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KRIENS, Richard Duane, 1932–
EFFECTS OF METAL IONS IN FREE RADICAL
REACTIONS.

Iowa State University of Science and Technology
Ph.D., 1963
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

EFFECTS OF METAL IONS IN FREE RADICAL REACTIONS

by

Richard Duane Kriens

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
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1963

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PART I: REACTIONS OF RADICALS WITH METAL SALTS

INTRODUCTION

The purpose of this study was to determine the effects of metal salts on free radical reactions. More specifically, it was of interest to study the ability of metal salts to act as trapping agents for organic free radicals in solution, i.e., to see if they can remove radicals from solution. The metal salts studied were of the type $M^{+n} X_n$ where M is a metal with more than one common valence state, such as copper and iron, and where X is a group common to organic molecules, such as the halides and the cyano group. It was believed that these salts could trap the radicals by undergoing an oxidation-reduction reaction with the radical, i.e., a reaction of the type:

$$R\cdot + M^{+n} X_n \longrightarrow RX + M^{n-1} X_{n-1}$$

The amount of trapping could be determined by measuring the amount of RX and $M^{n-1} X_{n-1}$ formed. In the present work gas-liquid chromatography was used to measure the amount of RX formed. At the time this work was started, several examples of this type of reaction were known, but no systematic study had been made. Not only was there interest in finding which metals were effective in trapping radicals, but also there was interest in elucidating the mechanism of the trapping reaction.

REVIEW OF LITERATURE

Since the discovery of the reaction of cuprous chloride with benzene diazonium salts by Sandmeyer in 1884, there has been interest in the use of metal salts, both as reactants and catalysts, in organic chemistry. In the area of free radical chemistry, there has been considerable interest in the use of metal salts to generate free radicals and in the reaction of radicals with metal ions.

Perhaps the best known example of the use of metal salts to generate free radicals is the use of Fenton's reagent as a mild oxidizing agent. Fenton's reagent is a solution of hydrogen peroxide and ferrous sulfate. The manner in which it produces hydroxylations or dehyrogenations of species is given by the Haber-Weiss Mechanism (1)

$$H_2O_2 + Fe^{++} \longrightarrow HO\cdot + OH^- + Fe^{+++}$$

$$HO\cdot + Fe^{++} \longrightarrow OH^- + Fe^{+++}$$

$$HO\cdot + H_2O_2 \longrightarrow H_2O + HO_2\cdot$$

$$HO_2\cdot + H_2O_2 \longrightarrow H_2O + HO\cdot + O_2$$

In a similar manner, the ferrous ion induced decomposition of hydroperoxides takes place. That the first step produces an alkoxy radical is shown

$$Fe^{+2} + ROOH \longrightarrow (FeOH)^{+2} + RO\cdot$$

by the fact that this system can initiate polymerization of vinyl compounds and end group analysis of the polymer shows the presence of the alkoxy group (1, 2). Subsequent steps depend upon the environment. In the presence of a hydrogen donor, it will abstract a hydrogen atom

$$RO\cdot + SH \longrightarrow ROH + S\cdot$$

$$S\cdot \longrightarrow \text{Products}$$

If nothing is present that will absorb the alkoxy radical or donate a hydrogen atom, then one of the following takes place

$$RO\cdot + Fe^{++} \longrightarrow RO^{-} + Fe^{+++} \text{ (reduces chain length)}$$

$$R^1_3CO\cdot \longrightarrow R^1_2C{=}O + R^1\cdot \text{ (or } \longrightarrow R^1_2\dot{C}OR^1 \longrightarrow \text{dimer)}$$

$$R^1_3CO\cdot + R^1_3COOH \longrightarrow R^1OH + R^1_2C{=}O + R^1_3CO\cdot$$

The last equation illustrates a chain-sustaining process by which the alkoxy radical can induce decomposition of the hydroperoxide.

Some metal salts, notably those of cobalt, can initiate long chains because they can act as both reductants and oxidants. In the higher valence state, they act as oxidants

$$ROOH + Co^{+++} \longrightarrow ROO\cdot + H^{+} + Co^{++}$$

$$RO_2\cdot + Co^{+++} \longrightarrow R^{+} + O_2 + Co^{++}$$

If a hydrogen donor is present that can yield an alkyl radical by loss of a hydrogen atom, this reaction can be used to form dialkyl peroxides by the overall stoichiometric reaction (1, 2)

$$2\ RO_2H + SH \longrightarrow ROOS + ROH + H_2O$$

There has been considerable interest in recent years in the reaction of metal ions with radicals. Most of this interest has been in the use of copper and iron salts, particularly the former, and stems from interest in the elucidation of the mechanism of the Sandmeyer and related Meerwein Reaction as well as the facile substitution reactions of peroxides catalyzed by copper salts discovered by Kharasch _et al_. (3, 4, 5).

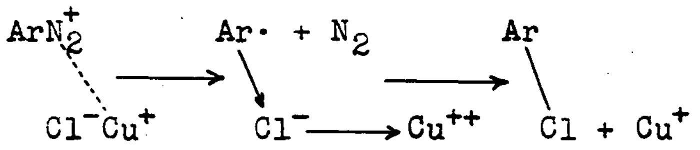
The Sandmeyer reaction

$$Ar\overset{+}{N}_2Cl^- \xrightarrow{Cu_2Cl_2} ArCl + N_2$$

(where Ar is an aryl group) was first postulated to involve a complex intermediate between the diazonium compound and the cuprous chloride with the chlorine in the final product coming from the cuprous chloride (6). Interest was renewed in the mechanism in 1941 when Hodgson _et al_. (7-10) postulated that CuX_4^{-3} (where X is Cl or Br) is the copper species involved and which forms an intermediate complex with the diazonium cation. It was also postulated that in this complex a free chlorine atom is formed by loss of an electron to the diazonium ion, evolution of nitrogen leaving an aryl radical, and a coupling of the aryl radical and chlorine atom. They found that $FeCl_3$, $CoCl_2$, and $CuCl_2$, would also work if the diazonium cation contained electron withdrawing groups and if heat were applied.

In contrast to this, Cowdry and Davies (11) found that $CuCl_2^-$ was the active copper species.

Waters (12, 13) favors a one electron transfer mechanism which is shown schematically as



These electron movements are envisioned as occurring in the immediate locus of a decomposing double diazonium salt $ArN_2^+,CuCl_2^-$ so that no free electrons and few free aryl radicals escape from the surrounding cage of solvent molecules. Evidence that some free radicals did escape was that several different aryl diazonium fluoroborates in dilute aqueous solution in the complete absence of oxygen would initiate polymerizations of acrylonitrile and methyl methacrylate. Polymerizations under such conditions cannot involve ionic mechanisms. If cupric or ferric salts were added to such polymerizations, the molecular weight of the polymer decreased. Furthermore, the yield of ArCl could be increased by addition of cupric chloride. This suggests that the reaction

$$Ar\cdot + CuCl_2 \longrightarrow ArCl + CuCl$$

is important.

Further evidence for the radical mechanism was given by Kochi (14) and Dickerman *et al*. (15). In each case, a reaction between a free radical and cupric chloride was said to be involved in the mechanism.

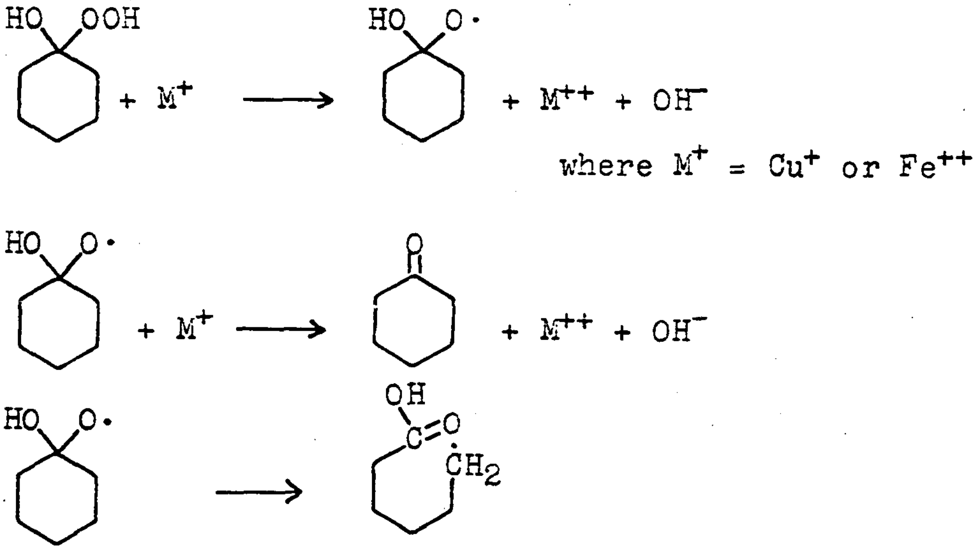
The Meerwein Reaction

$$ArN_2^+Cl^- + R_2C{=}CR_2 \xrightarrow{Cu_2Cl_2} Ar\text{-}CR_2CR_2Cl$$

is similar to the Sandmeyer reaction. This reaction was studied by Kochi (16-18) and it first was thought to go by an ionic mechanism and involved a pi-complex between the olefin and the cuprous salt (17). Later he favored a radical mechanism (18).

An instance wherein a radical reacted with ferric chloride was in the polymerization of acrylonitrile, methacrylonitrile, and styrene in N,N-dimethylformamide at 60° reported by Bamford et al. (19). The ferric chloride entered into the termination step and was reduced to ferrous chloride. The styryl radicals were much more reactive toward the ferric chloride than the other two. In fact, they were so reactive that this reaction caused an induction period. Later, they discuss this in terms of resonance contributions in the transition state and in this case feel the transition state involves contributions from the resonance structures (20) $R\cdot Fe^{+3} \longleftrightarrow R^{+}Fe^{+2}$.

In somewhat the same manner, Minisci and his coworkers (21-25) have developed the synthesis of ω-chlorohexanoic acids from cyclohexane. They state that the chlorine is added by reaction of a chlorinated ferric species. They draw an anology with the Sandmeyer reaction not only for the mechanism, but also from the fact that the experimental procedure is practically identical. The actual reactions studied are the reactions of 1-hydroxycyclohexyl hydroperoxide and 1-hydroxy-1'-hydroperoxycyclohexylperoxide which are obtained from cyclohexanone and hydrogen peroxide. The reaction is performed by adding the peroxide to an aqueous hydrohalic acid containing ferrous or cuprous salts. The mechanism given is similar to that given by Kochi which will be discussed later. In reactions where no halide ions are present, the products are different for the ferrous and cuprous salts. In the cuprous case, it appears that it can readily reduce the radical and thus prevent dimerization which occurs extensively with the ferrous salt.



where $M^+ = Cu^+$ or Fe^{++}

$$2\ HOOC(CH_2)_4CH\cdot_2 \longrightarrow HOOC-(CH_2)_{10}-COOH$$

(occurs only with ferrous salt)

$$HOOC(CH_2)_4-CH\cdot_2 + M^+ + H_2O \longrightarrow HOOC(CH_2)_4CH_3 + M^{++} + {}^-OH$$

The last equation represents the important step when $M^+ = Cu^+$, but is only of minor importance when $M^+ = Fe^{++}$.

From a series of reactions with alpha substituted cyclic peroxides and unsymmetrical acyclic 1-hydroxyhydroperoxides, it was found in the case of the cyclic compound, that the ring opened between the carbon containing the alkoxy radical and the most substituted adjacent carbon atom, and in the case of acyclic compound, cleavage to give an alkyl radical took place between the carbon containing the alkoxy-radical and the adjacent carbon atom containing the fewest hydrogens.

This reaction has been extended to include other groups besides halides, notably azides and cyanides. They have also found that under similar conditions t-butyl hydroperoxide in the presence of butadiene leads to addition of the _t_-butoxy radical to the end carbon followed by addition of chlorine to give either 1,4 or 3,4 addition (azide and thiocyanate give only 1,4 addition). Using radicals generated from several 1-hydroxy-hydroperoxides in the presence of acrylonitrile or acrylic acid ester, addition of the radical takes place at the carbon atom beta to the cyano and carboxy group.

Kovacic _et al_. (26, 27) have studied the reaction of ferric chloride with alkylbenzene and alkanes to give various products and reduction of ferric chloride to ferrous chloride. These reactions are believed to proceed via an ionic mechanism.

The first report in the literature of a study of the use of ferric chloride and cupric chloride as radical traps was by Kumamoto et al. (28), although at the time of their publication many of the important reactions involving cupric and ferric chloride reported in this thesis had already been carried out (see Results and Discussion for Part I). They ran a series of reactions with different radicals and either cupric chloride or ferric chloride in which significant yields of alkyl chlorides are reported in each case. At the time, they favored a mechanism involving a chlorine-bridged transition state in which chlorine is transferred to an alkyl radical by an oxidizing metal ion. They draw an analogy with the results of Taube's study (29) of some inorganic one electron oxidation-reduction reactions.

The discovery by Kharasch et al. (3, 4, 5) that small amounts of copper salts have a marked effect on rates and products of well known free radical reactions has aroused interest in the mechanism of this reaction. In the presence of terminal olefins, they found that the decomposition of peresters led only to the unrearranged secondary allylic esters. From this they felt that the abstraction of the allylic hydrogen must take place in a concerted manner. Otherwise, an allylic radical formation would give rise to a mixture of allylic olefins. Similar results were reported by Denney et al. (30). However, the stereoselectivity reported by these workers was shown not to be a general phenomenon by Kochi (31, 32). He found that 1-butene and 2-butene (55% cis, 45% trans) reacted with t-butyl perbenzoate catalyzed by cuprous bromide led to the same yield of butenyl benzoates having the same ratio of 1 and 3 substituted butenes (12% crotyl benzoate:88% 3-benzoyloxy-1-butene). Later work by Denney et al. (33) with tri- and tetramethylethylene under similar conditions also led predominately to the less thermodynamically stable 3-benzoyloxy substituted butene. Kochi (32, 34) gives the following general mechanism to explain some of the apparent dissimilarities among these reactions:

$$\mathrm{XOOY} + \mathrm{Cu}^{\mathrm{I}} \longrightarrow \mathrm{XOCu}^{\mathrm{II}} + \mathrm{YO}\cdot \qquad (1)$$

$$\mathrm{RH} + \mathrm{YO}\cdot \longrightarrow \mathrm{R}\cdot + \mathrm{YOH} \qquad (2)$$

$$\mathrm{R}\cdot + \mathrm{XOCu}^{\mathrm{II}} \longrightarrow \mathrm{ROX} + \mathrm{Cu}^{\mathrm{I}} \text{ etc.} \qquad (3)$$

For step 1 the case where the peroxide is a hydroperoxide has been discussed earlier in this section. The case where disubstituted peroxides are involved is less well documented but does occur by such a reaction (34) -- usually much slower and sometimes requiring heat. With unsymmetrical peroxides, two modes of reduction are possible.

$$\mathrm{XOOY} + \mathrm{M}^{+n} \longrightarrow \begin{cases} \xrightarrow{a} \mathrm{XOM}^{n+1} + \mathrm{YO}\cdot \\ \xrightarrow{b} \mathrm{YOM}^{n+1} + \mathrm{XO}\cdot \end{cases}$$

In the case of t-butyl perbenzoate ($X = t\text{-BuO}$, $Y = C_6H_5CO_2$), the path (b) giving t-butoxy radicals is the one commonly observed.

The radicals formed in step 2 depend on what kind of compound is present and on the attacking radical. In the case of olefins, either chain transfer by hydrogen abstraction or radical addition to the double bond is possible. The relative rates of each reaction is a function of the alkoxy radical structure. t-Butoxy radicals from t-butyl peresters react with butenes primarily by hydrogen abstraction (34) while benxoyloxy radicals from benzoyl peroxide react with butenes primarily by addition (35). If a suitable chain transfer agent is absent, the alkoxy radicals cleave to form a stable product and another radical which can react with the oxidizing metal by step 3.

Step 3, which is a redox reaction between a radical and a cupric salt, has been described in terms of ligand transfer and electron transfer processes (32, 34, 36-39). In ligand transfer, a bridged ligand is involved in the transition state and can be depicted as

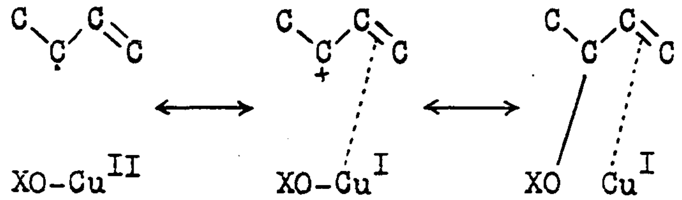
$$\left[R\cdot X \text{———} Cu^{II} \longleftrightarrow R\text{–}XCu^{I}\right]$$

Most carbon radical types that were studied can take part in such reactions, but the ligand being transferred is very important. Bromine and chlorine are very effective while sulfates and perchlorates are not. In electron transfer, an electron is supposed to transfer from the free radical to the cupric salt. Hence there is a transition state with a high degree of carbonium ion character. This can be depicted as

$$\left[R^{+}YCu^{I} \longleftrightarrow R\cdot YCu^{II}\right]$$

Actually, these are thought to be the two extreme modes of reaction and that most reactions catalyzed by copper salts involve some hybrid of the two. In ligand transfer, bond making between free radical and ligand is an important part of the driving force of the reaction and in electron transfer, formation of a carbonium ion is one of the controlling factors. The degree to which each participates in a particular system depends on the ligand being transferred as well as the ionization potential of the intermediate free radical. The electron transfer mechanism is probably most important with radicals that can lead to resonance stabilized carbonium ions and cupric salts with poor ligand transfer properties.

The copper catalyzed reaction of butenes with peresters is an example of a case in which both ligand transfer and electron transfer contributions must be considered in the transition state. Kochi (32, 37) pictures the transition state as an electron transfer-ligand transfer hybrid



To show that this cannot be exclusively an electron transfer process, he used a complexed (fully coordinated) copper catalyst as the copper salt and found that the allylic isomer ratio had been diastically changed (37) (the ratio of the isomers was now around one). The reaction with the complexed copper salt is cited as a true example of an electron transfer process and that an allylic carbonium ion is actually formed.

$$\underline{t}\text{-BuOOX} + \text{Cu}^{I}(\text{phen})n \longrightarrow \underline{t}\text{-BuO}\cdot + \text{Cu}^{II}(\text{phen})n + \text{XO}^{-}$$

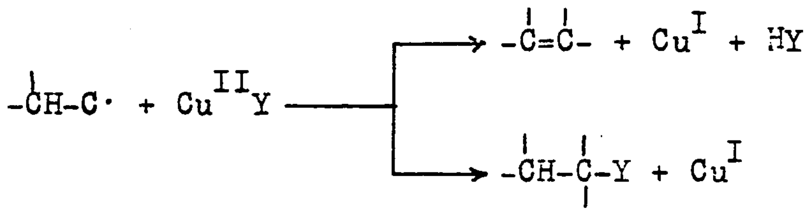
$$\underline{t}\text{-BuO}\cdot + C_4H_8 \longrightarrow \underline{t}\text{-BuOH} + C_4H_7\cdot$$

$$C_4H_7\cdot + \text{Cu}^{II}(\text{phen})n \longrightarrow C_4H_7^{+} + \text{Cu}^{I}(\text{phen})n \qquad \text{etc.}$$

where phen is 1,10-phenanthroline.

The best model for ligand transfer is the halide transfer between metal halides and carbon free radicals such as observed by Kumamoto et al. (28).

Alkyl free radicals were observed to reduce inorganic oxidizing agents by Haines and Waters (40). Where these alkyl radicals possess beta hydrogens, they may be oxidized by electron transfer and undergo either an elimination or a substitution reaction



$$-\overset{|}{C}H-C\cdot + \text{Cu}^{II}Y \longrightarrow \begin{cases} -\overset{|}{C}=\overset{|}{C}- + \text{Cu}^{I} + \text{HY} \\ -\overset{|}{C}H-\underset{|}{\overset{|}{C}}-Y + \text{Cu}^{I} \end{cases}$$

Elimination takes place most readily with primary alkyl radicals. The amount of substitution increases in the order ethyl < sec-butyl < t-butyl < allyl. The amount of substitution product appears to increase as the ionization potential decreases, or it can be stated that the more stable the radicals or the incipient carbonium ion formed, the more probable that the products will be those expected from the solvolsis of a classical carbonium ion (39). Thus, oxidation of ethyl and *t*-butyl radicals by cupric sulfate in water leads to ethylene and *t*-butanol respectively (in methanol, ethylene and *t*-butyl methyl ether form respectively). Whether the reaction goes by a two-step mechanism involving a carbonium ion or two concurrent reactions having a similar transition state cannot be decided. Individual cases can be found which favor each mechanism. However, Kochi (38, 39) seems to favor the idea of related transition states in which resonance contributions from ligand transfer and electron transfer vary with the structure of the radical and the identity of the metal species and counter ions.

Walling (41) has proposed a mechanism for the copper-catalyzed reaction of peresters with hydrocarbons similar to that proposed by Kochi (also see footnote 6 of reference 33).

$$CH_3COOOC(CH_3)_3 + Cu^{I} \longrightarrow CH_3CO_2^- + Cu^{II} + (CH_3)_2CO\cdot \quad (4)$$

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \quad (5)$$

$$R\cdot + Cu^{II} \longrightarrow R^+ + Cu^{I} \quad (6a)$$

$$R^+ + CH_3CO_2^- \longrightarrow RO_2CCH_3 \quad (6b)$$

$$\text{or} \quad R\cdot + Cu^{II}O_2CCH_3 \longrightarrow RO_2CCH_3 + Cu^{I} \quad (7)$$

He reports that the relative reactivities of seven hydrocarbons (olefins and aralkyl compounds) in the t-butyl peracetate and t-butyl perbenzoate reactions is the same as in t-butyl hypochlorite chlorination. He strongly favors an electron transfer to give a realtively free carbonium ion over a ligand transfer although the distribution of allylic acetates is essentially the same as reported by Kochi. He does not believe that the results with the complexed copper is necessarily indicative of the results expected from a free carbonium ion. Another argument in favor of a relatively free carbonium ion is the observation of 1,2 alkyl shifts in several instances. When t-butyl peracetate is treated with 6,6-dimethyl-1,3-cyclohexadiene, a 6% yield of o-xylene is found, but none when either perester or copper is not used. Another case of an apparent 1,2 shift is in the copper catalyzed decomposition of 2,4,4-trimethyl-2 pentyl hydroperoxide which gave some 2-methyl-2-butene and 2-methyl-1-butene. Actually, the latter example is consistent with Kochi's work on oxidation of alkyl radicals generated in a similar manner (39) which would form a carbonium ion by electron transfer. This argument is based on evidence that radical rearrangements occurring via 1,2-shifts do not compete with other radical processes at ordinary temperatures.

RESULTS AND DISCUSSION

Radicals were generated in the presence of metal salts to ascertain whether such salts have the ability to trap free radicals. Since such trapping would occur as an oxidation-reduction reaction, the metal had to be one with more than one common valence state. The obvious metals which fit this requirement are the transition metals. In addition to these metals, the elements phosphorus and sulfur also have several common valence states and several compounds of each were used. As a radical source, it was decided to use the 2-cyano-2-propyl radical because it was simple to generate in solution. The source of this radical, 2,2'-azo-bis-isobutyronitrile (henceforth designated as AIBN), is commercially available and easily purified.

The amount of trapping of the radicals by the metal salts can be determined by product analysis. Ideally, this would include analysis of both the organic products and the amount of the metal in the reduced state. Unfortunately, quantitative analysis of metals in mixtures containing organic residues is difficult or impossible without removing these residues. Removal of the organic residues is again almost impossible without affecting the valence state of the metals. This point was evident from the first reaction run using cupric salts when standard methods of analysis for copper gave impossible results. Fortunately, quantitative analysis of the organic products by use of gas-liquid chromatography (henceforth designated as GLC) is possible and this method was used.

The results of the decomposition of AIBN in the presence of various metal salts in benzene at 80^o is given in Table 1. It will be noticed that in several cases metal salts of the lower valence state were also run. It was gratifying to find that in those cases where salts of the higher valence state were able to trap some of the radicals, the corresponding lower valence salts did not. (Sulfur would appear to be an exception, but due to the nature of the sulfur compounds, they probably should not be compared with the others.) In most cases, identification of the product due to radical trapping is based solely on retention time compared to a known compound. In the case for cupric chloride dihydrate, one reaction was run on a large scale and the 2-chloro-2-cyanopropane isolated and its physical constants and infrared spectrum compared with 2-chloro-2-cyanopropane synthesized independently (see Experimental section). In some cases where the expected product was not available, a new peak (or lack of one) was taken to be that of the product due to trapping. In view of the results with the phenyl radical and ferric thiocyanate (Table 7), the assumption that lack of a new peak indicated no product due to trapping might be questioned.

Except in those cases where the metal compound was a

Table 1. Comparison of yields of $(CH_3)_2C(CN)X$ (designated RX in table) from reaction of compounds of type MX_n with 2-cyano-2-propyl radicals formed from decomposition of AIBN at 80° in benzene[a]

Compound $M^{+n}X_n$	Moles AIBN x 10^2	Moles MX_n x 10^2	Moles RX formed x 10^3[b]	% yield of RX	Type of reaction mixture
CCl_4	6.10	3.05	0	0	homogeneous[c]
CH_3COCl	2.82	1.41	0	0	homogeneous
PCl_5	2.44	1.22	15.8	64.8	heterogeneous
PCl_3	2.29	1.15	0	0	homogeneous[d]
$POCl_3$	2.18	1.09	0	0	homogeneous
S_2Cl_2	2.50	1.25	11.9	48.6	homogeneous
SCl_2	3.14	1.57	9.37	29.8	homogeneous
$SOCl_2$	2.46	1.23	7.17	29.1	homogeneous
	2.46	1.23	5.33	21.6	homogeneous
$TiCl_4$	12.2	6.10	1.79	1.47	homogeneous
$TiCl_3$	3.04	1.52	0[e]	0	heterogeneous
VCl_4	1.88	0.94	1.74	9.24	hemogeneous[f]

---

[a] Except where indicated 200 ml of benzene were used.

[b] GLC conditions I used for analysis, except where indicated.

[c] 190 ml benzene used.

[d] 190 ml of benzene used.

[e] GLC conditions V used for analysis.

[f] 210 ml of benzene used.

Table 1. (Continued)

Compound $M^{+n}X_n$	Moles AIBN$_2$ x 10^2	Moles MX_{n_2} x 10^2	Moles RX formed x 10^3	% yield of RX	Type of reaction mixture
$CrCl_3 \cdot 6H_2O$	2.44	1.22	0	0	heterogeneous
$Cr(acac)_3$[g]	2.44	1.22	0	0	heterogeneous
$FeCl_3 \cdot 6H_2O$[h]	2.44	1.22	11.3	46.3	heterogeneous
$FeCl_3$[h]	2.44	1.22	4.36	17.9	heterogeneous
$Fe(OCH_3)_3$	>3.44	1.72	0	0	homogeneous[i]
$Fe(OCH_2CH_3)_3$	>3.66	1.83	0	0	homogeneous[i]
$Fe(acac)_3$[g]	2.44	1.22	0	0	heterogeneous
$Fe(SCN)_3$	1.93	0.61	0[e]	0	heterogeneous[j]
$(CO(NH_3)_6)Cl_3$	2.22	1.22	0	0	heterogeneous
$(CO(NH_3)_5H_2O)Cl_3$	2.44	1.22	0	0	heterogeneous
$(CO(NH_3)_5Cl)Cl_2$	2.44	1.22	0	0	heterogeneous
$CO(acac)_3$[g]	2.44	1.22	0	0	heterogeneous
$CuF_2 \cdot 2H_2O$[k]	2.44	1.22	0	0	heterogeneous
$CuCl_2 \cdot 2H_2O$[h]	2.44	1.22	5.22	21.4	heterogeneous
$CuCl_2$	2.44	1.22	2.72	11.2	heterogeneous

---

[g] acac is acetylacetonate moiety.

[h] One of several runs, see Table 2.

[i] 250 ml of benzene used.

[j] 100 ml of benzene used.

[k] Reaction run in 200 ml pyridine.

Table 1. (Continued)

Compound $M^{+n}X_n$	Moles AIBN x 10^2	Moles MX x 10^2	Moles RX formed x 10^3	% yield of RX	Type of reaction mixture
$CuCl_2\cdot 2Py$	2.44	1.22	15.1	62.0	heterogeneous
$LiCuCl_3\cdot H_2O$	0.625	0.312	0	0	heterogeneous
$CuBr_2$	2.44	1.22	6.25	25.6	heterogeneous[l]
	4.88	1.22	11.1	45.5	heterogeneous
$Cu(CH_3CO_2)_2\cdot H_2O$	2.44	1.22	0	0	heterogeneous
$Cu(CN)_2$	2.60	1.22	0	0	heterogeneous
$Cu(OCH_3)_2$	2.44	1.22	0[e]	0	heterogeneous
$MoCl_5$	2.44	1.22	3.80	15.6	heterogeneous
$MoCl_3$	2.44	1.22	0	0	heterogeneous
$AgCl$	7.32	3.56	0	0	heterogeneous[l]
AgF_2[m]	2.44	1.22	1.56	6.39	heterogeneous
$SnCl_4\cdot 5H_2O$	4.88	1.22	0	0	heterogeneous
$SnCl_4$	2.60	1.30	0	0	homogeneous
$SbCl_5$	2.35	1.18	8.95	29.6	homogeneous
SbF_5	2.75	1.38	0	0	homogeneous
$TeCl_4$	1.86	0.93	6.98	37.6	heterogeneous
$HgCl_2$	9.74	4.87	0	0	heterogeneous
$HgCl$	2.44	1.22	0	0	heterogeneous

---

[l] 230 ml benzene used.

[m] Reaction run in 200 ml benzotrifluoride.

Table 1. (Continued)

Compound $M^{+n}X_n$	Moles AIBN $\times 10^2$	Moles MX $\times 10^2$	Moles RX formed $\times 10^3$	% yield of RX	Type of reaction mixture
$Hg(CH_3CO_2)_2$	2.44	1.22	0	0	heterogeneous
$Pb(CH_3CO_2)_4$	1.22	0.61	0	0	heterogeneous

liquid, they were not soluble in benzene and hence these were heterogeneous reaction mixtures. The reaction mixture was stirred at the same rate in all reactions, but no attempt was made to see if the rate of stirring had any effect on the amount of trapping that occurred. Even under identical reaction conditions, duplicate experiments were not very reproducible (see Table 3). This is attributed to the heterogeneous reaction conditions since in those reactions run in other solvents where the solubility of the metal salts was greater, the reproducibility was much better (see Table 4). It is also apparent that the anion of the salt is important and this will be discussed later.

