PREPARATION AND THERMAL DECOMPOSITION OF SOME UNSYMMETRICAL THENOYL BENZOYL PEROXIDES

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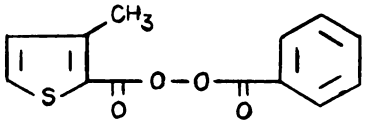
ABSTRACT

PREPARATION AND THERMAL DECOMPOSITION OF SOME UNSYMMETRICAL THENOYL BENZOYL PEROXIDES

by Delos Russell Byrne

This investigation deals with the preparation and thermal decomposition of a new series of unsymmetrical peroxides of the structure shown below, containing one benzene and one hetero-aromatic ring.



A total of eight compounds were synthesized and six were selected for kinetic investigation. With one exception the compounds investigated kinetically were derivatives of 2-thenoyl benzoyl peroxide either unsubstituted or substituted in the 5-position of the hetero-aromatic ring. 3-Thenoyl benzoyl peroxide was included for comparison.

In all cases investigated the thermal decomposition followed strict first-order kinetics. The rate constants and half-lives at 82.17° in presence of styrene as a radical scavenger are listed below:

Peroxide	$k \times 10^3$ ($min.^{-1}$)	$T_{1/2}$ (min.)
2-Thenoyl Benzoyl	4.00	173
3-Thenoyl Benzoyl	3.62	191
(5-Methyl-2-Thenoyl) Benzoyl	5.01	139
(5-Ethyl-2-Thenoyl) Benzoyl	5.19	134
(5-t-Butyl-2-Thenoyl) Benzoyl	4.69	148
(5-Nitro-2-Thenoyl) Benzoyl	4.93	141

The kinetic experiments were conducted at three temperatures: 72.90, 82.17 and 90.35° in Spectrograde carbon tetrachloride, 0.1000 molar in peroxide and 0.2 molar in styrene. The experiments were conducted in a purified nitrogen atmosphere in the absence of light to prevent decomposition. Peroxide concentrations were determined by infrared technique; rate constants and activation energies were calculated by the least square method using a 3600 CDC computer at Michigan State University. Frequency factors and activation entropies were then calculated from the Eyring absolute rate equation.

The data indicated that substituents increase the decomposition rate regardless of the electron donating or withdrawing character of the group. It appears that the increase in reaction rate is related to the displacement of the bonding electrons in one direction or the other from the central oxygen-oxygen bond. There may be a steric effect involved, specifically a case of "steric assistance."

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By

Delos Russell Byrne

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To My Mother, Mrs. Annabelle Tenney

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INTRODUCTION AND HISTORICAL

Interest in the behavior of peroxy compounds has been shown by those concerned with their theoretical aspects and those interested in their industrial applications. Free radical reactions are often catalyzed by peroxides and this has made such peroxides as cumyl peroxide, bis-t-Butyl peroxide, and benzoyl peroxide important catalytic reagents.

The initial thermal reaction of the peroxide is the unimolecular cleavage of the oxygen-oxygen bond and first order kinetics would be expected for practically all peroxide decompositions. This is true for the thermal decompositions of di-alkyl peroxides, but complications appear to interfere with the clear-cut unimolecular decompositions for acyl derivatives of the aromatic series. Both Brown (1) and Erlenmeyer and Schoenauer (2) determined that the decomposition reactions of aromatic acyl peroxides were complex in order, a higher order induced reaction being superimposed upon the first order oxygen-oxygen bond scission process. A study of these complications was made by Bartlett and Nozaki (3) who showed from their data that the assumption of the previous authors was essentially correct, and orders varying from

0.5 to 2.0 could be observed. There was also considerable variation in the kinetic picture as the solvent was varied. The work of Swain, Stockmeyer and Clark (4) was essentially responsible for isolating the unimolecular oxygen-oxygen bond cleavage reaction from the induced decompositions, by introducing a free radical scavenger, such as 3,4-dichlorostyrene or methyl methacrylate. The addition of these inhibitors increased the decomposition half-life of benzoyl peroxide at 80°C. by a factor of ten, and the variability of the reaction rate in different solvents became almost negligible. These investigators (4) varied the solvent from benzene to acetophenone; if one considers the large difference in polarity between these solvents, it suggests the almost complete absence of any ionic chemical species at any stop within the decomposition mechanism.

Later studies by Swain (4) as well as Blomquist and Buselli (5) were directed toward an examination of the relationship of peroxide decompositions and the Hammett Law (6). For the substituted derivatives of benzoyl peroxide, provided the substituents were located meta- and para- with respect to the peroxide linkage, these investigators found that the Hammett Law was fairly well obeyed. A reaction constant rho of -0.38 indicated that the cleavage is favored by an increase of electron density at the reaction site. The small value of rho

also indicated that the decompositions were not strongly influenced by the electron donating or attracting properties of the substituent in question.

The similarities between the benzenoid system and the heteroaromatic system of thiophene are rather striking. Thus, it was anticipated that the behavior of the peroxides derived from either 2-thenoic or 3-thenoic acid would show certain similarities to the benzoyl peroxides. Only one peroxide of this type, namely bis-(2-thenoyl) peroxide had been prepared prior to 1959 (7); Schuetz and Teller (8) reported the preparation and kinetic studies of the thermal decompositions for ten compounds; derivatives of bis-(2-thenoyl) peroxide. They also included a study of the peroxide derived from the unsubstituted 3-thenoic acid, as well as one unsymmetrical compound, 5-methyl-bis(2-thenoyl) peroxide. These investigators found that for the series of symmetrical compounds under investigation the Hammett equation was followed reasonably well, a rho value of -0.44 being obtained by a plot of $sigma_1$ plus $sigma_2$ for the substituents involved against log k. The work of Schuetz and Teller was extended to compounds derived from substituted 3-thenoic acids as well as additional substituted 2-thenoyl peroxides by Schuetz, Gruen, Byrne and Brennan (9). A total of nine new peroxides were prepared and the thermal decomposition rates of eight of these compounds were

examined. Five of these peroxides were derivatives of 3-thenoic acid, three of 2-thenoic acid; all were symmetrical about the oxygen-oxygen bond. It was found that, in general, electron donating groups accelerated decompositions whereas electron attractors retarded the decomposition rates. This was especially true of the peroxides with substituent halogens which showed the preponderance of an inductive effect over the resonance effect in these reactions. A notable exception was bis-(5-nitro-3-thenoyl) peroxide; the nitro group seemed to enhance the decomposition greatly, quite contrary to expectation, which was explained by a possible reversal of the dipole from a negative polarity toward the oxygens to a positive charge at the central bond (10, 11). In this series of peroxides it was also found that the Hammett Law was generally not applicable. It should be noted that for quite a few of the compounds studies by these investigators an "ortho-effect" would be expected. An attempt was made to calculate rho values for the two compounds for which such an effect would be absent, namely bis-(5-chloro) and bis-(5-bromo-3-thenoyl) peroxide, but even in these cases it was found that the calculated rho values varied from -0.087 to -0.123. Activation energies and entropies were calculated and found to vary from 38.1 to 20.1 kilocal. per mole for the activation energies and from -22 to +30 e.u. for the entropies of activation.

The present investigation is essentially concerned with a study of a new series of peroxide compounds, unsymmetrical peroxides bearing a benzene and a thiophene ring, and being substituted, if at all, in the heterocyclic system only. It seemed of interest and value to study this series of compounds from several points of view, as peroxides intermediate between the bis-(benzoyl) peroxides and the symmetrical peroxides in the thiophene series; they would afford an opportunity to study the effects on the decomposition rates due to the presence of substituents in only one of the two ring systems present. Leffler (12) carried out a study on unsymmetrical peroxides in the benzenoid series, but had employed different reaction conditions favoring an ionic mechanism. As mentioned previously, the only unsymmetrical peroxide studies to this point in the thiophene series was 5-methylbis(2-thenoyl) peroxide (8). The investigation reported here, it is felt, is therefore unique, as it involves, for the first time, a carbocylic aromatic as well as a hetero-aromatic system studied under conditions favoring free radical decompositions which are homolytic at the oxygen-oxygen bond. A total of eight new peroxides were prepared and the kinetics of decomposition of six of these compounds were studied. These compounds were chosen as they all bear either no substituent or substituents in the 5-position of the heterocylic ring. For comparison

3-thenoyl benzoyl peroxide was included. Three of the substitutents chosen were typical electron releasers: methyl, ethyl, and t-butyl; one, the nitro group, was a typical electron attractor. Infrared spectroscopy was employed for the analysis in this series of compounds (9), an I.R.5 Beckmann Spectrophotometer being employed; the solvent was M.C.B. Spectroquality carbon tetrachloride. The solutions were kept exactly at 0.1000 molar concentration, in the presence of 0.2 molar styrene as a free-radical scavenger. Strict precautions were observed to keep the ampoules free of dirt, dust and oxygen, and a constant temperature bath employed was set up in a dark room, to avoid complications due to photochemical reactions of any kind.

First order kinetics were found to be obeyed by all compounds under investigation. It was felt that the use of a larger temperature span than that employed in previous investigations of peroxide decompositions was preferable (8, 9). The total temperature span was extended to eighteen degrees, with a difference of about nine degrees being used between kinetic determinations. Duplicate determinations were employed for each temperature. Activation energies and entropies were calculated, the former by a plot of the logarithm of the rate constant against the reciprocal of the absolute temperature, the latter by the use of the Eyring equation (13).

Slopes were determined from the kinetic plots by the method of least squares, employing a CDC 3600 computer at the Michigan State University computer center. The author is greatful for the help of Mrs. Norma Ray of that office and her unselfish cooperation.

EXPERIMENTAL

Chemical Reagents

The carbon tetrachloride used as a solvent in the kinetic determinations was MCB Spectrograde CX 415. The 3-bromothiophene was purchased from the Aldrich Chemical Corporation, their White Label product.

The 5-t-butyl-2-acetylthiophene was donated as a sample by the Pennsalt Corporation; 2-furoic acid was an Eastman Kodak product, reagent grade. The writer is indebted to Dr. Fred M. Gruen of Olivet College for samples of 5-methyl-2-thenoic acid and 3-methyl-2-thenoic acid.

The styrene used as a free radical scavenger was Eastman Kodak White Label material, stabilized with t-butyl catechol. It was distilled *in vacuo* and stored in a refrigerator, in the dark, without inhibitor.

Syntheses

2-Acetylthiophene

The method of Hartough and Kosak (14) was employed in the preparation of this compound. A solution of 252 g. (3.0 moles) of thiophene and 117 g. (1.1 mole) of acetic anhydride was stirred and heated to 70° in a one-liter, three-necked flask. Ten grams of orthophosphoric

acid were then added cautiously from a dropping funnel during fifteen minutes. The temperature rose to 87-88° during the addition of the acid and the mixture was immersed in an ice-bath to prevent further rise in temperature. After completion of the addition the mixture was refluxed at 95-96° for two hours, during which time it turned dark in color. The mixture was then allowed to cool, water (200 ml.) was added and the aqueous mixture stirred for thirty minutes. The organic layer was separated, washed several times with 200 ml. portions of 10% sodium corbonate solution and then with water. The mixture was distilled at atmospheric pressure to remove the thiophene-water azeotrope and the residue was distilled in vacuo through a 6 inch Vigreux column to obtain 103 g. (0.82 mole, 74%) of 2-acetylthiophene, b.p. 79-81°/6 mm. Literature value (14): 77°/4 mm.

2-Thenoic Acid

In a four-liter beaker were placed 440 g. (11 moles) of sodium hydroxide pellets in 600 ml. of water and 2,500 g. of ice. The beaker was tared and 332 g. (4.53 moles) of chlorine gas were passed from a cylinder into the basic solution. The hypochlorite solution was heated to 60° and transferred to a five-liter three-necked standard taper flask fitted with mechanical stirrer, dropping funnel and reflux condenser. Acetylthiophene

(73.0 g., 0.58 mole) was added dropwise to the hypochlorite solution. During the addition of the ketone, the temperature of the reaction mixture rose to 67-68°, and was maintained by means of a cooling bath. Rapid refluxing due to the evolution of chloroform could be observed. The mixture was stirred and allowed to cool. A solution of 100 g. of sodium bisulfite in 200 ml. of water was added to destroy the hypochlorite. Careful acidification under cooling gave a heavy white precipitate. After standing overnight, the solid was recovered by filtration. Recrystallization from hot water gave white needles (0.52 moles, 67 g., 90.4%), melting at 127-218°. Literature value: (15) 128-129°.

3-Cyanothiophene

A mixture of 3-bromothiophene (115.2 g., 0.71 mole), cuprous cyanide (80 g.) and quinoline (Eastman Technical grade) (480 ml.) was heated under reflux in a two-liter, three-necked standard taper flask for three hours. The color of the reaction mixture changed from a dark green to a yellowish brown in an hour under reflux. After reflux the mixture was allowed to cool and then 400 ml. of liquid were removed by vacuum distillation, during which the temperature of the residual liquid reached approximarely 180°. The distillation was carefully acidified with 1:1 hydrochloric acid and set aside overnight in a refrigerator. It was then extracted with ether and washed

twice with 6 N. hydrochloric acid and finally with water. After having been dried over anhydrous calcium chloride, the solvent was removed from the ether extract and the residual oil was vacuum distilled to yield: 74 g. (0.679 mole, 96.1%) of the crude product.

3-Thenoic Acid

The crude 3-cyanothiophene was placed in a three-liter, three-necked standard-taper flask and 1,480 ml. of concentrated hydrochloric acid were added. The mixture was then refluxed for 3.5 hours. Following this the mixture was cooled very slowly to allow the slow crystallization of the product. The product was recovered by filtration and extraction of the mother liquor with ether to yield a total of 79.0 g. (0.616 mole, 90.8%) of 3-thenoic acid, mp. 136-137°. Literature value (17): mp. 137-138°.

2-Ethylthiophene

Using the experimental procedure of King and Nord (18) a mixture of 100 g. (0.79 mole) of 2-acetylthiophene, 155.1 ml. of 85% hydrazine hydrate and 617.1 ml. of ethylene glycol was stirred and heated to 170° to remove excess hydrazine and water. About 120 ml. of distillate was collected, and the residue was allowed to stand overnight protected from moisture by means of a calcium chloride tube. The distilling head was replaced

by a reflux condenser and 55.4 g. (0.99 mole) of potassium hydroxide pellets were added. The stirred mixture was heated to a temperature of 120° when the evolution of nitrogen began. The temperature was maintained at 120-140° for approximately two hours after which time the mixture was allowed to cool; it was observed that the solution had changed to a two-phase liquid mixture during nitrogen evolution.

After standing overnight the reaction mixture was distilled through a six-inch Vigreux column until the vapor temperature had reached 140°. The distillate was extracted twice with ether, the ether solution washed once with 1:1 hydrochloric acid and twice with water and dried over anhydrous calcium chloride. The ether was removed on a steam-bath and the product distilled at stmospheric pressure to yield 76 g. (0.68 mole, 86%) of product boiling at 133-135°. Literature value (19): b.p. 132-134°.

5-Ethyl-2-Acetylthiophene

The apparatus and general method described for the preparation of 2-acetylthiophene (14) was used to prepare this compound. Orthophosphoric acid (5 g.) was added at room temperature to a well stirred mixture of 56 g. (0.5 mole) of 2-ethylthiophene and 55 g. (0.540 mole) of acetic anhydride. During the addition of the catalyst the temperature rose spontaneously to 37-38°. The mixture

was then heated with vigorous stirring to 135-140°, its reflux temperature. The mixture was then refluxed for three hours. After cooling to room temperature, water was added to the mixture and it was stirred for an additional fifteen minutes. The organic layer was separated, washed with 10% sodium carbonate to basic reaction and then twice with water. The brown oil was dried over anhydrous magnesium sulfate and distilled in vacuo to yield, after a small forerun, 47.6 g. (0.317 mole, 58.7%) of water-clear liquid, boiling at 100°/10 mm.

5-Ethyl-2-Thenoic Acid

Using the experimental procedure described for the preparation of 2-thenoic acid (15), 47.6 g. (0.317 mole) of 5-ethyl-2-acetylthiophene were used to prepare this acid. The 5-ethyl-2-acetylthiophene was added dropwise to a solution of sodium hypochlorite prepared from 132 g. (3.30 moles) of sodium hydroxide, 94.5 g. (1.35 moles) of chlorine and 800 g. of ice. The initial temperature of the reaction mixture was 52°, but it had to be raised to 78-80° before the reaction commenced, as evidence by reflux (chloroform). The reaction temperature was controlled at 75-78° by means of alternate heating and cooling. The temperature was maintained for two hours, and then the mixture was cooled to room temperature. A solution of 35 g. of sodium bisulfite in 100 ml. of water was added. The

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solution was tested with potassium iodide-starch paper to assure complete reduction of the hypochlorite. The reaction mixture was transferred to a four liter beaker and acidified cautiously with concentrated hydrochloric acid, yielding a white precipitate. Yield: 40.7 g. (0.269 mole, 84.8%) of product melting at 67-70°. Literature value (20): 71°.

5-t-Butyl-2-Thenoic Acid

Using the experimental procedure described previously for the preparation of 2-thenoic acid (21), 54.6 g. (0.30 mole) of 5-t-butyl-2-acetylthiophene (supplied as a sample by the Pennsalt Corporation) were added dropwise during approximately 30 minutes to a solution of sodium hypochlorite. The latter was prepared from 132 g. (3.30 moles) of sodium hydroxide, 96 g. (1.35 moles) of chlorine and 800 g. of ice. The temperature of the mixture was maintained at 50-55° during the addition of the ketone. Following the addition of the ketone the mixture was heated to 75°. At this point the temperature began to rise rapidly, indicating that the reaction had been initiated. To control the exothermic initial reaction it was necessary to apply alternate cooling and heating to keep the reaction temperature in the range of 75-85°. During the reaction the color of the solution changed from a foggy yellow to a clear yellow and finally violent

bubbling due to the evolution of chloroform could be observed. The reaction mixture was set aside overnight and a solution of 30 g. of sodium bisulfite in 100 ml. of water was added. The mixture was extracted with ether to remove neutral materials. The aqueous layer was then transferred to a three-liter, three-necked flask fitted with a stirrer and 500 ml. of ethyl ether were added under stirring. The mixture was carefully acidified with concentrated hydrochloric acid. After separation of the ether extract, the water layer was again extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate, and the ether was removed leaving an orange-white liquid which solidified after being transferred to a beaker. Recrystallization of the material from ligroin (b.p. 90-120°) gave 18 g. (9.1 mole, 33%) of a crystalline material, melting at 124-125°. Literature value (21): 128-128.5°.

