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# Cerium (IV) oxidation of organic compounds: I. Benzyl and related alcohols, II. Cycloheptatriene

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CERIUM(IV) OXIDATION-OF ORGANIC COMPOUNDS .

I. BENZYL AND RELATED ALCOHOLS.

II. CYCLOHEPTATRIENE

by

Lewis Brewster Young

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
The Requirements for the Degree of  
DOCTOR OF PHILOSOPHY  
Major Subject: Organic Chemistry

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## INTRODUCTION

The use of cerium(IV) as an oxidant of organic compounds was reported as early as 1905, when ceric oxide in sulfuric acid was reported to oxidize toluene to benzaldehyde, anthracene to 9,10-anthraquinone, and naphthalene to 1,4-naphthoquinone (1,2). No yields or procedures were given, however. Later the use of cerium(IV) as an analytical reagent for the determination of organic compounds gained prominence, and this subject was reviewed by G. F. Smith in 1942 (3).

More recently several kinetic studies of the oxidation of aldehydes, ketones, alcohols, glycols, and other organic compounds by cerium(IV) have appeared in the chemical literature (4). Many of these studies are of only limited usefulness because the products of the reaction of these compounds with cerium(IV) are not known. Much of the impetus behind these studies seems to have been supplied by the ease with which oxidations by cerium(IV) can be followed (cerium(IV) is orange and cerium(III) is colorless).

The investigations reported in this dissertation were inspired by the finding of W. S. Trahanovsky that ceric ammonium nitrate converts benzyl alcohol to benzaldehyde. A study of the scope of the reaction with alcohols is reported in Part I. In general only benzylic-type alcohols are converted to the corresponding carbonyl compound. Ordinary aliphatic alcohols give starting material and few other

products.

When an alcohol and a cerium(IV) solution are mixed, the orange cerium(IV) color deepens to dark red. This color change is due to the formation of a 1:1 cerium(IV)-alcohol complex as has been demonstrated by us and by several other workers. A study of the effect of alcohol structure on the magnitude of the equilibrium constants for cerium(IV)-alcohol complex formation is presented in Part II. Such a study should be useful for predicting and rationalizing effects found in other metal ion oxidations of alcohols, for example the lead tetraacetate and chromium(VI) oxidations, where metal ion-alcohol complexes are believed to exist but can only be inferred from kinetic data.

Part III of this dissertation discusses a kinetic study of the mechanism of oxidation of benzyl alcohols. Of the several kinetic studies of cerium(IV) oxidations of organic compounds in the literature, studies of alcohol oxidation are by far the most numerous. In nearly all the studies the oxidation of only one alcohol is studied, generally with the conclusion being reached that oxidation occurs via formation of a 1:1 alcohol-cerium(IV) complex, and rate determining oxidative decomposition of the complex. The mechanism of oxidative decomposition of the 1:1 alcohol-cerium(IV) complex has received essentially no attention, and it is this point which the study presented in Part III pursues. In the benzyl

alcohol system the products of oxidation are known and a systematic variation of substituents can be made to ascertain the best formulation for the transition state for the oxidation of alcohols. This is important because it establishes the electronic behavior of an oxidant which is believed to be a simple one electron oxidant and sets a precedent for what might be expected from other oxidants.

In Part IV is presented a study of the novel oxidative ring contraction which occurs when cycloheptatriene is oxidized by ceric ammonium nitrate. The products of the reaction, benzaldehyde, the major product, and benzene are formed in nearly quantitative yield. The reaction is inherently interesting because it was not anticipated that a one electron oxidant would lead to appreciable yields of products in a triene system where polymerization is a likely possibility. In addition there was no precedent for the formation of benzene from cycloheptatriene. The invariance of the benzaldehyde/benzene ratio strongly implicated the involvement of nitrate ion in the reaction.

The results of this study taken as a whole indicate that cerium(IV) oxidations of organic compounds can be expected to lead to novel reactions as well as synthetically useful products.

PART I. SYNTHESIS OF ALDEHYDES AND KETONES FROM BENZYL  
AND RELATED ALCOHOLS

It has been found that ceric ammonium nitrate (CAN) in water or 50% aqueous acetic acid converts many benzyl and related alcohols to the corresponding aldehyde or ketone (Equation 1) (5,6). The results are summarized in Tables 1 and 2. In addition, it has been found that CAN in aqueous



64%

solution converts cyclopropanemethanol to cyclopropanecarbaldehyde in 64% yield (Equation 2) (7). The details of these reactions have been published elsewhere (5-7).

Table 1. Oxidation of benzyl and related alcohols to aldehydes or ketones by aqueous ceric ammonium nitrate

Alcohol	Product	Yield, %
Benzyl	Benzaldehyde	87 <sup>a</sup>
<u>p</u> -Xylyl	<u>p</u> -Tolualdehyde	86 <sup>b</sup>
2,4,6-Trimethylbenzyl	Mesitaldehyde	35 <sup>b</sup>
<u>o</u> -Chlorobenzyl	<u>o</u> -Chlorobenzaldehyde	77 <sup>b</sup> , 62 <sup>a</sup>
<u>p</u> -Bromobenzyl	<u>p</u> -Bromobenzaldehyde	83 <sup>b</sup>
<u>m</u> -Nitrobenzyl	<u>m</u> -Nitrobenzaldehyde	94 <sup>b</sup>
<u>p</u> -Nitrobenzyl	<u>p</u> -Nitrobenzaldehyde	81 <sup>b</sup>
<u>p</u> -Methoxybenzyl	Anisaldehyde	80 <sup>a</sup>
<u>p</u> -(Methylthio)benzyl	<u>p</u> -(Methylthio)benzaldehyde	0 <sup>b</sup>
<u>m</u> -Hydroxybenzyl	<u>m</u> -Hydroxybenzaldehyde	0 <sup>b</sup>
Veratryl	Veratraldehyde	30 <sup>b</sup>
Phthalyl	Phthalaldehyde	23 <sup>b</sup>
	Phthalide	42 <sup>b</sup>
Terephthalyl	Terephthalaldehyde	90 <sup>b</sup>
3-Pyridylmethanol	Nicotinaldehyde	75 <sup>b</sup> , 50 <sup>a</sup>
2-Thiophenemethanol	2-Thiophenecarbaldehyde	58 <sup>a</sup>
Furfuryl	Furfural	0 <sup>b</sup>
2-Naphthylmethanol	2-Naphthylcarbaldehyde	21 <sup>b</sup>
Cinnamyl	Cinnamaldehyde	0 <sup>b</sup>
Benzhydryl	Benzophenone	60 <sup>b</sup>
1-Phenethyl	Acetophenone	55 <sup>b</sup>
Cyclopropanemethanol	Cyclopropanecarbaldehyde	64 <sup>a</sup>

<sup>a</sup>Yield of distilled product.

<sup>b</sup>Yield of undistilled product, corrected for impurities by nmr.

Table 2. Oxidation of benzyl and related alcohols to aldehydes or ketones by ceric ammonium nitrate in 50% aqueous acetic acid

Alcohol	Product	Yield, %
Benzyl	Benzaldehyde	94 <sup>a</sup> , 72 <sup>b</sup>
<u>p</u> -Xylyl	<u>p</u> -Tolualdehyde	94 <sup>a</sup> , 74 <sup>c</sup>
2,4,6-Trimethylbenzyl	Mesitaldehyde	89 <sup>c</sup>
<u>o</u> -Chlorobenzyl	<u>o</u> -Chlorobenzaldehyde	89 <sup>a</sup> , 85 <sup>c</sup>
<u>p</u> -Bromobenzyl	<u>p</u> -Bromobenzaldehyde	93 <sup>a</sup>
<u>o</u> -Nitrobenzyl	<u>o</u> -Nitrobenzaldehyde	100 <sup>a</sup>
<u>m</u> -Nitrobenzyl	<u>m</u> -Nitrobenzaldehyde	79 <sup>a</sup>
<u>p</u> -Nitrobenzyl	<u>p</u> -Nitrobenzaldehyde	92 <sup>a</sup> , 77 <sup>c</sup>
<u>m</u> -Methoxybenzyl	<u>m</u> -Methoxybenzaldehyde	25 <sup>c</sup>
<u>p</u> -Methoxybenzyl	Anisaldehyde	94 <sup>a</sup>
<u>p</u> -(Methylthio)benzyl	<u>p</u> -(Methylthio)benzaldehyde	0 <sup>c</sup>
<u>m</u> -Benzoyloxybenzyl	<u>m</u> -Benzoyloxybenzaldehyde	18 <sup>c</sup>
Furfuryl	Furfural	0 <sup>c</sup>
2-Naphthylmethanol	2-Naphthylcarbaldehyde	28 <sup>d</sup>
Cinnamyl	Cinnamaldehyde	0 <sup>c</sup>
Benzhydryl	Benzophenone	57 <sup>c</sup>

<sup>a</sup>Yield obtained by glpc analysis of at least two runs.

<sup>b</sup>Yield of distilled product.

<sup>c</sup>Yield of undistilled product, corrected for impurities by nmr.

<sup>d</sup>Yield obtained by addition of a standard and nmr analysis.



PART II. A SPECTROPHOTOMETRIC STUDY OF CERIVM(IV) -  
ALCOHOL COMPLEXES

## INTRODUCTION

The use of cerium(IV) as a colorimetric reagent for the detection of alcohols has been known for quite a while (8). Other workers have developed methods for the quantitative analysis of alcohols utilizing the red cerium(IV)-alcohol complex color (9,10).

It has been demonstrated that the cerium(IV)-alcohol complex is a 1:1 complex involving one molecule of alcohol and one of cerium(IV) (Equation 3) (11-14). The purpose of this study was to determine what effect structural variation of the alcohol has on the position of the equilibrium



An attempt was also made to determine the solvent effect and the effect of added nitrate ion on the position of equilibrium.

Most of the equilibrium constants were measured at 21.0° C. in 70% aqueous acetonitrile containing ca. 0.5 M nitric acid. A few were measured in 70% aqueous acetic acid-0.5 M nitric acid and in water-0.5 M nitric acid. 70% Aqueous acetonitrile was chosen for the majority of the measurements because it approximated the conditions under which the kinetic study described elsewhere in this dissertation was carried out. In addition it afforded a medium in which all the alcohols were soluble and which was reasonably resistant to oxidation.

It is hoped that the equilibrium constants derived in this study will be useful in predicting and rationalizing results obtained in other metal ion-alcohol studies where it is not possible to measure the magnitude of any metal ion-alcohol interaction. The chromium(IV) and lead(IV) oxidations of alcohols are two cases where a metal ion-alcohol complex has been postulated (15), but no direct evidence for either the existence of a complex or the amount of complexation if a complex exists has been obtained.

## HISTORICAL

## Cerium(IV)-Alcohol Complexes

Although the existence of cerium(IV)-alcohol complexes had been well established by 1940 (8), the first complete study of cerium(IV)-alcohol complexation was carried out by Ardon in 1957 (11). He studied the kinetics of the ethanol-ceric perchlorate reaction and found that the oxidation proceeds via 1:1 complex formation between alcohol and cerium(IV). He derived an equilibrium constant from both kinetic and spectrophotometric data in 3.2 M perchloric acid of 4.3.

Rao and Muhammad measured the methanol-cerium(IV) equilibrium constant in perchloric acid at 20° C. (12). From kinetic measurements in 1 M perchloric acid they arrived at a value of K of 1.36. From spectrophotometric measurements in 3 M perchloric acid they found a value of 2.97. The decrease in K with decreasing concentration of hydrogen ion is probably due to a change in the uncomplexed cerium(IV) species, since it was found that the rate of decomposition (oxidation) of the complex remains the same with a change in [H+], implying that the complex species remains relatively constant.

Muhammad and Rao also found that the ceric sulfate-methanol system (0.5 M-2 M sulfuric acid) contained no cerium(IV)-alcohol complex (16). This is undoubtedly due to

the relatively strong binding of sulfate ion to cerium(IV) preventing alcohol from complexing. In contrast with Muhammad and Rao's results in sulfuric acid, Littler found that in 0.24 M sulfuric acid and 0.0218 M ceric sulfate at 50°, cyclohexanol complexes with cerium(IV) with  $K=13.0$  (17). This equilibrium constant was derived from kinetic data and is suspect since Hintz and Johnson found values of only 2.9 (kinetic) and 3.9 (spectrophotometric) for the cyclohexanol-ceric perchlorate equilibrium constant in 1 M perchloric acid at 15° (14). Since it is generally found that sulfate ion strongly depresses complex formation compared to perchlorate ion, it is obvious that Littler's value for  $K$  is much too high. Even if the temperature difference between Littler's and Hintz and Johnsons' studies is taken into account, Littler's value comes out much too high.

Sethuram studied the kinetics of the ceric nitrate oxidation of allyl alcohol in nitric acid at 20° (18). The nitric acid concentration was not reported but may have been 1 M based on an earlier study (19). He found a value for  $K$  of 3.1 from his kinetics.

Rangaswamy and Santappa studied the kinetics of the oxidation of benzyl alcohol by ceric perchlorate in 1-1.5 M perchloric acid (20). They found that a plot of  $1/k_{\text{obs}}$  vs.  $1/[\text{PhCH}_2\text{OH}]$  (where  $k_{\text{obs}}$  is the pseudo first order rate constant for the disappearance of cerium(IV) in the presence

of excess alcohol) had a y-intercept of zero, indicating no complex formation between cerium(IV) and benzyl alcohol. They did not report a verification of their conclusion of no complex formation by an independent spectrophotometric measurement, probably for a very good reason. If one mixes a solution of 0.05 M ceric perchlorate in 0.5 M perchloric acid and benzyl alcohol, it is observed that the orange color of cerium(IV) changes immediately to extremely deep red, the color of a cerium(IV)-alcohol complex (21). It is thus apparent that these authors' kinetics is in rather serious error and that there is in fact complex formation in this system.

Offner and Skoog have measured equilibrium constants for a few alcohols with ceric perchlorate in 1.6-1.7 M perchloric acid and with ceric ammonium nitrate in 2 M nitric acid (13). In ceric perchlorate-perchloric acid the equilibrium constants for n-butanol, sec-butanol, and tert-butanol were 16, 11, and 13, respectively. In ceric ammonium nitrate-nitric acid the equilibrium constants were 1, 1, and 0.6 for n-butanol, sec-butanol, and tert-butanol, respectively.

Sethuram and Muhammad determined equilibrium constants for isopropanol and sec-butanol in 1 M nitric acid and for isopropanol in 1 M perchloric acid (19,22). They found values for K at 22° in 1 M nitric acid of 2.07 for isopropanol and 2.213 for sec-butanol. These are apparently

extrapolated values since values of 1.38 (kinetic) and 1.40 (spectrophotometric) are reported earlier in the paper for the equilibrium constant of isopropanol, and 1.84 (kinetic) and 1.82 (spectrophotometric) are reported in the same place for sec-butanol, all measured at 28° in the medium. These two sets of data indicate that K must increase with a decrease in the temperature. However, a graph of  $1/K$  vs.  $1/T$  in the same paper reveals that K increases with increasing temperature and furthermore, extrapolation of this graph leads to the unlikely conclusion that  $K=\infty$  at 20° C. It seems likely that the graph referred to is in reality intended to be labelled  $\log K$  vs.  $1/T \times 10^3$ , however the prediction that K should increase with an increase in temperature still results, in conflict with the other results reported in the paper. It is concluded that the information reported in this paper is of no value because of its inconsistencies.

Sethuram and Muhammads' results in the second paper of this series (22) are apparently more meaningful than those in the first paper (19). They found that for isopropanol at 22° C. the equilibrium constant with ceric perchlorate-1 M perchloric acid was 2.3, with ceric nitrate-nitric acid was 2.1, and with ceric sulfate-sulfuric acid was zero. The change of the equilibrium constants with the different ligands can be explained as an increase in metal-ligand bond strength in going from perchlorate to nitrate to sulfate re-

sulting in less cerium(IV)-alcohol complex going along the series. The sulfate-cerium(IV) bonding is apparently sufficiently strong to exclude cerium(IV)-alcohol bonding.

A summary of alcohol-cerium(IV) equilibrium constants is presented in Table 3.

#### Cerium(IV)-Glycol Complexes

Duke and Forist studied the kinetics of the ceric nitrate oxidation of 2,3-butanediol (23). They found that a 1:1 cerium(IV)-glycol complex is formed in 0.5 M nitric acid with the total nitrate ion concentration 1.0-0.5 M, with the equilibrium constant equal to 24-25. They also studied the effect of hydrogen ion and nitrate ion concentration on the equilibrium constant and the rate of oxidative decomposition of the complex and reached the following conclusions: 1) there are different complexes present in the presence of different hydrogen ion concentrations; 2) nitrate ion is bound to cerium(IV) in the complex.

Duke and Bremer studied the kinetics of the ceric perchlorate oxidation of 2,3-butanediol (24). They found that in addition to a 1:1 complex, a 2:1 glycol:cerium(IV) complex and probably a 3:1 glycol:cerium(IV) complex were present. They supported a value of  $K=15$  for formation of the 1:1 complex and  $K=2.3$  for formation of the 2:1 complex in 0.1-1 M perchloric acid. From the effect of added perchlorate they



Table 3. Summary of equilibrium constants for cerium(IV)-alcohol complexes reported in the literature

Alcohol	Medium	$K_{eq}$	Method <sup>a</sup>	Ref.
Ethanol	CP <sup>b</sup> , 3.2 M HClO <sub>4</sub>	4.3	K,S	- <sup>c</sup>
Methanol	CP, 1 M HClO <sub>4</sub>	1.36	K	- <sup>d</sup>
	CP, 3 M HClO <sub>4</sub>	2.97	S	- <sup>d</sup>
	CS <sup>e</sup> , 0.5-2 M H <sub>2</sub> SO <sub>4</sub>	0	K	- <sup>f</sup>
Cyclohexanol	CS, 0.24 M H <sub>2</sub> SO <sub>4</sub>	13.0	K	- <sup>g</sup>
	CP, 1 M HClO <sub>4</sub>	2.9	K	- <sup>h</sup>
	CP, 1 M HClO <sub>4</sub>	3.9	S	- <sup>h</sup>
Allyl alcohol	CN <sup>i</sup> , 1 M HNO <sub>3</sub> <sup>j</sup>	3.1	K	- <sup>k</sup>
Benzyl alcohol	CP, 1-1.5 M HClO <sub>4</sub>	0	K	- <sup>l</sup>
<u>n</u> -Butanol	CP, 1.6-1.7 M HClO <sub>4</sub>	16	S	- <sup>m</sup>
	CAN, 2 M HNO <sub>3</sub>	1	S	- <sup>m</sup>
<u>sec</u> -Butanol	CP, 1.6-1.7 M HClO <sub>4</sub>	11	S	- <sup>m</sup>
	CAN, 2 M HNO <sub>3</sub>	1	S	- <sup>m</sup>
<u>t</u> -Butanol	CP, 1.6-1.7 M HClO <sub>4</sub>	13	S	- <sup>m</sup>
	CAN, 2 M HNO <sub>3</sub>	0.6	S	- <sup>m</sup>

<sup>a</sup>K=kinetic data; S=spectrophotometric data.

<sup>b</sup>CP is ceric perchlorate.

<sup>c</sup>Ref. 11.

<sup>d</sup>Ref. 12.

<sup>e</sup>CS is ceric sulfate.

<sup>f</sup>Ref. 16.

<sup>g</sup>Ref. 17.

<sup>h</sup>Ref. 14.

<sup>i</sup>CN is ceric nitrate.

<sup>j</sup>This may not be the correct acid concentration (see historical).

<sup>k</sup>Ref. 18.

<sup>l</sup>Ref. 20.

<sup>m</sup>Ref. 15.

Table 3 (Continued)

Alcohol	Medium	$K_{eq}$	Method <sup>a</sup>	Ref.
Isopropanol	CP, 1 <u>M</u> HClO <sub>4</sub>	2.3	K,S	- <sup>n</sup>
	CN, 1 <u>M</u> HNO <sub>3</sub>	2.1	K,S	- <sup>n</sup>
	CS, H <sub>2</sub> SO <sub>4</sub>	0	K	- <sup>n</sup>
2,3-Butanediol	CN, 0.5 <u>M</u> HNO <sub>3</sub>	24-25	K	- <sup>o</sup>
	CP, 0.1-1 <u>M</u> HClO <sub>4</sub>	15(K <sub>1</sub> )	K	- <sup>p</sup>
		2.3(K <sub>2</sub> )	K	- <sup>p</sup>
Glycerol	CS, H <sub>2</sub> SO <sub>4</sub>	0	K	- <sup>q</sup>
	CP, 0.5 <u>M</u> HClO <sub>4</sub>	20	K,S	- <sup>q</sup>
<u>cis</u> -1,2-Cyclohexanediol	CP, 1 <u>M</u> HClO <sub>4</sub>	29.0	K	- <sup>h</sup>
	CP, 1 <u>M</u> HClO <sub>4</sub>	29.3	S	- <sup>h</sup>
<u>trans</u> -1,2-Cyclohexanediol	CP, 1 <u>M</u> HClO <sub>4</sub>	18.0	K	- <sup>h</sup>
	CP, 1 <u>M</u> HClO <sub>4</sub>	18.6	S	- <sup>h</sup>
<u>trans</u> -2-Methoxycyclohexanol	CP, 1 <u>M</u> HClO <sub>4</sub>	2.1	K	- <sup>h</sup>
	CP, 1 <u>M</u> HClO <sub>4</sub>	2.9	S	- <sup>h</sup>
1,3-Butanediol	CP, 1.6-1.7 <u>M</u> HClO <sub>4</sub>	30	S	- <sup>m</sup>
	CAN, 2 <u>M</u> HNO <sub>3</sub>	3.1	S	- <sup>m</sup>
1,4-Butanediol	CP, 1.6-1.7 <u>M</u> HClO <sub>4</sub>	14	S	- <sup>m</sup>
	CAN, 2 <u>M</u> HNO <sub>3</sub>	2.6	S	- <sup>m</sup>
Diethylene glycol	CP, 1.6-1.7 <u>M</u> HClO <sub>4</sub>	40	S	- <sup>m</sup>
	CAN, 2 <u>M</u> HNO <sub>3</sub>	3.2	S	- <sup>m</sup>
Veratrol	CAN, 0.5 <u>M</u> H <sub>2</sub> SO <sub>4</sub> , 4% aqueous HOAc	490	S	- <sup>m</sup>

<sup>n</sup>Refs. 19 and 22.

<sup>o</sup>Ref. 23.

<sup>p</sup>Ref. 24.

<sup>q</sup>Ref. 25.

determined that the glycol was not displacing perchlorate from the complex.

Guilbault and McCurdy studied the ceric sulfate and ceric perchlorate oxidations of glycerol (25). They found no complex formation with ceric sulfate. In 0.5 M perchloric acid at 20° they found a value of  $K=20$  for the ceric perchlorate-glycerol complex. This value was determined both kinetically and spectrophotometrically. They did not detect any 2:1 or higher order complexes.

Hintz and Johnson measured equilibrium constants in 1.0 M perchloric acid at 15° C. for cyclohexanol, cis- and trans-1,2-cyclohexanediols, and trans-2-methoxycyclohexanol using both spectrophotometric and kinetic techniques (14). They found the following values for  $K$  in the 1:1 complex: cyclohexanol, 2.9 (kinetic), 3.9 (spectrophotometric); cis-1,2-cyclohexanediol, 29.0 (kinetic), 29.3 (spectrophotometric); trans-1,2-cyclohexanediol, 18.0 (kinetic), 18.6 (spectrophotometric); trans-2-methoxycyclohexanol, 2.1 (kinetic), 2.9 (spectrophotometric). Thus it is apparent that a second hydroxyl group adjacent to the first substantially increases the equilibrium constant for complex formation, possibly due to a chelate effect. Substitution of a methyl group for a hydroxyl hydrogen in trans-1,2-cyclohexanediol substantially decreases the stability of the complex, probably indicating that the substitution of a methyl group for a hydrogen prevents

chelate formation. The equilibrium constant for cis-1,2-cyclohexanediol is larger than that for trans-1,2-cyclohexanediol, consistent with chelate formation. This is expected since the formation of a five membered chelate ring fused to the cyclohexane ring results in a relatively rigid system with the trans isomer, whereas the complex with the cis isomer is relatively flexible. This greater flexibility of the complex with the cis isomer thus contributes to its somewhat greater stability.

Hintz and Johnson also attempted to measure the equilibrium constants for the cis- and trans-1,2-cyclopentanediols but found that they were oxidized too readily (14). However, from measurement of the activation parameters for oxidation of the cis and trans glycols they concluded that the cis glycol is oxidized via a cyclic mechanism while the trans glycol is oxidized via an acyclic mechanism.

Offner and Skoog measured equilibrium constants for a few glycols with ceric ammonium nitrate in 2 M nitric acid and with ceric perchlorate in 1.6-1.7 M perchloric acid using a spectrophotometric technique (13). They found the following values for K at room temperature (CAN is ceric ammonium nitrate, CP is ceric perchlorate): 1,3-butanediol, 3.1 (CAN), 30 (CP); 1,4-butanediol, 2.6 (CAN), 14 (CP); diethylene glycol, 3.2 (CAN), 40 (CP). They also measured the equilibrium constant for veratrol (o-dimethoxybenzene) with ceric

ammonium nitrate in 4% aqueous acetic acid and 0.5 M sulfuric acid and found  $K=490$ .

Littler and Waters concluded from a kinetic study using ceric sulfate and ethanol, ethylene glycol, and 2-methoxyethanol, that there is no cerium(IV)-alcohol complexation in this medium (26). Other workers have concluded that there is no complex formation in the oxidation of ethylene glycol (27) and pinacol (28) by ceric sulfate in sulfuric acid.

A summary of glycol-cerium(IV) equilibrium constants reported in the literature is presented in Table 3.

#### Other Rare Earth Ion Complexes

It is well known that the coordination chemistry of the rare earth metal ions is rather limited in scope. Appreciably stable complex species are formed only when the ligands contain highly electronegative donor atoms (e.g., oxygen and nitrogen). This subject has been thoroughly reviewed by Moeller (29).

The stability constants of several  $\alpha$ -hydroxycarboxylate complexes with lanthanide tripositive ions have been measured. Since bonding of ligands with lanthanide ions is believed to be essentially electrostatic in character, trends found with the tripositive lanthanides should also be applicable to the tetrapositive lanthanides. Choppin and Chopoorian found that the stability constants for complexes of the tripositive

lanthanides with  $\alpha$ -hydroxyisobutyrate, lactate ( $\alpha$ -hydroxypropionate), and glycolate ( $\alpha$ -hydroxyacetate) decrease in the order given (30). That is, the compound with two methyl groups at the  $\alpha$ -position forms a stronger complex than the one with one methyl group at the  $\alpha$ -position, and that in turn forms a stronger complex than the compound with only hydrogens at the  $\alpha$ -position. They explained this trend as a result of the inductive effect of the methyl groups, the electron donating properties of the methyl group resulting in a higher electron density at the ligand donor atoms in the more highly substituted compound, thus resulting in a more stable complex.

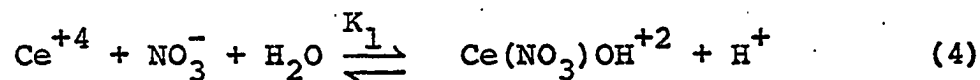
Powell and Fleischer (31) and Powell and Schoeb (32) extended this study to include several other substituents at the  $\alpha$ -position of  $\alpha$ -hydroxycarboxylates. If the ligands are considered to be substituted glycolates ( $\alpha$ -hydroxyacetates), the following order of stability constants for the tripositive lanthanides is found for the light rare earths: MeMe $\sim$ MeH $\sim$ HH $\sim$ MeEt $\sim$ tetramethylene $\sim$ EtH $\sim$ i-ProH $\sim$ i-ProMe $\sim$ EtEt $\sim$ t-BuMe $\sim$ t-BuH $\sim$ pentamethylene $\sim$ i-ProEt. For the heavy rare earth ions the order of stability constants is not the same, but is as follows: MeMe $\sim$ EtMe $\sim$ EtEt $\sim$ MeH $\sim$ HH $\sim$ tetramethylene $\sim$ EtH $\sim$ i-ProMe $\sim$ i-ProEt $\sim$ t-BuMe $\sim$ t-BuH $\sim$ pentamethylene. The trends can be explained by postulating that the stability constant increases with increasing substitution at the  $\alpha$ -carbon until the steric

effect of the substituents begins to overbalance the favorable inductive effect.

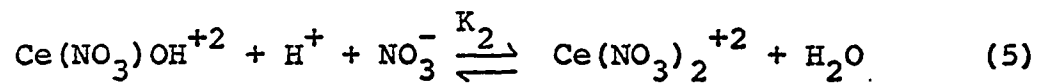
Powell and Kovar studied the stability of acetate, iodoacetate, chloroacetate, and formate complexes with tri-positive lanthanides (33). They found the following order of stability constants: acetate > iodoacetate > chloroacetate > formate. It might be anticipated that the stability constant of the complex should be directly related to the basicity of the ligand since factors which increase the basicity of a ligand (e.g., electron donating substituents) also increase the electron density on the donor atom. However, the order of basicity of the ligands cited above is acetate > formate > chloroacetate > iodoacetate. Thus it is found that the stability constants for the haloacetates, especially iodoacetate, are greater than anticipated. This may be indicative of complexing by the halogen in addition to the carboxylate.

Powell and Paul found that the stabilities of a number of rare earth propionates were less than the corresponding rare earth acetates (34). They suggested that this was due to a steric effect of the additional methyl group.

Duke and Tuazon studied the nature of cerium(IV) in aqueous nitric acid solution (35). They derived a value of  $K_1=171$  for the equilibrium



and a value of  $K_2$  of 0.6-1.0 for the equilibrium



using a spectrophotometric technique which measured the absorbance of a solution of cerium(IV) and nitrate ion relative to isolated solutions of cerium(IV) and nitrate ion.



## TREATMENT OF DATA

Equilibrium constants were calculated from absorption data using a linear least squares treatment and either of two equations. The one usually used was that of Ardon (11) which is derived as follows.



$$A = C_m \epsilon_{\text{complex}} X + C_m \epsilon_m (1-X) \quad (7)$$

where X is the fraction of M complexed.

$$K = \frac{X}{(1-X) [S]^n} \quad (8)$$

$$X = \frac{K[S]^n}{1 + K[S]^n} \quad (9)$$

Substituting Equation 9 into Equation 7 gives

$$A = \frac{C_m \epsilon_{\text{complex}} K[S]^n}{1 + K[S]^n} + C_m \epsilon_m - \frac{C_m \epsilon_m K[S]^n}{1 + K[S]^n} \quad (10)$$

Since  $C_m \epsilon_m = A_0$ ,

$$A - A_0 = \frac{\Delta \epsilon C_m K[S]^n}{1 + K[S]^n} \quad (11)$$

$$1/\Delta A = \frac{1 + K[S]^n}{\Delta \epsilon C_m K[S]^n} \quad (12)$$

$$= \frac{1}{[S]^n} \cdot \frac{1}{\Delta\epsilon C_m K} + \frac{1}{\Delta\epsilon C_m} \quad (13)$$

For a 1:1 cerium(IV)-alcohol complex, this equation can be rewritten

$$1/\Delta A = 1/[ROH] \cdot 1/\Delta\epsilon [Ce^{+4}]_T + 1/\Delta\epsilon [Ce^{+4}]_T \quad (14)$$

If  $1/\Delta A$  is plotted vs.  $1/[ROH]$ , the slope of the line is

$$1/\Delta\epsilon [Ce^{+4}]_T$$

and the intercept is

$$1/\Delta\epsilon [Ce^{+4}]_T$$

from which it can be seen that intercept/slope = K.

Some spectrophotometric data was treated using the modified equation derived below. Using the same symbols as above, for the equilibrium  $Ce^{+4} + ROH \rightleftharpoons$  complex

$$A = \epsilon_m [Ce^{+4}] + \epsilon_{\text{complex}} [\text{complex}] \quad (15)$$

$$= \epsilon_m [Ce^{+4}]_T \cdot \frac{1}{1+K[ROH]} + \epsilon_{\text{complex}} [Ce^{+4}]_T \cdot \frac{K[ROH]}{1+K[ROH]} \quad (16)$$

The apparent extinction coefficient,  $\bar{\epsilon}$ , is defined as  $A/[Ce^{+4}]_T$ , so that with Equation 16

$$\bar{\epsilon} = \frac{\epsilon_m + \epsilon_{\text{complex}} K[\text{ROH}]}{1 + K[\text{ROH}]} \quad (17)$$

Rearranging Equation 17 gives

$$\bar{\epsilon} + \bar{\epsilon} K[\text{ROH}] = \epsilon_m + \epsilon_{\text{complex}} K[\text{ROH}] \quad (18)$$

and

$$\bar{\epsilon} K[\text{ROH}] = -\bar{\epsilon} + \epsilon_{\text{complex}} K[\text{ROH}] + \epsilon_m \quad (19)$$

Dividing both sides of the equation by  $K[\text{ROH}]$  gives

$$\bar{\epsilon} = \epsilon_{\text{complex}} - \frac{\bar{\epsilon} - \epsilon_m}{[\text{ROH}]} \frac{1}{K} \quad (20)$$

From Equation 20 it can be seen that a plot of  $\bar{\epsilon}$  vs.  $(\bar{\epsilon} - \epsilon_m)/[\text{ROH}]$  has a slope of  $-1/K$  and an intercept of  $\epsilon_{\text{complex}}$ .

## RESULTS AND DISCUSSION

## General Considerations

The bonding model which will be assumed in the following discussion of stabilities of various cerium(IV)-alcohol complexes is one of mainly electrostatic attraction between the donor atom, oxygen, and cerium(IV). It is felt by most authors that the amount of covalent bonding between rare earth ions and electronegative atoms is quite small due to the shielding of the 5s and 5p orbitals by the diffuse 4f orbitals, thus forcing any covalent bonding with the metal ion to occur with the metal's higher energy 6s and 6p orbitals, an energetically unfavorable process (29). In the case of cerium(IV), the 4f orbitals are not occupied, but any covalent bonding of a donor atom to ceric ion would require the use of the diffuse 4f orbitals or the higher energy 6s or 6p orbitals, a situation which must be energetically unfavorable, since few stable ceric ion complexes are known (29).

Several factors must be considered in attempting to rationalize the changes in K with changes in the alcohol structure. These are a steric effect, an inductive effect, size of chelate ring, if any, and solvation effects. The latter factor, solvation effects, is the hardest factor to predict and may well be the most important one in determining the stability of a complex.

In comparing the magnitude of equilibrium constants of

several different systems, it is important to note that it is the ratio of  $K_1/K_2$ , or more properly  $\log(K_1/K_2)$ , which is proportional to the overall free energy change in going from uncomplexed alcohol and cerium(IV) to the cerium(IV)-alcohol complex. This follows from the equations below.

$$-\Delta F = RT \ln K \quad (21)$$

$$\Delta F_2 - \Delta F_1 = (-RT \ln K_2) - (-RT \ln K_1) \quad (22)$$

$$\Delta F_2 - \Delta F_1 = -RT \ln (K_2/K_1) \quad (23)$$

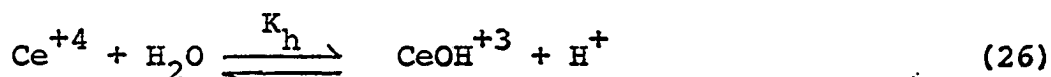
$$\Delta \Delta F \text{ (kcal./mole)} = -1.5 \log (K_2/K_1) \quad (24)$$

Thus in the following discussions, the effect of substitution in a given system will be discussed in terms of the ratio  $K_2/K_1$  rather than the difference  $K_2 - K_1$ .

It was anticipated in this study that we would be dealing with a 1:1 cerium(IV)-alcohol complex, since several other workers had established that a 1:1 complex exists in a wide variety of media (11,13-18,20). To substantiate this expectation one set of data for 2-methoxyethanol was plotted assuming a 1:1 complex and then a 2:1 alcohol-cerium(IV) complex. This data is illustrated in Figures 1 and 2. It can be seen that the plot of the data assuming a 1:1 complex yields a straight line, while that assuming a 2:1 complex yields a curved line. Thus in this case a 1:1 cerium(IV)-alcohol complex must be formed. It has been assumed that 1:1 complexes are formed for all the other alcohols since treat-

ment of the data assuming a 1:1 complex yields straight lines.

The equilibrium constants treated in this study are "apparent" equilibrium constants (12). That is, they measure the position of the equilibrium of all cerium(IV) species with alcohol to form a 1:1 cerium(IV)-alcohol complex. Some authors have made an attempt to break down the apparent equilibrium constant into the "true" formation constant for the complex,  $\bar{K}$ , and a hydrolysis equilibrium constant,  $K_h$  (12). The equilibria defined by  $\bar{K}$  and  $K_h$  are indicated in Equations 25 and 26. According to this line of reasoning, the



apparent equilibrium constant,  $K$ , can be broken down into  $[\text{H}^+]$ -dependent and  $[\text{H}^+]$ -independent parts as illustrated in Equations 27 and 28.

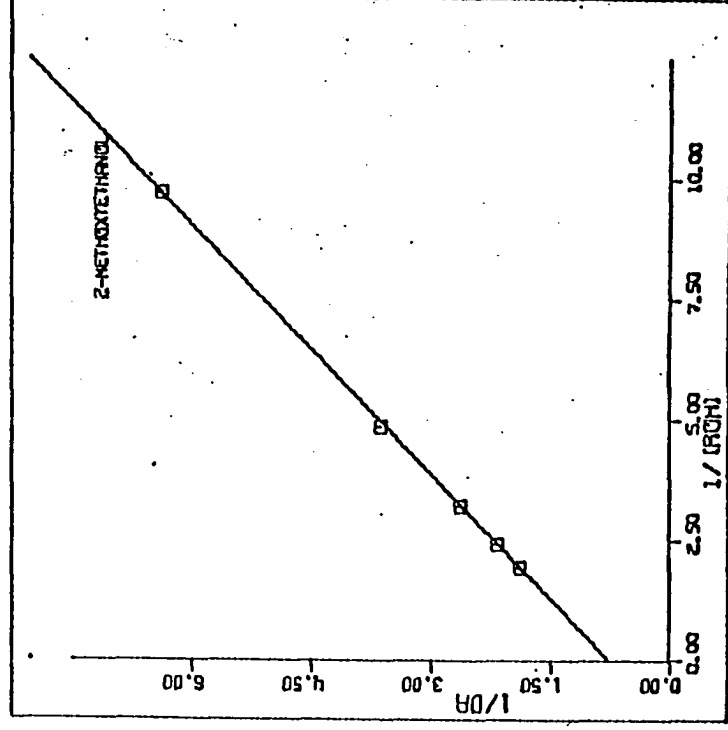
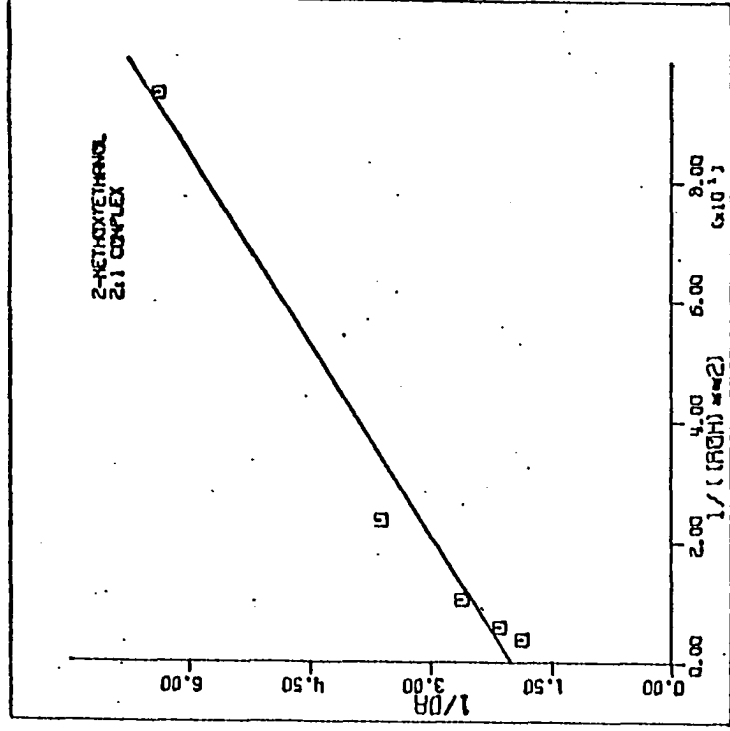
$$K = \frac{[\text{complex}]}{[\text{Ce}^{+4}][\text{ROH}]} + \frac{[\text{complex}][\text{H}_2\text{O}]}{[\text{ROH}][\text{CeOH}^{+3}]} \quad (27)$$

$$K = \bar{K} + \frac{\bar{K}[\text{H}^+]}{K_h} \quad (28)$$

The supposed advantage of this sort of treatment is that once  $\bar{K}$  and  $K_h$  are obtained for a given system, it should be

Figure 1. Plot of spectrophotometric data for 2-methoxyethanol assuming 2:1 complex formation

Figure 2. Plot of spectrophotometric data for 2-methoxyethanol assuming 1:1 complex formation





possible to predict  $K$ , the apparent equilibrium constant, in a similar medium of any acidity. The assumption made in deriving these  $\bar{K}^S$  and  $K_h^S$  in perchloric acid solution has been that only the two cerium(IV) species, the totally aquated species and the monohydroxy aquated species, are in equilibrium with the alcohol to form the complex (12).