Since the trapping occurs with a reduction of the metal, it would be expected that there should be a good correlation between the amount of trapping and the reduction potential of the metal. Such a comparison is difficult to make since the known reduction potentials have been determined in aqueous solution. Even in aqueous solution, the value of the reduction potential depends on the reaction conditions. For example, values of the reduction potential for silver of 0.779, 0.344, 0.222, 0.073, and -0.151 can be found depending on whether halides are present and if the reaction medium is acidic or basic (42). A comparison between yields of chloride compounds and reduction potentials is given in Table 2, where the elements are listed in order of increasing reduction potential. The couple was picked that most closely resembled the actual conditions used here. For copper, silver, and cobalt, reduction potentials for two couples have been included. While no clear-cut correlation is found, it is interesting to observe that chlorides of antimony and tellurium, which have about the same reduction potential as copper, are effective in trapping radicals. Earlier, Waters had remarked that perhaps the reason cuprous salts were so effective in the Sandmeyer reaction was that cuprous copper had just the right oxidation potential for the release of an electron under Sandmeyer conditions (12).

It was also thought that there might be some correlation between the electronegativity of an element and the ability of its salts to act as radical traps. Column 4 of Table 2 gives the values for the electronegativities of the elements. A study of the last two columns will show that there is no apparent relationship between the electronegativity and the amount of trapping.

Table 2. Comparison of yields of 2-chloro-2-cyanopropane with the reduction potential and electronegativity of the metals used

Element	Couple	Reduction potential[a]	Electro-negativity[b]	% yield 2-chloro-2-cyanopropane
Cr	$Cr^{+3} + e = Cr^{+2}$	-0.41	1.56	0
P	$H_3PO_4 + 2H^+ + 2e = H_3PO_3$	-0.276	2.06	64.8
Mo	$MoO_2^+ + 4H + 2e = Mo^{+3} + 2H_2O$	ca. 0.0	1.30	15.6
Ti	$TiO_2 + 4H^+ + e = Ti^{+3} + H_2O$	0.1	1.32	1.47
Co	$Co(NH_3)_6^{+3} + e = Co(NH_3)_6^{+2}$	0.1	1.70	0
C	$C + 4H^+ + e = CH_4$	0.13	2.50	0
Sn	$Sn^{+4} + 2e = Sn^{+2}$	0.15	1.72	0
Cu	$Cu^{++} + e = Cu^+$	0.153	1.75	21.4
Ag	$AgCl + e = Ag + Cl^-$	0.222	1.42	0
Hg	$HgCl_2 + 2e = 2Hg + 2Cl^-$	0.268[c]	1.44	0

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[a] Values from Latimer, Wendell M., The Oxidation States of the Elements and their Potentials in Aqueous Solution, 2nd Ed., New York, N. Y., Prentice-Hall, Inc., 1952.

[b] Values from Day, M. Clyde, Jr. and Joel Selbin, Theoretical Inorganic Chemistry, New York, N. Y., Reinhold Publishing Corp., 1962.

[c] Values from Lange, Norbert Adolph, Handbook of Chemistry, 10th Ed., Sandusky, Ohio, Handbook Publishers, Inc., 1961.

Table 2. (Continued)

Element	Couple	Reduction potential	Electro-negativity	% yield 2-chloro-2-cyanopropane
V	$VO^{+2} + 2H^{+} + e = V^{+3} + H_2O$	0.361	1.45	9.24
Sb	$Sb_2O_5 + 4H^{+} + 2e = Sb_2O_4 + H_2O$	0.48	1.82	29.6
Cu	$Cu^{+2} + Cl^{-} + e = CuCl$	0.538	1.75	21.4
Te	$TeCl_6^{-2} + 4e = Te + 6Cl^{-}$	0.55	2.01	37.6
Fe	$Fe^{+3} + e = Fe^{+2}$	0.771	1.64	46.3
Ag	$Ag^{+} + e = Ag$	0.779	1.42	0
Hg	$2Hg^{+2} + 2e = Hg_2^{+2}$	0.920	1.44	0
S	$S_2Cl_2 + 2e = 2S + 2Cl^{-}$	1.23	2.44	48.6
Pb	$Pb^{+4} + 2e = Pb^{+2}$	1.69[c]	1.55	0
Co	$Co^{+3} + e = Co^{+2}$	1.82	1.56	0
Ag	$Ag^{+2} + e = Ag^{+}$	1.98	1.42	6.39[d]

[d] Reaction run with AgF_2 in benzotrifluoride, this is yield of 2-fluoro-2-cyanopropane.

It will be noticed from Table 3 and Figures 1 and 2 that the neutral ligands (water and pyridine (Py) in the case of copper) coordinated with the metal salt effect the ability of the salt to act as a radical trap. It will be noticed that water as a ligand increases the amount of trapping that occurs with both ferric and cupric chlorides although it is much more evident in the ferric chloride case.

This is a reflection of the manner in which metal salts act as radical traps. The effect of ligands is to increase the electron density around the metal atom and thus the chloride ions are less strongly attracted to the metal. This enables a more facile formation of a bridge between the chlorine and the radical and reaction by ligand transfer is accomplished. In the case of the dipyridene copper chloride, a second factor that can be involved is the possibility of the formation of a pi-complex between the radical and the pyridine which will hold the radical in the proximity of the chlorine until it can form a chlorine bridge to bring about ligand transfer. Although such pi-complexes have not been postulated for the 2-cyano-2-propyl radical, an analogy can be made with the use of such complexes by Russell to explain the solvent effects in the chlorinations of hydrocarbons (43). From all indications, the three different copper salts are soluble to the same extent in benzene (little, if any goes into solution) so in this case the increase in yield cannot

Table 3. Comparison of yields of 2-chloro-2-cyanopropane from decomposition of AIBN at 80° in benzene[a] containing cupric and ferric chlorides at different halide:AIBN ratios

MX_n	Moles $MX_n \times 10^2$	Moles AIBN $\times 10^2$	Ratio	Moles RX formed $\times 10^3$	% yield RX
$CuCl_2 \cdot 2H_2O$	1.22	1.22	1	0.613	2.51
	1.22	1.22	1	0.958	3.94
	2.44	2.44	1	7.03	14.4
	1.22	0.61	2	0.847	6.94
	2.44	1.22	2	5.22	21.4
	2.44	1.22	2	0.767	3.14
	3.66	1.83	2	4.99	13.6
	4.88	2.44	2	8.01	16.4
	6.01	3.05	2	21.4	35.0
	4.88	1.22	4	6.21	25.4
	6.10	1.22	5	5.43	22.2
	7.32	1.22	6	9.42	38.5
	8.54	1.22	7	6.47	26.5
	9.76	1.22	8	7.48	30.6
	9.76	1.22	8	9.02	36.9
	12.2	1.22	10	9.17	37.6
$CuCl_2$	1.22	1.22	1	4.39	18.0
	2.44	1.22	2	2.72	11.2

---

[a] 200 ml. benzene used in each reaction.

Table 3. (Continued)

MX_n	Moles $MX_n \times 10^2$	Moles AIBN $\times 10^2$	Ratio	Moles RX formed $\times 10^3$	% yield RX
$CuCl_2$	2.44	1.22	2	2.64	10.8
	4.88	1.22	4	4.79	19.6
$CuCl_2 \cdot 2Py$	1.22	1.22	1	9.49	38.9
	2.44	1.22	2	15.1	62.0
	4.88	1.22	4	14.4	58.9
	9.76	1.22	8	14.4	58.9
$FeCl_3 \cdot 6H_2O$	1.22	1.22	1	9.96	40.8
	1.22	1.22	1	11.1	45.6
	2.44	2.44	1	19.8	40.7
	9.74	4.87	2	46.2	47.4
	2.44	1.22	2	11.3	46.3
	4.88	1.22	4	11.9	49.0
	9.76	1.22	8	12.4	50.9
$FeCl_3$	1.22	1.22	1	4.27	17.5
	2.44	1.22	2	4.36	17.9
	4.88	1.22	4	8.33	34.1

be attributed to solubility. Anhydrous ferric chloride is known to form _pi_-complexes with benzene so it is more soluble in benzene than the hydrated ferric chloride.

It does appear that solubility is important as can be

Figure 1. Dependence of yields of 2-chloro-2-cyanopropane on coordinated neutral ligand of cupric chloride; reactions run in benzene at 80° and reaction mixture heterogeneous; 0.0122 moles AIBN in 200 ml benzene used in each case

△ $CuCl_2\cdot 2Py$

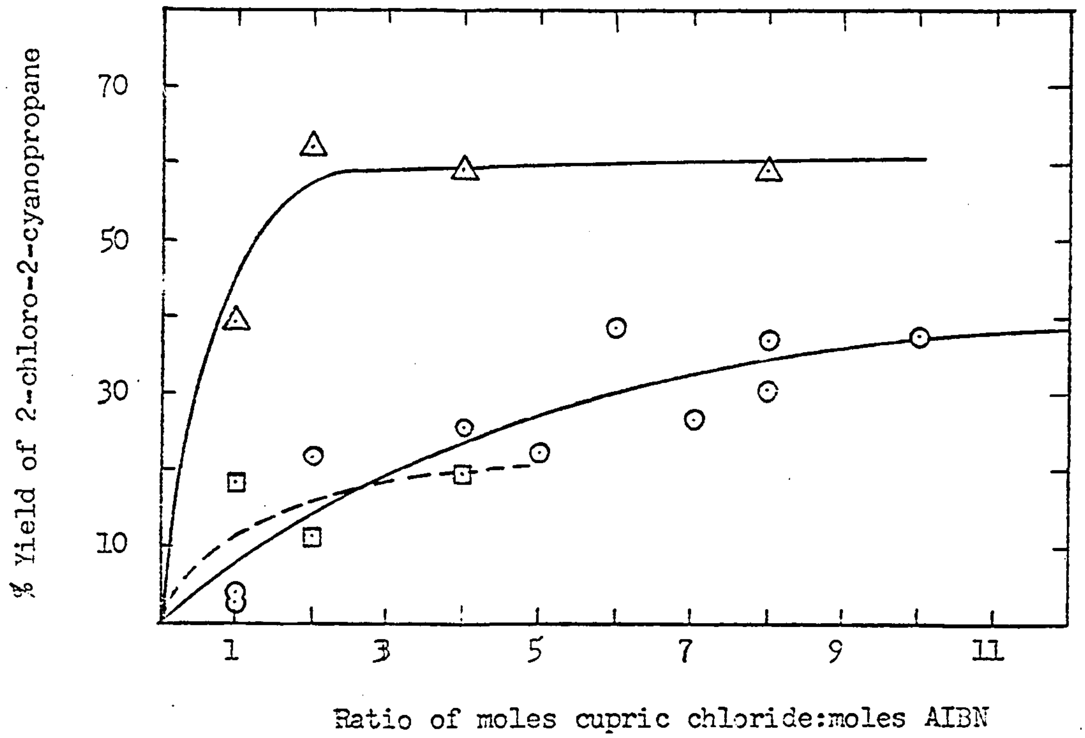
⊙ $CuCl_2\cdot 2H_2O$

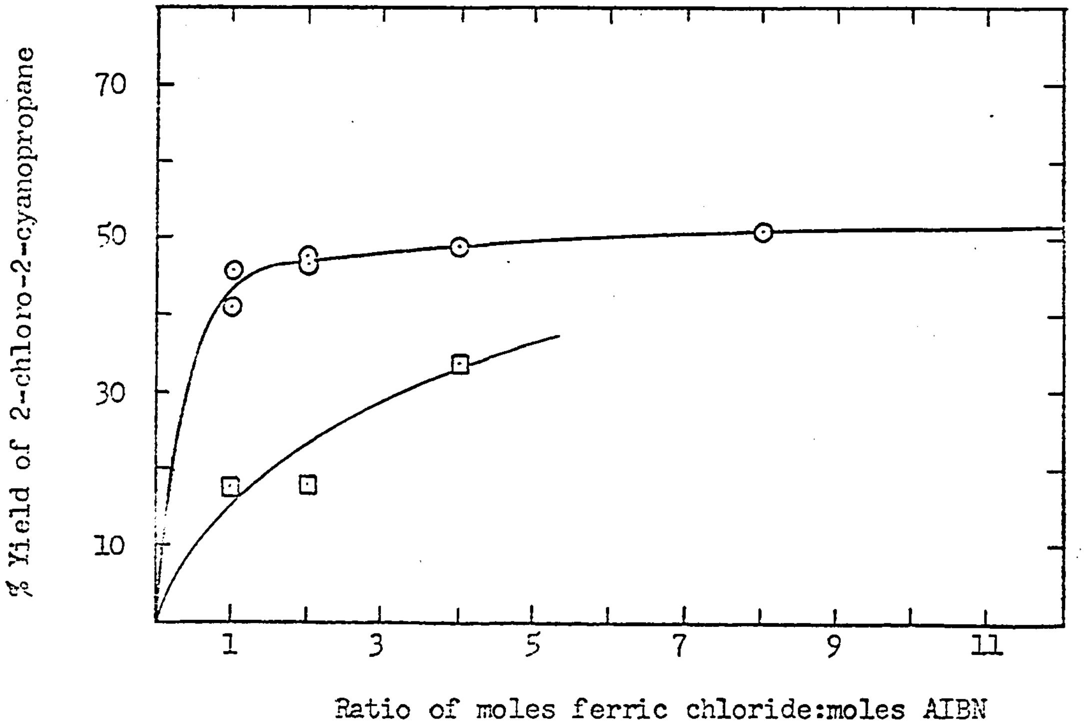
⊡ $CuCl_2$

Figure 2. Dependence of yields of 2-chloro-2-cyanopropane on coordinated neutral ligand of ferric chloride; reactions run in benzene at 80° and reaction mixture heterogeneous; 0.0122 moles AIBN in 200 ml benzene used in each case

⊙ $FeCl_3\cdot 6H_2O$

⊡ $FeCl_3$


% Yield of 2-chloro-2-cyanopropane
70
50
30
10
1
3
5
7
9
11
Ratio of moles cupric chloride:moles AIBN


% Yield of 2-chloro-2-cyanopropane
70
50
30
10
1
3
5
7
9
11
Ratio of moles ferric chloride:moles AIBN

seen from Tables 4 and 5 and Figures 3 and 4. Cupric chloride is fairly soluble in acetonitrile at 80°, but it is doubtful if the solubility in acetonitrile exceeds that in isopropanol. Yet the amount of trapping in acetonitrile is significantly higher than in isopropanol. It is known from the work of Hammond et al. (44) that the efficiency of radical production by AIBN is solvent dependent, but the highest efficiency factor reported was 0.75. Cupric chloride diacetonitrile can be isolated and undoubtedly exists in acetonitrile solution. Since the cyano group is a good complexing agent, the high amount of radical trapping by cupric chloride in acetonitrile is further evidence for the importance of a pi-complex between radical and neutral ligand coordinated with copper.

It was expected that the radicals that were not trapped by the cupric chloride would dimerize to form tetramethylsuccinonitrile (henceforth designated TMSN). A check of this showed that only with the reactions using cupric chloride in acetonitrile did these two reactions come close to accounting for all the radicals produced. The results for selected experiments are given in Table 6. Some of the missing radicals undoubtedly could be accounted for by a disproportionation process to give isobutyronitrile and methacrylonitrile. These compounds were qualitatively observed in the reactions in benzene, but the actual amounts of the two would account for less than 10% of the radicals. No attempt was made to

Table 4. Comparison of yields of 2-chloro-2-cyanopropane from decomposition of AIBN at 80° in several solvents[a] containing $CuCl_2$ at several different $CuCl_2$:AIBN ratios

Moles $CuCl_2$ x 10^2	Moles AIBN x 10^2	Moles 2-chloro-2-cyanopropane x 10^3					
		Benzene	Solvent	*i*-PrOH	Solvent	CH_3CN	Solvent
1.22	1.22	4.39	18.0%				
2.44	1.22	2.72	11.2%	14.5	59.5%	14.6	59.8%
						20.5	84.0%
2.44	1.22	2.64	10.8%	14.2	58.3%	19.8	81.4%
4.88	1.22	4.79	19.6%	13.6	55.9%	19.4	79.4%
4.88	1.22			14.4	59.0%		
9.76	1.22			14.5	59.5%	20.2	82.4%

[a] 200 ml. of solvent used in each case.

Table 5. Comparison of yields of 2-chloro-2-cyanopropane from decomposition of AIBN at 80° in several solvents[a] containing $FeCl_3$ at several different $FeCl_3$:AIBN ratios

Moles $FeCl_3$ x 10^2	Moles AIBN x 10^2	Moles 2-chloro-2-cyanopropane x 10^3					
		Benzene	Solvent	*i*-PrOH	Solvent	CH_3CN	Solvent
1.22	1.22	4.27	17.5%				
2.44	1.22	4.36	17.9%	12.7	52.1%	10.6	43.9%
4.88	1.22	8.33	34.1%	14.4	59.0%		
9.76	1.22			12.0	49.4%		
9.76	1.22			16.1	65.9%		

[a] 200 ml. of solvent used in each case.

Figure 3. Dependence of yields of 2-chloro-2-cyanopropane on the solvent in reactions run with cupric chloride at 80°; ability to solvate $CuCl_2$ is in the order isopropanol $\geq$ acetonitrile $\gg$ benzene; 0.0122 moles AIBN per 200 ml. solvent in each case

⊙ Acetonitrile

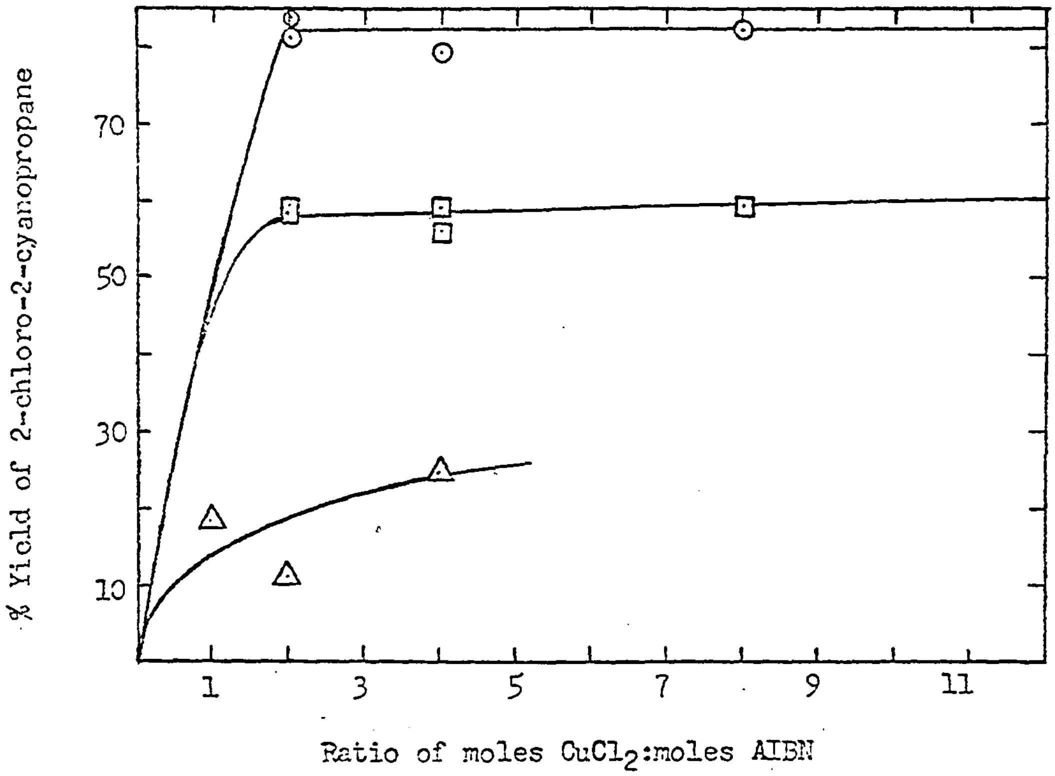
□ Isopropanol

△ Benzene

Figure 4. Dependence of yields of 2-chloro-2-cyanopropane on the solvent in reactions run with ferric chloride at 80°; ability to solvate $FeCl_3$ is in the order isopropanol $\gg$ benzene; 0.0122 mole AIBN per 200 ml solvent in each case

□ Isopropanol

⊙ Benzene


% Yield of 2-chloro-2-cyanopropane
70
50
30
10
1
3
5
7
9
11
Ratio of moles CuCl2:moles AIBN

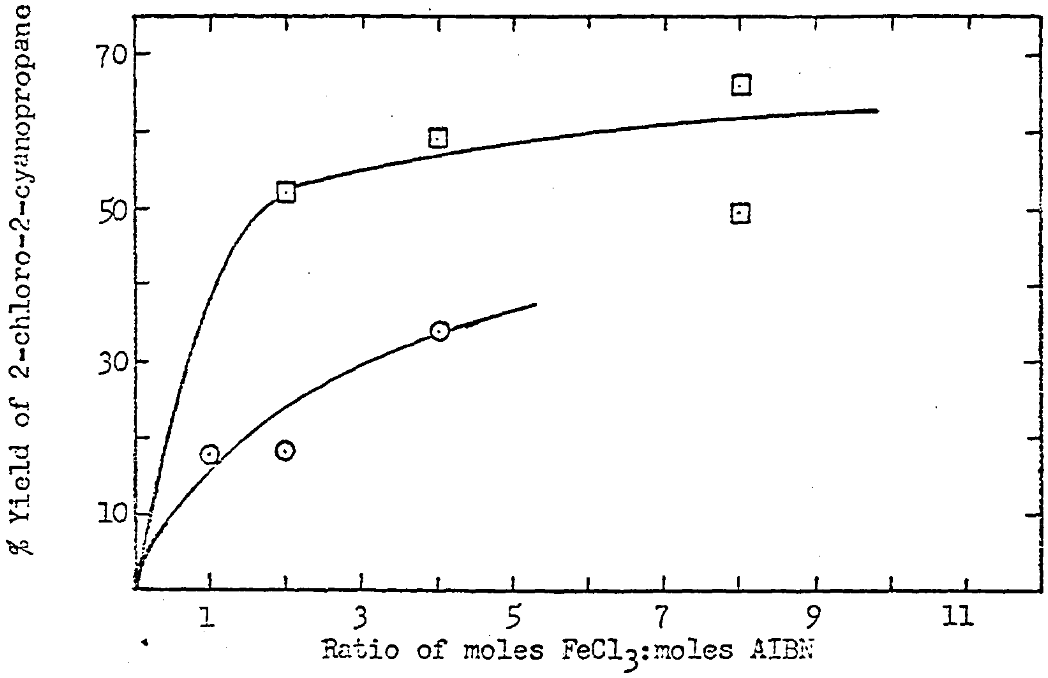

% Yield of 2-chloro-2-cyanopropane
70
50
30
10
1
3
5
7
9
11
Ratio of moles FeCl3:moles AIBN

Table 6. A comparison of the number of radicals accounted for by 2-chlorocyanopropane and tetramethylsuccinonitrile in selected typical reactions of metal halides with the 2-cyano-2-propyl radical generated by thermolysis of AIBN at 80°

				2-Chloro-2-cyanopropane		Tetramethylsuccinonitrile		
Halide	Solvent[a]	Moles halide x 10^2	Moles AIBN x 10^2	Moles x 10^2	% Yield	Moles x 10^4	% Yield	% 2-Cyano-2-propyl radicals accounted for
$CuCl_2$	CH_3CN	2.44	1.22	1.98	81.4	15.4	12.6	94.0
$CuCl_2$	CH_3CN	2.44	1.22	2.05	84.0	12.5	10.2	94.2
$CuCl_2$	CH_3CN	9.76	1.22	2.02	82.8	12.8	10.5	93.3
$CuCl_2$	*i*-PrOH	9.76	1.22	1.45	59.3	6.37	5.2	64.7
$CuCl_2\cdot 2Py$	benzene	9.76	1.22	1.44	58.9	18.2	14.9	73.8
$FeCl_3\cdot 6H_2O$	benzene	9.76	1.22	1.24	50.9	21.6	17.7	68.6
$FeCl_3$	*i*-PrOH	4.88	1.22	1.44	59.0	3.62	2.97	62.0
$FeCl_3$	*i*-PrOH	9.76	1.22	1.61	65.9	0	0	65.9

[a] 200 ml. of solvent used in each case.

work out the analytical conditions for quantitative determination of these disproportination products. The small amount of TMSN formed in the reactions run in isopropanol is surprising. After heating TMSN and $FeCl_3$ in isopropanol at 80° for 24 hours, the amount of TMSN remained unchanged. This showed that any TMSN formed in the above reactions could not disappear by this route. No further attempt was made to find out what happened to the other radicals and no good rationalization of the low yield of TMSN in isopropanol can be given.

A few reactions of the above type were run using phenyl radicals generated from thermolysis of phenylazotriphenylmethane (henceforth designated PAT) at 60°. The results are tabulated in Table 7. These reactions give us further insight on the importance of the anion part of the metal salt in addition to that already observed for the 2-cyano-2-propyl radical. The fact that the phenyl radical is a more reactive radical explains why it reacts with some of the copper salts that did not react before. It is interesting to note the difference in reaction between cupric and ferric thiocyanate based on the yield of C_6H_5NCS. It should be pointed out that the deep red color of ferric thiocyanate which was present at the start of the reaction had disappeared when the reaction was stopped, but GLC analysis showed no phenyl isothiocyanate formed. As soon as the reaction mixture was exposed to air, the red color of ferric thiocyanate returned. No explanation

Table 7. Yields of C_6H_5X from reactions of compounds of type MX_n with phenyl radicals generated from thermolysis of PAT in acetonitrile[a] at 60°

MX_n	Moles $MX_n \times 10^3$	Moles PAT $\times 10^3$	Moles $C_6H_5X \times 10^4$	% Yield C_6H_5X
$CuCl_2$	4.35	1.44	12.1	84[b]
CuCN	11.5	2.88	0	0
$Cu(CN)_2$	8.65	2.88	1.05	3.64
$Cu(OCH_3)_2$[c]	5.38	2.88	0	0
CuSCN	11.5	2.88	0	0
$Cu(SCN)_2$[d]	11.6	2.88	7.4	25.7
$Cu(CH_3CO_2)_2 \cdot H_2O$[e]	2.88	1.44	0.737	5.1
$Cu(C_6H_5CO_2)_2$	8.64	2.88	2.63	9.1
$Fe(SCN)_3$	11.5	2.88	0	0
$Fe(SCN)_3$	11.5	2.88	0	0
$(CH_3)_2Hg$[f]	5.76	2.88	0	0

[a] Except where indicated, 50 ml. of acetonitrile used.

[b] Results of Bridger using isopropanol as solvent (63).

[c] 60 ml. of acetonitrile used.

[d] 55 ml. of acetonitrile used.

[e] 25 ml. of acetonitrile used.

[f] Reaction run in 50 ml. of benzene.

of this can be given at this time.

The effect of anions observed reflects the ability of the various anions to act as bridging ions during a ligand transfer process. From the results found, it appears that the order of bridging ability is: $Br>Cl>SCN\gg RCO_2>CN>OCH_3,CH_3$. Perhaps this difference might be an indication of the relative rates of the ligand transfer reactions rather than the bridging ability of the anions. Actually it is probably an indication of both. This agrees well with Kochi's prediction that the rate of ligand transfer from cupric salt, $Cu^{II}S$, to radical in the reaction

$$R\cdot + Cu^{II}S \longrightarrow RS + Cu^{I}$$

should be in the order: $Br>Cl\gg RCO_2>OH>OCH_3$ (32).

It was known (45, 46, 47) that dimethyl-N-(2-cyano-2-propyl)-ketenimine, $(CH_3)_2C{=}C{=}N{-}C(CH_3)_2CN$, (henceforth designated KeIm) formed as an intermediate in the decomposition of AIBN. It was thought that a study of the rate of the reaction of KeIm with $CuCl_2$ might give us some information on the mechanism of the reaction between the metal halides and radicals.

When the KeIm was generated in situ by decomposing AIBN in acetonitrile at 80° and adding $CuCl_2$ when the KeIm concentration was at a maximum, it was found that the reaction rate was too great to follow by our method (see Experimental section). When the reaction was run at room temperature using pure KeIm, it was found that the rate of the reaction was still too fast for us to measure. This was a disappointment, but not too surprising. What was surprising, though, was the fact that neither 2-chloro-2-cyanopropane nor TMSN was formed in the reaction, not even when the reaction mixture was heated at 80° for 20 hours. When methylene chloride was used as a solvent in which case the cupric chloride was insoluble, little reaction was observed up to 17 hours later. The reaction mixture was stirred continuously during this time. It was apparent that this study was not going to shed any light on the mechanism of the metal salt-radical reaction. The only new information it gives along this line is that little if any KeIm is formed in the reaction of cupric chloride with AIBN in acetonitrile. Since 94% of the radicals are accounted for as 2-chloro-2-cyanopropane and TMSN, less than 6% of the radicals could form KeIm. This might be used as further evidence that complexing between ligands and radicals is important in radical trapping by metal halides. The argument is that such complexes form and prevent any electron density from the odd electron on the nitrogen in the radical, *i.e.*, there can be little contribution from the resonance form, $(CH_3)_2C{=}C{=}N\cdot$, in the radical if we write the radical as the resonance hybrid: $(CH_3)_2(CN)C\cdot \longleftrightarrow (CH_3)_2C{=}C{=}N\cdot$

Even though this did not give any information on the mechanism of the metal salt-radical reaction, it was interesting and some time was spent trying to shed some light on just what was happening. In one of the early reactions, two moles $CuCl_2$ per mole KeIm was found to be insufficient to react with all the KeIm. An experiment (Job's law plot) was performed to determine the number of moles $CuCl_2$ needed per mole of KeIm. The plot is shown in Figure 5. The combining ratio is found by the calculation

$$\frac{\text{Moles of } CuCl_2}{\text{Moles of KeIm}} = \frac{\text{flask no. intercept}}{10 - \text{flask no. intercept}} \times \frac{(CuCl_2)_i}{(\text{KeIm})_i}$$

This gives a value of 3 moles $CuCl_2$ per mole of KeIm (see Experimental section for further details). When the solvent from a reaction mixture was evaporated under reduced pressure, a black amorphous mass was left in the flask. Attempts to isolate a crystalline material from this mass using a variety of solvents were unsuccessful. A copper determination gave a result that did not fit any expected combinations of $CuCl_2$, KeIm, CH_3CN, or H_2O. In a later reaction, it was found that the weight of this residue is greater than the sum of the $CuCl_2$ and KeIm added initially indicating that it contained some acetonitrile.

