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ABSTRACT

SYNTHESIS AND STUDY OF DECOMPOSITION RATES OF SOME BIS(THENOYL)-PEROXIDES

by Fred Martin Gruen

This study concerns the effects of various substituents on the rates of decomposition of substituted bis(thenoyl)peroxides.

Interest in the rates and mechanisms of decomposition of the thenoyl peroxides is based on the possible feasibility of using these compounds commercially as initiators of free radical type polymerizations, or as catalysts in other polymerization processes.

The investigation involved a) the first syntheses and characterization of thenoyl chlorides, and bis thenoyl peroxides, and b) comparisons of the rates of decomposition of the peroxides as affected by (or governed by) the substituted groups.

The prepared thenoyl peroxides, all of which are derivatives of 2- and 3-thenoic acids, are listed in Table I.

As intermediates in preparing the peroxides, the following acid chlorides were prepared for the first time:

5-bromo-3-thenoyl chloride
5-chloro-3-thenoyl chloride
3-methyl-2-thenoyl chloride
5-nitro-3-thenoyl chloride
2,5-dichloro-3-thenoyl chloride
4,5-dibromo-2-thenoyl chloride
5-ethyl-4-bromo-2-thenoyl chloride
5-phenyl-2-thenoyl chloride
2,5-dimethyl-3-thenoyl chloride.

The general method of preparing the thenoyl peroxides was to add the appropriate thenoyl chloride, dissolved in a suitable solvent to an ice cold aqueous solution of sodium peroxide, and to let the mixture

stand until the reaction was completed. The formed, solid material was filtered off, washed with ice water and the product purified by recrystallization from an organic solvent.

The thenoyl peroxide decomposition rate determinations were carried out in a carbon tetrachloride solution, with the exception of the decomposition of bis(5-nitro-3-thenoyl)peroxide, which was insoluble in this solvent; the solvent used for this latter compound was chloroform. Styrene was employed with all peroxide decomposition rate determinations as a free radical scavenger, to eliminate induced decomposition and make certain that only the spontaneous thermal decomposition would be occurring. Infrared spectroscopy was employed as an analytical tool, the "peroxide peak" at a wavelength of 5.7 microns being observed. The absorption peak intensity was used as a measure of the concentration of peroxide remaining after various reaction periods, at a specific temperature, for each kinetic run. The absorption coefficient A equal to log I_0/I was computed, where I was the distance of the peak from some arbitrary zero line, and I_0 the distance of the base line from the same arbitrary line. The logarithm of A was then plotted against the time, in order to obtain first order rate constants.

The rate constants and corresponding half lives obtained, at 79.6°, for the various peroxides investigated are given in Table I. These data indicate that, in general, electron releasing substituents tend to increase the decomposition rate, whereas electron attracting groups decrease the rate with one exception; that one being the peroxy compound bearing the nitro-group as a substituent.

Table I. Rate constants and corresponding half lives obtained for the various peroxides investigated.

Peroxide	k x 10^3 (min.$^{-1}$)	$T_{1/2}$ (min.)
Bis(5-bromo-3-thenoyl)	2.031	341.2
Bis(5-chloro-3-thenoyl)	1.862	372.4
Bis(3-methyl-2-thenoyl)	2.699	256.7
Bis(5-nitro-3-thenoyl)	5.849	118.5
Bis(5-ethyl-4-bromo-2-thenoyl)	3.120	222.1
Bis(2,5-dichloro-3-thenoyl)	1.681	412.3
Bis(5-phenyl-2-thenoyl)	8.580	80.8
Bis(2,5-dimethyl-3-thenoyl)	3.789	182.9
Bis(2-thenoyl)*	2.550	271.8
Bis(3-thenoyl)*	2.360	293.6

*For comparison (10).

Activation energies were obtained by plotting the logarithms of the rate constants against the reciprocal of the absolute temperature. It was found that they varied over a rather wide range, from 20.135 kilocalories per mole for bis(5-chloro-3-thenoyl)peroxide to 38.140 kilocalories per mole for bis(5-phenyl-2-thenoyl)peroxide. The entropies of activation were calculated and it was found that they varied from -22.22 entropy units for the first of the above mentioned compounds to plus 29.72 entropy units for the latter compound mentioned. It is significant that a plot of the entropies of activation against energies of activation gives a straight line, indicating the possibility of an "isokinetic" reaction series for the sulfur heterocyclic peroxides studied in the present investigation.

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To My Wife Marian

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INTRODUCTION AND HISTORICAL

Organic peroxides have been of both theoretical and practical interest to the chemist for quite some time. The oxygen-oxygen bond being relatively weak (36.0 kcal. mole^{-1}), is capable of fission by thermal and photochemical methods with relative ease. Evidence of the interest in peroxides of this type is the 1964 symposium "Development, Stabilization and Uses of Organic Peroxides"(1). One of the papers by Guillett was of particular interest and value because of its relation to the present work. This paper dealt with the determination of decomposition rates of diacyl peroxides and presented clear evidence that the relative stabilities of aliphatic and aromatic peroxides are,

Alkyl-Peroxides > Aromatic Acyl Peroxides > Aliphatic Acyl Peroxides.

The aromatic and hetero aromatic acyl peroxides, such as benzoyl, furoyl, and thionyl peroxides apparently occupy a middle position in this stability series. This behavior may eventually add to their importance as initiators of free radical type polymerizations, which occupy an importand place in present industrial chemistry. It was brought out repeatedly during the symposium, that a careful study of the decomposition rates and mechanisms of as many of these compounds as is feasible should provide a sound basis for the choice of catalysts and optimum reaction temperatures for use in polymerization processes.

The only compound in the aromatic acyl peroxide group which had been studied originally in any detail was benzoyl peroxide. It appeared that, whereas the decomposition of di-_t_-butyl peroxide followed a strictly first order rate law, the kinetics of the thermal decomposition of benzoyl peroxide was much more complex. Brown (2) demonstrated that at least two simultaneous reactions were occurring in the decomposition of the aromatic acyl peroxide, one exhibiting first order kinetics, the other following a rate law of an order higher than first. Product analysis, as reported by Erlenmeyer and Schwenauer (3) substantiated Brown's hypothesis. An initial fission of the peroxide linkage resulting in benzoyl free radicals was postulated by Hey and Waters (4), with secondary reactions initiated by the acyl radicals initially formed leading to complications in the kinetic results. Bartlett and Nozaki (5) soon after interpreted the results of kinetic experiments by considering the overall reaction to consist of the sum of a spontaneous cleavage of the peroxide into acyl radicals followed by a radical induced chain reaction, the rate of which was different from first order and varied greatly with the reaction solvent. Kinetic orders varying from 0.5 to 2.0 were observed. The spontaneous cleavage, on the other hand, appeared to vary very slightly with the solvent employed. Attempts were made to kinetically isolate the spontaneous cleavage from the radical induced chain reaction by the addition of suitable inhibitors, such as oxygen, hydroquinone, _p_-_t_-butyl catechol or methyl methacrylate. Swain, Stockmayer, and Clarke (6) found that 3,4-dichlorostyrene and methyl methacrylate would suppress the induced reaction to such an extent as to make the overall reaction rate practically identical with the rate of spontaneous cleavage of the oxygen-oxygen bond. The effectiveness of these inhibitors, was demonstrated by the observation that the half life of a 0.05 M benzoyl peroxide was 23 minutes at 80° in the absence of inhibitors, but 275 minutes, or approximately twelve times as long, in the presence of 0.2 M, styrene, 2,4-dichlorostyrene, 1,4-diphenyl butadiene, or acrylonitrile. Variations in the rate with different solvents in the presence of the above inhibitors was found to be negligible, e.g. the specific rate constant for the decomposition was found to be 4.3×10^{-3} min.$^{-1}$ in benzene (6), and 4.32×10^{-3} min.$^{-1}$ in acetophenone (7), both determined at 80°. If one considers the wide difference in polarity of the two solvents, these results show clearly both the relative independence of the reaction from the solvent, and the absence of polar steps in the reaction mechanism.

An interesting study has been reported on the relative effect of substituents on the rate of the decomposition reaction of symmetrically substituted bis(benzoyl)peroxides. Swain and his coworkers (6) as well as Blomquist and Buselli (7) found that the Hammett equation (8) is rather well obeyed for meta and para substituted benzoyl peroxides. A reaction constant ρ of -0.38 indicates that the spontaneous cleavage reaction is favored by high electron density at the reaction site and thus, electron releasing substituents such as alkyl groups should accelerate the process, whereas electron attractors, such as the halogens and nitro substituents should retard the decomposition. The small value of the rho would indicate a relatively low susceptibility of this reaction to electronic effects (9).

In these laboratories Schuetz and his collaborators have extended these studies to the hetero aromatic systems, specifically to the derivatives of thiophene. In such systems two series of peroxides could be prepared and investigated; those derived from 2-thenoic acid and those prepared from 3-thenoic acid. The only peroxide reported prior to the work of Schuetz and his coworkers (10) was bis(2-thenoyl-) peroxide which had been prepared by the Austrian chemists Breitenbach and Karlinger (11) for use as an initiator in the free radical polymerization of styrene. These investigators synthesized the peroxide by the interaction of hydrogen peroxide and 2-thenoyl chloride in pyridine as a solvent. Schuetz and Teller (12) prepared a total of ten derivatives of bis(2-thenoyl) peroxide, as well as the unsubstituted bis(3-thenoyl)peroxide, using aqueous sodium peroxide which was allowed to react with the corresponding acid chloride dissolved in a dry inert organic solvent such as toluene or cyclohexane. This procedure had been originally used by Price and Krebs (13) in the preparation of bis-(p-nitrobenzoyl)peroxide. It is this experimental procedure which was employed, at times with some variation, in the present work for the synthesis of the peroxides described in the present study. The peroxides studied by Schuetz and Teller were in the main derivatives of bis(2-thenoyl)peroxide with substituents in the 5-position. Their work also included two sulfur heterocyclic peroxides having substituents (bromo and methyl respectively) in the 4-position. The decomposition reaction rates for these compounds were determined kinetically at three different temperatures in carbon tetrachloride as a reaction media. Reaction rates were followed by analyzing for unreacted peroxide employing the iodometric determination of the peroxide linkage. Activation energies were estimated by plotting the logarithm of the rate constants against the reciprocal of the absolute temperature. The inhibitor, 3,4-dichlorostyrene was used as a free radical scavenger, and under these experimental conditions it was found that the first order rate law was obeyed for all the peroxides studied except for the case of bis(5-nitro-2-thenoyl)peroxide. It was also determined that for these compounds the Hammett equation was followed reasonably well; a plot of $\sigma_1 + \sigma_2$ against log k gave rho values close to -0.44. It was noted by Teller, however, that the activation energy was remarkably constant for all the peroxides of the parent and substituted 2-thenoic acids studied, at a value of 29.3 kcal. mole^{-1}. This points to a variation in the frequency factor, which in turn indicated that the Hammett equation can only be obeyed approximately for these heterocyclic peroxides (14). The reaction constant rho of -0.44, as obtained by Schuetz and Teller compares well with that obtained by Blomquist and Buselli (7) for the m- and p-substituted benzoyl peroxides; it is interesting to note that Jaffe (15) in his review article reports -0.20 as a value of rho for the decomposition of substituted benzoyl peroxides.

The present study was undertaken to extend the investigation of heterocyclic peroxides to include,

a. derivatives of substituted 3-thenoic acids,

b. peroxides comparable to ortho substituted benzoyl derivatives, and

c. a phenylated thenoyl peroxide.

The preparation of these compounds, especially of those derived from 3-thenoic acid, presented some difficult synthetic problems. The parent acids of this series are not as readily accessible as are the 2-thenoic acids. This is due to the fact that the alpha positions in thiophene are considerably more active toward aromatic electrophilic substitution than are the beta positions. All beta derivatives have therefore to be prepared by indirect methods, usually involving several steps, and consequently lower over-all yields. Several improvements in these synthetic methods have been developed during the preparation of these compounds. To indicate only a few: Dodson (16) had prepared 3-bromothiophene, an important intermediate in the synthesis of 3-thenoic acid and its derivatives, from 2,5-dibromothiophene through a bromination-debromination reaction sequence with an overall yield of 35%. In the present work by careful control of experimental conditions in each it was possible to increase the yield, following essentially the analogous procedure, to an overall yield of 71%. The nitrile synthesis of 3-thenoic acid from 3-bromothiophene reported by Nishimura, Motoyama and Imoto (17) with an overall yield of 64%, has been increased in this study to 85% by eliminating the purification of the intermediate 3-thenonitrile. Attempts to prepare 2-ethyl-3-thenoic acid failed, when 2-ethyl-3-bromothiophene was allowed to react with a lithium Grignard (<u>n</u>-butyl-lithium) at -70°. The only acid that could be isolated, in relatively small yield, was 5-ethyl-4-bromo-2-thenoic acid. A peroxide was prepared and studied from this latter acid instead of from the one originally desired. On the suggestion of Schuetz and Shea of these laboratories the analytical procedure used by Schuetz and Teller in their initial studies of thiophene peroxide was not employed in the present work. The analytical kinetic results were determined from infrared spectra. Shea (18) used infrared techniques successfully in his study of the decomposition rates of <u>t</u>-butyl perthenoates. His help in acquainting the author with the experimental techniques needed for this study is herewith gratefully acknowledged. The iodate titration analytical technique was only used for assaying the purity of the peroxides; all kinetic data were obtained by infrared techniques, and are described in the experimental portion of the thesis.

EXPERIMENTAL

Chemical Reagents and Apparatus

The solvent carbon tetrachloride used in the kinetic determinations was purified by a method slightly modified from that described by Teller (12). A two liter quantity of C.P. grade carbon tetrachloride was heated at 60^{o} for 30 min., with an alkaline solution prepared by dissolving 20 g. (0.357 mole) of potassium hydroxide in a mixture of 150 ml. of ethyl alcohol (95%) and 150 ml. of water. This alkaline treatment was repeated; the carbon tetrachloride layer was separated and washed thoroughly with water to remove the ethyl alcohol. It was then shaken with 50 ml. portions of concentrated sulfuric acid until only a very faint ivory colored tinge remained in the acid layer. The sulfuric acid was then removed by washing with water; the carbon tetrachloride was dried in contact with potassium hydroxide pellets and finally distilled from the solid base using a 12 in. Vigreux column.

The chloroform employed in the rate determinations of the decomposition of bis(5-nitro-3-thenoyl)peroxide only, was purified by washing 2 liters of C.P. chloroform with small portions of concentrated sulfuric acid, until no yellow color was observable in the acid layer; the chloroform layer was subsequently washed with water to remove the sulfuric acid, and dried with anhydrous calcium chloride. The chloroform was then distilled from phosphorus pentoxide using a 12 in. Vigreux column.

The styrene, employed as a radical trap, in the kinetic determination, was Eastman Kodak, white label brand, containing <u>t</u>-butylcatechol as a stabilizer. It was vacuum distilled, and then stored in the refrigerator, in a brown bottle, without an inhibitor.

The toluene, cyclohexane, and benzene used in the preparation of the various peroxides were C.P. grade; they were dried in contact with anhydrous calcium chloride.

The 2,5-dibromothiophene was "practical" grade and purchased from the Eastman Kodak Corporation; 2,5-dimethylthiophene was a product of the Aldrich corporation; thiophene and 3-methyl-2-acetylthiophene were purchased from the Pennsalt Corporation. All these materials were used directly in the experimental work without any further purification. The 2,5-dichlorothiophene and 5-phenyl-2-thenoic acid were furnished to us by Dr. Schuetz of the Department of Chemistry, Michigan State University; these materials were also used without purification.

Thionyl chloride, practical grade, was purchased from Matheson, Coleman and Bell, and distilled at atmospheric pressure immediately prior to use.

Dimethylformamide was purchased from Eastman Kodak Company, as their white label product.

Phosphorus oxychloride was a Baker Product, Analytical Reagent.

Sodium peroxide was purchased from Mallinckrodt Company, their best Analytical Reagent Product.

All melting points were determined on a Fisher-Jones melting point apparatus and are reported uncorrected.

3-Bromothiophene

The method used here differed slightly in detail from that reported by Gronowitz (19); it was originally used at Michigan State University by Dodson (16), but the yields obtained in the present work were somewhat improved.

To a 485 g. (2 moles) quantity of 2,5-dibromothiophene contained in a 1 l. three-necked flask fitted with condenser, dropping funnel, and mechanical stirrer, were added, with vigorous stirring, 332 g. (2.2 moles) of bromine during an hour while the reaction flask was cooled by immersion in an ice-bath. The reaction solution was stirred for an additional 3 hrs. without external cooling. During, and following the addition of the bromine copious quantities of hydrogen bromide were evolved. The reaction solution was set aside at room temperature overnight (16 hrs.) without stirring. To the cooled solution was added methanolic potassium hydroxide (120 g. of potassium hydroxide pellets dissolved in 250 ml. of methanol). The alkaline mixture was heated to and held at its reflux temperature for 3 hrs., and then exhaustively steam distilled to isolate the crude product.

The yellow oil was separated from the water (approximately 615 g.) and transferred to a 3 l. three-necked flask fitted with a mechanical stirrer and reflux condenser. To the oil were added, 320 ml. of glacial acetic acid, 1,200 ml. of water, and 235 g. of metallic zinc dust. The latter was added carefully in small quantities through a powder funnel. An initial spontaneous exothermic reaction occurred, which raised the reaction mixture's temperature to its reflux point. This subsided in about 40 min. and the mixture was then held at this temperature for an additional 18 hrs. by the application of external heat.

The mixture was then steam distilled using a 6 in. Vigreux column until the vapor temperature in the distillation head reached 103°. The light colored oily product was separated, dried in contact with anhydrous calcium chloride, and redistilled at atmospheric pressure to obtain a pure product boiling at 156-160°, n_D^{20} 1.5915, yield: 237.8 g. (1.42 moles, 71%).

3-Thenoic Acid

Two different experimental procedures were used in converting 3-bromothiophene to 3-thenoic acid.

The first of these suggested by Zabik at Michigan State University (20) and also employed by Gronowitz (21) with slight modifications was used in the preparation of about half the 3-thenoic acid used in the present work.

A 500 ml. three-necked flask was equipped with a mechanical stirrer, an adapter carrying a -100° thermometer and a dropping funnel. A 100 ml. volume of anhydrous ether was introduced into the flask, and 6.8 g. (0.98 mole) of finely cut lithium metal added to the ether. A calcium chloride tube was placed on top of the dropping funnel and a solution containing 61.6 g. (0.45 mole) of n-butyl bromide dissolved in 60 ml. of anhydrous ether was placed in the dropping funnel. About 10 ml. of this solution was admitted to the reaction flask. The stirrer was then started and after a few minutes the reaction mixture became cloudy with spots appearing on the lithium metal indicating that reaction had been initiated. The reaction temperature was lowered to -10 - -20° by means of a dry-ice-isopropyl alcohol bath, and the remainder of the n-butyl bromide solution was added at a constant rate during an hour, after which the solution was stirred for an additional two hours, while the temperature was allowed to rise to 10°. The n-butyl lithium solution, colored an intense violet, was then filtered through glass wool into a 1 l. three-necked flask equipped with a stirrer and dropping funnel, which had been precooled to -70° by means of a dry-ice-acetone bath. The remaining neck in the reaction flask was fitted with a -100 - 0° thermometer. An additional 300 ml. of anhydrous ethyl ether was added to the n-butyl lithium solution, and it was cooled to -70°. In the dropping funnel was placed a solution containing 52.2 g. (0.32 mole) of 3-bromothiophene dissolved in 320 ml. of anhydrous ether. This solution was run into the stirred reaction mixture in a steady stream, while the reaction temperature was carefully maintained at -70° (30 min.). Following the addition of the bromothiophene the reaction mixture was stirred for an additional 3 hrs. at -70°, and then it was poured over powdered dry ice. At this point the solution changed color from purple to white. The carbonated mixture was then allowed to warm to 0° and then a mixture of 200 ml. of 6 N hydrochloric acid and 100 g. of ice was added to it. A white precipitate formed in the water layer, which redissolved in the ether layer on stirring. The ether layer was then separated and the water layer extracted twice with 200 ml. portions of ether. The combined ether layers were extracted with 250 ml. of 2 N sodium hydroxide solution. The aqueous alkaline layer was separated and acidified with 6 N hydrochloric acid at 0°. A white precipitate formed, which was recovered by filtration and washed with 50 ml. of ice-cold water. The crude solid was recrystallized from hot water, to obtain 34 g. (0.27 mole) of 3-thenoic acid, m.p. 135-36°. From the filtrate there was isolated an additional 3 g. of acid, total yield 37 g. (0.29 mole, 90%).

The second method used is that reported by Nishimura, Motoyama and Imoto (17), based on 3-cyanothiophene. In a 500 ml. single necked reaction flask fitted with two efficient reflux condensers fitted on top of one-another there were added 28.8 g. (0.18 mole) of 3-bromothiophene, 20 g. of cuprous cyanide and 120 ml. of quinoline. The mixture was first heated slowly and cautiously. It was observed that the initially yellowish green heterogenous mixture slowly changed its color to a canary yellow, in about a half hour. Violent bumping of the reaction mixture was evident during this period, but the reaction remained under control throughout this period. The reaction mixture was held at its reflux temperature an additional 3 hrs., and it was then vacuum distilled without prior cooling, to avoid solidification. Approximately 100 ml. of distillate was collected. Acidification of the distillate with 1:1 hydrochloric acid, caused a yellowish orange oil to separate from the reaction mixture. This was extracted with ether and the extract washed once with 1:1 hydrochloric acid and three times with water. The ethereal solution was dried in contact with anhydrous sodium sulfate. After removal of the ether on a water bath, there remained 18 g. of crude 3-cyanothiophene as an oil. This material was not further purified, yield, 18g. (0.165 mole, 93%).

A mixture of 18 g. of crude 3-cyanothiophene and 360 ml. of concentrated hydrochloric acid (ap. gr. 1.19) was placed in a single necked 1 l. flask, fitted with two efficient reflux condensers above one another, and heated at its reflux temperature for 3.5 hrs. The top of the reflux condensers was fitted with a sodium hydroxide trap to neutralize the evolving hydrogen chloride gas. After the 3.5 hrs. of heating at its reflux temperature the mixture was cooled very slowly. Within minutes long white needle like crystals began to form. The crystals were separated from the mother liquor by filtration. The mother liquor was extracted with ether, dried and the ether removed to obtain additional quantities of product. Total yield, 18.7 g. (0.147 mole) of 3-thenoic acid (83.45%), m.p. 136-37°, literature value, m.p. 137-38° (22).

5-Bromo-3-Thenoic Acid

The method of Campaigne and Bourgeous (23) was employed in the preparation of this acid. A solution containing 9.2 g. (0.058 mole) of bromine dissolved in 45 ml. of glacial acetic acid was carefully added at room temperature, from a dropping funnel, to a stirred solution of 7.6 g. (0.060 mole) of 3-thenoic acid dissolved in 70 ml. of glacial acetic acid. The mixture was stirred for 15 min. at room temperature, and then poured into 400 ml. of ice-cold water.

