1971

# Kinetic studies on the ozonation of organomercurials

Joseph Torres Rivera

*The University of Montana*

## Recommended Citation

Rivera, Joseph Torres, "Kinetic studies on the ozonation of organomercurials" (1971). *Graduate Student Theses, Dissertations, & Professional Papers*. 8302.
https://scholarworks.umt.edu/etd/8302

# KINETIC STUDIES ON THE OZONATION OF ORGANOMERCURIALS

by

Joseph T. Rivera

B.S., University of Southern California, 1968

Presented in partial fulfillment of the requirements

for the degree of

Master of Science

UNIVERSITY OF MONTANA

1971

Approved by:

William L. Waters

Chairman, Board of Examiners

John M. Stewart

Dean, Graduate School

Mar 16, 1971

Date

# ACKNOWLEDGEMENTS

I wish to express my gratitude to my adviser, Dr. W. L. Waters, for his advice and help in this research.

I am grateful to Paul Pike for his suggestions and aid, to Gale M. Sherrodd for his syntheses of the compounds, and to Robert Clark for his aid in processing the data.

# TABLE OF CONTENTS

## CHAPTER I

## INTRODUCTION

### Objective of the Research

The objective of this research was to measure the rates of cleavage of various carbon-mercury bonds in their reaction with ozone. The differences in rate were to be noted and compared as the ligands of the alkylmercury group were changed from a similar alkyl substituent to chlorine, bromine, and iodine.

In general, this research was performed to further elucidate the mechanism of ozonation of the carbon-mercury bond.

### Background

The only definitive work on the reaction of organomercurials with ozone was performed recently by Paul E. Pike.[1] The general subject of electrophilic substitution of organomercurials has, however, been well documented in the literature. Specifically, the cleavage of the carbon-mercury bond by protic acid, halogen, and mercuric salt have been shown to involve electrophilic reaction.[2]

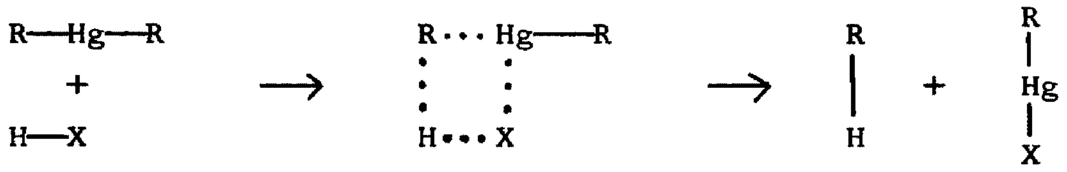
Reaction with Protic Acids. The reaction of organomercurials with protic acids produces alkanes and mercuric salts (see below). This reaction shows a decreased reactivity for alkylmercuric halides relative to dialkylmercurials.

$$R_2Hg + HX \longrightarrow RH + RHgX$$

$$RHgX + HX \xrightarrow[\text{slow}]{\text{very}} RH + HgX_2$$

The alkylmercuric iodides are the only compounds of this series which cleave with protic acids below decomposition temperatures.[3] These two bits of evidence lend support to an electrophilic cleavage mechanism. The presence of an electronegative element on mercury causes decreased electron density at the site of reaction and would therefore retard electrophilic cleavage. The compound with the least electronegative element would be expected to cleave most readily.

The reaction with protic acid is currently believed to proceed by a four-center or similar mechanism.



As mentioned by Jensen and Rickborn,[4] compounds containing atoms with valences greater than one would be subject to electrophilic cleavage depending on the electronegativity of the groups attached to such atoms. The carbon-mercury bond in C-Hg-C consists of about 8% ionic character, and this value decreases in the case of the carbon-mercury bond in C-Hg-Cl, thereby reducing the negative charge on carbon. Consequently, electrophilic cleavage reactions with organomercurials should exhibit a sequence of relative rates according to C-Hg-C > C-Hg-I > C-Hg-Br > C-Hg-Cl > C-Hg-F.

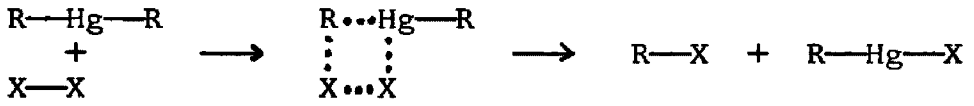
<u>Reaction with Halogen</u>. The reaction of organomercurials with

halogen produces alkyl halides and mercuric salts according to the equations below. For this reaction alkylmercuric halides react more slowly than dialkylmercurials, again substantiating an electrophilic reaction mechanism.

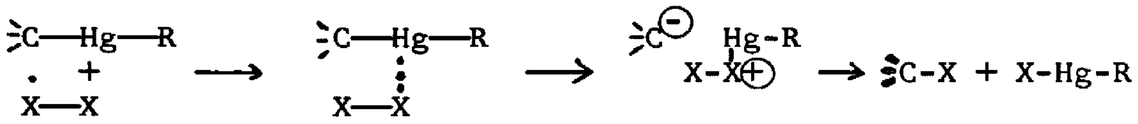
$$R_2Hg + X_2 \rightarrow RX + RHgX$$

$$RHgX + X_2 \rightarrow RX + HgX_2$$

$S_Ei$ and four-center processes are invoked as reaction mechanisms.



(four-center)



($S_Ei$)

These two mechanisms predict retention of configuration in reactions involving optically active compounds. Electrophilic cleavage of the carbon-mercury bond by bromine does indeed proceed with retention of configuration, as shown by Jensen and Gale.[5] Chlorine cleavage of the C-Hg bond is also completely stereospecific, but there is some doubt that this is always true for the reaction with iodine.[5]

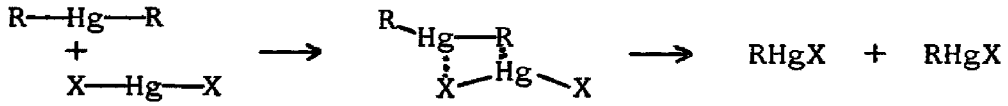
Reaction with Mercuric Salt. The reaction of dialkylmercurials and alkylmercuric salts with mercuric salts produces new salts through carbon-mercury bond cleavage (see below). Support for an electrophilic mechanism for the cleavage reaction is given by the fact that mercuric iodide reacts 125 times faster with diphenyl mercury than with diethyl mercury. This result agrees with the generalization that electrophilic substitution occurs more rapidly at an aryl site than at an alkyl site.

$$R_2Hg + HgX_2 \longrightarrow 2\ RHgX$$

$$RHgBr + {}^{*}HgBr_2 \longrightarrow R{}^{*}HgBr + HgBr_2$$

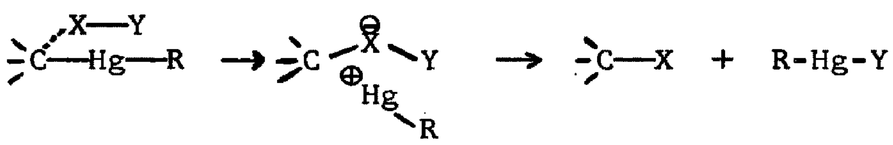
where $^{*}Hg = Hg^{203}$

A four-center mechanism is the most common one proposed for these reactions.



Support for this mechanism is given by the stereochemistry of the reaction of several optically active mercurials with various mercuric salts. A very high degree of retention of configuration is consistently observed.[6]

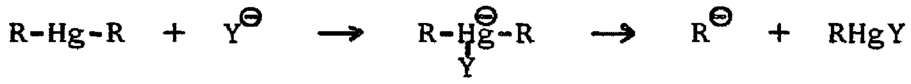
<u>Other Mechanisms</u>. In addition to the $S_Ei$ and four-center mechanisms described, there exists the possibility of the $S_E2$ mechanism, i.e.,



(with or without inversion).

To date, however, there is no substantiated example of a pure $S_E2$ reaction of an organomercurial.

The above bimolecular reaction mechanisms do not complete the possibilities for aliphatic electrophilic substitution reactions. In those cases where a carbanion can be sufficiently stabilized, it is important that the $S_E1$ mechanism be considered.



$$R\text{-}Hg\text{-}R + Y^{\ominus} \longrightarrow R\text{-}\underset{Y}{\overset{\ominus}{Hg}}\text{-}R \longrightarrow R^{\ominus} + RHgY$$

Relation of Rate Dependence with Mechanism

The rate of an $S_E1$ mechanism, in the case of mercurials, is dependent mainly on electronic factors since initial attack of the electrophile occurs at mercury, rather than at carbon. Following the rate-determining cleavage of the carbon-mercury bond, there is formation of a carbanion. Stabilization of this species requires the presence of electron-withdrawing groups on carbon, which in turn increases the rate of reaction. Therefore, the observed rate sequence should be t-butyl $<$ isopropyl $<$ ethyl, that is, $3° < 2° < 1°$.

The $S_E2$ mechanism is usually more dependent on steric factors, rather than on electronic factors since, theoretically, there should be no charge build-up in the concerted, pure $S_E2$ process. However, not much is known about this particular mechanism and exact electronic or steric predictions are virtually impossible. One complicating factor which must be accounted for by the $S_E2$ mechanism is that, in contrast to $S_N2$ processes, retention of configuration is the general rule.

Since reactions involving $S_Ei$ and various cyclic concerted mechanisms are limited to the carbon-mercury bond region of organomercurials, steric inhibition plays virtually no part. Electronically, a slight polarization of charge must at least exist in this bond region to promote the initial attack by an electrophile. Following this attack, the transition states of a concerted and an $S_E$i reaction are very similar. The only distinction lies solely in the order of bond-making versus bond-breaking.