It is hard to see why the combining ratio of copper (II) chloride and KeIm is 3:1. About the only possibility that could be seen at this time was the possibility of a <u>pi</u>-complex at each of the points of unsaturation

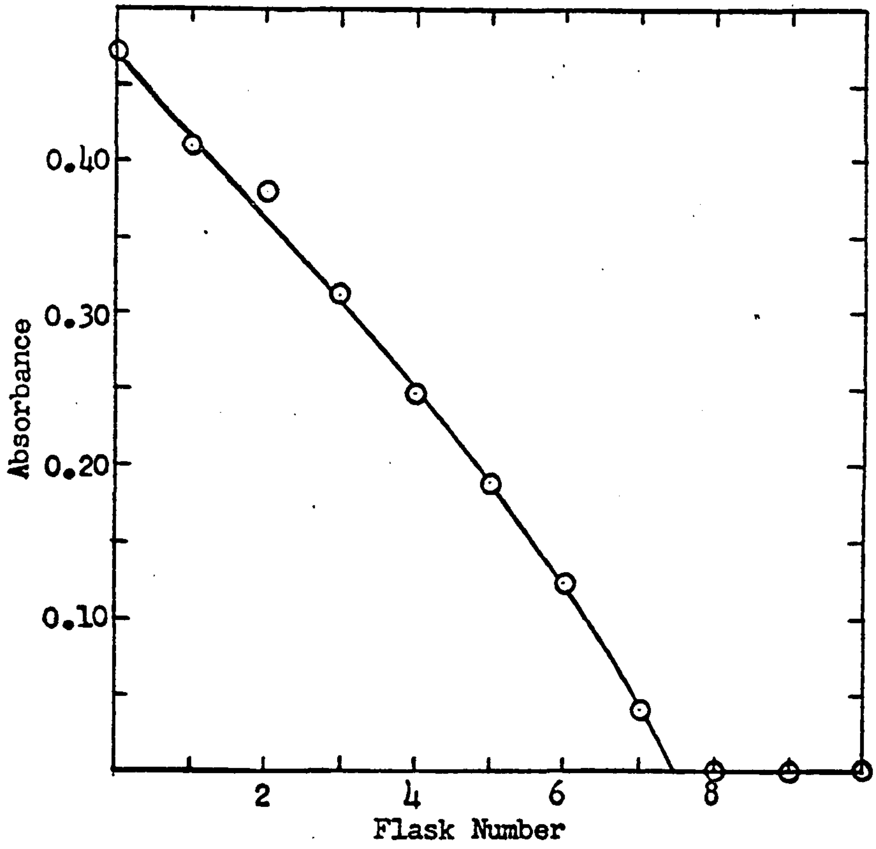
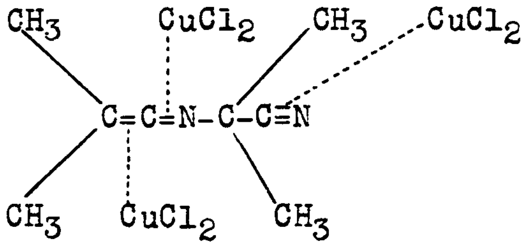


Figure 5. Job's law plot of the reaction of dimethyl-N-(2-cyano-2-propyl)-ketenimine with $CuCl_2$ in acetonitrile

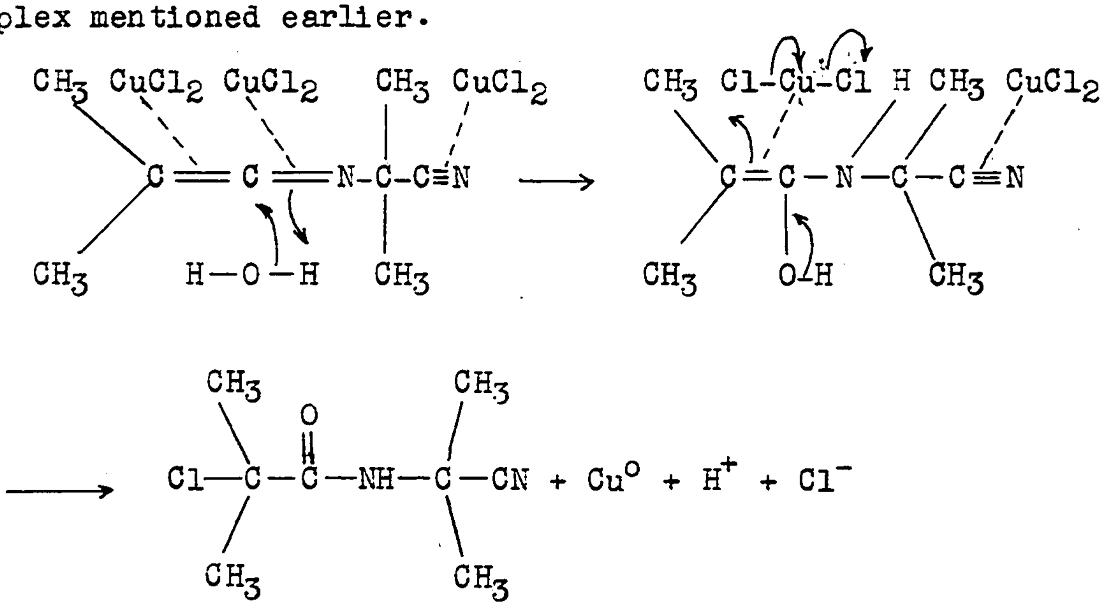


If such a pi-complex is formed, then a polarographic study should be able to verify it since the formation of such a complex causes a change in the half-wave potential of the complexed metal. Such a study was made; however the results are not as reliable as one would desire since non-aqueous polarography requires ultra-pure solvents and some experience in polarographic work. In all probability, both were below that desired. Nonetheless, there appears to be no change in half-wave potential ($E_{1/2}^{(1)} = -0.062$, $E_{1/2}^{(2)} = -0.38$ for $CuCl_2$ alone compared to $E_{1/2}^{(1)} = -0.063$, $E_{1/2}^{(2)} = -0.43$ when KeIm added) which would indicate copper has not formed a pi-complex in the KeIm reaction. On reflection, it is difficult to see why the cupric chloride would not form a pi-complex with the nitrile group of the acetonitrile if it forms one with the nitrile of the ketenimine compound. If it does, then the half-wave potentials would not be expected to change when KeIm is added.

The next reaction was to add the black amorphous material to water and see if any hydrolysis products could be isolated. An ether extraction yielded a white crystalline material. On the basis of IR and NMR spectra and elemental analysis, this material was 2-chloro-2-methyl-N-(2-cyano-2-propyl)-propionamide, $(CH_3)_2(Cl)CCONHC(CH_3)_2CN$. After chloroform was added to the black residue and the mixture stood overnight in a stoppered flask, the chloroform was decanted. The same amide as before was found upon evaporation of the chloroform. It is believed that moisture present in the chloroform or absorbed from the air would be large enough to cause the hydrolysis to produce the amide. At this point, it was decided not to spend any more time on this interesting sidelight, but it is hoped that someday more work will be done on this.

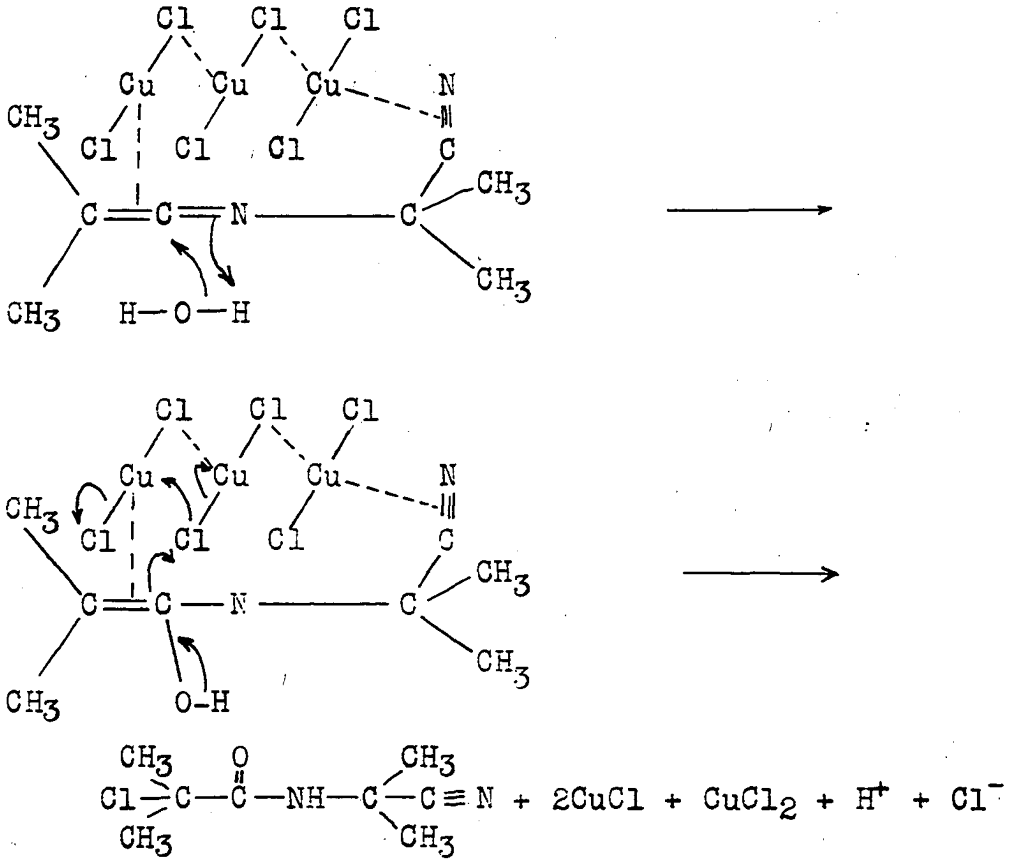
At this time, one can only speculate on the mechanism by which this amide is formed. Certainly, it must involve a reduction of the copper. Three possibilities come to mind, two of which assume that the KeIm-$CuCl_2$ residue is the *pi*-complex mentioned earlier.

A.



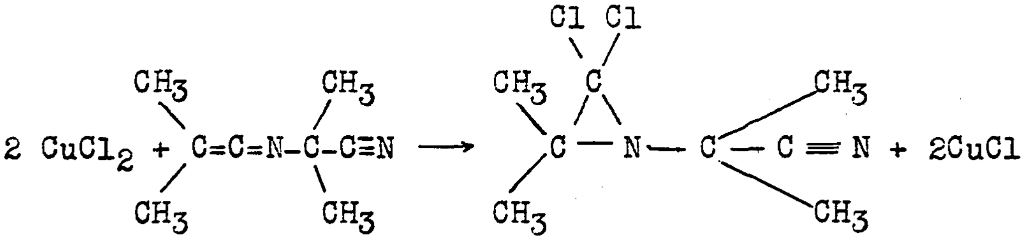
$$Cu^o + CuCl_2 \longrightarrow 2CuCl$$

B.

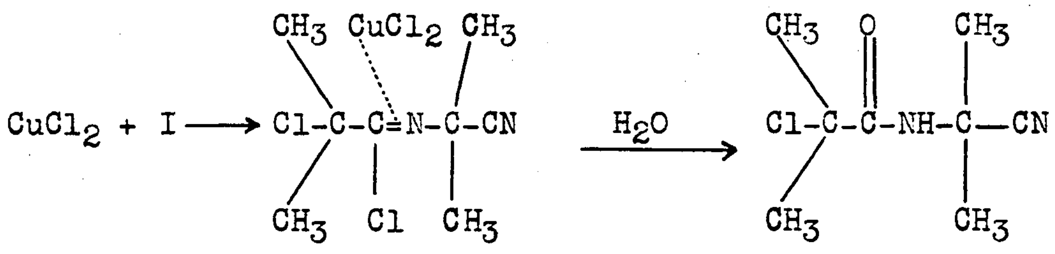


In B, a polymeric cupric chloride species is required. A trimer is shown, but a dimer or higher polymer would also work.

The third possibility is the formation of a transient aziridine, 1-(2-cyano-2-propyl)-2,2-dichloro-3,3-dimethylaziridine (I) which immediately converts to N-(2-cyano-2-propyl)-1-chloroisobutyroimidoyl chloride (II).

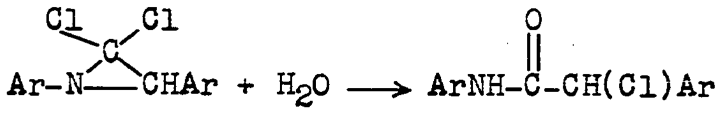


I



II

It is reported that 2,2-dichloroaziridines absorb at 13.6μ (48) while the imidoyl chlorides absorb at 5.95μ. However, it also shows a broad peak at 2.83μ. Although an effort was made to maintain anhydrous conditions, this might be due to water present as part of a hydrated copper chloride species. It is thought that it is this rather than an N-H absorption from 2-chloro-2-methyl-N-(2-cyano-2-propyl)-propionamide formed from hydrolyses of II since the N-H absorption is a sharp peak at 2.92μ in the spectrum of the amide in chloroform (see Figure 14 in Experimental section). A second argument for this not being an N-H absorption is that this absorption at 2.83μ is missing from the reaction mixture of the reaction in methylene chloride ($CuCl_2$ filtered off before introduction of sample into IR cell) although the same doublet appears at 5.85μ and 5.95μ. (Even though there is only a slight reaction in this case, it is felt that water would be more apt to be present in this reaction and if any amide were formed in a hydrolysis reaction, the N-H absorption would be strong enough to be seen.) Then too, the 5.95μ carbonyl peak in the amide is a strong singlet rather than a doublet although it could be argued that the doublet is due to the overlapping of an amide carbonyl absorption peak and an imidoyl chloride absorption peak which has been shifted to a shorter wavelength due to the <u>pi</u>-complex formed with $CuCl_2$. A comparison of the IR spectrum of the amide in acetonitrile with the IR spectrum of the reaction mixture (see Figures 7 and 8) show that the peaks at 2.83μ and 5.85μ are not the same as those of the N-H and carbonyl peaks of the amide in acetonitrile. Furthermore, there is a shoulder on the 2.83μ peak at 2.92μ and a 5.95μ peak on the reaction mixture spectrum which come at the same respective wavelengths as the N-H peak and carbonyl peak in the amide spectrum. This could be interpreted as an indication that some amide is present which formed as a result of hydrolysis of the imidoyl chloride. It is reported by Fields and Sandri (48) and also by Cook and Fields (49) that hydrolysis of 1,3-diaryl-2,2-dichloroaziridine (III) yields the chloroamide



where Ar = aryl

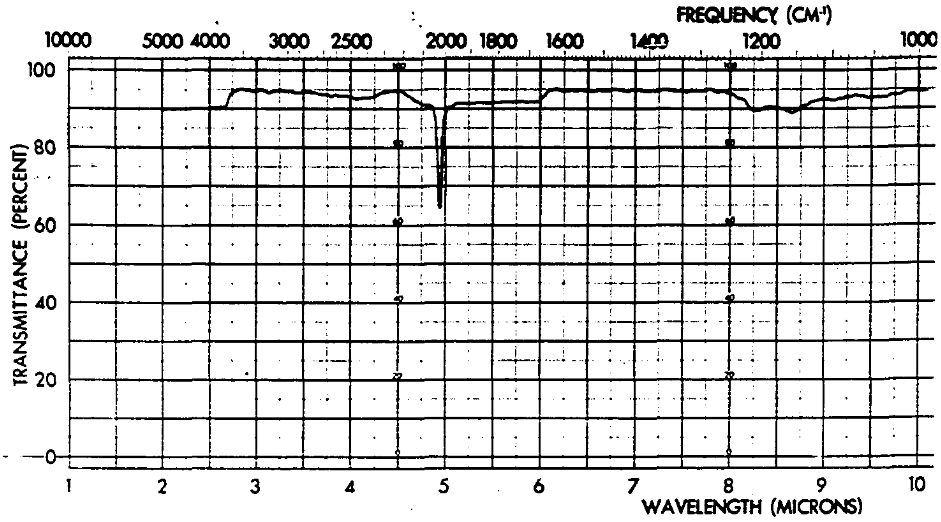
III

Heine and Smith (50) suggest that this hydrolysis involves rearrangement to the imidoyl chloride. In the case where Ar is the phenyl group, they were able to bring about this conversion (aziridine to imidoyl chloride) thermally by refluxing in toluene for 24 hours.

Figure 6. Infrared spectrum of dimethyl-N-(2-cyano-2-propyl)-ketenime in acetonitrile solution

Figure 7. Infrared spectrum of the reaction mixture of $CuCl_2$ with dimethyl-N-(2-cyano-2-propyl)-keteninime in acetonitrile

Figure 8. Infrared spectrum of 2-chloro-2-methyl-N-(2-cyano-2-propyl)-propionamide in acetonitrile


FREQUENCY (CM⁻¹)
10000
5000
4000
3000
2500
2000
1800
1600
1400
1200
1000
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
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2
3
4
5
6
7
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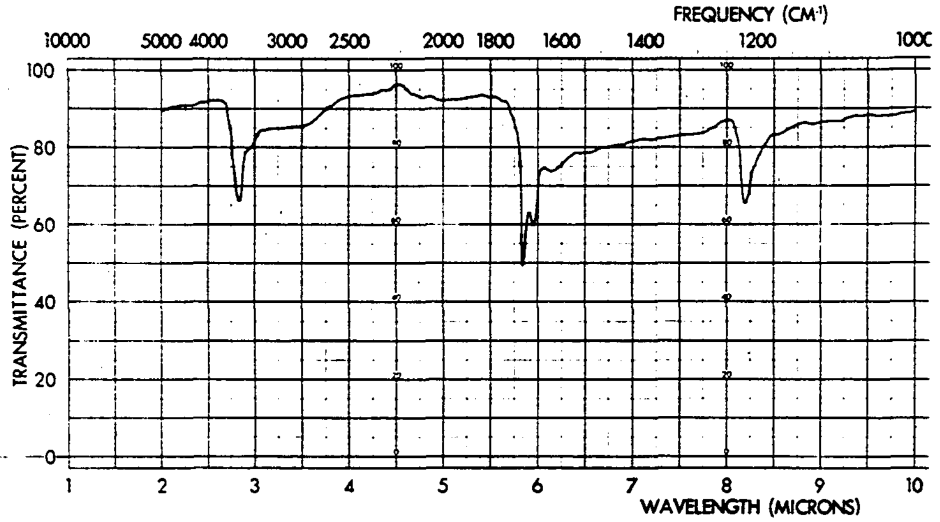
9
10
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
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TRANSMITTANCE (PERCENT)
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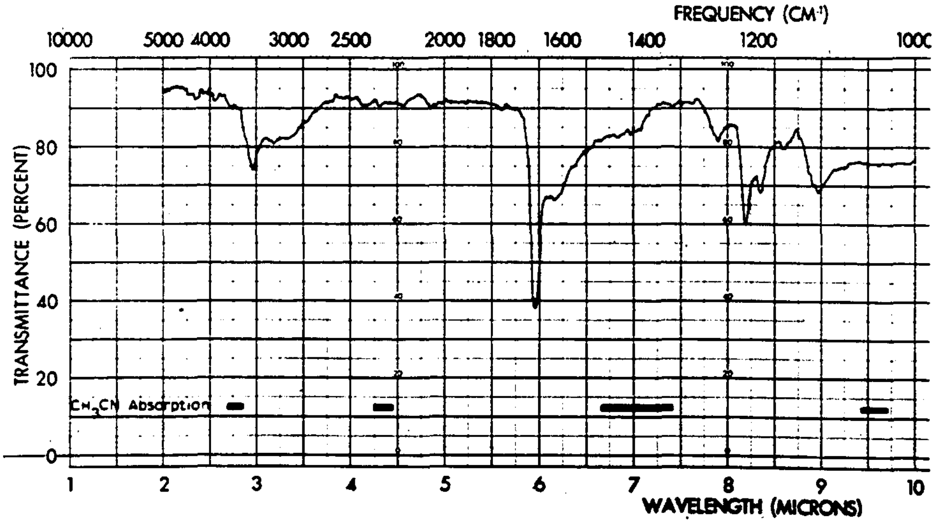
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
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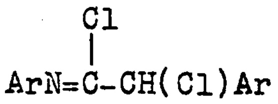
1800
1600
1400
1200
1000
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
CH_3CN Absorption
1
2
3
4
5
6
7
8
9
10
WAVELENGTH (MICRONS)

III ⟶ 

$$\mathrm{ArN{=}\overset{\displaystyle Cl}{\overset{|}{C}}{-}CH(Cl)Ar} \qquad \text{where Ar} = \mathrm{C_6H_5}$$

While there is no conclusive evidence for either of these three possible mechanisms, the best explanation of the spectral data favors the latter one.

There has been some speculation on the metal species which is important in the Sandmeyer reaction. CuX_4^{-3}, where X is Cl or Br, (7-10) and $CuCl_2^-$ (11) were mentioned in the Review of Literature section of this thesis as the form of the copper species necessary for the reaction. Waters (12, 13) does not state what he thinks is the metal species but he mentions the formation of a double diazonium salt, $ArN_2^+,CuCl_2^-$, while from his schematic picture of the mechanism one gets the idea that a transient $(CuCl)^+$ species is important in the reaction. Kochi (17) favors the $CuCl_2^-$ species for the Sandmeyer product, but thinks other species such as $CuCl_4^-$, $CuCl^+$, Cu_2Cl_3 are necessary to take part in reactions to give what he thinks is the important species in the Meerwein reaction, namely $(CuCl_2{\cdot}\text{olefin})^-$. In reactions of peroxides which he says are similar (identical) to the Sandmeyer reaction, Minisci _et al_. (24) show the metal species to be CuX^+ and FeX^{++}. In hydrohalic acids, ferrous sulfate works as well as ferrous chloride.

To test whether the species CuX^+ is the important form of the copper salt in the Sandmeyer reaction, the following experiment was devised. Phenyl radicals were generated by thermolysis of PAT in acetonitrile at 60° in the presence of a cuprous salt and a peroxide to act as an oxidizing agent to oxidize the copper to the cupric valence state. A large excess of both cuprous salt and peroxide (mole ratio of 4:1 with PAT) were used and peroxide was added throughout the reaction to ensure a fresh supply of MX^+ all during the reaction. The results of the experiments are given in Table 8. Note that the reactions run with AIBN were at 80°. There are several things of interest to be noticed. Comparison of yields of C_6H_5X with those from the reactions with CuX_2 (see Table 7) shows that the yield of benzonitrile is much better in this case (16.2% compound to 3.69) while the yield of phenyl isothiocyanate is slightly less (23.6% compared to 25.7%). With AIBN, the yield of 2-chloro-2-cyanopropane) is significantly lower (55.4% compared to 82.7%, Table 4) in this case. Two different peroxides were used, t-butylhydroperoxide and t-butyl perbenzoate. The latter is a possible source of phenyl radicals. If the yield of C_6H_5X from each peroxide is compared for each case (X = CN and X = SCN), it will be seen that t-butyl perbenzoate gives more phenyl radicals when X = SCN than when X = CN. The change in yield is 38.9% and 3.1% respectively.

These results support strongly that the active metal species in the Sandmeyer reaction is of the form CuX^+. The

Table 8. The importance of CuX$^+$ in the Sandmeyer reaction; comparison of the yield of RX from reaction of phenyl radical at 60° and 2-cyano-2-propyl radical at 80° with cuprous salt in acetonitrile with and without added peroxide

CuX	Moles x 10^2	Source of radical, R·	Moles x 10^3	R'OOR''	Moles x 10^2	Moles RX formed x 10^3	% RX formed	Ml. CH_3CN used
CuCN	4.60	PAT	11.5	*t*-BUOOH	4.60	2.01	17.5	300
CuCN	4.60	PAT	11.5	*t*-BUOOH	4.60	1.73	15.0	230
CuCN	1.15	PAT	2.88	none		0	0	50
CuCN	2.03	PAT	5.75	*t*-$BUOOCC_6H_5$	2.30	1.11	19.3	135
CuSCN	2.03	PAT	5.75	*t*-$BUOOCC_6H_5$	2.30	3.59	62.5	100
CuSCN	1.15	PAT	2.88	none		0	0	50
CuSCN	2.30	PAT	5.75	*t*-BUOOH	2.30	1.36	23.6	110
CuCl	5.00	AIBN(80°)	12.2	*t*-BUOOH	5.00	1.35	55.4	100
CuCN	5.00	AIBN(80°)	12.2	*t*-BUOOH	5.00	0	0	100
CuSCN	5.00	AIBN(80°)	12.2	*t*-BUOOH	5.00	0	0	95

difference in yields have several possible explanations. While no quantitative data is available, cupric thiocyanate appears to be more soluble than cupric cyanide. The purity of the thiocyanate was better also. Hence the increase in benzonitrile and decrease in phenyl isothiocyanate might be a reflection of the effect of solubility. In the case of the nitrile, the solubility of $CuCN^+$ is greater than that of $Cu(CN)_2$ and in the case of the thiocyanate, the $CuSCN^+$ is about the same as that of $Cu(SCN)_2$. The results with AIBN in the case where X is chloride could also point toward the difference in solubility of CuCl and $CuCl_2$ in acetonitrile where $CuCl_2$ is more soluble and the concentration of $CuCl^+$ produced would not be expected to attain the same concentration as the $CuCl_2$ used in the reactions with it.

The drop in yield of 2-chloro-2-cyanopropane in this case might even be considered further proof for formation of a chlorine bridge in the transition state. Even if the concentration of $CuCl^+$ was equal to that of $CuCl_2$ used before, the possibility of forming a chlorine bridge would be one half if judged solely on the number of chlorines available for bridging. The fact that the actual yield is greater than one half that found before can be rationalized by the formation of a <u>pi</u>-complex between radical and acetonitrile ligand which would make the radical less reactive (more selective) and also hold the radical in the proximity of the chlorine that is there until it can react with it. If we assume that the $CuCl_2 \cdot 2CH_3CN$ and the $CuCl^+ \cdot 2CH_3CN$ structure is tetrahedral (51) in acetonitrile solution and further assume that direct attack of the radical at any of the four corners of the tetrahedron will result in the formation of 2-chloro-2-cyanopropane when $CuCl_2 \cdot 2CH_3CN$ is the species present, then in the case where chlorine is missing from one corner, the yield would be expected to be one-fourth less than that when an equal concentration of $CuCl_2 \cdot 2CH_3CN$ is present. If the concentration were equal, this would be a decrease of 21.4%. The actual decrease is 27.3. It has already been speculated that the concentrations would not be equal so the larger decrease found would be in the right direction for the smaller solubility expected. However, it is thought that the <u>pi</u>-complexing of radical and ligand is not as great as the assumption above states although it is difficult to estimate this effect. The greater yield of C_6H_5X from <u>t</u>-butyl perbenzoate when X = SCN than when X = CN is a reflection of the fact that SCN is a better bridging ligand than CN.

EXPERIMENTAL

Melting points and boiling points given are uncorrected.

Chemicals

All chemicals were used as received unless otherwise specified.

Cupric chloride dihydrate was Baker Analyzed Reagent and Mallinckrodt Reagent Grade.

Cupric chloride (anhydrous) was from Fisher Scientific Co.

Ferric chloride hexahydrate was Baker and Adamson (Allied Chemical, General Chemical Division) Reagent Grade.

Ferric chloride (anhydrous) was from Fisher Scientific Co., Purified Grade.

Carbon tetrachloride was Mallinckrodt Reagent Grade.

Acetyl chloride was Baker Reagent Grade.

Phosphorus pentachloride was Baker Reagent Grade; phosphorus trichloride was Mallinckrodt Reagent Grade; and phosphorus oxychloride was from Matheson, Coleman, and Bell.

Sulfur monochloride (S_2Cl_2) was from Baker and Adamson (Allied Chemical, General Chemical Division); sulfur dichloride was from the British Drug Houses, Ltd. (Poole, England); sulfurous oxychloride (thionyl chloride) was from Matheson, Coleman, and Bell; and sulfuric oxychloride (sulfuryl chloride) was from Eastman Organic Chemicals, practical grade.

Titanium tetrachloride was from Matheson, Coleman, and Bell, 99.5% purity; and titanium trichloride was from an unknown source.

Vanadium tetrachloride was practical grade from Anderson Chemical Co. (Division of Stauffer Chemical Co., Weston, Michigan).

Chromic chloride hexahydrate was Baker and Adamson (Allied Chemical, General Chemical Division) Reagent Grade.

Chromium (III) acetylacetonate was made by the method given in <u>Inorganic Synthesis</u> (52).

Ferric acetylacetonate was made using the procedure given in an unpublished thesis of Norris A. Mendelsohn (53). To a solution of 27.8 g $FeCl_3$ (0.21 mole) (Fisher Scientific Purified Grade, anhydrous, sublimed) in 220 ml distilled water was added a solution of 100 g acetylacetone (0.96 mole) in 220 ml methanol. To the resulting solution, 180 g $NaC_2H_3O_2 \cdot 3H_2O$ (1.28 mole) dissolved in 440 ml of distilled water was added slowly with vigorous stirring. The mixture was warmed to 50-75° for about 15 minutes and placed in a refrigerator for several hours. The red solid was separated on a Büchner funnel, washed with water and petroleum ether, and dried over Drierite in a vacuum desiccator at a high vacuum (ca. 0.1 mm) for at least 24 hours at room temperature. After recrystallizing twice from a benzene, petroleum ether solvent pair, the chelate was dried at a high vacuum (ca. 0.1 mm) for 2 days.

The recrystallized yield was about 50%.

Ferric thiocyanate was made by the method of Schlesinger and Van Valkenburgh (54) and obtained from K and K Laboratories, Inc. Ferric benzoate was from K and K Laboratories, Inc.

Ferric ethoxide and ferric methoxide was made by the method of Bradley _et al_. (55). No attempt was made to isolate them, but an aliquot of the benzene solution in which they were made was used in the reaction run with them.