The white precipitate was recovered by filtration, washed with cold water and recrystallized from hot water, yielding 9.0 g. (0.435 mole, 72%) of a white crystalline product, m.p. 138-40°. Literature value (23) 140-142°.

5-Chloro-3-Thenoic Acid

The method of Campaigne and Bourgeois (23) was again used, with slight modifications, to obtain this acid. The quantity 30 g. (0.230 mole) of 3-thenoic acid was dissolved in a liter of glacial acetic acid, and chlorine gas was bubbled through the previously tared solution, until the weight increase amounted to 16 g. (0.23 mole of chlorine). After being set aside a few minutes the mixture was poured into three liters of ice water and stirred for a few minutes. A snowy white, fluffy precipitate was obtained immediately. The mixture was allowed to remain in the refrigerator overnight. The crystals formed were separated by filtration and the mother liquors were extracted with ether. Recrystallization of the original crystalline material, as well as of the solid material obtained from the ether extract, yielded 14.0 g. (0.086 mole, 37.3%) of a white, crystalline product, m.p. 154-56°. Literature value (23) 156-57°.

5-Nitro-3-Thenoic Acid

This acid was also prepared according to the procedure suggested by Campaigne and Bourgeois (23). A mixture of 80 ml. of conc. nitric acid (sp. gr. 1.42) and 11.5 ml. of conc. sulfuric acid was mechanically stirred in a tall beaker and cooled to -10° by means of a dry-ice isopropanol bath. The temperature of the acid mixture was maintained at -5°, while 20 g. (0.156 mole) of 3-thenoic acid were added in small portions. The reaction mixture was then poured into ice-water and steam distilled to remove any unreacted 3-thenoic acid. The residual liquid crude acid was separated from the steam distillation flask. It solidified on cooling, weight 20.0 g. (0.0115 mole, 74.0%). A 3 g. quantity was recrystallized from benzene, m.p. 144-46°. Literature value (23) 145-6°.

2-Acetylthiophene

The method of Hartough and Kosak(23a) was employed in the preparation of this material. A stirred solution containing 504 g. (6.0 moles) of thiophene and 234 g. (2.2 moles) of acetic anhydride was heated to 70° in a two-liter three-necked flask equipped with a dropping funnel, stirrer and thermometer, and 20 g. of 85% ortho-phosphoric acid were added to this mixture during a period of 15 min. There was a slight rise in reaction temperature during the initial addition of the acid, and external cooling, with an ice-bath, was essential, to hold the temperature at 88 - 90°. The reaction mixture was then heated to its reflux temperature (96°) for 2 hrs. A 400 ml. volume of water was then added. The mixture was stirred for an additional 25 min. The organic layer was separated, washed with 400 ml. of a 10% sodium carbonate solution, and then three times with 400 ml. portions of water. Drying was not necessary, as the thiophene water azeotrope would distill at 68°, followed by practically pure thiophene; the fraction boiling at 84° was collected. The residue was distilled using a 6 in. Vigreux column to obtain 238 g. (1.88 moles, 94%) of 2-acetylthiophene b.p. 79.5° (6 mm.). Literature value (23a) 77° (4mm.).

2-Thenoic Acid

The method of Hartough and Conley (24) was employed to convert 2-acetylthiophene to 2-thenoic acid. A solution was prepared containing 440 g. (11.0 moles) of sodium hydroxide dissolved in 600 ml. of water. A 2,500 g. quantity of chipped ice was weighed directly into the alkaline solution, contained in a 4 l. beaker. This was tared and 332 g. (4.68 mole) of chlorine gas was allowed to flow into the solution from a cylinder, employing two gas addition tubes, linked through a T-type joint. The sodium hypochlorite solution was then warmed on a water bath to 60-62° and rapidly transferred to a 5 l. flask (three-necked) equipped with dropping funnel, stirrer and two reflux condensers placed vertically on top of one another. The flask was then immersed in a cooling bath and 126 g. (1.0 mole) of acetylthiophene were added from the dropping funnel at a rate as to maintain the reaction temperature between 65-72°. Emission of chloroform in rather copious quantities could be observed. Following the addition of the acetylthiophene stirring was continued for an additional 3 hrs., until the reaction temperature had dropped to 25-30°, without the aid of external cooling. The excess hypochlorite was destroyed by the addition of a solution of sodium bisulfite (100 g. of salt to 200 ml. of water). The solution was transferred to a 4 l. beaker and carefully acidified with conc. hydrochloric acid (sp. gr. 1.19). The crude product was collected on a Buchner funnel and recrystallized from 1200 ml. of hot water. The mother liquor was made alkaline with sodium hydroxide (to pH about 8) and concentrated to one quarter of its volume, and extracted with ether. The total yield of product obtained was 112 g. (0.87 mole, 87%). It melted at 125-127°. Literature value (24) 128-29°.

4,5-Dibromo-2-Thenoic Acid

This halogenated acid was prepared from 2-thenoic acid utilizing the method of Jacob, Steinkopf, and Penz (25) with some modifications. A 224 g. (1.4 moles) quantity of bromine was placed in a 1 l. three-necked flask; the latter was fitted with a stirrer, reflux condenser and a flexible rubber tube, to which was attached a 125 ml. Erlenmeyer flask containing 28.5 g. (0.225 mole) of 2-thenoic acid. The acid was added slowly from the Erlenmeyer flask to the vigorously stirred bromine. During the addition of the acid the reaction flask was cooled by immersion in an ice bath. Following the addition of the halogen, the cooling bath was removed, and the reaction mixture was stirred at room temperature for an additional hour. The excess bromine was removed by evaporation with a water aspirator vacuum. To remove the final traces of bromine the white residual acid was stirred with 100 ml. of 10% ammonium carbonate solution, followed by acidification with conc. hydrochloric acid. The white solid product was recovered by filtration on a Buchner funnel, washed with cold water and recrystallized from absolute ethanol. Yield, 45.2 g. (0.158 mole, 70.2%); m.p. 223-225°. Literature value (25) 225-227°.

3-Bromothiophene from 4,5-Dibromo-2-thenoic Acid

The method suggested by Nishimura, Motayama and Imoto (17) was used in the preparation of this material. In a 1 l. three-necked flask fitted with a thermometer and distilling head there were placed 140 g. (1.09 moles) of previously distilled (b.p. 238-240°) quinoline and a mixture of 60 g. (0.21 mole) of 4,5-dibromo-2-thenoic acid and 10 g. of copper powder; the two latter substances had been previously ground together in a mortar, to assure intimate mixture. The reaction mixture was carefully heated, and at 75-80° it was observed that a fairly vigorous bubbling was occurring. The color of the reaction mixture turned at this point from a yellow to a brownish-black. The reaction temperature rose to 145°, the reflux temperature of the reaction mixture. The mixture was held at its reflux temperature for an hour, and then it was heated until distillation occurred. About 70-75 ml. of distillate was collected. This was acidified with 1:1 hydrochloric acid, to separate the 3-bromothiophene from the quinoline. The acidified distillate was extracted with ether, the ether layer was separated and washed twice with 1:1 hydrochloric acid and once with water. After having been dried in contact with anhydrous calcium chloride the ether layer was decanted from the drying agent and the ether evaporated. Vacuum distillation of the product gave 26.7 g. (0.16 mole, 78%) of 3-bromothiophene, b.p. 53-55°/15 mm. Literature value (17) 66-68.5°/31 mm.

3-Acetyl-2,5-dichlorothiophene

This ketone was prepared by the procedure originally described by Steinkopf and Kohler (26) and modified by Hartough and Conley (24,27).

A mixture of 153 g. (1.0 mole) of 2,5-dichlorothiophene, 150 g. (1.9 moles) of acetyl chloride, and 750 ml. of petroleum ether was placed in a 3 l. three-necked flask fitted with a stirrer, thermometer and powder addition funnel. A 150 g. (1.13 moles) quantity of anhydrous aluminum chloride was added to the reaction mixture, which had been precooled to -15°. The metal halide catalyst was added in portions from the powder funnel slowly and carefully during a 15 min. period, at which point the evolution of hydrogen chloride gas became rather vigorous. The powder funnel was replaced by a condenser fitted with a sodium hydroxide trap and the temperature of the stirred reaction mixture was maintained at 15° for 2 hrs. At this point the reaction temperature was permitted to slowly rise to room temperature and maintained there for 3.5 hrs. Finally the reaction mixture was heated at 40° for 30 min. It was then cooled to about 10° and carefully poured over 1 l. of crushed ice. The petroleum ether layer was separated and washed three times with water and dried over anhydrous calcium chloride. The solvent was removed by distillation at atmospheric pressure and the residue was distilled in vacuum from a Claissen flask directly connected to a receiver; the latter was cooled by a stream of water. The product solidified in the receiver flask to a yellowish white crystalline material: m.p. 35-37°. Literature value (27) 38-38.5°. No recrystallization was attempted. Yield: 141 g. (0.72 mole, 72%).

2,5-Dichloro-3-thenoic Acid

The experimental procedure described here is analogous to that discussed previously for the preparation of 2-thenoic acid. A mixture of sodium hypochlorite was prepared by using 180 g. (4.5 moles) of sodium hydroxide, 1,023 g. of ice and bubbling into the alkaline solution, chlorine gas until 131 g. (1.85 moles) of the halogen had been absorbed. The hypochlorite solution was heated to 65°, transferred to a three-necked 5 l. flask and 88 g. (0.41 mole) of 2,5-dichloro-3-acetylthiophene was added slowly through a powder funnel fitted on top of a short Allhijn condenser. The color of the reaction mixture changed from pale yellow to orange rose and chloroform evolved in rather copious quantities. The reaction temperature remained at 70-73° during the chloroform evolution and then decreased. The mixture was set aside at room temperature over night. A solution of sodium bisulfite (41 g. (0.394 mole) of bisulfite in 82 ml. of water) was then added, and the mixture was acidified with conc. hydrochloric acid (sp. gr. 1.19). The solid product was recovered by filtration and recrystallized from ethanol. Recrystallization presented some difficulties and had to be repeated several times in order to obtain a pure crystalline product. Yield, 36.8 g. (0.19 mole, 46.3%), m.p. 145-46°. Literature value (24) m.p. 147-48°.

2-Thenal

The method suggested by Campaigne and Archer (28) was employed in the preparation of the heterocyclic aldehyde. A solution of 252 g. (3.0 moles) of thiophene and 276 g. (3.84 moles) of N,N-dimethylformamide was cooled to 0° in a 3 l. three-necked flask fitted with a stirrer, reflux condenser and a 500 ml. dropping funnel. A total of 576 g. (3.72 moles) of phosphorus oxychloride was added to the cooled, stirred solution during a 2 hr. period. The color of the originally colorless mixture changed to straw yellow during this addition of the chloride. The reaction mixture was then heated at its reflux temperature on a water bath for an additional 2 hrs., and then set aside overnight at room temperature. During the time the reaction mixture was heated at its reflux temperature it turned first red, then brown, and finally almost black in color. The reaction solution was next carefully poured onto 3,000 g. of ice. The heat of reaction between the excess phosphorus oxychloride and the water was sufficient to melt all the ice and heat the water almost to its boiling point. After being set aside for a short period, the mixture was steam distilled, as recommended in the literature (28), since direct separation of the organic layer from the water was impossible. The oily liquid was readily separated from the water in the distillate. The impure product was stored over calcium chloride in a brown bottle. Further purification of the crude product was not attempted. Yield, 255 g. (2.58 moles, 74%) of unpurified product, a light yellow oil, which darkened slightly on storage.

2-Methylthiophene

The experimental procedure of King and Nord (29) was employed in the reduction of 2-thenal to obtain this alkyl thiophene. A solution was prepared containing 224 g. (2.0 moles) of 2-thenal, 400 ml. of 85% hydrazine hydrate and 1,600 ml. of ethylene glycol. This reduction solution was placed in a 5 l. three-necked flask fitted with a stirrer, thermometer and Vigreux column carrying a distilling head. The reaction solution was then heated to 160-170°, to remove water and excess hydrazine by direct distillation. The mixture was then set aside overnight to cool. The distillation head was replaced by two condensers one placed on top of the other and 400 g. (0.714 mole) of potassium hydroxide pellets were added to the reaction mixture while cooling the latter, care being taken to hold the temperature below 40°. After adding the base, the stirred mixture was carefully heated to 90°, at which temperature nitrogen gas evolution commenced. The nitrogen evolution was rather vigorous for about 2 hrs. When the most vigorous evolution of gas had subsided, the mixture was heated at its reflux temperature for 2 hrs. at 105-110°. The mixture was then set aside at room temperature to cool. The condensers were replaced by a Vigreux column, fitted with a distillation head, and the mixture was distilled. The distillate boiling up to 140° was collected. This was extracted three times with 100 ml. portions of ether. The extracts were combined and washed with 6 N hydrochloric acid and finally with water. The ether solution was dried over anhydrous calcium chloride, filtered, and the ether was removed on the water bath. The product was distilled at atmospheric pressure using an 8 in. Vigreux column. The yield of product was 110 g. (1.12 moles, 56.4%) of a colorless liquid, boiling at 110-110.5°.

3,5-Dibromo-2-methylthiophene

The method originally described by Steinkopf (30) after considerable modification was used in this preparation. To a solution of 50 g. (0.51 mole) of 2-methylthiophene and 250 ml. of carbon disulfide contained in a 1 l. three-necked flask fitted with a stirrer, condenser and dropping funnel were added 180 g. (1.1 moles) of bromine during an hour; the reaction flask was kept cool by immersion in an ice-bath. Following the addition of the halogen, the ice-bath was removed and the reaction mixture was stirred for 3 hrs. at room temperature; hydrogen bromide was emitted copiously, throughout the reaction period. The reaction was set aside over night at room temperature, then washed three times with water, next three times with 10% aqueous potassium hydroxide solution, and finally three times with water. With efficient stirring the washed reaction mixture was then cooled by immersion in an ice-bath and to it were added 100 ml. of methanolic potassium hydroxide (60 g. of potassium hydroxide pellets dissolved in 126 ml. of methanol) , slowly and carefully to avoid any rise in the reaction temperature. The mixture was then heated at its reflux temperature for an hour. Sufficient water was then added to double the volume of the mixture, and the carbon disulfide was removed by steam distillation on a water bath. The oily residue was exhaustively steam distilled (for about 9 hrs.). The oil product was separated from the water layer, dried over anhydrous calcium chloride, and distilled under reduced pressure, to obtain 63 g. of a heavy oil, with a density of 2.1 g. $ml.^{-1}$ A small sample of this material distilled at atmospheric pressure boiled at 220-226°. Literature value (30) 227.5-230°.

3-Bromo-2-methylthiophene

The procedure used by Gronowitz was followed to obtain this material (31). A 60 g. (0.234 mole) quantity of 3,5-dibromo-2-methylthiophene was added to a refluxing mixture of 77 ml. of water, 25.5 g. (0.390 g. atoms) of zinc powder and 32 ml. of glacial acetic acid. The reaction mixture was heated at its reflux temperature for 24 hrs. and the product was isolated by steam distillation. The organic layer, was separated, washed with 10% sodium carbonate solution and water, dried over anhydrous calcium chloride and fractionated to yield 36.4 g. (0.207 moles, 88.6%) of pure product boiling at 169-173°. Literature value (31) b.p. 173-174°.

2-Methyl-3-thenoic Acid

A procedure essentially analogous to the one described previously for the preparation of 3-thenoic acid was followed. A 500 ml. three-necked flask was equipped with a mechanical stirrer, reflux condenser, dropping funnel, and a -20 to -35° thermometer. A 100 ml. volume of anhydrous ether, previously dried over sodium wire, was introduced into the flask and 6.8 g. (0.98 g. atoms) of lithium metal were cut into small pieces and added to the ether. A solution containing 61.6 g. (0.45 moles) of n-butyl bromide dissolved in 60 ml. of absolute ether was placed in the dropping funnel, and about 10 ml. of this solution were admitted to the flask. Stirring was initiated and after a few minutes it was observed that the liquid turned dark and cloudy in appearance with discolored spots appearing on the lithium metal surface. The reaction temperature was lowered to -10- -20° by means of a dry ice-isopropanol bath, and the remainder of the n-butyl bromide solution was added at a constant rate during an hour. The reaction solution was stirred for an additional 2 hrs. during which its temperature was allowed to rise to 10°. As the temperature increased the color of the originally dark gray reaction mixture turned to a deep violet-purple. The n-butyl lithium solution was then filtered through glass wool into a 1 l. three-necked flask equipped with stirrer, dropping funnel, and a -100 to 10° thermometer. This reaction flask had been cooled previously to -70° in a dry ice-isopropanol bath, contained in an unbreakable polystyrene cookie jar, which had good insulating properties. An additional 300 ml. of absolute ether was then added to the solution of n-butyl lithium and it was then cooled to -70°. In the dropping funnel there were placed 30 g. (0.17 mole) of 2-methyl-3-bromothiophene dissolved in 320 ml. of ether. This solution was run into the well stirred n-butyl lithium solution in the flask in a steady stream, while the reaction temperature was held below -70° (30 min.). Following the addition of the alkylhalothiophene solution the reaction mixture was stirred for an additional 3 hrs. at -70°. It was then poured over powdered dry ice and allowed to warm up to 0°. The violet color of the mixture changed to almost pure white on the addition to the dry ice. After the solution had warmed to 0° a mixture of 200 ml. of 6 N hydrochloric acid and 100 g. of ice was slowly poured into it. A white precipitate was formed initially, but this dissolved in the ether. The ether layer was separated, and the water layer was extracted twice with 200 ml. portions of ether. The combined ether extracts were then extracted with 250 ml. of 2 N sodium hydroxide. The aqueous layer was separated and acidified with 6 N hydrochloric acid at 0°. The precipitate, which formed immediately on acidification was recovered by filtration and washed with ice-cold water. The solid product was recrystallized from hot water, to yield 18.5 g. (0.13 mole, 68%) of pure 2-methyl-3-thenoic acid, melting at 103-110°. Literature value (32) 115-117°.

Calculated for $C_6H_6O_2S$:	C, 50.7; H, 4.2; S, 22.5
Found:	C, 49.7; H, 4.3; S, 22.3.

2-Ethylthiophene

The procedure of King and Nord (29) previously described was employed to prepare this alkylthiophene. Acetylthiophene instead of 2-thenal was used as a starting material for the Wolff-Kishner reaction. A mixture of 200 g. of 2-acetylthiophene (1.58 moles), 310.18 ml. of hydrazine hydrate and 1,234.2 ml. of ethylene glycol was heated to 170°

to remove the excess hydrazine and water, and then it was cooled to 40°. Potassium hydroxide pellets (110.8 g., 1.98 moles) were then added and the stirred reaction mixture was cautiously heated to 120°. Nitrogen gas evolution was initiated at 120° and external heating was removed and the mixture was set aside overnight. The reaction solution was then heated at its reflux temperature for three hours followed by distillation to collect the product. Distillation was continued until the vapor temperature in the distillation head reached 135°. The distillate was extracted with ether; the ether extract was washed twice with 6 N hydrochloric acid and once with water, and dried over anhydrous calcium chloride. The ether was removed on a steam bath, and the product was distilled at atmospheric pressure to obtain 144 g. (1.36 moles, 86%) of the desired product boiling at 130-133°. Literature value (32) b.p. 132-134°.

3,5-Dibromo-2-ethylthiophene

Direct bromination of 2-ethylthiophene in a manner analogous to that described above for the preparation of 3,5-dibromo-2-methylthiophene was used to obtain 3,5-dibromo-2-ethylthiophene.

A solution containing 57 g. (0.5 mole) of 2-ethylthiophene dissolved in 250 ml. of carbon disulfide was placed in a 1 l. three-necked flask fitted with a mechanical stirrer and dropping funnel. The dropping funnel was charged with 180 g. (1.1 moles) of bromine dissolved in 125 ml. of carbon disulfide. The experimental procedure followed in conducting the bromination reaction was exactly analogous to that previously described for the preparation of 2-methyl-3,5-dibromothiophene. Steam distillation of the bromination reaction mixture yielded 222 g.

of yellow oil, which was separated from the distillate, dried, and used immediately, without further purification, in the next reaction of the synthesis.

3-Bromo-2-ethylthiophene

The crude oil, essentially 3,5-dibromo-2-ethylthiophene, isolated as described above was introduced into a 1 l. three-necked flask and a solution containing 48 ml. of glacial acetic acid and 180 ml. of water was added to the oil. To the stirred solution, from a powder funnel, there was slowly added 35.25 g. (0.538 g. atoms) of zinc powder. The reaction mixture was then heated carefully to its reflux temperature and kept at that temperature 3 hrs. The desired monobromo product was isolated from the reaction mixture by steam distillation, decanted from the water layer, dried and twice vacuum distilled, using a 6 in. Vigreux column in both distillations. The yield obtained was, 79 g. (0.41 mole, 82%), b.p. 56-60° 20mm. The material boiled, with some decomposition, at 174-175° at atmospheric pressure by a boiling point determination employing a small sample. Literature value (34) 180-190°.

Calculated for C_6H_7SBr: Br, 42.07; Found: Br, 42.67.

Attempts to Prepare 2-Ethyl-3-thenoic acid

A procedure analogous to that previously described for the preparation of 2-methyl-3-thenoic acid by the "lithium-butyl-process" was followed in attempting to synthesize 2-ethyl-3-thenoic acid. However, the product obtained in small yield was not the expected 2-ethyl-3-thenoic acid but 5-ethyl-4-bromo-2-thenoic acid. Yield, 2.5 g. (0.011 mole, 2.6%) of 5-ethyl-4-bromo-2-thenoic acid, m.p. 198-202°, dec.

Calculated for $C_7H_7O_2BrS$: C, 35.75; H, 3.0; S, 14.31

Found: C, 36.53; H, 3.25; S, 14.25.

Further, the preparation of the desired acid by the nitrile synthesis could not be effected either.

3-Methyl-2-thenoic Acid

A completely analogous experimental procedure was followed in converting 3-methyl-2-acetyl thiophene to the corresponding carboxylic acid as has been described in the oxidation of 2-acetylthiophene and 2,5-dichloro-3-acetylthiophene to 2-thenoic and 2,5-dichloro-3-thenoic acids. A 140 g. (1.0 mole) qunatity of 3-methyl-2-acetylthiophene (sample generously furnished from Pennsalt Chemical Company) was employed in the oxidation and the yield obtained after a single recrystallization from hot water was 127 g. (0.89 mole, 89%) of 3-methyl-2-thenoic acid, m.p. 145-147°. Literature value (32) m.p. 148°.

Preparation of the Thenoyl Chlorides

All of the thenoylchlorides employed in the present work were prepared from the corresponding carboxylic acids by interaction with thionyl chloride. A typical procedure is described as an example of these preparations.

5-Bromo-3-thenoyl Chloride

In a 100 ml. one-necked flask fitted with a reflux condenser having a sodium hydroxide trap attached to it, there were placed 10 g. (0.0483 mole) of 5-bromo-3-thenoic acid and 25 g. (0.209 mole) of thionyl chloride. A rather vigorous initial reaction occurred with the immediate evolution of hydrogen chloride gas. When this had subsided the

Table I. Rate constants and half lives for the decomposition of substituted thenoyl peroxides at 79.6°.

