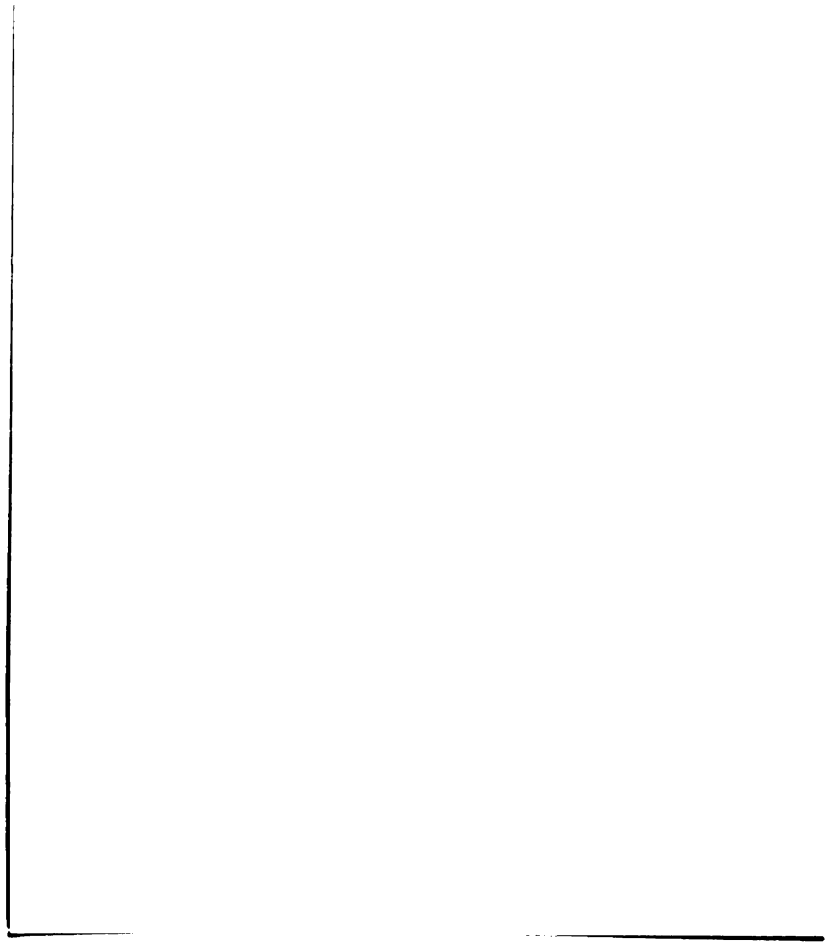


I. THE DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE

II. THE DECOMPOSITION OF SOME t-BUTYL PERESTERS DERIVED FROM ALICYCLIC ACIDS

By

Romeo A. Cipriani

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1961

ACKNOWLEDGMENT

The author wishes to express his appreciation to Professor Hart, for his assistance throughout this investigation, and to the Monsanto Chemical Company, for its financial aid during the academic year of 1958-1959.

I. THE DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE

II. THE DECOMPOSITION OF SOME t-BUTYL PERESTERS DERIVED FROM ALICYCLIC ACIDS

By

Romeo A. Cipriani

AN ABSTRACT

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1961

Approved_____

AN ABSTRACT

The purpose of this investigation was two-fold: to obtain more information about the decomposition of cyclopropaneacetyl peroxide and to study the decomposition of t-butyl peresters of cycloalkanecarboxylic acids. In connection with the work on cyclopropaneacetyl peroxide, it was necessary to develop a reliable method for the preparation of cyclopropaneacetic acid in quantity.

A two-step procedure for the preparation of cyclopropaneacetic acid was developed. Cyclopropyl chloride was converted to cyclopropyllithium using lithium sand in ether and was then treated with ethylene oxide to produce β-cyclopropylethanol in 66% yield. Alternatively cyclopropylmagnesium chloride, prepared from cyclopropyl chloride and magnesium in tetrahydrofuran and entrained with benzyl bromide, when treated with ethylene oxide produced this alcohol; however, the procedure was lengthier and the yield somewhat lower (42%). Oxidation of β-cyclopropylethanol with sulfuric acid-chromium trioxide in aqueous acetone provided cyclopropaneacetic acid in 57% yield.

The decomposition of cyclopropaneacetyl peroxide in carbon tetrachloride at various temperatures and concentrations was found to follow first-order kinetics. The principal products of the reaction were carbon dioxide and an ester, probably cyclopropylcarbinyl

cyclopropaneacetate, along with lesser amounts of cyclopropaneacetic acid and a substance of undetermined structure derived from the alkyl part of the peroxide. Phosgene and hexachloroethane were also produced, but in undetermined quantities. Whereas the carboxyl group was quantitatively accounted for, only three-fourths of the alkyl portion was detected.

The rate of decomposition of cyclopropaneacetyl peroxide was unaffected by the presence of either acetic or trimethylacetic acid. However, trichloroacetic acid accelerated the decomposition, the rate increase being proportional to the concentration of acid. A similar, though not quite so large, effect was obtained in the case of cyclohexaneacetyl peroxide. Accompanying a decrease in yield of carbon dioxide was the appearance of an ester of trichloroacetic acid, the nature of the alkyl group not determined. An accelerated decomposition was also noted in the presence of pyridine, but here a comparable effect was obtained with cyclohexaneacetyl peroxide. The implication of these results on the mechanism of decomposition of cyclopropaneacetyl peroxide is discussed.

The decomposition rates of t-butyl peresters of cyclopropanecarboxylic acid and cyclohexanecarboxylic acid were measured in carbon tetrachloride. At 110°, t-butyl cyclohexanepercarboxylate decomposed three times faster than t-butyl cyclopropanepercarboxylate; extrapolated to

70°, the difference is a factor of five. The corresponding rate difference for the acyl peroxides at 70° is about 140. The enthalpies of activation, ΔH^*, for the reactions were 28.7 and 30.7 kcal./mole respectively, a somewhat smaller difference than in acyl peroxides. The results are consistent with some carbon-carbon bond stretching in the transition state leading to decomposition of the t-butyl peresters.

TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

TABLE OF CONTENTS - Continued

LIST OF TABLES

LIST OF TABLES - Continued

LIST OF TABLES - Continued

LIST OF TABLES - Continued

LIST OF FIGURES

LIST OF FIGURES - Continued

INTRODUCTION

This thesis deals with the preparation of cyclopropaneacetic acid, the decomposition of cyclopropaneacetyl peroxide and the decomposition of t-butyl peresters of certain alicyclic acids.

In the decomposition of peroxides derived from alicyclic acids, Hart and Wyman (3) noted that the behavior of cyclopropaneacetyl peroxide was incongruous, both in rapid rate of decomposition and in the high yield of ester, with other cycloalkaneacetyl peroxides studied. Furthermore, the rates were erratic, suggesting that the peroxide contained either an accelerator or an inhibitor of an undetermined nature. The purpose of this investigation then was to re-examine the decomposition to better understand the role of the cyclopropylcarbinyl system in free radical reactions. Rate constants and products were to be re-determined, paying special heed to the purity of the peroxide, possible catalysis by acid or base, induced decomposition and the energetics of the decomposition.

The relatively large amounts of cyclopropaneacetic acid needed for preparation of cyclopropaneacetyl peroxide in sufficient quantity for rate and product studies required the development of a reliable synthetic procedure adaptable to large quantities; initial efforts were directed towards this goal and a method superior to those

in the literature was developed. Study of the peroxide decomposition then became possible.

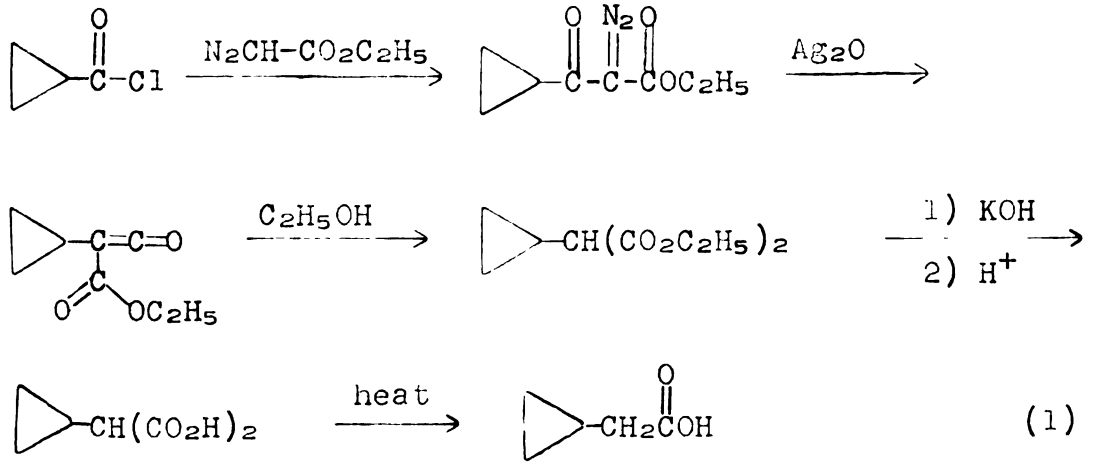
Acyl peroxides derived from cycloalkanecarboxylic acids decomposed at different rates, depending upon the size of the ring (1). This suggests that the stability of the alkyl radical which is produced when an acyl peroxide decomposes influences the rate. The effect was extensively studied by Bartlett and co-workers (2, 3, 4) using a wide variety of peresters. It was of interest to determine whether peresters were more or less sensitive to changes in structure of the alkyl group than were acyl peroxides. Towards this end, t-butyl peresters of cyclopropanecarboxylic and cyclohexanecarboxylic acids were synthesized and their rates of decomposition compared with those of the corresponding peroxides.

RESULTS AND DISCUSSION

A. The Preparation of Cyclopropaneacetic Acid

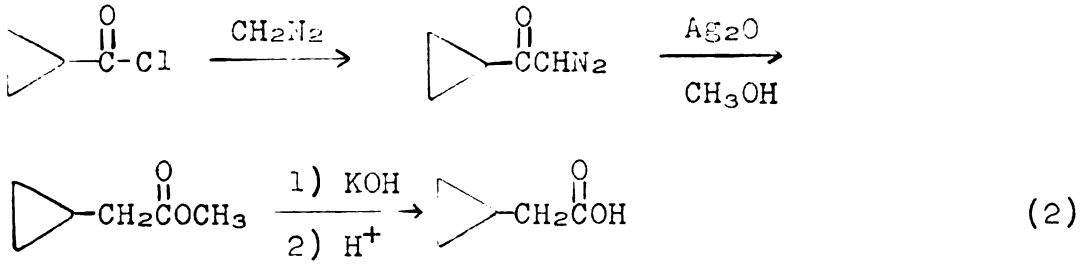
Cyclopropaneacetic acid is perhaps one of the most difficult of the simple acids to prepare in good yield and large quantity, for most of the conventional methods fail. Because of the unreactivity of cyclopropyl halides in displacement reactions, procedures such as condensation of cyclopropyl chloride with malonic ester do not work. Grignard reagents are easily formed from cyclopropyl bromide and iodide, but these are not readily available; cyclopropyl chloride, which is readily available, could be converted to the Grignard reagent only in small yield, using ether as the solvent (5). Carbonation of the Grignard reagent obtained from cyclopropylcarbinyl bromide produces allylacetic acid exclusively (6).

The first unequivocal synthesis of cyclopropaneacetic acid was that of Smith and MacKenzie (6), who prepared it according to equation 1; the overall yield was low. Two



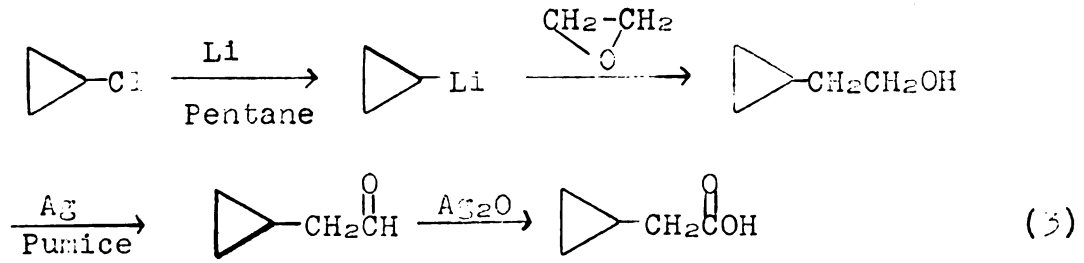
(1)

subsequent methods, though useful, possessed undesirable features. Wallis and Turnbull (7) used the Arndt-Eistert reaction (equation 2), which is good for only small



(2)

quantities because of the hazards involved in using diazomethane. To obtain cyclopropaneacetic acid, Hart and Wyman (1) treated cyclopropyllithium with ethylene oxide, dehydrogenated the resulting alcohol and oxidized the corresponding aldehyde (equation 3). Although this



(3)

route is adaptable to a large scale, the preparation of cyclopropyllithium, which was done in pentane, was found to be erratic. Furthermore, the procedure used to prepare the dehydrogenation catalyst lacked sufficient detail for successful reproduction of the yield.

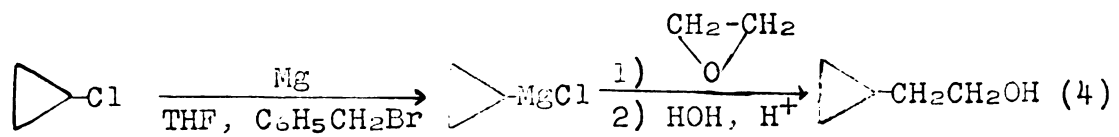
In the attempt to find another practical procedure, cyclopropylcarbinyl benzenesulfonate was treated with potassium cyanide in order to obtain cyclopropane-acetonitrile and, subsequently, the acid; this was

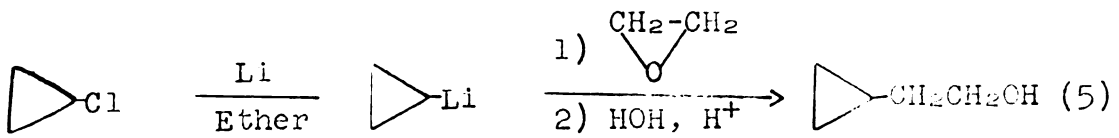
abandoned, for only a small amount of crude acidic material was obtained. Similar treatment of the cyclopropylcarbinyl tosylate also was unsuccessful because the tosylate was unstable (46). Extending the side chain of cyclopropanecarboxaldehyde using rhodanine, an excellent method for aromatic aldehydes, also was futile because the intermediates were ill-defined and obtained in poor yield.

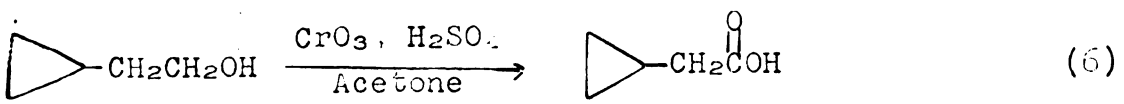
The success in preparing the Grignard reagent of vinyl chloride using tetrahydrofuran as the solvent (8) encouraged work on the preparation of cyclopropylmagnesium chloride. It was found that cyclopropyl chloride, entrained with one-fifth of a mole of benzyl bromide, reacted with magnesium in tetrahydrofuran to give the combined Grignard reagents in 76% yield. Treatment with ethylene oxide produced β-cyclopropylethanol in 42% yield, based on cyclopropyl chloride. Ethylene chlorohydrin was formed as a co-product, and, because of the closeness of the boiling point to that of the desired product, had to be removed by treatment with sodium hydroxide. The discovery that ether could be used as a solvent to prepare cyclopropyllithium (9) consistently eliminated the problem with ethylene chlorohydrin and β-cyclopropylethanol could be obtained in 66% yield.

Oxidation of the alcohol to the acid presented other difficulties, for acidic oxidizing agents attack the

cyclopropane ring, resulting in ring opening. Oxidation with basic potassium permanganate produced a mixture of cyclopropanecarboxylic and cyclopropaneacetic acids. However, a chromic oxide and sulfuric acid solution in water added slowly to an acetone solution of β-cyclopropylethanol, a method previously used for the oxidation of unsaturated alcohols (10), produced cyclopropaneacetic acid in 57% yield. The total reaction is shown in equations 4-6.







B. The Decomposition of Acyl Peroxides

Detailed discussions of acyl peroxide decompositions can be found in several textbooks (11, 12, 13, 14). In order to introduce the reader to certain phases of the field, the mechanisms of these reactions will be briefly discussed.

The decomposition of acyl peroxides can occur in a variety of ways. Primarily, there are the spontaneous reactions, in which the oxygen-oxygen bond breaks homolytically to form radicals

$$RC(=O)OOC(=O)R \longrightarrow 2\ RC(=O)O\cdot \qquad (7)$$

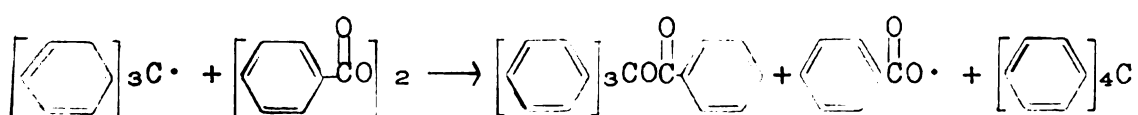
or heterolytically to form ions (15).

$$RC(=O)OOC(=O)R' \longrightarrow RC(=O)O^{\oplus} + {}^{-}OC(=O)R' \qquad (8)$$

In addition to these modes of decomposition, the acyl peroxide can undergo induced decomposition either by radicals (16, 17) or by ions (18).

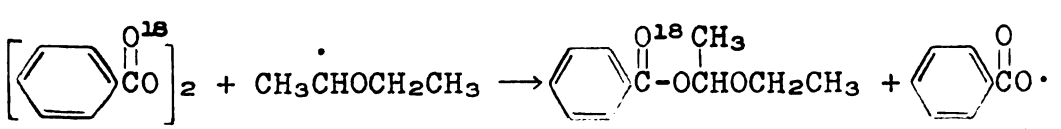
Spontaneous homolytic cleavage prevails when a symmetrical peroxide undergoes decomposition in a relatively non-polar solvent, such as benzene or carbon tetrachloride. This is probably the result of the small bond dissociation energy of the oxygen-oxygen linkage. For example, the bond dissociation energies of acetyl and benzoyl peroxides have been estimated to be 27-35 kcal./mole (19). This type of decomposition will be discussed further in later sections.

Often accompanying this reaction is induced decomposition caused by the presence of radicals in solution. The relative contribution depends upon the temperature (20) and the initial peroxide concentration, as well as on the solvent employed (17). Since this gives rise to higher order reactions, thereby complicating kinetics, it must be eliminated in order to simplify the study of the spontaneous decomposition. Either kinetic analysis (17) or the addition of a radical trap such as styrene or iodine (21), which intercepts the radicals, is effective. The point of attack of such a decomposition does vary: in the decomposition of benzoyl peroxide in benzene containing the triphenylmethyl radical, attack is both on the ring and on the oxygen (22)



(9)

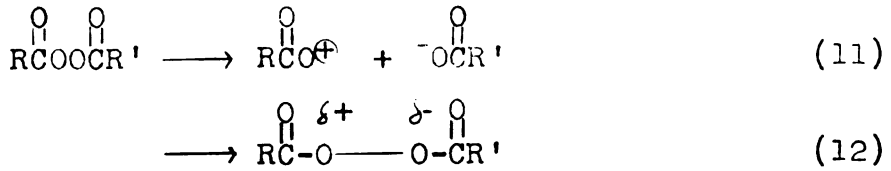
whereas in ethyl ether, attack occurs at the peroxide oxygen (23).



(10)

A decrease in symmetry of the molecule is accompanied by an increasing tendency for the reaction to proceed heterolytically. This type of decomposition may run the gamut from complete dissociation into ions, through intermediate stages, to a slight polarization of the

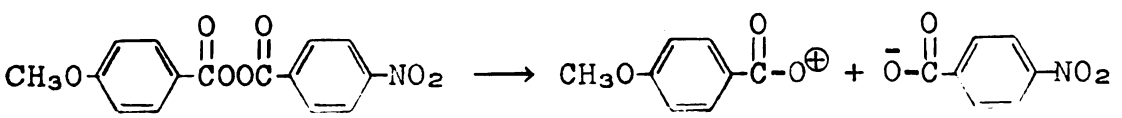
oxygen-oxygen bond (15).



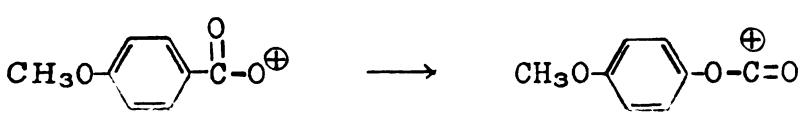
(11)

(12)

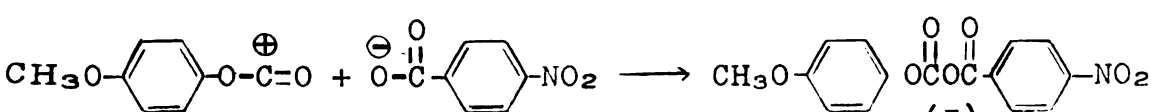
As would be expected, solvents of high dielectric constant favor this mode of reaction. An example is the decomposition of p-methoxy-p'-nitrobenzoyl peroxide studied by Leffler (18). In benzene, this peroxide decomposes at the same rate as benzoyl peroxide; in nitrobenzene, however, the decomposition proceeds eight times faster, the increase being attributed to an ionic mechanism operating in polar solvents. The postulated mechanism is shown in equations 13 to 15.



(13)



(14)



(15)

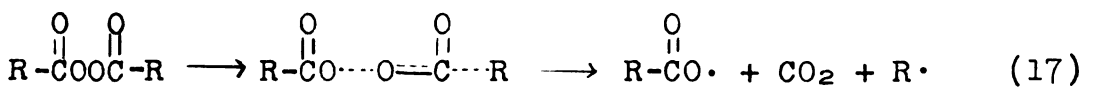
(I)

This was substantiated by isolation of (I) in 38% yield when thionyl chloride was used as the solvent. The peroxide is also susceptible to induced decomposition by acids. Whereas benzoyl peroxide is virtually insensitive to the presence of all but strong mineral acids, the rate of decomposition of p-methoxy-p'-nitrobenzoyl peroxide is proportional to the acidity constant of the acid. Similar

catalysis occurs with phenylacetyl peroxide, the spontaneous decomposition being autocatalytic because of the acid formed during the reaction (24).