The advantage of this sort of treatment completely breaks down in a medium as complex as aqueous acetonitrile containing nitric acid. Here one would have to postulate several cerium (IV) species in equilibrium with the complex and any conclusions would be speculative at best. Thus only apparent equilibrium constants are dealt with in this study.

#### Cerium Species in Solution

Beineke has found using x-ray crystallographic techniques that solid CAN has six nitrate ions surrounding each cerium atom (36). The nitrates are coordinated to the cerium in a bidentate fashion so that the coordination number of cerium is twelve (37). The average Ce-O distance is  $2.508 \pm 0.007 \text{ \AA}$ . It is obvious that great caution must be exercised in extrapolating from the solid state to solution, but it should at least be noted that there is definitive evidence for bidentate coordination of nitrate ion to cerium(IV) in the solid state.

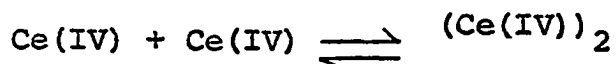
Larsen and Brown carried out an x-ray diffraction study of CAN in aqueous solution (38). They note that as of 1964, "no

direct structural evidence exists on this compound in either state," i.e., solid or solution. They found that there are twelve cerium-oxygen interactions within a distance of 2.85 Å<sup>0</sup> in 1.45 N aqueous CAN solution. In addition they found interactions attributable to the N-O and O-O of the nitrate ion, confirming its proximity to the cerium(IV) ion. This data is consistent with the presence of six bidentate nitrates around the cerium, although some of the coordination sites may be occupied by water.

Miller and Irish studied the i.r. attenuated total reflection spectra of CAN solutions of concentrations as low as 0.4 M (39). They found evidence for the existence of cerium-nitrate species and advanced the postulate that the nitrates were coordinated in a bidentate fashion.

Henshall carried out some measurements on CAN solutions in glacial acetic acid (40). He found from ion migration experiments that an uncharged species, possibly  $\text{Ce}(\text{NO}_3)_4$ , was present. Freezing point depression measurements lead to the conclusion that three particles were present, consistent with the dissociation of CAN to two ammonium nitrate molecules and one ceric nitrate molecule.

Blaustein and Gryder measured the equilibrium constant for the equilibrium



potentiometrically in 5.5 F nitric acid at 30° C. and found a value for K of  $17 \pm 2$  (41). That is, under these conditions the cerium(IV) is about 80% dimer. An independent kinetic study of the cerium(IV)-thallium(I) system in 6.2 F nitric acid by Dorfman and Gryder gave a value of 18 for the monomer-dimer equilibrium constant (42).

It thus appears that CAN in solution exists as a highly nitrated ion. The cerium(IV)-alcohol complexes may be formed by replacement of a mono- or bidentate nitrate ion or a water molecule by an alcohol molecule.

#### Benzyl Alcohols

A summary of the equilibrium constants for 1:1 cerium(IV)-alcohol complex formation of benzyl alcohols with ceric ammonium nitrate in 70% aqueous acetonitrile and 0.5 M nitric acid at 21.0° C. is presented in Table 4. The value of K changes little with ring substitution as might be expected, however there is a trend established with p-methyl > benzyl > m-chloro > p-chloro > p-nitro > m-nitro. There is a crude correlation of the values of K calculated from the slope-intercept equation with Hammett's sigma constants (43) as illustrated in Figure 3. There is also a correlation of the equilibrium constants of the para substituted alcohols (calculated from the slope-intercept equation) with Taft's polar substituent constants (44,45),  $\sigma'$ , as shown in Figure 4. Hammett's rho

value for the first case is -0.18 and for the second case -0.13. Thus the stability of the complex is increased slightly by electron donating substituents on the ring as might have been anticipated.

The effect of substitution at the  $\alpha$ -position is more impressive. The equilibrium constants for  $\alpha$ -methylbenzyl alcohol and benzhydrol are 1.8 and 1.4, respectively, compared to 0.7 for benzyl alcohol. As will be seen later, this is the trend usually found in going from a primary to a secondary alcohol. The fact that the stability of the  $\alpha$ -methylbenzyl alcohol complex is somewhat greater than the stability of the benzhydrol complex may be due to a steric effect or an inductive effect of the second phenyl group.

#### Aliphatic Alcohols

Equilibrium constants for several aliphatic alcohols with ceric ammonium nitrate at 21.0° C. in 70% aqueous acetonitrile and 0.5 M nitric acid are summarized in Table 4. All the equilibrium constants tabulated in this table were calculated using the slope-intercept equation (Equation 14). In order to facilitate discussion of the large number of equilibrium constants an attempt will be made to discuss one aspect of structural change at a time.

Table 4. Equilibrium constants for the cerium(IV)-alcohol complex in 70% aqueous acetonitrile at 21.0° C. and  $[\text{HNO}_3]=0.49 \text{ M}$

Alcohol	Equilibrium Constant	Standard Deviation	Equation	$\Delta F$ (kcal./mole)
Benzyl	0.73	0.01	S-I <sup>a</sup>	+0.20
	0.75	0.05	S <sup>b</sup>	+0.19
<u>p</u> -Methylbenzyl	0.80	0.01	S-I	+0.14
	0.78	0.04	S	+0.16
<u>o</u> -Chlorobenzyl	0.52	0.01	S-I	+0.42
	0.54	0.02	S	+0.40
<u>m</u> -Chlorobenzyl	0.72	0.01	S-I	+0.21
	0.71	0.03	S	+0.22
<u>p</u> -Chlorobenzyl	0.69	0.01	S-I	+0.24
	0.71	0.02	S	+0.22
<u>m</u> -Nitrobenzyl	0.46	0.03	S-I	+0.50
	0.48	0.05	S	+0.47
<u>p</u> -Nitrobenzyl	0.62	0.01	S-I	+0.31
	0.61	0.02	S	+0.32
$\alpha$ -Methylbenzyl	1.76	0.01	S-I	-0.36
	1.83	0.07	S	-0.39

<sup>a</sup>S-I is the equation which uses both slope and intercept of a plot to give K.

<sup>b</sup>S is the equation which uses slope only to give K.

Table 4 (Continued)

Alcohol	Equilibrium Constant	Standard Deviation	Equation	$\Delta F$ (kcal./mole)
Benzhydrol	1.37	0.01	S-I	-0.20
	1.43	0.06	S	-0.23
Methanol	0.51	0.03	- <sup>c</sup>	+0.43
Ethanol	0.72	0.01		+0.21
<u>n</u> -Hexanol	1.52	0.04		-0.27
<u>n</u> -Nonanol	1.84	0.01		-0.39
Neopentanol	2.7	0.01		-0.64
2-Cyclohexylethanol	1.89	0.00		-0.41
Cyclopropylcarbinol	0.86	0.01		+0.10
Cyclobutylcarbinol	1.4	0.02		-0.22
Cyclopentylcarbinol	2.59	0.04		-0.61
Cyclohexylcarbinol	2.46	0.05		-0.58
3-Butenol	0.98	0.01		0.00
5-Hexenol	1.42	0.03		-0.22
2-Phenylethanol	2.24	0.04		-0.52
4-Phenylbutanol	1.60	0.02		-0.30
Ethylene glycol	3.00	0.01		-0.70
1,3-Propanediol	4.38	0.01		-0.95
1,4-Butanediol	2.64	0.03		-0.62
1,5-Pentanediol	3.26	0.01		-0.76
2-Methoxyethanol	1.32	0.03		-0.18

<sup>c</sup>The following equilibrium constants were derived from the slope-intercept equation.

Table 4 (Continued)

Alcohol	Equilibrium Constant	Standard Deviation	Equation	$\Delta F$ (kcal./mole)
2-Chloroethanol	0.13	0.2 <sup>d</sup>		+1.31
3-Ethoxypropanol	1.09	0.01		-0.01
Isopropanol	1.45	0.02		-0.24
3-Heptanol	3.71	0.02		-0.84
Cyclopentanol	2.9	0.1 <sup>d</sup>		-0.68
Cyclohexanol	4.30	0.02	- <sup>c</sup>	-0.93
Cycloheptanol	4.5	0.2 <sup>d</sup>		-0.96
Cyclooctanol	5.38	0.02		-1.08
<u>t</u> -Butanol	2.69	0.02		-0.63
1-Methylcyclohexanol	8.80	0.01		-1.39

<sup>d</sup>This is not a standard deviation but an estimated error.

#### Primary alcohols, nonfunctionalized

This group includes the first ten alcohols from methanol to cyclohexylcarbinol in Table 4. The equilibrium constants are summarized below in Table 5 for convenience. These equilibrium constants measured in 70% aqueous acetonitrile and 0.5 M nitric acid-ceric ammonium nitrate can be compared to values of 4.3 for ethanol in 3.2 M perchloric acid-ceric perchlorate (11), 1.36 for methanol in 1 M perchloric acid-ceric perchlorate (12), 2.97 for methanol in 3 M perchloric acid-ceric perchlorate (12), 16 for n-butanol in 1.6-1.7 M perchloric acid-ceric perchlorate (13), and 1 for n-butanol

Figure 3. Correlation of  $K_{eq}$  for benzyl alcohols with Hammett's sigma constants

Figure 4. Correlation of  $K_{eq}$  for para substituted benzyl alcohols with Taft's polar substituent constants



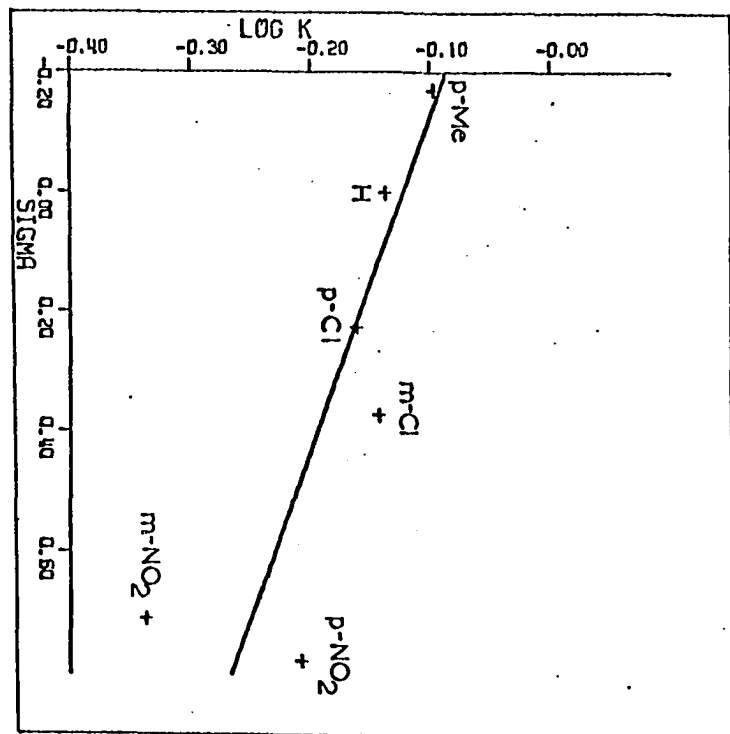
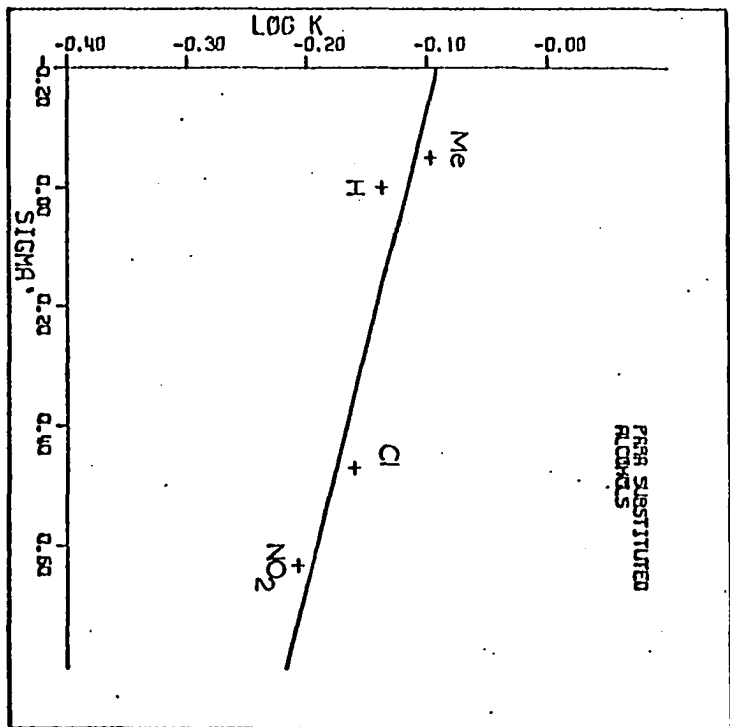


Table 5. Equilibrium constants for nonfunctionalized, primary alcohols in 70% aqueous acetonitrile

Alcohol	Equilibrium Constant
Methanol	0.51
Ethanol	0.72
<u>n</u> -Hexanol	1.52
<u>n</u> -Nonanol	1.84
Neopentanol	2.7
2-Cyclohexylethanol	1.89
Cyclopropylcarbinol	0.86
Cyclobutylcarbinol	1.4
Cyclopentylcarbinol	2.59
Cyclohexylcarbinol	2.46

in 2 M nitric acid-ceric ammonium nitrate (13).

The value of  $l$  for n-butanol in 2 M nitric acid-ceric ammonium nitrate is close to what would be predicted for n-butanol under our conditions, while constants measured in perchloric acid are significantly higher than ours due to the fact that perchlorate ion competes less effectively than nitrate ion with the alcohol for coordination sites around the cerium(IV) ion.

A comparison of the first four alcohols in Table 5 indicates that the chain length of a primary alcohol has a significant effect on the equilibrium constant, even in going

from the  $C_6$  to the  $C_9$  normal alcohol. Up to  $C_6$  the increase for each carbon added is about 0.2 units and from  $C_6$  to  $C_9$  is about 0.1 units. This effect does not seem to be purely an inductive effect since the inductive effect should fall off rather rapidly as carbons are added to the end of the chain. The most reasonable explanation would seem to lie in a solvent effect which either raises the free energy of the long-chain uncomplexed alcohol with respect to the shorter chain alcohol or lowers the free energy of the long-chain alcohol-cerium(IV) complex with respect to the shorter chain alcohol or both. This possible solvent effect will be discussed later in this dissertation.

The equilibrium constant for cyclopropylcarbinol is 0.86. The constants for ethanol and n-hexanol are 0.72 and 1.52, respectively, leading to the prediction that  $K$  for the straight-chain  $C_4$  alcohol should be about 1.1, if it is assumed that the increase in  $K$  with the addition of carbon atoms is approximately linear over the range  $C_2$ - $C_6$ . In addition, cyclobutylcarbinol which contains five carbon atoms gives an equilibrium constant for complex formation of 1.4. Thus the  $K$  for cyclopropylcarbinol is somewhat less than anticipated and is close to the equilibrium constants found for the benzylic alcohols. This may be a reflection of the special character of the cyclopropane ring.

The effect of branching at the  $\beta$ -position of primary

alcohols can be determined from the equilibrium constants presented in Table 5. If a comparison is made between the  $K$  for n-hexanol (1.5), cyclobutylcarbinol (2.6), and neopentanol (2.7), the conclusion is reached that as the amount of branching at the  $\beta$  position increases with the total number of carbon atoms constant, the equilibrium constant of the cerium(IV)-alcohol complex increases (in 70% aqueous acetonitrile); i.e.,  $K(\text{neopentanol}) > K(\text{cyclobutylcarbinol}) > K(\text{n-hexanol})$ . This is just the opposite of what would be predicted on steric grounds and, indeed, may indicate that the close proximity of the hydrocarbon portion of the molecule to the donor atom (oxygen) is an energetically favorable situation, possibly because of a unique solvent effect.

The same type of effect shows up in a comparison of 2-cyclohexylethanol ( $K=1.9$ ) and cyclohexylcarbinol ( $K=2.5$ ). Here again, moving the branching point nearer to the donor atom increases the equilibrium constant for formation of the cerium(IV)-alcohol complex.

The effect of replacing an  $\alpha$  hydrogen in methanol ( $K=0.5$ ) with methyl to give ethanol ( $K=0.7$ ) and with phenyl to give benzyl alcohol ( $K=0.7$ ) illustrates that the overall effect of a methyl and a phenyl substituent in the  $\alpha$  position is about the same. Since the net inductive effect of a phenyl group with respect to a methyl group is electron withdrawing ( $\sigma_m(\text{phenyl})=0.218$  (46),  $\sigma_m(\text{methyl})=-0.069$  (47) and

$\sigma^*$  (phenyl)=0.600 (48),  $\sigma^*$  (methyl)=0.00 (48), there must be some other effect, possibly a solvation effect, compensating for the electron withdrawing nature of the phenyl group and causing the stabilities of the ethanol and benzyl alcohol complexes to be the same with respect to the uncomplexed alcohols. An alternative explanation is that the phenyl group interacts favorably with the metal ion to a large enough extent to negate some of the destabilization caused by the close proximity of an electron withdrawing group to the donor atom. If this sort of interaction does exist it is not a very large effect since the saturated analog of benzyl alcohol, cyclohexylcarbinol, has  $K=2.5$  compared to 0.7 for benzyl alcohol, indicating that the overall effect of the phenyl group is destabilizing.

#### Secondary alcohols

The equilibrium constants measured for secondary alcohols in 70% aqueous acetonitrile and 0.5 M nitric acid at 21.0° C. are summarized in Table 6. These values may be compared with literature values of 11 for sec-butanol in 1.6-1.7 M perchloric acid-ceric perchlorate (13), 1 for sec-butanol in 2 M nitric acid-ceric ammonium nitrate (13), 2.07 and 1.40 for isopropanol in 1 M nitric acid-ceric nitrate (19) (see historical for discussion of the discrepancy in these reported values), 2.2 and 1.8 for sec-butanol in 1 M nitric acid-ceric nitrate (19) (see historical for discussion of the dis-

Table 6. Equilibrium constants for secondary alcohols in 70% aqueous acetonitrile

Alcohol	Equilibrium Constant
Isopropyl	1.45
3-Heptyl	3.71
Cyclopentyl	2.9
Cyclohexyl	4.30
Cycloheptyl	4.5
Cyclooctyl	5.38

crepancy in these reported values), 2.3 for isopropanol in 1 M perchloric acid-ceric perchlorate (19), 2.1 for isopropanol in 1 M nitric acid-ceric nitrate (19), and 2.9 (kinetic) and 3.9 (spectrophotometric) for cyclohexanol in 1 M perchloric acid-ceric perchlorate (14). There are several inconsistencies in these data, especially in perchloric acid, which make them almost useless for comparative purposes.

A comparison of the equilibrium constants for isopropanol (1.45) and 3-heptanol (3.71) reveals that the same trend evident with primary alcohols is also evident in the secondary alcohols; i.e., lengthening the chain increases the formation constant of the cerium(IV-alcohol complex).

The effect of tying back the ends of the chain may be seen by comparing 3-heptanol ( $K=3.71$ ) and cycloheptanol ( $K=4.5$ ). This may be evidence for the operation of a steric effect, the conformation of cycloheptanol being more favorable than that

of 3-heptanol. The trend with increasing ring size in the cycloalkanols is one of increasing values of the equilibrium constant. Thus the equilibrium constants are 2.9 for cyclopentanol, 4.30 for cyclohexanol, 4.5 for cycloheptanol, and 5.38 for cyclooctanol. The large jump from cyclopentanol to cyclohexanol may well be a conformational effect, since the cyclopentane ring is rather rigid while the  $C_6$ ,  $C_7$ , and  $C_8$  rings are conformationally mobile. Again, the trend with an increasing number of carbon atoms is towards increasingly large values of  $K$ .

#### Tertiary alcohols

The equilibrium constants measured for tertiary alcohols in 70% aqueous acetonitrile-0.5  $M$  nitric acid at 21.0° C. were 2.69 for t-butanol and 8.80 for 1-methylcyclohexanol. Offner and Skoog measured equilibrium constants for t-butanol in 1.6-1.7  $M$  perchloric acid-ceric perchlorate and in 2  $M$  nitric acid-ceric ammonium nitrate and found values of 13 and 0.6, respectively (13). The discrepancy between our value and Offner and Skoogs' value for the equilibrium constant for t-butanol in 2  $M$  nitric acid-ceric ammonium nitrate is probably a solvation effect due to the acetonitrile.

The large increase in  $K$  in going from t-butanol to 1-methylcyclohexanol is rather hard to explain. The addition of three more carbons to t-butanol would be expected to have the effect of increasing  $K$ , but based on the increases

observed for primary and secondary alcohols a greater than three-fold change is entirely unexpected. It is suggested that there may be an effect operating whereby the more carbon atoms there are near to the donor atom, the higher the value of  $K$ . Thus lengthening the chain of a primary alcohol has the effect of increasing  $K$  (a change by a factor of 2.1 from ethanol to n-hexanol), but to a lesser extent than with secondary alcohols (a change by a factor of 2.6 from isopropanol to 3-heptanol). The changes in the primary and secondary alcohols are less in turn than with tertiary alcohols (a change of a factor of 3.3 from t-butanol to 1-methylcyclohexanol). This change may be due to a solvation effect as discussed later.

Comparisons of equilibrium constants for primary, secondary, and tertiary alcohols in 70% aqueous acetonitrile

Offner and Skoog measured equilibrium constants for n-, sec-, and t-butanol-cerium(IV) complexes in 1.6-1.7 M perchloric acid and in 2 M nitric acid (13). In perchloric acid they found that the constant for n-butanol ( $K=16$ ) > t-butanol ( $K=13$ ) > sec-butanol ( $K=11$ ), i.e.,  $1^{\text{a}} > 3^{\text{a}} > 2^{\text{a}}$ . In nitric acid they found that n-butanol ( $K=1$ ) = sec-butanol ( $K=1$ ) > t-butanol ( $K=0.6$ ), i.e.,  $1^{\text{a}} = 2^{\text{a}} > 3^{\text{a}}$ . In general, then, they found that in aqueous solution the equilibrium constant for a primary alcohol-cerium(IV) complex was greater than for a secondary or tertiary alcohol-cerium(IV) complex in a series where all the alcohols had the same number of carbon atoms.



Other 1<sup>o</sup>-2<sup>o</sup>-3<sup>o</sup> alcohol comparisons among literature values are considerably complicated by the fact that the equilibrium constants have been measured under different conditions.

We have found that in 70% aqueous acetonitrile-0.5 M nitric acid-ceric ammonium nitrate at 21.0° C. tertiary alcohol-cerium(IV) complexes have higher formation constants than secondary alcohol-cerium(IV) complexes which in turn have greater formation constants than primary alcohol-cerium(IV) complexes among alcohols with approximately the same number of carbon atoms. This is illustrated by the series t-butanol (K=2.7) > isopropanol (K=1.45) > ethanol (K=0.7). This trend, 3<sup>o</sup> > 2<sup>o</sup> > 1<sup>o</sup>, is nearly the opposite of that found by Offner and Skoog (13).

Several other series of alcohols may be cited which support this trend, for example 1-methylcyclohexanol (K=8.8) > cyclohexanol (K=4.3), 3-heptanol (K=3.7) > n-hexanol (K=1.5), 1-methylcyclohexanol (K=8.8) > 3-heptanol (K=3.7) > cyclohexylcarbinol (K=2.5), cyclohexanol (K=4.3) > n-hexanol (K=1.5), cyclooctanol (K=5.4) > 2-cyclohexylethanol (K=1.9), cycloheptanol (K=4.5) > cyclohexylcarbinol (K=2.5), cyclohexanol (K=4.3) > cyclopentylcarbinol (K=2.6), cyclopentanol (K=2.9) > cyclobutylcarbinol (K=1.4).

However, this generalization breaks down badly when alcohols which differ in the total number of carbon atoms as well as the amount of branching at the  $\alpha$ -carbon are considered.

For example, the primary alcohol neopentanol has an equilibrium constant ( $K=2.7$ ) which is greater than the secondary alcohol isopropanol ( $K=1.45$ ), and equal to the tertiary alcohol t-butanol ( $K=2.7$ ). Furthermore, all the primary alcohols with six carbons or more have equilibrium constants greater than that of the secondary alcohol isopropanol.

The general trend of  $3^{\text{a}} > 2^{\text{a}}$  also breaks down when secondary and tertiary alcohols with different numbers of carbon atoms are considered. For example, all the secondary alcohols with five carbons or more have cerium(IV)-alcohol equilibrium constants greater than that of t-butanol.

It is apparent that both the total number of carbon atoms and the amount of chain branching are of the same relative importance in determining the equilibrium constants for cerium(IV)-alcohol complexes. An attempt at a more quantitative treatment of the effect of chain substitution will be made later in this dissertation.

#### Alcohols with two oxygen atoms

The equilibrium constants measured for glycol and glycol monoalkyl ether complexes with cerium(IV) in 70% aqueous acetonitrile-0.5 M nitric acid at 21.0° C. are summarized in Table 7.

Several equilibrium constants for cerium(IV)-glycol complexes have been reported in the literature. These are tabulated in Table 3. The equilibrium constant for 2,3-

Table 7. Equilibrium constants for glycols and glycol mono-alkyl ethers in 70% aqueous acetonitrile

Alcohol	Equilibrium Constant
Ethylene glycol	3.00
1,3-Propanediol	4.38
1,4-Butanediol	2.64
1,5-Pentanediol	3.26
2-Methoxyethanol	1.32
3-Ethoxypropanol	1.09

butanediol of 24-25 was obtained from kinetic measurements and seems too high based on our results and the findings of Offner and Skoog who found values of  $K=3.1$  for 1,3-butanediol,  $K=2.6$  for 1,4-butanediol, and  $K=3.2$  for diethylene glycol. The values reported by Offner and Skoog (13) seem more in line with our values. The equilibrium constants measured in perchloric acid cannot be compared with ours since ours were measured in nitric acid.

Comparison of the equilibrium constants for diols with those for the corresponding mono-ols shows that the equilibrium constants for the diols are several times as great as the constants for the mono-ols having about the same number of carbon atoms (Table 3). For example, the equilibrium constant for ethanol is 0.72 and that for ethylene glycol is 3.00; the constant for 1,3-propanediol is 4.38 and for n-butanol is 1.1 (predicted value); the constant for

1,4-butanediol is 2.64 and for n-pentanol is 1.3 (predicted value); the constant for 1,5-pentanediol is 3.26 and for n-hexanol is 1.52. It should be noted, however, that on a statistical basis the constants for the diols should be twice as great as those for the corresponding mono-ols if the second hydroxyl group has no stabilizing effect on the complex, and significantly more than twice as great if there is chelate formation. Inspecting the diol-mono-ol comparisons made directly above in this light reveals that the second hydroxyl group has a stabilizing effect of 0.47 kcal./mole comparing ethylene glycol and ethanol, 0.44 kcal./mole comparing 1,3-propanediol and n-butanol, but no stabilizing effect when comparing 1,4-butanediol and n-pentanol and 1,5-pentanediol and n-hexanol. Thus the second hydroxyl group has a significant stabilizing effect in the ethylene glycol-cerium(IV) and 1,3-propanediol-cerium(IV) complexes, but not in the four and five carbon diol complexes. It appears, then, that there is no bidentate complexing of cerium(IV) with the four and five carbon diols. However, the extra stability of the two and three carbon diol-cerium(IV) complexes remains to be explained. The most obvious explanation is that both hydroxyl groups in the diol are bound to the cerium(IV). This postulate has been advanced in the literature (4). However, an alternate explanation is that one hydroxyl group is bound to the cerium(IV) while the

second is hydrogen bonded to ligands in the first coordination sphere of the metal ion.

The subject of bidentate complexing in the diol-cerium(IV) complexes should be critically examined in light of our results and results already recorded in the literature. As previously mentioned, our results indicate that the addition of a second hydroxyl group at C<sub>2</sub> or C<sub>3</sub> of a mono-ol increases the free energy change for complexation with cerium(IV) by an amount 0.4-0.5 kcal./mole greater than predicted on a statistical basis. Introduction of a second hydroxyl at C<sub>4</sub> or C<sub>5</sub> has essentially no extra stabilizing effect and gives only the statistical doubling of the equilibrium constant. It is apparent that the second hydroxyl group in the C<sub>2</sub> and C<sub>3</sub>- $\alpha,\omega$ -diols is somehow contributing extra stability to the C<sub>2</sub> and C<sub>3</sub> diol-cerium(IV) complexes. As suggested above, this may be explained in two ways: 1) both hydroxyl groups are bound to the metal ion; 2) one hydroxyl is bound to the metal ion and the second interacts in a favorable fashion, possibly through hydrogen bonding, with the first coordination sphere of the metal ion.

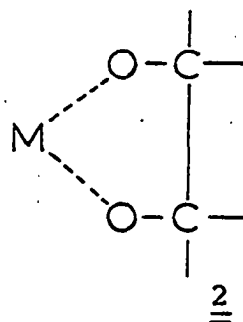
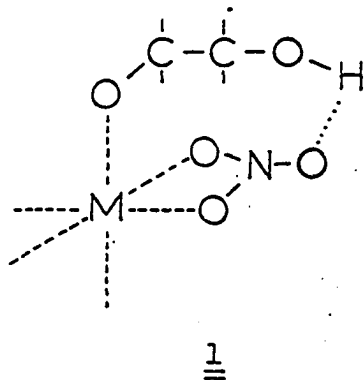
The question of bidentate vs. monodentate complexing will not be an easy one to answer, since the  $\Delta G$  for complex formation is only ca. -0.5 kcal./mole for typical mono-ols while hydrogen bonding (in ethanol) can amount to ca. 5 kcal./mole (49). It is easy to see that even a weak hydrogen bond by

the second hydroxyl group to the first coordination sphere of the metal ion could easily contribute as much stabilization to the cerium(IV)-glycol complex as the formation of a second metal-hydroxyl bond. Thus comparisons of equilibrium constants for various cis, trans pairs of glycols must be used with caution since the same stereochemical feature which may prevent the second hydroxyl from bonding with the metal ion may also prevent hydrogen bonding with the first coordination sphere of the metal ion.

While several authors have suggested the formation of a bidentate diol-cerium(IV) complex on the basis of the relatively large values of the diol-cerium(IV) equilibrium constant observed (4), the study of Hintz and Johnson is the most complete with regard to establishing bidentate complexation (14). They measured equilibrium constants for the cis- and trans-1,2-cyclohexanediols and for trans-2-methoxycyclohexanol and cyclohexanol with ceric perchlorate in perchloric acid and found values of  $K$  of 29.3 for cis-1,2-cyclohexanediol, 18.6 for trans-1,2-cyclohexanediol, 2.9 for trans-2-methoxycyclohexanol, and 3.9 for cyclohexanol from spectrophotometric data. These results would seem to argue for bidentate complexing in the 1,2-diols but not with trans-2-methoxycyclohexanol. The higher value of  $K$  for cis-1,2-cyclohexanediol as compared to trans-1,2-cyclohexanediol was explained on the basis of a conformationally mobile bidentate

complex being formed with the cis diol while the trans diol would lead to a conformationally rigid bidentate complex. Entropy factors would then favor the cis diol complex over the trans. This seems to be a reasonable argument for bidentate complexing since there should be little, if any, stereochemical preference for hydrogen bonding of the second hydroxyl to the first coordination sphere of the metal ion (1), whereas the more restricted bidentate complex 2 should show the entropy effects that were found. This, then, seems to be a strong, if not conclusive, argument for the binding of both hydroxyls to the metal ion.

Hintz and Johnson also investigated the cis- and trans-1,2-cyclopentanediol systems. These diols were sufficiently unstable with respect to oxidation that entropies of activation had to be used as a probe for bidentate complexation. They found that the entropies of activation were approximately the same for cis- and trans-1,2-cyclopentanediols and suggested that these diols are oxidized via an acyclic (i.e., monodentate) mechanism.



It thus seems from the work of Hintz and Johnson that there is evidence for bidentate coordination of 1,2-diols to ceric ion (14). However, the additional stability of the ceric ion-glycol complexes relative to ceric ion-alcohol complexes, ca. 0.5 kcal./mole, is sufficiently small that the possibility of monodentate coordination of glycols with ceric ion must be considered.

The effect of substitution of a methyl group for one hydroxyl hydrogen of a glycol is shown in the equilibrium constant for 2-methoxyethanol ( $K=1.32$ ) as compared to ethylene glycol ( $K=3.00$ ). The change decreases the stability of the complex, but it is interesting to note that the equilibrium constant for 2-methoxyethanol is still greater than those for ethanol ( $K=0.72$ ) and n-butanol ( $K=1.1$ ), indicating that the methoxyl group has some stabilizing effect when compared to hydrogen or ethyl.

The substitution of an ethyl group for one of the hydroxyl hydrogens in 1,3-propanediol ( $K=4.38$ ) decreases the equilibrium constant substantially to 1.09. This value of the equilibrium constant for 3-ethoxypropanol may be compared to values of 0.72 for ethanol, 0.9 (predicted value) for n-propanol, and 1.52 for n-hexanol. Since 3-ethoxypropanol can be considered a 4-oxahexanol, n-hexanol might be a good alcohol with which to compare it. If this is done it is seen that the oxygen atom of the ethoxy moiety has a destabilizing



effect and is almost certainly not coordinating with the metal ion in a bidentate fashion.

$\beta$ -Substituted ethanols

A series of  $\beta$ -substituted ethanols was investigated in order to ascertain whether bidentate-type complexing occurs in systems other than glycols. The results in 70% aqueous acetonitrile, 0.5 M nitric acid, and ceric ammonium nitrate at 21.0° C. are presented in Table 8.

The equilibrium constants for 3-buten-1-ol and 2-phenylethanol with cerium(IV) were measured in order to ascertain whether a pi electron system can interact with a

Table 8. Equilibrium constants for  $\beta$ -substituted ethanols in 70% aqueous acetonitrile

Alcohol	Equilibrium Constant
Ethanol	0.72
3-Buten-1-ol	0.98
2-Phenylethanol	2.24
2-Cyclohexylethanol	1.89
2-Chloroethanol	0.13 <sup>a</sup>
Ethylene glycol	3.00
2-Methoxyethanol	1.32

<sup>a</sup>The experimental error in this measurement may be as large as +0.4.

cerium(IV) ion in a fashion so as to increase the formation constant of the complex. It is apparent that the constant for 3-buten-1-ol is greater than that for ethanol. However, due to the trend towards larger equilibrium constants with increasing chain length discussed earlier, comparison of the equilibrium constant for 3-buten-1-ol with that for n-butanol should be a better indication of whether any favorable interaction between pi system and metal ion can occur. The equilibrium constant for n-butanol in 70% aqueous acetonitrile was not measured, but a value of 1.1 can be arrived at by interpolation between ethanol and n-hexanol. If 1.1 is a valid value for the n-butanol-cerium(IV) complex formation constant in this medium, then the value of 0.98 for 3-buten-1-ol indicates that the unsaturation has a destabilizing effect as compared to the saturated system and hence in this system no favorable pi-metal ion interaction occurs.

The equilibrium constant for 2-phenylethanol was measured because this alcohol provided a more extensive pi system than did 3-buten-1-ol. The high value of  $K=2.24$  for 2-phenylethanol compared to 0.72 for ethanol seems to indicate that the phenyl substitution has a favorable effect on  $K$ . A better alcohol with which to compare 2-phenylethanol is 2-cyclohexylethanol, the saturated analog. A value of  $K=1.89$  was found for 2-cyclohexylethanol. Thus substitution of a phenyl group for a

cyclohexyl group results in an increase in  $K$  of 0.35 units, which represents a stabilization of 0.11 kcal./mole. Models of 2-phenylethanol indicate that the aromatic ring and the hydroxyl group can be positioned in such a fashion that the metal ion can be sandwiched between them. However, there is no way to demonstrate that the extra stability of the 2-phenylethanol-cerium(IV) complex is not due to a secondary interaction of the aromatic ring with ligands in the first coordination sphere of the metal ion or some similar effect.

The question of bidentate complexing of ethylene glycol and 2-methoxyethanol with cerium(IV) has been discussed in the previous section. Suffice it to repeat here that there may be bidentate complexing in the ethylene glycol-cerium(IV) system and that this is attenuated to a large extent in going to 2-methoxyethanol.

The equilibrium constant for 2-chloroethanol, 0.13, appears to be sufficiently low that any significant amount of chlorine-cerium(IV) interaction can be ruled out. It should be noted, however, that the experimental error in this measurement was rather large (see Table 8).

#### Other functionalized alcohols

Equilibrium constants were measured for 4-phenylbutanol and 5-hexenol to determine whether a pi system several carbons removed from the donor atom might interact with the metal ion. The values determined in 0.5 M nitric acid-ceric ammonium

nitrate in 70% aqueous acetonitrile at 21.0° C. were 1.42 for 5-hexenol and 1.60 for 4-phenylbutanol.

Comparison of the equilibrium constant for 5-hexenol with that of n-hexanol ( $K=1.52$ ) shows that the introduction of unsaturation decreases the formation constant for the complex by a slight amount. Introduction of a phenyl substituent into the 4-position of butanol seems to have little effect on the formation constant of the complex. When compared to n-butanol ( $K=1.1$ , predicted), it appears that the phenyl group has some stabilizing influence. However, when compared with the nine carbon straight chain alcohol, n-nonanol, for which  $K=1.84$ , the effect of the phenyl group appears to be destabilizing. Thus it appears that in 5-hexenol and 4-phenylbutanol there is no stabilization of the complex by the pi system.

