PRODUCTS AND RATES OF DECOMPOSITION OF SOME t-BUTYL PERTHENOATES

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Joseph L. Shea
1963

THESIS

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Joseph L. Shea

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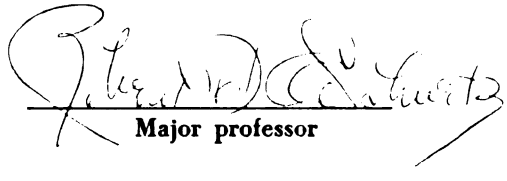

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ABSTRACT

PRODUCTS AND RATES OF DECOMPOSITION OF SOME t-BUTYL PERTHENOATES

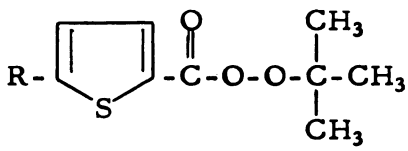
by Joseph L. Shea

The purpose of this investigation was to obtain information concerning the behavior of free radicals in the t-butyl perthenoate system. Six t-butyl perthenoates were prepared, and their rates and products of decomposition in carbon tetrachloride were studied. The kinetic determinations were carried out both in the presence and absence of a radical scavenger.

In the presence of a radical scavenger, the rates of decomposition are first order. In the absence of a scavenger, the rates of decomposition are faster than first order and increase with increasing initial perester concentration. This is good evidence for an induced decomposition step superimposed upon the first order, spontaneous cleavage of the oxygen-oxygen bond.

The Guggenheim method was used to treat the kinetic data in those determinations conducted in the absence of a radical scavenger. The relative rates of decomposition of the various t-butyl perthenoates at 124.5° in carbon tetrachloride are given below.

In the presence of a radical scavenger, examination of the rate constants shows that the presence of electron-donating substituents on the thiophene ring accelerates the rate of decomposition, while electron-withdrawing substituents have the opposite effect. In the absence of a scavenger, the slight decrease in rate of the alkyl-substituted perthenoates may be the result of a self-inhibition process.



Compound	Relative Rate 0.2M in Styrene	Relative Rate No Scavenger
R = H	1	1
CH_3	1.16	0.915
C_2H_5	1.15	0.915
Cl	0.642	0.642
Br	0.626	0.428

The products of decomposition of the unsubstituted t-butyl perthenoate in carbon tetrachloride include carbon dioxide, 2-thenoic acid, acetone and 2-t-butylthenoate. When the same compound is decomposed in chlorobenzene, carbon dioxide, 2-thenoic acid, and, most probably, a mixture of two esters, 2-phenylthenoate and 2(p-chlorophenyl) thenoate are isolated.

Several miscellaneous experiments involving the decomposition in several solvents of thiophene-2-sulfonyl chloride and the attempted preparation of 2(2-thienyl) thiirane are described.

PRODUCTS AND RATES OF DECOMPOSITION OF SOME t-BUTYL PERTHENOATES

By

Joseph L. Shea

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INTRODUCTION AND HISTORICAL

The chemistry of peroxyesters has been studied by only a few investigators. In 1951 Blomquist (1, 2, 3) and co-workers published the results of their studies on the thermal decomposition of t-butyl perbenzoate esters. During the last several years Bartlett (4, 5, 6) and his collaborators have investigated several series of peroxyesters including the t-butyl arylpersulfonates, t-butyl peracetates, and t-butyl peroxylates. Recently, Pincock (7) reported the preparation of t-butyl peroxyformate, which proved to be a highly stable perester. Other peroxyester systems have been reported, among them the 9-decalyl perbenzoate system (8). However, at present, there have been no reports of any detailed investigation of a peroxyester system containing a heterocyclic ring in the molecule. One purpose of the work discussed here was to investigate the feasibility of preparing and studying the chemistry of such compounds.

Due to previous interest in thiophene and its chemical properties in these laboratories the t-butyl perthenoates were selected for the initial study. This thesis, then, describes the preparation of several members of this series, their rates of thermal decomposition, and some of their decomposition products. Further, this work continues and expands the chemical studies of heterocyclic peroxides initiated in these laboratories by Schuetz and Teller (9) with their investigation of the bis(2-thenoyl) peroxides. Their investigation was the first published detailed study of such compounds, although the parent compound, bis-(2-thenoyl) peroxide, had been previously mentioned in the literature (10).

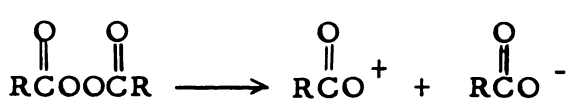
The decomposition of benzoyl peroxide has received exhaustive study in the past quarter of a century. The decomposition of the peroxide

provides a classic case of the thermal decomposition of an organic molecule in solution into reactive free radicals.

The decomposition of benzoyl peroxide follows a first order rate law in the majority of reaction media although the rate increases somewhat with increasing initial peroxide concentration in a given solvent and varies widely from one solvent to another. These facts indicate that the unimolecular cleavage of the peroxide is accompanied by a higher order reaction, which appears to be a radical-induced attack on undecomposed peroxide (11, 12). The induced decomposition can be effectively eliminated by the use of radical traps (12, 13) which inhibit the induced process, or by kinetic analysis (11, 14). Even then, the rate varies somewhat with the particular reaction solvent used, although the activation energy remains constant at approximately 30 kilocalories per mole.

Thus, it can be concluded that there are essentially two modes of diacyl peroxide decomposition, a spontaneous fission of the oxygen-oxygen bond homolytically to form radicals, equation (1), or heterolytically to form ions, equation (2), and the corresponding induced decomposition

(1)

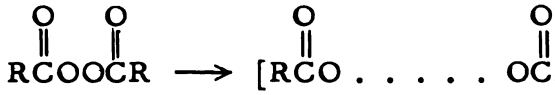


(2)

by radicals (11) or ions (15).

The decomposition of a dilute solution of a symmetrical peroxide in a non-polar solvent provides the most favorable experimental conditions for homolytic fission, while heterolytic fission is favored by a decrease in the symmetry of the molecule and the use of solvents of high polarity.

A major problem in an investigation of the homolytic mode of decomposition is the extent to which carbon-carbon bond breakage occurs in the rate-determining step. The peroxide decomposition can proceed in any or all of the three possible paths shown in equations (3), (4), and (5).



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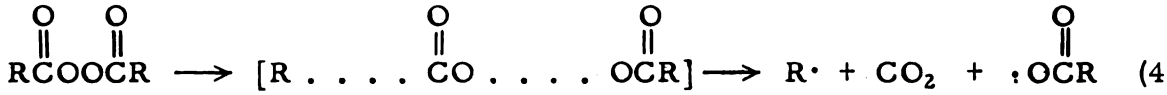

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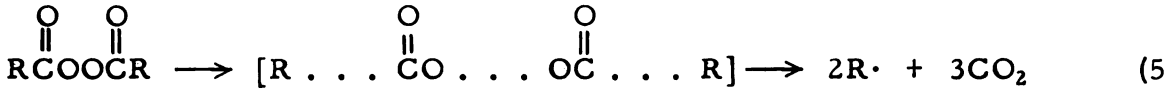
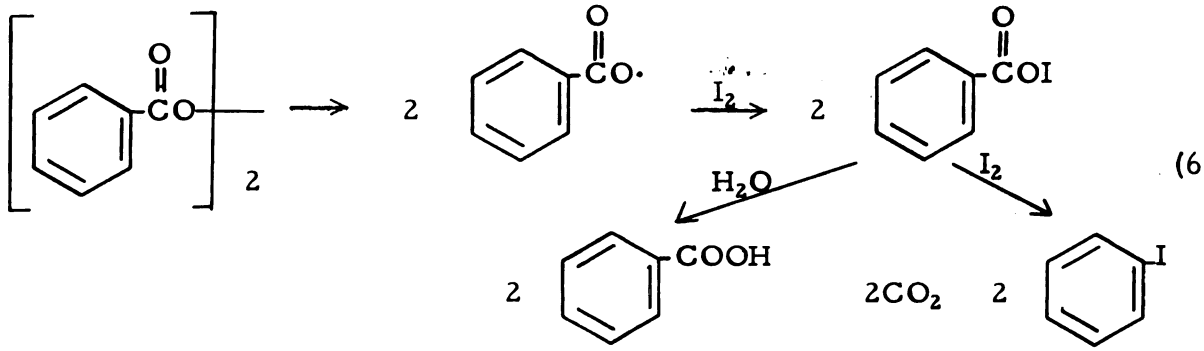


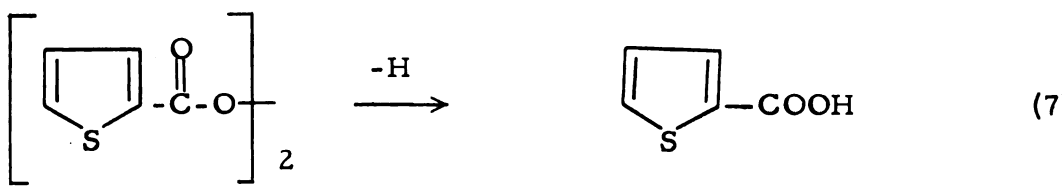
(5)

When R is an aryl group, equation (3) appears to best describe the spontaneous decomposition. Hammond and Sofer (13) obtained benzoic acid quantitatively by decomposing benzoyl peroxide in the presence of iodine and water. In the absence of water, iodobenzene was obtained in better than a 90% yield.



(6)

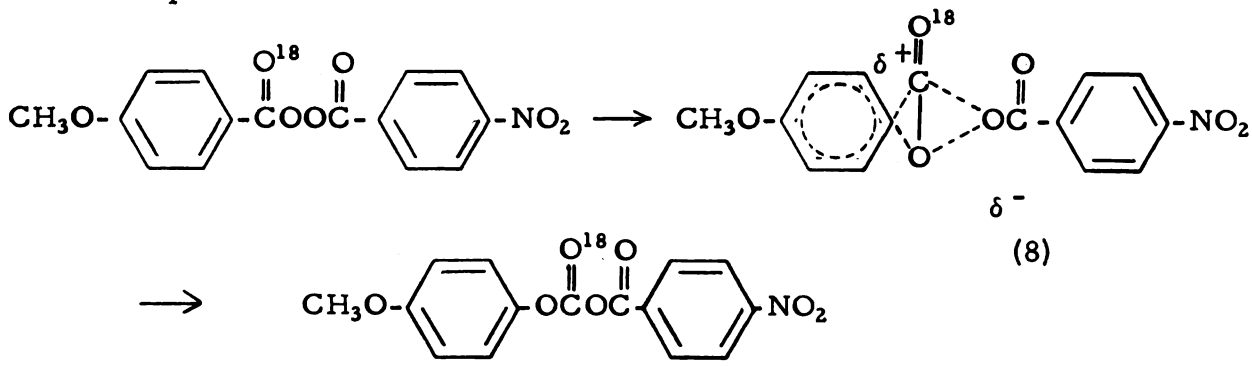
With the heterocyclic peroxides, Schuetz and Teller (9) have shown that even in the absence of inhibitors only small amounts of carbon dioxide are liberated. The major decomposition product in such systems is the corresponding acid.



(7)

On the other hand, Walling and Hodgdon (16) isolated methyl iodide as the major product from the decomposition of acetyl peroxide in the presence of iodine and water; no acetic acid was isolated. This result would support equation (5) as the mode of decomposition in this case. However, Szwarc (17) and also DeTar and Weis (18) have presented evidence which indicated that the failure of acetic acid to be formed from acetyl peroxide decomposition is due to the rapid loss of carbon dioxide from the acyloxy radical. Recently, Shine and Hoffman (19) have provided evidence for the existence of the acetoxy free radical.

In the heterolytic mode of decomposition of a peroxide the transition state can vary from a slight polarization of the oxygen-oxygen bond to complete dissociation into ions. In his study of the unsymmetrical 4-methoxy-4'-nitrobenzoyl peroxide, Leffler (15) found that this peroxide decomposes at the same rate as benzoyl peroxide in non-polar solvents. In polar solvents, however, the rate is increased markedly. Leffler attributed this rate enhancement to an ionic mechanism (equation 2) supplanting the homolytic fission. This conclusion is supported by the ability to induce decomposition by acids at a rate proportional to the acidity constant of the acid. Denney (20) further studied the mechanism of the decomposition of 4-methoxy-4'-nitrobenzoyl peroxide using isotopic tracer techniques. Using oxygen^{18}, he has shown that the oxygens do not equilibrate. This means the ions are not free, showing that the decomposition is not completely described by equation (2). Denney postulated the following mechanism for the decomposition of Leffler's unsymmetrical peroxide.



(8)

A number of textbooks contains excellent reviews of diacyl peroxide decompositions (21, 22, 23).

Of the diakyl peroxides, di-t-butyl peroxide has been studied in considerable detail. In the gas phase its decomposition follows a first order process and is independent of pressure (24). In various solvents it decomposes at essentially the same rate (25) as it does in the gas phase. This observation suggests as a rate-determining step a simple unimolecular process, equation (9), uncomplicated by any sort of induced

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (9)$$

chain process.

Blomquist and his collaborators (1, 2, 3) chose to investigate the t-butyl perbenzoates which, in a sense, are intermediate between the diacyl and the dialkyl peroxides. He and his co-workers have shown that the thermal decomposition of some t-butyl perbenzoates proceeds at about the same rate in aromatic solvents and at much faster and widely different rates in aliphatic solvents. They also observed that the overall rate of decomposition was dependent upon the initial perester concentration. Free radical inhibitors decreased the over-all rate of decomposition. Blomquist concluded from these results that the perester decomposition was essentially of the same complex nature as that of benzoyl peroxide; that is, a radical-induced decomposition superimposed upon the homolytic, unimolecular cleavage of the oxygen-oxygen bond. Blomquist has also found in his studies that trichloroacetic acid, but not dichloroacetic acid, accelerates perbenzoate decomposition, which suggested that a strong acid is necessary to make any part of the decomposition proceed by an ionic path. Surprisingly, he found the amount by which the rate increased was proportional to the square of the acid concentration, thus making the acid catalyzed decomposition of perbenzoates a third-order reaction;

second-order with respect to acid and first-order with respect to perbenzoate.

When a series of para-substituted perbenzoates was thermally decomposed under conditions in which only the spontaneous fission of the oxygen-oxygen bond was measured, Blomquist found an acceleration in rate when the substituent was electron-releasing and a decrease in rate when the substituent was electron-withdrawing. These results parallel those found in the benzoyl peroxide system. The rate constants and thermodynamic parameters for the thermal decomposition of the para-substituted perbenzoates are found in Table 1.

Since the decompositions all followed a first-order rate law, Blomquist assumed that no appreciable amount of induced decomposition was occurring under the experimental conditions employed; namely, dilute perester solutions in a non-polar solvent, diphenyl ether. However, he conducted several experiments employing the p-nitro perbenzoate ester, the most electrically unsymmetrical perester and hence the most susceptible to induced decomposition. In the benzoyl peroxide system, Swain and his co-workers (12) have shown that the bis(p-nitrobenzoyl) peroxide is most susceptible to induced radical attack. To the p-nitro perbenzoate ester, such known radical traps as ethyl urethan, acetanilide, styrene and dimethylfumerate were added, and the disappearance of perester was measured. In all cases, not one of the supposed inhibitors lowered the rate of decomposition. In fact, each one actually increased it. While no explanations for this rate enhancement were offered by Blomquist, the very fact that no decrease in rate was observed strongly supported the assumption that no appreciable amount of induced decomposition was occurring in this system and that, indeed, kinetic measurements were determining only the rate of the spontaneous fission of the oxygen-oxygen bond.

Table 1. Energy of Activation and Entropy of Activation and Rate Constants for the Decomposition of Various t-Butyl Perbenzoates in Diphenyl Ether

Compound	t, °C.	k, hr.$^{-1}$	E_a kcals, mole^{-1}	ΔS^* e.u.
p-Methoxy	100.1	.0386	35.8 ± .7	12.2 ± 1.5
	110.1	.150		
	120.2	.461		
	130.9	1.54		
p-Methyl	100.0	.0339	36.1 ± .7	12.6 ± 1.5
	110.0	.115		
	120.2	.380		
	130.9	1.17		
Unsubstituted	100.0	.0241	37.5 ± .7	15.8 ± 1.5
	110.1	.820		
	120.2	.324		
	130.9	1.05		
p-Chloro	100.0	.0410	39.3 ± .7	19.7 ± 1.5
	110.1	.0665		
	120.2	.230		
	130.9	.871		
p-Nitro	110.1	.0272	41.3 ± .7	23.7 ± 1.5
	120.2	.115		
	130.9	.401		
	141.5	1.41		

The rates of decomposition of the peresters were correlated very closely by means of the Hammett equation. A plot of log k/k_0 versus sigma had a negative slope, meaning that rho has a negative value as would be expected. The magnitude of rho was not given, however.

Blomquist also had assumed that no significant amount of heterolytic decomposition occurred when the peresters were decomposed in diphenyl

ether. An investigation of the activation energies for the peresters substituted with electron-withdrawing groups (Table 1) shows these values to be greater than the activation energy of the unsubstituted perester and the peresters substituted with electron-releasing groups. Since the greatest amount of ionic decomposition should occur in the most electrically unsymmetrical molecules, that is, those containing electron-withdrawing groups, lower rather than higher values for the activation energy of the negatively substituted molecules would be expected if there was appreciable heterolytic cleavage in their decomposition.

RESULTS AND DISCUSSION

I. Decomposition Products from t-Butyl Perthenoate

A. Products from Decomposition in Carbon Tetrachloride

A reasonably complete decomposition product study was carried out only with the unsubstituted perester, t-butyl perthenoate. In many respects, the products of this decomposition were consistent with the type of products obtained in the decomposition of aromatic diacyl peroxides. Unfortunately, a more direct comparison with aromatic t-butyl peresters was not possible since Blomquist and his co-workers did not report any products in their studies on aromatic peresters, nor have such reports appeared elsewhere in the literature. The decomposition products from the t-butyl perthenoate which were positively identified were acetone, thenoic acid, t-butyl 2-thenoate and carbon dioxide. Only the carbon dioxide was measured quantitatively since the decomposition was not clear-cut but involved the formation of considerable amounts of a black, insoluble material. The amount of thenoic acid could be estimated, however, by calculating the absorbance of the acid peak at 5.9 microns at the end of the kinetic run and relating absorbance to concentration. For all the peresters (in the absence of a radical scavenger) the amount of acid exceeded 60%. Usually, the combined acid and carbon dioxide accounted for approximately 75% of the decomposition products. The amount of t-butyl 2-thenoate was very small.

Acetone was an expected product since t-butoxy radicals are known to decompose to acetone and methyl radicals (24), equation (10).

$$(CH_3)_3C\text{-}O\cdot \longrightarrow CH_3COCH_3 + \cdot CH_3 \qquad (10)$$

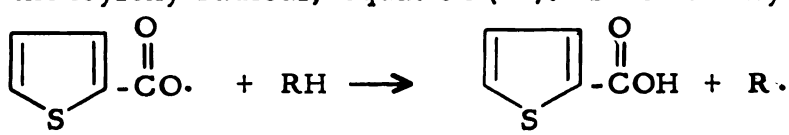
The activation energy of this reaction has been estimated at 11.2 ± 2 kcals. (26), but at the temperatures employed (> 100°) this energy barrier should be easily overcome, and reaction (10) would be expected to be very fast.

The t-butoxy radicals could also react by hydrogen abstraction from the solvent or some other species in the reaction mixture, and form t-butyl alcohol, equation (11). In a reaction mixture containing a

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \qquad (11)$$

source of readily abstractable hydrogen, it would be expected that reaction (11) would predominate over reaction (10) since the activation energy for the former reaction should be much less. Under the experimental conditions employed the only sources of abstractable hydrogen atoms are the thiophene ring and the t-butyl group. In the case of the thiophene ring the hydrogens are aromatic and in that of the t-butyl group they are all primary. Neither type of hydrogen is easily abstracted, so apparently the t-butoxy radicals decomposed by reaction (10) to the exclusion of reaction (11) since no t-butyl alcohol was isolated in the perthenoate decomposition.

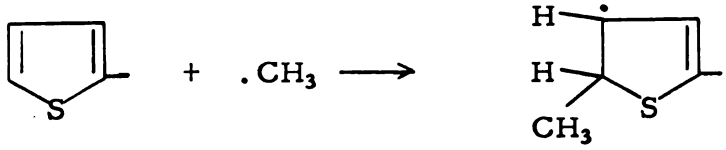
The formation of thenoic acid also involves hydrogen abstraction by the thenoyloxy radical, equation (12). Since the hydrogens from the



(12)

thiophene ring and the t-butyl group are not easily abstracted, the large amount of acid isolated requires that another source of abstractable hydrogen be available. This source can be postulated by considering the fate of the methyl radicals formed in equation (10). Levy and Szwarc (27) used acetyl peroxide as a source of methyl radicals. Upon decomposing acetyl peroxide in benzene, they showed that only about 25% of the methyl

radicals formed appeared as methane. Thus, methyl radical addition to the benzene ring must have been the chief path for the consumption of the methyl radicals. However, Levy and Szwarc did not determine the final products. The thiophene ring should be more susceptible to radical attack than benzene and the following equations illustrate the possible fate of the methyl radicals formed in reaction (10).



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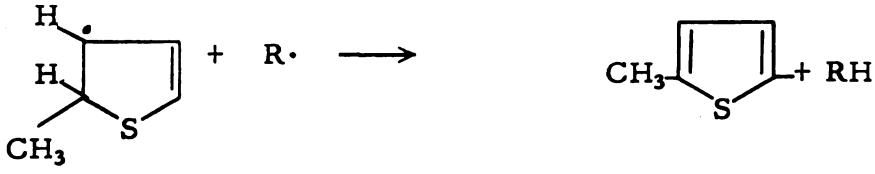
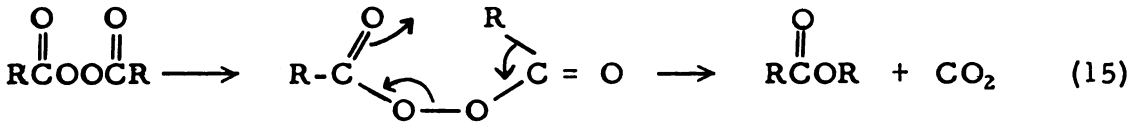


(14)

The initial addition product formed in equation (13) now contains an easily abstractable hydrogen and could be dehydrogenated easily by another radical as in equation (14). If this other radical was the thenoyloxy radical, this could account for the formation of acid. As no methylated thiophene derivatives were isolated from the perthenoate decomposition mixture, this scheme is, at best, only suggestive.

The formation of t-butyl 2-thenoate must occur by a mechanism different from that postulated for ester formation in the diacyl peroxide systems. In these systems two mechanisms have been postulated to account for the appearance of ester, a cyclic intramolecular process (18), equation (15) and a geminate recombination process (28), equation (16).



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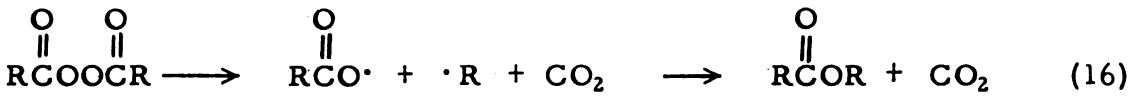
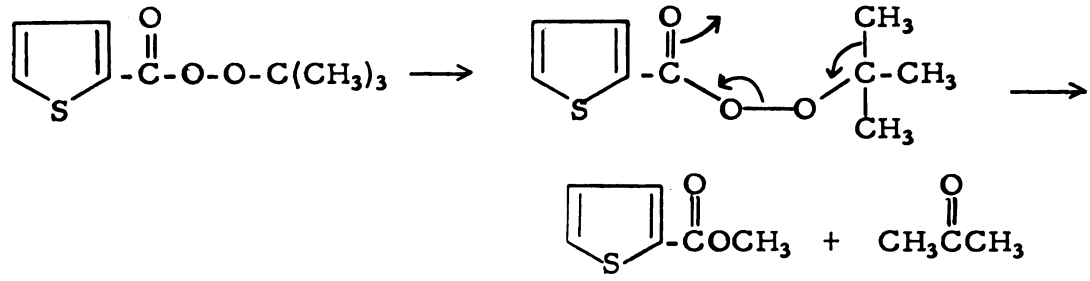


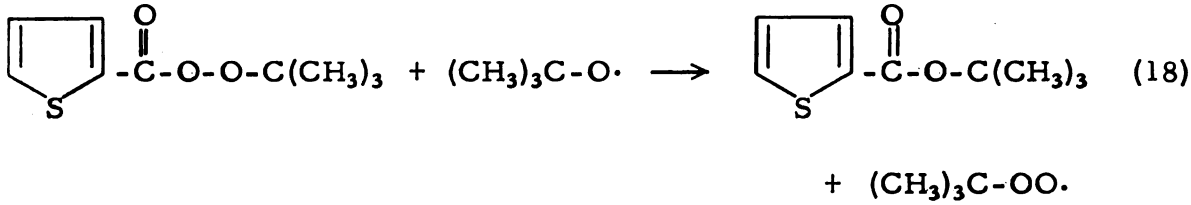
(16)

Obviously, a mechanism similar to equation (16) could not be written for the t-butyl perthenoate decomposition, but a mechanism similar to equation (15) could be written that would account for the formation of methyl 2-thenoate and acetone, equation (17). However, methyl



(17)

observed among the products. Perhaps the t-butyl 2-perthenoate was formed by a direct attack of a t-butoxy radical on the carbonyl group of a perester molecule, equation (18).



(18)

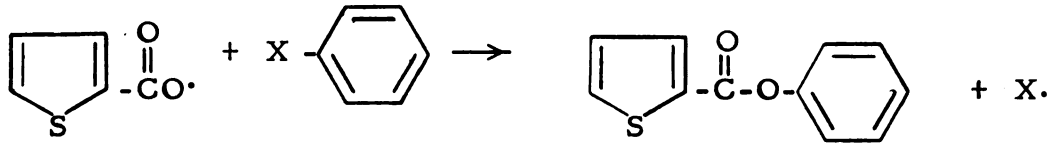
While it is desirable to write a mechanism for the t-butyl perester decomposition, the data presently at hand are insufficient for this purpose. A more thorough investigation of the decomposition products of the perthenoates is necessary before even a suggestive mechanism can be written.