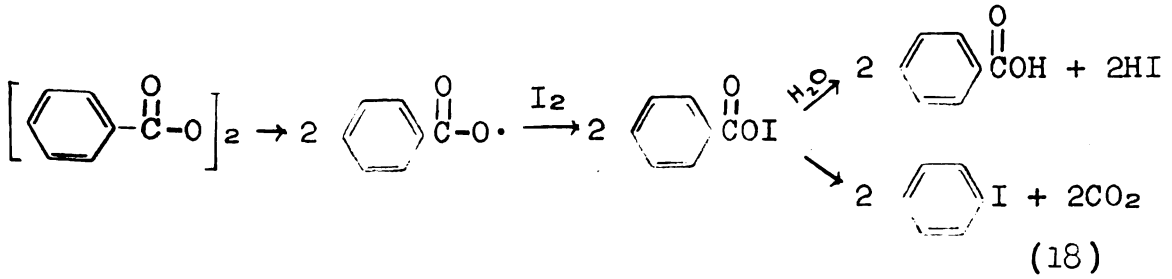
In the spontaneous homolytic cleavage of acyl peroxides in non-polar solvents, a major problem is the number of bonds broken in the rate-determining step. The decomposition can proceed by one- or by two-bond scission, as shown in equations 16 and 17.

(16)



(17)

Hammond and Soffer (21) demonstrated that the decomposition of benzoyl peroxide results in the formation of two benzoyloxy radicals which, in the presence of iodine and water, quantitatively produce benzoic acid. These results demonstrate the complete capture of the benzoyloxy radical as the hypoiodite; one concludes that initial reaction involves the rupture solely of the oxygen-oxygen bond (equation 18). The decomposition of acetyl peroxide in moist carbon tetrachloride containing iodine, however, produced principally methyl iodide,



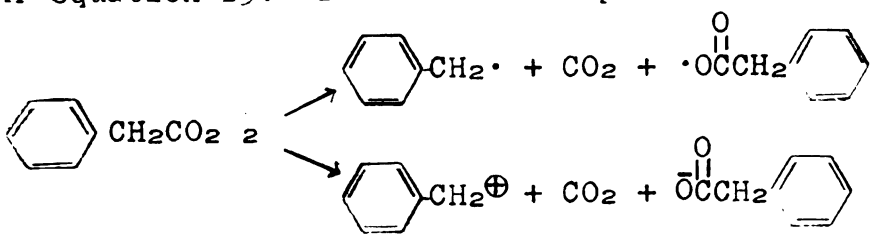
(18)

possibly indicating multiple scission (25). But Szwarc found that the activation energies of propionyl and butyryl peroxides are, within experimental error, the same as for acetyl peroxide and this is assumed to be the oxygen-oxygen bond energy in acyl peroxides (26). The absence of acetic acid in the reaction products is attributed to the extreme instability of the resulting acetoxy radical, the decomposition being strongly exothermic (25).

A very detailed study of the products of decomposition of delta-phenylvaleryl peroxide in carbon tetrachloride was made by DeTar and Weis (27). The major products were carbon dioxide (84%), acid (4%), ester (17.5%), 1,8-diphenyloctane (21.5%) and 1-chloro-4-phenylbutane (41%). They concluded that two acyloxy groups were initially formed and subsequent loss of carbon dioxide was very rapid. With the exception of 1-chloro-4-phenylbutane, which resulted from chlorine abstraction from the solvent by the δ-phenylbutyl radical, the products were formed entirely within the solvent cage.

Other cases show the carbon-carbon cleavage to be important, especially where the resulting radical is stable. Bartlett and Leffler (24) found that the decomposition of phenylacetyl peroxide proceeds more rapidly at 0° than benzoyl peroxide at 80° and attributed the increase to the formation of the benzyl radical in the rate-determining step. The decomposition scheme is shown

in equation 19. The relationship between the stability



(19)

of the resulting radical and the ease of decomposition has been demonstrated in the study of the decomposition of t-butyl peresters (2). This effect has also been noticed by Hart and Wyman (1), who found that the peroxides derived from cycloalkanecarboxylic acids decomposed at a rate which depended on the size of the ring. Furthermore, acyl peroxides which gave secondary alkyl radicals decomposed more rapidly than those which gave primary radicals (acyl peroxides derived from cycloalkaneacetic acids). Their results are listed in Table 1. The rate of decomposition and the heats of

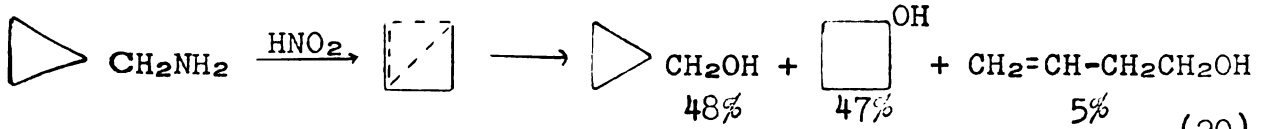
TABLE 1

THE DECOMPOSITION OF ACYL PEROXIDES, $(RCO_2)_2$, IN CARBON TETRACHLORIDE AT 70° (1)

R	Relative Rate	ΔH^* kcal/mole
Cyclopropyl (abs. rate const. = $4.8 \times 10^{-4} sec^{-1}$)	1	28.3
Cyclobutyl	16.8	26.6
Cyclopentyl	72.3	25.0
Cyclohexyl	137.2	26.1
Cycloheptyl	161	24.8
Cyclobutylcarbinyl	6.4	25.7
Cyclopentylcarbinyl	4.1	26.3
Cyclohexylcarbinyl	5.9	25.7

activation of the cycloalkanecarboxylyl peroxides decrease with increasing stability of the cycloalkyl radical. In the cycloalkaneacetyl peroxides, $((CH_2)_nCH\text{-}CH_2CO_2)_2$, however, an anamolous effect was obtained. Where n = 3, 4 or 5, the cyclobutyl, cyclopentyl or the cyclohexyl derivative, the peroxides decomposed at essentially the same rate; where n = 2, the cyclopropylcarbinyl system, extremely fast rates were obtained. It is this case which is of prime interest in this thesis.

There are many reactions in which rates are greatly accelerated by the presence of a cyclopropane ring. Under ionizing conditions, the cyclopropylcarbinyl system often undergoes rearrangement to allylcarbinyl and cyclobutyl derivatives (28) and these reactions proceed faster than the corresponding allyl compounds (29). In the diazotization of cyclopropylcarbinylamine, Roberts et. al. (30) showed that the cyclopropylcarbinyl cation rearranges extensively to produce a mixture of products (equation 20).



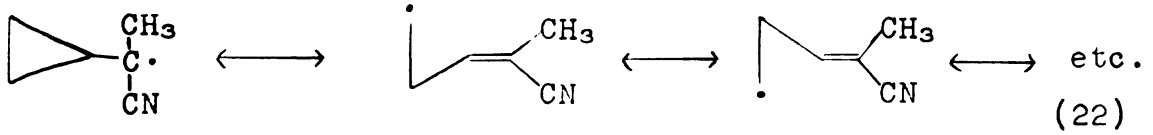
(20)

However, in reversible reactions, a multiplicity of products is not obtained; instead, the most stable derivative is produced, as in the treatment of cyclopropylcarbinol with Lucas reagent, where 4-chloro-1-butene is obtained exclusively.

The presence of such an equilibrium in free radical reactions has not been established, although several reactions involving the cyclopropylcarbinyl system have been reported. Overberger and Lebovitz (31), in a study of the decomposition of several alicyclic substituted azo-bisnitriles, found results similar to those reported by Hart and Wyman (1) on the decomposition of analogous acyl peroxides.

(21)

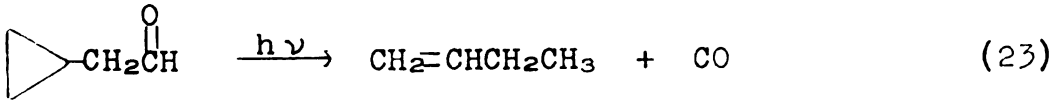
When R was cyclobutyl, cyclopentyl, cyclohexyl or isopropyl, the decomposition proceeded at approximately the same rate; when R was cyclopropyl, a 15-fold increase in rate was obtained. This acceleration was ascribed to resonance stabilization of the radical produced.



(22)

Unfortunately, products were not determined and the question of rearrangement was unanswered. However, in the photolytic chlorination of methylcyclopropane, much 4-chloro-1-butene was produced along with the expected cyclopropylcarbinyl chloride, indicating that the cyclopropylcarbinyl radical does rearrange considerably (32). During the course of the present work, Roberts and Schuster (33) noted that in the photolysis of cyclo-

propaneacetaldehyde, the cyclopropylcarbinyl radical rearranged to produce exclusively 1-butene.



(23)

Notably absent from both reactions was the cyclobutyl derivative, which indicates that an equilibrium similar to that in the ionic series does not exist.

The fast rate for the decomposition of cyclopropaneacetyl peroxide was approximately 400 times larger than the other cycloalkaneacetyl peroxides; the amount of ester produced also was abnormally high, accounting for 85% of the peroxide, as opposed to 30% for cyclohexaneacetyl peroxide. Later, Lau (34), who carefully washed the peroxide with aqueous sodium carbonate, stated that the rate of decomposition was less than that reported by Wyman, but still ten times faster than the homologous peroxides. These high ester yields and rapid rates indicate a potential ionic mode of decomposition, such as that for p-methoxy-p'-nitrobenzoyl peroxide and phenylacetyl peroxide, where high ester yields and rapid rates were obtained when the peroxides were decomposed in the presence of acids. Possibly, the cyclopropaneacetyl peroxide used for earlier kinetics and products experiments was contaminated with cyclopropaneacetic acid. It was therefore of interest to re-investigate the kinetics and products of decomposition.

The acyl peroxides used in this work were prepared by treating the corresponding acid chloride with sodium peroxide in anhydrous ether. Cyclopropaneacetyl and

$$2\ R\text{-}\overset{O}{\overset{\|}{C}}Cl\ +\ Na_2O_2 \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}\text{-}R\ +\ 2\ NaCl \qquad (24)$$

cyclohexaneacetyl peroxides, which were liquids at room temperature. were purified by crystallization from pentane at dry-ice temperatures; the other peroxides were crystallized from pentane or hexane. The purities of the peroxides, as determined by titration of liberated iodine, were 85-100% (see page 67).

The kinetics experiments were performed in dilute purified (35) carbon tetrachloride solutions, the concentration of peroxide ranging from 0.02-0.09 N. Most of the decompositions were followed by measuring the rate of disappearance of the 5.62μ peroxide band in the infrared. The remainder were followed by determining, using the method of Silbert and Swern (36), the amount of iodine liberated upon treatment of the peroxide solution with sodium iodide in acetic acid. When the spectrophotometric method was used, the rate constants were obtained from the slope of the equation listed on page 87; in the titrimetric procedures, the log of the titer was plotted directly against time, and the rate constants were calculated from the slope of the resulting line.

Cyclopropaneacetyl peroxide was decomposed between 44°

and 56°; as can be seen in Table 2, the rate doubles for approximately every 6° increase in temperature. For comparison, the data for cyclohexaneacetyl peroxide are also included; the increase in rate with increasing temperature is larger for the former peroxide than for the latter. The rate constants, measured to about 50%

TABLE 2

THE EFFECT OF TEMPERATURE UPON THE DECOMPOSITION OF CYCLOALKANEACETYL PEROXIDES

Peroxide	Temp.°	Rate Constant $\times 10^5$, $sec.^{-1}$	Data From Table
Cyclopropaneacetyl	44.0	5.30	14
	44.0	5.07	15
	49.8	11.1	16
	50.8	12.4	17
	50.8	13.0	18
	50.8	12.3	19
	56.7	25.8	20
	56.7	25.7	21
Cyclohexaneacetyl	44.4	0.308	36
	64.3	1.14	37
	71.8	2.95	39

decomposition of the peroxide and extrapolated to 25°, were a factor of 10^3 smaller than those reported by Hart and Wyman, and slightly larger than those of Lau, but the fact that cyclopropaneacetyl peroxide decomposes appreciably faster than cyclohexaneacetyl peroxide is

confirmed. The validity of these results is substantiated by the reproducibility of the rate constant in a number of runs from various batches of peroxide. To ensure that systematic errors were not involved using the infrared technique, titrimetric analysis was occasionally employed. These results are listed in Table 3. The data are in good

TABLE 3

RATE CONSTANTS FOR THE DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE DETERMINED BY INFRARED AND TITRIMETRIC TECHNIQUES

Run	Analytical Method	Temp.°	Rate Constant x 10^5, $sec.^{-1}$	Data From Table
1.	Iodometric	44.5	5.07	27
2.	Iodometric	44.5	4.93	26
	Infrared	44.5	5.03	26
3.	Infrared	44.0	5.30	14

agreement with each other; this is especially evident when both methods were run concurrently. Because the rate constants were lower than previously claimed, it was necessary to recalculate the energetics of the reaction. The enthalpy of activation was 24.3 kcal./mole, or approximately 2 kcal./mole less than that reported for the other cycloalkaneacetyl peroxides. The activation entropy was 3.1 cal./deg. mole. The enthalpy of activation obtained from the meager decomposition data for cyclohexaneacetyl peroxide (26 kcal./mole) was in good agreement with the 25.7 kcal./mole reported previously (1).

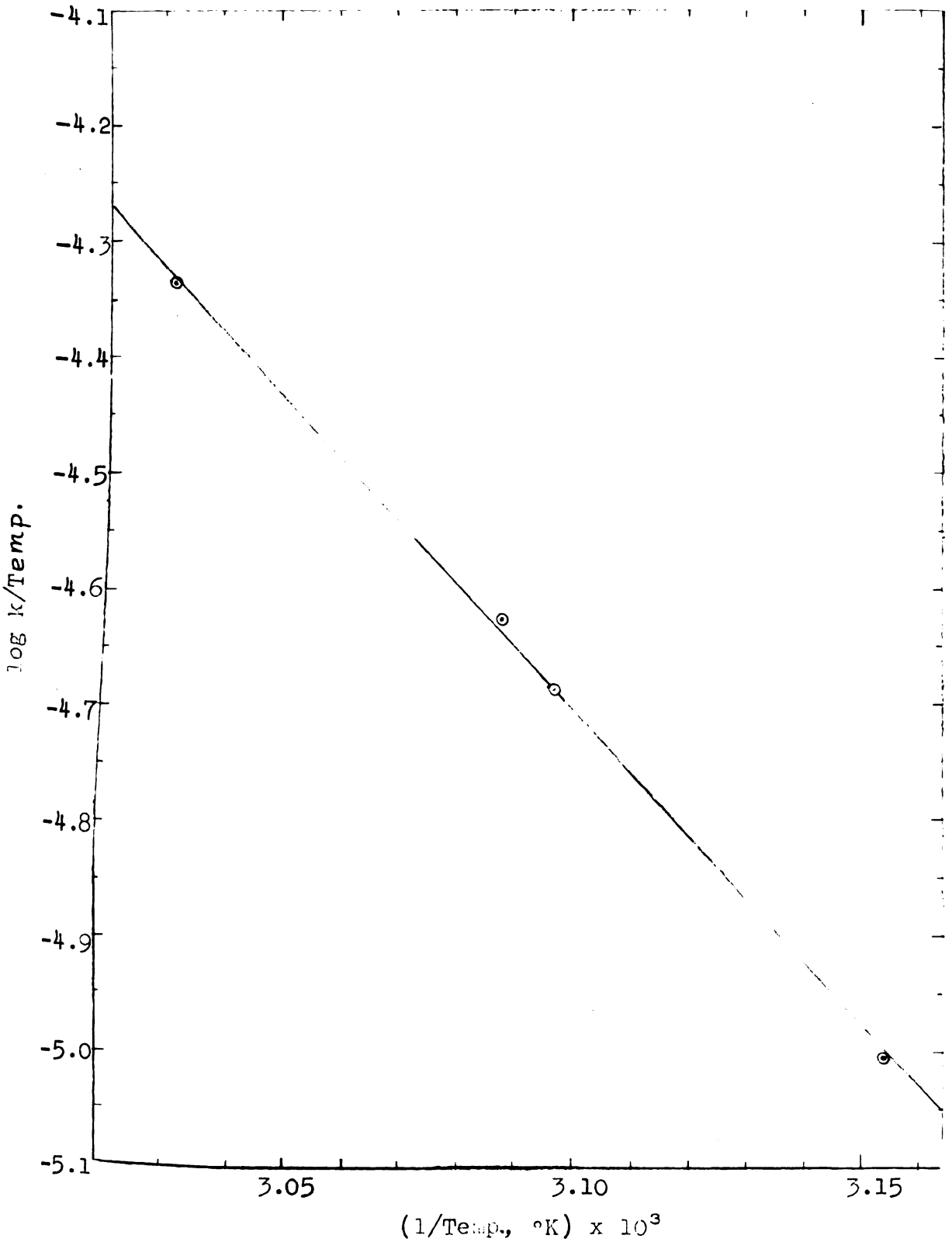


Figure 1. Arrhenius Plot for the Decomposition of Cyclopropanceacetyl Peroxide.

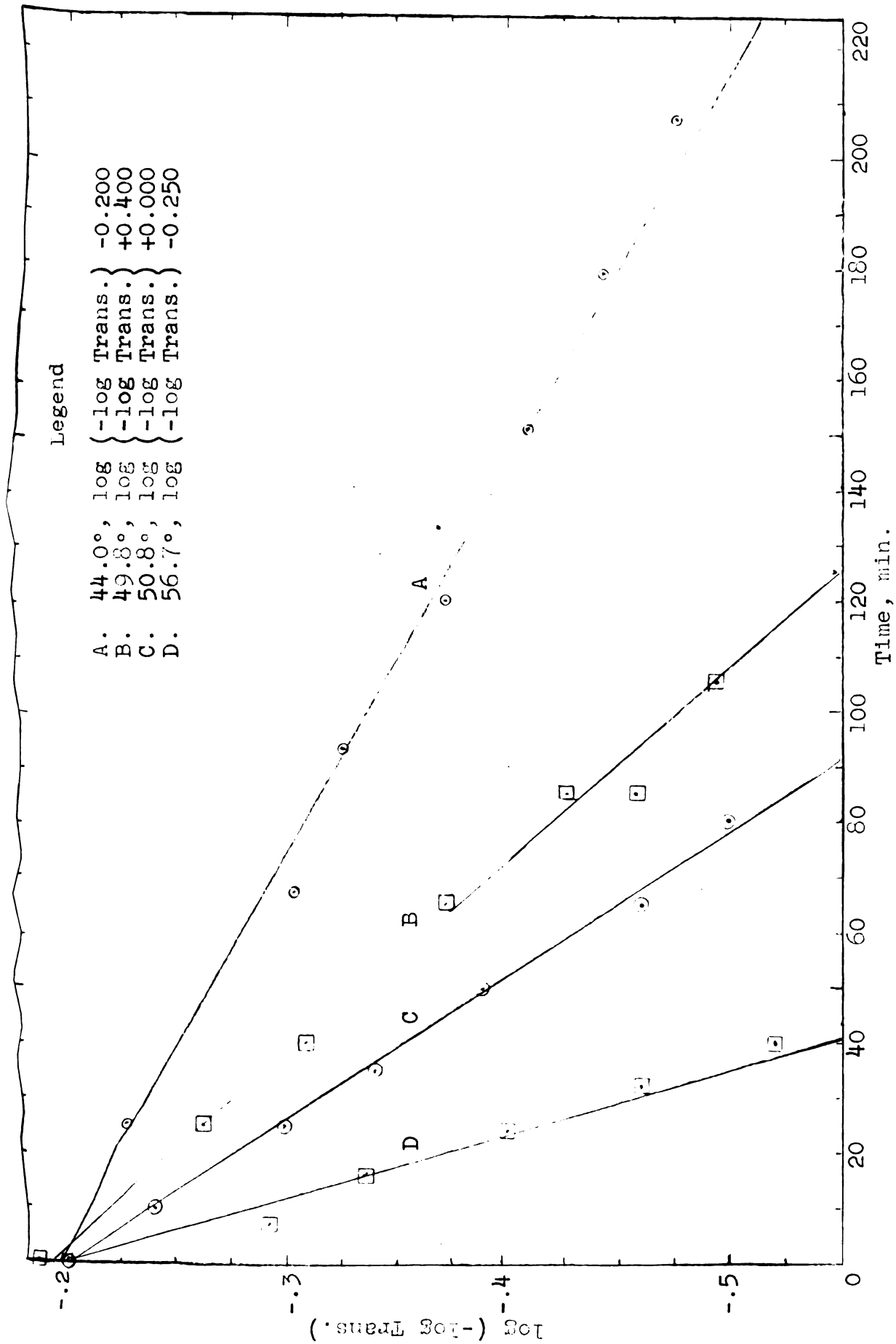


Figure 2. First-order Rate Curves for the Decomposition of Cyclopropaneacetyl Peroxide at Various Temperatures.

To determine the extent to which induced decomposition affected the rate constants, the decomposition was studied in the presence of iodine, a radical scavenger. The results in Table 4 show that the

TABLE 4

EFFECT OF IODINE ON THE DECOMPOSITION RATE OF CYCLOALKANEACETYL PEROXIDES

Peroxide	Temp. °C	Normality Peroxide	Normality Iodine	Rate Constant x 10^5, $sec.^{-1}$	Data From Table
Cyclopropane-acetyl	56.5	0.09	....	2.78	22
	56.5	0.09	0.07	2.94	23
	56.5	0.05	0.05	2.80	24
Cyclohexane-acetyl	64.3	0.06	....	1.14	37
	64.3	0.06	0.18	1.23	38

addition of iodine does not decrease the rate, as would be expected if there were induced decomposition; indeed, a slight increase in the rate constant was observed. Since a slight increase was also obtained with cyclohexaneacetyl peroxide, the possibility remains that interactions of the carbonyl group with the iodine caused an increase in the transmission at the wave-length used (5.62μ); iodine alone in carbon tetrachloride does not absorb in that region. Additional evidence for the absence of induced decomposition in the concentration range used (0.02-0.09 N) is the invariability of the rate constant with the initial peroxide concentration (see

Table 5). At 0.18 N, the rate constant was appreciably

TABLE 5

THE EFFECT OF CONCENTRATION UPON THE RATE OF DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

Temp.°	Normality of Peroxide	Rate Constant x 10^5, $sec.^{-1}$	Data From Table
49.8	0.018	11.1	16
50.8	0.046	12.4	17
50.8	0.055	13.0	18
50.8	0.092	12.3	19
44.5	0.06	5.30	14
44.5	0.186	(a)	29

(a). Initially very rapid, but approaches 5 x 10^{-5} $sec.^{-1}$ as concentration approaches 0.09 N.

larger, presumably because of induced decomposition. As the reaction proceeded, however, the rate constant gradually approached those obtained at lower concentrations. It can be stated with certainty that the decomposition, at the concentrations used, is free of induced decomposition.

The decomposition of cyclopropaneacetyl peroxide then is indeed faster than the higher members of the series, and these rapid rates are a reflection of the lower activation energy. If the reaction is free radical, and not ionic, there must be some particular stability associated with the cyclopropylcarbinyl radical. A distinction between these mechanisms could be made by determining whether the peroxide initiates the

polymerization of styrene. Two equal portions of styrene were placed in separate flasks, one containing cyclopropaneacetyl peroxide; the flasks were heated to 50-70° and cooled occasionally to check the viscosity and clarity of the reaction mixtures. The styrene containing the peroxide was somewhat more viscous and opaque throughout the observation period. The ability of cyclopropaneacetyl peroxide to initiate polymerization, though sluggish, shows that the decomposition proceeds at least in part with the production of radicals.