#### Effect of added nitrate ion

The equilibrium constants for the t-butanol-cerium(IV) complex were measured in water with  $[\text{HNO}_3]=0.5 \text{ M}$  and [ceric ammonium nitrate]= $0.02 \text{ M}$  at 21.0° C. with and without added salt. The results are summarized in Table 9.

The addition of  $0.2 \text{ M}$  sodium perchlorate has essentially no effect on the equilibrium constant since the values with and without added sodium perchlorate are the same within experimental error. The addition of  $0.2 \text{ M}$  sodium nitrate, however, depressed the equilibrium constant by an amount which

seems to be outside of experimental error. Thus increasing the total concentration of nitrate ion from 0.8 M to 1.0 M depresses the equilibrium constant a significant amount. This is postulated to be the result of competition between nitrate ion and alcohol for coordination sites around the metal ion. This observation is consistent with the results of Sethuram and Muhammad (19) who found that the rates of oxidation of isopropanol and sec-butanol by ceric nitrate are inversely proportional to the square of the nitrate ion concentration, consistent with a competition between nitrate ion and alcohol for coordination sites around the ceric ion.

Equilibrium constants in water and 70% aqueous acetic acid

A series of equilibrium constants was measured in water and in 70% aqueous acetic acid at 21.0° C. with the concentration of nitric acid 0.5 M and the concentration of ceric ammonium nitrate 0.02 M. The results along with the equilibrium constants measured in 70% aqueous acetonitrile are summarized in Table 10.

Table 9. Effect of added salt on the cerium(IV)-t-butanol complex in water at 21.0° C.

Additive	[NO <sub>3</sub> <sup>-</sup> ]	Equilibrium Constant
None	0.8 <u>M</u>	0.53
0.2 <u>M</u> NaClO <sub>4</sub>	0.8 <u>M</u>	0.49
0.2 <u>M</u> NaNO <sub>3</sub>	1.0 <u>M</u>	0.33

Table 10. Equilibrium constants in water, 70% aqueous acetic acid, and 70% aqueous acetonitrile

Alcohol	Equilibrium Constant		
	Water	70% Aqueous Acetic Acid	70% Aqueous Acetonitrile
Ethanol	1.2	0.15	0.72
<u>n</u> -Butanol	1.6	0.40	1.1 <sup>a</sup>
Isopropanol	0.82	0.43	1.45
<u>t</u> -Butanol	0.53	0.65	2.69

<sup>a</sup>Predicted value.

It is interesting to note the trends in each solvent system as the alcohol is changed from primary to secondary to tertiary. The trend found in acetonitrile is tertiary > secondary > long-chain primary > short-chain primary. In 70% aqueous acetic acid the trend is about the same, tertiary > secondary ~ long-chain primary > short-chain primary. The fact that the trend observed in 70% aqueous acetonitrile is about the same as that found in 70% aqueous acetic acid might be due to the fact that acetic acid and acetonitrile have similar structural features, i.e., a hydrocarbon portion attached to a polar part. The lower values of K in 70% aqueous acetic acid may well be due to the formation of cerium(IV)-acetate complexes (see historical) which reduce the amount of cerium(IV)-alcohol complex formation.

The trend observed in water is long-chain primary > short-chain primary > secondary > tertiary. This is similar

to the trend observed by Offner and Skoog for constants measured in 2 M nitric acid (13) where they found  $K(\underline{n}\text{-butanol}) > K(\underline{\text{sec}}\text{-butanol}) > K(\underline{t}\text{-butanol})$ . The actual values found by Offner and Skoog were 1, n-butanol; 1, sec-butanol; 0.6, t-butanol. These values compare favorably with ours.

It is apparent that the trend for 1<sup>d</sup> vs. 2<sup>d</sup> vs. 3<sup>d</sup> cerium(IV)-alcohol complexes is completely reversed in aqueous solution from what it is in 70% aqueous acetic acid or 70% aqueous acetonitrile. Whereas the tertiary alcohol-cerium(IV) complexes have the highest formation constants in the aqueous organic solvents, the primary alcohol-cerium(IV) complexes have the highest formation constants in aqueous solution. This reversal is difficult to understand and will be discussed in a later section.

It is interesting to note that the tendency for the equilibrium constants for long-chain primary alcohol-cerium(IV) complexes to be greater than for short-chain primary alcohol-cerium(IV) complexes exists in water as well as in the aqueous organic solvents. The simplest way to explain this tendency is that it is the result of the additional electron donating inductive effect of the extra part of the chain resulting in an increase in electron density at the donor atom thus increasing the equilibrium constant. However, this is probably an oversimplification since the effect is rather

large for a purely inductive effect.

#### Solvent effect

As has been seen earlier in this discussion, equilibrium constants for alcohol-cerium(IV) complex formation in 70% aqueous acetonitrile and 70% aqueous acetic acid conform to the trend tertiary alcohol > secondary alcohol > primary alcohol, while in water the trend is primary ~ secondary > tertiary. In rationalizing these solvent effects the free energies of uncomplexed alcohol, uncomplexed cerium(IV), and cerium(IV)-alcohol complex must be considered since the equilibrium constant is a function of the total free energy difference between uncomplexed reactants and complexed products.

The fact that equilibrium constants in 70% aqueous acetonitrile and 70% aqueous acetic acid follow the trend tertiary alcohol > secondary alcohol > primary alcohol may be due to steric effects on solvation of the uncomplexed alcohol being more important than steric effects on solvation of the complex. That is, the equilibrium constant for tertiary alcohol-cerium(IV) complex formation would be greater than for primary alcohol-cerium(IV) complex formation because the uncomplexed tertiary alcohol is of higher energy than the primary alcohol while the energy of the complex remains relatively constant.

In water this effect is reversed. The fact that primary



alcohol  $\sim$  secondary alcohol  $>$  tertiary alcohol could be explained as due to steric effects on solvation of the complex being more important than steric effects on solvation of the uncomplexed alcohol. Thus the primary alcohol-cerium(IV) complex would be more stable (lower energy) than the tertiary alcohol-cerium(IV) complex while the uncomplexed alcohols remain about the same energy, making the equilibrium constant for primary alcohol-cerium(IV) complex formation greater than that for tertiary alcohol-cerium(IV) complex formation.

Since the hydroxyl group of the alcohol is in rather different steric and electronic environments in uncomplexed alcohol and in the alcohol-cerium(IV) complex, it is quite reasonable that there should be a marked solvent effect on the magnitude of the equilibrium constants.

#### Semiquantitative Treatment of the Effect of Substitution on the Equilibrium Constant

The free energy changes,  $\Delta F(\text{kcal./mole})$ , associated with each equilibrium constant measured in 70% aqueous acetonitrile are summarized in Table 3.

#### Effect of addition of carbon atoms

It is of interest first to examine the effect of addition of carbon atoms to the alcohol on the free energy change for complex formation. If the assumption is made that the free energies of uncomplexed alcohol and cerium(IV) are rela-

tively constant throughout the series of alcohols, then the free energy change can be taken as a measure of the stability of the cerium(IV)-alcohol complex.

The effect of lengthening a normal chain alcohol in 70% aqueous acetonitrile is indicated by the following (free energies are given in kcal./mole): methanol to ethanol,  $\Delta\Delta F=0.12/\text{carbon}$ ; n-hexanol to n-nonanol,  $\Delta\Delta F=0.4/\text{carbon}$ . Thus it is seen that the effect per added carbon atom decreases as the chain length increases. The effect of lengthening the chain in a secondary alcohol is seen in the series isopropanol to 3-heptanol where  $\Delta\Delta F=0.15/\text{carbon}$ , about the same as found in the ethanol to n-hexanol series.

In water as solvent the effect of chain lengthening is slightly less than in 70% aqueous acetonitrile as illustrated by the series ethanol to butanol,  $\Delta\Delta F=0.10/\text{carbon}$ . In 70% aqueous acetonitrile the effect of chain lengthening in the ethanol to n-hexanol series is 0.12/carbon.

The effect of branching at the position  $\alpha$  to the hydroxyl group is seen in the following series in 70% aqueous acetonitrile: methanol to ethanol,  $\Delta\Delta F=0.22/\text{carbon}$ ; ethanol to isopropanol,  $\Delta\Delta F=0.45/\text{carbon}$ ; isopropanol to t-butanol,  $\Delta\Delta F=0.39/\text{carbon}$ . The average  $\Delta\Delta F$  in this methanol to t-butanol series is 0.35/carbon. It can be seen by comparison of this value with those found for chain lengthening cited above (0.22-0.04/carbon), that  $\alpha$ -branching has a larger effect on K

and (probably) the stability of the alcohol-cerium(IV) complex than does chain lengthening in 70% aqueous acetonitrile.

The effect of  $\alpha$  branching is further illustrated by the following examples: benzyl alcohol to  $\alpha$ -methylbenzyl alcohol,  $\Delta\Delta F=0.56/\text{carbon}$ ; cyclohexanol to 1-methylcyclohexanol,  $\Delta\Delta F=0.46/\text{carbon}$ . The effect of  $\alpha$  substitution upon K appears to become larger as the size of the alcohol increases as is illustrated by comparison of the effect per carbon in these series and in the methanol to t-butanol series discussed above.

The effect of  $\beta$  substitution is illustrated by the ethanol-neopentanol series where three methyl groups are added to ethanol to give neopentanol. Here the  $\Delta\Delta F$  is 0.28/carbon.

A comparison of the effect on K of chain lengthening,  $\alpha$  substitution and  $\beta$  substitution in the alcohol thus leads to the conclusion that  $\alpha$  branching is more important and has a greater stabilizing influence than  $\beta$  branching which, in turn, is more important than chain lengthening (in 70% aqueous acetonitrile). In aqueous solution in the one series available, chain lengthening appears to have about the same effect as in 70% aqueous acetonitrile. However,  $\alpha$  branching has a definite destabilizing effect with the t-butanol-cerium(IV) complex having the lowest K of the series.

Effect of rearrangement of the carbon skeleton of the alcohol in 70% aqueous acetonitrile

It is also interesting to examine the effect on  $K$  of changing the arrangement of the carbon skeleton of the alcohol while maintaining the number of carbon atoms constant. The effect of changing from a normal chain alcohol to an  $\alpha$ -branched alcohol is illustrated by the following:  $n$ -hexanol - cyclohexanol,  $\Delta\Delta F=0.66$  kcal./mole;  $n$ -pentanol (predicted value) - cyclopentanol,  $\Delta\Delta F=0.51$  kcal./mole. The change from a secondary  $\alpha$  position to a tertiary  $\alpha$  position is illustrated by cycloheptanol - 1-methylcyclohexanol where  $\Delta\Delta F=0.43$  kcal./mole.

The effect of rearrangement of the carbon skeleton of the alcohol to give  $\beta$  branching is illustrated by the series  $n$ -pentanol (predicted value) - cyclobutylcarbinol,  $\Delta\Delta F=0.05$  kcal./mole; cyclobutylcarbinol - neopentanol,  $\Delta\Delta F=0.42$  kcal./mole. Thus it is apparent that rearrangement of the carbon skeleton of the alcohol to give  $\alpha$  branching has a greater stabilizing effect than rearranging it to give  $\beta$  branching.

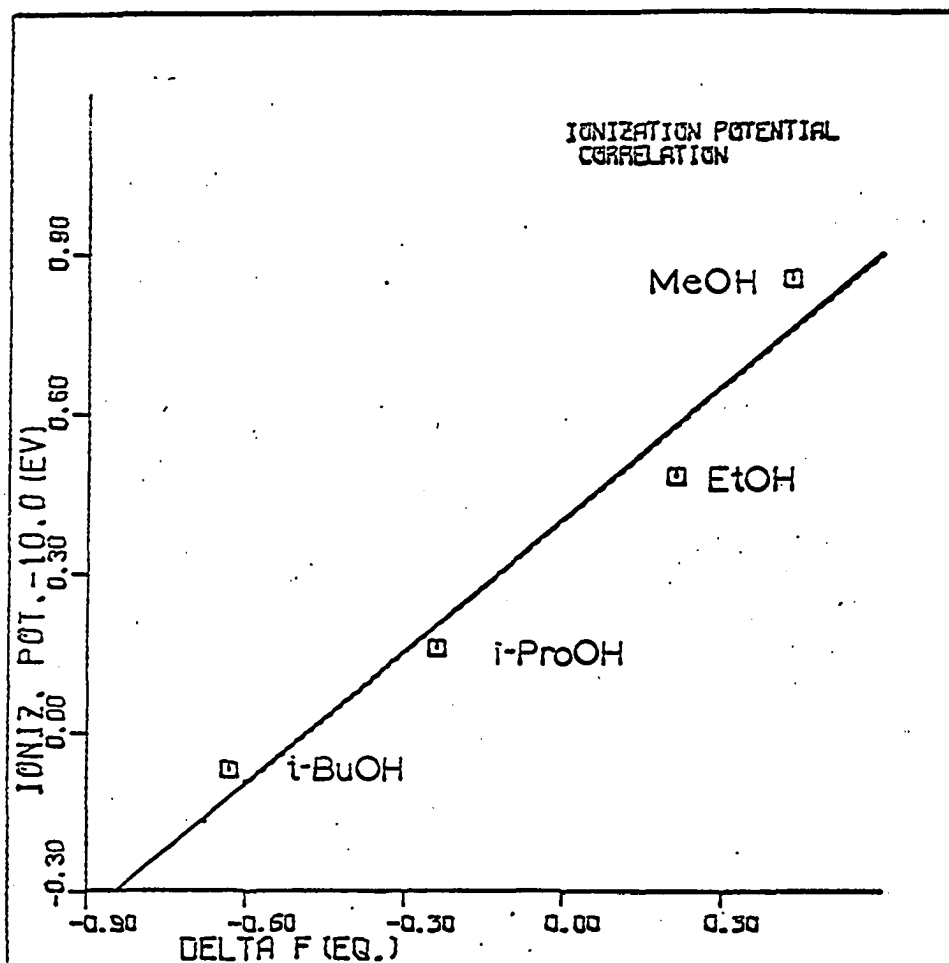
Correlation of  $K$  with ionization potentials

Ionization potentials for several alcohols have been derived from alcohol-iodine charge transfer complexes by Kurylo and Jurinski (50). There is an interesting correlation between  $\Delta F_{eq}$  for cerium(IV)-alcohol complex formation and

the ionization potential of the alcohol as illustrated in Figure 5. This correlation can be rationalized on the following basis.

The ionization potential of an alcohol should be a function of the electron density on oxygen. The electron density on oxygen should increase with increasing substitution due to the electron donating capabilities of the additional substituents. Thus one expects a decrease in the I.P. of an alcohol with increasing substitution. Likewise one expects the strength of the metal ion-oxygen interaction to increase with increasing substitution thus increasing  $K$ . These trends are evidenced in Figure 5.

Figure 5. Correlation of  $\Delta F_{eq}$  with ionization potentials of some alcohols



## EXPERIMENTAL

General Procedure for Measurement  
of Equilibrium Constants

A solution of 0.0666 M ceric ammonium nitrate (CAN) was prepared by dissolving ca. 0.913 g. CAN in 1.637 M nitric acid solution, the total volume being 25 ml. A 1-2 M solution of the alcohol was prepared by dissolving the appropriate amount of alcohol in acetonitrile, the total volume of solution being 25 ml. A quantity of 3.0 ml. of the CAN solution was pipetted into a 10-ml. volumetric flask and the solution was diluted to 10 ml. with acetonitrile. The absorbance at 520  $\mu$  was measured as rapidly as possible.

A quantity of 3.0 ml. of the CAN solution was pipetted into a 10 ml. volumetric flask, a few ml. of acetonitrile was added, and 1.0 ml. of the alcohol solution was added. The time was noted and the solution was diluted to 10.0 ml. with acetonitrile. A portion of the solution was transferred to a cuvette (1 cm.) and the absorbance at 520  $\mu$  was measured at 1.0 min., 1.5 min., and 2.0 min. after the first time noted. This procedure was repeated using 2.0 ml., 3.0 ml., 4.0 ml., and 5.0 ml. of the alcohol solution.

If there was a decrease in absorbance of the cerium(IV)-alcohol solution during the time the absorbance was measured, the absorbance value used in calculating the equilibrium constant was determined by extrapolating absorbance to zero time, usually assuming that absorbance decreased linearly with



time. In a few cases the solution faded so rapidly during the absorbance measurement at the highest alcohol concentration that this point could not be used in determining the equilibrium constant.

The concentrations of CAN and alcohol and the calculated data are summarized in Table 11.

#### Modified Procedures

In addition to 70% aqueous acetonitrile as a solvent for the equilibrium constant measurements, 70% aqueous acetic acid, water, and water with added salts were used. For the measurements in 70% aqueous acetic acid and water, glacial acetic acid and water were substituted for acetonitrile in the general procedure described above. For measurements in water with added salt, the appropriate amount of salt was added to the solid CAN before dissolution and dilution.

In the experiment with added sodium perchlorate, 2.1327 g. of anhydrous sodium perchlorate was added to the solid CAN making the concentration 0.2090 M in the cerium(IV)-alcohol solutions. In the experiment with added sodium nitrate, 1.4219 g. was added, making the concentration of sodium nitrate 0.2010 M in the cerium(IV)-alcohol solutions.

Table 11. CAN and alcohol concentrations and calculated data for equilibrium constant measurements

Alcohol	[CAN] <sup>a</sup>	[Alcohol] <sup>b</sup>	Slope+ St. Dev. <sup>c</sup>	Intercept+ St. Dev. <sup>c</sup>
Benzyl	0.0205	1.9958	0.4536±0.0051	0.3324±0.0139
	0.0205	1.9958	-1.3380±0.0874	148.98±6.73 <sup>d</sup>
p-Methylbenzyl	0.0201	1.0319	0.3148±0.0015	0.2523±0.0081
	0.0201	1.0319	-1.2768±0.0595	205.67±7.63 <sup>d</sup>
o-Chlorobenzyl	0.0207	1.0082	0.7140±0.0022	0.3736±0.0118
	0.0207	1.0082	-1.8428±0.0542	130.13±3.20 <sup>d</sup>
m-Chlorobenzyl	0.0206	1.9901	0.5670±0.0037	0.4098±0.0100
	0.0206	1.9901	-1.4091±0.0553	124.44±3.41 <sup>d</sup>
p-Chlorobenzyl	0.0206	2.0998	0.4600±0.0023	0.3201±0.0062
	0.0206	2.0998	-1.4139±0.0442	154.38±3.38 <sup>d</sup>
m-Nitrobenzyl	0.0205	1.6086	0.8425±0.0095	0.3880±0.0321
	0.0205	1.6086	-2.0726±0.2330	125.32±1.11 <sup>d</sup>
p-Nitrobenzyl	0.0208	1.3669	0.7246±0.0024	0.4521±0.0095
	0.0208	1.3669	-1.6504±0.0421	113.40±2.26 <sup>d</sup>
α-Methylbenzyl	0.0206	2.0177	0.2712±0.0077	0.5641±0.0205
	0.0206	2.0177	-0.4544±0.0354	88.412±3.149 <sup>d</sup>

<sup>a</sup>CAN concentration in the CAN-alcohol solution.

<sup>b</sup>Alcohol concentration before dilution.

<sup>c</sup>Slope and intercept are calculated from slope-intercept equation unless otherwise indicated.

<sup>d</sup>Calculated from slope equation.

Table 11 (Continued)

Alcohol	[CAN] <sup>a</sup>	[Alcohol] <sup>b</sup>	Slope+ St. Dev. <sup>c</sup>	Intercept+ St. Dev. <sup>c</sup>
$\alpha$ -Methylbenzyl	0.0202	1.0738	0.3043+0.0026	0.5369+0.0131
	0.0202	1.0738	-0.5462+0.0200	94.675+2.170 <sup>d</sup>
Benzhydrol	0.0207	1.4628	0.2211+0.0022	0.3311+0.0091
	0.0207	1.4628	-0.6483+0.0301	147.57+4.42 <sup>d</sup>
Benzhydrol	0.0206	1.0474	0.2374+0.0020	0.3250+0.0105
	0.0206	1.0474	-0.7003+0.0311	149.72+4.60 <sup>b</sup>
Methanol	0.0204	1.5629	1.204+0.009	0.6134+0.0321
Ethanol	0.0200	1.0129	0.7898+0.0010	0.5717+0.0533
<u>n</u> -Hexanol	0.0202	1.0274	0.3509+0.0057	0.5333+0.0301
<u>n</u> -Nonanol	0.0200	1.0109	0.3381+0.0019	0.6147+0.0103
Neopentyl	0.0206	0.9827	0.1785+0.0012	0.4926+0.0069
2-Cyclohexyl- ethanol	0.0201	0.9614	0.2702+0.0006	0.5105+0.0032
Cyclopropyl- carbinol	0.0200	1.0933	0.7143+0.0022	0.6109+0.0107
Cyclobutyl- carbinol	0.0200	0.8602	0.3078+0.0024	0.4448+0.0151
Cyclopentyl- carbinol	0.0205	1.0228	0.2615+0.0059	0.6775+0.0310
Cyclohexyl- carbinol	0.0199	1.0112	0.1945+0.0008	0.4786+0.0045
3-Butenol	0.0201	1.0005	0.5358+0.0019	0.5226+0.0105
5-Hexenol	0.0201	0.9930	0.3906+0.0055	0.5534+0.0300
2-Phenylethanol	0.0205	1.0433	0.3930+0.0082	0.8811+0.0426
4-Phenylbutanol	0.0206	1.0660	0.3165+0.0032	0.5070+0.0162

Table 11 (Continued)

Alcohol	[CAN] <sup>a</sup>	[Alcohol] <sup>b</sup>	Slope St. Dev. <sup>c</sup>	Intercept+ St. Dev. <sup>c</sup>
Ethylene glycol	0.0197	0.9243	0.2146+0.0007	0.6483+0.0040
1,3-Propanediol	0.0203	1.1248	0.1418+0.0024	0.6202+0.0117
1,4-Butanediol	0.0200	1.0680	0.2251+0.0034	0.5930+0.0172
1,5-Pentanediol	0.0203	0.9895	0.2011+0.0023	0.6555+0.0128
2-Methoxyethanol	0.0202	1.0305	0.5795+0.0051	0.7621+0.0267
2-Chloroethanol	0.0199	1.2536	2.610+0.045	0.3298+0.1951
3-Ethoxypropanol	0.0201	0.9187	0.5211+0.0037	0.5698+0.0190
Isopropanol	0.0208	1.9848	0.4904+0.0073	0.7124+0.0200
3-Heptanol	0.0206	1.0246	0.1551+0.0021	0.5758+0.0109
Cyclopentanol	0.0201	1.0543	0.1276+0.0018	0.3692+0.0100
Cyclohexanol	0.0202	1.0035	0.1415+0.0030	0.6080+0.0163
Cycloheptanol	0.0205	1.0153	0.1241+0.0040	0.5544+0.0263
Cyclooctanol	0.0202	0.5530	0.1142+0.0026	0.6149+0.0161
<u>t</u> -Butanol	0.0202	1.7449	0.3234+0.0044	0.8708+0.0135
1-Methylcyclohexanol	0.0200	1.0054	0.6300+0.0017	0.5543+0.0091
Ethanol/HOAc	0.0201	1.2424	1.871+0.019	0.2806+0.0808
Ethanol/H <sub>2</sub> O	0.0201	1.0488	0.4274+0.0033	0.4941+0.0168
<u>n</u> -Butanol/HOAc	0.0200	0.9821	1.025+0.008	0.4075+0.0444
<u>n</u> -Butanol/H <sub>2</sub> O	0.0199	0.7338	0.2798+0.0033	0.4502+0.0244
Isopropanol/HOAc	0.0203	1.0919	1.243+0.008	0.5373+0.0419
Isopropanol/H <sub>2</sub> O	0.0200	1.0007	0.5451+0.0074	0.4462+0.0403

Table 11 (Continued)

Alcohol	[CAN] <sup>a</sup>	[Alcohol] <sup>b</sup>	Slope St. Dev. <sup>c</sup>	Intercept+ St. Dev. <sup>c</sup>
<u>t</u> -Butanol/HOAc	0.0200	0.9433	0.8351±0.0110	0.5414±0.0632
<u>t</u> -Butanol/H <sub>2</sub> O	0.0204	1.0151	0.7945±0.0059	0.4213±0.0316
<u>t</u> -Butanol/H <sub>2</sub> O/ NaClO <sub>4</sub>	0.0201	0.9949	0.8156±0.0063	0.4001±0.0345
<u>t</u> -Butanol/H <sub>2</sub> O/ NaNO <sub>3</sub>	0.0203	0.9904	0.8306±0.0102	0.2732±0.0559

## Chemicals

Table 12. Chemicals

Chemical	Source	Purification Procedure
Benzyl alcohol	Eastman	None
<u>p</u> -Methylbenzyl alcohol	Aldrich	None
<u>o</u> -Chlorobenzyl alcohol	<u>o</u> -Chloro- benzyl chloride <sup>a</sup>	Recrystallization <sup>a</sup>
<u>m</u> -Chlorobenzyl alcohol	Aldrich	None
<u>p</u> -Chlorobenzyl alcohol	Aldrich	None
<u>m</u> -Nitrobenzyl alcohol	Eastman	None
<u>p</u> -Nitrobenzyl alcohol	Aldrich	Two recrystallizations from aqueous ethanol; m.p. 92-92.5°, lit. 93° <sup>b</sup>
$\alpha$ -Methylbenzyl alcohol	Aldrich	None
Benzhydryl	Matheson, Coleman, and Bell	None

<sup>a</sup>See below for procedure.  
<sup>b</sup>See reference 51.

Table 12 (Continued)

Chemical	Source	Purification Procedure
Methanol	Baker	None
Ethanol	Matheson, Coleman, and Bell	None
<u>n</u> -Hexanol	Matheson, Coleman, and Bell	Distilled
<u>n</u> -Nonanol	Aldrich	None
Neopentanol	Matheson, Coleman, and Bell	None
2-Cyclohexylethanol	Aldrich	None
Cyclopropylcarbinol	Aldrich	None
Cyclobutylcarbinol	Prepared <sup>a</sup>	Distilled
Cyclopentylcarbinol	K. & K.	Distilled
Cyclohexylcarbinol	Aldrich	None
3-Butenol	Aldrich	None
5-Hexenol	Columbia	None
2-Phenylethanol	Matheson, Coleman, and Bell	None
4-Phenylbutanol	Prepared <sup>a</sup>	Distilled
Ethylene glycol	Matheson, Coleman, and Bell	None
1,3-Propanediol	Matheson, Coleman, and Bell	None
1,4-Butanediol	Aldrich	None
1,5-Pentanediol	Aldrich	None

Table 12 (Continued)

Chemical	Source	Purification Procedure
2-Methoxyethanol	Aldrich	Distilled, b.p. 125° (760 mm.)
2-Chloroethanol	Baker	None
3-Ethoxypropanol	Aldrich	Distilled, b.p. 160-1° (760 mm.)
Isopropanol	Fisher	None
3-Heptanol	Matheson, Coleman, and Bell	Distilled, b.p. 154° (760 mm.)
Cyclopentanol	Aldrich	Distilled, b.p. 139-40° (760 mm.)
Cyclohexanol	Matheson, Coleman, and Bell	None
Cycloheptanol	Aldrich	Distilled
Cyclooctanol	Aldrich	None
<u>t</u> -Butanol	Eastman	None
1-Methylcyclohexanol	Aldrich	Distilled, b.p. 62° ( <u>ca.</u> 20 mm.)
<u>n</u> -Butanol	Baker	None
<u>o</u> -Chlorobenzyl chloride	Aldrich	None
CAN	G.F. Smith, Certified Primary Standard	None, 99.99% pure
Acetonitrile	Baker	None
Acetic acid	Mallinckrodt	None
4-Phenylbutyric acid	Aldrich	None

o-Chlorobenzyl alcohol

A mixture of 80.5 g. (0.50 mole) o-chlorobenzyl chloride, 52 g. (0.53 mole) potassium acetate, and 750 ml. 95% ethanol was refluxed for 8 hrs. The mixture was filtered, 33.6 g. potassium hydroxide was added to the filtrate, and it was refluxed for 6 hrs. The mixture was diluted with ca. 2 l. water and extracted with chloroform. Concentration of the chloroform solution gave 30 g. (42%) o-chlorobenzyl alcohol. The product was recrystallized successively from ligroin, heptane, 75% aqueous ethanol, and ligroin, m.p. 69-70°, lit. 69° (52).

Cyclobutylcarbinol

Cyclobutylcarbinol was prepared by R. Shaw. Cyclobutane-carboxylic acid was prepared from diethylmalonate and trimethylene dibromide using the method of Cason and Rapoport (53). The acid was reduced to the alcohol using lithium aluminum hydride (54). The alcohol was distilled at reduced pressure, b.p. 53-5° (7 mm.).

4-Phenylbutanol

To 10.5 g. (0.26 mole) lithium aluminum hydride in 800 ml. ether was added 50 g. (0.30 mole) 4-phenylbutyric acid in 250 ml. ether. The mixture was refluxed for 2 hr. after addition was complete and then moist ether was added to destroy excess hydride. Ca. 25 ml. water and then 400 ml. 2 M sulfuric acid were added and the mixture was stirred



until the solid dissolved. The ether layer was separated, washed once with saturated sodium bicarbonate solution, and dried over magnesium sulfate. The ether was evaporatively distilled through a Vigreux column and the last traces were removed on a rotary evaporator. The resulting yellow-brown liquid was distilled under reduced pressure, b.p.  $105^{\circ}$  (1.6 mm.), lit. b.p.  $140^{\circ}$  (14 mm.) (55).

#### Equipment

Absorption measurements were made at 520 m $\mu$  using a Beckman Model D.U. spectrophotometer using Beckman 1 cm. matched silica cells. The temperature of the cell holder was maintained at  $21.0^{\circ}$  with a Haake constant temperature circulator to circulate water through the cell holder jackets.

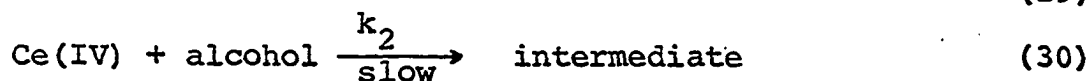
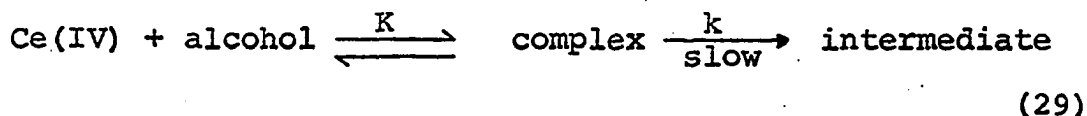
Most of the calculations were done by an I.B.M. Series 360 Model 50 computer using the least squares computer programs RAWDAT and PLOT. Plotting was done by a Cal-Comp Digital Incremental Data Plotter in conjunction with program PLOT using the Simplotter routines at Iowa State University.

PART III. THE MECHANISM OF CERIVM(IV) OXIDATION OF  
BENZYL ALCOHOLS

## INTRODUCTION

The use of cerium(IV) as an oxidant in analytical chemistry has been thoroughly explored. However, only recently has there been any interest in the mechanisms of cerium(IV) oxidation of organic compounds (4).

The findings of other workers concerning the mechanisms of oxidation of alcohols by cerium(IV) may be summarized briefly. The general finding is that in perchloric and nitric acids, oxidation of alcohols proceeds via 1:1 complex formation between cerium(IV) and the alcohol. The slow step of the oxidation is the unimolecular decomposition of the alcohol-cerium(IV) complex. In sulfuric acid, alcohol-cerium(IV) complex formation does not in general occur and the reaction is found to be overall second order, first order in alcohol and first order in cerium(IV). These two mechanisms are illustrated in Equations 29 and 30. In all but one kinetic study (11) of the cerium(IV) oxidation of alcohols reported in



the literature, the authors assume that the first formed intermediate is an alkoxy radical, RO·.

In our study of the synthetic application of cerium(IV) oxidations to benzylic-type alcohols (Part I) (5,6) we made

an observation which was clearly inconsistent with alkoxy radical formation in the slow step of the reaction. This was that there was a rather large substituent effect on the rate of oxidation of substituted benzyl alcohols by ceric ammonium nitrate in a variety of media. *p*-Methoxybenzyl alcohol was oxidized to *p*-anisaldehyde in a few minutes at room temperature, whereas benzyl alcohol required several minutes at steam bath temperature for oxidation to benzaldehyde. *p*-Nitrobenzyl alcohol required even longer than benzyl alcohol for oxidation. Thus it was apparent that the oxidation of benzyl alcohols by ceric ammonium nitrate is accelerated by electron donating substituents such as *p*-methoxy and retarded by electron withdrawing substituents such as *p*-nitro.

This observation seemed to us more consistent with the development of free radical or carbonium ion character on the  $\alpha$ -carbon in the transition state of the slow step of the reaction than with alkoxy radical formation. Indeed, Littler had measured a deuterium isotope effect for the ceric sulfate oxidation of cyclohexanol and 1-deuterocyclohexanol in sulfuric acid and found  $k_H/k_D = 1.9$  (17), indicating that there is some C-H bond breakage at the  $\alpha$ -carbon in the transition state of the slow step. However, this experimental fact has been generally ignored by other workers (12,16, 18-20,22,56,57) and a study of the kinetics of oxidation of

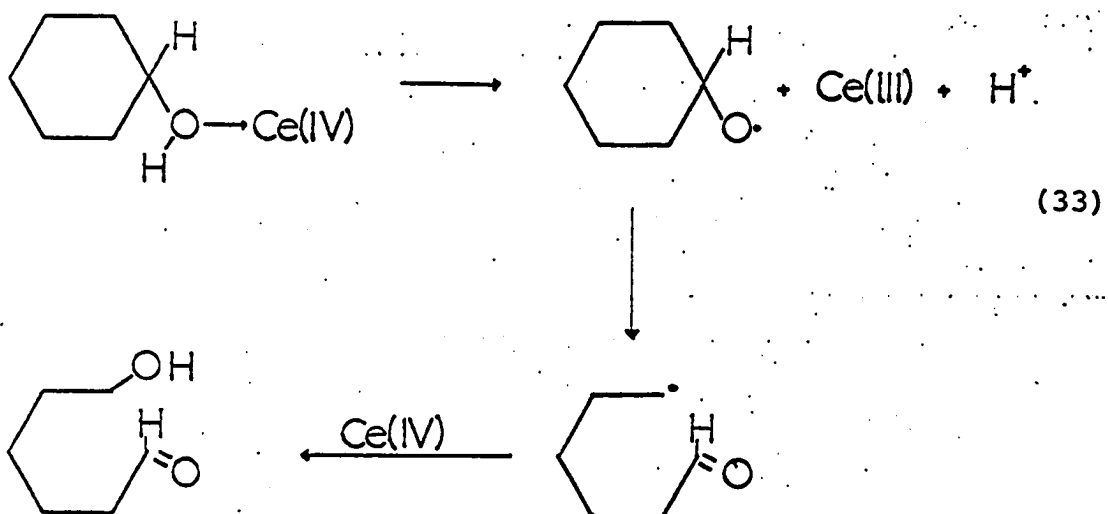
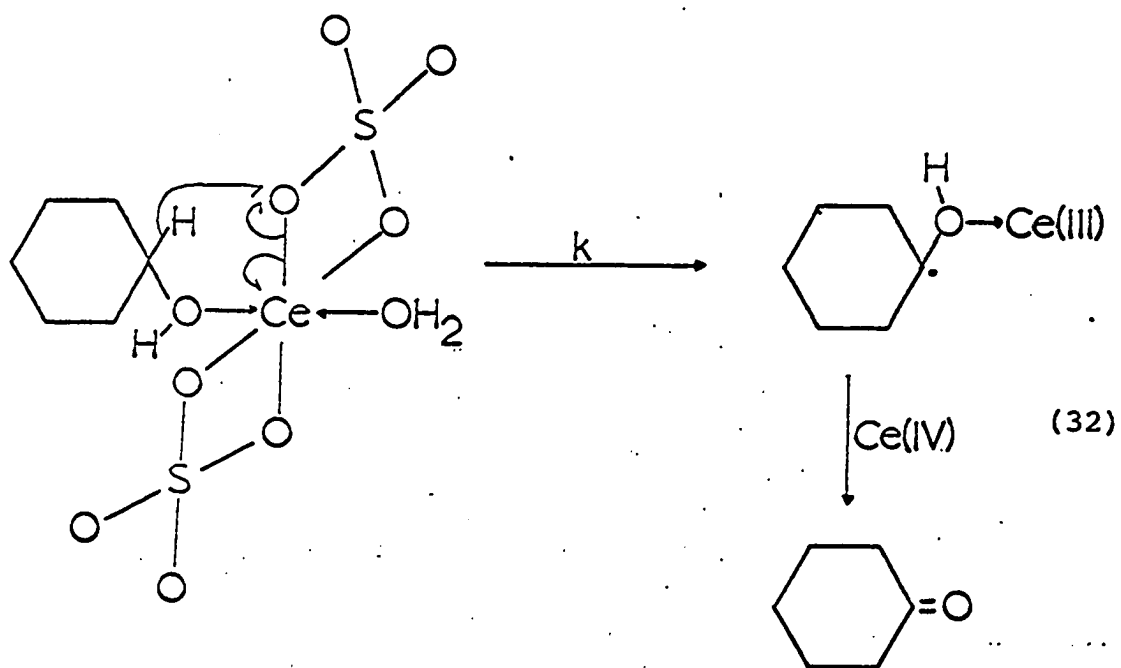
substituted benzyl alcohols seemed to offer an excellent system to thoroughly explore the mechanism of cerium(IV) oxidation of alcohols. It offers the advantages that the oxidation of benzyl alcohols proceeds cleanly to the corresponding benzaldehydes (Part I), and substituents can be systematically varied and their effect on the rate of oxidation noted.

## HISTORICAL

The first study of the mechanism of oxidation of alcohols by cerium(IV) was that of Ardon (11), who studied the ceric perchlorate oxidation of ethanol in 3.2 M perchloric acid. He found that the kinetics were consistent with the intermediacy of a 1:1 cerium(IV)-alcohol complex and confirmed the presence of the complex spectrophotometrically. Thus the mechanism was proposed to be

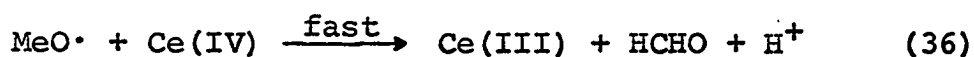
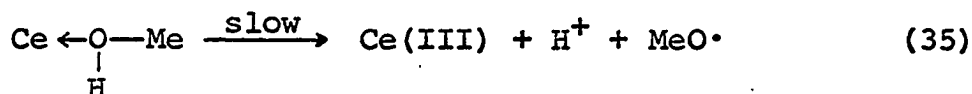
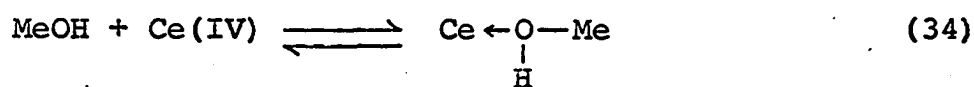


Littler investigated the ceric sulfate oxidation of cyclohexanol in 0.24 M sulfuric acid at 50° C. and found complex formation kinetics similar to Ardon's (17) with  $K=13.0$  and  $k=1.38 \times 10^{-4} \text{ sec}^{-1}$  compared to  $K=4.3$  and  $k=67 \times 10^{-4} \text{ sec}^{-1}$  at 20° found by Ardon (11). Littler found a deuterium isotope effect,  $k_{\text{H}}/k_{\text{D}}$ , of 1.9 for the oxidation of 1-deuterocyclohexanol by ceric sulfate (17) and suggested that this indicates that the oxidation step probably involves one-electron transfers within a cyclic alcohol-cerium (IV) complex (Equation 32). However the low value of  $k_{\text{H}}/k_{\text{D}}$  for cerium(IV) ( $k_{\text{H}}/k_{\text{D}}=3.6$  in perchloric acid and 4.5 in sulfuric acid for the vanadium(V) oxidation of 1-deuterocyclohexanol (57) shows the possibility of concurrent oxidation by an acyclic mechanism such as that suggested by Bawn and White for the cobalt(III) oxidation of alcohols



(Equation 33) (58).