Chloropentaminocobalt chloride, $(Co(NH_3)_5Cl)Cl_2$, was obtained from the G. Frederick Smith Chemical Co.; hexaminocobalti chloride, $(Co(NH_3)_6)Cl_3$, and hydropentaminocobalti chloride, $(Co(NH_3)_5H_2O)Cl_3$, were donated by Dr. Byron G. Kratochvil, graduate student under Dr. Harvey Diehl, Professor of Analytical Chemistry at Iowa State University, at the time they were used in this work.

Cobalt (III) acetylacetone was made by the method given in _Inorganic Synthesis_ (56).

Cupric chloride dipyridine was made by the method of Lang (57). To a solution of 48 g anhydrous cupric chloride (0.0298 mole) in 200 ml absolute methanol was added 48 ml of pyridine (0.596 mole) which resulted in the precipitation of a blue substance (contrary to the beautiful, brilliant, silky, greenish blue needles reported, this has no definite crystalline structure). This is dissolved in boiling ethanol (it is not very soluble and a large amount of alcohol was necessary) and cooled which results in the precipitation of fluffy blue (greenish-blue) needles.

Lithium copper chloride dihydrate $LiCuCl_32H_2O$ was a gift from Dr. Robert E. Rundle, Professor of Physical Chemistry at Iowa State University.

Cupric bromide, 98.0% minimum purity, and cupric fluoride dihydrate, technical grade, was from Baker and Adamson (Allied Chemical, General Chemical Division); cupric thiocyanate and cupric benzoate were from K and K Laboratories, Inc.; and cupric acetate monohydrate was from Fisher Scientific Co., reagent grade.

Cupric cyanide was made by double displacement reaction of copper sulfate and potassium cyanide. A solution of 3.96 g KCN (0.0610 mole) in 15 ml of distilled water is added to a solution of 7.28 g $CuSO_4 \cdot 5H_2O$ (0.0305 mole) in 50 ml of distilled water with vigorous stirring. The $Cu(CN)_2$ precipitates immediately and this is filtered off and washed several times with small amounts of distilled water. The $Cu(CN)_2$ is then air dried for several hours. $Cu(CN)_2$ should be used soon after being made because it decomposes to cuprous cyanide and cyanogen over a period of time.

Cupric methoxide was made by the double displacement reaction of lithium methoxide and cupric chloride. To 100 ml of absolute methanol 5.52 g. of lithium (0.797 mole) was added slowly. The resulting solution was added slowly with rapid stirring to a solution of 53.5 g of $CuCl_2$

(0.398 mole) in absolute methanol which resulted in immediate precipitation of cupric methoxide (% Cu found 48.25, theoretical % Cu 50.58).

Cuprous chloride was Mallinckrodt Reagent Grade; cuprous cyanide was Baker Reagent Grade; and cuprous thiocyanate was K and K Laboratories, Inc.

Molybdenum trichloride and molybdenum pentachloride were from L. Light and Co., Ltd.

Silver chloride, reagent grade, was from Baker and Adamson (Allied Chemical, General Chemical Division); and silver difluoride was from General Chemical Division, Allied Chemical and Dye Corp,, Baton Rouge Development Laboratory.

Stannic chloride, anhydrous, was from General Chemical Co.; and stannic chloride pentahydrate, reagent grade was from Baker Chemical Co.

Antimony pentachloride, reagent grade, was from Baker and Adamson (Allied Chemical, General Chemical Division); and antimony tetrafluoride was from General Chemical Division, Allied Chemical and Dye Corp., Baton Rouge Development Laboratory.

Tellurium tetrachloride was from K and K Laboratories, Inc.

Mercuric chloride, reagent grade, was from Baker Chemical Co.; mercurous chloride, reagent grade, was from Merck and Co., Inc.; and mercuric acetate, reagent grade, was from

Baker Chemical Co.

Diethyl mercury and dimethyl mercury were gifts from Jerry D. Hunt, graduate student under Dr. Glen A. Russell, Professor of Organic Chemistry at Iowa State University. They were made by the method of Gilman and Brown (58) with slight modification (59).

Lead tetraacetate was from Arapahoe Chemicals, Inc. It was recrystallized from glacial acetic acid. It turns brown if filtered in the air so filtration must be done under an inert atmosphere.

2,2'-Azo-bis-isobutyronitrile (AIBN) was from Chemical Intermediates and Research Laboratories, Inc. and from Monomer-Polymer Laboratories, The Borden Co.--Chemical Division. It was recrystallized from absolute methanol. The methanol was saturated with AIBN at room temperature and left in the freezing compartment of a refrigerator overnight. The needle shaped crystals were filtered off in a Büchner funnel and air dried for about an hour. The AIBN thus obtained melted with decomposition at 102-103°. It was stored in a refrigerator when not in use.

2-Chloro-2-cyanopropane was made by the method of Stevens (60). A mixture of 9.4 g isobutyronitrile (0.136 mole) and 28.2 g PCl_5 (0.136 mole) was heated to the refluxing temperature. HCl was evolved smoothly and within an hour the PCl_5 could no longer be seen. After refluxing the clear solution until the HCl ceased to be evolved (ca. 3 hours), the reaction mixture was fractionated in a Todd Distillation Apparatus containing a column which had a monel metal spiral as packing. The 2-chloro-2-cyanopropane was the fraction collected from 114-116° and had a refractive index, n_D^{25} = 1.4048 (reported: b.p. 114-116, n_D^{25} = 1.4048). The gas liquid chromatogram indicates greater than 99.9 mole per cent purity.

The isobutyronitrile used in the above synthesis of 2-chloro-2-cyanopropane was obtained from two sources. One source was a three step synthesis starting with isobutyric acid using the procedure given in <u>Organic</u> <u>Synthesis</u> (61, 62). This was the source of the isobutyronitrile used in the synthesis of 2-chloro-2-cyanopropane having the physical properties given above. The other source was Eastman practical grade. This source gave 2-chloro-2-cyanopropane containing an impurity present in the amount of about 5% which could not be separated by distillation.

Dimethyl-N-(2-cyano-2-propyl)-ketenimine (designated KeIm) was made by two methods. The first method employed was that of Hammond <u>et</u> <u>al</u>. (47). The second method employed was the photolysis of AIBN in cyclohexane. This method was suggested by a kinetic study of the photolysis of AIBN in benzene by Smith and Rosenberg (63). Benzene was first tried as a solvent but it appeared to azeotrope with the KeIm and prevented isolation of the KeIm (contrary to the note by Smith et al. (64)). A solution of 30 g of AIBN (0.183 moles) (used as received from Chemical Intermediates and Research Laboratories Inc.) in 2 liters of cyclohexane in a Pyrex irradiation vessel was stirred by means of a magnetic stirrer (Teflon coated stirring bar) while nitrogen was bubbled through it for 30 minutes to remove any dissolved oxygen. A positive nitrogen pressured was maintained throughout the irradiation by means of a gas bubbler and the stirring was also continued throughout the irradiation. The irradiation was done with a mercury arc lamp (Hanovia Type A, 550 watts) which was inserted in a Pyrex immersion well that was cooled with water. The progress of the irradiation was followed by the disappearance of the 345 mμ band and the appearance of the 290 mμ band in the ultraviolet. The irradiation was stopped at 540 minutes. The cyclohexane was removed by vacuum distillation at room temperature by means of a "roto-vac" attached to a water aspirator. The remaining liquid was introduced into a vacuum rack capable of maintaining a pressure of 10^{-6} mm. of mercury where three one-plate distillations were carried out. The KeIm collected is a water-white liquid which melts at 15° (determined using a crude method, could be off by several degrees) and having a refractive index, $n_D^{25°}$ = 1.4475 (reported: m.p. 12.7°, n_D^{25} = 1.4473) (47). The yield of KeIm was raised from 10% by the first method to 30% by the second method.

Tetramethylsuccinonitrile (TMSN) was made by decomposing AIBN in toluene at 80° for 24 hours. The liquid portion distilled off and the solid recrystallized from ethanol. The crystals collected were further purified by sublimation, m.p. 169-169.5°.

Phenylazotriphenylmethane (PAT) was prepared by the method of Cohen and Wang (65). To a solution of 100 g triphenylchloromethane (0.359 mole) in 1100 ml of ether, 71.5 ml of phenylhydrazine (0.718) was added with stirring (glass stirrer with a Teflon paddle and a glycerol lubricated glass bushing driven by a Waco stirring motor (fast shaft)) over a 5 minute time interval. The flask was also equipped with a reflux condenser. The reaction mixture was stirred overnight at room temperature (ca. 29°) and the white precipitate was removed by suction filtration. The majority of the ether was evaporated at reduced pressure. The crude N-phenyl-N'-tritylhydrazine was separated from the small amount of liquid remaining by suction filtration and recrystallized from methylene chloride-ethanol solvent pair. Two crops of crystals were collected. The two crops of crystals were combined and dissolved in 1100 ml ether in a flask equipped with a stirrer (same as above) and a reflux condenser. To this, 500 ml of saturated aqueous sodium bicarbonate was added, followed by dropwise addition of 34 ml of 30% hydrogen peroxide with stirring over a period of 30 minutes. The stirring was continued overnight at room temperature. The ether layer was separated and was washed once with water, three times with 5% aqueous sodium hydroxide solution (200 ml. each time) and once with water. Treatment of a small sample of the ether solution with anhydrous hydrogen chloride resulted in the precipitation of a hydrochloride. This indicated the oxidation was not complete so the ether solution was returned to the reaction flask and the oxidation procedure was repeated. This time the flask was heated gently on a steam bath with stirring for only two hours. After separating the ether and washing as before, the anhydrous hydrogen chloride test gives almost no precipitate. The ether is removed under reduced pressure (water aspirator) by a series of steps in which the majority of the ether is removed, the solid separated by filtration and the process repeated on the filtrate. The last treatment left a small amount of oily residue which was discarded. The crude PAT was recrystallized from a methylene chloride-ethanol solvent pair. Three crops of crystals were collected: 1st crop - 22.84 g, m.p. 109-110; 2nd crop - 11.19 g, m.p. 107-108; 3rd crop - 2.56 g, m.p. 106-108. Each crop was tested for purity by using the method of decomposition in carbon tetrachloride developed by Bridger (66). The 1st and 2nd crops gave values for per cent benzene equivalent to those of Bridger. (During recrystallization a small amount of a white compound precipitated out. This was filtered off before completing recrystallization.)

t-Butyl hydroperoxide and t-butyl perbenzoate were from Lucidol Division, Wallace and Tiernan, Inc.

Acetonitrile was from Matheson, Coleman, and Bell, practical grade, or from Eastman Organic Chemicals, practical grade. The majority was purified by distilling twice from phosphorus pentoxide, once from potassium carbonate, and once by itself. Each fraction was checked for purity by GLC and only those of greater than 99.9 mole % purity were used. More recently, the acetonitrile was purified by the method of Coetzee et al. (67).

Benzene, thiophene free, reagent grade, was from Mallinckrodt Chemical Works.

Isopropanol, 99%, was from Chicago Apparatus Company.

Pyridine, reagent grade, was from Mallinckrodt Chemical Works.

Benzotrifluoride, practical grade, was from Eastman Organic Chemicals. GLC spectrum showed it to be greater than 99.9% pure so it was used as received.

Dimethyl sulfoxide was from Crown Zellerback. It was distilled once from calcium hydride.

Benzonitrile, white label, was from Eastman Organic Chemicals.

Toluene used as GLC standard was from an unknown source.

GLC analysis showed it to be greater than 99.5% pure.

Phenyl isothiocyanate, white label, was from Eastman Organic Chemicals.

2-Methyl-N-(2-cyano-2-propyl)-propionamide, $(CH_3)_2CHCO-NHC(CH_3)_2CN$, was synthesized by the reaction of 2-amino-2-cyanopropane with isobutyryl chloride.

2-Amino-2-cyanopropane was synthesized by the method given in Organic Synthesis (68). For this synthesis, 87.5 g of acetone (1.5 moles) were used and proportional amounts of the other materials used. In the final step, most of the solvent, methyl alcohol, was removed but no attempt was made to isolate the product in pure form. The final mixture was placed in a 1 liter, 3-necked, round-bottomed flask equipped with a dropping funnel, a reflux condenser and a stirrer. The mixture was diluted with 300 ml of toluene. To the dropping funnel 65 g of isobutyryl chloride (procedure ref. 58) was added and this was added dropwise with stirring to the toluene solution. The temperature was kept between 15^{o} and 30^{o} by the use of a water bath. Stirring was continued for several hours after the last of the isobutyryl chloride had been added. The solid was removed by filtration and the toluene was evaporated from the filtrate leaving an orange-red oil. Separation of the desired product from the oil proved rather difficult, but a small amount was obtained by dissolving some of the oil in benzene and adding ethanol which precipitated a small amount of brownish solid. This solid was sublimed yielding a white crystalline compound with m.p. of 105-107 (reported 108). No attempt to isolate any more of the amide was made.

Apparatus and Procedure

Reactions of compounds with the 2-cyano-2-propyl radical

In a typical reaction, 200 ml of solvent were placed in a 500 ml round-bottomed, 3-necked flask equipped with a stirrer, a reflux condenser, and a thermometer. The thermometer was long enough that its bulb would be immersed in the liquid during the reaction. It was not placed into position until the following preliminary operations were carried out. A nitrogen source was connected to the top of the reflux condenser so a nitrogen atmosphere could be maintained throughout the time of reaction. The nitrogen system contained a gas bubbler so a constant positive pressure could be maintained. Nitrogen was bubbled through the solvent for 20 to 30 minutes prior to starting the reaction to remove any dissolved oxygen and then was flushed through the reflux condenser and the flask while the AIBN and other compound was added through the neck that would hold the thermometer. The thermometer was put in place, the stirrer started, and heat applied. The actual amounts of AIBN and other compounds can be found in Tables 1, 3, 4 and 5. The reaction mixture was heated at 80° for 24 hours and was stirred continuously during this time. In most cases the heat was supplied by an electric heating mantle, but in a few cases, the reaction flask was immersed in an oil bath at 80°. The reaction was stirred using a glass stirrer having a Teflon paddle and a glycerol lubricated glass bushing and driven by a Waco stirring motor (slow shaft). In a few instances, a mercury seal stirrer was used which was driven by a Waco stirring motor. After the reaction was stopped and the temperature had dropped to room temperature, any solid was removed by filtration. A GPC spectrum was run on the filtrate to ascertain an appropriate compound to use as an internal standard for GLC analysis. (In most cases, this turned out to be toluene. Actual GLC conditions used are given in the section on GLC analysis.) If the GLC spectrum showed that some of the expected product was formed, an internal standard was added and a GLC analysis was made.

Reactions of compounds with the phenyl radical

The reactions were run in a flask in a constant temperature oil bath maintained at $60.0 \pm 0.1^{\circ}$. The bath was stirred by a metal blade connected to an Eberbach motor which had had the original bearings replaced by ball bearings because of an undue amount of trouble with it as received. The heat was supplied by two 125 watt blade heaters connected to a Cenco

Electronic relay actuated by a Thermoregulator thermometer adjustable by a rotating magnet over a temperature range of 0° to $100^{\circ} \pm 0.1^{\circ}$.

In a typical reaction, a 100 ml round-bottomed, 3-necked flask was equipped with a stirrer and a reflux condenser. A nitrogen source was connected to the top of the reflux condenser to maintain a nitrogen atmosphere during the reaction. The nitrogen system contained a gas bubbler so a constant positive nitrogen pressure could be maintained. The system was flushed with nitrogen and the solid reactants added to the flask while nitrogen was passing slowly through the system. The solvent, which has had nitrogen bubbling through it for 20-30 minutes to remove any dissolved oxygen was then added and the flask stoppered. The reaction flask was then immersed in the constant temperature bath, the mercury seal stirrer adjusted, and the stirrer started. The reaction was stirred continuously during the 4 hour reaction time. In all cases, a mercury seal stirrer (Teflon blade) attached to the fast shaft of a Waco stirring motor was used. The actual amounts of PAT and other materials used are given in Table 7. After the reaction was stopped and the temperature had dropped to room temperature, any solid was removed by filtration. A GLC spectrum was run on the filtrate to see if any of the expected product had been formed and to ascertain an appropriate compound to use as an internal standard (see section on GLC analysis). If the GLC spectrum showed some of the expected product, an internal standard was added and a GLC analysis was made.

Procedure for Sandmeyer type reaction

The reaction was run in round-bottomed, 3-necked flask equipped with a reflux condenser, a mercury stirrer, and a dropping funnel having a pressure equalizing side arm. A nitrogen atmosphere was maintained for the duration of the reaction by attaching a nitrogen inlet to the top of the condenser. The positive nitrogen pressure was held constant by the use of a gas bubbler in the nitrogen system. The radical source and the reduced metal salt were placed in the reaction flask and the deoxygenated solvent was added. The oxidizing peroxide dissolved in the solvent was then placed in the dropping funnel, the funnel stoppered, the reaction flask put in an oil bath ($60.0^{\circ} \pm 0.1^{\circ}$ for the phenyl radical reaction and $80.0^{\circ} \pm 0.1^{\circ}$ for the 2-cyano-2-propyl radical), and the stirrer adjusted and started. A mercury seal stirrer (Teflon blade) attached to the fast shaft of a Waco stirring motor was used to stir the reaction mixture throughout the time of heating (4 hours for the phenyl radical reactions and 24 hours for the 2-cyano-2-propyl radical reactions). The oxidizing peroxide is added rapidly at first when the concentration of the radical is at a maximum and then slowly so the total time of addition was about 2 half-lives. The actual amounts of reactants are given in Table 8. The amounts of acetonitrile used are a ratio of 200 ml per 0.0115 moles of PAT for the reaction flask and a ratio of 100 ml per 0.0115 moles of PAT for the amount used to make the peroxide solution. The flask used was roughly twice the size of the total amount of acetonitrile used. After the reaction was stopped and the temperature had dropped to room temperature, any solid was removed by filtration. A GLC spectrum was run on the filtrate to see if any of the expected product had formed and to ascertain an appropriate compound to use as an internal standard. If the GLC spectrum showed some of the expected product was formed, an internal standard was added and a GLC analysis was made.

Procedure for reactions with dimethyl-N-(2-cyano-2-propyl)-ketenimine (KeIm)

The initial experiments carried out were to watch the growth and decay of KeIm during the decomposition of AIBN in acetonitrile at 80° by measuring the absorbance at 4.96μ in the infrared spectrum of aliquots periodically removed from the reaction vessel. This was done both with and without cupric chloride, but in the latter case no absorbance at 4.96μ was observed so a new experiment was tried. This new experiment was to add cupric chloride to the decomposition reaction at the time when the KeIm was at a maximum, remove aliquots and measure the rate of its disappearance as above.

Since the build-up and decay of KeIm was known to be solvent dependent (69), it was first necessary to study the build up and decay of KeIm in acetonitrile. Because the method of determining absorbance (see section on Infrared (IR) analysis) differed from that used by Trapp (69), a Beer's Law plot was made using solutions made from pure KeIm. There was also the possibility that the same kind of experiment would be done in isopropanol, so a Beer's Law plot was made for the case when isopropanol was solvent as well. It was surprising to find the two plots were different. In the case of acetonitrile, Beer's Law holds at the lower concentrations, but in isopropanol, a straight line relationship does not seem to hold anywhere. This is shown in Table 9 and Figures 9 and 10. As it turned out, further experiments in isopropanol were not carried out, but the build up and decay of KeIm in acetonitrile at 80^{o} is shown in Table 10 and Figure 11. Similar curves for benzene and carbon tetrachloride can be found on page 67 of Trapp's thesis (69)..

The copper chloride was added at the time of maximum concentration of KeIm and an aliquot removed a minute later. By the time this could be measured, the infrared absorbance at 4.96μ had disappeared so the procedure given below was tried.

A solution of KeIm in acetonitrile was added to a

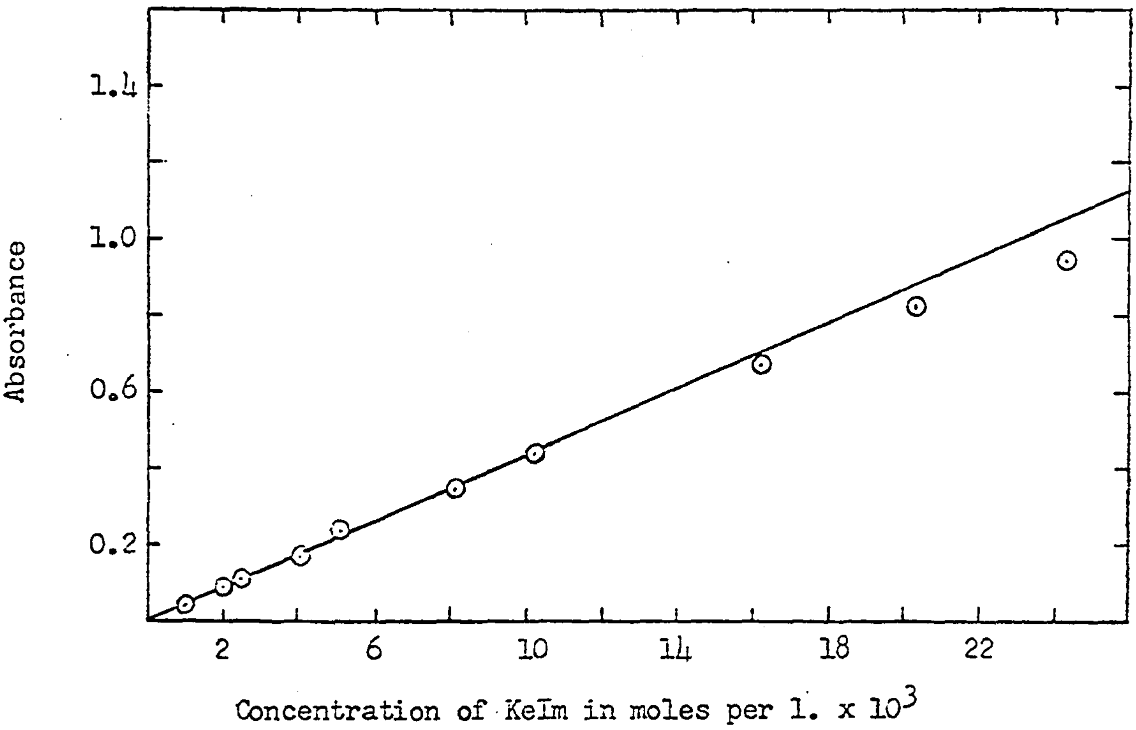
Table 9. Comparison of molar concentration of KeIm with infrared absorbance at 4.96μ when solvent is acetonitrile and isopropanol

Acetonitrile		Isopropanol	
Molar concentration x 10^3	Absorbance	Molar concentration x 10^3	Absorbance
1.015	0.043	1.057	0.029
2.03	0.092	2.113	0.072
2.537	0.110	2.641	0.095
4.06	0.172	4.226	0.115
5.075	0.235	5.282	0.196
8.11	0.353	8.456	0.304
10.15	0.437	10.57	0.383
16.2	0.670	16.89	0.573
20.3	0.826	21.13	0.681
24.3	0.938	25.36	0.810
32.4	1.121	33.81	0.947
40.59	1.290	42.26	0.948

3-necked, round-bottomed flask equipped with a mercury seal stirrer and a nitrogen inlet while nitrogen was being flushed through the system. No other attempt was made to remove dissolved oxygen, but a nitrogen atmosphere was maintained during the reaction. A bent tube containing the copper chloride was added to the third neck which was tipped to add

Figure 9. Relationship between KeIm concentration and infrared absorbance at 4.96μ when solvent is acetonitrile

Figure 10. Relationship between KeIm concentration and infrared absorbance at 4.96μ when solvent is isopropanol


1.4
1.0
0.6
0.2
Absorbance
2
6
10
14
18
22
Concentration of KeIm in moles per l. x 10^3

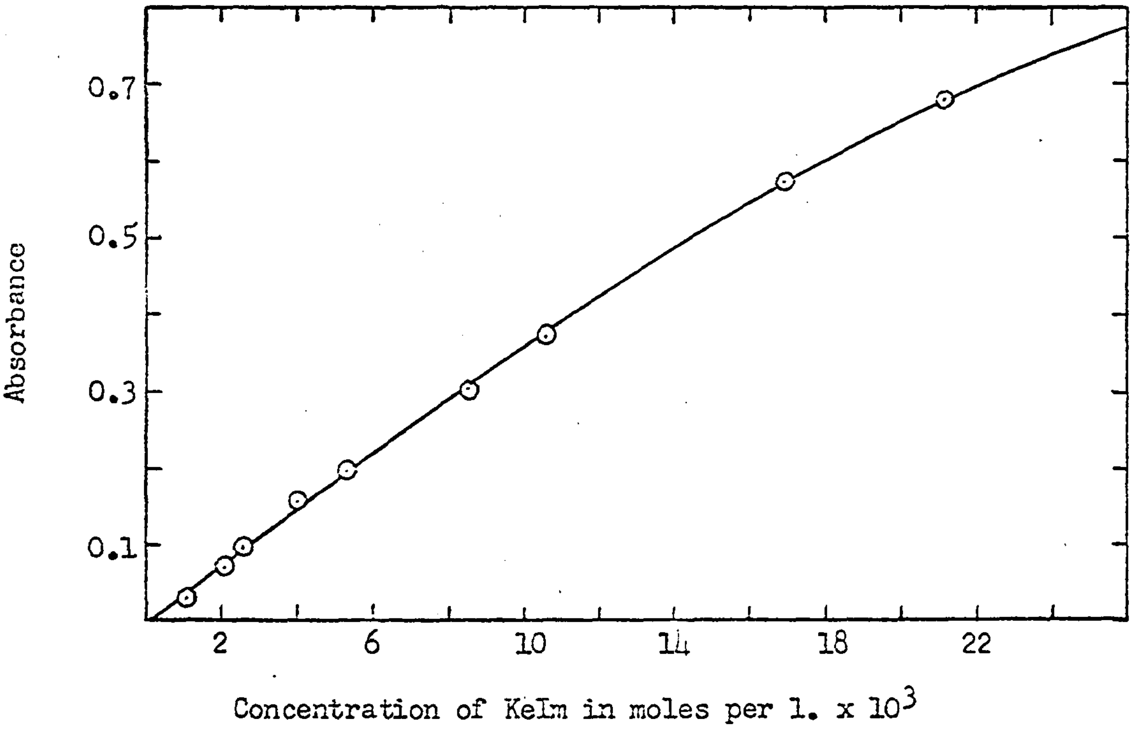

0.7
0.5
0.3
0.1
Absorbance
2
6
10
14
18
22
Concentration of KeIm in moles per l. x 10^3

Table 10. KeIm formation and subsequent disappearance in the decomposition of AIBN in acetonitrile at 80°

Time in minutes	Absorbance	KeIm concentration in moles/l x 10^3
20	0.112	2.4
40	0.256	5.8
60	0.331	7.5
80	0.376	8.5
100	0.386	8.8
120	0.396	9.0
140	0.385	8.8
160	0.370	8.4
180	0.348	7.9
200	0.332	7.5
220	0.310	7.0
240	0.289	6.5
260	0.274	6.2
280	0.259	5.8
300	0.245	5.5
780	0.063	1.3
1080	0.026	0.6
1400	0.012	0.1
1640	0.009	0
2240	0.003	0

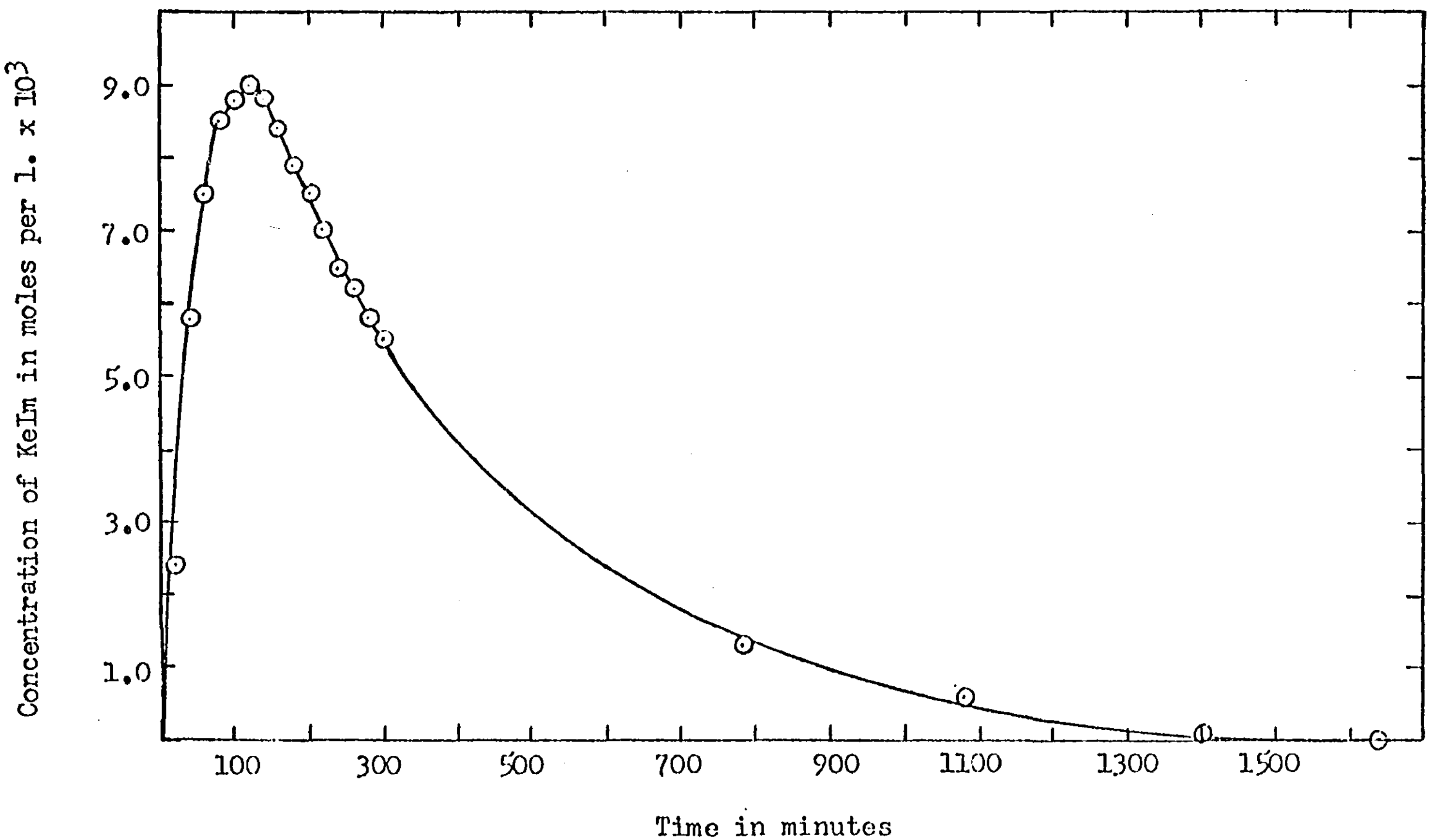


Figure 11. KeIm formation and subsequent disappearance in the decomposition of AIBN in acetonitrile at 80°

the copper chloride. Aliquots were removed and filtered to remove any undissolved cupric chloride, but the results were unsatisfactory and seemed to indicate some dependence on the rate of dissolution of the cupric chloride. This procedure was modified by adding the cupric chloride in solution and in this case the KeIm peak had disappeared by the time the first aliquot had been put in the IR cell and the spectrum run. In an attempt to speed up the process of sample taking and spectrum taking, it was discovered that a ratio of $\frac{CuCl_2}{KeIm} = 2$ was not enough to cause the KeIm peak to disappear. A Job's law plot showed that the ratio needed was 3.