The possibility still remains that the decomposition also proceeds ionically, as in the case of phenylacetyl peroxide, which decomposes simultaneously by both mechanisms (24). Acid catalysis may have been the cause of earlier erratic results with cyclopropaneacetyl peroxide: if any unreacted acid chloride remained in the preparation of the peroxide and were incompletely removed upon hydrolysis, erratic results could have been obtained, for peroxides capable of decomposing by ionic mechanisms are sensitive to the presence of acid (18). Alternatively, the reaction may have been autocatalyzed by the cyclopropaneacetic acid formed during the decomposition. To explore this possibility, the decomposition was carried out in the presence of several acids of varying acidity.

As is shown in Table 6, the weak acids acetic and trimethylacetic had little effect upon the rate of decomposition of cyclopropaneacetyl peroxide. Although

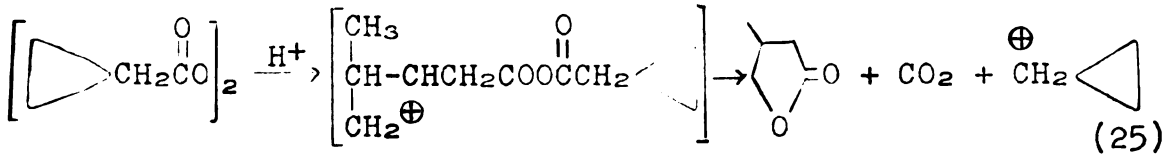
TABLE 6

THE EFFECT OF ACIDS UPON THE DECOMPOSITION OF CYCLOALKANEACETYL PEROXIDES, $(RCH_2CO_2)_2$

R	Temp.°	Normality of Peroxide	Normality of Acid	Rate Constant x 10^5, $sec.^{-1}$	Data From Table
Cyclopropyl	44.5	0.06	.....	5.07	15
	44.5	0.042	Acetic, 0.014	4.65	30
	44.5	0.048	Trimethylacetic 0.043	4.64	31
	44.5	0.061	Trichloroacetic 0.061	65-80 (a)	33
	44.5	0.061	Trichloroacetic 0.030	33 (a)	34
	44.5	0.061	Trichloroacetic 0.015	13 (a)	35
Cyclohexyl	64	0.06	.....	1.14	37
	64	0.06	Trichloroacetic 0.068	4.47	41

(a). Followed iodometrically. Points were erratic. The rate constant was approximated by initial consumption of thiosulfate.

cyclopropaneacetic acid was not studied, a comparable effect would be likely. Catalysis by carboxylic acids does not seem to be the cause of the erratic rates reported. The stronger acid, trichloroacetic acid, however, did accelerate the rate, the increase being proportional to the initial concentration of acid. For equivalent amounts of peroxide and trichloroacetic acid, the increase was a factor of 12-15. The rate effect was considerably larger than that obtained with cyclohexaneacetyl peroxide. Since the decomposition of benzoyl peroxide is unaffected by all but the strong mineral acids (18), the increase in rate for cyclopropaneacetyl peroxide could be the result of ring protonation. If ring protonation were the cause of rate enhancement, β-methyl-γ-butyrolactone would be the expected decomposition product (equation 25). Absence of the lactone band in the

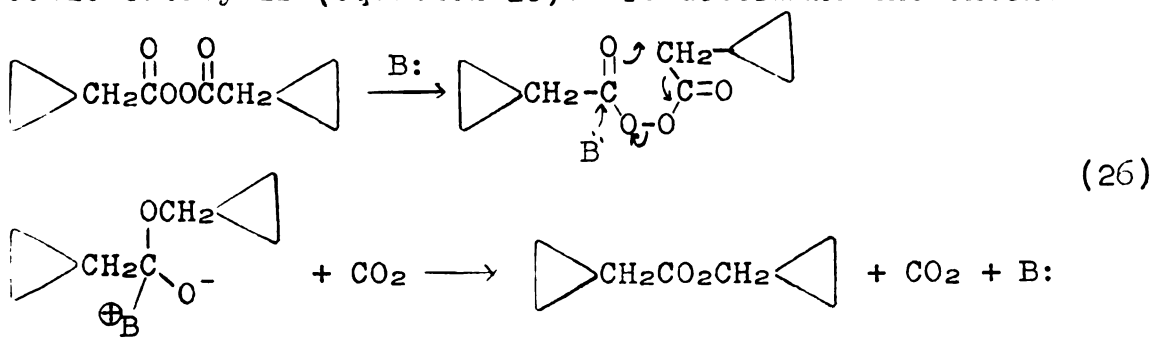


(25)

infrared is evidence that ring protonation is not the cause of the extremely rapid rates. The products are, however, appreciably different from those obtained from the spontaneous decomposition, especially in the formation of esters of trichloroacetic acid. This may be due to an ionic mechanism and will be discussed later.

Since the presence of acid is not the cause of the high rates for the decomposition of cyclopropaneacetyl

peroxide, the possibility of catalysis by dissolved base, which would result from the incomplete removal of the sodium carbonate or sodium peroxide, was examined in an effort to reconcile these results with those previously reported. Because of the polarization of the cyclopropylcarbinyl group, a reasonable mechanism can be drawn for basic catalysis (equation 26). To determine the extent



(26)

of this, the decomposition was run after washing the peroxide solution in carbon tetrachloride with 10% aqueous sodium carbonate and in the presence of pyridine. The results are listed in Table 7. For comparison cyclohexaneacetyl peroxide also was decomposed in the presence of pyridine.

The results show that the presence of neither inorganic nor organic base inexplicably altered the rate constant. Washing of the peroxide solution with aqueous sodium carbonate before had no effect on the decomposition rate. Although pyridine accelerated the rate, the increase was comparable to that resulting from the treatment of cyclohexaneacetyl peroxide with pyridine. Tertiary amines are known to react with acyl peroxides (37) as is illustrated in equation 27. The use of pyridine has also

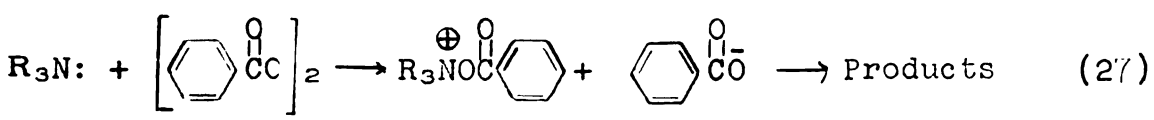
TABLE 7

THE EFFECT OF BASE UPON THE DECOMPOSITION OF CYCLOALKANEACETYL PEROXIDES, $(RCH_2CO_2)_2$

R	Temp°	Normality Peroxide	Normality Pyridine	Rate Constant x 10^5, $sec.^{-1}$	Data From Table
Cyclopropyl	44.5	0.06	....	5.07	15
	44.5	0.05	0.03	6.86	32
	44.5	0.06	(a)	5.30	28
Cyclohexyl	71.8	0.06	....	2.93	39
	71.8	0.06	0.056	4.83	40

(a). After washing the peroxide solution with sodium carbonate and drying.

been reported; although the rate of reaction is increased,



(27)

the nature of the products is unknown (38). It would be expected that if cyclopropaneacetyl peroxide were susceptible to basic catalysis, the effect would be considerably larger than obtained. The relative ease of decomposition of this peroxide then cannot be attributed to basic catalysis.

The cause of earlier high rates is not clear. The work reported in this thesis shows that the decomposition is catalyzed neither by carboxylic acids initially present or formed during the reaction nor by bases. They may have been due to other impurities, such as unhydrolyzed acid

chloride, which, on occasion, was present in peroxides used in this work and gave rapid rates.

Earlier product studies showed that ester (85%) and carbon dioxide (85%) were the major products; alkyl halides resulting from the reaction of an alkyl radical with the solvent were not found (1). The absence of alkyl chloride indicates that the cyclopropylcarbinyl radical, if formed, reacts in other ways than by abstraction of a chloride atom from the carbon tetrachloride. Since the decomposition rates reported here are substantially lower than those reported by Wyman, it was important to verify the product composition, with emphasis on the ester produced.

The major products of the decomposition of cyclopropaneacetyl peroxide in carbon tetrachloride were carbon dioxide and an ester, probably cyclopropylcarbinyl cyclopropaneacetate; in addition, there was a small amount of cyclopropaneacetic acid. The average results from several experiments are shown in Table 8. Carbon dioxide was determined gravimetrically; the ester and the acid were determined spectrophotometrically using respectively the 5.75μ and the 5.85μ bands in the infrared. Together, these accounted for 97.5% of the initial carbonyl group, while the acid and the ester contained 59.5% of the alkyl group initially present in the peroxide. Approximately 10 ml. of carbon tetrachloride solution was distilled directly from the decomposed peroxide solution; 1-butene,

TABLE 8

PRODUCTS OF DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE AFTER THREE HOURS AT 78° (2.45 mmoles of peroxide in 50 ml. of carbon tetrachloride)

Product	mmoles.	mmoles/mmole peroxide
Carbon dioxide	3.24	1.32
Ester (ϵ = 489 l/mole-cm.)	1.37	.56
Acid (ϵ = 539 l/mole-cm.)	.17	.07
Alkyl chloride (a)	....	.17

(a). It is not known whether this is actually an alkyl chloride or a dialkyl.

if formed, would appear in this fraction. Because of the low concentration and the absence of an appreciable olefinic peak in the infrared, the presence of small amounts of pentane, which was used in the preparation of the peroxide, could not be excluded. The remainder of the carbon tetrachloride solution was distilled under reduced pressure to remove higher boiling materials; redistillation of most of the solvent (75 ml.) through a packed column afforded fractions whose infrared spectra possessed insignificant carbon-hydrogen absorption peaks. The spectrum of the remaining carbon tetrachloride had a strong carbon-hydrogen peak, which, after correction for a small amount of ester present, accounted for 8.5% of the initial peroxide; whether an alkyl chloride or a dialkyl was present was not determined. The remainder of the cyclopropaneacetyl peroxide was probably tar, which, along

with hexachloroethane, was undetermined.

The results verify the higher ester and lower carbon dioxide yields than expected for the decomposition of acyl peroxides, although a considerable difference still was obtained from the results of Hart and Wyman (85% vs. 56% for ester and 85% vs. 66% for carbon dioxide). For comparison, the yields of ester, carbon dioxide and alkyl chloride for peroxides derived from other alicyclic acids are shown in Table 9. Yields of 75-80% of alkyl chloride

TABLE 9 •

PRODUCTS FROM THE DECOMPOSITION OF CERTAIN ACYL PEROXIDES IN CARBON TETRACHLORIDE

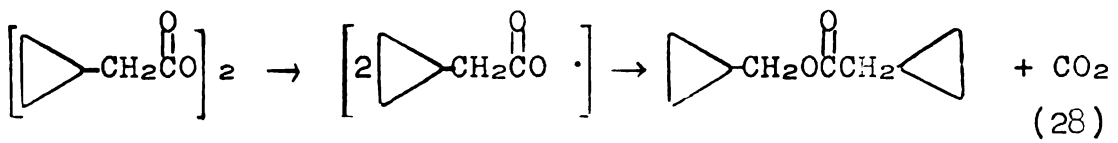
Peroxide	Temp°	Ester [a]	Carbon Dioxide [a]	Alkyl Chloride [a]
Cyclopropaneacetyl [b]	78	0.56	1.32	0.17
Cyclopropaneformyl [c]	70	0.16	1.61	1.33
Cyclohexaneformyl [c]	70	0.23	1.87	1.53
Cyclohexaneacetyl [c]	70	0.30	1.77	1.32
Benzoyl [c]	70	0.26	1.72	1.27

(a). Moles produced per mole of peroxide decomposed.
(b). This work.
(c). Ref. 1.

were obtained for the other peroxides, whereas in the decomposition of cyclopropaneacetyl peroxide, the alkyl chloride, if formed at all, was a minor product.

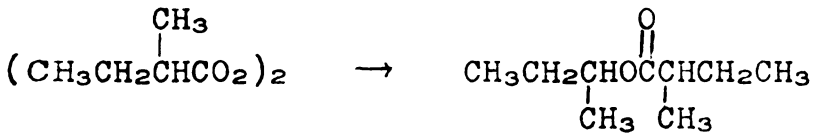
The ester obtained is probably cyclopropylcarbinyl cyclopropaneacetate, since the infrared spectrum was

similar to that of authentic cyclopropylcarbinyl cyclopropaneacetate and passage of the higher boiling materials from the decomposition through a vapor-phase chromatograph showed the existence of almost entirely one product. The production of ester is a geminate reaction and is probably explained by equation 28.



(28)

The immediate recombination of the radicals within the solvent cage has been demonstrated by Kharasch and co-workers (39), who obtained from optically active α-methylbutyryl peroxide an ester in which both the acid and the alcohol portions retained their optical activity.

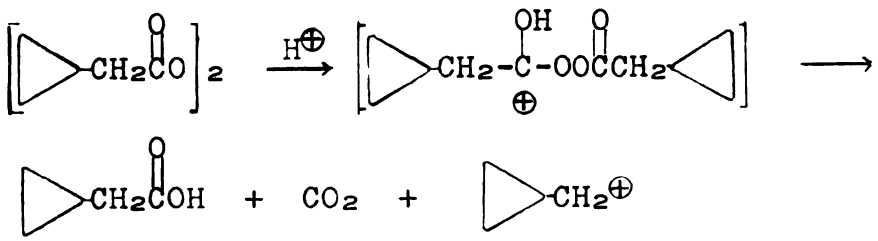


(29)

The larger quantity of ester produced from the decomposition of cyclopropaneacetyl peroxide shows that the reaction between the alkyl and the acyloxy radicals occurs rapidly, before reaction with the solvent can occur. The small amount of acid present could result from abstraction of a hydrogen atom within the solvent cage (27) or from reaction of the acyloxy radical with a small amount of water present (40).

The question of acceleration of the rate by trichloroacetic acid being due to attack at the ring rather than

carbonyl group demanded a study of the decomposition products under these conditions. Since cyclopropane derivatives are sensitive to ring opening reactions by strong acids (18), the decomposition might be expected to proceed either by proton attack at the ring or the carbonyl group. The products obtained from the decomposition



(30)

varied considerably from those of the spontaneous decomposition; along with less carbon dioxide, the type and quantity of ester were altered. The products are listed in Table 10. The mechanism chosen must explain the

TABLE 10

PRODUCTS OF DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE IN THE PRESENCE OF TRICHLOROACETIC ACID, 76°, 3 HOURS (2.5 mmoles of peroxide and 5.00 mmoles of trichloroacetic acid in 40 ml. of carbon tetrachloride)

Product	Mmoles	Mmoles per mmole peroxide
Carbon dioxide	3.06	1.22 (a)
Ester (5.76μ, ϵ = 489 l/mole-cm.)	0.74	0.30
Ester (5.67μ, ϵ = 525 l/mole-cm.)	1.44	0.58
Acid not determined		

(a). Average of two runs.

decrease in the carbon dioxide and the ester (5.76μ) produced, as well as the appearance of a material absorbing at 5.67μ.

Formation of β-methyl-γ-butyrolactone was excluded, since the action of concentrated sulfuric acid on cyclopropaneacetic acid produced a substance which absorbed at 5.63μ, the same absorption peak possessed by γ-butyrolactone. The presence of the 5.67μ band was attributed to an ester of trichloroacetic acid, since cyclopropylcarbinyl trichloroacetate possessed the same peak. The reaction then must be described by equation 30, with the cyclopropylcarbinyl cation resulting as a trichloroacetate ester. The extent of rearrangement was not determined. Such a mechanism would also explain a decrease in the yield of carbon dioxide. The ester absorbing at 5.76μ was probably a cyclopropaneacetate; the nature of the alkyl group was not determined, but the cyclopropylcarbinyl derivative could result from the concurrent spontaneous reaction. The amount of cyclopropaneacetic acid is expected to be at least equivalent to the trichloroacetate ester formed. Assuming this value, 90% of the initial carboxyl and 70% of the initial alkyl radicals would be accounted for.

THE DECOMPOSITION OF OTHER ACYL PEROXIDES.

With a change in solvents, a change occurs both in the product composition and in the rates of decomposition

of acyl peroxides. For example, the amount of carbon dioxide evolved from the decomposition of benzoyl peroxide increases in the order olefins < paraffins < aromatics < carbon tetrachloride. Factors influencing this change are the relative reactivity of the solvent with the radical formed and the extent of induced decomposition, which becomes important at concentrations used to determine products (41).

The decomposition of trans-4-t-butylcyclohexanecarboxylyl peroxide in tetrabromoethane produced a quantitative yield of trans-4-t-butylcyclohexyl trans-4-t-butylcyclohexanecarboxylate (42), whereas in carbon tetrachloride only 47% of presumably the same ester was formed. The decrease in yield might be the result of higher temperatures and induced decomposition rather than increased reactivity with the solvent. Since the radical transfer constants of tetrabromoethane was approximated to be slightly larger than that of carbon tetrachloride at the same temperature, the effect would be attributed to the difference in reaction temperature (78° for the decomposition in carbon tetrachloride vs. 50.7° for that in tetrabromoethane (42)), with induced decomposition by the trichloromethyl radical playing the greater role. Hence, the yield of ester would be smaller.

In the decomposition of cyclopropanecarboxylyl peroxide in carbon tetrachloride, a highly reactive solvent, cyclopropyl chloride was the major product (1).

Decompositions performed in the presence of iodine showed that most of the cyclopropyl radicals exist outside of the solvent cage. By using a less reactive solvent, coupling of the radicals could conceivably be forced, presenting a new method for the synthesis of dicyclopropyl.

Cyclopropanecarboxylyl peroxide was decomposed in chlorobenzene and in t-butylbenzene, solvents with low radical transfer constants (43). In the decomposition in t-butylbenzene, acid (8%), ester (37%) and presumably carbon dioxide appeared as the major products, with no dicyclopropyl being detected. Similar results were obtained in chlorobenzene as the solvent. In spite of the low radical transfer constants, the solvents were too reactive to permit the coupling of the alkyl radicals, the major reaction probably involving attack at the benzene ring.

C. The Decomposition of t-Butyl Peresters of Some Alicyclic Acids.

In contrast to acyl peroxides, relatively little work had been done on the decomposition of t-butyl peresters, R-C(=O)-O-Ot-Bu, until recently. Their decompositions parallel those of the corresponding acyl peroxides but proceed more slowly.

The most extensive work on the mechanism of decomposition was conducted by Bartlett and co-workers (2, 3, 4). Considerable evidence was presented by Bartlett and Hiatt (2) for the importance of carbon-carbon stretching in the decomposition transition state. Their results are listed in Table 11. With increasing stability of the resulting radical, there is a decrease in the heat of activation and the stability of the perester for a given series. The peracetate and the perbenzoate are particularly resistant to decomposition because they would produce the poorly stabilized methyl and phenyl radicals respectively. A concerted decomposition was further demonstrated by Bartlett and Rüchhardt (3) in the decomposition or substituted t-butyl phenylperacetates, where the rate was decreased by electronegative groups on the benzene ring and increased by electropositive ones.

These results helped put the concept of a concerted decomposition of acyl peroxides on a firmer basis. However, a work relating the two decompositions has not been reported. As was mentioned previously (p. 12), a

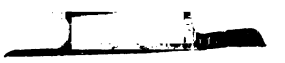


TABLE 11

DECOMPOSITION OF t-BUTYL PERESTERS, RCO_3t-Bu, IN CHLOROBENZENE (2)

R	Half-life Min., 60°	ΔH^* kcal./mole	ΔS^* cal./deg. mole
(Di-t-butyl peroxide)	10^7	37.8	13.8
CH_3	5×10^5	38	17
C_6H_5	3×10^4	33.5	7.8
(Benzoyl peroxide)	6000	32.7	13.3
$C_6H_5CH_2$	1700	28.7	3.9
Cl_3C	970	30.1	8.9
$(CH_3)_3C$	300	30.6	13
$C_6H_5CH{=}CHCH_2$	100	23.5	-5.9
$(C_6H_5)_2CH$	26	24.3	-1.0
$C_6H_5(CH_3)_2C$	12	26.1	5.8
$(C_6H_5)_2CH_3C$	6	24.7	3.3
$C_6H_5(CH_2{=}CH)CH$	4	23.0	-1.1

difference of 2.5 kcal./mole for the heats of activation and a factor of 137 for the rates of decomposition of cyclopropanecarboxylyl and cyclohexanecarboxylyl peroxides were obtained. These were attributed to a decrease in stability of the cyclopropyl radical relative to the cyclohexyl radical and to some carbon-carbon stretching occurring in the rate-determining step. Bartlett (44) had reported that the decomposition of t-butyl cyclohexanepercarboxylate proceeded at 100° in chlorobenzene a factor of 120 times faster than the t-butyl peracetate.

with an activation enthalpy of 31.3 kcal./mole and an activation entropy of 8.6 e.u. It was then a matter of interest to compare the relative sensitivity of the peroxide and perester decompositions to the same change in the structure of the alkyl group.

The t-butyl peresters of cyclopropanecarboxylic and cyclohexanecarboxylic acids were prepared by the reaction of t-butyl hydroperoxide in a pyridine-ether solution with the appropriate acid chloride and were purified by passing through a chromatographic column containing Florisil, using pentane as the eluent. Removal of the pentane afforded t-butyl cyclohexanepercarboxylate of 77% purity and t-butyl cyclopropanepercarboxylate of 76% purity. Portions of a solution of the peroxide in carbon tetrachloride were sealed in ampoules and placed in a constant temperature bath. Individual samples were removed periodically and frozen in dry-ice until use. Transmissions of the melted samples at 5.62μ were determined and the rate constants and heats of activation determined in a manner similar to those of the acyl peroxides (p. 87). The rate data and the energetics for the decomposition are shown in Tables 12 and 13.

From the work of Bartlett and Hiatt and of Hart and Wyman, these results are to be expected. A comparison of the peresters with the corresponding acyl peroxides in carbon tetrachloride is shown in Table 13. The t-butyl peresters are definitely more stable than the

TABLE 12

THE DECOMPOSITION OF t-BUTYL CYCLOALKANEPERCARBOXYLATE IN CARBON TETRACHLORIDE

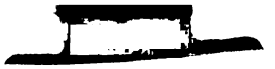
Temp.°	Cyclopropane k x 10^5, $sec.^{-1}$	Data From Table	Temp.°	Cyclohexane k x 10^5, $sec.^{-1}$	Data From Table
110	6.86	48	90	2.35	42
110	6.68	49	90	2.33	43
120	20.7	50	100	9.48	44
120	20.2	51	100	9.28	45
129	48.3	52	110	20.0	46
129	49.8	53	110	22.0	47

TABLE 13

COMPARISON OF THE DECOMPOSITION OF t-BUTYL PERESTERS AND ACYL PEROXIDES

	Half-life sec., 70°	ΔH^* $kcal.mole^{-1}$	ΔS^*, cal. $deg.^{-1} mole^{-1}$
Cyclopropanecarboxylyl Peroxide (a)	1.41 x 10^5	28.3	-5.7
Cyclohexanecarboxylyl Peroxide (a)	1.03 x 10^3	26.1	-3.1
t-Butyl Cyclopropane-percarboxylate	1.2 x 10^6 (b)	30.7	2.1
t-Butyl Cyclohexane-percarboxylate	2.4 x 10^5 (b)	28.7	-0.6

(a). Ref. 40.
(b). Extrapolated from higher temperatures.