Peroxide	$k \times 10^3 (\text{min.}^{-1})$	$T_{1/2}$(minutes)
Bis-(5-bromo-3-thenoyl)	2.031	341.2
Bis-(5-chloro-3-thenoyl)	1.862	372.4
Bis-(5-nitro-3-thenoyl)	5.849	118.5
Bis-(3-methyl-2-thenoyl)	2.699	256.7
Bis-(5-ethyl-4-bromo-2-thenoyl)	3.120	222.1
Bis-(2,5-dichloro-3-thenoyl)	1.681	412.3
Bis-(5-phenyl-2-thenoyl)	8.580	80.8
Bis-(2,5-dimethyl-3-thenoyl)	3.789	182.9
Bis-(2-thenoyl)*	2.55	271.8
Bis-(3-thenoyl)*	2.36	293.6

*For comparison (12).

Table II. Bis(thenoyl) peroxides.

Peroxide[a]	Solvent for Recrystallization	Yield %	M.P.[b]	Purity[c] %	Carbon		Hydrogen		Sulfur	
					calc.	found	calc.	found	calc.	found
Bis(5-bromo-3-thenoyl)	Chloroform n-butyl ether	44	102-103	98.0	29.14	28.98	0.978	1.10	15.56	15.56
Bis(5-chloro-3-thenoyl)	Pet. ether[d]	58	72-73	99.5	37.16	37.43	1.25	1.66	19.84	19.84
Bis(5-nitro-3-thenoyl)	Chloroform Pet. ether	80	153-154	98.9	34.78	35.02	1.16	1.21	18.61	18.57
Bis(3-methyl-2-thenoyl)	Benzene Pet. ether	35	92-93	97.5	51.05	51.12	3.75	3.62	22.72	22.58
Bis(2,5-Dichloro-3-thenoyl)	Pet. ether	70	92-93	94.7	30.61	30.51	0.51	0.71	16.33	16.28
Bis(4,5-dibromo-2-thenoyl)	None	59	158-159 (decomp.)	97.5	21.05	20.96	0.35	0.31	11.23	10.67
Bis(5-phenyl-2-thenoyl)	Chloroform	80	81 (decomp.)	98.3	65.0	61.0	3.40	3.42	15.80	15.98
Bis(5-ethyl-4-bromo-2-thenoyl)	Pet. ether	82	98-102	99.9	35.89	35.36	2.56	2.62	13.68	13.29
Bis(2,5-dimethyl-3-thenoyl)	Pet. ether	82		96.7	54.19	53.94	4.82	4.52	20.65	20.17

[a] For the mono-and dihalogenated peroxides cyclohexane was used as the solvent for the acid chloride, whereas toluene was employed in the case of the remaining peroxides with the exception of the Bis(2,5-dimethyl-3-thenoyl)peroxide for which carbon tetrachloride was employed.

[b] All melting points are uncorrected. [c] Purity after one recrystallization with the exception of Bis(4,5-dibromo-2-thenoyl)peroxide which could not be recrystallized.

[d] Pet. ether (b.p. 30-60°).

dark mixture was heated at its reflux temperature for 4 hrs. The excess thionyl chloride was removed by distillation at atmospheric pressure and the residue was distilled using a 4 in. Vigreux column to obtain 12 g. of crude product containing some thionyl chloride. This material distilled at 120 - 130° 10-15 mm. The exact yields obtained were difficult to determine as the heterocyclic acid chlorides were not further purified to remove the thionyl chloride completely, since its presence offered no experimental difficulties in using these impure acid chlorides to prepare their corresponding heterocyclic peroxides.

Bis-(5-bromo-3-thenoyl Peroxide)

A vigorously stirred 25 ml. volume of water contained in a 300 ml. three-necked reaction flask fitted with a stirrer, thermometer and dropping funnel was cooled to 0° in an ice-sodium chloride bath and 1.95 g. (0.025 mole) of sodium peroxide were dissolved in it in small portions, care being taken that each portion was completely dissolved in the water, before additional sodium peroxide was added. To the cold peroxide solution, a second solution containing 10.0 g. (0.044 mole) of 5-bromo-3-thenoyl chloride dissolved in 35 ml. of dry cyclohexane was added in one portion. A colorless solid precipitated immediately. The mixture was then stirred at 0° for an additional 1.5 hrs. The colorless, crystalline product was removed by filtration, washed with ice water, and dried at 0°, for 48 hrs. in a vacuum desiccator. The product was recrystallized from the minimum amount of n-butyl ether, preheated to 50°, and then reprecipitated by the addition of chloroform. The yield of colorless peroxide obtained was 4.0 g. (0.0097 mole, 44%), melting at 102-103°. On melting, the material turned red in color and detonated, after having been maintained at its melting temperature for about 2 min.

Calculated for $C_{10}H_4Br_2O_4S_2$: C, 29.14; H, 0.978; S, 15.56; Br, 38.65

Found: C, 28.98; H, 1.10; S, 15.56; Br, 38.65.

Bis-(5-chloro-3-thenoyl peroxide)

Using apparatus and experimental conditions analogous to those described for the synthesis of bis-(5-bromo-3-thenoyl peroxide) 2.50 g. (0.032 mole) of sodium peroxide were dissolved, at 0°, in small portions in 35 ml. of water. A solution of 10.0 g. (0.056 mole) of 5-chloro-2-thenoyl chloride dissolved in 35 ml. of dry cyclohexane was added, all at once, to the vigorously stirred aqueous peroxide solution. A colorless solid immediately precipitated. The reaction mixture was stirred at 0° for 1.5 hrs. to complete the reaction. The colorless crystalline solid was collected by filtration on a sintered glass funnel and washed with ice water, then four times with 25 ml. portions of ice-cold petroleum ether, to remove any unreacted 5-chloro-3-thenoyl chloride. After drying for 48 hrs. in a vacuum desiccator, the crude product was recrystallized from petroleum ether (b.p. 30-60°). The yield obtained was 5.2 g. (0.0163 mole, 58%), m.p. 72-73°. It melted into a clear liquid without detonation.

Calculated for $C_{10}H_4Cl_2O_4S_2$:

C, 37.16; H, 1.25; S, 19.84; Cl, 21.94

Found:

C, 37.48; H, 1.66; S, 19.84; Cl, 21.86.

Bis-(3-methyl-2-thenoyl peroxide)

Following the general procedure in the two previous preparations just described, 3.1 g. (0.040 mole) of sodium peroxide were added at 0^{o} in small portions to 30 ml. of water. A solution containing 10 g. (0.062 mole) of 3-methyl-2-thenoyl chloride dissolved in 30 ml. of dry toluene was added dropwise, at 0^{o}, during 15 min., to the vigorously stirred aqueous sodium peroxide solution. The reaction mixture was then stirred, at 0^{o}, for an additional 2.5 hrs. to complete the reaction. About 15 min. after the addition of acid chloride, a colorless solid material began to separate from solution. The crystalline product was recovered by filtration and thoroughly washed with ice-water. After drying for 48 hrs. at 0^{o}, in a vacuum desiccator, the crude product was recrystallized from a minimum quantity of benzene by the addition of petroleum ether (b.p. $30\text{-}60^{o}$). The yield of colorless peroxide obtained was 3.1 g. (0.0110 mole, 35%), melting at 104^{o}. This heterocyclic peroxide on melting turned red in color and detonated.

Calculated for $C_{12}H_{10}O_4S$: C, 51.05; H, 3.75; S, 22.72.
Found: C, 51.12; H, 3.62; S, 22.58.

Isopropyl-2-thienyl Ketone

The general acylation procedure as described by Hartough and Kosak (23a) was used in the synthesis of this ketone. A 142 g. (1.0 mole) quantity of phosphorus pentoxide was weighed directly into a solution prepared from 600 ml. of benzene and 600 ml. of thiophene. Isobutyric acid (88 g., 1.0 mole)(Eastman Organic Chemical Division Product) was added very carefully to the acylation mixture. The reaction temperature was held under control by immersing the reaction flask in an ice bath, and no appreciable heat of reaction could be observed. A short time after initiating the reaction, the reaction mixture turned a turbid purple in color, and separated into two phases. One phase was straw color, the other a deep purple solid. After heating the reaction mixture at its reflux temperature for 4 hrs. the liquid was decanted from the solid mass, and extracted with 10% sodium hydroxide. Experimental difficulties were encountered in this as the alkali extraction resulted in the formation of a thick emulsion, which necessitated it being set aside for several hours to effect a phase separation. The organic phase was finally separated; the thiophene was removed by distillation, and the crude product was purified by distillation in vacuo, b.p. 137-39°/35mm. Yield: 87.5 g. (0.59 mole, 59%).

2-Isobutyl thiophene

The Wolff-Kishner reduction described previously in the preparation of 2-methyl-thiophene and originally reported by King and Nord (29), was used for the reduction of 2-isopropylthienyl ketone to 2-isobutyl thiophene. A solution containing 87.5 g. (0.57 mole) of 2-isopropylthienyl ketone, 543.4 ml. of ethylene glycol and 135.97 ml. of 85% hydrazine hydrate was stirred in a 2 l. three-necked reaction flask, fitted with a stirrer, thermometer, and a 12 in. Vigreux column fitted with a distillation head. The reaction solution was heated to 130-160° to remove water and excess hydrazine, by distillation and then it was allowed to cool to 50°. The Vigreux column was replaced by two reflux condensers mounted on top of one-another. While vigorously stirring 50 g. of potassium hydroxide pellets were added slowly to the reaction mixture, then it was heated carefully at about 100° until the slow evolution of nitrogen gas commenced. The reaction proceeded smoothly with no vigorous gas evolution occurring at any time. After being heated at its reflux temperature for 24 hrs. the solution was allowed to cool to room temperature. The condensers were replaced by the Vigreux column and the product was isolated by distillation. The major portion of the pure product distilled at 165-173°. Yield: 62 g. (0.44 mole, 77%) of colorless clear liquid.

5-Isobutyl-2-acetylthiophene

The procedure described above for the synthesis of 2-acetylthiophene was employed for the preparation of this ketone. A 6 g. quantity of 85% phosphoric acid was added slowly at 80° to a mixture of 62 g. (0.44 mole) of 2-isobutylthiophene, and 73.5 g. (0.72 mole) of acetic anhydride under vigorous stirring. An immediate color change in the reaction mixture from colorless to light red to deep red-black, was observed. The temperature of the mixture initially rose rapidly to 135°, its temperature of reflux. After the refluxing had subsided, the temperature was allowed to drop to 110°, and was maintained there for 3 hrs. after which it was again heated at its reflux temperature for 30 min. The mixture was allowed to cool to room temperature, 100 ml. of water were added to the mixture and it was stirred for an additional 15 min. A clear, green oil separated from solution at this point. The mixture was washed with water and separation of the phases required the emulsion to be set aside for several hours. The crude product was purified by distillation. A water-product azeotrope initially distilled as a small forerun from the organic phase. The pure product was collected boiling in the range 168-172°/25 mm. Yield: 61 g. (0.33 mole, 75%).

5-Isobutyl-2-thenoic acid

This acid was prepared by the hypochlorite oxidation of 5-isobutyl-2-acetylthiophene in a manner described above for synthesis of 2-thenoic acid. The yield of acid obtained from 60 g. (0.340 mole) of starting material was 42 g. (0.234 mole, 71%), m.p. 67-69°.

Bis(2,5-dichloro-3-thenoyl)peroxide

Apparatus and methods analogous to those described for the preparation of bis(5-bromo-3-thenoyl)peroxide above were used to obtain the peroxide. A 25 ml. volume of water was cooled to 0° and 1.66 g. (0.021 mole) of sodium peroxide were dissolved in the water, the solid being added in small portions and under vigorous stirring. A second solution containing 4.9 g. (0.022 mole) of 2,5-dichloro-3-thenoylchloride dissolved in 22 ml. of dry cyclohexane was added, in one portion, to the aqueous solution of sodium peroxide. A white solid separated from solution immediately. The reaction mixture was then stirred for an additional 1.5 hrs. at 0°. The white, crystalline product was recovered by filtration, washed thoroughly with ice water, dried 48 hrs. at 0° in a vacuum desiccator, and recrystallized from petroleum ether to obtain 3.0 g. (0.00766 mole, 70%) of a pure, crystalline product, m.p. 92-95°.

Calculated for $C_{10}H_2Cl_4O_4S_2$: C, 30.61; H, 0.51; S, 16.33; Cl, 36.92.

Found: C, 30.51; H, 0.71; S, 16.28; Cl, 36.12.

Bis-(4,5-dibromo-3-thenoyl)peroxide

Apparatus and experimental procedures entirely analogous to the above preparation were employed to prepare this peroxide. A solution containing

Table III. Preparation of thenoyl chlorides

Thenoyl Chloride	Yield %	Boiling Point °C.
5-Bromo-3-thenoyl chloride	64	99-100/ 8 mm.
5-Chloro-3-thenoyl chloride	94	124-125/ 15 mm.
3-Methyl-2-thenoyl chloride	88	125-130/ 15 mm.
5-Nitro-3-thenoyl chloride	67	120-130/10 - 15 mm.
2,5-Dichloro-3-thenoyl chloride	66	135-140/ 15 mm.
4,5-Dibromo-2-thenoyl chloride	54	167-168/ 0.1 mm.
5-Ethyl-4-bromo-2-thenoyl chloride	45	102-104/ 15 mm.
5-Phenyl-2-thenoyl chloride	69	12-22/ 10 mm.
2,5-Dimethyl-3-thenoyl chloride	80	110-111/ 5 mm.

2.1 g. (0.027 mole) of sodium peroxide dissolved in 30 ml. of ice-cooled water was prepared. A second solution prepared from 19 g. (0.0062 mole) of 4,5-dibromo-3-thenoyl chloride and 35 ml. of dry cyclohexane was added to the aqueous peroxide in one portion. A white solid precipitated immediately. After the reaction mixture had been stirred for 2 hrs. at 0° the white solid product was removed by filtration and washed with ice water. The yield of peroxide was 10.2 g. (0.00183 mole, 59%), melting at 158-159° while turning red in color.

Caculated for $C_{10}H_2Br_4S_2O_4$:	C, 21.05; H, 0.35; Br, 56.14; S, 11.23.
Found:	C, 20.96; H, 0.31; Br, 53.7; S, 10.67.

Bis-(5-phenyl-2-thenoyl)peroxide

A 6 g. (0.027 mole) quantity of 5-phenyl-2-thenoyl chloride was dissolved in 20 ml. of dry toluene. This solution was then added to a second solution containing 1.0 g. (0.013 mole) of sodium peroxide dissolved in 35 ml. of ice cold water. A yellowish solid precipitated about a minute after mixing the two solutions. The reaction mixture was allowed to stir at 0° for 2 hr. to insure completeness of reaction. The solid material was removed by filtration, washed with ice water, set aside in a vacuum desiccator at 0° for 48 hrs. and recrystallized from chloroform. The yield of pure product was 5 g. (0.012 mole, 80%), melting at 81° with decomposition.

Calculated for $C_{22}H_{14}O_4S_2$:	C, 65.0; H, 3.40; S, 15.80.
Found:	C, 61.0; H, 3.42; S, 15.98.

Bis-(5-ethyl-4-bromo-2-thenoyl)peroxide

The general method for the synthesis of peroxide described above was again followed. The aqueous solution of sodium peroxide was prepared by dissolving 1.2 g. (0.016 mole) of the solid in 35 ml. of ice-cold water. A second solution containing 7.5 g. (0.030 mole) of 5-ethyl-4-bromo-2-thenoyl chloride dissolved in 35 ml. of dry toluene was added dropwise to the rapidly stirred aqueous peroxide solution. In this case about 15 min. of reaction time elapsed before a white precipitate separated from solution. The reaction mixture was stirred at 0° for an additional 2 hrs. to complete the reaction. The solid was then recovered by filtration. The product after recrystallization from petroleum ether melted at 102-5°, with decomposition. The yield obtained was 3.6 g. (0.0077 mole, 51%).

Calculated for $C_{14}H_{12}Br_2S_2O_4$:	C, 35.89; H, 2.56; S, 13.68; Br, 34.19.
Found:	C, 35.36; H, 2.62; S, 13.29; Br, 33.56.

2,5-Dimethyl-3-acetylthiophene

The procedure employed by Goldfarb, Litvinoff, and Shedov (35) was used in this preparation. A 40 g. (0.357 mole) quantity of 2,5-dimethylthiophene was placed in a 1 l. four-necked flask fitted with mechanical stirrer, calcium chloride drying tube, thermometer and dropping funnel. With the aid of a special graduated pipet 480 ml. of chlorobenzene, and 0.48 mole of acetyl chloride were added to the flask. The mixture was cooled to 0° under stirring (the cooling was achieved by means of a dry ice isopropanol bath), and during the course of 1.5 hrs. 0.24 mole of stannic chloride dissolved in 120 ml. of chlorobenzene was added, the temperature being maintained at 0-3°. The mixture was allowed to warm to room temperature and the stirring was continued for an additional hour. A hydrochloric acid solution (20 ml. of conc. (sp. gr. 1.19) acid in 180 ml. of water) was then added at 10-15° in order to decompose the complex salt. The acid layer was then separated and extracted with 280 ml. of chlorobenzene.

The chlorobenzene layer was washed with water, then with 10% sodium hydroxide, and twice more with water. The wash liquors were again extracted with 280 ml. of chlorobenzene. The chlorobenzene layers were combined and dried over anhydrous calcium chloride. The chlorobenzene was removed in vacuo and the ketone distilled in a micro distillation apparatus, yielding 46 g. (0.299 mole, 83.7%) of product boiling at 120-122°/25 mm. Literature value (35) 128-130°/30 mm.

2,5-Dimethyl-3-thenoic acid

A variation of the method of Hartough and Conley (24) was used in the preparation of the acid.

A solution of sodium hypochlorite was prepared by passing 160 g. (0.225 mole) of chlorine gas into a solution of 220 g. (5.5 moles) of sodium hydroxide in 300 ml. of water to which 1,000 g. of ice had been added. The chlorine addition was completed in 25 min., after which the hypochlorite solution was heated to 60° on a steam bath. The solution was then transferred to a 3 l. four-necked flask, fitted with a mechanical stirrer, dropping funnel, thermometer and reflux condenser. The mixture was then slowly heated under stirring to 85°. A quantity of 46 g. (0.2923 mole) of 2,5-dimethyl-3-acetylthiophene was then added dropwise from the addition funnel at a rate sufficient to maintain the reaction temperature between 85-95°. After the addition was completed the mixture was stirred at 95° for 10 hrs., and then cooled to room temperature. The cooled solution was washed with ether to remove any residual starting material, and the ether layer was discarded.

A solution containing 50 g. of sodium bisulfite dissolved in 100 ml. of water was then added to the washed reaction mixture and the resulting solution was transferred into a 4 l. beaker. It was acidified with conc. hydrochloric acid and the white solid product, which precipitated at this point, was recovered by filtration, washed, and recrystallized from hot water. This yielded 3.9 g. (0.0025 mole, 8.55%) of product melting at 107-108°. Literature value (24) 119-120°.

Bis-(2,5-dimethyl-3-thenoyl)peroxide

A volume of 80 ml. of water, contained in a 300 ml. three-necked flask fitted with stirrer, thermometer and dropping funnel was cooled to 0° by means of an ice bath. Under vigorous stirring 7 g. (0.089 mole) of sodium peroxide were added in small portions. A solution prepared from 3.5 g. (0.2008 mole) of 2,5-dimethyl-3-thenoyl chloride in 10 ml. of dry carbon tetrachloride was added dropwise, at 0° to the aqueous peroxide solution with stirring over a period of 15 min. A white insoluble material began to form about 30 min. after the addition of the acid chloride solution had been completed. The reaction mixture was stirred at 0° for an additional 4 hrs. and the white, crystalline product was recovered by filtration, washed with ice water yielding 3.2 g. (0.0103 mole, 82.4%) of product.

Calculated for $C_{14}H_{14}O_4S_2$:	H, 4.52; S, 20.65.
Found:	H, 4.82; S, 20.17.

Analytical Titration Procedures Employed for Determination of the Purity of the Thenoyl Peroxides

The peroxide analyses were performed by Mr. James Stoia and Mr. Anton Westveld at the laboratories of Olivet College.

The analytical results obtained for the substituted thenoyl peroxides prepared are summarized in Table IV. The experimental procedure used was taken from the Ph.D. Thesis of Joseph Shae (18).

A sample of peroxide (170.9 mg. (0.526 millimole) in the case of bis-(5-chloro-3-thenoyl)peroxide) was accurately weighed and transferred to a 25 ml. volumetric flask. It was dissolved in specially purified carbon tetrachloride and made up to volume.

Four aliquots of 4 ml. each were then removed with a pipet and transferred to clean, dry 125 ml. Erlenmeyer flasks. A 10 ml. volume of glacial acetic acid containing 0.005% ferric chloride and a small piece of dry ice were then added to each aliquot. The dry ice was added to displace the atmospheric oxygen with carbon dioxide. The flasks were then shaken to make certain that all the dry ice had sublimed (to avoid the displacement of iodine vapor later), and finally 1.0 ml. of saturated sodium iodide solution was added to each sample. A blank solution was also prepared containing all the reactants except the peroxide sample.

The samples were set aside in the dark for a period of 45 min., with occasional shaking, and were then titrated with standard sodium thiosulfate. Just prior to titration 25 ml. of water was added to each sample. Starch solution was added just before the end point had been reached (light straw yellow color). The sodium thiosulfate had been standardized against potassium iodate as a primary standard.

Kinetic Determinations

The thermal decomposition rates of the various substituted thenoyl peroxides were followed by a study of their infrared spectra at 5.5 to 6.1 microns of carbon tetrachloride solutions containing 0.2 mole of purified styrene to inhibit induced decompositions. The typical "peroxide peak" occurred at approximately 5.7 microns with a slight shifting from compound to compound. The samples were exposed to the required reaction temperatures for definite times, extending from "zero time" to the estimated half life of the compound. The decompositions were conducted in an electrically heated mineral oil bath, the temperature of which was controlled to ± 0.2^{o} by a relay supplied by Central Scientific Company.

The peroxide solutions were prepared, using specially purified carbon tetrachloride for all the peroxides except bis-(5-nitro-3-thenoyl)peroxide, which was only slightly soluble in carbon tetrachloride. For this peroxide purified chloroform was used as a solvent. The concentration of the peroxide solutions were prepared as closely to 0.01 M as was feasable for all compounds. They were transferred into ampoules of approximately 1 ml. capacity employing a hypodermic syringe, frozen in dry ice, and immediately sealed with the gas flame torch. The samples were then introduced into the constant temperature bath which had been preheated to the desired reaction temperature. A 3 min. period was allowed for the peroxide solutions to come to thermal equilibrium. Duplicate samples were removed from the thermostatted bath for all determinations at this "zero time". The results of the kinetic runs are shown in Tables V through XXVIII. They were determined from the respective infrared spectra obtained on a Perkin-Elmer 21 spectrograph in the region of 5.5 to 6.1 microns. Base-lines were determined using solvent for both the sample and the reference beams. The values I and I_0 represent the distances of the peak and corresponding base-line values from some arbitrary zero line (see photographs of spectra in Appendix). These distances on the graphs were determined with a ruler, designated as I_0 and I respectively and the absorption coefficients were calculated as log I_0/I. (A). The logarithms of the absorption coefficients were then computed and plotted against the time in minutes, to determine the rate constants initially. (See appendix.) All final values of the rate constants were calculated using the method of least squares. Only for one compound, namely bis-(5-chloro-3-thenoyl)peroxide, were the rate values calculated manually, all others were programmed and calculated in a Burroughs B-500 type computer. These calculations were carried out by the offices of Mr. Thomas Aird of Detroit to whom we are most grateful.