Concerted cyclic reactions, such as the four-center process, require bond-formation and bond-cleavage to occur simultaneously. Since no build-up of charge occurs in these purely concerted processes (as mentioned above), electronic factors would not be expected to influence the reaction rates to any great extent.

The $S_E$i mechanism, on the other hand, demands that carbon-mercury bond cleavage be well onto completion before bond-formation to carbon occurs. The latter mechanism is accompanied by the appearance of an intimate ion-pair, including a carbanion-like species, as an intermediate. In this case, the presence of electron-donating substituents on carbon destabilize such incipient carbanions in the transition state, thereby decelerating the reaction rate. The expected rates of such a reaction should therefore follow the general order predicted for the $S_E1$ mechanism above.

# CHAPTER II

## EXPERIMENTAL

### Instrumentation

The rate data were determined by nuclear magnetic resonance with a Varian Associates Model HA-60 Analytical NMR Spectrometer. The probe temperatures for all spectra were between 33-37°C. Solutions for analysis utilized chloroform as the solvent, as well as the lock signal. An internal standard of nitromethane ($CH_3NO_2$) was added before each rate experiment to measure relative concentrations of mercurial. Nitromethane was determined to be impervious to ozone.

All melting points were determined with a Meltemp melting point apparatus. The melting points were not corrected.

### Experimental Apparatus

The ozone was produced by a Welsbach T-408 electric discharge ozonator. The flow rate of ozone through the solutions was determined by the standard iodide-thiosulfate method. The ozone was passed through a KI solution for a few minutes, the solution was subsequently acidified and then titrated with a 0.1 M solution of sodium thiosulfate. The equation used to determine the flow rate was:

$$(\text{Liters})\ (\text{Molarity})\ (\tfrac{1}{2})\ \left(\frac{1}{\text{time}}\right) = \text{moles } O_3/\text{minute}.$$

Liters = liters of $Na_2S_2O_3$ used in the titration.

OZONATION APPARATUS

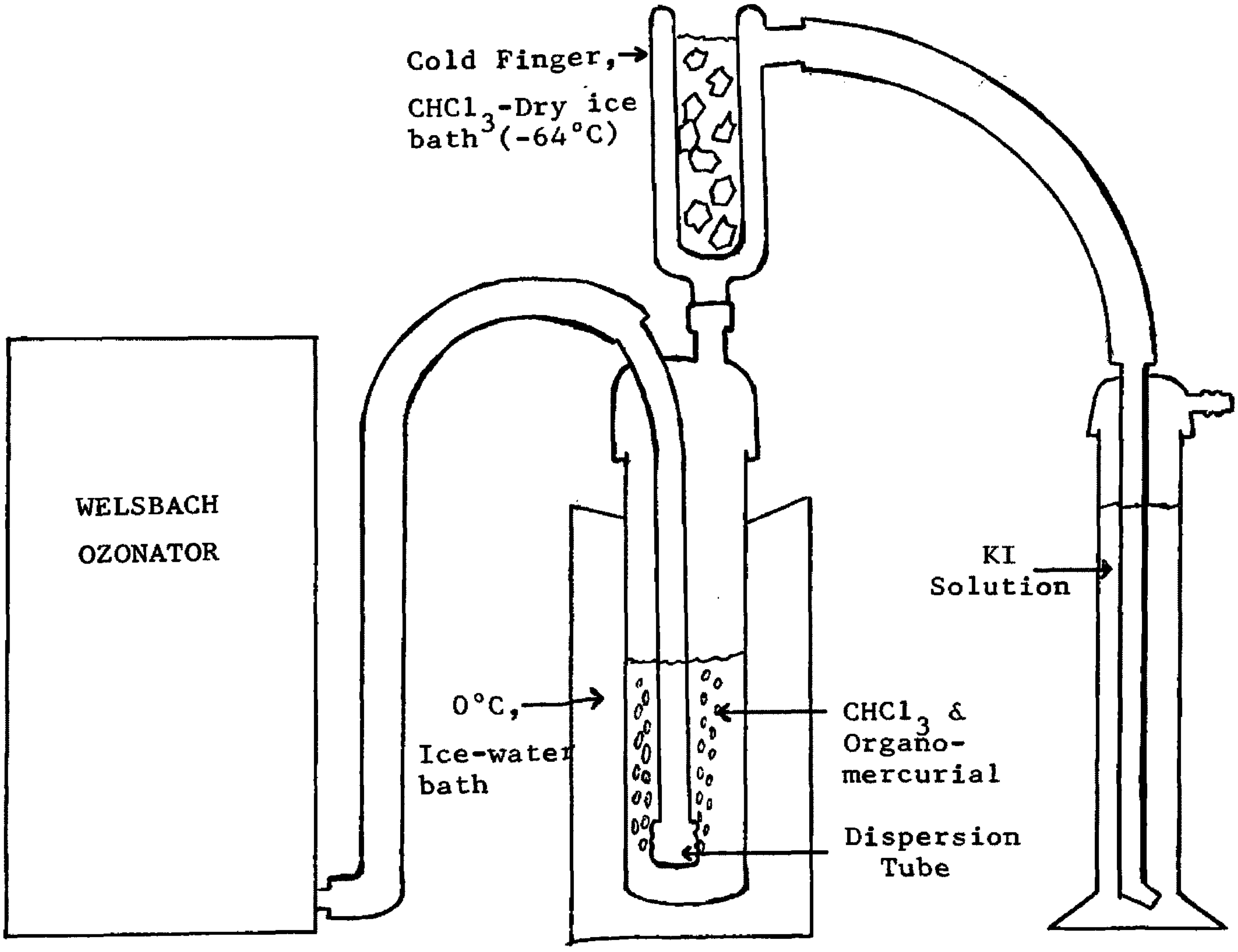


Fig. 1

Molarity = molarity of $Na_2S_2O_3$.

time = number of minutes $O_3$ was bubbled through KI solution.

The flow rates for the experiments ranged from 32 to 70 millimoles of ozone per minute.

Oxygen was the carrier gas in all cases, with the temperature of ozonation maintained at 0° by an ice-water bath.

## Chemicals

The chloroform solvent used in the experiments was J. T. Baker reagent grade. Further purification of the $CHCl_3$ was necessary to remove the 1% ethanol added to maintain stability. This was done to eliminate the appearance, and subsequent interference, of the ethanol multiplets in the NMR spectra. Purification was accomplished following the procedure outlined in Purification of Laboratory Chemicals.[7] The $CHCl_3$ was washed with portions of water to remove the EtOH, followed by one washing with a saturated $NaHCO_3$ solution. The $CHCl_3$ was then dried over calcium chloride, and distilled from $P_2O_5$. To retard decomposition, nitrogen gas was passed through the $CHCl_3$ for several minutes, after which the solvent was frozen in dry ice until needed.

The diethyl ether used to prepare the Grignard reagents was anhydrous Baker Analytical Reagent and was stored over sodium wire without further purification. The magnesium for the Grignard reagents was J. T. Baker purified magnesium chips, which were stored in a dessicator containing $P_2O_5$. The mercuric bromide was from Alfa Inorganics. The mercuric chloride was J. T. Baker brand. These mercuric salts were used without further purification. The nitromethane used as the internal standard was judged to be pure by NMR, and no further purification was performed.

## Preparation of Organomercurials

The dialkylmercurials were prepared using the Grignard method described by Gilman and Brown[8] and the references noted therein. The organomercuric halides were mainly prepared using the Grignard method described by C. S. Marvel, C. G. Gauerke, and E. L. Hill[9] and the references noted therein. In addition, some alkylmercuric halides were prepared by reaction of the dialkylmercurial with the appropriate mercury dihalide[10] or by a halide exchange using the silver nitrate procedure.[11]

Diisopropyl Mercury. Eastman 2-bromopropane was purified following the procedure outlined for 1-bromohexane in Purification of Laboratory Chemicals.[12] The 2-bromopropane was shaken with sulfuric acid. It was then washed three times with distilled water, dried with $K_2CO_3$, and distilled. The boiling point of the purified 2-bromopropane was 55.5°C at 682 mm. (lit.[13] b.p. 59.4°C at 760 mm.).

The procedure to prepare diisopropyl mercury was that as described by Gilman and Brown.[14] The Grignard reagent was prepared by adding 123 g. (1.0 mole) of 2-bromopropane, diluted to 250 ml. with diethyl ether, to a vigorously stirred mixture of 28 g. (1.15 mole) of magnesium chips in 250 ml. of diethyl ether. Addition was completed within two hours. After refluxing the Grignard reagent solution for an additional 10 to 12 hours, it was filtered through glass wool into a

2 liter, three-neck distilling flask. This was done to remove unreacted magnesium, since the metallic magnesium will reduce mercuric salts to the mercurous valence state[15] and effect a lower yield of organomercurial. The solution was then diluted to 1000 ml. with diethyl ether.

A Soxhlet extractor was used to add 95 g. (0.35 mole) of mercuric chloride to the rapidly stirred Grignard reagent solution. After addition of the mercuric halide was complete, the Soxhlet extractor was replaced by two condensers. The reaction mixture was then refluxed for 50 hours.

The mixture was cooled in an ice bath, and 300 ml. of water was added slowly through the condenser. The organic layer was separated from the water layer. The water layer was extracted with two 25 ml. portions of diethyl ether. Following one washing of the combined diethyl ether solution with saturated sodium chloride, the solution was dried over anhydrous calcium chloride. The ether was removed by rotary evaporation, yielding 80.3 g. of raw product. This raw product was redistilled through a six inch Vigreaux column at 37-39° and 2 mm. to yield 74.5 g. (74%) of diisopropyl mercury, lit.[16] b.p. 63° at 10 mm.