The Job's law plot was made by the procedure that follows. Separate solutions of $CuCl_2$ and KeIm in acetonitrile of about equal concentration were made up. Eleven 10 ml. volumetric flasks were numbered from zero to ten. The number of ml. of $CuCl_2$ solution equivalent to the flask number were added to each volumetric flask. The flask was then diluted to the mark with the KeIm solution, the flask shaken and the IR spectrum from 4.00 to 5.50μ taken from which the absorbance was determined. In a Job's law plot a graph of flask number versus absorbance is made and a smooth curve (usually a straight line) drawn from each end connecting the points. The flask number value at the point of intersection of the two curves is then used in the equation below to find the combining ratio.

$$\frac{\text{Moles of } CuCl_2}{\text{Moles of KeIm}} = \frac{\text{flask no. at intersection}}{10 - \text{flask no.}} \times \frac{(CuCl_2)i}{(KeIm)i}$$

In this case:

$$\frac{\text{Moles of } CuCl_2}{\text{Moles of KeIm}} = \frac{7.5}{2.5} \times \frac{1.528}{1.545} = 2.97$$

The data is given in Table 11 and the plot in Figure 5 in the Results and Discussion section.

GLC spectra taken of the reaction solution and of an aliquot which had been heated at 80° for 24 hours showed that no 2-cyano-2-chloropane and no tetramethylsuccinonitrile had

Table 11. Data for Job's law plot

Flask number	($CuCl_2$) x 10^3	(KeIm) x 10^3	Absorbance
0	0	15.4	0.471
1	1.53	13.9	0.408
2	3.06	12.3	0.379
3	4.59	10.8	0.310
4	6.12	9.24	0.248
5	7.65	7.70	0.188
6	9.18	6.16	0.123
7	10.7	4.62	0 041
8	12.2	3.08	0
9	13.8	1.54	0
10	15.3	0	0

formed in the reaction. A reaction using 1 g of KeIm and 3 g of cupric chloride was run and the solvent (CH_3CN) was evaporated under reduced pressure. The residue remaining was a black amorphous mass which was insoluble in cyclohexane, ether, benzene, carbon disulfide, carbon tetrachloride, and chloroform and which appeared to react with water, tetrahydrofuran, dimethylformamide, and 1,2-dimethoxyethane (might be due to water in some of these). Thus, acetonitrile is the only known solvent for this black amorphous material. This amorphous material appeared to have a melting point range of 135-150°. A copper determination by titration with ethylenediaminetetraacetic acid (EDTA) (PAN indicator) showed that this material contained 39.2% copper. Attempts to isolate a crystalline material from the substance by the use of benzene-acetonitrile and ether-acetonitrile solvent pairs were unsuccessful. The material was redissolved in acetonitrile and benzene added until some of the material came out of solution, the liquid decanted, the precipitate dried by removal of the solvent under reduced pressure, and the process repeated on the decantate. A copper determination of the first two precipitates formed in this way (titration with EDTA using PAN indicator) showed that they contained 38.8% and 40.3% copper respectively. Since these values are essentially the same as that for the original material, no attempt was made to repeat the procedure so a copper analysis could be run on the material that remained in solution when water was accidentally added to the remaining decantate. In this reaction where large amounts of cupric chloride were used without increasing the amount of acetonitrile, most of the cupric chloride did not go into solution when added to the acetonitrile, but after addition of the KeIm, almost all of the cupric chloride dissolved.

A polarographic study was made to see if this might tell us if we had a copper complex or a compound, but the results were unsatisfactory. The half-wave potentials did not appear to change which implies that the copper was not present as a copper complex.

Some of the black amorphous material was added to water and stirred vigorously. The water became a blue color and a small amount of a greenish colored precipitate formed which was filtered off. The filtrate was extracted three times with ether. The ether was evaporated from these ether extracts leaving a white solid tinged with green, m.p. 98-101. A sodium fusion of this solid gives a weak positive test for chlorine and nitrogen. An IR spectra taken in carbon tetrachloride shows a strong absorption peak at 5.91μ which is typical of amide carbonyl absorption. This material was recrystallized from carbon tetrachloride and then sublimed giving a white solid, m.p. 103-104. An NMR (see Figure 12) of this purified material shows a broad NH peak (equivalent to 1 proton) and a doublet or two singlets (equivalent to 12 protons or each singlet equivalent to 6 protons). An IR spectra taken in chloroform (see Figure 13) shows a weak nitrile absorption at 4.46 which was not present in CCl_4 spectra (probably due to larger concentration possible in $CHCl_3$). A basic hydrolysis of the material was made, but no compounds could be isolated from the hydrolysis. An elemental analysis was run by Schwartzkopf Microanalytical Laboratory: % expected for $C_8H_{13}ClN_2O$, C 50.96, H 6.896, Cl 18.80, N 15.92; % found, C 50.66, H 7.06, Cl 18.78, N 15.73. All the above data fit the compound 2-chloro-2-methyl-N-(2-cyano-2-propyl)-propionamide, $(CH_3)_2CClCONHC(CH_3)_2CN$.

The NMR and IR spectra for 2-chloro-2-methyl-N-(2-cyano-2-propyl)-propionamide (Figures 12 and 14) were compared with the NMR and IR spectra of 2-methyl-N-(2-cyano-2-propyl)-propionamide (Figures 13 and 15).

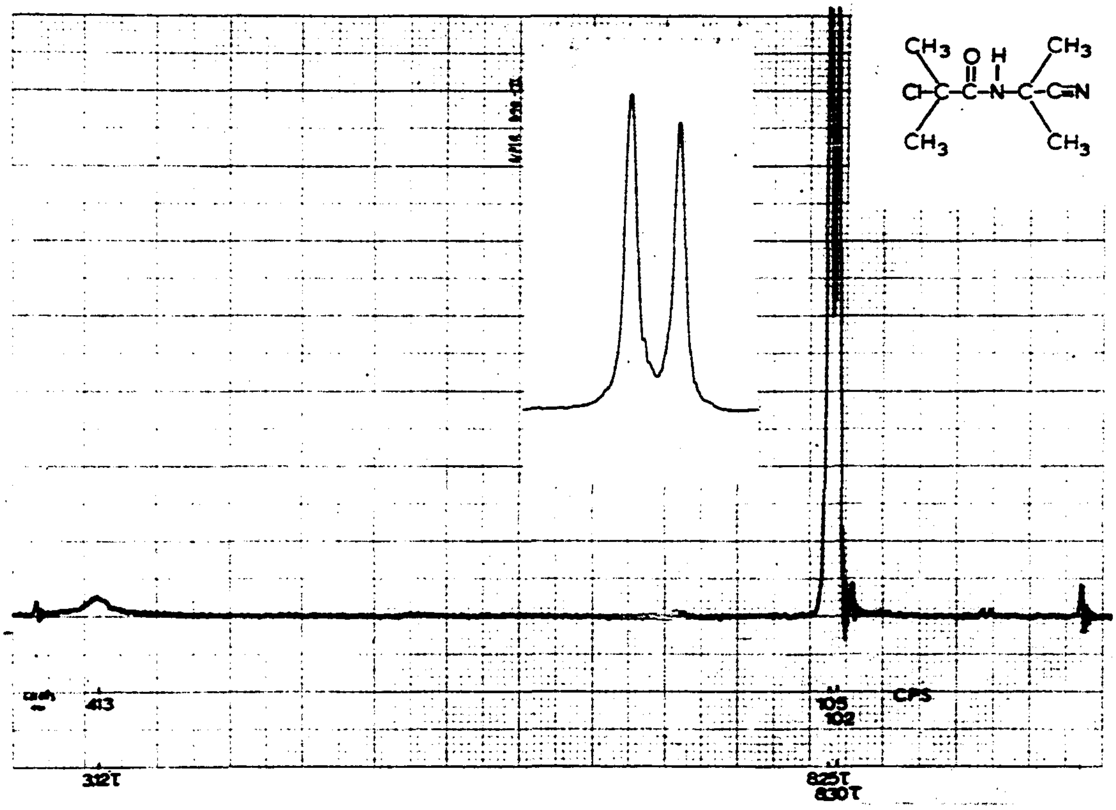
Gas liquid chromatographic (GLC) analysis

The gas chromatographic analysis was done on two different instruments: a model constructed by Professor Glen A. Russell (henceforth designated Russell model) employing a hot wire thermal-conductivity detector and a Perkin-Elmer Vapor Fractometer Model 154-D (henceforth designated P-E 154-D). All columns were constructed of 1/4 inch O.D. metal tubing.

GLC conditions I A 2-meter Perkin-Elmer B column

Figure 12. Nuclear magnetic resonance spectrum of 2-chloro-2-methyl-N-(2-cyano-2-propyl)-propionamide

Figure 13. Nuclear magnetic resonance spectrum of 2-methyl-N-(2-cyano-2-propyl)-propionamide


CH3 O H CH3
Cl-C-C-N-C-C≡N
CH3 CH3
413
105
102
CPS
312τ
825τ
830τ

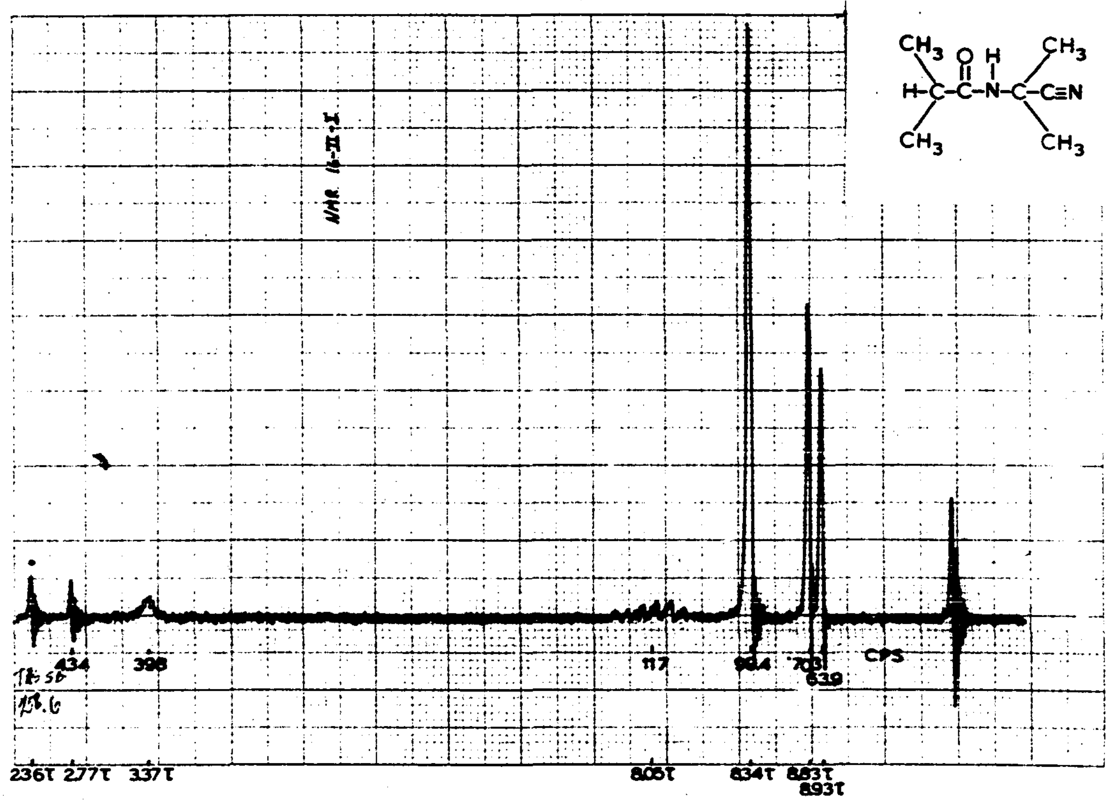
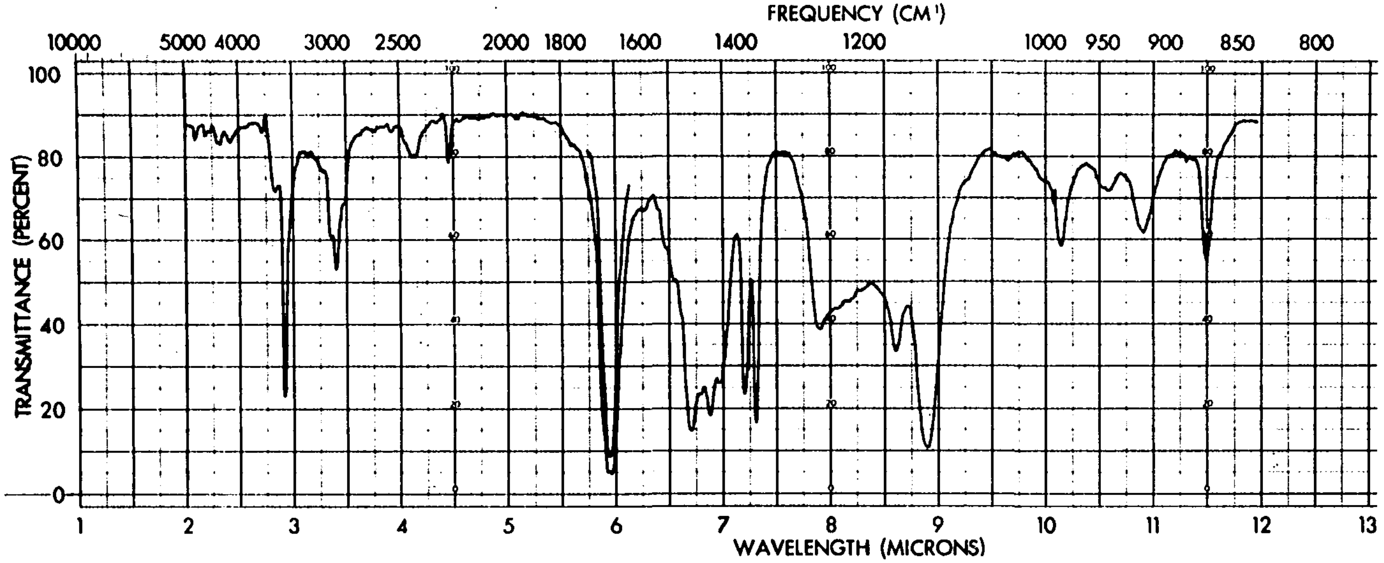
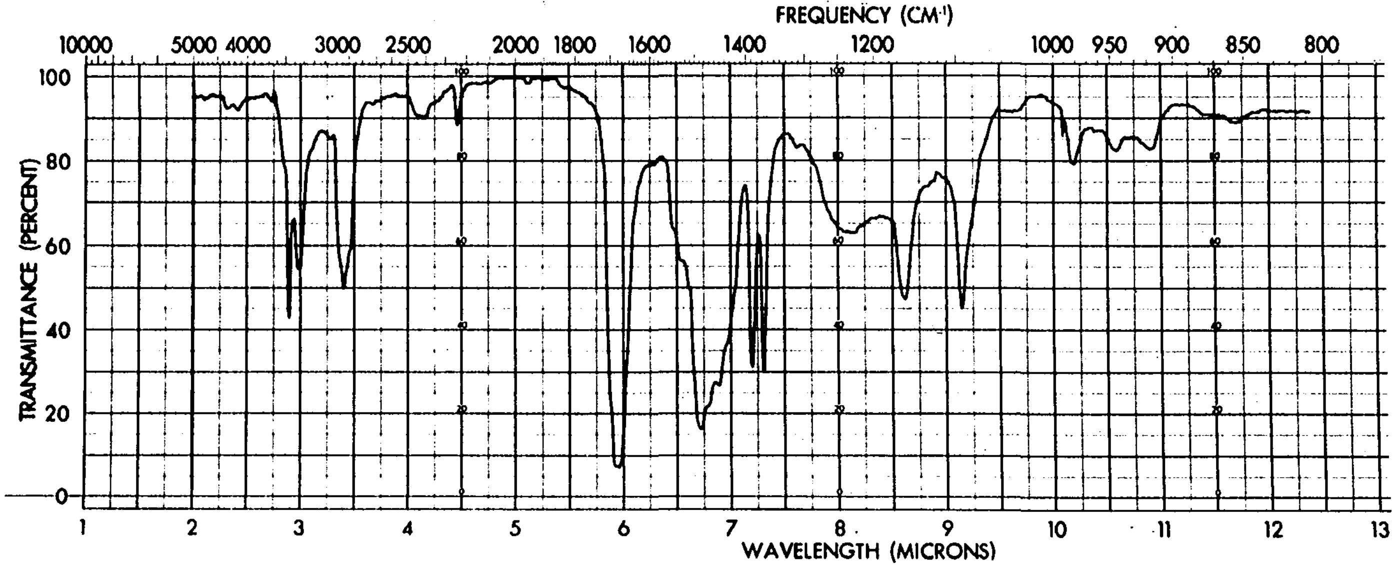

CH3 O H CH3
H-C-C-N-C-C≡N
CH3 CH3
434
398
117
98.4
70.3
63.9
CPS
236τ
277τ
337τ
805τ
834τ
883τ
893τ

Figure 14. Infrared spectrum of 2-chloro-2-methyl-N-(2-cyano-2-propyl)-propionamide in chloroform solution

Figure 15. Infrared spectrum of 2-methyl-N-(2-cyano-2-propyl)-propionamide in chloroform solution


FREQUENCY (CM^{-1})
10000
5000
4000
3000
2500
2000
1800
1600
1400
1200
1000
950
900
850
800
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
10
11
12
13
WAVELENGTH (MICRONS)


FREQUENCY (CM^{-1})
10000
5000
4000
3000
2500
2000
1800
1600
1400
1200
1000
950
900
850
800
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
10
11
12
13
WAVELENGTH (MICRONS)

(di-2-ethylhexyl sebacate on diatomaceous earth) was used in the Russell model with a column temperature of 120°, a detector temperature of 140°, and an injector temperature of 135° and with a helium flow rate of 61 cc/min measured at ambient conditions.

GLC conditions II A 2-meter Perkin-Elmer B column (di-2-ethylhexyl sebacate on diatomaceous earth) was used in the Russell model with a column temperature of 119°, a detector temperature of 137°, and an injector temperature of 146° and with a helium flow rate of 74 cc/min measured at ambient conditions.

GLC conditions III A 1-meter Perkin-Elmer O column (silicone grease on diatomaceous earth) was used in the Russell model with a column temperature of 165°, a detector temperature of 175°, and an injector temperature of 190° and with a helium flow rate of 35 cc/min measured at ambient conditions.

GLC conditions IV A 2-meter Perkin-Elmer R column (polypropylene glycol (UCON LB-550-X) on diatomaceous earth) was used in the P-E 154-D with a column temperature of 148° and with a helium flow rate of 34 cc/min measured at ambient conditions.

GLC conditions V A 2-meter Perkin-Elmer R column (polypropylene glycol on diatomaceous earth) was used in the P-E 154-D with a column temperature of 80° and with a flow rate of 86 cc/min measured at ambient conditions.

GLC conditions VI A Perkin-Elmer O column was used in the P-E 154-D with a column temperature of 150° and with helium flow rate of 88 cc/min measured at ambient conditions.

GLC conditions VII A Perkin-Elmer O column was used in the P-E 154-D with a column temperature of 125° and a helium flow rate of 132 cc/min measured at ambient conditions.

GLC conditions VIII Either two 1-meter 3,3'-oxydipropionitrile (ODPN) columns (70), 20% by weight on 80/100 mesh firebrick in series or one 2-meter ODPN column was used in the P-E 154-D with a column temperature of 80° and a helium flow of 84 cc/min measured at ambient conditions.

GLC conditions IX Either two 1-meter ODPN columns in series or one 2-meter ODPN column was used in the P-E 154-D with a column temperature of 70° and a flow rate of 86 cc/min measured at ambient conditions.

GLC conditions X A 2-meter ODPN column was used in the P-E 154-D with a column temperature of 55° and a helium flow rate of 53 cc/min measured at ambient conditions.

GLC conditions XI Two columns were used in series in the P-E 154-D. A 2-meter R column was followed by a 1-meter ODPN column. The column temperature was 72° and the helium flow rate was 57 cc/min measured at ambient conditions.

GLC conditions XII Two columns were used in series in the P-E 154-D. A 1-meter ODPN column was followed by a

1-meter di-N-propyl tetrachlorophthalate column (71). The column temperature was 85° and the helium flow rate was 66 cc/min measured at ambient conditions.

Retention times A list of retention times is given in Table 12 and Table 22. Table 12 gives retention times for GLC conditions I-VII which were used for the GLC analyses of reaction run in the first part of this thesis. Table 22 appears at the end of the section on apparatus and procedure in the second part of this thesis and gives retention times for GLC conditions VIII-XII which were used for the GLC analysis of reactions run in that part of this thesis. The retention times given can only be considered approximate since no effort was made to determine retention times accurately with very dilute samples. The retention times for reaction products and internal standards are fairly accurate, however, since in these cases they are present in fairly small concentrations. In Table 12, actual retention times in minutes are given and in Table 22 they are given relative to acetone. In cases of compounds which have high retention times that were not known, a known minimum is indicated.

Correction factors Correction factors given in Table 13 are calculated from the formula

$$K = \frac{\text{Moles A}}{\text{Area A}} \times \frac{\text{Area B}}{\text{Moles B}}$$

In all instances compound B was used as the internal standard in a GLC analysis. In some cases where GLC conditions XI were

Table 12. Retention times of selected compounds

Compound	GLC conditions	Retention times in minutes
Acetonitrile	I,III,IV,V,VII	1.9,0.18,0.96,5.0, 0.5
i-Propanol	I,II,III,IV	2.0,1.1,0.2,1.24
2-Fluoro-2-cyanopropane	I	4.6
Benzene	I,III,IV,VI	5.1,0.4,0.98,0.4
Benzotrifluoride	I	6.3
2-Chloro-2-cyanopropane	I,II,V	7.9,4.2,11.0
Acetone	V	2.2
Toluene	I,II,V	10.8,5.6,14.0
Pyridene	I	10.1
2-Bromo-2-cyanopropane	I	13.3
Dimethyl sulfoxide	II	19.3
o-Dichlorobenzene	VII	2.5
Phenyl isothiocyanate	VII	5.8
Tetramethylsuccinonitrile	III,VI	1.9,1.52
o-Nitrotoluene	III,VI	3.3,2.94
Biphenyl	VI	7.79
Chlorobenzene	IV	5.6
Benzonitrile	IV	16.7

Table 13. Correction factors for GLC

Compound A	Compound B	Correction factor	GLC conditions
2-Chloro-2-cyanopropane	Toluene	1.10	I
2-Chloro-2-cyanopropane	Carbon tetrachloride	1.04	I
Tetramethyl-succinonitrile	o-Nitrotoluene	1.01	III,VI
Benzonitrile	Chlorobenzene	0.950	IV
Phenyl isothiocyanate	o-Dichlorobenzene	1.07	VII
Phenyl benzoate	Diphenyl	1.07	0,202°
Benzene	Toluene	1.08	Ref. 16
Chlorobenzene	Toluene	0.98	Ref. 16
_t_-Butyl chloride	Toluene	1.05	VIII
Acetone	Toluene	1.29	VIII
_t_-Butanol	Toluene	1.14	VIII
Acetone	Ethylbenzene	1.37	VIII
_t_-Butanol	Ethylbenzene	1.23	VIII
Acetone	Cumene	1.42	VIII
_t_-Butanol	Cumene	1.24	VIII
Acetone	Benzene	1.10[a]	XI
_t_-Butanol	Benzene	1.08[a]	XI
_t_-Butyl chloride	Benzene	0.933	XI
Acetone	Benzene	1.15	XI

---

[a] Cyclohexane present which affects this value.

Table 13. (Continued)

Compound A	Compound B	Correction factor	GLC conditions
_t_-Butanol	Benzene	1.07	XI
Acetone	Benzotrifluoride	1.40[a]	XI
_t_-Butanol	Benzotrifluoride	1.28[a]	XI
_t_-Butyl chloride	Carbon tetrachloride	1.07	XI
Acetone	Carbon tetrachloride	1.29[a]	XI
_t_-Butanol	Carbon tetrachloride	1.29[a]	XI

used, the absence of cyclohexane would probably give different correction factors. Those correction factors so affected are indicated in Table 13. In all cases, the GLC conditions used in determining these correction factors is given under the heading GLC conditions.

Infrared (IR) analysis

A Perkin-Elmer Model 21 double beam infrared spectrophotometer was used for all IR spectra. For the quantitative IR work with the KeIm work, matched 1.0 mm sodium chloride cells were used. The absorbance was calculated by using the "base line density" method (72).

Ultraviolet (UV) analysis

A Beckman DK-2A Recording Spectrophotometer was used for all UV analyses.

SUMMARY

The ability of transition metal salts to act as traps for organic free radicals depends on several things:

1. The cation. There is no apparent general relationship between the ability to trap radicals and the reduction potential or electronegativity. The apparent order of ability judged from reaction in benzene using chloride salts is $P^{+5} > Fe^{+3} > Te^{+4} > Sb^{+5} > Cu^{+2} > Mo^{+5} > V^{+4} > Ti^{+4}$. All the sulfur chlorides tried gave good yield of RX.
2. The anion. Judging from the results with cupric salts and phenyl radicals and 2-cyano-2-propyl radicals, the importance of anions in radical trapping ability of metal salts is in the order $Br > Cl > SCN > RCO_2 > CN > OCH_3, CH_3$. Since the reaction is postulated to go through a ligand transfer mechanism, i.e., $R\cdot + MX_n \longrightarrow (R\cdots X\cdots MX_{n-1}) \longrightarrow RX + M^{m-1} X_{m-1}$, this reflects the ability of the anion to form a ligand bridge in the transition state.
3. The neutral ligand coordinated with the metal. The amount of trapping found is in the order $CuCl_2\cdot 2PY > FeCl_3\cdot 6H_2O > CuCl_2\cdot 2H_2O > FeCl_3 > CuCl_2$. This reflects the ability of the neutral ligand to increase the electron density around the metal and its ability to form a transient <u>pi</u>-complex with the

radical involved.

4. The solvent or the solubility of the metal salt in the solvent. The amount of trapping is greater with a homogeneous reaction mixture than with a heterogeneous reaction mixture. In the case of $CuCl_2$, the amount of trapping with a given solvent is in the order acetonitrile > isopropanol > benzene. Since isopropanol is probably a slightly better solvent than acetonitrile, this is taken as further support for the importance of the ability of coordinated neutral ligands to form transient pi-complexes with the radical.

Dimethyl-N-(2-cyano-2-propyl)-ketenimine, $(CH_3)_2C{=}C{=}N{-}C(CH_3)_2CN$, known to be an intermediate in the decomposition of AIBN does not form any 2-chloro-2-cyanopropane or tetramethylsuccinonitrile when reacted with cupric chloride in acetonitrile. This indicates that it is not a stable product when AIBN is decomposed in the presence of cupric chloride. Hydrolysis of the residue left after acetonitrile is removed from the reaction mixture above gave 2-chloro-2-methyl-N-(2-cyano-2-propyl)propionamide, $(CH_3)_2CClCONHC(CH_3)_2CN$.

Experimental evidence supports the idea that CuX^+ is the important copper species in the Sandmeyer reaction.

PART II. SOLVENT EFFECTS IN REACTIONS OF t-BUTOXY RADICALS

INTRODUCTION

In an exploratory experiment to determine the feasability of a study of the effect of aromatic metal pi-complexes on the t-butoxy radical, an unexpected solvent effect was noted in acetonitrile. This led to the present study of solvent effects.

The purpose of this study was to determine what effect the polarity of the solvent (dielectric constant) had on the mode of reaction of the t-butoxy radical generated by thermolysis of di-t-butyl peroxide and in conjunction with this, to study the effect, if any, of aromatic metal pi-complexes on the reactivity of the t-butoxy radical.

REVIEW OF LITERATURE

Since free radical intermediates do not usually have a positive or negative charge, they would not be expected to be sensitive to the polarity of the solvent (73, 74). There have been several cases where the effect of solvent on reaction rates of free radical processes has been insignificant (75-80). These include a study of the overall rate of styrene polymerization (75), a study of rate and copolymer structure in vinyl copolymerization (76, 77), and a study of the rate of decomposition of various azo compounds (78-80). However, in the latter case, other workers have observed a small solvent effect (81-83). They also report relatively large but compensating changes in the entropy and enthalpy of activation which have been questioned and appear to be the result of experimental error (84).

It seems certain that the alternating effect observed in vinyl copolymerization is due to polar contributions to the transition state (74). One explanation is that electron-withdrawing and electron-supplying groups set up permanent charge distributions in monomer and radical which would increase or decrease the energy required to bring the two species together in the transition state. This would predict a pronounced dependence of monomer reactivity ratios upon the dielectric constant of the medium. This is not observed. To explain this, a mutual polarization of radical and olefin as they approach the transition state is assumed. This becomes important only as the separation of the reactants becomes very small with the result that few lines of force radiate into the surrounding medium. Another explanation is that the energy of the transition state is lowered by the participation of resonance structures in which electron transfer has occurred between radical and olefin.