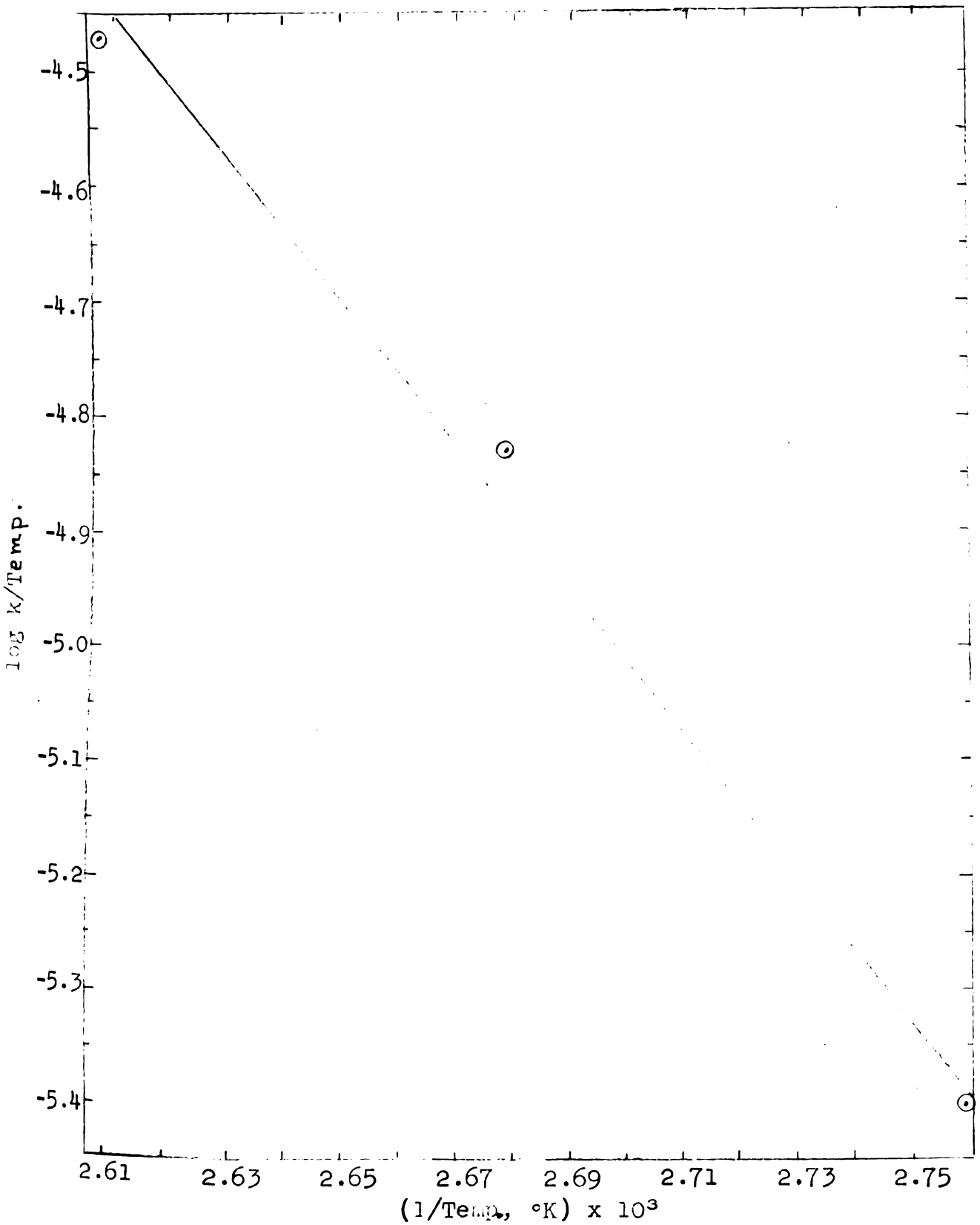


Figure 3. Arrhenius Plot for the Decomposition of t-Butyl Cyclohexanepercarboxylate.

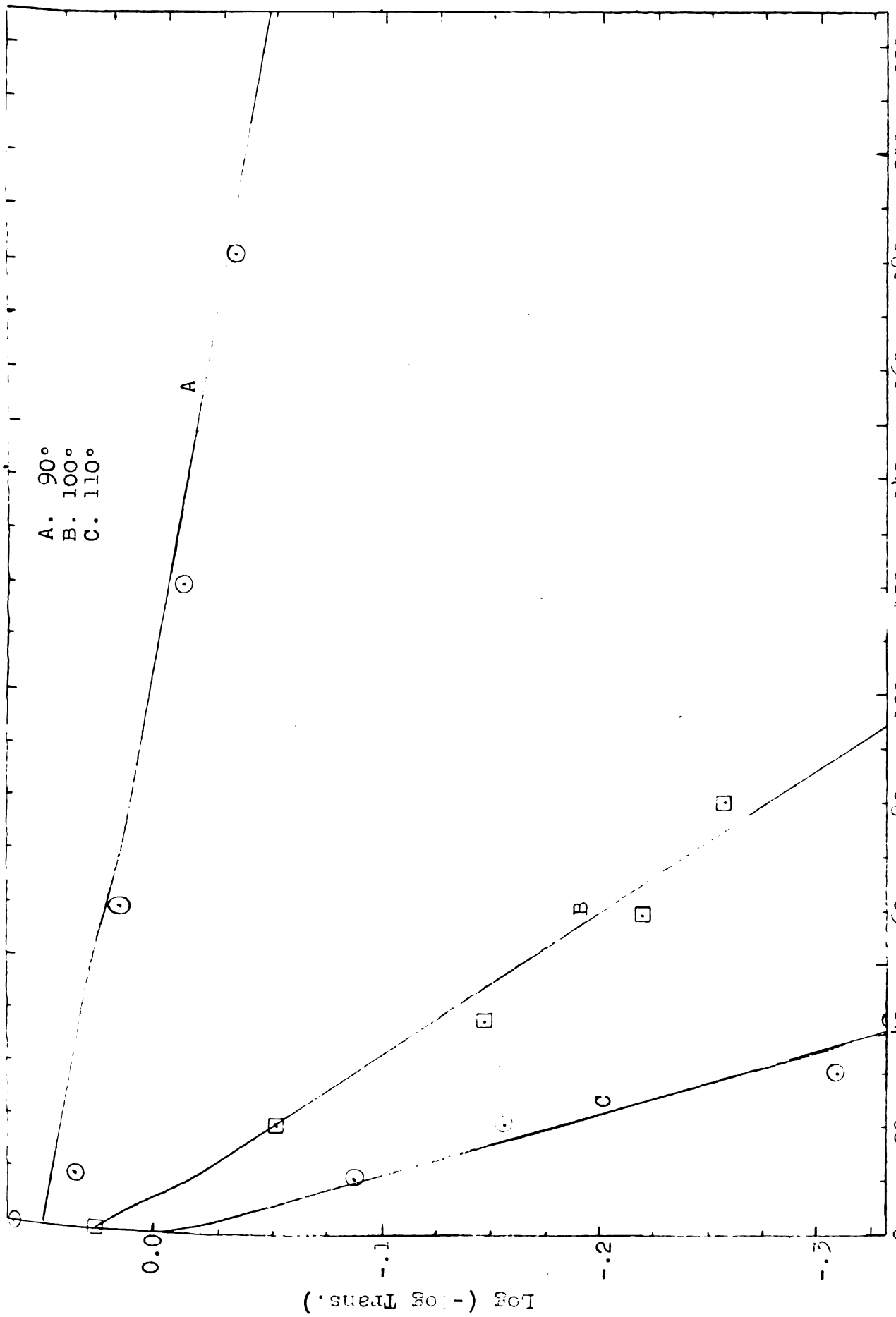


Figure 4. First-order Rate Curves for the Decomposition of t-Butyl Cyclohexaneperoxycarboxylate at Various Temperatures.

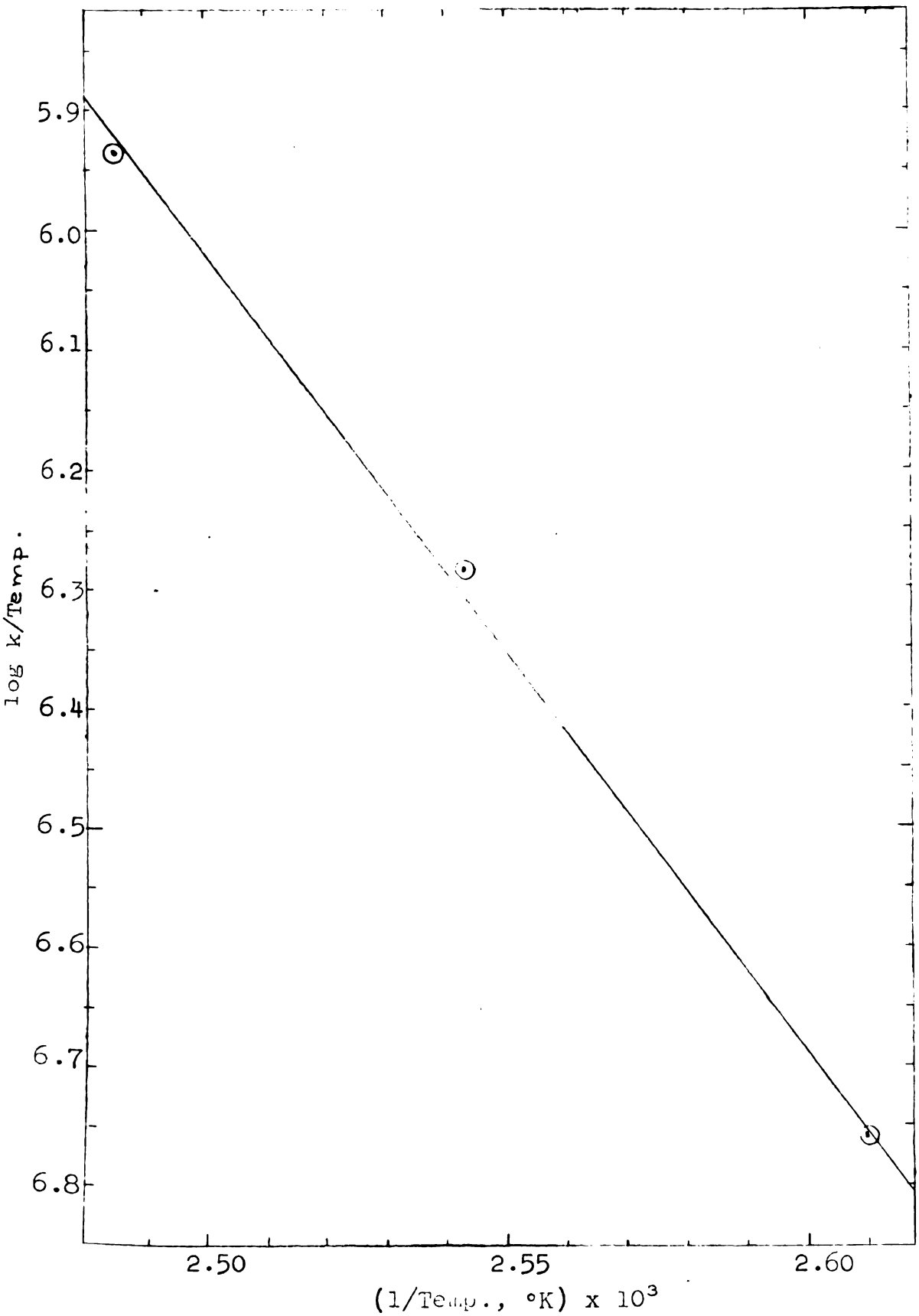


Figure 5. Arrhenius Plot for the Decomposition of t-Butyl Cyclopropanepercarboxylate.

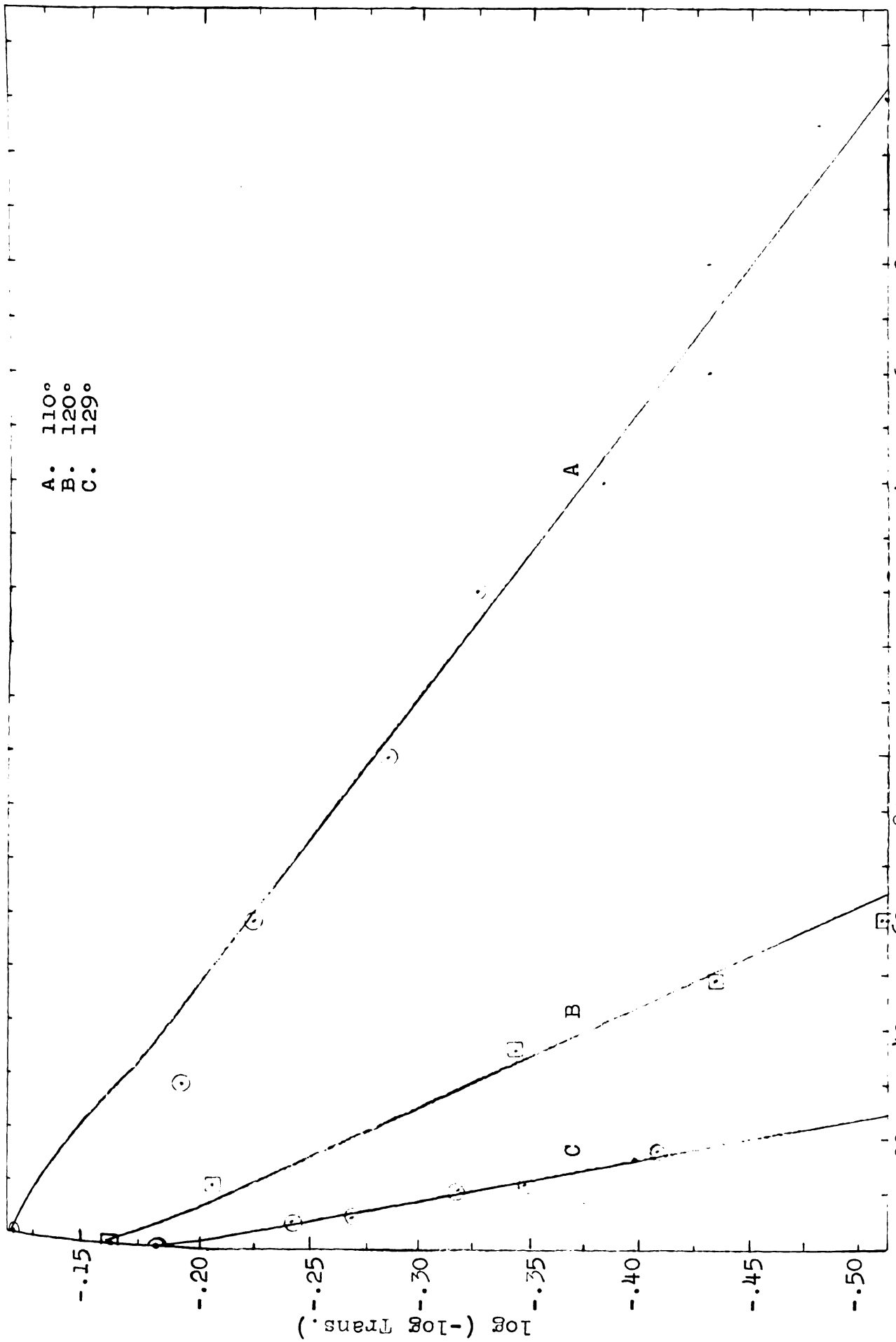


Figure 6. First-order Rate Curves for the Decomposition of t-Butyl Cyclopropanepercarboxylate at Various Temperatures.

corresponding acyl peroxides. At 70°, t-butyl cyclopropanepercarboxylate would decompose at about one-eighth the rate for cyclopropanecarboxylyl peroxide; the effect is even greater for the cyclohexane derivative. Although the enthalpy of activation of t-butyl cyclopropanepercarboxylate is 2 kcal./mole larger than that for t-butyl cyclohexanepercarboxylate, the inversion of entropies partially nullifies the expected differences in decomposition rates.

That the differences in the decomposition rates of t-butyl peresters is not the same as for the corresponding acyl peroxides is not extraordinary. Whereas benzoyl peroxide and acetyl peroxide decompose at essentially the same rate and, within experimental error, possess the same energy of activation (45), t-butyl peracetate decomposes approximately 16 times slower than t-butyl perbenzoate (Table 10). Also, phenylacetyl peroxide decomposes 80 times faster at 0° than benzoyl peroxide at 80°, but the difference for the corresponding t-butyl peresters at 60° is only a factor of four. Although the general effects operative in acyl peroxide decompositions are present in the decomposition of t-butyl peresters, their magnitudes are not comparable.

The decrease of the heat of activation in going from a three- to a six-membered ring, in conjunction with the work of Hart and Wyman (1), is evidence that there is some carbon-carbon stretching in the transition state of the

decomposition of t-butyl peresters. The explanation of I-strain they offer for the decomposition of acyl peroxides is also applicable here. In the cyclohexane derivative, the bond angles are 109° and the carbon atoms possess tetrahedral configurations. As the carbon-carbon bond stretches, the carbon involved becomes trigonal and expands its bond angles to 120°, thereby introducing strain into the ring. In the case of the cyclopropane derivative, however, the strain produced is of more importance. Using the conventional bond angles of 109° for saturated carbon atoms, there is an existing strain of 49° in the molecule. Upon transformation into the cyclopropyl radical, the bond angles cannot expand as they do in cyclohexane and the internal strain would increase to 60°, which would impede carbon-carbon stretching.

SUMMARY

1. A reliable procedure for the synthesis of cyclopropaneacetic acid on a moderately large scale has been developed. Cyclopropyl chloride gave a good yield of cyclopropyllithium, using ether as the solvent; treatment with ethylene oxide gave β-cyclopropylethanol in 66% yield. Cyclopropylmagnesium chloride can be prepared, using benzyl bromide as an entraining agent and tetrahydrofuran as solvent; it also gave β-cyclopropylethanol when treated with ethylene oxide, but the overall yield was lower and the reaction less clean than with the lithium reagent. β-Cyclopropylethanol can be oxidized by chromium trioxide and sulfuric acid to cyclopropaneacetic acid in 57% yield.

2. The decomposition of cyclopropaneacetyl peroxide proceeds by first-order kinetics, slower than previously reported (1), but still 18 times faster than other cycloalkaneacetyl peroxides. The reaction, at the concentrations used, (0.02-0.09 N), is free of induced decomposition, will initiate the polymerization of styrene and results in the production of large amounts of ester, with low yields of carbon dioxide. Also produced in the reaction were a small amount of acid and an unidentified material, either an alkyl chloride or a hydrocarbon from the coupling of two alkyl groups. Whereas the carboxyl group was quantitatively accounted for, only three-quarters of the

cyclopropylcarbinyl radical was detected; the remainder escaped detection, possibly as tar.

3. The decomposition of cyclopropaneacetyl peroxide is insensitive to weak acids such as acetic or trimethylacetic acid. In the presence of trichloroacetic acid, however, there is an acceleration in the rate of decomposition, the increase being proportional to the concentration of acid. A similar effect, though not so large, was obtained in the decomposition of cyclohexaneacetyl peroxide. This action results in a decrease in the yield of carbon dioxide and cyclopropylcarbinyl cyclopropaneacetate, as well as in the formation of an ester of trichloroacetic acid, the nature of the alkyl group not being determined.

4. Pyridine also accelerates the decomposition of cyclopropaneacetyl peroxide. Cyclohexaneacetyl peroxide behaved similarly; the effect, however, was not large.

5. t-Butyl cyclohexanepercarboxylate decomposed three times faster than t-butyl cyclopropanepercarboxylate in carbon tetrachloride at 110°. The enthalpies of activation for the reactions were 28.7 and 30.7 kcal./mole respectively.

6. An improved procedure was developed for the preparation of cyclopropanecarboxaldehyde. Cyclopropylcarbinol was catalytically dehydrogenated over a copper-zinc catalyst at 300° to give the aldehyde in 81% yield.

EXPERIMENTAL

I. THE PREPARATION OF CYCLOPROPANEACETIC ACID

A. Displacement Reaction of Cyclopropylcarbinyl Benzenesulfonate with Potassium Cyanide.

Cyclopropylcarbinyl benzenesulfonate was prepared according to the procedure of Bergstrom and Siegel (46). A mixture of 53 ml. of 2,4,6-collidine and 15.8 g. (0.22 moles) of cyclopropylcarbinol was cooled to -5° and 38.7 g. (0.22 moles) of benzenesulfonyl chloride was added at such a rate that the temperature was maintained between 0-5°. Methylene chloride (50 ml.) was added as solvent. The temperature was allowed to rise to 12°, where it was maintained for one hour. The 2,4,6-collidine was slowly neutralized with 50 ml. of ice-cold 10 N sulfuric acid, so that the temperature did not rise. The resulting layers were separated and the water layer was extracted with several portions of methylene chloride. The combined extracts were then washed several times with cold 2.5 N sulfuric acid.

After removing the methylene chloride, 40 ml. of water and 50 g. of potassium cyanide were added to the residue and the mixture was stirred for several days at room temperature. Sufficient water was then added to dissolve the inorganic salts and the mixture was extracted with ether until the extracts were colorless. The extracts were combined and dried over potassium carbonate. After the drying agent was filtered, the ether was removed

on a steam bath and the remaining liquid distilled under reduced pressure. One fraction, boiling from 43-63°/20 mm., was collected, the remainder being tar and high boiling materials. The infrared of the distillate indicated a preponderance of an isonitrile, along with small amounts of nitrile, alcohol and olefin.

Refluxing this mixture with aqueous potassium hydroxide, followed by acidification, afforded a small amount of crude acid, which was not identified (Figure 7).

B. Attempted Condensation of Cyclopropanecarboxaldehyde with Rhodanine.

1. The Preparation of a Copper-Zinc Catalyst.

The method used was essentially that of Fenske and Hart (47). Cupric nitrate trihydrate (1044 g., 3.54 moles) and zinc nitrate hexahydrate (136 g., 0.56 moles) were dissolved in one liter of distilled water. The solution was heated to 70°, filtered to remove insoluble particles and treated at 70° with concentrated ammonium hydroxide. Before an excess of ammonium hydroxide was added, the precipitated hydroxides were filtered. The addition was continued until precipitation no longer occurred and the mixture of hydroxides was filtered. The hydroxides were washed with 1.5 liters of water and dried in an oven at 125° for 6 hours. The cake was ground to a powder, which was dried at 125° for an additional 24 hours.