B. Products from Decomposition in Chlorobenzene

The various perthenoates were decomposed in chlorobenzene at its reflux temperature and analyzed for carbon dioxide. The analysis is discussed in a later section of this thesis. The chlorobenzene solution

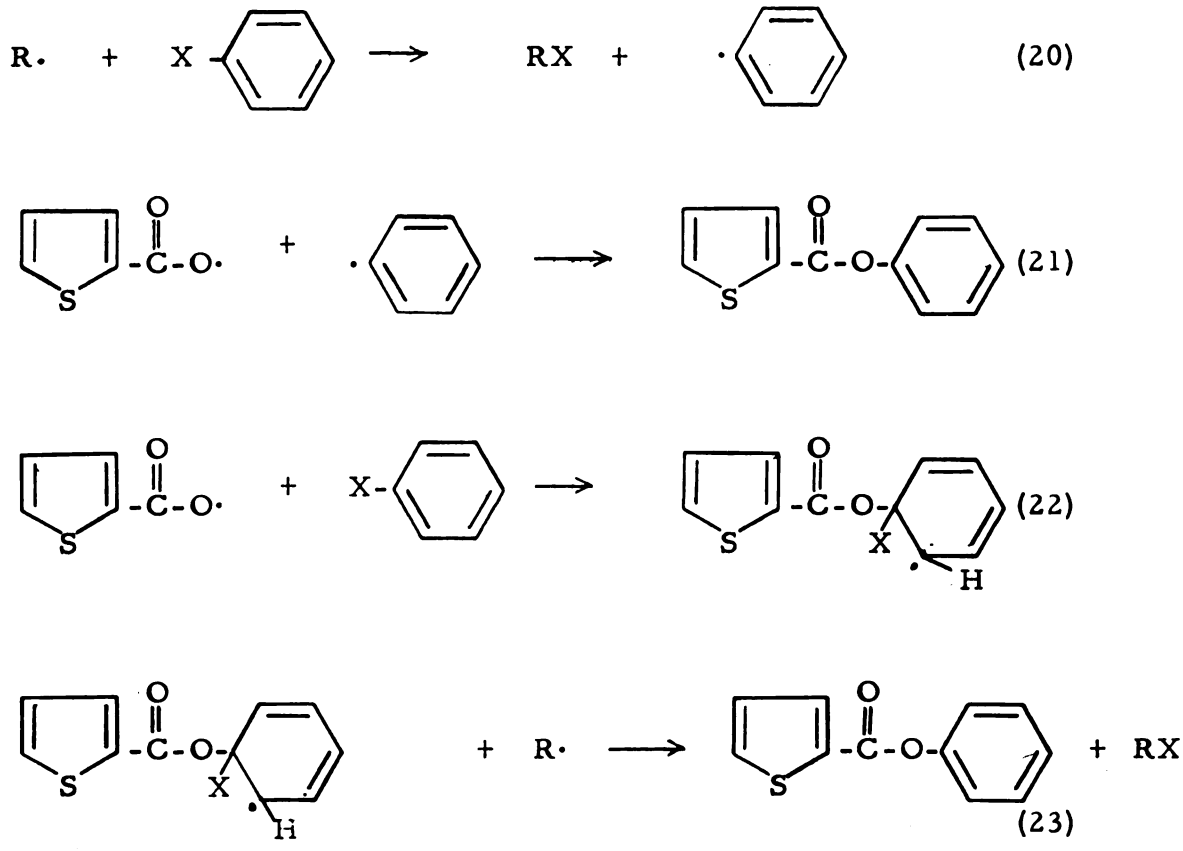
of t-butyl 2-perthenoate, after total perester decomposition, was investigated with the aim of isolating a product or products which would show the fate of the thenoyloxy radical generated in the aromatic solvent. Besides thenoic acid, the only other product isolated was most probably phenyl 2-thenoate, although some p-chlorophenyl 2-thenoate could also have been present. The proof of structure of this compound rests solely on its infrared spectrum, which makes positive identification impossible since the spectra of pure, known samples of phenyl 2-thenoate and p-chlorophenyl 2-thenoate are very similar.

Ford and Mackay (10) decomposed 2-thenoyl peroxide in chlorobenzene, bromobenzene and iodobenzene. They isolated p-chlorophenyl 2-thenoate and phenyl 2-thenoate from the chlorobenzene decomposition, p-bromophenyl 2-thenoate and phenyl 2-thenoate from bromobenzene along with the evolution of hydrogen bromide. With iodobenzene, only phenyl 2-thenoate and free iodine were isolated. In chlorobenzene and bromobenzene, the unsubstituted ester was the predominant ester product, while with iodobenzene the unsubstituted ester was the only ester product. These observations indicate that the primary ester-forming reaction involves a displacement of the halogen of the solvent by the thenoyloxy radical, equation (19).



(19)

This is not to imply that the formation of phenyl 2-thenoate is actually a bimolecular radical displacement reaction. The ester formation could just as well involve either or both of the following mechanisms, equations (20) and (21) or (22) and (23).



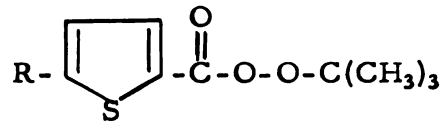
Equations (22) and (23) appears to be the most probable scheme since this is the presently accepted method of radical attack on an aromatic ring.

C. Carbon Dioxide Analyses

The quantitative determination of the carbon dioxide liberated during decomposition of the various peresters was made by decomposing a chlorobenzene solution of the perthenoate at the reflux temperature of the solvent for a period of at least ten half-lives of the perester. Carbon dioxide evolved was absorbed on Ascarite and weighed. The results are listed in Table 2.

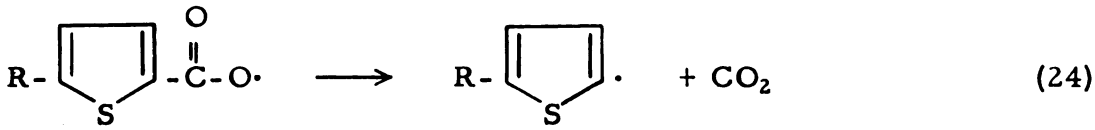
These data are somewhat difficult to rationalize. It can be said that when R = H, CH_3, C_2H_5, and NO_2, the amount of carbon dioxide evolved is essentially constant, about 15%. When R = Cl and Br, the amount

Table 2. Amount of Carbon Dioxide Evolved from the Decomposition of t-Butyl Perthenoates in Chlorobenzene



Perester	Percent Carbon Dioxide
R = H	15.7 ± 3
Br	28.7 ± 3
Cl	32.0 ± 3
CH_3	15.5 ± 3
C_2H_5	15.0 ± 3
NO_2	18.3 ± 3

evolved is about 30%. These results could mean that the activation energy for reaction (24) is less when the substituent is a halogen than when the



(24)

substituent is alkyl or nitro. Perhaps the thienyl radical is stabilized more when substituted with a halogen than with an alkyl substituent. The results obtained with the nitro group are anomolous, however, since the nitro group should be able to stabilize the thienyl radical at least as well as the halogen substituents.

In the presence of a radical scavenger, a decrease in the amount of carbon dioxide liberated would be expected, since the thenoyloxy radical would react with the scavenger rather than decarboxylate. Several attempts to measure the amount of carbon dioxide liberated when the perester solutions were made 0.2M in styrene led to unreproducible results, although the amount of carbon dioxide liberated was reduced to only a very few percent.

II. Rates of Decomposition of t-Butyl Perthenoates

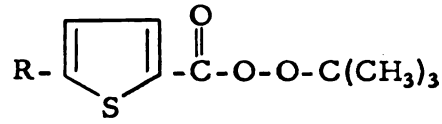
The rates of decomposition of the various t-butyl perthenoates were followed by measuring the rate of disappearance of the 5.7 micron perester carbonyl peak in the infrared. Initially, the analyses were made iodometrically, but this procedure proved to be unreliable and not reproducible. The iodometric method, therefore, cannot be used with the t-butyl perthenoates.

The decompositions containing no radical scavenger were followed for three or four half-lives of the peresters. Those kinetic runs containing 0.2M styrene as a radical scavenger could be followed only for about one half-life of the perester due to interference of the peak at 5.8 microns caused by the styrene esters formed as a reaction product. The rate data and activation parameters are summarized in Tables 3 and 4 respectively. The data and infrared curves for a representative kinetic determination of each type appear in the Appendix.

The measurements were conducted by purging the perester solution, approximately 0.03M in carbon tetrachloride, with purified nitrogen for ten minutes. The solutions were then placed in small, constricted ampules prepared from 9 mm Pyrex tubing and the ampules sealed at -70°. Sufficient solution was placed in each ampule to fill the infrared cell. The ampules were placed in an oil bath controlled to $\pm 0.2^{\circ}$ and two minutes were allowed to equilibrate the ampules to the bath temperature. The ampules were removed at definite time intervals and frozen in dry ice until completion of the kinetic run. The tips of the ampules were then broken and the contents transferred directly to the infrared cell using a hypodermic needle and syringe.

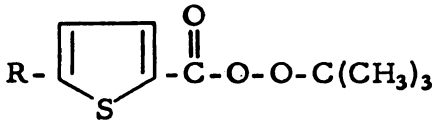
The kinetic determinations were not first order due very probably to induced decomposition, but a Guggenheim treatment (29) of the data permitted a calculation of an apparent first order rate constant. It should

Table 3. Rate Constants for the Decomposition of Various t-Butyl Perthenoates in Carbon Tetrachloride



Compound R	Temp. °C.	No Inhibitor		0.2M in Styrene	
		k x 10^3 min.$^{-1}$	$t_{\frac{1}{2}}$ min.	k x 10^3 min.$^{-1}$	$t_{\frac{1}{2}}$ min.
H	99.2	1.02	681	.201	3448
	112.0	3.77	184	1.00	693
	124.5	16.4	42.3	4.14	165
CH_3	99.2	.764	908	.281	2452
	112.0	3.02	231	1.17	592
	124.5	15.0	46	4.79	145
C_2H_5	99.2			.325	2132
	112.0	2.30	301	1.28	544
	124.5	15.0	46	4.77	145
Cl	99.2	.924	750	.138	5022
	112.0	2.88	240	.576	1205
	124.5	10.4	67	2.66	260
Br	99.2	.470	1475	.135	5134
	112.0	1.69	410	.714	972
	124.5	7.00	100	2.59	268

Table 4. Activation Parameters for the Decomposition of Various t-Butyl Perthenoates in Carbon Tetrachloride, 0.2M in Styrene



Compound	E_a kcal. mole^{-1}	S^* e.u.
H	35.2 ± 1	16.8 ± 3
Cl	34.3 ± 1	13.8 ± 3
Br	34.3 ± 1	14.0 ± 3
CH_3	32.9 ± 1	11.4 ± 3
C_2H_5	31.2 ± 1	7.07 ± 3

be emphasized that since these kinetic runs were not first order, the apparent first order rate constant has no real significance. However, within the series of peresters, these apparent constants do show the relative rate of decomposition and in this sense are meaningful. On the other hand, the kinetic runs containing 0.2M styrene were first order as shown by a plot of the log absorbance versus time being linear. Further, the rate of decomposition remained unchanged when the initial perester concentration was varied. Solutions of the unsubstituted perester at concentrations of 0.04M, 0.015M and 0.005M were decomposed at 123.5° and the rate constant was calculated. The first two solutions gave the same rate constant within experimental error. The rate constant for the most dilute solution could not be calculated however, since the perester carbonyl peak was very small initially due to the low concentration and became only a shoulder on the styrene ester peak early in the kinetic run.

It was observed that the t-butyl 2-perthenoate was very susceptible to induced decomposition in the absence of a radical scavenger since increasing the perester concentration led to an appreciable rate acceleration. A series of solutions of known concentrations was decomposed for an identical period of time and the absorbance was calculated. The results are summarized in Table 5.

Table 5. Decomposition of t-Butyl 2-perthenoate at 124.5° for Thirty Minutes

Initial Conc., Moles/liter	Percent Perester Decomposed
0.0431	29.3
0.0216	27.8
0.0108	22.5
0.00540	13.5
0.00270	3.8

While the peak for the most dilute solution was very small and hence may be in considerable error, the trend toward increasing decomposition with increasing concentration is unmistakable and considerable in magnitude.

An investigation of the rates of decomposition of the perthenoates containing 0.2M styrene as a radical scavenger showed that the peresters containing electron-releasing groups decompose faster than the unsubstituted perester, while the reverse was true for those peresters containing electron-withdrawing groups. These results parallel those obtained by Blomquist (1, 2, 3) in his studies of the t-butyl perbenzoate systems and by Swain (12) in his investigation of the benzoyl peroxide systems. The substitutent effect is not large, however, being less than a factor of two between the fastest and slowest compound investigated.

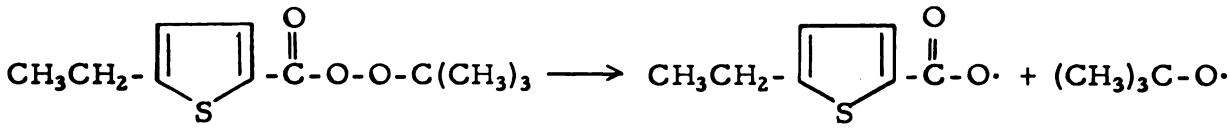
The apparent first-order rate constants obtained in the kinetic runs containing no styrene are overall rate constants for the perester decomposition and are the sum of at least two rates, namely, the spontaneous cleavage of the oxygen-oxygen bond and the induced cleavage caused by radical attack on the undecomposed perester. In their work on the decomposition of benzoyl peroxide, Nozaki and Bartlett (11) separated the contribution of the spontaneous decomposition and the induced decomposition to the overall rate expression using a kinetic analysis and found the expression

$$-\frac{dP}{dt} = k_s P + k_i P^{\frac{3}{2}} \qquad (25)$$

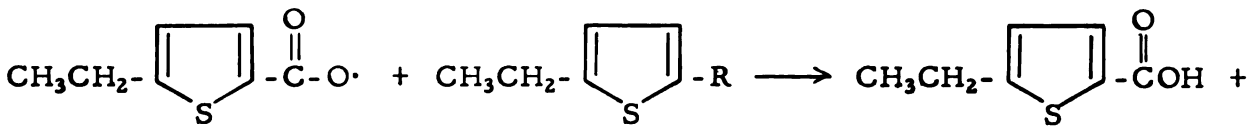
was applicable to the decomposition in a variety of solvents, where k_s corresponds to the spontaneous decomposition and k_i to the induced. In carbon tetrachloride, at 80°, the induced reaction amounted to only a few percent of the total decomposition rate at 0.01M peroxide concentration. Application of this kinetic analysis to the decomposition of

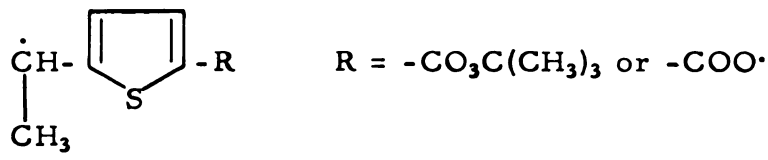
t-butyl 2-perthenoate was unsuccessful, probably due to a change in the mechanism of the decomposition. A complete kinetic run did show that the rate of decomposition increased with increasing concentration which is very good evidence for an induced step being involved in the decomposition mechanism. A solution 0.032M in t-butyl 2-perthenoate had a half-life of 259 minutes at 112.0°, while a solution 0.038M had a half-life of 184 minutes.

When the rate of decomposition of the ethyl-substituted perthenoate, in the absence of a scavenger, was compared with that of the unsubstituted perester, an anomoly was apparent. At the highest temperature employed, 124.5°, their decomposition rates were the same. At the intermediate temperature, 112.0°. the ethyl compound decomposed more slowly, which was not anticipated. At the lowest temperature, 99.2°, the rate constant could not be calculated for the ethyl compound since the slope of the plot of absorbance versus time was very gradual and application of the Guggenheim procedure to calculate the apparent rate constant failed to give a straight line. The fact that the ethyl-substituted compound decomposed more slowly than the unsubstituted compound at 112.0° tends to indicate that there is less induced decomposition in the former compound since the spontaneous cleavage should be expected to be faster in the substituted perester. Such a conjecture would require the removal, from the reaction medium, of the radical or radicals which are inducing perester decomposition. Since the thenoyloxy radical is very probably responsible for most of the induced decomposition, its removal should result in a slower rate of decomposition. An examination of the reacting species showed a source of easily abstractable hydrogen is available from the ethyl substituent and the following reactions, equations (26) and (27) may be of importance in the decomposition of the ethyl substituted perester.



(26)

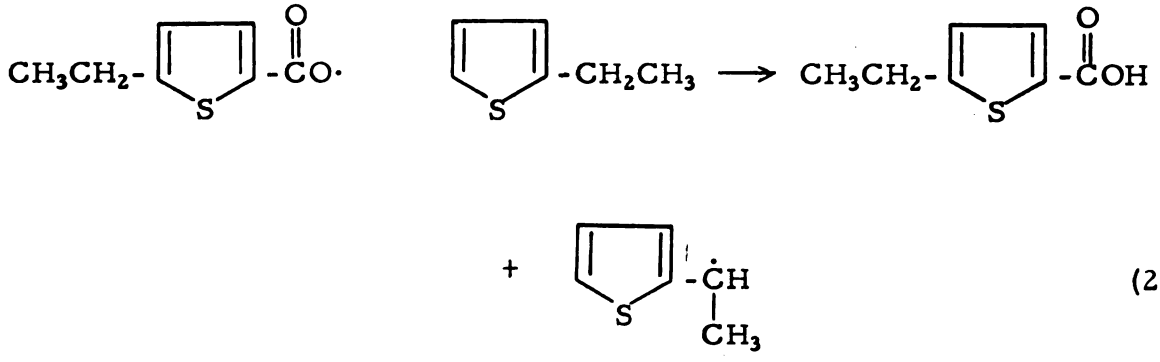




(27)

Equation (27) allows for the removal of the 5-ethylthenoyloxy radical by hydrogen abstraction from an undecomposed perester molecule or another 5-ethylthenoyloxy radical. The radical formed as a product in equation (27) should be a stable radical, since the unpaired electron can be delocalized by resonance with the aromatic thiophene pi electrons. The end result is a removal of a reactive radical causing less induced decomposition and a slower rate of decomposition. This process could be termed an example of "self-inhibition."

This concept was further examined by decomposing a 0.031M solution of the 5-ethyl substituted perester in the presence of 0.2M 2-ethylthiophene. The large excess of ethylthiophene should be an efficient source of abstractable hydrogen, and the decomposition should become slower. An examination of the quantitative infrared spectra of the kinetic run showed that the acid formed much faster than usual, as was anticipated, equation (28), and, in fact, the reaction was first-order for about a one-fourth life of the decomposition with a rate constant of 1.65×10^{-3} min.$^{-1}$ and $t_{\frac{1}{2}}$ of 420 minutes at 112.0°.

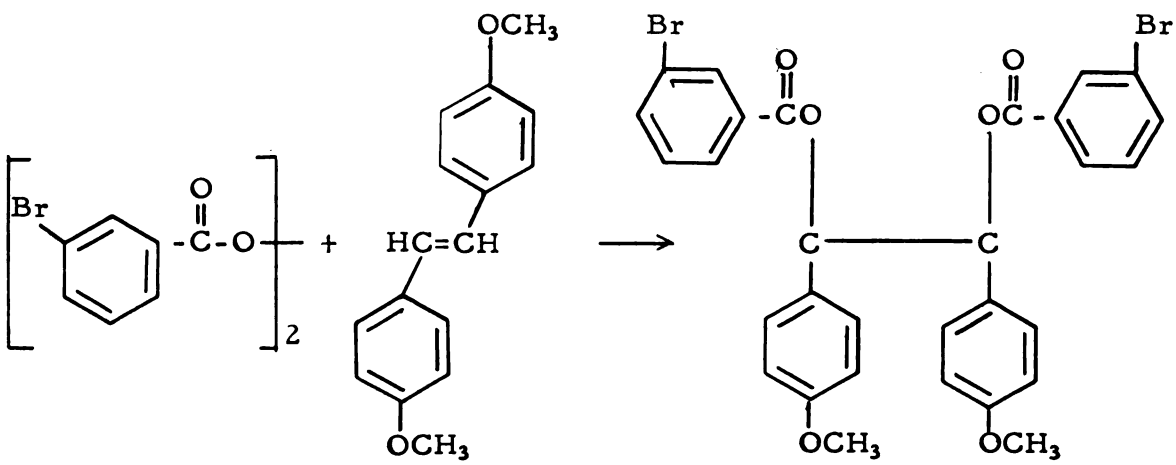


(28)

The t-butyl 5-nitro-2-perthenoate gave markedly different results than the other peresters investigated. When a 0.032M solution of this perester was decomposed in the presence of 0.2M styrene at 124.5°, the reaction was much faster than expected and kinetically was not first order. After 100 minutes of reaction, 40% of the perester had decomposed, while an interpolation of the kinetic data on the unsubstituted perester showed that it would require about 130 minutes to decompose 40% of the unsubstituted perester. Hence, in the presence of a radical scavenger, the nitro-substituted perester decomposes faster than the unsubstituted perester. This result strongly suggests that the styrene is not only acting as a radical scavenger, but in some manner is entering into a direct reaction with the perester accelerating its decomposition. Blomquist (3) reported similar accelerating effects on the rate of decomposition when known radical traps were added to a solution of t-butyl p-nitroperbenzoate. Swain (12) found a similar acceleration when he employed p-nitrobenzoyl peroxide. Both Blomquist and Swain imply that this rate acceleration is due to a rapid, induced decomposition brought about by the electrical unsymmetry of the nitro-substituted compounds which makes them very susceptible to induced radical attack. It is also possible to consider the fact that such a strongly electron-attracting group could cause a rather polar oxygen-oxygen bond in the

transition state which could result in at least partial ionic decomposition and facilitate the direct interaction of the now polar peroxide linkage with the radical scavenger.

Greene (30) and his co-workers have reported definite evidence for a direct peroxide-olefin reaction in a benzoyl peroxide-stilbene system. Since a direct reaction between peroxide and olefin is most favorable when the peroxide contains electron-withdrawing groups and the olefin electron-releasing groups, Greene used m,m'-dibromobenzoyl peroxide and p,p'-dimethoxy-trans-stilbene in his principal investigations. When decomposed at 45°, the reaction was first order in each component and 84% of the products were two 1:1 adducts of peroxide and olefin, the meso- and dl-benzoates, equation (29). The acid derived from the



(29)

peroxide, m-bromobenzoic acid, was isolated in only 7% yield. Since it is possible to write a radical mechanism to account for the product in equation (29), the peroxide and olefin were decomposed in the presence of the radical scavenger galvinoxyl, which was shown to be efficient in this system by other experiments. By observing the disappearance of the galvinoxyl the number of radicals in the system could be determined. The results indicated that only a very small number of radicals appeared

from the peroxide, showing that direct, ionic interaction between olefin and peroxide was the most important reaction occurring. The ratio of the rates of the direct reaction and free radical reaction between olefin and peroxide was found to be 40:1.

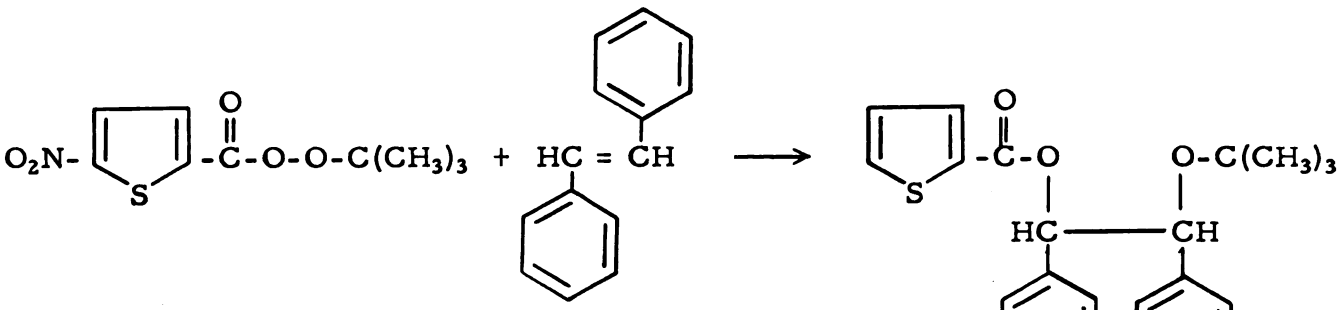
The application of Greene's procedure to the thiophene perester series was not possible since galvinoxyl is not stable at the temperatures required to decompose the thiophene peresters. With the aim of obtaining additional information concerning the decomposition of the nitro-substituted perthenoate in the presence of an olefin such as styrene, the decomposition was carried out in the presence of p-methoxystyrene and p-nitrostyrene, as it was anticipated that the p-methoxy substituent should make the direct reaction more feasible, and the p-nitro group should make it less feasible. The results of these experiments are recorded in Table 6.

Table 6. Decomposition of 0.032M t-Butyl 5-Nitro-2-perthenoate at 124.5° after 100 Min.

Scavenger, 0.2M	Percent Perester Decomposed
Styrene	40
p-Methoxystyrene	22
p-Nitrostyrene	23

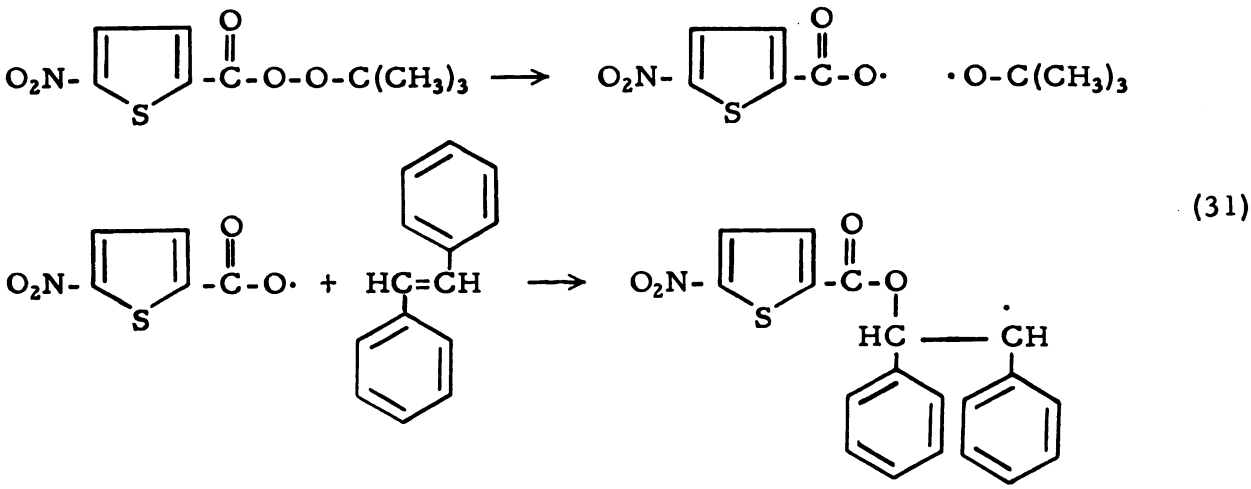
The results were not as expected since less perester was decomposed in the presence of p-methoxystyrene than in the presence of styrene itself. Actually, it might have been rash to expect any correlation with Greene's results, since the work described here was done at a reaction temperature 80° higher than Greene's and similarity in the mechanisms of two different systems with such a large temperature differential would be unexpected.

Surprisingly, when a 0.032M solution of the 5-nitro perester was decomposed in the presence of 0.2M trans-stilbene, the disappearance of perester was first-order in perester with $k = 1.85 \times 10^{-3}$ min.$^{-1}$ and $t_{\frac{1}{2}}$ of 373 min. The infrared spectra showed that thenoic acid was not formed but the ester peak at 5.85 microns constantly increased as did a peak at approximately 10.4 microns, characteristic of an ether linkage. This would be the expected result of a direct reaction between the perester and the stilbene, equation (30).