2-Thenal

The method of Campaigne and Archer (22) was employed in the preparation of this aldehyde. In a liter, three-necked flask fitted with a mechanical stirrer, reflux condenser and dropping funnel were placed 84 g. (1.0 mole) of thiophene and 92 g. (1.28 moles) of N,N-dimethylformamide and the mixture was cooled by immersion in an ice-bath. To the stirred mixture there was added 192 g. (1.24 moles) of phosphorus oxychloride during two hours.

During the addition of the inorganic chloride the reaction mixture underwent a change from clear white to canary yellow. Following the addition of the phosphorus oxychloride the mixture was refluxed for an hour and a half on a steam bath during which it underwent further coloration changes from yellow to reddish-black. The reaction mixture was then cooled, partially neutralized with 10% sodium hydroxide solution and then completely neutralized by the addition of solid sodium carbonate. The mixture was next extracted with ether, the ether extract was washed with water and set aside in contact with anhydrous sodium sulfate overnight. The ether was removed on a steam bath leaving a reddish black oily residue. The latter was distilled in vacuo using a six-inch Vigreux column and the fraction distilling at 82-84°/20 mm. was collected as product. The yield was 73.5 g. (0.654 mole, 65.4%). Literature value (22): 44-45°/1mm.

5-Nitro-2-Thenal

The experimental method of Buu Hoi (23) was employed for the preparation of this aldehyde. A 250 ml. flask was equipped with a mechanical stirrer, dropping funnel, and Allihn condenser. The flask was cooled by immersion in an ice-bath. Into the flask was placed a solution of 26 g. (0.232 mole) of 2-thenal in 50 g. (0.490 mole) of acetic anhydride. To the cold aldehyde

solution there was added a mixture of 50 g. of glacial acetic acid and 19.8 g. of fuming nitric acid (sp.g. 1.49) during a half hour in which time the reaction mixture changed from a light brownish red to a clear canary yellow. Care was taken to keep the reaction temperature below 0° during the entire experiment. Following addition of the nitrating mixture the solution was stirred at 0° for an additional hour and a half and then poured into approximately 200 ml. of a crushed ice slurry. Initially the mixture became cloudy and a reddish oil separated from solution. This, after brief stirring, solidified to a crystalline solid. This was removed by filtration and washed several times with distilled water. The filtrate which had a turbid yellow-green color was again poured into water and the additional product was recovered by filtration. The combined solid product was air-dried for several hours and then recrystallized from 95% ethanol by dissolving it in ethanol, concentrating the solution on a steam-bath, and allowing the concentrated solution to stand overnight. The pale-brown crystalline product was recovered by filtration. The yield was 29.8 g. (0.189 mole, 82%). The melting point was 72°. Literature value (23): 77°.

5-Nitro-2-Thenoic Acid

The experimental procedure was adapted from the general method described by Migridichian (24). Into a

two-liter, three-necked flask fitted with a stirrer, Allihn condenser, thermometer and dropping funnel was introduced a mixture of 400 ml. of water and 400 ml. of 95% ethanol containing 18.8 g. (0.12 mole) of 5-nitro-2-thenal. A 40.8 g. (0.24 mole) quantity of silver nitrate was then added to the reaction mixture, at which point the mixture had a slight pale brown-yellow color. A solution of 19.2 g. (0.48 mole) of sodium hydroxide in 400 ml. of water was then placed in the dropping funnel and allowed to drip slowly into the well-stirred mixture during a half hour while holding the reaction mixture below 50°. Following addition of the base the mixture was stirred for fifteen minutes, then cooled in an ice-bath for thirty minutes and filtered. The large cake of silver remaining on the filter was washed several times with hot water and the washings were added to the filtrate. As the filtrate was still turbid, it was refiltered several times through a finer filter by using a piece of filter paper placed inside the "coarse grade" sintered glass funnel. After several filtrations the filtrate had a slight yellow-green color, but was clear. Its total volume was approximately 1,500 ml. The filtrate was concentrated until the volume had been reduced to 500 ml. and 500 ml. of ethyl ether were added. The mixture was carefully acidified with concentrated hydrochloric acid. A cloudy white material precipitated, but quickly dissolved in the ether layer. The

ether layer was separated and the aqueous solution was extracted with several portions of ether. The ether extracts were combined and dried over anhydrous magnesium sulfate. The ether was removed on a steam bath, leaving a yellow-brown solid. During the evaporation of the solvent a brown gas was observed indicating the presence of residual nitric acid. The solid was recrystallized from hot water to obtain pure product in the form of yellow needles, melting at 158-159°. Literature value (25): 158°. The yield was 11.0 g. (0.064 mole, 53%).

Preparation of Acid Chlorides

The thenoyl chlorides used in this work were prepared by reaction of the corresponding carboxylic acids with thionyl chloride; their properties are summarized in Table 1. A typical preparation follows:

2-Thenoyl Chloride (26)

In a 100 ml. flask fitted with an Allihn condenser and heating mantle, there were placed 12.8 g. (0.1 mole) of 2-thenoic acid and 46.0 g. (0.39 mole) of thionyl chloride. The mixture was heated under reflux for ten hours, during which it became a clear orange colored solution. After cooling, the excess thionyl chloride was removed by distillation at atmospheric pressure using an eight-inch Vigreux column.

Table 1. Preparation of the Acid Chlorides.

Acid Chloride	Yield Percent	B.P. °C	Literature Reference
2-Thenoyl Chloride	95	58.5-59.5/1.5 mm.	(27)
3-Thenoyl Chloride	81	73/4.5-5.0 mm.	(17)
3-Methyl-2-Thenoyl Chloride	93	91-93/6 mm.	(9)
5-Methyl-2-Thenoyl Chloride	77.1	87-88/3.1 mm.	(33)
5-Ethyl-2-Thenoyl Chloride	92.7	97-98/3 mm.	Not Reported
5-t-Butyl-2-Thenoyl Chloride	81.4	119/4.5 mm.	(34)
5-Nitro-2-Thenoyl Chloride	62.5	114-116/2.5 mm.	(25)
2-Furoyl	98	43/1.5 mm.	(35)

The residual dark colored oil was distilled *in vacuo*, yielding 14.1 g. (0.095 mole, 95%) of clear colorless liquid which solidified immediately on immersion of the receiver in a dry-ice isopropanol bath. The boiling point was 58.5-59.5°/1.5 mm. (McLeod gauge). The distillation of this product was carried out in a micro apparatus using a fraction cutter. The product was stored in the dark at 0° and protected from moisture by a calcium chloride drying tube. Literature value (27): 92°/18 mm.

Sodium Perbenzoate

The material was prepared by the experimental procedure originally reported by Braun (28). In a 500 ml. Erlenmeyer flask, cooled by immersion in an ice-salt bath, and fitted with a calcium chloride drying tube there were placed 100 ml. of absolute methanol in which 5.2 g. (0.22 g. atom) of sodium metal had been dissolved. A 50 g. (0.21 mole) quantity of benzoyl peroxide was dissolved in 200 ml. of pure chloroform and the solution chilled by immersion in an ice-salt bath. The benzoyl peroxide-chloroform solution was then added quickly to the sodium methoxide solution and the resulting mixture was vigorously stirred for four to five minutes while immersed in an ice-salt bath. The mixture turned turbid and after several minutes a curdy, cheese-like solid had formed. The mixture was transferred to a two-liter separatory funnel and the

sodium perbenzoate was extracted with 500 ml. of ice-cold water. The aqueous extract was washed with two 100 ml. portions of chloroform and used directly in the preparation of the unsymmetrical peroxides.

2-Thenoyl Benzoyl Peroxide

The aqueous sodium perbenzoate solution was maintained at -5 to 0° by immersion in an ice-salt bath and then introduced into a 500 ml., three-necked, standard taper flask fitted with a mechanical stirrer, Allihn condenser and dropping funnel. The flask was chilled by immersion in an ice-salt bath. A solution containing 14.1 g. (0.095 mole) of 2-thenoyl chloride in 50 ml. of dry cyclohexane was added dropwise during fifteen minutes to the perbenzoate solution. Precipitation of a white material was observed almost immediately. The reaction mixture was stirred vigorously for an additional hour and the solid product was recovered by filtration on a sintered glass funnel. The colorless, fluffy, extremely hydrophobic peroxide was washed several times with 100 ml. portions of ice-cold water and dried in a vacuum disiccator at 0°, while being protected from light. The yield of product was 20.9 g. (0.084 mole, 88.4%, based on 2-thenoyl chloride), which melted sharply at 92.0-92.5°. After melting, the liquid turned red, but did not detonate.

Calculated for $C_{12}H_8O_4S$: C, 58.06; H, 3.23; S, 12.90.

Found: C, 57.44; H, 3.20; S, 12.84.

3-Thenoyl Benzoyl Peroxide

The sodium perbenzoate solution was introduced into a 500 ml., three-necked, standard-taper flask, fitted with a mechanical stirrer, Allihn condenser, and dropping funnel and cooled to -5 to 0° by immersion in an ice-bath. To the vigorously stirred solution was added a solution containing 12.0 g. (0.081 mole) of 3-thenoyl chloride in 50 ml. of dry cyclohexane. Within minutes a white solid formed which had a cheese-like appearance. The reaction product was stirred at -5 to 0° for an additional hour, after which the solid product was recovered by filtration on a sintered glass funnel. The white, fluffy, hydrophobic solid was washed several times with 100 ml. portions of ice-cold water. The yield was 18.3 g. (0.073 mole, 90.1% based on 3-thenoyl chloride) of a snow-white solid melting sharply at 101-101.5°. The peroxide, after melting, did not detonate, but turned red in color. The product was placed in a vacuum desiccator, evacuated for two hours and then stored in a refrigerator in the dark a 0°.

Calculated for $C_{12}H_8O_4S$: C, 58.06; H, 3.23; S, 12.90.

Found: C, 57.90; H, 3.24; S, 12.98.

(3-Methyl-2-Thenoyl) Benzoyl Peroxide

The sodium perbenzoate solution was placed in a 500 ml., three-necked, standard taper flask fitted with a reflux condenser, stirrer and dropping funnel. The flask

was immersed in a dry-ice isopropanol bath in order to maintain the temperature at -5 to 0°. A solution containing 16 g. (0.106 mole) of 3-methyl-2-thenoyl chloride in 50 ml. dry cyclohexane was added dropwise to the reaction mixture. The mixture was stirred for an additional hour and the precipitated white solid was recovered by filtration and washed with several portions of ice-cold water. It was dried in vacuo, yielding 15.0 g. (0.056 mole, 53% based on 3-methyl-2-thenoyl chloride) of product, melting at 49.5-50.0°. The white material, upon melting, did not detonate or turn color.

Calculated for $C_{13}H_{10}O_4S$: C, 59.53; H, 3.84; S, 12.22.
Found: C, 59.44; H, 3.84; S, 12.24.

(5-Methyl-2-Thenoyl) Benzoyl Peroxide

The sodium perbenzoate solution prepared as indicated previously, was introduced into a 500 ml., three-necked, round bottomed flask, fitted with a mechanical stirrer, Allihn condenser, and dropping funnel. The flask was cooled by immersion in an ice-bath and 3.9 g. (0.027 mole) of 5-methyl-2-thenoyl chloride dissolved in 50 ml. of dry cyclohexane was added to the perbonzoate solution through the dropping funnel during one hour under vigorous stirring. Precipitation of the product initiated almost immediately. The entire system had been kept at -5 to 0° during the whole experiment. The solid was recovered by filtration

and washed several times with cold water. The yield of peroxide was 4.25 g. (0.016 mole, 59.2%) of a colorless solid, which melted at 82-83°. A small portion of the product held in a Bunsen flame acted in a manner typical of this type of peroxide. The solid turned deep-red in color on melting, but did not detonate.

Calculated for: $C_{13}H_{10}O_4S$: C, 59.53; H, 3.84; S, 12.22.
Found: C, 59.49; H, 3.79; S, 11.95.

(5-Ethyl-2-Thenoyl) Benzoyl Peroxide

A method analogous to that described for the synthesis of (5-methyl-2-thenoyl) benzoyl peroxide was used to prepare this compound. In the apparatus described above there was added dropwise 18.1 g. (0.103 mole) of 5-ethyl-2-thenoyl chloride in 50 ml. of dry cyclohexane to the perbenzoate solution. The reaction mixture became turbid, but no precipitation occurred. The mixture was stirred for one and a half hours while immersed in an ice-salt bath. The cyclohexane layer was separated and reduced to about one half of its volume by removal of solvent in an air stream. The residual material was set aside in a refrigerator overnight; some crystallization of the product from solution was observed the following morning. However, when a drop of the mother liquid was placed in the flame of a Bunsen burner, a large flash was observed, indicating the presence of peroxide in solution. The

solution was then placed in a dry-ice isopropanol bath where a yellowish solid crystallized from solution. The solid was extracted into petroleum ether (b.p. 30-60°) and set aside overnight at 0° in the dark to allow crystallization of the product to occur. The yield of peroxide obtained was 15.5 g. (0.056 mole, 54.4%) of a lightly orange colored crystalline solid, melting at 52-53°. On melting the product turned deep red in color and decomposed at 100°. After drying the peroxide in vacuo for several days at 0°, an analytical sample was obtained.

Calculated for $C_{14}H_{12}O_4S$: C, 60.84; H, 4.37; S, 11.62.
Found: C, 59.93; H, 4.33; S, 11.74.

(5-t-Butyl-2-Thenoyl) Benzoyl Peroxide

Using the apparatus described above, there was added during an hour 8.25 g. (0.0407 mole) of 5-t-butyl-2-thenoyl chloride in 50 ml. dry cyclohexane to the precooled and vigorously stirred sodium perbenzoate solution. During the addition of the acid chloride no precipitation of product occurred. The reaction mixture was stirred for an additional hour, after which time the cyclohexane layer was separated and its volume was reduced to about 25 ml. by evaporation of the solvent in an air stream. The residual liquid was set aside overnight in the refrigerator, to permit crystallization of the peroxide product. This was recovered by filtration, washed with

cold water and dried for several hours in a vacuum desiccator under reduced pressure. The yield of pure product was 3.7 g. (0.012 mole, 29.7%) of yellow colored crystals melting at 50°. Identification of the peroxide was confirmed by means of its infrared spectrum (Beckman IR # 5). When a small quantity of the peroxide was held in a Bunsen flame, it behaved typically. After melting, the compound turned red and decomposed above 80°. The compound was highly hydrophobic.

Calculated for $C_{16}H_{16}O_4S$: C, 63.13; H, 5.30; S, 10.55.
Found: C, 62.70; H, 5.43; S, 10.98.

(5-Nitro-2-Thenoyl) Benzoyl Peroxide

The sodium perbenzoate solution was placed in a 500 ml. flask as described above. A solution containing 7.15 g. (0.040 mole) of 5-nitro-2-thenoyl chloride in 100 ml. of dry cyclohexane was added dropwise during one hour to the vigorously stirred, prechilled perbenzoate solution. A beige colored solid precipitated from solution during the addition of the acid chloride. The mixture was stirred during an additional hour and the rather hydrophobic, beige colored solid was recovered by filtration and washed several times with 200 ml. portions of ice water. The solid was dried in a vacuum disiccator overnight in the dark. The solid melted sharply at 82.5-83°. The yield of pure product was 7.8 g. (0.026 mole, 65%). After melting the solid turned red and detonated.

Table 2. Peroxides prepared.

Peroxide	Formula	Yield %	M.P.* °C	Carbon** Calc.	Found	Hydrogen Calc.	Found	Sulphur Calc.	Found	Nitrogen Calc.	Found
2-Thenoyl Benzoyl	$C_{12}H_8O_4S$	88	92.0-92.5	58.06	57.44	3.23	3.20	12.90	12.84	--	--
3-Thenoyl Benzoyl	$C_{12}H_8O_4S$	90	101.0-101.5	58.06	57.90	3.23	3.24	12.90	12.98	--	--
(5-Methyl-2-Thenoyl) Benzoyl	$C_{13}H_{10}{}^4{}_4S$	59	83	59.53	59.49	3.84	3.79	12.22	11.95	--	--
(5-Ethyl-2-Thenoyl) Benzoyl	$C_{14}H_{12}O_4S$	54	52-53	60.84	59.93	4.37	4.33	11.62	11.74	--	--
(5-t-Butyl-2-Thenoyl) Benzoyl	$C_{16}H_{16}O_4S$	30	50	63.13	62.70	5.30	5.43	10.55	10.98	--	--
(5-Nitro-2-Thenoyl) Benzoyl	$C_{12}H_7O_6NS$	65	82.5-83.0	49.15	48.86	2.41	2.28	10.93	10.79	4.78	4.79

* All melting points uncorrected.
** Analyses performed by Microtech. Laboratories, Skokie, Illinois.

Calculated for $C_{12}H_7O_6NS$:
C, 49.15; H, 2.41; N, 4.78; S, 10.93.
Found: C, 48.86; H, 2.28; N, 4.79; S, 10.79.

2-Furoyl Benzoyl Peroxide

The aqueous perbenzoate solution was maintained at -5 to 0° by immersion in an ice-salt bath and introduced into a 500 ml., three-necked, standard-taper flask fitted with a mechanical stirrer, reflux condenser and dropping funnel. Eleven grams (0.083 mole) of furoyl chloride dissolved in 50 ml. of dry cyclohexane was added dropwise to the sodium perbenzoate solution. The mixture was stirred at 0° for an additional hour. The organic layer was sepatated and filtered. A white solid material was isolated. The solid was washed with ice-cold water and dried in a vacuum disiccator. The yield was 5.4 g. (0.023 mole, 20.8%, based on furoyl chloride) melting sharply at 57.5-58°. A small sample, dropped into a Bunsen flame, gave a typical burst of flame. After drying, the material had a powdery appearance and was snowy-white.
Calculated for $C_{12}H_8O_5$: C, 62.07; H, 3.42.
Found: C, 61.96; H, 3.58.

Kinetic Determinations

A typical kinetic determination is described, (2-thenoyl-benzoyl peroxide) at 72.90°.

A 0.6231 g. (0.1000 mole) quantity of 2-thenoyl benzoyl peroxide was weighed on a single pan (Mettler) balance and transferred to a 25 ml. volumetric flask. The solution was made up to volume using carbon tetrachloride (MCB Spectroquality CX 415), which contained sufficient styrene to make it 0.2 molar in concentration. Samples, 0.4 ml. in volume, were introduced into ampoules which were then cooled in dry ice. After flushing each ampoule with pure dry nitrogen (prewashed with concentrated sulfuric acid and dried with sodium hydroxide pellets) the ampoules were sealed with a gas-oxygen torch and transferred to a constant temperature bath (temp. ±0.05°). Duplicate samples were removed at each temperature determination. A "zero-time" of three minutes was assumed sufficient for the samples to reach thermal equilibrium with the bath. The initial duplicate samples were removed at this point, designated zero time; samples were removed at three-hour intervals thereafter. Each set of samples was quenched immediately by immersion in an ice-bath and the adherent mineral oil from the bath was washed off with petroleum ether (b.p. 30-60°). The samples were then stored in dry ice until analyzed in the Beckman I.R. 5. The infrared region from 5.5 to 6.1 microns was scanned to determine the peroxide concentration. A total of six duplicate samples were removed in each

determination. As a three hour interval was kept between removals of samples, the total time span investigated for the temperature of 72.90° was fifteen hours.