Muhammad and Rao studied the kinetics of the ceric perchlorate oxidation of methanol in varying concentrations of perchloric acid (12). Their kinetics were consistent with a mechanism involving 1:1 cerium(IV)-alcohol complex formation and unimolecular decomposition of the complex. They suggest that the oxidation of both ethanol and methanol proceeds via formation of an alkoxy radical, RO·, in the slow step of the reaction with the following step being a rapid oxidation of the alkoxy radical (Equations 34-36). An activation energy of 14.45 kcal./mole was found in 1 M

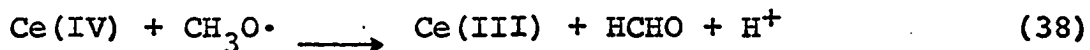
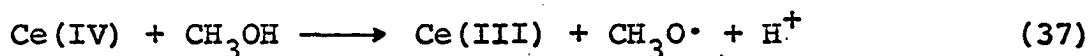


perchloric acid.

Muhammad and Rao also studied the kinetics of the ceric sulfate oxidation of methanol in 0.5-2 M sulfuric acid at 55° (16). A search for cerium(IV)-alcohol complex formation indicated that there was none. The rate of disappearance of cerium(IV) was overall second order, first order in alcohol and first order in cerium(IV). The difference between the kinetics observed in sulfuric acid and in perchloric acid



was postulated to be due to the strong binding of sulfate ion with cerium(IV) preventing alcohol-cerium(IV) complex formation in sulfuric acid. They again postulated the intermediacy of an alkoxy radical in the ceric sulfate oxidation of methanol (Equations 37 and 38). An activation energy of 26.3 kcal./mole was reported for the ceric sulfate oxidation of methanol.



Rangaswamy and Santappa have studied the kinetics of the ceric perchlorate oxidation of n-butanol in 0.5-2.0 M perchloric acid at 10-15° C. (56). They found that the reaction is first order in cerium(IV) in the presence of excess alcohol and ca. 0.5 order in n-butanol. They found that plots of 1/rate vs. 1/(n-butanol) as well as 1/rate vs. 1/(H<sup>+</sup>) are linear. These results are consistent with the formation of a 1:1 complex between aquated cerium(IV) and alcohol which then undergoes rate determining unimolecular decomposition. They suggest with no justification that the initial step of the reaction is O-H bond fission in the alcohol leading to an alkoxy radical which with further oxidation is converted to n-butyraldehyde and then to "stable" n-butyric acid. In fact, Trahanovsky and M. G. Young (59) have found

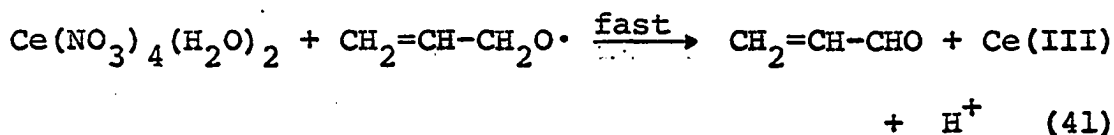
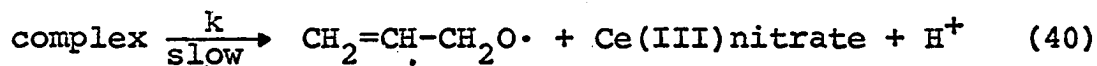
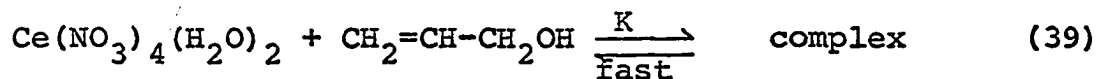
that the oxidation of n-pentanol produces no n-valeraldehyde or n-valeric acid shedding some doubt on Rangaswamy and Santappas' assumed products.

Sethuram and Muhammad have investigated the oxidation of isopropanol and sec-butanol by ceric nitrate in 1 M nitric acid (19). They found that the oxidation of isopropanol produced approximately one mole of acetone for every two moles of cerium(IV) consumed. In the presence of excess alcohol the reaction is first order in cerium(IV), 0.70 order in n-butanol and 0.625 order in isopropanol. This is consistent with the formation of a 1:1 complex and rate determining decomposition of the complex. They also found that the rate of reaction is inversely proportional to the square of the nitrate ion concentration due to competition of the nitrate ion with alcohol for coordination sites around the ceric ion. As usual, the intermediacy of an alkoxy radical is postulated without justification. They assumed that the cerium(IV) species in solution was  $\text{Ce}(\text{NO}_3)_4(\text{H}_2\text{O})_2$  and concluded that alcohol is displacing water and not nitrate ion from the cerium(IV) species.

In a following paper, Sethuram and Muhammad studied the kinetics of oxidation of isopropanol by various ceric salts (22). They found that in ceric perchlorate-perchloric acid and ceric nitrate-nitric acid the reaction follows kinetics characteristic of 1:1 cerium(IV)-alcohol complex formation

and rate determining decomposition of the complex, while in ceric sulfate-sulfuric acid medium the reaction is first order in each reactant. They also found that there is more alcohol-cerium(IV) complex present in ceric perchlorate-perchloric acid than in ceric nitrate-nitric acid and attributed this to the competition of nitrate ion with alcohol for coordination sites around the metal ion. In all three systems, the first-formed intermediate was assumed to be the alkoxy radical which underwent rapid oxidation to acetone.

Sethuram studied the ceric nitrate oxidation of allyl alcohol in nitric acid (18). He found that the oxidation of allyl alcohol by ceric nitrate was faster than the oxidation of *n*-propanol, but he doesn't reveal how much faster. The kinetics were consistent with 1:1 complex formation and rate determining unimolecular decomposition of the complex. The mechanism suggested is outlined in Equations 39-41. A priori, formation of the alkoxy radical derived from allyl



alcohol should be energetically less favorable than formation of the alkoxy radical from n-propanol because the electron withdrawing pi system in allyl alcohol should increase the ionization potential of the alcohol. Thus one would expect allyl alcohol to be oxidized at a slower rate than n-propanol. On the other hand, if there is some charge development on the  $\alpha$ -carbon atom in the transition state of the rate determining step, allyl alcohol should be oxidized more rapidly than n-propanol, as is observed. Thus there is reason to believe that a simple alkoxy radical is not the first-formed intermediate in this reaction.

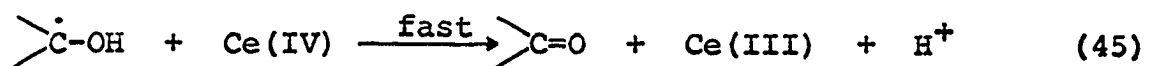
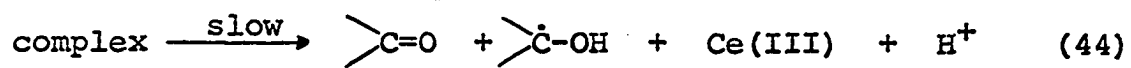
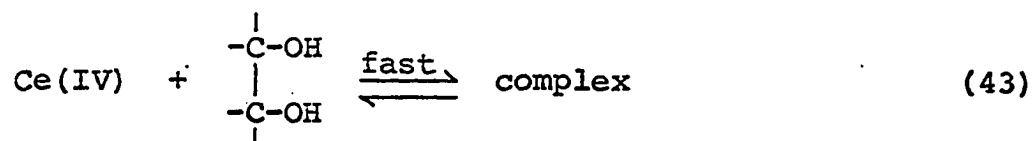
Rangaswamy and Santappa carried out a kinetic study of the oxidation of benzyl alcohol by ceric perchlorate in 1.0-1.5 M perchloric acid at 10-20° C. (20). Their kinetics indicated that the reaction was first order in cerium(IV) and first order in benzyl alcohol. They suggest that the absence of complexing between cerium(IV) and the alcohol is due to the electron withdrawing nature of the phenyl group. That there actually is cerium(IV)-alcohol complexation in this medium is apparent from visual observation of the color change upon adding benzyl alcohol to a 0.05 M ceric perchlorate solution in 0.5 M perchloric acid (see experimental section). Thus these authors' kinetics may be in error, although it is possible that the use of low alcohol concentrations could lead to the erroneous conclusion that there is no complex formation

if the denominator of the rate expression in Equation 42 remains nearly constant.

$$-d[\text{Ce(IV)}]/dt = \frac{kK [\text{Ce(IV)}] [\text{ROH}]}{1 + K[\text{ROH}]} \quad (42)$$

Hintz and Johnson studied the mechanism of oxidation of glycols by ceric perchlorate in 1.0 M perchloric acid and in 0.75 M perchloric acid-0.25 M sulfuric acid (14). Their main concern was with the mechanism of oxidation of 1,2-diols, but they also examined the kinetics of oxidation of cyclohexanol. They observed kinetics consistent with formation of a cerium(IV)-alcohol complex and rate determining unimolecular decomposition of the complex in 1.0 M perchloric acid. They found an equilibrium constant for complex formation of 2.9 (from kinetic data) and a rate constant of  $0.13 \text{ min.}^{-1}$  at  $15.0^\circ \text{ C}$ .

Several workers have studied the mechanism of glycol cleavage by cerium(IV) (4,60). It is generally found that no glycol-cerium(IV) complex forms in sulfuric acid, whereas in nitric and perchloric acids a complex usually forms. The mechanism generally agreed upon for glycol cleavage in nitric and perchloric acids is presented in Equations 43-45. The intermediacy of a free radical in the cerium(IV)-glycol cleavage reaction has been demonstrated by showing that the yield of carbonyl containing product is reduced by one half



when the oxidation is carried out in the presence of the free radical trap acrylamide (60).

## RESULTS

Rate measurements were carried out at 55.0° C. in 75% aqueous acetonitrile containing 0.95 M nitric acid with ceric ammonium nitrate (CAN) as oxidant. Reactions were followed spectrophotometrically, usually at 458 m $\mu$  for a CAN concentration of 0.005 M.

## Order in Cerium(IV)

In the presence of excess benzyl alcohol (0.10 M) and 0.005 M CAN at 55.0° C., the rate of disappearance of cerium(IV) is first order with respect to cerium(IV), since a plot of log absorbance vs. time is linear for at least two half-lives (Figure 6). All other rates which were measured for benzyl alcohols also showed first order dependence on cerium(IV). The pseudo first order rate constants obtained are summarized in Table 13.

A further attempt was made to demonstrate that the cerium(IV)-benzyl alcohol reaction is first order in cerium (IV) by measuring rates with varying concentrations of cerium(IV) in the presence of a constant excess of alcohol. These results are summarized in Table 14.

## Order in Alcohol

A graph of the pseudo first order rate constant vs. the concentration of benzyl alcohol has a non-zero intercept and slight curvature (Figure 7) illustrating that the reaction

Figure 6. Pseudo first order rate data for benzyl alcohol. [Benzyl alcohol] = 0.0501 M  
[CAN] = 0.005 M, 55.0° C.

Figure 7. Pseudo first order rate constant vs. alcohol concentration for benzyl alcohol



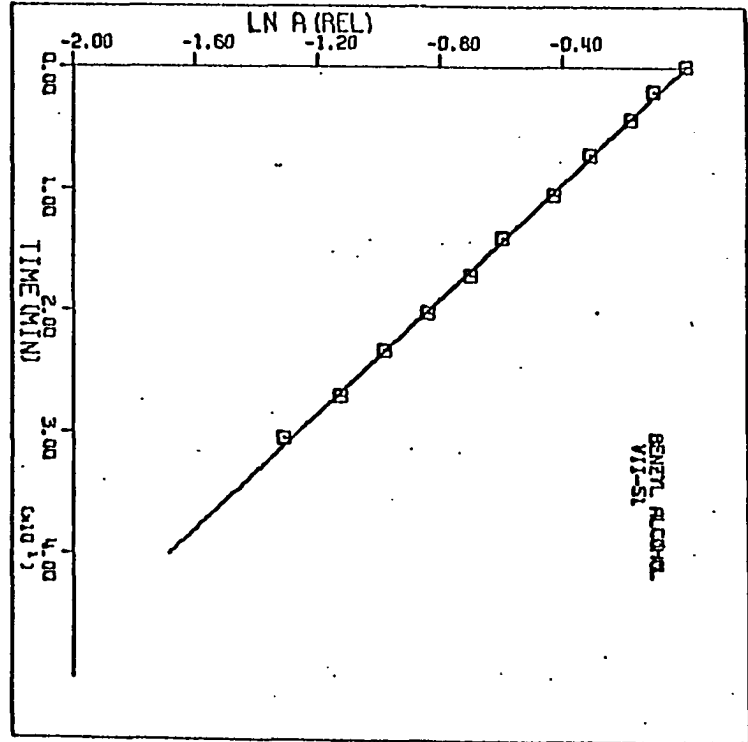
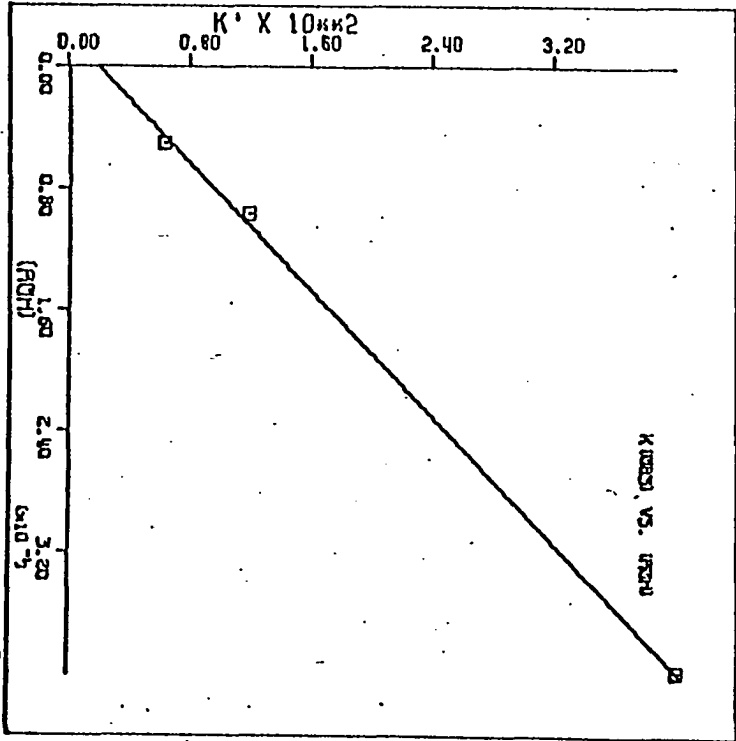


Table 13. Pseudo first order rate constants for the cerium (IV) oxidation of benzyl alcohols<sup>a</sup>

Alcohol	[Alcohol] <sup>b</sup>	$k' \times 10^2$ <sup>c</sup> (min. <sup>-1</sup> )
Benzyl	0.05012	0.623
	0.09676	1.185
	0.39795	3.997
<u>m</u> -Methylbenzyl	0.04923	1.387
	0.06570	1.827
	0.09217	2.545
	0.13100	3.523
	0.27442	7.196
<u>p</u> -Methylbenzyl	0.04865	5.504
	0.05178	5.809
	0.09758	10.412
<u>p</u> -Chlorobenzyl	0.06803	0.466
	0.17714	0.895
	0.35246	1.631
<u>m</u> -Chlorobenzyl	0.06760	0.786
	0.10900	1.236
	0.24573	2.060

<sup>a</sup>The reaction medium was 75% aqueous acetonitrile, 0.95 M nitric acid, 0.005 M CAN. Temperature = 55.0° C. unless noted otherwise.

<sup>b</sup>Average concentration of alcohol during the kinetic run.

<sup>c</sup>Rate constants are corrected for concurrent solvent oxidation.

Table 13 (Continued)

Alcohol	[Alcohol] <sup>b</sup>	$k' \times 10^2$ <sup>c</sup> (min. <sup>-1</sup> )
<u>p</u> -Chlorobenzyl	0.09811	0.988
	0.16682	1.591
	0.39484	3.724
<u>p</u> -Bromobenzyl	0.06769	1.023
	0.09727	1.406
	0.29672	5.099
<u>m</u> -Nitrobenzyl	0.06333	0.426
	0.10143	0.598
	0.25577	1.406
<u>m</u> -Nitrobenzyl <sup>d</sup>	0.05738	2.165
	0.10198	3.670
	0.22755	8.050
<u>p</u> -Nitrobenzyl	0.07146	0.582
	0.14987	1.104
	0.26066	1.945
<u>e</u>	0.0	0.218
<u>f</u>	0.0	1.079

<sup>d</sup>Temperature is 70.0° C.

<sup>e</sup>Rate of solvent oxidation in the absence of alcohol at 55.0° C.

<sup>f</sup>Rate of solvent oxidation in the absence of alcohol at 70.0° C.

Table 14. Pseudo first order rate constants for the cerium(IV) oxidation of benzyl alcohol at 55.0° C.<sup>a</sup>

Benzyl alcohol concentration (M)	CAN concentration (M)	$k' \times 10^2$ <sup>b</sup> (min. <sup>-1</sup> )
0.40	0.04	3.35
0.40	0.005 <sup>c</sup>	3.85
0.40	0.005 <sup>d</sup>	3.32

<sup>a</sup>In 75% aqueous acetonitrile, 0.95 M nitric acid, ceric ammonium nitrate.

<sup>b</sup>Uncorrected for solvent oxidation.

<sup>c</sup>Cerous nitrate (0.034 M) added.

<sup>d</sup>Cerous nitrate (0.035 M) and ammonium nitrate (0.070 M) added.

is not first order in alcohol. However, a plot of  $1/k'$  vs.  $1/[ROH]$  is linear (Figure 8). This observation is consistent with the kinetic expression

$$1/k' = 1/k + 1/kK[ROH] \quad (46)$$

which is derivable from the kinetic situation where reactants are in equilibrium with a 1:1 complex with equilibrium constant K, which undergoes rate determining decomposition with a rate constant k. The intercept of this plot gives  $1/k$  and intercept/slope gives K. The rate constants and equilibrium constants calculated using this rate expression are summarized in Table 15.

Rate constants for unimolecular decomposition of the alcohol-cerium(IV) complex were also calculated using the

slope of the  $1/k'$  vs.  $1/[ROH]$  plots and the spectrophotometric equilibrium constants measured elsewhere in this dissertation. These are summarized in Table 16.

#### Temperature Dependence of Rate

The rate of oxidation of m-nitrobenzyl alcohol was measured at 55.0° C. and 70.0° C. in 75% aqueous acetonitrile and 0.95 M nitric acid with the concentration of ceric ammonium nitrate 0.005 M. The error in measuring  $K$  and  $k$  is expected to be large since the correction of  $k'$  for solvent oxidation amounted to ca. 30% of the total rate of oxidation (see Table 13). Activation parameters were calculated assuming that  $K$  remains essentially constant in the temperature range 55.0° to 70.0°. The calculated parameters are summarized in Table 17.

#### Deuterium Isotope Effect

The pseudo first order rate constant,  $k'$ , measured for  $\alpha$ ,  $\alpha$ -dideuterobenzyl alcohol in 75% aqueous acetonitrile and 0.95 M nitric acid at 55.0° C. was  $1.28 \times 10^{-2} \text{ min.}^{-1}$  at an alcohol concentration of 0.1877 M. Using the equation derivable for complex-formation kinetics (Equation 46), and assuming that the equilibrium constants for benzyl and  $\alpha$ ,  $\alpha$ -dideuterobenzyl alcohol are the same, the rate constant for decomposition of the complex,  $k$ , is calculated to be  $10.1 \times 10^{-2} \text{ min.}^{-1}$  for  $\alpha$ ,  $\alpha$ -dideuterobenzyl alcohol. This gives a value of  $k_H/k_D=2.0$  for benzyl alcohol at 55.0° C. The kinetic isotope effects

Figure 8.  $1/k'$  vs.  $1/[ROH]$  for benzyl alcohol

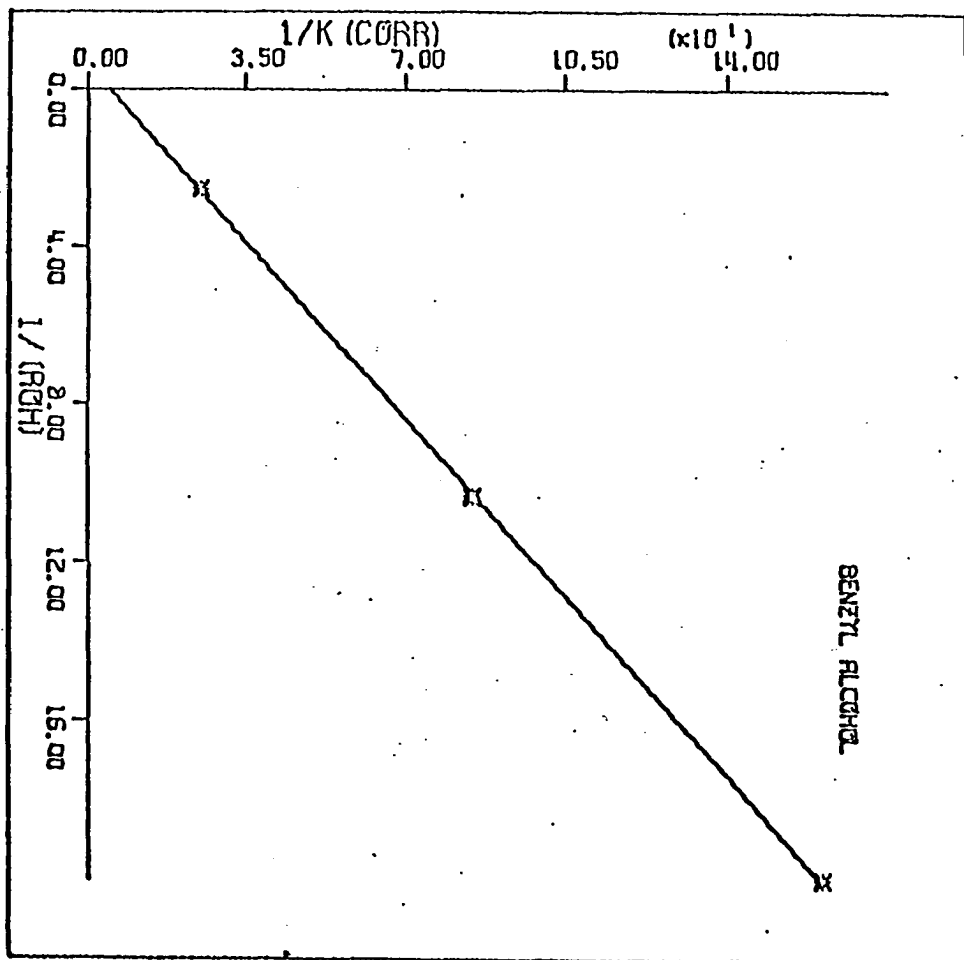


Table 15. Equilibrium constants for 1:1 alcohol-cerium(IV) complex formation and rate constants for unimolecular complex decomposition derived from kinetic data<sup>a</sup>

Alcohol	$k \times 10^2$ (min. <sup>-1</sup> )	K (liters/mole)
Benzyl	20.1	0.64
<u>m</u> -Methylbenzyl	68.1	0.42
<u>p</u> -Methylbenzyl	94.5	1.27
<u>o</u> -Chlorobenzyl	3.09	2.58
<u>m</u> -Chlorobenzyl	5.94	2.29
<u>p</u> -Chlorobenzyl	31.4	0.33
<u>p</u> -Bromobenzyl	<u>b</u>	<u>b</u>
<u>m</u> -Nitrobenzyl	4.55	1.59
<u>m</u> -Nitrobenzyl <sup>c</sup>	72.5	0.53
<u>p</u> -Nitrobenzyl	11.0	0.77

<sup>a</sup>In 75% aqueous acetonitrile, 0.95 M nitric acid, 0.005 M CAN at 55.0° C.

<sup>b</sup>The graph of  $1/k'$  vs.  $1/[ROH]$  had a negative intercept.

<sup>c</sup>Measured at 70.0° C.

for m-chloro- and p-methylbenzyl alcohols were measured and calculated to be 2.2 and 1.3, respectively, at 55.0° C.



Table 16. Rate constants for complex decomposition calculated using spectrophotometric equilibrium constants

Alcohol	$k \times 10^2$ (min. <sup>-1</sup> ) <sup>a</sup>	$K$ (liters/mole) <sup>b</sup>
Benzyl	17.62	0.73
<u>m</u> -Methylbenzyl	37.24	<u>ca.</u> 0.77 <sup>c</sup>
<u>p</u> -Methylbenzyl	149.79	0.80
<u>m</u> -Chlorobenzyl	18.89	0.72
<u>p</u> -Chlorobenzyl	14.96	0.69
<u>p</u> -Bromobenzyl	20.69	<u>ca.</u> 0.70 <sup>c</sup>
<u>m</u> -Nitrobenzyl	15.78	0.46
<u>p</u> -Nitrobenzyl	13.79	0.62

<sup>a</sup>Rate measurements were in 75% aqueous acetonitrile, 0.95 M nitric acid, 0.005 M CAN at 55.0° C.

<sup>b</sup>Equilibrium constants were measured in 70% aqueous acetonitrile, 0.50 M nitric acid, 0.02 M CAN at 21.0° C.

<sup>c</sup>Estimated value.

Table 17. Activation parameters for the cerium(IV) oxidation of m-nitrobenzyl alcohol<sup>a</sup>

Parameter	From "kinetic" <sup>b</sup> rate constants	From "spectrophotometric" rate constants <sup>c</sup>
$E_a$	41.3 kcal./mole	25.0 kcal./mole
$\Delta H^*$	40.7 kcal./mole	24.3 kcal./mole
$\Delta S^*$	59.1 e.u.	11.7 e.u.
$\Delta F^*$	21.6 kcal./mole	20.5 kcal./mole

<sup>a</sup>In 75% aqueous acetonitrile, 0.95 M nitric acid at 50.0° C.

<sup>b</sup>Rate constants,  $k$ , from purely kinetic data.

<sup>c</sup>Rate constants,  $k$ , calculated using spectrophotometric equilibrium constants.

### Rate of Oxidation of *p*-Methoxybenzyl Alcohol

An attempt was made to follow the rate of oxidation of *p*-methoxybenzyl alcohol (0.05 M) by CAN (0.005 M) in 75% aqueous acetonitrile and 0.95 M nitric acid at room temperature. The result was that complete fading occurred within one minute. Assuming a half-life of 0.5 min.,  $k'$ , the pseudo first order rate constant, is calculated to be  $1.5 \text{ min.}^{-1}$ . Assuming an equilibrium constant of  $0.5 \text{ l.mole}^{-1}$ , a value of  $61.5 \text{ min.}^{-1}$  is calculated for  $k$ , the rate constant for unimolecular decomposition of the alcohol-cerium(IV) complex, at room temperature.

### Rate of Oxidation of Ethanol

The pseudo first order rate constant,  $k'$ , for the oxidation of ethanol (0.1008 M) in 75% aqueous acetonitrile and 0.95 M nitric acid at  $55.0^\circ \text{ C}$ . was found to be  $0.925 \times 10^{-2} \text{ min.}^{-1}$ . Assuming that the equilibrium constant for the formation of the ethanol-cerium(IV) complex is the same as that found kinetically for the benzyl alcohol-cerium(IV) complex ( $K=0.64$ ), a value of  $k=12.3 \times 10^{-2} \text{ min.}^{-1}$  is calculated for ethanol. The assumption that  $K(\text{ethanol})=K(\text{benzyl alcohol})$  is probably a good one since spectrophotometric values of 0.73 and 0.72 were found for benzyl alcohol and ethanol, respectively, at  $21.0^\circ \text{ C}$ . in 70% aqueous acetonitrile and 0.5 M nitric acid. The ratio of  $k(\text{benzyl alcohol})/k(\text{ethanol})=1.6-1.7$ .

## DISCUSSION

## Overall Reaction Mechanism

Spectrophotometric evidence

A spectrophotometric study reported in Part II of this study describes the determination of equilibrium constants for the formation of the 1:1 cerium(IV)-alcohol complex for several benzyl alcohols in 70% aqueous acetonitrile containing 0.5 M nitric acid at 21.0° C. (Equation 47). These constants ranged from 0.46 to 0.80,



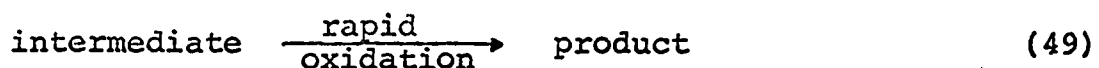
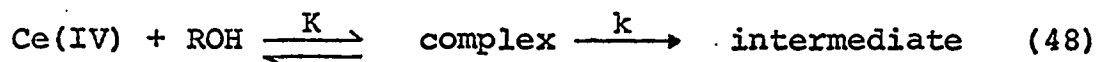
with electron donating substituents facilitating complex formation to a small extent (see Table 4). It is interesting to note that with initial concentrations of cerium(IV) and alcohol of 0.02 M and 0.50 M, respectively, and an equilibrium constant of 0.80, about 29% of the cerium(IV) is present in the form of a cerium(IV)-alcohol complex. Thus it was anticipated that complex formation should also be evidenced by the kinetics of the cerium(IV) oxidation of alcohols.

Kinetic evidence

The cerium(IV) oxidation of benzyl alcohols in 75% aqueous acetonitrile and 0.95 M nitric acid at 55.0° C. is pseudo first order with respect to cerium(IV) in the presence of excess alcohol, as evidenced by the linearity of log absorbance vs. time plots (Figure 6). That the reaction is

first order in cerium(IV) is further supported by the observation that the pseudo first order rate constants for the oxidation of benzyl alcohol remain approximately constant when the cerium(IV) concentration is varied in the presence of a constant excess of alcohol with the ionic strength maintained constant (Table 14).

A plot of the pseudo first order rate constants vs. alcohol concentration for benzyl alcohol illustrates that the reaction is non-first order in alcohol since the plot has a non-zero intercept and slight curvature (Figure 7). However, a plot of the reciprocal of the pseudo first order rate constant vs. the reciprocal of the alcohol concentration results in a straight line (Figure 8). This is consistent with the kinetic situation observed by Ardon for the ceric perchlorate oxidation of ethanol in perchloric acid (11), where there is an equilibrium established between cerium(IV) and alcohol to form a 1:1 complex, with the rate determining step of the oxidation being unimolecular decomposition of the complex (Equations 48 and 49).



The kinetic expression for this mechanistic situation is derivable in the following manner. In the presence of excess alcohol,

$$-d[\text{Ce(IV)}]_{\text{T}}/dt = k' [\text{Ce(IV)}]_{\text{T}} \quad (50)$$

where  $k'$  is the pseudo first order rate constant obtained in the presence of excess alcohol and  $[\text{Ce(IV)}]_{\text{T}}$  is the total cerium(IV) concentration. The rate expression corresponding to the mechanism given in Equations 48 and 49 is

$$-d[\text{Ce(IV)}]_{\text{T}}/dt = k [\text{complex}] \quad (51)$$

$$K = \frac{[\text{complex}]}{([\text{Ce(IV)}]_{\text{T}} - [\text{complex}]) [\text{ROH}]} \quad (52)$$

Solving for [complex] and substituting into Equation 51,

$$\frac{-d[\text{Ce(IV)}]_{\text{T}}}{dt} = \frac{kK[\text{ROH}]}{1 + K[\text{ROH}]} [\text{Ce(IV)}]_{\text{T}} \quad (53)$$

From Equations 50 and 53 it can be seen that

$$k' = \frac{kK[\text{ROH}]}{1 + K[\text{ROH}]} \quad (54)$$

Rearranging this expression gives

$$\frac{1}{k'} = \frac{1}{k} + \frac{1}{kK[\text{ROH}]} \quad (55)$$

A plot of  $1/k'$  vs.  $1/[\text{ROH}]$  has a slope of  $1/kK$  and an intercept of  $1/k$ .

Equilibrium constants derived from spectrophotometric measurements in 70% aqueous acetonitrile-0.5 M nitric acid

at 21.0° C. and from kinetic measurements in 75% aqueous acetonitrile-0.95 M nitric acid at 55.0° C. are summarized in Table 18. Agreement between some of the spectrophotometric and kinetic values of K is quite good. However, there are rather large deviations between some of the values. This is due to the relatively large experimental error encountered in these measurements. Correction of the pseudo first order rate constants for concurrent solvent oxidation is significant ( $0.22 \times 10^{-2} \text{ min.}^{-1}$  at 55.0° C.) and is probably the major source of error. In addition, the method of treating the data (i.e., plotting  $1/k'$  vs.  $1/[\text{ROH}]$ ) magnifies systematic errors, since any error which increases the value of the intercept of the plot will in general also decrease the slope, and  $K = \text{intercept/slope}$ . It is noteworthy that the largest deviations between spectroscopically and kinetically derived equilibrium constants are found for the more slowly oxidized alcohols o-chloro-, m-chloro-, and m-nitrobenzyl alcohols, where the corrections for solvent oxidation are most important.

The observation of 1:1 alcohol-cerium(IV) complex formation in the present system is consistent with the majority of cerium(IV)-alcohol studies reported in the literature (see historical). One major exception is the report by Rangaswamy and Santappa of a kinetic study of the ceric perchlorate oxidation of benzyl alcohol in perchloric acid

at 10-20° C. (20). They report that there is no complex formation between benzyl alcohol and cerium(IV) in this medium, although we have shown that there is visual evidence for complex formation in this medium. It is possible that their kinetics are in error, or that the low alcohol concentrations at which they worked (the maximum alcohol concentration was 0.025 M) did not allow the detection of the complex. This could occur if  $K[\text{ROH}] \ll 1$  in Equation 53, since second order kinetics would result.

Table 18. Equilibrium constants for cerium(IV)-alcohol complex formation

Alcohol	Equilibrium constants (liter mole <sup>-1</sup> )	
	Spectrophotometric <sup>a</sup>	Kinetic <sup>b</sup>
Benzyl	0.73	0.64
<u>m</u> -Methylbenzyl	ca. 0.77 <sup>c</sup>	0.42
<u>p</u> -Methylbenzyl	0.80	1.27
<u>o</u> -Chlorobenzyl	0.52	2.58
<u>m</u> -Chlorobenzyl	0.72	2.29
<u>p</u> -Chlorobenzyl	0.69	0.33
<u>p</u> -Bromobenzyl	ca. 0.70 <sup>c</sup>	<u>d</u>
<u>m</u> -Nitrobenzyl	0.46	1.59
<u>p</u> -Nitrobenzyl	0.62	0.77

<sup>a</sup> Measured at 21.0° C. in 70% aqueous acetonitrile, 0.5 M nitric acid,  $[\text{Ce(IV)}] = 0.02 \text{ M}$ .

<sup>b</sup> Measured at 55.0° C. in 75% aqueous acetonitrile, 0.95 M nitric acid,  $[\text{Ce(IV)}] = 0.005 \text{ M}$ .

<sup>c</sup> Estimated value.

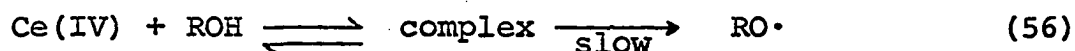
<sup>d</sup> This graph of  $1/k'$  vs.  $1/[\text{ROH}]$  had a negative intercept.

All information available from this study is thus consistent with the mechanism generally found by other workers; i.e., 1:1 alcohol-cerium(IV) complex formation in a rapid preequilibrium step followed by rate determining unimolecular decomposition of the complex.

### Mechanism of Complex Decomposition

#### Popular opinion

The mechanism most commonly proposed in the literature for the cerium(IV) oxidation of alcohols involves the formation of an alkoxy radical as the first intermediate, via either unimolecular cerium(IV)-alcohol complex decomposition or bimolecular reaction of alcohol and cerium(IV) (Equations 56 and 57). The alkoxy radical intermediate has been pro-



posed by Muhammad and Rao for the ceric perchlorate and ceric sulfate oxidations of methanol (12,16), by Rangaswamy and Santappa for the ceric perchlorate oxidation of n-butanol and benzyl alcohol (20,56), by Sethuram and Muhammad for the ceric nitrate oxidation of isopropanol and sec-butanol (19) and for the ceric sulfate and ceric perchlorate oxidations of isopropanol (22), and by Sethuram for the ceric nitrate

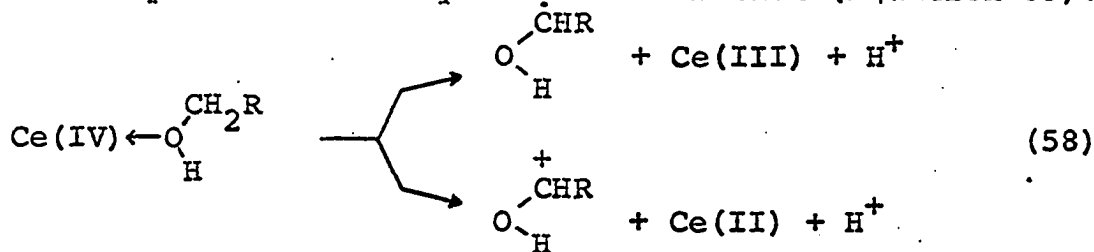


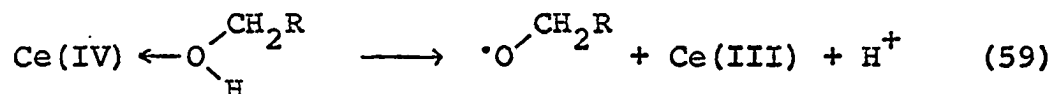
oxidation of allyl alcohol (18).

Littler, on the other hand, found a kinetic isotope effect for the oxidation of 1-deuterocyclohexanol by ceric sulfate of 1.9 (17). He suggested that the oxidation might proceed by two concurrent mechanisms: 1) removal of the  $\alpha$ -hydrogen in the transition state to give a carbon radical as the first intermediate, and 2) alkoxy radical formation. This deuterium isotope effect indicates that there must be some degree of  $\alpha$ -C-H bond breakage in the transition state of the slow step (although the possibility that this is a secondary kinetic isotope effect cannot be rigorously excluded). Unfortunately, this kinetic isotope effect has been completely ignored by the several Indian chemists and consequently some questionable mechanisms have been placed in the chemical literature.