(30)

Since acid was not observed after one half-life of the perester, the direct reaction must be quite efficient. Of course, thenoyloxy radicals could also react with the stilbene by a homolytic route, equation (31).



(31)

which would also result in the appearance of no acid. However, if the disappearance of perester resulted from a combination of reactions (30) and (31), first-order kinetics could probably not be expected.

When cis-stilbene was substituted for trans-stilbene, the disappearance of perester was slower, and was not first-order. Table 7 summarizes the results obtained in these experiments. Greene also found that the rate of reaction was slower when he used p, p'-dimethoxy-cis-stilbene in place of the trans-isomer in their reactions with the substituted benzoyl peroxides.

Table 7. Decomposition of t-Butyl 5-Nitro-2-perthenoate at 124.5° in the Presence of cis- and trans-Stilbene

Scavenger, 0.2M	Percent Perester Decomposed	
	100 Min.	300 Min.
trans-Stilbene	15	30
cis-Stilbene	6	36

The activation parameters show that the effect of the substituent on the thiophene ring has only a small effect on the rate of the reaction. This was expected since the influence of substituents was small in the t-butyl perbenzoates (Table 1') and should be smaller in the thiophene series. For the substituents H, Br, and Cl, the activation energy and entropy values are all actually within experimental error, although the unsubstituted perester has the highest activation energy and the most favorable entropy value. The slightly lower activation energies of the chloro and bromo peresters could possibly be indicative of a small amount of heterolytic cleavage of the peroxide linkage in these two systems, but it is probably more realistic to account for these differences as

experimental error. In fact, an investigation of Blomquist's data (Table I) showed that the negatively-substituted perbenzoates had higher activation energies than the unsubstituted perbenzoate. As previously stated, this rules out any appreciable amount of heterolytic decomposition in the perbenzoates. Since the effect of the substituent is less in the thiophene series than in the benzene compounds, no appreciable amount of heterolytic decomposition should be occurring in the heterocyclic series of compounds. It seems best, therefore, to consider the activation energies of the unsubstituted, 5-bromo, and 5-chloro peresters to be essentially the same, showing, then, very little substituent effect on the rate of the decompositions. The methyl and ethyl substituted perthenoates had lower activation energies than the unsubstituted and halogen substituted peresters. This was expected, since the electron-releasing groups facilitate the decomposition. The activation parameters for the alkyl substituted perthenoates were very similar and almost within experimental error.

A Hammett plot of the decomposition rates of the perthenoates in the presence of 0.2M styrene gave a reasonably straight line when the sigma values for para-substituted benzenes were used. While these results indicate that a Hammett correlation does exist for this series of compounds, no meaningful value for rho could be assigned since the improper sigma values were used. Unfortunately, the sigma values for substituents on a thiophene ring have not been reported. While the entropy term is not constant throughout the series, the Hammett relationship is meaningful since the activation energy varies linearly with the entropy of activation (31).

EXPERIMENTAL

I. Reagents

A. Carbon Tetrachloride

Carbon tetrachloride was purified according to the method of Fieser (32). A two liter volume of carbon tetrachloride was mixed with 200 ml. ethanol, 200 ml. water, and 80 g. potassium hydroxide. This mixture was warmed to 60° for a half hour. The carbon tetrachloride layer was separated and the above treatment was repeated. The carbon tetrachloride was then washed successively with water and 50 ml. portions of concentrated sulfuric acid. The acid washings were repeated until the acid was colorless or, at most, had a very light yellow coloration. The carbon tetrachloride was dried over anhydrous calcium chloride and distilled from phosphorus pentoxide through a column packed with glass helices.

B. Chlorobenzene

Chlorobenzene was dried over anhydrous calcium chloride and distilled from phosphorus pentoxide through a column packed with glass helices.

C. Styrene

Eastman reagent grade styrene was fractionated through a column packed with glass helices and that material with a boiling point of 143-144° was used in this work. Stock solutions of 0.2M styrene in carbon tetrachloride were prepared and stored at 0° in the dark.

D. Substituted Styrenes

Para-nitrostyrene was obtained from Monomer-Polymer Laboratories and was distilled immediately before use. The material boiling at 83°/1 mm. was used.

Para-methoxystyrene was obtained from Monomer-Polymer Laboratories and was distilled immediately before use, employing the material with a boiling point of 110°/25 mm.

E. Stilbenes

Trans-stilbene was obtained from Eastman as their Scintillation Grade and was used as received.

Cis-stilbene was obtained from Aldrich Chemical Company and was used as received.

F. Standardization of Sodium Thiosulfate Solution

In a typical standardization procedure, four liters of approximately 0.01N sodium thiosulfate solution was prepared 48 hours prior to the standardization and stabilized with approximately 0.25 g. of sodium carbonate.

Standardization of the solution was conducted as follows. A sample of previously dried, reagent grade potassium iodate was weighed out exactly and transferred to a 50 ml. volumetric flask. This was filled to the mark with distilled water. Several aliquots of a 5 ml. volume were transferred by a pipette to a small Erlenmeyer flask. To this aliquot were added 8 ml. carbon tetrachloride and 10 ml. glacial acetic acid containing 0.0005% ferric chloride hexahydrate. A few very small pieces of dry ice and one ml. saturated sodium iodide solution was added and the iodine liberated was titrated immediately with the thiosulfate solution using the starch endpoint.

The normality of the thiosulfate solution was calculated from the following equation:

$$N = \frac{\text{g. } KIO_3}{\text{meq. wt. } KIO_3 \times \text{ml. } Na_2S_2O_3}$$

where the meq. wt. of potassium iodate equals the molecular wt./6000.

G. Standardization of Perester Solutions

The method of Silbert and Swern (33) was used to determine the concentration of the perester solutions used in the kinetic determinations.

A measured aliquot (4 ml.) of the carbon tetrachloride solution of the perester was placed in an Erlenmeyer flask. Acetic acid (10 ml.) containing 0.0005% ferric chloride hexahydrate, a few small pieces of dry ice and one ml. saturated sodium iodide solution was added. This mixture was allowed to stand in the dark for 30 min. with occasional agitation. Water (25 ml.) was added, and the magnetically stirred mixture was titrated with the standard thiosulfate solution. Starch solution (3 ml.) was added near the end point and the end point was taken at the disappearance of the purple starch-iodine color.

II. Preparation of t-Butyl Perthenoates

A. Preparation of Acids

The substituted thenoic acids previously prepared by Teller (34) were available in these laboratories. These included 5-chloro-2-thenoic acid, 5-bromo-2-thenoic acid and 5-methyl-2-thenoic acid.

1. Preparation of 5-Ethyl-2-thenoic Acid

A liter, three-necked flask was fitted with a stirrer, reflux condenser and dropping funnel. The flask was charged with 6.9 g. (1.0 g. atom)

of lithium chips and 100 ml. anhydrous ether. A solution containing 86 g. (0.55 mole) of freshly distilled bromobenzene dissolved in 200 ml. anhydrous ether was slowly added to the suspension of the alkali metal. The metallation reaction was allowed to proceed at the reflux temperature of the reaction mixture. After the addition of the bromobenzene was completed, the reaction mixture was heated at its reflux temperature for a half hour and cooled to room temperature. A solution containing 56 g. (0.5 mole) of freshly distilled 2-ethylthiophene (35) dissolved in 100 ml. anhydrous ether was slowly added to the phenyllithium solution. The reaction mixture was then heated at its reflux temperature for a half hour, cooled to room temperature, and poured cautiously into a well-stirred slurry of 300 g. of dry ice in anhydrous ether. The vigorously stirred mixture was allowed to warm to room temperature and 300 ml. water were added dropwise to it to destroy excess lithium. The reaction mixture was filtered, the water layer separated and the ether layer extracted twice with 10% aqueous sodium hydroxide. The basic extracts were combined with the water layer and acidified with concentrated hydrochloric acid. An orange oil which initially formed solidified after being set aside for several hours. This was isolated by filtration and recrystallized from 60-90^{o}ligroin, after being decolorized with Norite, to obtain a tan solid melting at 64-67^{o}. Three additional recrystallizations from ligroin gave 30 g. (0.192 mole, 40%) of an almost white solid which had a melting point of 69-70^{o}. Literature value (36): melting point 71^{o}.

2. Preparation of 2-Acetothienone

A liter, three-necked flask was equipped with a stirrer, reflux condenser and thermometer. The flask was charged with 168 g. (2 moles) of thiophene and 107 g. (one mole) acetic anhydride. The reaction mixture was heated to 70^{o} on a steam bath, the source of heat removed and 6 ml. of

85% phosphoric acid was added as a catalyst to the acetylation mixture. The exothermic reaction initiated after a few minutes required external cooling to control the rate of the reaction. After the initial reaction had subsided the mixture was heated at its reflux temperature for two hours. After cooling, the mixture was transferred to a separatory funnel and 250 ml. water was added. The mixture was washed twice with 5% sodium carbonate solution, once with water, and then dried over anhydrous sodium sulfate. The drying agent was removed by filtration and excess thiophene was recovered by distillation at atmospheric pressure. The residue was vacuum distilled collecting the product boiling at 88-89°/9 mm. Literature value (37): boiling point 88-90°/10 mm. The yield of product was 74.0 g. (0.59 mole, 59%).

3. Preparation of 2-Thenoic Acid

The acid was prepared by the hypochlorite oxidation of 2-acetothienone. A solution of sodium hypochlorite was prepared by dissolving 160 g. (4 moles) of sodium hydroxide in 600 ml. of water. Chlorine gas was introduced into the basic solution until the mixture gained 107 g. in weight, corresponding to 1.5 moles of chlorine. To this well-stirred solution was slowly added 42 g. (0.333 mole) of 2-acetothienone maintaining the temperature below 60°. After the addition was complete, the reaction mixture was stirred for one hour then reduced in volume to about 200 ml. Ether (100 ml.) was added to the concentrate which was then carefully acidified with concentrated hydrochloric acid. The ether layer was separated and the aqueous layer was extracted three times with ether and set aside overnight in contact with anhydrous magnesium sulfate. The ether was removed leaving 27 g. of a brown solid. Two recrystallizations from hot water gave 21 g. (0.167 mole, 50%) of white crystals, melting at 127-128°. Literature value (38): melting point 129-130°.

4. Preparation of 2-Thenal

Into a liter, three-necked flask fitted with a stirrer, reflux condenser and dropping funnel were placed 126 g. (1.5 moles) of thiophene and 138 g. (1.92 moles) of dimethylformamide. After pre-cooling this mixture to ice-bath temperature, 288 g. (1.86 moles) of phosphorus oxychloride was added to the reaction mixture during an hour while maintaining the temperature at 0°. The reaction mixture was heated at its reflux temperature for 2 hrs., cooled to room temperature and poured over 1500 g. of ice. The entire mixture was steam distilled until oil failed to appear in the distillate. The organic layer of the distillate was separated and the water layer was extracted with ether. The combined product layer and the ether extracts were washed twice with 10% sodium carbonate solution, twice with water and then dried over anhydrous magnesium sulfate. Following removal of the ether the residue was vacuum distilled to obtain 130 g. (1.16 moles, 77%) of a colorless oil, boiling at 69-71°/4 mm. Literature value (39): boiling point 66-67°/4 mm.

5. Preparation of 5-Nitro-2-thenal

A three-necked, 300 ml. round-bottomed flask was fitted with a stirrer, thermometer, reflux condenser and dropping funnel. The flask was charged with 37 g. (0.33 mole) of 2-thenal dissolved in 60 g. of reagent grade acetic anhydride. The flask and its contents were cooled to 0° in an ice bath and 25.2 g. (0.40 mole) of fuming nitric acid dissolved in 60 g. of glacial acetic acid was added during 15 min. while maintaining the reaction temperature at 0°. After the addition of the nitrating agent, the reaction mixture was stirred for an additional hour at 0°. The reaction mixture was then poured into 200 ml. of distilled water which caused the immediate precipitation of a yellow solid. This was recovered by filtration and recrystallized from ethanol to obtain 36.0 g. (0.23 mole, 70%)

of a yellow-colored solid product, melting at 71°. Literature value (40): 77°.

6. Preparation of 5-Nitro-2-thenoic Acid

A solution of silver nitrate was prepared by dissolving 92 g. (0.48 mole) of silver nitrate into a mixture a 500 ml. of water and 500 ml. of ethanol. In this solution was suspended 36 g. (0.23 mole) of 5-nitro-2-thenal. This oxidation mixture was transferred to a 3 liter, three-necked flask equipped with stirrer, thermometer, reflux condenser and dropping funnel and heated on a steam bath to 45° while being vigorously stirred. To the well-stirred, warm reaction mixture a solution containing 40 g. (1 mole) of sodium hydroxide dissolved in 400 ml. of water was added at a rate sufficient to maintain the reaction temperature at 60°. Following the addition of the basic solution, the reaction mixture was kept at 50-60° for an additional half-hour, then cooled and filtered to remove silver. The latter was washed with hot water and the washings added to the filtrate. The combined filtrate and washings were concentrated to about 500 ml. Ether (500 ml.) was added to the concentrate and the mixture was carefully acidified with concentrated hydrochloric acid. The ether layer was separated and the water layer was extracted three times with ether. The ether extracts were combined with the original ether product fraction and dried in contact with anhydrous magnesium sulfate. Removal of the ether yielded 22 g. (0.127 mole, 56%) of a yellow-colored solid product melting at 146-147°. Literature value (41): melting point 156.5-158°.

B. Preparation of Acid Chlorides

The acid chlorides were prepared by heating at its reflux temperature a mixture of the acid and thionyl chloride and isolating the acid chloride by vacuum distillation.

In a typical synthesis a 500 ml. round-bottomed flask was fitted with a reflux condenser and charged with 26 g. (0.15 mole) of 5-chloro-2-thenoic acid and 71 g. (0.60 mole) of freshly distilled thionyl chloride. The reaction mixture was heated at its reflux temperature on a steam bath for three hours, then set aside overnight in contact with anhydrous magnesium sulfate. Excess thionyl chloride was removed by distillation and the residue was distilled at reduced pressure to obtain 22 g. (0.123 mole, 80%) of a colorless product, boiling at 96-98°/11 mm.

Immediately after distillation the acid chlorides were sealed in glass ampules and stored in the dark until used.

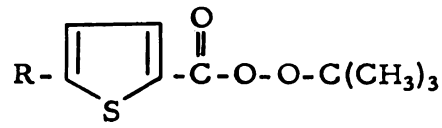
C. Preparation of t-Butyl Perthenoates

The peroxyesters were prepared by an adaptation of the method of Blomquist and Berstein (3).

In a typical preparation a 25 ml. Erlenmeyer flask was cooled in an ice bath. The flask was charged with 0.63 g. (0.007 mole) of t-butyl-hydroperoxide and 0.42 g. of distilled water to obtain a 60% hydroperoxide solution. To this solution, stirred by a magnetic stirrer, were added simultaneously 1.0 g. (0.0068 mole) of 2-thenoyl chloride and 1.5 g. of a 30% aqueous potassium hydroxide solution, the additions being accomplished with medicine droppers. The reaction mixture was stirred for an hour at 0° and transferred to a small separatory funnel. Approximately 10 ml. of pentane was added and the aqueous layer was discarded. The pentane solution was then washed five times or more with small portions of 5% sodium carbonate solution and then five times or more with small portions of water. The pentane solution was set aside overnight in contact with anhydrous magnesium sulfate. The drying agent was removed by filtration and the pentane was removed on a rotary evaporator retaining the colorless liquid residue on the evaporator for several hours.

The peresters prepared in this fashion were all colorless liquids except for the nitro-substituted perester, which was a very light-yellow solid, melting point 55.5-56°. At dry-ice temperature, the liquid peresters became glassy but would not crystallize. All of the peresters gave acceptable carbon, hydrogen and sulfur or functional group analysis. The infrared spectra of the peresters showed no contamination by hydroperoxide or acid.

Table 8. Elemental Analyses of the Various t-Butyl Perthenoates



Compound	Carbon		Hydrogen		Sulfur		Halogen/Nitrogen	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
R = H	53.98	53.95	6.04	5.85	16.01	16.12		
CH_3	55.79	56.00	6.56	6.50	14.89	14.96		
C_2H_5	57.87	57.60	7.06	6.86	14.04	14.21		
Cl	46.06	45.76	4.72	4.62			15.11	15.38
Br	38.72	39.01	3.97	4.14			28.63	28.50
NO_2	44.07	44.28	4.52	4.69			5.71	5.60

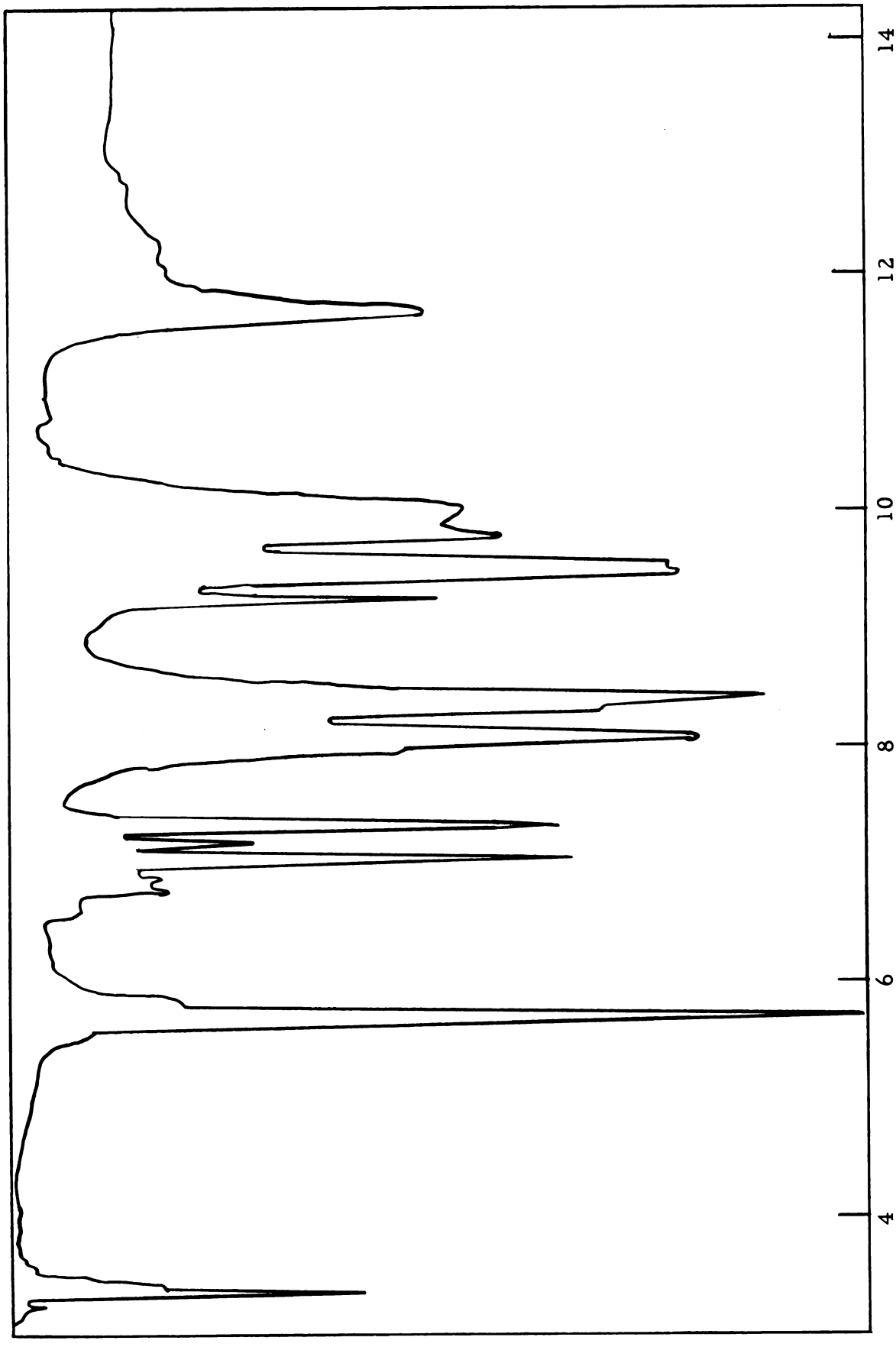


Figure 1. Infrared Spectrum of t-Butyl 2-Perthenoate.

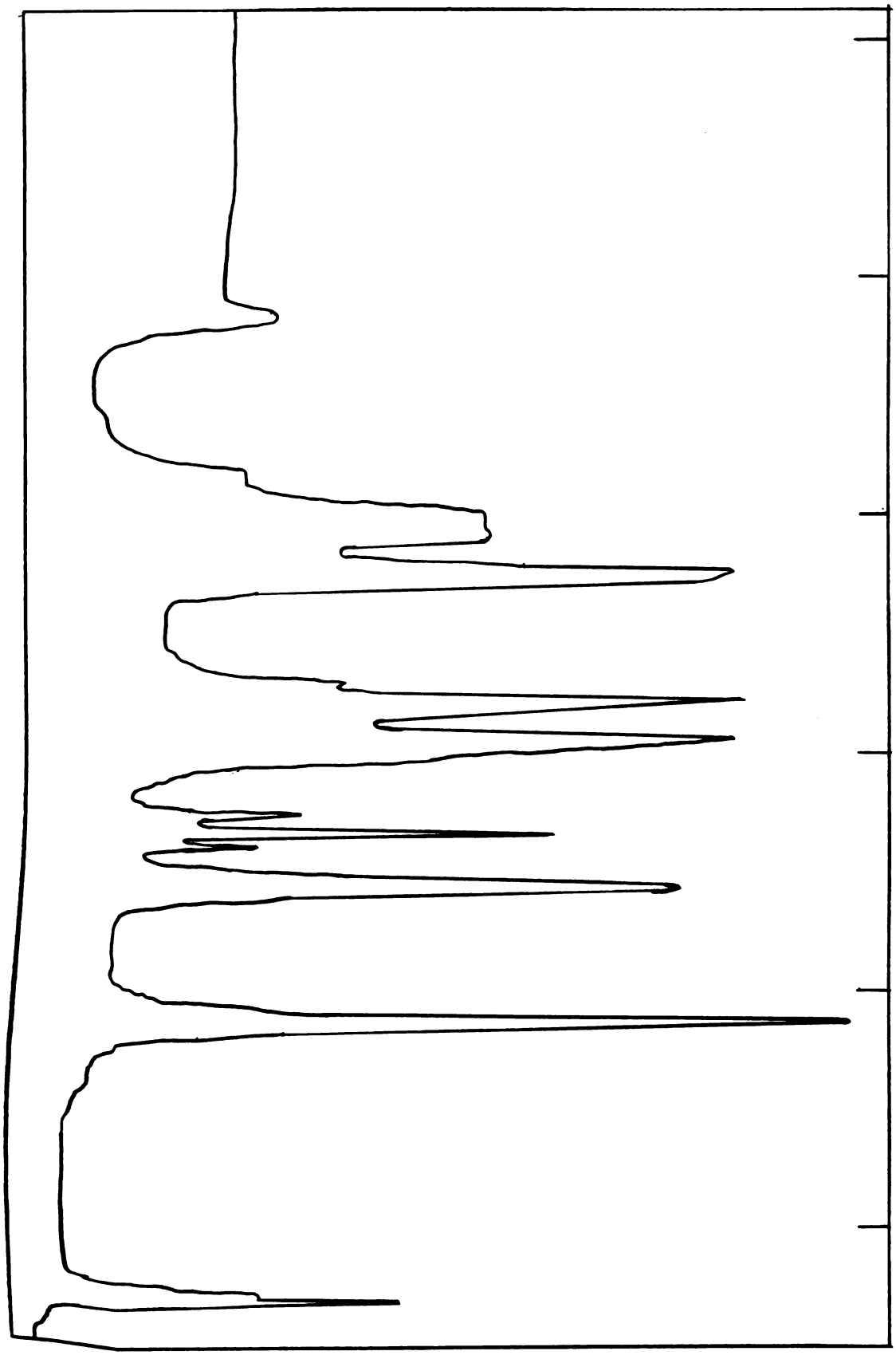


Figure 2. Infrared Spectrum of t-Butyl 5-Methyl-2-perthenoate.

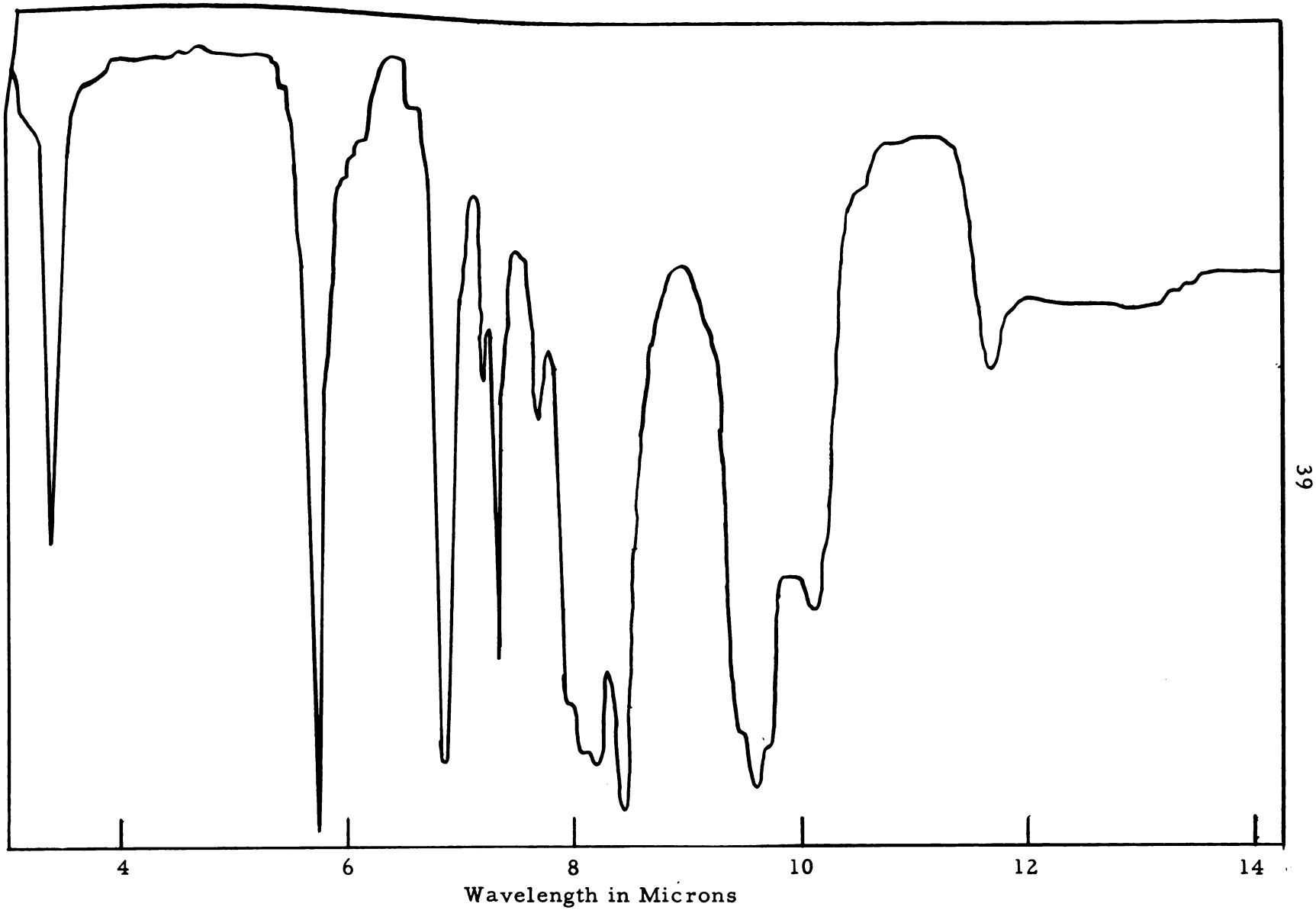


Figure 3. Infrared Spectrum of t-Butyl 5-Ethyl-2-perthenoate.