Further evidence of polar effects in free radical reactions was observed by Hendry in the autoxidation of cyclohexene and cumene (85). He found that there is a relationship between the dielectric constant of the solvent and the rate of oxidation. The rate of oxidation increases as the dielectric constant increases. Although the points are somewhat scattered, it appears that there is a linear relationship between $\log(\text{rate} - R_i/2)$ and $(d/M)(D - 1)/(2D + 1)$ where R_i is the rate of initiation of free radicals, d is the density of the pure solvent, M is the molecular weight of the pure solvent, and D is the dielectric constant of the pure solvent. The scatter of the points is explained as probably resulting from the approximation of the physical constants (d, M, and D) for solutions 2M in cyclohexene by use of the constants for the pure solvent. The variation of the Kirkwood-Onsager parameter (86, 87) employed by Hendry was developed by Powling and Bernstein (88, 89).

The most pronounced effect of solvent on free radical reactions is that observed by Russell in the photochlorination of hydrocarbons (90-92). Here the ability of the solvent to effect the reaction is dependent on its ability to form a complex with the chlorine atom rather than its dielectric constant (ionizing power). In the case where 2,3-dimethylbutane is the hydrocarbon carbon being chlorinated, the relative reactivities of the tertiary and primary hydrogens toward the chlorine atom at 55°C increases from 3.5:1 in aliphatic solvents to 32:1 in 8M benzene. In the case of aromatic solvents, there is a quantitative relationship between the magnitude of the solvent effect and the basicity of the solvent determined by the equilibrium constant for interaction with hydrogen chloride. This is strong evidence for formation of a _pi_-complex between the aromatic solvent and the chlorine atom since the stability of the _pi_-complex should increase with the basicity or electron density of the aromatic ring. While many non-aromatic solvents have little effect on this reaction, some of them, notably _t_-butyl alcohol, dioxane, _n_-butyl ether, dimethylformamide, thionyl chloride, sulfur monochloride, carbon disulfide, and some alkyl iodides, do show a solvent effect. Some of these will undergo acid-base interactions with chlorine atoms at the most electron rich site similar to the _pi_-complexes observed for aromatic solvents. Carbon disulfide which produces a large solvent effect, however, probably involves formation of a _sigma_-complex and the effect of the alkyl iodides is probably due to a complex with an expanded valence shell for the iodine atom.

From this study, it appears possible to separate inductive effects and resonance effects in complexing solvents, at least qualitatively. This is given by the rule: relative reactivities that are determined mainly by the availability of electrons in the carbon-hydrogen bond are not particularly sensitive to solvent effects while relative reactivities that are determined mainly by the stabilities of the incipient free radicals are very sensitive to changes in solvent (91). The relative reactivities of primary and tertiary hydrogen atoms of 2,3-dimethylbutane toward the chlorine atom at 25 degrees increases from 4.2:1 to 20:1 to 225:1 as the solvent changes from aliphatic to 4M benzene to 12M carbon disulfide. Here the strengths of the carbon-hydrogen bonds being ruptured are mainly responsible for the observed reactivities. The relative reactivities of the hydrogen atoms of tetramethylsilane and trimethylchlorosilane toward the chlorine atom at 25^{o} remain practically the same as the solvent changes from aliphatic to 4M benzene to 12M carbon disulfide, 6.5:1 to 6.9:1 to 5.1:1. While presumably the polar nature of the chlorine substituent causes the lower reactivity in the case of the trimethylchlorosilane, only a small solvent effect was observed. Further support for this rule is found in the data on photochlorination of n-butyl chloride in various solvents

(93). In the absence and in the presence of carbon disulfide at 0°, the following relative reactivities of the carbon-hydrogen bonds were observed:

CH_3-CH_2-CH_2-CH_2-Cl ·Cl in aliphatic solvent

1.0 3.1 1.35 0.3

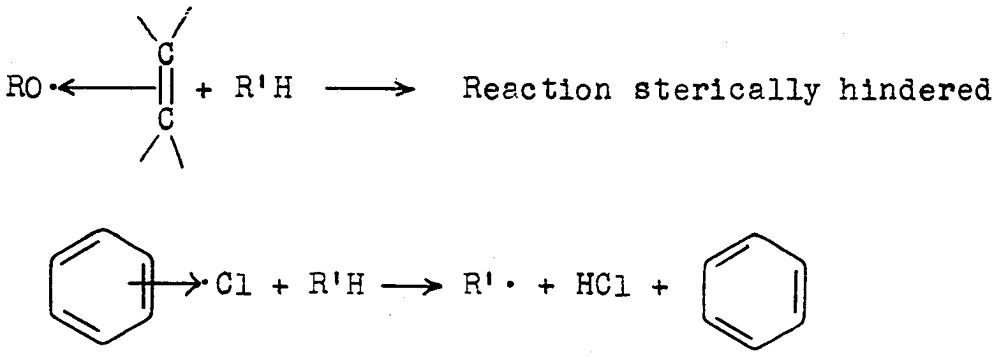
CH_3-CH_2-CH_2-CH_2-Cl ·Cl in 11.1M carbon disulfide

1.0 8.1 2.4 0.5

Here the relative reactivities at the 1, 2, and possibly 3, positions are determined mainly by the polar effect of the chlorine substituent. The change in ratios at the 1 and 2 position is 4.5 to 4.8 and at the 2 and 3 position is 2.3 to 3.4 in the absence and presence of carbon disulfide illustrating the small solvent effect. In the 3 and 4 positions, relative reactivities are determined by differences in bond dissociation energy and the relative ratios change from 3.1 to 8.1 in the absence and presence of carbon disulfide which is a fairly large solvent effect (94).

A study of the effect of aromatic solvents on the _t_-butoxy radical generated by thermolysis of di-_t_-butyl peroxide shows a similar effect although much smaller. Several possible explanations for the decrease are that the temperature employed (130°) may cause extensive dissociation of the hydrocarbon-_t_-butyl radical _pi_-complex and that the driving force for the formation of this complex may be considerably less for a t-butoxy radical than a chlorine atom since the desire of a t-butoxy radical for an electron is less than that of a chlorine atom (95).

A rather pronounced effect of olefins on the mode of reaction of the t-alkoxy radical generated from the t-alkyl hypochlorite has been reported (96, 97). For example, the photoinduced decomposition of benzyl-dimethylcarbinyl hypochlorite at 40° in $C_2F_3Cl_3$ containing cyclohexane gives a ratio of acetone:alcohol of 1.28 while the presence of a small amount of cyclohexene increases this ratio to greater than 40. In the presence of as little as 3.6 mole % cyclohexene in the hydrocarbon mixture, only cleavage products resulted, no hydrocarbon was chlorinated, and the cyclohexene was recovered unchanged. Acrylonitrile and methyl acrylate, which have strong electron-withdrawing groups, were the only olefins of those tried which gave traces of alcohols. Here too, a pi-complex is believed to occur. This is a rapid reversible process and the solvent effects will be determined solely by solvation effects on the transition states involved. Thus, solvent molecules would be sterically excluded from close vicinity to the alkoxy radical favoring the beta-scission process. This difficulty should not arise with halogen atom reactions since presumably the "back side" of a complexed halogen atom is still available to attack a carbon-hydrogen bond.


RO·
C
C
+ R'H
Reaction sterically hindered
·Cl + R'H
R'· + HCl +

RESULTS AND DISCUSSION

Di-t-butyl peroxide is known to decompose by a first order process in the gas phase. Since the rate in solution is essentially the same, the rate determining step is the scission of the oxygen-oxygen bond

$$(CH_3)_3C\text{-}O\text{-}O\text{-}C(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot$$

In solution, the t-butoxy radical can react further in one of two ways. It can decompose to acetone and a methyl radical

$$(CH_3)_3CO\cdot \xrightarrow{k_1} (CH_3)_2C = O + CH_3\cdot$$

or it can abstract a hydrogen atom from the solvent or other hydrogen donor present in solution (74)

$$(CH_3)_3CO\cdot + RH \xrightarrow{k_2} (CH_3)_3COH + R.$$

From the ratio of acetone and t-butyl alcohol formed, it is possible to calculate the ratio of k_1/k_2 provided that the products do not result from radical-radical interaction and provided that acetone and t-butyl alcohol are formed only in the above reactions. The former requirement will always be satisfied when the ratio of acetone and t-butyl alcohol is independent of the t-butoxy radical concentration, while the latter requirement will nearly always be satisfied when the combined yield of acetone and t-butyl alcohol is quantitative based on the starting di-t-butyl peroxide (95). Russell has shown that the k_1/k_2 value is independent of the concentration of di-t-butyl peroxide (95). In the work reported here, it was observed that if the ratio of cyclohexane (the hydrogen donor) to di-t-butyl peroxide used was 5 or less, k_1/k_2 was not independent of the concentration of di-t-butyl peroxide (Table 14). From the data using acetonitrile as solvent, it appears that if this ratio is greater than 7, then the k_1/k_2 ratio is independent of the concentration of di-t-butyl peroxide. For the comparisons made in this study, the value of this ratio was kept around 13. In most cases, all of the di-t-butyl peroxide could be accounted for, within experimental error, in the combined yield of acetone and t-butyl alcohol.

The data for a number of solvents is given in Table 14. It will be noticed that except for a few questionable cases, the value of k_1/k_2 increases as the dielectric constant increases. An examination of the anomalous cases, pyridine, nitrobenzene, dimethyl sulfoxide, and nitromethane is necessary.

In addition to the solvents given in Table 14, 88% formic acid, pyridine N-oxide, acetamide, malononitrile, and succinonitrile were also tried. They were unsatisfactory because cyclohexane was insoluble in them both at room temperature and at 135°.

In the case of dimethyl sulfoxide, it will be noticed that only 48% of the di-t-butyl peroxide is accounted for. The value of k_1/k_2 is calculated on the assumption that the

Table 14. Products from decomposition of di-t-butyl peroxide in presence of cyclohexane in various solvents at 135°[a]

	Moles used x 10^4			Moles produced x 10^4		%$(\underline{t}\text{-BuO})_2$ accounted		
Solvent	Solvent	C_6H_{12}[b]	$(\underline{t}\text{-BuO})_2$[c]	t-BuOH[d]	Acetone	for	k_1/k_2[e]	D[f]
Cyclohexane	440.3	440.7	11.70	21.2	1.43	96.6	0.518	2.05
	450.0	450.0	4.482	7.92	0.545	95.9	0.548	2.05
Pyridine	527.5	60.5	4.438	5.50	2.98	95.4	0.585	12.5
Nitrobenzene	413.7	60.45	4.465	5.56	3.13	97.3	0.614	35.7
	483.6	60.3	11.78	13.7	6.23	84.4	0.495	35.7
Benzene	461.2	59.9	11.72	12.9	8.97	93.7	0.716	2.283
--[g]	216.2	90.09	4.434	6.67	1.91	96.7	0.739	2.283

[a] Initial volume of solution at room temperature was 5 ml. except where indicated.

[b] Cyclohexane.

[c] di-t-Butyl peroxide.

[d] t-Butyl alcohol.

[e] $$\frac{k_1}{k_2} = \frac{\text{acetone}}{\underline{t}\text{-BuOH}} \times \left[C_6H_{12}\right]_{135^\circ}; \quad \left[C_6H_{12}\right]_{135^\circ} = \frac{\text{moles used}}{\text{ml. used} \times \frac{\text{density at } 25^\circ}{\text{density at } 135^\circ}} \times \frac{1000 \text{ ml.}}{\text{liter}}$$

[f] Dielectric constant, for further information see Table 23, p. 156.

[g] Only 3 ml. of solution used.

Table 14. (Continued)

	Moles used x 10^4			Moles produced x 10^4		%($\underline{t}$-BuO)$_2$ accounted		
Solvent	Solvent	C_6H_{12}	($\underline{t}$-BuO)$_2$	$\underline{t}$-BuOH	Acetone	for	k_1/k_2	D
Dimethyl sulfoxide	686.7	60.13	4.462	0(4.67)[h]	4.25	47.6	0.872[i,j]	45
	669.9	59.35	11.80	0.162(13.1)	10.5	44.5	0.760[i,j]	45
	670	59.96	11.76	0.120(13.1)	10.4	44.4	0.759[i,j]	45
Nitromethane	899.0	60.05	4.42	2.91	2.58	61.8	0.809[j]	39.4
	903.5	61.51	4.500	2.78	2.56	59.4	0.873[j]	39.4
Acetophenone	364.5	59.80	4.445	4.61	3.93	96.0	0.930	17.0
Acetylacetone	410.8	60.0	4.482	4.63	4.40	100.5	1.02	24.5
Benzonitrile	413.3	60.0	4.432	3.91	4.53	95.2	1.16	26.5
Nitroethane	726	60.0	4.476	3.82	4.81	96.4	1.31	30.0
	705.5	60.0	11.72	11.1	9.86	89.8	0.93	30.0

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[h] Number in parenthesis is 2 x ($\underline{t}$-BuO)$_2$-acetone and the value used in calculation of k_1/k_2.

[i] Using value of $\underline{t}$-BuOH found as in h.

[j] Cyclohexane and solvent immiscible at room temperature. Assume total volume equal to the sum of the individual volumes.

Table 14. (Continued)

Solvent	Moles used x 10^4			Moles produced x 10^4		%$(\underline{t}\text{-BuO})_2$ accounted for	k_1/k_2	D
	Solvent	C_6H_{12}	$(\underline{t}\text{-BuO})_2$	$\underline{t}$-BuOH	Acetone			
Acetonitrile	804	60.3	4.445	3.11	5.80	100	1.88	37.5
	773	71.1	6.94	5.18	8.21	96.4	1.89	37.5
--g	477.6	36.12	5.085	3.52	6.52	98.8	1.87	37.5
	774	59.8	11.71	7.99	13.7	92.7	1.72	37.5
	772	59.7	11.71	8.23	14.1	95.3	1.72	37.5
Dimethylformamide	533	60.4	11.74	19.5	1.99	91.3	0.123[k]	
Octafluorodithiane	271.2	60.1	4.520	0.332	2.71	33.6		2.0
	271.4	60.05	4.425	0.472	2.79	36.8		2.0

[k] Calculated on molar concentration at room temperature, high value for $\underline{t}$-BuOH assumed due to hydrogen abstraction from methyl groups on DMF.

peroxide not accounted for had formed t-butyl alcohol which was dehydrated to isobutylene. The experimental procedure for finding the amount of isobutylene was not worked out so it is not known whether the amount of isobutylene formed would account for the rest of the di-t-butyl peroxide. However, when 5 ml. of a solution containing 6.75×10^{-4} moles of t-butyl alcohol in dimethyl sulfoxide was subjected to the same reaction conditions as the decomposition reactions, analysis showed that 6.13×10^{-4} or 90.7% of the t-butyl alcohol was unchanged. Furthermore, a similar reaction using 9.82×10^{4} moles of acetone showed 9.43×10^{-4} moles of acetone or 96.0% was unchanged. While this data does not prove anything conclusively, it certainly casts doubt on the validity of the assumption on which k_1/k_2 is calculated.

In the case of nitromethane, the value of k_1/k_2 is calculated from data which only accounts for 60% of the di-t-butyl peroxide. Thus the reliability of this value is very questionable.

In the case of nitrobenzene and pyridine, possible explanations will be discussed a little later. It should be noted, however, that Hendry also observed an anomalous behavior with nitrobenzene but of a much smaller magnitude (85).

The correlation between the value of k_1/k_2 and several functions containing the dielectric constant is given in Table 15 and shown graphically in Figures 16-18. The values for

Table 15. Comparison of k_1/k_2 values with several functions of the dielectric constant and with Hendry's Rate - $R_1/2$ data

Solvent	D[a]	(D-1)/ (2D+1)	(d/M)(D-1)/ (2D+1)[b]	k_1/k_2	Rate-$R_1/2$ from Hendry[c]
Cyclohexane	2.05	0.206	1.89(1.62)[d]	0.55	3.06
Pyridine	12.5	0.443	5.47(4.89)	0.58	
Nitrobenzene	35.7	0.479	4.68(4.33)	0.61	6.36
Benzene	2.28	0.230	2.58(2.21)	0.72	3.42
Dimethyl sulfoxide	45	0.483	6.77(6.10)	0 87	10.5
Nitromethane	39.4	0.481	8.91(7.66)	0.84	8.78
Acetophenone	17.0	0.457	3.90(3.53)	0.93	
Acetylacetone	24.5	0.470	4.57(4.12)	1.02	
Benzonitrile	26.5	0.472	4.58(4.13)	1.16	
Nitroethane	30.0	0.475	6.58(5.73)	1.31	7.49
Acetonitrile	37.5	0 481	9.10(7.64)	1.84	9.21

[a] Dielectric constant.

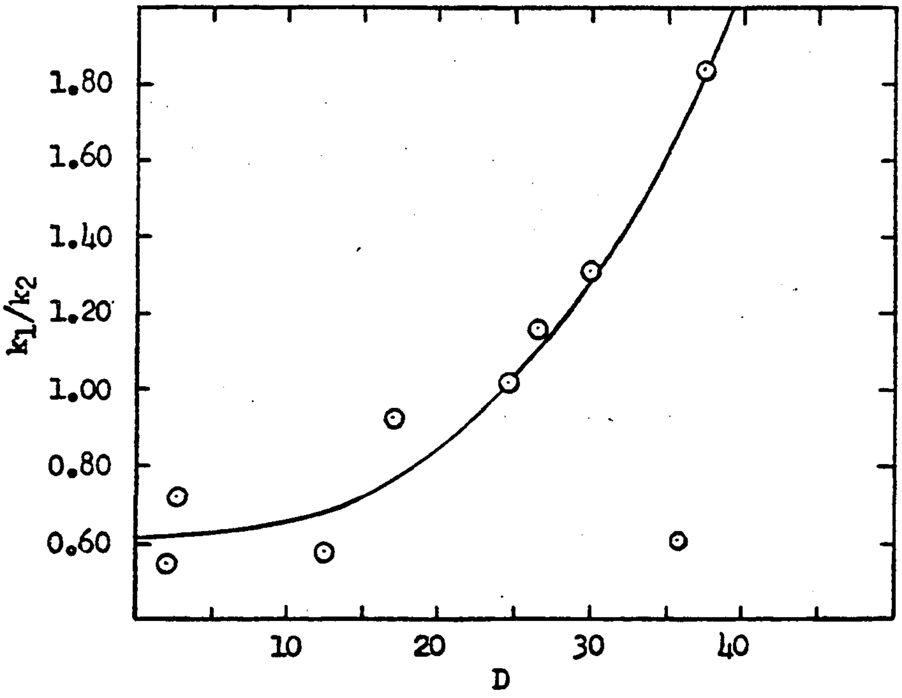
[b] d stands for density and M stands for molecular weight.

[c] See reference 85.

[d] Values in parenthesis were obtained using density at 135°; the others using density at 25°.

Figure 16. Decomposition of di-_t_-butyl peroxide at 135° in various solvents containing cyclohexane; comparison of k_1/k_2 values with the dielectric constant

Figure 17. Decomposition of di-_t_-butyl peroxide at 135° in various solvents containing cyclohexane; comparison of k_1/k_2 values with the Kirkwood-Onsager parameter according to Laidler and Eyring


k1/k2
1.80
1.60
1.40
1.20
1.00
0.80
0.60
10
20
30
40
D

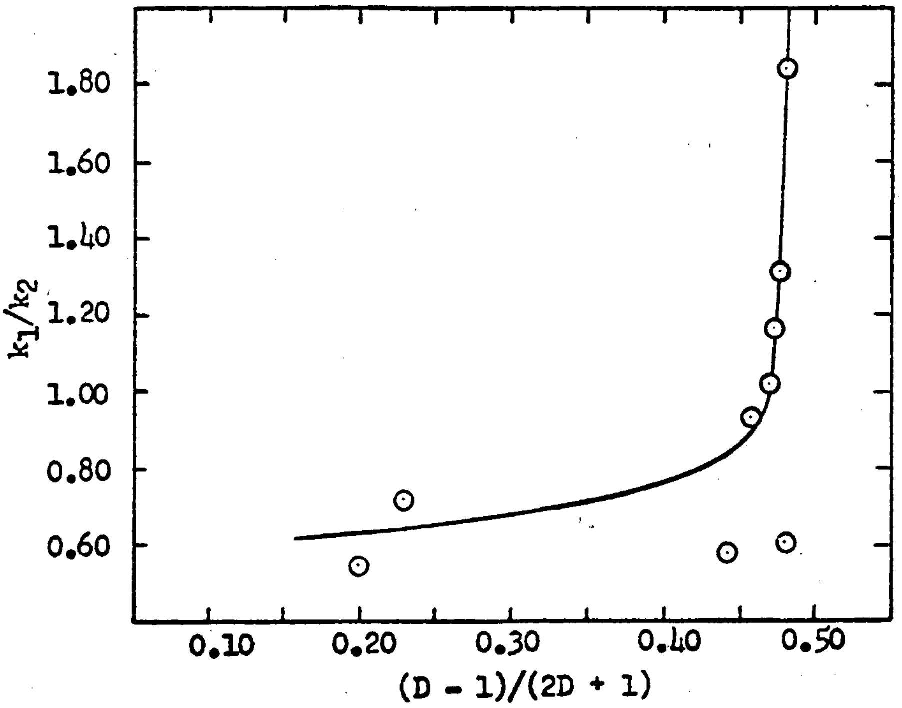
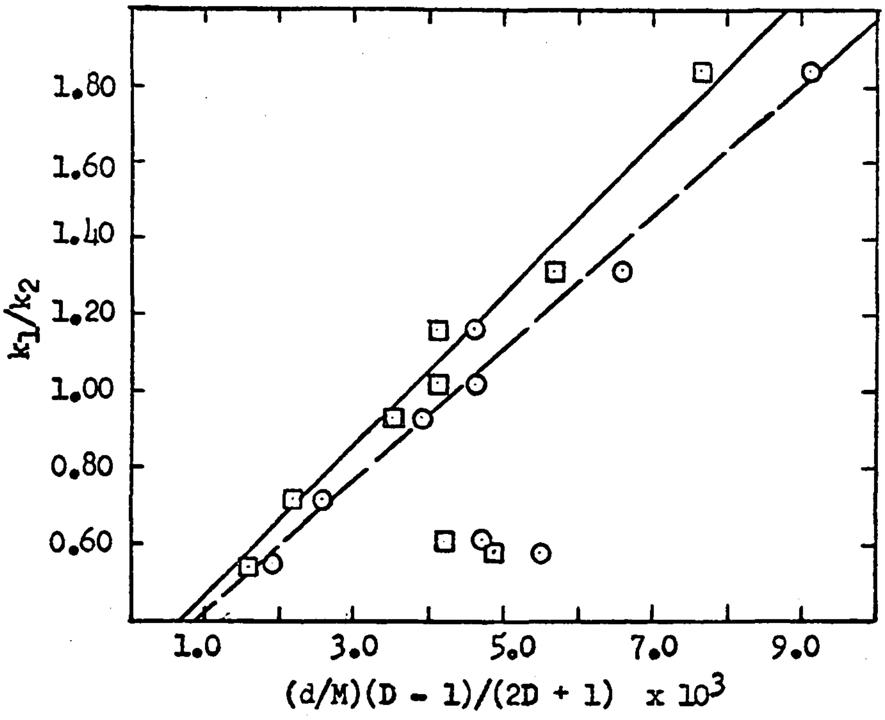

k1/k2
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.10
0.20
0.30
0.40
0.50
(D - 1)/(2D + 1)

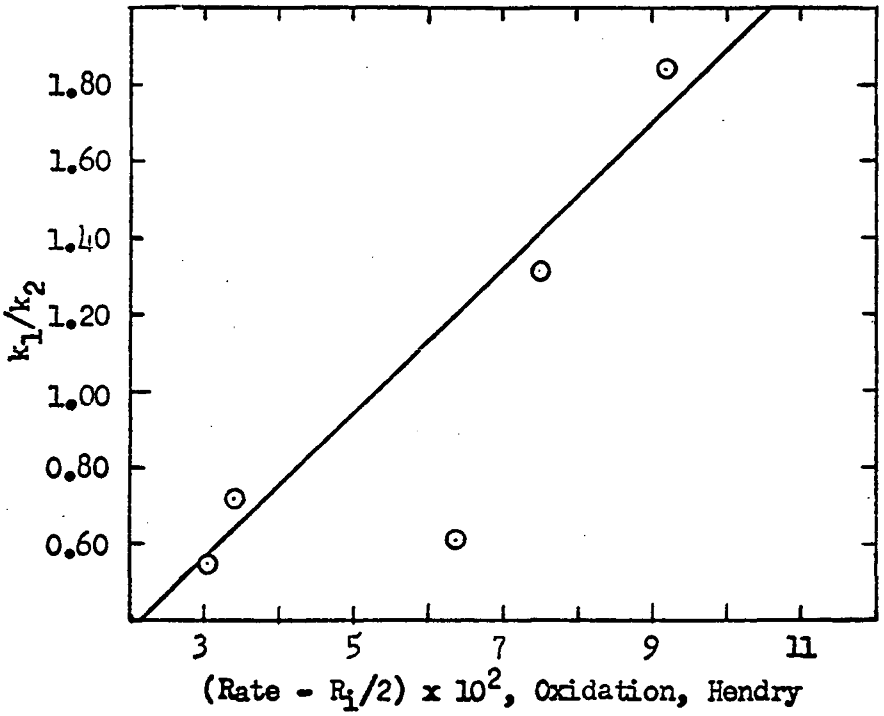
Figure 18. Decomposition of di-_t_-butyl peroxide at 135° in various solvents containing cyclohexane; comparison of k_1/k_2 values with the Kirkwood-Onsager parameter according to the method of Powling and Bernstein

⊙ —— using density at 25°

⊡ —— using density at 135°

Figure 19. Decomposition of di-_t_-butyl peroxide at 135° in various solvents containing cyclohexane; comparison of k_1/k_2 values with Hendry's values of (Rate - $R_1/2$) for the oxidation of cyclohexene


1.80
1.60
1.40
1.20
1.00
0.80
0.60
k1/k2
1.0
3.0
5.0
7.0
9.0
(d/M)(D - 1)/(2D + 1) x 10³


1.80
1.60
1.40
1.20
1.00
0.80
0.60
k1/k2
3
5
7
9
11
(Rate - R1/2) x 10², Oxidation, Hendry

dimethyl sulfoxide and nitromethane are not included in these figures. In the graph of k_1/k_2 vs D, Figure 16, where D is the dielectric constant of the pure solvent, the point for nitrobenzene was practically ignored when the curve was drawn. In the graph of k_1/k_2 vs $(D-1)/(2D+1)$, Figure 17, there were not enough intermediate points to warrant drawing a curve, but it was drawn anyway.

In the graph of k_1/k_2 vs $(d/M)(D-1)/(2D+1)$, Figure 18, where d is the density and M the molecular weight of the pure solvent, the lines drawn are the lines determined by the method of least squares ignoring the points for nitrobenzene and pyridine. The equations are:

using d at 25°

$$k_1/k_2 = \left[1.71 \times 10^2\ (d/M)(D-1)/(2D+1)\right] + 0.264$$

using d at 135°

$$k_1/k_2 = \left[1.99 \times 10^2\ (d/M)(D-1)/(2D+1)\right] + 0.250$$

If the points for nitrobenzene and pyridine are included, the equations for the lines determined by the method of least squares become:

using d at 25°

$$k_1/k_2 = \left[1.27 \times 10^2\ (d/M)(D-1)/(2D+1)\right] + 0.357$$

using d at 135°

$$k_1/k_2 = \left[1.83 \times 10^2\ (d/M)(D-1)/(2D+1)\right] + 0.194$$

When the points for nitrobenzene and pyridine are ignored, the linear correlation in this case is very good. Since the values of the physical constants, d, D, and M used are those of the pure solvent at room temperature (in most cases 20°, see Table 23) while the k_1/k_2 values refer to reactions run at 135° in which the solvent contains sizeable amounts of other materials (7 to 17 mole %), some scatter of the data is expected. It is difficult to see why nitrobenzene and pyridine would be affected so much more than the others, however, so there must be some other reason for their anomalous behavior. This function of the dielectric constant is a modification of the Kirkwood-Onsager parameter (86, 87) according to Powling and Bernstein (88, 89). Both an electrostatic factor and a non-electrostatic factor are involved in this formulation. The non-electrostatic factor is important for nitrobenzene (85) and perhaps is also important for pyridine.

Figure 19 shows the comparison of k_1/k_2 with Hendry's values (85) of (Rate - $R_1/2$) in the oxidation of cyclohexene for the solvents: cyclohexane, benzene, nitrobenzene, nitroethane, and acetonitrile. Here too, the nitrobenzene peak was ignored in drawing the line and intermediate points are needed for justifying the line at all.

To be sure that hydrogen abstraction would occur primarily from the cyclohexane, di-t-butyl peroxide was decomposed at 135° in most of the solvents in which hydrogen abstraction could occur. The results are given in Table 16. Results with some of the chlorohydrocarbon solvents are included. They

Table 16. Products from decomposition of di-*t*-butyl peroxide in various solvents at 135°

Solvent	Solvent		$(t\text{-BuO})_2$[a]		Moles produced x 10^4			%$(t\text{-BuO})_2$ accounted for	$\frac{k_1}{k_2}$
	Moles x 10^2	Molar conc.	Moles x 10^4	Molar conc. x 10^2	*t*-BuCl[b]	*t*-BuOH[c]	Acetone		
Cyclohexane	4.403	8.807	11.70	23.39	--	21.2	1.43	96.6	0.518
	4.500	9.000	4.482	8.8965	--	7.94	0.545	95.9	0.548
Acetophenone	4.186	8.372	4.493	8.986	--	2.13	6.26	93.3	22.3
Acetylacetone	4.758	9.517	4.476	8.952	--	2.76	6.37	102	19.6
Dimethyl sulfoxide[e]	5.494	13.734	3.570	8.924	--	0(4.57)	4.35	53.4	9.40
Acetonitrile	9.19	18.4	6.946	13.9	--	1.06	12.0	94.4	17.5
	9.02	18.0	11.71	23.4	--	2.20	20.2	95.8	13.9
	9.0	18.0[e]	11.70	23.4	--	2.38	20.5	97.8	13.0
--[f]	5.31	17.70	10.35	34.5	--	2.57	16.7	93.3	9.68
	9.2	18.4[e]	4.455	8.910	--	0.734	7.77	95.4	16.4

---

[a] di-*t*-Butyl peroxide.

[b] *t*-Butyl chloride.

[c] *t*-Butyl alcohol.

[d] 4 ml. of reaction mixture used.