#### Analysis of existing literature

The purpose of this section is to examine the results of cerium(IV) studies already in the literature and show that there is as much reason to postulate formation of a carbon radical (Equation 58) in the slow step of the reaction as there is to postulate alkoxy radical formation (Equation 59).





That the presence of an  $\alpha$ -hydrogen is a necessary requirement for facile oxidation of an alcohol can be seen by comparison of the rates of oxidation of ethanol and t-butanol under conditions of identical ceric sulfate ( $4.4 \times 10^{-3}$  M) and sulfuric acid (0.272 M) concentrations. The pseudo first order rate constants for ethanol and t-butanol are  $2.57 \times 10^{-4}$  and  $0.05 \times 10^{-4}$  sec.<sup>-1</sup>, respectively, at alcohol concentrations of 0.100 M and 0.058 M, respectively (4,26).

Sethuram has reported that the oxidation of allyl alcohol by ceric nitrate is faster than the ceric nitrate oxidation of n-propanol (18). No rate constants are reported, however. This is the expected trend if oxidation occurs at the  $\alpha$ -carbon since the carbon-carbon double bond can help stabilize an incipient radical or carbonium ion to a greater extent than a saturated system. On the other hand, it might be expected that oxidation of the oxygen atom of allyl alcohol would be retarded with respect to n-propanol because of the electron withdrawing nature of the carbon-carbon double bond.

The rate accelerating effect of substitution of a phenyl group for a hydrogen can be seen by comparing the rates of oxidation of methanol and benzyl alcohol by ceric perchlorate

in 1 M perchloric acid. For a cerium(IV) concentration of 0.1 M and an alcohol concentration of 0.24 M, the rate of disappearance of ceric ion is calculated to be  $0.41 \times 10^{-2}$  and  $2.25 \times 10^{-2}$  mole l.<sup>-1</sup> sec.<sup>-1</sup> for methanol (20° C.) (12) and benzyl alcohol (15° C.) (20), respectively. This is the effect predicted for  $\alpha$ -carbon radical or carbonium ion formation, but not for alkoxy radical formation.

Another report gives the activation energies for the ceric sulfate oxidation of several alcohols (4,61). It was found that the total  $E_a$  for the oxidation of n-propanol (20.1 kcal./mole) > isopropanol (19.0 kcal./mole) > benzyl alcohol (18.5 kcal./mole). This is more consistent with  $\alpha$ -carbon radical formation rather than alkoxy radical formation.

Thus it seems apparent that there is substantial if not compelling evidence for the formation of an  $\alpha$ -carbon radical or carbonium ion in the slow step of the cerium(IV) oxidation of alcohols. However, of the mechanistic studies of the cerium(IV)-alcohol reaction now extant in the chemical literature, nearly all have favored alkoxy radical formation (12,16,18-20,22,56), while only one has suggested that part of the reaction may occur via  $\alpha$ -carbon radical formation (17).  
The substituent effect

In the course of synthetic applications of the cerium(IV) oxidation to the benzyl alcohol-benzaldehyde conversion (Part

I), it was noted that benzyl alcohols containing electron releasing groups are oxidized at an appreciably faster rate than those containing electron withdrawing groups (5,6). For example, *p*-methoxybenzyl alcohol is oxidized to *p*-anisaldehyde in a few minutes at room temperature while *p*-nitrobenzyl alcohol is converted to *p*-nitrobenzaldehyde only after 10-15 minutes at steam bath temperature (6). Kinetic measurements in 75% aqueous acetonitrile-0.95 M nitric acid have also conformed to this trend. Hammett rho-sigma plots for the kinetically derived rate constants are shown in Figures 9 and 10. The Hammett rho values derived from these plots are  $-1.13 \pm 0.33$  for the  $\log k$  vs.  $\sigma$  plot and  $-1.07 \pm 0.28$  for the  $\log k$  vs.  $\sigma^+$  plot. The  $\sigma$  and  $\sigma^+$  constants used are summarized in Table 19 (62,63). All Hammett rho-values  $\pm$  standard deviation were evaluated by a linear least squares treatment.

The following discussion of the substituent effect will be based on the rate constants derived using spectrophotometric equilibrium constants (Table 16) rather than those derived entirely from kinetic data (Table 15). This is probably justified because the kinetically derived equilibrium constants for the more slowly oxidized alcohols deviate rather widely from the spectrophotometric equilibrium constants (Table 18), while the more rapidly oxidized alcohols yield kinetic equilibrium constants which are approxi-

Figure 9. Hammett plot for benzyl alcohols using rate constants derived from kinetic data.  
 $\rho = -1.13$

Figure 10. Hammett plot for benzyl alcohols using rate constants derived from kinetic data.  $\rho^{\ddagger} = -1.07$

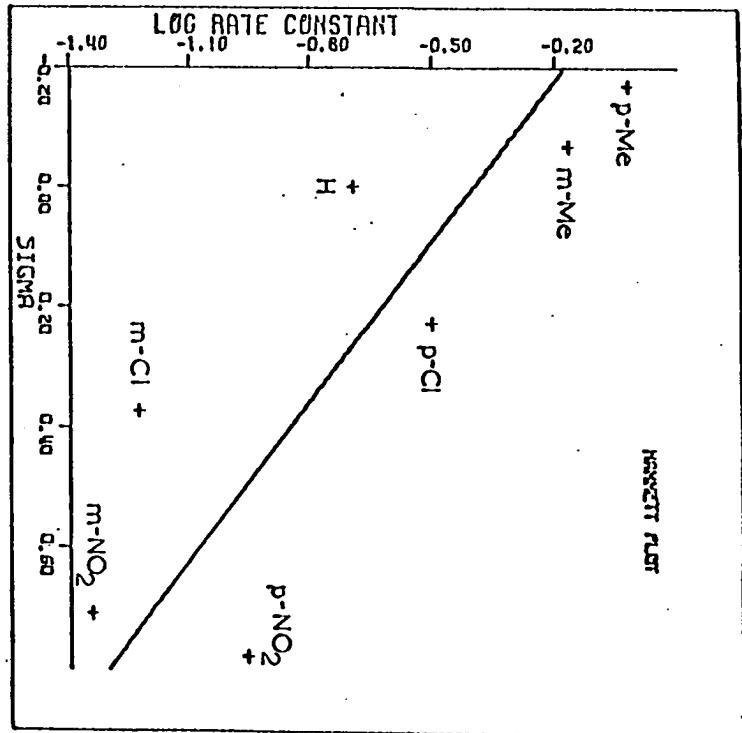
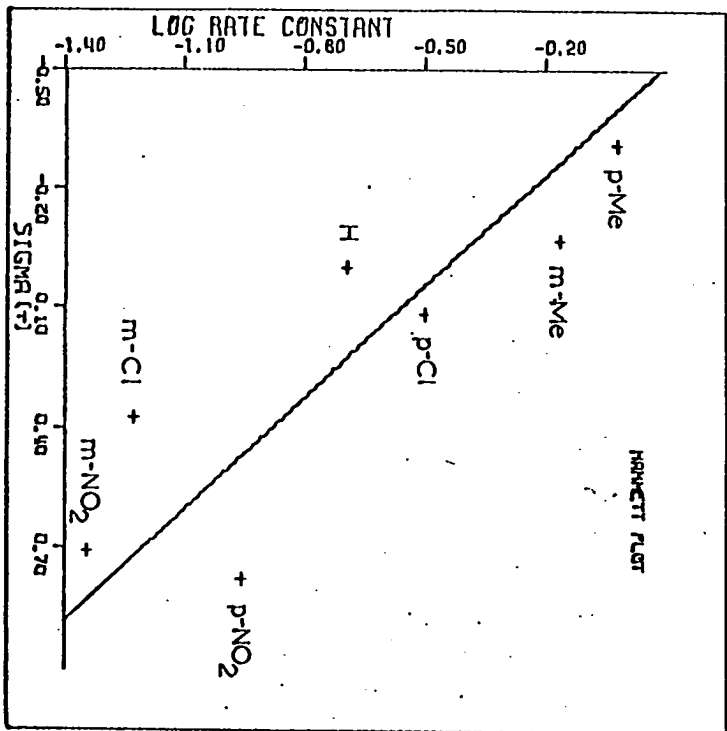


Table 19. Hammett  $\sigma$  and  $\sigma^+$  constants

Substituent	$\sigma^a$	$\sigma^{+b}$
<u>m</u> -CH <sub>3</sub>	-0.069	
<u>p</u> -CH <sub>3</sub>	-0.170	-0.311
<u>m</u> -Cl	+0.373	
<u>p</u> -Cl	+0.227	+0.114
<u>p</u> -Br	+0.232	+0.150
<u>m</u> -NO <sub>2</sub>	+0.710	
<u>p</u> -NO <sub>2</sub>	+0.778	
<u>p</u> -CH <sub>3</sub> O	-0.268	-0.778

<sup>a</sup>From reference 62.

<sup>b</sup>From reference 63.

mately the same as those derived spectrophotometrically. Thus there seems to be a larger experimental error associated with the more slowly oxidized alcohols as would be expected since solvent oxidation becomes more important in these cases. This error can be avoided to a large extent by using the slopes of the  $1/k'$  vs.  $1/[ROH]$  plots,  $1/kK$ , and the spectrophotometric equilibrium constant,  $K$ , to evaluate the unimolecular rate constants, making the assumption that the relative values of the equilibrium constants will not vary significantly from the spectrophotometric conditions to the kinetic conditions.

The use of the "spectrophotometric" rate constants

(those derived using spectrophotometric equilibrium constants) rather than "kinetic" rate constants (those derived from kinetic data alone) can be further justified by comparing the activation parameters for the cerium(IV) oxidation of m-nitrobenzyl alcohol calculated from "kinetic" and "spectrophotometric" rate constants (Table 17) with those reported in the literature for other alcohols. Muhammad and Rao reported an activation energy of 26.3 kcal./mole for the ceric sulfate oxidation of methanol (16). Hintz and Johnson reported an activation energy of 27.5 kcal./mole and an entropy of activation of 16.5 e.u. for the ceric perchlorate oxidation of cyclopentanol in mixed perchloric and sulfuric acids (14). Comparison of these values with those calculated in this study using "kinetic" rate constants,  $E_a=41.3$  kcal./mole and  $\Delta S^*=59.1$  e.u., and using "spectrophotometric" rate constants,  $E_a=25.0$  kcal./mole and  $\Delta S^*=11.7$  e.u., demonstrates that the "spectrophotometric" rate constants are more in line with what has been reported in the literature and thus are probably more reliable.

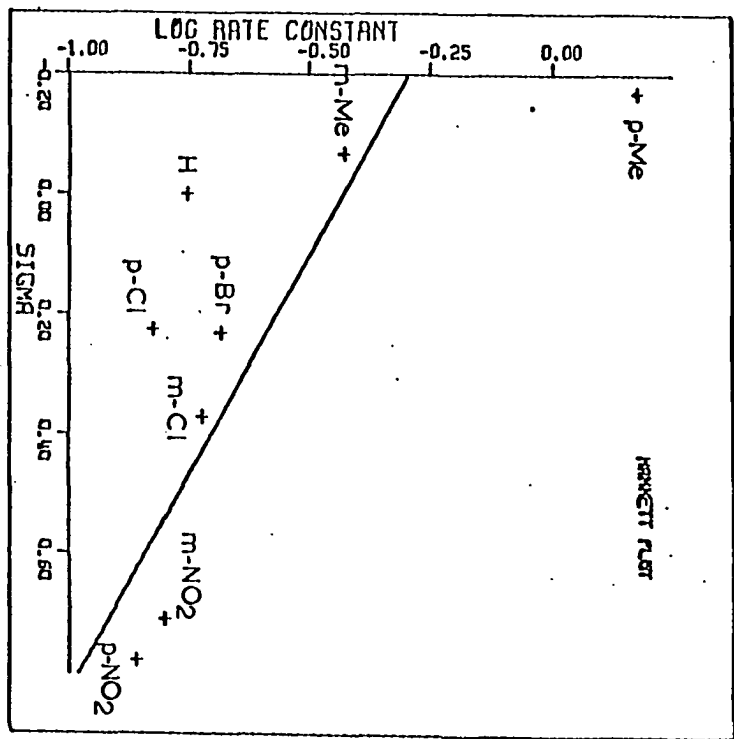
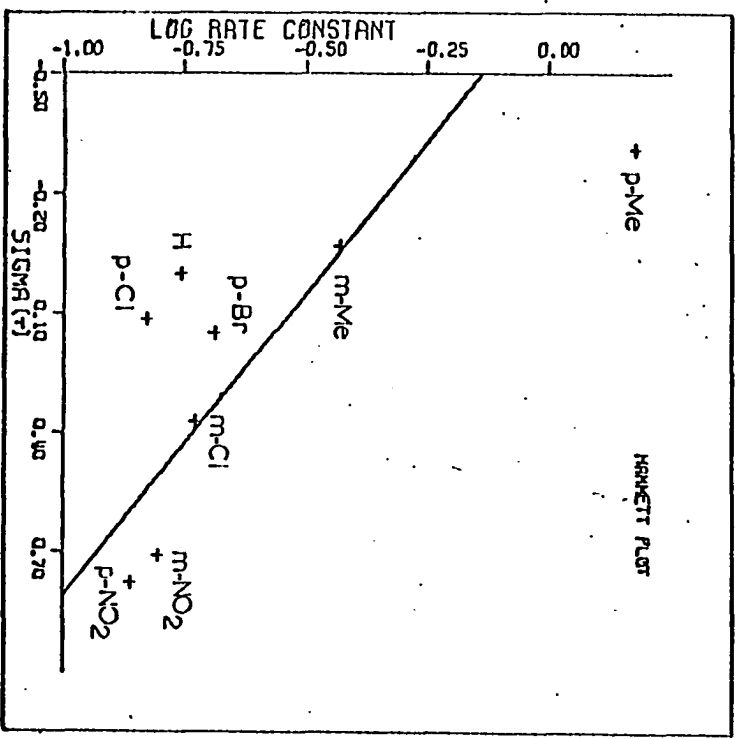
Hammett plots of  $\log k$  (from spectrophotometric equilibrium constants) vs.  $\sigma$  and  $\sigma^+$  are shown in Figures 11 and 12. the  $\sigma$  and  $\sigma^+$  values are summarized in Table 19. The slopes of the plots are  $\rho = -0.69 \pm 0.29$  and  $\rho^+ = -0.66 \pm 0.26$ , seemingly consistent with the development of a small amount of free radical character at the  $\alpha$ -carbon in the transition state.

If the rate constants for the alcohols with electron



Figure 11. Hammett plot for benzyl alcohols. Rate constants derived using spectrophotometric equilibrium constants.  $\rho = -0.69$

Figure 12. Hammett plot for benzyl alcohols. Rate constants derived using spectrophotometric equilibrium constants.  $\rho^{\ddagger} = -0.66$



donating substituents (p-methyl, m-methyl, plus benzyl alcohol) are plotted separately from those for benzyl alcohols with electron withdrawing substituents (m-chloro, p-chloro, p-bromo, m-nitro, and p-nitro), an interesting trend is observed as is illustrated in Figures 13-16. Hammett's rho for the electron donating substituents is  $-5.51 \pm 0.35$  (Figure 13) and rho(plus) is  $-2.86 \pm 0.40$  (Figure 14). For the alcohols with electron withdrawing substituents, Hammett's rho is  $-0.12 \pm 0.09$  (Figure 15) and rho(plus) is  $-0.11 \pm 0.08$  (Figure 16). Thus the substituent effect seems to vary with the nature of the substituent on the aromatic ring.

In order to determine whether the rates of oxidation of alcohols with electron donating substituents correlate better with  $\sigma$  or  $\sigma^+$  an attempt was made to measure the rate of oxidation of p-methoxybenzyl alcohol at 25° C. However, complete oxidation occurred in less than one minute at alcohol and cerium(IV) concentrations of 0.05 M and 0.005 M, respectively. If the half-life of the reaction is estimated to be 0.5 min. (it is probably less than this),  $k'$ , the pseudo first order rate constant, is calculated to be 1.5 min.<sup>-1</sup>. Assuming a value for the equilibrium constant of 0.5 l. mole<sup>-1</sup>, a value of 61.5 l.mole<sup>-1</sup> min.<sup>-1</sup> is calculated for the rate constant for unimolecular decomposition of the cerium(IV)-alcohol complex at ca. 25° C. The actual rate

Figure 13. Hammett plot for benzyl, m-methylbenzyl,  
and p-methylbenzyl alcohols.  $\rho = -5.51$

Figure 14. Hammett plot for benzyl, m-methylbenzyl,  
and p-methylbenzyl alcohols.  $\rho^{\ddagger} = -2.86$

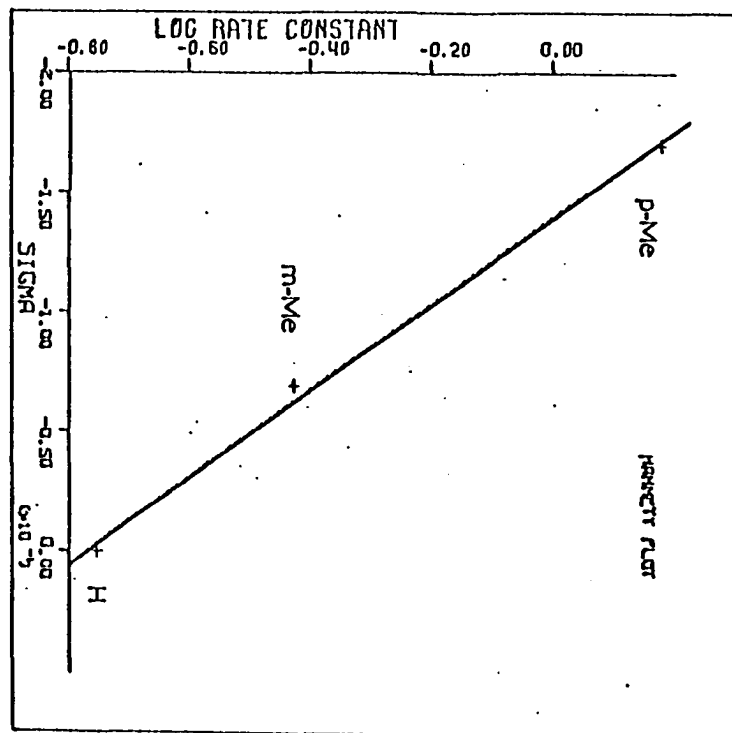
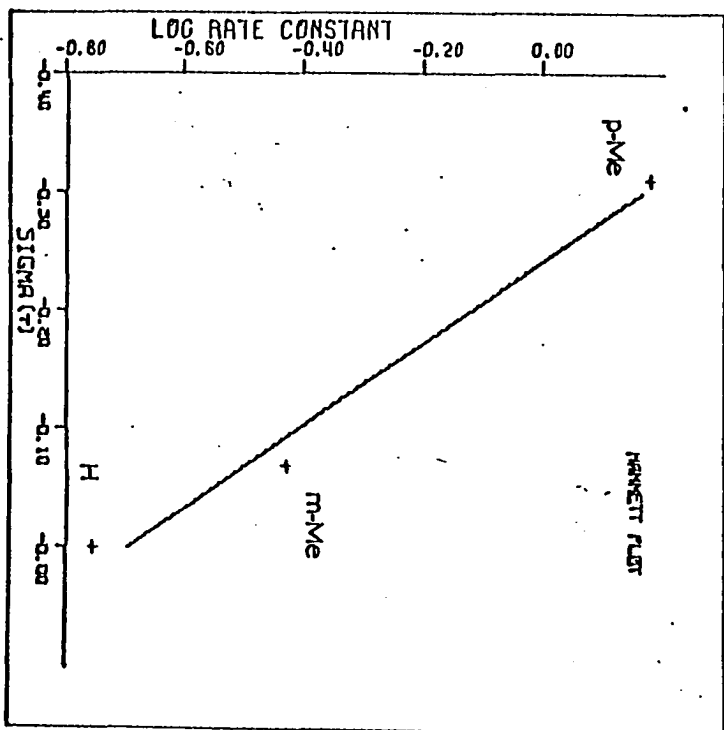
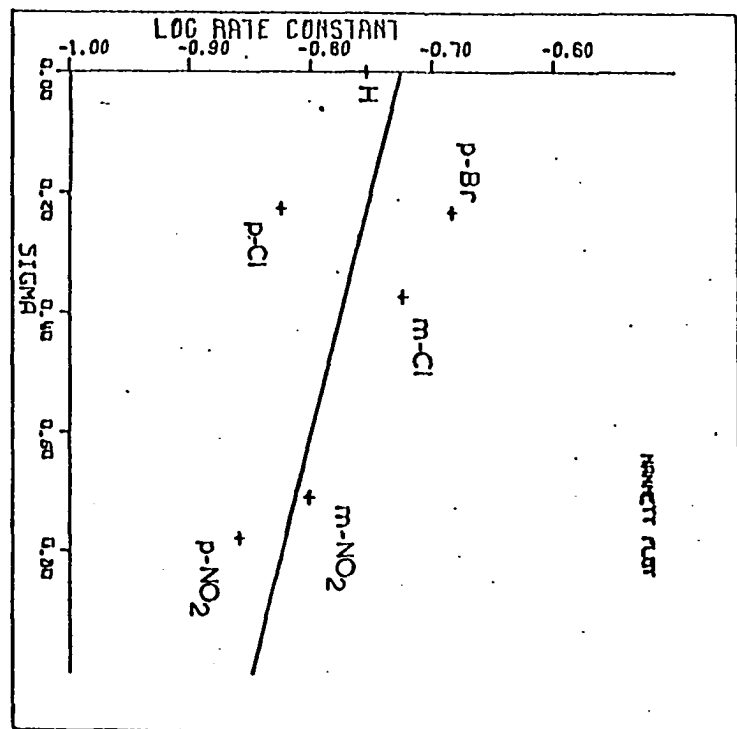
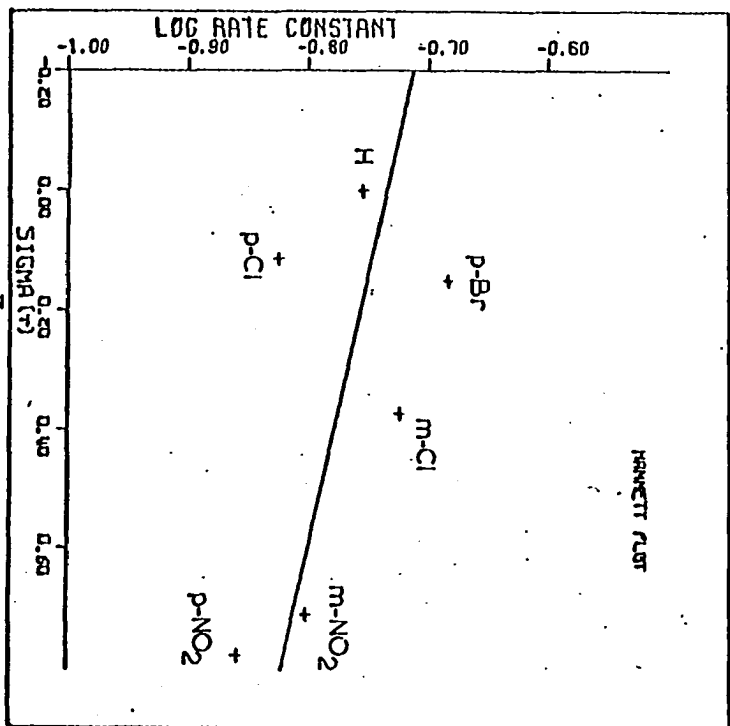


Figure 15. Hammett plot for benzyl alcohols with  
electron withdrawing substituents.  
 $\rho = -0.12$

Figure 16. Hammett plot for benzyl alcohols with  
electron withdrawing substituents.  
 $\rho^+ = -0.11$



constant may be larger than this since the half-life was probably less than 0.5 min.

Assuming a two-fold change in the rate constant,  $k$ , for each 10 degree change in temperature (a factor of four change over a 15 degree range was found for m-nitrobenzyl alcohol; see results, Table 15), a unimolecular rate constant,  $k$ , of  $492 \text{ l.mole}^{-1} \text{ min.}^{-1}$  is calculated for p-methoxybenzyl alcohol at  $55^\circ \text{ C.}$ , giving  $k(\text{p-methoxy})/k(\text{H}) = 2800$ . The value of the rate ratio  $k(\text{p-methoxy})/k(\text{H})$  is predicted to be 30 using  $\rho = -5.51$  and  $\sigma$  (Figure 13) and 166 using  $\rho^+ = -2.86$  and  $\sigma^+$  (Figure 14). Thus p-methoxybenzyl alcohol seems to be oxidized much faster than predicted from Hammett plots. If the rates of oxidation of p-methoxybenzyl alcohol and p-methylbenzyl alcohol and  $\sigma^+$  values are used to calculate a value of  $\rho^+$ , the result is  $\rho^+ = -5.25$ .

The various values of  $\rho$  and  $\rho^+$  calculated from the Hammett plots using a linear least squares treatment are summarized in Table 20. These may be compared with some values cited in the literature (Table 21). Hydrogen atom abstractions from a benzylic position typically correlate with  $\sigma^+$  and give  $\rho^+$  -values of ca. -1. Development of a full-fledged carbonium ion at the  $\alpha$ -position gives rise to  $\rho^+$  -values of ca. -5, while chromic acid oxidations give  $\rho$  -values of ca. -1. Thus it appears that the cerium(IV) oxidation of benzyl alcohol proceeds through transition states with varying amounts of charge on the  $\alpha$ -position depending on



Table 20. Hammett  $\rho$  values for the cerium(IV) oxidation of benzyl alcohols

Plot <sup>a</sup>	Fig.	$\rho$ or $\rho^+$
Log k <u>vs.</u> $\sigma$ ; all alcohols	6	-0.69 $\pm$ 0.29
Log k <u>vs.</u> $\sigma^+$ ; all alcohols	7	-0.66 $\pm$ 0.26
Log k <u>vs.</u> $\sigma$ ; H, <i>m</i> -CH <sub>3</sub> , <i>p</i> -CH <sub>3</sub>	8	-5.51 $\pm$ 0.35
Log k <u>vs.</u> $\sigma$ ; electron withdrawing substs.	10	-0.12 $\pm$ 0.09
Log k <u>vs.</u> $\sigma^+$ ; H, <i>m</i> -CH <sub>3</sub> , <i>p</i> -CH <sub>3</sub>	9	-2.86 $\pm$ 0.40
Log k <u>vs.</u> $\sigma^+$ ; electron withdrawing substs.	11	-0.11 $\pm$ 0.08
Log k <u>vs.</u> $\sigma^+$ ; <i>p</i> -CH <sub>3</sub> , <i>p</i> -CH <sub>3</sub> O	-	-5.52

<sup>a</sup>All rate constants derived using spectrophotometric equilibrium constants.

the nature of the substituent. With a *p*-methoxy substituent, the  $\rho^+$  -value (ca. -5) indicates nearly full carbonium ion character on the  $\alpha$ -position, while the nitrobenzyl alcohols ( $\rho$  ca. -0.1) may have no appreciable charge buildup at the  $\alpha$ -position.

#### k(Ethanol)/k(benzyl alcohol)

The finding that the rate constant for unimolecular complex decomposition in the cerium(IV) oxidation of ethanol is 1.6-1.7 times less than that for benzyl alcohol is consistent with the postulate of charge development on the  $\alpha$ -carbon during oxidation. It is clearly inconsistent with alkoxy formation in the rate determining step of the reaction

Table 21. Hammett  $\rho$  values reported in the literature

Reaction	$\rho$ or $\rho^+$
$z\text{-C}_6\text{H}_4\text{-CH}_2\text{CH}_3 + \text{Br}\cdot$ ( $\sigma^+$ )	$-0.69^a$
$z\text{-C}_6\text{H}_4\text{-CH}_2\text{-C}(=\text{O})\text{-O-O-}$ (56°) ( $\sigma^+$ )	$-1.20^b$
(100°) ( $\sigma^+$ )	$-1.04^b$
$z\text{-C}_6\text{H}_4\text{-CH}_3 + \text{Cl}\cdot$	$-0.66^c$
Br $\cdot$	$-1.46^c$
$\text{CCl}_3\cdot$	$-1.46^c$
$\text{---O}\cdot$	$-0.83^c$
$\text{Ar}_2\text{CHCl} + \text{EtOH}$	$-5.09^d$
$\text{Ar}_2\text{CHOH} \rightleftharpoons \text{Ar}_2\text{CH}^+$	$-6.7^d$
$\text{ArCHOHCH}_3 + \text{CrO}_3$ ; aqueous acetic acid, 30°	$-1.01^e$
; pyridine/benzene, 30°	$-0.52^e$
; benzene, 30°	$-0.37^e$
$\text{ArCHOHCF}_3 + \text{CrO}_3$ ; 77% aqueous acetic acid	$-1.01^f$

<sup>a</sup>Reference 64.<sup>b</sup>Reference 65.<sup>c</sup>Reference 66.<sup>d</sup>Reference 43.<sup>e</sup>Reference 67.<sup>f</sup>Reference 68.

since the electron withdrawing phenyl group should hinder alkoxy radical formation relative to a methyl group. However, the magnitude of this effect is also inconsistent with complete carbonium ion or free radical formation on the  $\alpha$ -position, since the ability of a phenyl group to stabilize positive charge and free radical character is far greater than that of a methyl group.

#### The deuterium isotope effect

Deuterium isotope effects of  $k_H/k_D = 2.2, 2.0,$  and  $1.3$  were found for *m*-chlorobenzyl, benzyl, and *p*-methylbenzyl alcohols, respectively. These compare favorably with the value of  $1.9$  found by Littler for the ceric sulfate oxidation of cyclohexanol- $\alpha$ - $d_1$  (17).

Other deuterium isotope effects reported in the literature for alcohol oxidations are  $16$  for the permanganate oxidation of  $C_6H_5CDOHCF_3$  at  $25^\circ$  (69),  $7$  for the chromic acid oxidation of 2-propanol-2- $d_1$  in water (70),  $9.5$  for the chromic acid oxidation of benzhydrol- $\alpha$ - $d$  (4),  $1.6$  for the manganese(III) oxidation of cyclohexanol- $\alpha$ - $d$  in sulfuric acid (71),  $4.5$  and  $3.6$  for the vanadium(V) oxidation of cyclohexanol- $\alpha$ - $d$  in sulfuric acid and perchloric acid, respectively (57),  $1.7$  for the cobalt (III) oxidation of cyclohexanol- $\alpha$ - $d$  in perchloric acid (72),  $1.4$  for the cobalt(III) oxidation of 3-methyl-2-butanol-2- $d_1$  in perchloric acid (73), and  $1.0$  for the cobalt (III) oxidation of 3-pentanol-3- $d_1$  in perchloric

acid (74).

Some deuterium isotope effects reported in the literature for hydrogen atom abstractions by free radicals are 2.0 for the reaction of chlorine atoms with toluene (75), 4.6 for bromine atoms with toluene (76), 9.9 for methyl radicals with toluene (77), and 1.8 for chlorine atoms with isobutane (75).

It is apparent that the kinetic isotope effect found for the cerium(IV) oxidation of benzyl alcohols is small compared to the isotope effects usually found for alcohol oxidations by other oxidants. The behavior of cerium(IV) parallels most closely that of cobalt(III), an oxidant usually acknowledged to produce alkoxy radicals in the oxidation of alcohols (4), and manganese(III), another one electron oxidant (78), but deviates rather widely from the isotope effects found for chromium(VI) and manganese(VII). The isotope effect for chlorine atom abstraction of benzylic hydrogen atoms is close to that found for the cerium(IV)-alcohol reaction. The magnitude of the kinetic isotope for the cerium(IV)-alcohol reaction seems to demand some participation of the  $\alpha$ -hydrogen in the slow step of the reaction, but the extent of  $\alpha$ -C-H bond breakage is probably small.

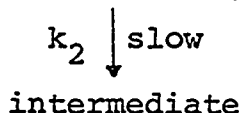
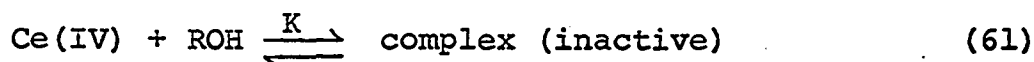
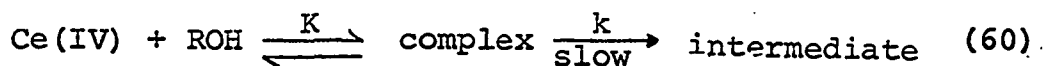
The substituent effect on the kinetic isotope effect ( $k_H/k_D$  for m-chloro > H > p-methyl) might have been anticipated since it is generally found that reactions with the

lowest activation energy give the smallest isotope effect (77). For example, in the chromic acid oxidation of  $\text{ArCHOHCF}_3$  and  $\text{ArCDOHCF}_3$  ( $\rho = -1.01$ ) it is found that  $k_{\text{H}}/k_{\text{D}}$  for 3,5- $(\text{NO}_2)_2$  >  $\underline{\text{m}}\text{-NO}_2$  >  $\underline{\text{m}}\text{-Br}$  > H >  $\underline{\text{p}}\text{-CH}_3$  (68).

### Mechanistic Conclusions

#### Complex formation

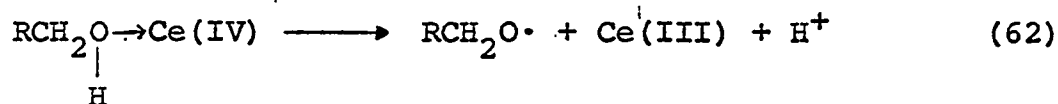
The evidence for 1:1 cerium(IV)-alcohol complex formation as the first step in the cerium(IV) oxidation of alcohols seems conclusive. In this study and in several other studies reported in the literature (4,11,12,16-20,22,56), both spectrophotometric and kinetic data indicate complex formation. It may be pointed out, however, that the two situations --- where unimolecular decomposition of the complex is the rate determining step of the reaction (Equation 60) and where the 1:1 complex is an inactive species and oxidation occurs via bimolecular collision (Equation 61) --- are kinetically and spectrophotometrically indistinguishable. However, it seems only reasonable



that if a molecule of substrate and a metal ion are bound together, that oxidation should occur from this species and not from a random collision of alcohol and metal ion.

#### Complex decomposition

Several possible modes of decomposition exist for the cerium(IV)-alcohol complex. The one most commonly suggested in the literature is simple alkoxy radical formation (Equation 62) (4). While this may occur with some alcohols, Littler's



finding of  $k_{\text{H}}/k_{\text{D}} = 1.9$  for the ceric sulfate oxidation of cyclohexanol- $\alpha$ -d (17) and our finding that  $k_{\text{H}}/k_{\text{D}} = 1.3\text{-}2.2$  for benzyl alcohols seems to argue against simple alkoxy radical formation. In addition, the observed substituent effect and our finding that benzyl alcohol is oxidized faster than ethanol also argue against simple alkoxy radical formation. However, one experimental observation seems to demand an alkoxy radical-like species. The oxidation of n-pentanol leads to 1-methyltetrahydrofuran in ca. 20% yield based on consumed alcohol (79). This is best explained by the mechanism outlined in Chart 1, although a free alkoxy radical is not necessarily an intermediate.

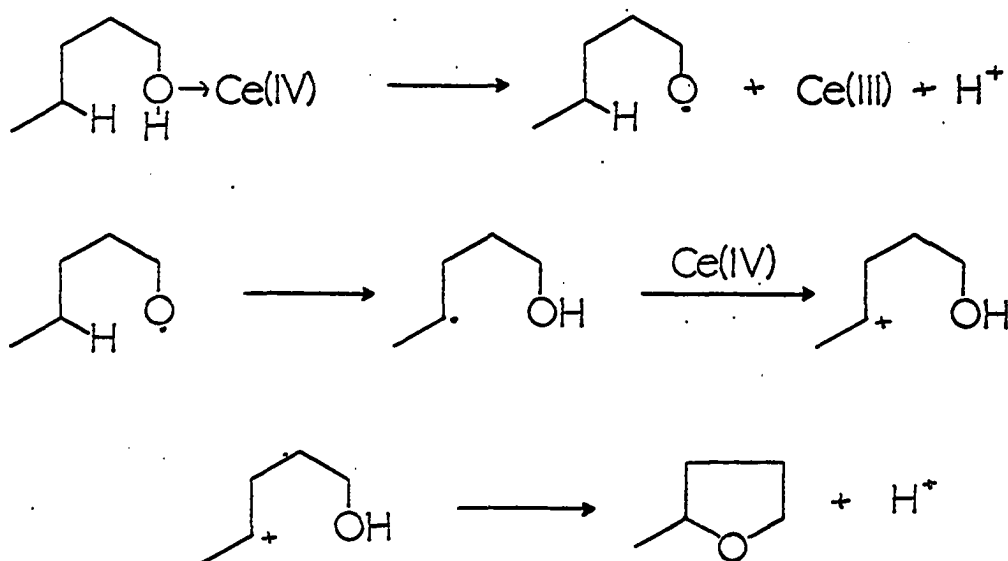


Chart 1. CAN oxidation of 1-pentanol

The small substituent effect observed for the cerium(IV) oxidation of benzyl alcohols with electron withdrawing substituents might be explicable as due to alkoxy radical formation if it were not for the deuterium isotope effect of 2.2 found for the oxidation of *m*-chlorobenzyl alcohol. This indicates that there must be some C-H bond breakage in the transition state of the slow step of the reaction. Thus it is likely that the first formed intermediate in these cases is the carbon radical 3, which may or may not be coordinated to a

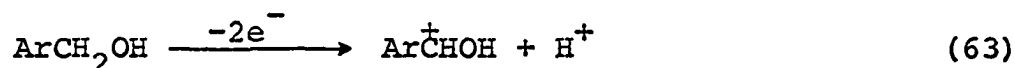


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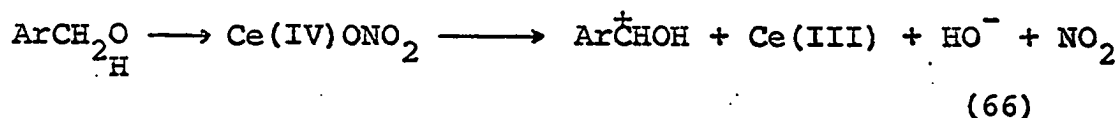
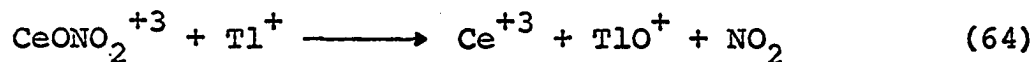
cerium(III). The small substituent effect is then due to the fact that there is essentially no charge development on the

$\alpha$ -carbon in the transition state.

The large substituent effect observed for the oxidation of benzyl alcohols with strongly electron donating substituents is most simply explained as the formation of a carbonium ion as the first intermediate (Equation 63). This, however, would require a two electron oxidation by cerium(IV),



an occurrence which appears to be unlikely since the existence of cerium(II) in solution, even as a transient intermediate, has never been demonstrated. It should be noted, however, that Gryder and Dorfman have suggested that in the cerium(IV) oxidation of thallium(I) to thallium(III) a small part of the oxidation occurs in a one step process (80). They have suggested that the two electron oxidation occurs with the aid of coordinated nitrate (Equation 64). Two possible two electron oxidation mechanisms are illustrated in Equations 65 and 66. The possibility that a two electron oxidation of the benzyl alcohol occurs via a





cerium(IV) dimer can be eliminated on the basis of the pseudo first order kinetics observed for the oxidation.