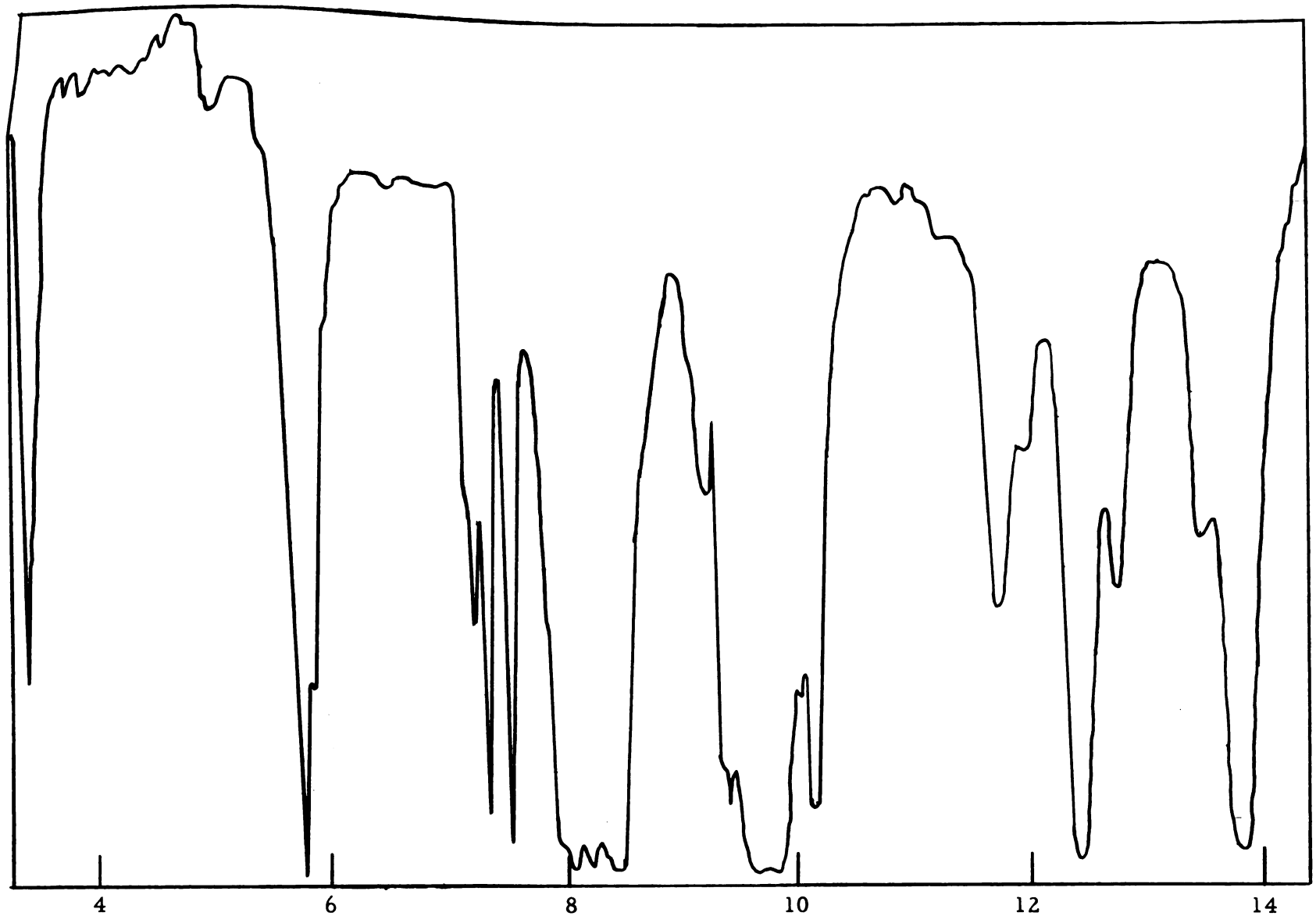


Figure 4. Infrared Spectrum of t-Butyl 5-Chloro-2-perthenoate taken in Carbon Disulfide.

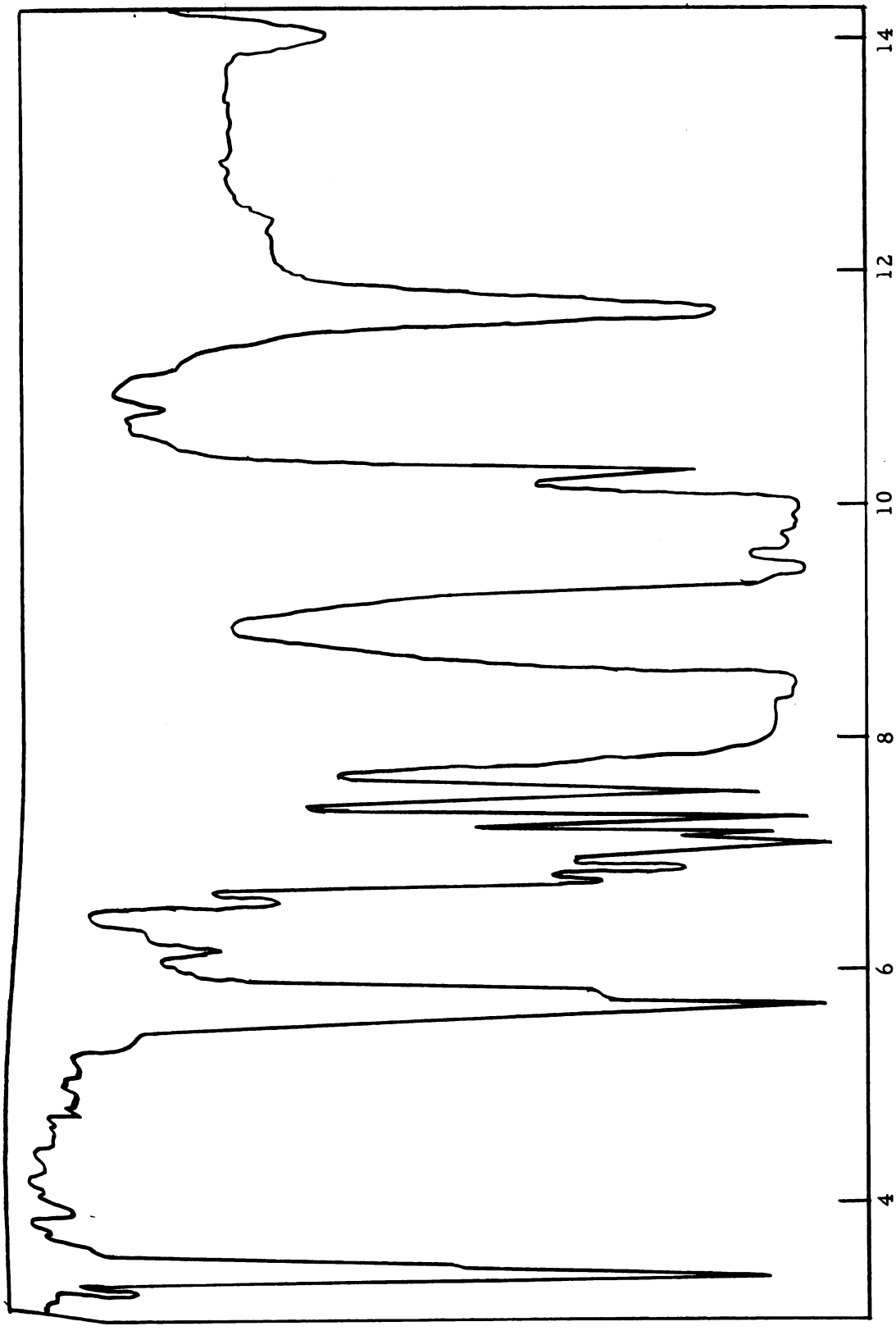


Figure 5. Infrared Spectrum of t-Butyl 5-Bromo-2-perthenoate.

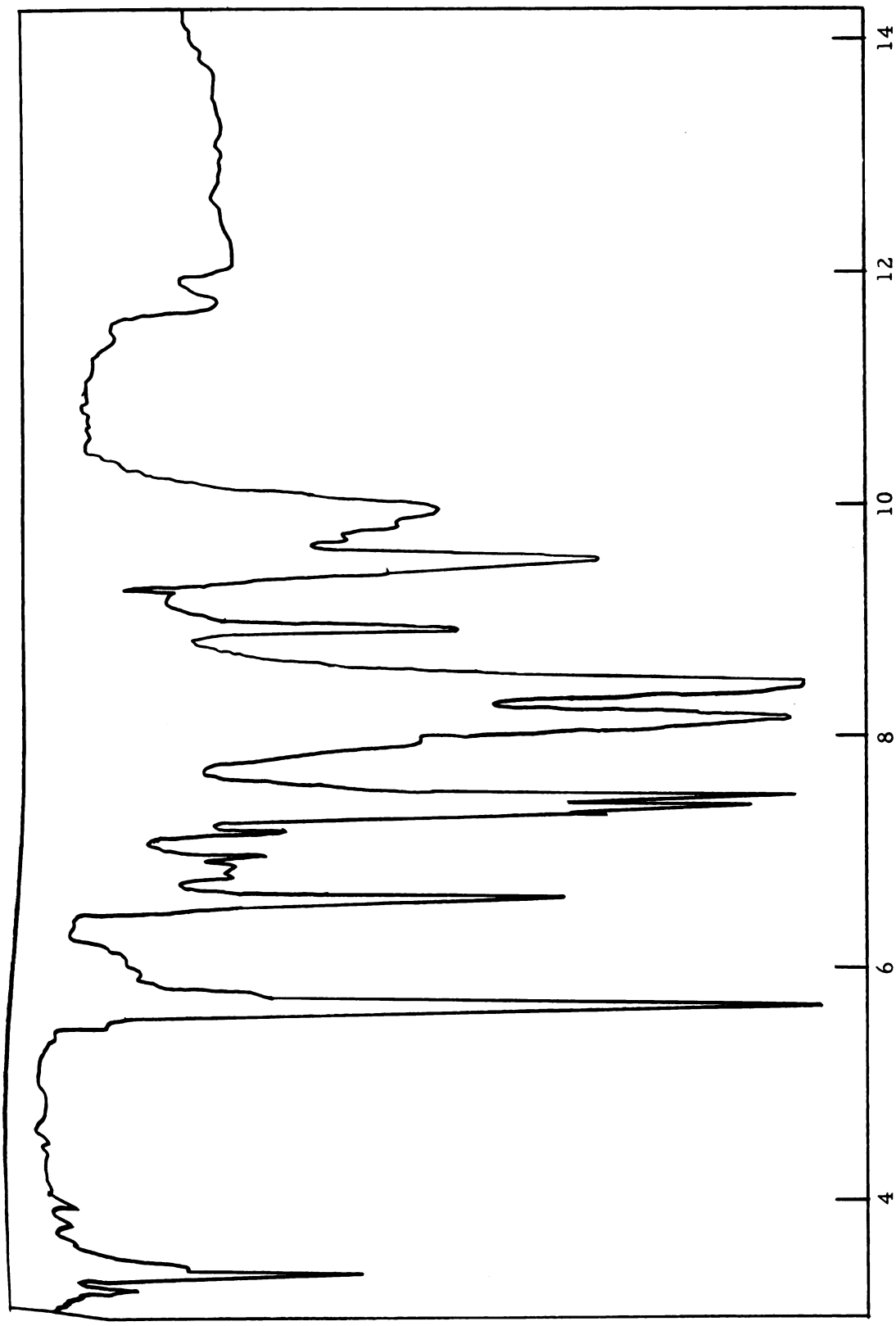


Figure 6. Infrared Spectrum of t-Butyl 5-Nitro-2-perthenoate.

III. Preparation of Esters

A. Preparation of t-Butyl 2-Thenoate

A 300 ml. three-necked flask was equipped with a stirrer and reflux condenser. The flask was charged with 15 g. (0.20 mole) of t-butyl alcohol, 6.3 g. (0.08 mole) of anhydrous pyridine and 50 ml. of purified carbon tetrachloride. The solution was heated to its reflux temperature and 10 g. (0.07 mole) of 2-thenoyl chloride was added rapidly to the flask and the reaction mixture was kept at its reflux temperature for twenty hours. After cooling, the pyridinium hydrochloride formed during the reaction was removed by filtration and the filtrate was washed three times with 1N hydrochloric acid, twice with water, and set aside overnight in contact with anhydrous magnesium sulfate and Norite. The drying agent and Norite were removed by filtration and the solvent by distillation at atmospheric pressure. Vacuum distillation of the residue gave a colorless, liquid product boiling at 112-113°/15 mm. The infrared spectrum of the product proved it to be an ester having a t-butyl group present in the structure. The elemental analysis for this compound is found in Table 9.

B. Preparation of Phenyl 2-Thenoate

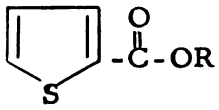
To the stirred mixture containing 6.8 g. (0.07 mole) of phenol, 5.5 g. (0.07 mole) of pyridine and 50 ml. of carbon tetrachloride heated to its reflux temperature and contained in a 300 ml. flask was added 10.0 g. (0.07 mole) of 2-thenoyl chloride. The reaction mixture was held at its reflux temperature for 5 hr., then cooled. The pyridinium hydrochloride was removed by filtration and the filtrate was washed twice with 5% sodium hydroxide solution to remove excess phenol, and then with water. Removal of the carbon tetrachloride on a rotary evaporator left a white, solid residue. This was dissolved in ether and the solution set

aside overnight in contact with anhydrous magnesium sulfate. Removal of the ether left a white, solid product melting at 43.5-45°. Literature Value (42): melting point 53°. Recrystallization of the product twice from petroleum ether narrowed the melting point range to 45-45.5°. The infrared spectrum of the product showed it to be an ester. Hydroxyl absorption bands in the 2 micron region were absent showing no contamination of the product by phenol. The elemental analysis of the material was acceptable.

C. Preparation of 2(p-Chlorophenyl) Thenoate

To a mixture containing 9.0 g. (0.07 mole) of p-chlorophenol, 5.5 g. (0.07 mole) of pyridine and 50 ml. of carbon tetrachloride heated to its reflux temperature was added 10.0 g. (0.07 mole) of 2-thenoyl chloride. The mixture was held at its reflux temperature for seven hours, then cooled to room temperature and the pyridinium hydrochloride was removed by filtration. The carbon tetrachloride was washed successively with small quantities of 5% sodium hydroxide solution, water, very dilute hydrochloric acid, and finally with water. The solution was set aside overnight in contact with anhydrous magnesium sulfate. Removal of the carbon tetrachloride left a white, solid residue. This was recrystallized twice from methanol to obtain a proeuct in the form of white needles, melting at 82-83°. Literature value (42): melting point 84-84.5°.

Table 9. Elemental Analyses of the Various Esters



Compound	Carbon		Hydrogen		Sulfur		Halogen	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
R = t-Bu	58.66	58.64	6.56	6.37	17.40	17.69		
C_6H_5	64.70	64.79	3.92	4.11	15.70	15.89		
C_6H_5Cl	55.35	55.52	2.96	3.08	13.43	13.13	14.85	14.53

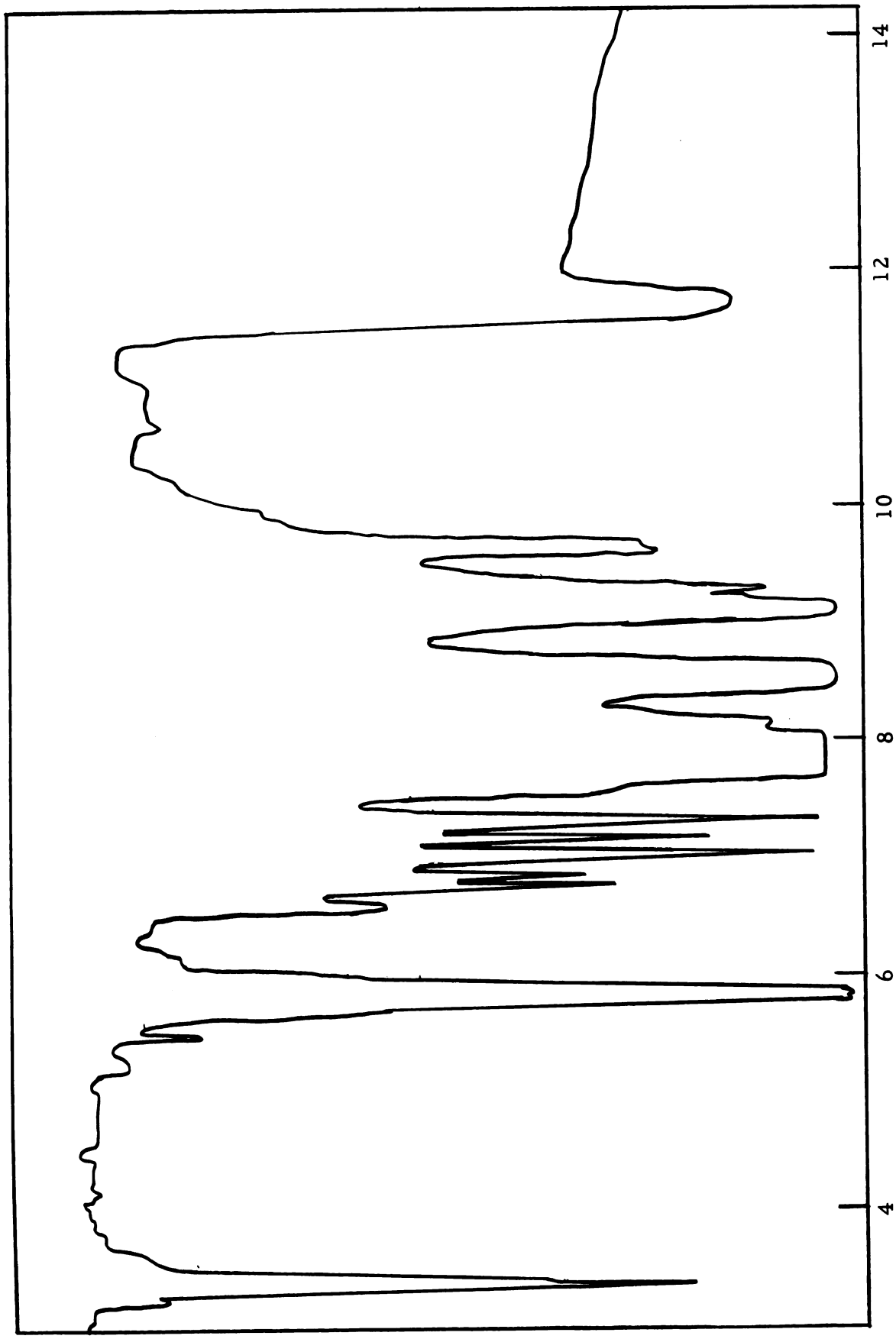


Figure 7. Infrared Spectrum of t-Butyl 2-Thenoate.

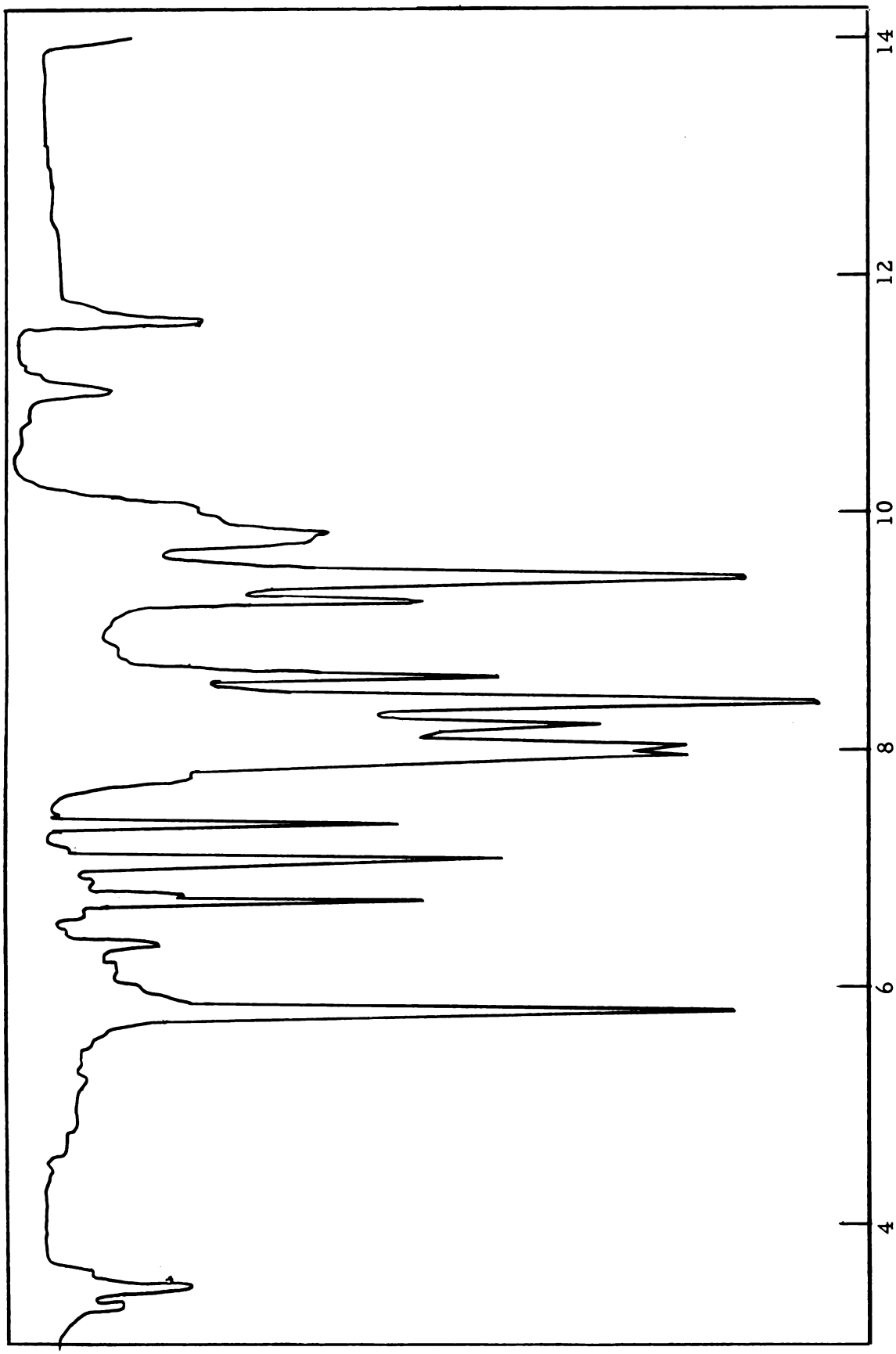


Figure 8. Infrared Spectrum of Phenyl 2-Thenoate.

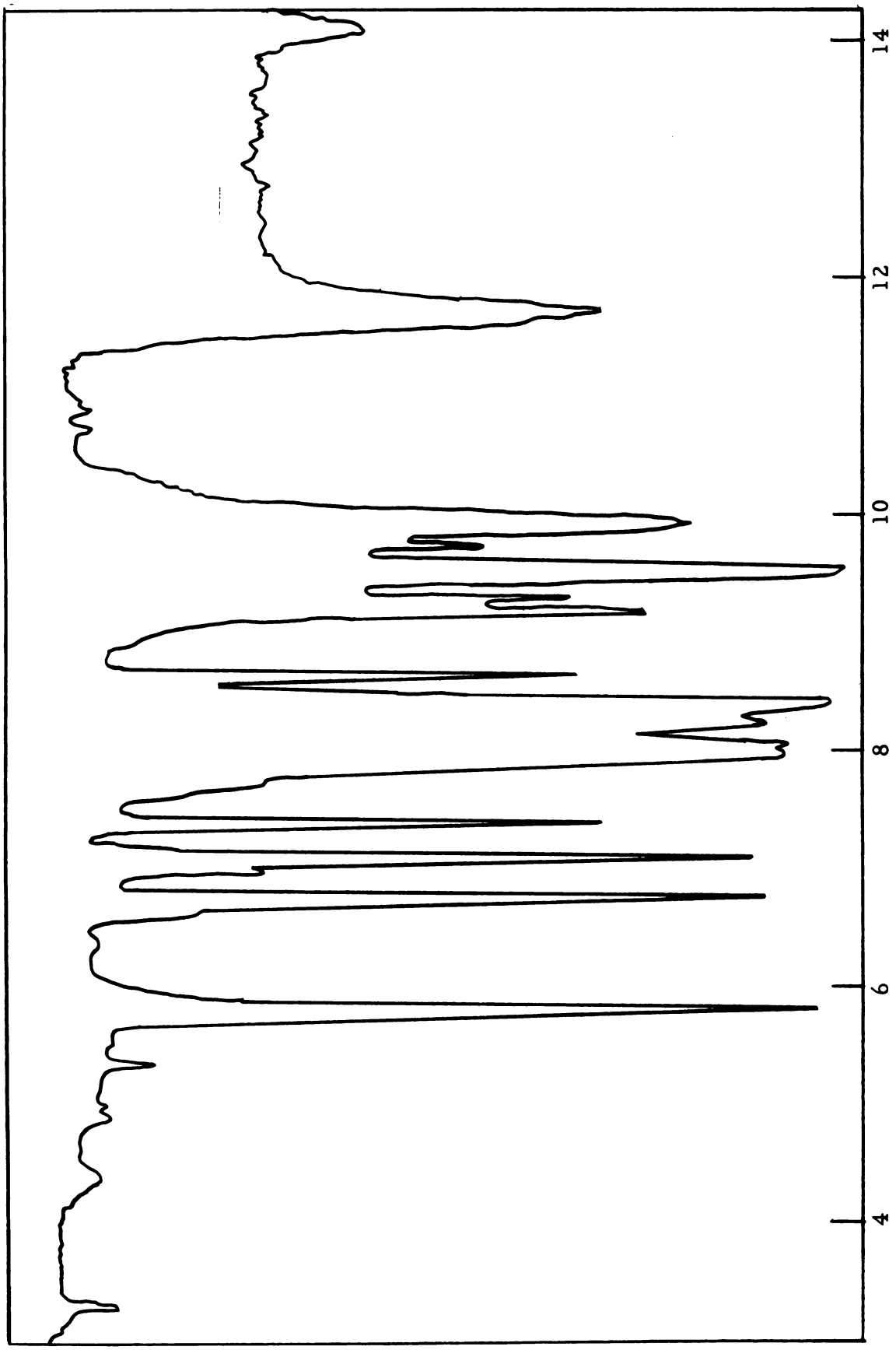


Figure 9. Infrared Spectrum of 2(p-Chlorophenyl) Thenoate.

