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Oxidative and electrophilic pathways in the reactions of organochromium(III) complexes with nitrous acid and tris(2,2'-bipyridyl)ruthenium(III)

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**OXIDATIVE AND ELECTROPHILIC PATHWAYS IN THE REACTIONS OF
ORGANOCHROMIUM(III) COMPLEXES WITH NITROUS ACID AND TRIS(2,2'-
BIPYRIDYL)RUTHENIUM(III)**

Iowa State University

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Oxidative and electrophilic pathways in the reactions
of organochromium(III) complexes with nitrous acid and
tris(2,2'-bipyridyl)ruthenium(III)

by

Jon David Melton

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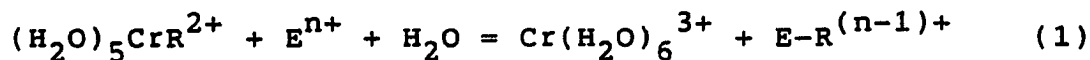
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GENERAL INTRODUCTION

Organochromium(III) complexes of the type $(\text{H}_2\text{O})_5\text{CrR}^{2+}$, where R is a sigma-bonded organic group, have been shown to undergo a number of reactions resulting in cleavage of the Cr-C bond.¹ Two closely related families of reactions of CrR^{2+} complexes are its reactions with electrophiles and with oxidants.

The reaction of CrR^{2+} with electrophiles^{2,3} can be thought of as an electrophilic substitution at the α -carbon as described by eq 1 where E^{n+} represents electrophilic reagents such as Br_2 , Hg^{2+} , Tl^{3+} , and NO^+ . Part I of this



thesis deals with the reactions of a variety of organochromium(III) complexes with nitrous acid in which both electrophilic and oxidative pathways have been found. The kinetics and mechanisms of these reactions are discussed as well as the factors which favor each mechanism.

With strong outer-sphere oxidants alkylmetals can be made to react exclusively by an oxidative pathway.^{4,5,6} Most of the work in this area has been done on organocobalt

macrocycles and alkylmetals of main group metals. Part II describes the kinetics and mechanisms of the reactions of CrR^{2+} complexes with tris(2,2'-bipyridyl)ruthenium(III).

CHAPTER I KINETICS AND MECHANISMS OF THE REACTIONS OF
PENTAAQUOROORGANOCHROMIUM(III) COMPLEXES WITH NITROUS
ACID

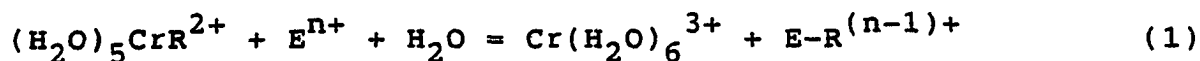
INTRODUCTION

One of the most common reactions which alkylmetal compounds undergo is their reaction with electrophiles.¹⁻⁴ Mechanistic studies have been done on the reactions of organometallic complexes with a variety of electrophilic reagents such as Br_2 , Hg^{2+} , Tl^{3+} , and NO^+ . These reactions vary a great deal in terms of rates, selectivity, and stereochemistry, but each involves an electrophilic substitution at the α -carbon of the alkylmetal complex.

One class of compounds which is particularly well-suited for the study of electrophilic substitution reactions consists of organochromium(III) complexes¹ of the type $(\text{H}_2\text{O})_5\text{CrR}^{2+}$. The chemistry of these complexes is somewhat simplified by the fact that chromium is substitutionally inert so that the electrophile attacks at the α -carbon rather than at the metal. The latter reaction can occur for alkylmetals which contain an electron-rich metal possessing a vacant coordination site.^{3,4} The presence of only one

alkyl group and the difficulty of oxidizing CrR^{2+} with electrophiles^{1,3} also has simplified the study of electrophilic reactions of organochromium complexes.

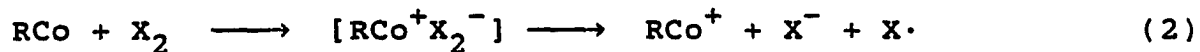
Electrophilic substitution reactions of CrR^{2+} can be described by eq 1. E^{n+} in this equation represents Hg^{2+} ,



RHg^+ , Br_2 , I_2 , IBr , NO^+ , Tl^{3+} , and H^+ . These reactions show second order kinetics, and in the case of aralkylchromium complexes of the type $\text{CrCH}_2\text{C}_6\text{H}_4\text{X}^{2+}$, a small substituent effect can be observed as X is varied.^{1,3} The reaction constants ρ for the electrophiles Br_2 , I_2 , Hg^{2+} , and MeHg^+ are -1.29, -0.81, -0.62, and -0.85, respectively. The negative ρ values are consistent with an electrophilic mechanism in which there is a build up of positive charge on the α -carbon in the transition state. An alternative explanation is that electron-withdrawing groups stabilize the ground state CrR^{2+} complex toward heterolytic cleavage.

Since electrophiles are often oxidants, reactions of alkylmetals with electrophilic reagents can occur via oxidative pathways.^{3,4} For example, $\text{RCo}(\text{dmgH})_2^7$ reacts with ICl by both an oxidative and electrophilic pathway^{8,9} (schemes I and II):

Scheme I

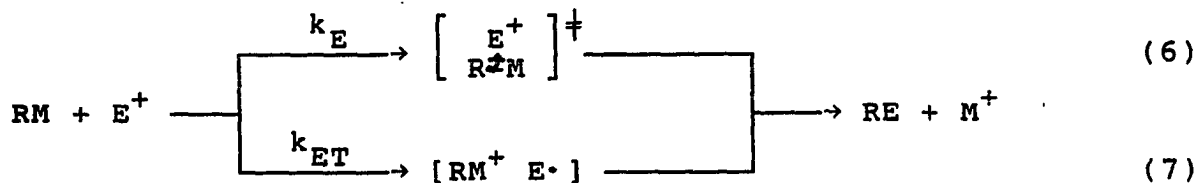


Scheme II



In scheme I the halogen oxidizes the organocobalt(III) complex by one electron to produce an unstable Co(IV) intermediate. This intermediate is then susceptible to nucleophilic attack by X^- (or H_2O) to give RX and Co(II) which then traps $\text{X}\cdot$. Scheme II, on the other hand, involves a concerted electrophilic substitution at the α -carbon to give RI and ClCo .

Kochi⁴ has compared electron transfer mechanisms with electrophilic mechanisms in more general terms using Scheme III:



In eq 6 the transition state shown in brackets involves a transfer of two electrons from the organometal R-M to the electrophile E^+ . In this process an R-E bond is being formed while the metal to carbon bond is concurrently being broken. No intermediates are formed in this pathway.

Eq 7 shows an initial one electron oxidation of R-M by E^+ to form a radical ion pair intermediate. The detection of any of these radical intermediates can serve as the basis for distinguishing an electron transfer mechanism from an electrophilic mechanism. However, if collapse of the radical ion pair is more rapid than diffusion of radicals from the solvent cage, then eq 6 and 7 can only be differentiated by selectivity studies since each pathway leads to the same products. Although the two pathways cannot be distinguished on the basis of electronic effects alone,¹⁰ reactions occurring by the the electrophilic pathway will be much more sensitive to steric interactions since they involve an inner-sphere process.

Although the reactions of CrR^{2+} with mercury(II) and halogen electrophiles have been fairly well studied, only one example has been reported in the literature of an organochromium(III) complex being reacted with HONO, a source of NO^+ in acidic aqueous solutions. Bartlett and Johnson¹¹ have studied the kinetics and mechanism of the reaction of 4-pyridinomethylchromium(III) with HONO and

found the rate law to be first-order in $[H^+]$, $[HONO]$, and $[CrCH_2pyH^{3+}]$:

$$-\frac{[CrR^{2+}]}{dt} = (k_1[H^+][HONO] + k_2[Cl^-][H^+][HONO])[CrR^{2+}] \quad (6)$$

The two terms of this rate law are believed to correspond to attack on $CrCH_2pyH^+$ by H_2ONO^+ and $NOCl$, respectively. The remainder of this chapter describes an attempt to extend this reaction to a series of CrR^{2+} complexes.

RESULTS

Products

The inorganic products in these reactions were determined by reacting solutions of $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ with HONO, separating the chromium products on a cation-exchange column, and then identifying the products on the basis of their visible spectra. The reactions can be divided into two classes on the basis of the chromium product formed. A somewhat different classification will be used later when the mechanisms are discussed. However, this is a useful way of organizing the data from the product analyses. The first class consists of reactions of organochromium complexes having an alkoxy or hydroxy group on the α -carbon. These complexes react with nitrous acid to give $(\text{H}_2\text{O})_5\text{CrNO}^{2+}$ as the major product with traces of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, probably arising from decomposition of CrR^{2+} by acidolysis. The other class comprises the reactions of the other organochromium complexes studied, and the product for these reactions is $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. These products provide important clues regarding the mechanism of the reactions in which they are formed since they are stable products¹² which are not interconvertible. That is to say, $(\text{H}_2\text{O})_5\text{CrNO}^{2+}$ is a very stable complex which, on the time scale of the analysis, does not decompose to Cr^{3+} . Likewise, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is

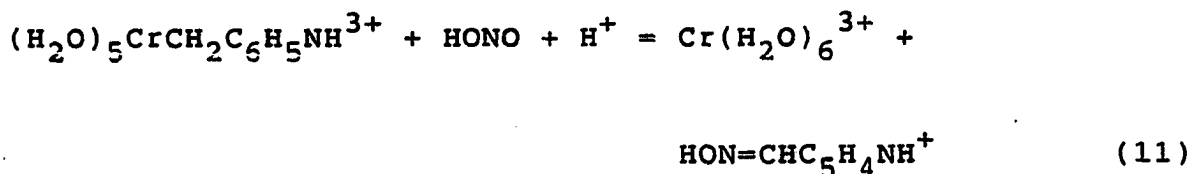
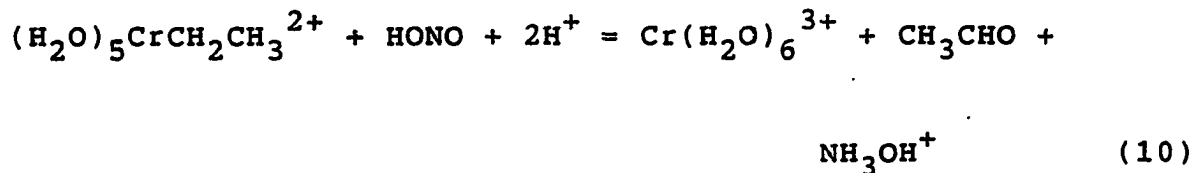
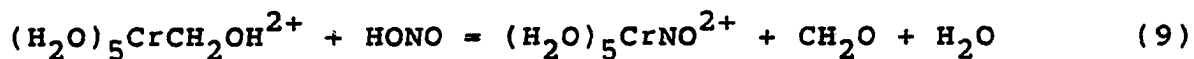
substitutionally inert and there is no known reaction of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ with NO or HONO which would lead to the formation of CrNO^{2+} .

In order to account for the formation of CrNO^{2+} in the reactions of the α -hydroxy- and α -alkoxyalkylchromium complexes, Cr^{2+} was proposed as an intermediate since it is known to react¹³ with both HONO and NO to produce CrNO^{2+} . This possibility was tested by reacting $\text{CrCH}_2\text{OCH}_3^{2+}$ with HONO in the presence of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, which rapidly reacts¹⁴ with Cr^{2+} to form CrBr^{2+} and Co^{2+} . Analysis for cobaltous at the end of the reaction indicated that 58% of the Cr^{2+} formed was trapped by $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$. Kinetic runs carried out in the presence of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ showed that the cobalt complex had no effect on the rate constant. When the same reaction was carried out in an oxygen-saturated solution, no CrNO^{2+} could be detected after ion-exchanging the products. These results suggest that the reactions of compounds in the first class proceed via a Cr^{2+} intermediate.

Organic products were determined either spectrophotometrically or by gas chromatographic analysis. In studying the reaction of nitrous acid with 4-pyridinomethylchromium, Bartlett and Johnson¹¹ identified 4-pyridinoaldoxime as the organic product by its U.V. spectrum and we have verified this finding.

Gas chromatography was used to identify the products for the reactions of ethyl- and 2-propylchromium ions, and acetaldehyde and acetone were identified as the major organic products. For the reaction of methoxymethylchromium ion, methanol was identified as a product by G.C. and formaldehyde was detected in a 87.5% yield using the chromotropic acid method.¹⁵ These results are summarized below in Table I-1.

Thus, three types of reactions can be identified which are given below in eq 9 - 11:



All of the products in the equations above were detected with the exception of hydroxylamine, although this is a reasonable product in light of the mechanism proposed below.

Table I-1 Products of the Reaction of HONO with CrR^{2+}

R	Cr Product ^a	Organic Product
CH_2OH	CrNO^{2+}	CH_2O^b
CH_2OCH_3	CrNO^{2+}	$\text{CH}_2\text{O},^b \text{CH}_3\text{OH}^c$
$\text{CHCH}_3\text{OCH}_2\text{CH}_3$	CrNO^{2+}	$[\text{CH}_3\text{CO}, \text{CH}_3\text{CH}_2\text{OH}]^d$
CH_3	Cr^{3+}	$[\text{CH}_2\text{O}]^d$
CH_2CH_3	Cr^{3+}	CH_3CHO^c
$\text{CH}(\text{CH}_3)_2$	Cr^{3+}	$\text{CH}_3\text{COCH}_3^c$
$p\text{-CH}_2\text{C}_6\text{H}_5$	Cr^{3+}	$[\text{HON}=\text{CHC}_6\text{H}_5]^d$
$4\text{-CH}_2\text{pyH}^+$	Cr^{3+}	$\text{HON}=\text{CHpyH}^+ \text{ a}$

^aDetermined by U.V.-visible spectroscopy.

^bDetermined by the chromotropic acid method.

^cDetermined by G.C.

^dThe organic product was not determined for this reaction, but the presumed product is given in brackets.

Stoichiometry

The stoichiometry of the reaction of $\text{CrCH}_2\text{OCH}_3^{2+}$ with HONO was determined by a spectrophotometric titration. A plot of the absorbance at λ 386 nm vs $[\text{HONO}]/[\text{CrCH}_2\text{OCH}_3^{2+}]_0$ is shown in Figure I-1. The stoichiometry of the reaction was found to be 0.95 mol of HONO to 1 mol of CrR^{2+} , i.e. 1 : 1.

Kinetics

Kinetic studies were conducted on the reactions of nitrous acid with various $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ complexes. The kinetic runs were carried out by reacting an excess of HONO with CrR^{2+} and monitoring the loss of CrR^{2+} by using the U.V. peak of CrR^{2+} between λ 260 nm and 290 nm. The concentrations used were typically in the following ranges: $[\text{CrR}^{2+}] = (0.3 - 9) \times 10^{-4}$ M, $[\text{HONO}] = (3 - 200) \times 10^{-4}$ M, $[\text{HClO}_4] = (0.01 - 0.1)$ M. Runs were conducted at constant temperature (23.4 °C) and a constant ionic strength of 0.10 M; maintained with perchloric acid and lithium perchlorate. Pseudo-first-order rate constants were obtained from the kinetic data by standard methods. Tables are given in Appendix I containing the observed rate constants (k_{obs}) for the reactions of the different organochromium complexes as a function of reagent concentrations.

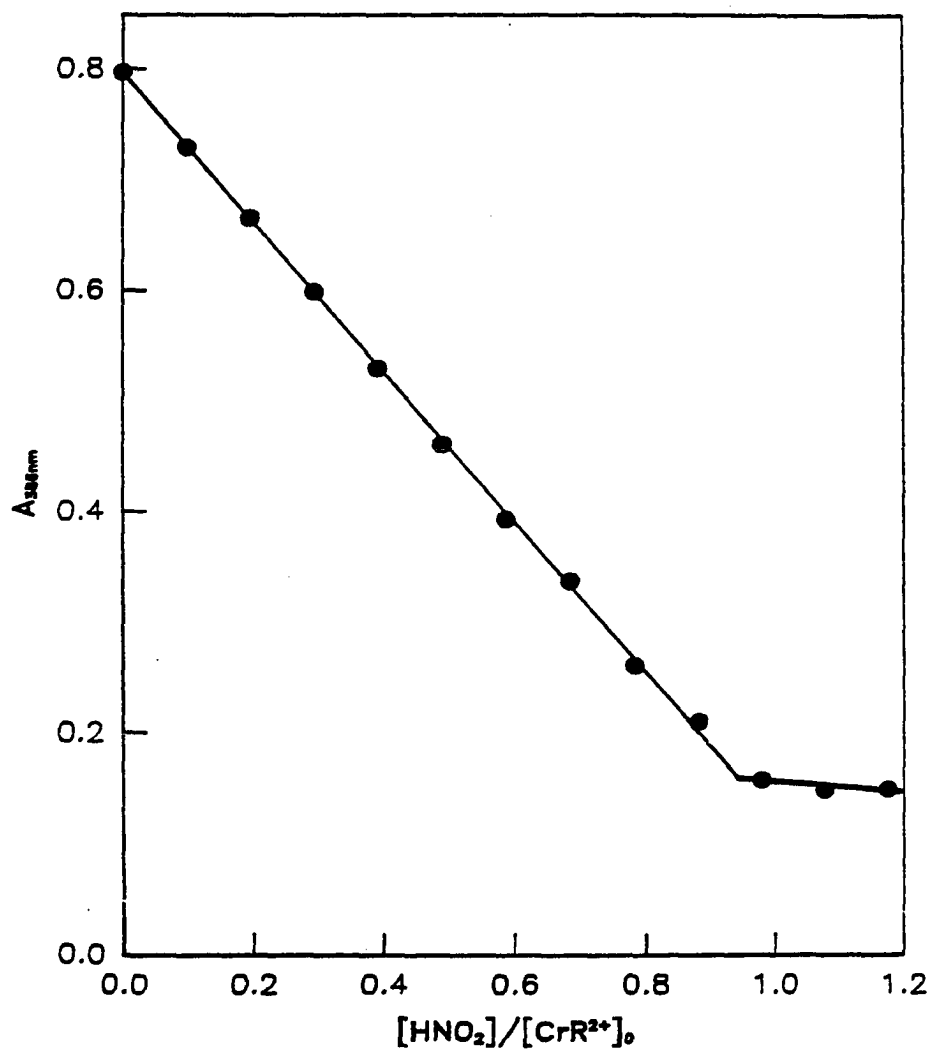


Figure I-1 Plot of absorbance at λ 386 nm vs $[\text{HONO}]/[\text{CrCH}_2\text{OCH}_3^{2+}]_0$ for the spectrophotometric titration of $\text{CrCH}_2\text{OCH}_3^{2+}$ by HONO. The endpoint indicates a 1 : 1 stoichiometry for the reaction

The observed rate constants were corrected for acidolysis (k_A) and homolysis (k_H),¹ and the "corrected" rate constants obtained ($k_C = k_{Obs} - k_A - k_H$) were found to increase with both $[HONO]$ and $[H^+]$. This is illustrated in Figures I-2 and I-3 which show plots of $(k_{Obs} - k_H - k_A)/[HONO]$ vs $[H^+]$ for the reactions of $CrCH_2OCH_3^{2+}$ and $CrCH_2C_6H_5^{2+}$ with HONO. The linearity of these plots leads to the rate law given in eq 12:

$$-\frac{d[CrR^{2+}]}{dt} = (k_A + k_H + k_1[H^+][HONO] + k_1'[HONO])[CrR^{2+}] \quad (12)$$

This is the form of the rate law found for all of the organochromium complexes studied. The first two terms of the rate law correspond to decomposition of the organochromium complex by acidolysis and homolysis¹ and the second two terms arise from the reaction with nitrous acid. Table I-2 gives the values of k_1 and k_1' for the organochromium complexes studied.

Several observations can be made regarding the rate law and rate constants in Table I-2. The third term in the rate law shows a first-order dependence on $[H^+]$ which suggests that this reaction occurs via an NO^+ intermediate as do many nitrosation reactions in the literature.^{16,17} A second observation which can be made relates to the relative values of the rate constants in Table I-2. It is rather surprising

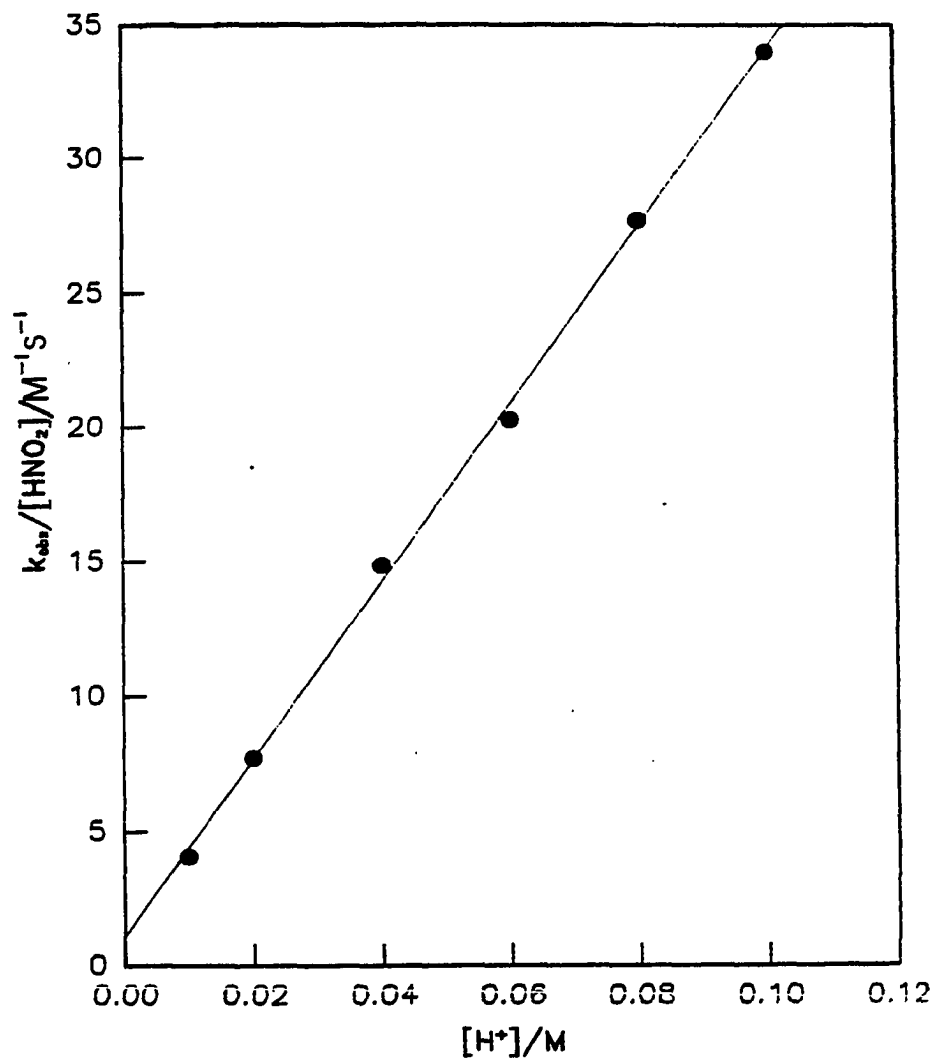


Figure I-2 Plot of $k_c/[\text{HONO}]$ vs $[\text{H}^+]$ for the reaction of $\text{CrCH}_2\text{OCH}_3^{2+}$ with HONO. Apparent second-order rate constant varies linearly with $[\text{H}^+]$ and shows an intercept which is zero within experimental error. Data were taken at 23.4 °C and $I = 0.10 \text{ M}$