An eighteen-inch glass column equipped with a

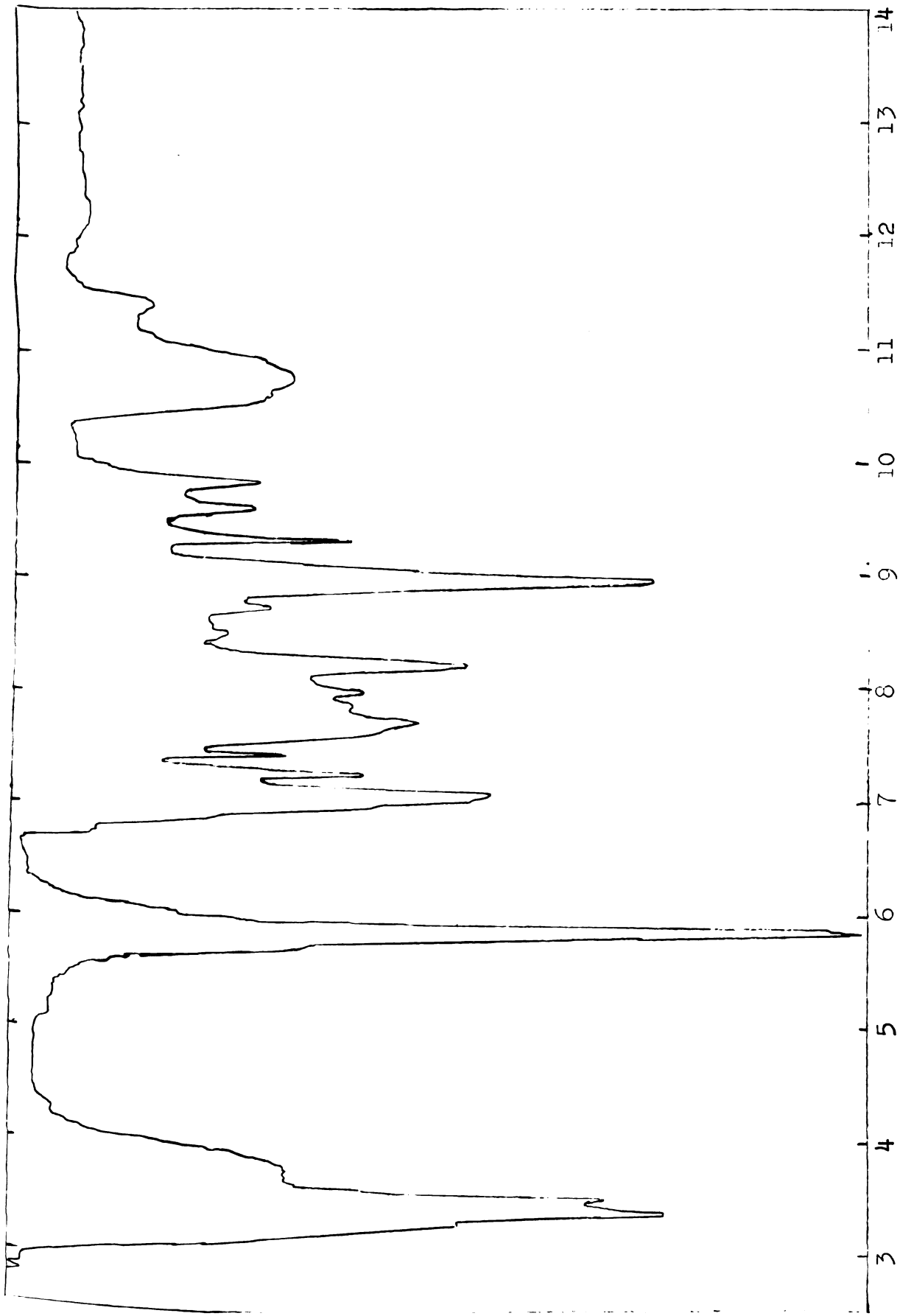


Figure 7. Infrared Spectrum of Acid Obtained from Reaction Product of Cyclopropylcarbinyl Benzenesulfonate and Potassium Cyanide.

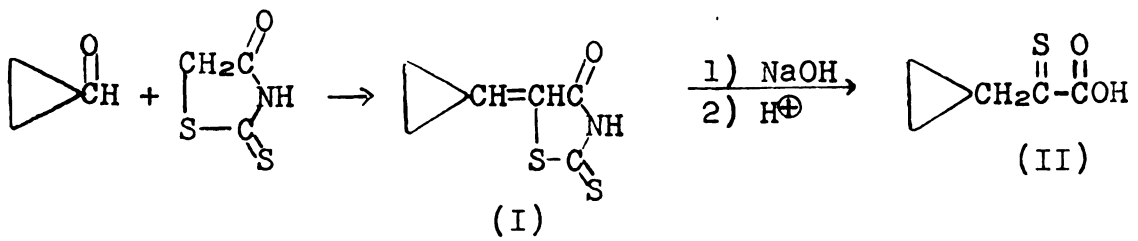
thermocouple and wound with Nichrome wire was packed with the powdered hydroxides, using a glass wool support. The column was heated to 325°, and air, previously dried by phosphorus pentoxide, was passed through until evolution of oxides of nitrogen ceased. The column was then allowed to cool to room temperature.

The packed column was flushed with hydrogen while being gradually heated to 200°. At this temperature, water was evolved and the temperature rose abruptly to 250°, where it remained until the evolution of water ceased. The column was then allowed to cool and the flow of hydrogen stopped.

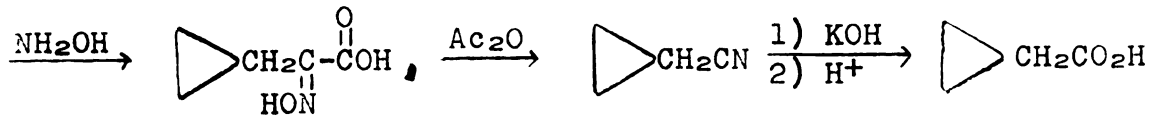
2. Dehydrogenation of Cyclopropylcarbinol.

To the packed column was attached a dropping funnel and a condenser. The column was heated to 300° and 60 g. (0.83 moles) of cyclopropylcarbinol (46) were added dropwise. The reaction was followed by measuring the amount of hydrogen liberated by means of a flowmeter. The yield of aldehyde (b.p. 100°/744 mm.; n_D^{25} 1.4265) was 33.1 g., 81% conversion based on 42 g. of unrecovered alcohol.

3. Attempted Condensation of Cyclopropanecarboxaldehyde with Rhodanine.



(I) (II)



(III)

To a solution of 10 g. (0.075 moles) of rhodanine and 5.3 g. (0.076 moles) of cyclopropanecarboxaldehyde in 25 g. of glacial acetic acid was added 20 g. of freshly fused sodium acetate. The mixture was refluxed for 35 minutes with occasional stirring. Upon addition of the mixture to 150 ml. of water, a reddish-black gum, presumably I, separated. Attempts to crystallize the gum failed. It was then dissolved in 200 ml. of 2 N sodium hydroxide and the solution was refluxed for twenty minutes filtered and allowed to cool. Upon rapid neutralization with 2 N hydrochloric acid, 7 g. of a rust colored powder, presumably II, was obtained. Attempts to crystallize this also failed.

The powder (7 g.) was added to 5.0 g. of hydroxylamine in ethanol, prepared by mixing 10.4 g. of hydroxylamine hydrochloride and 3.45 g. of sodium in 100 ml. of ethanol and filtering the sodium chloride formed. The mixture was heated until hydrogen sulfide ceased being evolved; the alcohol was then removed by evaporation under reduced pressure. The residue was dissolved in 100 ml. of 2 N sodium hydroxide. After filtration, the solution was cooled and acidified with 1.5 N hydrochloric acid to a Congo Red endpoint, yielding 4.5 g. of a yellow

precipitate, presumably III.

The oximino-acid (III) was refluxed with 23 g. of acetic anhydride for twenty minutes and steam-distilled, 250 ml. of distillate being collected. A carbonaceous residue remained in the reaction flask. The distillate was neutralized with sodium carbonate and extracted with three 35 ml. portions of ether, which were combined and dried over magnesium sulfate. The drying agent was filtered and the ether evaporated. A small amount of liquid, whose infrared spectrum contained no nitrile band, was obtained.

C. The Preparation of β-Cyclopropylethanol.

1. Using Cyclopropylmagnesium Chloride.

In a two-liter three-necked round-bottomed flask equipped with stirrer, dropping funnel and dry-ice condenser was placed 49.6 g. (2.04 g. at.) of magnesium turnings. To this was added slowly, with stirring, a mixture of 125 g. (1.63 moles) of cyclopropyl chloride (48) and 50 g. (0.29 moles) of freshly distilled benzyl bromide in 376 g. of dry tetrahydrofuran. After the addition was complete, the mixture was refluxed for 18 hours. Treatment of the mixture with standard acid and back-titration showed that 1.46 moles (76%) of Grignard reagent was present.

To the ice-cold mixture was added dropwise a solution of 64.4 g. (1.46 moles) of ethylene oxide in 300 g. of dry tetrahydrofuran. After the addition was complete, the

mixture was refluxed for two hours. It was then allowed to cool to room temperature, filtered through glass wool to remove unreacted magnesium, poured onto ice and acidified with 10% sulfuric acid. After the layers were separated, the aqueous layer was saturated with sodium chloride and extracted with three 100-ml. portions of ether. The ethereal extracts were combined with the tetrahydrofuran layer and the solvents were removed by distillation through a Vigreux column. To the remaining solution was added 250 ml. of 4 N sodium hydroxide and the mixture was refluxed for four hours. After cooling, the layers were separated and the aqueous layer was extracted with three 50-ml. portions of ether. The extracts were added to the organic layer and dried over magnesium sulfate. The ether was removed and the residue was distilled through a packed column to yield 59 g. (42%) of β-cyclopropylethanol, b.p. 73-75°/50 mm.; n_D^{20} 1.4328.

2. Using Cyclopropyllithium.

The method used for the preparation of cyclopropyllithium is that developed by Hart and Holzschuh (9). A typical preparation is described.

To a flame-dried one-liter three-necked round-bottomed flask continuously flushed with argon and equipped with a high-speed stirrer and a reflux condenser was added 7.3 g. (1.06 g. at.) of lump lithium and 250 ml. of mineral oil, which had been dried by heating over

sodium. The flask was heated by means of a Fisher burner until the lithium melted, at which time the mixture was vigorously stirred. When the lithium was thoroughly dispersed, the heating was discontinued, but the rapid stirring was maintained for a short period to prevent the lithium sand from fusing. After the mixture cooled to room temperature, most of the mineral oil was removed by the addition of anhydrous ether in portions, followed by the application of suction, until 500 ml. of ether had been used.

To the lithium sand was added 250 ml. of anhydrous ether. A thermometer and a dropping funnel were attached to the flask, which was cooled to 2°. A mixture of 46.3 g. (0.60 moles) of cyclopropyl chloride in 150 ml. of anhydrous ether was added slowly so that the temperature of the reaction mixture never exceeded 10°. After the addition was complete (about three hours), the mixture was stirred for an additional hour. The cyclopropyllithium was then ready for use.

To the ethereal suspension of cyclopropyllithium was added a dry-ice-cold mixture of 53.2 g. (1.21 moles) of ethylene oxide in 300 ml. of anhydrous ether at such a rate that the temperature of the mixture never exceeded 10°. After the addition was complete, the stirring was continued for an additional hour at 2°.

The mixture was poured into water and acidified with ice-cold 10% sulfuric acid. The layers were separated and

the aqueous portion was saturated with sodium chloride. The water layer was then extracted with three 75-ml. portions of ether; the extracts were combined with the ether layer and dried with anhydrous potassium carbonate. After filtration, the ether was removed by distillation through a Vigreux column. Distillation of the residue under reduced pressure afforded 30 g. (66%) of β-cyclopropylethanol. The infrared spectrum is shown in Figure 8.

D. Oxidation of β-Cyclopropylethanol.

1. With Potassium Permanganate.

In a two-liter three-necked round-bottomed flask equipped with stirrer, dropping funnel and condenser was placed 27 g. (0.31 moles) of β-cyclopropylethanol and a solution of 7.0 g. of sodium carbonate in 70 ml. of water. To this was added dropwise, over a period of 2.5 hours, a solution of 66 g. (0.42 moles) of potassium permanganate in 1800 ml. of water. After the addition was complete, the flask was cooled to ice temperature and then stirred at room temperature for a day.

The precipitate of manganese dioxide was then filtered. The filtrate, which was still purple, was heated to boiling, at which time the color disappeared. The solution was refiltered and the filtrate was evaporated to 150 ml. The solution was cooled and washed with 50 ml. of ether. It was then covered with 100 ml. of

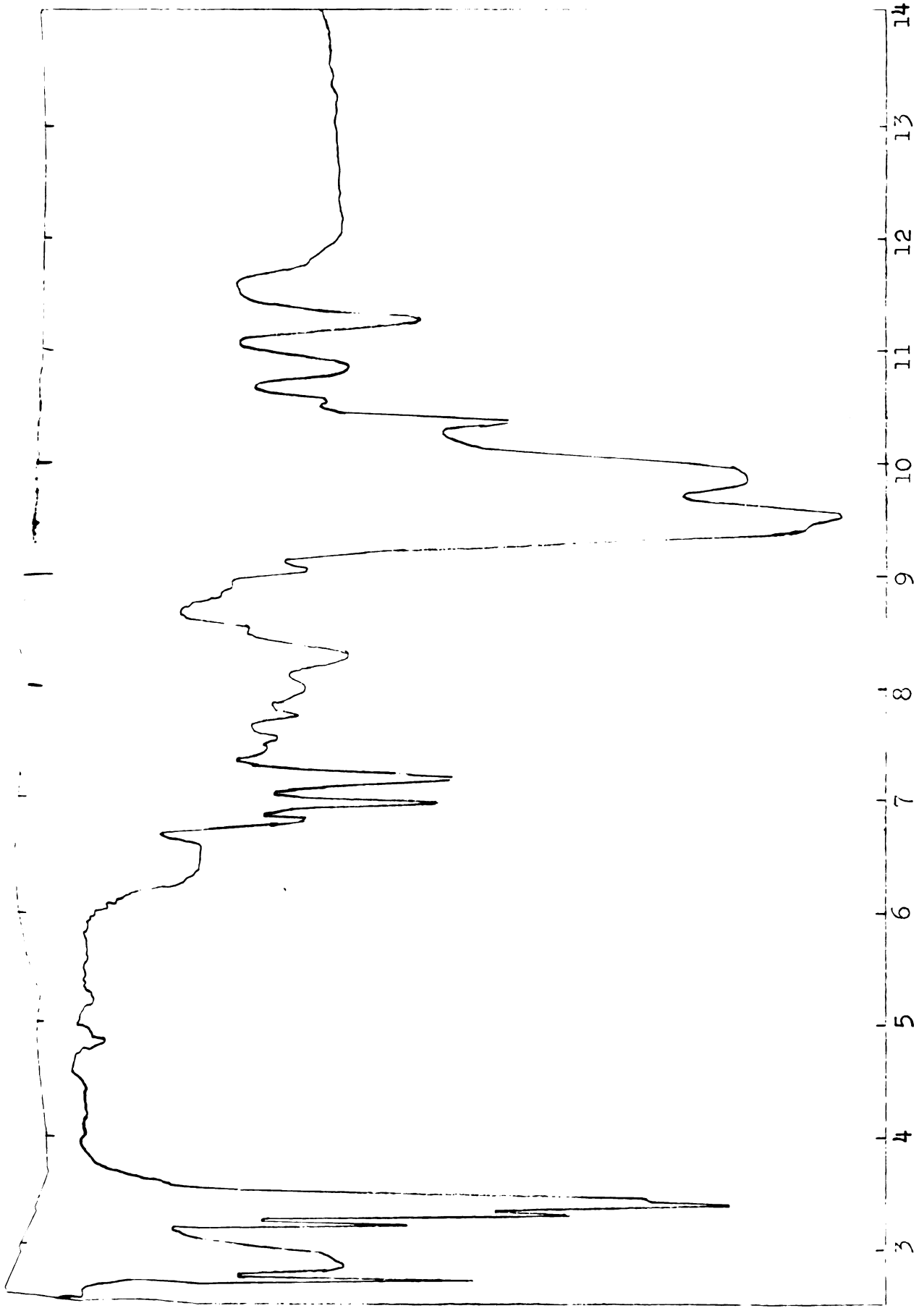


Figure 8. Infrared Spectrum of β-Cyclopropylethanol in Carbon Tetrachloride.

ether and acidified with 6 N sulfuric acid to the Congo Red endpoint. The layers were separated and the aqueous portion was extracted several times with ether. The combined ether extracts were dried over magnesium sulfate.

After filtration, the ether was removed by distillation. Distillation of the remaining liquid afforded 11.5 g. of acidic material, b. p. 92-93°/15 mm.; n_D^{21} 1.4375. The index of refraction indicated that it was a mixture of cyclopropanecarboxylic and cyclopropaneacetic acids.

Cyclopropanecarboxylic acid	n_D^{20} 1.4390	b.p. 81°/15mm.	(7)
Cyclopropaneacetic acid	n_D^{21} 1.4340	b.p. 89°/15mm.	(7)

2. Oxidation Using Chromium Trioxide-Sulfuric Acid.

To a one-liter three-necked round-bottomed flask equipped with reflux condenser, dropping funnel and magnetic stirrer and set in a water bath was added 39.5 g. (0.46 moles) of β-cyclopropylethanol and 92.5 ml. of acetone. To this well-stirred solution was added slowly a solution of 61.5 g. (0.615 moles) of chromium trioxide and 95.8 g. (1.04 moles) of sulfuric acid in 405 ml. of water. The addition required approximately thirteen hours; the temperature of the bath was never allowed to exceed 30°. Water (100 ml.) was added and the mixture stirred for an additional hour; the aqueous layer was still acid to Congo Red. The layers were separated and the water layer extracted with three 100-ml. portions of ether.

The ether extracts were added to the organic layer and the solvents were removed by distillation on a steam bath. To the residue was added 300 ml. of 4 N sodium hydroxide and the whole was refluxed for 5 hours. After the mixture cooled, it was extracted with three 50-ml. portions of ether. The ether extracts were combined, dried over potassium carbonate, and filtered. The ether was removed by distillation. The residue yielded 6 g. of unreacted alcohol.

The alkaline solution was acidified to Congo Red and was extracted with four 75-ml. portions of ether. The extracts were combined, dried over magnesium sulfate, filtered and the ether removed by distillation. The residue afforded 22.3 g. (57%, based on unrecovered alcohol) of cyclopropaneacetic acid. The infrared spectrum is shown in Figure 9.

b.p. 91°/15 mm. n_D^{25} 1.4321 Neut. Eq. 100.1

Lit. Values (7) b.p. 89°/15 mm.; n_D^{25} 1.4320 Neut. Eq. 100.1

II. THE PREPARATION OF ACYL PEROXIDES.

A. Preparation of the Acid Chlorides.

The acid chlorides were prepared from the corresponding acids either by reaction with thionyl chloride or by exchange with benzoyl chloride.

1. Preparation of Cyclopropanecarboxylyl Chloride

To a 100-ml. round-bottomed flask equipped with a distillation head was added 10.0 g. (0.12 moles) of

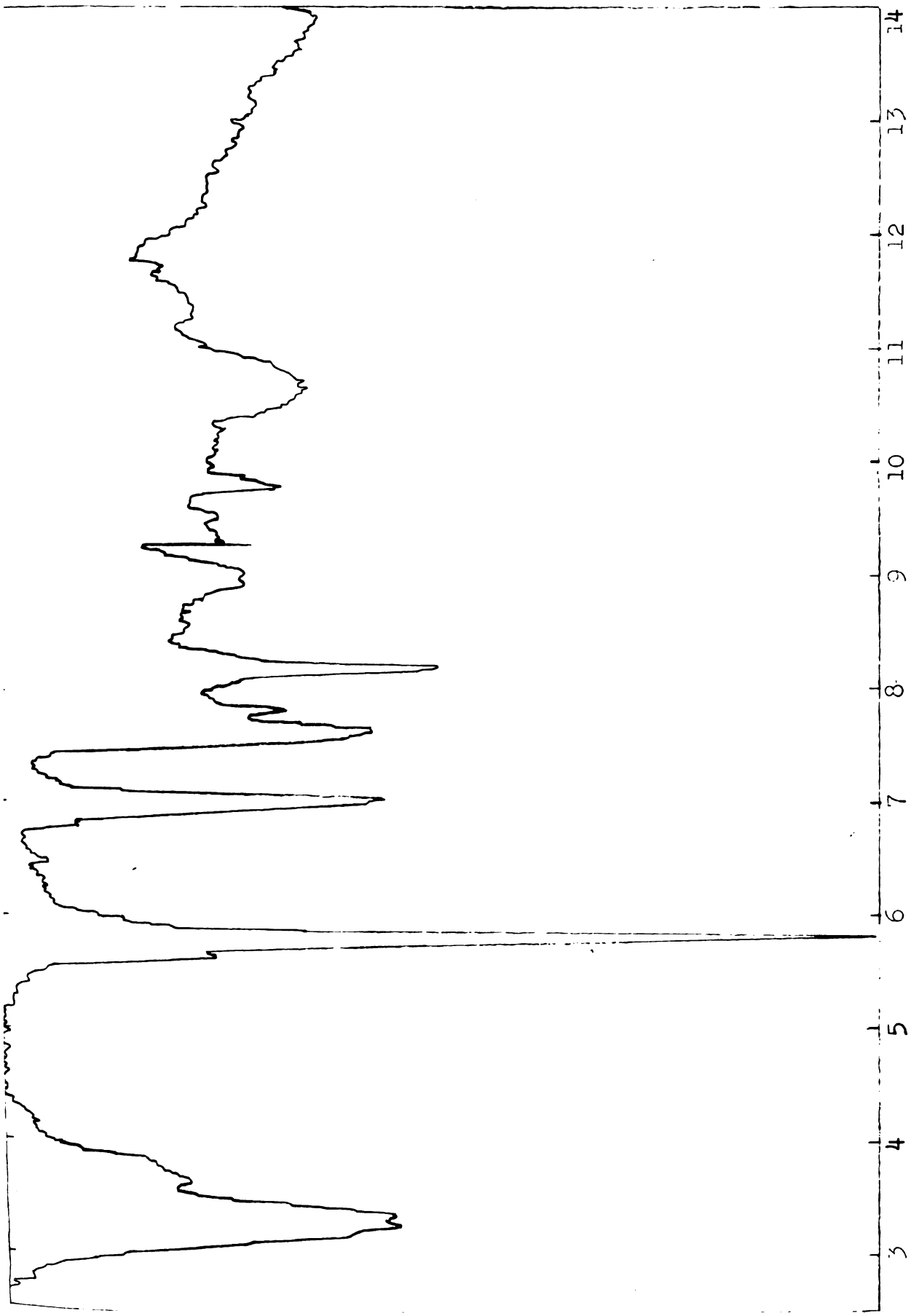


Figure 9. Infrared Spectrum of Cyclopropaneacetic Acid in Carbon Tetrachloride.

cyclopranecarboxylic acid (49) and 33 g. (0.24 moles) of benzoyl chloride. The mixture was heated and the distillate was collected until the temperature of the distillation head began to drop. Redistillation yielded 7.0 g. (57%) of cyclopropanecarboxylyl chloride, b.p. 113-5°. Lit. Value (40) 112-5°.