RESULTS AND DISCUSSION

The rate constants, half lives, frequency factors, energies and entropies of activation, calculated from the decomposition kinetic determinations of the peroxides studied in the course of this investigation are summarized in Table 22. It can be seen from this data that all the peroxides carrying substituents decompose at a rate greater than the unsubstituted parent compounds, regardless of the electron attracting or repelling character of the substituent. The unique structural feature of this series of peroxides compared with those investigated previously (9, 26) is that here there are two different ring systems in the same peroxide (benzenoid as well as hetero-aromatic), and additionally there is only a single substituent in one of the rings (the hetero-aromatic). This intrinsic difference between these unsymmetrical peroxides and their symmetrical counterparts (benzenoid as well as heterocyclic) suggests that the increase in reaction rate is in some way related to the shift of electrons in either direction from the centrally located oxygen to oxygen peroxide bond. It can also be noted from the data in Table 22 that the increase in the decomposition rate due to the substitution of either alkyl

groups or the nitro group is relatively small in magnitude; as the data show, the ratio between the rate constant of the substituted compound and the k factor of the parent peroxide never exceeds the value of two at any particular reaction temperature. The difference in reaction rates for the symmetrical series of peroxides are more pronounced (9, 26). This may be due to the fact that the unsymmetrical peroxides carry only one substituent, whereas the symmetrical compounds are substituted in each ring system. It appears that for the case of the symmetrical peroxides there is either an accumulation of electrons, if the substituent is electron repelling at the central linkage, or a decrease of electron density at the same bond, if the group is electron attracting (10). For the compounds discussed in the present work there is, due to their unsymmetrical nature, a shift of electrons in either direction of the central oxygen-oxygen linkage. Another interesting fact shown by the data is the striking regularity in the increase of the rate constant from temperature to temperature with all compounds. The rate constant is approximately tripled by a temperature increase of about nine degrees throughout the series, with the possible exception of the nitro derivative.

The fact that the influence of the substituents on the rate is practically independent of the electronic character of the group in question may be reasonably

accounted for on the basis of steric considerations. Since there is an increase in the rate of the peroxide decomposition due to the presence of substituents, a case of "steric assistance" (29) may exist. The size of the nitro substituent is comparable to that of the methyl group (30), and the data show that the energies of activation and the entropies of activation in this series are practically the same. As a decrease in the entropy parameter would lead to a decrease in reaction rate, the observed rate enhancement must be due to a decrease in energy of activation. It can be seen from the data that both the energy and entropy of activation decrease in going from the unsubstituted peroxides to those bearing the various types of substituents. In another series of free radical decompositions, previously reported by Bartlett (31), it was observed that the entropies of activation were decreasing with increasing resonance stabilization of the free radicals forming in the decompositions. There is a possibility that this resonance effect is here superimposed upon the steric assistance effect discussed. It should also be noted that the ethyl substituent should be capable of higher resonance stabilization (hyperconjugation) than is the t-butyl group. This may be responsible for the relatively low value of the entropy of activation for the ethyl derivative in the series of compounds examined here.

Another reason for the extreme values of the activation parameters for the ethyl derivative may be the increased possibility of varying conformations in the linearly shaped ethyl group as compared to the more spherical methyl- and t-butyl substituents.

In Table 3 a comparison has been made between some of the symmetrical (both benzoyl, and 2-thenoyl) peroxides and the unsymmetrical "mixed" compounds studied in the present work. Rate constants have been corrected to a temperature of 80° by means of the integrated Arrhenius equation (32).

The energies and entropies of activation are also given for comparison in Table 3. The most striking fact of the data shown in the table is the small differences in magnitude of the entropy of activation values between the unsymmetrical thenoyl-benzoyl peroxides and the derivatives of bis-(2-thenoyl) peroxide on one hand, and the striking difference in magnitude of these values between the two series and the derivatives of benzoyl peroxide. This strongly suggests that the hetero-atom (sulfur) leads to the high entropy of activation values for the two series containing this hetero-atom. It may be the close proximity of the sulfur atom to the acyl peroxide linkage imposes additional restraint on the peroxides, which is released in their change toward the transition state; this may well lead to entropy of

Table 3. Comparison data of symmetrical and unsymmetrical peroxides. All data at 80°C.

Compound, Peroxide	k x 10^3(min.$^{-1}$)	Energy of Act. (kcal. mole^{-1})	Entropy of Activation e.u.
Bis-Benzoyl) [5]	2.59	30.2	4.5
Bis-(2-Thenoyl) [26]	2.43	29.5	10.22
Thenoyl Benzoyl	3.33	32.9	12.24
Bis-(p-Methyl-Benzoyl)	3.55	30.2	4.3
Bis-(5-Methyl-2-Thenoyl)	4.64	29.5	11.63
(5-Methyl-2-Thenoyl) Benzoyl	3.80	31.8	10.21
Bis-(5-t-Butyl-2-Thenoyl)	4.24	29.5	11.41
(5-t-Butyl-2-Thenoyl) Benzoyl	3.57	31.3	9.10
Bis-(p-Nitro-Benzoyl)	2.60	29.9	4.8
(5-Nitro-3-Thenoyl) Benzoyl	3.73	31.9	10.36

activation values differing by five to seven entropy units, as shown by the data in Table 3.

These observations and results indicate that it would be informative to make a study of decomposition rates of additional compounds in the series of peroxides described above as well as in additional mixed series of heterocyclic peroxides, such as symmetrical and unsymmetrical compounds containing oxygen and nitrogen hetero-atoms.

SUMMARY

(1) Eight previously unreported unsymmetrical peroxides containing one benzene and one hetero-aromatic ring were prepared and the kinetics of the decomposition of six of these peroxides were investigated.

(2) For the compounds investigated the kinetics was found to be first order in presence of a free radical scavenger.

(3) Energies of activation, frequency factors and entropies of activation were calculated and conclusions were drawn from the values obtained as to the influence of substituents on the rate constants and the kinetic parameters.

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APPENDIX

Table 4. Spectroscopic measurements leading to kinetic data.

2-thenoyl benzoyl peroxide

Temp.: 72.90°C.±0.05°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	117.8	3.0	39.27	1.59406	0.20249
2	180	118.6	7.5	15.81	1.19893	0.07846
3	360	118.4	15.5	7.638	0.88298	-0.05409
4	540	118.4	23.0	5.147	0.71155	-0.14283
5	720	118.9	30.0	3.963	0.59802	-0.22330
6	900	117.8	39.0	3.021	0.48015	-0.31876
Slope: -5.72×10^{-4}				$k = 1.32 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	118.3	6.6	17.92	1.25334	0.09795
2	180	118.9	8.7	13.67	1.13577	0.05538
3	360	116.0	16.1	7.261	0.86100	-0.06500
4	540	118.3	22.9	5.116	0.71315	-0.14685
5	720	117.8	30.8	3.825	0.58263	-0.23463
6	900	117.8	39.0	3.0205	0.48015	-0.31858
Slope: -4.63×10^{-4}				$k = 1.07 \times 10^{-3}$ min.$^{-1}$		

Table 5. Spectroscopic measurements leading to kinetic data.

2-thenoyl benzoyl peroxide

Temp.: 82.17°C.±0.02°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	118.8	1.4	84.86	1.92870	0.28533
2	60	117.8	8.0	14.73	1.16820	0.06744
3	120	117.8	16.2	7.272	0.86165	-0.06464
4	180	118.4	25.5	4.643	0.66680	-0.17600
5	240	118.5	33.4	3.548	0.54998	-0.25964
6	300	117.6	41.5	2.834	0.45240	-0.34448
Slope: -1.70×10^{-3}				$K = 3.91 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	118.7	2.7	43.96	1.64306	0.21564
2	60	119.2	9.9	12.04	1.08063	0.02383
3	120	118.9	15.2	7.822	0.89332	-0.04900
4	180	119.0	24.9	4.779	0.67934	-0.16794
5	240	118.3	34.1	3.469	0.54020	-0.23745
6	300	118.5	42.4	2.795	0.44638	-0.35028
Slope: -1.78×10^{-3}				$k = 4.09 \times 10^{-3}$ min.$^{-1}$		

Table 6. Spectroscopic measurements leading to kinetic data.

2-thenoyl benzoyl peroxide

Temp.: 90.35°C.±0.05°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	120.4	3.6	33.44	1.52427	0.18298
2	15	120.0	9.0	13.33	1.12483	0.05115
3	30	120.4	12.7	9.480	0.97681	-0.01019
4	45	120.1	18.6	6.457	0.81003	-0.09151
5	60	120.7	21.9	5.511	0.74123	-0.13006
6	75	120.2	30.2	3.980	0.59988	-0.22192
Slope: -5.05×10^{-3}				$k = 1.16 \times 10^{-2}$ min.$^{-1}$		
Run No. 2						
1	0	120.5	3.5	34.43	1.43694	0.18667
2	15	120.4	7.7	15.64	1.19424	0.07700
3	30	120.2	11.8	10.20	1.00860	0.00389
4	45	118.9	18.4	6.462	0.81037	-0.09130
5	60	119.8	-2.4	5.348	0.72819	-0.13775
6	75	120.7	29.8	4.050	0.60746	-0.21345
Slope: -5.22×10^{-3}				$k = 1.20 \times 10^{-2}$ min.$^{-1}$		

Table 7. Spectroscopic measurements leading to kinetic data.

3-thenoyl benzoyl peroxide

Temp.: 72.90°C.±0.05°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	119.2	6.7	17.79	1.25018	0.09691
2	180	119.0	10.8	11.02	1.04218	0.00787
3	360	119.1	16.0	7.444	0.87181	-0.05958
4	540	119.4	24.4	4.893	0.68958	-0.16140
5	720	118.9	32.0	3.716	0.57008	-0.24405
6	900	118.9	38.2	3.113	0.49318	-0.30698
Slope: -4.57×10^{-4}				$k = 1.05 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	118.7	5.1	23.28	1.36698	0.13577
2	180	118.3	10.4	11.38	1.05614	0.02366
3	360	118.2	16.4	7.207	0.85775	-0.06661
4	540	118.0	23.2	5.086	0.70638	-0.15095
5	720	118.1	32.5	3.634	0.56038	-0.25150
6	900	117.5	38.9	3.021	0.48015	-0.31858
Slope: -5.05×10^{-4}				$k = 1.16 \times 10^{-3}$ min.$^{-1}$		

Table 8. Spectroscopic measurements leading to kinetic data.

3-thenoyl benzoyl peroxide

Temp.: 82.17°C.±0.02°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	117.8	4.3	27.40	1.43775	0.15776
2	60	118.2	8.8	13.43	1.23808	0.05231
3	120	118.5	16.9	7.012	0.84584	-0.07273
4	180	118.4	23.6	5.017	0.70044	-0.15465
5	240	117.9	30.8	3.828	0.58297	-0.23433
6	300	118.6	40.0	2.965	0.47202	-0.34606
Slope: -1.60×10^{-3}				$k = 3.69 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	117.6	4.5	26.13	1.41714	0.15137
2	60	118.0	10.0	11.80	1.07188	0.03019
3	120	117.5	16.7	7.036	0.84733	-0.07196
4	180	119.0	24.0	4.958	0.69531	-0.15783
5	240	118.7	31.4	3.780	0.57749	-0.23845
6	300	118.3	39.2	3.018	0.47972	-0.31903
Slope: -1.55×10^{-3}				$k = 3.62 \times 10^{-3}$ min.$^{-1}$		

Table 9. Spectroscopic measurements leading to kinetic data.

3-thenoyl benzoyl peroxide

Temp.: 90.35°C.±0.05°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	119.9	4.0	29.98	1.47683	0.16938
2	15	120.5	8.2	14.70	1.16732	0.06707
3	30	119.9	12.4	9.669	0.98538	-0.00643
4	45	120.4	18.0	6.688	0.82530	-0.08339
5	60	119.7	22.8	5.250	0.72016	-0.21063
6	75	119.7	29.0	4.128	0.61574	-0.21063
Slope: -4.96×10^{-3}				$k = 1.14 \times 10^{-2}$ min.$^{-1}$		
Run No. 2						
1	0	119.5	4.8	24.90	1.39620	0.14489
2	15	119.4	9.4	12.70	1.10380	0.04297
3	30	120.3	13.1	9.183	0.96298	-0.01637
4	45	120.5	17.1	7.047	0.84800	-0.07160
5	60	119.6	22.8	5.246	0.71983	-0.14229
6	75	119.9	27.3	4.392	0.64266	-0.19199
Slope: -4.37×10^{-3}				$k = 1.01 \times 10^{-2}$ min.$^{-1}$		

Table 10. Spectroscopic measurements leading to kinetic data.

(5-methyl-2-thenoyl) benzoyl peroxide

Temp.: 72.90°C.±0.05°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	123.2	3.7	33.30	1.52244	0.18241
2	180	123.2	12.3	10.02	1.00087	0.00043
3	360	123.7	24.6	5.029	0.70148	-0.15397
4	540	123.6	34.2	3.614	0.55799	-0.25337
5	720	123.0	46.7	2.634	0.42062	-0.37613
6	900	123.5	58.5	2.111	0.32449	-0.48829
Slope: -7.27×10^{-4}				$k = 1.68 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	123.5	5.0	24.70	1.39270	0.14395
2	180	123.9	14.3	8.664	0.93772	-0.02794
3	360	123.4	25.0	4.936	0.69338	-0.15902
4	540	123.8	35.2	3.517	0.54617	-0.26265
5	720	123.1	46.3	2.659	0.42472	-0.37192
6	900	123.5	57.8	2.137	0.32980	-0.48175
Slope: -6.77×10^{-4}				$k = 1.56 \times 10^{-3}$ min.$^{-1}$		

Table 11. Spectroscopic measurements leading to kinetic data.

(5-methyl-2-thenoyl) benzoyl peroxide

Temp.: 82.17°C.±0.02°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	122.4	5.0	24.48	1.38881	0.14270
2	60	122.7	13.3	9.226	0.96501	-0.01547
3	120	121.1	23.3	5.197	0.71575	-0.14521
4	180	120.8	37.0	3.265	0.51388	-0.28912
5	240	121.0	47.6	2.542	0.40518	-0.39233
6	300	121.4	61.0	1.990	0.29885	-0.52447
Slope: -2.20×10^{-3}				$k = 5.06 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	121.7	5.2	23.40	1.36922	0.13640
2	60	121.3	14.5	8.365	0.92247	-0.03503
3	120	121.5	24.8	4.899	0.69011	-0.16109
4	180	121.2	36.2	3.348	0.52479	-0.28001
5	240	121.9	48.7	2.503	0.39846	-0.39957
6	300	121.3	60.8	1.995	0.29994	-0.52302
Slope: -2.15×10^{-3}				$k = 4.95 \times 10^{-3}$ min.$^{-1}$		

Table 12. Spectroscopic measurements leading to kinetic data.

(5-methyl-2-thenoyl) benzoyl peroxide

Temp.: 90.35°C.±0.05°C. Solvent: CCl_4 plus 0.2M. sytrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	120.4	6.3	19.11	1.28126	0.10755
2	15	120.6	9.5	12.70	1.10380	0.04297
3	30	120.4	17.4	6.920	0.84011	-0.07567
4	40	120.2	25.8	4.659	0.66829	-0.17503
5	60	120.5	45.0	3.442	0.53681	-0.27019
6	75	120.2	41.9	2.869	0.45773	-0.33942
Slope: -6.24×10^{-3}				$k = 1.44 \times 10^{-2}$ min.$^{-1}$		
Run No. 2						
1	0	120.5	4.2	28.69	1.45773	0.16376
2	15	120.0	10.1	11.88	1.07782	0.03141
3	30	120.0	18.6	6.452	0.80969	-0.09168
4	45	120.6	25.8	4.674	0.66969	-0.17412
5	60	120.2	35.1	3.425	0.53466	-0.27189
6	75	120.5	43.0	2.802	0.44747	-0.34921
Slope: -6.78×10^{-3}				$k = 1.56 \times 10^{-2}$ min.$^{-1}$		

Table 13. Spectroscopic measurements leading to kinetic data.

(5-ethyl-2-thenoyl) benzoyl peroxide

Temp.: 72.90°C.±0.05°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	119.4	4.9	24.37	1.38686	0.14208
2	120	119.5	10.4	11.49	1.06032	0.02531
3	240	119.9	16.6	7.223	0.85872	-0.06616
4	360	120.1	25.8	4.655	0.66792	-0.17529
5	480	120.0	36.4	3.279	0.51812	-0.28559
6	600	119.9	43.4	2.763	0.44138	-0.35517
Slope: -8.40×10^{-4}				$k = 1.94 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	120.2	5.2	23.12	1.36399	0.13481
2	120	120.0	12.1	9.917	0.99638	-0.00157
3	240	120.7	18.6	6.489	0.81218	-0.09034
4	360	118.9	24.1	4.934	0.69320	-0.15914
5	480	120.2	35.7	3.367	0.52724	-0.27802
6	600	119.8	42.5	2.819	0.45010	-0.34669
Slope: -7.87×10^{-4}				$k = 1.81 \times 10^{-3}$ min.$^{-1}$		

Table 14. Spectroscopic measurements leading to kinetic data.

(5-ethyl-2-thenoyl) benzoyl peroxide

Temp.: 82.17°±0.02°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	118.9	4.8	24.77	1.39393	0.14426
2	60	119.0	15.5	7.677	0.88519	-0.05296
3	120	118.8	27.2	4.368	0.64028	-0.19362
4	180	118.7	36.8	3.226	0.50866	-0.29354
5	240	118.5	50.9	2.328	0.36698	-0.56193
6	300	119.0	63.3	1.880	0.27416	-0.56193
Slope: -2.28×10^{-3}				$k = 5.24 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	118.9	6.0	19.82	1.29710	0.11294
2	60	118.1	15.7	7.522	0.87633	-0.05735
3	120	118.5	26.2	4.523	0.65543	-0.18349
4	180	118.1	40.5	2.916	0.46479	-0.33273
5	240	118.3	52.2	2.266	0.35526	-0.44940
6	300	118.0	62.6	1.885	0.27531	-0.56019
Slope: -2.23×10^{-3}				$k = 5.14 \times 10^{-3}$ min.$^{-1}$		

Table 15. Spectroscopic measurements leading to kinetic data.