The n.m.r. spectrum of this product showed a singlet at 1.33$\delta$. The $\alpha$ mercury satellites could not be distinguished from the spectrum noise. However, about the singlet there were two sets of mercury satellites with $J_{Hg^{199}-H^{1}} = 115$ c.p.s. indicative of $\beta$ coupling. This value is near that reported by Dessy and others.[17]

The presence of satellite peaks is caused by the mercury-199 isotope, which has a nuclear spin number of ½, a negligible quadrupole moment, and a natural abundance of 17%. Mercury-199 can, therefore, couple with hydrogen nuclei on adjacent carbon atoms.

Di-n-propyl Mercury. The synthesis, physical properties, and spectral parameters of this compound are fully described in the thesis by Paul E. Pike.[18]

Diethyl Mercury. The diethyl mercury and all the remaining dialkylmercurials were prepared by Mr. Gale M. Sherrodd. The ethyl bromide was Baker and Adams Reagent Grade and was used without further purification. The boiling range was 38-40°C at 687 mm.

This compound was prepared following the procedure outlined for diisopropyl mercury. Ethyl bromide (125 g., 1.15 mole), magnesium (60 g., 2.47 mole), and mercuric chloride (97 g., 0.358 mole) were used to give 10.5 g. (11%) of diethyl mercury. The b.p. of this compound was 73-74°C at 35 mm. (lit.[19] b.p. 97-99°C at 125 mm.).

The n.m.r. spectrum showed a multiplet centered at 1.20 $\delta$ with a sharp central peak of the methyl protons appearing at 1.30$\delta$ . Symmetrically positioned about this peak were a set of mercury satellite triplets with $J_{Hg^{199}-H^{1}}$ = 126 c.p.s. The satellites of the methylene protons were not distinct enough to measure the coupling constant.

Dineopentyl Mercury. The procedure for preparation followed that outlined for diisopropyl mercury. Chemical Samples Co. 1-chloro-2, 2-dimethylpropane was used without further purification.

The reaction of 1-chloro-2,2-dimethylpropane (75 g., 0.70 mole), magnesium (34 g., 1.40 mole), and mercuric chloride (32 g., 0.118 mole) yielded 28.8 g. (72%) of dineopentyl mercury. The melting point of this compound was recorded as 33-36°C (lit.[20] m.p. 31-33°C).

The n.m.r. spectrum showed a methyl singlet at 1.00 $\delta$ integrating for 18 protons and a methylene singlet at 1.10 $\delta$ with an integration of 4 protons. About the methyl singlet was a symmetrical pair of satellite singlets with $J_{Hg^{199}-H^{1}}$ = 28.0 c.p.s. About the methylene signal was a set of satellites with $J_{Hg^{199}-H^{1}}$ = 93.6 c.p.s.

<u>Di-sec-butyl Mercury</u>. The procedure for preparation followed that for diisopropyl mercury. Aldrich white label 2-bromobutane was used without further purification.

2-Bromobutane (96 g., 0.70 mole), magnesium (34 g., 1.40 moles), and mercuric chloride (60 g. 0.22 mole) yielded 58 g. (84%) of di-<u>sec</u>-butyl mercury with a boiling range of 40-41°C at 2 mm. (lit.[21] b.p. 93-96°C at 18 mm.).

The n.m.r. spectrum showed the appearance of a multiplet at 1.00 $\delta$ which strongly resembled a triplet, but with additional splitting. This multiplet was assigned to the methyl protons adjacent to the methylene group. At 1.34 $\delta$ a strong singlet with slight additional splitting was determined to belong to the methyl group adjacent to the methine carbon. Symmetrically disposed about this singlet was a set of mercury satellites, doublets in nature, with a $J_{Hg^{199}-H^{1}}$ = 116.7 c.p.s. At 1.95 $\delta$ a broad multiplet accounting for the methine and methylene protons appeared. No other mercury satellite peaks could be identified.

Dibenzyl Mercury. The benzyl chloride used without further purification for the preparation of this compound was J. T. Baker reagent grade. The boiling range was 177-179°C at 679 mm.

In the preparation, anhydrous benzene was added to the Grignard reagent prior to reaction with mercuric chloride. This was done to prevent the precipitation of benzylmercuric chloride from solution, due to its minimal solubility in ether. Otherwise, the procedure was the same as described for diisopropyl mercury.

Following that procedure, 89 g. (0.70 mole) of benzyl chloride, 34 g. (1.40 moles) of magnesium, and 49 g. (0.18 mole) of mercuric chloride yielded 21 g. (0.055 mole, 31.3%) of dibenzyl mercury. The melting point of the compound was 106-108°C (lit.[22] m.p. 110-111°C).

The n.m.r. spectrum showed a singlet at 7.12 $\delta$ accounting for the 10 ring protons and a singlet downfield at 2.38$\delta$ accounting for the remaining 4 protons. A symmetrical set of mercury satellites was positioned about this downfield singlet with $J_{Hg^{199}-H^{1}}$ = 132.4 c.p.s.

2-Chloromercuripropane. This compound was prepared by Mr. P. G. Marsh and also by Mr. Gale M. Sherrodd. The 2-bromopropane used was the same as that described in the preparation of diisopropyl mercury.

The Grignard reagent was prepared in the usual manner by adding 61.5 g. (0.5 mole) of 2-bromopropane, diluted to 250 ml. with diethyl ether, to 200 ml. of ether containing 12.15 g. (0.5 mole) of magnesium chips. Addition was performed with vigorous stirring over a period of 2 to 3 hours. The solution of the Grignard reagent was then filtered through glass wool to remove any unreacted magnesium.[23] This filtered solution was then diluted to 1000 ml. with diethyl ether and cooled in an ice bath. Finely ground mercuric chloride (135.8 g., 0.50 mole) was then added through an efficient condenser in 5 g. portions at 5 minute intervals. Constant, vigorous stirring was necessary to prevent caking. After addition of the total amount of mercuric halide, the condenser was rinsed with diethyl ether, and the reaction mixture was refluxed for 2 hours. Longer reflux times gave reduced yields due to formation of some dialkyl compounds. This time of reflux was therefore deemed to be the maximum allowable for optimum yields.

The reaction mixture was again cooled in an ice bath, and 300 ml. of ice water was added slowly through the condenser to destroy any unreacted Grignard reagent and to dissolve the inorganic salts.

Following separation of the aqueous and the organic layers, the water layer was washed twice with 100 ml. portions of chloroform. The chloroform and ether portions were combined. The product was isolated by flash evaporation to remove the volatile solvents. A yield of 76.1 g. (51%) of a mixture of 2-bromomercuripropane and 2-chloromercuripropane was obtained (m.p. 78-83°C).

Since a pure compound was necessary, the procedure outlined by Robson and Wright[24] was followed. The mixture of halides was dissolved in methanol, and a 10% molar excess of silver nitrate was added with stirring. After filtration of this mixture to remove the insoluble silver halides, excess reagent grade sodium chloride was added to the methanol solution. After heating to reflux temperature, the solution was filtered once again. Upon cooling, the pure chloride product precipitated. Eighty percent of the mass of the mixture was recovered as 2-chloromercuripropane with a melting point of 94-95°C (lit.[25] m.p. 94.5-95.5°C).

The n.m.r. spectrum of the product showed a doublet at 1.51$\delta$ and a multiplet at 2.53$\delta$ with an area ratio of 6 to 1 respectively. About the low field peaks there was a set of mercury satellites with $J_{Hg^{199}-H^{1}}$ = 185.0 c.p.s. indicating $\alpha$ coupling. About the upfield doublet there was a set of mercury satellites with $J_{Hg^{199}-H^{1}}$ = 288.5 c.p.s. indicating $\beta$ coupling.

In addition to the above preparation of 2-chloromercuripropane, this compound was also prepared using the reaction of the dialkylmercurial with a 10% molar excess of mercuric chloride.[26] By this method, 9.90 g. (0.035 mole) of diisopropyl mercury was placed in a flask with 10.28 g. (0.038 mole) of mercuric chloride using chloroform as the solvent. The reaction mixture was stirred under reflux for 4 to 5 hours. Following rotary evaporation of the chloroform, the 2-chloromercuripropane product was then recrystallized from methanol. The compound was placed under vacuum to remove any residual methanol. The resultant yield was 17.25 g. (90%) of white crystals of 2-chloromercuripropane, m.p. 93-94°C (lit.[27] m.p. 94.5-95.5°C).

<u>2-Bromomercuripropane</u>. This compound was prepared exclusively by the silver nitrate method outlined above.

2-Chloromercuripropane (5.58 g., 0.02 mole) was heated and stirred in methanol with 3.74 g. (0.022 mole) of silver nitrate, followed by filtration and subsequent reaction with 2.26 g. (0.022 mole) of reagent grade sodium bromide. Following recrystallization, a yield of 6.04 g. (93%) of 2-bromomercuripropane was obtained. The white crystals melted at 92-93°C (lit.[28] m.p. 90.5-91.5°C).

The n.m.r. spectrum showed a multiplet at 2.59 $\delta$ and a doublet at 1.51 $\delta$ with respective areas of 1 to 6. About the doublet were mercury satellites with $J_{Hg^{199}-H^{1}}$ = 281.6 c.p.s. indicating $\beta$ coupling. No satellites were determined for the multiplet.

2-Iodomercuripropane. Following the silver nitrate method of preparation outlined above, 5.58 g. (0.020 mole) of 2-chloromercuripropane were reacted with a 10% molar excess of silver nitrate, followed with 10% molar excess reagent grade sodium iodide. After evaporation of solvent and recrystallization, 5.38 g. (80%) of 2-iodomercuripropane were obtained. The yellow-green crystals had a melting point of 124-126°C (lit.[29] m.p. 123-124°C).