Activation energies were determined from a plot of the logarithm of the rate constants determined, at three different reaction temperatures, against the reciprocal of the absolute temperature. These are shown in Table XXIX. Using the formula,

$$\Delta S^{\#}/4.576 = \log k - 10.753 - \log T + E/4.576T \qquad (36)$$

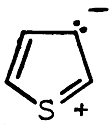
the entropies of activation were then calculated for each case. These, as well as the frequency factors, are summarized in Table XXX.

Table IV. List of peroxides prepared.

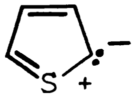
Peroxide	Yield %	Melting Point °C.	Solvent(s) used for Recrystallization
Bis-(5-bromo-3-thenoyl) peroxide	44	102-103	Chloroform *n*-butyl ether
Bis-(5-chloro-3-thenoyl) peroxide	58	72-73	Petroleum ether
Bis-(5-nitro-3-thenoyl) peroxide		153-154 det. at 157	Chloroform Petroleum ether
Bis-(3-methyl-2-thenoyl) peroxide	35	104- (Decomp.)	Benzene Petroleum ether
Bis-(2,5-dichloro-3-thenoyl) peroxide	70	92-93	Petroleum ether
Bis-(4,5-dibromo-2-thenoyl) peroxide	59	158-159 (Decomp.)	Not recrystallized
Bis-(5-phenyl-2-thenoyl) peroxide	80	81- (Decomp.)	Chloroform
Bis-(5-ethyl-4-bromo-2-thenoyl)peroxide	51	102-105	Petroleum ether

DISCUSSION AND RESULTS

Essentially the work described in this thesis involved two main tasks. Initially to develop suitable synthetic procedures for the preparation of the thenoyl peroxides studied, and secondly an investigation of their decomposition rates. Originally the object of the present investigation was to extend the studies of sulfur heterocyclic peroxides initated by Schuetz and Teller (12). It was planned to prepare a complete series of substituted 3-thenoyl peroxides, containing both electron repelling and electron attracting substituents attached to suitable positions in the heterocyclic ring. Once the parent acids to these peroxides are prepared, the synthesis of the corresponding peroxides themselves is a relatively easy task, provided the right solvent media is chosen for reaction involving the intermediate acyl chlorides. The best solvents for the reactions of the acyl chlorides with aqueous inorganic peroxide are those in which the acyl chlorides are highly soluble, but in which the final peroxide product is sufficiently insoluble to allow it to precipitate from the medium immediately after it has been produced. Toluene, cyclohexane, benzene, and carbon tetrachloride were found suitable for different compounds, after considerable "trial and error". The parent acids having the carboxyl group in the three position are relatively difficult to obtain, compared to their corresponding isomeric 2-thenoic acids. The reason for this is that the canonical forms (37) of the type I contribute considerably less to the final resonance hybrid of thiophene than do the structures typified by II. As thiophene has only a single uncharged canonical



I



II

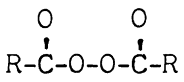
form contributing to the resonance hybrid, those charged forms which have their charges closer together are known to contribute more to the hybrid than those having the centers of charge further removed from one another (38). As long as the alpha positions are free of substituents, practically all electrophylic substitutions will occur in these positions; this is true of halogenation, acylation, and sulfonation, etc.

The parent, 3-thenoic, acid was originally prepared by the side-chain oxidation of 3-methylthiophene, itself a substance rather difficult to obtain. Permanganate oxidation, known to be so successful in the preparation of benzoic acid and its derivatives, by oxidation of alkyl side chains had given only a very poor yield (8%) of the theoretical amount of 3-thenoic acid by oxidation of 3-methylthiophene (39). Campaigne and Le Suer (22) prepared 3-thenoic acid by a side chain bromination of 3-methylthiophene, followed by the Sommelett reaction and subsequent oxidation of the resulting 3-thenal. In the present work 3-bromothiophene was used as a starting material, from which 3-thenoic acid was prepared in good yields by two different methods. A Grignard type reaction using n-butyl lithium (20), and a nitrile synthesis (17), employing cuprous cyanide in quinoline, followed by hydrolysis of the nitrile with concentrated acid. Primarily through the efforts of Byrne, working in the laboratories of Olivet College (40), the yields in the latter process have been improved considerably above those indicated in in the literature (19). Fortunately, the 5-substituted bromo-, chloro-, and nitro-3-thenoic acids can be prepared by simple (23) procedures from the parent acid directly, as the meta directing influence of the carboxy group augments alpha orienting character of the heterocyclic sulfur, directing the substituents into the five position exclusively. On the other hand, the synthesis of simple derivatives of 3-thenoic acid, having electron releasing substituents, is a rather lengthy, difficult process, requiring numerous steps resulting in relatively low overall yields. An attempt to prepare 2-ethyl-3-thenoic acid from the corresponding brominated precursor, 2-ethyl-3-bromothiophene, by the "lithium-butyl" procedure was unsuccessful. In a second attempt to obtain the alkyl substituted 3-thenoic acid by this procedure, the resulting product proved to be 5-ethyl-4-bromo-2-thenoic acid, obtained in low yield. Apparently the ortho-directing influence of the halogen collaborates with the alpha orienting power of the hetero atom to yield the acid obtained. It should be emphasized here that according to the findings of Gronowitz (41), 3-bromothiophene, when treated with butyl lithium at 0°, yield, after carbonation, 3-bromo-2-thenoic acid, whereas at -70° 3-thenoic acid is the product; mixtures of the acids are presumably obtained at intermediate temperatures. These results suggest that under the activating influence of the ethyl substituent, an even lower temperature of reaction may be indicated in order to obtain the desired 2-ethyl-3-thenoic acid. Since 5-ethyl-4-bromo-2-thenoic acid was obtained, it was decided to use this acid as a starting material for the preparation of its corresponding peroxide, and for this reason bis-(4-bromo-5-ethyl-2-thenoyl)peroxide was included in the kinetic studies.

Further it was decided that it was better to use the alpha-alpha substituted thiophenes as starting materials for further 3-substituted acids, as 2,5-dichloro- (24), as well as 2,5-dimethylthiophenes (35), both commercially available can easily be acylated in the 3-position, yielding methylketones which could be readily oxidized by hypo-iodite oxidation to the corresponding carboxylic acids. Peroxides were prepared from these acids, yielding the desired substituted thenoyl peroxide examples for comparison between electron attracting (chlorine) substituents and electron releasing (methyl) groups. A thenoyl peroxide was also prepared from 4,5-dibromo-2-thenoic acid, readily available through direct bromination of 2-thenoic acid. However, this peroxide, evidently due to its high molecular weight, could not be dissolved in any solvent compatible with infrared techniques. It was therefore not included in the kinetic investigations. All other peroxides, with the exception of bis-(5-nitro-3-thenoyl)peroxide, were easily soluble in carbon tetrachloride. The latter peroxide had to be dissolved in chloroform.

Considering the results obtained from the kinetic determinations, the following generalizations can be suggested.

In contrast to the compounds investigated by Schuetz and Teller (10), the majority of the compounds studied in the present investigation would not be expected to decompose at rates following the Hammett equation. Only the derivatives of 5- substituted 3-thenoic acids could be expected to follow this law, as they are comparable to the "meta"-substituted analogues in the benzenoid series. The results of the present study show that bis-(5-nitro-3-thenoyl)peroxide decomposes at a faster rate than the peroxide obtained from unsubstituted 3-thenoic acid; $T_{1/2}$ for the nitro derivative equals 118.5 minutes, for the "parent" peroxide 293.5 minutes. This result is contrary to that normally expected, since the nitro group is typically electron withdrawing (-I, -T). A reasonable explanation for this has been given by Hine (42). If the spontaneous decomposition can be assumed to be due to the repulsion of two dipoles joined at their negative ends,



$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R$$

then the rate of decomposition should be proportional to the magnitude of these dipoles. Electron releasing groups would therefore increase the rate, whereas electron attracting substituents would retard the reaction. Blomquist and Buselli (7) found however that for p,p'-, as well as m,m'-dinitrobenzoyl peroxides the rates were considerably higher than predicted by the Hammett equation. Similar results were found to be true for the bis-(5-nitro-3-thenoyl)peroxide in the studies described here. The above authors point out that they believe the nitro group may be such a strong electron withdrawing group that the direction of the dipole is actually reversed. There is also the possibility that, in spite of the presence of styrene as a free radical scavenger, the induced part of the reaction may not have been completely suppressed in the case of the nitro-derivatives under consideration. According to Swain and Stockmeyer (6), electron withdrawing substituents aid, rather than hinder, the induced decomposition. It should also be mentioned here that Schuetz and Teller (10) found that bis-(5-nitro-2-thenoyl)peroxide does not decompose according to a strict first order law in the presence of 3,4-dichlorostyrene as a scavenger, whereas all other compounds they investigated did follow a first order pattern. The only two remaining peroxides in the series which might decompose according to the Hammett equation are bis-(5-chloro) and bis-(5-bromo)thenoyl peroxides. The values which should be used for these compounds are 0.373 for Cl and 0.391 for Br. Thus, for these two halo substituted heterocyclic peroxides, the results are,

Substituent	$\sigma 1 + \sigma 2$	$\log k/k_0$	Calc'd.
Cl	0.746	-0.065	-0.087
Br	0.782	-0.093	-0.123

As can be readily seen from these data, the Hammett equation is obeyed only to a very rough approximation. This is not too surprising, as Imoto (43) and his coworkers found that a linear plot is not obtained when the rates of hydrolysis of 5-substituted-3-thenoic esters are plotted against the acidity constants of the corresponding acids in a Hammett type plot.

Blomquist and Buselli (7) make the statement that for those aromatic and hetero-aromatic compounds whose reactions obey the Hammett equation the frequency factor of the Eyring equation (44), and therefore the entropy of activation, should be constant, or at least nearly so. For the peroxides studied in the present investigation both energies and entropies of activation vary over a rather wide range (Table XXIX). A number of the peroxides, such as bis-(3-methyl-2-thenoyl)-, bis-(2,5-dichloro-3-thenoyl)-, and bis-(25,-dimethyl-3-thenoyl)-, bear substituents on carbons next to the atoms bearing the peroxyl group. A considerable "ortho effect" (8) is therefore to be anticipated. However, it was of interest to determine that if the energies of activation are plotted against the entropies of activation in the entire series studied a rather good straight line results (see Figure 30). This points toward an "isokinetic" relationship as discussed by Bunnett (45) in his article of the "Interpretation of Rate Data".

The above author talks about "Reaction Series" and classifies them into four categories:

1) Changes of reaction rate are due mainly to changes in the enthalpy of activation, with the entropy of activation remaining essentially constant. It is for these reactions that the Hammett Law is essentially obeyed.

2) Changes in reaction rate are due mainly to changes in the entropy of activation, with the energy factor being practically constant. Such reactions are relatively rare, but they do occur.

3) Reactions for which both the entropy and the enthalpy of activation change in a rather random fashion.

4). Reactions for which the changes in reaction rate are due to a change in both factors, but for which a linear relationship can be found to exist between the entropy and the enthalpy factor. The probability that the reaction series investigated in the present study falls into the last mentioned type is apparently given.

Leffler (46), as well as Wilmarth and Schwartz (47) have investigated this type of reaction series. In Leffler's paper a total of eighty-one reaction series were investigated; the authors employed either the simple Arrhenious equation (48)

$$k = A\ e^{-E/RT}$$

or the modified collision approach (49)

$$k = P\ Z\ e^{-E/RT}$$

where P is the "probability factor", and Z the "collision frequency".

Leffler used for his plots of reaction data either log A, log PZ or directly the entropy of activation as abscissa, and the energy of activation as ordinate for the reaction series under study and obtained good straight line plots in the majority of cases. The various methods of treating rate data used by Leffler are equivalent as A is quite apparently equal to PZ and PZ is related to the entropy of activation by the relationship:

$$PZ = (\kappa kT/h)\ e^{-\Delta S/R}\ (49)$$

where k is the Boltzmann constant, R is the molar gas constant, and κ is the "transmission" coefficient (49). Included in the studies made by Leffler (46) was the series investigated by Blomquist and Buselli (7), on the decomposition rates of substituted benzoyl peroxides. In this series it was found that two separate straight lines were obtained, when the entropies of activation were plotted against the energies of activation, one for the meta- and para- substituted benzoyl peroxides, and a second one for those peroxides bearing the substituents ortho relative to the peroxy linkage.

It is particularly noteworthy that for the reactions investigated in this study only one straight line is obtained, and that the experimental points show an almost perfect fit to this line, although there were included in this study compounds which would be expected to show marked "ortho" effects (8); these compounds are bis(2,5-dichloro-3-thenoyl), bis(2,5-dimethyl-3-thenoyl), bis(4-bromo-5-ethyl-2-thenoyl), and bis(3-methyl-2-thenoyl) peroxides. If the pattern shown for the substituted benzoyl peroxides (7) were followed, one would expect two separate straight lines to result, one for the above mentioned heterocyclic peroxides, and one for the remaining compounds investigated in this work as the latter group would be comparable to the meta- and para- derivatives in the benzenoid series. This is apparently not the case for the substituted thenoyl peroxides investigated. Leffler (46) states that "moderate changes in the degree of steric hindrance do not remove a reaction from the isokinetic line, but merely move it to a different position on the same line. One would expect with a considerable increase in steric hindrance in the transition state an increase in the enthalpy of activation and decrease in the entropy of activation." From the data obtained in this investigation this seems to apply mainly for the case of bis(5-phenyl-2-thenoyl)peroxide, where a steric hindrance factor appears to play only a minor role. Further investigation is quite obviously indicated, and is planned for the future study.

The slope of the "isokinetic line" has the dimensions of temperature and is called the "isokinetic temperature". It is denoted by the symbol β (46). For the straight line plot:

$$\Delta H^{\#} = \beta \Delta S^{\#} + \text{constant}$$

for two points on the line:

$$\Delta H_2^{\#} - \Delta H_1^{\#} = \beta(\Delta S_2^{\#} - \Delta S_1^{\#})$$

but

$$\Delta H^{\#} = \Delta F^{\#} + T\Delta S^{\#}$$

and

$$\Delta H_2^{\#} - \Delta H_1^{\#} = T\ (\Delta S_2^{\#} - \Delta S_1^{\#}) + T(\Delta F_2^{\#} - \Delta F_1^{\#})$$

therefore,

$$\beta(\Delta S_2^{\#} - \Delta S_1^{\#}) = T\ (\Delta S_2^{\#} - \Delta S_1^{\#}) + (\Delta F_2^{\#} - \Delta F_1^{\#})$$

Thus, it is apparent that

if $\Delta F_2^{\#} = \Delta F_1^{\#}$, then $\beta = T$

and at the temperature β all the reactions in the series should occur at the same rate, as their free energies of activation would then be equal.

For the reaction series under investigation in the present study the slope of the line, (Fig. 15) is 369.4°K. or 96.2°C. If the series follows a true isokinetic behavior all the heterocyclic peroxides under investigation should decompose at equal rates at 96.2°. There should also be, above the isokinetic temperature, an inversion of relative rates; the compounds showing the fastest rate below 96.2° should decompose at the slowest rate above that temperature and vice versa (45). Again it is rather apparent that the present study has opened a wide field for further investigation.

SUMMARY

1. Nine previously unreported bis thenoyl peroxides were prepared; four of these were derivatives of 2-thenoic acid and five were derived from 3-thenoic acid. All the intermediate acid chlorides used to synthesize the peroxides were also new compounds, characterized for the first time.

2. The rates of thermal decomposition, in carbon tetrachloride, of eight of the nine above mentioned peroxides were studied, the only peroxide not so investigated being bis(4,5-dibromo-2-thenoyl)peroxide for which a solvent compatible with infra-red technique could not be found. The first order law was found to be obeyed for all compounds studied. Rate constants determined at 79.6° are,

Peroxide	$k \times 10^3$ (min.$^{-1}$)
Bis(5-bromo-3-thenoyl)	2.031
Bis(5-chloro-3-thenoyl)	1.862
Bis(3-methyl-2-thenoyl)	2.699
Bis(5-nitro-3-thenoyl)	5.849
Bis(5-ethyl-4-bromo-2-thenoyl)	3.120
Bis(2,5-dichloro-3-thenoyl)	1.681
Bis(5-phenyl-2-thenoyl)	8.580
Bis(2,5-dimethyl-3-thenoyl)	3.789

3. Activation energies were determined and found to vary over a wide range, from 20.1 to 38.1 kilocalories per mole. This fairly well precluded the applicability of the Hammett equation. A Hammett type relationship was not expected, as several of the peroxides studied could be related to ortho-substituted benzenoid compounds. Entropies of activation were also computed which varied from -22 to plus 30 entropy units. When the entropies of activation were plotted against the energies of

activation a straight line plot was obtained, which pointed toward an "isokinetic" reaction series, with the "isokinetic" temperature being equal to the slope of the straight line obtained -369.4°K. (or 96.2°C.). This opened possibilities for further investigation.

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APPENDIX

Table V. Spectroscopic information leading to kinetic data.

Bis-(5-bromo-3-thenoyl)peroxide.

Code No. A - 1 - a

Temperature: 74.3°C ± 0.1. Solvent: CCl_4 plus 0.2 M styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	13.2	1.1	1.12057	0.04139	1.07928	0.02310
2	60	12.8	0.9	1.10721	-0.04576	1.15297	discard
3	180	13.2	1.3	1.12057	0.11394	1.01663	0.00715
4	300	13.1	1.8	1.11757	0.25527	0.86230	-0.06434
5	420	13.4	2.6	1.12710	0.41497	0.71313	-0.14683
6	540	13.2	3.0	1.12057	0.47712	0.64345	-0.19148

Slope: 3.5590×10^{-4} k = 8.195×10^{-4} min.$^{-1}$ $T_{1/2}$ = 846 minutes.

Run No. 2. Code No. A - 1 - b

1	0	13.6	1.4	1.13354	0.14613	0.98741	-0.00550
2	60	13.1	1.2	1.11727	0.07918	0.93809	-0.02275
3	180	13.35	1.8	1.12548	0.25527	0.87021	-0.06037
4	300	13.35	2.5	1.12548	0.39794	0.72754	-0.13815
5	420	13.5	2.8	1.13033	0.44716	0.68317	-0.16185
6	540	13.35	3.4	1.12548	0.53148	0.59400	-0.22621

Slope: - 4.0707×10^{-4} k = 9.375×10^{-4} min.$^{-1}$. $T_{1/2}$ = 740 minutes.

Sum of square error (to indicate accuracy of data) = 5.746×10^{-4}.

Table VI. Spectroscopic information leading to kinetic data.

Bis-(5-bromo-3-thenoyl-) peroxide.

Code No. A - 2 - a

Temperature: 79.6°C ± 0.1 Solvent: CCl_4 plus 0.2 <u>M</u> styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	13.9	1.3	1.14301	0.11394	1.02907	0.01245
2	60	13.8	2.3	1.13988	0.36173	0.77815	-0.10899
3	180	14.2	3.3	1.15229	0.51851	0.63378	-0.19807
4	300	14.0	4.5	1.14613	0.65321	0.49292	-0.30722
5	420	14.4	5.6	1.15836	0.74819	0.41017	-0.38703
6	540	14.2	6.6	1.15229	0.81954	0.33275	-0.47788
Slope:	-8.5972×10^{-4}			$k = 1.980 \times 10^{-3}$ min.$^{-1}$		$T_{1/2}$ = 350.0 minutes.	
Run No. 2.				Code No. A - 2 - b			
1	0	14.1	1.0	1.14922	0.00000	1.14922	0.06040
2	60	14.0	2.3	1.14613	0.36173	0.78440	-0.10546
3	180	14.3	3.5	1.15534	0.54407	0.61127	-0.21377
4	300	14.2	4.5	1.15229	0.65321	0.49908	-0.30183
5	420	14.5	5.7	1.16137	0.75587	0.40550	-0.39201
6	540	14.4	6.6	1.15836	0.81954	0.33882	-0.47003
Slope:	-9.0475×10^{-4}			$k = 2.090 \times 10^{-3}$ min.$^{-1}$		$T_{1/2}$ = 331.1 minutes.	

Table VII. Spectroscopic information leading to kinetic data.

Bis-(5-bromo-3-thenoyl-) peroxide.

Code No. A - 3 - a

Temperature: 85.0^{o}C ± 0.1 Solvent: CCl_4 plus 0.2 M styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	13.1	1.0	1.1271	0.00000	1.12710	0.10415
2	60	13.3	2.4	1.2385	0.38021	0.74364	-0.12864
3	180	13.6	4.4	1.3354	0.64345	0.49009	-0.30972
4	300	13.3	6.1	1.12385	0.78533	0.33852	-0.47042
5	420	13.9	7.6	1.14301	0.88081	0.26220	-0.58137
6	540	13.1	8.7	1.11727	0.93952	0.17775	-0.75260

Slope: 1.4635×10^{-3} k = 3.370×10^{-3} min.$^{-1}$ $T_{1/2}$ = 205.6 minutes.

Run No. 2. Code No. A - 3 - b

1	0	13.8	1.5	1.13988	0.17609	0.96379	-0.01601
2	60	13.5	2.7	1.13033	0.43136	0.69897	-0.15554
3	180	13.9	5.1	1.14301	0.70757	0.43544	-0.36107
4	300	13.9	6.6	1.14301	0.81954	0.32347	-0.49017
5	420	14.2	8.0	1.15229	0.90309	0.24920	-0.60345
6	540	14.0	9.1	1.14613	0.95904	0.18709	-0.72795

Slope: -1.2756×10^{-3} k = 2.937×10^{-3} min.$^{-1}$ $T_{1/2}$ = 241.4 minutes.

Table VIII. Spectroscopic information leading to kinetic data.

Bis-(5-chloro-3-thenoyl)peroxide

Code No. B - 1 - a

Temperature: 73.6°C. ± 0.1 Solvent: CCl_4 plus 0.2M styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	15.4	1.0	1.18752	0.00000	1.18752	0.07452
2	60	15.15	2.20	1.18041	0.34242	0.83799	-0.07676
3	180	15.8	2.95	1.19866	0.46982	0.72884	-0.13737
4	300	15.75	4.40	1.19728	0.64345	0.55383	-0.25663
5	420	15.9	4.45	1.20140	0.64836	0.55304	-0.25724
6	540	16.0	4.95	1.20412	0.69461	0.50951	-0.29285

Slope: -4.032×10^{-4} $k = 9.288 \times 10^{-4}$ min.^{-1} $T_{1/2}$ = 746.1 minutes.