(5-ethyl-2-thenoyl) benzoyl peroxide

Temp.: 90.35°C.±0.05°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	120.7	3.7	32.62	1.51348	0.18013
2	15	120.3	12.5	9.624	0.98336	-0.00727
3	30	119.7	18.9	6.333	0.80161	-0.09604
4	45	120.5	26.9	4.480	0.65128	-0.18622
5	60	120.5	34.6	3.483	0.54195	-0.26600
6	75	120.3	46.2	2.604	0.41564	-0.38132
Slope: -7.00×10^{-3}				$k = 1.61 \times 10^{-2}$ min.$^{-1}$		
Run No. 2						
1	0	121.2	4.2	28.86	1.46030	0.16435
2	15	121.3	10.3	11.78	1.07115	0.02979
3	30	121.4	19.0	6.390	0.80550	-0.09393
4	45	121.6	26.7	4.554	0.65839	-0.18151
5	60	120.5	35.1	3.433	0.53567	-0.27108
6	75	121.0	44.2	2.738	0.43743	-0.35912
Slope: -6.87×10^{-3}				$k = 1.58 \times 10^{-2}$ min.$^{-1}$		

Table 16. Spectroscopic measurements leading to kinetic data.

(5-t-butyl-2-thenoyl) benzoyl peroxide

Temp.: 72.90°C.±0.05°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	120.3	4.7	25.60	1.40824	0.14860
2	180	120.5	13.9	8.669	0.97797	-0.02780
3	360	120.9	23.2	5.221	0.71775	-0.14400
4	540	119.7	33.4	3.584	0.55437	-0.25618
5	720	120.1	42.0	2.860	0.45637	-0.34065
6	900	120.2	53.1	2.364	0.35488	-0.44989
Slope: -6.42×10^{-4}				$k = 1.48 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	121.3	6.0	20.22	1.30578	0.11594
2	180	120.6	12.9	9.349	0.97077	-0.01287
3	360	121.0	23.4	5.171	0.71357	-0.14655
4	540	120.8	33.7	3.585	0.55449	-0.25610
5	720	120.1	43.0	2.793	0.44607	-0.35057
6	900	120.5	52.8	2.282	0.35832	-0.44575
Slope: -6.24×10^{-4}				$k = 1.44 \times 10^{-3}$ min.$^{-1}$		

Table 17. Spectroscopic measurements leading to kinetic data.

(5-t-butyl-2-thenoyl) benzoyl peroxide

Temp.: 82.17°C.±0.02°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	120.3	5.3	22.70	1.35603	0.12226
2	60	120.4	14.0	8.600	0.93450	-0.02942
3	120	120.7	25.7	4.697	0.67182	-0.17276
4	183	120.1	37.6	3.194	0.50433	-0.29731
5	240	120.4	46.9	2.567	0.40943	-0.38285
6	300	120.4	57.8	2.083	0.31869	-0.49662
Slope: -2.04×10^{-3}				$k = 4.69 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	119.8	5.3	22.60	1.35411	0.13162
2	60	120.3	15.5	7.761	0.88992	-0.05066
3	120	120.8	26.2	4.611	0.66380	-0.17796
4	183	119.8	36.3	3.300	0.51851	-0.28525
5	240	120.2	47.4	2.536	0.40415	-0.39340
6	300	120.2	58.0	2.072	0.31639	-0.49976
Slope: -2.04×10^{-3}				$k = 4.70 \times 10^{-3}$ min.$^{-1}$		

Table 18. Spectroscopic measurements leading to kinetic data.

(5-t-butyl-2-thenoyl) benzoyl peroxide

Temp.: 90.35°C.±0.05°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	120.1	6.2	19.37	1.28713	0.10958
2	15	120.2	10.8	11.13	1.04650	0.01995
3	30	120.0	18.8	6.383	0.80502	-0.09420
4	45	120.1	25.5	4.710	0.67302	-0.17198
5	60	120.2	33.6	3.577	0.55108	-0.25877
6	75	120.2	40.9	2.939	0.46820	-0.32957
Slope: -5.92×10^{-3}				$k = 1.36 \times 10^{-2}$ min.$^{-1}$		
Run No. 2						
1	0	120.0	7.1	16.90	1.22789	0.08920
2	15	120.4	11.9	10.12	1.00518	0.00217
3	30	119.9	18.2	6.588	0.81875	-0.08682
4	45	120.6	26.9	4.483	0.65157	-0.18602
5	60	120.4	32.8	3.671	0.56478	-0.24811
6	75	120.5	40.1	3.005	0.47784	-0.32075
Slope: -5.52×10^{-3}				$k = 1.27 \times 10^{-2}$ min.$^{-1}$		

Table 19. Spectroscopic measurements leading to kinetic data.

(5-nitro-2-thenoyl) benzoyl peroxide

Temp.: 72.90°C.±0.05°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	120.0	13.4	8.955	0.95207	-0.02.32
2	120	119.0	23.4	5.086	0.70638	-0.15095
3	240	119.9	35.7	3.359	0.52621	-0.27885
4	360	119.9	46.9	2.557	0.40773	-0.38966
5	480	120.2	53.5	2.247	0.35160	-0.45395
6	600	120.2	60.1	2.000	0.30103	-0.52143
Slope: -8.38×10^{-4}				$k = 1.93 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	121.3	11.5	10.55	1.02325	0.00988
2	120	120.8	24.3	4.971	0.69644	-0.15714
3	240	119.8	36.6	3.273	0.51495	-0.28819
4	360	119.5	42.5	2.812	0.44902	-0.34775
5	480	119.9	54.0	2.220	0.34635	-0.46042
6	600	117.5	59.7	1.968	0.29403	-0.53165
Slope: -9.76×10^{-4}				$k = 2.02 \times 10^{-3}$ min.$^{-1}$		

Table 20. Spectroscopic measurements leading to kinetic data.

(5-nitro-2-thenoyl) benzoyl peroxide

Temp.: 82.17°C.±0.02°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	121.9	12.5	9.752	0.98909	-0.00476
2	60	122.0	32.0	3.813	0.58127	-0.23560
3	120	122.0	46.3	2.635	0.42078	-0.37592
4	180	119.0	56.2	2.117	0.32572	-0.48718
5	240	119.9	64.2	1.868	0.27138	-0.56639
6	300	119.1	72.9	1.364	0.21325	-0.67101
Slope: -2.11×10^{-3}				$k = 4.86 \times 10^{-3}$ min.$^{-1}$		
Run No. 2						
1	0	119.0	12.8	9.297	0.96834	-0.01399
2	60	118.5	30.4	3.898	0.59084	-0.22856
3	120	118.7	44.3	2.680	0.42813	-0.36845
4	180	119.0	57.3	2.077	0.31744	-0.49839
5	240	118.6	65.4	1.814	0.25864	-0.58737
6	300	118.8	73.7	1.612	0.20737	-0.68319
Slope: -2.17×10^{-3}				$k = 4.99 \times 10^{-3}$ min.$^{-1}$		

Table 21. Spectroscopic measurements leading to kinetic data.

(5-nitro-2-thenoyl) benzoyl peroxide

Temp.: 90.35°C.±0.05°C. Solvent: CCl_4 plus 0.2M. styrene

Sample Number	Time Min.	I_o	I	I_o/I	A	log A
Run No. 1						
1	0	120.6	11.1	10.87	1.03623	0.01536
2	11	121.1	20.9	5.794	0.76298	-0.11748
3	20	121.5	27.0	4.500	0.65321	-0.18495
4	30	121.1	33.4	3.626	0.55943	-0.25228
5	40	120.9	40.7	2.971	0.47290	-0.38891
6	50	120.9	47.2	2.561	0.40841	-0.38891
Slope: -7.83×10^{-3}				$k = 1.80 \times 10^{-2}$ min.$^{-1}$		
Run No. 2						
1	0	121.0	10.8	11.20	1.04922	0.02078
2	11	122.6	18.0	6.811	0.83321	-0.07925
3	20	120.4	26.3	4.578	0.66068	-0.18000
4	30	121.7	35.1	3.467	0.53995	-0.26761
5	40	121.5	41.4	2.935	0.46761	-0.33013
6	50	120.8	47.0	2.570	0.40993	-0.38732
Slope: -8.30×10^{-3}				$k = 1.91 \times 10^{-2}$ min.$^{-1}$		

Table 22. Kinetic data of peroxides.

Compound	Temperature in Degrees C.	k in min.$^{-1}$ (x 103)	Half Life in Minutes	Energy* of Activation (Kcal. mole^{-1})	s (sec.$^{-1}$)	Entropy of Activation** (e.u.)	Entropy of Activation (Average e.u.)
2-Thenoyl	72.90	1.19	595		8.71×10^{15}	12.12	
Benzoyl	82.17	4.00	173	32.9	9.62×10^{15}	12.30	12.2
	90.35	11.82	58.6		1.00×10^{16}	12.29	
3-Thenoyl	72.90	1.11	625		6.37×10^{15}	11.49	
Benzoyl	82.17	3.62	191	32.5	6.04×10^{15}	11.34	11.5
	90.35	10.75	58.6		6.46×10^{15}	11.42	
(5-Methyl-	72.90	1.62	429		3.29×10^{15}	10.25	
2-Thenoyl)	82.17	5.01	139	31.8	3.14×10^{15}	10.04	10.2
Benzoyl	90.35	14.98	46.2		3.77×10^{15}	10.35	
(5-Ethyl-	72.90	1.87	370		6.10×10^{14}	6.83	
2-Thenoyl)	82.17	5.19	134	30.6	6.46×10^{14}	6.78	6.82
Benzoyl	90.35	15.97	43.4		5.56×10^{14}	6.85	
(5-t-Butyl-	72.90	1.46	475		1.99×10^{15}	9.06	
2-Thenoyl)	82.17	4.69	148	31.3	1.91×10^{15}	9.19	9.10
Butyl	90.35	13.18	52.3		1.17×10^{15}	9.06	
(5-Nitro-	72.90	1.97	351		4.34×10^{15}	10.63	
2-Thenoyl)	82.17	4.93	141	31.9	3.24×10^{15}	9.83	10.4
Benzoyl	90.57	18.57	37.3		4.42×10^{15}	10.67	

* Obtained from a plot of log k against 1/T.
** Obtained from the Eyring equation (13).


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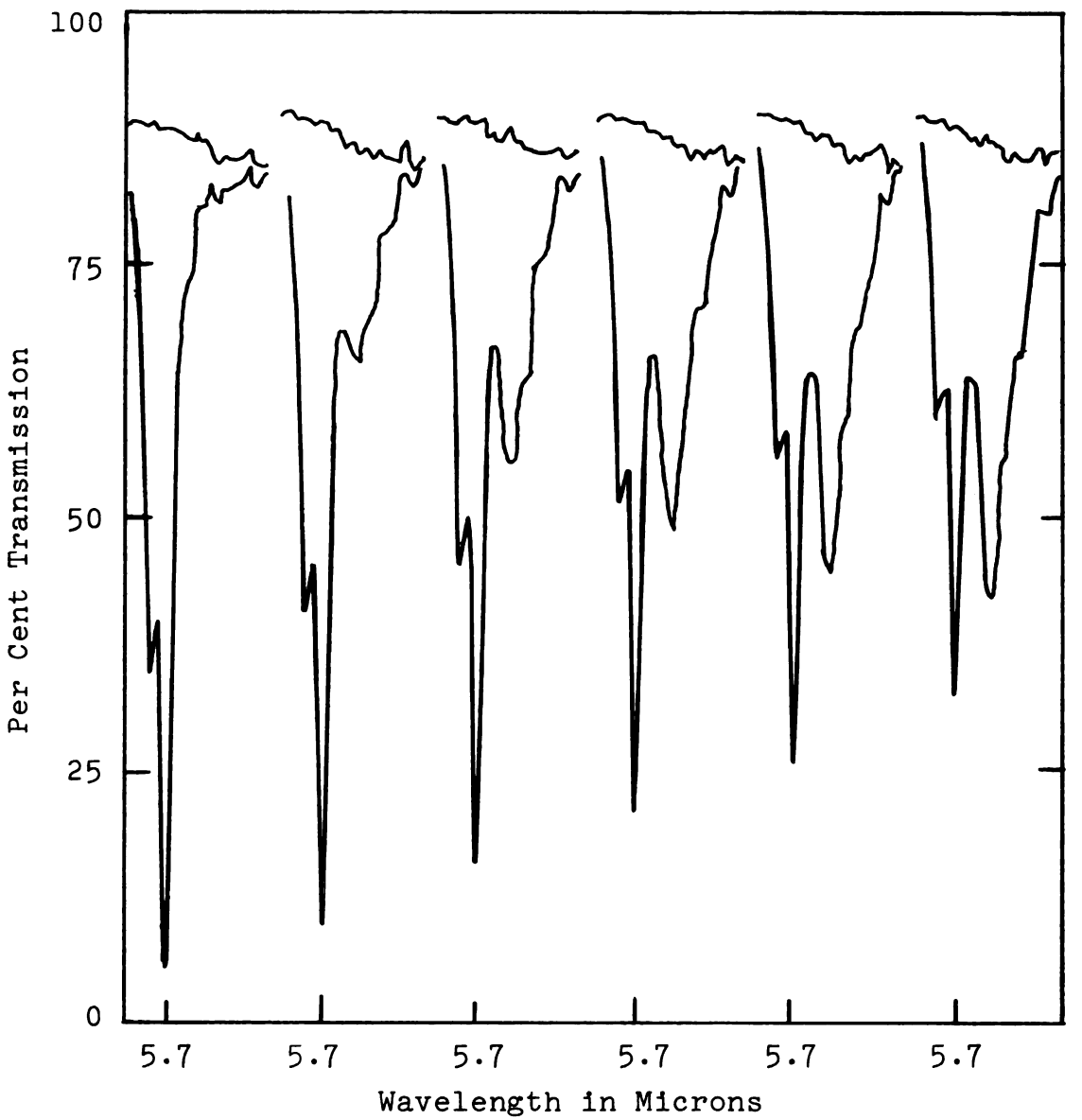

Figure 1. Quantitative infrared spectra of the decomposition of 2-thenoyl benzoyl peroxide at 72.90° in carbon tetracloride, 0.2M. in styrene.

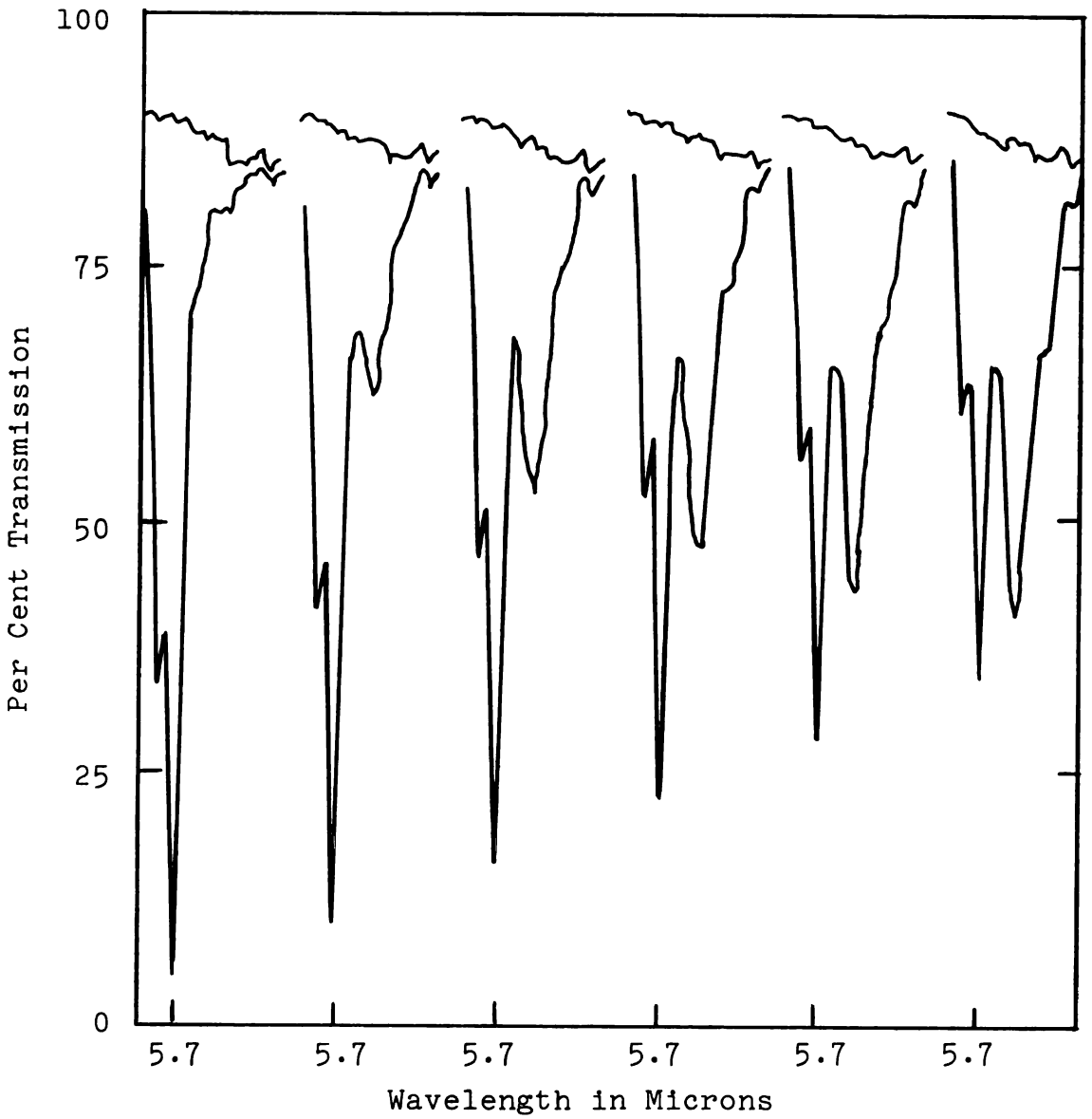

Figure 2. Quantitative infrared spectra of the decomposition of 2-thenoyl benzoyl peroxide at 82.17° in carbon tetrachloride, 0.2M. in styrene.