The n.m.r. spectrum showed a doublet at 1.52 $\delta$ and a multiplet at 2.70 $\delta$ . There were no distinct satellites for the doublet, but instead broadened areas symmetrically positioned. The $J_{Hg^{199}-H^{1}}$ was determined to be 282.6 c.p.s. as measured from the center of the broadening. It is thought that the presence of iodine, with its large quadrupole moment, accounts for the observed broadening.

Chloromercuriethane. The preparation of the compound followed that procedure outlined above for 2-chloromercuripropane using the dialkyl compound.

The reaction of diethyl mercury (3.234 g., 0.0125 mole) and

3.80 g. of mercuric chloride (0.0137 mole) yielded 6.448 g. (97%) of chloromercuriethane. The white crystals of chloromercuriethane had a melting point of 195-197°C (lit.[30] m.p. 192°C).

The n.m.r. spectrum showed a quartet at 2.00 $\delta$ and an upfield triplet at 1.37 $\delta$ . About the quartet was a set of satellites with $J_{Hg^{199}-H^{1}}$ = 204.8 c.p.s. indicating $\alpha$ coupling. The triplet showed mercury satellites with $J_{Hg^{199}-H^{1}}$ = 293.1 c.p.s. indicating $\beta$ coupling. The upfield satellites of both multiplets overlapped.

<u>Bromomercuriethane</u>. This compound was prepared by Mr. Gale M. Sherrodd. The bromoethane was the same as used previously in preparing diethyl mercury.

Following the procedure of 2-chloromercuripropane, 10.89 g. (0.10 mole) of bromoethane, 48.6 g. (0.20 mole) of magnesium chips, and 27.0 g. (0.075 mole) of mercuric bromide yielded 2.32 g. (10%) of pure white crystals of bromomercuriethane, m.p. 195-196°C.

Since more of this compound was needed, the preparation involving diethyl mercury and mercuric bromide was also utilized. Diethyl mercury (3.234 g., 0.0125 mole) and mercuric bromide (4.96 g., 0.0137 mole) gave 7.50 g. (97%) of bromomercuriethane with a melting point of 191-193°C (lit.[31] m.p. 198°C).

The n.m.r. spectrum showed a quartet at 2.06 $\delta$ and a triplet at 1.40 $\delta$ . About the triplet were mercury satellites with $J_{Hg^{199}-H^{1}}$ = 294.6 c.p.s., and about the quartet a set of satellites with $J_{Hg^{199}-H^{1}}$ = 194.2 c.p.s. The upfield satellites of both groups overlapped.

Chloromercurimethane. This compound was purchased from Alfa Inorganics Inc. and used without further purification. The white crystals showed a melting point of 168-170°C (lit.[32] m.p. 170°C).

The n.m.r. spectrum showed a singlet at 1.13$\delta$. Symmetrically positioned about the singlet were a set of mercury satellites with $J_{Hg^{199}-H^{1}}$ = 201.6 c.p.s.

1-Chloromercuri-2,2-dimethylpropane. This compound was prepared by Mr. Paul E. Pike. Its synthesis, physical properties, and spectral parameters are fully described in the latter's thesis.[33]

2-Chloromercuributane. This compound was prepared by Mr. Gale M. Sherrodd. The dialkylmercurial was used to prepare the alkylmercuric halide.

Following the procedure previously described, 9.45 g. (0.030 mole) of di-sec-butyl mercury and 8.95 g. (0.033 mole) of mercuric chloride yielded 5.13 g. (59%) of white crystals, m.p. 28°C (lit.[34] m.p. 28°C).

The n.m.r. spectrum of the product showed a triplet at 1.08$\delta$, a doublet at 1.49$\delta$, a multiplet at 1.83$\delta$, and a multiplet at 2.76$\delta$ accounting for areas of 3, 3, 1, and 2, respectively. The only set of mercury satellites determined was for the methyl doublet. This set had a $J_{Hg^{199}-H^{1}}$ value of 275.0 c.p.s. indicating $\beta$ coupling.

2-Chloromercuri-2-methylpropane. The t-butyl chloride used for this preparation was prepared by Mr. Paul E. Pike.[35]

With the exception that the Grignard reagent was prepared in a more concentrated form, the procedure was the same as described for

2-chloromercuripropane. t-Butyl chloride (23.60 g., 0.255 mole), magnesium (12.0 g., 0.50 mole) and powdered mercuric chloride (81.3 g., 0.30 mole) yielded white crystals which decomposed without melting. After recrystallization from methanol, total yield was 20.9 g. (28%) of product which decomposed without melting (lit.[36] 2-chloromercuri-2-methylpropane decomposed without melting).

The n.m.r. spectrum of the product showed a singlet at 1.50 $\delta$. About this peak was a set of mercury satellites with $J_{Hg^{199}-H^{1}}$ = 255.5 c.p.s. indicative of $\beta$ coupling.

Benzylmercuric chloride. Benzylmercuric chloride was prepared by Mr. Galé M. Sherrodd. The benzyl chloride used was the same as that utilized in preparing dibenzyl mercury.

The procedure for preparation was the same as outlined for 2-chloromercuripropane. Benzyl chloride (31.7 g., 0.25 mole), magnesium (12.16 g., 0.50 mole), and mercuric chloride (59.7 g., 0.22 mole) were used to yield 51.6 g. (72%) of white crystals, m.p. 95-97°C (lit.[37] m.p. 104°C).

The n.m.r. spectrum of the product showed a singlet at 3.27 $\delta$ and at 7.18 $\delta$. About the upfield singlet was a set of mercury satellites with $J_{Hg^{199}-H^{1}}$ = 253.6 c.p.s. showing $\alpha$ coupling. No other satellites could be determined.

## Ozonation of the Organomercurials

A solution of the organomercurials was prepared using 100 ml. of pure chloroform and sufficient compound to make an approximately 0.10 M solution. To this solution was added 1.90 grams of nitromethane as an internal NMR standard. Flow rates of ozone were determined, and all the solutions were then ozonized at 0°C. Aliquots were withdrawn at spaced intervals of time and were subsequently shaken with solid potassium iodide to quench the reaction with ozone. The potassium iodide reduced any remaining ozone similar to its action as an $O_3$ trap (see Fig. 1). Since it was noted that iodine was liberated by this quenching, and that some unexplained n.m.r. peaks were later traced to formation of RI via the reaction of $I_2$ with unreacted RHgX, later rate reactions were treated with a mixture of solid potassium iodide and solid sodium thiosulfate. The sodium thiosulfate reduced any liberated iodine to the iodide form of the element.

This quenching of the solutions with potassium iodide caused formation, in the case of the alkylmercuric halides, of the corresponding alkylmercuric iodide. Consequently, it was noted that a "loss" of mercury satellites occurred in the n.m.r. spectra of these products. This in no way affected the results, since all the original organomercurial was still present, albeit as the iodide.

## Rate Determination of the Organomercurials

Using the n.m.r. method, the decreasing concentration of organomercurial was measured by comparison with the constant concentration of the nitromethane standard. This method gave a relative ratio of loss of mercurial versus time. Since the original concentration was known, the actual loss of concentration versus time could be easily determined.

The method of determining the ratios of nitromethane to mercurial involved integration of the areas under the peaks using the electronic analog integrator of the HA-60 spectrometer. Employing the field sweep technique for constant phase reasons, the nitromethane peak was first integrated and then the organomercurial peak. After waiting 10 to 15 seconds, so the protons could regain a relaxed state, the respective peaks were again integrated. Usually, six pairs of integrations were taken for each sample.

This series of concentrations was plotted for the individual organomercurial to give a graph depicting the loss of reactant versus time. This graph was exactly linear for the dialkylmercurials. In the case of the alkylmercuric halides, this graph yielded a curve.

To obtain rate data for the alkylmercuric halides, the actual concentrations were obtained from the relative values by noting that the original concentration in all cases (time = 0) was 0.10 M. These actual concentrations, along with the respective interval of time each value was obtained, were submitted to a least-squares computer program. Using an IBM 1620 computer, the natural logarithm of the concentration was compared to the time of reaction to give a linear graph. From this plotting the least-squares slope, y-intercept, absolute rate constant, and correlation coefficient of the line were determined.

## Oxygenation of Organomercurials

The gas stream from the Welsbach ozonator contains only 3 to 4% ozone. The remaining 96 to 97% is oxygen. Therefore, it is important to determine the effect of oxygen on organomercurials.

To determine this effect, 1.39 g. (0.005 mole) of 2-chloromercuripropane was placed in 50 ml. of chloroform containing 0.90 g. of nitromethane. Pure oxygen was passed through this solution for two hours.

The relative ratios of the samples were determined by n.m.r. spectroscopy. It was discovered that the loss of 2-chloromercuripropane amounted to approximately 4%. Only acetone was seen as a product of the oxygenation; no 2-propanol was found.

It is concluded that oxygen has a much reduced effect on the carbon-mercury bond compared to the latter's reaction with ozone.

## Attempted 2nd Order Rate Determination

To accomplish a second-order rate study, equimolar concentrations of ozone and organomercurial were allowed to react.

The solubility of ozone in chloroform at -64°C was measured to determine its concentration at saturation. One hundred ml. of pure chloroform was placed in a water-ice bath, and ozone was passed through the solvent for one-half hour. The solution at that time showed the deep blue coloration characteristic of ozone solutions. The reaction tube was then allowed to warm to room temperature while nitrogen gas was passed through the solution to expel the ozone. The released ozone was trapped in a KI solution, and the amount of ozone present was then determined by the standard thiosulfate titration. The concentration of ozone was 0.0140 M.

Using diisopropyl mercury as the dialkylmercurial, a saturated solution of ozone was prepared at -64°C, to which the mercurial was added with stirring. Aliquots at 2, 5, and 7 minutes were analyzed by n.m.r. spectroscopy. No reactant peaks could be found, so the experiment was run a second time. This time the solution was noticed to be completely decolorized in less than one minute. These results implied that the reaction of the dialkylmercurials with ozone occurred very rapidly.