2. Preparation of Cyclopropaneacetyl Chloride

(a) By Exchange with Benzoyl Chloride

The reaction was similar to the one above. Cyclopropaneacetic acid (10 g., 0.10 moles) and benzoyl chloride (29 g., 0.21 moles) afforded 6.0 g. (51%) of the acid chloride, b.p. 132-134°. Lit. Value (40) b.p. 132-133°.

(b) By Reaction with Thionyl Chloride

A mixture of 10 g. (0.1 moles) of cyclopropaneacetic acid, 13.1 g. (0.11 moles) of thionyl chloride and 25 ml. of chloroform was refluxed for 4 hours. After cooling, the chloroform and the excess thionyl chloride were removed by distillation through a small Vigreux column. The fraction boiling at 132-33° was collected and amounted to 7.5 g. (63%). The infrared spectrum is shown in Figure 10.

3. Preparation of Cyclohexanecarboxylyl Chloride

A 50-ml. round-bottomed flask was charged with 6.5 g. (0.05 moles) of cyclohexanecarboxylic acid and 6.4 g. (0.054 moles) of thionyl chloride. After the initial reaction subsided, the mixture was refluxed on a steam bath for an hour. The mixture was then distilled. Upon

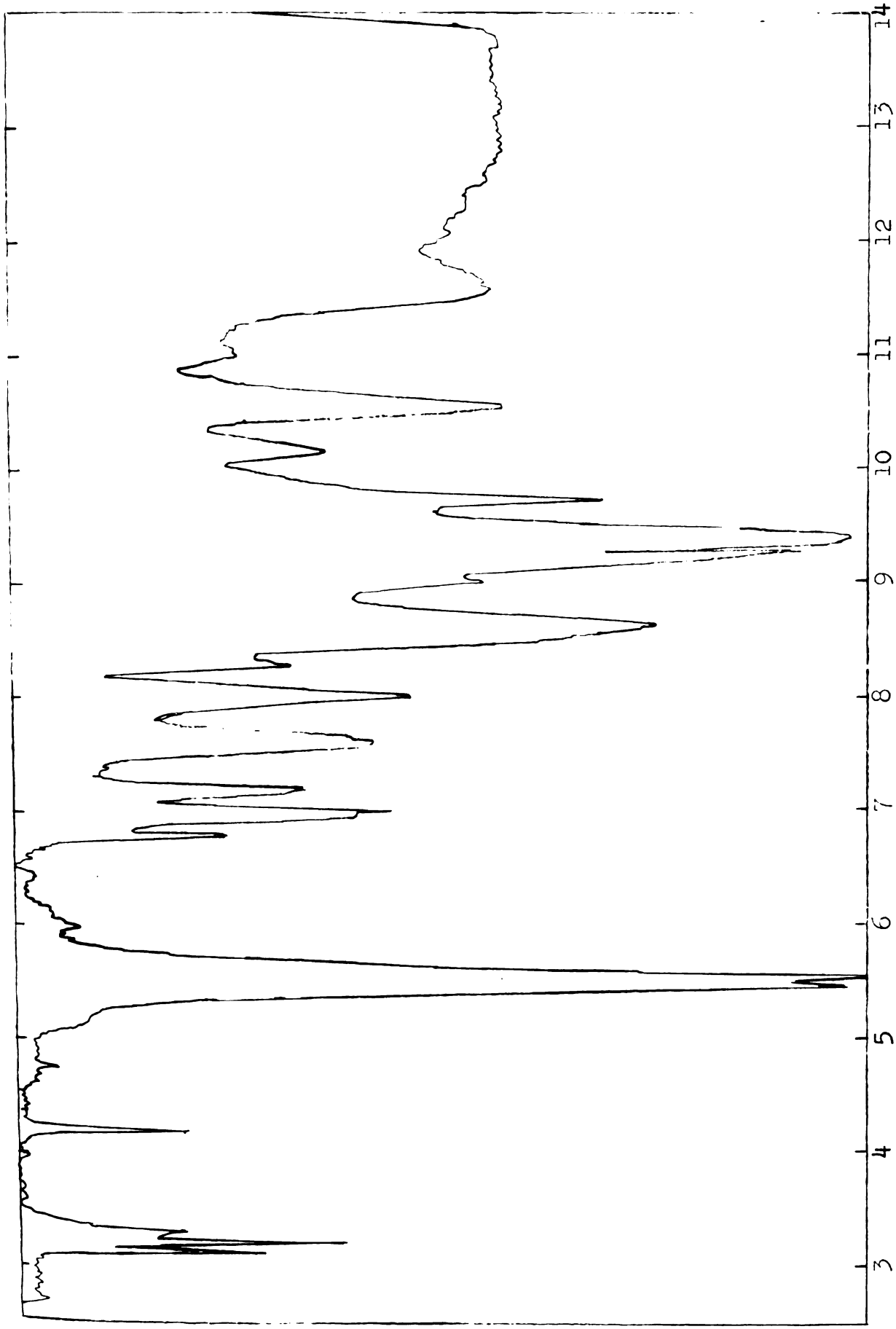


Figure 10. Infrared Spectrum of Cyclopropaneacetyl Chloride in Carbon Tetrachloride.

redistillation, the fraction boiling from 77-80°/20mm. was collected. This amounted to 5.7 g. (0.039 moles) or 78% of the theoretical amount.

4. Preparation of Cyclohexaneacetyl Chloride

Cyclohexaneacetic acid (10 g., 0.07 moles) and thionyl chloride (9.5 g., 0.08 moles) were treated as described above, except that after the reaction was complete a partial vacuum of 2 mm. was applied for one hour to ensure the complete removal of the excess thionyl chloride. Distillation of the residue afforded 9.5 g. (0.059 moles, 84%) of the acid chloride, b.p. 114-6°/15 mm.

5. Preparation of Trans-4-t-Butylcyclohexanecarboxylyl Chloride

The procedure was identical to that of cyclohexaneacetyl chloride. Three grams (0.016 moles) of the corresponding acid (42) and 1.9 ml. (0.024 moles) of thionyl chloride yielded 2.75 g. (0.013 moles, 84%) of the acid chloride, b.p. 85°/1 mm.

B. Preparation of Acyl Peroxides

The acyl peroxides were prepared by treating the acid chloride in ether with an equivalent amount of sodium peroxide. Details of the preparation of cyclopropaneacetyl peroxide are given as an example.

In a 300-ml. three-necked round-bottomed flask, ice-cooled and equipped with a magnetic stirrer, reflux condenser, dropping funnel and thermometer there was placed 2.0 g. (0.026 moles) of sodium peroxide and 40 ml. of anhydrous ether. To this was added 5.8 g. (0.049 moles) of cyclopropaneacetyl chloride and the reaction was initiated by the addition of several drops of water, with additional drops added later to keep the reaction going. The reaction was assumed to be complete when the yellow color of the sodium peroxide had disappeared and the addition of water no longer caused the temperature to rise.

Cold water was added to dissolve the salt. The mixture was stirred for several minutes and the layers were separated. If the aqueous layer was not basic to litmus, the ether layer was washed with 10% sodium carbonate solution. The ether layer was then dried over calcium chloride.

The mixture was filtered and the ether removed on a Rinco evaporator. The remaining liquid was dissolved in 20 ml. of pentane and crystallized at dry-ice temperature in an atmosphere of carbon dioxide. The peroxide would remain crystalline if stored at -20°, but melted when warmed to room temperature. Titration of the peroxide according to the method of Silbert and Swern (96) indicated a peroxide content of 85%. The infrared spectra in carbon tetrachloride and carbon disulfide are shown in

Figures 11 and 12. On one or two occasions, unreacted acid chloride appeared as an impurity and was removed by washing with sodium carbonate solution; this was necessary for the acid chloride accelerated the decomposition rate of the peroxide.

The other peroxides used were prepared in a similar manner. Cyclohexaneacetyl peroxide, also a liquid, was crystallized in an identical fashion and possessed a peroxide content of 88%. Cyclopropaneformyl and trans-4-t-butylcyclohexaneformyl peroxides, which were solids at room temperature, were recrystallized from n-hexane and possessed purities of 99+%.

III. THE DECOMPOSITION OF ACYL PEROXIDES

A. Kinetics of Decomposition

The decompositions were performed in the apparatus illustrated in Figure 13. The peroxides were used in the form of a standard solution in carbon tetrachloride. A 20-ml. portion of the solution was placed in the reaction flask; the flask was then set in a constant-temperature bath and allowed to attain thermal equilibrium. The first sample was taken to be zero-time; samples were withdrawn periodically, placed into vials and frozen in dry-ice until analyzed.

For analysis, the samples were allowed to thaw and the peroxide content was determined either spectrophotometrically by following the disappearance of the 5.62μ

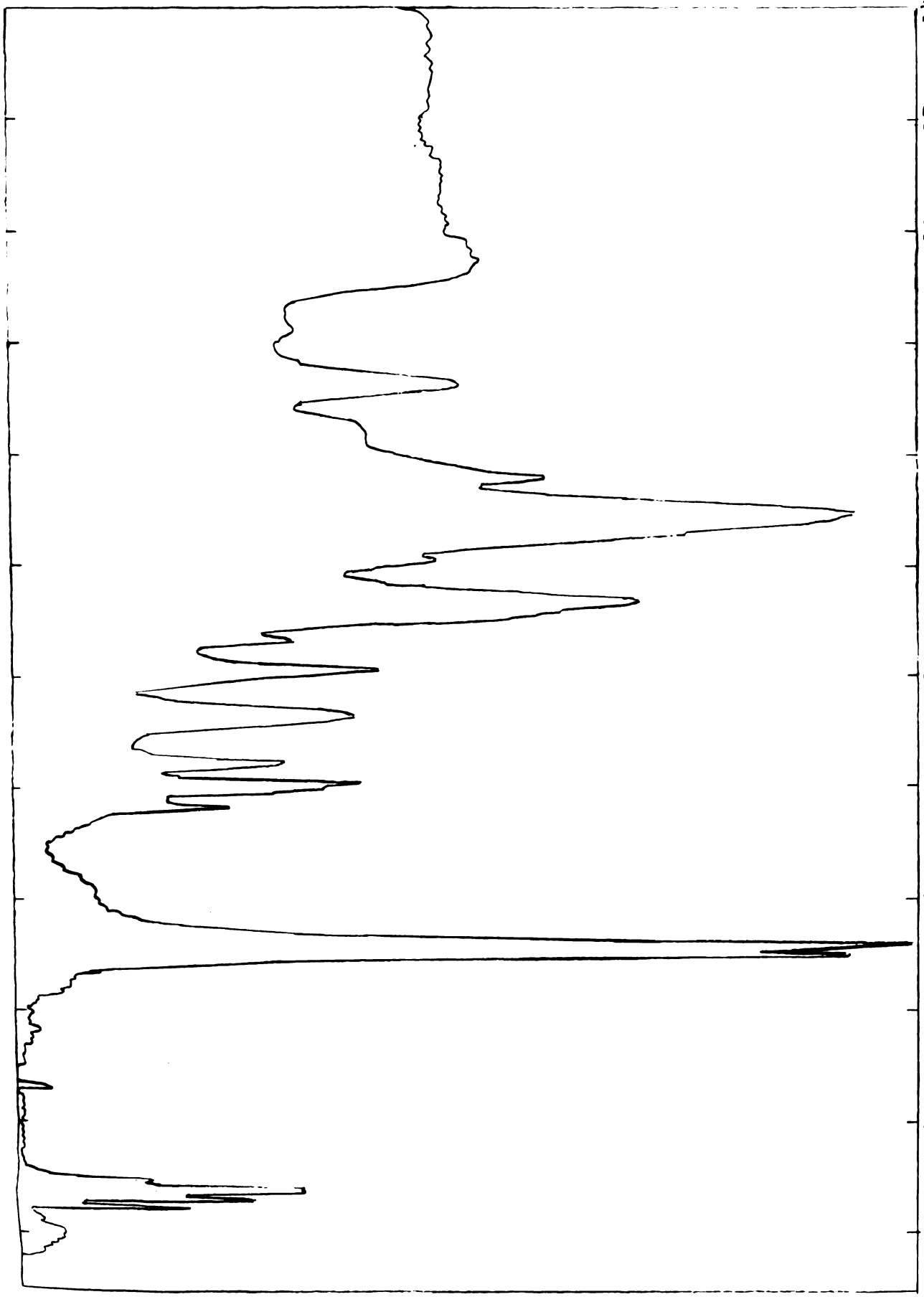


Figure 11. Infrared Spectrum of Cyclopropaneacetyl Peroxide in Carbon Tetrachloride.

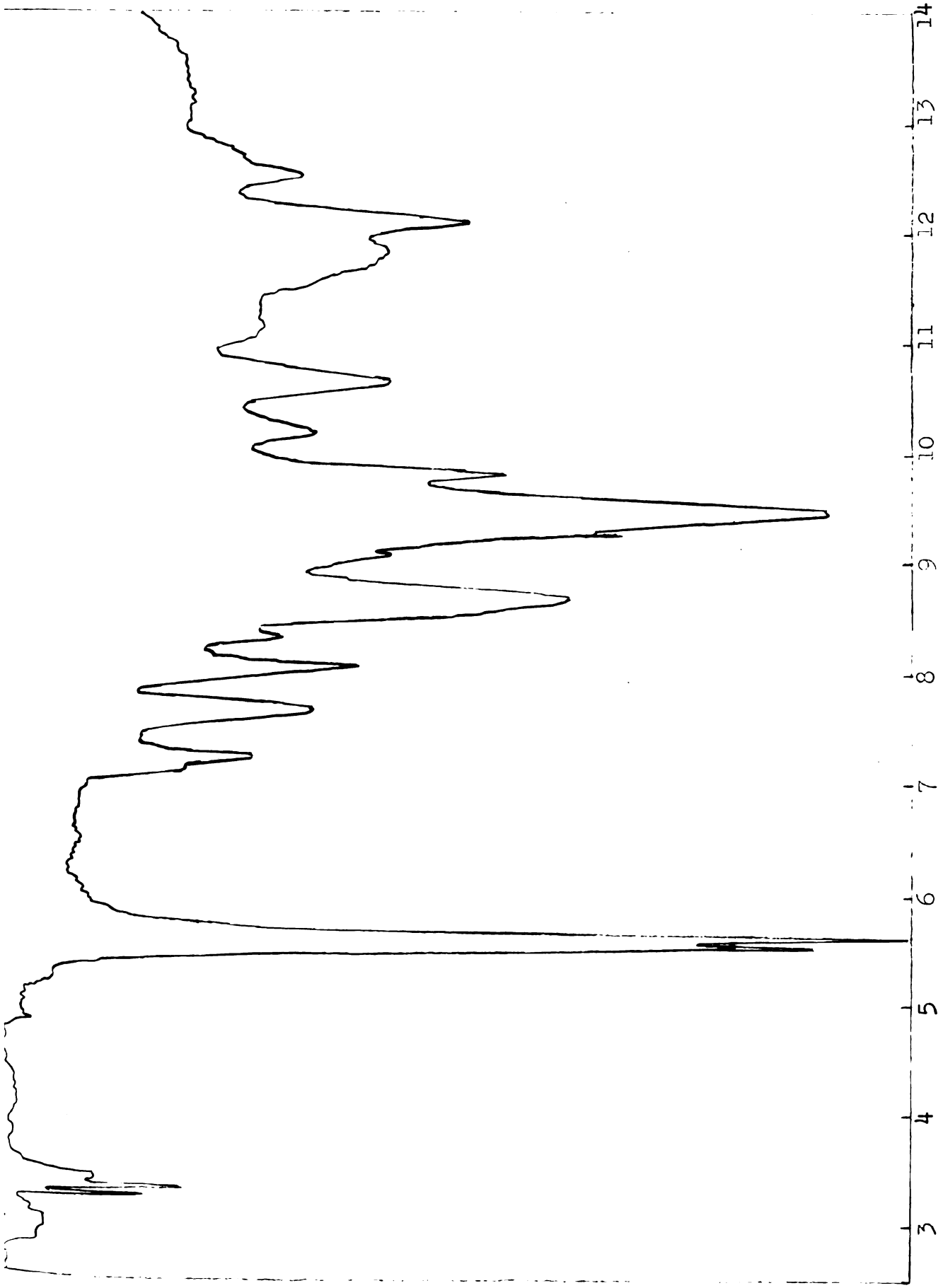
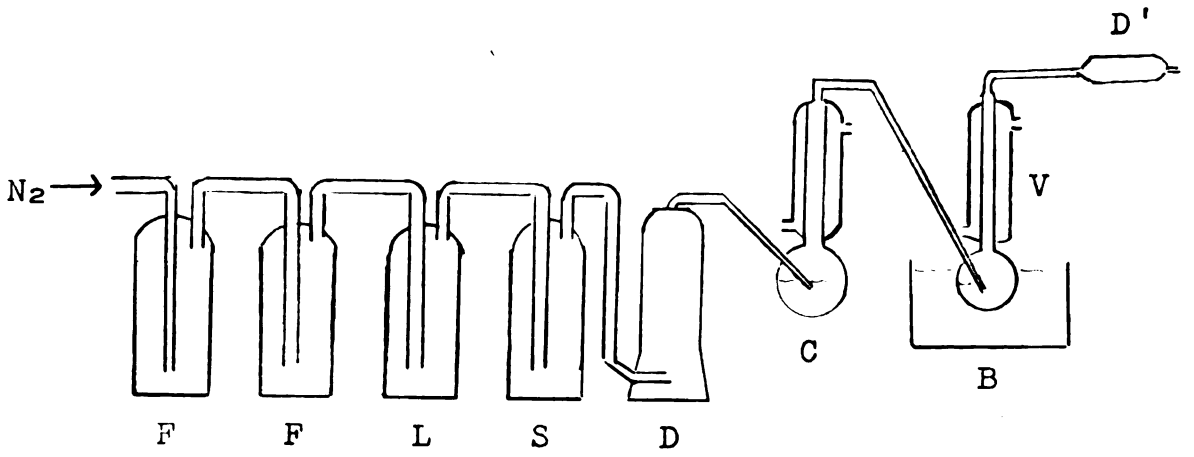


Figure 12. Infrared Spectrum of Cyclopropaneacetyl Peroxide in Carbon Disulfide.



F - Fieser's solution, to remove oxygen.
L - Saturated lead acetate in water, to remove sulfur compounds.
S - Sulfuric acid, to dry nitrogen.
D - Calcium chloride.
D' - Drierite.
C - Flask equipped with condenser and containing carbon tetrachloride to saturate nitrogen.
V - Reaction vessel.
B - Bath maintained at desired temperature.

Figure 13. Diagram of the Apparatus Used for Decomposition Runs.

band, or by iodometric titration, using the method of Silbert and Swern (36).

The iodometric titrations were performed in the following manner. A 1-ml. portion of the peroxide solution was dissolved in 5 ml. of glacial acetic acid containing 0.0005% ferric chloride hexahydrate, $FeCl_3 \cdot 6H_2O$. The solution was degassed with carbon dioxide, 0.5 ml. of water saturated with sodium iodide was added and the mixture was placed in the dark for twenty minutes. After the addition of 5 ml. of water, the mixture was titrated with standard thiosulfate, with 2 ml. of starch being added shortly before the end-point was reached. Standardization of the thiosulfate solution using this method with benzoyl peroxide produced results identical, within experimental error, to those obtained using potassium iodate.

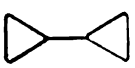
B. Products of Decomposition of Peroxides

1. Trans-4-t-butylcyclohexanecarboxylyl Peroxide in Carbon Tetrachloride

A solution of 0.041 g. (0.11 mmoles) of the peroxide and 4.5 ml. of purified carbon tetrachloride (35) in a 50-ml. flask was refluxed in a nitrogen atmosphere for five hours. After the mixture cooled, the ester content was determined by measuring the intensity of the 5.75μ band and translating this into concentration using a standardization curve prepared from pure trans-4-t-butylcyclohexyl trans-4-t-butylcyclohexanecarboxylate; this

showed that 0.053 moles of ester, or 48.8% of theoretical, was obtained.

2. Cyclopropanecarboxylyl Peroxide in t-Butylbenzene

Cyclopropanecarboxylyl peroxide was decomposed in t-butylbenzene with the hope of obtaining dicyclopropyl,  . A 300-ml. three-necked flask equipped with reflux condenser, dropping funnel and nitrogen inlet tube and maintained at 78° was charged with 50 ml. of t-butylbenzene. To this was added over a period of five hours a solution of 5 g. (0.03 moles) of the peroxide in 90 ml. of t-butylbenzene. The mixture was heated for an additional seven hours. The infrared spectrum of the reaction mixture indicated that the peroxide was not entirely decomposed and that the principal products were ester and acid. The solution was refluxed for two hours longer and the infrared spectrum of the first few milliliters of distillate indicated that no dicyclopropyl was formed.

The reaction mixture was shaken with 150 ml. of 1 N sodium hydroxide for fifteen minutes. The alkaline solution was acidified and extracted with ether. The extract was dried with magnesium sulfate and filtered and the ether evaporated. The residue was titrated with standard base and contained 0.4 g. of acid, calculated as cyclopropanecarboxylic acid. Distillation of the dried t-butylbenzene solution did not separate the ester from the solvent. The yield of ester was estimated from the infrared spectrum to

be 1.4 g., or 37% of theoretical, calculated as cyclopropanecarboxylate.

Decomposition of the peroxide in refluxing chlorobenzene yielded similar results, with no dicyclopropyl being detected.

3. Decomposition of Cyclopropaneacetyl Peroxide in Carbon Tetrachloride

The apparatus used for determining the products of the decomposition was essentially that used for kinetics runs (Figure 13), except that two dry-ice traps and a tube containing Ascarite and Anhydrone for the determination of carbon dioxide were placed, in that order, between the reaction vessel V and the drying tube D'. A known amount of a standard solution of peroxide in carbon tetrachloride was refluxed for three hours in a stream of purified dry nitrogen (50). The flow of nitrogen was continued for a half-hour while the reaction mixture cooled. The carbon dioxide evolved was determined by the increase in weight of the Ascarite tube, while the ester and acid were determined spectrophotometrically, using the 5.75μ and the 5.87μ bands respectively. The results are listed in Table 8, page 29.