A mechanistic possibility which seems intuitively more satisfying than the clean-cut two-electron and one-electron oxidation mechanisms is one whereby the metal ion can accept varying amounts of electronic charge depending on the availability of the electrons. The transition state would then be represented as 4 or as a resonance hybrid (Chart 2). If there are electron donating substituents on the aromatic ring which can stabilize positive charge on the  $\alpha$ -position

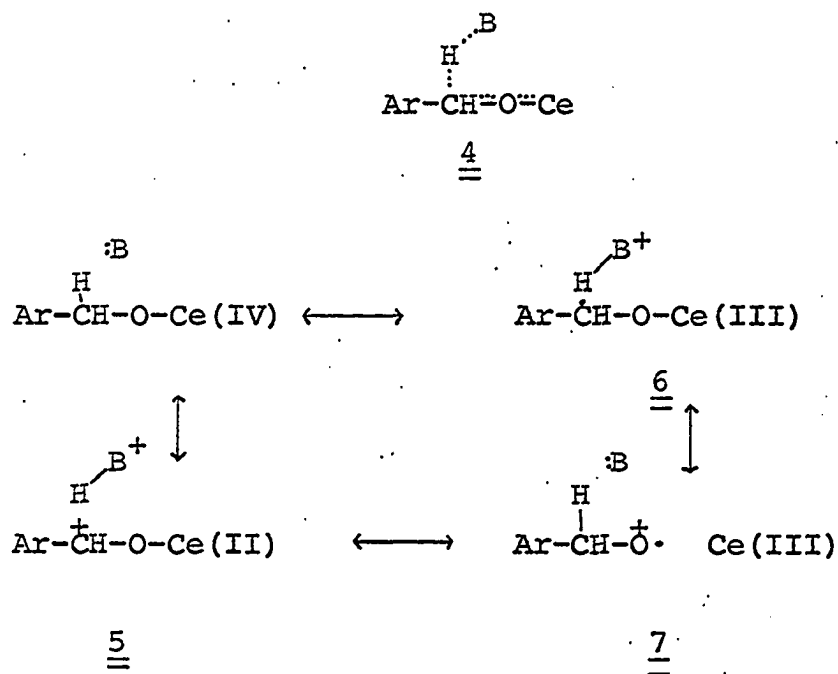


Chart 2. Transition state for the cerium(IV) oxidation of arylcarbinols

then the transition state will look more like resonance hybrid 5, whereas the presence of electron withdrawing groups on the aromatic ring will cause the transition state

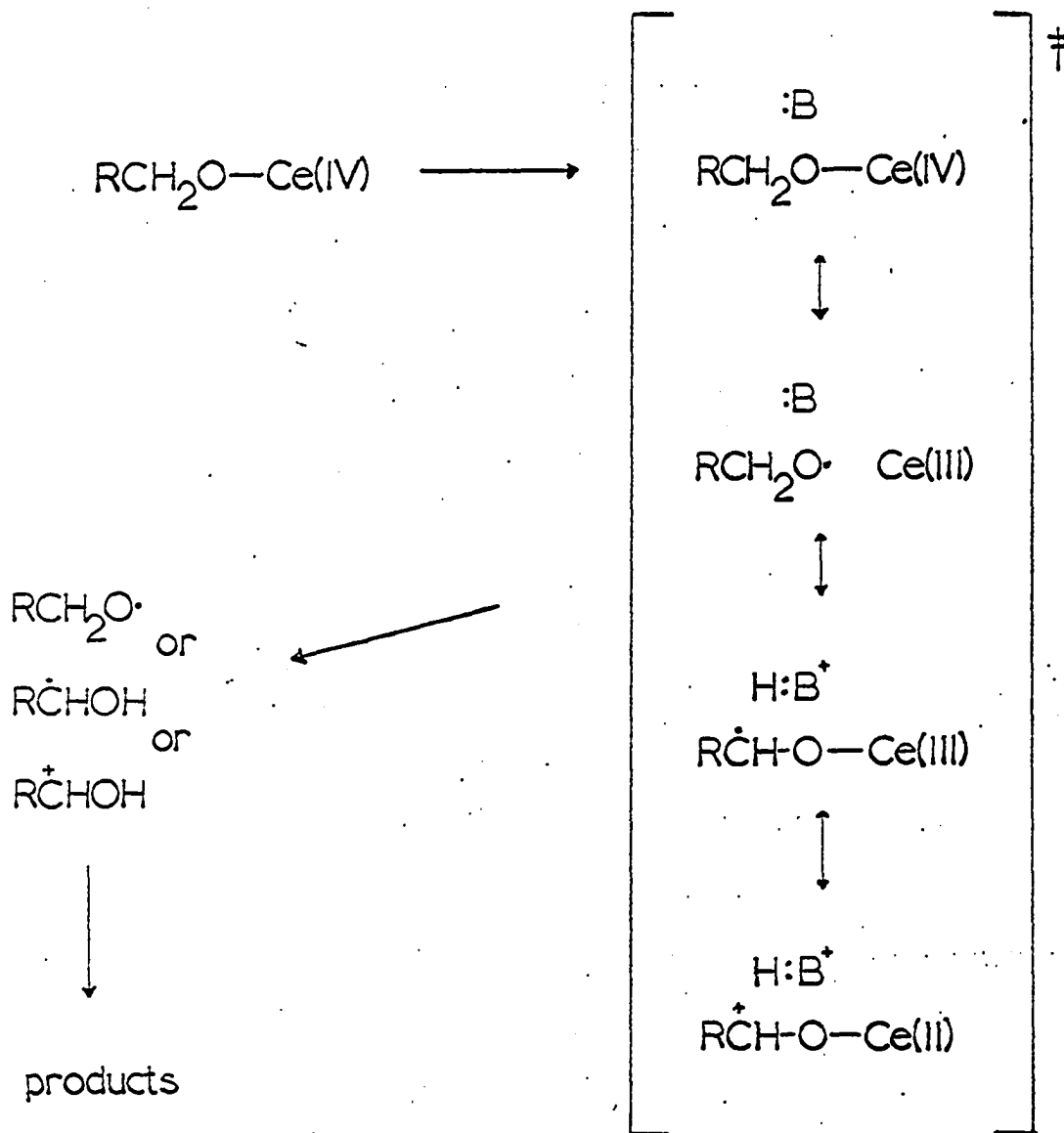
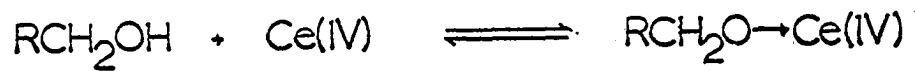
to look more like resonance hybrids 6 and 7. The base (:B) in this chart might well be a ligand (e.g. nitrate) attached to the metal ion. In this mechanistic scheme, normal aliphatic alcohols which are not capable of supporting much positive charge on the  $\alpha$ -position would have transition states contribution from resonance hybrids 4 and 5.

Thus the overall mechanism for the oxidation of alcohols by cerium(IV) may be pictured as in Chart 3.

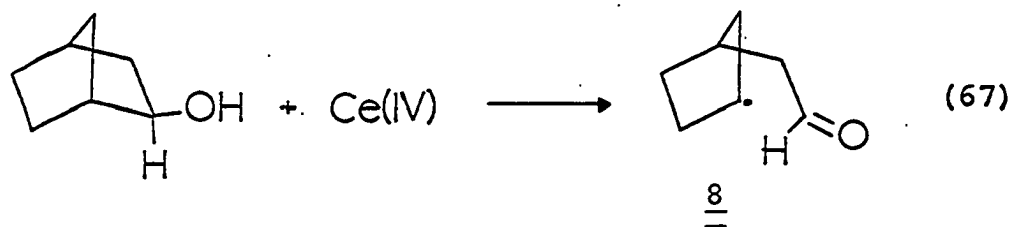
That no single mechanism accounts for the reactions of cerium(IV) with alcohols becomes obvious when the various reactions are surveyed. The cerium(IV) oxidation of *n*-pentanol leads to 1-methyltetrahydrofuran in 20% yield (81). This product is most simply explained as arising from an alkoxy radical intermediate. The oxidation of substituted benzyl alcohols is subject to a large substituent effect, this being largest for electron donating substituents, and an  $\alpha$ -deuterium isotope effect. These results are consistent with a large amount of carbonium ion character developing at the  $\alpha$ -carbon in the transition state of the slow step. Benzyl alcohols with electron withdrawing substituents are subject to a smaller substituent effect along with a deuterium isotope effect, possibly indicating a small amount of free radical character on the  $\alpha$ -carbon in the transition state.

Norborneol is oxidized by cerium(IV) to give products formally derived from the radical (or cation), 8 (Equation 67)

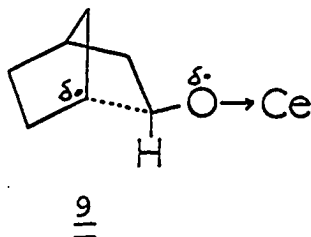
Chart 3. Mechanism of the cerium(IV) oxidation of alcohols



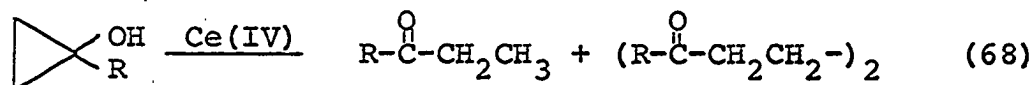
(79). While formation of an alkoxy radical followed by ring cleavage would give the radical 8, the rapid rate of oxidation



of the alcohol probably indicates that ring opening is occurring in the transition state, which might be pictured as 9. In a similar reaction, the oxidation of cyclopro-



panols with cerium(IV) leads to monomeric and dimeric ring-opened ketones (Equation 68) (82).



Thus the variable mechanism outlined in Chart 3 seems to be required to account for the varied reactions of cerium(IV) with alcohols. On the basis of the results of this study the mechanistic conclusions of several workers concerning the cerium(IV) oxidation of alcohols must be seriously questioned. The intermediacy of a simple alkoxy radical no longer seems adequate to account for all experimental observations,

although it seems to be a reasonable intermediate in several cases. The ability of a one electron oxidant to behave like a two electron oxidant as in the case of benzyl alcohols with electron denating substituents suggests further investigation into reaction mechanisms of cerium(IV) oxidations.

## EXPERIMENTAL

## Rate Measurements

The reaction medium was prepared by mixing three parts (by volume) acetonitrile and one part (by volume) 3.81 M nitric acid in aqueous solution. Solutions of alcohol and ceric ammonium nitrate were prepared by dissolving the appropriate amount of reagent in the solution described above in 25 ml. volumetric flasks. The ceric ammonium nitrate concentration was usually 0.005 M; the alcohol concentration was usually 0.3-0.05 M.

The two volumetric flasks were placed in a constant temperature bath ( $T. = 55.0^{\circ}$  C. for most runs) for at least ten minutes before mixing. The contents of both flasks were then mixed in a 100 ml. volumetric flask and the time was noted. At appropriate time intervals 3-4 ml. aliquots were removed and put in a 25 ml. Erlenmeyer flask to cool. The time at which the aliquot was removed was noted. The aliquot was transferred from the Erlenmeyer flask to a cuvette and the absorbance of the solution was measured one minute after the aliquot was taken. Absorbance measurements were usually made at 458  $m\mu$  for 0.005 M cerium(IV). The rates were followed for at least two half-lives and pseudo first order rate constants were obtained by least squares treatment of log absorbance vs. time plots. The pseudo first order rate constants were corrected for concurrent solvent oxidation by

subtracting the pseudo first order rate constant for solvent oxidation (Table 13).

Rate constants for unimolecular decomposition of the complex were calculated in two ways. In the first, plots of the reciprocal of the pseudo first order rate constant vs. the reciprocal of the alcohol concentration gave the intercept of  $1/k$  and slope of  $1/kK$ . This method is very sensitive to errors in  $k'$  and gave values of  $K$  which were not in very good agreement with the values of  $K$  measured spectrophotometrically (Table 18). The second method of calculating  $k$  utilized spectrophotometric equilibrium constants and the slope of the  $1/k'$  vs.  $1/(ROH)$  plots.

#### Benzyl Alcohol-Ceric Perchlorate Complex Formation

To 50 ml. of a solution of 0.1 M ceric perchlorate in 1 M perchloric acid was added a few drops of benzyl alcohol. Upon mixing, the solution exhibited the orange to red-orange color change associated with alcohol-cerium(IV) complex formation.

#### Chemicals

Ceric ammonium nitrate was from the G. F. Smith Chemical Co. and was analyzed primary standard grade material with a purity of 99.99%. Acetonitrile was Baker Analyzed Reagent and was used without purification. Benzyl alcohol was



Matheson, Coleman, and Bell material and was distilled before use. p-Methylbenzyl alcohol was prepared by the saponification of p-methylbenzyl acetate (83) obtained from Aldrich. The product was recrystallized from heptane, m.p. 57.5-59.0°, lit. 59° (84). m-Methylbenzyl alcohol was prepared by the lithium aluminum hydride reduction of methyl m-toluate using the procedure of Nystrom and Brown (54). The product was distilled prior to use. p-Chlorobenzyl alcohol was from Aldrich and was recrystallized from benzene-ligroin, m.p. 70-71°, lit. 71-72.5° (85). p-Bromobenzyl alcohol was prepared from p-bromobenzyl bromide (Aldrich) by conversion to the acetate and saponification of the acetate (86). The product was recrystallized from ligroin-benzene, m.p. 76-77.5°, lit. 76-76.5° (85). m-Chlorobenzyl alcohol was from Aldrich and was used without purification. o-Chlorobenzyl alcohol was obtained from E. Geels, m.p. 70-71°, lit. 69° (52). m-Nitrobenzyl alcohol was Eastman Co. "yellow label" material and was distilled before use.  $\alpha,\alpha$ -Dideuterobenzyl alcohol was prepared by the lithium aluminum deuteride (Ventron) reduction of methyl benzoate and was distilled prior to use. N.m.r. analysis of the product indicated the presence of 6 mole % methyl benzoate in the product.  $\alpha,\alpha$ -Dideutero-p-methylbenzyl alcohol was prepared by the lithium aluminum deuteride (Ventron) reduction of p-toluic acid (Matheson, Coleman, and Bell), m.p. 57.5-58.5°. The alcohol contained >

97% deuterium in the  $\alpha$ -position as shown by n.m.r.  $\alpha,\alpha$ -Dideutero-m-chlorobenzyl alcohol was prepared by the lithium aluminum deuteride (Ventron) reduction of m-chlorobenzoic acid (Matheson, Coleman, and Bell), b.p. 90-91<sup>0</sup> (0.7 mm.). The product contained greater than 97% deuterium in the  $\alpha$ -position as shown by n.m.r. p-Nitrobenzyl alcohol was from Aldrich and was recrystallized twice from aqueous ethanol, m.p. 92-92.5<sup>0</sup>, lit. 93<sup>0</sup> (51).

#### Equipment

A Beckman model DU spectrophotometer fitted with a tungsten filament source was used to measure the absorbance of the solutions. Least squares calculations were performed by an IBM Series 360 Model 50 computer using the program PLOT. The graphs were executed by a Cal-Comp Digital Incremental Data Plotter in conjunction with program PLOT. Activation parameters were calculated using the computer program ACTPAR.

PART IV. CERIUM(IV) OXIDATION OF CYCLOHEPTATRIENE

## INTRODUCTION

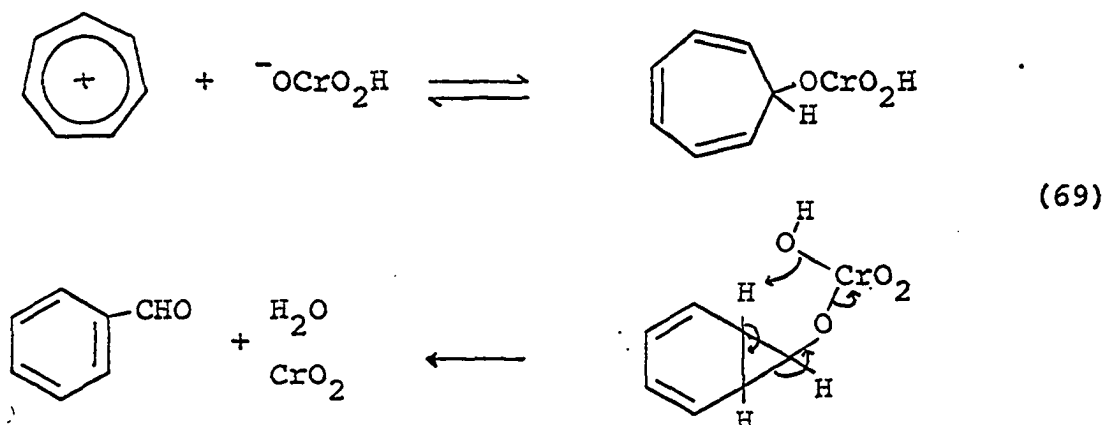
Oxidations of Cycloheptatriene and Related  
Compounds Involving Ring Contraction

The earliest reported oxidation of cycloheptatriene (CHT) is that of Merling in 1891 (87). He found that CHT is oxidized to a "considerable yield" of benzaldehyde and benzoic acid and a small amount of carbon dioxide by potassium dichromate in aqueous sulfuric acid. The oxidation of CHT by potassium permanganate led to no isolable products (87). Büchner in 1896 oxidized cycloheptatriene-7-carboxylic acid ("pseudophenylacetic acid") with alkaline potassium permanganate and found the products to be terephthalic acid and benzoic acid (88). It is interesting to note that the structure of the starting acid was postulated to be 7-norcaradiene carboxylic acid and it was not until the advent of nuclear magnetic resonance that the structure was unequivocally shown to be cycloheptatriene-7-carboxylic acid.

Juppe and Wolf in 1961 investigated the chromium trioxide oxidation of cycloheptatriene-7-C-14 (89). They obtained benzoic acid in 21% yield and determined that six sevenths of the carbon-14 label was contained in the aromatic ring, and one seventh was present in the carboxyl carbon. Their data suggests that a symmetrical intermediate, most likely tropylium ion, is an intermediate in the reaction. Dewar, Ganellin, and Pettit investigated the products of

oxidation of cycloheptatriene-7-carboxylic acid by several oxidants (90). Among the products were tropylium ion, terephthalic acid, benzaldehyde, and benzoic acid. In no case was the total yield of products from any one oxidation greater than 40% and most oxidants gave only low yields of isolable products. In particular, ceric ammonium nitrate (CAN) in 2 N nitric acid in acetone oxidized cycloheptatriene-7-carboxylic acid to tropylium ion in 30% yield. No other products were identified. The authors suggest that tropylium ion formation results from the oxidative decarboxylation of the starting material, i.e.,  $\text{RCO}_2\text{H} \longrightarrow \text{R}^+ + \text{CO}_2\text{H}^+ + 2\text{e}^-$ . Benzaldehyde and benzoic acid probably arise from further oxidation of tropylium ion (vide infra), while terephthalic acid formation probably occurs via epoxidation of one of the double bonds of the starting material followed by acid catalyzed rearrangement and further oxidation.

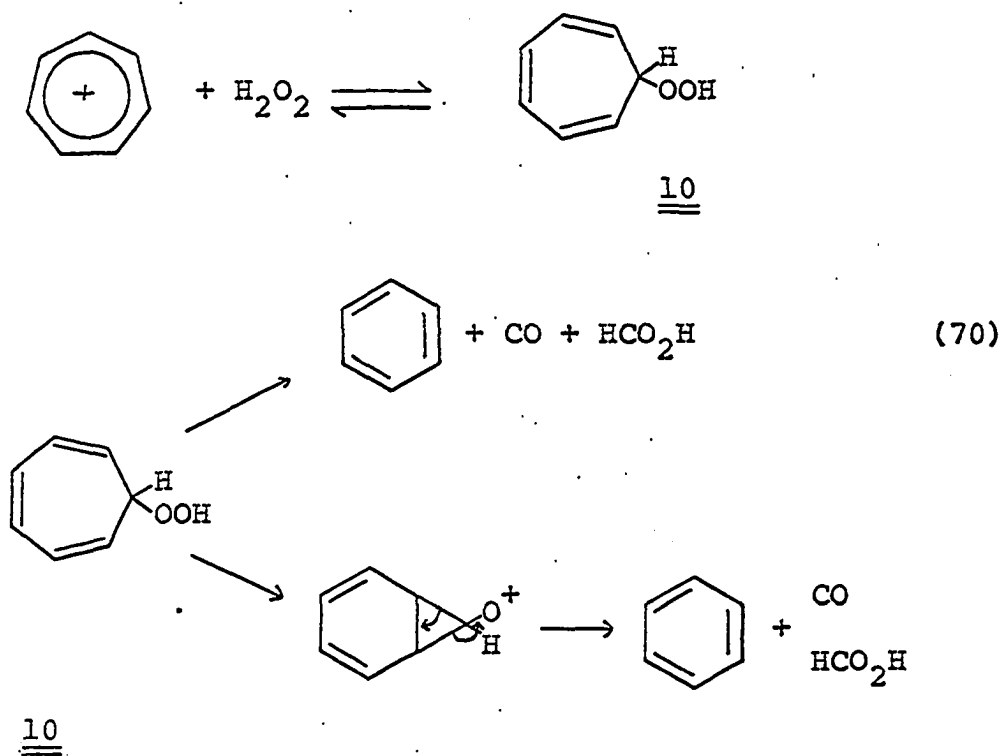
Tropylium ion may be converted to ring-contracted products upon reaction with oxidizing agents. Doering and Knox found that chromium trioxide and silver oxide convert tropylium bromide to benzaldehyde in 71% yield and 46% yield, respectively (91). The authors suggest that the rearrangement in the chromic acid oxidation may occur via a norcaradiene valence tautomer as illustrated in Equation 69. Like other aromatizing rearrangements in the tropilidene and tropolone field, expression in terms of the norcaradiene



valence tautomer although never necessary is simplest. The oxidation by silver oxide may occur via troyl alcohol, but there is no evidence relating to the mechanism.

Volpin and Kursanov found that troylium ion reacts rapidly with hydrogen peroxide to give high yields of benzene (92,93). The source of troylium ion does not affect the course of the reaction since both troylium bromide and perchlorate behave similarly. The reaction does not proceed via troyone or benzaldehyde as shown by control experiments and the reaction ceases in weakly alkaline media, indicating that oxidation of the troylium ion and not troyl alcohol occurs. The reaction is apparently not free radical in nature since addition of ferrous sulfate which promotes the free radical decomposition of peroxides inhibits the reaction. Volpin and Kursanov suggest that the reaction proceeds via formation of 10 and that either concerted or stepwise decomposition of 10 leads to the observed product, benzene

(Equation 70).

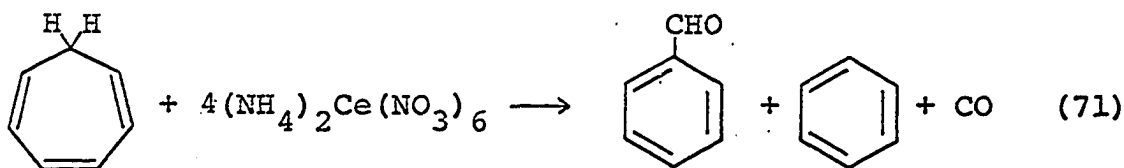


Oxidations of Cycloheptatriene and Related  
Compounds not Involving Ring Contraction

Nozoe, Mukai, Tezuka, and Osaka found that oxidation of CHT by chromic acid in pyridine gave tropone in 30% yield (94). Oxidation of tropylium ion under the same conditions gave a 40% yield of tropone (94). Radlick found that selenium dioxide in buffered aqueous dioxane oxidizes CHT to tropone in 25% yield (95). The oxidation of CHT by potassium permanganate gave  $\alpha$ -tropolone in 6.3% yield (96).

## RESULTS AND DISCUSSION

The oxidation of cycloheptatriene (CHT) by four equivalents of ceric ammonium nitrate (CAN) in aqueous acetic acid and other solvents gives nearly quantitative yields of benzaldehyde (major product), benzene, and carbon monoxide (Equation 71). The results are summarized in Table 22. The



reaction is quite facile (6 minutes, 90° C.), being more rapid in 50% aqueous acetic acid than the oxidation of benzyl alcohol.

The oxidation of a CHT-related compound by cerium(IV) has been reported only for the oxidative decarboxylation of cycloheptatriene-7-carboxylic acid where the product was found to be tropylium ion in 30% yield (vide supra) (90). The CAN oxidation of CHT is unique in that almost quantitative conversion to products occurs. It seems a priori rather surprising that a one electron oxidant such as cerium(IV) should lead to a high yield of products in a system where polymerization should be a facile process. In the other oxidative aromatizations of CHT reported, products are generally obtained in only moderate to low yields (vide supra).



Table 22. Oxidation of CHT by cerium(IV)

Oxidant (Conc.) <sup>a</sup>	Medium	Temp. (deg.)	PhCHO/ PhH	Yield, %	
				PhCHO	PhH
CAN(1N)	water	25	87/13		
CAN(0.5N)	water	95	85/15	64	11
CAN(0.4N)	water + 0.15N KOH	75	86/14		
CAN(0.5N)	water + 0.5N HClO <sub>4</sub>	95	87/13	58	9
CAN(0.5N)	10% aq. HOAc	95	88/12	46	6
CAN(0.5N)	50% aq. HOAc	25	80/20		
"	"	25	80/20	60	14
"	"	95	78/22	72	20
"	"	30	83/17	79	16
CAN(0.5N)	50% aq. HOAc + 0.15N NaOAc	75	78/22		
CAN(0.5N)	80% aq. HOAc	95	70/30		
"	"	95	77/23	70	21
CAN(0.5N)	100% HOAc	95	70/30		
"	"	95	73/27	56	21
CAN(0.5N)	50% aq. HOAc + 3N HNO <sub>3</sub>	95	75.5/24.5	45	14.7
"	"	95	69/31	47	21.4
CP <sup>b</sup> (0.5N)	50% HOAc + 3N HClO <sub>4</sub>	95	69/31	3.2	
CAN(0.5N)	50% aq. sulfolane	75	83/17		
CAN(0.5N)	50% aq. sulfolane + 3N HNO <sub>3</sub>	75	79/21		
CP(0.5N)	50% aq. sulfolane + 3N HClO <sub>4</sub>	75	82/18		
CAN(0.5N)	100% sulfolane	75	80/20	61.4	14.9

<sup>a</sup>All reactions were carried out using four equivalents of cerium(IV) unless otherwise specified.

<sup>b</sup>CP is ceric perchlorate.

<sup>c</sup>Two equivalents of oxidant were used.

Table 22 (Continued)

Oxidant (Conc.) <sup>a</sup>	Medium	Temp. (deg.)	PhCHO/ PhH	Yield, %	
				PhCHO	PhH
CAN (0.5N) <sup>c</sup>	100% sulfolane	75	63/37 <sup>d</sup>	32.8 <sup>d</sup>	18.9 <sup>d</sup>
"	"	75	65/35 <sup>d</sup>	22.5 <sup>d</sup>	12.2 <sup>d</sup>
CAN (0.5N)	100% MeCN	75	81.5/18.5 <sup>e</sup>	79.5 <sup>e</sup>	17.5 <sup>e</sup>
"	"	75	80/20 <sup>e</sup>		
"	"	75	72/28 <sup>e</sup>		
CAN (0.5N) <sup>f</sup>	100% MeCN	75		43.6	
CAN (0.5N) <sup>c</sup>	100% MeCN	75		2	
CAN (0.5N) <sup>g</sup>	100% MeCN	75	85/15	85	
CAN (0.5N) <sup>c</sup>	50% aq. MeCN	25	85/15	30-50	
CAN (0.5N) <sup>c</sup>	water, TroBF <sub>4</sub> <sup>h</sup>	25		35	
CAN (0.5N) <sup>c</sup>	50% aq. HOAc, TroBF <sub>4</sub> <sup>h</sup>	75	80/20		
CAN (0.5N) <sup>c</sup>	50% aq. HOAc, TroOEt <sup>i</sup>	75	86/14		
KMnO <sub>4</sub>	dil. sulfuric acid, acetone	25		0	0
KMnO <sub>4</sub>	water	25		0	0
CrO <sub>3</sub>	80% aq. HOAc	25	91/9	34.4	3.3
CrO <sub>3</sub>	80% aq. HOAc	25	93.3/6.7		

<sup>d</sup>These numbers were obtained from duplicate analyses of the same reaction mixture.

<sup>e</sup>Same as <sup>d</sup>.

<sup>f</sup>Three equivalents of oxidant were used.

<sup>g</sup>Two equivalents of oxidant were added and the reaction was allowed to go to completion, and then two more equivalents were added.

<sup>h</sup>Tropylium fluoborate was oxidized.

<sup>i</sup>Tropylethyl ether was oxidized.

The formation of benzene from the oxidation of CHT has not previously been reported. However, we have found that in addition to the CAN oxidation of CHT, the chromium trioxide oxidation of CHT also leads to benzene as a minor product (3% yield). It is apparent that the advent of vapor phase chromatography (v.p.c.) as a routine method of analysis has allowed the detection of benzene as a product in our work, while earlier workers have failed to find it. It is therefore quite likely that other oxidative aromatizations, for example the chromium trioxide (86) and silver oxide (86) oxidations of tropylium ion, also lead to benzene as a minor product.

#### Cerium Species in Solution

For a discussion of relevant literature see page 32.

Certain inferences can be made about the cerium(IV) species present from the results of the oxidation of CHT by CAN. The results obtained in a wide variety of solvent systems are presented in Table 22.

The oxidation of CHT by four equivalents of CAN in 50% aqueous acetic acid-3 N nitric acid led to a 45-7% yield of benzaldehyde. However, the oxidation of CHT by four equivalents of ceric perchlorate led to only 3.2% benzaldehyde. Thus the substitution of perchlorate for nitrate leads to a drastic reduction in the yield of benzaldehyde. If the

oxidizing species in both cases is the hexaquo cerium(IV) ion, it is difficult to see why the yield of benzaldehyde should change drastically from one system to the other. However, if the oxidizing species in the first case is the hexanitratocerate(IV) ion or a nitratocerio(IV) species and in the second case is a hexaquo cerium(IV) ion, one might expect a difference in the oxidizing behavior in the two systems. However, one must consider the possibility that the different behavior in the two systems is due to the decrease in the oxidation potential of cerium(IV) in going from perchloric acid to nitric acid (97).

The constancy of product distributions and yields of products from the CAN oxidation of CHT in media varying from entirely aqueous to anhydrous strongly suggest that the cerium(IV) species remains nearly constant with varying solvents. The data presented in Table 23 illustrate that the benzaldehyde/benzene ratio and the yields of benzaldehyde and benzene remain relatively constant in solvents of widely different characteristics. It seems reasonable to postulate that the cerium(IV) species in anhydrous acetonitrile is some sort of nitratocerio(IV) species (ceric tetranitrate and the hexanitratocerate(IV) ion being the most likely) since acetonitrile should not compete effectively with nitrate ion for coordination sites around the cerium. If this is the case, the similarity of product

Table 23. Oxidation of CHT by four equivalents of CAN

Medium	PhCHO/PhH	Yield, %	
		PhCHO	PhH
Water	85/15	65	11
50% Aqueous HOAc	78/22	72	20
Anh. MeCN	81.5/18.5	79.5	17.5

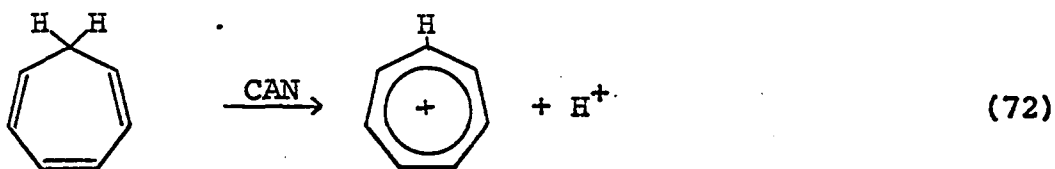
ratios and yields in anhydrous acetonitrile and 50% aqueous acetic acid and water suggests that similar cerium(IV) species are present in both anhydrous and aqueous solvents.

On the basis of the evidence presented in this and previous sections it will be assumed in the following discussion that each ceric ion has coordinated to it several nitrate ions. Further evidence which supports the postulate will be presented in the following sections.

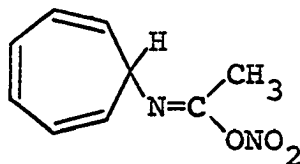
#### The First Steps of the Reaction

The evidence accumulated in this study implicates the tropylium ion or some closely related species as an intermediate in the oxidation of CHT by CAN (Equation 72).

The major evidence is from oxidations carried out in anhydrous acetonitrile. It was observed that four equivalents of CAN in anhydrous acetonitrile oxidized CHT to 79.5%



benzaldehyde and 17.5% benzene. The oxidation of CHT by two equivalents of CAN in anhydrous sulfolane led to half the yield of benzaldehyde obtained when four equivalents were used. Thus it was expected that the oxidation of CHT by two equivalents of CAN in anhydrous acetonitrile would also lead to one half the amount of benzaldehyde formed when four equivalents were used. However it was found that two equivalents of CAN in anhydrous acetonitrile consumed all the CHT and produced only 2% benzaldehyde. In addition, three equivalents of CAN produced one half the amount of benzaldehyde produced when four equivalents were used. That a stable species which could be oxidized to benzaldehyde was produced in the oxidation with two equivalents of CAN in anhydrous acetonitrile was demonstrated by adding two equivalents of CAN, allowing the reaction to go to completion (as evidenced by the fading of the orange cerium(IV) color to colorless cerium(III)), and then adding two more equivalents of CAN. The net result was that benzaldehyde was produced in the same yield as if all four equivalents of CAN had been added at once. An obvious possibility is that the intermediate produced in the oxidation of CHT by two equivalents of CAN in anhydrous acetonitrile is tropylium ion formed via a two electron oxidation of CHT. An alternate possibility is that the intermediate is the imidol nitrate, 11, analogous to the structure proposed by Cristol for the

11

product of the reaction of trityl chloride with silver nitrate in acetonitrile (98). Compound 11 might undergo reversible dissociation to give tropylium ion or might be oxidized in the imidol nitrate form to give the observed products.

The presence of tropylium ion or a closely related species in the reaction mixture from the oxidation of CHT by two equivalents of CAN in anhydrous acetonitrile was confirmed in the following way: Tropylium fluoborate was dissolved in aqueous ethanol and the solution was neutralized with solid sodium bicarbonate. From this solution was isolated a 53.6% yield of troyl ethyl ether, identified by comparison of its n.m.r. spectrum with that of an authentic sample. The reaction mixture from the oxidation of CHT by two equivalents of CAN was extracted with ether to remove all ether soluble materials, aqueous ethanol was added, and the solution was neutralized with solid sodium bicarbonate producing a flocculent precipitate of cerous hydroxide. From this mixture was obtained a 35.2% yield (based on CHT) of troyl ethyl ether. Comparison of this yield with that obtained from pure tropylium ion shows that the amount of tropylium ion present in the CAN-CHT-anhydrous acetonitrile reaction mixture is at least 66% based on starting CHT.

Further evidence for the intermediacy of tropylium ion or a closely related species is that tropylium fluoborate in aqueous solution is rapidly oxidized (less than one minute at room temperature) by two equivalents of CAN to a 35% yield of benzaldehyde with a benzaldehyde to benzene ratio of 80/20. In addition, troyl ethyl ether which should give tropylium ion upon protonation is oxidized to benzaldehyde and benzene in the ratio of 86/14.

The intermediacy of tropylium ion or a closely related species in the oxidation of CHT is consistent with the findings of Juppe and Wolf whose results indicated a symmetrical intermediate in the chromium trioxide oxidation of CHT to benzoic acid (vide supra) (89).

As is the usual case in reactions of organic compounds with metal ions, the detailed mechanism by which cerium(IV) converts CHT to tropylium ion or a closely related species can only be speculated upon. The rapidity of the reaction of CHT with CAN is somewhat unexpected. Normal olefins, for example cyclohexene, are rather unreactive and give mixtures of many products when the reaction is forced to completion (99).

The initial step of the reaction may be complex formation between CHT and a cerium(IV) atom. Stable CHT-metal complexes are well known for metals other than cerium (100). There is no physical evidence for such complexing, however,



and it must be admitted that the chemical behavior of cerium, a rare earth metal, and the transition metals, for which stable CHT-metal complexes are known, is drastically different. A major difference can be expected because of the differing electronic configurations around the metal ions. The stabilities of coordination compounds of the d-type transition metal ions are related to participation of the d electrons in the metal-ligand bond through hybridization of metal electronic orbitals and overlap of these hybrid orbitals with appropriate ligand orbitals (29). If overlap of rare earth metal ion hybrid orbitals with ligand orbitals is to occur, it must of necessity involve normally unoccupied higher energy orbitals (e.g., 5d, 6s, 6p), and hybridization of this type can be expected only with the most strongly coordinating ligands (29). Hence it seems unlikely that a CHT molecule would be able to compete effectively with water or nitrate ions for coordination sites around the cerium(IV) ion.

The most reasonable first step for the CAN-CHT reaction, then, seems to be an outer sphere reaction of the metal ion aggregate. That is, the CHT molecule never enters the first coordination sphere of the metal ion and electron transfer occurs through the ligands coordinated to the metal ion. While this argument for an outer sphere oxidation by CAN is certainly not rigorous, it seems much more likely than an

inner sphere process, i.e., one involving direct coordination of a CHT molecule to the cerium(IV) ion.

The following possibilities then exist for the CHT  $\rightarrow$  tropylium ion conversion:

1) The first step is a one-electron transfer from CHT to the cerium(IV) via a ligand to give a radical cation. Loss of a proton from the radical cation gives a radical which is rapidly oxidized to tropylium ion via another one-electron oxidation.

2) Proton removal by a base, possibly a ligand, occurs concurrently with the initial one-electron oxidation to give a troyl radical directly. Oxidation of the radical gives tropylium ion. These two possibilities are summarized in Chart 4.