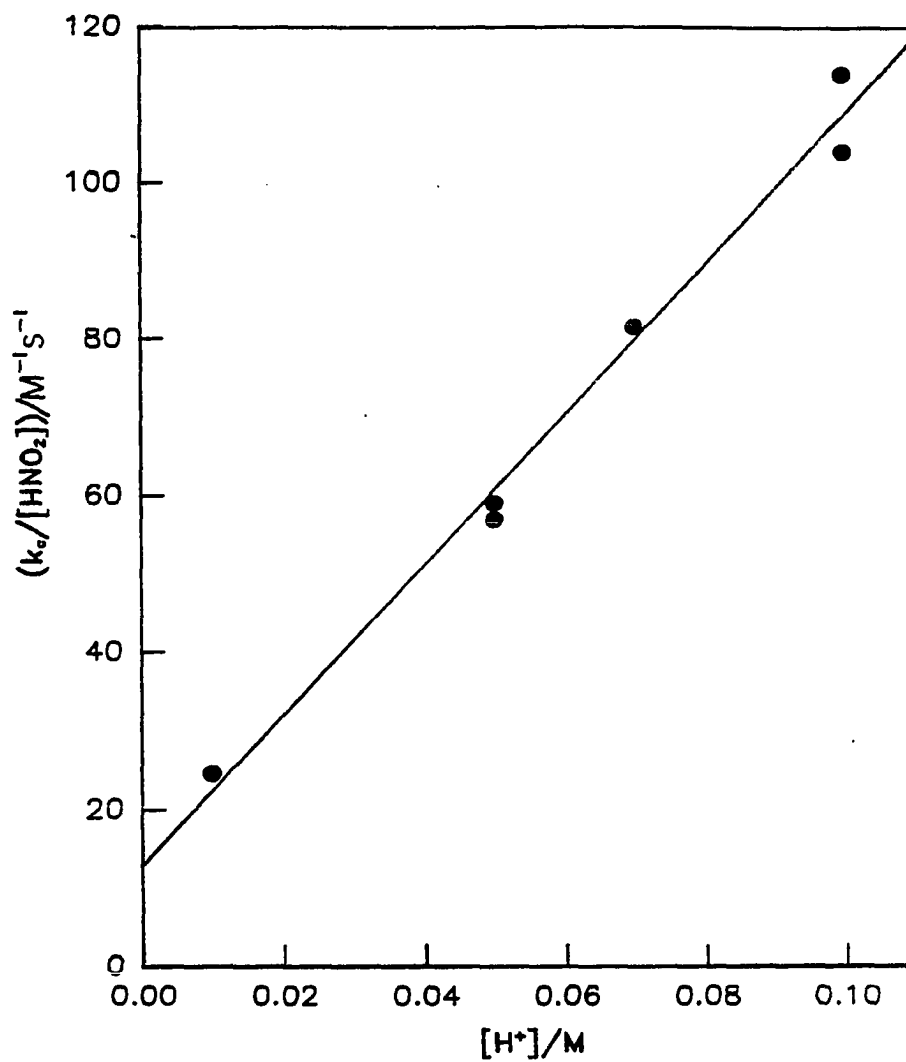


Figure I-3 Plot of $k_c/[\text{HONO}]$ vs $[\text{H}^+]$ for the reaction of $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ with HONO. Apparent second-order rate constant varies linearly with $[\text{H}^+]$ and shows an intercept which is zero within experimental error. Data were taken at 23.4 °C and $I = 0.10 \text{ M}$

Table I-2 Rate Constants for the Reactions of Nitrous Acid with Organochromium(III) Complexes^a

R	$k/M^{-2}s^{-1}$	$k'/M^{-1}s^{-1}$	$k_{Hg}^b/M^{-1}s^{-1}$
CH ₂ OH	745 ± 26	5.1 ± 1.8	2.28 × 10 ²
CH ₂ OCH ₃	330 ± 6	1.1 ± 0.4	9.05 × 10 ¹
CHCH ₃ OCH ₂ CH ₃	45 ± 2	2.5 ± 0.1	0.535/[H ⁺] ^c
CH ₃	38.8 ± 0.8	0	1.0 × 10 ⁷
CH ₂ CH ₃	87 ± 5	0.6 ± 0.4	1.40 × 10 ⁵
CH ₂ CH ₂ CH ₃	15.1 ± 0.8	0	3.50 × 10 ⁴
CH(CH ₃) ₂	17.9 ± 0.5	0.076 ± 0.027	1.56
CH ₂ Cl	0.46 ± 0.02	0	5.90 × 10 ⁻¹
CH ₂ Br	0.12 ± 0.01	0.005 ± 0.001	4.68 × 10 ⁻¹
CH ₂ I	0.247 ± 0.006	0	
p-CH ₂ C ₆ H ₄ CH ₃	1010 ± 31	0	5.22 × 10 ⁴
CH ₂ C ₆ H ₅	956 ± 56	13 ± 4	4.87 × 10 ⁴
p-CH ₂ C ₆ H ₄ CF ₃	241 ± 2	0	2.10 × 10 ⁴
p-CH ₂ C ₆ H ₄ CN	92 ± 3	0	1.64 × 10 ⁴
4-CH ₂ C ₅ H ₅ NH ⁺	0.561 ± 0.005	0	5.0 × 10 ²

^aT = (23.4 ± 0.1) °C, I = 0.10 M.

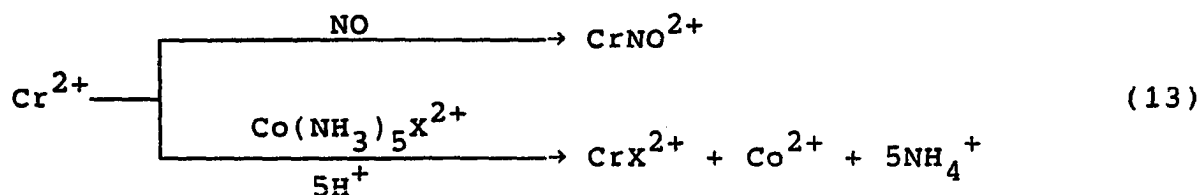
^bref. 1.

^cCrCHMeOEt²⁺ reacts with Hg²⁺ by an electron transfer mechanism. All other organochromium complexes listed in this table react by an S_E2 mechanism.

that the benzylchromium complex reacts with HONO much more rapidly than the methylchromium complex does since the reverse behavior is seen for the corresponding reactions of mercury(II) electrophiles.¹ This difference suggests that at least some of the reactions of HONO with CrR^{2+} complexes proceed by a different mechanism than the related Hg(II) reactions (Hg^{2+} reacts with both alkyl- and aralkylchromium complexes by an $\text{S}_{\text{E}}2$ mechanism). Both of these points will be discussed in greater detail below.

Competition Studies to Determine the Rate Constant for the Reaction of Cr^{2+} with NO

Cr^{2+} and NO have been proposed as intermediates in the reactions of α -hydroxy- and α -alkoxyalkylchromium complexes. This reaction has been mentioned several times in the literature,¹² but no rate constant has been reported. The fast rate of the reaction and the lack of a suitable wavelength for monitoring the kinetics spectrophotometrically makes this rate constant difficult to measure directly. We have, however, been able to determine the rate constant indirectly by competition experiments using $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ to compete with NO for Cr^{2+} :



The competition experiments were carried out by slowly injecting Cr^{2+} into a well-stirred solution of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ saturated with NO. The number of moles of Cr^{2+} injected was less than or equal to 10% of the number of moles of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ initially present so $[\text{Co}(\text{NH}_3)_5\text{X}^{2+}]_{\text{av}}$ was used for the concentration of halopentamminecobalt(III) in the calculations. After the Cr^{2+} was injected, $[\text{Co}^{2+}]_{\infty}$ was determined by the thiocyanate method ($\lambda_{\text{max}} 623$, $\epsilon = 1.842 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ in 1 : 1 acetone/water).

The data from the competition experiments are shown in Tables I-3 and I-4. One can show that eq 14 is valid in these experiments, where $[\text{Cr}^{2+}]_{\text{T}}$ is the total amount of Cr^{2+} added and k_{NO} and k_{X} represent the rate constants for

$$\frac{[\text{Cr}^{2+}]_{\text{T}}}{[\text{Co}^{2+}]_{\infty}} = 1 - \frac{k_{\text{NO}}}{k_{\text{X}}} \times \frac{[\text{NO}]_0}{[\text{Co}(\text{NH}_3)_5\text{X}^{2+}]_{\text{av}}} \quad (14)$$

the reaction of Cr^{2+} with NO and $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$, respectively. Thus, a plot of $[\text{Cr}^{2+}]_{\text{T}}/[\text{Co}^{2+}]_{\infty}$ vs $[\text{NO}]_0/[\text{Co}(\text{NH}_3)_5\text{X}^{2+}]_{\text{av}}$ will have an intercept of 1 and a slope equal to $k_{\text{NO}}/k_{\text{X}}$. The plots for $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ are shown in Figure I-4. The least squares fit for for each of the two lines gives a unit intercept and the slopes of the lines yield the ratios $k_{\text{NO}}/k_{\text{Br}} = 1.8 \pm 0.1$ and $k_{\text{NO}}/k_{\text{Cl}} = 3.0 \pm 0.2$. From the literature¹⁴ one obtains the rate constants $k_{\text{Br}} = (1.4 \pm 0.4) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ and $k_{\text{Cl}} = (6 \pm 1) \times 10^5$

Table I-3 Data from Competition Experiments with
 $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$

$10^3[\text{Co}^{\text{III}}]_{\text{a}}/\text{M}$	$10^4[\text{Cr}^{2+}]_{\text{T}}/\text{M}$	$10^4[\text{Co}^{2+}]_{\text{M}}$	$\frac{[\text{Cr}^{2+}]_{\text{T}}}{[\text{Co}^{2+}]_{\infty}}$	$\frac{[\text{NO}]_0}{[\text{Co}^{\text{III}}]_{\text{av}}}$
0.89	1.00	2.19	4.57	1.91
1.06	1.00	2.75	3.64	1.60
1.52	1.00	3.53	2.83	1.12
1.94	3.01	1.13	2.66	0.876
2.91	3.01	1.24	2.43	0.584
3.94	3.01	1.21	2.49 ^b	0.431 ^b
5.91	3.01	1.73	1.74	0.288
9.89	3.01	2.22	1.36	0.172

^a $\text{Co}^{\text{III}} = \text{Co}(\text{NH}_3)_5\text{Br}^{2+}$. The concentration given is the average concentration during the experiment.

^bThis point was not used in the calculation of the slope of the line in Fig. I-4.

Table I-4 Data from Competition Experiments with
 $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$

$10^3[\text{Co}^{\text{III}}]^a/\text{M}$	$10^4[\text{Cr}^{2+}]_{\text{T}}/\text{M}$	$10^4[\text{Co}^{2+}]/\text{M}$	$\frac{[\text{Cr}^{2+}]_{\text{T}}}{[\text{Co}^{2+}]_{\infty}}$	$\frac{[\text{NO}]_0}{[\text{Co}^{\text{III}}]_{\text{av}}}$
1.97	2.04	0.530	3.85	0.863
1.97	2.04	0.566	3.60	0.863
2.46	2.04	0.753	2.71	0.691
2.95	3.06	1.05	2.91	0.576
3.94	3.01	1.13	2.66	0.431
4.93	3.06	1.35	2.27	0.345
5.91	3.01	1.80	1.67	0.288
7.90	3.06	1.90	1.61	0.215

$^a\text{Co}^{\text{III}} = \text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$. The concentration given is the average concentration during the experiment.

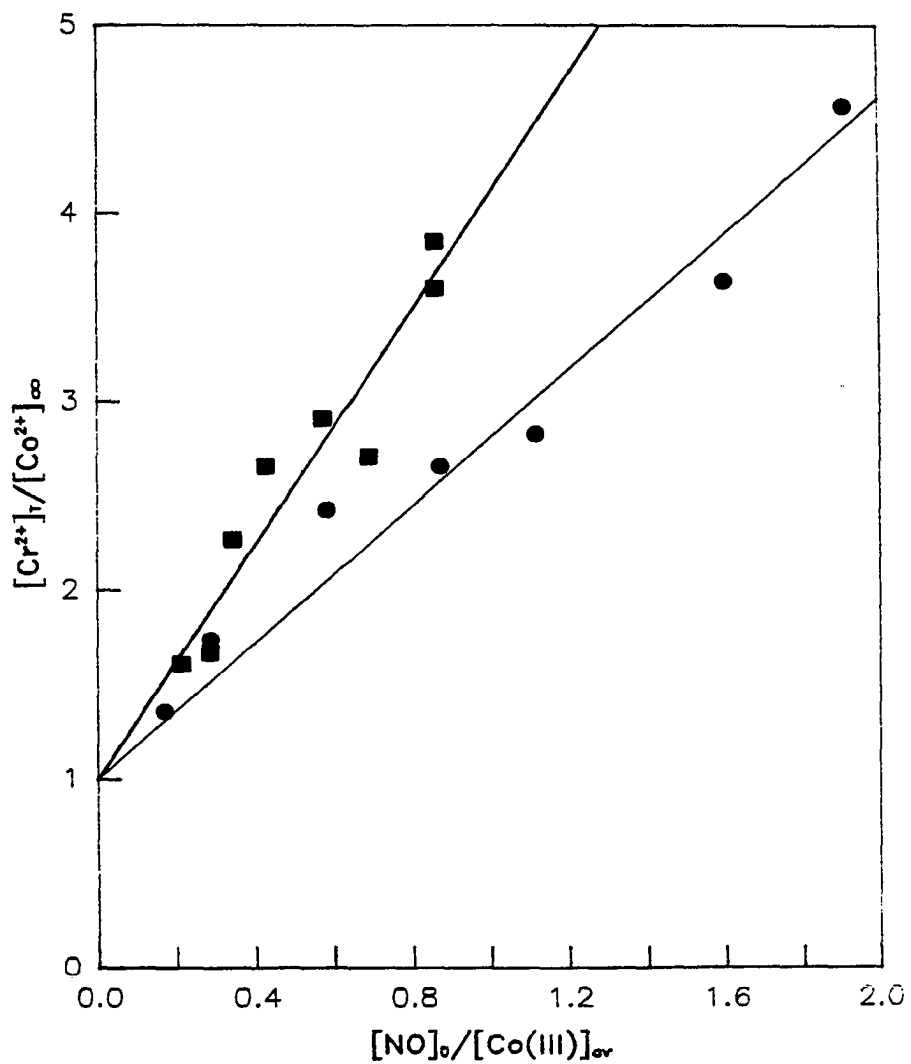


Figure I-4 Plots of $[\text{Cr}^{2+}]_T/[\text{Co}^{2+}]_\infty$ vs $[\text{NO}]_0/[\text{Co}(\text{NH}_3)_5\text{X}^{2+}]_{av}$ where $\text{X} = \text{Cl} \blacksquare, \text{Br} \bullet$. The slopes of the lines correspond to $k_{\text{NO}}/k_{\text{Cl}}$ and $k_{\text{NO}}/k_{\text{Br}}$ and are equal to 3.0 ± 0.2 and 1.8 ± 0.1 , respectively

$M^{-1}s^{-1}$ which lead to values of $(2.5 \pm 0.7) \times 10^6 M^{-1}s^{-1}$ and $(1.8 \pm 0.3) \times 10^6 M^{-1}s^{-1}$ for k_{NO} . This gives an average value of $2.2 \times 10^6 M^{-1}s^{-1}$ for k_{NO} . Although the two sets of competition experiments yield somewhat different values for k_{NO} , one cannot conclude that the values are significantly different because of the rather large standard deviations for k_{Br} and k_{Cl} . It should be noted that the results reported here yield the ratio $(k_{NO}/k_{Cl})/(k_{NO}/k_{Br}) = k_{Br}/k_{Cl} = 1.67 \pm 0.14$ which agrees with the value of 1.44 ± 0.02 determined by Moore and Keller¹⁸ in competition experiments involving various Co(III) complexes.

DISCUSSION

Classification of Organochromium Complexes

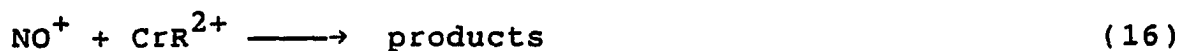
The results described above can best be understood if we divide the organochromium complexes into two main classes. The first class will be referred to as the aliphatic CrR^{2+} complexes in which R is an alkyl or substituted alkyl group. The second class is made up of aralkylchromium complexes of the type $\text{CrCH}_2\text{Ar}^{2+}$ where Ar = p- $\text{C}_6\text{H}_4\text{X}$, or 4- $\text{C}_5\text{H}_4\text{NH}^+$.

The first class can be further subdivided into two classes according to the nature of the R group. α -Hydroxyalkyl and α -alkoxyalkyl radicals are generally regarded as strongly reducing radicals,^{19,20} this property being due in part to the electron-donating ability of the oxygen on the α -carbon. Organochromium complexes possessing a reducing radical as an R group will be referred to as "strongly reducing" aliphatic CrR^{2+} complexes. On the other hand, alkyl radicals²⁰ are much more difficult to oxidize and can be considered to be oxidizing radicals. Thus, the organochromium complexes with R = alkyl or α -haloalkyl radicals will be classified as "weakly reducing" aliphatic complexes.

Aliphatic Organochromium Complexes

The strongly reducing aliphatic complexes will be considered first, although reference will be made to the other organochromium complexes. As mentioned earlier, the first two terms in the rate law for the reaction of nitrous acid with organochromium ions (eq 12) result from the heterolytic and homolytic decomposition of CrR^{2+} , and it is the last two terms in the rate law which arise from the reaction with nitrous acid. The third term represents the major pathway in the reaction and is the one which will be discussed below.

NO^+ Intermediate The first-order dependence on $[\text{H}^+]$, $[\text{HONO}]$, and $[\text{CrR}^{2+}]$ suggest that the reaction involves a rapid pre-equilibrium (eq 15) to form NO^+ followed by a rate-determining reaction between NO^+ and CrR^{2+} (eq 16)



analogous to numerous nitrosation reactions in the literature.¹⁷ Although H_2ONO^+ has been proposed as an intermediate in nitrosation reactions, there is no spectroscopic evidence for this species^{17b} and the reaction probably occurs through an NO^+ intermediate. The equilibrium constant for reaction 15 has been reported in

the literature²¹ and has the value $K_{15} = 3 \times 10^{-7} \text{ M}^{-1}\text{s}^{-1}$. Using this value and the values for $K_{15}k_{16}$ (the measured rate constant k) given in Table I-2 we can calculate k_{16} and see that it approaches the diffusion controlled limit in the fastest reactions. It is very doubtful that such a rapid reaction would involve substitution of NO^+ at the metal center although substitution of the trans water molecule is known²² for SCN^- . Reaction 16 is still slow enough, however, to be rate-limiting. This can be shown by using the value of $k_{15} = 617 \text{ M}^{-1}\text{s}^{-1}$ obtained by Benton and Moore²³ to calculate a value of $2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for k_{15} . Since the reactions show a first-order dependence on $[\text{CrR}^{2+}]$ and since $k_{15} \gg k_{16}[\text{CrR}^{2+}]$, it is clear that the equilibrium in reaction 15 is rapid relative to reaction 16 which is rate-limiting.

NO^+ is both a better oxidant²⁴ and electrophile^{17b} than HONO which explains why it is the reactive form of N(III) . Since NO^+ typically reacts as either an oxidant or an electrophile, one would expect its reactions with CrR^{2+} to involve either electrophilic substitution at the α -carbon or an outer-sphere oxidation of the organochromium complex.

Steric Effects One should be able to distinguish between these two possibilities by considering the sensitivity of the rate constants to steric crowding at the α -carbon. Rate constants for an outer-sphere electron

transfer should show little sensitivity to steric effects whereas rate constants for substitution reactions at sp^3 hybridized C atoms are very sensitive to the degree of substitution of the carbon.⁴ Table I-2 shown above gives the rate constants for the reactions of alkylchromium complexes with Hg^{2+} and HONO. Hg^{2+} is known to react with alkylchromium complexes by an S_E2 mechanism²⁵ and this is reflected in the large variations in the rate constant for the series $R = CH_3, CH_2CH_3, CH(CH_3)_2$. In contrast, steric effects do not seem to be important for the reactions with HONO which suggests that NO^+ is acting as an outer-sphere oxidant. Inner-sphere electron transfer through a bridging water ligand would also give rise to small steric effects, but this type of mechanism is unlikely since the basicity of coordinated water is so small making water a very poor bridging ligand.

Linear Free Energy Correlations In order to gain a better understanding of the mechanism for the reaction of HONO with CrR^{2+} an attempt was made to correlate the rate constants with the properties of the R groups. Of the different correlations attempted, the only successful one involved a plot of $\log(k_N)$ vs $\sigma_p(X)$ where k_N is the rate constant for the reaction of HONO with $CrCH_2X^{2+}$ and $\sigma_p(X)$ is the Hammett substituent constant for X.²⁶ Such a plot is shown in Fig. I-5. The slope was calculated by a least-

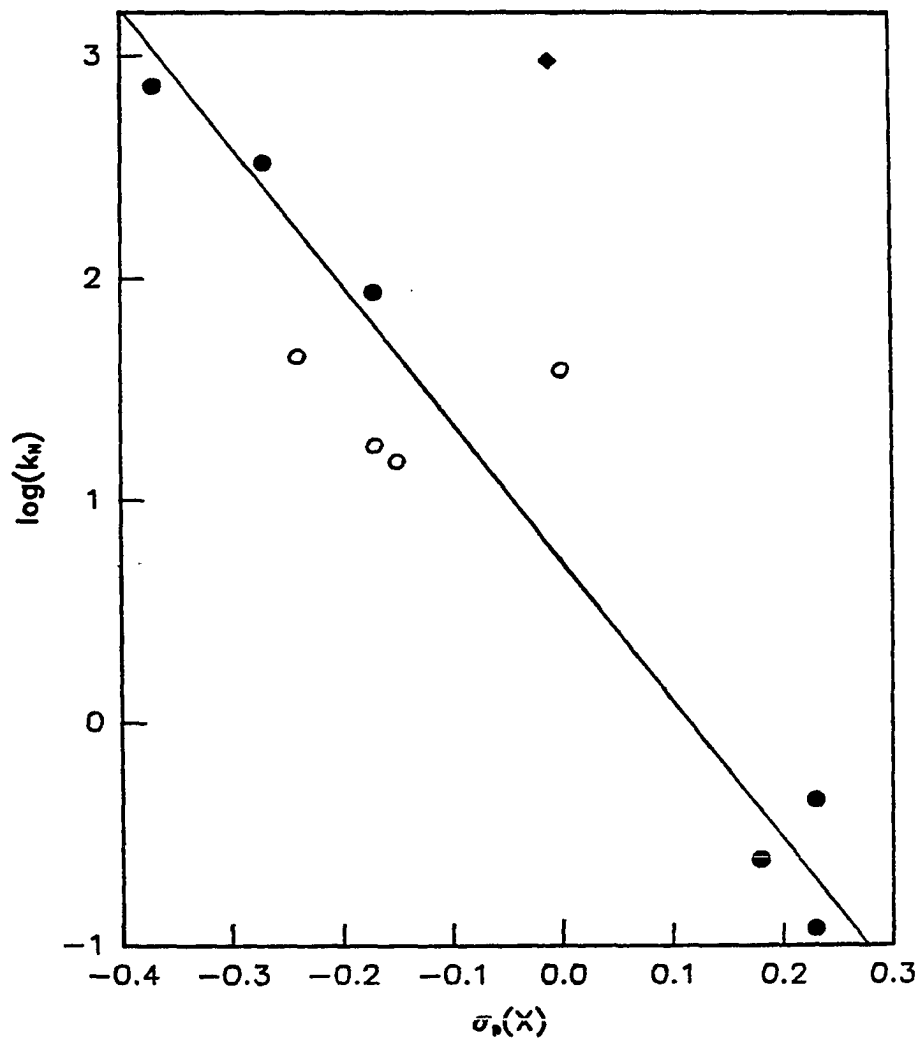


Figure I-5 Plot of $\log(k_N)$ vs $\sigma_p(X)$ for the reactions of $(H_2O)_5CrCH_2X^{2+}$ with HONO. The line drawn is from a least-squares fit of the points when $X = CH_3, OCH_3, OH, Cl, Br, I$. Other points are shown for $R = CH_3, CH_2CH_3, CH_2CH_2CH_3$, and $CH(CH_3)_2$ (open circles) and $R = CH_2C_6H_5$ (diamond).

squares fit of the points (filled circles) representing reactions of organochromium complexes having only one substituent on the α -carbon. This was done to minimize differences due to steric effects. This leads to a ρ value of -6.2 ± 0.4 . Since the Hammett σ values are normally used only for substituents on an aromatic ring, this correlation is only semi-quantitative, but it does suggest that the reactions of the aliphatic organochromium complexes go through a common transition state. One can also conclude that the large negative ρ value is consistent with either an oxidative or an electrophilic mechanism. The points for $R = \text{CH}_3$, $\text{CH}(\text{CH}_3)_2$, $\text{CH}_2\text{CH}_2\text{CH}_3$, and $\text{CH}(\text{CH}_3)(\text{OCH}_2\text{CH}_3)$ (open circles) deviate somewhat from the line, but this can be attributed to a small steric effects seen for groups larger than or smaller than CH_2CH_3 . A point was plotted for $R = \text{CH}_2\text{C}_6\text{H}_5$ (diamond) which shows a large deviation from the line. This deviation, which cannot be accounted for by steric effects, suggests that $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ reacts with HONO by a different mechanism than the aliphatic organochromium complexes.