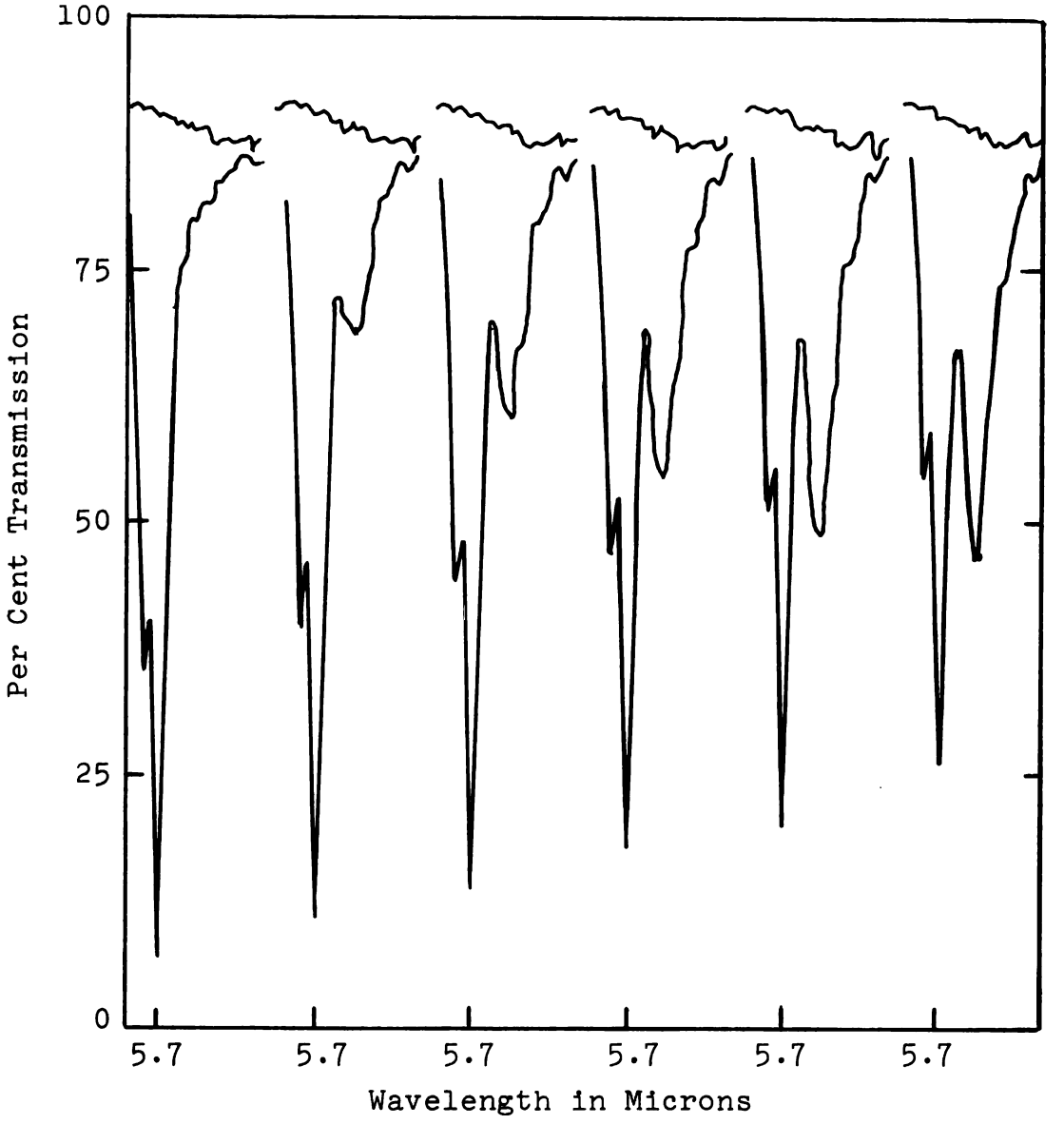

Figure 3. Quantitative infrared spectra of the decomposition of 2-thenoyl benzoyl peroxide at 90.35° in carbon tetrachloride, 0.2M. in styrene.

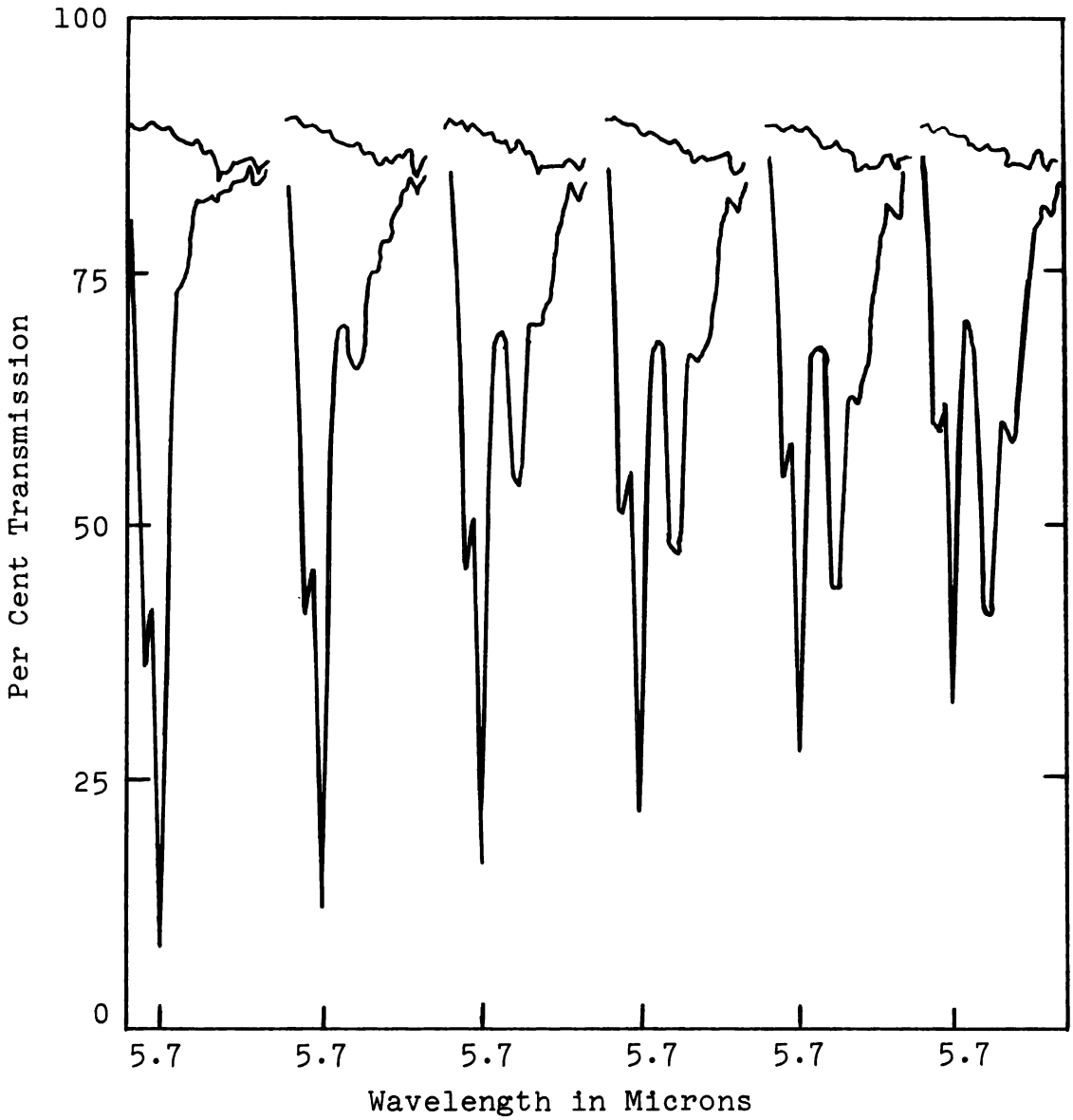

Figure 4. Quantitative infrared spectra of the decomposition of 3-thenoyl benzoyl peroxide at 72.90° in carbon tetrachloride, 0.2M. in styrene.

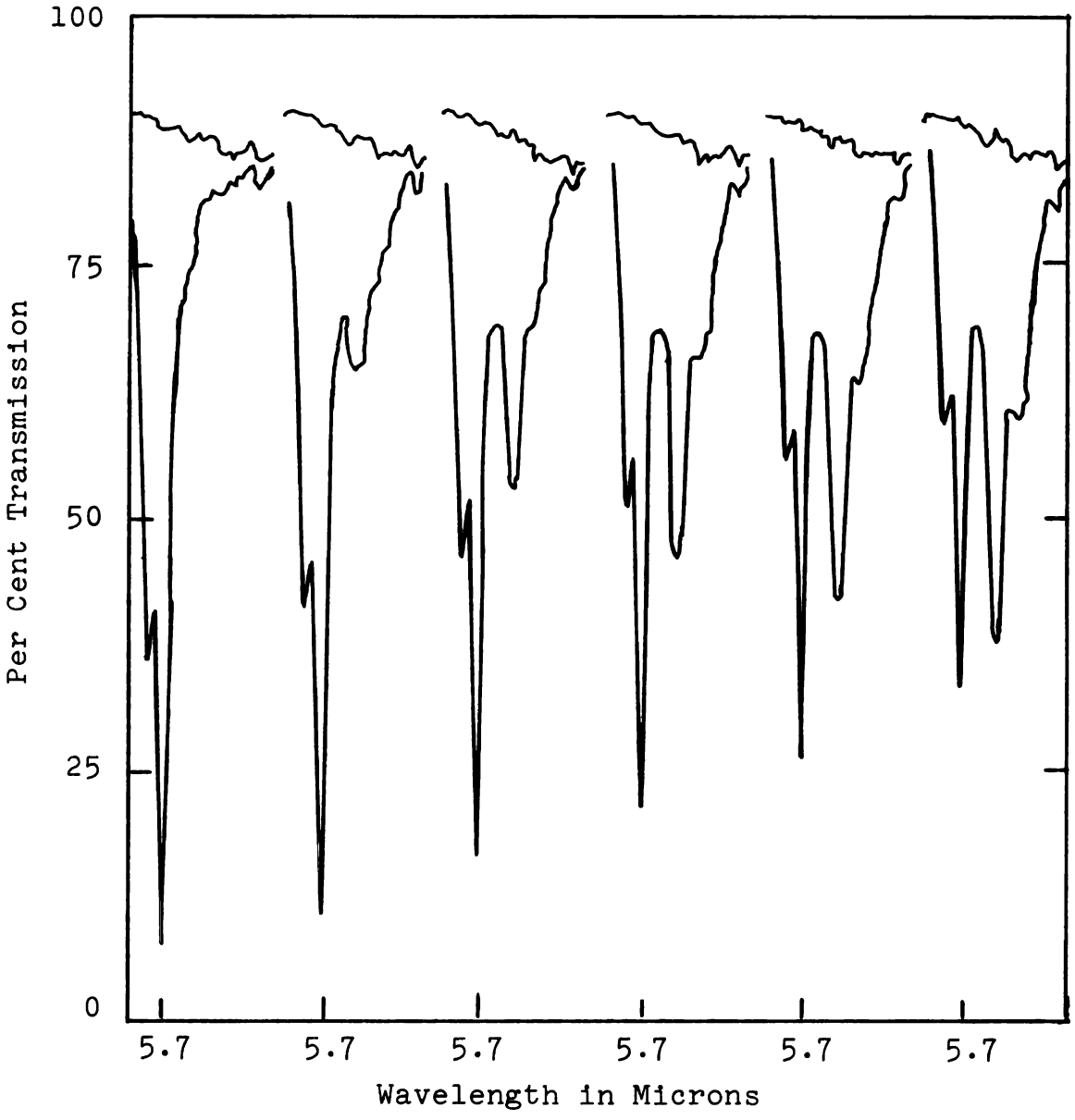

Figure 5. Quantitative infrared spectra of the decomposition of 3-thenoyl benzoyl peroxide at 82.17° in carbon tetrachloride, 0.2M. in styrene.

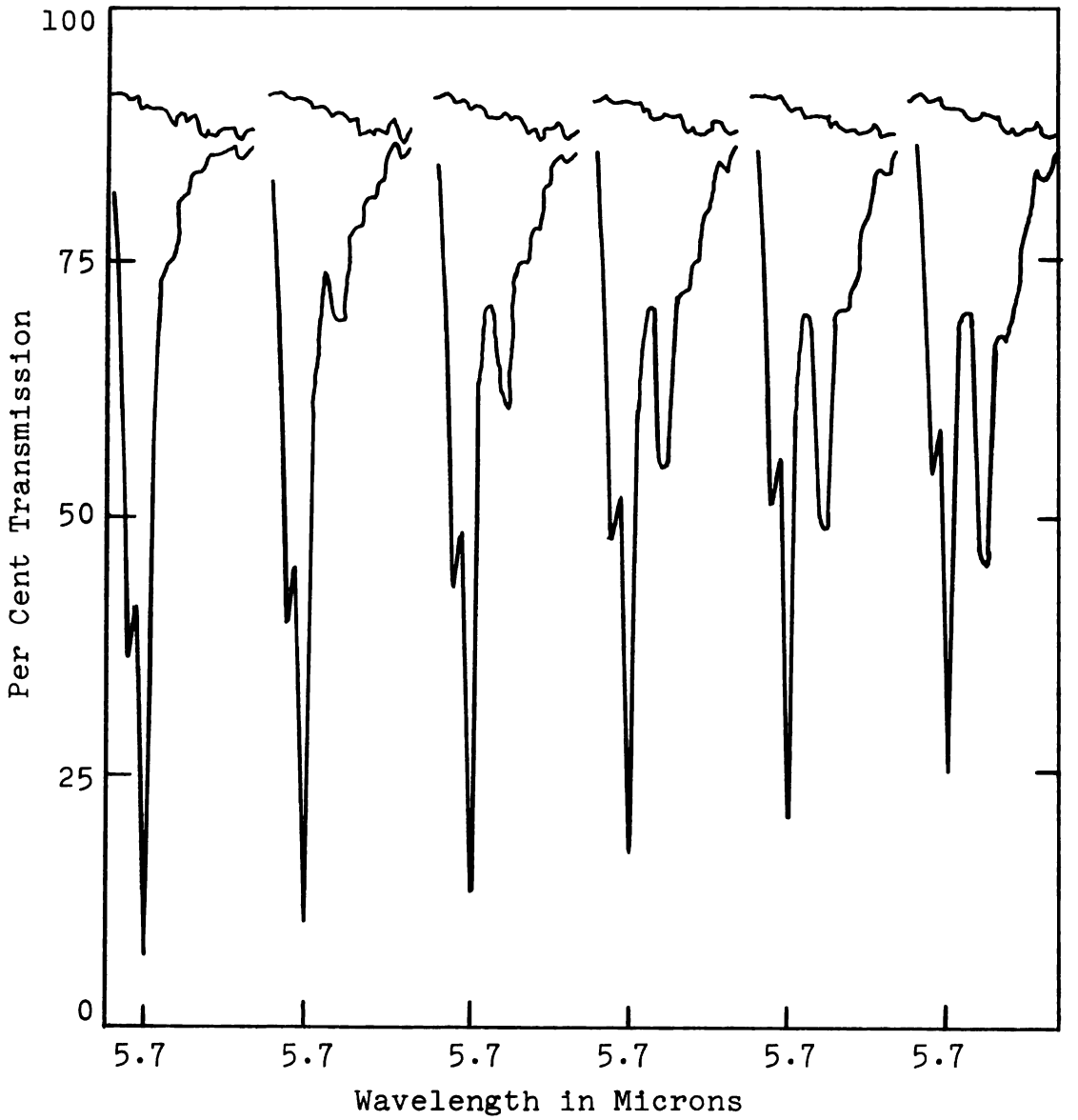

Figure 6. Quantitative infrared spectra of the decomposition of 3-thenoyl benzoyl peroxide at 90.35° in carbon tetrachloride, 0.2M. in styrene.

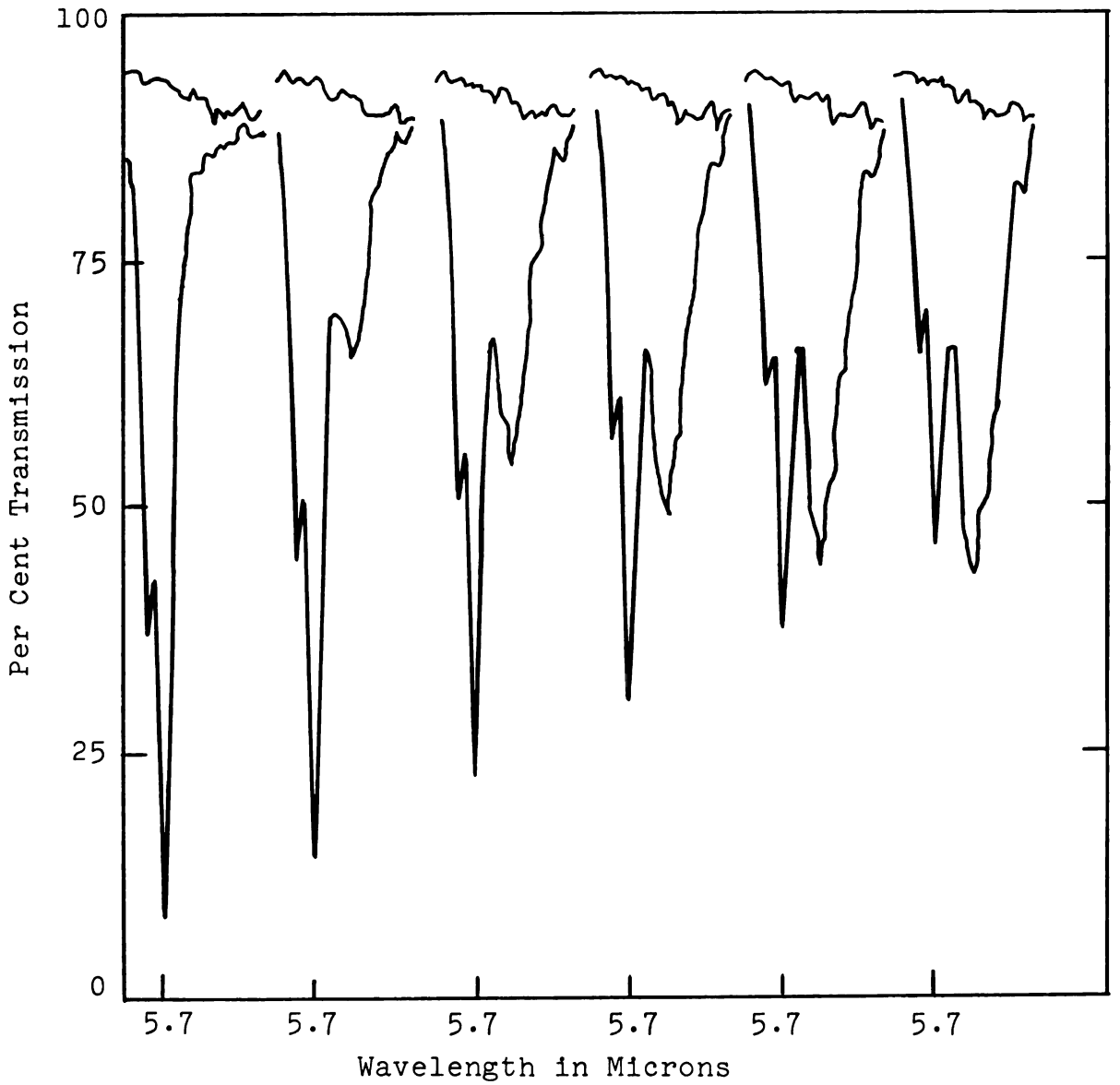

Figure 7. Quantitative infrared spectra of the decomposition of (5-methyl-2-thenoyl) benzoyl peroxide at 72.90° in carbon tetrachloride, 0.2M. in styrene.