To obtain more information regarding the nature of the ester, most of the carbon tetrachloride was distilled through a packed column. The remaining liquid was washed with 10% sodium carbonate solution and dried over calcium sulfate. The filtered liquid was distilled under reduced

pressure and, upon redistillation, yielded a material whose infrared spectrum was somewhat similar to that of cyclopropylcarbinyl cyclopropaneacetate. The mixture consisted of almost entirely one product, as was indicated by the vapor-phase chromatograph; purification of the compound using this method was impossible because of extensive decomposition occurring in the column. A spectrum of the high boiling material appears in Figure 14.

For the determination of alkyl chloride, 96 ml. of a 0.076 N peroxide solution in carbon tetrachloride was refluxed for three hours. The infrared spectrum of the first ten milliliters obtained on distillation through a packed column possessed a small carbon-hydrogen absorption peak. A partial vacuum was applied to the remainder of the solution and everything volatile at room temperature and 5 mm. of pressure was collected in a dry-ice trap. Most of carbon tetrachloride was fractionated; each of the fractions possessed a slight carbon-hydrogen absorption peak in the infrared. The remaining liquid (10 ml.) was distilled, not allowing the temperature of the oil bath to exceed 100°. The temperature of the distillate gradually rose from 76-80°, after which it dropped slowly. The infrared spectrum showed that, in addition to small amounts of ester and acid, a substance, either an alkyl halide or a hydrocarbon, was present. The amount, calculated as alkyl chloride, was estimated from the

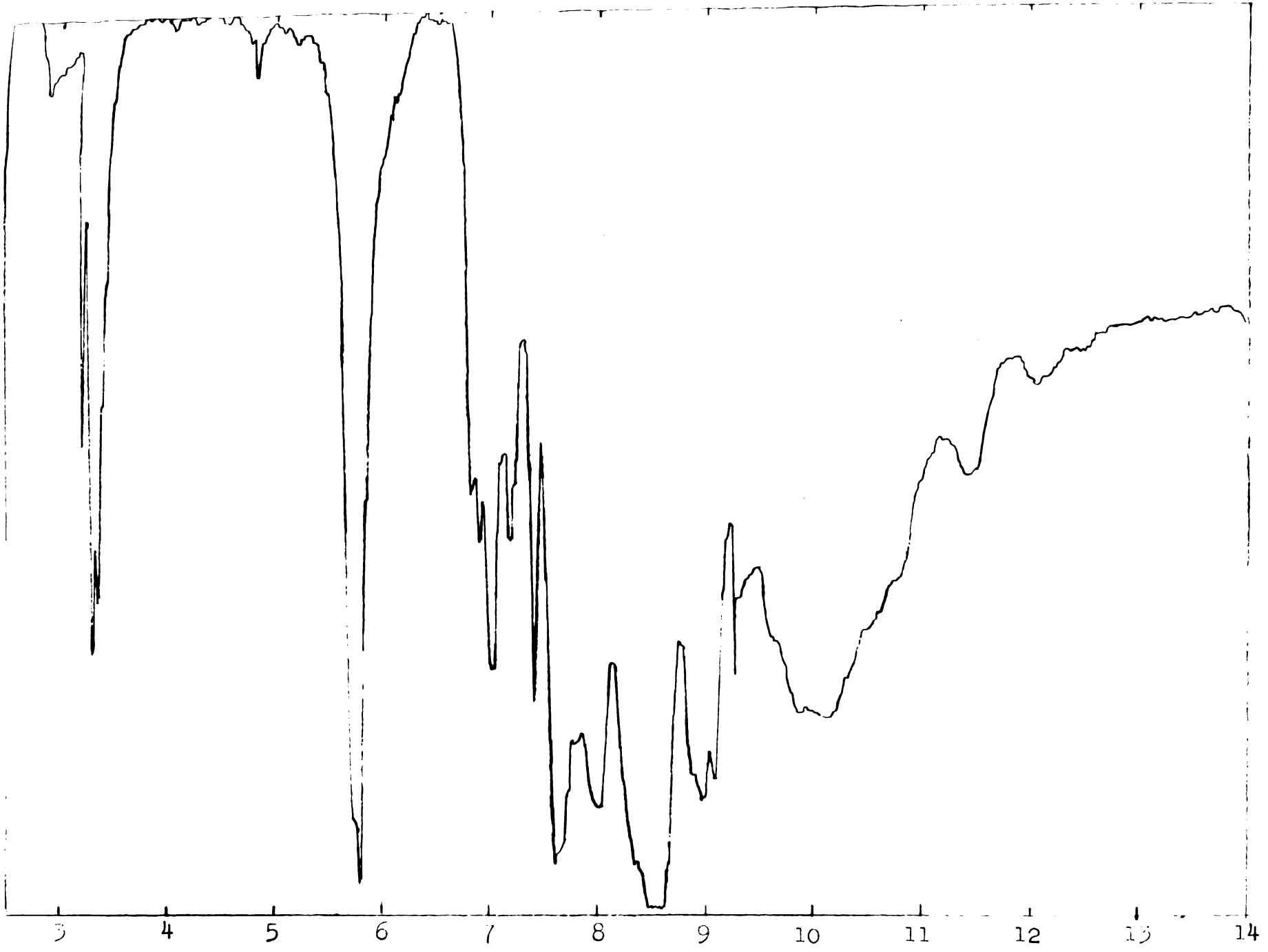


Figure 14. Infrared Spectrum of the High Boiling Material Obtained from the Decomposition of Cyclopropanecacetyl Peroxide in Carbon Tetrachloride.

carbon-hydrogen absorption. Absence of an olefinic peak indicated that the compound was saturated.

4. Decomposition of Cyclopropaneacetyl Peroxide in the Presence of Trichloroacetic Acid

The apparatus used for the decomposition is that described above. A mixture of carbon tetrachloride solutions of the peroxide and of trichloroacetic acid was refluxed for three hours and the carbon dioxide evolved determined by the increase in weight of the Ascarite tube. The solution was cooled, washed with 10% sodium carbonate solution and dried; the filtered solution was then diluted to 50.0 ml. The ester produced was determined by infrared; two ester bands were present, one at 5.67μ and another at 5.76μ. The data are listed in Table 10, page 32.

5. Initiation of the Polymerization of Styrene by Cyclopropaneacetyl Peroxide

Two flasks were each charged with twenty grams of freshly distilled styrene; to one was added one gram of cyclopropaneacetyl peroxide. The flasks were placed in a water bath maintained at 40-60°. The extent of polymerization was noted by cooling the flasks at intervals and comparing the viscosities and opaqueness of the solutions; the flasks were then returned to the water bath. Throughout the four hour observation period, the styrene containing cyclopropaneacetyl peroxide was both more viscous and opaque. At the end of four hours, this solution required twice the time as the uncatalyzed

styrene to drain approximately the same length.

IV. PREPARATION OF t-BUTYL PERESTERS OF SOME ALICYCLIC ACIDS

A. Purification of t-Butyl Hydroperoxide

t-Butyl hydroperoxide (Lucidol Corp.) was dried by refluxing at 40 mm. and removing the water as it was collected in a distillation head. The hydroperoxide was then distilled and the material boiling at 51-52°/40 mm. was collected; n_D^{19} 1.3995. Lit. value n_D^{25} 1.3986 (51).

B. Preparation of the t-Butyl Peresters

The peresters were prepared by treating the appropriate acid chloride (prepared as described above) with t-butyl hydroperoxide in the presence of pyridine. This is based on the method of Bartlett and Hiatt (2). The preparation of t-butyl cyclohexanepercarboxylate is described.

In a 100-ml. round-bottomed flask was placed 25 ml. of dry pyridine, 25 ml. of anhydrous ethyl ether and 10 g. (0.11 moles) of t-butyl hydroperoxide. The solution was stirred with a magnetic stirrer and was cooled to -6 to -8° by means of an ice-salt mixture. Cyclohexanecarboxylyl chloride (10.1 g., 0.97 moles) was added at such a rate that the temperature did not rise above 5°. After the addition was complete, the reaction mixture was placed in the freezer compartment of a refrigerator (-17°) for sixty hours. During this period, a white precipitate,

presumably pyridine hydrochloride, had separated. The mixture was washed with small portions of iced 10% sulfuric acid to remove the pyridine, then with 10% sodium carbonate to remove any acid present and finally with water. The ether layer was then dried over magnesium sulfate. The solution was filtered and the ether removed by a jet of dry air. The residue was passed through a column of Florisil and eluted with pentane. The first fifty milliliters, after removal of the pentane by evaporation, gave a residue of 6.5 g. Its infrared spectrum (carbon tetrachloride) possessed no extraneous acid or hydroxyl peaks and is shown in Figure 15. Titration of the perester using a method based on a note of Simon (52) indicated a peroxide content of 77%.

The t-butyl perester of cyclopropanecarboxylic acid was prepared in an analogous manner. Its infrared spectrum is shown in Figure 16. The purity of the perester was 76%, as indicated by titration.

C. Method of Titration of the Peresters

Aliquots of carbon tetrachloride containing a known amount of perester were added to flasks containing a solution of 10 ml. of acetic anhydride, 10 ml. of glacial acetic acid, 30 ml. of absolute alcohol, 6 g. of potassium iodide and 20 ml. of water. The mixture was degassed with carbon dioxide and was allowed to stand for two hours with occasional shaking. Water (150 ml.) was added to the

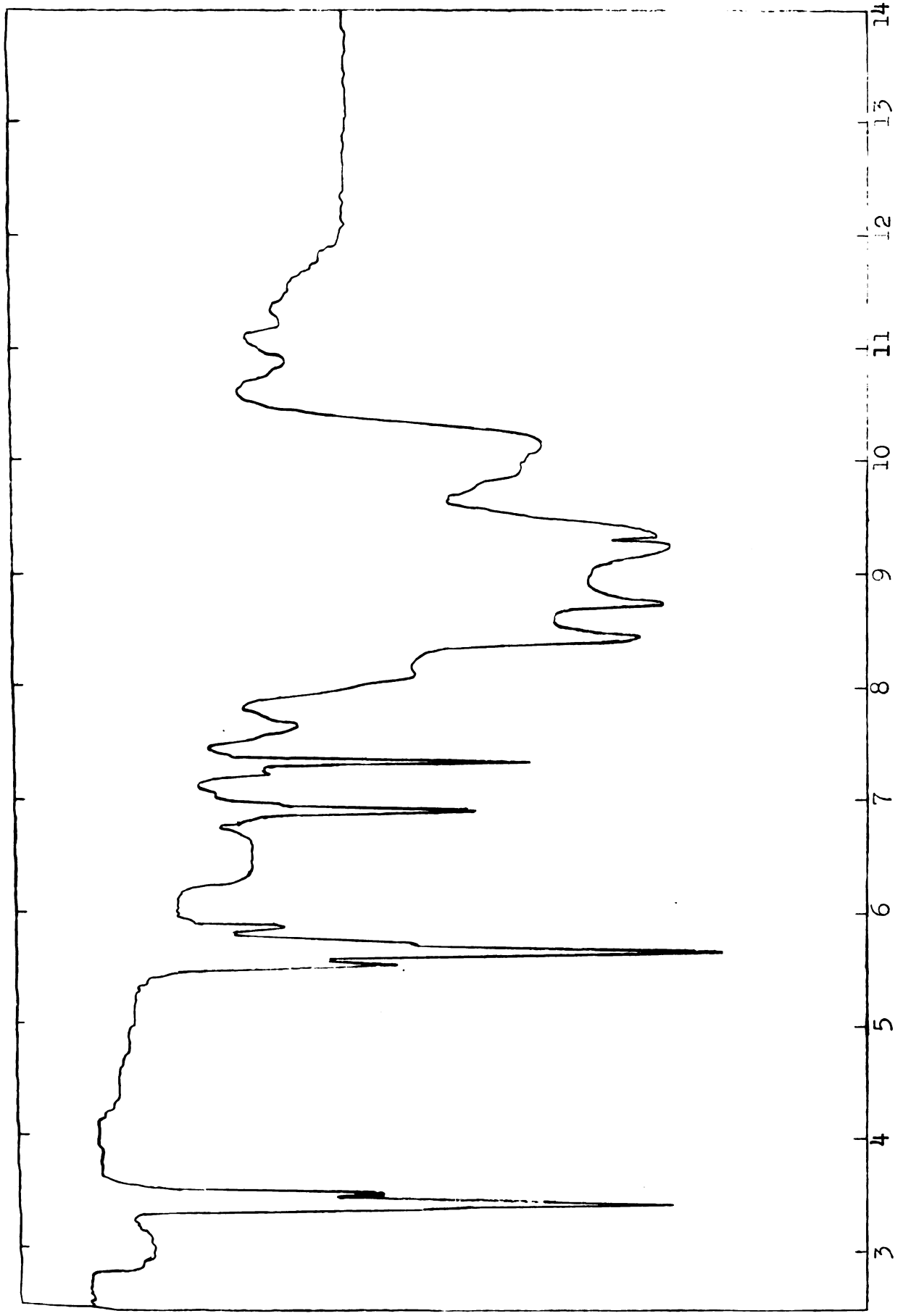


Figure 15. Infrared Spectrum of t-Butyl Cyclohexanepercarboxylate in Carbon Tetrachloride.

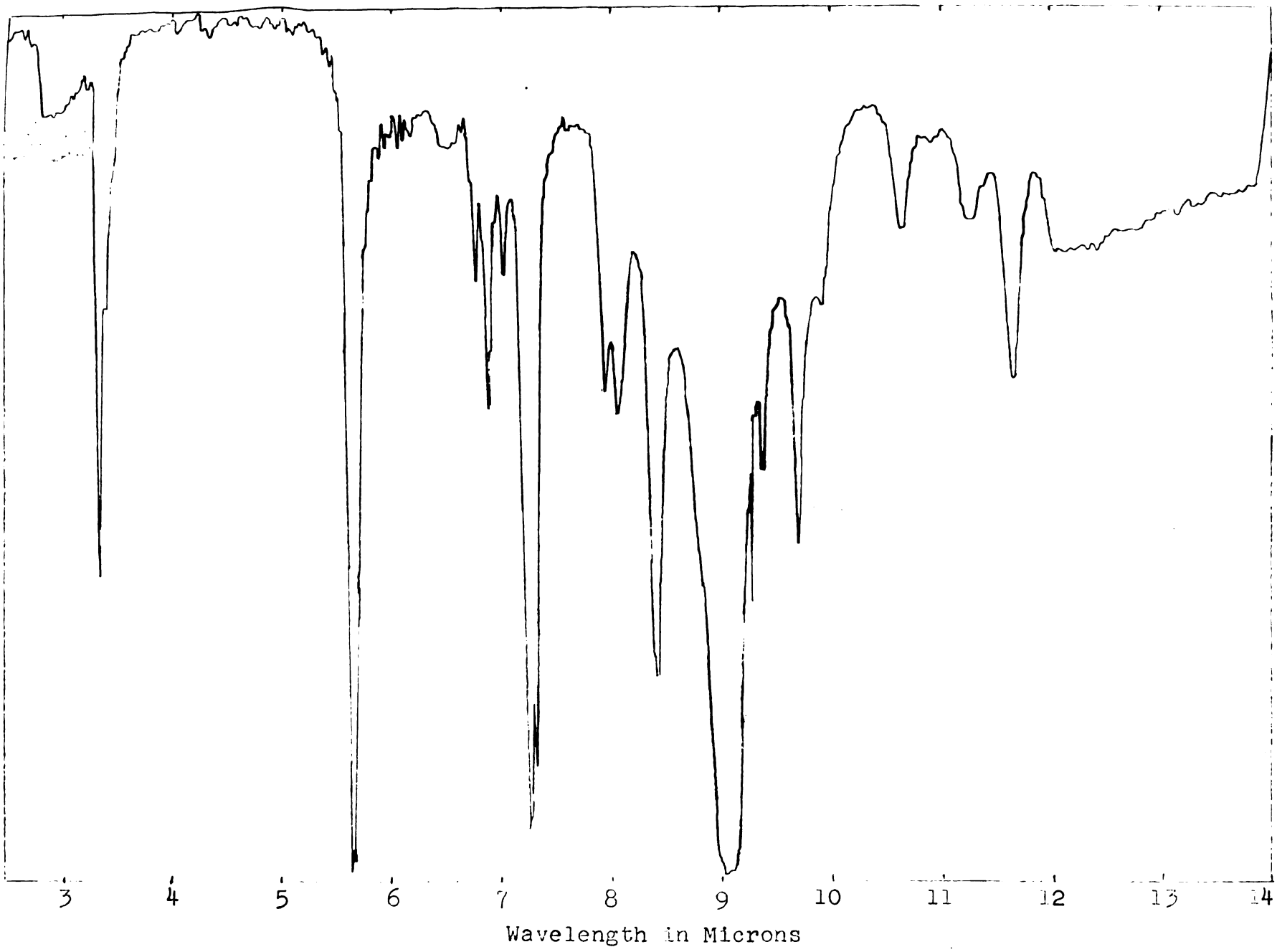


Figure 16. Infrared Spectrum of t-Butyl Cyclopropanepercarboxylate in Carbon Tetrachloride.

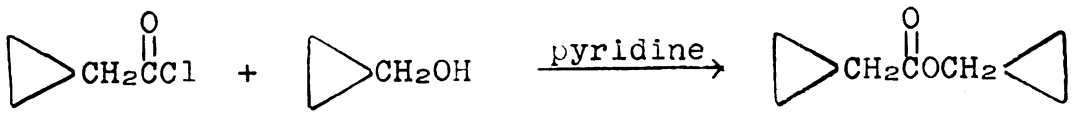
solution, which was then titrated with standard thiosulfate. Starch was used as the indicator, although the color was brown instead of purple.

V. THE DECOMPOSITION OF PERESTERS

The perester was dissolved in sufficient carbon tetrachloride to make an approximately 0.06 N solution. Portions of this solution were sealed in ampoules, placed in an oil bath maintained at the desired temperature and allowed ten minutes to attain thermal equilibrium. The first sample was taken as zero-time; samples were taken at intervals and frozen in dry-ice until analyzed. They were thawed and the peroxide content determined spectrophotometrically. The kinetics were determined by following the rate of disappearance of the 5.62μ band, which is characteristics of peroxide carbonyls. The rate constants were obtained from the transmissions by means of the equation listed on page 87.

VI. MISCELLANEOUS EXPERIMENTS

A. The Preparation of Cyclopropylcarbinyl Cyclopropaneacetate



A 125-ml. Erlenmeyer flask was charged with 20 ml. of dry pyridine, 2.6 g. (0.022 moles) of cyclopropaneacetyl chloride and 1.6 g. (0.022 moles) of cyclopropylcarbinol.

The flask was stoppered and the mixture was allowed to stand at room temperature for two hours, after which it was diluted with 50-ml. of ether. The ether solution was washed with two 50-ml. portions of water, then with 25 ml. of 10% sodium carbonate and again with 50-ml. of water. After drying over magnesium sulfate and filtering, the ether was removed under reduced pressure. The remaining liquid was distilled through a small Vigreux column and 2.1 g. (62%) of the ester was obtained, b.p. 65-66°/2 mm.; n_D^{25} 1.4470.

Lit. values (40) b.p. 63-65°/2 mm.; n_D^{25} 1.4475

The infrared spectrum of the ester is shown in Figure 17.

B. <u>The Preparation of Cyclopropylcarbinyl Trichloroacetate</u>

A mixture of 4 g. (0.024 moles) of trichloroacetyl chloride, prepared by the action of thionyl chloride on trichloroacetic acid, and 1.8 g. (0.025 moles) of cyclopropylcarbinol in twenty milliliters of dry pyridine was allowed to stand, with occasional shaking, for three hours. Fifty milliliters of ether were added and the mixture was washed successively with 50 ml. of water, 25 ml. of cold 10% sulfuric acid, 25 ml. of 10% sodium carbonate solution and finally again with 50 ml. of water. After the ether solution was dried and filtered, the solvent was removed under reduced pressure. Distillation of the remaining liquid through a small Vigreux column afforded 2.8 g. (0.014 moles) of material boiling from 81-85°/5 mm.;

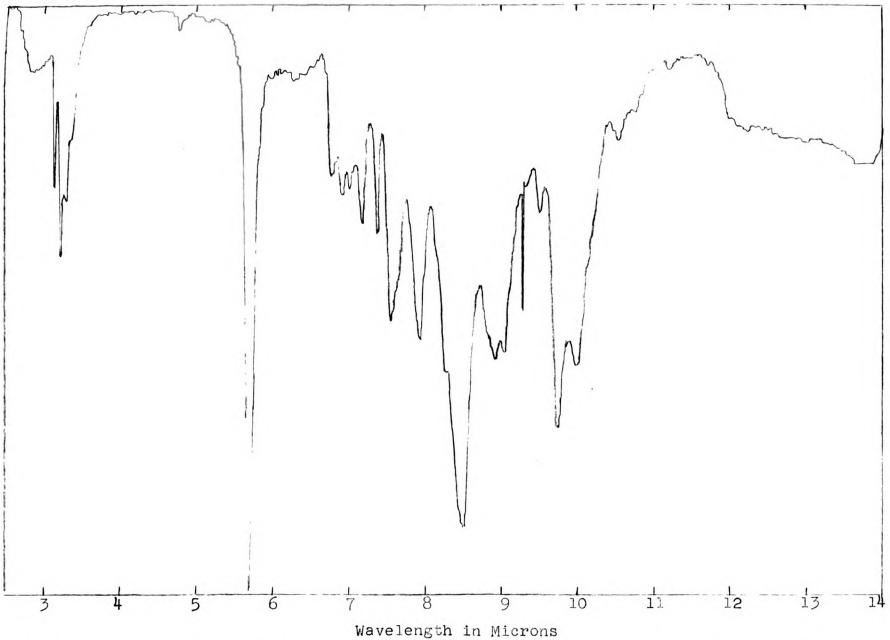


Figure 17. Infrared Spectrum of Cyclopropylcarbinyl Cyclopropaneacetate in Carbon Tetrachloride.

n_D 1.4690. The infrared spectrum (Figure 18) showed a carbonyl absorption at 5.67μ.

C. Reaction of Cyclopropaneacetic Acid with Sulfuric Acid

A mixture of 1 g. of cyclopropaneacetic acid and 15 ml. of 20% sulfuric acid was refluxed for thirty minutes and, upon cooling, extracted with 25 ml. of carbon tetrachloride. After the extract was dried over calcium sulfate and filtered, an infrared spectrum was taken. In addition to an acid carbonyl peak (5.87μ), a band at 5.63μ was present. This is the range of γ-lactones and the peak is ascribed to the presence of β-methyl-γ-butyrolactone.