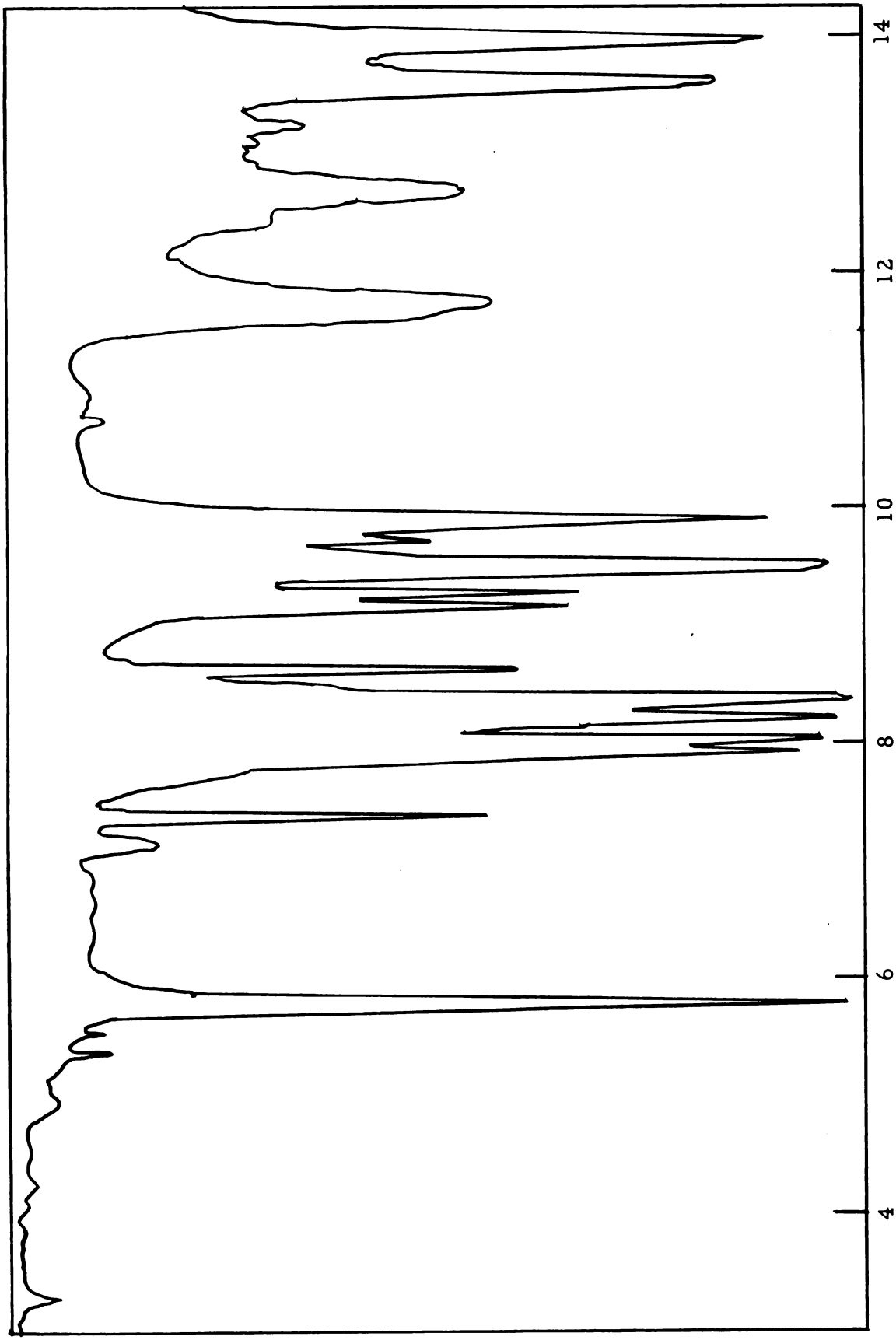


Figure 10. Infrared Spectrum of 2(p-Chlorophenyl) Thenoate taken in Carbon Disulfide.

IV. Product Analyses

A. Decomposition of t-Butyl-2-perthenoate in Carbon Tetrachloride

A solution containing 2 g. of t-butyl perthenoate in approximately 40 ml. of carbon tetrachloride was sealed in a Pyrex combustion tube. The tube was heated in an oven at 140° for 20 hrs. The tube was cooled in liquid air and cautiously opened. Considerable pressure was built up in the tube due to the evolution of carbon dioxide during the decomposition of the perester. The black, decomposition mixture was placed in contact with Norite and anhydrous magnesium sulfate for 48 hrs. The mixture was filtered and the filtrate was slowly distilled through a short Vigreaux column. The material (approximately 2 ml.) collected below the boiling point of carbon tetrachloride was analyzed. An infrared spectrum of this material showed definite carbonyl absorption peaks and possible hydroxyl peaks. Vapor phase chromatography (10% silicone column) gave three peaks with retention times of 3 min., 4 min., and 12 min. Samples of pure acetone, t-butyl alcohol and carbon tetrachloride gave retention times of 4 min., 5 min., and 12 min., respectively. From the relative areas under the peaks it was calculated that more than half the sample analyzed was carbon tetrachloride. These observations strongly suggested that acetone was present in the sample but no definite conclusion could be reached concerning the presence of t-butyl alcohol. If any of the alcohol was present, the amount must have been very small.

Acetone was identified by preparation of its 2,4-dinitrophenylhydrazone. Approximately 0.5 ml. of the low-boiling distillate was diluted with about a ml. of ethanol and treated with several drops of 0.25M Johnson's Reagent (43). In approximately 15 min. crystallization began and after allowing about an hour for completion of the reaction the crystalline product was collected on a fritted glass filter and dried in a vacuum desiccator. Recrystallization of the material from ethanol gave a pure derivative which

melted at 124.5-126°. Literature value (44): melting point 126°. A mixed melting point with an authentic sample of acetone-2,4-dinitrophenylhydrazone gave no melting point depression. This established acetone as a decomposition produce of t-butyl perthenoate in carbon tetrachloride.

After the greater part of the carbon tetrachloride was removed from the decomposition mixture, the residual liquid was washed twice with 50 ml. portions of 10% sodium hydroxide solution. The combined basic washings were then acidified with concentrated hydrochloric acid and extracted with ether. The ether solution was placed in contact with anhydrous magnesium sulfate and Norite. Following filtration, the ether was removed leaving a small amount of a yellow-colored solid. This was crystallized twice from ligroin to obtain a white solid melting at 124-125°. A mixed melting point with an authentic sample of thenoic acid showed no depression in the melting point. This established 2-thenoic acid as a decomposition product of t-butyl perthenoate in carbon tetrachloride.

Following extraction with base to remove the thenoic acid, the residual liquid of the decomposition mixture was washed twice with water and set aside overnight in contact with anhydrous magnesium sulfate and Norite. The small amount of carbon tetrachloride remaining was removed leaving a very small amount of a dark, brown-colored oil. The oil was dissolved in ether and set aside overnight in contact with magnesium sulfate and Norite. After filtration and removal of the ether, a yellow-colored, sweet-smelling oil remained. Repeated attempts to crystallize this material were unsuccessful. The oil was distilled using a molecular still at approximately 1 mm and an oil bath temperature of 100°. One drop of a colorless oil was collected whose infrared spectrum was found to be essentially identical with a spectrum of an authentic sample of t-butyl thenoate.

A few milligrams of a very dark-colored, intractable material, which slowly dissolved in acetone, remained after the distillation. This was not further investigated.

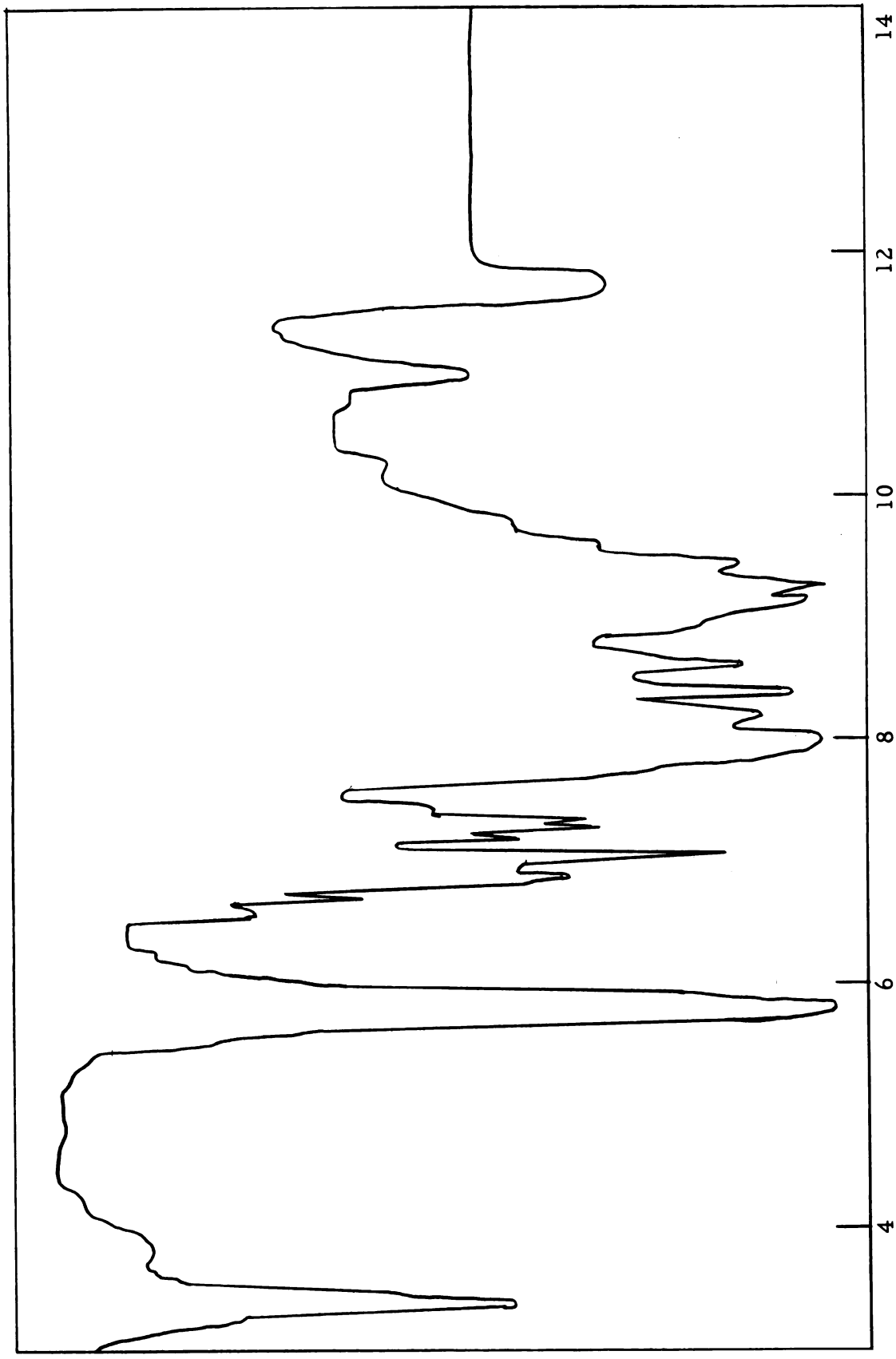


Figure 11. Infrared Spectrum of the Residue Obtained from the Decomposition of t-Butyl 2-Perthenoate in Carbon Tetrachloride Solution.

B. Decomposition of t-Butyl-2-perthenoate in Chlorobenzene

Approximately 4 g. of t-butyl perthenoate was dissolved in 100 ml. of chlorobenzene. This solution was heated at its reflux temperature for 8 hrs., cooled, treated with Norite and filtered.

The thenoic acid was isolated as described earlier, that is, by extraction with sodium hydroxide solution followed by acidification of the basic washings and recovery of the precipitated acid by filtration. The acid was recrystallized from hot water to obtain a white, crystalline solid melting at 124-125°. A mixed melting point with an authentic sample of thenoic acid showed no melting point depression.

After the extraction procedure, the chlorobenzene layer was washed with water and set aside overnight in contact with anhydrous magnesium sulfate and Norite. Removal of the chlorobenzene on a rotary evaporator left approximately a ml. of a brown oil. The oil was dissolved in a small amount of ether and chromatographed on alumina. The column was successively eluded with petroleum ether, carbon tetrachloride, cyclohexane, carbon disulfide, benzene, toluene, ether, acetone, ethyl acetate, ethanol and finally with methanol. From the benzene, toluene, and ether fractions, brown-colored oils were recovered. These oils were all shown to be identical by their infrared spectra which were very similar to the spectra of authentic samples of phenyl 2-thenoate and 2(p-chlorophenyl) thenoate. A very small amount of a light brown-colored solid was recovered from the ethanol fraction. By melting point and infrared spectrum, this solid was shown to be 2-thenoic acid.

Thus, the oily residue was not satisfactorily purified by chromatography on alumina. The infrared spectra of the brown oil, phenyl thenoate and p-chlorophenyl thenoate are quite similar so that the brown oil could not be positively identified. The area of the spectrum between 9 and 10 microns of the decomposition product was almost identical with

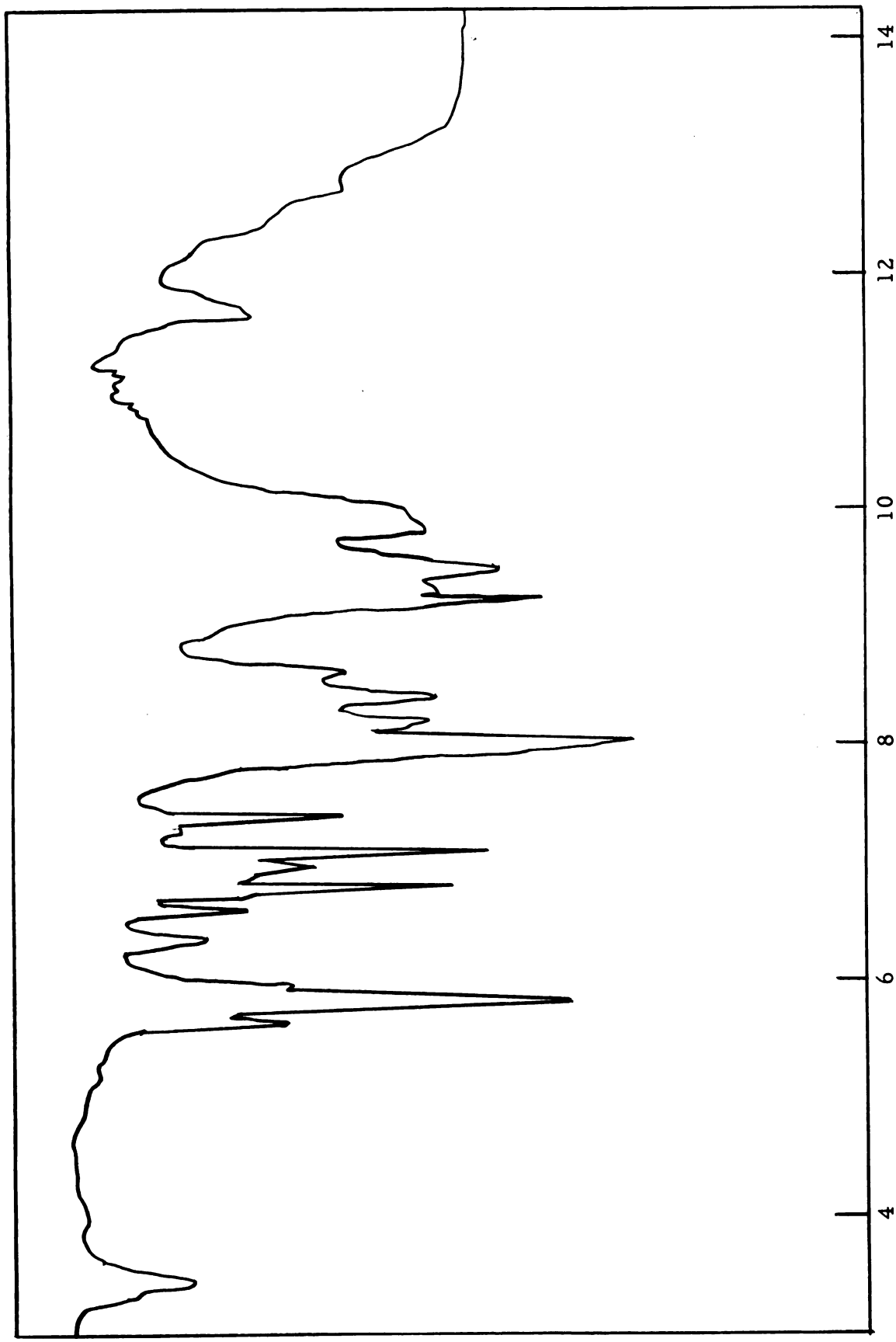


Figure 12. Infrared Spectrum of the Residue Obtained from the Decomposition of t-Butyl 2-Perthenoate in Chlorobenzene Solution.

the same region in the spectrum of phenyl thenoate but somewhat different in this region from the spectrum of p-chlorophenyl thenoate. The decomposition product could possibly be a mixture of the two esters. These same two esters were isolated by Ford and Mackay (10) when they decomposed 2-thenoyl peroxide in chlorobenzene.

The thenoic acid isolated from the ethanol fraction apparently was the result of incomplete removal of the acid during the extraction with sodium hydroxide solution as previously described.

C. Determination of Carbon Dioxide in Perester Decomposition

Using the apparatus illustrated in Figure 13, a measured aliquot of a standard chlorobenzene solution of the perester was introduced into the reaction flask and the system was swept with nitrogen for an hour. The absorption tube, packed with a 2:1 mixture of ascarite and anhydrous magnesium perchlorate, was then removed, weighed, and returned to the system. The perester solution was heated at its reflux temperature for a minimum period equivalent to 10 half-lives of the perester under a continuous stream of nitrogen. The heating was discontinued and the dry ice traps allowed to stand at room temperature for 30 min. The absorption tube was then reweighed and the gain in weight of the tube was taken as equivalent to the weight of carbon dioxide liberated by the perester during its decomposition. The results are tabulated in Table 2.

V. Kinetics of Decomposition of the Peresters

The rates of the thermal decomposition of the peresters were followed by measuring the rate of disappearance of the perester absorption band at approximately 5.7 microns employing a Perkin-Elmer model 21 recording infrared spectrophotometer. This method was chosen after initial attempts

to use the iodometric method of Silbert and Swern (33) proved unfeasible in its attempted application to this system.

The perester solutions used in the kinetic determinations were contained in ampules prepared from 9 mm Pyrex tubing. The tubing was cleaned prior to preparation of the ampules by immersion in hot, concentrated sulfuric acid for 24 hrs., followed by several washings with water, then immersion into concentrated ammonium hydroxide to remove any traces of sulfuric acid which is a catalyst for perester decomposition, followed by several washings with water and a final rinse with acetone. The tubing was dried at 130° for 12 hrs.

The nitrogen used to purge the perester solutions of oxygen was purified in the same manner as in the carbon dioxide determinations (Figure 13).

The following experimental procedure was used in a typical kinetic run. The carbon tetrachloride solution, approximately 0.03M in perester, was purged of oxygen by bubbling purified nitrogen into the solution for about 15 min. at room temperature. Approximately 0.3 ml. of the solution was introduced into each ampule with a hypodermic syringe and needle. In the determinations not containing a radical scavenger, nine ampules per determination were used, while in the determinations employing a scavenger, six ampules per determination were used. The ampules were sealed at -70° with an oxygen-gas torch, secured with string and completely immersed into an electrically heated mineral oil bath controlled to ± 0.2° by means of a Fisher-Serfass Electronic Relay. A period of 2 min. was allowed for the samples to reach the bath temperature, zero time being assumed to be 2 min. after the immersion of the ampules into the bath. At definite time intervals an ampule was removed from the bath and the reaction was immediately quenched by immersion of the ampule into ice water. The ampules were marked and stored at -70° until completion of the kinetic determination. The tips of the ampules were

broken and the samples were transferred into the infrared cell with a hypodermic syringe and needle and the rate of disappearance of the per-ester absorption band was measured. The rate of appearance of the acid peak at approximately 5.95 microns could also be measured.

For the kinetic determinations containing a radical scavenger, the data were plotted as a log absorbance versus time curve. For those determinations not containing a radical scavenger, the data were plotted as an absorbance versus time curve and the method of Guggenheim (29) was employed to calculate the apparent first-order rate constants.

The energies of activation were calculated from a plot of the log of the rate constants versus the reciprocal of the absolute temperature employing the method of least squares to determine the slopes. The entropies of activation were calculated by the method of Foster, Cope and Daniels (45).

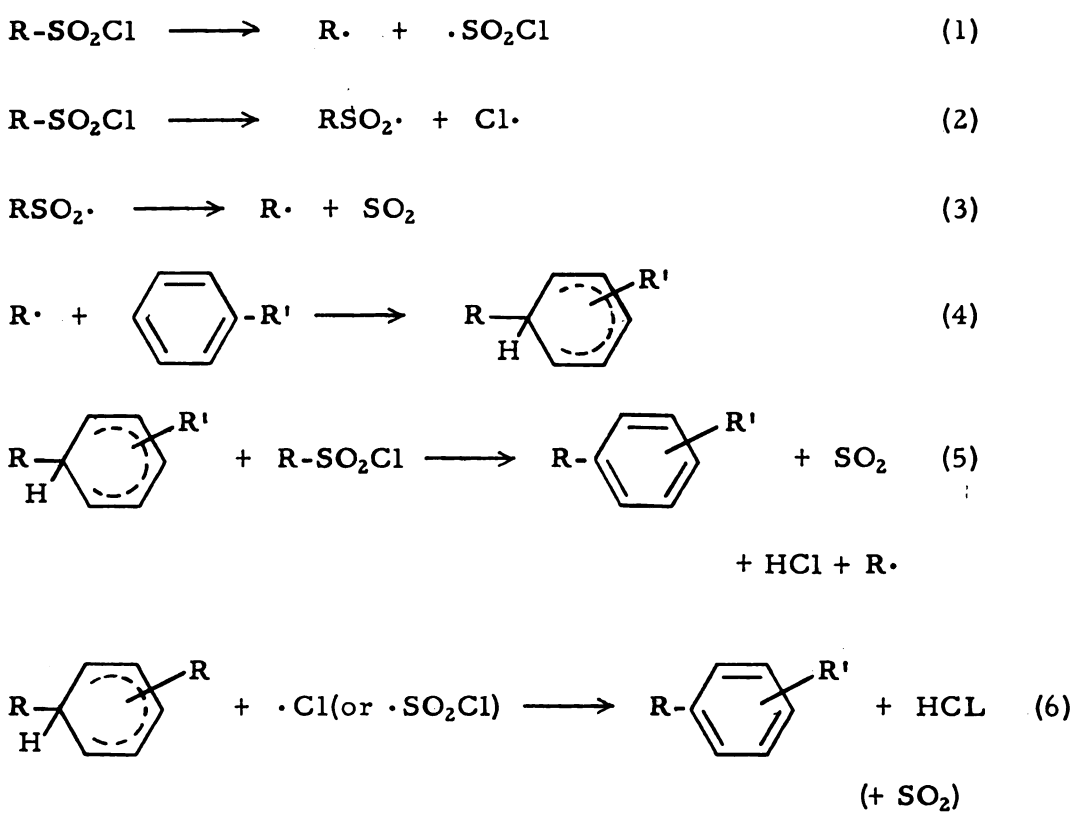
Derivation of the rate expressions and data for representative kinetic determinations are given in the Appendix.

VI. Miscellaneous Experiments

A. Decomposition of Thiophene-2-sulfonyl Chloride

1. Introduction and Results. A new and convenient process for free-radical substitution of aromatic compounds based on the thermal homolysis of sulfonyl halides was recently reported in the literature (46). In a typical reaction, one mole of benzenesulfonyl chloride in 15 moles boiling biphenyl completely decomposed in four hours at 255° with the evolution of nearly quantitative amounts of sulfur dioxide and hydrogen chloride. Mixed terphenyls were isolated in 75% yield. In general, this reaction gave good yields of arylated products when various benzene-sulfonyl chlorides were decomposed in a variety of high-boiling solvents such as p-dibromobenzene, mesitylene, and 1, 3, 5-trichlorobenzene.

The following mechanism was suggested (46) for the thermal decomposition of aromatic sulfonyl chlorides:



It appeared feasible, therefore, to investigate this type of decomposition reaction using thiophenesulfonyl chloride. A study of the reaction products, it was hoped, would give definite indications as to the fate of the thiophene radical.

The thiophene-2-sulfonyl chloride was decomposed in three different solvents whose boiling points varied considerably. These solvents were benzene (b.p. 80°), mesitylene (b.p. 165°), and biphenyl (b.p. 256°). The sulfonyl chloride was decomposed in a large excess of the solvent. Purified nitrogen was bubbled through the decomposition solution at a reasonably rapid rate to entrain volatile decomposition products.

The course of the reaction was followed by leading the gaseous reaction products (hydrogen chloride and sulfur dioxide) into a solution of standard sodium hydroxide.

The results of these experiments were unrewarding. In the lowest boiling solvent, benzene, no reaction occurred after heating the reaction mixture at its reflux temperature for two days. No sodium hydroxide was consumed and the thiophene-1-sulfonyl chloride was recovered almost quantitatively. At the reflux temperature of mesitylene, 5% of the sulfonyl chloride decomposed after 68 hrs. The solution began to darken shortly after it reached reflux temperature and was black at the end of the heating period. After removal of excess mesitylene, an intractable, black material was obtained. No sulfonyl chloride was recovered. Decomposition of the sulfonyl chloride in biphenyl at its reflux temperature led immediately to excessive tar formation. After two days, the entire reaction mixture became a sticky, semi-solid tar, and heating was discontinued. Surprisingly, no base was consumed.

These results indicated that the thermal decomposition of thiophene-2-sulfonyl chloride did not appear to proceed by a smooth decomposition into hydrogen chloride, sulfur dioxide, and the thiophene radical. Apparently, the boiling point of benzene was not high enough to cause any decomposition of the sulfonyl chloride. In mesitylene, one can suggest that only a small portion (5%) of the total decomposition was of the type desired, and the great bulk of the sulfonyl chloride was decomposed in fashions which led to the formation of the intractable tar. In the high-boiling biphenyl, the decomposition must have been of a totally undesired nature, since all the sulfonyl chloride was consumed, but no base eas consumed.