An attempt was made to correlate the rates of the reactions of HONO with aliphatic CrR^{2+} complexes with those of the corresponding reactions with Hg^{2+} . One can see by inspection of the rate constants in Table I-2 that no such correlation is possible since HONO reacts more rapidly with

α -hydroxy- and α -alkoxychromium complexes than with alkylchromium complexes while the reverse is true for the reactions of Hg^{2+} . This also suggests that HONO does not react with aliphatic organochromium complexes by an electrophilic substitution mechanism as has been established for the reactions of mercury(II).²⁵

Outer-Sphere Electron Transfer The evidence presented thus far implies that HONO is reacting with aliphatic organochromium by an electron transfer mechanism in which NO^+ is formed as an intermediate which then oxidizes CrR^{2+} by one electron. NO^+ acts as a one electron oxidant in reactions with a variety of reagents^{17,27-29} although it probably reacts by an inner-sphere mechanism in most of these reactions.³⁰ Two reactions which might be expected to proceed by an outer-sphere mechanism are the reactions of HONO with $\text{Fe}(\text{phen})_2(\text{CN})_2$ ³¹ and $[\text{IrCl}_6]^{3-}$.²⁹ Both of these metal complexes are substitutionally inert and generally react as outer-sphere electron transfer reagents.

Ram and Stanbury²⁹ have analyzed their data for the hexachloroiridate system in terms of the the Marcus theory³² which relates the rate constant for an outer-sphere electron transfer reaction to the equilibrium constant of that reaction and the rate constants of the exchange reactions of the two redox couples involved:

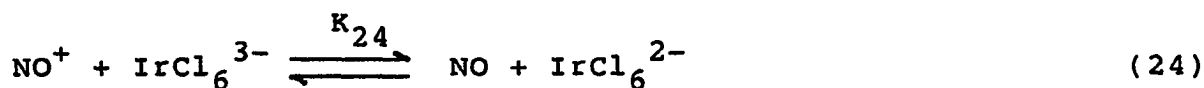
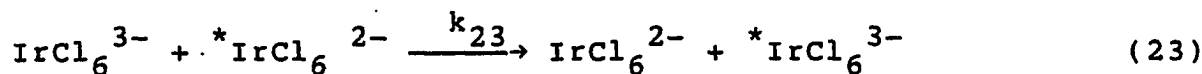




$$k_{19} = (k_{17}k_{18}K_{19}f)^{1/2} \quad (20)$$

$$\log(f) = \frac{(\log K_{19})^2}{4 \log(k_{17}k_{18}/Z^2)} \quad (21)$$

The reactions of interest are therefore given in eq 22 - 24:



Using eq 20 and 21 they estimated a value of 4×10^8 $M^{-1}s^{-1}$ for k_{22} , the exchange rate for the NO/NO^+ couple. This value for k_{22} is much higher than the value of ≈ 0.01 $M^{-1}s^{-1}$ estimated by Ebersson and Radner²⁷ using a classical valence force-field model. They attribute this difference to strong overlap of the orbitals of NO^+ with those of one of the Cl atoms on $IrCl_6^{3-}$. In other words, Cl acts as a bridging ligand allowing the oxidation to occur by an inner-

sphere pathway, thereby increasing the rate of the reaction over that which would be expected for an outer-sphere electron transfer.

Reveco and Stedman³¹ have studied the reaction between HONO and $\text{Fe}(\text{phen})_2(\text{CN})_2$ and obtained a value of $6.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for the second-order rate constant for the reaction of NO^+ with $\text{Fe}(\text{phen})_2(\text{CN})_2$. We can estimate the exchange rate for the $\text{Fe}(\text{phen})_2(\text{CN})_2/\text{Fe}(\text{phen})_2(\text{CN})_2^+$ couple ($E^\circ = 0.80 \text{ V}$) to have a value of $\approx 10^5 \text{ M}^{-1}\text{s}^{-1}$ using the known values of $1.9 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ and $1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ for the exchange reactions of the $\text{Fe}(\text{CN})_6^{3-/2-}$ and $\text{Fe}(\text{phen})_3^{2+/3+}$, respectively. This leads to a value of $k_{22} = 1.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ which is also much higher than the one calculated by Ebersson and Radner. However, here again there is a possibility that the NO^+ attacks at the nitrogen on one of the cyanide ligands which would give rise to a rate constant much higher than that predicted by Marcus theory.

Consideration of the two reactions cited above lead one to conclude that either the reactions proceed by an inner-sphere mechanism or the exchange rate for the NO/NO^+ couple is a great deal larger than the value of $0.01 \text{ M}^{-1}\text{s}^{-1}$ calculated by Ebersson and Radner. Perhaps, the difficulty in determining k_{22} stems from the large change in solvation which occurs in going from NO to NO^+ . This is the reason given for the large range in values (10^{-8} to $10^7 \text{ M}^{-1}\text{s}^{-1}$) for

the calculated self-exchange rate for the O_2/O_2^- couple.³³ It is argued that the neutral O_2 and the charged, hydrogen bonded O_2^- differ greatly in their degree of solvation. Thus, when O_2^- is reacted with diverse oxidizing agents the transition states occur at different points along the reaction coordinate which vary significantly with regard to the degree of desolvation of $O_2(H_2O)_n^-$. These variations in the calculated exchange rate are therefore due to large differences in the extent of desolvation of $O_2(H_2O)_n^-$ in the transition state (leading to large differences in reorganization energy) which are not adequately accounted for by Marcus theory which is usually applied to charged coordination complexes in which changes in the degree of solvation are much less.

This sort of problem may also be occurring with the NO/NO^+ couple making it difficult to obtain a meaningful value for k_{22} . Thus, NO^+ may undergo outer-sphere electron transfer more readily than is implied by Marcus theory and the small self-exchange rate calculated by Ebersson and Radner.

A comparison of the rates of the reactions of CrR^{2+} with NO^+ and $Ru(bpy)_3^{3+}$ (the latter reaction being discussed in Chapter II) also suggest that NO^+ does not conform to Marcus theory. Although neither the exchange rate nor the reduction potential of the CrR^{3+}/CrR^{2+} couple is known, it

is possible to use eq 20 and 21 to calculate an apparent self-exchange rate constant for the NO^+/NO couple. The reactions of $\text{CrCH}_2\text{OCH}_3^{2+}$ with NO^+ and $\text{Ru}(\text{bpy})_3^{3+}$ will be used as an example. The rate constants for the reactions of $\text{CrCH}_2\text{OCH}_3^{2+}$ with NO^+ and $\text{Ru}(\text{bpy})_3^{3+}$ are $1.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $1.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, respectively. Also known are the reduction potentials for the $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}$ and NO^+/NO couples (1.26 V and 1.21 V) and the exchange rate for the $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}$ couple ($k = 1.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$).³⁴ Eq 20 and 21 can then be applied using this information to calculate an apparent rate constant $(k_{\text{NO}^0/+})_{\text{app}}$ for the exchange reaction of the NO^+/NO couple. This treatment of the data leads to a value of $2.1 \times 10^{12} \text{ M}^{-1}\text{s}^{-1}$ for the apparent rate constant for the NO^+/NO self-exchange reaction.

This large value for $(k_{\text{NO}^0/+})_{\text{app}}$ is unusual, for it exceeds not only the estimated value of $k_{\text{NO}^0/+}$ given by Ebersson and Radner²⁷ ($0.015 \text{ M}^{-1}\text{s}^{-1}$) but also the diffusion controlled limit of $10^{10} \text{ M}^{-1}\text{s}^{-1}$ for bimolecular reactions in aqueous solution. This suggests that at least one of these two reactions either does not occur by an outer-sphere mechanism or does not obey Marcus theory. The trends in the rate constants for the reactions of $\text{Ru}(\text{bpy})_3^{3+}$ with CrR^{2+} complexes (discussed in Chapter II), as well as the usual behavior of $\text{Ru}(\text{bpy})_3^{3+}$ in other reactions imply that this

reaction is occurring by an outer-sphere mechanism and is obeying Marcus theory. The arguments presented above indicated that NO^+ oxidizes aliphatic organochromium ions by an outer-sphere pathway, although the rate constant appeared to be rather large in view of the small self-exchange rate constant $k_{\text{NO}^0/\text{NO}^+} = 0.015 \text{ M}^{-1}\text{s}^{-1}$ calculated by Ebersson and Radner.

All of this suggests that for various reasons Marcus theory cannot be applied to the reaction of HONO (NO^+) with CrR^{2+} . One reason for this large deviation from Marcus theory was discussed above, i.e., large differences in the solvent reorganization energy for reactions involving the NO^+/NO couple.

Another reason for the apparent failure of the reaction of HONO with CrR^{2+} to conform to Marcus theory could be that NO^+ can hydrogen bond to the bound water molecules on the CrR^{2+} complex. Hydrogen bonds generally have bond strengths in the range of 1 to 10 kcal which could increase the rate constant by seven orders of magnitude. The contribution of hydrogen bonding would not be reflected in the rate constants for the self-exchange reactions and therefore would not be accounted for by Marcus theory.

A third reason for the very rapid rates for the reactions of HONO with CrR^{2+} may be that NO^+ is small and has a poorly defined coordination sphere as compared to

transition metal complexes. This might lead to significant overlap between the π^* LUMO on NO^+ and the t_{2g} HOMO on the CrR^{2+} . Marcus theory assumes that the donor and acceptor orbitals in electron transfer have the proper symmetry, but that there is no significant orbital overlap. If some orbital overlap is occurring in the reaction between NO^+ and CrR^{2+} , the experimental rate constant would be greater than that predicted by Marcus theory. Kochi has argued³⁵ that inner- and outer-sphere electron transfer mechanisms may be simply two extremes along a continuum. According to this theory, inner- and outer-sphere electron transfer differ mainly in the magnitude of separation between the oxidant and reductant in the transition state for electron transfer. Thus, there may be significant orbital overlap in the transition state for the reaction of NO^+ with CrR^{2+} such that the reaction is not purely "outer-sphere" and therefore occurs at a rate which exceeds that predicted by Marcus theory. This would also account for the small steric effect seen for the reactions of HONO with aliphatic CrR^{2+} complexes.

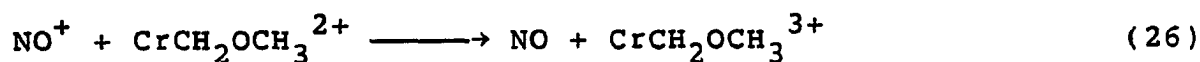
In summary, the reactions of CrR^{2+} with $\text{Ru}(\text{bpy})_3^{3+}$ and NO^+ both occur by an outer-sphere electron transfer mechanism, but one of the reactions, presumably the reaction of NO^+ , does not conform to Marcus theory. Several reasons can be offered to account for this discrepancy: a large

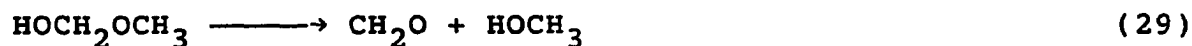
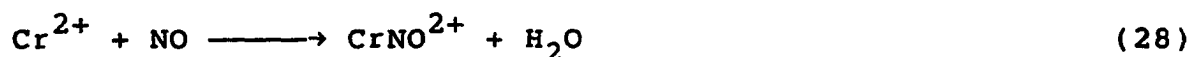
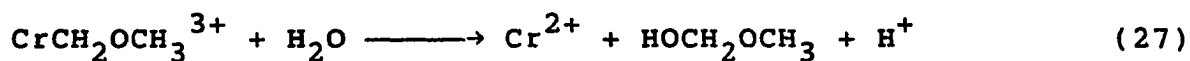
difference between the solvation of NO^+ and NO ; hydrogen bonding between NO^+ and bound water molecules on the CrR^{2+} complex; and strong orbital overlap.

In the next chapter some other comparisons will be made between the reactions of NO^+ and $\text{Ru}(\text{bpy})_3^{3+}$ with CrR^{2+} .

Mechanism for Strongly Reducing Organochromium

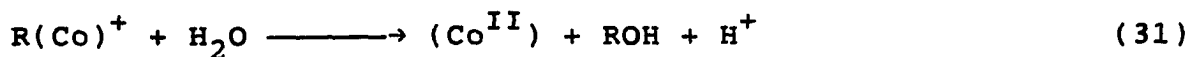
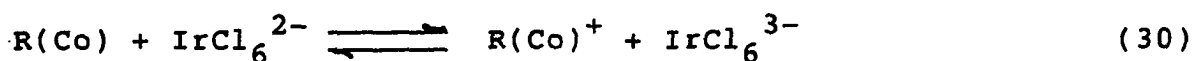
Complexes The product analyses for the reactions of the strongly reducing CrR^{2+} complexes also imply an electron transfer mechanism. As mentioned above, CrNO^{2+} is the chromium product for the reactions of HONO with $\text{CrCH}_2\text{OCH}_3^{2+}$, $\text{CrCH}_2\text{OH}^{2+}$, and $\text{CrCH}(\text{CH}_3)(\text{OCH}_2\text{CH}_3)^{2+}$. This product is very difficult to explain in terms of an electrophilic mechanism in which NO^+ would preferentially attack at the site of greatest electron density, i.e., the α -carbon giving substitutionally inert $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ as the product. The alternatives are NO^+ attacking at the metal or oxidizing CrR^{2+} by one electron by an outer-sphere mechanism. For the reasons given above, it is unlikely that substitution occurs at the metal center. Electron transfer is more reasonable in terms of the known chemistry of NO^+ . The following mechanism accounts for the detection Cr^{2+} as an intermediate as well as the formation of CrNO^{2+} :





Although the above mechanism is written for the oxidation of $\text{CrCH}_2\text{OCH}_3^{2+}$, it should be general for the reactions of all the α -alkoxy- and the α -hydroxyalkylchromium complexes with nitrous acid. A similar type of mechanism has been proposed by Bakac and Espenson^{20a} for the oxidation of α -alkoxy- and α -hydroxyalkylchromium complexes by Fe^{3+} and Cu^{2+} . In the mechanism which they propose, Cr^{2+} is formed after an inner-sphere oxidation of the organochromium complex.

Reactions 26 and 27 are also analogous to steps occurring in the mechanism for the oxidation of organocobalt(III) macrocycles by IrCl_6^{2-} studied by Halpern:⁵

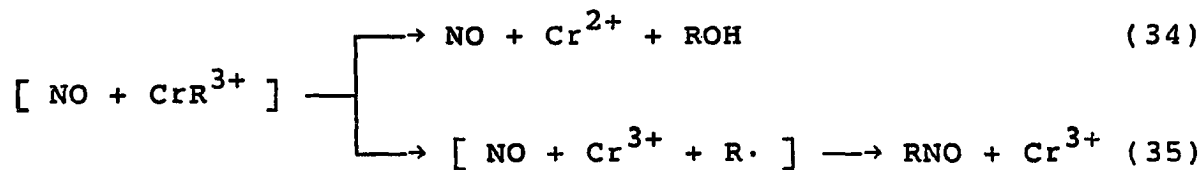
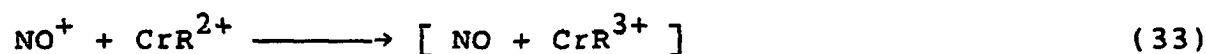


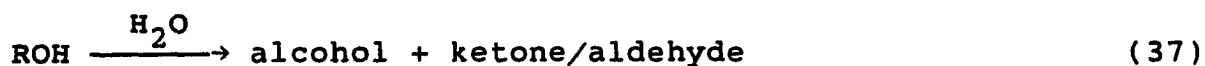
Mechanism for Weakly Reducing Organochromium

Complexes The weakly reducing organochromium complexes (alkyl- and α -haloalkylchromium complexes) probably have a

similar mechanism. The correlation described earlier between $\log(k_N)$ and $\sigma_p(X)$ suggests that all the aliphatic organochromium complexes pass through a common transition state. Additionally, the lack of a large steric effects with bulky R groups is more consistent with outer-sphere electron transfer than with electrophilic substitution. On the other hand, the products obtained are different for the alkylchromium complexes than for the α -alkoxy- and α -hydroxyalkylchromium complexes.

General Mechanism for the Reaction of Aliphatic Organochromium Complexes with Nitrous Acid These facts can be reconciled if the mechanisms for both types of organochromium complexes involve the formation of the one electron oxidation product CrR^{3+} which then decays to different products depending on the nature of the R group. The mechanism given below is consistent with the products and the relative reducing abilities of the free radicals $R\cdot$.





In this mechanism only the strongly reducing radicals reduce chromium to Cr^{2+} which then reacts with NO with the rate constant $k = 2.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. In contrast, alkylchromium complexes decay to Cr^{3+} and $\text{R}\cdot$ which apparently reacts with NO within the solvent cage to form RNO. These rate constants are very rapid in the gas phase³⁶ and should be diffusion controlled in solution. This would account for the failure to observe other free radical products such as the dimer R_2 .

According to this mechanism the organic products observed in these reactions are therefore actually secondary products. The alcohols formed in the reactions of the α -alkoxy- and α -hydroxyalkylchromium complexes are hemiacetals (or a hydrate in the case of $\text{CrCH}_2\text{OH}^{2+}$) which decompose to the alcohols and aldehydes or ketones from which they are formally derived, e.g., $\text{HOCH}_2\text{OCH}_3$ decomposes to CH_3OH and CH_2O . The nitrosoalkanes formed in the reactions of alkylchromium complexes are also unstable under the reaction conditions. RNO is known to isomerize to an oxime in acidic solution³⁷ which then hydrolyzes to hydroxylamine and an aldehyde or ketone. Although no attempt was made to analyze

for hydroxylamine, the observed organic products are consistent with the mechanism given above.

Reactions of aralkylchromium complexes

The second type of organochromium complex studied is of the form $\text{CrCH}_2\text{Ar}^{2+}$ where $\text{Ar} = \text{p-C}_6\text{H}_4\text{X}$ or $4\text{-C}_5\text{H}_4\text{NH}^+$. The reactions of aralkylchromium complexes with HONO follow the same rate law as the aliphatic organochromium complexes. This is evident from the plot of $(k_{\text{obs}} - k_{\text{H}})/[\text{HONO}]$ vs $[\text{H}^+]$ for the reaction of $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ with HONO shown earlier in Figure I-3. Again, this type of rate law indicates that the reaction occurs via an NO^+ intermediate, but does not allow one to distinguish between an electrophilic and an electron transfer mechanism.

In order to make this distinction one must consider the same sort of correlations described earlier. Unfortunately, in this case, one cannot examine the effect of steric crowding at the α -carbon on the rate constants since only primary aralkylchromium complexes are known. An attempt to synthesize CrCHBrPh^{2+} was unsuccessful.

One can, however, compare the electronic effects of these reactions with those of others. It was mentioned earlier that the rate constants for the reactions of aliphatic organochromium complexes can be correlated by plotting $\log(k_{\text{N}})$ vs $\sigma_{\text{p}}(\text{X})$. Since $\sigma_{\text{p}}(\text{X}) = 0$ and -0.01 for X

= H and Ph, respectively, one might expect, on the basis of electronic effects alone, that CrCH_3^{2+} and $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ would react at comparable rates. If one takes into account steric crowding at the α -carbon by the phenyl group, a smaller rate constant might be predicted for the reaction of $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ with HONO. Indeed, in its reaction with Hg^{2+} , CrCH_3^{2+} reacts much more rapidly ($k = 1.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) than $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ ($k = 4.87 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$) presumably because of less steric hindrance with the methyl group.

The results for the nitrous acid reaction, however, are quite surprising in light of these considerations. As shown in Table I-2, $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ reacts with HONO more rapidly than does CrCH_3^{2+} . This can also be seen in the failure of $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ to fit the correlation mentioned above for the aliphatic organochromium complexes (Fig. I-5). This indicates that the aralkylchromium complexes do not react with HONO by the same mechanism as the aliphatic organochromium complexes. This suggests that the reaction is probably occurring by an electrophilic substitution mechanism of the type proposed by Bartlett and Johnson¹¹ for the reaction of HONO with $\text{CrCH}_2\text{pyH}^{3+}$.