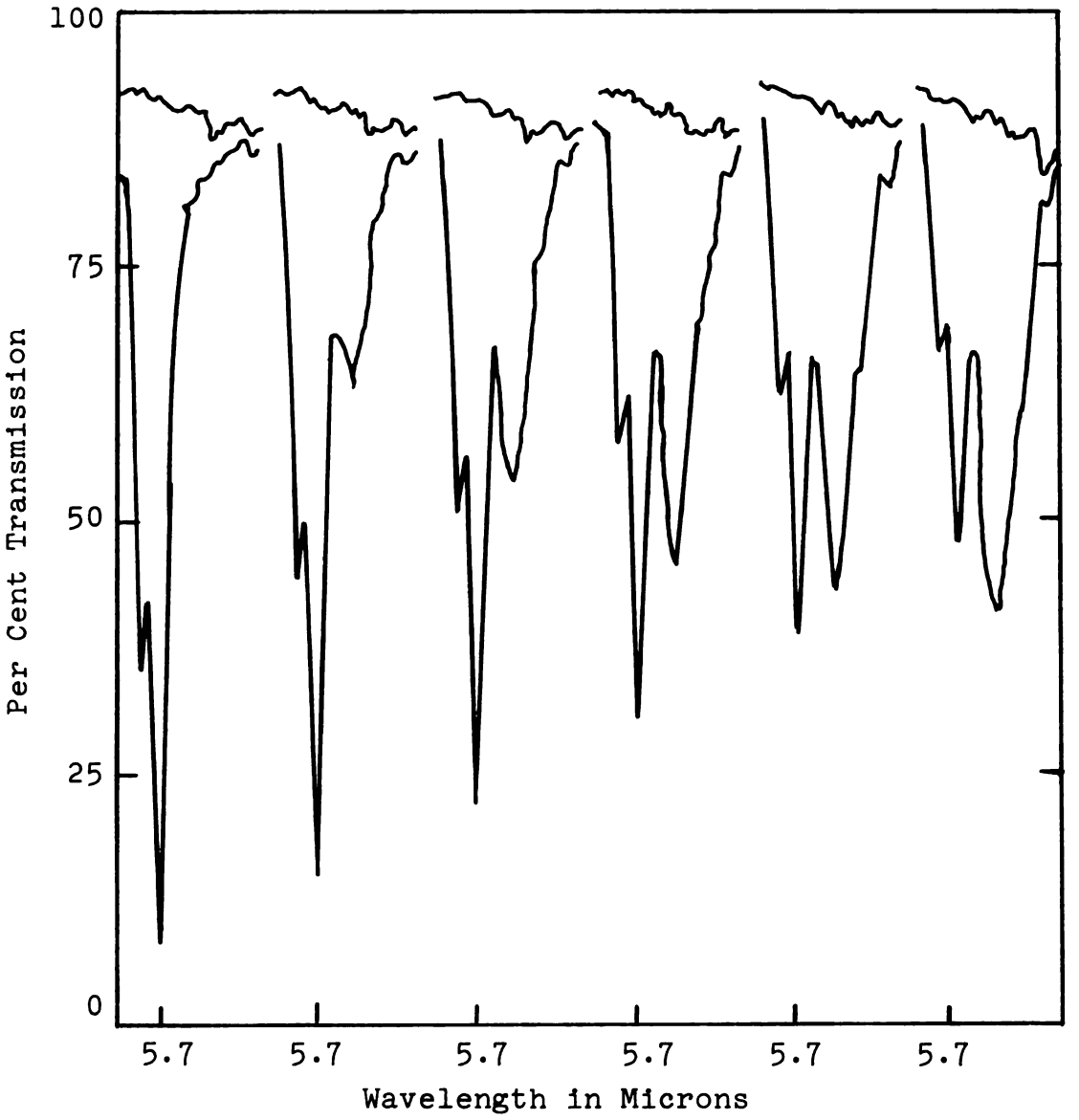

Figure 8. Quantitative infrared spectra of the decomposition of (5-methyl-2-thenoyl) benzoyl peroxide at 82.17° in carbon tetrachloride, 0.2M. in styrene.

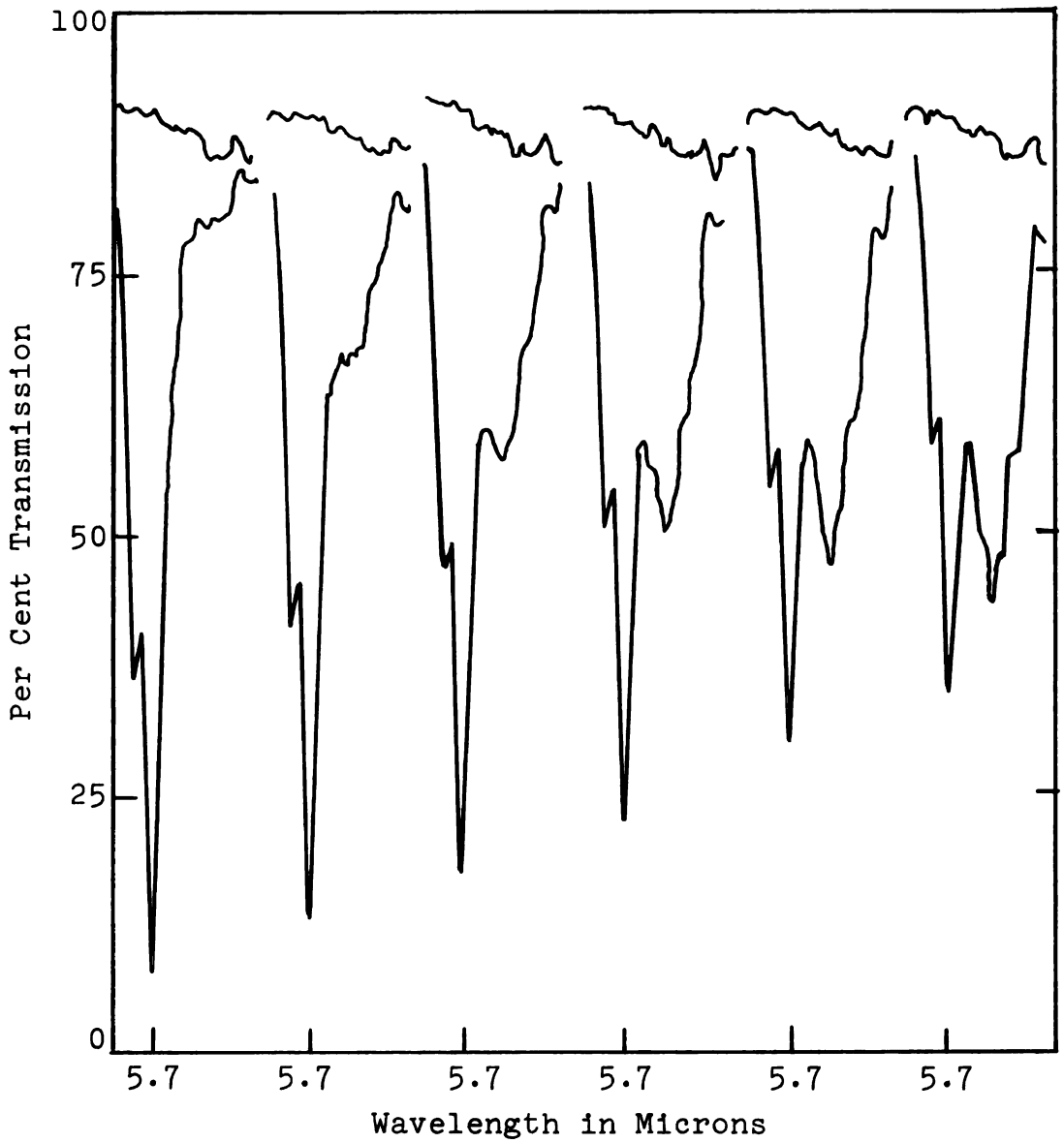

Figure 10. Quantitative infrared spectra of the decomposition of (5-ethyl-2-thenoyl) benzoyl peroxide at 72.90° in carbon tetrachloride, 0.2M. in styrene.

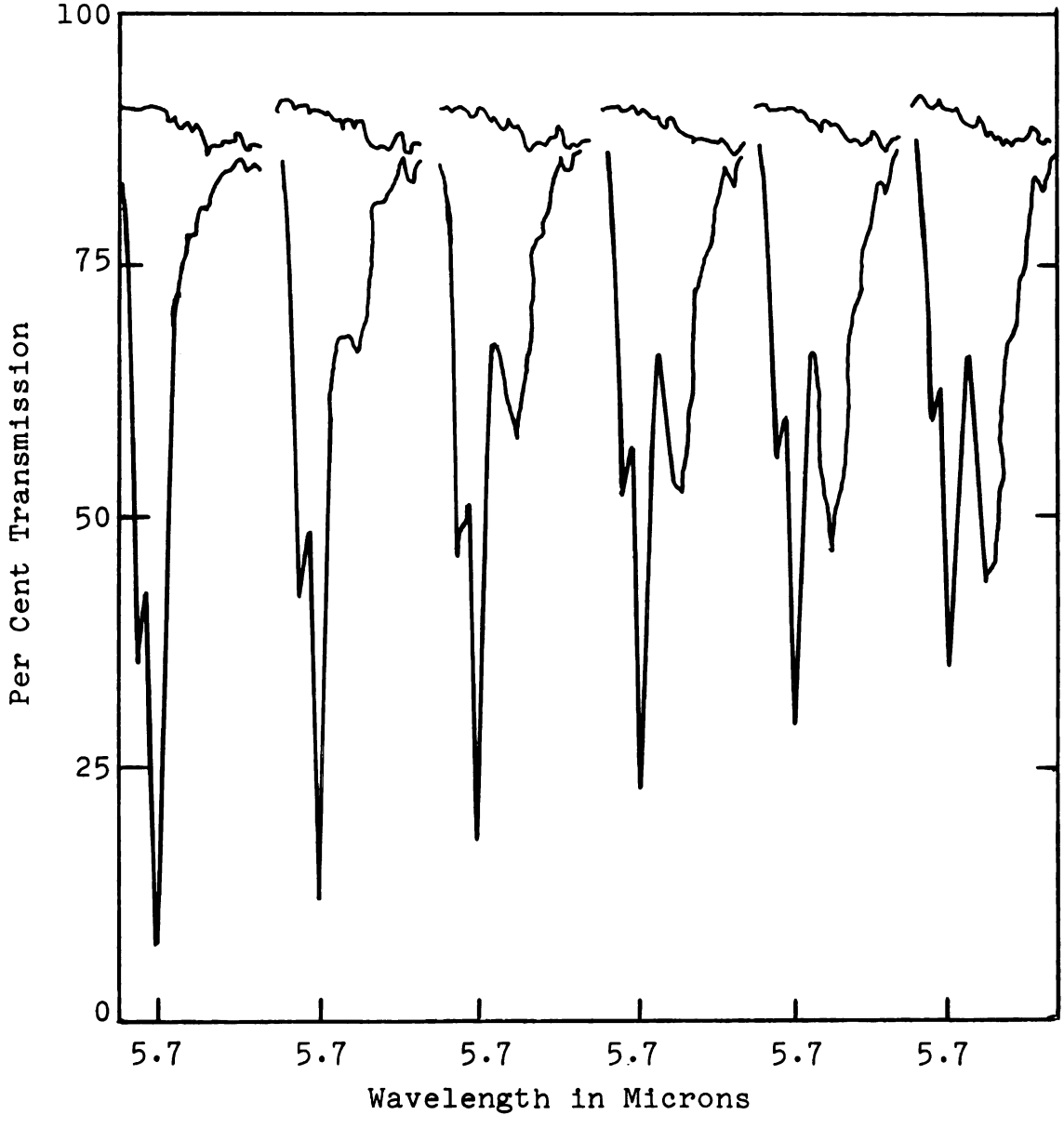

Figure 9. Quantitative infrared spectra of the decomposition of (5-methyl-2-thenoyl) benzoyl peroxide at 90.35° in carbon tetrachloride, 0.2M. in styrene.

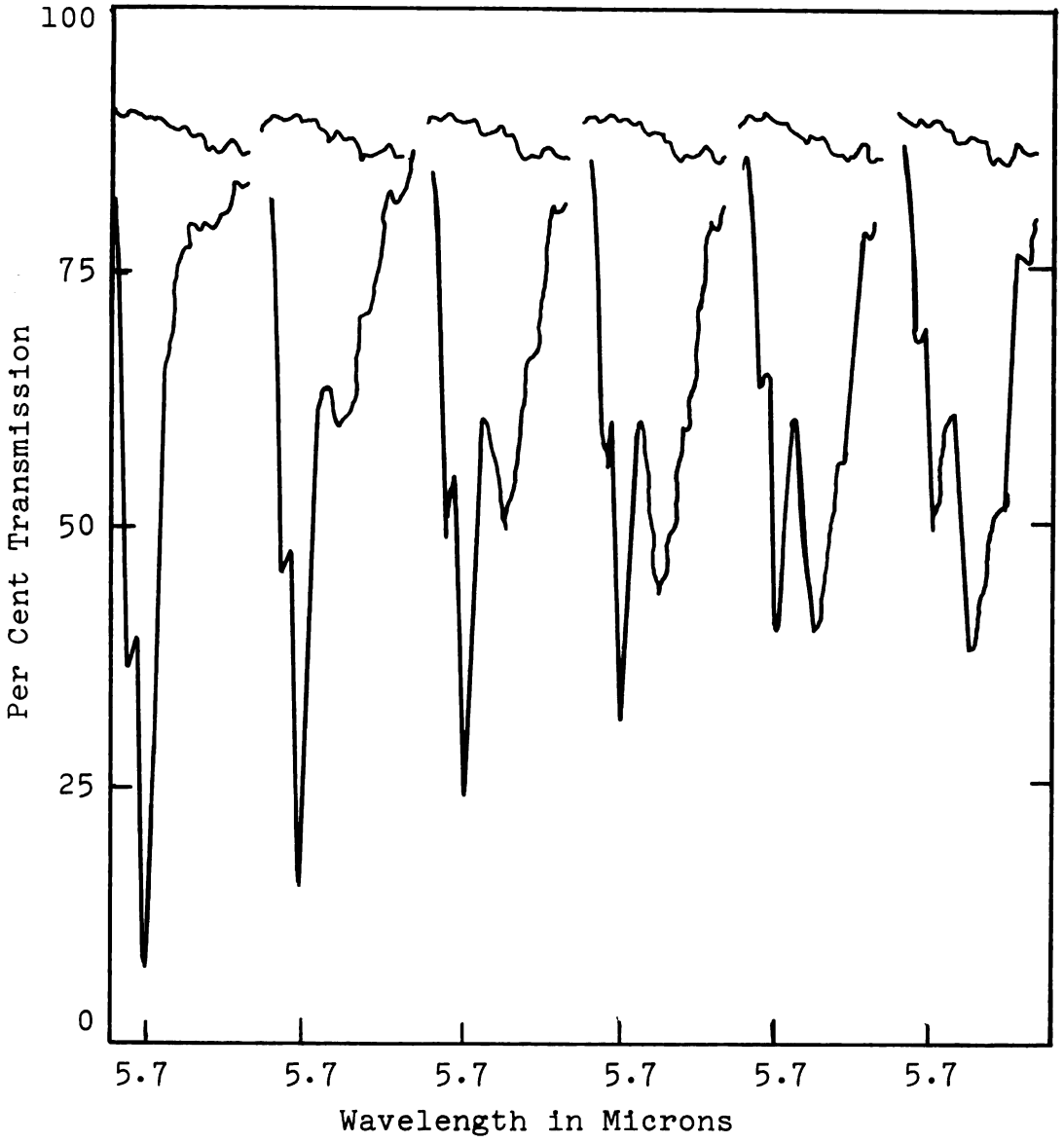

Figure 11. Quantitative infrared spectra of the decomposition of (5-ethyl-2-thenoyl) benzoyl peroxide at 82.17° in carbon tetrachloride, 0.2M. in styrene.

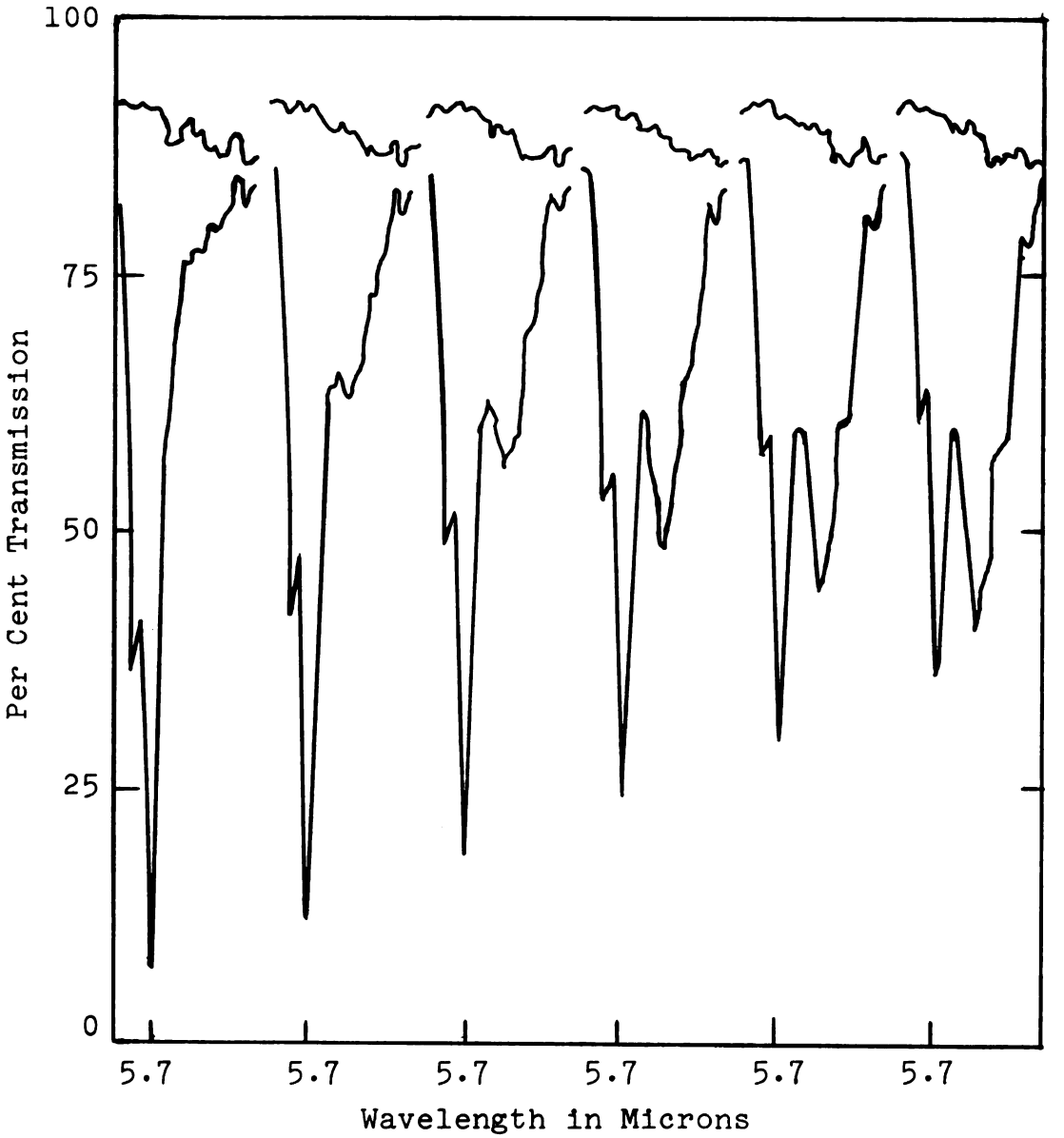

Figure 12. Quantitative infrared spectra of the decomposition of (5-ethyl-2-thenoyl) benzoyl peroxide at 82.17° in carbon tetrachloride, 0.2M. in styrene.