Run No. 2. Code No. B - 1 - b

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
1	0	15.2	1.9	1.18184	0.27875	0.90309	-0.04436
2	60	15.3	2.0	1.18469	0.20103	0.88366	-0.05372
3	180	15.25	2.65	1.18327	0.42325	0.76002	-0.11918
4	300	15.4	3.05	1.18752	0.48430	0.70322	-0.15297
5	420	15.5	3.85	1.19033	0.58546	0.60487	-0.21834
6	540	15.55	4.25	1.19173	0.62839	0.56334	-0.24923

Slope: -3.889×10^{-4} $k = 8.956 \times 10^{-4}$ sec.^{-1} $T_{1/2}$ = 829.1 minutes.

Table IX. Spectroscopic information leading to kinetic data.

Bis-(5-chloro-3-thenoyl)peroxide

Code No. B - 2 - a

Temperature: 79.6°C. ± 0.1 Solvent: CCl_4 plus 0.2M styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	13.5	1.4	1.13033	0.14613	1.00420	0.00182
2	60	13.4	1.0	1.12710	0.00000	1.12710	0.05195
3	180	13.7	2.3	1.13672	0.36173	0.77499	-0.11070
4	300	13.6	3.4	1.13354	0.53148	0.60206	-0.22036
5	420	13.5	4.6	1.13033	0.66276	0.46757	-0.33015
6	540	13.8	5.8	1.13988	0.76343	0.37645	-0.42429
Slope: -9.167×10^{-4}		$k = 2.111 \times 10^{-3}$ sec.$^{-1}$			$T_{1/2}$ = 328.3 minutes.		
Run No. 2.		Code No. B - 2 - b					
1	0	13.95	1.4	1.14457	0.14613	0.99844	-0.00062
2	60	14.0	2.0	1.14613	0.30103	0.84510	-0.07304
3	180	14.2	2.8	1.15229	0.44716	0.70513	-0.15173
4	300	14.0	3.8	1.14613	0.57978	0.56635	-0.24616
5	420	14.3	5.2	1.15534	0.71600	0.43934	-0.37720
6	540	14.25	6.1	1.15381	0.78533	0.36848	-0.43358
Slope: -7.50×10^{-4}		$k = 1.727 \times 10^{-3}$ sec.$^{-1}$			$T_{1/2}$ = 401.3 minutes.		

Table X. Spectroscopic information leading to kinetic data.

Bis-(5-chloro-3-thenoyl)peroxide

Code No. B - 3 - a

Temperature 85°C. ± 0.1 Solvent CCl_4 plus 0.2M styrene.

Run No. 1.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
1	0	14.0	1.0	1.14613	0.00000	1.14613	0.16474
2	60	13.8	1.9	1.13988	0.27875	0.86113	-0.06493
3	180	14.1	3.9	1.14922	0.59106	0.55816	-0.25324
4	300	14.0	5.2	1.14613	0.71600	0.43013	-0.36640
5	420	14.4	7.7	1.15836	0.88649	0.27187	-0.56564
6	540	14.3	9.2	1.15534	0.96379	0.19155	-0.71771

Slope: -1.3889×10^{-3} $k = 3.1986 \times 10^{-3}$ sec.$^{-1}$ $T_{1/2} = 216.7$ minutes.

Run No. 2. Code No. B - 3 - b

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
1	0	14.6	1.6	1.16435	0.20412	0.96023	-0.01758
2	60	14.4	2.6	1.15836	0.41497	0.66339	-0.17823
3	180	14.8	4.8	1.17026	0.68124	0.48902	-0.31067
4	300	14.7	6.6	1.16732	0.81954	0.34778	-0.45867
5	420	14.8	8.7	1.17026	0.93952	0.23074	-0.63688
6	540	14.8	9.8	1.17026	0.99123	0.17903	-0.74708

Slope: -1.2222×10^{-3} $k = 2.8148 \times 10^{-3}$ sec.$^{-1}$ $T_{1/2} = 246.2$ minutes.

Table XI. Spectroscopic information leading to kinetic data.

Bis-(5-nitro-3-thenoyl)peroxide

Code No. C - 1 - a

Temperature: 73.8°C ± 0.1 Solvent: $CHCl_3$ plus 0.2M styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	12.0	0.7	1.07918	9.84510 -10	1.23408	0.08132
2	60	12.1	1.1	1.08279	0.04139	1.04140	0.01745
3	180	12.2	1.45	1.08636	0.16137	0.92499	-0.03386
4	300	12.1	2.3	1.08279	0.36173	0.72106	-0.14200
5	420	12.3	3.95	1.08991	0.59660	0.49331	-0.30689
6	540	12.0	4.8	1.07918	0.68124	0.39794	-0.40017

Slope: -8.9769×10^{-4} k = 2.067×10^{-3} min.^{-1} $T_{1/2}$ = 335.2 minutes.

Run No. 2. Code No. C - 1 - b

1	0	12.1	0.3	1.08279	9.47712 -10	1.66567	0.20575
2	60	11.9	0.45	1.07555	9.65321 -10	1.42234	0.15290
3	180	12.1	1.3	1.08279	0.11394	0.96885	-0.01572
4	300	11.95	2.4	1.07237	0.38021	0.69716	-0.15664
5	420	12.1	3.1	1.08279	0.49136	0.59143	-0.22812
6	540	11.9	4.65	1.07555	0.66745	0.40810	-0.38923

Slope: -1.123×10^{-3} k = 2.586×10^{-3} min.^{-1} $T_{1/2}$ = 268 minutes.

Table XII. Spectroscopic information leading to kinetic data.

Bis-(5-nitro-3-thenoyl)peroxide

Code No. C - 2 - a

Temperature: 79.6°C ± 0.1 Solvent: $CHCl_3$ plus 0.2$\underline{M}$ styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	7.5	0.1	0.87506	-1.00000	1.87506	0.27300
2	60	7.5	0.7	0.87506	-0.15490	0.97996	-0.02877
3	120	7.5	0.9	0.87506	-0.0510	0.88383	-0.05314
4	180	7.4	1.2	0.86923	0.07918	0.79005	-0.10237
5	240	7.4	2.5	0.86923	0.39794	0.47129	-0.32670
6	300	7.2	3.0	0.85733	0.47712	0.38021	-0.42998

Slope: -2.1526×10^{-3} $k = 4.957 \times 10^{-3}$ min.^{-1} $T_{1/2}$ = 139.8 minutes.

Run No. 2. Code No. C - 2 - b

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
1	0	7.4	0.2	0.86923	-0.69897	1.56820	0.19540
2	60	7.8	1.3	0.89209	0.11394	0.77815	-0.01893
3	120	7.9	2.0	0.89763	0.30103	0.59660	-0.22432
4	180	7.5	2.65	0.87506	0.42325	0.45181	-0.34504
5	240	7.6	3.6	0.88081	0.55030	0.33051	-0.48082
6	300	7.5	4.9	0.87506	0.69020	0.18486	-0.73316

Slope: -2.9281×10^{-3} $k = 6.771 \times 10^{-3}$ min.^{-1} $T_{1/2}$ = 102.4 minutes.

Table XIII. Spectroscopic information leading to kinetic data.

Bis-(5-nitro-3-thenoyl)peroxide

Code No. C - 3

Temperature: 85.0°C. ± 0.1 Solvent: $CHCl_3$ plus 0.2$\underline{M}$ styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	7.9	0.1	0.89763	-1.00000	1.89763	0.27821
2	60	7.7	1.6	0.89763	0.20412	0.69351	-0.15894
3	120	7.7	3.0	0.88649	0.47712	0.40937	-0.38788
4	180	7.9	4.0	0.89763	0.60206	0.29557	-0.52934
5	240	7.85	5.25	0.89487	0.72016	0.17471	-0.75768
6	300	7.5	666	0.87506			

Slope: -4.0703×10^{-3} $k = 9.374 \times 10^{-3}$ min.$^{-1}$ $T_{1/2}$ = 74.50 minutes.

Table XIV. Spectroscopic information leading to kinetic data.

Bis-(3-methyl-2-thenoyl)peroxide

Code No. D - 1 - a

Temperature: 74.3°C. ± 0.1 Solvent: CCl_4 plus styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	15.0	0.8	1.17609	-0.09691	1.17300	0.06930
2	60	15.0	1.05	1.17609	0.02119	1.15490	0.06629
3	180	15.0	1.95	1.17609	0.29063	0.88546	-0.05283
4	300	14.6	2.25	1.16435	0.35218	0.81217	-0.09035
5	420	14.6	3.0	1.16435	0.47712	0.68723	-0.16270
6	540	14.6	3.7	1.16436	0.56820	0.59615	-0.22464
Slope: -5.31777×10^{-4} k = 1.225×10^{-3} min.$^{-1}$ $T_{1/2}$ = 565.9 minutes.							
Run No. 2.			Code No. D - 1 - b				
1	0	15.1	0.9	1.17869	-0.04576	1.22445	0.08794
2	60	15.0	1.6	1.17754	0.20412	0.97342	-0.01170
3	180	14.8	1.8	1.17026	0.25527	0.91499	-0.03858
4	300	14.8	2.5	1.17026	0.39794	0.77794	-0.10905
5	420	14.8	2.95	1.17026	0.46982	0.70044	-0.15488
6	540	14.8	3.8	1.17026	0.57978	0.59048	-0.22879

Slope: -5.25994×10^{-4} k = 1.211×10^{-3} min.$^{-1}$ $T_{1/2}$ = 603.5 minutes.

Table XV. Spectroscopic information leading to kinetic data.

Bis-(3-methyl-2-thenoyl)peroxide

Code No. D - 2 - a

Temperature: 79.6°C. ± 0.1 Solvent: CCl_4 plus 0.02M styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	12.45	0.95	1.09517	-0.02228	1.11745	0.04823
2	60	12.3	1.75	1.08991	0.24304	0.86687	-0.06204
3	180	12.4	3.15	1.09342	0.49831	0.59511	-0.22530
4	300	12.25	4.50	1.08849	0.65321	0.43528	-0.36123
5	420	12.3	5.10	1.08991	0.70757	0.38234	-0.41755
6	540	12.35	6.5	1.09167	0.81291	0.27876	-0.55477

Slope: -1.0704×10^{-3} $k = 2.465 \times 10^{-3}$ $min.^{-1}$ $T_{1/2}$ = 281.1 minutes.

Run No. 2. Code No. D - 2 - b

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
1	0	12.1	0.9	1.08279	-0.04576	1.12855	0.05252
2	60	11.8	1.3	1.07188	0.11394	0.95794	-0.01866
3	180	11.8	2.7	1.07188	0.43136	0.64052	-0.19347
4	300	11.85	4.1	1.07372	0.61278	0.46094	-0.33635
5	420	11.95	5.4	1.07737	0.73239	0.34498	-0.46281
6	540	11.95	7.0	1.07737	0.84510	0.22627	-0.64538

Slope: -1.2725×10^{-3} $k = 2.930 \times 10^{-3}$ $min.^{-1}$ $T_{1/2}$ = 247.6 minutes.

Table XVI. Spectroscopic information leading to kinetic data.

Bis-(3-methyl-2-thenoyl)peroxide

Code No. D - 3 - a

Temperature: 85.0°C. ± 0.1   Solvent: CCl_4 plus 0.02M styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	11.9	0.2	1.07555	-0.69897	1.77452	0.24908
2	30	12.1	0.8	1.08279	-0.09691	1.17970	0.07177
3	60	11.5	0.9	1.06070	-0.04576	1.10646	0.04394
4	90	11.3	1.8	1.05308	0.25527	0.79781	-0.09806
5	120	11.5	2.0	1.06070	0.30103	0.75452	-0.12233
6	150	11.5	2.9	1.06070	0.46240	0.59030	-0.22308

Slope: -2.9381×10^{-3} $k = 6.767 \times 10^{-3}$ min.$^{-1}$ $T_{1/2}$ = 102.4 minutes.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 2.			Code No. D - 3 - b				
1	0	12.7	0.6	1.0380	-0.22185	1.22565	0.08837
2	30	12.5	1.15	1.09691	0.06070	1.03621	0.01545
3	60	12.5	2.1	1.09691	0.32222	0.77469	-0.11082
4	90	12.0	2.3	1.07918	0.36173	0.71745	-0.14421
5	120	12.8	3.65	1.10721	0.56229	0.54492	-0.26366
6	150	11.8	4.0	1.07188	0.60206	0.46982	-0.32807

Slope: -2.8123×10^{-3} $k = 6.477 \times 10^{-3}$ min.$^{-1}$ $T_{1/2}$ = 107.0 minutes.

Table XVII. Spectroscopic information leading to kinetic data.

Bis-(5-ethyl-4-bromo-2-thenoyl)peroxide

Code No. F - 1 - a

Temperature: 73.8°C. ± 0.1 Solvent: CCl_4 plus styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	13.3	0.4	1.12385	-0.39794	1.52179	0.18235
2	120	12.8	0.75	1.10721	-0.12494	1.23215	0.08066
3	240	13.1	0.85	1.11727	-0.07058	1.04663	0.01979
4	360	12.4	1.45	1.09342	0.16137	0.93205	-0.03056
5	480	12.8	1.5	0.17609	0.93112	0.93112	-0.03099
6	600	12.5	2.2	1.09691	0.32242	0.75449	-0.12235

Slope: -4.4873×10^{-4} k = 1.0334×10^{-3} min.^{-1} $T_{1/2}$ = 670.6 minutes.

Run No. 2. Code No. F - 1 - b

1	0	14.1	1.4	1.11727	0.14613	1.00309	0.00004
2	120	12.9	1.0	1.11059	0.00000	1.11059	0.04554
3	240	13.4	1.5	1.12710	0.17609	0.95101	-0.02181
4	360	12.8	1.6	1.10721	0.20412	0.90309	-0.04426
5	480	13.2	2.25	1.12057	0.35218	0.76839	-0.11448
6	600	12.85	2.6	1.10890	0.41497	0.69393	-0.15868

Slope: -4.17592×10^{-4} k = 9.615×10^{-4} min.^{-1} $T_{1/2}$ = 720.7 minutes.

Table XVIII. Spectroscopic information leading to kinetic data.

Bis-(5-ethyl-4-bromo-2-thenoyl)peroxide

Code No. F - 2 - a

Temperature 79.6°C. ± 0.1 Solvent: CCl_4 plus styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	11.35	0.45	1.05500	-0.34679	1.40179	0.14669
2	60	11.35	0.75	1.05500	-0.12494	1.17994	0.07187
3	120	11.35	1.6	1.05500	0.20412	0.85088	-0.07013
4	180	11.45	2.1	1.05881	0.32222	0.73659	-0.13278
5	240	11.2	2.35	1.04922	0.37107	0.67845	-0.16848
6	300	11.65	3.0	1.06633	0.47712	0.58921	-0.22973
Slope: -1.2694×10^{-3}		k = 2.923×10^{-3} min.$^{-1}$			$T_{1/2}$ = 237.1 minutes.		
Run No. 2.			Code No. F - 2 - b				
1	0	11.35	0.45	1.05500	-0.34679	1.14079	0.14669
2	60	10.95	0.9	1.03941	-0.04576	1.08517	0.03390
3	120	11.15	1.6	1.04727	0.20412	0.84315	-0.07409
4	180	11.0	1.85	1.04139	0.26717	0.77422	-0.11114
5	240	10.5	2.15	1.02119	0.33244	0.68875	-0.16194
6	300	10.35	2.6	1.01494	0.41497	0.59997	-0.22187
Slope: -1.1749×10^{-3}		k = 2.706×10^{-3} min.$^{-1}$			$T_{1/2}$ = 262.1 minutes.		

Table XIX. Spectroscopic information leading to kinetic data.

Bis-(5-ethyl-4-bromo-2-thenoyl)peroxide

Code No. F - 3 - a

Temperature: 85.0°C. ± 0.1 Solvent: CCl_4 plus Styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	12.5	1.35	1.09691	0.13033	0.96558	-0.01522
2	60	12.35	2.2	1.09167	0.34242	0.74925	-0.12531
3	120	12.35	3.7	1.09167	0.56820	0.52347	-0.28028
4	180	12.65	4.6	1.10209	0.66276	0.43933	-0.35724
5	240	12.5	5.2	1.09691	0.71600	0.38091	-0.41918
6	300	12.6	5.75	1.10037	0.75967	0.34070	-0.46763

Slope: -1.53363×10^{-3} $k = 3.578 \times 10^{-3}$ min.$^{-1}$ $T_{1/2}$ = 193.1 minutes.

Run No. 2. Code No. F - 3 - b

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
1	0	11.4	0.5	1.05690	-0.30103	1.35793	0.13288
2	60	11.05	1.5	1.04336	0.17609	0.86667	-0.06214
3	120	11.5	2.8	1.06070	0.44716	0.61354	-0.21273
4	180	11.35	3.5	1.05500	0.54407	0.51093	-0.29164
5	240	11.4	4.4	1.05690	0.64345	0.41345	-0.38357
6	300	11.25	4.9	1.05115	0.69020	0.35895	-0.44497

Slope: -1.8726×10^{-3} $k = 4.293 \times 10^{-3}$ min.$^{-1}$ $T_{1/2}$ = 161.4 minutes.

Table XX. Spectroscopic information leading to kinetic data.

Bis-(2,5-dichloro-3-thenoyl)peroxide

Code No. G - 1 - a

Temperature: 73.8°C. ± 0.1 Solvent: CCl_4 plus sytrene.

Run No. 1.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
1	0	9.0	0.8	0.95424	-0.09691	1.05115	0.02166
2	60	9.1	0.85	0.95904	-0.07058	1.02962	0.01268
3	180	9.10	1.2	0.95904	0.07918	0.87986	-0.05559
4	300	9.05	1.4	0.95665	0.14613	0.81052	-0.09124
5	420	8.75	1.8	0.94201	0.25527	0.68674	-0.16384
6	540	9.25	2.25	0.96614	0.35218	0.61396	-0.21186

Slope: -4.824×10^{-4} k = 1.111×10^{-3} min.$^{-1}$ $T_{1/2}$ = 624.3 minutes.

Run No. 2. Code No. G - 1 - b

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
1	0	9.0	0.8	0.95424	-0.09691	1.05115	0.02116
2	60	9.2	1.05	0.96379	0.02119	0.94260	-0.02567
3	180	9.15	1.3	0.96142	0.11394	0.84748	-0.07187
4	300	9.1	1.65	0.95904	0.21748	0.74356	-0.12868
5	420	9.1	2.2	0.95904	0.34242	0.61662	-0.20999
6	540	8.9	2.35	0.94939	0.37107	0.57832	-0.23790

Slope: -4.581×10^{-4} k = 1.055×10^{-3} min.$^{-1}$ $T_{1/2}$ = 657.4 minutes.

Table XXI. Spectroscopic information leading to kinetic data.

Bis-(2,5-dichloro-3-thenoyl)peroxide

Code No. G - 2 - a

Temperature: 79.8°C. ± 0.1 Solvent: CCl_4 plus styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	9.3	1.15	0.96848	0.06070	0.90778	-0.04202
2	60	9.3	1.65	0.96848	0.21748	0.75100	-0.12436
3	180	9.35	2.25	0.97081	0.35218	0.61863	-0.20857
4	300	9.35	3.1	0.97081	0.49136	0.47945	-0.31925
5	540	9.1	3.9	0.95904	0.59106	0.36798	-0.43417
6	660	9.1	4.45	0.95904	0.64836	0.31068	-0.50769

Slope: -7.095×10^{-4} k = 1.634×10^{-3} min.$^{-1}$ $T_{1/2}$ = 424.1 minutes.

Run No. 2. Code No. G - 2 - b

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
1	0	9.1	0.9	0.95904	-0.04576	1.00480	0.00208
2	60	9.15	1.3	0.96142	0.11394	0.84748	-0.07187
3	180	9.05	2.0	0.95665	0.30103	0.65562	-0.18335
4	300	9.0	2.7	0.95424	0.43136	0.52529	-0.27960
5	540	9.1	3.9	0.95904	0.59106	0.36798	-0.43417
6	660	8.8	4.4	0.94448	0.64345	0.30103	-0.52139

Slope: -7.499×10^{-4} k = 1.727×10^{-3} min.$^{-1}$ $T_{1/2}$ = 401.3 minutes.

Table XXII. Spectroscopic information leading to kinetic data.

Bis-(2,5-dichloro-3-thenoyl)peroxide

Code No. G - 3 - a

Temperature: 85.0°C. ± 0.1 Solvent: CCl_4 plus styrene

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	9.15	0.95	0.96142	-0.02228	0.98370	-0.02747
2	60	9.05	1.65	0.95665	0.21748	0.73917	-0.13126
3	180	9.1	3.1	0.95904	0.49136	0.46768	-0.33005
4	300	9.05	4.3	0.95665	0.63347	0.32318	-0.49056
5	420	9.0	4.85	0.95424	0.68574	0.26850	-0.57106
6	540	9.0	5.5	0.95424	0.74036	0.21388	-0.67893

Slope: -1.255 x 10^{-3} k = 2.891 x 10^{-3} min.$^{-1}$ $T_{1/2}$ = 239.7 minutes.

Run No. 2. Code No. G - 3 - b

1	0	9.15	1.0	0.96142	0.00000	0.96142	-0.03709
2	60	8.9	1.5	0.94939	0.17609	0.77330	-0.11165
3	180	8.8	3.0	0.94448	0.47712	0.46736	-0.33035
4	300	8.8	3.9	0.94448	0.59106	0.35342	-0.45170
5	420	9.15	4.9	0.96142	0.69020	0.27122	-0.56668
6	540	9.0	5.5	0.95424	0.74036	0.21388	-0.66983

Slope: -1.330 x 10^{-3} k = 3.063 x 10^{-3} min.$^{-1}$ $T_{1/2}$ = 237.0 minutes.

Table XXIII. Spectroscopic information leading to kinetic data.

Bis-(5-phenyl-2-thenoyl)peroxide

Code No. H - 1 - a

Temperature: 73.8°C. ± 0.1 Solvent: CCl_4 plus 0.2 M styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	12.4	3.25	1.09342	0.51188	0.58154	-0.23542
2	30	12.5	3.55	1.09691	0.55023	0.54668	-0.26227
3	60	12.5	4.10	1.09691	0.61278	0.48413	-0.31504
4	90	12.8	4.60	1.10721	0.66276	0.44445	-0.35218
5	120	12.4	4.80	1.09342	0.68124	0.41218	-0.38491

Slope: -1.33×10^{-3} $k = 3.056 \times 10^{-3}$ $min.^{-1}$ $T_{1/2} = 226.8$ minutes.

Run No. 2. Code No. H - 1 - b

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
1	0	6.9	1.7	0.83885	0.23046	0.60840	-0.21581
2	30	7.0	1.9	0.84510	0.27875	0.56645	-0.24684
3	60	6.85	2.25	0.83569	0.35218	0.48351	-0.31559
4	90	7.0	2.3	0.84510	0.36173	0.48337	-0.31571
5	120	7.05	2.75	0.84819	0.43933	0.40886	-0.38842
6	150	Reduced to shoulder.					

Slope: -1.40×10^{-3} $k = 3.224 \times 10^{-3}$ $min.^{-1}$ $T_{1/2} = 214.9$ minutes.