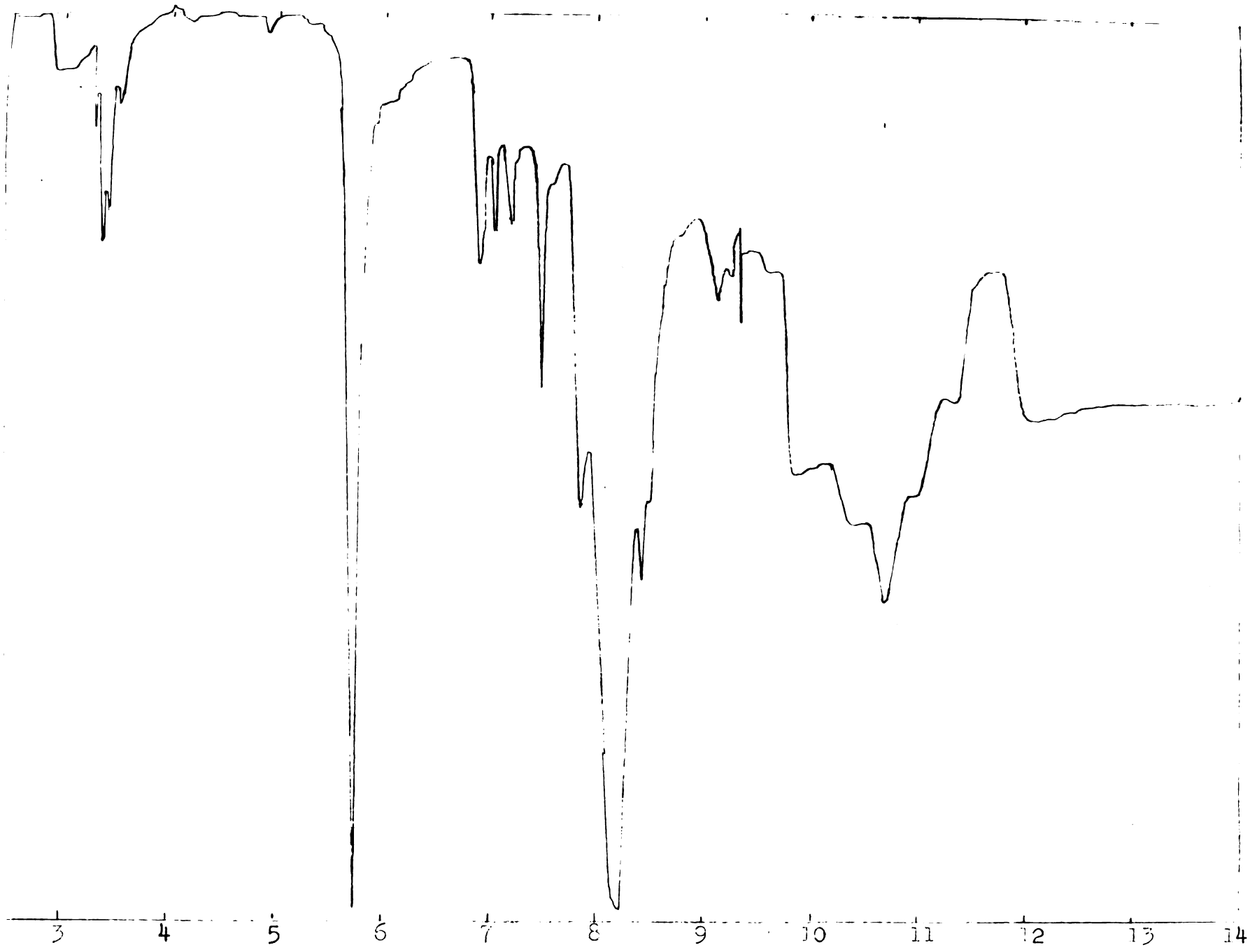


Figure 18. Infrared Spectrum of Cyclopropylcarbinyl Trichloroacetate in Carbon Tetrachloride.

LITERATURE CITED

1. H. Hart and D. P. Wyman, J. Am. Chem. Soc., 81, 4891 (1959).

2. P. D. Bartlett and R. R. Hiatt, J. Am. Chem. Soc., 80, 1398 (1958).

3. P. D. Bartlett and D. M. Simons, J. Am. Chem. Soc., 82, 1753 (1960).

4. P. D. Bartlett and C. Rüchhardt, J. Am. Chem. Soc., 82, 1756 (1960).

5. J. D. Roberts and V. C. Chambers, J. Am. Chem. Soc., 73, 3176 (1951).

6. L. I. Smith and S. MacKenzie, J. Org. Chem., 15, 74 (1950).

7. J. H. Turnbull and E. S. Wallis, J. Org. Chem., 21, 663 (1956).

8. S. D. Rosenburg, A. J. Gibbons, Jr., and H. E. Ramsden, J. Am. Chem. Soc., 79, 2137 (1957).

9. H. Hart and A. Holzschuh, unpublished results.

10. K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Wilson, J. Chem. Soc., 39, (1946).

11. C. Walling, "Free Radicals in Solution", John Wiley and Sons, Inc., New York, 1957, pp. 474-503.

12. A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides", Interscience Publishers, Inc., New York, 1954, pp. 72-87.

13. J. Hine, "Physical Organic Chemistry", McGraw-Hill Book Co., Inc., New York, 1956, pp. 412-419.

14. E. S. Gould, "Mechanisms and Structure in Organic Chemistry", Henry Holt and Comp., New York, 1959, pp. 714-720.

15. A. V. Tobolsky and R. B. Mesrobian, loc. cit., p. 107.

16. W. E. Cass, J. Am. Chem. Soc., 68, 1976 (1946).

17. K. Nozaki and P. D. Bartlett, J. Am. Chem. Soc., 68, 1686 (1946).

18. J. E. Leffler, J. Am. Chem. Soc., 72, 67 (1950).

19. M. Szwarc, Chem. ~~Revs~~ Rev., 47, 75 (1950).

20. C. Walling, loc. cit., p. 478.

21. G. S. Hammond and L. M. Soffer, J. Am. Chem. Soc., 72, 4711 (1950).

22. G. S. Hammond, J. T. Rudesill, and F. J. Modic, J. Am. Chem. Soc., 73, 3929 (1951).

23. D. B. Denney and G. Feig, J. Am. Chem. Soc., 81, 5322 (1959).

24. P. D. Bartlett and J. E. Leffler, J. Am. Chem. Soc., 72, 3030 (1950).

25. C. Walling, loc. cit., p. 493.

26. A. Rembaum and M. Szwarc, J. Chem. Phys., 23, 909 (1955).

27. D. F. DeTar and C. Weis, J. Am. Chem. Soc., 78, 4296 (1956).

28. J. D. Roberts and V. C. Chambers, J. Am. Chem. Soc., 73, 5034 (1951).

29. A. Streitwieser, Chem. ~~Revs~~ Rev., 56, 571 (1956).

30. R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, J. Am. Chem. Soc., 81, 4390 (1959).

31. C. G. Overberger and A. Lebowits, J. Am. Chem. Soc., 76, 2722 (1954).

32. J. D. Roberts and R. H. Mazur, J. Am. Chem. Soc., 73, 2509 (1951).

33. Private Communication to Professor Hart.

34. H. Hart and H. H. Lau, unpublished results.

35. L. F. Fieser, "Experiments in Organic Chemistry", 2nd. Edit., D. C. Heath Comp., Boston, 1941, p. 365.

36. L. S. Silbert and D. Swern, J. Am. Chem. Soc., 81, 2364 (1959).

37. D. B. Denney and D. Z. Denney, J. Am. Chem. Soc., 82, 1389 (1960).

38. L. Horner and H. Junkermann, Ann., 591, 53 (1955).

39. M. S. Kharasch, J. Kuderna and W. Nudenberg, J. Org. Chem., 19, 1283 (1954).

40. D. P. Wyman, Doctoral Thesis, Michigan State Univ., 1957.

41. C. Walling, loc. cit., p. 476.

42. H. H. Lau and H. Hart, J. Am. Chem. Soc., 81, 4897 (1959).

43. C. Walling, loc. cit., p. 152.

44. P. D. Bartlett, Organic Symposium, Seattle, June, 1957.

45. C. Walling, loc. cit., p. 491.

46. C. G. Bergstrom and S. Siegel, J. Am. Chem. Soc., 74, 145 (1952).

47. M. R. Fenske and H. Hart; unpublished results.

48. J. D. Roberts and P. H. Dirstine, J. Am. Chem. Soc., 67, 1281 (1945).

49. "Organic Syntheses", 24, 36 (1944).

50. L. Fieser, loc. cit., p. 395.

51. P. D. Bartlett and R. R. Hiatt, loc. cit., p. 1403.

52. Reference 2, footnote 6.

53. A. R. Frost and R. G. Pearson, "Kinetics and Mechanisms", John Wiley and Sons, Inc., New York, 1953, p. 96.

APPENDIX

Derivation of Equation Used in Calculating Rate Constants.

The equation used to follow the decomposition spectrophotometrically was obtained by the following manipulations. From the equation for a first-order reaction, one has

$$\log c = \frac{-kt}{2.303} + \log c_o \ , \tag{1}$$

where c_o is the initial concentration of peroxide and c the concentration at time t. From Beer's law,

$$c = \frac{2.303}{k'l'} \log \frac{I_o}{I} = \frac{2.303}{k'l'} \log \frac{1}{Tr} \ , \tag{2}$$

where I and I_o are the intensities, k' the absorption coefficient, l' the length of the cell and Tr the transmission. Combining (1) and (2), one obtains

$$\log(\frac{2.303}{k'l'} \log \frac{1}{Tr}) = \frac{-kt}{2.303} + \log c_o \ . \tag{3}$$

Further,

$$\log \log \frac{1}{Tr} = \frac{-kt}{2.303} + \log c_o - \log \frac{2.303}{k'l'} \ . \tag{4}$$

Then

$$\log(-\log Tr) = \frac{-kt}{2.303} + \log c_o - \log \frac{2.303}{kl'} \ . \tag{5}$$

Combining all of the constants,

$$\log(-\log Tr) = \frac{-kt}{2.303} + K \ . \qquad (6)$$

The rate constants were obtained by plotting log (-log Tr) versus t and multiplying the slope of the line, which was obtained by the method of least squares, by 2.303.

The enthalpy of activation, ΔH^*, was calculated using a form of the Eyring equation (53)

$$\log \frac{k}{T} = \frac{-\Delta H^*}{2.303\ RT} + Z \ , \qquad (7)$$

where R is the gas constant, T the temperature in degrees Kelvin and Z a constant.

The entropy of activation, ΔS^*, was calculated directly from the Eyring Equation (53)

$$k = \frac{k_b T}{h} e^{\Delta S^*/R} e^{- \Delta H^*/RT} \ , \qquad (8)$$

where h is Planck's constant, 6.62×10^{-27} erg. sec., and k_b is Boltzmann's constant, 1.37×10^{-16} erg. $deg.^{-1}$.

DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 14

Temp. 44.0° Conc. 0.06 N
$k = 5.30 \pm .30 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.072
2.	20	.080
3.	39	.109
4.	57	.119
5.	93	.152
6.	108	.159
7.	133	.189
8.	165	.219
9.	200	.259
10.	264	.318

TABLE 15

Temp. 44.0° Conc. 0.06 N
$k = 5.07 \pm .21 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.090
2.	26	.115
3.	67	.162
4.	93	.177
5.	120	.211
6.	151	.239
7.	179	.264
8.	207	.294
9.	233	.314
10.	257	.338

DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 16

Temp. 49.8° Conc. 0.018 N
$k = 1.11 \pm .02 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	25	.605
2.	40	.637
3.	65	.681
4.	85	.726
5.	105	.745
6.	125	.771

TABLE 17

Temp. 50.8° Conc. 0.046 N
$k = 1.24 \pm .04 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	10	.264
2.	25	.314
3.	35	.338
4.	50	.388
5.	75	.463
6.	90	.498
7.	105	.532
8.	120	.562
9.	140	.597

DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 18

Temp. 50.8° Conc. 0.055 N
$k = 1.30 \pm .06 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	20	.218
2.	35	.282
3.	45	.317
4.	60	.356
5.	80	.428
6.	90	.450
7.	106	.485
8.	125	.515
9.	140	.364

TABLE 19

Temp. 50.8° Conc. 0.092 N
$k = 1.23 \pm .07 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	15	.099
2.	30	.122
3.	45	.150
4.	60	.205
5.	80	.258
6.	100	.302
7.	120	.340
8.	150	.395

DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 20

Temp. 56.7° Conc. 0.09 N
$k = 2.58 \pm .18 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.075
2.	7	.102
3.	16	.150
4.	24	.195
5.	32	.240
6.	40	.290
7.	48	.320

TABLE 21

Temp. 56.7° Conc. 0.09 N
$k = 2.57 \pm .24 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.072
2.	7	.105
3.	13	.135
4.	20	.170
5.	28	.228
6.	37	.278
7.	45	.322
8.	51	.345
9.	62	.380
10.	73	.420

DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 22

Temp. 56.5°
Conc. Peroxide 0.09 N

$k = 2.78 \pm .03 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.075
2.	7	.092
3.	14	.136
4.	21	.178
5.	28	.201
6.	35	.236
7.	43	.286
8.	50	.321

TABLE 23

Temp. 56.5°
Conc. Peroxide 0.09 N
Conc. Iodine 0.07 N
$k = 2.94 \pm .12 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.079
2.	6	.112
3.	12	.137
4.	19	.172
5.	28	.224
6.	34	.259
7.	41	.292

DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 24

Temp. 56.5°
Conc. Peroxide 0.055 N
Conc. Iodine 0.05 N
$k = 2.80 \pm .26 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.208
2.	6	.248
3.	12	.294
4.	18	.338
5.	25	.378
6.	31	.408
7.	37	.445
8.	43	.472
9.	50	.500

TABLE 25

Temp. 56.5°
Followed Titrimetrically
$N(Na_2S_2O_3) = 0.0115$
$k = 2.55 \pm .14 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Titer, ml.
1.	0	4.40
2.	9	3.72
3.	16	3.38
4.	27	2.78
5.	35	2.48
6.	42	2.35

DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 26

Temp. 44.5°
Followed Titrimetrically
$N(Na_2S_2O_3) = 0.0115$
$k = 4.93 \pm .12 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Titer, ml.
1.	60	2.15
2.	120	1.73
3.	256	1.19
4.	331	0.96

Using the infrared technique
$k = 5.03 \pm .24 \times 10^{-5}$ sec.$^{-1}$

TABLE 27

Temp. 44.5°
Followed Titrimetrically
$N(Na_2S_2O_3) = 0.0115$
$k = 5.07 \pm .32 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Titer, ml.
1.	0	2.84
2.	30	2.57
3.	62	2.40
4.	90	2.19
5.	120	2.04

DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 28

Temp. 44.5°
Solution washed with aqueous 10% sodium carbonate.
$k = 5.03 \pm .19 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.251
2.	30	.280
3.	60	.315
4.	87	.345
5.	120	.390

TABLE 29

Temp. 44.5° Conc. 0.186 N

Followed Titrimetrically
$N(Na_2S_2O_3) = 0.0115$ N

Sample	Time, min.	Titer, ml.
1.	0	16.12
2.	68	11.38
3.	124	8.34
4.	189	6.00
5.	243	5.04
6.	362	4.17
7.	440	3.11
8.	536	2.59

As the concentration approached 0.09 N, the rate constant approached 5×10^{-5} sec.$^{-1}$

DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 30

Temp. 44.5°
Conc. Peroxide 0.042 N
Conc. Acetic Acid 0.014 N
$k = 4.65 \pm .18 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.239
2.	30	.271
3.	59	.307
4.	88	.336
5.	123	.336
6.	149	.397
7.	177	.447
8.	211	.447

TABLE 31

Temp. 44.5°
Conc. Peroxide 0.048 N
Conc. Trimethylacetic Acid 0.043 N
$k = 4.64 \pm .14 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.201
2.	30	.231
3.	80	.286
4.	107	.307
5.	127	.332
6.	158	.362
7.	194	.402
8.	226	.432
9.	265	.460

DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 32

Temp. 44.5°
Conc. Peroxide 0.05 N
Conc. Pyridine 0.03 N
$k = 6.86 \pm .12 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.297
2.	40	.352
3.	80	.414
4.	104	.453
5.	128	.492
6.	170	.542
7.	198	.543
8.	218	.591

TABLE 33

Temp. 44.5°
Conc. Peroxide 0.061 N
Trichloroacetic Acid 0.061 N
Followed Titrimetrically
$N(Na_2SO_2O_3) = 0.0115$
$k = 6\text{-}8 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Titer, ml.
1.	0	8.93
2.	19	3.95
3.	48	1.80
4.	69	0.98
5.	91	0.51

DECOMPOSITION OF CYCLOPROPANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 34

Temp. 44.5°
Conc. Peroxide 0.061 N
Trichloroacetic Acid 0.030 N
Followed Titrimetrically
$N(Na_2SO_2O_3)$ = 0.0115
$k = 3 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Titer, ml.
1.	0	8.87
2.	15	6.17
3.	30	5.48
4.	45	3.75
5.	61	3.38

TABLE 35

Temp. 44.5°
Conc. Peroxide 0.061 N
Trichloroacetic Acid 0.015 N
Followed Titrimetrically
$N(Na_2SO_2O_3)$ = 0.0115
$k = 1.3 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Titer, ml.
1.	0	9.71
2.	20	7.48
3.	41	6.14
4.	67	5.17
5.	93	4.83

DECOMPOSITION OF CYCLOHEXANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 36

Temp. 44.4°
Conc. Peroxide 0.06 N
$k = 3.08 \pm .08 \times 10^{-6}$ sec.$^{-1}$

Sample	Time, hrs.	Trans.
1.	24	.145
2.	46.5	.240
3.	67.5	.310
4.	90	.400

TABLE 37

Temp. 64.3°
Conc. Peroxide 0.06 N
$k = 1.14 \pm .53 \times 10^{-6}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.061
2.	90	.080
3.	180	.102
4.	270	.114
5.	360	.124
6.	460	.142
7.	540	.157
8.	630	.175
9.	720	.188

DECOMPOSITION OF CYCLOHEXANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 38

Temp. 64.3°
Conc. Peroxide 0.06 N
Conc. Iodine 0.18 N
$k = 1.23 \pm .04 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.113
2.	90	.139
3.	210	.165
4.	330	.191
5.	450	.222
6.	570	.247
7.	690	.278
8.	785	.299

TABLE 39

Temp. 71.8°
Conc. Peroxide 0.06 N

$k = 2.95 \pm .11 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.137
2.	90	.185
3.	180	.251
4.	270	.307
5.	360	.368
6.	495	.455
7.	570	.497
8.	655	.550
9.	770	.593

DECOMPOSITION OF CYCLOHEXANEACETYL PEROXIDE IN CARBON TETRACHLORIDE

TABLE 40

Temp. 71.8°
Conc. Peroxide 0.06 N
Conc. Pyridine 0.056 N
$k = 4.83 \pm .21 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.129
2.	87	.191
3.	180	.296
4.	238	.345
5.	302	.412
6.	350	.474
7.	437	.570
8.	498	.634
9.	585	.704
10.	692	.732

TABLE 41

Temp. 64.3°
Conc. Peroxide 0.06 N
Trichloroacetic Acid 0.068 N
Followed Titrimetrically
$N(Na_2SO_2O_3) = 0.0115$
$k = 4.47 \pm .15 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Titer, ml.
1.	0	4.72
2.	120	3.79
3.	211	3.00
4.	300	2.20
5.	390	1.85
6.	493	1.37
7.	634	0.95

DECOMPOSITION OF t-BUTYL CYCLOHEXANEPERCARBOXYLATE IN CARBON TETRACHLORIDE

TABLE 42

Temp. 89.6°
$k = 2.35 \pm .15 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, hrs.	Trans.
1.	0	.119
2.	1	.146
3.	2	.167
4.	3	.182
5.	4	.221
6.	5	.253
7.	6	.303
8.	7	.316
9.	8	.322

TABLE 43

Temp. 89.6°
$k = 2.33 \pm .11 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, hrs.	Trans.
1.	0	.135
2.	2.2	.201
3.	3.5	.239
4.	5	.276
5.	6.5	.338
6.	8	.369
7.	10	.425

DECOMPOSITION OF t-BUTYL CYCLOHEXANEPERCARBOXYLATE IN CARBON TETRACHLORIDE

TABLE 44

Temp. 100°
$k = 9.48 \pm .72 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	20	.093
2.	40	.121
3.	60	.170
4.	80	.226
5.	100	.262
6.	120	.296
7.	140	.343
8.	160	.383
9.	180	.411
10.	240	.497

TABLE 45

Temp. 100°
$k = 9.28 \pm .67 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.196
2.	20	.247
3.	40	.325
4.	60	.386
5.	80	.419
6.	100	.450
7.	120	.510
8.	140	.531
9.	160	.550
10.	180	.588
11.	240	.673
12.	270	.696

DECOMPOSITION OF t-BUTYL CYCLOHEXANEPERCARBOXYLATE IN CARBON TETRACHLORIDE

TABLE 46

Temp. 110°
$k = 2.00 \pm .34 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.062
2.	15	.175
3.	30	.266
4.	45	.375
5.	60	.416
6.	75	.477
7.	90	.507
8.	105	.562

TABLE 47

Temp. 110°
$k = 2.20 \pm .34 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	10	.136
2.	20	.182
3.	30	.300
4.	40	.338
5.	50	.388
6.	60	.476
7.	70	.497
8.	80	.526
9.	90	.536
10.	105	.549

DECOMPOSITION OF t-BUTYL CYCLOPROPANEPERCARBOXYLATE IN CARBON TETRACHLORIDE

TABLE 48

Temp. 110°
$k = 6.86 \pm .38 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.177
2.	30	.227
3.	60	.252
4.	90	.302
5.	120	.336
6.	140	.385
7.	160	.427
8.	180	.427
9.	210	.491

TABLE 49

Temp. 110°
$k = 6.68 \pm .29 \times 10^{-5}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.188
2.	30	.245
3.	30	.234
4.	60	.271
5.	80	.294
6.	80	.307
7.	100	.330
8.	110	.346
9.	110	.340
10.	150	.408
11.	180	.458

DECOMPOSITION OF t-BUTYL CYCLOPROPANEPERCARBOXYLATE IN CARBON TETRACHLORIDE

TABLE 50

Temp. 120°
$k = 2.07 \pm .14 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.205
2.	12	.237
3.	36	.343
4.	48	.429
5.	60	.492
6.	72	.528
7.	72	.515
8.	84	.542

TABLE 51

Temp. 120°
$k = 2.02 \pm .14 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.190
2.	12	.235
3.	13	.244
4.	25	.270
5.	26	.304
6.	38	.345
7.	39	.359
8.	51	.415
9.	52	.410
10.	66	.474
11.	78	.513
12.	79	.529

DECOMPOSITION OF t-BUTYL CYCLOPROPANEPERCARBOXYLATE IN CARBON TETRACHLORIDE

TABLE 52

Temp. 129°
$k = 4.83 \pm .10 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	0	.219
2.	5	.265
3.	6	.289
4.	11	.333
5.	12	.355
6.	17	.397
7.	18	.406

TABLE 53

Temp. 129°
$k = 4.98 \pm .10 \times 10^{-4}$ sec.$^{-1}$

Sample	Time, min.	Trans.
1.	5	.251
2.	10	.313
3.	15	.366
4.	20	.415
5.	25	.472

CHEMISTRY LIBRARY