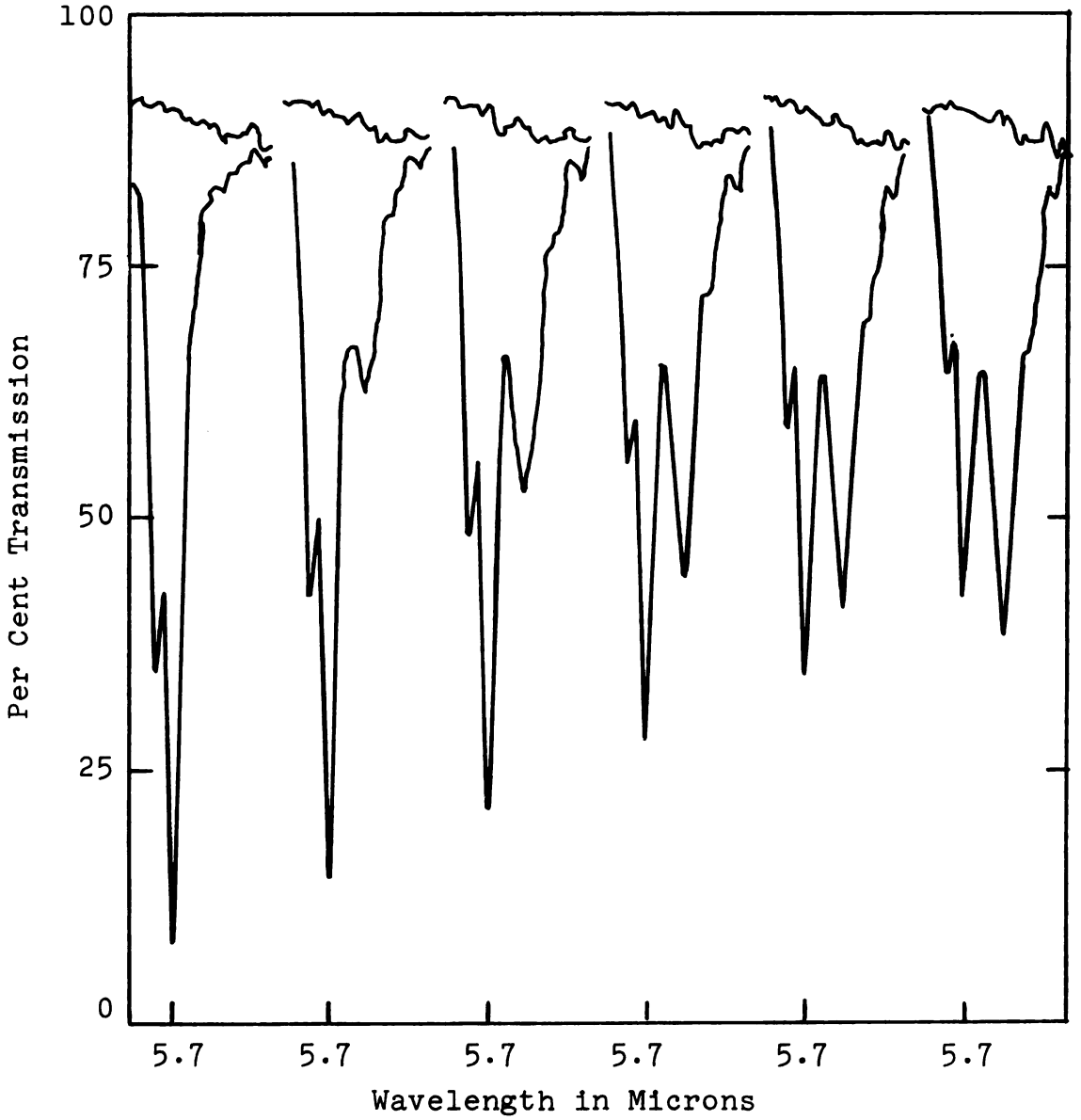

Figure 13. Quantitative infrared spectra of the decomposition of (5-t-butyl-2-thenoyl) benzoyl peroxide at 72.90° in carbon tetrachloride, 0.2M. in styrene.

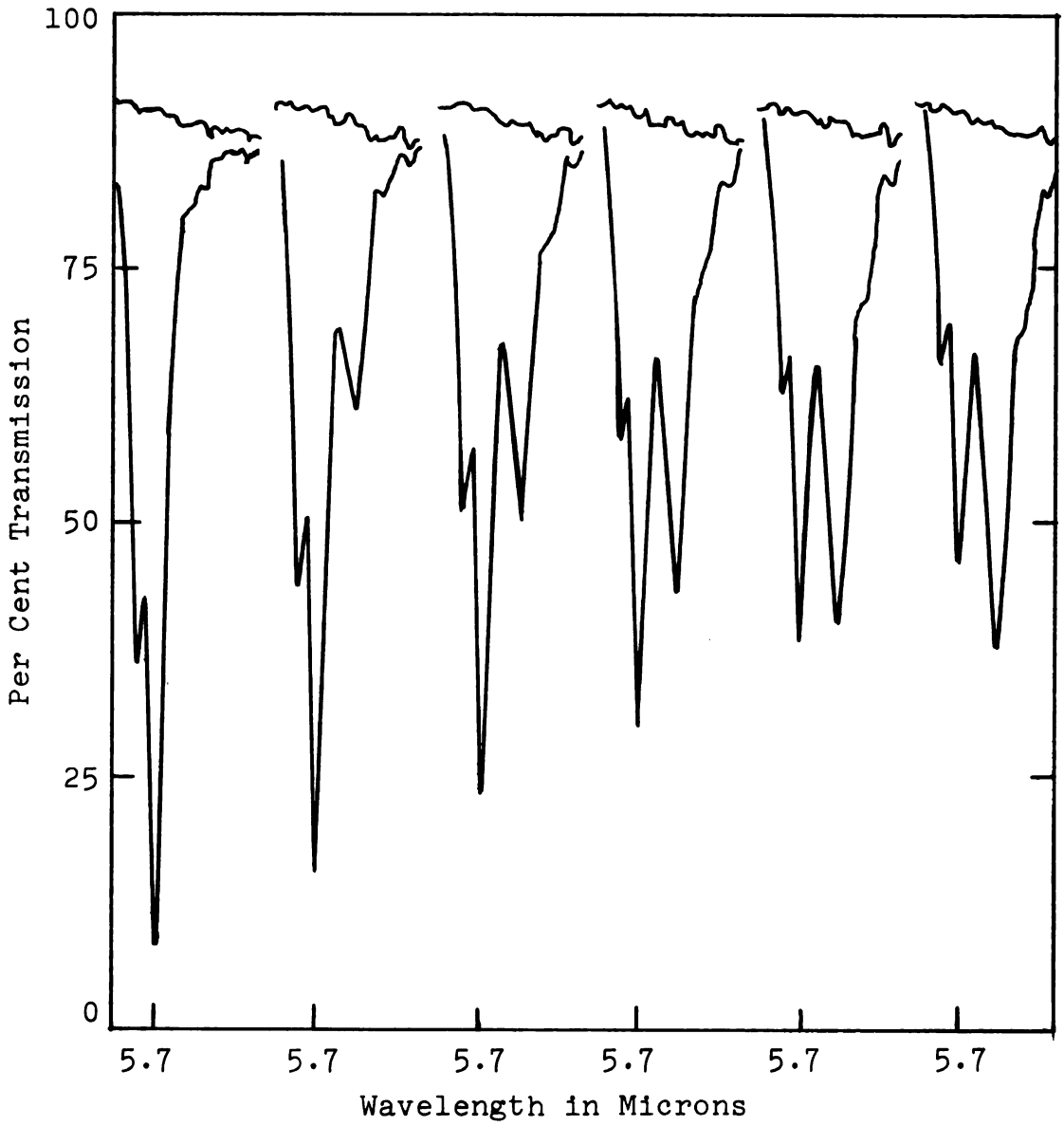

Figure 14. Quantitative infrared spectra of the decomposition of (5-t-butyl-2-thenoyl) benzoyl peroxide at 82.17° in carbon tetrachloride, 0.2M. in styrene.

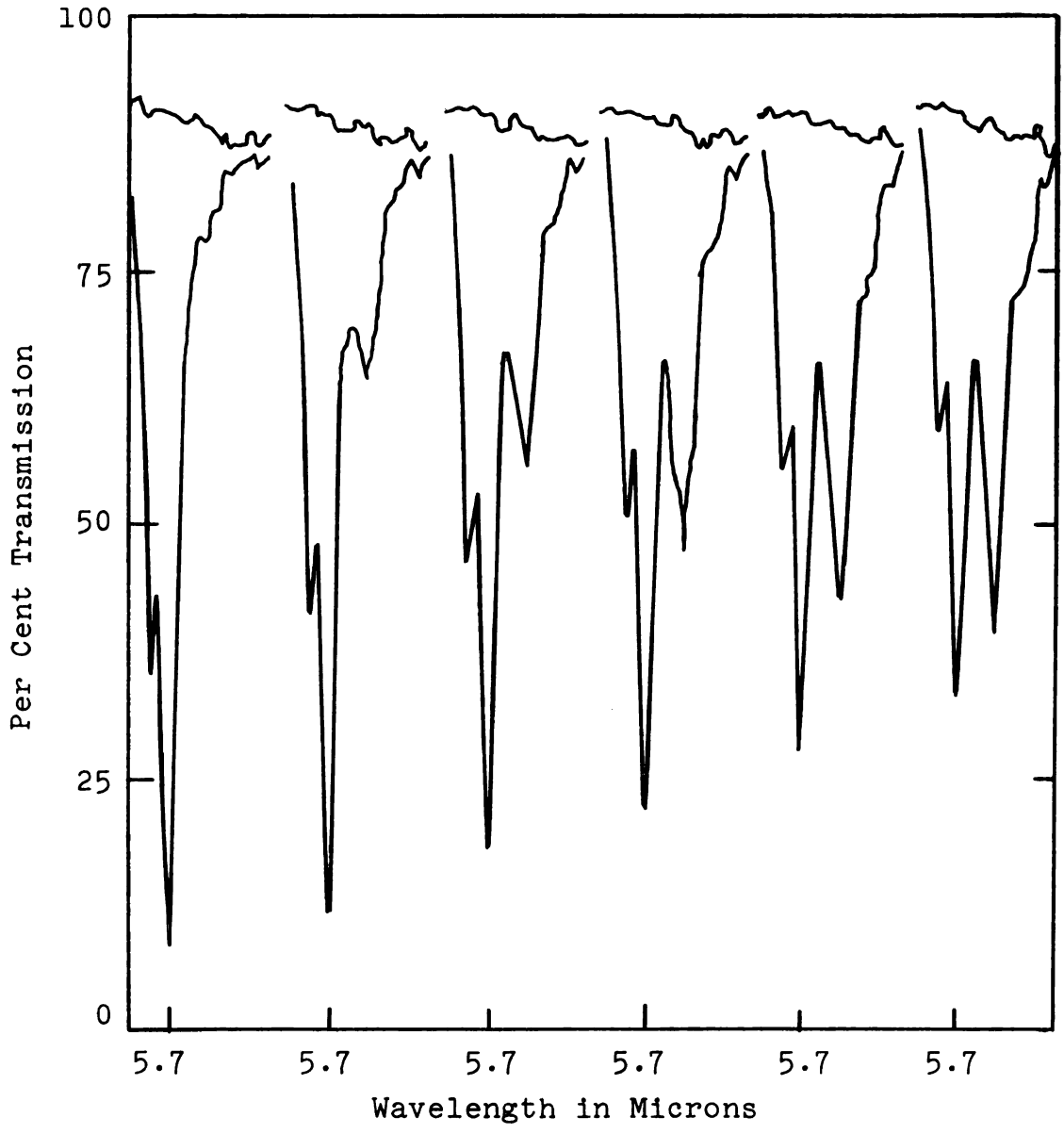

Figure 15. Quantitative infrared spectra of the decomposition of (5-t-butyl-2-thenoyl) benzoyl peroxide at 90.35° in carbon tetrachloride, 0.2M. in styrene.

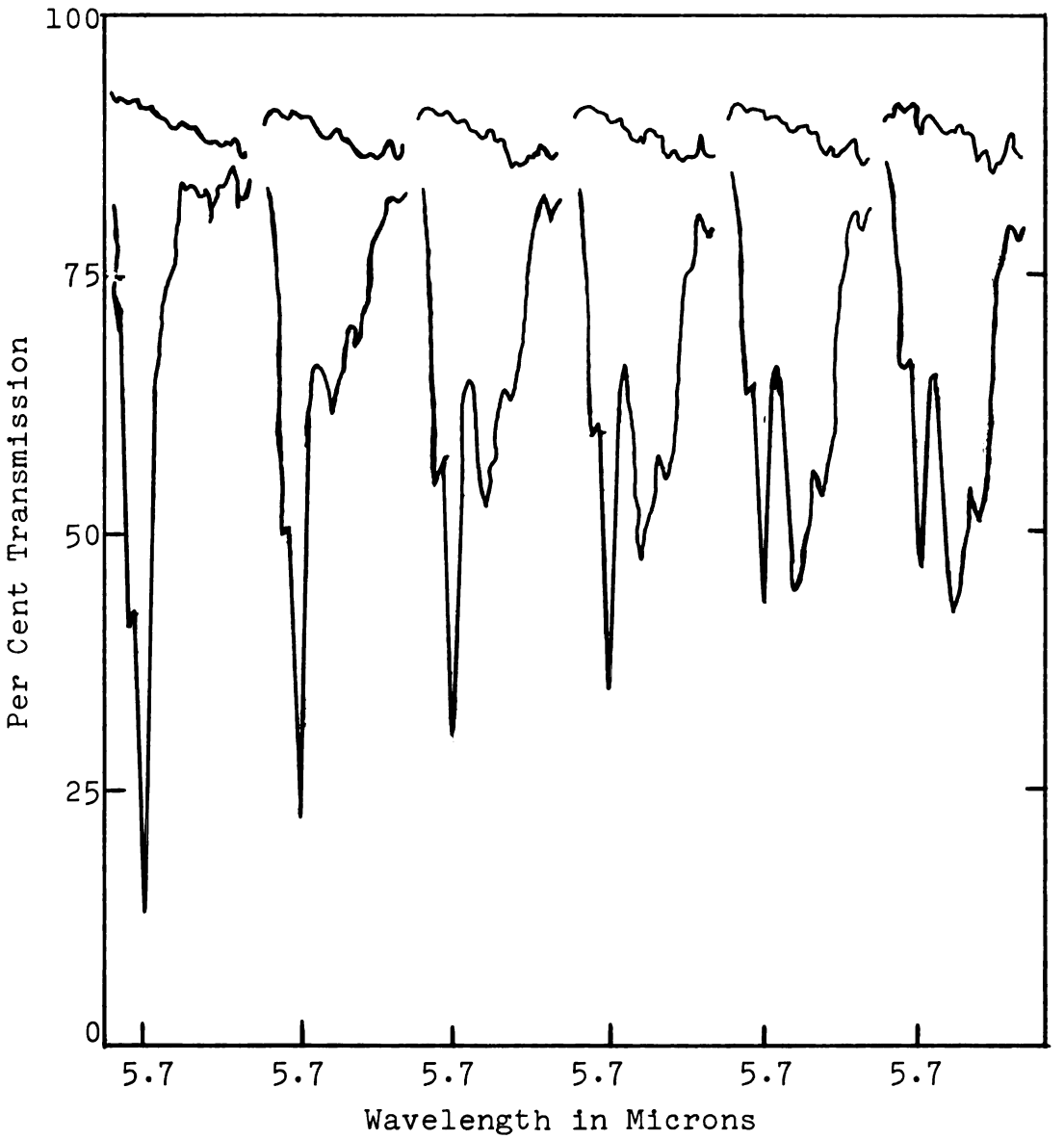

Figure 16. Quantitative infrared spectra of the decomposition of (5-nitro-2-thenoyl) benzoyl peroxide at 72.90° in carbon tetrachloride, 0.2M. in styrene.