This possibility was tested by comparing the rate constants for the nitrous acid reactions of $\text{CrCH}_2\text{Ar}^{2+}$ with those of the corresponding mercury(II) reactions (Table I-2). A plot of $\log(k_N)$ vs $\log(k_{\text{Hg}})$ yields a line (Fig. I-6)

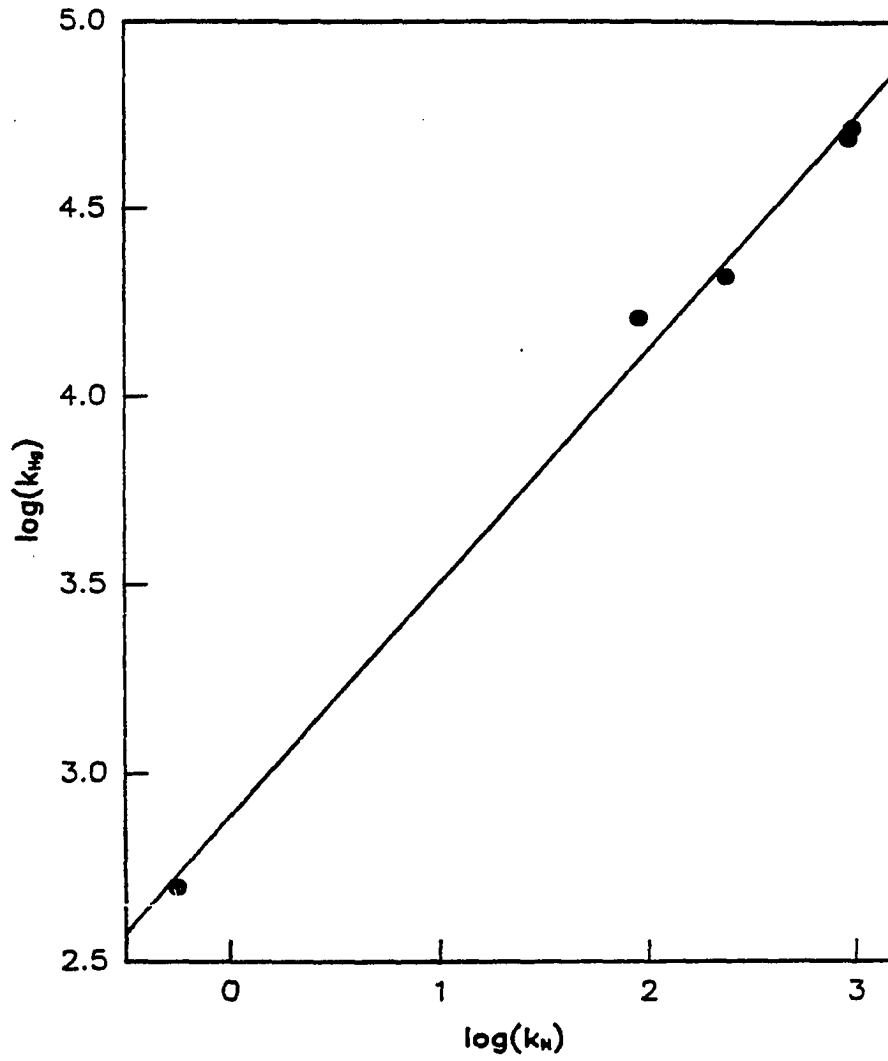


Figure I-6 Plot of $\log(k_N)$ vs $\log(k_{Hg})$ for the reactions of $CrCH_2Ar^{2+}$ with HONO and Hg(II)

indicating that the reactions of HONO with $\text{CrCH}_2\text{Ar}^{2+}$ occur by an electrophilic mechanism, which has already been established in the case of the mercury(II) reactions.^{1,25} Another comparison between the nitrous acid and the mercury reactions can be seen in Figure I-7 in which $\log(k)$ is plotted against the Hammett substituent parameter σ_p for the group on the para position of the benzene ring in benzylchromium or one of its derivatives. The nitrous acid reaction has a reaction constant $\rho = -1.26$ as compared to values of -1.29 and -0.62 for Br_2 and Hg^{2+} , respectively. All of these reactions have similar reaction constants although NO^+ and Br_2 show somewhat more sensitivity to substituents than mercury does.

Thus it appears that NO^+ , like Br_2 and Hg^{2+} , reacts with aralkylchromium complexes by an electrophilic substitution mechanism. The Cr^{3+} product detected in the nitrous acid reactions is also consistent with this interpretation. The greater reactivity of $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ than CrCH_3^{2+} in the nitrous acid reactions is still puzzling, however, in view of the greater steric crowding at the α -carbon in $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$. A possible explanation for this difference is that NO^+ , a π -acid, could form an intermediate π -complex with the benzene ring of $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$. NO^+ could then attack the α -carbon of $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ displacing Cr^{3+} in an electrophilic substitution (Figure I-8). The weak bond

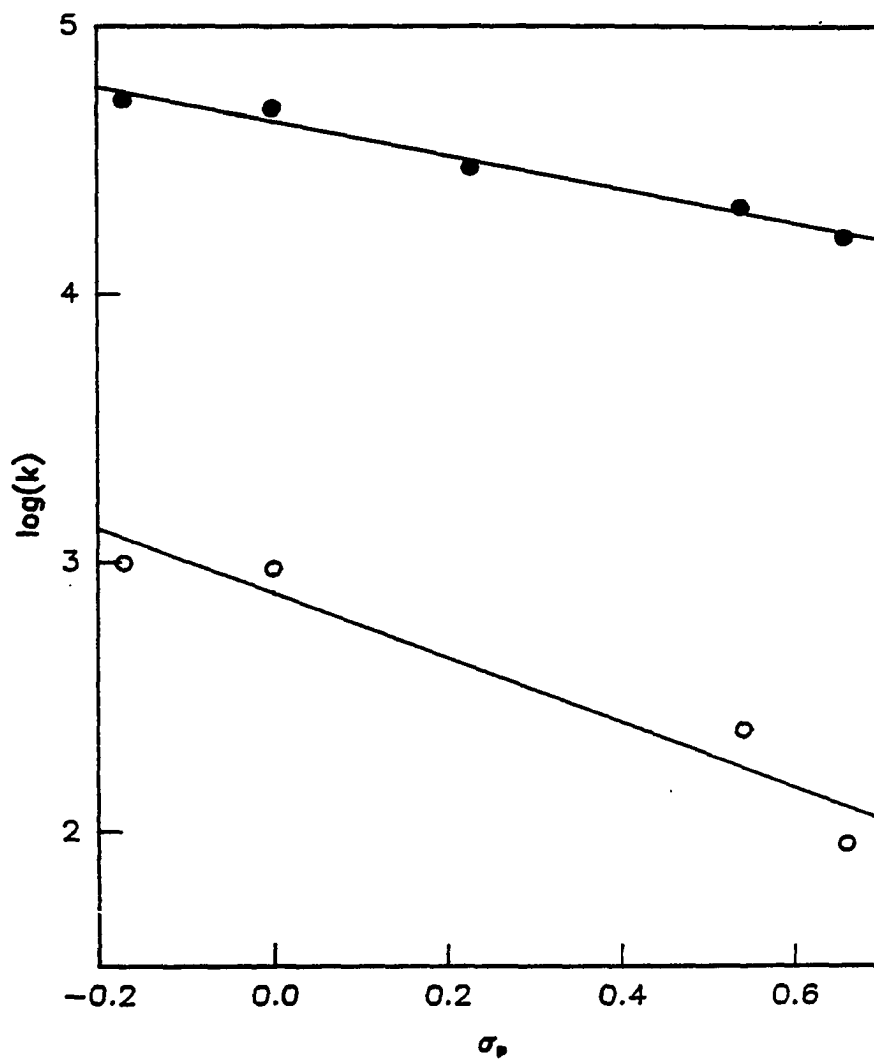


Figure I-7 Plots of $\log(k)$ vs $\sigma_p(X)$ for the reactions of $\text{CrCH}_2\text{C}_6\text{H}_4\text{X}^{2+}$ with Hg^{2+} (filled circles) and HONO (open circles). $X = \text{CH}_3, \text{H}, \text{Br}, \text{CF}_3,$ and CN

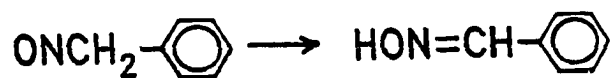
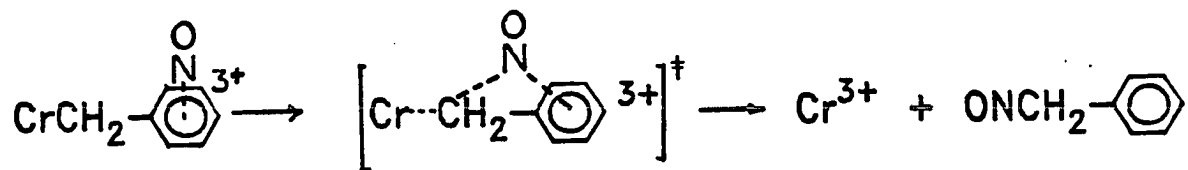
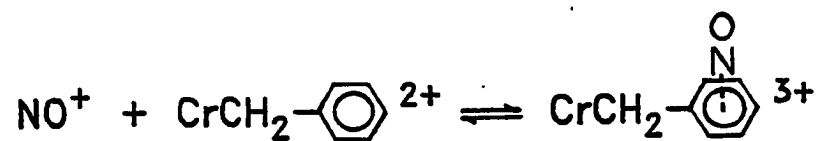


Figure I-8 Mechanism for the reaction of HONO with $\text{CrCH}_2\text{Ar}^{2+}$

between NO^+ and the benzene ring should lower the energy of the activated complex thus making electrophilic substitution occur more readily for $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ than for CrCH_3^{2+} in which such an interaction is not possible. Thus the presence of the aromatic ring should facilitate electrophilic substitution. On the other hand, this π -complex would not aid electron transfer by either a chemical mechanism or a resonance mechanism.³⁸ A chemical mechanism would necessitate oxidation by NO^+ of an aromatic ring, which is part of a dipositive cation. This should be a very unfavorable process thermodynamically. The other possibility, a resonance mechanism, is not likely either since the aromatic ring is not conjugated with the d orbitals on the Cr from which the electrons are presumably removed.

This type of interaction has been proposed in organic chemistry to explain the greater rate of N-nitrosation of aromatic amines as compared with aliphatic amines and to account for certain substituent effects.³⁹ NO^+ forms a π -complex with, for example, anilinium ion ($\text{H}_3\text{NC}_6\text{H}_5^+$), and then in the rate-determining step displaces a proton from the nitrogen. A π -complex between a π -acid / electrophile and an aromatic ring seems reasonable, but one might ask what experimental evidence there is for such an interaction. Although there is no direct spectroscopic evidence for a π -

complex intermediate in nitrosation reactions this type of complex is known in the gas phase. A π -complex between NO^+ and benzene in the gas phase has been detected by mass spectrometry.⁴⁰

Summary

Nitrous acid has been shown to react with pentaquoorganochromium(III) complexes via NO^+ by either an electrophilic or electron transfer mechanism depending on the particular complex involved. The rate constants for all of the aliphatic organochromium complexes can be correlated by plotting the logarithms of the rate constants against the corresponding Hammett substituent constants for the substituent on the α -carbon which yields a straight line. This indicates a common transition state for the nitrous acid reaction of aliphatic CrR^{2+} complexes. The lack of steric effects with the alkylchromium complexes, the detection of Cr^{2+} as an intermediate in the reaction of $\text{CrCH}_2\text{OCH}_3^{2+}$, and the formation of CrNO^{2+} in the reactions of α -hydroxy- and α -alkoxyalkylchromium complexes suggest that these complexes react with HONO by an electron transfer mechanism. In the proposed mechanism NO^+ oxidizes CrR^{2+} by one electron to form CrR^{3+} which, in the case of the alkylchromium complexes, decays to Cr^{3+} and R \cdot which combines with NO within the solvent cage to form RNO. This

species is unstable in acidic aqueous solution and decomposes to an aldehyde or ketone and hydroxylamine. When R· is one of the more strongly reducing α -hydroxy- or α -alkoxyalkyl radicals, Cr^{2+} and ROH are formed. The Cr^{2+} formed reacts with NO to give CrNO^{2+} .

Aralkylchromium complexes on the other hand react with nitrous acid by an electrophilic substitution mechanism as indicated by its correlation with reactions of mercury(II) with $\text{CrCH}_2\text{Ar}^{2+}$ which are known to proceed by an $\text{S}_{\text{E}}2$ mechanism and by the formation of Cr^{3+} , the expected product for an electrophilic mechanism. This pathway is favored by the interaction of NO^+ with the aromatic ring which would be expected to stabilize the transition state for an electrophilic substitution reaction.

EXPERIMENTAL

Materials

CrR^{2+} complexes where $\text{R} = \text{CH}_2\text{OH}$, CH_2OCH_3 , or $\text{CH}(\text{CH}_3)\text{OCH}_2\text{CH}_3$ were prepared by the modified Fenton's reagent method.⁴¹ In each case the appropriate alcohol or ether (R-H) was added to a deaerated aqueous solution containing hydrogen peroxide and perchloric acid. Chromium(II) perchlorate was then injected into this solution with stirring. The reaction mixture was then loaded onto a column of Sephadex SP C-25 cation exchange resin and washed with dilute HClO_4 (0.005 to 0.01 M). The organochromium complex was then eluted with 0.10 M or 0.50 M HClO_4 . Ion-exchanging was not possible in the case of $\text{CrCH}_2\text{OH}^{2+}$ owing to its high rate of acidolysis. Both the reaction and ion-exchanging were carried out under nitrogen.

Concentrations of the organochromium complexes were determined spectrophotometrically from the U.V.-visible spectra.^{20a} The absorption maxima are as follows:
 $\text{CrCH}_2\text{OH}^{2+}$, λ 282 nm (ϵ $2.4 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 392 nm ($5.7 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$); $\text{CrCH}_2\text{OCH}_3^{2+}$, λ 270 nm (ϵ $2.59 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 385 nm (ϵ $4.04 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$), λ 530 nm (ϵ $15.3 \text{ M}^{-1}\text{cm}^{-1}$); $\text{CrCH}(\text{CH}_3)\text{OCH}_2\text{CH}_3^{2+}$, λ 290 nm (ϵ $2.27 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 390 nm (ϵ $4.68 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$).

CrR^{2+} complexes where $\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{CH}_2\text{CH}_3,$ or $\text{CH}(\text{CH}_3)_2$ were prepared by a method similar to that used by Leslie and Espenson.²⁵ Chromium(II) perchlorate was injected into a well stirred aqueous solution containing perchloric acid, the appropriate hydroperoxide ($\text{RC}(\text{CH}_3)_2\text{OOH}$) and acetone (20% by volume in the final reaction mixture). The stoichiometry of the reaction is $2\text{Cr}^{2+} : 1\text{RC}(\text{CH}_3)_2\text{OOH}$ and best results were obtained when a slight excess of Cr^{2+} was used. The following procedure for making $\text{CrCH}_2\text{CH}_2\text{CH}_3^{2+}$ is typical. A 50 mL flask containing 0.13 mL of 4.46 M 2-methyl-2-pentyl hydroperoxide (0.580 mmol), 5 mL acetone, .22 mL of 5.588 M HClO_4 (0.05 M), and 6.8 mL of water was deaerated. 12.8 mL of 0.0997 M Cr^{2+} (1.28 mmol) was then injected into the flask with stirring and the reaction was complete upon mixing. The reaction mixture was chilled in an ice bath and air was bubbled through the solution to react with any excess Cr^{2+} (this was not done in the case of $\text{CrCH}(\text{CH}_3)_2^{2+}$ because of its reactivity with O_2). The reaction mixture was then loaded onto a Sephadex column, washed with 0.005 M HClO_4 , and eluted with 0.50 M NaClO_4 in 0.005 M HClO_4 (sometimes 0.25 M or 0.50 M HClO_4 was used to elute). This procedure was modified slightly in the case of $\text{CrCH}(\text{CH}_3)_2^{2+}$ in that the column separation was carried out under nitrogen. All of the organochromium complexes were stored under nitrogen and frozen when not in use. CrCH_3^{2+}

was also prepared from the reaction of Cr^{2+} with H_2O_2 in the presence of DMSO.

Concentrations were determined spectrophotometrically using following absorption maxima:²⁵ CrCH_3^{2+} , λ 258 nm (ϵ $2.4 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 392 nm (ϵ $2.46 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$), λ 550 nm (ϵ $12.0 \text{ M}^{-1}\text{cm}^{-1}$); $\text{CrCH}_2\text{CH}_3^{2+}$, λ 275 nm (ϵ $2.4 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 394 nm (ϵ $3.90 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$), λ 560 nm (ϵ $8.5 \text{ M}^{-1}\text{cm}^{-1}$); $\text{CrCH}_2\text{CH}_2\text{CH}_3^{2+}$, λ 276 nm (ϵ $2.65 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 393 nm (ϵ $3.8 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$), λ 550 nm (ϵ $8.3 \text{ M}^{-1}\text{cm}^{-1}$); $\text{CrCH}(\text{CH}_3)_2^{2+}$, λ 290 nm, (ϵ $2.33 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 400 nm, (ϵ $4.88 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$), λ 560 nm (ϵ $10 \text{ M}^{-1}\text{cm}^{-1}$).

Complexes of the type $\text{CrCH}_2\text{X}^{2+}$, where X = Cl, Br, or I were prepared by a modification of the literature method⁴² in which chromium(II) perchlorate was injected into a deaerated aqueous solution containing HClO_4 , acetone (20% by volume in the final reaction mixture), and either CH_2I_2 , CH_2Br_2 , or CH_2BrCl depending on the organochromium complex being made. The resulting organochromium complexes were purified by ion-exchanging on Sephadex.

Concentrations were determined spectrophotometrically using following absorption maxima⁴²: $\text{CrCH}_2\text{Cl}^{2+}$, λ 260 nm (ϵ $3.56 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 393 nm (ϵ $2.25 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$), λ 517 nm (ϵ $23.5 \text{ M}^{-1}\text{cm}^{-1}$); $\text{CrCH}_2\text{Br}^{2+}$, λ 266 nm (ϵ $3.28 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 397 nm (ϵ $2.55 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$), λ 490 nm (ϵ $43.2 \text{ M}^{-1}\text{cm}^{-1}$); $\text{CrCH}_2\text{I}^{2+}$, λ 264 nm (ϵ $2.19 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 295

nm (ϵ $2.34 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 396 nm (ϵ $2.63 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$),
 λ 524 nm (ϵ $26.3 \text{ M}^{-1}\text{cm}^{-1}$).

Benzylchromium and its derivatives were synthesized by a modification of the literature method⁴³ in which a slight excess (< 5%) of chromium(II) perchlorate was injected into a deaerated aqueous solution containing HClO_4 , acetone (20% by volume in the final reaction mixture), and $p\text{-BrCH}_2\text{C}_6\text{H}_4\text{X}$ ($\text{X} = \text{CH}_3, \text{H}, \text{CF}_3, \text{CN}$; $2\text{Cr}^{2+} : 1p\text{-Br-CH}_2\text{C}_6\text{H}_4\text{X}$). The reaction mixture was then stirred for about ten minutes and then ion-exchanged on Sephadex under nitrogen. This same procedure was used to prepare $\text{CrCH}_2\text{pyH}^{3+}$ except that no acetone was used and the complex was ion-exchanged aerobically.

Concentrations were determined spectrophotometrically using following absorption maxima⁴⁴: $\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CH}_3^{2+}$, λ 276 nm (ϵ $4.8 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 300 nm (ϵ $4.2 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 360 nm (ϵ $1.2 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$); $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$, λ 240 nm (ϵ $7.5 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 274 nm (ϵ $7.67 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 297 nm (ϵ $6.97 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 356 nm (ϵ $2.2 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$); $\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CF}_3^{2+}$, λ 280 nm (ϵ $2.4 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 298 nm (ϵ $2.36 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 354 nm (ϵ $5.0 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$); $\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CN}^{2+}$, λ 260 nm (ϵ $1.9 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 285 nm (sh), λ 312 nm (ϵ $3.2 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 360 nm (sh); $\text{Cr-4-CH}_2\text{pyH}^{3+}$, λ 225 nm (ϵ $6.75 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$), λ 308 nm (ϵ $1.56 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), λ 550 nm ($92 \text{ M}^{-1}\text{cm}^{-1}$).

$\text{Co}(\text{NH}_3)_5\text{Cl}(\text{ClO}_4)_2$ and $\text{Co}(\text{NH}_3)_5\text{Br}(\text{ClO}_4)_2$ were prepared from their halide salts⁴⁵ using perchloric acid and were recrystallized twice. $\text{Co}(\text{NH}_3)_5\text{Br}_3$ was synthesized by a modification of the literature method in which CoBr_2 was used instead of CoCO_3 . The products were characterized by U.V.-visible spectroscopy.

Chromium(III) perchlorate was prepared by the reaction of CrO_3 with H_2O_2 in perchloric acid. The product was recrystallized twice using dilute perchloric acid. Chromium(II) perchlorate was prepared by reduction of chromium(III) perchlorate over zinc amalgam.

LiClO_4 was prepared by the addition of Li_2CO_3 to 70% HClO_4 until the acid was neutralized. This was followed by recrystallization. This compound was donated by Ron McHatton.

2-methyl-2-butyl hydroperoxide, 2,3-dimethyl-2-butyl hydroperoxide, and 2-methyl-2-pentyl hydroperoxide were prepared from the corresponding alcohols by a slight modification of the the method described by Leslie and Espenson.²⁵ The procedure given below for 2,3-dimethyl-2-butyl hydroperoxide is typical. 10 mL of water was added to 11 mL of concentrated H_2SO_4 in a 125 mL Erlenmeyer flask and chilled to 0 °C in an ice bath. 21.8 mL of 2,3-dimethyl-2-butanol was added dropwise with stirring over a 30 - 40 min period. Then 30.4 mL of 8.23 M H_2O_2 was added dropwise for

45 min. The mixture was then stirred for \approx 14 hrs at zero degrees. The aqueous phase was discarded and the organic phase was washed several times with water. The concentrations of the hydroperoxides were determined by an iodometric titration as described by Leslie and Espenson.

Acetone (Fischer), acetaldehyde (Kodak), diethyl ether (Fischer), dimethyl ether (Matheson), methanol (Fischer), 2-methyl-2-butanol (Chemical Samples Co.), 2,3-dimethyl-2-butanol (Chemical Samples Co.), 2-methyl-2-pentanol (Chemical Samples Co.), CH_2I_2 , CH_2Br_2 , CH_2BrCl , dimethyl sulfoxide (Fischer), NaNO_2 (Fischer), HClO_4 (Fischer), NO (Matheson), and 30% hydrogen peroxide (Fischer) were available commercially as reagent grade chemicals and were used as received with the following exceptions. CH_2BrCl had a slight yellow color and was therefore washed with concentrated H_2SO_4 , with water, dried with MgSO_4 , and then distilled. CH_2I_2 (B.P. 182 °C) was purified by vacuum distillation followed by washing with saturated Na_2SO_3 solution to remove any iodine formed by decomposition during distillation. A small amount of copper powder was added to the purified CH_2I_2 to inhibit decomposition. The 30% H_2O_2 was used to make a 0.1M stock solution which was standardized by iodometric titration. NO gas was passed through a solution of 2M NaOH to remove higher oxides of nitrogen.

4-BrCH₂pyHBr was prepared by refluxing α -HO-4-methylpyridinium bromide with HBr.

Kinetics

Kinetic runs were carried out by reacting an excess amount of HONO (added to the reaction mixture as a solution of NaNO₂ since HONO is unstable over a long period of time) with the organochromium complex and monitoring the reaction on a Cary 219 spectrophotometer using the U.V. peak of CrR²⁺ between λ 260 nm and λ 290 nm. When Co(NH₃)₅Br²⁺ was present it was necessary to monitor the reaction at λ 400 nm. All kinetic runs were carried out under nitrogen at 23.4 °C with LiClO₄ being used to maintain an ionic strength of 0.10 M. The reactions followed pseudo-first-order kinetics and the data were analyzed by standard methods. Only the data from the first half-life were used for calculating the rate constants for the slow reactions of CrCH₂X²⁺ (X = Cl, Br, I) since the high concentration of HONO used in these runs led to significant decomposition of HONO after period of time.