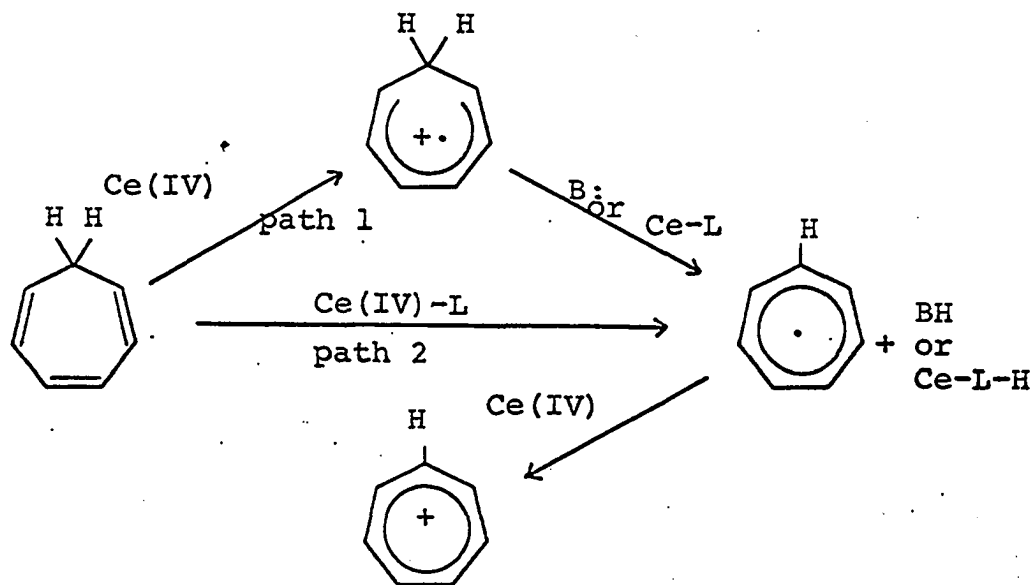


Chart 4. Oxidation of CHT to tropylium ion via stepwise one-electron oxidations

The intermediacy of a relatively long-lived free radical in this reaction seems unlikely because of the high recovery of products generally found. However, a free radical species might be an intermediate with its further oxidation to tropylium ion being sufficiently rapid to prevent typical free radical reactions from occurring. There is also the possibility that association of the free radical with a metal ion species stabilizes the radical towards side reactions, the result being a metal ion-free radical aggregate of the sort proposed by Kochi in the chromium(II) reductions of benzyl halides and other organic halides (101-103).

Hunter has studied the chemical and physical properties of the cycloheptatrienyl radical (104). He found that this free radical is not prone to undergo hydrogen atom abstraction reactions and that it has a relatively low reactivity with oxygen. He reported a resonance energy of 25.8 kcal./mole for the radical and concluded that the cycloheptatrienyl radical is a highly delocalized, probably planar radical whose chemical reactivity is apparently not high. Thus it seems possible that the cycloheptatrienyl radical might be an intermediate in the cerium(IV) oxidation of CHT.

3) The initial oxidation is a two-electron oxidation by one cerium(IV) ion with concurrent removal of a proton by a base to generate tropylium ion and a transient cerium(II)

species which is rapidly oxidized to cerium(III). This possibility is illustrated in Chart 5. Although cerium(II) is not known in solution, it is possible that the driving

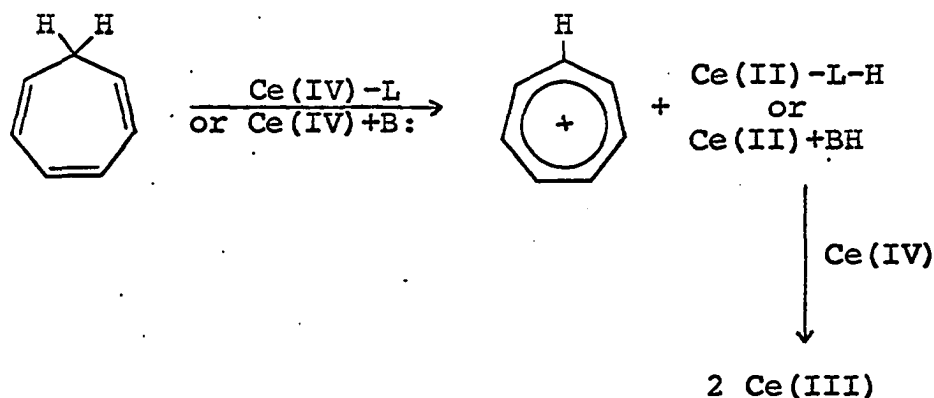
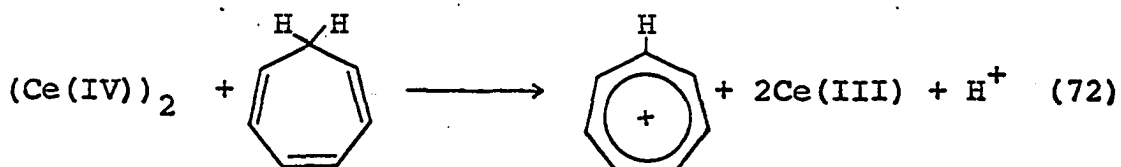


Chart 5. Oxidation of CHT to tropylium ion via a single two-electron oxidation by cerium(IV)

force afforded by the direct conversion of CHT to tropylium ion with its large resonance stabilization might favor this process.

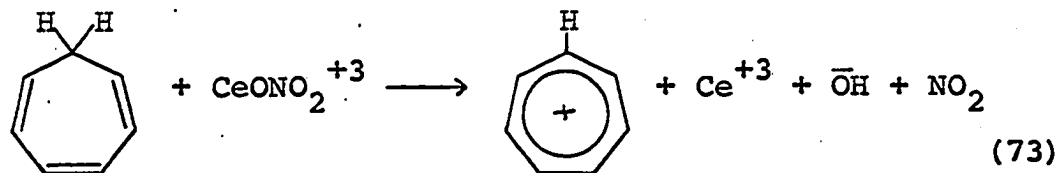
4) The initial oxidation is a two-electron oxidation by a cerium(IV) dimer to generate tropylium ion directly (Equation 72). Gryder has found that ca. 80% of the cerium(IV)



exists as a dimer in 5-6 F nitric acid, indicating that it is at least possible that the oxidant in this reaction is cerium(IV) dimer (42,80).

5) The initial oxidation is a two-electron oxidation

involving a one-electron reduction of cerium(IV) and a one-electron reduction of nitrate (Equation 73). The  $\text{NO}_2$



produced might escape from solution or be reoxidized by cerium(IV) to nitrate ion. This mechanism is analogous to that suggested by Gryder and Dorfman for the one step oxidation of thallium(I) to thallium(III) by cerium(IV) (Equation 74) (80).

A choice between the five mechanistic possibilities presented above is not possible with the information accumulated in this study. All have both good and bad points. The intermediacy of tropylium ion or a closely related species, however, seems to be firmly established and in discussion of the subsequent steps of the reaction it will be assumed that tropylium ion is involved.

#### The Final Steps of the Reaction

Assuming that tropylium ion, a tropylium ion-metal ion aggregate, or a tropylium-like species such as 11 is indeed an intermediate in the CHT-CAN reaction, a possible subsequent reaction is the combination of tropylium ion and water to form troyl alcohol (12). The troyl alcohol could then

be oxidized to the observed products, benzaldehyde and benzene (Chart 6).

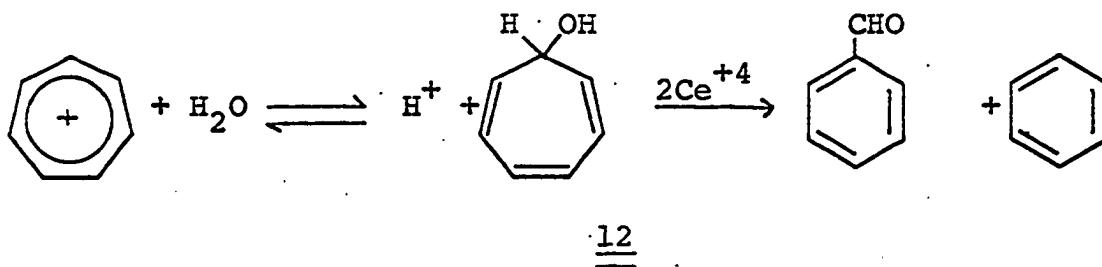


Chart 6. Oxidation of tropylium ion to benzene and benzaldehyde via tropylium alcohol

An alternative path is the reaction of tropylium ion with nitrate ion which may be complexed with cerium(IV) or uncomplexed. Further oxidation of this tropylium nitrate species (13 or 14) would lead to products (Chart 7). That 13 does not lead to the observed products in the absence of

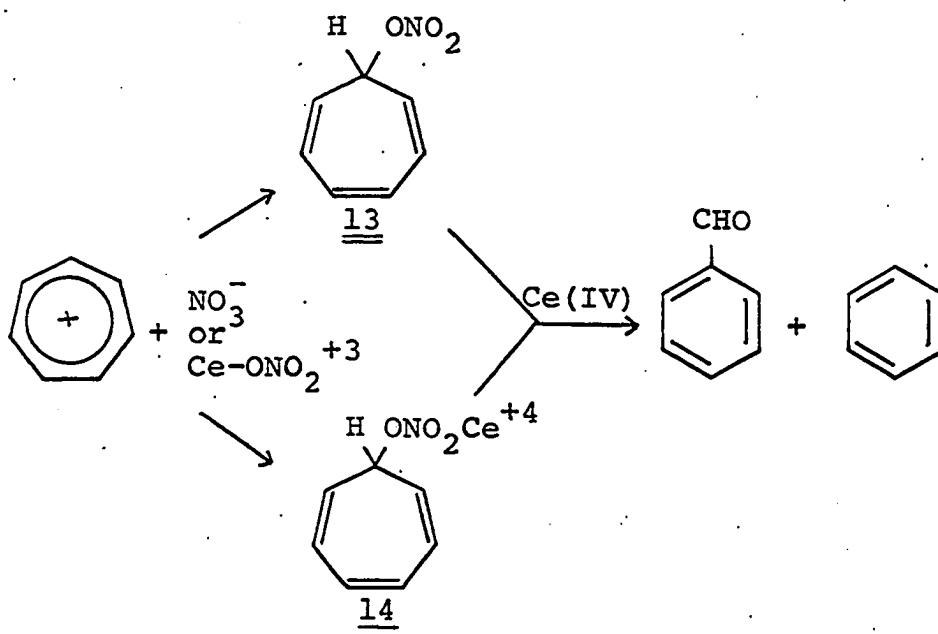


Chart 7. Oxidation of tropylium ion to benzene and benzaldehyde via tropylium nitrate

cerium(IV) has been demonstrated by heating sodium nitrate and tropylium bromide and showing that no benzaldehyde or benzene is produced.

A third possible reaction path involves the formation of tropone (15) and subsequent rearrangement of 15 to benzaldehyde and benzene (Chart 8). The formation of 15 from the oxidation of both CHT and tropylium ion has been reported. Radlick has reported that the selenium dioxide oxidation of CHT leads to 15 in 25% yield (95). Nozoe, Mukai, Tezuka, and Osaka found that chromium trioxide in pyridine converts CHT to 15 in 30% yield, and tropylium ion to 15 in 40% yield (94). The possible involvement of 15 in the CAN oxidation of CHT has been eliminated by demonstrating that 15 does not rearrange to benzaldehyde and/or benzene under the reaction conditions.

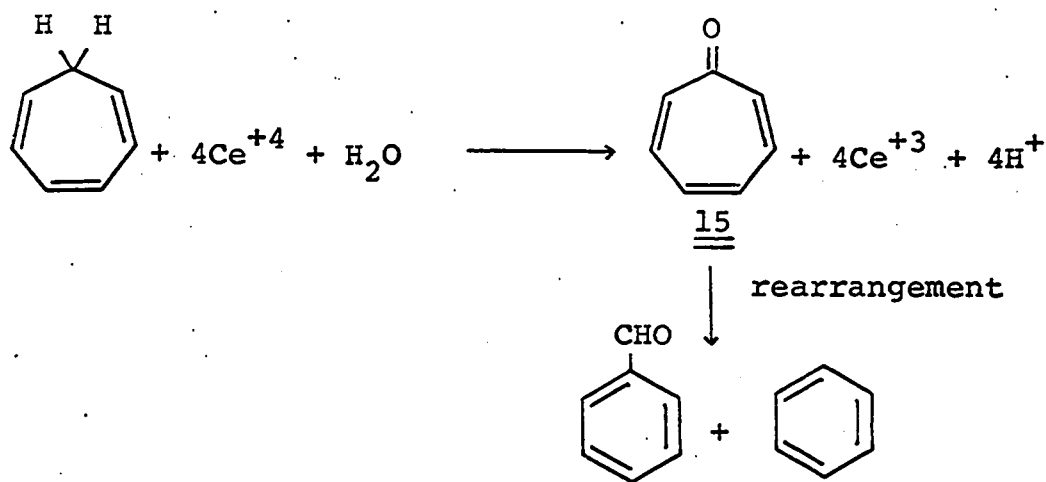


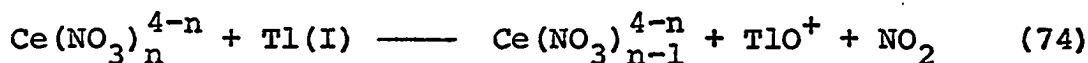
Chart 8. Oxidation of CHT to benzene and benzaldehyde via tropone

The choice between the mechanistic paths illustrated in Charts 6 and 7 is not easy, however all available evidence implicates the involvement of nitrate in the reaction (i.e., Chart 7). When the oxidation of CHT is carried out in anhydrous acetonitrile, the products are still benzaldehyde (79.5% yield) and benzene (17.5% yield), the same as in aqueous media. The only possible source of the oxygen incorporated into the benzaldehyde is nitrate ion. The possibility that oxygen incorporation into the benzaldehyde occurred during aqueous workup of the reaction mixture was eliminated by i.r. analysis of the anhydrous reaction mixture before workup, which showed the characteristic absorption band of the carbonyl group. The possibility of incorporation of molecular oxygen into the product was eliminated by showing that benzaldehyde was still a major product when the reaction was carried out under nitrogen in degassed acetonitrile.

Since the product ratio and total yield of products are very nearly the same in solvents ranging from anhydrous to entirely aqueous (see Table 22) the involvement of nitrate ion complexed with cerium(IV) in all these reaction seems likely. Additional support for nitrate involvement is given by the low yield (3.2%) of benzaldehyde obtained from the oxidation of CHT by ceric perchlorate in perchloric acid. If the oxidation was occurring via troyl alcohol (Chart 6) one



might expect that ceric perchlorate should oxidize CHT to benzaldehyde in high yield. However if a tropylium nitrate intermediate is involved in the reaction (Chart 7) it is easy to explain the low yield of benzaldehyde in the ceric perchlorate oxidation. A two electron oxidation involving a cerium(IV)-nitrate species has been proposed by Gryder for the oxidation of thallium(I) by cerium(IV) (Equation 74) (80).



The oxidation of tropylium nitrate (or tropylium ion) to benzaldehyde or benzene is an overall two electron oxidation. As suggested by Doering and Knox for the chromic acid oxidation of tropylium bromide to benzaldehyde (91), the reaction can be pictured as proceeding via a norcaradiene intermediate (Chart 9), although this is not strictly necessary.

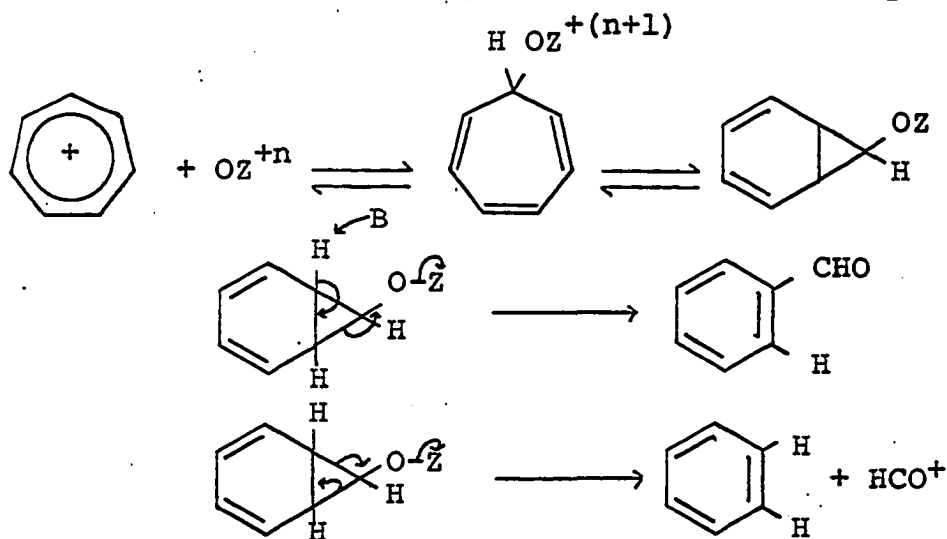


Chart 9. Oxidation of tropylium ion to benzene and benzaldehyde via a norcaradiene intermediate

In the case of the CAN oxidation of CHT it is not clear whether one concerted two-electron oxidation or two successive one-electron oxidations occur in the conversion of tropylium ion to benzaldehyde and benzene. Since cerium(IV) has always been considered to be a one-electron oxidant, it is expected that the tropylium ion to benzene-benzaldehyde conversion should occur via two one-electron oxidations. However, it is simpler to imagine the reaction occurring via a single two-electron oxidation as illustrated in Chart 9.

Since a tropylium nitrate intermediate has been implicated by previously cited evidence, the two-electron oxidation might be represented as in Chart 10. The cerium species initially formed, 16, can be thought of as a cerium(IV)-nitrite ion complex or a cerium(III)-nitrogen dioxide complex. The

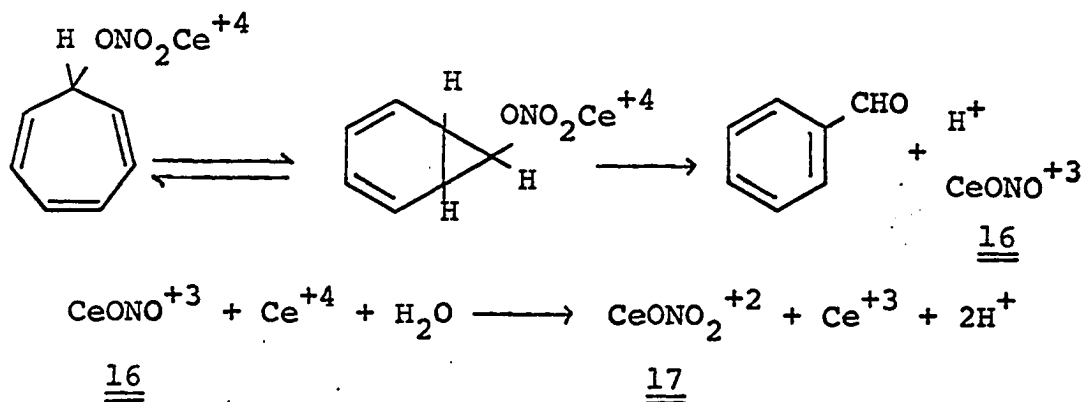
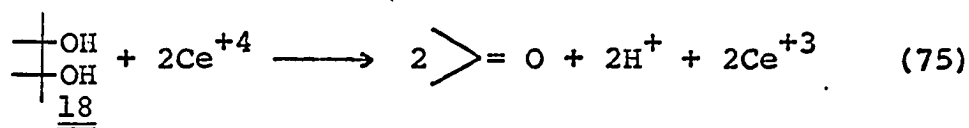


Chart 10. Oxidation of tropylium nitrate to benzaldehyde

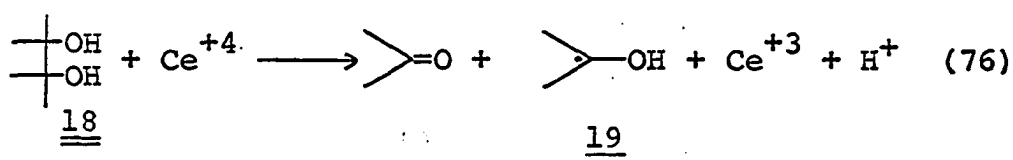
species 16 would then be rapidly oxidized to 17, a cerium(III)-nitrate ion aggregate. We have independently shown that nitrite ion is rapidly oxidized to nitrate ion by two equivalents of cerium(IV), illustrating that it is at least possible that a change in the formal oxidation state of nitrogen may be occurring in this reaction.

The possibility that the oxidation of tropylium ion to benzene and benzaldehyde occurs via two consecutive one-electron transfers also exists. It might be argued that if a free radical is formed it should undergo some side reactions typical of free radicals resulting in a low yield of benzene and benzaldehyde or it should be capable of being trapped by some free radical trap. However, if the free radical undergoes further oxidation before side reactions or trapping can occur, high yields of products might be obtained.

Some experimental results which give an indication of the small tendency for free radicals to undergo side reactions (i.e., reactions other than further oxidation) in the presence of cerium(IV) have been obtained by Bierman and Trahanovsky (105) and L. H. Young and Trahanovsky (60). One part of their study concerned the oxidation of pinacol (18) to acetone by cerium(IV) (Equation 75). They repeated the work of Mino (28) and found that CAN oxidizes 18 to acetone in 84% yield. The initial step of the reaction was shown to be the oxidation of 18 by one equivalent of cerium(IV).



to one equivalent of acetone and one equivalent of the radical 19 by demonstrating that the yield of acetone was reduced to 47% in the presence of acrylamide, a free radical scavenger (Equation 76). The feature of this reaction which should be noted is that relatively large amounts of a free



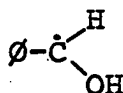
radical, 19, are being generated, yet these radicals are very efficiently oxidized to acetone by cerium(IV) in the absence of a free radical trap before other typical free radical reactions occur. That is, one may expect that if free radicals are generated in the cerium(IV) oxidation of tropylium ion and CHT, they will probably be rapidly oxidized further by cerium(IV) before any side reactions can occur.

In addition, Bierman and Trahanovsky have demonstrated that some "free" radicals may not be trappable by normal means in the presence of cerium(IV) and hence are not prone to undergo typical free radical reactions in preference to further oxidation. They found that similar to pinacol (18), meso-hydrobenzoin (20) is oxidized to benzaldehyde by two equivalents of cerium(IV) (Equation 77).



20

Since it was demonstrated that in the oxidation of pinacol one free radical (19) was produced for every molecule of pinacol oxidized, it is likely that a free radical is produced in the oxidation of 20, presumably 21. However, it was found that acrylamide which scavenged the radical 19



21

produced in the oxidation of pinacol (18) was ineffective in scavenging a radical from the oxidation of 20. Thus, either no free radical is produced in the oxidation of 20, or more likely, based on analogy with the pinacol oxidation, the stability of radical 21 has tipped the balance in favor of further oxidation of 21 by cerium(IV) rather than addition of the radical to acrylamide.

Thus it may be strongly argued that a reaction which does indeed proceed via two consecutive one-electron oxidations may have all the characteristics of a concerted two-electron oxidation. The conclusion which must be reached re-

garding whether the oxidation of tropylium ion or tropylium nitrate to benzene and benzaldehyde by cerium(IV) occurs via a single two-electron transfer or two stepwise one-electron transfers must be that it is impossible to distinguish between the two possibilities with the data accumulated in this study.

The question of whether a norcaradiene-type intermediate is involved in the reaction or not is impossible to answer. Corey found no evidence for any norcaradiene in CHT using n.m.r. (106). The only known stable norcaradienes are those which contain strongly electron withdrawing groups at C-7, for example 7,7-dicyanonorcaradiene, (107,108). The use of the norcaradiene structure in previous and following schemes should only be considered as a convenient manner in which to view the reaction, since the same products could just as well be formed in a concerted ring contraction-oxidation process as illustrated in Chart 11.

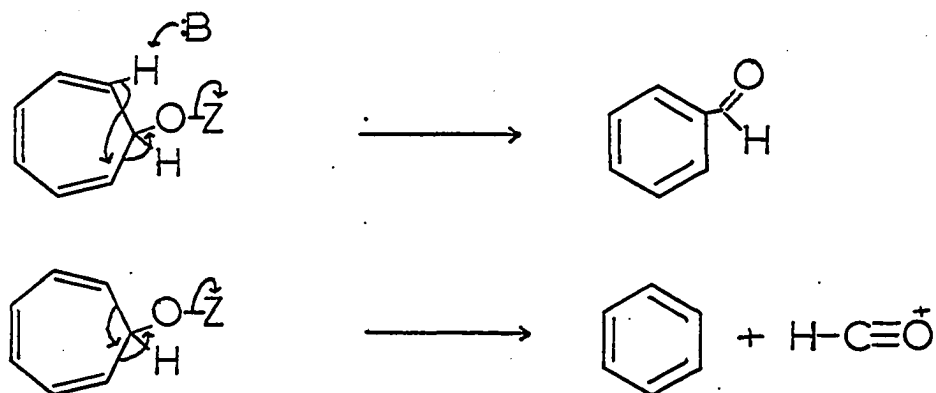


Chart 11. Concerted ring contraction-oxidation mechanisms for benzaldehyde and benzene formation

The identity of the base which removes the proton on C-1 in the transition state leading to benzaldehyde may be speculated upon. Inspection of the data in Tables 22 and 23 reveals that the benzene/benzaldehyde ratio remains remarkably constant in solvents of widely varying basicities. The transition state for formation of benzaldehyde involves removal of a proton by base while that leading to benzene involves no base (see Chart 9). The most reasonable explanation for this constant benzene/benzaldehyde ratio is that the solvent itself is not acting as base, but rather some species which is constant from one solvent to another removes the proton. A likely candidate is a ligand, probably nitrate, which is attached to the cerium. If any other species were acting as a base to remove the proton on C-1, it would be extremely coincidental if the benzene/benzaldehyde ratio remained so nearly constant. Thus the transition state leading to benzaldehyde can be pictured as in Chart 12. A similar process could be drawn for two consecutive one-electron transfers

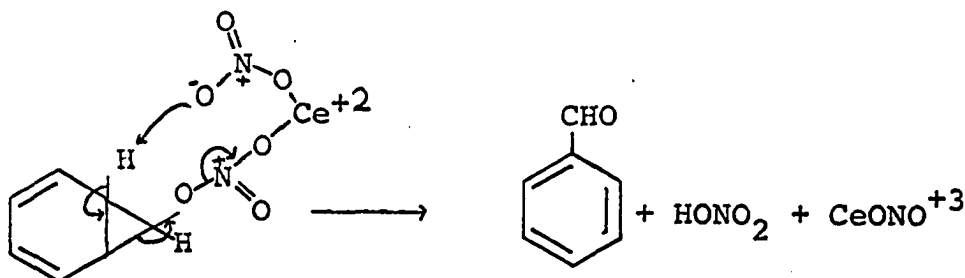


Chart 12. Mechanism for benzaldehyde formation showing ligand participation

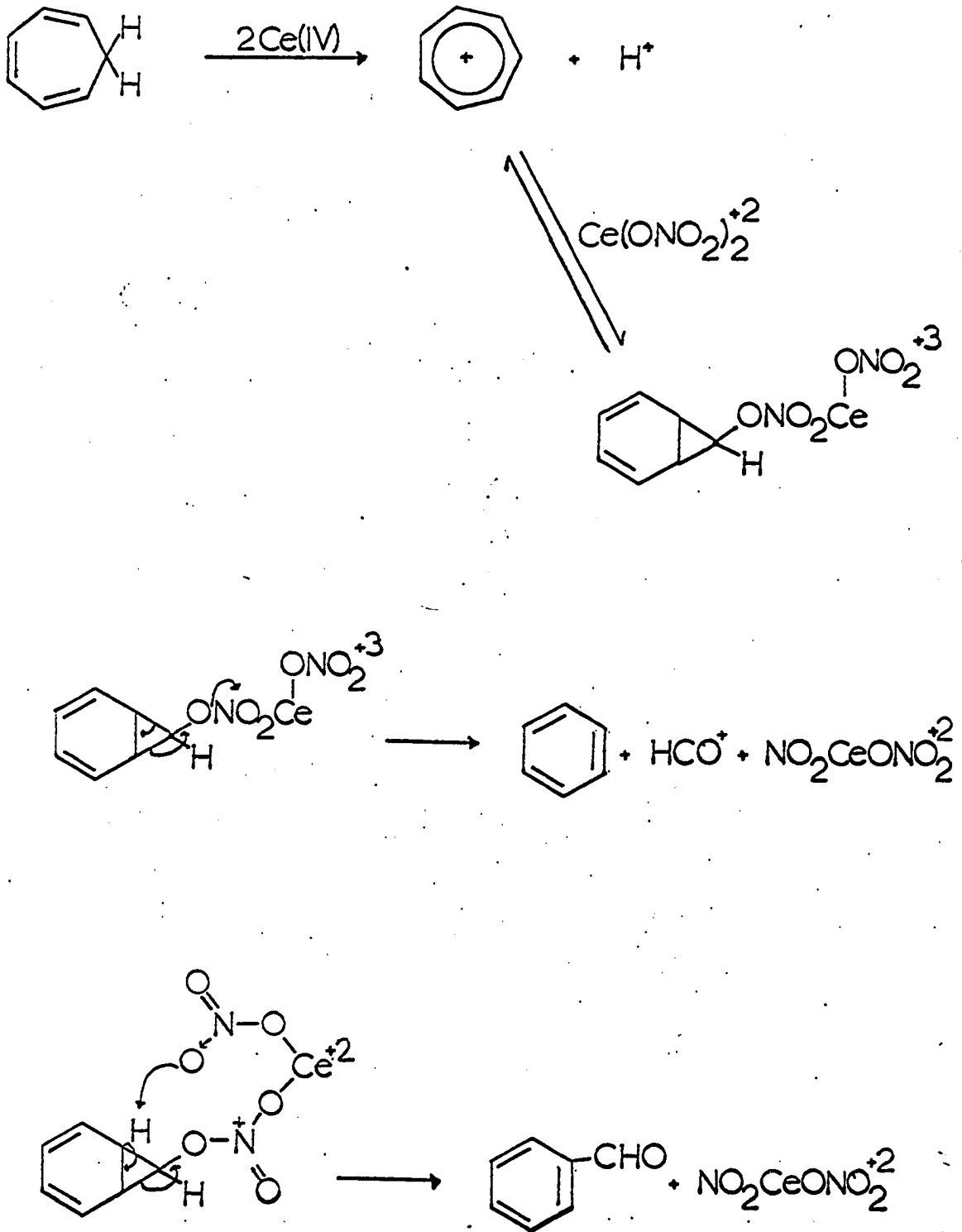
instead of a two electron transfer. Although the atoms in-

volved in the cyclic transition state constitute an apparently unfavorable ten membered ring, it must be remembered that cerium probably has a coordination number of at least six and probably more. Since several of the ligands will be nitrates, there will be several conformations of the metal ion aggregate which allow the close proximity of a nitrate to the proton to be removed.

The mechanism supported by the results of this study is illustrated in Chart 13. The oxidation of tropylium ion is illustrated as a two electron oxidation occurring via a norcaradiene intermediate for convenience.



Chart 13. Proposed mechanism for the oxidation of CHT  
by CAN



## EXPERIMENTAL

## Materials

Cycloheptatriene (CHT) was either Shell technical grade (91-92% pure) or Aldrich (96% pure) and was used unpurified or after distillation, b.p. 114-116° (1 atm.), lit. (87) b.p. 117° (749 mm.). The absence of benzene as an impurity was shown by v.p.c. and n.m.r. The major impurity was toluene. Ceric ammonium nitrate (CAN) and 0.5 N ceric perchlorate in 6 N perchloric acid were from G. F. Smith Chemical Co. Glacial acetic acid and potassium permanganate were Mallinckrodt analytical grade reagents. Chromic acid was Baker and Adamson reagent grade. Palladium chloride was from Matheson, Coleman, and Bell. Tropone was obtained from Dr. T. H. Kinstle. Acetonitrile was used without distillation or after distillation from calcium chloride and was Baker analyzed reagent. The same results were obtained whether purified or unpurified acetonitrile was used. Sulfolane was from the Phillips Petroleum Co. and was purified by distillation from calcium hydride, b.p. 111° (0.07 mm.). Tropylium fluoborate was prepared using the method of Conrow (109) or Dauben (110). Ethyl tropylium ether was obtained from tropylium fluoborate using the method of Conrow (111), b.p. 64° (8.5 mm.), lit. (111) b.p. 62° (8 mm.).

## Standardization of Cerium(IV) Solutions

Reagent grade ferrous ammonium sulfate hexahydrate was used as a primary standard. Freshly prepared 0.1 N solutions in ca. 1 N sulfuric acid were used to titrate cerium (IV) solutions to the ferroin end point (3).

Cerium(IV) Oxidations of  
Cycloheptatriene (CHT)In pure water

To 0.202 g. (2.2 mmoles.) CHT was added 9.2 ml. (8.9 mmoles.) 0.97 N CAN solution. The mixture was heated and stirred on a hotplate-stirrer for ca. 3.5 min. at which time the solution was light yellow. The mixture was cooled and extracted with 1.5 ml. carbon tetrachloride. Tetramethylsilane was added and the n.m.r. spectrum was obtained. The integrals for the benzene protons and the aldehyde proton were used to calculate relative yields. PhCHO/PhH = 87/13.

To 0.37 g. (4.1 mmoles.) CHT was added 33 ml. (16.0 mmoles.) of a 0.485 N CAN solution. The mixture was heated and stirred on a steam bath for 8 min. A quantity of 0.2165 g. xylene (standard) was added and the mixture was extracted with 25 ml. ether. The ether layer was dried over magnesium sulfate and analyzed by v.p.c. The peak areas of products were  $A_{\text{PhH}}=190$ ;  $A_{\text{PhCHO}}=1407$ ;  $A_{\text{xylene}}=1304$ ;

$$A_{\text{PhCH}_3 + \text{CMT}} = 63.$$

Control A quantity of 33 ml. 0.485 N CAN solution was reduced by heating with ca. 10 drops of acetone.

Benzene, benzaldehyde, and xylene were weighed into the solution and the solution was worked up as described above.

Wt. PhH=0.0721 g.; wt. PhCHO=0.1528 g.; wt. xylene=0.1473 g.;  $A_{\text{PhH}}=860$ ;  $A_{\text{PhCHO}}=1635$ ;  $A_{\text{xylene}}=1850$ . Yield PhCHO=64%, PhH=11%, PhCHO/PhH=85/15.

In 0.15 N potassium hydroxide

To 0.357 g. (3.9 mmoles.) CHT was added a solution of 33 ml. (16.0 mmoles.) 0.485 N CAN and 3.3 ml. (5.0 mmoles.) 1.5 N potassium hydroxide. The mixture was heated and stirred on a hotplate-stirrer for 25 min. A white precipitate formed on standing. The mixture was extracted with 25 ml. ether and the ether layer was dried over magnesium sulfate and analyzed by v.p.c. PhCHO/PhH=86/14.

In 0.5 N perchloric acid

To 0.3750 g. (4.1 mmoles.) CHT was added a solution of 16.5 ml. (16.1 mmoles.) 0.973 N CAN and 16.5 ml. (16.5 mmoles.) 1 N perchloric acid. The mixture was heated and stirred on a steam bath for 2 min. A quantity of 0.1970 g. xylene (standard) was added and the solution was extracted with 25 ml. of ether. The ether layer was washed with 25 ml. 1.5 N potassium hydroxide, dried over magnesium sulfate, and analyzed by v.p.c. The peak areas were  $A_{\text{PhH}}=141$ ;  $A_{\text{PhCH}_3 - \text{CMT}}=0$ ;

$A_{\text{xylene}}=1165$ ;  $A_{\text{PhCHO}}=1252$ .

Control A solution of 16.5 ml. 0.973 N CAN and 16.5 ml. 1 N perchloric acid was reduced to cerium(III) by heating with 10 drops of acetone. Benzene, benzaldehyde, and xylene (standard) were weighed in and the mixture was worked up as described above and analyzed by v.p.c. Wt. PhH=0.0868 g.; wt. PhCHO=0.2000g.; wt. xylene=0.2149 g.;  $A_{\text{PhH}}=465$ ;  $A_{\text{PhCHO}}=1060$ ;  $A_{\text{xylene}}=1340$ . Yield PhCHO=58%, PhH=9%, PhCHO/PhH=87/13.

In 10% aqueous acetic acid

To 0.3758 g. (4.0 mmoles.) CHT was added a solution of 16.5 ml. (16.1 mmoles.) 0.973 N CAN and 16.5 ml. 20% aqueous acetic acid. The mixture was heated and stirred on a steam bath for one hour. A quantity of 0.1985 g. xylene(standard) was weighed in and the mixture was added to 25 ml. of water and extracted with 25 ml. ether. The ether layer was washed with 35 ml. 1.5 N potassium hydroxide, dried over magnesium sulfate, and analyzed by v.p.c.  $A_{\text{PhH}}=121$ ;  $A_{\text{PhCH}_3\text{-CHT}}=42$ ;  $A_{\text{xylene}}=1620$ ;  $A_{\text{PhCHO}}=1390$ .

Control A solution of 16.5 ml. 0.973 N CAN and 16.5 ml. 20% aqueous acid was reduced to cerium(III) by heating with 10 drops of acetone. Benzene, benzaldehyde, and xylene (standard) were weighed in and the mixture was worked up as above, and analyzed by v.p.c. Wt. PhH=0.0843; wt. PhCHO=0.2251 g.; wt. xylene=0.2030 g.;  $A_{\text{PhH}}=480$ ;  $A_{\text{PhCHO}}=1308$ ;

$A_{\text{xylene}}=1385$ . Yield PhCHO=46%, PhH=6%, PhCHO/PhH=88/12.

In 50% aqueous acetic acid

A quantity of 0.368 g. (4.0 mmoles.) CHT was dissolved in 16.4 ml. glacial acetic acid and 16.4 ml. (16.1 mmoles.) of a 0.974 N solution of CAN was added. The solution was stirred at room temperature for 2 hrs. and then added to 50 ml. water and extracted with 30 ml. ether. The ether layer was washed with 40 ml. 1.5 N potassium hydroxide, dried over magnesium sulfate, and analyzed by v.p.c. PhCHO/PhH=80/20.

A quantity of 0.3567 g. (3.9 mmoles.) CHT was dissolved in 16.5 ml. glacial acetic acid and 16.5 ml. (16.1 mmoles.) of a 0.973 N solution of CAN was added. The solution was stirred at room temperature for 41 hrs. A quantity of 0.2055 g. xylene (standard) was added and the solution was poured into 50 ml. of water and extracted with 30 ml. ether. The ether layer was washed with 40 ml. 1.5 N potassium hydroxide, dried over magnesium sulfate, and analyzed by v.p.c.  $A_{\text{PhH}}=460$ ;  $A_{\text{PhCH}_3\text{-CHT}}=84$ ;  $A_{\text{xylene}}=2845$ ;  $A_{\text{PhCHO}}=2080$ .

Control A solution of 16.5 ml. 0.973 N CAN and 16.5 ml. glacial acetic acid was reduced to cerium(III) by heating with 10 drops of acetone. Benzene, benzaldehyde, and xylene were weighed in and the solution was worked up and analyzed as above. Wt. PhH=0.1989 g.; wt. PhCHO=0.1905 g.; wt. xylene=0.1788 g.;  $A_{\text{PhH}}=1575$ ;  $A_{\text{PhCHO}}=1025$ ;  $A_{\text{xylene}}=1425$ . Yield PhCHO=60%, PhH=14%. PhCHO/PhH=80/20.

A quantity of 0.368 g. (4.0 mmoles.) CHT was dissolved in 16.4 ml. glacial acetic acid and 16.4 ml. (16.0 mmoles.) of a 0.974 N solution of CAN was added. The solution was heated on a steam bath for 8 min., 200 microliters of xylene(standard) was added, and the solution was poured into 50 ml. water and extracted with 30 ml. ether. The ether layer was washed with 40 ml. 1.5 N potassium hydroxide, dried over magnesium sulfate, and analyzed by v.p.c.  $A_{\text{PhCHO}}/A_{\text{xylene}}=1.123$ ;  $A_{\text{PhH}}/A_{\text{xylene}}=0.314$ ;  $A_{\text{CHT}}/A_{\text{xylene}}=0.057$ .