Table XXIV. Spectroscopic information leading to kinetic data.

Bis-(5-pehnyl-2-thenoyl)peroxide

Code No. H - 2 - a

Temperature: 79.8°C. ± 0.1 Solvent: CCl_4 plus 0.2 M styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	7.2	0.7	0.85733	-0.15490	1.01223	0.00528
2	10	6.7	1.2	0.82607	0.07918	0.74689	-0.12675
3	20	6.35	1.0	0.80277	0.00000	0.80277	-0.09541
4	30	6.50	1.6	0.81291	0.20412	0.60870	-0.21554
5	40	6.35	1.3	0.80277	0.11394	0.68883	-0.16189
6	50	6.50	1.8	0.81291	0.25527	0.55764	-0.25365
Slope: -4.099×10^{-3}		$k = 9.44 \times 10^{-3}$ min.$^{-1}$			$T_{1/2}$ = 78.66 minutes.		
Run No. 2.			Code No. H - 2 - b				
1	0	7.25	1.40	0.86034	0.14613	0.71421	-0.14617
2	10	7.00	1.80	0.84510	0.25527	0.58983	-0.22928
3	20	7.30	1.95	0.86332	0.29003	0.57329	-0.24163
4	30	7.35	2.30	0.86629	0.36173	0.50456	-0.29708
5	40	7.35	2.30	0.86629	0.36173	0.50456	-0.29708
6	50	7.35	2.80	0.86629	0.44716	0.41913	-0.37765
Slope: -3.203×10^{-3}		$k = 7.377 \times 10^{-3}$ min.$^{-1}$			$T_{1/2}$ = 93.94 minutes.		

Table XXV. Spectroscopic information leading to kinetic data.

Bis-(5-phenyl-2-thenoyl)peroxide

Code No. H - 3 - a

Temperature: 85.0°C. ± 0.1 Solvent: CCl_4 plus styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	6.35	0.75	0.80277	-0.12494	0.92771	-0.03258
2	5	6.30	0.90	0.79934	-0.04576	0.84510	-0.07309
3	10	6.20	0.70	0.79239	-0.15390	0.94729	-0.02351
4	15	6.15	1.05	0.78888	0.02119	0.76770	-0.11481
5	20	6.20	1.30	0.79239	0.11394	0.67845	-0.16848
6	25	6.40	1.85	0.80618	0.25717	0.54901	-0.25972
Slope: -8.098×10^{-3}			k = 1.865×10^{-2} min.$^{-2}$			$T_{1/2}$ = 37.2 minutes.	
Run No. 2.							
1	0	6.35	0.70	0.80277	-0.15490	0.95767	-0.01879
2	5	6.30	0.90	0.79934	-0.04576	0.84510	-0.07309
3	10	6.25	0.75	0.79588	-0.12494	0.92082	-0.03518
4	15	6.20	1.10	0.79239	0.04139	0.75100	-0.12436
5	20	6.20	1.25	0.79239	0.09691	0.69548	-0.15771
6	25	6.20	1.75	0.79239	0.24304	0.54935	-0.26015
Slope: -9.206×10^{-3}			k = 2.12×10^{-2} min.$^{-1}$			$T_{1/2}$ = 34.2 minutes.	

Table XXVI. Spectroscopic information leading to kinetic data.

Bis-(2,5-dimethyl-3-thenoyl)peroxide

Code No. I - 1 - a

Temperature: 83.8°C. ± 0.1 Solvent: CCl_4 plus 0.2M styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	9.55	0.85	0.98000	-0.07058	1.05058	0.02142
2	60	10.15	1.25	1.00647	0.09691	0.90956	-0.04117
3	180	9.55	2.0	0.98000	0.30103	0.67897	-0.16815
4	300	10.1	2.6	1.00432	0.41497	0.58935	-0.22962
5	420	9.85	3.25	0.99344	0.51188	0.44156	-0.35501
6	540	10.2	3.9	1.00860	0.59106	0.41754	-0.38930

Slope: -1.0×10^{-3} $k = 2.303 \times 10^{-3}$ min.$^{-1}$ $T_{1/2}$ = 300.9 minutes.

Run No. 2. Code No. I - 1 - b

1	0	9.15	0.15	0.96142	-0.82391	1.78533	0.25172
2	60	9.1	0.3	0.95904	-0.52288	1.48192	0.17083
3	180	9.65	1.4	0.98453	0.14613	0.83840	-0.07655
4	300	9.60	2.0	0.98227	0.30103	0.68124	-0.16670
5	420	9.85	2.7	0.99344	0.43136	0.56098	-0.25105
6	540	9.15	3.15	0.96142	0.49831	0.46311	-0.33432

Slope: -1.25×10^{-3} $k = 2.896 \times 10^{-3}$ min.$^{-1}$ $T_{1/2}$ = 239.3 minutes.

Table XXVII. Spectroscopic information leading to kinetic data.

Bis-(2,5-dimethyl-3-thenoyl)peroxide

Code No. I - 2 - a

Temperature: 79.6°C. ± 0.1 Solvent: CCl_4 plus 0.2<u>M</u> styrene.

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
<u>Run No. 1.</u>							
1	0	9.4	0.2	0.97313	-0.69897	1.67210	0.22327
2	60	8.85	0.9	0.94694	-0.04576	1.09270	0.03850
3	180	9.15	2.4	0.96142	0.38021	0.62121	-0.20676
4	300	8.85	3.35	0.94694	0.52504	0.42190	-0.37479
5	420	9.45	4.4	0.97543	0.64345	0.33198	-0.47889
6	540	8.75	5.25	0.94201	0.72016	0.22185	-0.65394

Slope: -1.63×10^{-3} k = 3.754×10^{-3} min.$^{-1}$ $T_{1/2}$ = 184.6 minutes.

<u>Run No. 2.</u> Code No. I - 2 - b

1	0	9.35	0.25	0.97081	-0.60406	1.57487	0.19723
2	60	9.2	1.6	0.96379	0.20412	0.75967	-0.11938
3	180	8.85	1.4	0.94694	0.14613	0.80081	-0.09647
4	300	9.2	3.3	0.96379	0.51851	0.44528	-0.35137
5	420	9.25	4.6	0.96614	0.66216	0.30398	-0.51716
6	540	9.0	5.0	0.95424	0.69897	0.25527	-0.59300

Slope: -1.66×10^{-3} k = 3.823×10^{-3} min.$^{-1}$ $T_{1/2}$ = 181.3 minutes.

Table XXVIII. Spectroscopic information leading to kinetic data.

Bis-(2,5-dimethyl-3-thenoyl)peroxide

Code No. I - 3 - a

Temperature: 85.0°C. ± 0.1

Sample No.	Time min.	I_0	I	log I_0	log I	A	log A
Run No. 1.							
1	0	9.25	0.1	0.96614	-1.00000	1.96194	0.29268
2	60	9.0	1.7	0.95421	0.23045	0.72376	-0.14041
3	180	9.25	3.95	0.96614	0.59660	0.36954	-0.43234
4	300	8.65	5.5	0.93702	0.74036	0.19666	-0.70629
5	420	9.25	6.5	0.96614	0.81291	0.15323	-0.81466
Slope: -2.42×10^{-3}			k = 5.57×10^{-3} min.$^{-1}$		$T_{1/2}$ = 124.4 minutes.		
Run No. 2.			Code No. I - 3 - b				
1	0	9.4	0.2	0.97313	-0.69897	1.67110	0.22301
2	60	8.65	1.4	0.93702	0.14613	0.79089	-0.10188
3	180	9.05	4.25	0.95665	0.62839	0.32826	-0.48578
4	300	8.85	4.5	0.94694	0.65321	0.29373	-0.53205
5	420	8.85	6.0	0.94694	0.77815	0.16879	-0.77265
Slope: -2.5×10^{-3}			k = 5.75×10^{-3} min.$^{-1}$		$T_{1/2}$ = 120.5 minutes.		

Table XXIX. Summary of kinetic data for the thenoyl peroxides.

Compound (peroxide)	k (min.$^{-1}$)	log K	T (°K.)	1/T x 10^3	Code
Bis-(5-bromo-3-thenoyl)	8.79×10^{-4}	-3.05601	347.5	2.878	A-1
	2.031×10^{-3}	-2.69229	352.8	2.835	A-2
	3.589×10^{-3}	-2.55497	358.2	2.792	A-3
	Energy of activation: 24,818 cal. mole^{-1}				
	Entropy of activation (average): -8.823 e.u.				
Bis-(5-chloro-3-thenoyl)	1.355×10^{-3}	-2.86806	346.8	2.883	B-1
	1.862×10^{-3}	-2.73002	352.8	2.835	B-2
	3.268×10^{-3}	-2.48572	358.2	2.792	B-3
	Energy of activation: 20,135 cal. mole^{-1}				
	Entropy of activation (average): -22.22 e.u.				
Bis-(5-nitro-3-thenoyl)	2.329×10^{-3}	-2.63282	347.0	2.883	C-1
	5.849×10^{-3}	-2.23292	352.8	2.835	C-2
	9.373×10^{-3}	-2.02812	358.2	2.792	C-3
	Energy of activation: 30,202 cal. mole^{-1}				
	Entropy of activation (average): 7.589 e.u.				
Bis-(3-methyl-2-thenoyl)	1.535×10^{-3}	-2.81389	347.5	2.878	D-1
	2.699×10^{-3}	-2.56880	352.8	2.835	D-2
	6.333×10^{-3}	-2.19839	358.2	2.792	D-3
	Energy of activation: 29,836 cal. mole^{-1}				
	Entropy of activation (average): 5.739 e.u.				
Bis-(4-bromo-5-ethyl-2-thenoyl)	1.070×10^{-3}	-2.97062	347.0	2.882	F-1
	3.120×10^{-3}	-2.50585	352.8	2.835	F-2
	4.369×10^{-3}	-2.35962	358.2	2.792	F-3
	Energy of activation: 28,710 cal. mole^{-1}				
	Entropy of activation (average): 2.433 e.u.				
Bis-(2,5-dichloro-3-thenoyl)	1.080×10^{-3}	-2.96658	347.0	2.882	G-1
	1.681×10^{-3}	-2.77443	353.0	2.833	G-2
	2.976×10^{-3}	-2.52637	358.2	2.792	G-3
	Energy of activation: 23,063 cal. mole^{-1}				
	Entropy of activation (average): -14.71 e.u.				

Table XXIX. (Cont.)

Compound (peroxide)	k (min.$^{-1}$)	log K	T (°K.)	1/T x 10^3	Code
Bis-(5-phenyl-2-thenoyl)	3.140 x 10^{-3}	-2.50307	347.0	2.883	H-1
	8.580 x 10^{-3}	-2.06651	353.0	2.835	H-2
	2.000 x 10^{-2}	-1.69897	358.2	2.792	H-3
	Energy of activation: 38,140 cl. mole^{-1} Entropy of activation (average): 29.72 e.u.				
Bis-(2,5-dimethyl-3-thenoyl)	2.599 x 10^{-3}	-2.58519	347.0	2.883	I-1
	3.789 x 10^{-3}	-2.42148	352.8	2.833	I-2
	5.666 x 10^{-3}	-2.24672	358.2	2.792	I-3
	Energy of activation: 21,050 cal. mole^{-1} Entropy of activation (average): -20.47 e.u.				

Table XXX. Calculation of entropies of activation.

Compound (peroxide)	$E_{act.}$ cal.mole^{-1}	Temp. °K.	log k (sec.)	s (sec.$^{-1}$)	Entropy of Activation cal. deg.$^{-1}$ mole^{-1}
Bis-(5-bromo- 3-thenoyl)	24,818	347.5	-4.834	5.889×10^{10}	-9.555
		352.8	-4.470	7.943×10^{10}	-9.001
		358.2	-3.976	1.449×10^{11}	-7.925
Bis-(5-chloro- 3-thenoyl)	20,135	346.8	-4.646	1.099×10^{8}	-22.05
		352.8	-4.284	1.542×10^{8}	-22.41
		358.2	-4.264	1.645×10^{8}	-22.21
Bis-(5-nitro- 3-thenoyl)	30,202	347.0	-4.411	1.567×10^{14}	6.127
		352.8	-4.977	4.977×10^{14}	8.574
		358.2	-3.806	4.159×10^{14}	8.068
Bis-(3-methyl- 2-thenoyl)	29,836	347.5	-4.592	1.463×10^{14}	5.721
		352.8	-4.347	1.346×10^{14}	6.237
		358.2	-3.976	2.090×10^{14}	5.260
Bis-(4-bromo- 5-ethyl- 2-thenoyl	28,710	347.0	-4.749	2.143×10^{13}	2.173
		352.8	-4.284	3.083×10^{13}	2.850
		358.2	-4.138	2.383×10^{13}	2.306
Bis-(2,5-di chloro-3-thenoyl)	23,063	347.0	-4.745	6.012×10^{9}	-14.41
		353.0	-4.552	5.333×10^{9}	-15.50
		358.2	-4.305	5.821×10^{9}	-14.22
Bis-(5-phenyl- 2-thenoyl	38,140	247.0	-4.281	5.470×10^{19}	29.47
		353.0	-3.844	5.835×10^{19}	29.56
		358.2	-3.477	7.889×10^{19}	30.13
Bis-(2,5-di- methyl-3-thenoyl)	21,050	347.0	-4.136	7.835×10^{8}	-20.14
		352.8	-4.199	6.919×10^{8}	-20.43
		358.2	-4.025	6.547×10^{8}	-20.84

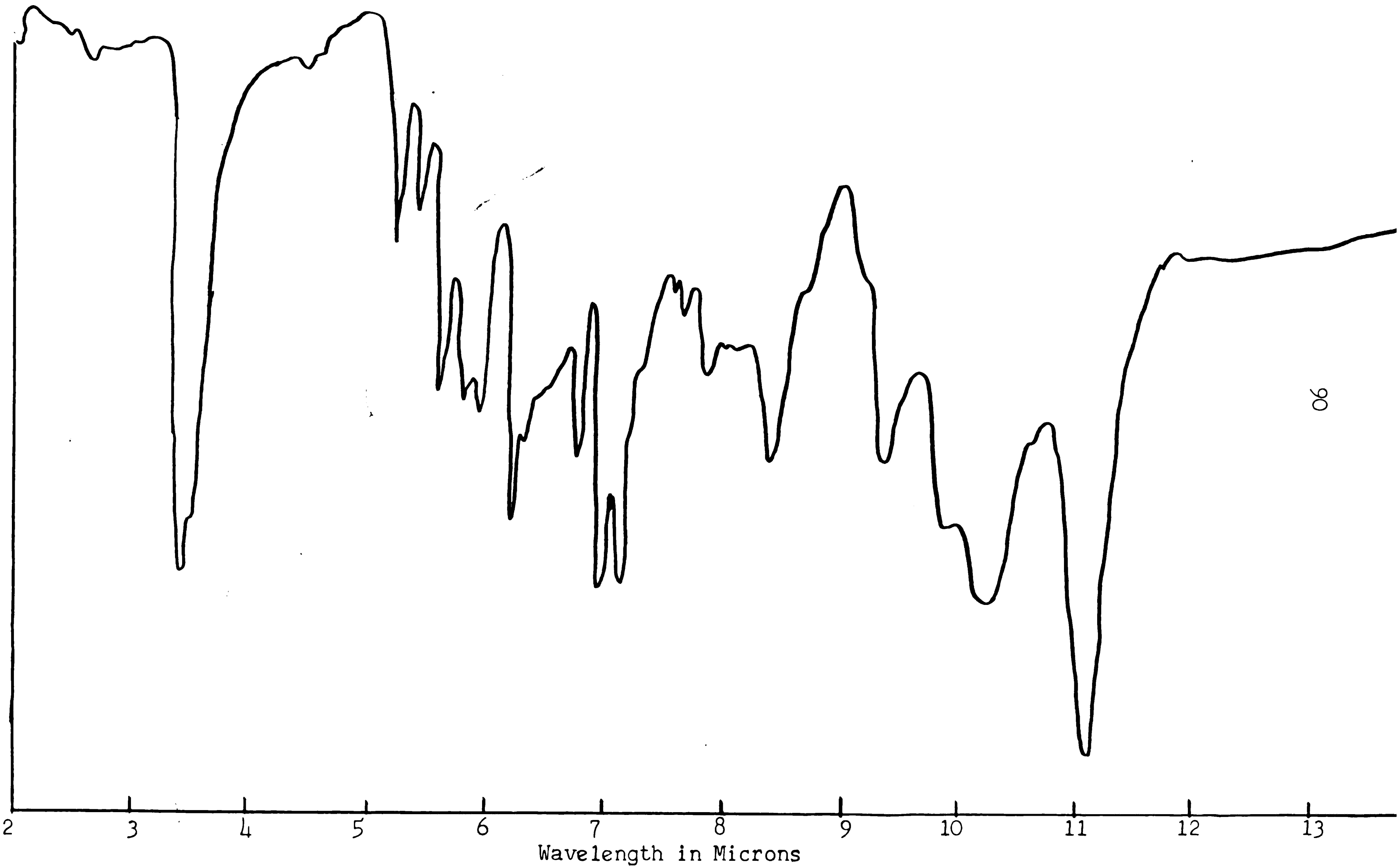

Figure 1. Infrared spectrum of bis(3-methyl-2-thenoyl)peroxide.

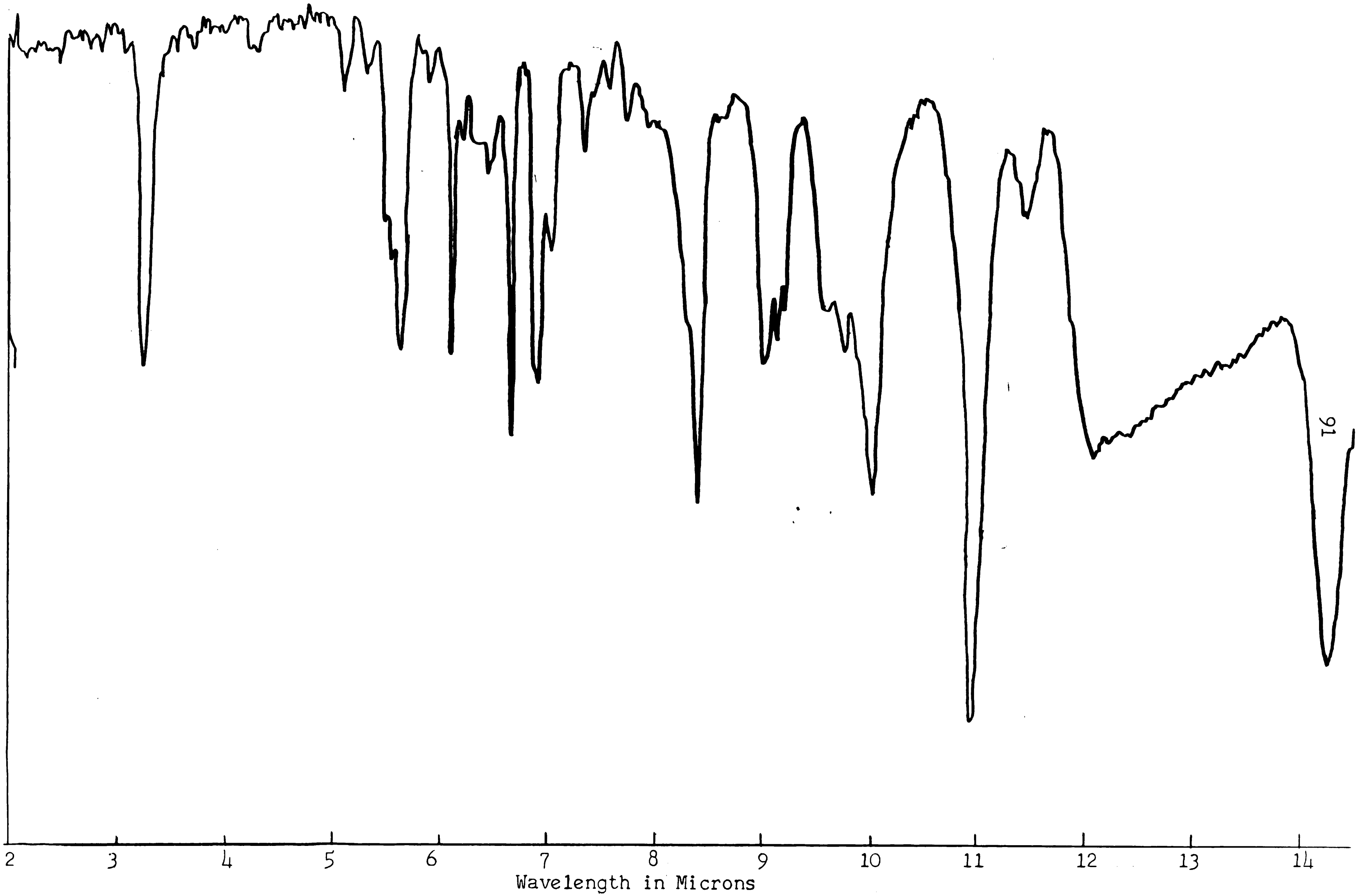

Figure 2. Infrared spectrum of bis(2,5-dichloro-3-thenoyl)peroxide.