Competition Experiments

In all competition experiments an aqueous solution of Co(NH₃)₅X²⁺ was prepared with enough perchloric acid added to make the ionic strength 0.10 M and this solution was then

deaerated and saturated with NO. Cr^{2+} was then slowly injected into the solution with rapid stirring while NO was continuously bubbled through the solution. After all the Cr^{2+} was added, the solution was deaerated and $[\text{Co}^{2+}]_{\infty}$ was determined by the thiocyanate method (λ 623 nm, $\epsilon = 1.842 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ in 1 : 1 acetone/water). A blank was done in which the procedure was identical except that no SCN^- was added.

Spectrophotometric Titration

A spectrophotometric titration of $\text{CrCH}_2\text{OCH}_3^{2+}$ by HONO was carried out by making successive injections of $12.0 \mu\text{L}$ of 0.0500 M NaNO_2 into a solution containing $9.88 \times 10^{-4} \text{ M CrCH}_2\text{OCH}_3^{2+}$ and 1.0 M HClO_4 (initial volume = 6.2 mL) and taking the spectrum between 360 nm and 440 nm . A plot of the absorbance at λ 386 nm vs $[\text{HONO}]/[\text{CrCH}_2\text{OCH}_3^{2+}]$ shows that the stoichiometry is $0.95 \text{ HONO} : 1.0 \text{ CrCH}_2\text{OCH}_3^{2+}$ or $1 : 1$.

Product Analysis

Inorganic Inorganic products were determined by ion-exchanging the reaction mixtures on a Sephadex SP C-25 cation exchange column and then taking the visible spectra of the products. The two types of chromium products found, Cr^{3+} and CrNO^{2+} , were identified by their visible spectra.⁴⁶

In the case of CrNO^{2+} the extinction coefficient at λ 449 nm was determined by a chromium analysis and found to have a value of $\epsilon = 117 \text{ M}^{-1}\text{cm}^{-1}$ which is within 3% of the literature value of $121 \text{ M}^{-1}\text{cm}^{-1}$.

Organic Organic products were determined by gas chromatography except for formaldehyde which was determined by the chromotropic acid method. Gas chromatography was carried out on a Hewlett Packard 5790A series gas chromatograph with a 3390A series integrator. A 10% FFAP column was used for the determinations. The following procedure for determining the products of the reactions of $\text{CrCH}_2\text{CH}_3^{2+}$ with HONO is typical. Two deaerated flasks were prepared, each containing $0.0117 \text{ M CrCH}_2\text{CH}_3^{2+}$ and 0.11 M HClO_4 . NaNO_2 was injected into the first flask so that $[\text{HONO}]_0 = 0.012 \text{ M}$. After the reaction had gone to completion, $1 \mu\text{L}$ of each of the solutions was gas chromatographed and the GC trace for the sample revealed a peak not found in the blank which had a retention time (0.91 min) identical to that of an authentic sample of acetaldehyde.

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APPENDIX I

Table AI-1 Rate Constants for the Reaction of HONO with $\text{CrCH}_2\text{OH}^{2+}$ a

$[\text{H}^+]/\text{M}$	$10^4[\text{HONO}]/\text{M}$	$10^2k_{\text{obs}}/\text{s}^{-1}$	$(k_c^b/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.010	5.30	0.650	11.2
0.010	7.56	0.906	11.2
0.010	9.18	1.05	10.8
0.010	20.2	2.25	10.8
0.050	3.80	1.80	45.8
0.050	5.40	2.47	44.6
0.050	7.70	3.82	48.8
0.050	9.33	3.94	40.2
0.050	20.2	8.00	39.3
0.10	1.98	1.54	74.6
0.10	2.90	2.28	75.5
0.10	3.75	3.39	88.8
0.10	3.85	3.16	80.5
0.10	5.65	4.38	76.4
0.10	7.50	5.78	76.2
0.10	9.50	7.07	73.8

^a $T = (23.4 \pm 0.1) \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$.

^b k_c is the observed rate constant corrected for acidolysis of the organochromium complex, i.e., $k_{\text{obs}} - k_A$.
 $k_A = 5.6 \times 10^{-4} \text{ s}^{-1} + 3.8 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}[\text{H}^+]$ (corrected for temperature).¹

Table AI-2 Rate Constants for the Reaction of HONO with
 $\text{CrCH}_2\text{OCH}_3^{2+}$ ^a

$[\text{H}^+]/\text{M}$	$10^4[\text{HONO}]/\text{M}$	$10^3k_{\text{obs}}/\text{s}^{-1}$	$(k_{\text{obs}}/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.010	9.12	3.74	4.10
0.020	9.12	7.06	7.74
0.040	9.12	13.6	14.9
0.060	9.12	18.5	20.3
0.080	9.12	25.3	27.7
0.10	1.9 - 50	10 - 170	34.0 ^b

^a $T = (23.4 \pm 0.1) \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$.

^bCalculated from the slope of a plot of k_{obs} vs $[\text{HONO}]$ using eight different concentrations of $[\text{HONO}]$.

Table AI-3 Rate Constants for the Reaction of HONO with
 $\text{CrCH}(\text{CH}_3)\text{OCH}_2\text{CH}_3^{2+}$ ^a

$[\text{H}^+]/\text{M}$	$10^3[\text{HONO}]/\text{M}$	$10^2 k_{\text{obs}}/\text{s}^{-1}$	$(k_c^b/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.0036	6.00	1.64	2.48
0.010	1.00	0.429	2.75
0.010	2.00	0.643	2.44
0.010	4.00	1.22	2.66
0.010	5.00	1.64	2.97
0.010	6.00	1.99	3.06
0.010	8.00	2.50	2.93
0.010	10.0	3.32	3.17
0.010	10.0	3.49	3.34
0.013	6.00	2.04	3.14
0.022	6.00	2.23	3.46
0.031	6.00	2.61	4.09
0.031	6.00	2.83	4.46
0.050	1.00	0.616	4.62
0.050	2.00	1.06	4.53
0.050	4.00	2.10	4.86
0.050	6.00	2.99	4.73
0.050	6.00	3.15	4.99
0.050	8.00	4.23	5.10
0.050	10.0	5.23	5.08
0.054	6.00	3.45	5.49
0.077	6.00	3.72	5.94
0.084	1.00	0.867	7.13
0.093	2.00	1.32	5.83
0.091	4.00	2.59	6.09
0.094	6.00	4.22	6.87
0.087	8.00	5.79	7.22
0.085	10.0	6.39	6.24

^a $T = (23.4 \pm 0.1) ^\circ\text{C}$, $I = 0.10 \text{ M}$.

^b k_c is the observed rate constant corrected for homolysis of the organochromium complex, i.e., $k_{\text{obs}} - k_{\text{H}}$.
 $k_{\text{H}} = 1.54 \times 10^{-3} \text{ s}^{-1}$ (corrected for temperature).¹

Table AI-4 Rate Constants for the Reaction of HONO with
 CrCH_3^{2+} a

$[\text{H}^+]/\text{M}$	$10^3[\text{HONO}]/\text{M}$	$10^3k_{\text{obs}}/\text{s}^{-1}$	$(k_{\text{c}}^{\text{b}}/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.020	0.95	1.18	0.786
0.050	0.95	2.28	1.88
0.050	5.00	10.6	2.02
0.10	0.95	4.14	3.72
0.10	5.00	20.8	4.04

^a $T = (23.4 \pm 0.1) \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$.

^b k_{c} is the observed rate constant corrected for acidolysis of the organochromium complex, i.e., $k_{\text{obs}} - k_{\text{A}}$.
 $k_{\text{A}} = 3.9 \times 10^{-4} \text{ s}^{-1} + 2.14 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}[\text{H}^+]$ (corrected for temperature).¹

Table AI-5 Rate Constants for the Reaction of HONO with
 $\text{CrCH}_2\text{CH}_3^{2+}$ a

$[\text{H}^+]/\text{M}$	$10^3[\text{HONO}]/\text{M}$	$10^3k_{\text{obs}}/\text{s}^{-1}$	$(k_c^b/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.050	0.95	5.09	5.12
0.050	2.00	9.78	4.78
0.10	0.45	4.56	9.62
0.10	0.95	9.00	9.23
0.10	2.00	18.3	9.03

^a $T = (23.4 \pm 0.1) \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$.

^b k_c is the observed rate constant corrected for acidolysis of the organochromium complex, i.e., $k_{\text{obs}} - k_A$.
 $k_A = 2.2 \times 10^{-4} \text{ s}^{-1} + 1.15 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}[\text{H}^+]$ ($T = (25.0 \pm 0.1) \text{ }^\circ\text{C}$).¹

Table AI-6 Rate Constants for the Reaction of HONO with
 $\text{CrCH}_2\text{CH}_2\text{CH}_3^{2+}$ ^a

$[\text{H}^+]/\text{M}$	$10^3[\text{HONO}]/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^2(k_c^b/[\text{H}^+])/\text{M}^{-1}\text{s}^{-1}$
0.050	0.95	1.13	1.66
0.10	0.95	1.93	1.62
0.10	3.00	4.23	3.92
0.10	5.00	7.64	7.33
0.10	7.00	10.7	10.4

^a $T = (23.4 \pm 0.1) \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$.

^b k_c is the observed rate constant corrected for acidolysis of the organochromium complex, i.e., $k_{\text{obs}} - k_A$.
 $k_A = 3.0 \times 10^{-4} \text{ s}^{-1} + 6.5 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}[\text{H}^+]$ ($T = (25.0 \pm 0.1) \text{ }^\circ\text{C}$).¹

Table AI-7 Rate Constants for the Reaction of HONO with
 $\text{CrCH}(\text{CH}_3)_2^{2+}$ a

$[\text{H}^+]/\text{M}$	$10^3[\text{HONO}]/\text{M}$	$10^3k_{\text{obs}}/\text{s}^{-1}$	$(k_c^b/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.020	8.00	3.66	0.430
0.040	4.00	3.32	0.774
0.040	8.00	6.74	0.815
0.060	4.00	4.93	1.18
0.060	8.00	9.33	1.14
0.080	4.00	6.27	1.51
0.080	8.00	12.9	1.58
0.10	1.00	2.18	1.96
0.10	3.00	6.14	1.97
0.10	5.00	8.90	1.74
0.10	7.00	12.0	1.68
0.10	8.00	15.9	1.96
0.10	9.00	17.0	1.86

^a $T = (23.4 \pm 0.1) \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$.

^b k_c is the observed rate constant corrected for homolysis and acidolysis of the organochromium complex, i.e., $k_{\text{obs}} - k_{\text{H}} - k_{\text{A}}$. $k_{\text{A}} = 8.9 \times 10^{-5} \text{ s}^{-1}$ and $k_{\text{H}} = 1.34 \times 10^{-4} \text{ s}^{-1}$ (corrected for temperature).¹

Table AI-8 Rate Constants for the Reaction of HONO with
 $\text{CrCH}_2\text{Cl}^{2+}$ a

$[\text{H}^+]/\text{M}$	$10^3[\text{HONO}]/\text{M}$	$10^4 k_{\text{obs}}/\text{s}^{-1}$	$10^2(k_{\text{obs}}/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.040	20.0	4.63	2.32
0.070	19.8	6.29	3.18
0.10	4.85	1.94	4.00
0.10	9.86	4.97	5.04
0.10	19.8	9.47	4.78

a_T = (23.4 ± 0.1) °C, I = 0.10 M.

Table AI-9 Rate Constants for the Reaction of HONO with
 $\text{CrCH}_2\text{Br}^{2+}$ a

$[\text{H}^+]/\text{M}$	$10^3[\text{HONO}]/\text{M}$	$10^4 k_{\text{obs}}/\text{s}^{-1}$	$10^2(k_{\text{obs}}/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.040	20.0	2.11	1.06
0.070	20.0	2.65	1.32
0.10	9.86	1.79	1.81
0.10	20.0	3.45	1.72

$a_T = (23.4 \pm 0.1) \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$.

Table AI-10 Rate Constants for the Reaction of HONO with
 $\text{CrCH}_2\text{I}^{2+}$ a

$[\text{H}^+]/\text{M}$	$10^3[\text{HONO}]/\text{M}$	$10^4 k_{\text{obs}}/\text{s}^{-1}$	$10^2(k_{\text{obs}}/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.040	20.0	2.09	1.04
0.070	20.0	3.20	1.60
0.10	9.83	2.52	2.56
0.10	20.0	4.88	2.44

^aT = (23.4 ± 0.1) °C, I = 0.10 M.

Table AI-11 Rate Constants for the Reaction of HONO with
 $\text{CrCH}_2\text{C}_6\text{H}_4\text{-p-CH}_3^{2+}$ ^a

$[\text{H}^+]/\text{M}$	$10^4[\text{HONO}]/\text{M}$	$10^2 k_{\text{obs}}/\text{s}^{-1}$	$(k_c^b/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.020	4.59	1.34	23.1
0.050	3.07	2.03	57.0
0.050	4.59	2.53	49.0
0.050	9.50	5.20	51.8
0.10	3.07	3.51	105
0.10	4.59	4.56	93.2

^a $T = (23.4 \pm 0.1) \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$.

^b k_c is the observed rate constant corrected for homolysis of the organochromium complex, i.e., $k_{\text{obs}} - k_{\text{H}}$.
 $k_{\text{H}} = 2.8 \times 10^{-3} \text{ s}^{-1}$ (corrected for temperature).¹

Table AI-12 Rate Constants for the Reaction of HONO with
 $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ ^a

$[\text{H}^+]/\text{M}$	$10^4[\text{HONO}]/\text{M}$	$10^2 k_{\text{obs}}/\text{s}^{-1}$	$(k_c^b/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.010	3.06	0.886	24.7
0.050	3.06	1.94	59.2
0.050	5.60	3.33	57.1
0.070	5.60	4.70	81.6
0.10	5.60	6.53	114
0.10	9.68	10.2	104

^a $T = (23.4 \pm 0.1) \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$.

^b k_c is the observed rate constant corrected for homolysis of the organochromium complex, i.e., $k_{\text{obs}} - k_{\text{H}}$.
 $k_{\text{H}} = 1.3 \times 10^{-4} \text{ s}^{-1}$ (corrected for temperature).¹

Table AI-13 Rate Constants for the Reaction of HONO with
 $\text{CrCH}_2\text{C}_6\text{H}_4\text{CF}_3^{2+}$ ^a

$[\text{H}^+]/\text{M}$	$10^4[\text{HONO}]/\text{M}$	$10^3k_{\text{obs}}/\text{s}^{-1}$	$(k_{\text{c}}^{\text{b}}/[\text{HONO}])/\text{M}^{-1}\text{s}^{-1}$
0.020	9.50	5.06	4.76
0.040	9.50	9.75	9.69
0.050	9.50	12.1	12.2
0.080	9.50	19.3	19.7
0.10	5.34	13.5	24.3
0.10	9.50	23.0	23.6

^aT = (23.4 ± 0.1) °C, I = 0.10 M.

^bk_c is the observed rate constant corrected for
homolysis of the organochromium complex, i.e., k_{obs} - k_H.
k_H = 5.4 × 10⁻⁴ s⁻¹ (corrected for temperature).¹

Table AI-14 Rate Constants for the Reaction of HONO with
 $\text{CrCH}_2\text{C}_6\text{H}_4\text{CN}^{2+}$ ^a

$[\text{H}^+]/\text{M}$	$10^4[\text{HONO}]/\text{M}$	$10^2 k_{\text{obs}}/\text{s}^{-1}$	$10^2(k_{\text{c}}^{\text{b}}/[\text{H}^+])/\text{M}^{-1}\text{s}^{-1}$
0.050	9.68	4.70	8.57
0.050	20.2	9.16	17.5
0.10	4.59	4.98	4.56
0.10	7.26	6.25	5.84
0.10	9.68	9.31	8.90
0.10	15.3	16.0	15.6
0.10	20.3	20.9	20.5

^a $\bar{T} = (23.4 \pm 0.1) \text{ }^\circ\text{C}$, $I = 0.10 \text{ M}$.

^b k_{c} is the observed rate constant corrected for homolysis of the organochromium complex, i.e., $k_{\text{obs}} - k_{\text{H}}$.
 $k_{\text{H}} = 4.15 \times 10^{-4} \text{ s}^{-1}$ (corrected for temperature).¹

Table AI-15 Rate Constants for the Reaction of HONO with
Cr-4-CH₂pyH³⁺ a

[H ⁺]/M	10 ³ [HONO]/M	10 ⁵ k _{obs} /s ⁻¹	10 ² (k _{obs} /[HONO])/M ⁻¹ s ⁻¹
0.020	8.00	9.37	1.17
0.10	8.00	44.8	5.60

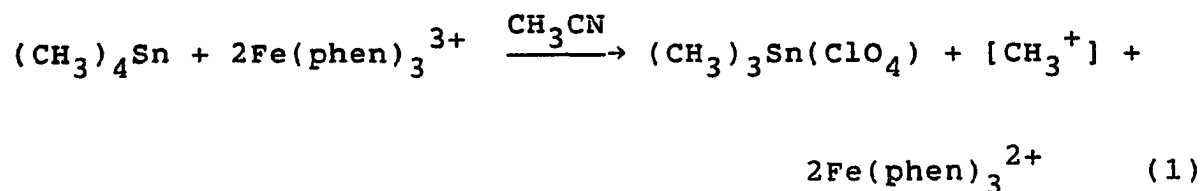
^aT = (23.4 ± 0.1) °C, I = 0.10 M. Only two runs were carried out since they are quite slow and the form of the rate law has already been established by Bartlett and Johnson.¹¹

CHAPTER II KINETICS AND MECHANISMS OF THE REACTIONS OF
 PENTAAQUOROORGANOCHROMIUM(III) COMPLEXES WITH TRIS(2,2'-
 BIPYRIDYL)RUTHENIUM(III)

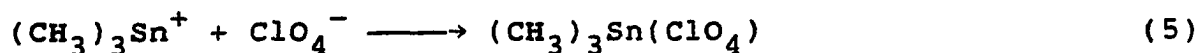
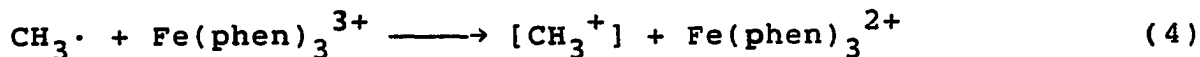
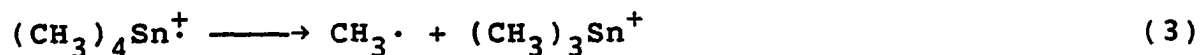
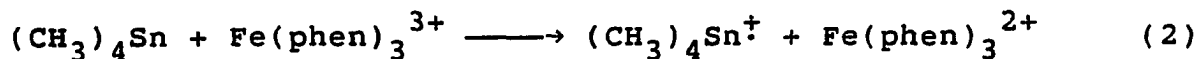
INTRODUCTION

One very important problem in organometallic chemistry involves studying the relationship between the lability of a metal to carbon bond in an alkylmetal complex and the oxidation state of the metal.^{1,2,3} A better understanding of this relationship should be helpful both in synthetic organometallic chemistry and in homogeneous catalysis since alkylmetal complexes are often intermediates in catalytic cycles.⁴

One way of labilizing metal to carbon bonds in alkylmetal complexes is by oxidizing the complex by one electron. This type of reaction has been fairly well studied for organometallic complexes of main group metals. A typical example is the reaction of $(\text{CH}_3)_4\text{Sn}$ with $\text{Fe}(\text{phen})_3^{3+}$ ⁵ which is a strong one electron outer-sphere oxidant (eq 1):



This reaction is believed to proceed by a mechanism involving a one electron oxidation of $(\text{CH}_3)_4\text{Sn}$ by $\text{Fe}(\text{phen})_3^{3+}$ to form the radical cation $(\text{CH}_3)_4\text{Sn}^{\cdot+}$ which then undergoes homolytic cleavage to give $(\text{CH}_3)_3\text{Sn}^+$ and $\text{CH}_3\cdot$ (eq 2 - 5):

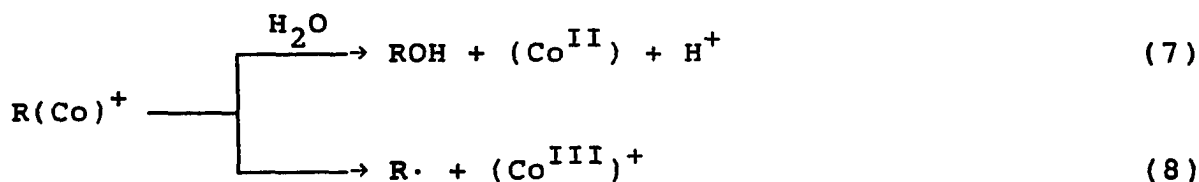


$[\text{CH}_3^+]$ represents oxidation products derived from the methyl radical (principally N-methylacetamide when the reaction is carried out in acetonitrile). Homolytic cleavage of the radical cation to give a free radical $\text{R}\cdot$ (eq 3) is a typical mode of decomposition for the radical cations of main group alkylmetals. When this reaction is carried out with other tetraalkyltin compounds in which methyl groups are replaced by ethyl groups, the reaction rate increases, which is consistent with an outer-sphere electron transfer mechanism rather than an electrophilic mechanism as is found for the reactions of alkylmetal compounds with $\text{Ag}(\text{I})$, $\text{Cu}(\text{I})$, or $\text{Cu}(\text{II})$.¹

Although there have been a number of studies concerning the oxidative cleavage reactions of main group alkylmetals, less work has been done on similar reactions of alkyl complexes of transition metals. Some of the studies in this area have dealt with one electron oxidations of dialkylplatinum⁶ and -iron⁷ complexes. These reactions resemble the oxidation reactions of main group alkylmetal complexes in that oxidation is followed by homolytic cleavage of the metal-carbon bond. They differ from the reactions of main group alkylmetal complexes, however, in that the oxidized species can also decompose by other routes such as reductive elimination of R₂ or nucleophilic attack at the α-carbon.

Much of the work done on transition metal complexes deals with the one electron oxidation reactions of R₂Co(chel)⁸ and RCo(chel)^{9,10} where chel is a tetradentate or bis-bidentate nitrogen macrocycle derived from a Schiff base, α-dioxime, or a corrin ring system. The oxidation reactions of RCo(chel) will be used to illustrate this type of chemistry. These macrocyclic organocobalt(III) complexes can be oxidized electrochemically or by oxidants such as IrCl₆²⁻ according to the general mechanism shown in eq 6 - 8:





When R(Co) complexes of the type $\text{RCo}(\text{dmgH})_2^{11}$ are reacted with IrCl_6^{2-} the reaction follows the pathway described by eq 6 and 7. In these reactions one electron oxidation of R(Co) yields R(Co)^+ which, because of its positive charge, becomes susceptible to nucleophilic attack by water at the α -carbon displacing (Co^{II}) to form the alcohol. Cyclic voltammetry has also been employed to reversibly oxidize $\text{RCo}(\text{dmgH})_2$ complexes by one electron to yield the radical cation $\text{RCo}(\text{dmgH})_2^+$. ESR studies have shown that $\text{RCo}(\text{dmgH})_2^+$ has one unpaired electron localized on cobalt which supports the formulation of the intermediate as $\text{RCo}^{\text{IV}}(\text{dmgH})_2^+$. The electron is presumably being removed from a nonbonding d orbital on the cobalt as is the case in the oxidation of many other transition metal complexes.¹² The strongly electron-donating R^- group undoubtedly helps to stabilize this high oxidation state of cobalt.