2. Experimental. The thiophene-2-sulfonyl chloride was prepared by the method of Blatt, et al. (47).

A 500 ml. round-bottomed flask was equipped with stirrer, dropping funnel and reflux condenser. All the glassware had been carefully dried. The flask was charged with 200 g. (1.72 mole) of chlorosulfonic acid and 100 ml. of anhydrous chloroform and the mixture was cooled to 0°. With efficient stirring, 50 g. (0.60 mole) of thiophene was added during 8 min. while holding the reaction temperature at 0° by immersion of the reaction flask into a dry ice-acetone bath. Following addition of the thiophene the mixture was allowed to warm to 10°. It was cooled again to 0° and held at this temperature while ice was added directly to the reaction mixture to decompose the excess chlorosulfonic acid (vigorous reaction). When no further reaction was apparent, the chloroform layer was separated and the aqueous layer was extracted twice with chloroform. The combined chloroform layers were placed in contact with anhydrous magnesium sulfate and Norite and set aside overnight. The chloroform was removed and distillation gave 46 g. (0.25 mole, 42%) of a light yellow-colored oil, boiling at $89\text{-}92^{\circ}/3$ mm. A sodium fusion and subsequent tests were positive for sulfur and halogen. An infrared spectrum of the product showed two strong absorption peaks at 7.3 and 8.5 microns which are characteristic of sulfonyl chlorides.

The sulfonyl chloride was then decomposed in the various aromatic solvents. Decomposition in benzene: thiophene-2-sulfonyl chloride, 27.4 g. (0.15 mole) was dissolved in 156 g. (2 moles) of benzene and the mixture was heated at its reflux temperature for two days. At the end of this time no base had been consumed by volatile products evolved from the mixture and the reaction mixture was still colorless. The benzene was removed on a rotary evaporator, leaving 26 g. (95% recovery) of unreacted sulfonyl chloride. Decomposition in mesitylene: thiophene-2-sulfonyl chloride, 18.2 g. (0.10 mole) and 180 g. (1.5 mole) of mesitylene were heated at the reflux temperature of the mixture for a total of 68 hrs. At the end of this heating period, the amount of base consumed corresponded

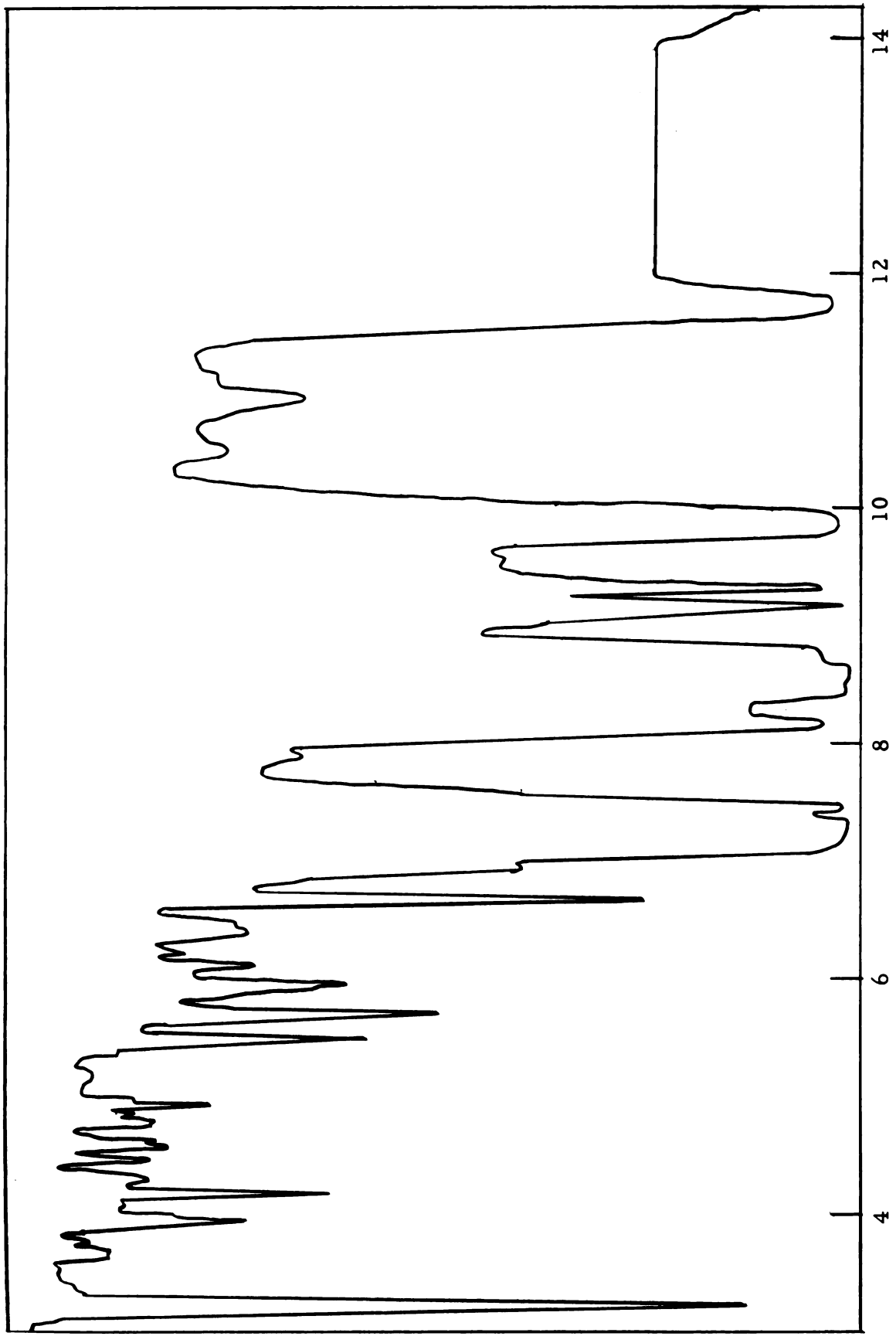


Figure 14. Infrared Spectrum of Thiophene-2-sulfonyl Chloride.

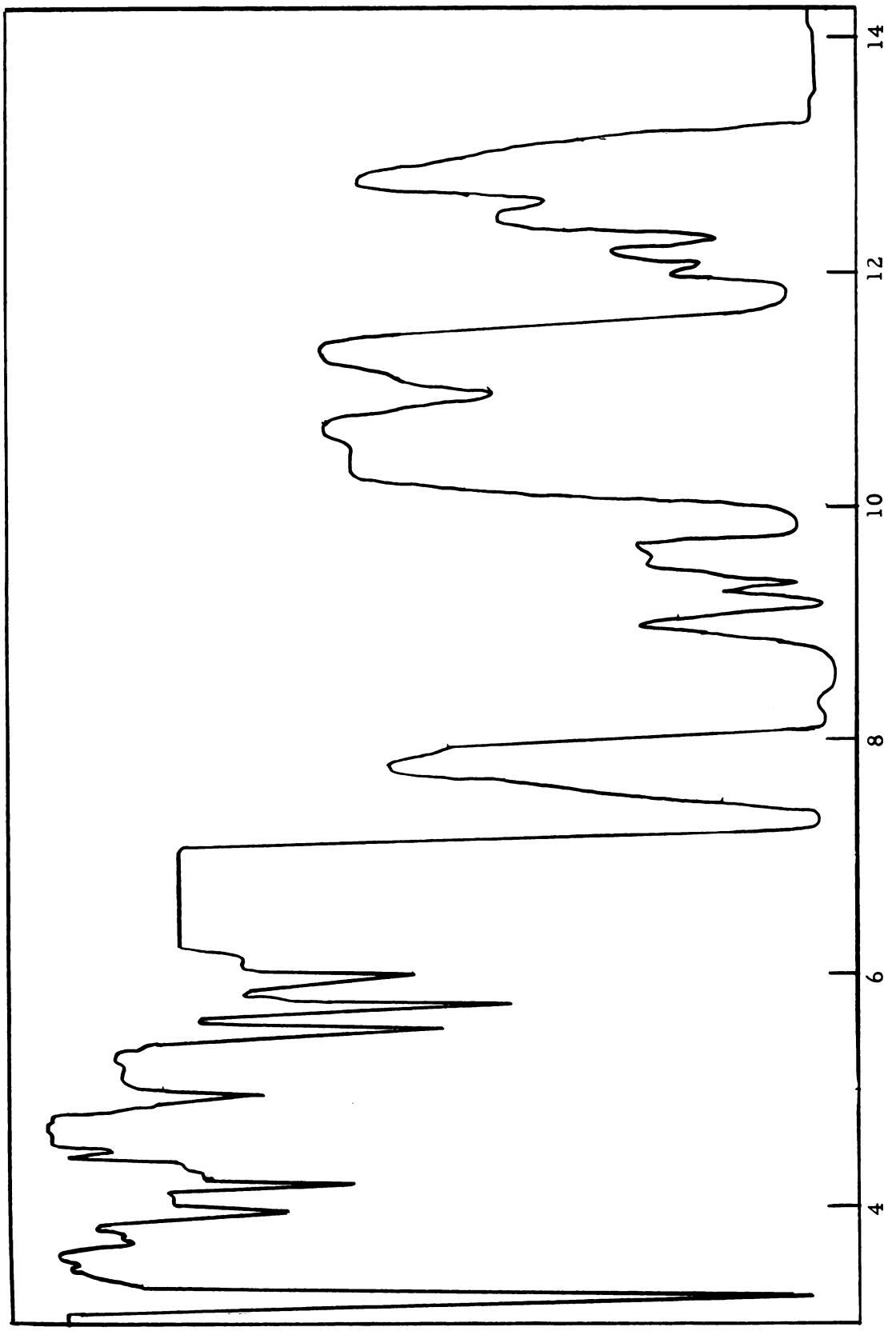
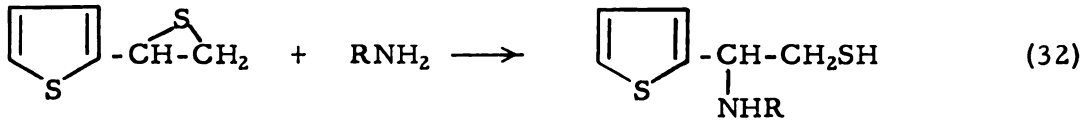


Figure 15. Infrared Specgrum of Thiophene-2-sulfonyl Chloride Taken in Carbon Disulfide.

to five millimoles of sulfonyl chloride or 5% decomposition. After removal of excess solvent, an intractable solid remained in the reaction flask. Decomposition in biphenyl: a mixture of thiophene-2-sulfonyl chloride, 27.4 g. (0.15 mole) and 230 g. (1.5 moles) of biphenyl was heated at its reflux temperature for 48 hrs. The solution began to darken in color almost immediately, and after two days became a sticky mass which completely blocked the flow of nitrogen through the reaction mixture. No measurable amount of base was consumed, indicating that no sulfur dioxide or hydrogen chloride had been evolved.

B. Attempted Preparation of 2(2-Thienyl) Thiirane

1. Introduction and Results. Compounds containing beta-amino-mercaptan linkages are known to possess physiological activity giving protection to biological systems against damage by high energy radiation (48, 49, 50, 51, 52). In an attempt to prepare such compounds containing a thiophene ring in the molecule, the reaction of a thienyl-substituted thiirane with an amine seemed to be a feasible path, equation (32).



(32)

This path necessitated the preparation of the unknown 2(2-thienyl) thiirane. The conversion of the also unknown 2(2-thienyl) oxirane to the thiirane by the classical reaction with thiourea (53) or with thiocyanate salts (54) appeared to be a good route to the desired thiirane.

The preparation of 2(2-thienyl) oxirane was attempted by three different methods. Each of these methods resulted in a very low yield of the desired product. Because of the poor yields none of the methods could be utilized on a reasonable preparative scheme. The oxirane was

very sensitive to heat which made purification by distillation unfeasible and it turned to a glassy resin after being set aside at room temperature for several days.

Several attempts to convert the oxirane to the thiirane resulted in rapid decomposition of the starting material with formation of black tars from which no product could be isolated nor any starting material recovered. No further attempts were made to prepare the oxirane nor the thiirane. The following experimental part describes the various methods used to prepare the oxirane and presents the proof of its structure.

2. Experimental. The oxirane was prepared, in poor yields, by three different reaction sequences, which are described as Methods I, II, and III. Method I involved the reaction of 2-thienylmagnesium bromide with chloroacetaldehyde and dehydrohalogenation of the resulting chlorohydrin. Method II was similar to Method I, except that 2-thienyllithium was used in place of the 2-thienylmagnesium bromide. Method III involved the epoxidation of 2-vinylthiophene with perbenzoic acid.

Method I. The starting materials for this reaction sequence were prepared in the following manner.

Preparation of Chloroacetaldehyde. A quantity of chloroacetaldehydr diethylacetal, 76.3 g. (0.50 mole) and 50 g. of anhydrous oxalic acid were placed in a 500 ml. round-bottomed flask fitted with a short Vigreaux column and distilling head. The flask was heated in an oil bath and the distillate boiling at 85-88° was collected. The yield of chloroacetaldehyde was very close to the theoretical amount each time this reaction was conducted. The aldehyde was immediately diluted with anhydrous ether and dried over anhydrous magnesium sulfate for several hours before use.

Preparation of 2-Bromothiophene. A liter, round-bottomed flask was fitted with a reflux condenser and charged with 500 g. (6.0 moles)

of thiophene and 178 g. (1.0 mole) of N-bromosuccinimide. This mixture was heated at its reflux temperature for 25 hrs., cooled, washed with 10% sodium hydroxide solution and then with water. After drying over anhydrous magnesium sulfate, the material was distilled, giving a product fraction weighing 98 g. (0.60 mole, 60%) boiling at 40-44°/12 mm.

Preparation of 2-Thienylmagnesium Bromide. A liter, round-bottomed flask was fitted with a stirrer, dropping funnel and a reflux condenser. The flask was charged with 12.8 g. of magnesium turnings and 50 ml. of anhydrous ether. The 2-bromothiophene, 65.5 g. (0.50 mole) was diluted with an equal volume of anhydrous ether and approximately 10 ml. of this solution was added to the magnesium turnings to start the reaction. The 2-bromothiophene was then added at such a rate sufficient to maintain the reaction mixture at its reflux temperature. The mixture was held at its reflux temperature for an additional hour, then chilled to ice bath temperature.

The 2-thienylmagnesium bromide was allowed to interact with the chloroacetaldehyde. To the chilled Grignard reagent was added dropwise 36.5 g. (0.468 mole) of chloroactaldehyde dissolved in 100 ml. of anhydrous ether during 2 hrs. A considerable amount of a brown, polymeric material formed during the addition of the aldehyde. After stirring for an hour at room temperature, the mixture was hydrolyzed with 500 ml. of 10% ammonium chloride solution. The ether layer was separated and the aqueous layer was extracted twice with ether. The extracts were combined with the main product layer and washed twice with 5% sodium carbonate solution and finally with water. The ether solution was set aside overnight in contact with anhydrous magnesium sulfate and Norite. The ether was removed on a rotary evaporator leaving 18 g. of a red oil. An infrared spectrum of this oil confirmed the presence of an alcohol function. Vacuum distillation was attempted on a small portion

of this oil. The material was very sensitive to heat, however, and decomposed immediately upon heating with excessive charring and the evolution of gases.

Since distillation proved impossible, the red oil was subjected to dehydrohalogenation without further purification. The oil, 15 g., was placed in a 300 ml. round-bottomed flask along with 100 ml. of water-saturated ether and cooled to 0° in an ice bath. A quantity of powdered potassium hydroxide, 17 g. (0.3 mole) was added in small amounts to the chilled, well-stirred solution during two hours. The ice bath was then removed and the reaction mixture was stirred overnight at room temperature. A 50 ml. quantity of water was added, the ether layer separated, and the water layer was extracted with ether. The extracts were combined with the product layer and placed in contact with anhydrous magnesium sulfate. After several hours the ether was removed on a rotary evaporator leaving a light red-colored oil with a sweet, floral odor. An infrared spectrum of the impure product showed no hydroxyl nor strong carbonyl absorption bands. Vacuum distillation gave a small forerun and 5 g. of a sweet-smelling, colorless oil, boiling at $82\text{-}85^{\circ}$/ 10 mm; n_D^{20} 1.5510. An infrared spectrum of the distilled product showed no hydroxyl absorption but showed three peaks of medium intensity in the carbonyl region, at 5.6, 5.75, and 5.95 microns. A spectrum of freshly distilled styrene oxide showed these same peaks at exactly the same wavelength and with about the same intensity. Anal. calcd. for C_6H_6OS: C, 57.11%; H, 4.79%; S, 25.42%. Found: C, 56.88%; H, 4.81%; S, 25.26%. On the basis of this physical data, the compound appeared to be an epxide. In a later portion of this work, several chemical tests are described which further substantiate the epoxide structure.

Method II. The general reaction scheme employed the use of n-butyllithium from which the 2-thienyllithium was prepared via an

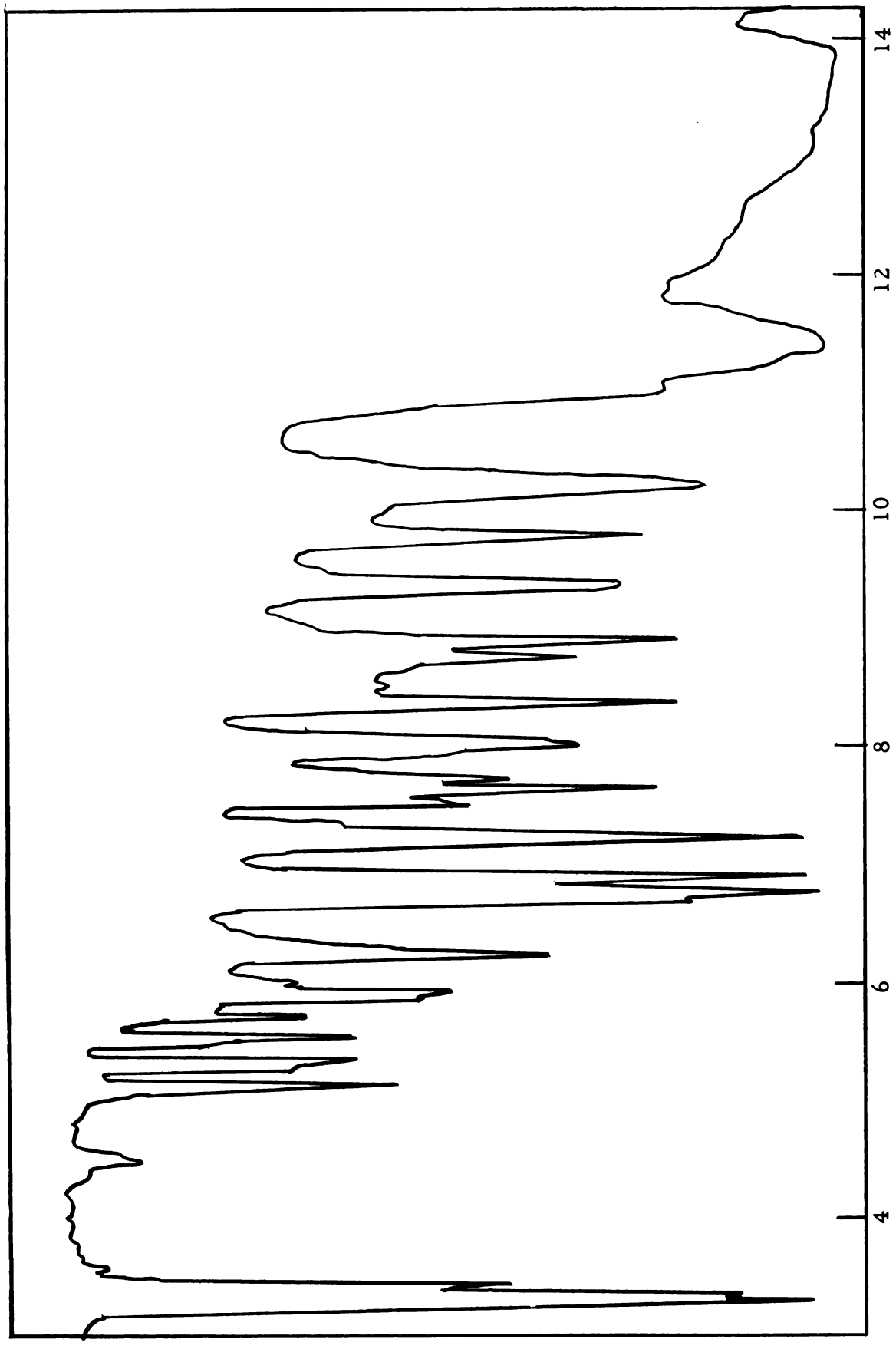


Figure 16. Infrared Spectrum of Styrene Oxide.

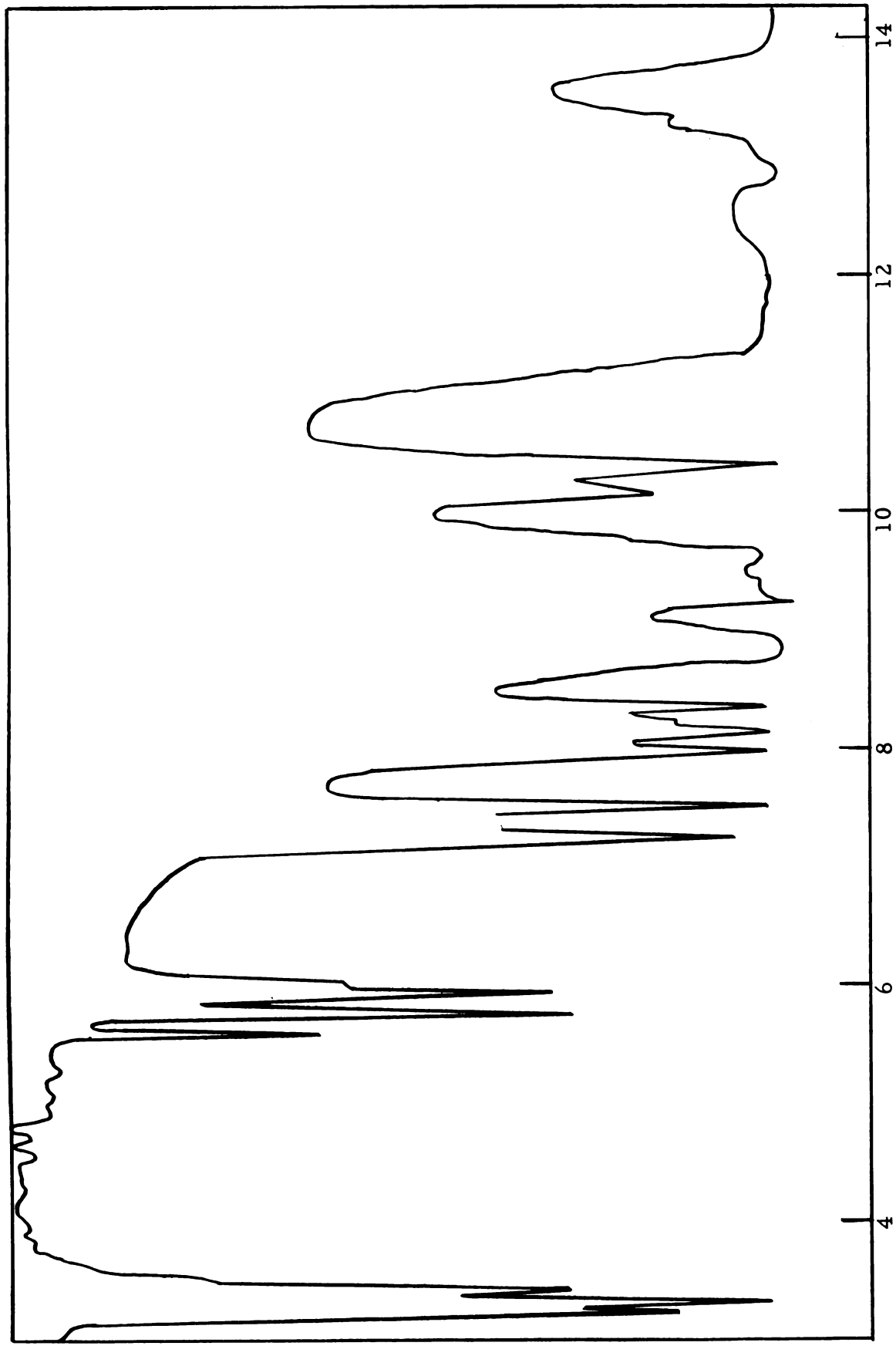


Figure 17. Infrared Spectrum of 2(2-Thienyl) Oxirane.

exchange reaction. This was allowed to react with chloroacetaldehyde and the resulting chlorohydrin was dehydrohalogenated with potassium hydroxide.

Preparation of n-Butyllithium. A quantity of lithium chips, 8.6 g. (1.23 g. atoms) and 100 ml. of anhydrous ether were placed in a 500 ml. round-bottomed flask equipped with a stirrer, reflux condenser, thermometer and dropping funnel. The flask was cooled in an isopropyl alcohol-dry ice bath to -10° and 68.5 g. (0.50 mole) of freshly distilled n-butyl bromide dissolved in 100 ml. of anhydrous ether was added slowly during an hour holding the temperature of the reaction mixture at -10°. Following the addition of the halide, the reaction mixture was stirred for an hour at -10°. Using nitrogen pressure, the n-butyllithium was filtered away from the unreacted lithium through a glass-wool plug into a liter flask previously cooled to -10° and equipped with a stirrer, reflux condenser, thermometer and dropping funnel.

Preparation of 2-Thienyllithium. With the temperature of the n-butyllithium solution cooled to -10°, 42 g. (0.50 mole) of freshly distilled thiophene dissolved in 50 ml. of anhydrous ether was added dropwise to the n-butyllithium solution during a half-hour. The mixture was then stirred for 5 hrs. while it was allowed to warm to room temperature.

Preparation of Chloroacetaldehyde. A quantity of 34 g. of chloroacetaldehyde was prepared as previously described, diluted with anhydrous ether and dried over magnesium sulfate.

The chloroacetaldehyde was then allowed to interact with 2-thienyllithium. The thienyllithium solution was cooled to -30° and held at this temperature while the chloroacetaldehyde was added during 2 hrs. The mixture was stirred for two hours while allowing it to warm to room temperature and then it was hydrolyzed by pouring it into 1 N hydrochloric acid. The red layer was separated, the aqueous layer was

extracted with ether and the extracts combined with the main product layer and placed in contact with anhydrous magnesium sulfate and Norite. The ether was removed on a rotary evaporator leaving 33.8 g. of a red-colored oil. An attempted distillation of a small amount of this oil led to immediate and rapid decomposition with excessive charring and the evolution of gases.

A dehydrohalogenation was attempted on 20 g. of this oil which was dissolved in 100 ml. of water-saturated ether. A quantity of powdered potassium hydroxide (14 g.) was added in small portions during 2 hrs. to the chilled reaction mixture. The mixture was stirred at room temperature overnight. Water was added and the product was isolated as described above. Distillation gave only 3 g. of a colorless oil whose boiling point, refractive index and infrared spectrum were identical to the product prepared in Method I.

Method III. This procedure involved the direct epoxidation of 2-vinylthiophene with perbenzoic acid. The vinylthiophene was prepared by the dehydration of 2-thienylmethylcarbinol; the alcohol was prepared by the interaction of the Grignard reagent prepared from 2-iodothiophene with acetaldehyde. The perbenzoic acid was prepared by standard procedures.