Similar second-order rate determinations were attempted with alkylmercuric halides. Three separate experiments with 2-chloromercuripropane and one experiment with benzylmercuric chloride were performed. In each case, the results showed random assortments of points; no reasonably good line or curve could be drawn. In particular, the benzylmercuric chloride experiment and one of the 2-chloromercuripropane experiments showed the bulk of points to be increasing with time. This last result definitely questioned the validity of these experiments.

The main problem associated with these latter experiments was the necessarily low concentration of alkylmercuric halide used. The peaks in the n.m.r. spectra were small and too close to the background noise to give consistent and reliable integration data. Increased concentrations of organomercurial would have altered the intent of the experiments by upsetting the equimolar ratio of the reactants.

The concentration of ozone at 0°C was determined by the method described and found to be 0.0163 M. Therefore, second-order attempts at 0°C were deemed impossible with the available instrumentation.

There is a discrepancy in the ozone concentrations noted above.

The general rule is that with decreasing temperature, the solubility of gases in liquids increases. However, the opposite result is noted above. This specious deviation from the rule may be the result of experimental error.

## Preliminary Data

The results presented in Table I show the average concentrations, relative and actual, of the mercurials during ozonation at 0°C.

The integration values were normalized with respect to nitromethane and then averaged. This average was reported in Table I as the relative concentration. For example, a series of integrations gave the following results:

| $CH_3NO_2$ | Mercurial |
|---|---|
| 181.0 | 121.5 |
| 173.0 | 119.0 |
| 180.0 | 119.0 |
| 180.5 | 120.5 |
| 181.5 | 118.5 |

(The numbers represent the height in millimeters of the respective integrations on the n.m.r. spectra.)

These numbers were then normalized to give $CH_3NO_2$ the value of 1.00 in all cases.

| $CH_3NO_2$ | Mercurial | |
|---|---|---|
| 1.00 | 0.671 | |
| 1.00 | 0.687 | |
| 1.00 | 0.661 | |
| 1.00 | 0.667 | |
| 1.00 | 0.653 | Average: 0.668 |

The actual concentration was determined by relating the relative concentration at any time with the relative concentration at time zero, where mercurial concentration is 0.10 M.

## TABLE I

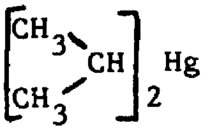
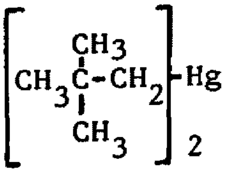
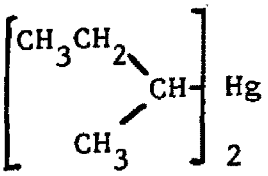
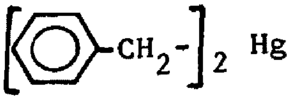
| Organo-mercurial | $O_3$ Flow Rate (mmole/min) | Time Minutes | Relative Conc. (cf. $CH_3NO_2$=1.00) | Actual Conc. (M) |
|---|---|---|---|---|
| 1.  | 34 | 0.0 | 1.199 | 0.100 |
| | | 5.0 | 0.975 | .087 |
| | | 10.0 | 0.697 | .062 |
| | | 15.0 | 0.506 | .045 |
| | | 20.0 | 0.229 | .021 |
| 2. $(CH_3CH_2CH_2)_2Hg$ | 50.7 | 0.0 | 1.156 | 0.100 |
| | | 5.0 | 1.062 | .087 |
| | | 10.0 | .947 | .082 |
| | | 15.0 | .787 | .068 |
| | | 20.0 | .731 | .063 |
| | | 25.0 | .642 | .055 |
| 3. $(CH_3CH_2)_2Hg$ | 44.0 | 0.0 | .775 | 0.100 |
| | | 5.0 | .623 | .080 |
| | | 10.0 | .495 | .064 |
| | | 15.0 | .389 | .050 |
| | | 20.0 | .198 | .026 |
| 4.  | 43.3 | 0.0 | 2.028 | 0.100 |
| | | 5.0 | 1.491 | .074 |
| | | 15.0 | .706 | .035 |
| | | 20.0 | .312 | .015 |
| | | 25.0 | .048 | .0024 |
| 5.  | 49.3 | 0.0 | 1.458 | 0.300[38] |
| | | 5.0 | 1.397 | .288 |
| | | 10.0 | 1.329 | .274 |
| | | 20.0 | 1.151 | .237 |
| | | 31.0 | 1.021 | .210 |
| | | 40.0 | .938 | .193 |
| 6.  | 42.9 | 0.0 | 0.393 | 0.300[38] |
| | | 10.0 | .342 | .261 |
| | | 20.0 | .315 | .241 |
| | | 30.0 | .226 | .173 |
| | | 40.0 | .178 | .136 |
| | | 50.0 | .132 | .101 |
| | | 75.0 | .043 | .0328 |

Table I (Continued)

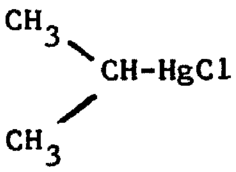
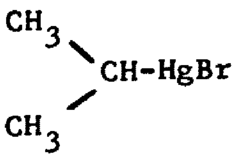
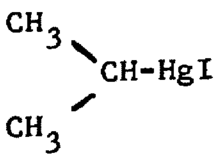
| Organomercurial | $O_3$ Flow Rate (mmole/min) | Time (min) | Rel. Conc. ($CH_3NO_2$=1.00) | Actual Conc. (M) |
|---|---|---|---|---|
| 7.  | 34.3 | 0.0 | 0.613 | 0.100 |
| | | 10.0 | .418 | .068 |
| | | 20.0 | .329 | .054 |
| | | 30.0 | .268 | .044 |
| | | 40.0 | .215 | .035 |
| | | 50.0 | .189 | .031 |
| | | 60.0 | .164 | .027 |
| " | - | 0.0 | 0.721 | 0.100 |
| | | 5.5 | .648 | .0899 |
| | | 10.0 | .603 | .0836 |
| | | 15.0 | .569 | .0789 |
| | | 20.0 | .526 | .0729 |
| | | 25.0 | .455 | .0631 |
| | | 30.0 | .445 | .0617 |
| | | 40.0 | .294 | .0408 |
| 8.  | 42.5 | 0.0 | 0.613 | 0.100 |
| | | 5.0 | .525 | .0857 |
| | | 15.0 | .336 | .0548 |
| | | 25.0 | .254 | .0414 |
| | | 35.0 | .235 | .0384 |
| | | 45.0 | .182 | .0297 |
| | | 60.0 | .144 | .0235 |
| | | 75.0 | .130 | .0212 |
| | | 90.0 | .105 | .0171 |
| 9.  | 55.4 | 0.0 | 0.556 | 0.100 |
| | | 5.0 | .465 | .0836 |
| | | 10.5 | .395 | .0710 |
| | | 20.0 | .315 | .0566 |
| | | 25.0 | .251 | .0451 |
| | | 30.0 | .238 | .0428 |
| | | 40.0 | .186 | .0335 |
| | | 52.0 | .125 | .0225 |
| | | 60.5 | .101 | .0182 |
| | | 70.0 | .0733 | .0132 |
| 10. $CH_3CH_2$-HgCl | 32.5 | 0.0 | 0.320 | 0.100 |
| | | 10.0 | .255 | .0797 |
| | | 20.0 | .239 | .0746 |
| | | 30.0 | .228 | .0713 |
| | | 50.0 | .195 | .0609 |
| | | 80.0 | .200 | .0625 |
| | | 135.0 | .174 | .0543 |

Table I (Continued)

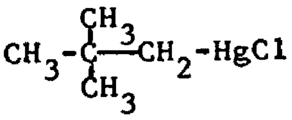
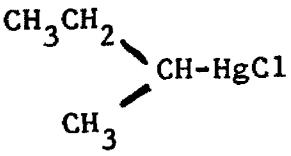
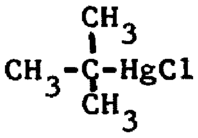
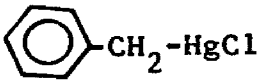
| | Organomercurial | $O_3$ Flow Rate (mmole/min) | Time (min) | Rel. Conc. $(CH_3NO_2=1.00)$ | Actual Conc. (M) |
|---|---|---|---|---|---|
| 11. | $CH_3CH_2$-HgBr | 37.3 | 0.0 | 0.430 | 0.100 |
| | | | 5.0 | .325 | .0756 |
| | | | 16.0 | .377 | .0876 |
| | | | 25.0 | .332 | .0773 |
| | | | 35.0 | .320 | .0744 |
| | | | 45.0 | .327 | .0760 |
| | | | 60.0 | .293 | .0682 |
| | | | 70.0 | .309 | .0719 |
| | | | 85.0 | .278 | .0647 |
| | | | 100.0 | .256 | .0595 |
| | | | 120.0 | .243 | .0566 |
| 12. | $CH_3$-HgCl | 46.2 | 0.0 | 0.443 | 0.100 |
| | | | 10.0 | .413 | .0932 |
| | | | 20.0 | .393 | .0887 |
| | | | 25.0 | .375 | .0846 |
| | | | 30.0 | .356 | .0804 |
| | | | 40.0 | .336 | .0758 |
| | | | 50.0 | .308 | .0695 |
| 13. |  $CH_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}HgCl$ | 31.2 | 0.0 | 0.853 | - |
| | | | 10.0 | .976 | 0.100 |
| | | | 30.0 | .955 | .0980 |
| | | | 40.0 | 1.022 | - |
| | | | 60.0 | .989 | - |
| | | | 90.0 | .956 | .0980 |
| | | | 165.0 | .907 | .0930 |
| | | | 780 | .707 | .0724 |
| 14. |  | 52.1 | 0.0 | 0.349 | 0.100 |
| | | | 10.0 | .304 | .0871 |
| | | | 16.0 | .279 | .0799 |
| | | | 23.0 | .275 | .0788 |
| | | | 30.0 | .229 | .0656 |
| | | | 40.0 | .207 | .0593 |
| | | | 50.0 | .177 | .0507 |
| | | | 60.0 | .146 | .0418 |
| | | | 70.0 | .125 | .0358 |
| | | | 80.0 | .0849 | .0243 |