Homolytic cleavage of the Co-C bond to give $\text{R}\cdot$ and $\text{Co}^{\text{III}}(\text{chel})^+$ (eq 8) occurs when chel = acacen [bis-(acetylacetonato)ethylenediimine], salen [bis-(salicylidenato)ethylenediimine] and $\text{R} = \text{CH}_3\text{CH}_2$ or CH_3 .¹³

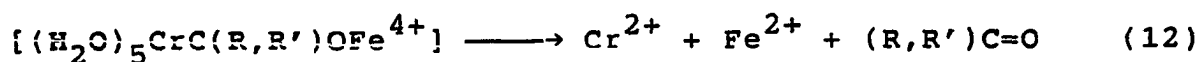
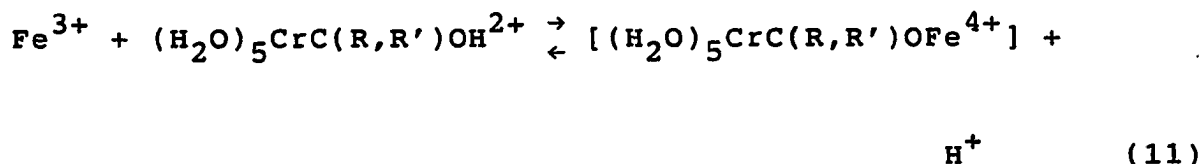
This mode of decomposition of the Co(IV) macrocycle is promoted by the high electron-donating ability of the macrocycle (which stabilizes Co(III) as opposed to Co(II)) and the high ionization potential of $\text{CH}_3\text{CH}_2\cdot$ and $\text{CH}_3\cdot$ ($I = 8.38$ eV and 9.84 eV) which makes oxidation to the alcohol more difficult. For comparison $\text{PhCH}_2\text{Co}(\text{dmgH})_2$ is oxidized by IrCl_6^{2-} to give $\text{Co}^{\text{II}}(\text{dmgH})_2$ and PhCH_2OH . The oxidation of the benzyl group to benzyl alcohol can be understood in terms of the lower ionization potential of benzyl radical ($I = 7.76$ eV).

Studies have also been conducted on the reactions of one electron oxidants with organochromium(III) complexes of the type $(\text{H}_2\text{O})_5\text{CrR}^{2+}$. CrR^{2+} usually reacts with oxidants by an indirect pathway in which the organochromium complex undergoes a rate-determining homolytic cleavage of the Cr-C bond to form Cr^{2+} and $\text{R}\cdot$ which then react rapidly with the oxidant (eq 9, 10):



A direct reaction has been shown to occur, however, between some CrR^{2+} complexes and Fe^{3+} , Cu^{2+} , Hg^{2+} , and VO^{2+} .¹⁴ These metal ions oxidize most α -hydroxy- and α -alkoxyalkyl-chromium complexes by one electron, although

there is a competing electrophilic pathway for some of the reactions of mercury(II). The reactions of Fe^{3+} and Cu^{2+} occur via a Cr^{2+} intermediate, show a stoichiometry of $2\text{M}^{n+} : 1\text{CrR}^{2+}$, and produce $2\text{M}^{(n-1)+}$, 1Cr^{3+} , and an organic product resulting from a one electron oxidation of R. In addition to this, the rate law for the reaction shows a first-order dependence on $[\text{M}^{n+}]$ and an inverse dependence on $[\text{H}^+]$. This suggests a rapid preequilibrium in which Fe^{3+} or Cu^{2+} substitute for the proton on the hydroxyl group of the organochromium complex to form a precursor complex which then undergoes internal electron transfer. The mechanism for Fe^{3+} is given below in eq 11 - 13:



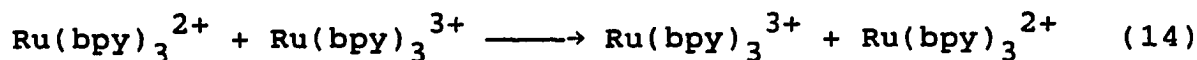
Thus, Fe^{3+} , Cu^{2+} , and Hg^{2+} oxidize α -hydroxy- and α -alkoxyalkylchromium complexes by one electron via an inner-sphere pathway.

This reaction, however, is not general for CrR^{2+} complexes and appears to be limited to the most easily

oxidized CrR^{2+} complexes which can react by an inner-sphere pathway involving coordination of the oxidant to the hydroxyl oxygen. Since there is no report in the literature of the direct oxidation of a wide range of $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ complexes, an outer-sphere oxidant was sought which would not only oxidize α -hydroxy- and α -alkoxyalkylchromium complexes but also some of the less easily oxidized complexes such as $\text{CrCH}_2\text{CH}_3^{2+}$. CrR^{2+} is in some respects more suited to the study of substituent effects than are the $\text{RCo}(\text{chel})$ complexes since α -hydroxy- and α -alkoxyalkylchromium complexes are known, but the corresponding organocobalt(III) macrocycles are not stable.¹⁵ The oxidation reactions of CrR^{2+} should also be somewhat more conducive to mechanistic studies since there is no possibility of interfering reactions involving a macrocycle.¹³

An oxidant suitable for this type of reaction should have a fairly large positive reduction potential and electronic and structural properties which make it a good outer-sphere oxidant. Tris(2,2'-bipyridyl)ruthenium(III) satisfies these requirements. $\text{Ru}(\text{bpy})_3^{3+}$ is a strong oxidant with the $\text{Ru}(\text{III})/\text{Ru}(\text{II})$ couple having a reduction potential of 1.26 v.¹⁶ The electronic configurations of the pseudooctahedral $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{3+}$ complexes are low-spin d^6 and d^5 , respectively. These electronic

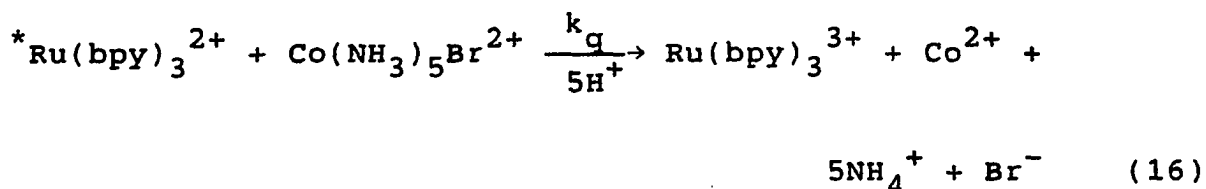
configurations and the chelating ability of the bipyridyl ligands make the complex substitutionally inert in both oxidation states which promotes oxidation by an outer-sphere pathway. The similarity of low-spin d^6 and d^5 electronic configurations also lead to relatively small differences in the metal to ligand bond distances for the ruthenium complex in the two different oxidation states. Another consequence of the similar electronic configurations of $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{3+}$ is the comparatively small change in solvation which occurs upon reduction of $\text{Ru}(\text{bpy})_3^{3+}$. Both of these factors are responsible for the high self-exchange rate for electron transfer for the $\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^{3+}$ couple ($k = 1.2 \times 10^9 \text{M}^{-1}\text{s}^{-1}$)¹² (eq 14):



All of these factors make $\text{Ru}(\text{bpy})_3^{3+}$ a good oxidant for outer-sphere electron transfer reactions.

A further advantage of using $\text{Ru}(\text{bpy})_3^{3+}$ as an oxidant is the convenient way in which it can be generated photochemically from $\text{Ru}(\text{bpy})_3^{2+}$.¹⁷ The photochemistry of $\text{Ru}(\text{bpy})_3^{2+}$ has been studied extensively^{16,18,19} because of its potential use in the photochemical production of O_2 and H_2 from water. This chemistry is based on the properties of the lowest-lying excited state of $\text{Ru}(\text{bpy})_3^{2+}$. The absorption spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ is shown below (Fig. II-

1). The peak at λ 450 nm represents a metal to ligand charge transfer band (ϵ $1.37 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$).²⁰ This transition involves the transfer of an electron from a t_{2g} orbital on the ruthenium to one of the bipyridyl rings to form $\text{Ru}^{\text{III}}(\text{bpy}^{\cdot-})(\text{bpy})_2^{2+}$ which is usually written as $^*\text{Ru}(\text{bpy})_3^{2+}$. Because the excited state of the ruthenium complex contains Ru(III) and a ligand radical anion ($\text{bpy}^{\cdot-}$) it is both a strong oxidant and reductant. $^*\text{Ru}(\text{bpy})_3^{2+}$ is rapidly oxidized by a number of Co(III) complexes to form $\text{Ru}(\text{bpy})_3^{3+}$. Therefore, it is possible to study the kinetics of reactions of $\text{Ru}(\text{bpy})_3^{3+}$ with other complexes by flash photolysis of solutions containing $\text{Ru}(\text{bpy})_3^{2+}$, Co(III), and the complex of interest. The set of reactions given below (eq 15 - 17; $\text{Co(III)} = \text{Co}(\text{NH}_3)_5\text{Br}^{2+}$) show how this method can be applied to the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with CrR^{2+} :



This reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ was studied mechanistically, and the results are reported and discussed below.

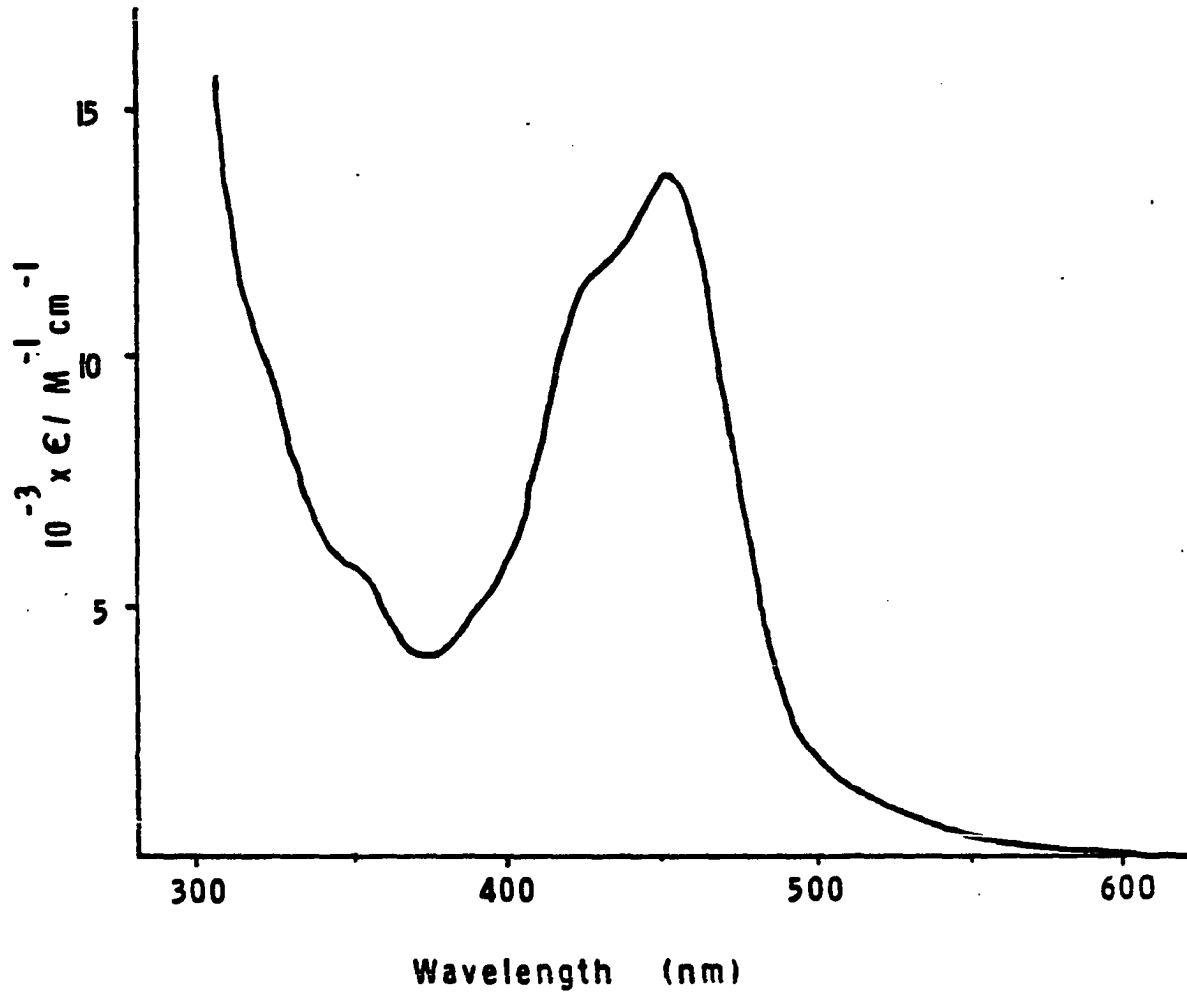


Figure II-1 Absorption spectrum of Ru(bpy)₃Cl₂ in water

RESULTS

Product Analysis

A product analysis was not feasible for many of the reactions studied, but an analysis was carried out to determine the organic product for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{CH}_3^{2+}$. An acidic solution containing $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, and excess $\text{CrCH}_2\text{CH}_3^{2+}$ was prepared in a spectrophotometric cell²¹ and irradiated with visible light. After the excess $\text{CrCH}_2\text{CH}_3^{2+}$ had decomposed to ethane and Cr^{3+} via acidolysis, the sample was analyzed by gas chromatography which indicated the formation of ethyl bromide as the organic product.

Kinetics

The kinetics of the reactions of $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ with $\text{Ru}(\text{bpy})_3^{3+}$ was studied by laser flash photolysis. $\text{Ru}(\text{bpy})_3^{2+}$ has a metal to ligand charge transfer band at λ 450 nm which can be irradiated with laser light to produce the charge transfer excited state, $^*\text{Ru}(\text{bpy})_3^{2+}$. This can be oxidatively quenched by $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ to produce $\text{Ru}(\text{bpy})_3^{3+}$ in solution. Thus, a cell containing an acidic solution of $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, and CrR^{2+} was irradiated by a 0.6 μs laser pulse (λ (461 \pm 20) nm). The decay and formation of $\text{Ru}(\text{bpy})_3^{2+}$ was followed by monitoring the absorbance of

the solution at λ 450 nm. There was a rapid initial drop in absorbance in the first one or two microseconds due to the conversion of $\text{Ru}(\text{bpy})_3^{2+}$ into $^*\text{Ru}(\text{bpy})_3^{2+}$ and then $\text{Ru}(\text{bpy})_3^{3+}$ after quenching by $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ ($\Delta\epsilon = 1.23 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ at λ 450 nm).²² This is then followed by a slower rise in absorbance which returns to the initial value or a value slightly less in some cases.

These changes in absorbance can be seen in Figure II-2 which shows a typical kinetic trace. The rise in absorbance is indicative of the reduction of the photochemically generated $\text{Ru}(\text{bpy})_3^{3+}$ to $\text{Ru}(\text{bpy})_3^{2+}$ by CrR^{2+} . Plots of $\ln|D_t - D_\infty|$ vs time are linear for three or more half lives indicating that the decay of $\text{Ru}(\text{bpy})_3^{3+}$ follows first-order kinetics. An exception to this is the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CH}_3^{2+}$ which showed biphasic kinetics. The kinetic data for this reaction were analyzed by standard methods and the rate constant reported is for the first reaction. Although the nature of the second reaction is unknown, the first reaction is assumed to be oxidation of CrR^{2+} .

The plot of k_{obs} vs $[\text{CrCH}_2\text{CH}_3^{2+}]$ given in Figure II-3 shows that the reaction is first-order in the concentration of $\text{CrCH}_2\text{CH}_3^{2+}$. This suggests a bimolecular reaction between $\text{Ru}(\text{bpy})_3^{3+}$ and CrR^{2+} which is in pseudo-first-order excess. This behavior was found for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with

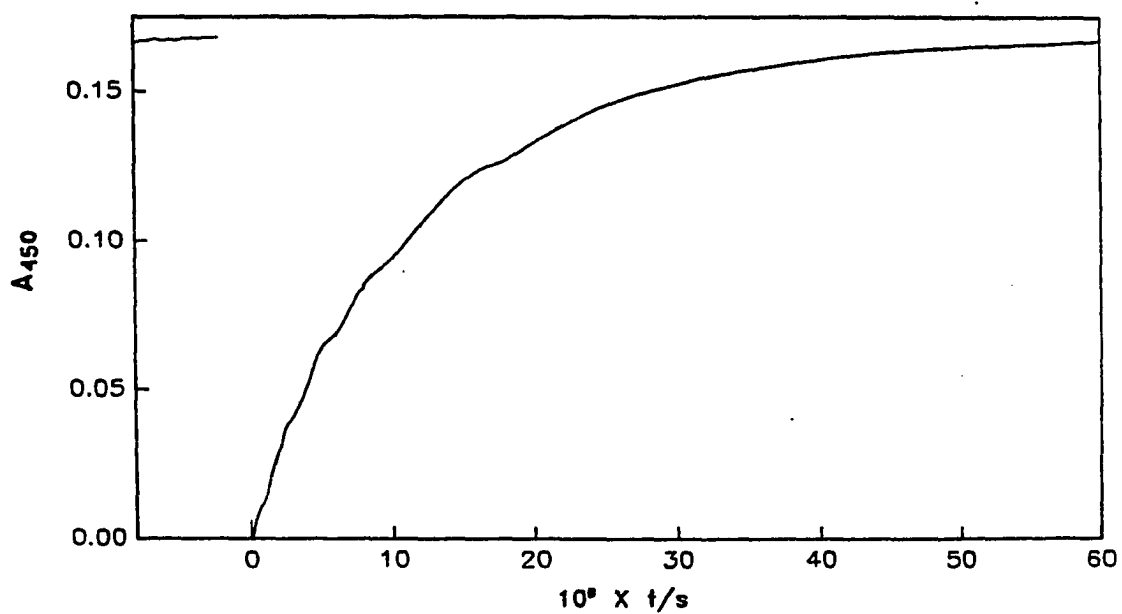


Figure II-2 Kinetic trace for the reaction of $\text{CrCH}_2\text{C}_6\text{H}_4\text{CN}^{2+}$ with $\text{Ru}(\text{bpy})_3^{3+}$. $T = 25\text{ }^\circ\text{C}$, $I = 0.10\text{ M}$, $[\text{CrCH}_2\text{C}_6\text{H}_4\text{CN}^{2+}] = 7.97 \times 10^{-4}\text{ M}$

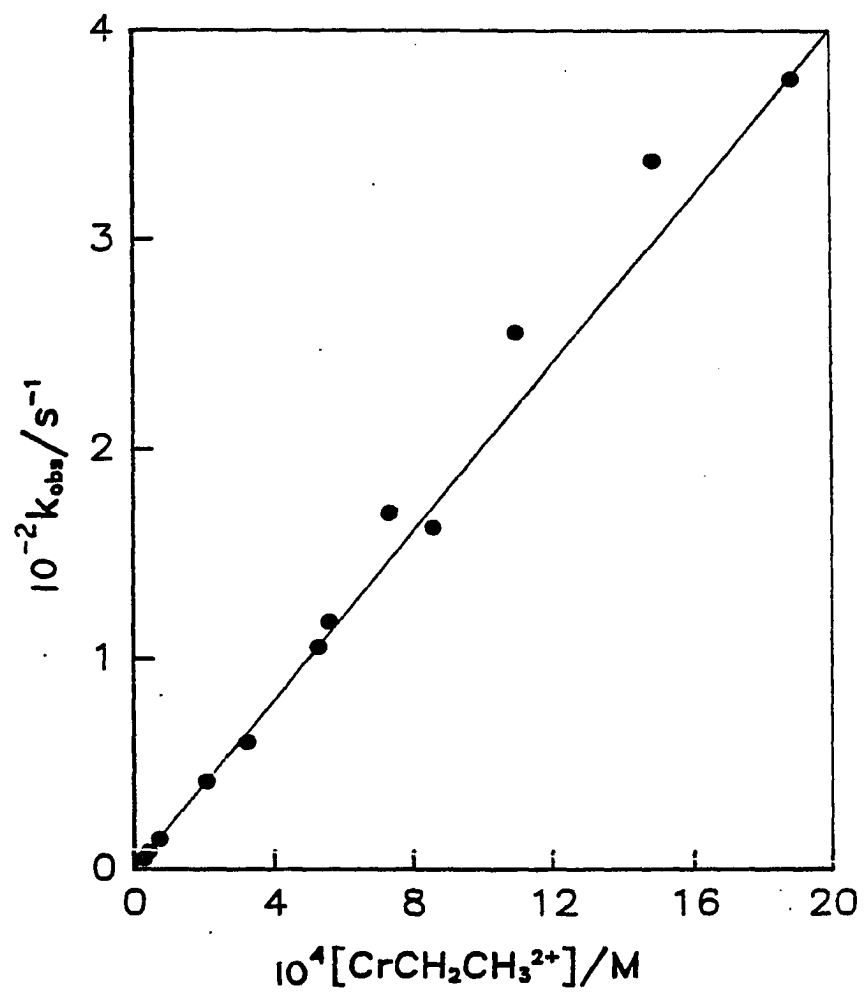


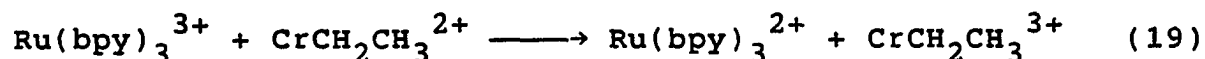
Figure II-3 Plot of k_{obs} vs $[\text{CrCH}_2\text{CH}_3^{2+}]$ for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{CH}_3^{2+}$

the other CrR^{2+} complexes as well which leads to the the rate law given below (eq 18):

$$-d[\text{Ru}(\text{bpy})_3^{3+}]/dt = k[\text{Ru}(\text{bpy})_3^{3+}][\text{CrR}^{2+}] \quad (18)$$

The rate constants for this reaction have been tabulated in Table II-1 below. It can be seen that the rate constants increase as electron donating groups are added to the α -carbon. This is consistent with an electron transfer mechanism and will be discussed in detail later.

If the reaction does indeed involve a one electron oxidation of CrR^{2+} by $\text{Ru}(\text{bpy})_3^{3+}$ then a question arises as to the fate of the CrR^{3+} formed. This reaction is shown in eq 19 for $\text{CrCH}_2\text{CH}_3^{2+}$. The results in Chapter I indicated that one electron oxidation of alkylchromium complexes by



NO^+ produces Cr^{3+} and $\text{R}\cdot$. Under the conditions of those experiments, the alkyl radical produced is scavenged by NO . However, in the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with CrR^{2+} there is a possibility that the alkyl radical would react with $\text{Ru}(\text{bpy})_3^{3+}$. Indeed, it is known that $\text{Fe}(\text{phen})_3^{3+}$ rapidly reacts with alkyl radicals.²³ Alternatively, $\text{R}\cdot$ might react with $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ which is present in the solution as a quencher. This type of reaction has precedents in the

Table II-1 Rate Constants for the Reactions of Tris(2,2'-bipyridyl)ruthenium(III) with $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ ^a

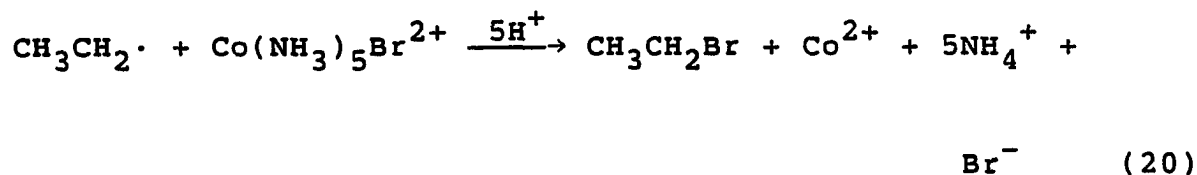
R	$k/\text{M}^{-1}\text{s}^{-1}$	σ_p^b
p-CH ₂ C ₆ H ₄ CH ₃	2.9×10^8	-0.17
CH ₂ C ₆ H ₅	5.3×10^8	0.0
p-CH ₂ C ₆ H ₄ CF ₃	1.71×10^7	0.54
p-CH ₂ C ₆ H ₄ CN	9.5×10^6	0.66
CH ₂ OCH ₃	1.04×10^7	
CH(CH ₃) ₂	4.25×10^7	
CH ₂ CH ₃	2.00×10^5	
CH ₃	$< 10^3$	

^aT = 25 °C, I = 0.10 M.