[e] Assumed.

[f] 3 ml. of reaction mixture used.

Table 16. (Continued)

	Solvent		$(t\text{-}BuO)_2$		Moles produced x 10^4			%$(t\text{-}BuO)_2$ accounted for	$\frac{k_1}{k_2}$
Solvent	Moles x 10^2	Molar conc.	Moles x 10^4	Molar conc. x 10^2	t-BuCl	t-BuOH	Acetone		
Toluene	4.470	8.92	1.170	23.4	--	14.0	7.24	90.6	ca. 4.61
Carbon tetrachloride	5.044	10.088	4.483	8.966	0.084	0.515	8.21	98.5	
Trichloroethylene	5.429	10.858	4.538	9.075	1.63	0	2.64	47.1 (54.3)[g]	
Tetrachloroethylene	4.772	9.543	4.718	9.437	1.90	0.095	2.73	50.0 (59.1)[g]	

[g] See Table 17.

will be discussed below.

When the decompositions were carried out in several chloro-substituted solvents, the results were rather surprising. The results are tabulated in Table 17. In all cases where cyclohexane was present, sizeable amounts of _t_-butyl chloride were formed. In the case of trichloroethylene and tetrachloroethylene, sizeable amounts of _t_-butyl chloride were formed even when cyclohexane was absent. In all cases where _t_-butyl chloride was formed, HCl was also formed but it was not determined quantitatively. The only case in which all of the di-_t_-butyl peroxide could be accounted for was in the decomposition carried out in carbon tetrachloride with no cyclohexane present. As expected in this case, mostly acetone was formed, but trace amounts of _t_-butyl chloride and alcohol were found which must mean that trace amounts of chlorinated acetones were also present. In all cases, a large number of products were formed, all of which were not identified and the analyses were not worked out for some that were known to be formed.

A decomposition with cyclohexane present was carried out on a large scale in 1,2-dichloroethylene (ca 80% _cis_ and 20% _trans_) by use of a bomb. It was hoped to be able to isolate and identify conclusively the products formed. An attempt to isolate the acetone and _t_-butyl chloride from the low boiling solvent and unreacted cyclohexane by distillation was

Table 17. Products from decomposition of di-t-butyl peroxide in various chloro-substituted solvents with and without cyclohexane present

			Cyclohexane			$(t\text{-BuO})_2$		Moles produced $\times 10^4$			%
Solvent	Moles $\times 10^2$	Molar conc.	Moles $\times 10^3$	Molar conc. 25°	Molar conc. 135°	Moles $\times 10^4$	Molar conc. $\times 10^2$	t-BuCl	t-BuOH	Acetone	$(t\text{-BuO})_2$ accounted for
CCl_4	5.044	10.088	none	0	0	4.483	8.966	0.084	0.515	8.21	98.3
	4.353	8.706	6.02	1.204		4.435	8.870	2.54	--[a]	3.43	67.3
$HClC=CCl_2$	5.429	10.858	none	0	0	4.538	9.075	1.63	0	2.64	47.1 (54.3)[b]
	4.699	9.397	6.03	1.205		4.452	8.904	6.96[c]	0	0.729	86.4
	4.690	9.379	6.03	1.206		4.476	8.952	6.58[c]	0	1.25	87.5
cis-$CHCl=CHCl$	5.584	11.167	5.997	1.1994		4.482	8.965	7.10[c,d]	0	0.675	86.8

---

[a] Chloroform peak has same retention times. Assuming conversion factor (k) of 1, moles of $CHCl_3$ + moles of t-BuOH = 13.70×10^{-4}. Moles C_6H_{11} and/or C_2Cl_6 = 7.60×10^{-4} (k = 1 assumed).

[b] If two other unidentified peaks are included and k = 1 assumed (GLC condition X 3.6 min., 0.185 moles; 10.7 min., 0.478 moles).

[c] HCl formed in Rx.

[d] Based on a value k = 1.14 for t-BuCl - ϕCF_3 system from a rough calculation based on relative conversion factors of t-BuOH and acetone for several compounds.

Table 17. (Continued)

Solvent	Moles x 10^2	Molar conc.	Moles x 10^3	Molar conc. 25^0	Molar conc. 135^0	$(t\text{-BuO})_2$ Moles x 10^4	$(t\text{-BuO})_2$ Molar conc. x 10^2	Moles produced x 10^4 t-BuCl	Moles produced x 10^4 T-BuOH	Moles produced x 10^4 Acetone	% $(t\text{-BuO})_2$ accounted for
			Cyclohexane								
C_2Cl_4	4.772	9.543	none	0	0	4.718	9.437	1.90	0.095	2.73	50.0 $(59.1)^{e}$
	4.150	8.300	6.023	1.2046		4.482	8.965	6.65^{c}	0	0.263	77.1
			p-xylene								
CCl_4	4.278	8.555	6.017	1.2034		4.424	8.849	2.50	? [f]	3.77	70.9 $(101)^{g}$
			Chlorocyclohexane								
C_6H_6	3.658	7.316	6.004	1.2007		4.476	8.952	$4.64^{c,h}$	2.02^{h}	4.82^{h}	128

[e] If two other unidentified peaks are included and k = 1 assumed (GLC condition XI 1.53 min., 0.467 moles; 13.6 min., 0.384 moles).

[f] Chloroform peak has same retention time. Assuming k = 1, moles $CHCl_3$ + moles t-BuOH = 17.7.

[g] If two other unidentified peaks are included and k = 1 assumed (GLC condition X 0.81 min., 0.610 moles; 1.45 min., 2.04 moles).

[h] Conversion factors used were those found when C_6H_{12} present. They are probably too large in this case where no C_6H_{12} is present. Two other unidentified peaks are present (assuming k = 1, GLC condition XI, k = 1 assumed; 1.6 min., 2.17 moles; 10.2 min., 2.07 moles).

unsuccessful. An attempt to separate the higher boiling components was only partially successful. The only product isolated in a pure enough form to identify was one that had not been expected, although it turned out later that this particular reaction had been reported in the literature in 1949 (98). When a GLC spectrum indicated a mixture of two compounds, an NMR spectrum (Figure 20) indicated a cyclohexyl group, and an IR spectrum (Figure 21) a double bond absorption and a possible C-Cl absorption, 1-chloro-2-cyclohexylethylene was indicated. In the process of searching for physical constants, the aforementioned article was found. The physical constants, boiling point and refractive index, agree with those reported. Further evidence of a cis and trans mixture of 1-chloro-2-cyclohexylethylene was given by the isolation of cyclohexane carboxylic acid from a permanganate oxidation of the compound. The mechanism proposed by Schmerling and West (98) is

$R'OOR' \longrightarrow 2R'O\cdot \qquad R' = $ *t*-butyl

$R'O\cdot + RH \longrightarrow R'OH + R\cdot \qquad RH = $ cyclohexane

$R\cdot + ClXC{=}CXCl \longrightarrow RClXC{-}\dot{C}XCl \qquad X = Cl$ or H

$RXClC{-}\dot{C}XCl \longrightarrow RClC{=}CXCl + Cl\cdot$

$Cl\cdot + RH \longrightarrow R\cdot + HCl$

process repeats

Higher boiling components proposed to be formed by the reaction

Figure 20. Nuclear magnetic resonance spectrum of a mixture of *cis*- and *trans*-1-chloro-2-cyclohexylethylene

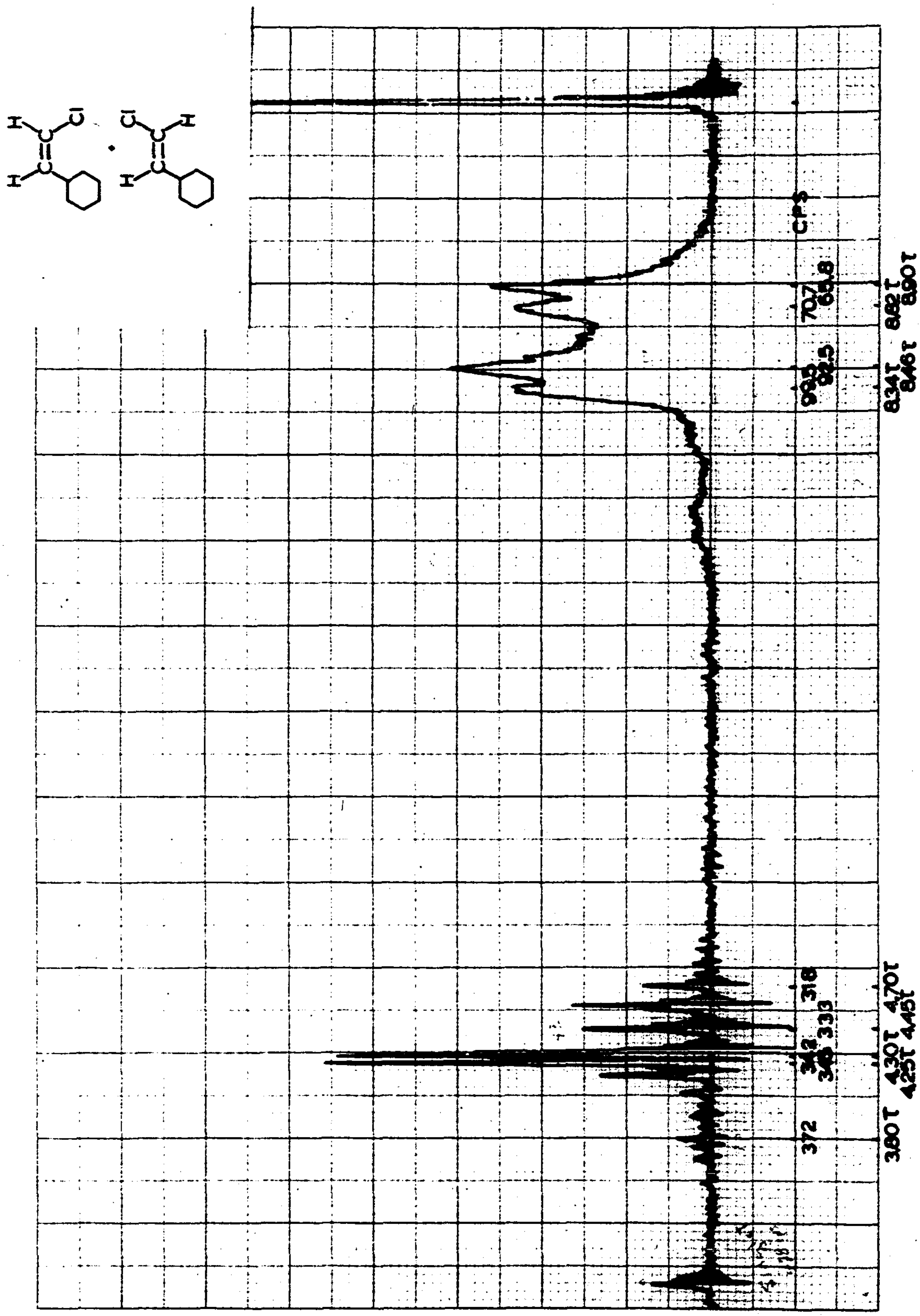
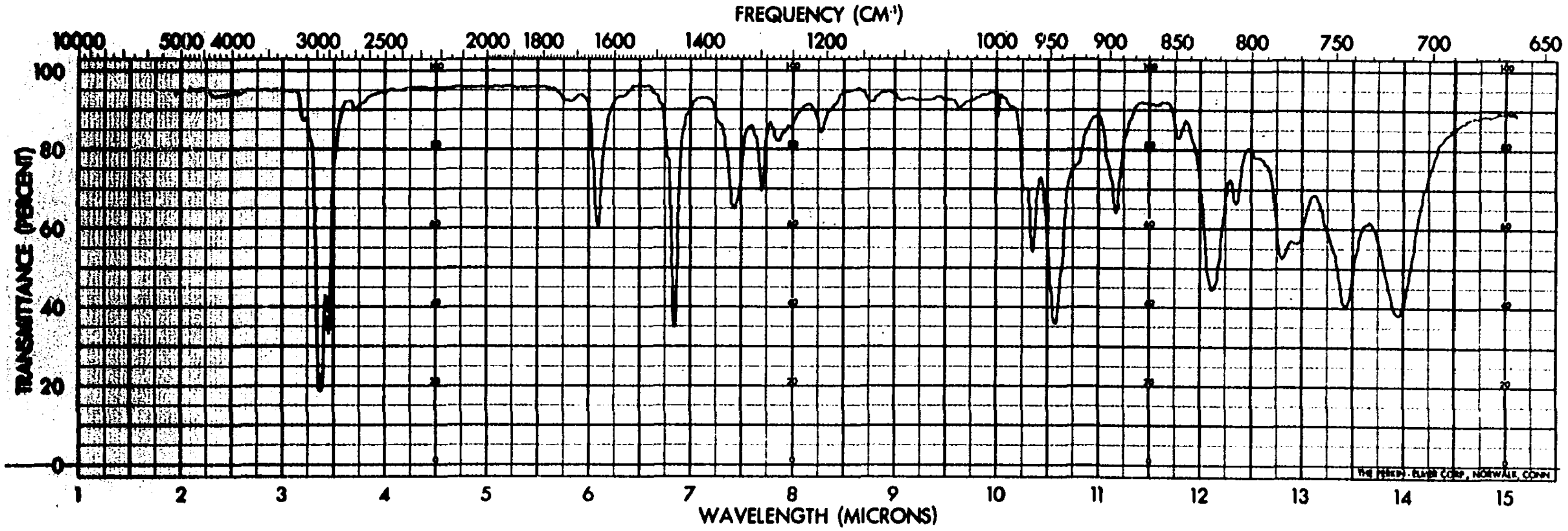

H
Cl
H
H
Cl
H
H
H
CPS
70.7
65.8
8.82T
8.90T
99.5
92.5
8.34T
8.46T
318
333
342
345
4.70T
4.45T
4.30T
4.25T
372
3.80T

Figure 21. Infrared spectrum of a mixture of *cis*- and *trans*-1-chloro-2-cyclohexylethylene

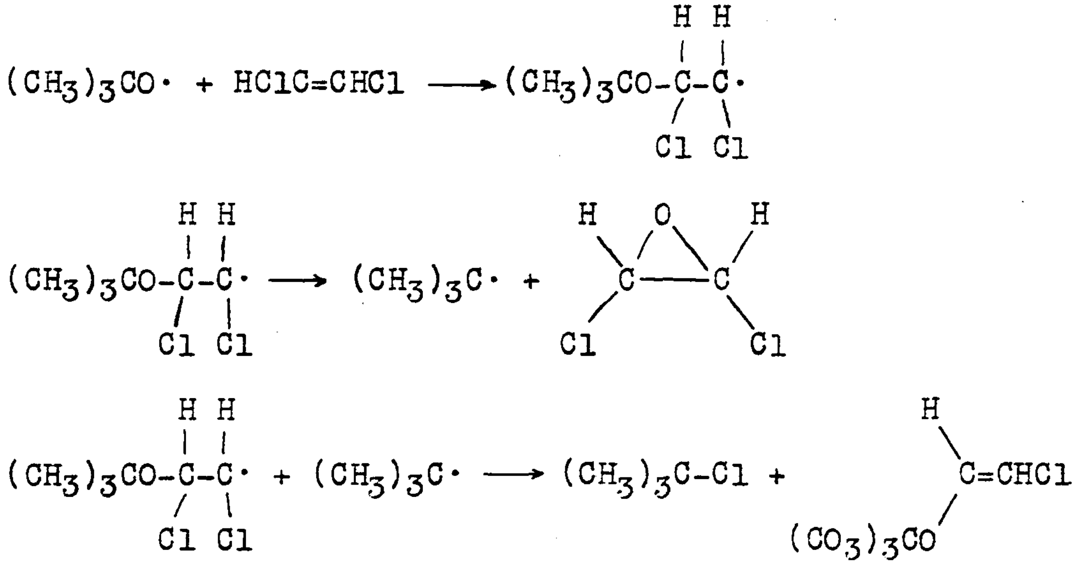

FREQUENCY (CM⁻¹)
10000
5000
4000
3000
2500
2000
1800
1600
1400
1200
1000
950
900
850
800
750
700
650
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)
THE PERKIN-ELMER CORP., NORWALK, CONN.

$$\mathrm{RXClC{-}\dot{C}XCl + ClXC{=}CXCl \longrightarrow RXClC{-}CXCl{-}CXCl{-}\dot{C}XCl}$$

$$\longrightarrow \mathrm{RXClC{-}CXCl{-}CX{=}CXCl + Cl\cdot}$$

In similar reactions in which the t-butoxy radical is generated by photolysis of t-butyl hypochlorite, Walling and Wagner do not mention any formation of t-butyl chloride (99). They give data for reactions at 0°, 40° and 100°. From this, it would appear that the difference in the manner of reaction observed here is due to the higher temperature at which the decomposition was carried out, but it is difficult to see why this should be so. A decrease in yield of t-butyl chloride might be expected, but a decrease to 0%, even at 100°, is unexpected. Of course, there might be a difference in the t-butoxy radicals generated in each case, but this seems very unlikely.

The mechanism given by Schmerling and West can explain the formation of t-butyl chloride in the decomposition of the peroxide in the chloroolefins carried out in the presence of cyclohexane. The HCl formed causes dehydration of the t-butyl alcohol to isobutylene which then adds HCl to give the t-butyl chloride. However it does not explain the formation of t-butyl chloride in these solvents in the absence of cyclohexane where acetone would be expected to be the only product. No good explanation is evident at this time. One possibility which might be plausible is shown in the reaction scheme below.

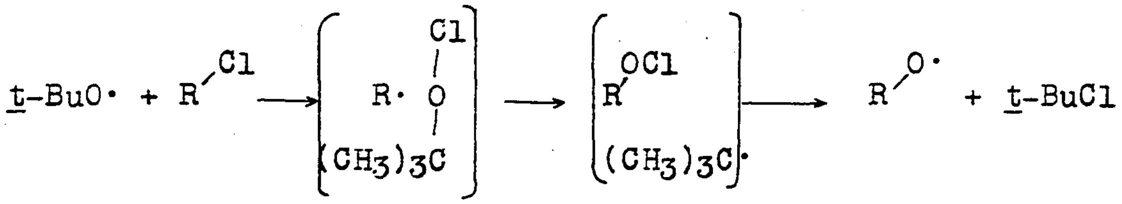


The last step would require the removal of a t-butoxy radical from solution for each t-butyl chloride molecule formed. Since only about 50% of the t-butoxy radicals are accounted for, this would also account for part of the other 50% of the t-butoxy radicals not accounted for in the reaction.

The formation of t-butyl chloride when the decomposition of di-t-butyl peroxide is carried out in carbon tetrachloride containing cyclohexane was also observed by Russell (95). He suggested as a possible explanation the abstraction of a chlorine atom from the solvent by the t-butoxy radical followed by the subsequent thermolysis of the t-butyl hypochlorite to give a chlorine atom which would go on to form HCl. The reaction of HCl and t-butyl alcohol then produces the t-butyl chloride. He also showed that chlorocyclohexane did not cause dehydration of the alcohol or form a detectable amount of HCl at 130°. From the present study, however, it appears that chlorocyclohexane may be involved since a decomposition of di-*t*-butyl peroxide in benzene containing chlorocyclohexane leads to sizeable amounts of *t*-butyl chloride (see Table 17). It should also be noted that *t*-butyl chloride is formed when *p*-xylene is used as the hydrogen donor in carbon tetrachloride (Table 17). Since the reaction

$$CCl_4 + C_6H_{12} \xrightarrow{\text{peroxide}} CHCl_3 + C_6H_{11}Cl$$

was observed to have a kinetic chain length of about 16 (95) and *p*-xylene would be expected to have one of comparable size, the concentration of the chlorinated hydrocarbons (call them RCl) could be large enough to be involved in the formation of the *t*-butyl chloride. It is difficult to conceive the manner in which this would occur using accepted radical reactions. One mode of transformation might be



$$\underline{t}\text{-BuO}\cdot + R{-}Cl \longrightarrow \left[\begin{array}{c} Cl \\ | \\ R\cdot\ O \\ | \\ (CH_3)_3C \end{array}\right] \longrightarrow \left[\begin{array}{l} R{-}OCl \\ \\ (CH_3)_3C \end{array}\right]\cdot \longrightarrow R{-}O\cdot + \underline{t}\text{-BuCl}$$

but there is no precedent for this type of reaction in the literature (at least, none that I know of).

No attempt was made to calculate k_1/k_2 values for the reactions in chloro substituted solvents primarily because of the large amount of the di-*t*-butyl peroxide unaccounted for. In addition to this, an experiment was carried out which shows that the HCl formed in the reaction is probably reacting with the acetone formed. The results are given in Table 18. On

Table 18. Affects of the other products on the acetone formed in the decomposition of di-_t_-butyl peroxide in tetrachloroethylene containing cyclohexane

Moles used x 10^4				Moles at end x 10^4		Δ
C_2Cl_4	C_6H_{12}	$(t\text{-}BuO)_2$	Acetone	t-BuCl	Acetone	Acetone[a]
409.9	51.00	4.531	0	6.92	0.26	0
409.9	51.00	4.531	1.86	7.12	1.26	0.86

[a] Δ Acetone = amt. added + amt. expected - amt. present at end.

the assumption that the same amount of acetone would be present at the end due to the di-_t_-butyl peroxide, almost half of the added acetone (0.86/1.86) has disappeared. Whatever the reaction is that caused the disappearance of the added acetone, the same reaction would be expected to occur with the acetone formed from the decomposition of the _t_-butoxy radical.

In conjunction with the study of solvent effects on the _t_-butoxy radical, a study was made of the effect of some aromatic metal _pi_-complexes on the mode of reaction of the _t_-butoxy radical. The most extensive one studied was cobaltocene, but ferrocene, and copper(II), iron(II), and cobalt(II) phthalocyanines were also used. The results are tabulated in Table 19.

It will be seen that in the decompositions carried out in acetonitrile, the presence of cobaltocene has a very

Table 19. Comparison of yields of acetone and _t_-butanol from decomposition of di-_t_-butyl peroxide at 135° in various solvents with and without cyclohexane and aromatic metal _pi_-complexes

Aromatic metal _pi_-complex (M.C.)	Moles used[a] x 10^4				Moles produced x 10^4		% $(t\text{-BuO})_2$ accounted for	Moles x 10^4 t-BuOH expected[b]	Δ t-BuOH x 10^4[c]	Δ t-BuOH / moles M.C.
	M.C.	CH_3CN	C_6H_{12}	$(t\text{-BuO})_2$	Acetone	t-BuOH				
None	0	902	0	11.71	20.2	2.20	95.8	2.20	0	--
None	0	902[d]	0	11.70	20.5	2.38	97.8	2.38	0	--
None	0	919	0	6.946	12.0	1.06	94.4	1.06	0	--
Cobaltocene[e]	5.82	902	0	11.70	0.22	23.0	99.2	2.20	20.8	3.58
Cobaltocene[e]	5.82	902[d]	0	11.70	0.43	23.0	100	2.29	20.7	3.56
Cobaltocene[f]	0.952	918	0	7.64	7.68	7.19	97.4	1.16	6.03	6.33
Cobaltocene[f]	5.288	913	0	9.445	0.23	18.2	109	1.85	16.4	3.10
Cobaltocene[f]	1.396	886	0	17.38	25.8	7.84	96.5	4.32	3.52	2.52

---

[a] Initial volume of solution at room temperature was 5 ml. except where indicated.

[b] Based on the amount found in a reaction run at the same time without added metal _pi_-complex where possible. Otherwise an average value computed.

[c] t-BuOH = (moles t-BuOH produced) - (moles t-BuOH expected).

[d] Assumed.

[e] As received.

[f] Purified by sublimation.

Table 19. (Continued)

Aromatic metal pi-complex (M.C.)	Moles used x 10^4				Moles produced x 10^4		% $(t\text{-BuO})_2$ accounted for	Moles x 10^4 t-BuOH expected	Δ t-BuOH x 10^4	$\frac{\Delta\ t\text{-BuOH}}{\text{moles M.C.}}$
	M.C.	CH_3CN	C_6H_{12}	$(t\text{-BuO})_2$	Acetone	t-BuOH				
Cobaltocene[f]	0.444	918	0	8.905	14.5	2.74	96.5	2.21	0.53	1.19
Cobaltocene[f]	0.862	885	0	17.25	20.8	6.98	80.5	4.28	2.70	3.14
Oxidized	0.616	901.9	0	12.43	20.4	3.26	95.2	2.44	0.82	1.33
cobaltocene	5.943	906	0	11.99	18.8	4.87	99.8	2.35	2.52	0.424
Cobaltocene[e]	5.82	775[d]	59.9	11.71	0.40	24.2	105	7.99	16.2	2.78
Cobaltocene[f]	0.423	796	60.2	8.475	8.96	7.16	95.2	5.87	1.29	3.05
Ferrocene	3.512	908	0	6.946	8.14	4.65	92.1	1.06	3.59	1.02
Ferrocene	3.480	846	27.97	6.946	6.50	5.69	87.8	3.06	2.63	0.755
CuPhth[g]	0.448	920[d]	0	4.455	7.64	1.21	99.4	0.734	0.48	1.07
Fe(II)Phth[g]	0.440	920[d]	0	4.455	7.51	1.48	101	0.734	0.75	1.70
CoPhth[g]	0.441	920[d]	0	4.455	7.67	1.01	97.4	0.734	0.28	0.635
CuPhth[g]	0.439	800[d]	59.99	4.452	5.20	3.62	99.1	3.32	0.30	0.682
Fe(II)Phth[g]	0.446	800[d]	59.99	4.452	5.09	3.86	100.5	3.32	0.54	1.21
CoPhth[g]	0.450	800[d]	59.99	4.452	5.86	3.36	103.5	3.32	0.04	0.089
		Toluene								
None	0	447	0	11.70	7.24	14.0	90.6	14.0	0	--
Cobaltocene[d]	5.82	447	0	11.70	0.113	21.1	90.6	14.0	7.1	1.22

---

[g] Phth moiety is phthalocyanine.

Table 19. (Continued)

Aromatic metal *pi*-complex (M.C.)	Moles used x 10^4				Moles produced x 10^4		% $(t\text{-}BuO)_2$ accounted for	Moles x 10^4 t-BuOH expected	Δ t-BuOH x 10^4	Δ t-BuOH / moles M.C.
	M.C.	CH_3CN	C_6H_{12}	$(t\text{-}BuO)_2$	Acetone	t-BuOH				
		Benzene								
None	0	461.2	59.9	11.72	8.97	12.9	93.7	12.9	0	--
Cobaltocene[d]	5.82	458.8	59.9	11.76	0.723	20.2	89.0	12.9	7.3	1.25
Cobaltocene[d]	1.116	343.5	149.9	13.88	3.33	21.3	88.5	20.9	0.4	0.36
None	0	168[h]	90.09	4.434	1.91	6.67	96.7	6.67	0	--
Cobaltocene[e]	0.370	360.3	150.2	7.39	2.87	11.2	95.3	11.1	0.1	0.27

[h] Reaction mixture was 3 ml.

pronounced effect on the amounts of acetone and t-butyl alcohol formed in the decomposition. When di-t-butyl peroxide is decomposed in acetonitrile nearly all acetone is formed, but when cobaltocene is present in a ratio of cobaltocene to peroxide of 0.5, the product is nearly all t-butyl alcohol. Similar results are seen in the cases where cyclohexane is present in each case. When the ratio of cobaltocene to peroxide is lowered (several reactions at different ratios are carried out) a comparison of the number of moles of t-butyl alcohol per mole of cobaltocene averages about 3, although the individual values vary from 1.2 to 6.3. The lack of reproducibility is probably due to the difficulty in working with cobaltocene. It is extremely sensitive to oxidation by air or water (100-103) and with the equipment available it was difficult to prevent complete exclusion of these substances during the course of setting up the reaction. When cobaltocene which had been air oxidized was used, there is still a change in the products with more t-butyl alcohol formed, but the change is not nearly as great. When the solvent is changed to toluene and benzene, the effect of cobaltocene is considerably less. In the latter cases, it compares with the effect of the oxidized cobaltocene as well as ferrocene and the metal phthalocyanines in acetonitrile.

In a crude kinetic experiment, it was found that cobaltocene causes an increase in the rate of decomposition of di-t-butyl peroxide. The results of this experiment are given in Table 20 and Figure 22. Whether a catalytic amount of cobaltocene will increase the rate of decomposition in a similar manner was not determined.

Table 20. Decomposition of 0.234 M di-t-butyl peroxide at 135° in acetonitrile and in acetonitrile containing 0.116 M cobaltocene

Acetonitrile		Acetonitrile containing cobaltocene	
Time in minutes	% di-t-Butyl[a] peroxide decomposed	Time in minutes	% di-t-Butyl peroxide decomposed
60	33.0	60	91.0
120	53.4	135	103
240	83.3	270	100
480	88.5	570	99.2
840	96.1	870	103
1,440	97.8	1,710	99.7
		28,840	100

[a] % di-t-butyl peroxide decomposed =

$$\frac{(\text{moles acetone}) + (\text{moles } t\text{-butanol})}{2\ (\text{initial moles peroxide})} .$$

In a manner similar to that proposed by Kochi for the effect of cuprous salts on the decompositions of peroxides (32, 34), the cobaltocene can react with the di-t-butyl peroxide as given below.