Control A solution of 16.4 ml. glacial acetic acid and 16.4 ml. 0.974 N CAN was reduced to cerium(III) by heating with 10 drops of 95% ethanol. A quantity of 0.337 g. benzaldehyde and 200 microliters xylene(standard) were added and the solution was worked up and analyzed as above.  $A_{\text{PhCHO}}/A_{\text{xylene}}=1.241$ . The yield of benzene was calculated by assuming that thermal conductivities and extraction ratios are the same for benzaldehyde and benzene. Yield PhCHO=72%, PhH=20%.  
PhCHO/PhH=78/22.

A quantity of 0.3670 g. (4.0 mmoles.) CHT was dissolved in 16.5 ml. glacial acetic acid and 16.4 ml. (16.1 mmoles.) of a 0.974 N solution of CAN was added. The solution was placed in an oil bath at 130° for 3 min., cooled, and 0.2073 g. xylene(standard) was added. The solution was poured into 50 ml. water and extracted with 30 ml. ether. The ether layer was washed with 1.5 N potassium hydroxide, dried over



magnesium sulfate and analyzed by v.p.c.  $A_{\text{PhH}}=336$ ;  $A_{\text{xylene}}=1690$ ;  $A_{\text{PhCHO}}=1660$ .

Control The following results were obtained: wt. PhH=0.1989 g., wt. PhCHO=0.1905 g.; wt. xylene=0.1788 g.;  $A_{\text{PhH}}=1575$ ;  $A_{\text{PhCHO}}=1025$ ;  $A_{\text{xylene}}=1425$ . Yield PhCHO=79%, PhH=16%. PhCHO/PhH=83/17.

In 50% aqueous acetic acid-0.15 N sodium acetate

To 0.357 g. (3.9 mmoles.) CHT was added a solution of 16.5 ml. (16.0 mmoles.) 0.9735 N CAN, 16.5 ml. glacial acetic acid, and 0.40 g. (4.9 mmoles.) sodium acetate. The solution was heated on a hotplate-stirrer for 18 min. and worked up using 50 ml. water, 25 ml. ether, and 35 ml. 1.5 N potassium hydroxide. The ether layer was dried over magnesium sulfate and analyzed by v.p.c. PhCHO/PhH=78/22.

In 80% aqueous acetic acid

To a solution of 0.368 g. (4.0 mmoles.) CHT in 25.6 ml. glacial acetic acid was added a solution of 8.992 g. (16.0 mmoles.) CAN in 6.4 ml. water. The solution was heated on a steam bath for 17 min. and worked up using 50 ml. water, 30 ml. ether, and 60 ml. 1.5 N potassium hydroxide. The ether layer was dried over magnesium sulfate and analyzed by v.p.c. PhCHO/PhH=70/30.

A solution of 0.3858 g. (4.0 mmoles.) CHT, 25.6 ml. glacial acetic acid, 6.4 ml. water, and 8.992 g. (16.0 mmoles.) CAN was heated on a steam bath for 12 min. A quantity of 0.200 g. xylene (standard) was added and the

solution was worked up using 80 ml. water, 30 ml. ether, and 70 ml. 1.5 N potassium hydroxide. The ether layer was dried over magnesium sulfate and analyzed by v.p.c.  $A_{\text{PhH}}=404$ ;

$A_{\text{PhCH}_3\text{-CHT}}=70$ ;  $A_{\text{xylene}}=1400$ ;  $A_{\text{PhCHO}}=1208$ .

Control A solution of 25.6 ml. glacial acetic acid, 6.4 ml. water, and 8.992 g. CAN was reduced to cerium(III) by heating with 10 drops acetone. Benzene, benzaldehyde, and xylene were weighed in and the solution was worked up and analyzed as described above. Wt. PhH=0.1317 g.; wt. PhCHO=0.2019 g.; wt. xylene=0.1867 g.;  $A_{\text{PhH}}=697$ ;  $A_{\text{PhCHO}}=705$ ;  $A_{\text{xylene}}=1120$ . Yield PhCHO=70%, PhH=21%. PhCHO/PhH=77/23.

In glacial acetic acid

To 0.368 g. (4.0 mmoles.) CHT dissolved in 32 ml. glacial acetic acid was added 8.99 g. (16 mmoles.) CAN. The mixture was heated and stirred for 33 min. at which time the solution was yellow and the undissolved solid was white. The mixture was added to 50 ml. of water and extracted with 30 ml. ether. The ether layer was washed with 1.5 N potassium hydroxide, dried over magnesium sulfate, and analyzed by v.p.c. PhCHO/PhH=70/30.

To 0.3712 g. (4.0 mmoles.) CHT dissolved in 32 ml. glacial acetic acid was added 8.99 g. (16 mmoles.) CAN. The mixture was heated and stirred on a steam bath for 1 hr. at which time the solution was orange and the undissolved yellow-white. A quantity of 0.2005 g. xylene(standard) was weighed in and the

reaction mixture was worked up using 100 ml. water, 40 ml. ether, and 75 ml. 1.5 N potassium hydroxide. The ether layer was dried over magnesium sulfate and analyzed by v.p.c.

$A_{\text{PhH}}=432$ ;  $A_{\text{xylene}}=1390$ ;  $A_{\text{PhCHO}}=960$ .

Control To a mixture of 32 ml. glacial acetic acid and 8.99 g. (16 mmoles.) CAN was added ca. 10 drops of acetone. The mixture was heated and stirred on a steam bath until the liquid was yellow and the solid yellow-white. Benzene, benzaldehyde, and xylene were weighed in and the solution was worked up as above. Wt. PhH=0.1303g.; wt. PhCHO=0.2040 g.; wt. xylene=0.1954 g.;  $A_{\text{PhH}}=774$ ;  $A_{\text{PhCHO}}=730$ ;  $A_{\text{xylene}}=1205$ . Yield PhCHO=56%, PhH=21%. PhCHO/PhH=73/27.

In 50% aqueous acetic acid containing 3 N nitric acid

To 0.184 g. (2.0 mmoles.) CHT in 15.3 ml. glacial acetic acid was added 15.3 ml. (8.0 mmoles.) 0.522 N CAN in 6 N nitric acid. The solution was heated on a steam bath for 13 min. and then cooled. A quantity of 100 microliters xylene(standard) was added and the reaction mixture was added to 100 ml. saturated sodium chloride solution and extracted with 25 ml. ether. The ether layer was washed with 55 ml. 1.5 N potassium hydroxide, dried over magnesium sulfate, and analyzed by v.p.c.  $A_{\text{PhH}}=181$ ;  $A_{\text{xylene}}=759$ ;  $A_{\text{PhCHO}}=587$ . In a duplicate experiment using 0.1896 g. (2.06 mmoles.) CHT, the following results were obtained:  $A_{\text{PhH}}=224$ ;  $A_{\text{xylene}}=770$ ;  $A_{\text{PhCHO}}=670$ .

Control A few drops of acetone were added to a solution of 15.3 ml. 0.522 N CAN solution in 6 N nitric acid and 15.3 ml. glacial acetic acid and the resulting solution was heated on a steam bath until it was reduced (colorless). To the resulting solution were added 0.1313 g. benzaldehyde, 0.0384 g. benzene, and 100 microliters xylene. The solution was worked up as described above and analyzed by v.p.c.

$A_{\text{PhH}}=340$ ;  $A_{\text{xylene}}=769$ ;  $A_{\text{PhCHO}}=869$ .

A second control experiment was carried out the same as above except that after the cerium(IV) solution was reduced, 0.1375 g. benzaldehyde and 0.0408 g. benzene were added and the resulting solution was heated on a steam bath for 20 min. The solution was cooled, 100 microliters xylene was added, and it was treated as described above.  $A_{\text{PhH}}=230$ ;  $A_{\text{xylene}}=712$ ;  $A_{\text{PhCHO}}=814$ .

The two control experiments demonstrate that no benzaldehyde is destroyed under the reaction conditions (e.g., through oxidation by nitric acid), but some benzene is lost. Using the average values from the oxidation experiments to calculate yields, the first control experiment gives 45% benzaldehyde, 14.7% benzene,  $\text{PhCHO}/\text{PhH}=75.5/24.5$ . Using the second control experiment, yield  $\text{PhCHO}=47\%$ ,  $\text{PhH}=21.4\%$ ,  $\text{PhCHO}/\text{PhH}=69/31$ .

In 50% aqueous acetic acid containing 3 N perchloric acid

To 0.1900 g. (2.1 mmoles.) CHT in 16.2 ml. glacial

acetic acid was added 16.2 ml. (8.1 mmoles.) 0.496 N ceric perchlorate in 6 N perchloric acid. The solution was heated on a steam bath for 5 min. and then cooled. A quantity of 100 microliters xylene(standard) was added and the solution was poured into 100 ml. saturated sodium chloride solution and extracted with 25 ml. ether. The ether layer was washed with 25 ml. water, 30 ml. 1.5 N potassium hydroxide, and dried over magnesium sulfate. V.p.c. analysis gave the following results:  $A_{\text{PhH}}=12.7$ ;  $A_{\text{xylene}}=465$ ;  $A_{\text{PhCHO}}=28$ .

Control experiments A few drops of acetone were added to a solution of 16.2 ml. glacial acetic acid and 16.2 ml. 0.496 N ceric perchlorate in 6 N perchloric acid. The resulting solution was heated on a steam bath until reduced (colorless) and then cooled. To the solution was added 0.1200 g. benzaldehyde, 0.0410 g. benzene, and 100 microliters xylene. The resulting solution was worked up and analyzed as above.  $A_{\text{PhH}}=381$ ;  $A_{\text{xylene}}=792$ ;  $A_{\text{PhCHO}}=851$ .

This control experiment was carried out the same as above except 0.1371 g. benzaldehyde and 0.0430 g. benzene were added to the reduced solution and the resulting solution was heated on a steam bath for 5 min. It was then cooled, 100 microliters xylene was added, and it was worked up and analyzed as above.  $A_{\text{PhH}}=428$ ;  $A_{\text{xylene}}=819$ ;  $A_{\text{PhCHO}}=904$ .

The two control experiments demonstrate that no benzaldehyde or benzene is lost or destroyed under these con-

ditions. PhCHO/PhH=69/31. Yield PhCHO=3.2%. These reaction conditions apparently allow polymerization of the starting material.

In 50% aqueous sulfolane

To 0.184 g. (2.0 mmoles.) CHT was added 8.7 ml. sulfolane and 8.7 ml. (8.7 mmoles.) 1.009 N CAN solution. The solution was heated on a hotplate-stirrer for 6-12 min. at which time the solution was pale yellow. The solution was cooled, poured into 30 ml. of saturated sodium chloride solution, and extracted with 15 ml. ether. The ether layer was dried over magnesium sulfate and analyzed by v.p.c. PhCHO/PhH=82.6/17.4.

Control A solution of 8.7 ml. sulfolane and 8.7 ml. 1.009 N CAN solution was reduced by heating with a small amount of acetone until the solution was colorless. Benzaldehyde and benzene were weighed in and the solution was worked up as described above and analyzed by v.p.c. Wt. PhCHO=0.1714 g.; wt. PhH=0.1000 g.;  $A_{\text{PhCHO}}=712$ ;  $A_{\text{PhH}}=540$ . Correction of the benzaldehyde/benzene ratio found in the oxidation experiment gives PhCHO/PhH=83.1/16.9.

In 50% aqueous sulfolane containing 3 N nitric acid

To 0.184 g. (2.0 mmoles.) CHT was added 15.3 ml. sulfolane and 15.3 ml. (8.0 mmoles.) of a CAN solution in 6 N nitric acid. The solution was heated and stirred on a hotplate-stirrer for 12 min., poured into 60 ml. cold saturated sodium chloride solution, and extracted with 20 ml. ether.

The ether layer was dried over magnesium sulfate and analyzed by v.p.c. PhCHO/PhH=79/21.

In 50% aqueous sulfolane containing 3 N perchloric acid

To 0.184 g. (2.0 mmoles.) CHT in 17.7 ml. sulfolane was added 17.7 ml. (8.8 mmoles.) of a 0.496 N solution of ceric perchlorate in 6 N perchloric acid. The solution was heated and stirred on a hotplate-stirrer for 5 min. at which time the solution was cloudy light yellow. The solution was cooled, poured into 60 ml. cold, saturated sodium chloride solution and extracted with 20 ml. ether. The ether layer was dried over magnesium sulfate and analyzed by v.p.c. A semiquantitative estimate of the total amount of benzene and benzaldehyde recovered indicated less than 10% total recovery. PhCHO/PhH=82/18.

In 100% sulfolane

To 0.184 g. (2.0 mmoles.) CHT dissolved in 16 ml. dry sulfolane was added 4.496 g. (8.0 mmoles.) CAN. Care was taken to exclude water from the reaction mixture. The mixture was heated and stirred on a hotplate-stirrer for 3.8 hr. during which time the solid CAN dissolved to give a homogeneous solution. The solution was cooled, 100 microliters xylene(standard) was added, the solution was poured into 50 ml. saturated sodium chloride solution, and extracted with 15 ml. ether. The ether layer was dried over magnesium sulfate and analyzed by v.p.c.  $A_{\text{PhH}}=338$ ;  $A_{\text{xylene}}=1193$ ;

$A_{\text{CHT}+\text{PhCH}_3}=121$ ;  $A_{\text{PhCHO}}=1241$ . PhCHO/PhH=79/21. In a duplicate experiment the following results were obtained:  $A_{\text{PhH}}=452$ ;

$A_{\text{xylene}}=991$ ;  $A_{\text{CHT}+\text{PhCH}_3}=100$ ;  $A_{\text{PhCHO}}=1078$ . PhCHO/PhH=70/30.

Control A quantity of 4.496 g. CAN in 16 ml. sulfolane was reduced to cerium(III) by heating with a small amount of acetone. Into the resulting solution were weighed 0.1128 g. benzene and 0.1563 g. benzaldehyde. A quantity of 100 microliters xylene was added and the solution was worked up as before.  $A_{\text{PhH}}/A_{\text{xylene}}=1.38$ ;  $A_{\text{PhCHO}}/A_{\text{xylene}}=1.28$ . Using the average values from the two oxidations, yield PhCHO=61.4%, PhH=14.9%. PhCHO/PhH=80/20.

In 100% sulfolane. Two equivalents of CAN

To 0.184 g. (2.0 mmoles.) CHT in 8 ml. sulfolane was added 2.248 g. (4.0 mmoles.) CAN and the mixture was heated and stirred on a hotplate-stirrer for 1.3 hr. during which time the CAN dissolved. A quantity of 100 microliters xylene (standard) was added and the solution was added to 25 ml. saturated sodium chloride solution and extracted with 10 ml. ether. The ether layer was dried over magnesium sulfate and analyzed by v.p.c. Experiment 1:  $A_{\text{PhH}}=150$ ;  $A_{\text{xylene}}=436$ ;  $A_{\text{PhCHO}}=291$ . Experiment 2:  $A_{\text{PhH}}=95$ ;  $A_{\text{xylene}}=436$ ;  $A_{\text{PhCHO}}=196$ .

Control experiment A quantity of 2.248 g. CAN, 8 ml. sulfolane, and a few drops of acetone were heated until the cerium(IV) was reduced. To the reduced solution were added 100 microliters xylene, and weighed amounts of benzene and



benzaldehyde. The solution was then worked up as described above and analyzed by v.p.c. Experiment 1: Wt. PhH=0.0848 g.; wt. PhCHO=0.1569 g.;  $A_{\text{PhH}}=365$ ;  $A_{\text{xylene}}=379$ ;  $A_{\text{PhCHO}}=530$ . Experiment 2: Wt. PhH=0.1010 g.; wt. PhCHO=0.1395 g.;  $A_{\text{PhH}}=444$ ;  $A_{\text{xylene}}=378$ ;  $A_{\text{PhCHO}}=521$ . Using average values from the two control experiments, the yields from the oxidation experiments are: experiment 1, PhCHO=32.8%, PhH=18.9%, PhCHO/PhH=63/37; experiment 2, PhCHO=22.5%, PhH=12.2%, PhCHO/PhH=65/35.

In 100% acetonitrile; four equivalents of CAN

To 0.184 g. (2.0 mmoles.) CHT was added 16 ml. acetonitrile and 4.496 g. (8.0 mmoles.) CAN. The mixture was heated and stirred on a hotplate stirrer for 1.75 hr. at which time the solid was white and the solution orange. The reaction mixture was filtered and the filtrate added to 50 ml. water and extracted with a few milliliters carbon tetrachloride. N.m.r. analysis of the carbon tetrachloride layer indicated the presence of benzene and benzaldehyde.

To 0.1814 g. (1.8 mmoles.) CHT in 13.0 ml. acetonitrile was added 3.94 g. (7.1 mmoles.) CAN. The mixture was heated and stirred for 8 min. on a hotplate-stirrer at which time the solid was white and the solution orange. The mixture was cooled, 100 microliters xylene(standard) was added, and the mixture was poured into 50 ml. water and extracted with 15 ml. ether. The ether layer was dried over magnesium

sulfate and analyzed by v.p.c.  $A_{\text{PhH}}=320$ ;  $A_{\text{xylene}}=1195$ ;  
 $A_{\text{PhCHO}}=1465$ .

Control experiment To 16 ml. acetonitrile and 4.77 g. CAN was added a few drops of acetone and the mixture was heated and stirred on a hotplate-stirrer until the solid was white. To this mixture was added benzaldehyde and 100 microliters xylene. The mixture was poured into 50 ml. water and extracted with 15 ml. ether. The ether layer was dried over magnesium sulfate and analyzed by v.p.c. Wt. PhCHO=0.1197 g.;  $A_{\text{xylene}}=537$ ;  $A_{\text{PhCHO}}=474$ . Yield PhCHO=79.5%; yield PhH=17.5% (calculated on the basis of no correction for extraction or thermal conductivity). PhCHO/PhH=81.5/18.5.

To 0.184 g. (2.0 mmoles.) CHT in 16 ml. acetonitrile was added 4.496 g. (8.0 mmoles.) CAN and the mixture was heated and stirred on a hotplate-stirrer for 10 min. The mixture was worked up using 50 ml. water and 15 ml. ether. The ether layer was dried over magnesium sulfate and analyzed by v.p.c. Two successive v.p.c. analyses gave the following results:  $A_{\text{PhH}}=238$ ;  $A_{\text{PhCHO}}=919$ .  $A_{\text{PhH}}=366$ ;  $A_{\text{PhCHO}}=883$ .

Control experiment To 4.496 g. CAN in 16 ml. acetonitrile was added a few drops of acetone and the mixture was heated and stirred until the solid was white. The mixture was cooled and 0.173 g. benzaldehyde and 0.099 g. benzene were added and the mixture was treated as above.  $A_{\text{PhH}}=723$ ;  
 $A_{\text{PhCHO}}=880$ . Correcting the benzaldehyde/benzene ratio for

extraction and thermal conductivity differences gives for the first v.p.c. analysis PhCHO/PhH=80/20; and for the second 72/28.

In 100% acetonitrile; three equivalents of CAN

To 0.3916 (3.88 mmoles.) CHT in 23 ml. acetonitrile was added 6.37 g. (11.65 mmoles.) CAN. The mixture was heated and stirred on a hotplate-stirrer for 8 min. at which time the solid was white. To the cooled mixture was added 100 microliters xylene (standard) and 50 ml. water and it was extracted with 20 ml. ether. The ether layer was dried over magnesium sulfate and analyzed by v.p.c.  $A_{\text{xylene}}=473$ ;  $A_{\text{PhCHO}}=776$ .

Control experiment To 6.37 g. CAN in 23 ml. acetonitrile was added a few drops of acetone and the mixture was heated and stirred on a hotplate-stirrer for 30-60 min. To the cooled mixture was added 0.1961 g. benzaldehyde and 100 microliters xylene and it was worked up as described above and analyzed by v.p.c.  $A_{\text{xylene}}=393$ ;  $A_{\text{PhCHO}}=705$ . Yield PhCHO=43.6%. The amount of benzene was not determined because of overlapping of solvent and benzene in the v.p.c. traces.

In 100% acetonitrile; two equivalents of CAN

To 0.3806 g. (3.78 mmoles.) CHT in 15 ml. acetonitrile was added 4.1419 g. (8.56 mmoles.) CAN and the mixture was heated and stirred on a hotplate-stirrer for 5 min. To the

cooled mixture was added 100 microliters xylene(standard) and the mixture was worked up using 50 ml. water and 25 ml. ether. The ether layer was dried over magnesium sulfate and analyzed by v.p.c.  $A_{\text{xylene}}=136$ ;  $A_{\text{PhCHO}}=10.7$ .

Control experiment To 4.1419 g. CAN in 15 ml. acetonitrile was added 2 ml. acetone and the mixture was heated and stirred on a stirrer-hotplate for a few hours until the solid was white. A quantity of 100 microliters xylene and 0.2657 g. (2.40 mmoles.) benzaldehyde were added and the mixture was treated as above.  $A_{\text{xylene}}=496$ ;  $A_{\text{PhCHO}}=1248$ . Yield PhCHO=2%.

In 100% acetonitrile; stepwise addition of four equivalents of CAN

To 0.202 g. (2.0 mmoles.) CHT in 8 ml. acetonitrile was added 2.248 g. (4.0 mmoles.) CAN. The mixture was heated and stirred on a stirrer-hotplate for 5 min. at which time the solid was white and the liquid orange. To this mixture was added 8 ml. acetonitrile and 2.248 g. (4.0 mmoles.) CAN and the mixture was heated and stirred for another 35 min. at which time the solid was white and the solution orange. To the cooled mixture was added 100 microliters xylene(standard). The mixture was poured into 50 ml. water and extracted with 15 ml. ether. The ether layer was dried over magnesium sulfate and analyzed by v.p.c.  $A_{\text{PhH}}=226$ ;  $A_{\text{xylene}}=891$ ;  $A_{\text{PhCHO}}=1185$ . The data for the control experiment for four

equivalents of CAN in 100% acetonitrile was used. Wt.

PhCHO=0.1197 g.;  $A_{\text{xylene}}=537$ ;  $A_{\text{PhCHO}}=474$ . Yield PhCHO=85%.

PhCHO/PhH=85/15.

In 50% aqueous acetonitrile; two equivalents of CAN

To 0.3917 g. (3.88 mmoles.) CHT in 7.8 ml. acetonitrile was added 7.8 ml. (7.8 mmoles.) 1 N CAN solution. The orange cerium(IV) color faded immediately to cloudy pale yellow. The solution warmed up slightly and two layers formed. The mixture was stirred for 2 min., 100 microliters xylene (standard) was added, and the mixture was added to 25 ml. water and extracted with 15 ml. ether. The ether layer was dried over magnesium sulfate and analyzed by v.p.c.  $A_{\text{PhH}}=100$ ;  $A_{\text{xylene}}=578$ ;  $A_{\text{PhCH}_3+\text{CHT}}=531$ ;  $A_{\text{PhCHO}}=553$ . Neglecting any correction for extraction or thermal conductivity differences, PhCHO/(CHT+PhCH<sub>3</sub>)=51/49; PhCHO/PhH=85/15. There may be an appreciable error in measuring  $A_{\text{PhH}}$  since it comes on the tail of the acetonitrile peak.

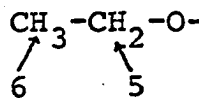
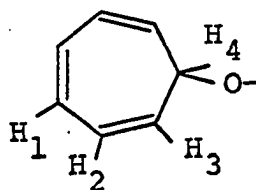
Isolation of tropyli ethyl ether from the oxidation of CHT by two equivalents of CAN in 100% acetonitrile

To a solution of 28.3 g. (50.0 mmoles.) CAN in 100 ml. acetonitrile at 30° C. was added dropwise with stirring 2.52 g. (27 mmoles.) CHT. Immediate reaction ensued upon addition with white solid precipitating. When addition of the CHT was complete, the mixture was stirred for a few minutes and then added to 500 ml. water and extracted three times with

ether. A quantity of 250 ml. absolute ethanol was added to the aqueous layer and solid sodium bicarbonate was added portionwise with stirring until the evolution of carbon dioxide ceased. The cerium salts which precipitated during the addition of sodium bicarbonate were filtered and the filtrate was extracted four times with ether. The ether layer was washed two times with water, dried over magnesium sulfate, and evaporatively distilled through a Vigreux column on a steam bath. A quantity of 100 microliters toluene(standard) was added to the resulting yellow-orange liquid and the resulting solution was analyzed by n.m.r. The chemical shifts, assignments, and corresponding n.m.r. integrals of the product were as follows:

Table 24. N.m.r. spectrum of tropylethyl ether isolated from the oxidation of CHT

Assignment	Chemical Shift	Integral
H <sub>1</sub>	6.63	175.5
H <sub>2</sub>	6.12	178
H <sub>3</sub>	5.48	178
H <sub>6</sub>	1.20	187
H <sub>4+5</sub>	ca. 3.6	195
PhCH <sub>3</sub>	2.30	18.2



Since the density of toluene is 0.867 g./ml.,  $9.4 \times 10^{-4}$  mole was added as standard. Based on the average integral for  $H_1$ ,  $H_2$ , and  $H_3$ , the amount of the 7-oxy-CHT moiety is  $9.4 \times 10^{-4} \times 3/2 \times 178/18.2 = 1.38 \times 10^{-2}$  mole. Based on the integral for  $H_6$ , the amount of the ethoxy moiety is  $9.4 \times 10^{-4} \times 187/18.2 = 9.65 \times 10^{-3}$  mole. The amount of CHT starting material was  $2.74 \times 10^{-2}$  mole. The n.m.r. spectrum is nearly identical to that of authentic troyl ethyl ether. In addition, there is no evidence for the presence of ethanol or diethyl ether in the n.m.r. sample. Yield of ethoxy moiety = 35.2%. Yield of 7-oxy-CHT moiety = 50.4%. The ethoxy moiety must be part of the troyl ethyl ether, while the extra 7-oxy-CHT moiety (15.2%) may be due to either ditroyl ether or troyl alcohol. Support for the presence of troyl alcohol is lent by the observation that the product formed a small second layer, probably water, on standing, possibly from the known reaction of two molecules of troyl alcohol to form one molecule of ditroyl ether and one of water.

Control experiment To a stirred solution of 500 ml. water and 250 ml. ethanol was added 4.86 g. (27.4 mmoles.) troylium fluoborate. To this solution solid sodium bicarbonate was added portionwise until carbon dioxide evolution ceased. The resulting mixture was added to 0.5-1 liter of water and extracted three times with ether. The

combined layers were washed two times with water and dried over magnesium sulfate. The ether was evaporatively distilled through a Vigreux column, the last traces of ether being removed on a rotary evaporator. Yield of crude product, 2.6807 g. The chemical shifts, assignments, and n.m.r. integrals of the crude product were as follows:

Table 25. N.m.r. spectrum of tropylethyl ether isolated in control experiment

Assignment	Chemical Shift	Integral
H <sub>1</sub>	6.63	163
H <sub>2</sub>	6.12	173
H <sub>3</sub>	5.48	180
H <sub>4+5</sub>	ca. 3.6	219
H <sub>6</sub>	1.20	201

To 0.15 g. crude sample dissolved in deuteriochloroform in an n.m.r. tube was added 50 microliters toluene (standard) and the n.m.r. integrals of H<sub>1</sub>, H<sub>2</sub>, H<sub>3</sub>, and toluene CH<sub>3</sub> were obtained. The average integral for H<sub>1</sub>, H<sub>2</sub>, and H<sub>3</sub> was 159 and for the toluene CH<sub>3</sub> was 106. Thus the yield of the 7-oxy-CHT moiety was 69% and of the ethoxy moiety (i.e., tropyl ethyl ether) was 53.6%.

Thus the amount of tropyl ethyl ether obtained from the oxidation of CHT by two equivalents of CAN in 100% acetonitrile is 66% (35.2/53.6 x 100) of theoretical. It is likely



that the surplus 7-oxy-CHT moiety observed in these reactions is tropyl alcohol.

I.r. and v.p.c. detection of benzaldehyde in the oxidation of CHT by four equivalents of CAN in 100% acetonitrile

To 1.0 g. (10.9 mmoles.) CHT in 87 ml. acetonitrile was added 24.4 g. (43.6 mmoles.) CAN. The mixture was heated and stirred on a hotplate-stirrer for 2 hr. The solid was removed by filtration. The i.r. spectrum of the liquid was obtained in a 0.5 mm. polyethylene cell and showed an absorption at  $1700\text{ cm}^{-1}$ . Control experiments showed that this was not due to the cell or acetonitrile or CAN and that an authentic sample of benzaldehyde in acetonitrile solution gave an absorption at  $1700\text{ cm}^{-1}$ .

In addition, a portion of the acetonitrile solution from the oxidation was injected directly into the v.p.c. A peak which was enhanced by an authentic sample of benzaldehyde was observed.

Oxidation of Tropol Ethyl Ether by CAN

To 0.27 g. (2.0 mmoles.) tropyl ethyl ether was added 4.3 ml. glacial acetic acid and 4.3 ml. (4.0 mmoles.) 0.93 N CAN solution. The solution was heated on a steam bath for 7 min. and then added to 25 ml. water and extracted with 20 ml. ether. The ether layer was washed with 40 ml. 1.5 N potassium hydroxide, dried over magnesium sulfate, and analyzed by.

v.p.c. The benzene/benzaldehyde ratio (peak areas) was 14/86.

Control To 0.27 g. (2.0 mmoles.) tropylium ethyl ether was added a solution of 4.3 ml. glacial acetic acid and 4.3 ml. 0.93 N CAN solution which had been reduced by heating with 10 drops ethanol. The solution was heated on a steam bath for 7 min. and worked up as above. V.p.c. analysis showed trace amounts of what may be benzene and benzaldehyde. These products were estimated to be less than 10% of the amount produced in the oxidation.

#### Oxidation of Tropylium Fluoborate by CAN

A quantity of 1.0 g. (5.68 mmoles.) tropylium fluoborate dissolved in ca. 10 ml. water was added with stirring to 10-11 ml. (10-11 mmoles.) 1 N CAN solution. Immediate evolution of gas occurred and the solution turned cloudy yellow. After stirring for 1 min. at room temperature, the mixture was extracted two times with ether. The ether layer was dried over magnesium sulfate and the ether was removed on a rotary evaporator. A quantity of 0.2079 g. toluene (standard) was added and the solution was analyzed by n.m.r. The integrals were as follows: methyl group of toluene: 191; CHO of benzaldehyde: 55. Yield PhCHO=35%.

To 0.711 g. (4.0 mmoles.) tropylium fluoborate was added 8.25 ml. 0.973 N CAN. The mixture was heated and stirred on a

hotplate-stirrer for 20 min. at which time the mixture was milky yellow. The mixture was extracted with ether and analyzed by v.p.c. PhCHO/PhH=80/20.

Reaction of Tropylium Fluoborate  
with Sodium Nitrate

A solution of sodium nitrate and tropylium fluoborate in water was allowed to react at steam bath temperature for 30 min. V.p.c. analysis of the ether extract of the reaction mixture showed no benzene or benzaldehyde.

Oxidation of CHT by CAN in Anhydrous  
Acetonitrile under Nitrogen

To 0.20 g. (2.18 mmoles.) CHT was added 10.0 ml. anhydrous acetonitrile in a 50 ml. Erlenmeyer flask. The flask was capped with a serum stopper and nitrogen was bubbled through the solution for 10 min. A quantity of 4.7 g. (8.6 mmoles.) CAN was added quickly and the flow of nitrogen was resumed. The mixture was heated and stirred under nitrogen on a hotplate-stirrer for 20 min. The mixture was cooled and 100 microliters toluene was added as a standard. The solution was analyzed by v.p.c. (SE-30, 6' x 1/4") without exposure to the air. Benzaldehyde was identified by its retention time (enhanced by authentic sample). The benzaldehyde peak area was approximately equal to the standard peak area indicating a yield of benzaldehyde of ca. 50%.

## Oxidation of CHT by Permanganate

Acidic medium

To 0.92 g. (10.0 mmoles.) CHT in 7 ml. acetone and 2 ml. 4 N sulfuric acid were added 1.58 g. (10.0 mmoles.) potassium permanganate in 39 ml. 2 N sulfuric acid. There was an immediate exothermic reaction. After 4 hr. at room temperature the reaction mixture was extracted with 3 ml. carbon tetrachloride. N.m.r. analysis showed the absence of benzene and benzaldehyde.

Neutral medium

To 0.92 g. (10.0 mmoles.) CHT was added 1.58 g. (10.0 mmoles.) potassium permanganate in 15 ml. water. After stirring at room temperature for 0.7 hr. the reaction mixture was filtered and extracted with 3 ml. carbon tetrachloride. N.m.r. analysis showed the absence of benzene and benzaldehyde and showed only starting material.

## Oxidation of CHT by Chromium(VI)

A quantity of 0.376 g. (4.0 mmoles.) CHT was weighed into a flask containing 0.82 g. (ca. 8 mmoles.) chromic acid dissolved in 11 ml. glacial acetic acid and 3 ml. water. Heat was evolved immediately and the solution turned dark. The solution was allowed to stand at room temperature for 42 hrs. After addition of a standard and workup, v.p.c. analysis indicated a 3.3% yield of benzene and a 34.4% yield of

benzaldehyde. PhCHO/PhH=91/9. Extraction of another reaction mixture with carbon tetrachloride and n.m.r. analysis gave a benzene/benzaldehyde ratio of 6.7/93.3.

#### Stability of Tropone to Cerium(III) Solutions

To a solution of 16.4 ml. (16.0 mmoles.) 0.974 N CAN and 16.4 ml. glacial acetic acid was added 13 drops of 95% ethanol and the solution was heated until it was colorless. This solution was added to ca. 0.3 g. tropone and the resulting solution was heated on a steam bath for 12 min. The solution was added to 40 ml. water and extracted with 30 ml. ether. The ether layer was washed with 40 ml. 1.5 N potassium hydroxide, dried over magnesium sulfate, and analyzed by v.p.c. The v.p.c. trace showed no benzene or benzaldehyde.

#### Determination of Carbon Monoxide

##### Presence of carbon monoxide

A quantity of 20 ml. of a palladium chloride solution (prepared from 0.5 g. palladium chloride, 150 ml. water, and 2.5 ml. concentrated hydrochloric acid) was placed in a 100 ml. round-bottom flask which was then evacuated. Into this flask was drawn the gas evolved during the oxidation of CHT by CAN in 50% aqueous acetic acid. After 45 min., palladium metal was floating on the surface of the solution. The re-

duction of palladium(II) indicates the presence of carbon monoxide (112).

#### Volume of gas evolved

The volume of gas evolved from the oxidation of 5 mmoles. CHT by CAN in 50% aqueous acetic acid was measured over water and found to be 18.7 ml. at 748 mm. Hg and 25° C. This quantity is corrected for the amount of gas evolved in a control experiment where no CHT was present. Correction for the water vapor pressure and to STP gives 0.73 mmoles. of gas. This corresponds to a 14.6% yield of benzene if the assumption is made that one molecule of carbon monoxide is evolved for each molecule of benzene formed.

#### Mass spectral analysis

The gas evolved from the oxidation of CHT by four equivalents of CAN in 50% aqueous acetic acid was collected and analyzed by mass spectrometry. The ratio of m/e 28 to m/e 32 from analysis of a sample of air was 84/16. The gas collected from the oxidation of CHT gave a ratio of 91.4/8.6, while the gas collected from a control experiment where everything was the same as in the oxidation experiment except for the absence of CHT gave a ratio of 82.6/17.4. Thus the oxidation of CHT produces a gas of mass 28, presumably carbon monoxide.

## Oxidation of Nitrite Ion by CAN

A ca. 1 N solution of sodium nitrite was prepared by dissolving 69.0 g. sodium nitrite in 1 l. solution. A quantity of 25 ml. of this solution was titrated with 1 N CAN solution. When 25 ml. of the 1 N solution had been added the solution was clear and colorless. This condition persisted until 50.0 ml. 1 N CAN solution had been added. Upon addition of more CAN solution the orange cerium(IV) color persisted.

## V.P.C. Methods

Routine analyses were carried out using a 6' x 1/4" column packed with 20% QF-1 on Chromosorb P (30/60 mesh) at 80-200° or a 5' x 1/4" column packed with 20% Apiezon L on Chromosorb P (60/80 mesh) at 100-225°. A 6' x 1/4" column packed with 20% Carbowax 20M on Chromosorb P (60/80 mesh) at 75° was used for the analysis of toluene in CHT.

Peak areas were determined either by cutting out and weighing or by multiplying the height times the width at half height. Yields were determined by using a control experiment to calculate the ratio of product/standard expected for a 100% yield of the product, and then comparing this ratio to that found in the reaction under consideration.

## Equipment

N.m.r. spectra were obtained on a Varian A-60 spectrometer. V.p.c. analyses were carried out on an Aerograph Model 200 fitted with dual thermal conductivity detectors. A Corning model PC-351 combination hotplate-stirrer was used to heat and stir several of the reactions. The polyethylene cells used for i.r. analysis of benzaldehyde in the CAN oxidation of CHT were far i.r. cells from Barnes Engineering.



## SUMMARY

Several benzyl and related alcohols are converted to the corresponding carbonyl compound by ceric ammonium nitrate in aqueous or 50% aqueous acetic acid solution. The reaction is synthetically useful in many cases since it is easy to follow and the product is obtained in a relatively pure form and in high yield.

Cyclopropanemethanol is oxidized to cyclopropanecarbaldehyde in 64% isolated yield by aqueous ceric ammonium nitrate (1 M). This conversion represents a convenient synthesis of cyclopropanecarbaldehyde from commercially available starting materials.

Equilibrium constants for the formation of the 1:1 cerium(IV)-alcohol complex were measured in 70% aqueous acetonitrile, 70% aqueous acetic acid, and water containing 0.5 M nitric acid utilizing a spectrophotometric technique. In 70% aqueous acetonitrile and 70% aqueous acetic acid a "reverse steric effect" was found whereby the equilibrium constants for tertiary alcohols > secondary > primary. In water the effect was reversed with primary > secondary > tertiary. For benzyl alcohols in 70% aqueous acetonitrile it was found that ring substitution causes little change in the equilibrium constant. Evidence is presented which excludes bidentate complexing of the 1,4- and 1,5- $\alpha,\omega$ -diols, but indicates some

extra stability of the 1,2- and 1,3-diols which may or may not be due to bidentate attachment of the glycol to cerium(IV).

The kinetics of the cerium(IV) oxidation of benzyl and substituted benzyl alcohols in 75% aqueous acetonitrile-1 M nitric acid was studied. It is concluded that the oxidation proceeds via rapid 1:1 alcohol-cerium(IV) complex formation and rate determining unimolecular decomposition of the complex. The substituent effect and deuterium isotope effect indicate that the  $\alpha$ -C-H bond is being broken in the transition state of the rate determining step and that the amount of charge development on the  $\alpha$ -carbon varies with the nature of the substituent. It is concluded that a mechanism involving varying amounts of charge development at the  $\alpha$ -carbon and on oxygen depending on the nature of the alcohol best explains the experimental results encountered in this study and in studies already in the literature.

Ceric ammonium nitrate in a variety of media oxidizes cycloheptatriene to benzaldehyde, benzene, and carbon monoxide in very high yield. All experimental evidence indicates that the reaction proceeds via tropylium ion formation and subsequent oxidation of tropylium ion to the observed products. Participation of nitrate ion in the reaction, probably as a ligand of the metal ion, is supported by the experimental results.

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