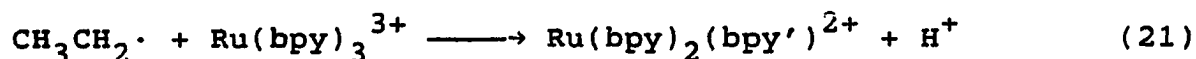
^bThis is the Hammett substituent parameter σ_p for para substituent on the benzyl group.

reactions of CH₃CH₂· with IrCl₆²⁻ and CuCl₂ which produce CH₃CH₂Cl as the organic product.²⁴ Perhaps a more significant precedent is the reaction of cyclopentyl radical with Co(NH₃)₅Br²⁺ to form cyclopentyl bromide.²⁵

The existence of two alternative reactions for R·, i.e., with $\text{Ru}(\text{bpy})_3^{3+}$ or $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, suggests a way of verifying the formation of an alkyl radical intermediate. If $\text{CrCH}_2\text{CH}_3^{2+}$ is reacted with $\text{Ru}(\text{bpy})_3^{3+}$ in the presence of an efficient scavenger, such as $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, the ethyl radical will be trapped by $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ (eq 20) and the



stoichiometry of the reaction will be $1\text{Ru}(\text{bpy})_3^{3+} : 1\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$. However, if a different quencher is used, such as $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$, which has a much less efficient bridging ligand for electron transfer (pyridine as opposed to bromide), then ethyl radical would react instead with $\text{Ru}(\text{bpy})_3^{3+}$ (eq 21), presumably by substitution on a



bipyridyl ring. If this reaction is rapid relative to reaction 19, then two $\text{Ru}(\text{bpy})_3^{3+}$ ions would be consumed for every $\text{CrCH}_2\text{CH}_3^{2+}$ ion oxidized thus making the stoichiometry $2\text{Ru}(\text{bpy})_3^{3+} : 1\text{CrCH}_2\text{CH}_3^{2+}$.

This change in stoichiometry as the quencher is changed would also be reflected in the kinetics. Since $\text{Ru}(\text{bpy})_3^{3+}$

is the limiting reagent for all of the runs, the measured rate constant k would be k_1 with 1 : 1 stoichiometry but with 2 : 1 stoichiometry k would have a value of $2k_1$ since an additional $\text{Ru}(\text{bpy})_3^{3+}$ ion is rapidly consumed each time the first step occurs. Thus, one predicts that the rate constant for the oxidation of $\text{CrCH}_2\text{CH}_3^{2+}$ by $\text{Ru}(\text{bpy})_3^{3+}$ will double when the quencher is changed from $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ to $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$.

This prediction has been confirmed experimentally. Figure II-4 shows plots of k_{obs} vs $[\text{CrCH}_2\text{CH}_3^{2+}]$ from two sets of kinetic runs. The upper line (symbol = \diamond) represents kinetic runs carried out using $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ as the quencher and the lower line (symbol = \bullet) represents runs using $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$. It is evident that the rate constant measured with $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ as the quencher ($k = (4.3 \pm 0.2) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) is twice what was found when $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ was used as the quencher ($k = (2.00 \pm 0.05) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$).

Similar experiments were carried out for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{OCH}_3^{2+}$. Plots of k_{obs} vs $[\text{CrCH}_2\text{OCH}_3^{2+}]$ for runs with the two quenchers $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ are shown in Figure II-5. In this case, the rate constants with $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ as quenchers were the same ($(1.04 \pm 0.2) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ and $(1.18 \pm 0.07) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, respectively) within experimental error.

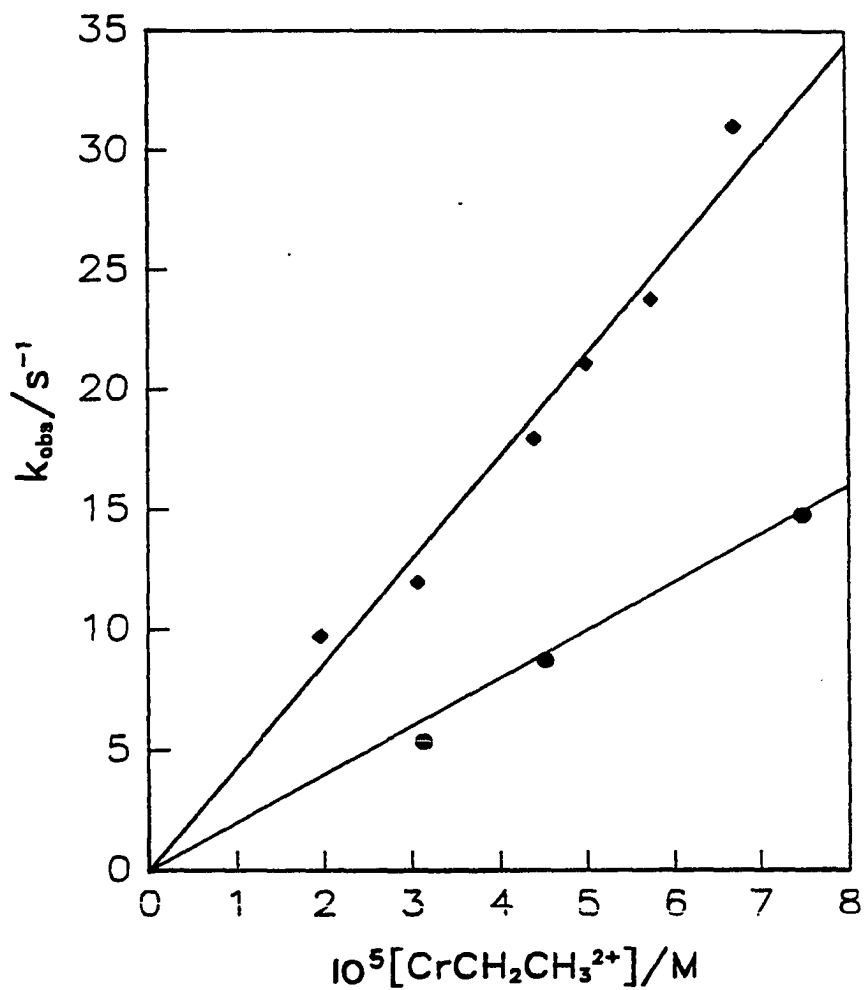


Figure II-4 Plots of k_{obs} vs $[\text{CrCH}_2\text{CH}_3^{2+}]$ for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{CH}_3^{2+}$ using two different quenchers. The circles represent kinetic runs using $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and the diamonds represent runs using $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$

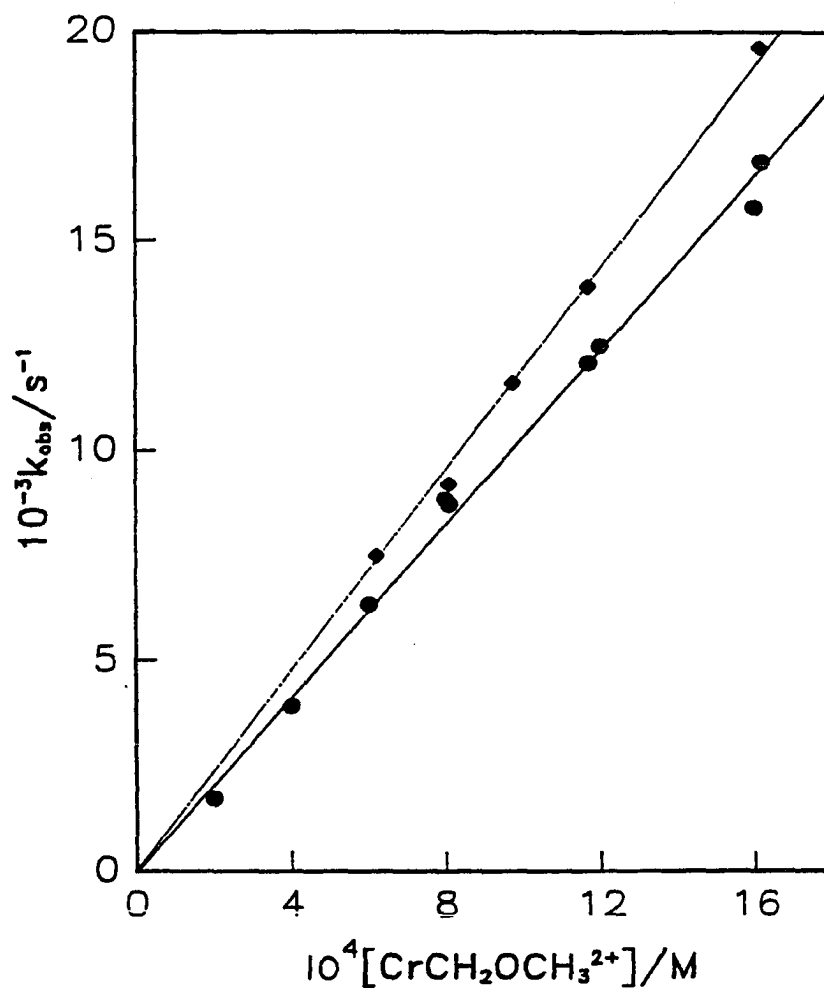


Figure II-5 Plots of k_{obs} vs $[\text{CrCH}_2\text{OCH}_3^{2+}]$ for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{OCH}_3^{2+}$ using two different quenchers. The circles represent kinetic runs using $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and the diamonds represent runs using $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$.

Since the reaction between $\text{Ru}(\text{bpy})_3^{3+}$ and some of the CrR^{2+} complexes may involve a Cr^{2+} intermediate capable of reacting with $\text{Ru}(\text{bpy})_3^{3+}$, kinetic runs were carried out to measure the rate constant between Cr^{2+} and $\text{Ru}(\text{bpy})_3^{3+}$ which does not appear to have been reported in the literature. We have measured this rate constant in much the same way as those of the reactions of $\text{Ru}(\text{bpy})_3^{3+}$ with CrR^{2+} . In this case excess Cr^{2+} was used instead of CrR^{2+} , and $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ was used as the quencher to minimize reaction with Cr^{2+} . A plot of k_{obs} vs $[\text{Cr}^{2+}]$ yielded a value of $(7.6 \pm 0.3) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ for the second-order rate constant for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with Cr^{2+} . This value is less than that predicted by Marcus theory²³ which may imply that the electron transfer is non-adiabatic, resulting from a mismatch in the symmetry of the HOMO of the Cr^{2+} (e_g^*) and the LUMO of the $\text{Ru}(\text{bpy})_3^{3+}$ (t_{2g}).

DISCUSSION

Product Analysis

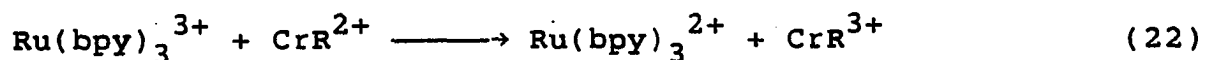
Ethyl bromide was detected as a product when an acidic solution of $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, and excess $\text{CrCH}_2\text{CH}_3^{2+}$ was irradiated with visible light. Since no free bromide was present in solution the bromine atom in $\text{CH}_3\text{CH}_2\text{Br}$ must have been derived from the $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ in solution. It is difficult to envision how bromine could be transferred from $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ to the ethyl group on $\text{CrCH}_2\text{CH}_3^{2+}$ unless ethyl radicals are involved as intermediates. Ethyl radicals would be expected to react with $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ by bromine atom abstraction to give $\text{CH}_3\text{CH}_2\text{Br}$. As mentioned earlier, this type of reaction has precedents in the literature such as the reaction of cyclopentyl radical with $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ which yields cyclopentyl bromide.²⁵ The proposed pathway by which ethyl radicals are formed in this mechanism will be discussed below.

Kinetics

Rate Law and Spectral Changes Kinetic studies of the reactions of $\text{Ru}(\text{bpy})_3^{3+}$ with $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ complexes indicate that the reaction rate is first-order in both $[\text{Ru}(\text{bpy})_3^{3+}]$ and $[(\text{H}_2\text{O})_5\text{CrR}^{2+}]$. This leads to the rate law given in eq 18:

$$-\text{d}[\text{Ru}(\text{bpy})_3^{3+}]/\text{dt} = k[\text{Ru}(\text{bpy})_3^{3+}][\text{CrR}^{2+}] \quad (18)$$

This rate law and the formation of $\text{Ru}(\text{bpy})_3^{2+}$, as shown by rise in absorbance at λ 450 nm, imply that the reaction involves a rate-determining bimolecular reaction between $\text{Ru}(\text{bpy})_3^{3+}$ and CrR^{2+} in which the ruthenium(III) oxidizes CrR^{2+} by one electron to form $\text{Ru}(\text{bpy})_3^{2+}$ and CrR^{3+} (eq 22):



This reaction is analogous to the reactions of IrCl_6^{2-} with organocobalt(III) macrocycles^{1,2,3} as well as one electron oxidation reactions of dialkylplatinum and -iron complexes.^{6,7}

Trends in the Rate Constants The trends in the rate constants also suggest that $\text{Ru}(\text{bpy})_3^{3+}$ reacts with CrR^{2+} by outer-sphere electron transfer. This is particularly evident in the rate constants for the reactions of alkylchromium complexes which have the ordering: $\text{CH}_3 \ll \text{CH}_2\text{CH}_3 < \text{CH}(\text{CH}_3)_2$. This order of reactivity is characteristic of outer-sphere electron transfer reactions¹ in which steric effects are not very important and electronic effects predominate. Thus, the addition of electron-donating methyl groups to the α -carbon of the organochromium complex increases the rate of oxidation of the complex by $\text{Ru}(\text{bpy})_3^{3+}$.

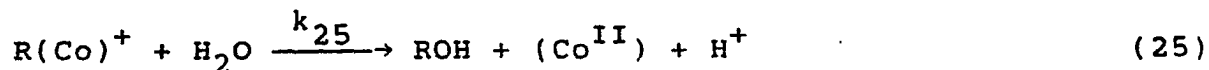
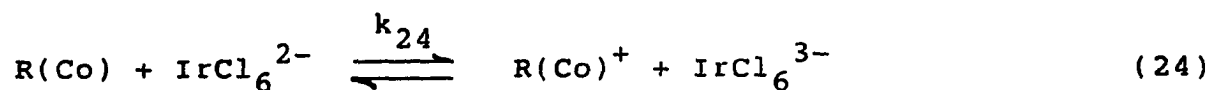
The decrease in the rate constants for the derivatives of $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ when electron-withdrawing groups are

substituted at the para position is also consistent with an oxidation of CrR^{2+} , although the effect of steric crowding cannot be examined for this series. There appears to be a slight anomaly in this series in that the rate constant for $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$ appears to be slightly higher ($k = 5.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) than the rate constant for $\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CH}_3^{2+}$ ($k = 2.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$). The reason for this anomaly is not known, although the value for the rate constant for $\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CH}_3^{2+}$ is probably less reliable since this reaction showed biphasic kinetics and may involve other reactions.

Although rate constants have been measured for only four organochromium complexes of the type $\text{CrCH}_2\text{C}_6\text{H}_4\text{X}^{2+}$, one can correlate these rate constants using the Hammett relation (eq 23):

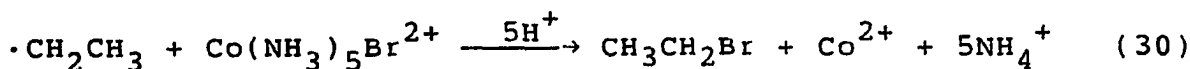
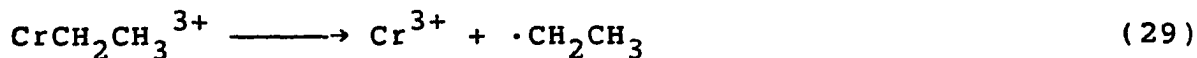
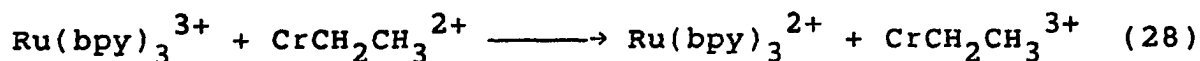
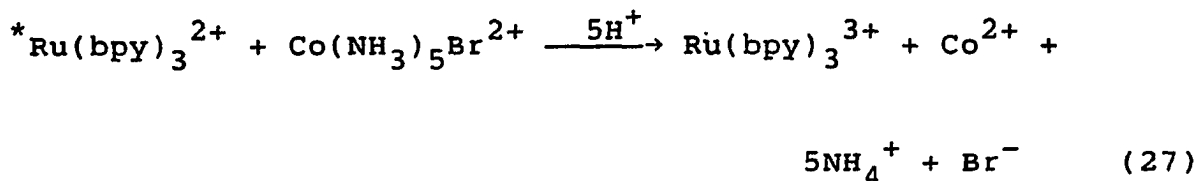
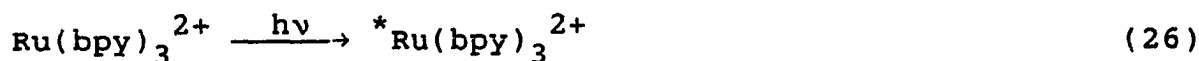
$$\log(k) = \log(k_0) + \rho\sigma \quad (23)$$

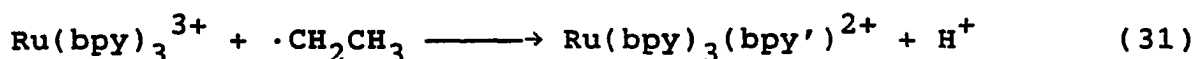
A plot of $\log(k)$ vs $\sigma_p(\text{X})$ yields the reaction constant $\rho = -2.3$. Although this value is only approximate, it can be compared to the reaction constant for the reaction of IrCl_6^{2-} with $\text{Co}(\text{dmgH})_2\text{CH}_2\text{C}_6\text{H}_4\text{X}$ mentioned earlier (eq 24, 25):¹⁰



A plot of $\log(k_{24})$ vs $\sigma_p(X)$ for this reaction yields a reaction constant ρ with a value of -3.0 . This reaction produces the transient $R(\text{Co})^+$ which has been shown to be a cobalt(IV) species implying that the electron is removed from the metal center. The reaction constant for the reactions of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{C}_6\text{H}_4\text{X}^{2+}$ is -2.3 which indicates that substituents have somewhat less effect on the rate of this reaction. This suggests that the electron is removed from the metal center for these reactions also.

Mechanism for the Reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{CH}_3^{2+}$ The product analysis for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{CH}_3^{2+}$ and the kinetic studies carried out on the reactions of the other CrR^{2+} complexes lead to the mechanism for $\text{CrCH}_2\text{CH}_3^{2+}$ given below in eq 26 - 31:





In this mechanism, $\text{Ru}(\text{bpy})_3^{3+}$ oxidizes $\text{CrCH}_2\text{CH}_3^{2+}$ by one electron to form $\text{CrCH}_2\text{CH}_3^{3+}$ which is formally $[\text{Cr}^{\text{IV}}\text{R}^-]^{3+}$. Cr^{IV} should be very strongly oxidizing and would be expected to oxidize the ligand R^- . Thus, the decomposition of $\text{CrCH}_2\text{CH}_3^{2+}$ to form Cr^{3+} and $\cdot\text{CH}_2\text{CH}_3$ seems reasonable. This is similar to the mode of decomposition of $\text{RCo}(\text{salen})^+$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3$) to form $\text{Co}^{\text{III}}(\text{salen})^+$ and $\text{R}\cdot$ as was mentioned earlier. The one electron oxidation of $\text{R}_2\text{Co}(\text{chel})$ also leads to homolytic cleavage of the cobalt-carbon bond.⁸

The ethyl radical formed in this mechanism can react in several different ways. In eq 30 $\cdot\text{CH}_2\text{CH}_3$ reduces $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ by an inner-sphere pathway to produce Co^{2+} and $\text{CH}_3\text{CH}_2\text{Br}$ which was the observed organic product. Alternatively, ethyl radicals could react with $\text{Ru}(\text{bpy})_3^{3+}$ by substitution on one of the bipyridyl rings (eq 31).²³ This reaction does not appear to be able to compete with reaction 30 when $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ is present at the concentrations normally used in the kinetic runs.

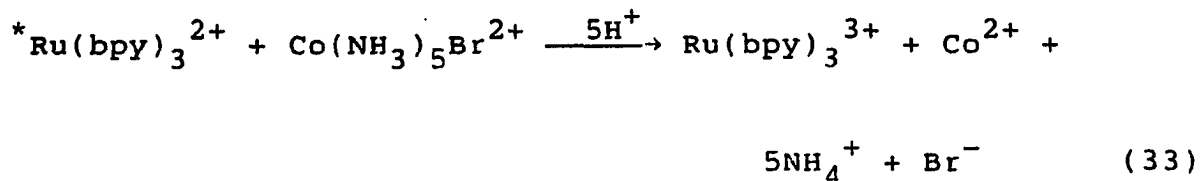
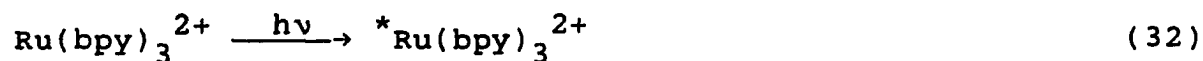
Kinetic runs carried out with the two different quenchers have confirmed the mechanism given in reactions 26 - 31. The measured rate constant is $(4.2 \pm 0.3) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ when $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ is used as the quencher whereas it has a value of $(2.00 \pm 0.05) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ when $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$

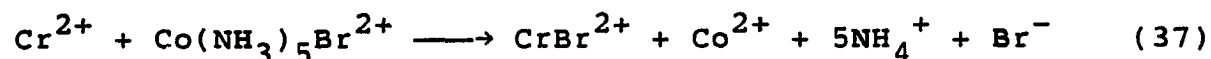
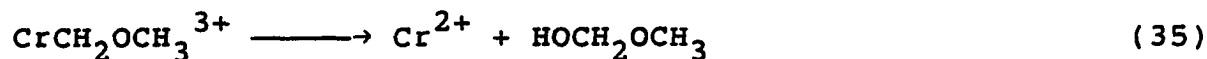
is used as the quencher. This doubling of the rate constant when $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ is absent can be explained as follows. One $\text{Ru}(\text{bpy})_3^{3+}$ ion is consumed each time the rate-determining step (reaction 28) occurs, and if the ethyl radical is trapped by $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ the measured rate constant will be equal to k_{28} . On the other hand, if $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ is absent and $\cdot\text{CH}_2\text{CH}_3$ is allowed to react with another $\text{Ru}(\text{bpy})_3^{3+}$ ion in a step (reaction 31) which is rapid relative to reaction 28, the rate of loss of $\text{Ru}(\text{bpy})_3^{3+}$ will be doubled and the measured rate constant will be equal to $2k_{28}$.