Preparation of 2-Iodothiophene. To the vigorously stirred mixture of 70 g. (0.84 mole) of thiophene and 100 ml. of benzene contained in a 500 ml. round-bottomed flask and cooled to 0° were added alternately in small portions 150 g. (0.70 mole) of mercuric oxide and 218 g. (0.86 mole) of iodine. The yellow mercuric oxide was replaced by the red mercuric iodide as the reaction proceeded. Following the addition of the mercuric oxide and the iodine, which required about an hour, the mixture was filtered and the solids were washed several times with small portions of ether. The ether washings were added to the filtrate which was washed

several times with 100 ml. portions of 5% sodium thiosulfate solution, and then with water. The organic material was dried over anhydrous calcium chloride and distilled to obtain 110 g. (62%) of a straw-colored oil, boiling at 78-80°/16 mm.

Preparation of 2-Thienylmagnesium Bromide. In a 500 ml. round-bottomed flask equipped with a stirrer, dropping funnel and reflux condenser were placed 19.3 g. of magnesium turnings and enough anhydrous ether to cover the magnesium. Then 156 g. (0.75 mole) of 2-iodothiophene dissolved in 150 ml. of anhydrous ether was added at such a rate sufficient to maintain the reaction mixture at a gentle reflux. Following the addition of the iodothiophene, the reaction mixture was heated at its reflux temperature for an hour and cooled to 0° by immersion into an ice bath.

Preparation of 2-Thienylmethylcarbinol. To the cooled Grignard reagent, 26.4 g. (0.60 mole) of freshly distilled acetaldehyde dissolved in 50 ml. of anhydrous ether was added slowly while maintaining the reaction temperature at 0°. Following addition of the aldehyde the reaction mixture was heated at its reflux temperature for 15 min., cooled to room temperature and hydrolyzed with 1N hydrochloric acid. The ether layer was separated, the aqueous layer was extracted several times with ether and the extracts combined with the main product fraction. This was washed with 10% sodium carbonate solution and water and dried over anhydrous magnesium sulfate. Distillation of the residue after removal of the ether gave 22 g. (28.5%) of a colorless oil, boiling at 68-70°/1.5 mm. An infrared spectrum of the oil confirmed the presence of the hydroxyl group. The yield of product was low due to a considerable amount of decomposition during its distillation.

Preparation of 2-Vinylthiophene. A quantity of 2-thienylmethylcarbinol weighing 22 g. was placed in a 50 ml. round-bottomed flask fitted with a short Vigreaux column and condenser arranged for distillation.

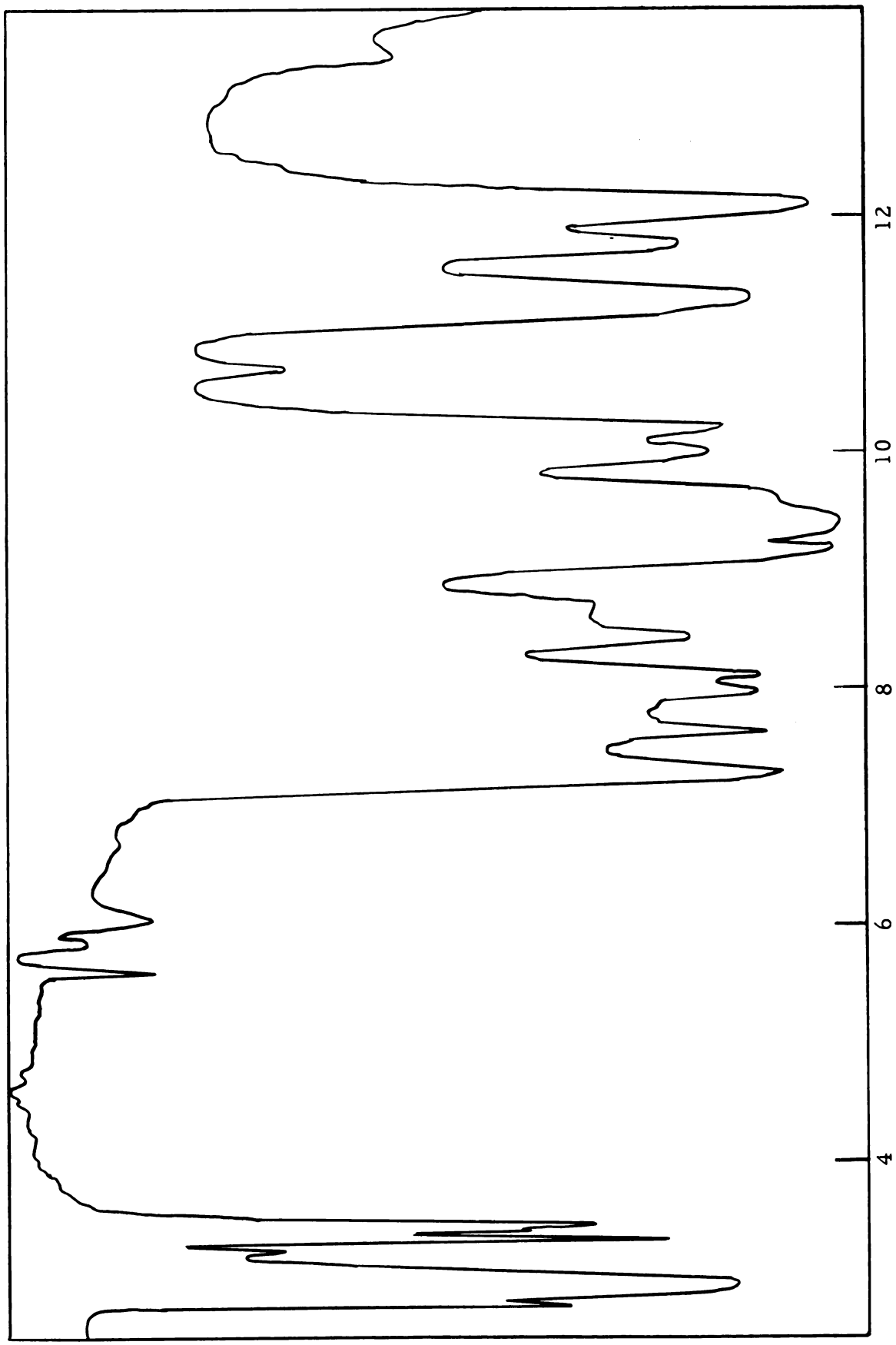


Figure 18. Infrared Spectrum of 2-Thienylmethylcarbinol Taken in Carbon Disulfide.

The alcohol was heated gently with a micro-burner, and a two-phase mixture was collected in the receiver. When the distillation appeared to be complete, heating was discontinued and the distillate was taken up in ether. The water layer was discarded and the ether layer was placed in contact with anhydrous magnesium sulfate. Distillation of the residue after removal of the ether gave 9.0 g. (0.082 mole, 41%) of a colorless oil boiling at 40-42°/12 mm., n_D^{20} 1.5720. The literature records (55): boiling point 77-78°/70 mm., n_D^{20} 1.5722. The infrared spectrum of the product supported its structure.

Preparation of Perbenzoic Acid. The perbenzoic acid was prepared by the method of Braun (56) using the modifications suggested by Koltoff, Lee, and Mairs (57).

In a 500 ml. Erlenmeyer flask, 3.91 g. (0.17 g. atom) of sodium was dissolved in 100 ml. of absolute methanol, which had been previously distilled from calcium hydride. The reaction flask was cooled to -5° in an ice-salt bath and a solution prepared from 35 g. (0.145 mole) of benzoyl peroxide dissolved in 200 ml. of purified chloroform and precooled to 0° was added through a separatory funnel to the sodium methoxide solution during 10 min. while vigorously shaking the flask. Following the addition of the peroxide, the reaction mixture was transferred to a liter separatory funnel and shaken with 500 ml. of an ice-water mixture. The chloroform layer was separated and the aqueous layer was extracted twice with carbon tetrachloride (to remove methyl benzoate). The aqueous layer contained the sodium salt of perbenzoic acid and the free acid was liberated by the addition of 1N sulfuric acid followed by extraction three times with 100 ml. portions of benzene. The benzene solution was washed twice with water, placed over anhydrous magnesium sulfate in a brown bottle, stored for several hours at 10°, then filtered and diluted to 500 ml. with benzene in a volumetric flask. A 3 ml. aliquot of this solution was titrated for peroxide content in the usual manner and

showed the peracid solution contained 0.0775 mole of peracid, which corresponds to a yield of 59% based on 0.145 mole of 94% pure benzoyl peroxide. (The benzoyl peroxide used was previously titrated for purity.)

The perbenzoic acid solution was then allowed to interact immediately with the vinylthiophene. The peracid solution was placed in a liter, round-bottomed flask equipped with a stirrer, reflux condenser and thermometer. After cooling the peracid solution to 5°, a 9 g. quantity (0.082 mole) of 2-vinylthiophene was added to the flask and the stirrer was started. The mixture was allowed to stir at 5° and aliquots of 3 ml. were removed at various time intervals and titrated for peracid content. After 24 hrs., the peracid was completely consumed and the reaction mixture was transferred to a separatory funnel and washed with 5% sodium hydroxide solution to remove benzoic acid, then with water, followed by a dilute ferrous sulfate solution to test for remaining peroxides (negative), then again with water. The yellow solution was placed in contact with anhydrous magnesium sulfate. The benzene was removed on a rotary evaporator leaving 6 g. of a light red-colored, floral-smelling oil. Attempted distillation caused rapid decomposition and only enough distillate was collected to obtain an infrared spectrum. This proved to be identical with the spectrum of the product obtained in Method I.

In an effort to present further proof that the product isolated by the preceding reaction schemes was the epoxide, the following chemical tests were performed.

Several drops of the product were mixed with 2 ml. of 1N hydrochloric acid and stirred for a few minutes in a small beaker. A white, pasty material precipitated. The dilute acid was decanted and the white precipitate was taken up in ether and dried over anhydrous magnesium sulfate. The ether was removed on a rotary evaporator and the residue was taken up in carbon disulfide. The infrared spectrum of this material showed strong hydroxyl absorption bands. This would be the expected

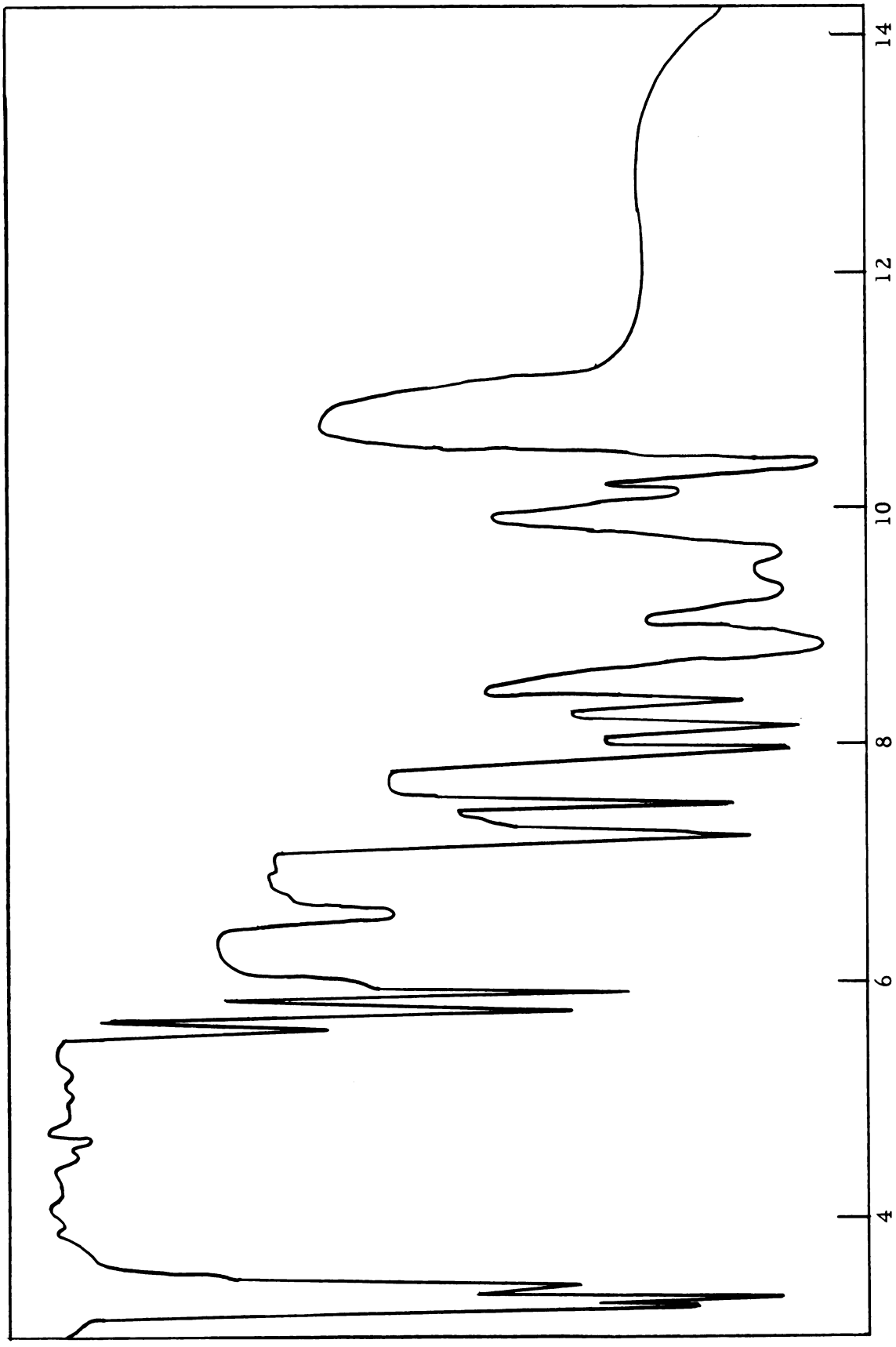


Figure 19. Infrared Spectrum of 2(2-Thienyl) Oxirane Prepared from 2-Vinylthiophene and Perbenzoic Acid.

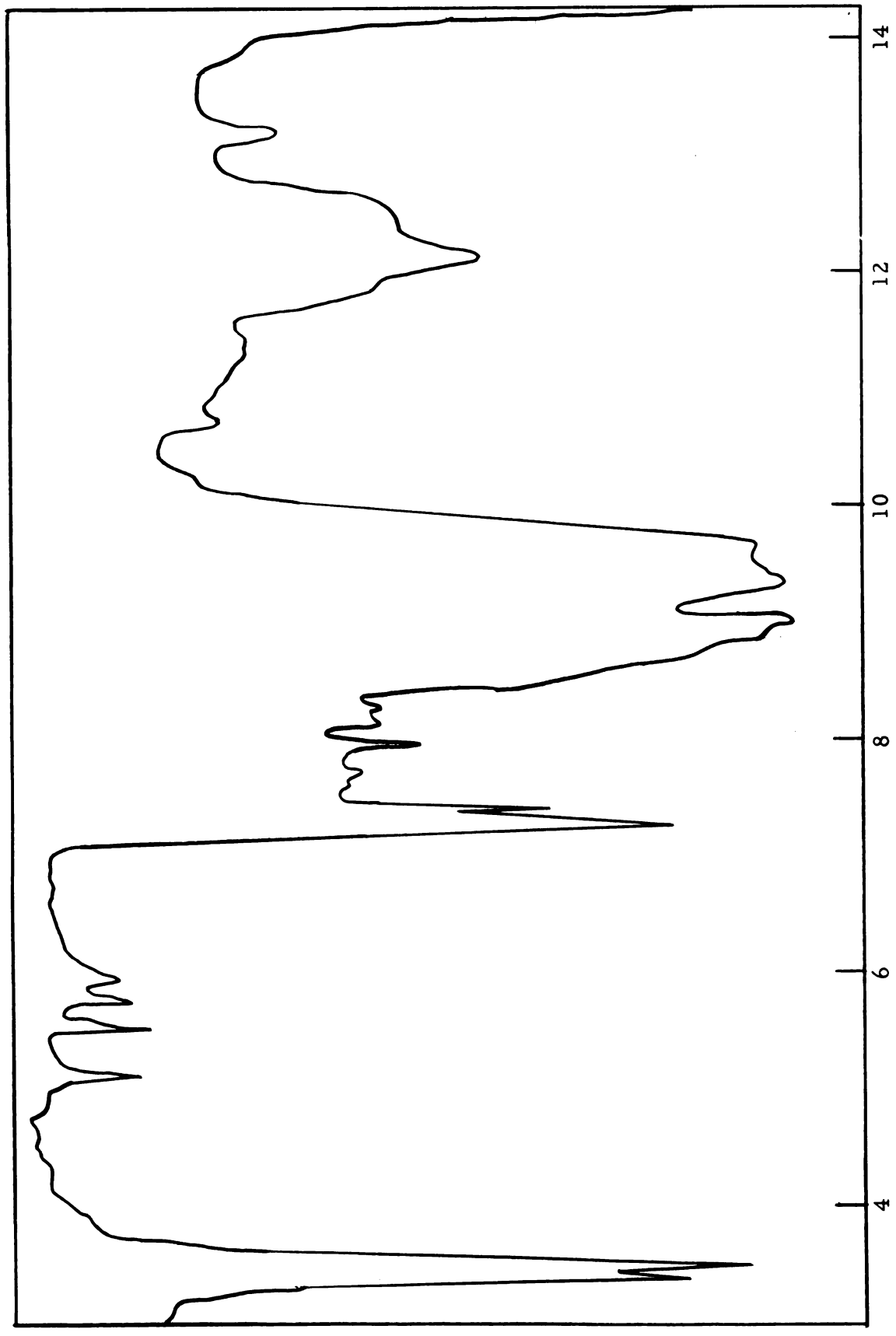


Figure 20. Infrared Spectrum of the Product Obtained from the Reaction of 2(2-Thienyl) Oxirane with Hydrochloric Acid.

result of the reaction of an epoxide with dilute, mineral acid, giving the diol as product.

Another sample of several drops of the original material was hydrolyzed as above, the white precipitate being taken up in ether. To the ether solution, a very dilute solution (1%) of potassium permanganate was added dropwise. Immediately, the permanganate was decolorized, as would be expected upon reacting a diol with permanganate.

Another sample of several drops of the original material was stirred for several minutes with 2 ml. of a 1:1 acetic acid-water solution containing 10% sodium acetate. The mixture was then poured into an equal volume of water and extracted with ether. The ether layer was washed several times with small portions of 5% sodium carbonate solution until the ether layer was slightly basic to litmus. The ether layer was then dried in contact with anhydrous magnesium sulfate, the ether removed, and the small amount of residue was taken up in carbon tetrachloride at its infrared spectrum was obtained. Absorption bands at 5.75 and 8.20 microns, characteristic of an ester linkage were observed along with the hydroxyl peak at 2.95 microns. This would be the expected result from the hydrolysis of an epoxide in an aqueous acetate solution, the product consisting, most likely, of a mixture of the diol, the mono-acetylated diol and the di-acetylated compound.

It appears reasonable, therefore, to assign the epoxide structure to the compound isolated in the preceding reaction schemes on the basis of the elemental analysis, infrared spectrum and chemical characterization. Unfortunately, the yields of the product were poor by the various methods used, and the instability of the product toward heat made its purification rather difficult.

Small portions of the epoxide (several grams) were reacted with thiourea and potassium thiocyanate in an attempt to prepare the thioepoxide or thiirane. The reaction temperature was varied from ambient to -15°,

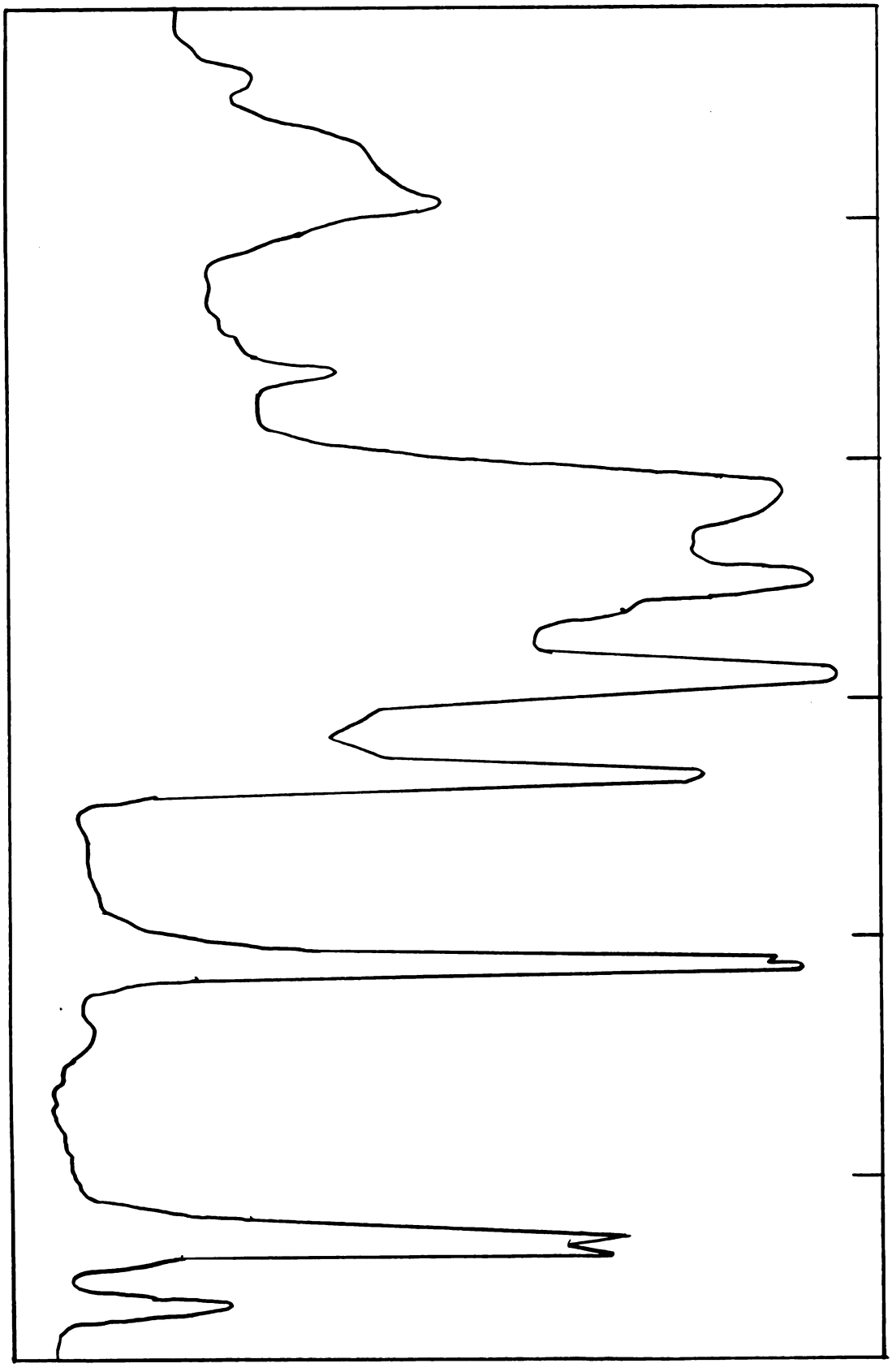


Figure 21. Infrared Spectrum of the Product Obtained from the Reaction of 2(2-Thienyl) Oxirane with Sodium Acetate and Acetic Acid.

but in all cases rapid decomposition of the starting material was observed in all the attempts and neither product could be isolated nor starting material recovered.

SUMMARY

1. Six new t-butyl peroxyesters, derived from 2-thenoic acid and substituted 2-thenoic acids were prepared, and their rates and products of decomposition in carbon tetrachloride were studied.

2. The rates of decomposition of the peroxyesters were first order in the presence of a radical scavenger, but were faster and not of any integral order in the absence of a radical scavenger. The rate of decomposition increased with increasing concentration in the absence of a radical scavenger. This was strongly suggestive of an induced decomposition step superimposed upon the spontaneous cleavage of the oxygen-oxygen bond.

3. The products of decomposition of the unsubstituted perester in carbon tetrachloride included carbon dioxide, 2-thenoic acid, acetone and phenyl 2-thenoate. When the same compound was decomposed in chlorobenzene, carbon dioxide, 2-thenoic acid and, most probably, a mixture of two esters, phenyl 2-thenoate and 2(p-chlorophenyl) thenoate were isolated.

4. Some miscellaneous experiments involving the decomposition of thiophene-2-sulfonyl chloride and the attempted preparation of 2(2-thienyl) thiirane were described.

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APPENDIX

Derivation of the Guggenheim Equation

The equation used to follow the decomposition of the peresters in the absence of a radical scavenger was obtained by the following manipulations. From the equation for a first order reaction one has

$$f(C) = f(C_0)\ e^{-kt} \tag{1}$$

where $f(C_0)$ is an appropriate function of the initial perester concentration and $f(C)$ is the same function at time t. If times t_1, t_2, t_3, etc., and $t_1 + \Delta$, $t_2 + \Delta$, $t_3 + \Delta$, etc., are selected where Δ is a constant increment, then the following equations are true:

$$(f(C_1) - f(C_\infty)) = (f(C_0) - f(C_\infty))\ e^{-kt_1} \tag{2}$$

$$(f'(C_1) - f(C_\infty)) = (f(C_0) - f(C_\infty))\ e^{-k(t_1 + \Delta)} \tag{3}$$

where $f(C_1)$ and $f'(C_1)$ are readings of the appropriate function at t_1 and $t_1 + \Delta$ respectively. Similar equations for t_2, t_3, etc., would also be true. Subtracting (3) from (2) gives

$$(f(C_1) - f'(C_1)) = (f(C_0) - f(C_\infty))\ e^{-kt_1}\ (1 - e^{-k\Delta}) \tag{4}$$

or

$$kt_1 + \ln (f(C_1) - f'(C_1)) = \ln\ [(f(C_0) - f(C_\infty))\ (1 - e^{-k\Delta})] \tag{5}$$

which can be generalized by dropping the subscript 1. The right hand side of the equation is a constant. Changing to base 10 logarithms and rewriting gives

$$\text{Log}\ (f(C) - f'(C)) = 2.303\ kt + A \tag{6}$$

where A incorporates the right hand term of equation (5) and factor 2.303.

In this investigation, absorbance was used as $f(C)$. The rate constants were obtained by plotting log ($f(C) - f'(C)$) versus t and multiplying the slope of the line by 2.303. It was previously established that the absorbance of the various peresters varies linearly with concentration throughout the concentration range employed.

The energy of activation, E_a, was calculated using equation (7)

$$k = se^{-E_a/RT} \tag{7}$$

where k is the first order rate constant, E_a is the experimental activation energy in calories, R is the gas constant per mole (1.987 calories/^{o}K), and s is the frequency factor. Rewriting to a more convenient form,

$$\log k = \log s + -E_a/2.303\ RT \tag{8}$$

and plotting log k versus 1/T, the energy of activation was obtained by multiplying the slope of the line, which was determined by the method of least squares, by -2.303 R.