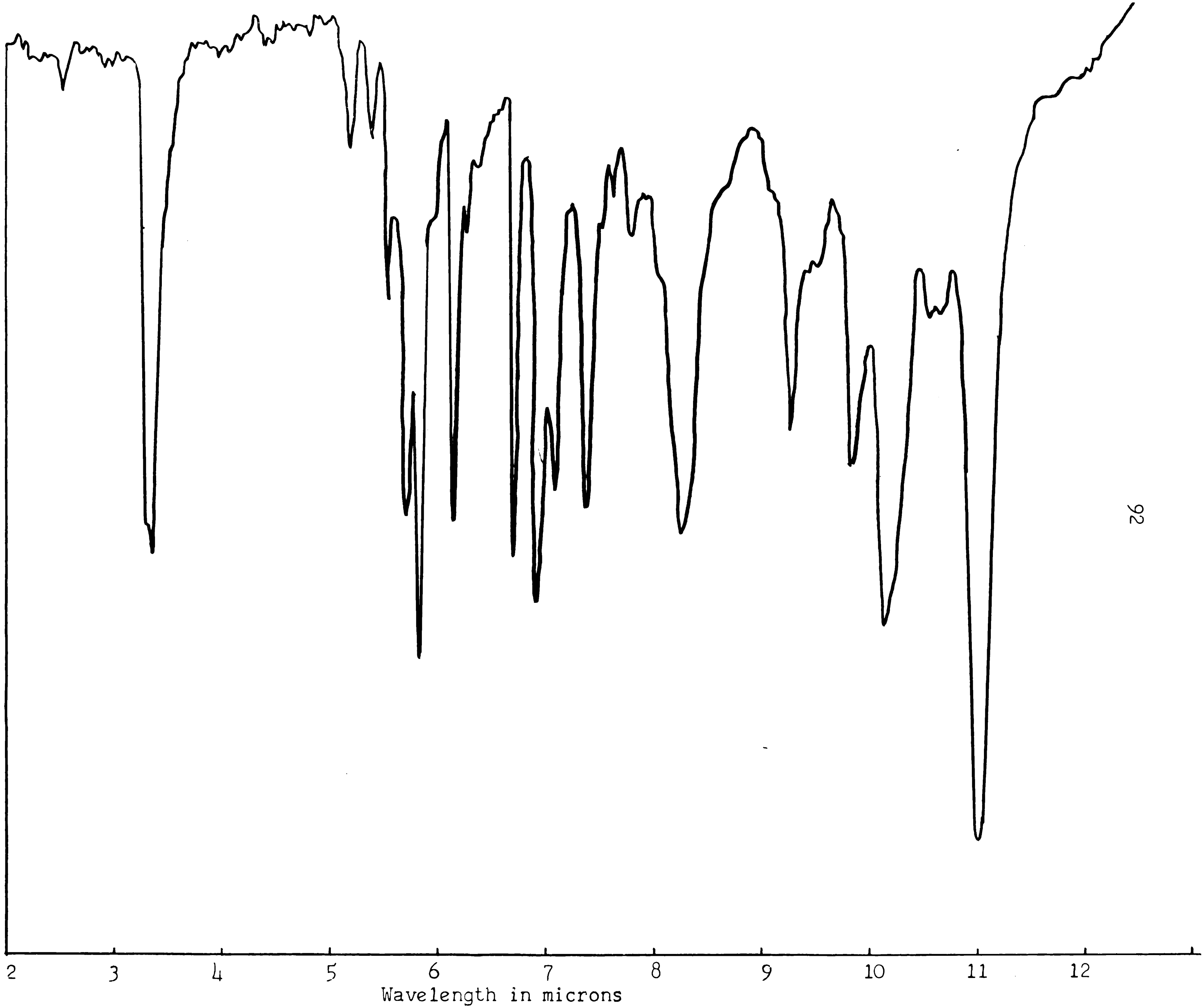

Figure 3. Infrared spectrum of bis(5-phenyl-2-thenoyl)peroxide.

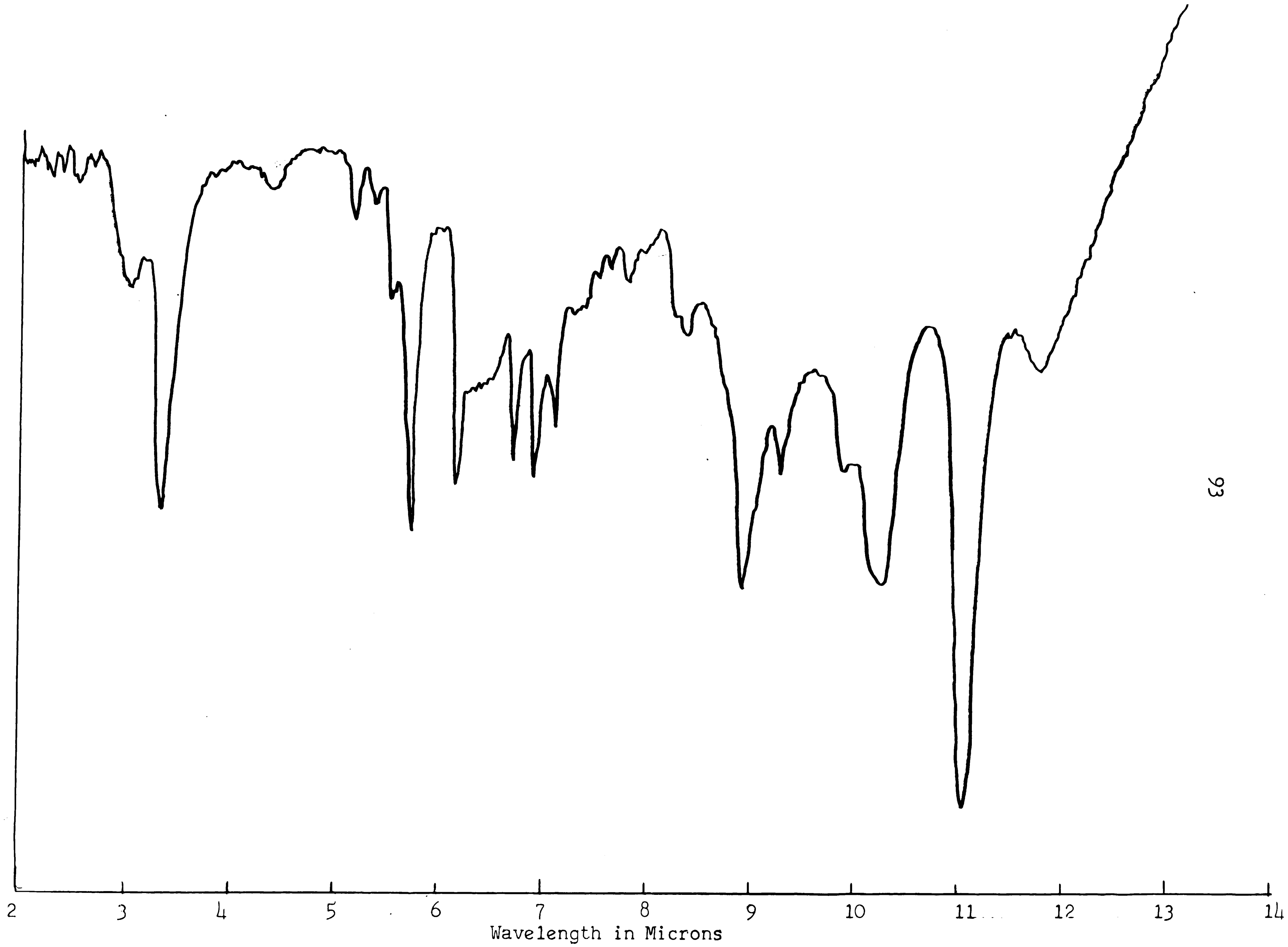

Figure 4. Infrared spectrum of bis(2,5-dimethyl-3-thenoyl)peroxide.

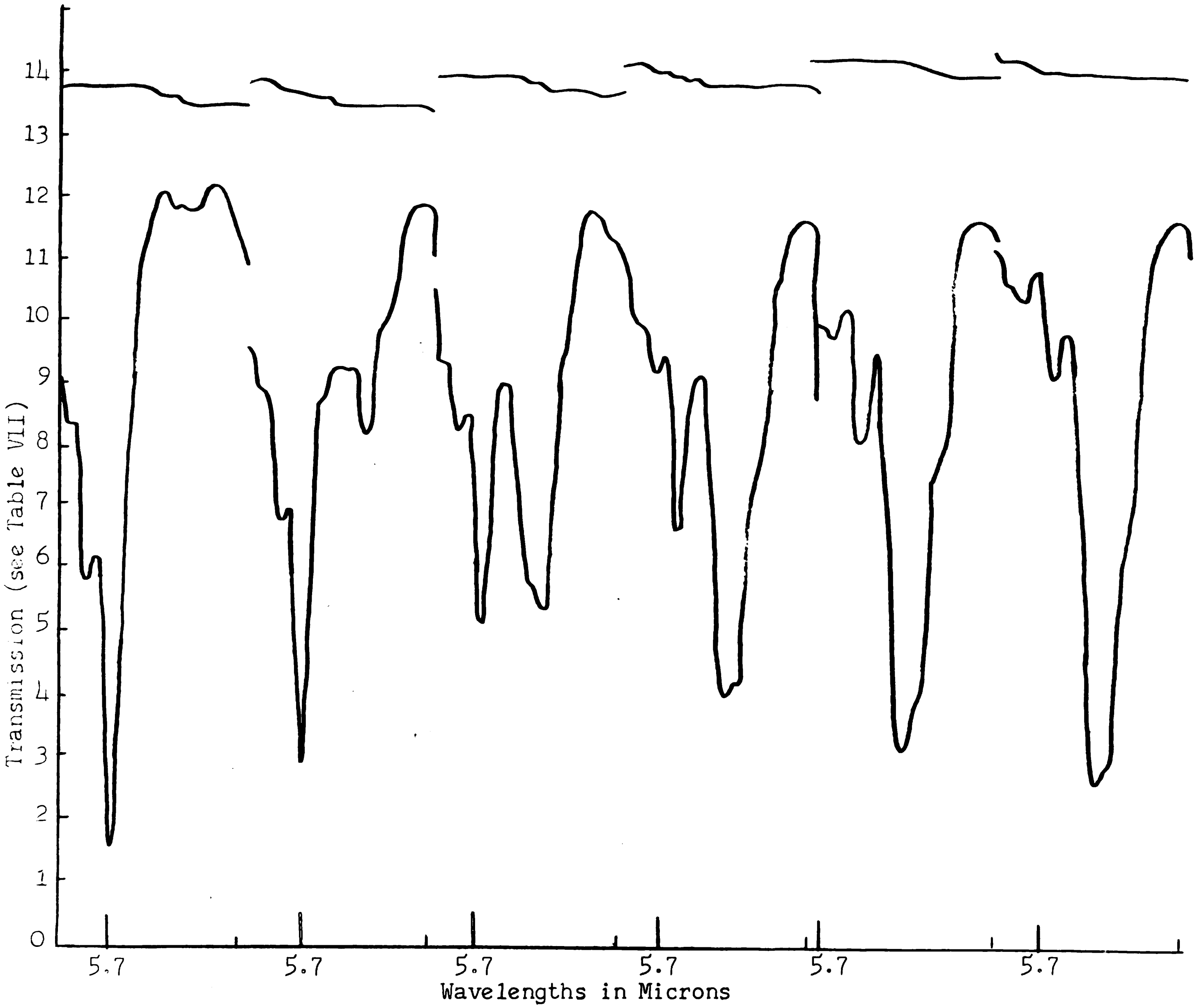

Figure 5. Quantitative infrared spectra on the decomposition of bis(5-bromo-3-thenoyl)peroxide

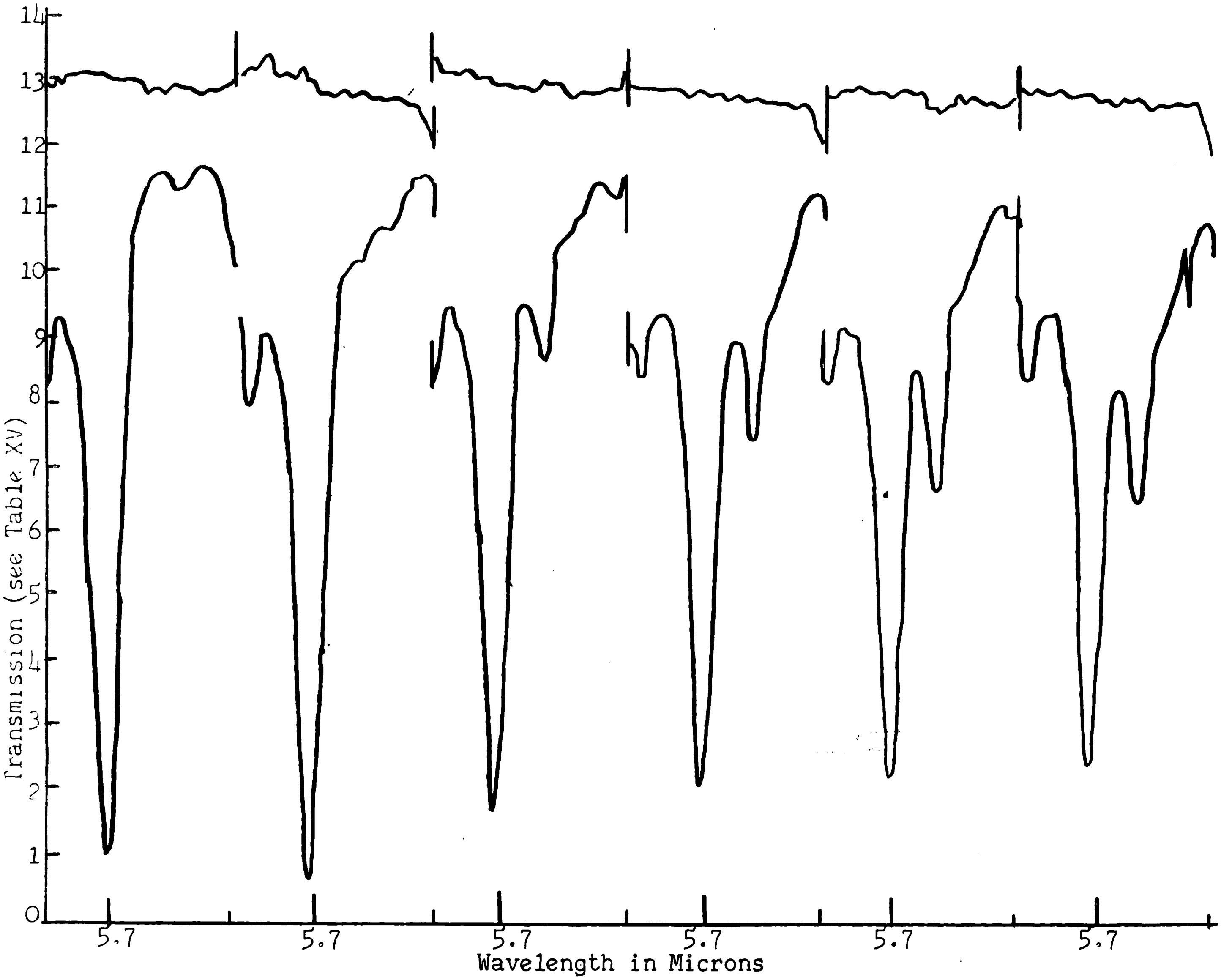

Figure 6. Quantitative infrared spectra of the decomposition of bis(3-methyl-2-thenoyl)peroxide.

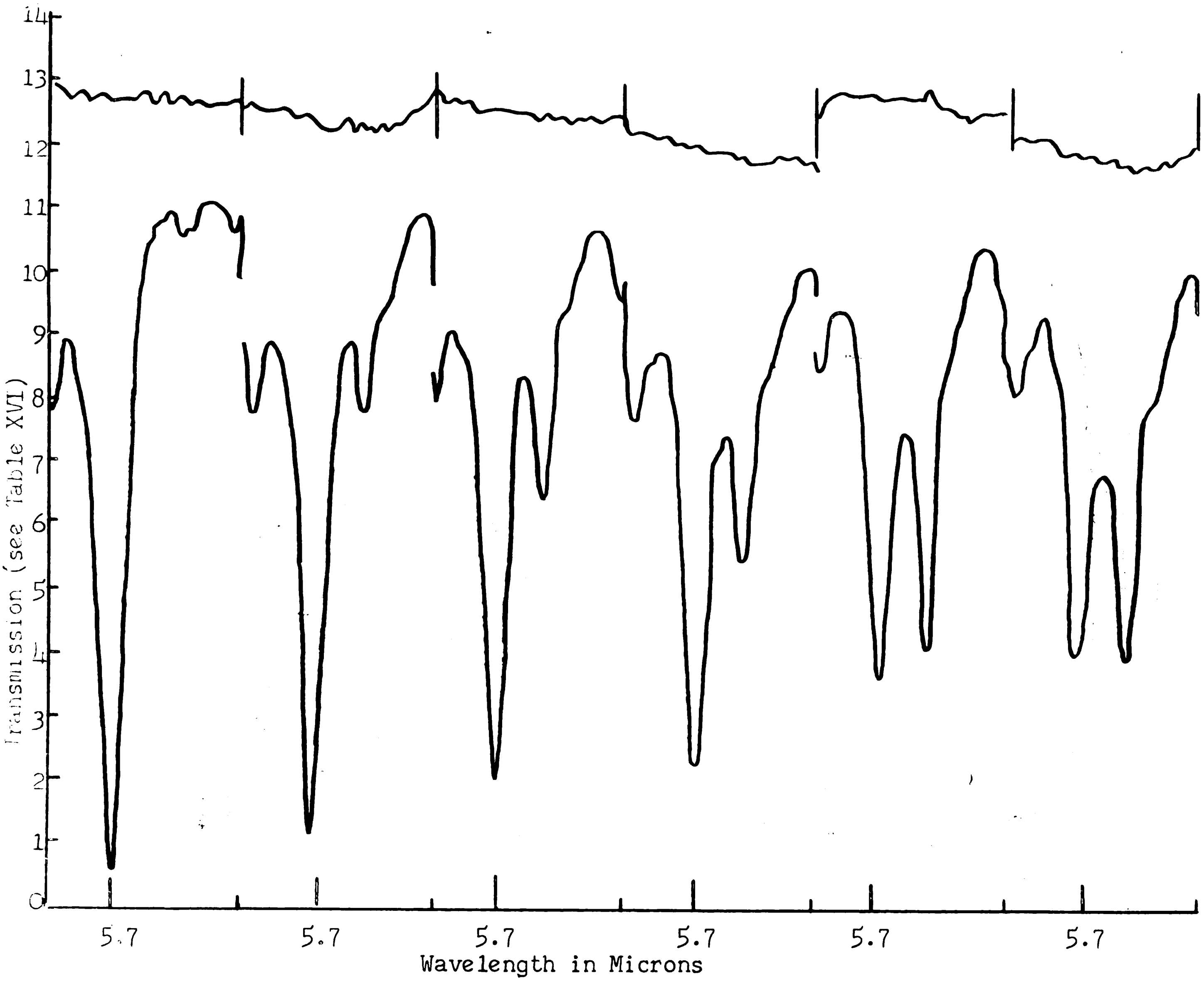

Figure 7. Quantitative infrared spectra of the decomposition of bis(3-methyl-2-thenoyl)peroxide.

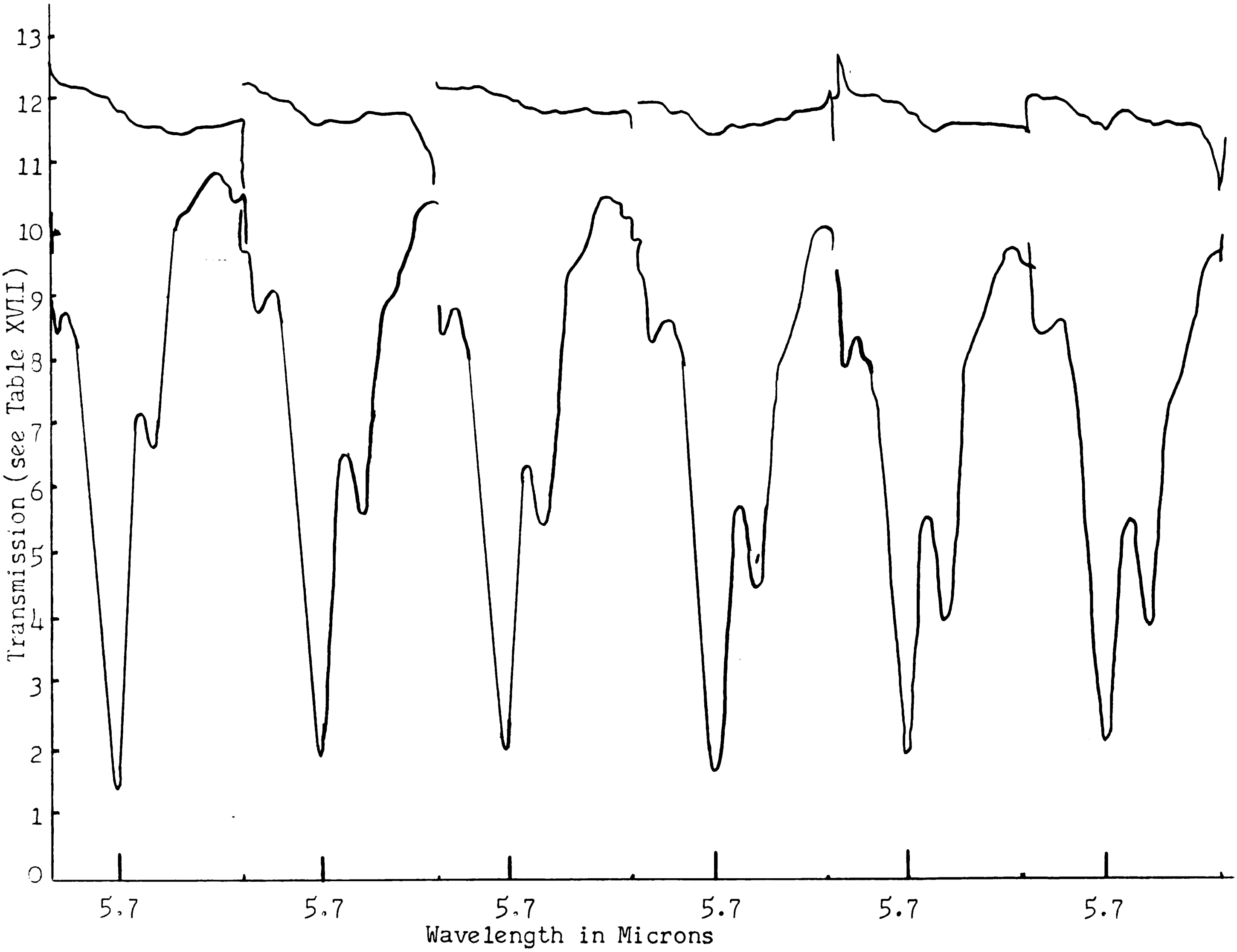

Figure 8. Quantitative infrared spectra of the decomposition of bis(4-bromo-5-ethyl-3-thenoyl)peroxide.

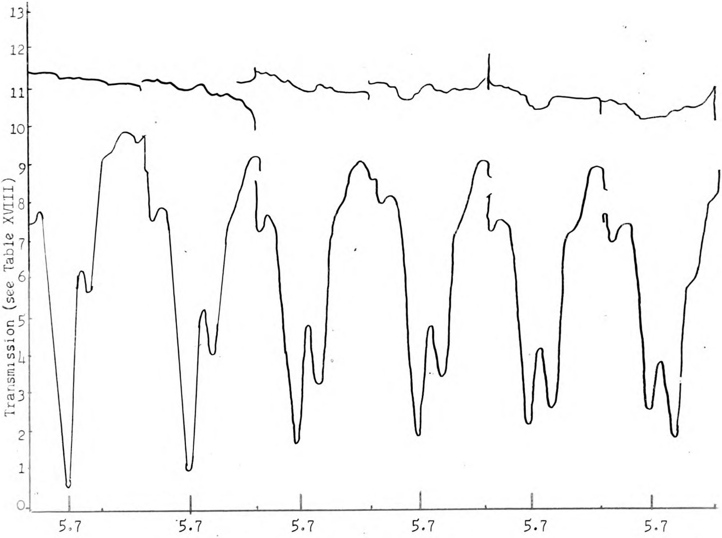

Figure 9. Quantitative infrared spectra of the decomposition of bis(4-bromo-5-ethyl-2-thenoyl)peroxide.