Table I (Continued)

| Organomercurial | $O_3$ Flow Rate (mmole/min) | Time (min) | Rel. Conc. ($CH_3NO_2$=1.00) | Actual Conc. (M) |
|---|---|---|---|---|
| 15.  $CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}HgCl$ | 41.5 | 0.0 | 0.914 | 0.100 |
| | | 5.0 | .682 | .0746 |
| | | 10.0 | .455 | .0498 |
| | | 15.0 | .303 | .0332 |
| | | 20.0 | .115 | .0126 |
| | | 25.0 | .046 | .00504 |
| | | 30.0 | .036 | .00394 |
| 16.  | 35.1 | 0.0 | 0.159 | 0.0927 |
| | | 5.0 | .171 | .100 |
| | | 10.0 | .139 | .0811 |
| | | 20.0 | .0938 | .0548 |
| | | 30.0 | .0464 | .0272 |

# CHAPTER III

# RESULTS

## Rates of Ozonation of Organomercurials

The rates of ozonation of six dialkylmercurials and ten alkylmercuric halides were determined at 0°C. Also, since it was later discovered that the 2-halomercuripropanes yielded 2-propanol as an intermediate product, the rate of ozonation of 2-propanol at 0°C was measured, thereby permitting a comparison of the ozonation rates of the organomercurial and the alcohol. From these data it was possible to assign the percentage of ketone product which was formed *via* the alcohol.

The rates of ozonation of the dialkylmercurials were indeterminable because of the extremely rapid ozonation of these compounds. Consequently, the kinetic order of the reaction was unknown. A plot of concentration of mercurial versus time yielded a linear relationship, illustrating the lack of mercurial concentration dependence at the experimental temperatures and $O_3$ concentration.

Consider the rate equation as

$$-d(RHgR)/dt = k\ (RHgR)\ (O_3).$$

After saturation was reached, ozone concentration was constant, therefore $k' = k(O_3)$ for most of the reaction. Therefore, because of the lack of concentration dependence on mercurial concentration,

$$-\int_{R_o}^{R} d(\text{RHgR}) = k' \int_{o}^{t} dt,$$

$$(\text{RHgR}) - (\text{RHgR})_o = -k't, \text{ and}$$

$$(\text{RHgR}) = -k't + (\text{RHgR})_o \ .$$

In consideration of the equation of a straight line ($y = mx + b$), a plot of (RHgR) versus time gave a linear graph with the initial concentration, $(\text{RHgR})_o$, as the y-intercept of the line and $-k'$ as the slope.

The slope of the line was meaningless in the case of the dialkylmercurials. The extremely facile ozonation of these compounds resulted in the slope depending not on the concentration of ozone in solution, but on the flow rate of ozone through the solution. Therefore, no rate constants were determinable for the dialkylmercurials.

The alkylmercuric halides, on the other hand, reacted at a more convenient rate with ozone (at 0°C and 0.1 M organomercurial concentration). Moreover, these compounds showed a definite rate-altered effect as the molecule was changed from one containing a tertiary carbon-mercury bond to one with a primary bond. This effect is clearly seen in Table II when, for example, the relative rates of the t-butyl, isopropyl, and ethyl compounds are compared.

A lesser, yet observable, rate effect was noted with a change in halide ligand from chloride to bromide to iodide (see Table II).

The kinetic data for the ozonation of alkylmercuric halides supported a pseudo-first-order process. Thus, plotting the natural logarithm of the concentration of mercurial versus time yielded a linear graph.

Assuming second-order kinetics overall, the rate equation describing the reaction is

$$-\frac{d(\mathrm{RHgX})}{dt} = k(\mathrm{O_3})\ (\mathrm{RHgX}).$$

Ozone concentration is a constant in the solution, so $k(\mathrm{O_3}) = k'$. Consequently,

$$-\frac{d(\mathrm{RHgX})}{(\mathrm{RHgX})} = k'\ dt,$$

$$\int_{R_o}^{R} \frac{d(\mathrm{RHgX})}{(\mathrm{RHgX})} = k' \int_{o}^{t} dt,$$

$$\ln\ (\mathrm{RHgX}) - \ln\ (\mathrm{RHgX})_o = -k't, \text{ or}$$

$$\ln\ (\mathrm{RHgX}) = -k't + \ln\ (\mathrm{RHgX})_o.$$

Again considering the equation of a straight line, the plot of ln (RHgX) versus time gave a slope equal to -k' and a y-intercept equal to $\ln(\mathrm{RHgX})_o$, the logarithm of the initial concentration. If the concentration of ozone in solution was known, the slope could then be used to determine the absolute rate constant, k.

In the case of the alkylmercuric halides, the slopes of the lines could be used to measure relative and absolute rates, since for those mercurials ozonation was relatively slow.

Inherent in the calculation of the absolute rate constant from the slope of the line was the assumption that the ozone saturates the solution within 5 to 10 minutes from the time it is first introduced (based upon an average flow rate of 35 millimoles ozone per minute). Although it has been found by Erickson[39] that up to one-half hour or more may be necessary to saturate a solvent with ozone, the graphs obtained show that any deviation from saturation in the early part of the reaction did not affect the data to any great extent.

## Intermediate and Final Products from Ozonation of Mercurials

Paul E. Pike,[40] in his work on the ozonolysis of organomercurials, determined the final products that were formed after several hours of ozonation. A fortunate bonus of using NMR in this study was that several intermediates of the reaction were discovered.

In the case of the dialkylmercurials, it was found that upon ozonation the respective alkylmercuric halide was formed from one half of the original molecule. The cleaved R-group went on to form the respective alcohol, acid, or ketone.[40] As an example, the ozonation of diisopropyl mercury yielded a 2-halomercuripropane and 2-propanol as intermediates which further reacted with ozone to form 2-propanone and acetic acid. The intermediates were identified by their chemical shift values. Of these, the alkylmercuric halide intermediate was believed to be the respective chloride, due to the availability of chlorine from the slow ozonation of the $CHCl_3$ solvent, which is known to yield phosgene and hydrogen chloride.

All the 2-halomercuripropanes showed 2-propanol as a definite intermediate product. To verify that the doublet at $1.20\delta$ was 2-propanol and not another isopropylmercuric salt, a solution of the mercurial was ozonized, followed by flash evaporation at room temperature and low pressure. In the flash distillate the presence of 2-propanol was proved by the appearance of a doublet at 1.20$\delta$ in the n.m.r. spectrum. The 2-propanol was also not an artifact of ozone quenching, since the solution was deliberately left untreated in the above-mentioned experiment.

Of the alkylmercuric halides ozonized, final products were noted in the case of the 2-halomercuripropanes, 2-chloromercuributane, 1-chloromercuri-2,2-dimethylpropane, 2-chloromercuri-2-methylpropane, and benzylmercuric chloride. These were the only compounds whose products had significantly different chemical shift values, thereby facilitating detection.

2-Chloromercuributane on reaction with ozone gave 2-butanone. Due to the similarity of this mercurial with the 2-halomercuripropanes, it was to be expected that 2-butanol should also be formed. However, the presence of this alcohol was not substantiated.

1-Chloromercuri-2,2-dimethylpropane gave 2-propanone as one of the products of ozonation. The other products could not be identified by their chemical shift values alone. Because of the unreactivity of this mercurial, the products appeared only after several hours of ozonation.

2-Chloromercuri-2-methylpropane yielded only 2-propanone and t-butanol as products of ozonation. This was in accord with the products found previously.[40] The appearance of 2-propanone occurred only after all the mercurial had reacted to form t-butanol, thus implying that 2-propanone was a product of the further ozonation of t-butanol.

The ozonation of benzylmercuric chloride gave benzaldehyde and benzoic acid as products. The appearance of benzyl alcohol was expected, but not substantiated by n.m.r. spectroscopy. Possibly the rate of ozonation of this alcohol was so great such that no sufficient build-up occurred to permit detection.

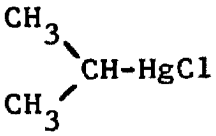
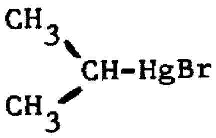
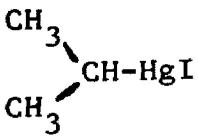
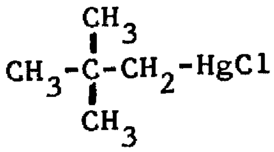
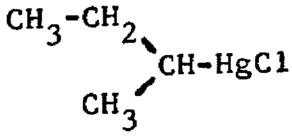
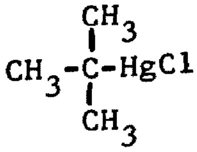
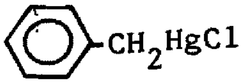
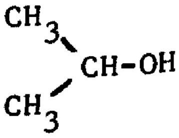
## Stoichiometry of the Ozonation of Organomercurials

The dialkylmercurials required only one equivalent of ozone for cleavage of one of the carbon-mercury bonds. This was demonstrated by the measurement of ozone flow rate and correlation with the amount of time necessary for the mercurial to reach zero concentration.