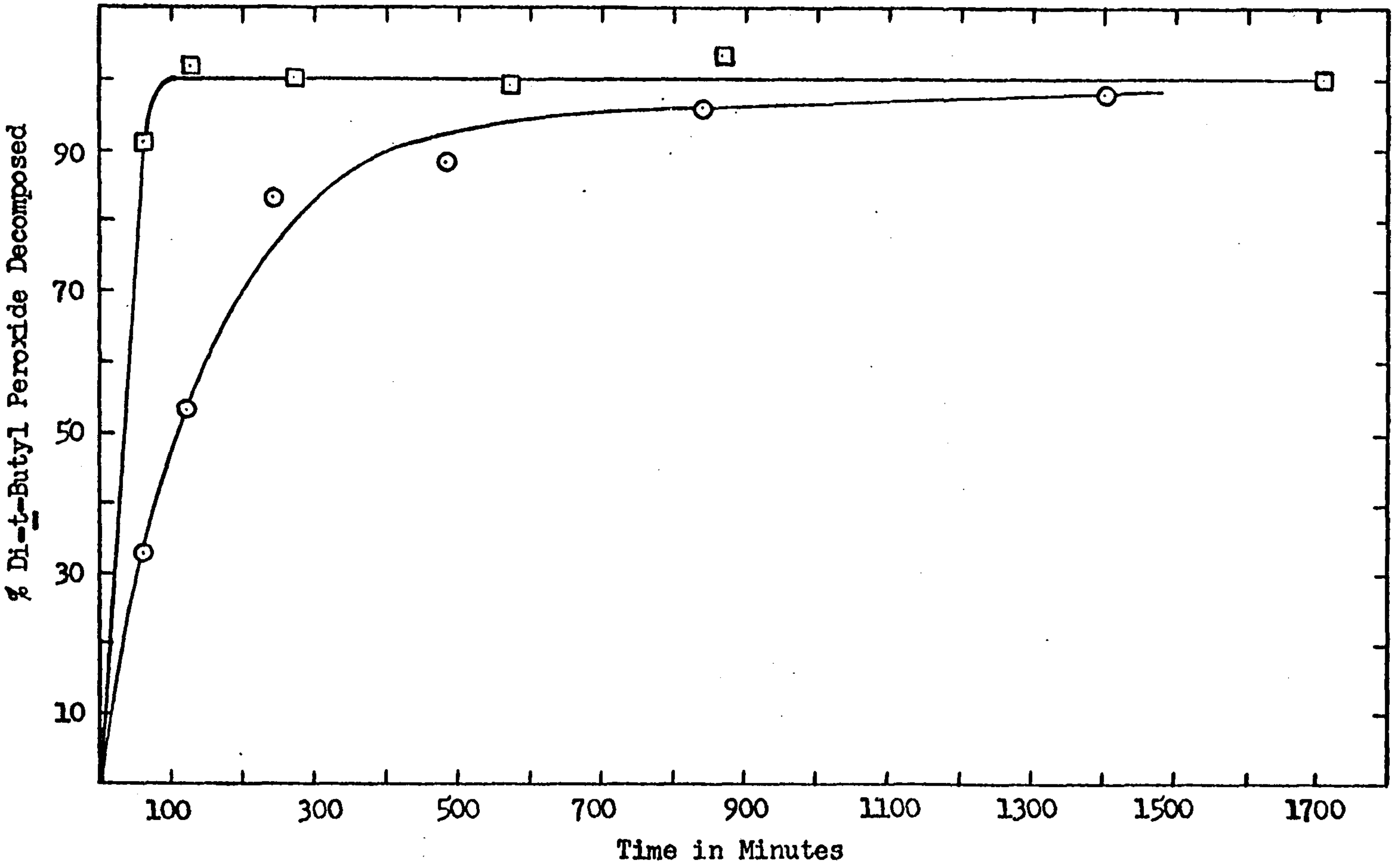


Figure 22. Decomposition of di-t-butyl peroxide in acetonitrile at 135° as a function of time

⊙ 0.234 M di-t-butyl peroxide

⊡ 0.234 M di-t-butyl peroxide and 0.116 M cobaltocene

$$(C_5H_5)_2Co^{II} + (CH_3)_3C\text{-}O\text{-}O\text{-}C(CH_3)_3 \longrightarrow$$

$$(C_5H_5)_2Co^{III}O\text{-}C(CH_3)_3 + (CH_3)_3C\text{-}O\cdot$$

$$(CH_3)_3C\text{-}O\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot$$

$$(C_5H_5)_2Co^{III}O\text{-}C(CH_3)_3 \longrightarrow (C_5H_5)_2Co^{II} + (CH_3)_3CO\cdot$$

Cobaltocene has two aromatic cyclopentadienyl groups capable of forming a pi-complex with the t-butoxy radical and the Co^{II} moiety capable of forming a sigma-complex with it. Thus we have a compound capable of catalyzing the decomposition of the peroxide and stabilizing the radicals produced. Furthermore, if the rationalization by Walling and Padwa (97) for their data is correct, this complex must not be involved in the transition state, but rather the complex is very transient and the less energetic free t-butoxy radical formed is involved in the transition state and preferentially undergoes a hydrogen abstraction reaction to a scission reaction.

What about the solvent effect observed? Why should this be more pronounced in acetonitrile than in benzene or toluene? The sigma-complex is quite polar in this case and the polar solvent has the effect of shifting the equilibrium away from the complex and again releasing a less energetic free t-butoxy radical which is involved in the transition state. In the less polar solvent, this sigma-complex does take part in the transition state in which case the scission reaction is favored.

In the other cases studied, more of the complexes formed are involved in the transition state. Or perhaps the decomposition occurs in the usual way and most of the radicals react in the usual manner. Only the radicals that have a chance to form the very transient complex with the aromatic metal pi-complex are able to increase the amount of t-butyl alcohol formed.

On the other hand, oxidation-reduction reactions of the cobalt atom might be used to explain these observations. A sequence of reactions such as that given below might be involved

$$\mathrm{Co^{II} + RO\cdot \longrightarrow RO^- + Co^{III}}$$

$$\mathrm{Co^{III} \xrightarrow{?} Co^{II}}$$

$$\mathrm{RO^- \xrightarrow[H^+]{\text{source of}} ROH}$$

Cobaltocene has a much greater effect in acetonitrile than in toluene or benzene. This might be taken as a reflection of its acidic properties and ability to act as a source of protons. However, the reaction

$$\mathrm{RO^- + CH_3CN \rightleftharpoons ROH + {}^-CH_2CN}$$

would be expected to go to the left on the basis of an acid-base reaction. If the $^-CH_2CN$ anion could act as a reducing agent for the Co^{III} species, this would act as a driving force to push the equilibrium to the right.

$$Co^{III} + {}^{\ominus}CH_2CN \longrightarrow Co^{II} + \cdot CH_2CN$$

$$\cdot CH_2CN \longrightarrow \text{unknown products, possibly } NC\text{-}CH_2\text{-}CH_2\text{-}CN$$

When cobaltocene and ferrocene are added to the reaction mixture for the decomposition of PAT in equal molar cyclohexane and carbon tetrachloride solvent, they have no effect on the value of k_H/k_{Cl}. The small amount of deviation seen in Table 21 is within the magnitude of experimental error. This is not surprising since the more reactive phenyl radical would be expected to be less susceptible to complexing of the type discussed above.

Table 21. The effect of ferrocene and cobaltocene upon the value of k_H/k_{Cl} when PAT is decomposed in an equal molar mixture of cyclohexane and carbon tetrachloride

Aromatic metal pi-complex (M.C.)	Moles used x 10^4				Moles produced x 10^4		k_H/k_{Cl}[a]
	M.C.	C_6H_{12}	CCl_4	PAT	Benzene	Chlorobenzene	
None	0	148	142	5.40	2.12(39.3%)	1.64(30.4%)	0.328
Ferrocene	2.72	148	142	5.40	2.11(39.1%)	1.60(29.6%)	0.334
Ferrocene	5.42	148	142	5.39	2.17(40.2%)	1.66(30.8%)	0.333
Cobaltocene	3.54	144	146	5.43	2.06(37.9%)	1.59(29.3%)	0.340
Cobaltocene	8.94	144	146	5.39	1.98(36.7%)	1.66(30.8%)	0.311

[a] $$\frac{12k_H}{3k_{Cl}} = \frac{(CCl_4)(\%\ \text{benzene} - 8.3\%^{b})}{(CCl_4)(\%\ \text{chlorobenzene})}$$

[b] This is the % benzene found when the decomposition of PAT is carried out in pure chlorobenzene.

EXPERIMENTAL

Melting points and boiling points given are uncorrected.

Chemicals

All chemicals were used as received unless otherwise specified. Some physical constants relating to compounds used as solvents are given in Table 23 at the end of this Experimental section.

Di-t-butyl peroxide was from the Lucidol Division, Wallace and Tiernan Inc. It was shaken three times with 30% sodium hydroxide followed by four extractions with water and then dried over anhydrous magnesium sulfate. This procedure removes hydroperoxide impurities (1). The peroxide treated above was distilled through an 11 inch by 1/4 inch silvered glass column filled with glass helices at a pressure of 25 mm of Hg. The middle fractions boiling from 25-28° were combined and used, $n_D^{20} = 1.3892$, reported $n_D^{20} = 1.3890$ (1).

Cyclohexane was from Matheson, Coleman and Bell. GLC analysis showed 99.5% purity.

Source of acetonitrile and method of purification are given in the Experimental section of Part I of this thesis.

The toluene used as a solvent was Reagent Grade from Fisher Scientific Company and that used as an internal standard for GLC analysis was from an unknown source, but GLC analysis showed greater than 99.5% purity.

Dimethylformamide, white label, was from Eastman Organic Chemicals.

Nitroethane, white label, was from Eastman Organic Chemicals. GLC analysis showed it contained 5 to 10% nitromethane. Nitromethane, spectro grade, was from Eastman Organic Chemicals. GLC analysis showed it contained 1-3% nitroethane.

Nitrobenzene was some that had been purified by Mr. Scotty Mak of this laboratory and donated by him.

Dimethyl sulfoxide was from Crown Zellerback Corp. It was distilled once from calcium hydride under vacuum.

Reagent grade 88% formic acid was from Mallinckrodt Chemical Works. An attempt was made to convert this to 100% formic acid by the method given in Reference 105. Formic acid, 200 ml. of 88%, was added to 500 ml. of di-n-butyl ether in a 2 liter 1-necked, round-bottomed flask and a 2-foot Vigreux column attached. The water, formic acid, and ether are supposed to form a low boiling azeotrope so the first 100 ml. was discarded and the next 30 ml. collected at a temperature of 100^o (reported 100.8^o).

Pyridine N-oxide was from Aldrich Chemical Company.

Benzene, thiophene free, reagent grade, was from Mallinckrodt Chemical Works. It was washed three times with concentrate sulfuric acid, several times with water, dried with anhydrous magnesium sulfate, distilled over calcium hydride, and stored over sodium.

Benzonitrile, white label, was from Eastman Organic Chemicals.

Acetylacetone (2,5-pentanedione) was from Matheson, Coleman and Bell.

Acetophenone was from Matheson, Coleman and Bell.

Pyridine, reagent grade, was from Mallinckrodt Chemical Works.

Acetamide, reagent grade, was from Baker and Adamson (Allied Chemical, General Chemical Division).

Malononitrile was from Aldrich Chemical Co.

Succinonitrile was from Aldrich Chemical Co.

Trichloroethylene was from Matheson, Coleman and Bell. It was distilled once through a 4-foot by 1/2 inch column filled with glass helices in a Todd Distillation Apparatus and the center fraction used.

cis-1,2-Dichloroethylene was from Aldrich Chemical Co. It was distilled as above and the fractions were used that GLC analysis showed greater than 99.9% pure and free from the *trans* compound (b.p. 60°).

trans-1,2-dichloroethylene was from Aldrich Chemical Company. It was distilled as above, but complete separation from the *cis* compound was difficult to attain. After several distillations in which the fractions having the least *cis* compound present from the prior distillation were combined and redistilled, 25 ml. of material containing less than 1% impurities (0.5% _cis_) were obtained and used (b.p. 46^o).

Octafluorodithiane was a gift from Dr. J. J. Drysdale of E. I. Dupont De Nemours and Company's Jackson Laboratory, Organic Chemicals Department, Wilmington, Delaware. The 2 lb. sample supplied was stirred vigorously with 253 ml. of ethylene diamine for approximately 18 hours, cooled, and poured into cold water. The mixture was poured into a separatory funnel and the heavier octafluorodithiane removed. It was then washed three times with water and dried by filtering through anhydrous magnesium sulfate.

Carbon tetrachloride, reagent grade, was from Mallinckrodt Chemical Works. It was passed through an alumina column before use. GLC analysis showed less than 0.1% impurities.

Tetrachloroethylene was from Matheson, Coleman and Bell. GLC analysis showed less than 0.5% impurities.

p-Xylene, research grade, 99.9% pure, was from Phillips Petroleum Company.

Chlorocyclohexane, white label, was from Eastman Organic Chemicals.

Acetone, reagent grade, was from Mallinckrodt Chemical Works.

_t_-Butanol, white label, was from Eastman Organic Chemicals.

Ethylbenzene was from Matheson, Coleman and Bell. It was distilled in the Todd Distillation Apparatus. The fraction used showed no impurity peaks in the GLC spectrum.

Cumene, white label, was from Eastman Organic Chemicals. It was distilled in the Todd Distillation Apparatus. The fraction used showed no impurities in the GLC spectrum.

Benzotrifluoride, practical grade, was from Eastman Organic Chemicals. GLC spectrum showed it to be greater than 99.9% pure.

Ferrocene was a gift from Dr. Frank Smentowski, Research Associate under Dr. Bernard Gerstein, Ames Laboratory.

Cobaltocene was a gift from Arapahoe Chemicals, Inc., 2855 Walnut Street, Boulder, Colorado. It was received as a benzene solution. Since it is sensitive to oxygen and moisture, a method had to be devised to transfer the solution and remove the benzene with a minimum amount of these present. It was further purified by sublimation (100, 103). (Some of each was used. This is discussed further in the section: Procedure in cobaltocene reactions) (m.p. 175-176°, reported 173-174° (100).)

The oxidized cobaltocene was obtained by exposing to the air the solid left after subliming away the benzene.

The phthalocyanines of copper, iron, and cobalt were gifts from Central Research Laboratory, Allied Chemical Corporation, Morristown, New Jersey.

Phenylazotriphenylmethane (PAT) was prepared as described in the Experimental section of Part I of this thesis.

Apparatus and Procedure

Procedure for reactions involving the *t*-butoxy radical

The decompositions were carried out in sealed tubes heated in an oil bath at 135° ± 1°. The oil bath containing mineral oil was stirred by a metal blade on a metal shaft connected to an Eberbach motor in which the original bearings had been replaced by ball bearings because the original bearings did not function properly. The heat was supplied by a 250 watt blade heater connected directly to a 110 volt source and a 500 watt blade heater connected to a regulator. Two types of regulators were used. One was a Fenwall Thermoswitch Control which was used initially. The other one was a Niatrol Proportional Control and was used for most of the reactions. The oil bath was set up in a hood and the position of the hood doors affected the temperature maintained. In most cases, the temperature was maintained at 135° ± 0.5°, but in several cases where other people using the hood had left one of the doors open, there were periods of from 3 to 6 hours in a run when the temperature was maintained at 137° ± 0.5°.

When the solvents were liquids at room temperature and the reactants were soluble in the solvent, the procedure given below was used. The reactants were weighed into a 10 ml. volumetric flask, the flask diluted to the mark with the solvent and the weight of the solvent determined. The mixture was shaken until a homogeneous solution was assured and then 5.00 ml. of this solution pipetted into the reaction tube. The actual amounts of reactants used are given in Table 14. In some cases of repeat runs used in conjunction with added metallic compounds, larger volumetric flasks were used in which case the solvent was not weighed and the molar concentration of the solvent was assumed to be the same as before.

The Pyrex reaction tube consisted of a 3 inch piece of 20 mm. Pyrex tubing connected to a 6 inch piece of 8 mm. thick-walled Pyrex tubing. The volume of the reaction tube when it was ready for insertion into the oil bath was approximately 18 ml.

After the reaction mixture was added to the reaction tube, the tube was connected by a piece of vacuum tubing to a two-way stopcock. The reaction mixture was degassed by immersing the tube in a Dry Ice-acetone mixture, evacuating to about 0.5 mm. pressure (vacuum pump connected 10 to 20 minutes), closing stopcock, removing the tube and warming to room temperature, and repeating the process once more. On the third evacuation, the tube was sealed off by heating with a torch in about the middle of thick-walled part of the reaction tube until a good seal is made (vacuum pump connected and stopcock open during this time). The seal was annealed with a cold flame for several minutes and the seal was allowed to cool to room temperature before the tube was removed from the Dry Ice-acetone bath and warmed to room temperature. After warming to room temperature, the sealed tube was immersed in the 135° oil bath and left for 48 hours to insure complete decomposition of the di-t-butyl peroxide. After removal from the oil bath, the tube was immersed in a Dry Ice-acetone mixture until ready for analysis. At that time, it is opened and capped with a rubber septum. As the contents warm to room temperature, the pressure is allowed to equalize from time to time by carefully removing the septum. No attempt was made to trap and analyze the gaseous products. After attaining room temperature, a GLC spectrum was run to determine a suitable internal standard to use, the standard was added, and the GLC analysis was made. The standard was added by making up a solution of it in the solvent used and pipetting an aliquot of this into the opened reaction tube.

When the solvents were solids at room temperature or the reactants were immiscible at room temperature, the materials were weighed directly into the reaction tube. The liquids were added by use of a graduated hypodermic syringe for small amounts and a pipette for large amounts. The rest of the procedure is the same as above.

A large scale reaction was carried out using a high pressure hydrogenation bomb as the reaction vessel. The reactants, 56.7 g. of cyclohexane (0.675 moles) and 7.34 g. di-t-butyl peroxide (0.050 moles), were weighed into a 250 ml. volumetric flask and diluted to the mark with cis-dichloroethylene (ca. 80% cis and 20% trans). The resulting solution was put in the glass liner of the bomb and the bomb assembled. The apparatus was purged of oxygen by hooking up a nitrogen tank to the apparatus and then alternately building up the pressure and releasing it several times. The temperature was attained by a built-in electric heater which did not function as expected so the temperature ranged from 110° up to 150° before the correct setting for 135° was found. An attempt to make a semi-quantitative measurement of the HCl formed was thwarted when it was discovered that the exit connection had a leak and no repairs were available. The reaction solution was separated into a low boiling and a high boiling fraction. The low boiling fraction was distilled through a Todd column filled with glass helices, but the separation of acetone and t-butyl chloride from the low boiling solvent and unreacted cyclohexane was unsuccessful. The high boiling fraction was vacuum distilled through a small Vigreaux column leaving a viscous tar-like residue in the pot which was not worked up. The distillate from this was then distilled through a small silvered column filled with glass helices. Four fractions with boiling points of 161-171°, 171-177°, 177-181°, and 181-191° were collected. A GLC spectrum showed all to contain the same two main fractions. An IR was taken of the 177-181° fraction which had a refractive index of n_D^{20} = 1.4820. The fractions were combined and vacuum distilled through a larger column, but the fractions collected were shown by GLC to be essentially the same as before. An NMR spectrum and an IR spectrum were taken of the fraction that contained roughly equal amounts of the two main components (by GLC). These are shown as Figures 20 and 21 found in the Results and Discussion section of this part. On the basis of these and the boiling point and refractive index, these compounds are the cis and trans form of 1-chloro-2-cyclohexylethylene (b.p. = 69-71° at 21 mm. and 174-176° at 760 mm., n_D^{20} = 1.4778 reported (98)). A permanganate oxidation yielded a compound whose IR spectrum matched that of cyclohexane carboxylic acid.

Procedure for the reactions with ferrocene and the phthalocyanines

These materials were weighed directly into the reaction tubes. The material adhering to the sides of the tubes were washed into the bottom by the liquid solution added later. The method of making up the solutions, degassing the reaction mixture, and sealing the tubes is the same as given above. The actual amounts of reactants are given in Table 19.

Procedure for the reactions with cobaltocene

As mentioned before, cobaltocene is extremely sensitive to moisture and oxygen. A scheme was devised whereby the benzene solution could be removed from the container and transferred to the reaction tube with a minimum of exposure to the atmosphere. The reaction tube was kept in a nitrogen atmosphere inside a larger tube which was inserted into a Dry Ice-acetone mixture until the solution was frozen. Then the container was attached to a vacuum pump and evacuated, the Dry Ice-acetone bath removed, and the vacuum pump left on until all of the benzene had sublimed into the cold trap in the vacuum line. When the pump was turned off, nitrogen was quickly introduced to maintain a nitrogen atmosphere. The tube was capped with a rubber septum and removed from the container. The reaction solution was introduced into the reaction tube by means of a 5 ml. hypodermic syringe. The needle was passed through the septum, thus avoiding contact with the air. The septum was removed and the reaction tube attached to the vacuum tubing connected to the stopcock quickly while nitrogen was passing through the tubing. The stopcock was closed and the tube inserted into a Dry Ice-acetone mixture. Except for the fact that the stopcock was not opened until the rest of the system was evacuated, the procedure of degassing and sealing was the same as before. The actual amounts of reactants used are given in Table 19.

The procedure for the reactions using cobaltocene that had been sublimed was the same except for the method of introducing the cobaltocene into the reaction tube. In this case, the sublimator and reaction tubes were put into a dry box having a helium atmosphere. The tubes had been weighed filled with helium prior to this by alternately evacuating and filling with helium several times and capping with a rubber septum. The sublimator was opened in the dry box and the cobaltocene introduced into the reaction tubes which were then capped with the same septum used before. The tubes were weighed after removal to determine the amount of cobaltocene introduced. The actual amounts of reactants used are given in Table 19.

For the reactions with PAT, the introduction of the cobaltocene from the sublimator to the reaction tubes was done in a glove bag having a nitrogen atmosphere. Prior to this, the PAT had been weighed into the reaction tube, the tube flushed with nitrogen, and capped with a rubber septum. After determining the amount of cobaltocene added, the other reactants were introduced with a hypodermic needle and syringe as before and the above procedure repeated. The actual amounts of reactants used are given in Table 21.

The procedure for the reactions using oxidized cobaltocene was the same as for those using ferrocene.

Procedure for reactions involving the phenyl radical

PAT was weighed directly into the reaction tube. Any adhering to the sides of the reaction tube was washed down by the reaction solution introduced volumetrically. In this case, 3.00 ml. of solution were introduced. Actual amounts of all reactants used are given in Table 21.

Gas-liquid chromatographic (GLC) analysis

The gas-liquid chromatographic analysis was done on a Perkin-Elmer Vapor Fractometer, Model 154-D. GLC conditions (conditions VIII-XII used in this section) are given under GLC analysis section of Part I as are the correction factors. Retention times of compounds pertinent to Part II are found in Table 22 at the end of this section. Except for GLC conditions XII, retention times are given relative to acetone. The retention times actually observed for these conditions were 6.6, 9.1, 13.6, and 6.2 minutes respectively. For condition XII, actual retention times are given.

Table 22. Relative retention times of selected compounds

Compound	GLC conditions	Retention time in minutes[a]
Octafluorodittheane	VIII	0.15
Cyclohexane	VIII,IX,X,XI,XII	0.20,0.16,0.13,1.18, 1.3
t-Butyl chloride	X,XI	0.19,0.68
t-Butanol	VIII,IX,X,XI	0.77,0.78,0.82,1.40
Carbon tetrachloride	X,XII	0.35,2.2
Benzene	VIII,IX,XI,XII	0.91,0.85,2.42,4.1
Acetone	VIII,IX,X,XI	(1.00)
Toluene	VIII,IX,X,XII	1.38,1.43,1.65,7.4
Ethylbenzene	VIII	2.10
Cumene	VIII	2.61
p-Xylene	VIII,X	2.72,2.65
Acetonitrile	VIII,IX	2.73,3.00
Pyridine	VIII	4.39
Nitroethane	VIII	6.07
Nitromethane	VIII	4.85
Dimethylformamide	VIII	>7.6
Acetylacetone	VIII	>7.6
Acetophenone	VIII	>9.1

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[a] For conditions VIII, IX, X, and XI, retention times are given relative to acetone. The actual retention times observed for these conditions were 6.6, 9.1, 13.6, and 6.2 minutes respectively. For condition XII, actual retention times are given.

Table 22. (Continued)

Compound	GLC conditions	Retention time in minutes
Benzonitrile	VIII	> 10.6
Dimethyl sulfoxide	VIII	>18.2
Nitrobenzene	VIII	>18.2
cis-Dichloroethylene	XI	1.97
Benzotrichloride	XI	2.86
Trichloroethylene	XI	2.88
Tetrachloroethylene	XI	5.00
Chlorocyclohexane	XI	11.29
Chlorobenzene	XII	15.0

Table 23. Physical constants of solvents used

Solvent	B.p.	M.p.	Dielectric constant			Density			
			Value	Temp.	Ref.	25°	Ref.	135°	Ref.
Cyclohexane	80.7	6.5	2.05	20°	(107) p. 91	0.7742	(106) p. 29	0.661 0.663[a]	(106) p.244 (106) p. 29
Pyridine	115.5	-41.5	12.5	20°	(107) p. 88	0.9781	(106) p. 33	0.873[a]	(106) p. 29
Nitrobenzene	210.9	5.7	35.7	20°	(107) p. 82	1.198	(106) p. 29	1.085 1.088[a]	(109) (106) p. 29
Benzene	80.1	5.5	2.283	20°	(107) p. 82	0.8734	(106) p. 29	0.750 0.750[a]	(108) p.1440 (106) p. 29
Dimethyl sulfoxide	--	--	45[b]		[b]	1.0956	(110)	0.986[a]	(110)
Nitromethane	101.3	-28.6	39.4	20°	(107) p. 83	1.1304	(106) p. 29	0.9724[a]	(106) p. 29

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[a] Calculated by assuming the equation for a lower temperature range can be extrapolated to 135°.

[b] Data sheet from Crown Zellerback Corp.

Table 23. (Continued)

Solvent	B.p.	M.p.	Dielectric constant Value	 Temp.	 Ref.	Density 25°	 Ref.	 135°	 Ref.
Acetophenone	202.0	19.6	17.0^c	20°	(107) p. 93	1.0238	(106) p.34	0.928	(109)
								0.923^a	(106) p. 29
Acetylacetone	139	-23.2	24.5^c	20°	(107) p. 88	0.972	(106) p. 29	0.869^a	(106) p. 29
Benzonitrile	191.1	-13.8	26.5	20°	(107) p. 91	1.0005	(106) p. 33	0.902^a	(106) p. 29
Nitroethane	114.8	-90	30.0	18°	(107) p. 85	1.038	(111)	0.906^a	(111)
Acetonitrile	81.6	-44.9	37.5^c	20°	(107) p. 84	0.7770	(106) p. 33	0.652	(106) p.237
								0.643^a	(106) p. 29
Octafluorodithiane			2.0^d	25°	--^{d}				
Carbon tetrachloride	76.8	-22.96	2.24	20°	(107) p. 83	1.5843	(106) p. 29	1.357	(106) p.245
								1.362^a	(106) p. 29
Tetrachloroethylene	121.2	-22.4	2.46	21°	(107) p. 83	1.6070	(106) p. 29	1.4288^a	(106) p. 29

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[c] Average of two values given.

[d] Data sheet from DuPont.

Table 23. (Continued)

			Dielectric constant			Density			
Solvent	B.p.	M.p.	Value	Temp.	Ref.	25°	Ref.	135°	Ref.
cis-Dichloroethylene	60.1	-80.5	9.22	20°	(107) p. 84	1.274	(112)	1.098[e]	(112)
trans-Dichloroethylene	48.4	-50	2.25	20°	(107) p. 84	1.249	(112)	1.064[e]	(112)
Trichloroethylene	87.2	-73	3.42	16°	(107) p. 84	1.454	(113)	1.273	(113)

[e] Reference 112 has _cis_ and _trans_ reversed.

SUMMARY

The mode of reaction of the t-butoxy radical generated by thermolysis of di-t-butyl peroxide at 135° is found to be dependent on the dielectric constant of the solvent. The value of k_1/k_2 where k_1 is the rate of scission to give acetone and a methyl radical and k_2 is the rate of hydrogen abstraction reaction with cyclohexane increases with an increase in the dielectric constant of the solvent. Except for the anomalous behavior of nitrobenzene and pyridine there is a linear correlation between k_1/k_2 and $(d/M)(D-1)/(2D+1)$ where d is the density, M the molecular weight, and D the dielectric constant of the solvent for the solvents that were tried except for the chloro-substituted solvents where the reaction does not proceed in the same manner. In the latter case, sizeable amounts of t-butyl chloride and HCl are formed. In the case of cis-, dichloro-, trichloro-, and tetrachloroethylene, it is surprising to find that these products occur even in the absence of cyclohexane. In carbon tetrachloride only a trace of t-butyl chloride is formed in the absence of cyclohexane.

The aromatic metal pi-complexes - cobaltocene, ferrocene, and Cu(II), Fe(II), and Co(II) phthalocyanines - are found to have the opposite effect, i.e., the presence of these materials increased the amount of t-butyl alcohol formed when the reactions are carried out in acetonitrile. The effect of

cobaltocene is much greater than the others and it is more effective in acetonitrile than in benzene or toluene. The presence of cobaltocene also increases the rate of decomposition of di-_t_-butyl peroxide. This is explained by the possible simultaneous formation of a transient _sigma_- and a _pi_-complex between the two _t_-butoxy radicals formed and the cobaltocene in its role of increasing the rate of decomposition. The radicals released when the complex breaks up are less energetic and prefer to undergo a hydrogen abstraction reaction to a scission reaction even when the hydrogen donor is acetonitrile. The collapse of the _sigma_-complex is expected to be more facile in a polar solvent.

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ACKNOWLEDGMENTS

Upon reaching another milestone on the journey through life and upon reflection of the events leading up to it, it is obvious to me that many people other than myself have made significant contributions in helping me to attain this goal. Like any task, it has not been without its moments of trial and frustration as well as the moments of satisfaction. In a sense, every one of my friends and acquaintances has contributed in some way or another. It would be impossible to mention them all individually, but I want those not listed specifically to know that I appreciate all the help and kindness they have given to me.

I am especially indebted to Professor Glen A. Russell for the suggestion of the problem and without whose patience, guidance, and understanding this work would not have been possible.

I want to thank all of the members of the Russell group for the sharing of their ideas, chemicals, and equipment. Of this group, I want particularly to thank Dr. Robert F. Bridger for many fruitful discussions and ideas on all phases of my graduate work; Dr. Dale G. Hendry and Dr. Akihiko Ito for help and discussions of course work problems; Dr. Edward G. Janzen and Mr. E. Thomas Strom for their assistance in the mechanics of the final stages of completing this manuscript as well as helpful discussions; and Dr. Roger C. Williamson for his advice and suggestions.

During my stay at Iowa State University, I have had the good fortune to have as roommates, Harold Saylor, Dale Hendry, and Jack Corey. I want to thank them for putting up with my idiosyncrasies and for making life in a college dormitory more interesting.

The aid and cooperativeness of the men in the Chemistry Shop and Glassblowing Shop as well as the Chemistry Department employees in making, repairing, and procuring equipment and supplies is very much appreciated.

Financial aid from the Sloan Foundation, The Petroleum Research Fund of the American Chemical Society, Allied Chemical Corporation, and The Proctor and Gamble Company are gratefully acknowledged.