The entropy of activation, ΔS^*, was calculated from the Eyring Equation

$$k = \frac{ek'T}{h}\left(e^{\Delta S^*/R}\right)\left(e^{-E_a/RT}\right) \tag{9}$$

where k is the first order rate constant, k' is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, ΔS^* is the difference in entropy between the initial and activated states in entropy units, E_a is the experimental activation energy in calories, R is the gas constant in calories/^{o}K, and e is the base of the natural logarithm system.

Combining equations (7) and (9) there is obtained

$$s = \frac{ek'T}{h}\ e^{\Delta S^*/R} \tag{10}$$

Taking logarithms of both sides and rearranging gives

$$\Delta S^* = R \ln s - R \ln (ek'T/h) \tag{11}$$

The entropy of activation was obtained by solving equation (8) for s at various T and K_2, and then using the average s in equation (11) to solve for ΔS^*. Suitable examples of these calculations follow.

Calculation of Rate Constant for the Decomposition of t-Butyl 5-Chloro-2-perthenoate at 99.2°, 0.2M in Styrene

Table 10. Decomposition of t-Butyl 5-Chloro-2-perthenoate at 99.2° in Carbon Tetrachloride, 0.2M in Styrene

Sample	Time/hrs.	Absorbancy	Log_{10}Absorbancy
1	0	0.61567	-0.21063
2	10	0.57331	-0.24162
3	21	0.52129	-0.28291
4	35	0.46163	-0.33533
5	50	0.41573	-0.38122
6	71	0.33947	-0.46916

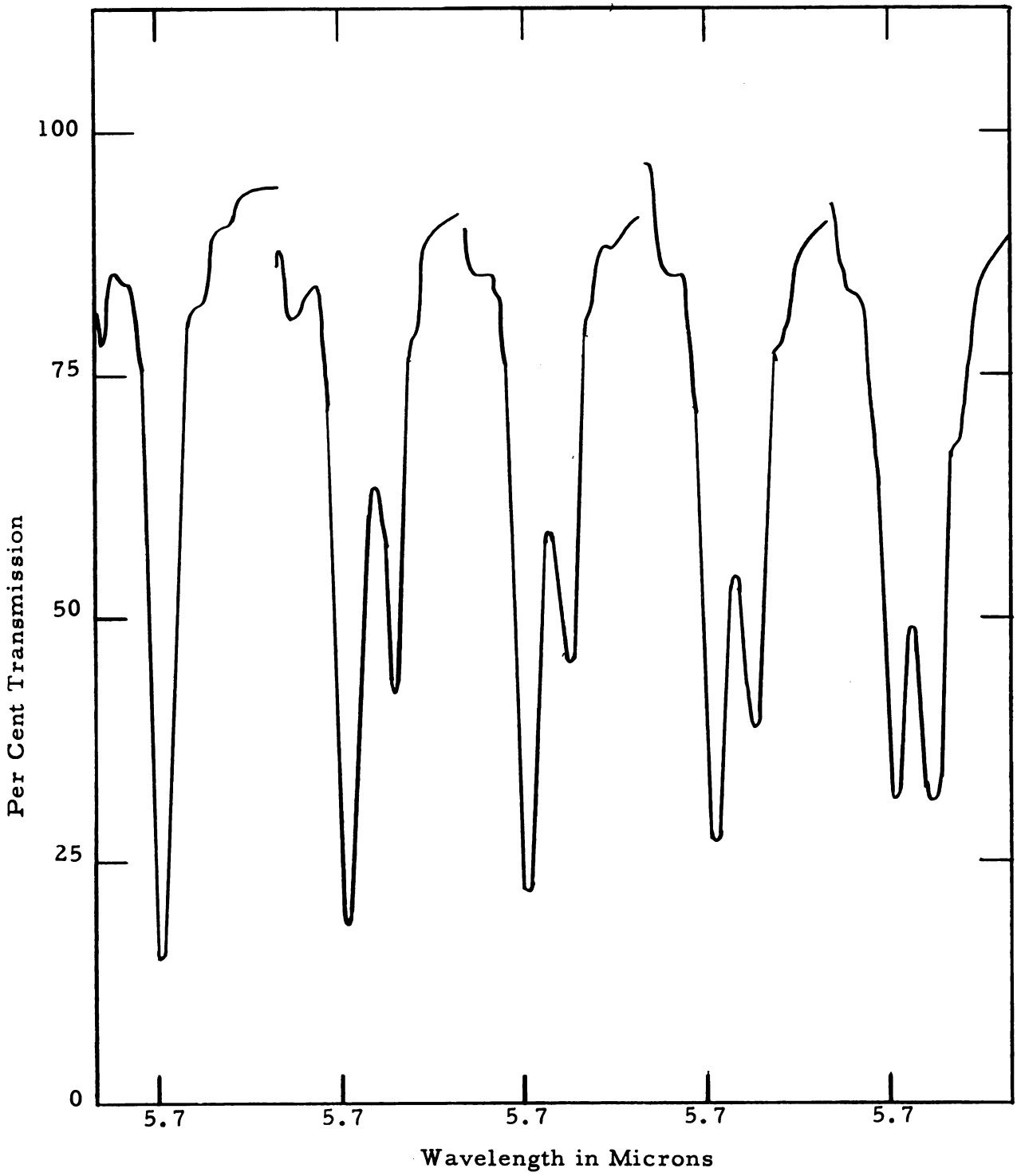

Figure 22. Quantitative Infrared Spectra of the Decomposition of t-Butyl 5-Chloro-2-perthenoate at 99.2° in Carbon Tetrachloride, 0.2M in Styrene.

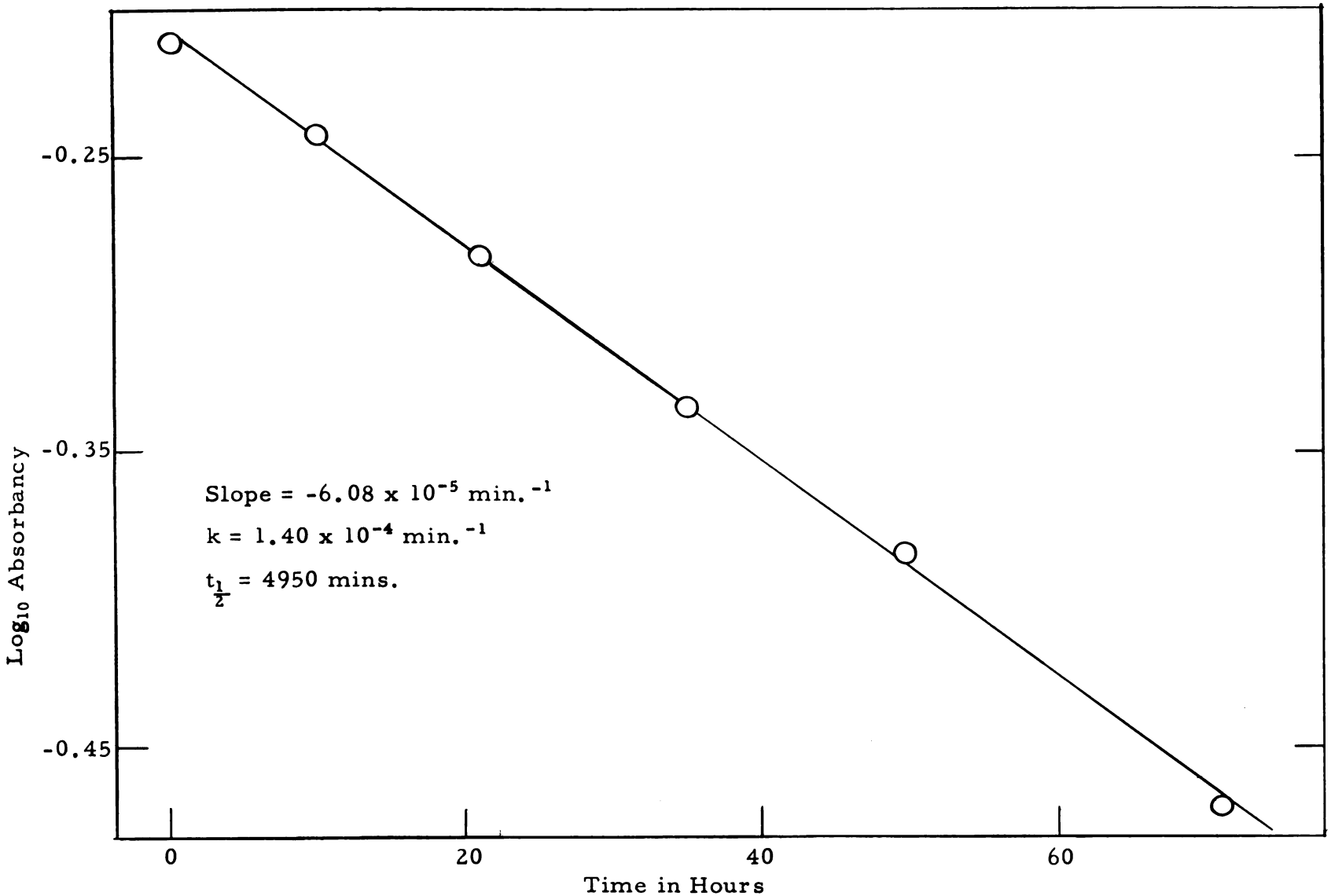

Figure 23. Log Absorbancy versus Time Curve for the Decomposition of t-Butyl 5-Chloro-2-perthenoate at 99.2° in Carbon Tetrachloride, 0.2M in Styrene.

Calculation of Rate Constant for the Decomposition of t-Butyl 5-Methyl-2-perthenoate at 124.5° in Carbon Tetrachloride

Table 11. Decomposition of t-Butyl 5-Methyl-2-perthenoate at 124.5° in Carbon Tetrachloride

Sample	Time/mins.	Absorbancy
1	0	0.73686
2	10	0.66643
3	20	0.61192
4	30	0.54995
5	55	0.45551
6	80	0.39284
7	100	0.35659
8	140	0.29377
9	175	0.27944

Table 12. Guggenheim Data for the Decomposition of t-Butyl 5-Methyl-2-perthenoate at 124.5° in Carbon Tetrachloride

Time/mins.	A_t	$A_{t+\Delta}$	$A_t - A_{t+\Delta}$	$\text{Log}_{10}(A_t - A_{t+\Delta})$
10	0.666	0.302	0.364	-0.43890
20	0.607	0.293	0.314	-0.50307
30	0.555	0.287	0.268	-0.57187
40	0.510	0.284	0.226	-0.64589
50	0.473	0.277	0.196	-0.70774

Δ = 125 minutes

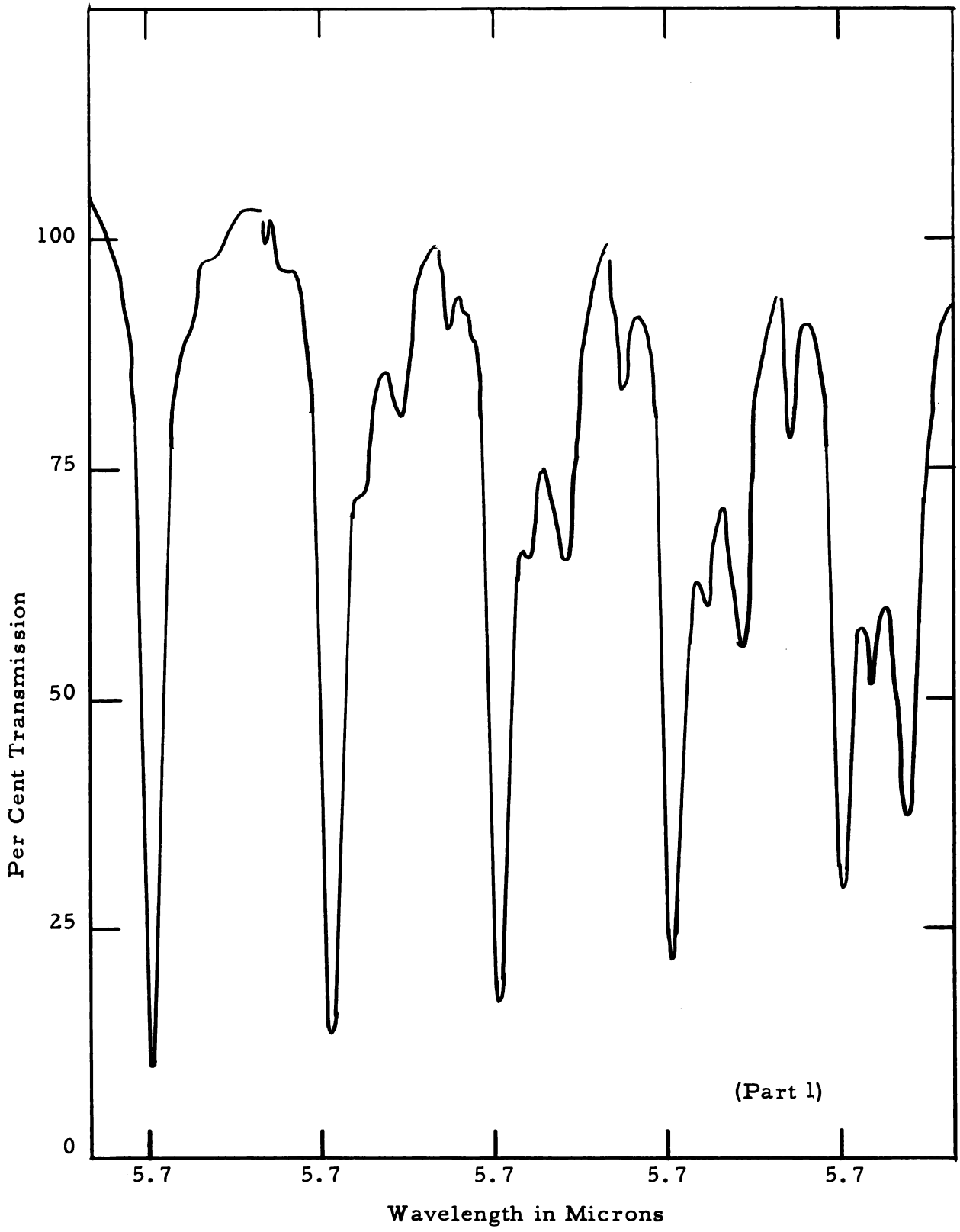

Figure 24. Quantitative Infrared Spectra of the Decomposition of t-Butyl 5-Methyl-2-perthenoate at 124.5° in Carbon Tetrachloride.

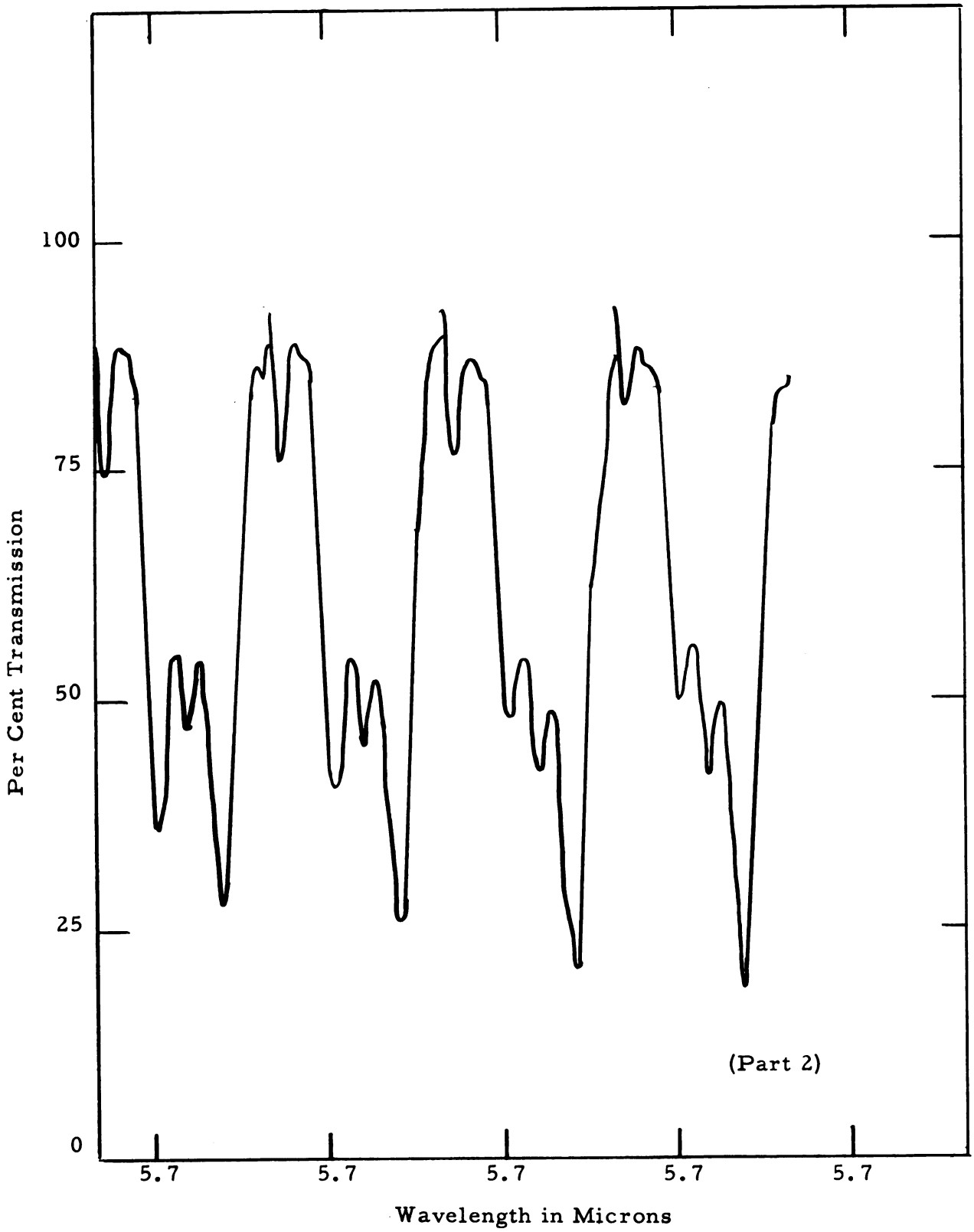

Figure 24 (cont'd). Quantitative Infrared Spectra of the Decomposition of t-Butyl 5-Methyl-2-perthenoate at 124.5° in Carbon Tetrachloride.

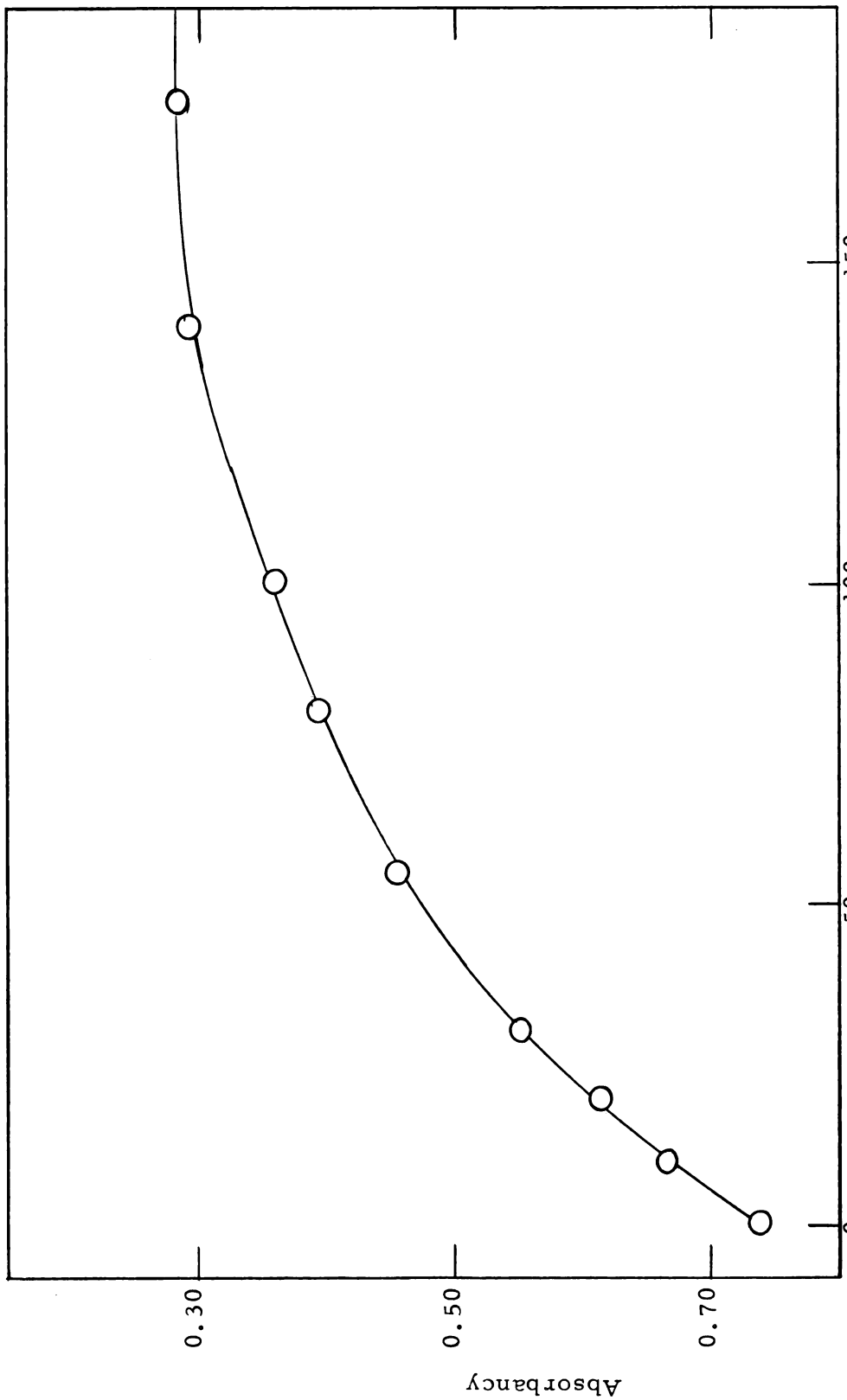

Figure 25. Absorbancy versus Time Curve for the Decomposition of t-Butyl 5-Methyl-2-perthenoate at 124.5° in Carbon Tetrachloride.

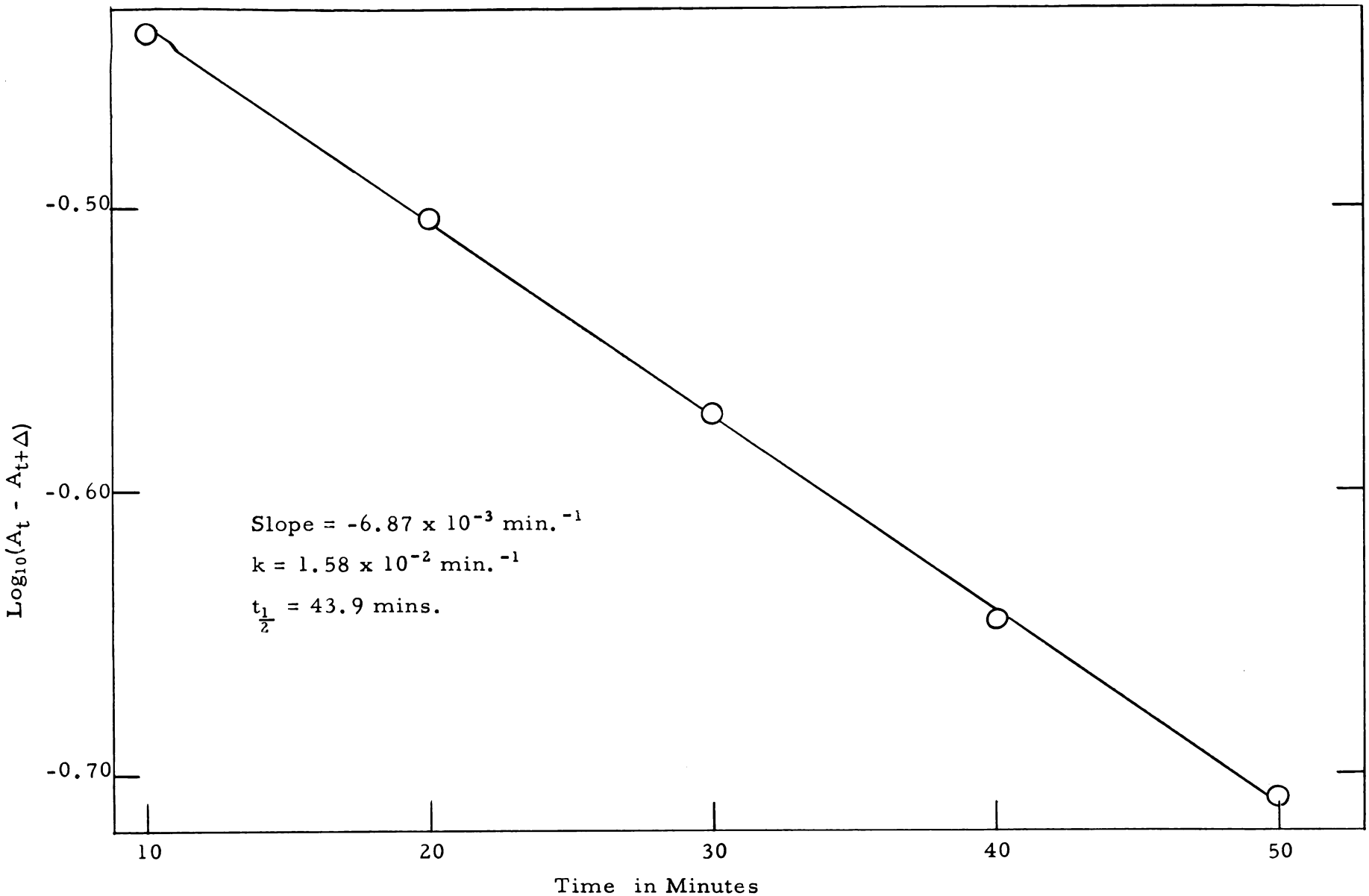

Figure 26. Guggenheim Plot for the Decomposition of t-Butyl 5-Methyl-2-perthenoate at 124.5° in Carbon Tetrachloride.

Table 13. Energy of Activation for the Decomposition of t-Butyl 2-Perthenoate in Carbon Tetrachloride, 0.2M Styrene

$T/^{o}K$	$T^{-1}/^{o}K^{-1}$	$k/mins.^{-1}$	$Log_{10}k$	$Slope/^{o}K$	E_a kcal./mole
372.3	2.68605×10^{-3}	2.01×10^{-4}	-3.69680		
381.5	2.59672×10^{-3}	1.00×10^{-3}	-3.00000	-7.68338×10^{3}	35.2
397.6	2.51509×10^{-3}	4.14×10^{-3}	-2.38360		

Table 14. Entropy of Activation for the Decomposition of t-Butyl 2-Perthenoate in Carbon Tetrachloride, 0.2M in Styrene

$k/mins.^{-1}$	$Log_{10}k$	$E_a/2.303RT$	$Log_{10}s$	Average $log_{10}s$	ΔS^{*} at $385.0^{o}K$/ e.u.
2.01×10^{-4}	-3.69680	20.63760	16.94080		
1.00×10^{-3}	-3.00000	20.13992	17.13992	17.00716	16.8
4.14×10^{-3}	-2.38360	19.32440	16.94080		

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