The alkylmercuric halides required from one to approximately two equivalents of ozone for the carbon-mercury cleavage, depending on the type of the carbon-mercury bond. The values were determined by correlation of the number of moles of ozone used, as measured by titration, to the loss of mercurial, as determined by n.m.r. spectroscopy.

Cleavage of the primary carbon-mercury bond required from 1.30, in the case of bromomercuriethane, to 1.95 equivalents of ozone, in the case of benzylmercuric chloride. The secondary carbon-mercury bond required 1.5 to 2 equivalents of ozone, as determined by two separate experiments with 2-chloromercuripropane. The tertiary carbon-mercury bond of 2-chloromercuri-2-methylpropane showed a requirement of approximately one equivalent of ozone. The method described for stoichiometric determination of the dialkylmercurials was applied in this instance. The ozonation of this mercurial was sufficiently rapid to warrant use of this procedure.

## TABLE II

| | Organomercurial | $10^3k'$ (min$^{-1}$) | k (l/mole-min) | Relative Rate | Correlation Coefficient[41] |
|---|---|---|---|---|---|
| 1. |  | 20.02 | 1.228 | 7.24 | 0.990 |
| 2. |  | 22.27 | 1.366 | 8.05 | 0.982 |
| 3. |  | 28.11 | 1.724 | 10.16 | 0.999 |
| 4. | $CH_3CH_2-HgCl$ | 2.766 | 0.169 | 1.00 | 0.989 |
| 5. | $CH_3CH_2-HgBr$ | 3.757 | 0.231 | 1.36 | 0.962 |
| 6. | $CH_3-HgCl$ | 7.245 | 0.444 | 2.62 | 0.997 |
| 7. |  $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-HgCl$ | ∼0.417 | — | <0.151 | — |
| 8. |  | 14.65 | 0.899 | 5.29 | 0.995 |
| 9. |  $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-HgCl$ | 117.6 | 7.217 | 42.51 | 0.981 |
| 10. |  | 51.29 | 3.147 | 18.54 | 0.989 |
| 11. |  | 41.71 | — | 15.1 | 0.994 |

# CHAPTER IV

# DISCUSSION

## Rates of Ozonation of Organomercurials

From the data in Table II, it is observed that the alkyl substituents demonstrate a substantial effect on the rates of ozonation. The order of reaction rate follows the sequence t-butyl > benzyl > isopropyl > sec-butyl > methyl > ethyl >> neopentyl. Also, the alkylmercuric iodides react faster than the bromides, which in turn react faster than the chlorides. In addition, a comparison of the dialkyl compounds with the alkylmercuric halides shows the former to be the faster reacting.

These relationships are very atypical of the expected results described in the introductory remarks concerning $S_E1$ and $S_Ei$ mechanisms of electrophilic substitution. For these mechanisms, partial negative charge is built up at carbon in the transition states. Such a charge would not be stabilized by alkyl groupings. The distinctions between the $S_E2$ and the concerted cyclic mechanisms are not clear. An alternative to these mechanisms is a free radical process, which is known to be assisted by alkyl groups. However such free radical reactions of ozone are uncommon.

Evidence for electrophilic substitution by ozone is clearly demonstrated. As noted by Jensen and Rickborn,[42] the rate of electrophilic cleavage of a carbon-metal bond increases as the polarization of the bond increases. This is a direct consequence of the electronegativity of the second atom attached to mercury.

$$\begin{array}{ccccc} & & \delta+ & & \delta- \\ C & \text{———} & Hg & \text{———} & Cl \\ 2.5 & & 1.9 & & 3.0 \end{array}$$

$$\begin{array}{ccccc} \delta- & & 2\delta+ & & \delta- \\ C & \text{———} & Hg & \text{———} & Br \\ 2.5 & & 1.9 & & 2.8 \end{array}$$

$$\begin{array}{ccccc} \delta- & & 2\delta+ & & \delta- \\ C & \text{———} & Hg & \text{———} & I \\ 2.5 & & 1.9 & & 2.5 \end{array}$$

$$\begin{array}{ccccc} \delta- & & 2\delta+ & & \delta- \\ C & \text{———} & Hg & \text{———} & C \\ 2.5 & & 1.9 & & 2.5 \end{array}$$

The chlorine atom, due to its larger electronegativity, pulls electron density from the carbon-mercury bond, thus making this bond less of an electron source. As the electronegativity of the halogens decreases, the carbon atom begins to assume more partial negative charge, that is, the C-Hg bond becomes more polarized. Finally, with symmetrical carbon groups attached to mercury, the carbon-mercury bond has reached a maximum polarization thereby producing a bond between carbon and mercury which is more rapidly attacked by an electrophile. Therefore, the dialkylmercurial is expected to cleave fastest, followed by the alkylmercuric iodide, bromide, and chloride, respectively. This order is held for electrophilic cleavage reactions by bromine, HX, and mercuric salts.[2]

At first glance one would assume that iodide compounds should be as reactive as the dialkyl compounds because of the similar Pauling electronegativity values of iodine and carbon. This is misleading however, as the iodine atom still exhibits the electron-pulling capabilities of the halogens, whereas carbon is not at all halogen-like in this respect. Also, the bonding orbitals in the carbon-mercury bond are very different than the bonding orbitals of the iodine-mercury bond. The two atoms, and the respective reaction rates, cannot be compared solely on the basis of electronegativity values.

A ground-state argument for the observed reaction rate differences is based on alkyl inductive effects. Namely, as the number of R-groups increases on the carbon of the carbon-mercury bond, increasing electron density is inductively placed in the bond region, and this in turn facilitates the initial attack by the electrophile ozone. Since the length of the carbon-mercury bond is almost one and one-half times larger than the length of the carbon-carbon bond (2.06-2.20 Å vs. 1.54 Å, respectively),[43] steric effects should not play too large a part in hindering ozone attack at the bond region. This ground-state approach shows that a tertiary carbon-mercury bond would facilitate initial attack better than a secondary and primary bond.

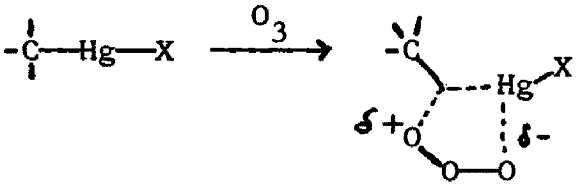
A transition-state argument for the rate sequence is that, in the four-center-like mechanism (see next section), the ozone-mercurial transition species has the carbon $sp^3$ orbital as the "fourth center".[44] Because of the presence of the electronegative oxygen atom, electronic changes occur in this orbital to give the carbon atom a partial positive charge in the transition state. This positive charge is stabilized best by a tertiary carbon, and in turn the rate is increased. The relative rates would then be as described above.

In these rate sequences the benzyl group fits in between the tertiary and secondary groups because of the usual resonance interactions of the aromatic ring.

## Mechanism of Ozonation of Organomercurials

The ozonation of organomercurials may proceed by an $S_E2$ mechanism or a polarized concerted cyclic mechanism. The concerted four-center-like mechanism is described below.

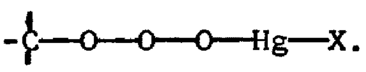
A high energy transition state arising from a 1,3-dipolar addition of ozone to the mercurial is very likely.



Of interest in this picture is the use of the carbon $sp^3$ atomic orbital as the "fourth center".[44] This orbital is represented by the normal dark line, showing that its charge density is changed mainly by electronic factors rather than by the bond cleavage and formation. This representation is similar to that presented by Jensen and Rickborn[44] when explaining the cleavage of organomercuric bromides with bromine.

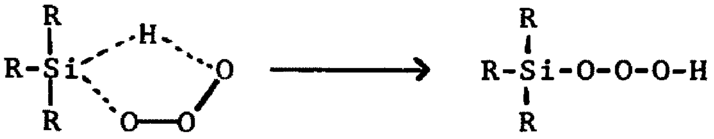
In this transition state, the high electronegativity of the oxygen atom can easily cause the carbon atom to bear a partial positive charge.

This transition state should then lead to an intermediate such as

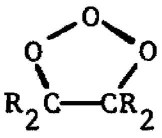


$-\overset{|}{\underset{|}{C}}-O-O-O-Hg-X.$

This is not without precedence. A similar mechanism is proposed for the ozonation of silicon compounds.[45]



Also, the 1,3-dipolar attack of ozone is well known in the case of olefins, where the ozonide intermediate

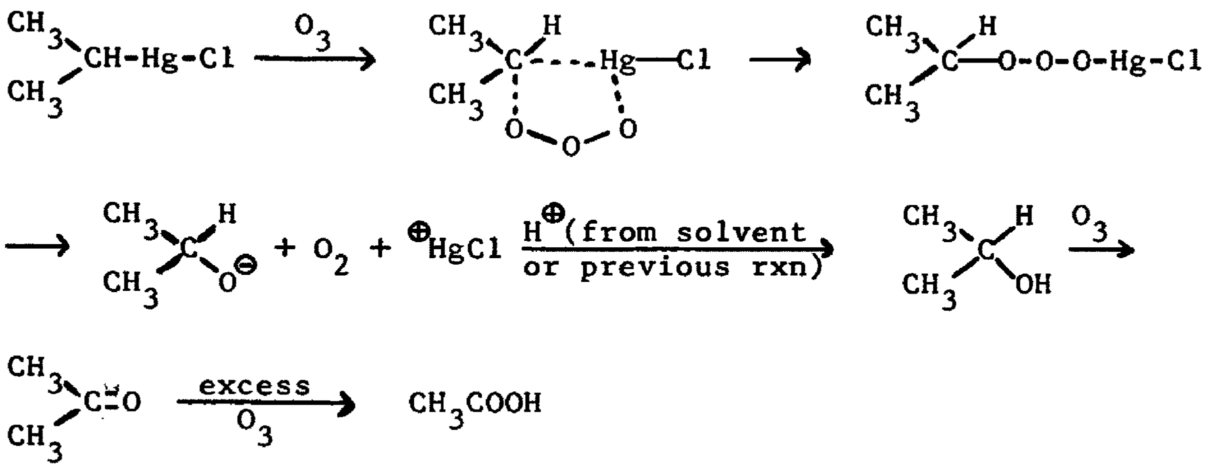


has been shown to exist.[46]

The existence of the ozone-mercurial intermediate has not, however, been proven. For example, an unquenched and partially ozonized solution of chloromercurimethane in chloroform showed no additional peaks besides starting material and formic acid in its n.m.r. spectrum. If such an intermediate were present in any appreciable concentration, one would expect a new methyl absorbance with a unique chemical shift value and with a quite different $Hg^{199}$-$CH_3$ spin-spin coupling constant.