Mechanism for the Reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{OCH}_3^{2+}$ It should be noted that the mechanism presented above has only been confirmed for $\text{CrCH}_2\text{CH}_3^{2+}$ although it probably also applies for the oxidation of $\text{CrCH}(\text{CH}_3)_2^{2+}$ by $\text{Ru}(\text{bpy})_3^{3+}$ since these two organochromium complexes are oxidized by NO^+ by the same mechanism. On the other hand, it is doubtful that $\cdot\text{CH}_2\text{OCH}_3$ is formed in the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{OCH}_3^{2+}$. It is more likely that $\text{Ru}(\text{bpy})_3^{3+}$ oxidizes $\text{CrCH}_2\text{OCH}_3^{2+}$ by one electron to give $\text{CrCH}_2\text{OCH}_3^{3+}$ which undergoes an internal redox reaction to form Cr^{2+} and $\text{HOCH}_2\text{OCH}_3$ (which decomposes to CH_2O and HOCH_3). This is the pathway for decomposition of $\text{CrCH}_2\text{OCH}_3^{3+}$ in the reaction of $\text{CrCH}_2\text{OCH}_3^{2+}$ with HONO . In the reaction with nitrous acid Cr^{2+} was proposed as an

intermediate in order to account for the formation of Co^{2+} when the reaction was carried out in the presence of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$. The proposal of Cr^{2+} as an intermediate also explains how CrNO^{2+} is formed in the reaction. It is more difficult, however, to distinguish between these possibilities for the $\text{Ru}(\text{bpy})_3^{3+}$ reaction. If $\cdot\text{CH}_2\text{OCH}_3$ is formed in this reaction it would react with $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ to form Co^{2+} and $\text{HOCH}_2\text{OCH}_3$ or $\text{BrCH}_2\text{OCH}_3$, either of which would decompose under the reaction conditions to give CH_2O and HOCH_3 as the organic products. These organic products would also be formed if the intermediate $\text{CrCH}_2\text{OCH}_3^{3+}$ decomposed to give Cr^{2+} and $\text{HOCH}_2\text{OCH}_3$.

Thus, it is difficult to determine experimentally the details of the mechanism for the oxidation of $\text{CrCH}_2\text{OCH}_3^{2+}$ by $\text{Ru}(\text{bpy})_3^{3+}$. Nevertheless, the formation of Cr^{2+} as an intermediate in the oxidation reactions of $\text{CrCH}_2\text{OCH}_3^{2+}$ when the oxidants are Fe^{3+} , Cu^{2+} , NO^+ suggest that this is also the case in the reaction with $\text{Ru}(\text{bpy})_3^{3+}$. Therefore, the following mechanism can be proposed for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{OCH}_3^{2+}$ (eq 32 - 37):





The intermediate formed in this mechanism, Cr^{2+} , is trapped by $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$. This reaction has a rate constant of $1.4 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$.²⁶ One may well ask whether or not Cr^{2+} can react with $\text{Ru}(\text{bpy})_3^{3+}$ under the conditions of these kinetic runs. The rate constant of this reaction has been determined and found to have a value of $(7.6 \pm 0.3) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$. Since the concentration of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ in the kinetic runs is 0.01 M whereas $\text{Ru}(\text{bpy})_3^{3+}$ is at a concentration of $\approx 10 \mu\text{M}$, it is clear that Cr^{2+} will react with $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ when it is present at these concentrations.

On the other hand, when $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ is the quencher, Cr^{2+} does not react with either the quencher (the rate constant for the reaction of Cr^{2+} with $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ is only $4.1 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$)²⁷ or $\text{Ru}(\text{bpy})_3^{3+}$. The rate constants for the reactions of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{OCH}_3^{2+}$ and Cr^{2+} are $1.04 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ and $7.6 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, respectively. In

the kinetic runs $[\text{CrCH}_2\text{OCH}_3^{2+}] \geq 2 \times 10^{-4} \text{ M}$ which implies that the steady state concentration of Cr^{2+} would have to be equal to $2.7 \times 10^{-6} \text{ M}$ in order for 10% of the $\text{Ru}(\text{bpy})_3^{3+}$ to react with Cr^{2+} . Since it is unlikely that the steady state concentration of Cr^{2+} is greater than this, the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with Cr^{2+} can be ignored. Therefore, one would predict that the measured rate constant for the reaction would be the same ($k = k_{34}$) whether $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ or $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ is used as the quencher.

This was indeed found to be the case when kinetic runs were carried out for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{OCH}_3^{2+}$ using $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ as the quencher. The rate constant with $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ is $(1.18 \pm 0.07) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ which is the same, within experimental error, as the rate constant obtained when $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ is used ($k = (1.04 \pm 0.2) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$).

The reactions of $\text{CrCH}_2\text{C}_6\text{H}_4\text{X}^{2+}$ complexes with $\text{Ru}(\text{bpy})_3^{3+}$ also involve an initial one electron oxidation of $\text{CrCH}_2\text{C}_6\text{H}_4\text{X}^{2+}$, but it is not possible to determine the decomposition pathway of $\text{CrCH}_2\text{C}_6\text{H}_4\text{X}^{3+}$ on the basis of the evidence presented. $\text{CrCH}_2\text{C}_6\text{H}_4\text{X}^{3+}$ could decompose either to Cr^{3+} and $\cdot\text{CH}_2\text{C}_6\text{H}_4\text{X}$ or Cr^{2+} and $\text{HOCH}_2\text{C}_6\text{H}_4\text{X}$.

Comparisons Between the HNO_2 and $\text{Ru}(\text{bpy})_3^{3+}$ Reactions

The reactions of $\text{Ru}(\text{bpy})_3^{3+}$ and NO^+ with CrR^{2+} can also be compared in terms of the trends in rate constants. The

rates of the reactions of both $\text{Ru}(\text{bpy})_3^{3+}$ and NO^+ with aliphatic CrR^{2+} complexes increase as electron donating groups are substituted on the α -carbon but the NO^+ reaction shows much less sensitivity to substituent effects. This can be attributed to the fact that the second-order rate constants for the NO^+ reactions are approaching the diffusion-controlled limit ($k_{\text{NO}^+} = 2.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for the reaction of $\text{CrCH}_2\text{OH}^{2+}$) which tends to compress the variations in rate constants along a series.

A more interesting comparison can be made between the mechanisms for the reactions of $\text{Ru}(\text{bpy})_3^{3+}$ and NO^+ with aralkylchromium complexes. $\text{Ru}(\text{bpy})_3^{3+}$ reacts with $\text{CrCH}_2\text{C}_6\text{H}_4\text{X}^{2+}$ by an electron transfer mechanism whereas NO^+ reacts with these organochromium complexes by electrophilic substitution at the α -carbon. The fact that $\text{Ru}(\text{bpy})_3^{3+}$ oxidizes aralkylchromium complexes much more rapidly than it does aliphatic CrR^{2+} complexes (e.g. $k = 5.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for $\text{CrCH}_2\text{C}_6\text{H}_5^{2+}$, while $k = 4.25 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ for $\text{CrCH}(\text{CH}_3)_2^{2+}$) suggests that aralkylchromium complexes may be inherently more easily oxidized than aliphatic organochromium complexes. If this is indeed the case, one might wonder why NO^+ does not react with $\text{CrCH}_2\text{C}_6\text{H}_4\text{X}^{2+}$ by an electron transfer mechanism.

The trend in the rate constants for the oxidation of macrocyclic organocobalt(III) complexes by IrCl_6^{2-} is the

reverse of the trend for the reactions of $\text{Ru}(\text{bpy})_3^{3+}$ with CrR^{2+} . The rate constant for the oxidation of $\text{Co}(\text{dmgH})_2\text{CH}(\text{CH}_3)_2$ by IrCl_6^{2-} has a value of $3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ whereas the rate constant for the oxidation of $\text{Co}(\text{dmgH})_2\text{CH}_2\text{C}_6\text{H}_5$ is $\approx 5 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$. Thus, the relative rates of oxidation of aralkylmetals vs alkylmetals can vary with the oxidant. $\text{Ru}(\text{bpy})_3^{3+}$ may react more rapidly with aralkylchromium complexes than with aliphatic organochromium complexes because of a greater interaction between the hydrophobic bipyridyl ligands and the aralkyl ligands which are more hydrophobic than the alkyl ligands studied.

This type of interaction would not occur in the case of the reactions of NO^+ which may oxidize aralkyl- and alkylchromium complexes at comparable rates. Presumably, the reaction of NO^+ with CrR^{2+} occurs by two parallel pathways with electron transfer dominating when R is aliphatic, but with electrophilic substitution dominating when $\text{R} = \text{C}_6\text{H}_4\text{X}$ since the transition state for electrophilic substitution can be stabilized by the formation of a π -complex intermediate. It is possible that electron transfer is occurring in the reactions of NO^+ with the aralkylchromium complexes but the pathway for electrophilic substitution predominates.

Summary

Photochemically generated $\text{Ru}(\text{bpy})_3^{3+}$ has been found to oxidize a wide range of $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ complexes. The first step in this reaction is the one electron oxidation of CrR^{2+} by $\text{Ru}(\text{bpy})_3^{3+}$ which is believed to involve removal of an electron from a d orbital on chromium. The trends in the rate constants ($\text{CH}(\text{CH}_3)_2 > \text{CH}_2\text{CH}_3 \gg \text{CH}_3$) and the usual behavior of $\text{Ru}(\text{bpy})_3^{3+}$ suggest that electron transfer occurs by an outer-sphere mechanism. The intermediate CrR^{3+} produced decays to Cr^{3+} and R. for alkylchromium complexes. In the case of $\text{CrCH}_2\text{CH}_3^{2+}$ the $\cdot\text{CH}_2\text{CH}_3$ produced can be trapped by $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ or, in the absence of a scavenger, it can react with $\text{Ru}(\text{bpy})_3^{3+}$ thereby doubling the measured rate constant. It has been suggested on the basis of precedents that $\text{CrCH}_2\text{OCH}_3^{3+}$ decays to Cr^{2+} and $\text{HOCH}_2\text{OCH}_3$. This mechanism is consistent with the failure to observe a change in the rate constant when the quencher is changed from $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ to $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$. Aalkylchromium complexes of the type $\text{CrCH}_2\text{C}_6\text{H}_4\text{X}^{2+}$ are also oxidized by $\text{Ru}(\text{bpy})_3^{3+}$. The rate constants for these reactions are more rapid than those of the alkylchromium complexes. This may be due in part to an interaction between the hydrophobic bipyridyl rings and the comparatively more hydrophobic aralkyl ligands.

EXPERIMENTAL**Materials**

$(\text{H}_2\text{O})_5\text{CrR}^{2+}$ complexes and $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ were prepared and characterized as described in the chapter I.

$\text{Ru}(\text{bpy})_3\text{Cl}_2$ (Aldrich), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Mallinckrodt), $(\text{NH}_4)_2\text{SO}_4$ (Baker), BaCO_3 (Fisher), HOSO_2CF_3 (Alpha Products), K_2CO_3 (Baker), KOH (Fisher), pyridine (Fisher), and ethyl bromide (Baker) are available commercially as reagent grade chemicals and were used as received with the exception of pyridine which was dried by KOH ,²⁸ distilled from KOH and stored over 4A molecular sieves.

$[\text{Co}(\text{NH}_3)_5\text{py}](\text{OSO}_2\text{CF}_3)_3$ was prepared from $[\text{Co}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{OSO}_2\text{CF}_3)_2$ ²⁹ by dissolving 1 g of the triflate complex in about 8 mL of dried and distilled pyridine and stirring until the color changed from red to orange (≈ 45 min). The $[\text{Co}(\text{NH}_3)_5\text{py}](\text{OSO}_2\text{CF}_3)_3$ was precipitated by adding diethyl ether to the pyridine solution and washing with ether three or four times. The resulting orange crystals were recrystallized several times from hot (45°C) methanol to remove any excess pyridine.

Other compounds used are listed in the experimental section of the first chapter.

Product Analysis

A product analysis for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with $\text{CrCH}_2\text{CH}_3^{2+}$ was carried out to determine the organic product. An acidic solution (0.20 M HClO_4) containing $\text{Ru}(\text{bpy})_3^{2+}$ (5.6×10^{-6} M), $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ (0.010 M), and excess $\text{CrCH}_2\text{CH}_3^{2+}$ (0.00495 M) was prepared in a jacketed spectrophotometric cell. The jacket of the cell contained ≈ 0.01 M $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ which acts as a filter for UV light to prevent photolysis of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ in the cell. The cell was irradiated for four minutes with a 275 W sunlamp placed ≈ 14 cm from the cell. The solution was then placed in the dark for several hours to allow the excess $\text{CrCH}_2\text{CH}_3^{2+}$ to decompose to $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and ethane by acidolysis. One microliter of the reaction mixture was then analyzed by gas chromatography on a Hewlett Packard 5790A series gas chromatograph equipped with a 3390A series integrator. A 10% FFAP column was used for the analysis. The GC trace for the sample showed a peak having the same retention time as an authentic sample of ethyl bromide.

Kinetics

Kinetic runs were carried out using laser flash photolysis. The laser system used has been described by Connolly³⁰ and is based on another system in the literature.³¹ In a typical kinetic run, an acidic solution

($[H^+] = 0.01 \text{ M} - 0.1 \text{ M}$)³² containing $\text{Ru}(\text{bpy})_3\text{Cl}_2$ ($(1.2 - 2.6) \times 10^{-5} \text{ M}$), $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ ($0.002 \text{ M} - 0.010 \text{ M}$), and CrR^{2+} ($(2.0 - 210) \times 10^{-5} \text{ M}$) was prepared in a square one cm quartz cell. The solution was then photolyzed by a $0.6 \mu\text{s}$ laser pulse from a Phase-R model DL-1100 pulsed dye laser. At right angles to the laser beam was a monitoring beam, provided by a 50 W quartz-halogen lamp, which passed through the cell. The light transmitted through the cell then passed through an Instruments SA grating monochromator, and was detected by a Hamamatsu R928 photomultiplier tube. The signal from the photomultiplier tube was collected and stored on a Nicolet model 2090-3A digitizing oscilloscope. The Nicolet oscilloscope was interfaced with an Apple II plus microcomputer which converted the voltage vs time data from the oscilloscope to absorbance vs time data (voltages being proportional to transmittance). Analysis of the absorbance vs time data indicated that the rise in absorbance at λ 450 nm follows first-order kinetics for at least three half lives.

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21. A jacketed cell was used for the experiment. The jacket was filled with 0.01 M $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ to filter U.V. light which might cause photolysis of the cobalt complex.
22. $\Delta\varepsilon = \varepsilon_{\text{Ru}^{\text{II}}} - \varepsilon_{\text{Ru}^{\text{III}}}$; for $\text{Ru}(\text{bpy})_3^{3+}$ spectrum see Watts, R.J. J. Chem. Ed. 1983, 60, 834 and references therein.
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1162; $k = 3.84 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$.
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32. HClO_4 and/or HCl were used to maintain 0.01 M ionic strength. No significant change was observed in the kinetics when HCl was used in place of HClO_4 .

APPENDIX II

Table AII-1 Rate Constants for the Reaction of $\text{Ru}(\text{bpy})_3^{3+}$
with $\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CH}_3^{2+}$ ^a

$10^4[\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CH}_3^{2+}]/\text{M}$	$10^{-4}k_{\text{obs}}/\text{s}^{-1}$
0.99	4.24
1.98	8.32
3.96	15.0
10.0	33.6
10.1	35.4
20.1	58.8

^aT = 25 °C, I = 0.10 M (maintained by HCl or HClO₄),
[Ru(bpy)₃²⁺] = (1.5 - 2.6) × 10⁻⁵ M, [Ru(bpy)₃³⁺] = 1 × 10⁻⁵
M (typical concentration), [Co(NH₃)₅Br²⁺] = (0.002 - 0.004)
M.

Table AII-2 Rate Constants for the Reaction of $\text{Ru}(\text{bpy})_3^{3+}$
with $\text{Cr-p-CH}_2\text{C}_6\text{H}_5^{2+}$ ^a

$10^4 [\text{CrCH}_2\text{C}_6\text{H}_5^{2+}] / \text{M}$	$10^{-4} k_{\text{obs}} / \text{s}^{-1}$
0.756	3.63
0.927	4.36
0.972	4.00
1.92	12.3
2.40	14.3
2.93	23.3
3.92	30.4

^a $T = 25$ °C, $I = 0.10$ M (maintained by HCl or HClO_4),
 $[\text{Ru}(\text{bpy})_3^{2+}] = (1.5 - 2.6) \times 10^{-5}$ M, $[\text{Ru}(\text{bpy})_3^{3+}] = 1 \times 10^{-5}$
M (typical concentration), $[\text{Co}(\text{NH}_3)_5\text{Br}^{2+}] = 0.01$ M.

Table AII-3 Rate Constants for the Reaction of $\text{Ru}(\text{bpy})_3^{3+}$
with $\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CF}_3^{2+}$ a

$10^4[\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CH}_3^{2+}]/\text{M}$	$10^{-4}k_{\text{obs}}/\text{s}^{-1}$
2.39	0.219
6.00	1.08
7.66	1.19
7.66	1.24
10.0	1.64
12.4	2.41
15.8	2.62

$t = 25^\circ\text{C}$, $I = 0.10 \text{ M}$ (maintained by HCl or HClO_4),
 $[\text{Ru}(\text{bpy})_3^{2+}] = (1.2 - 2.5) \times 10^{-5} \text{ M}$, $[\text{Ru}(\text{bpy})_3^{3+}] = 1 \times 10^{-5}$
 M (typical concentration), $[\text{Co}(\text{NH}_3)_5\text{Br}^{2+}] = 0.01 \text{ M}$.

Table AII-4 Rate Constants for the Reaction of $\text{Ru}(\text{bpy})_3^{3+}$
with $\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CN}^{2+}$ ^a

$10^4[\text{Cr-p-CH}_2\text{C}_6\text{H}_4\text{CN}^{2+}]/\text{M}$	$10^{-3}k_{\text{obs}}/\text{s}^{-1}$
1.67	0.606
3.19	1.61
4.78	3.67
7.97	8.07
9.92	9.00

^a $T = 25$ °C, $I = 0.10$ M (maintained by HCl or HClO_4),
 $[\text{Ru}(\text{bpy})_3^{2+}] = 1.5 \times 10^{-5}$ M, $[\text{Ru}(\text{bpy})_3^{3+}] = 1 \times 10^{-5}$ M
 (typical concentration), $[\text{Co}(\text{NH}_3)_5\text{Br}^{2+}] = 0.01$ M.

Table AII-5 Rate Constants for the Reaction of $\text{Ru}(\text{bpy})_3^{3+}$
with $\text{CrCH}_2\text{OCH}_3^{2+}$ ^a

$10^4[\text{CrCH}_2\text{OCH}_3^{2+}]/\text{M}$	$10^{-3}k_{\text{obs}}/\text{s}^{-1}$
2.00	1.75
4.00	3.94
6.00	6.35
8.00	8.86
8.10	8.74
11.7	12.1
12.0	12.5
16.0	15.8
16.2	16.9

^aT = 25 °C, I = 0.10 M (maintained by HCl or HClO₄),
 $[\text{Ru}(\text{bpy})_3^{2+}] = (1.8 - 2.5) \times 10^{-5}$ M, $[\text{Ru}(\text{bpy})_3^{3+}] = 1 \times 10^{-5}$
M (typical concentration), $[\text{Co}(\text{NH}_3)_5\text{Br}^{2+}] = 0.01$ M.

Table AII-6 Rate Constants for the Reaction of $\text{Ru}(\text{bpy})_3^{3+}$
with $\text{CrCH}_2\text{OCH}_3^{2+}$ a

$10^4[\text{CrCH}_2\text{OCH}_3^{2+}]/\text{M}$	$10^{-3}k_{\text{obs}}/\text{s}^{-1}$
6.20	7.5
8.10	9.2
9.74	11.6
11.7	13.9
16.2	19.6

^aT = 25 °C, I = 0.10 M (maintained by HCl or HClO₄),
[Ru(bpy)₃²⁺] = (1.5 - 1.8) × 10⁻⁵ M, [Ru(bpy)₃³⁺] = 1 × 10⁻⁵
M (typical concentration), [Co(NH₃)₅py³⁺] = 0.005 M.

Table AII-7 Rate Constants for the Reaction of $\text{Ru}(\text{bpy})_3^{3+}$
with $\text{CrCH}(\text{CH}_3)_2^{2+}$ a

$10^4[\text{CrCH}(\text{CH}_3)_2^{2+}]/\text{M}$	$10^{-3}k_{\text{obs}}/\text{s}^{-1}$
1.09	3.06
5.51	19.1
8.27	36.2
10.8	48.6
14.2	56.7
15.8	69.0
21.0	89.5

^aT = 25 °C, I = 0.10 M (maintained by HCl or HClO₄),
[Ru(bpy)₃²⁺] = 2.6 × 10⁻⁵ M, [Ru(bpy)₃³⁺] = 1 × 10⁻⁵ M
(typical concentration), [Co(NH₃)₅Br²⁺] = 0.002 - 0.003 M.

Table AII-8 Rate Constants for the Reaction of $\text{Ru}(\text{bpy})_3^{3+}$
with $\text{CrCH}_2\text{CH}_3^{2+}$ ^a

$10^5[\text{CrCH}_2\text{CH}_3^{2+}]/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$
3.14	5.38
4.52	8.76
7.48	14.8
21.1	42.2
32.5	60.9
53.0	106
56.0	118
73.5	170
86.2	163
110	256
149	338
189	377

^a $T = 25$ °C, $I = 0.10$ M (maintained by HCl or HClO_4),
 $[\text{Ru}(\text{bpy})_3^{2+}] = (1.5 - 2.6) \times 10^{-5}$ M, $[\text{Ru}(\text{bpy})_3^{3+}] = 1 \times 10^{-5}$
M (typical concentration), $[\text{Co}(\text{NH}_3)_5\text{Br}^{2+}] = 0.002$ M.

Table AII-9 Rate Constants for the Reaction of $\text{Ru}(\text{bpy})_3^{3+}$
with $\text{CrCH}_2\text{CH}_3^{2+}$ a

$10^5[\text{CrCH}_2\text{CH}_3^{2+}]/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$
1.97	9.75
3.08	12.0
4.40	18.0
5.00	21.1
5.74	23.8
6.71	31
8.4	27.3
11.6	40.3

^a $T = 25\text{ }^\circ\text{C}$, $I = 0.10\text{ M}$ (maintained by HCl or HClO_4),
 $[\text{Ru}(\text{bpy})_3^{2+}] = 1.5 \times 10^{-5}\text{ M}$, $[\text{Ru}(\text{bpy})_3^{3+}] = 1 \times 10^{-5}\text{ M}$
 (typical concentration), $[\text{Co}(\text{NH}_3)_5\text{py}^{3+}] = 0.005\text{ M}$.

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