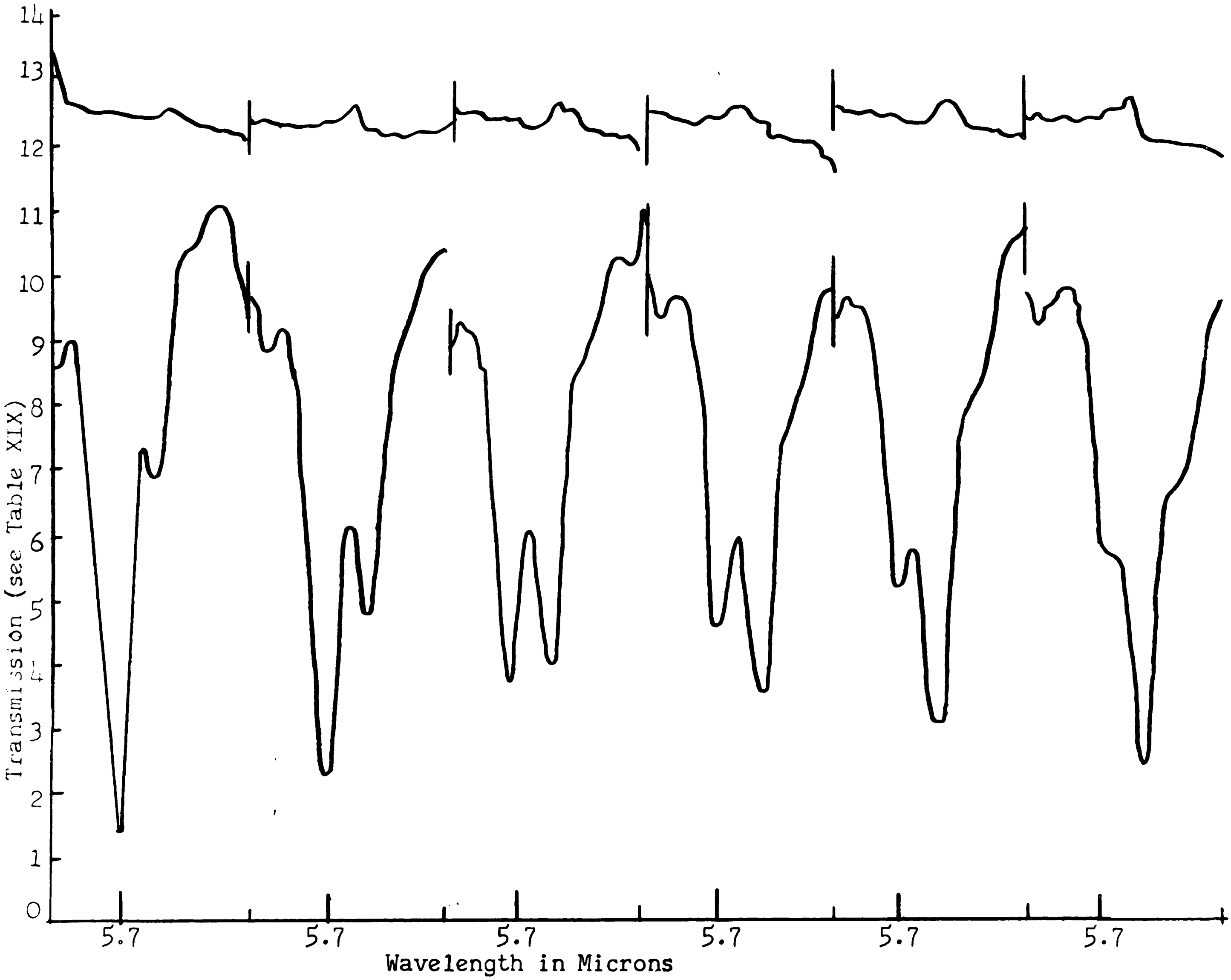

Figure 10. Quantitative infrared spectra on the decomposition of bis(5-ethyl-4-bromo-2-thenoyl)peroxide.

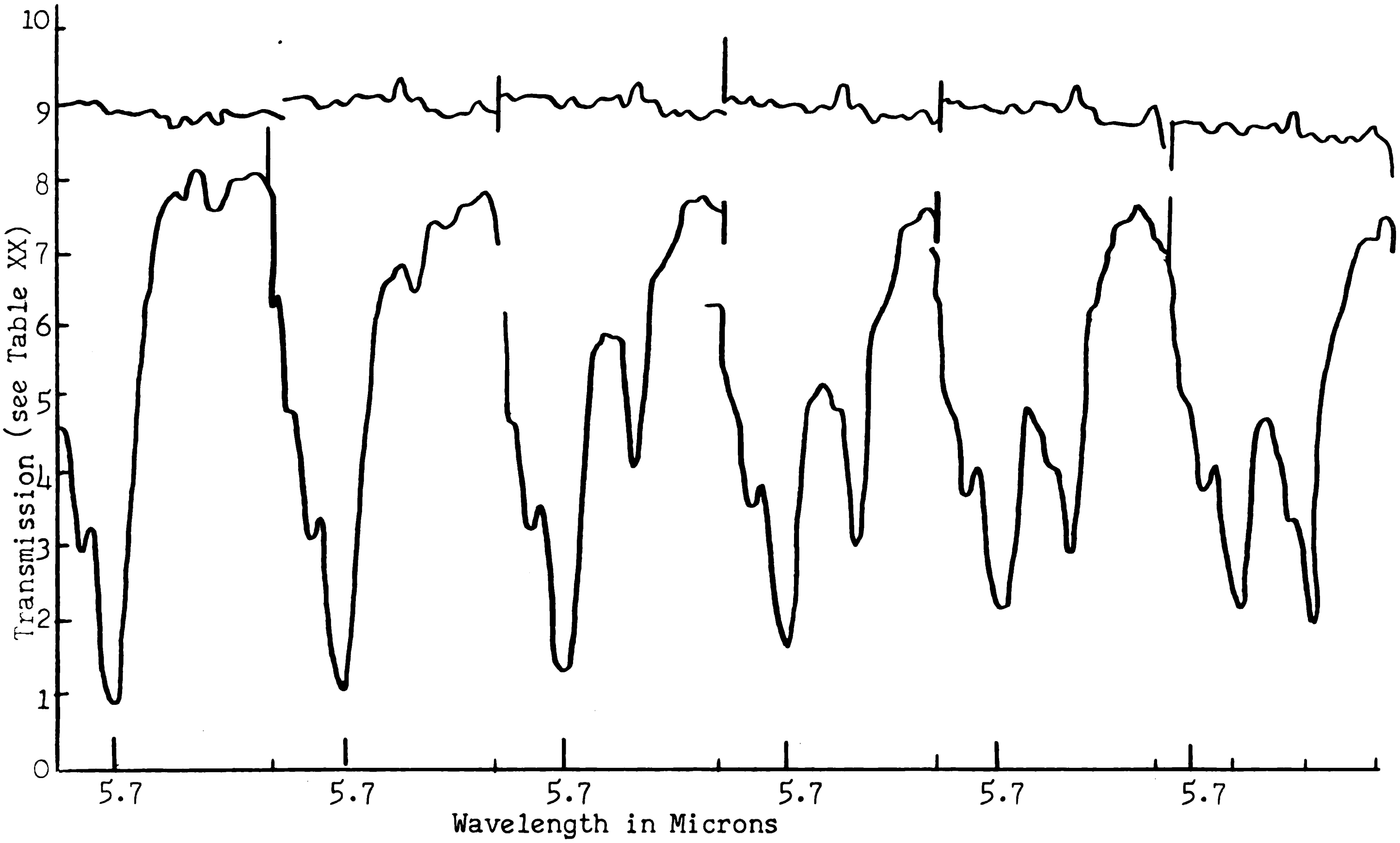

Figure 11. Quantitative infrared spectra on the decomposition of bis(2,5-dichloro-3-thenoyl)peroxide.

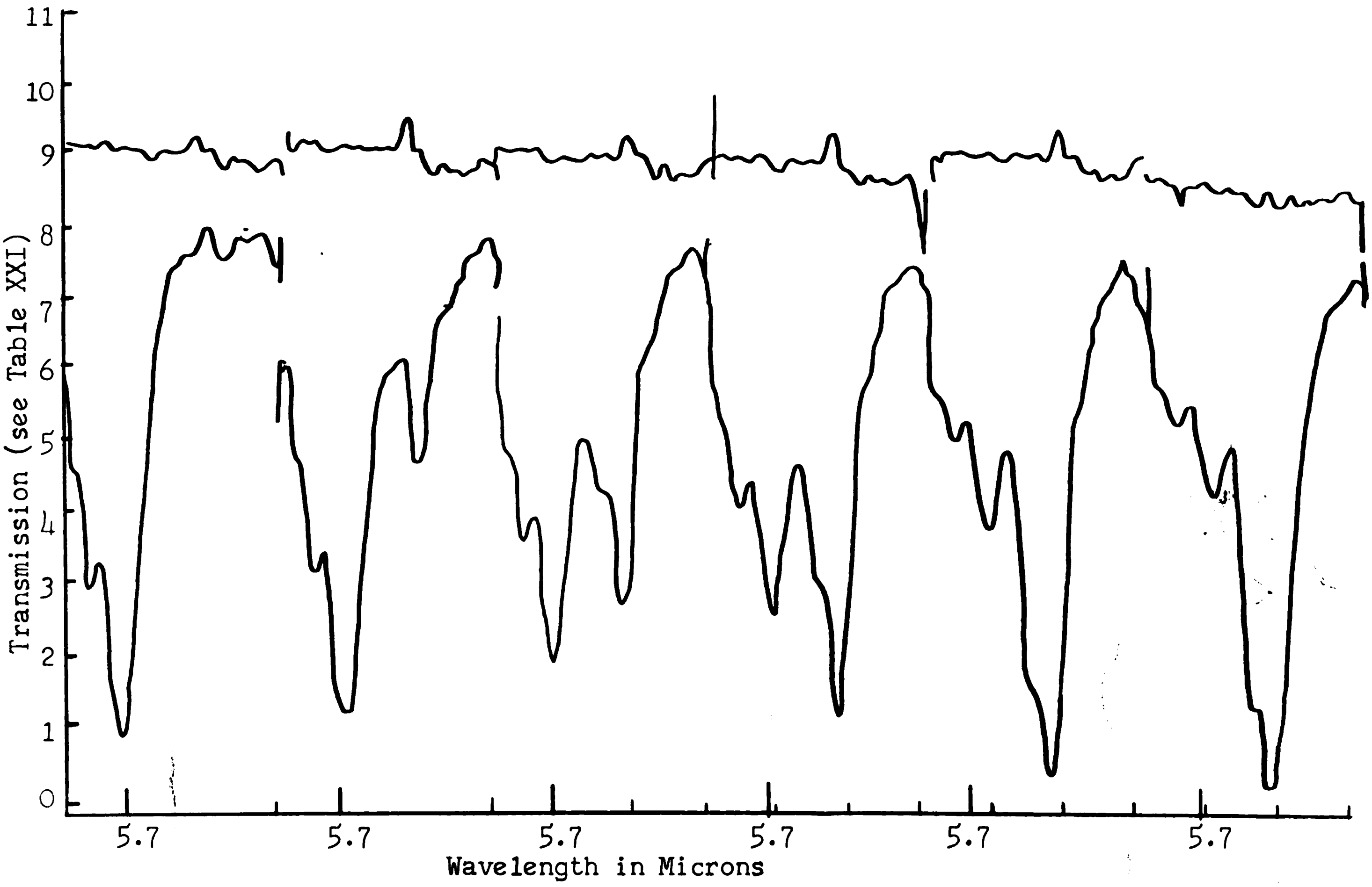

Figure 12. Quantitative infrared spectra on the decomposition of bis(2,5-dichloro-3-thenoyl)peroxide.

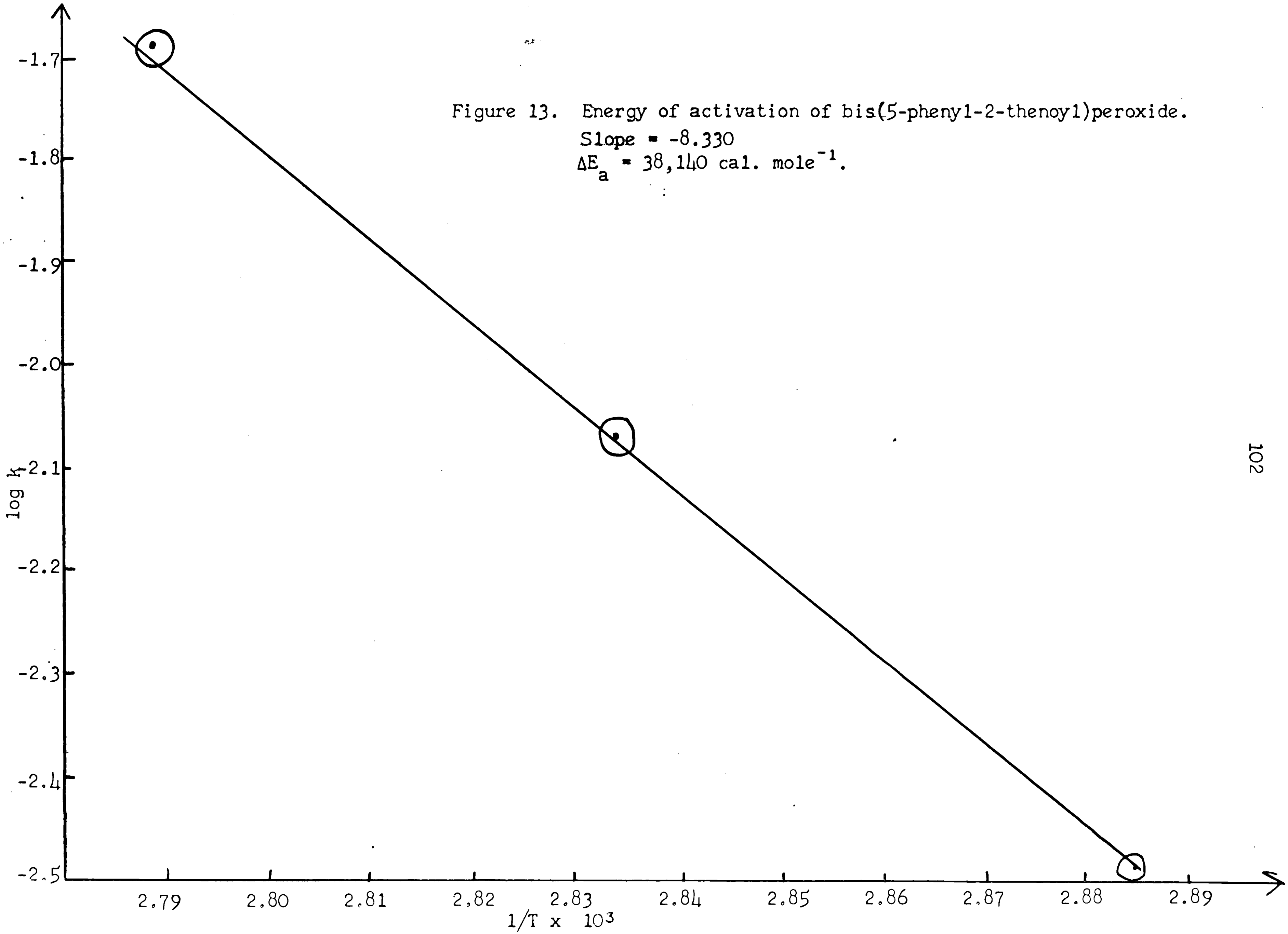

Figure 13. Energy of activation of bis(5-phenyl-2-thenoyl)peroxide.
Slope = -8.330
ΔE_a = 38,140 cal. mole^{-1}.

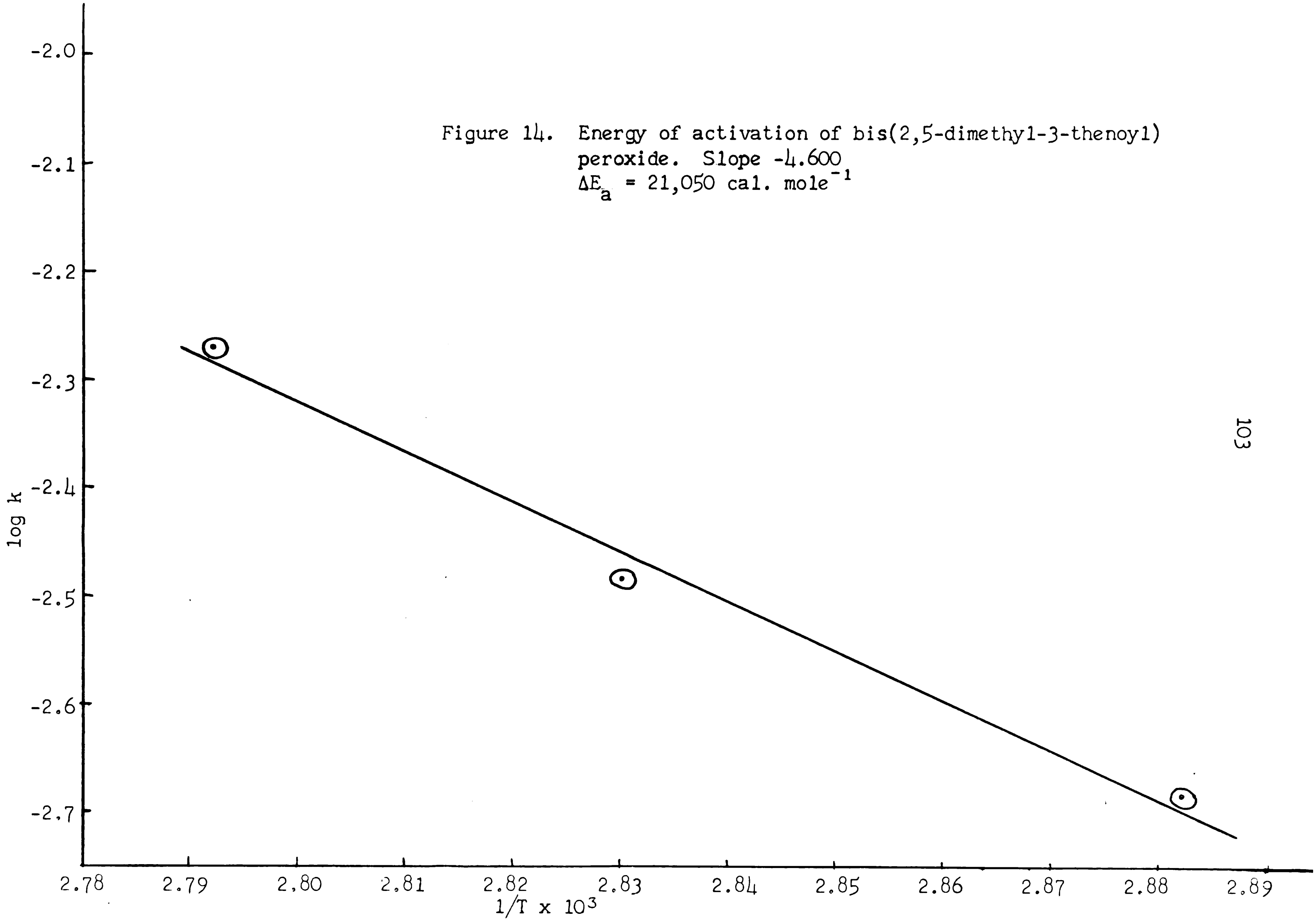

Figure 14. Energy of activation of bis(2,5-dimethyl-3-thenoyl) peroxide. Slope -4.600
ΔE_a = 21,050 cal. mole^{-1}

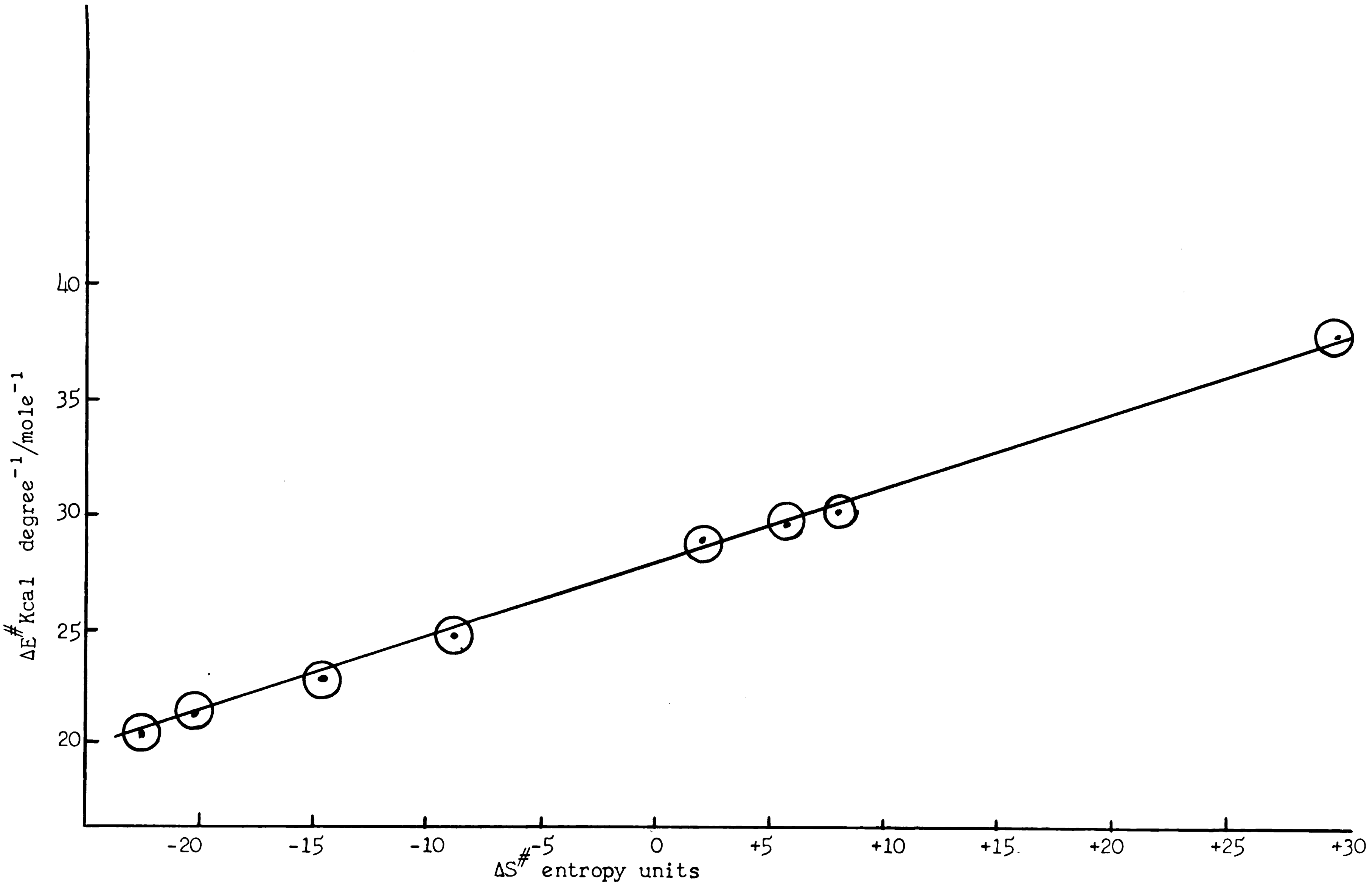

Figure 15. Plot of energy of activation *versus* entropy of activation.