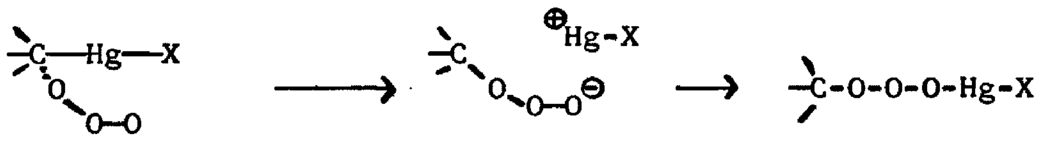
The implication from this negative data is that either such an intermediate $-\overset{|}{\underset{|}{C}}-O-O-O-Hg-$ species does not exist, or that it is so reactive or thermally unstable that it does not exist for an appreciable length of time, i.e., no large concentration builds up.

However, some indirect support for this high-energy intermediate was observed. The appearance of 2-propanol as an intermediate compound in the ozonation of 2-chloromercuripropane can be shown to form *via* the above transition state and intermediate.



In this sequence presented, it is likely that the ketone could be formed from the mercurial directly, and not necessarily be derived from the alcohol. It should be noted that Pike[47] found acetic acid to account for 10-20% of the reaction products of 2-chloromercuripropane, which implies that the acid results from further ozonation of the ketone or the alcohol.

A brief consideration of the $S_E2$ mechanism suggests that ozone must enter the bond region and attack carbon in a certain front-side manner as to allow for retention of configuration.



Since ozone is dipolar, the mercury atom with its cationic character will have an effect on the manner in which ozone reacts with the mercurial. However, a pure $S_E2$ reaction should involve reaction by the electrophile on carbon with no interactions occurring between the electrophile and the leaving group. There is no analogy between the $S_E2$ mechanism and other electrophilic cleavage mechanisms, and as yet no authenticated example of an $S_E2$ reaction of an organomercurial is known.

## Bond Strength and Relative Rates of Ozonation

The relative carbon-mercury bond strengths for some of the alkylmercurials were determined indirectly from polarographic data by Butin, Beletskaya, Kashin, and Reutov.[48]

As a bond becomes stronger, more voltage is necessary to achieve reduction of that bond. That is to say, the $E_{\frac{1}{2}}$ value becomes more negative. Polarographic data is therefore a good indication of bond strength.

For the reduction of dialkylmercurials, the data of interest is for R-groups of $CH_3$, iso-$C_3H_7$, $C_2H_5$, and $C_6H_5CH_2$. These compounds show respective $E_{\frac{1}{2}}$ values of - 2.880, - 2.861, - 2.859, and - 2.053 volts.

These few values show that there is a good correlation of carbon-mercury bond strength with the observed relative rates of ozonation. The polarographic reduction of the above species is a free radical (homolytic) process, however, it appears that the isopropyl value is out of sequence for such a process. No mention of this is brought up in the reference cited.

## Kinetics of Ozonation of Organomercurials

Without competitive rate data or fast reaction observation methods, nothing can be deduced concerning the kinetic order of the ozonation of the dialkylmercurials. It is expected that competitive data may show the same rate dependence on alkyl substituents as shown by the alkylmercuric halides.

The alkylmercuric halides show pseudo-first-order kinetics under constant ozone concentration conditions. It is only an assumption that the overall reaction is second-order, first in ozone concentration and first in mercurial concentration under normal conditions. This has no basis on experimental fact, since no simple method was devised to measure changes in concentration of ozone in solution.

## Stoichiometry of Ozonation of Organomercurials

Although the stoichiometry of the alkylmercuric halides varies from a value of 1 to approximately 2 equivalents of ozone, it is felt that cleavage of one carbon-mercury bond requires only one equivalent of ozone. This is shown to be the case with the dialkylmercurials and with 2-chloro-2-methylmercuripropane.

With the other mercurials tested, the discrepancy in values may be explained by consideration of the formation of intermediate products which have comparable rates of ozonation.

As an example of such possible discrepancies, one might consider the ozonation of 2-chloromercuripropane. The rate of ozonation of the intermediate 2-propanol was shown to be greater than that of the mercurial. As this alcohol accumulates, its ozonation can affect the apparent stoichiometric measurement. If a long enough time is allowed for ozonation, as was the case, it is very possible to see this effect coupled with the results of the organomercurial.

## CHAPTER V

## SUMMARY

The rates of ozonation of six dialkylmercurials and ten alkylmercuric halides were determined. According to the sequence of the relative rates of ozonation, the reactions were shown to be electrophilic in nature. Specifically, the ozonation of organomercurials was one of electrophilic substitution by means of an $S_Ei$ or concerted mechanism.

The dialkylmercurials exhibited the greatest rates of ozonation. The alkylmercuric iodides reacted faster than the bromides, and these in turn reacted faster than the chlorides. The rate differences with change in halide were not great, but they were significant.

Alkyl substituents provided the greatest effect on ozonation rates. The observed rates followed the sequence t-butyl $>$ benzyl $>$ isopropyl $>$ *sec*-butyl $>$ methyl $\geqslant$ ethyl $\gg$ neopentyl.

# BIBLIOGRAPHY

1. Paul E. Pike, Master's Thesis, University of Montana, 1970.
2. F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill Book Co., New York, 1968, pp. 45, 75, 100 and references cited therein.
3. H. Framherz and K. Lih, Z. Physik, Chem. (Leipzig), A167:103 (1933), as cited in ref. 2, p. 4.
4. Ref. 2, p. 4.
5. F. R. Jensen and L. H. Gale, J. Am. Chem. Soc., 81, 1261 (1959). Also, ref. 2, pp. 86-92.
6. Ref. 2, pp. 113-116, and references therein.
7. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, "Purification of Laboratory Chemicals," 1st Ed., Pergamon Press Inc., New York, 1966, p. 110.
8. Henry Gilman and Robert E. Brown, J. Am. Chem. Soc., 51, 928 (1929).
9. C. S. Marvel, C. G. Gauerke and E. L. Hill, J. Am. Chem. Soc., 47, 3009-11 (1925).
10. Ref. 2, p. 104.
11. J. H. Robson and George F. Wright, Can. J. Chem., 38, 29 (1960).
12. Ref. 5, p. 179.
13. R. C. Weast and others, "Handbook of Chemistry and Physics," 47th Ed., Chemical Rubber Co., Cleveland Ohio, 1966, p. C-487.
14. Ref. 6, and references therein.
15. C. S. Marvel and V. L. Gould, J. Am. Chem. Soc., 44, 153-5 (1922).
16. Ref. 11, p. C-667.
17. R. E. Dessy, T. J. Flautt, H. H. Jaffe and G. F. Reynolds, J. Chem. Physics, 30, 1422 (1959).
18. Ref. 1, p. 23-24.

19. Ref. 13, p. 155.

20. F. C. Whitmore and E. Rohrman, *J. Am. Chem. Soc.*, **61**, 592 (1939).

21. C. S. Marvel and H. D. Calvery, *J. Am. Chem. Soc.*, **45**, 821 (1922).

22. A. Barcia Banirs, *C. A.*, **17**, 2109 (1923).

23. Ref. 13, p. 154, and this thesis, p. 9.

24. Ref. 9, p. 38.

25. *Ibid*.

26. Ref. 2, p. 104.

27. Ref. 9, p. 38.

28. *Ibid*.

29. M. M. Kreevoy and R. L. Hansen, *J. Am. Chem. Soc.*, **83**, 629 (1961).

30. K. H. Slotta and K. R. Jacobi, *C. A.*, **23**, 1870 (1929).

31. *Ibid*.

32. Ref. 11, p. C-667.

33. Ref. 1, p. 15-16.

34. Charman, Hughes and Ingold, *J. Chem. Soc.*, 1962, 2528.

35. Ref. 1, p. 22.

36. W. K. Wilde, *J. Chem. Soc.*, 1949, 75.

37. Paul Wolf, *C. A.*, **7**, 1196 (1913).

38. Analysis of these compounds by an A-60 NMR spectrometer necessitated the use of greater concentrations.

39. R. E. Erickson, personal communication.

40. Ref. 1, p. 33 ff.

41. The correlation coefficient is a measure of the degree of scattering of points about a line. A value of 1.00 indicates a perfect straight line fit of all points.

42. Ref. 2, p. 4.

43. D. Grdenić, *Quart. Rev.*, *19*(3), 303-28 (1965).

44. Ref. 2, p. 96.

45. R. J. Ouellette and D. L. Marks, *J. Organometal. Chem.*, *11*, 407-13 (1968).

46. J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill Book Co., New York, 1968, p. 874.

47. Ref. 1, pp. 40-41.

48. K. P. Butin, I. P. Beletskaya, A. N. Kashin and O. A. Reutov, *J. Organometal. Chem.*, *10*(2), 197-210 (1967).