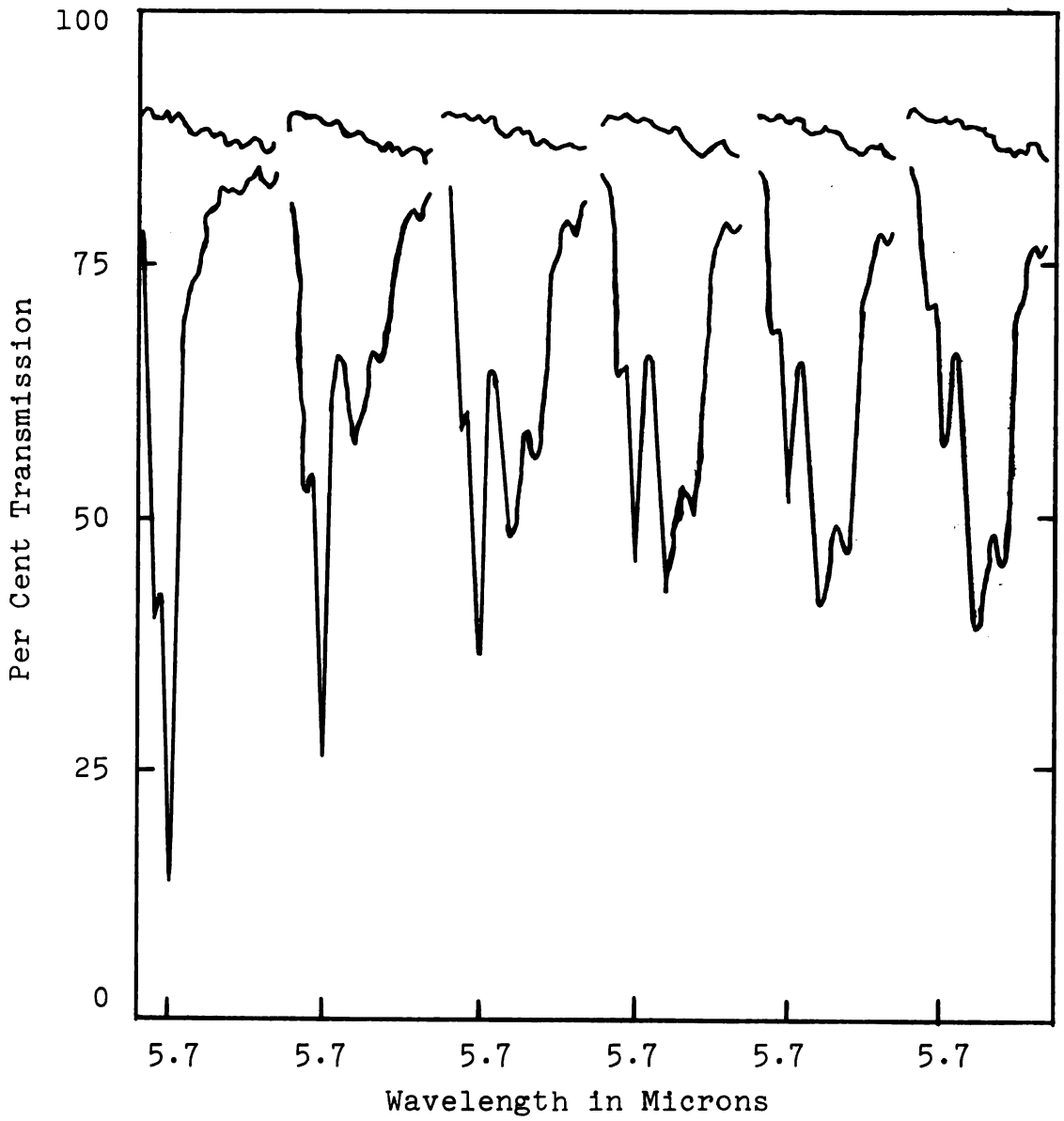

Figure 17. Quantitative infrared spectra of the decomposition of (5-nitro-2-thenoyl) benzoyl peroxide at 82.17° in carbon tetrachloride, 0.2M. in styrene.

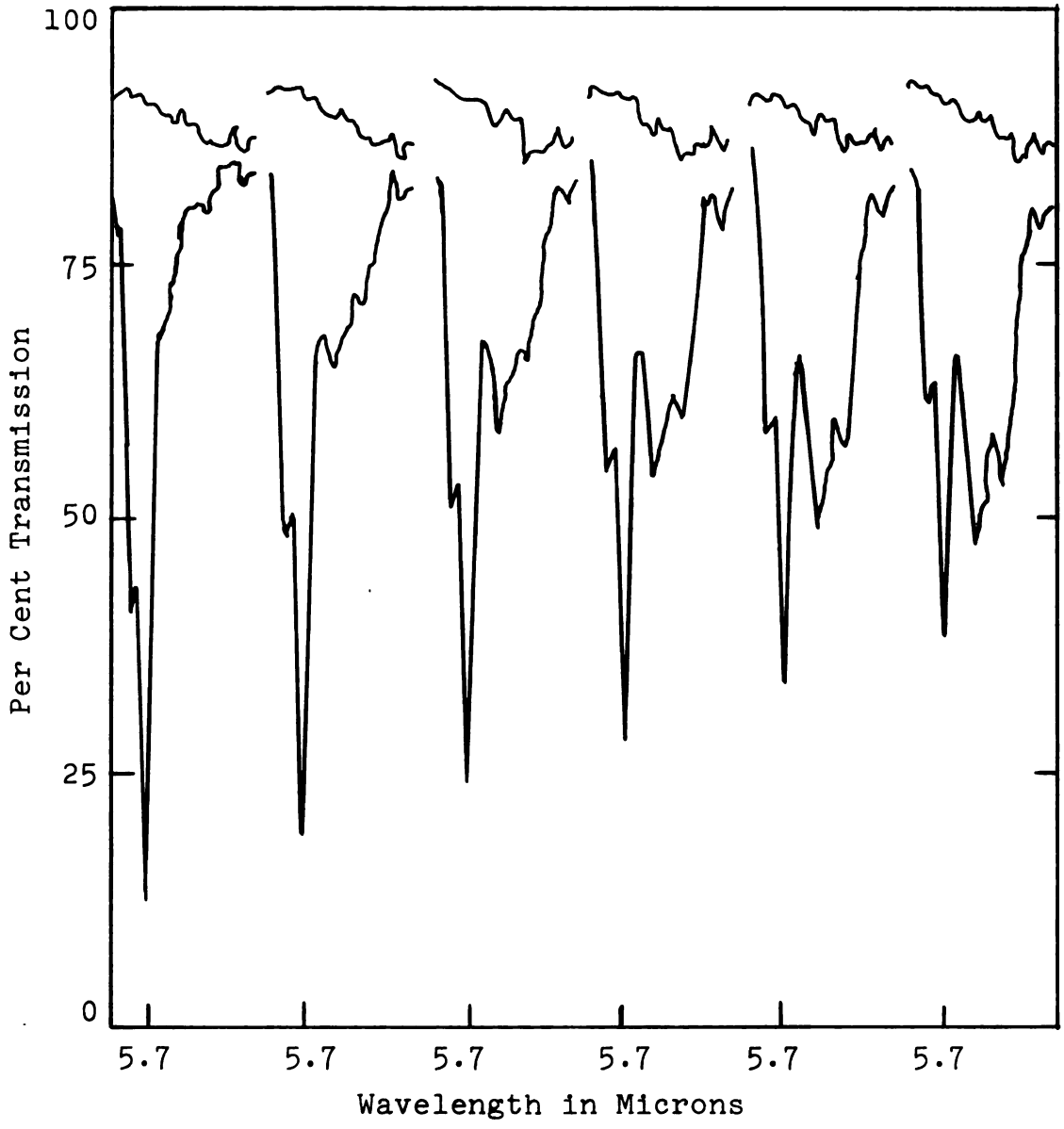

Figure 18. Quantitative infrared spectra of the decomposition of (5-nitro-2-thenoyl) benzoyl peroxide at 90.35° in carbon tetrachloride, 0.2M. in styrene.

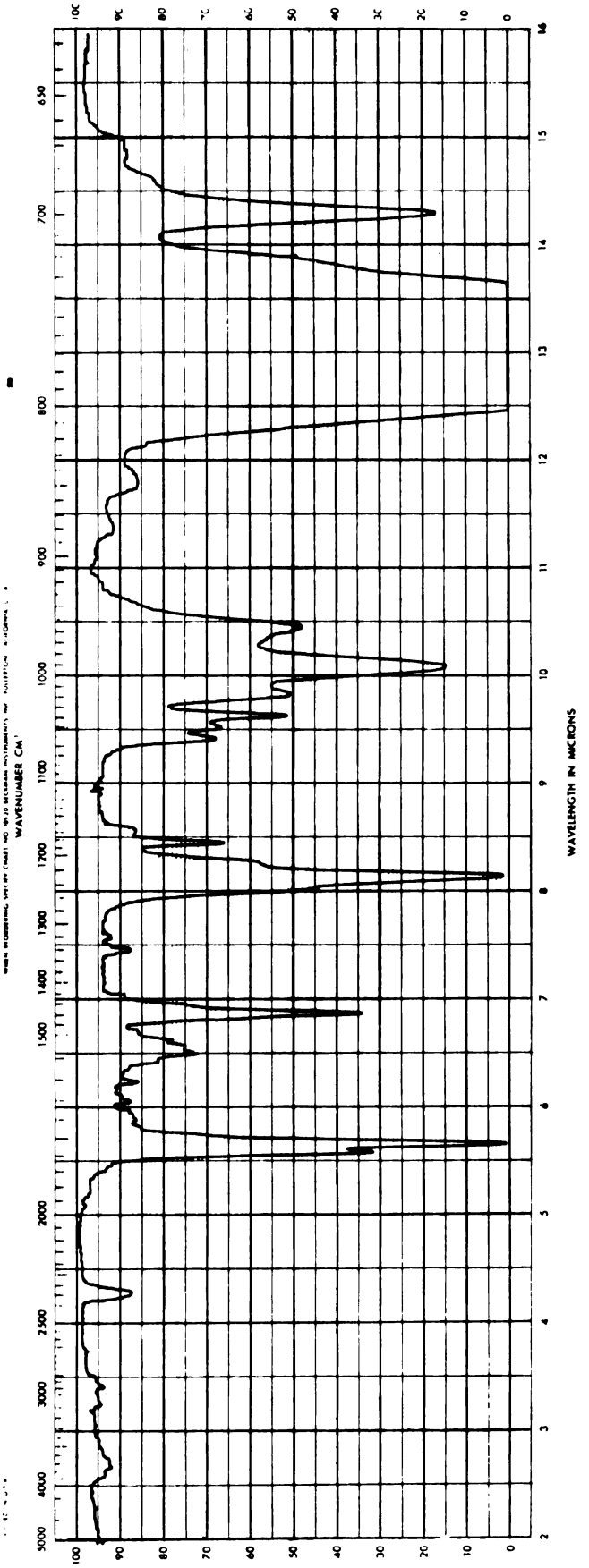

Figure 19. Infrared spectrum of (5-methyl-2-thenoyl) benzoyl peroxide in carbon tetrachloride.

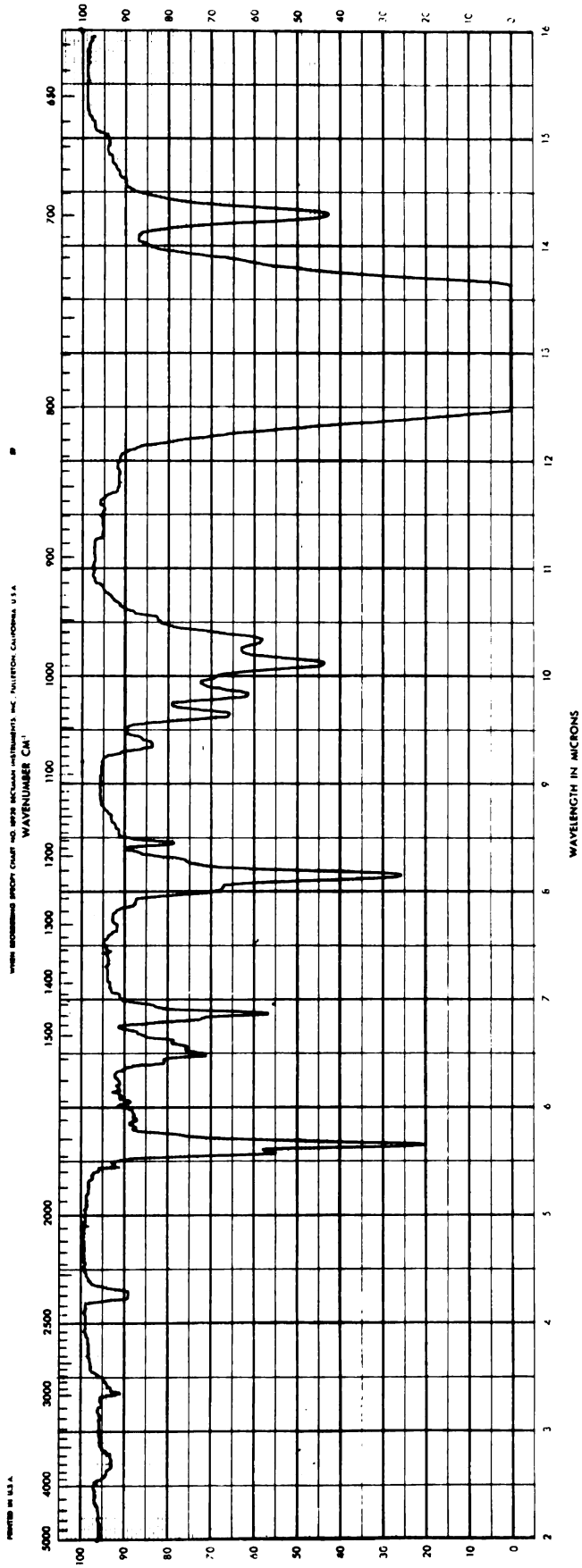

Figure 20. Infrared spectrum of (5-ethyl-2-thenoyl) benzoyl peroxide in carbon tetrachloride.

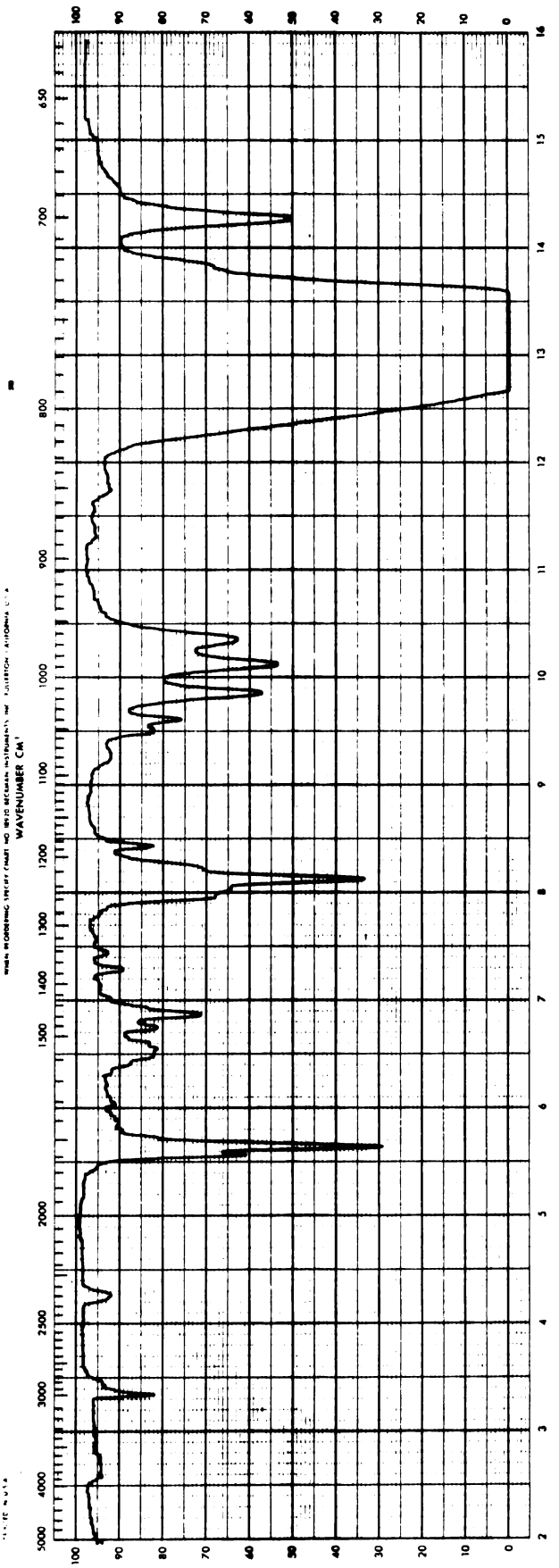

Figure 21. Infrared spectrum of (5-t-butyl-2-thenoyl) benzoyl peroxide in carbon tetrachloride.

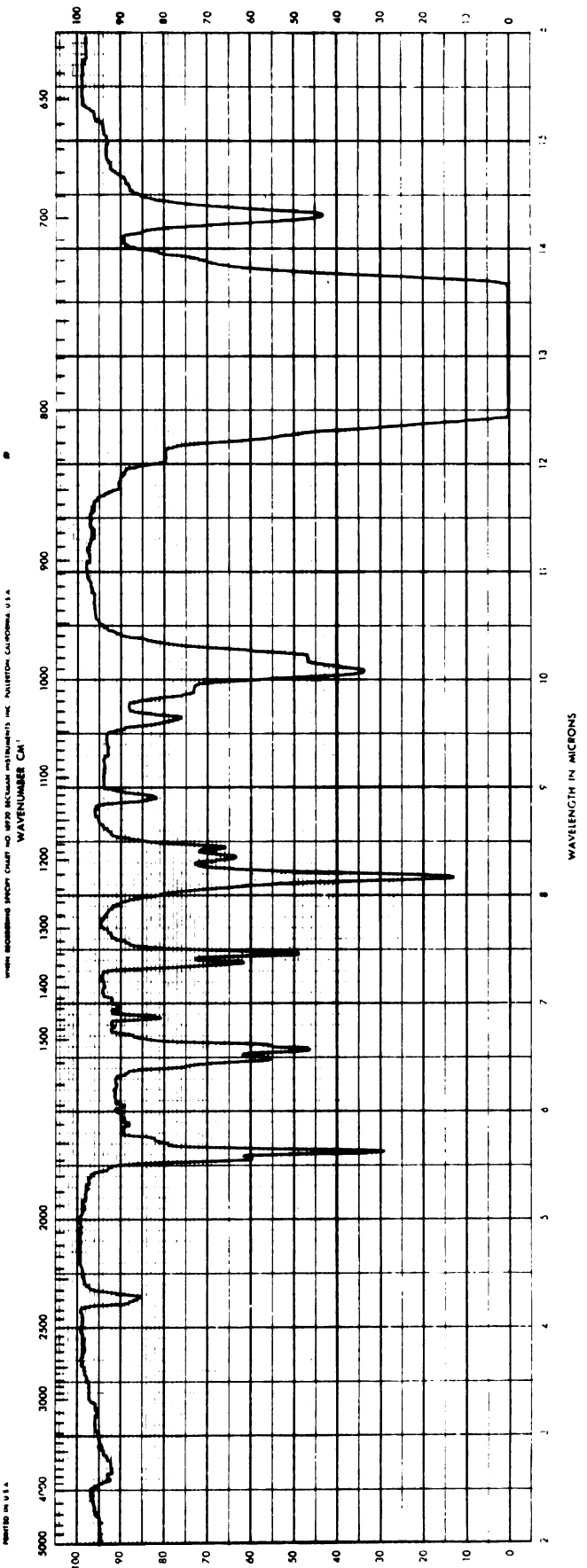

Figure 22. Infrared spectrum of (5-nitro-2-thenoyl) benzoyl peroxide in carbon tetrachloride.

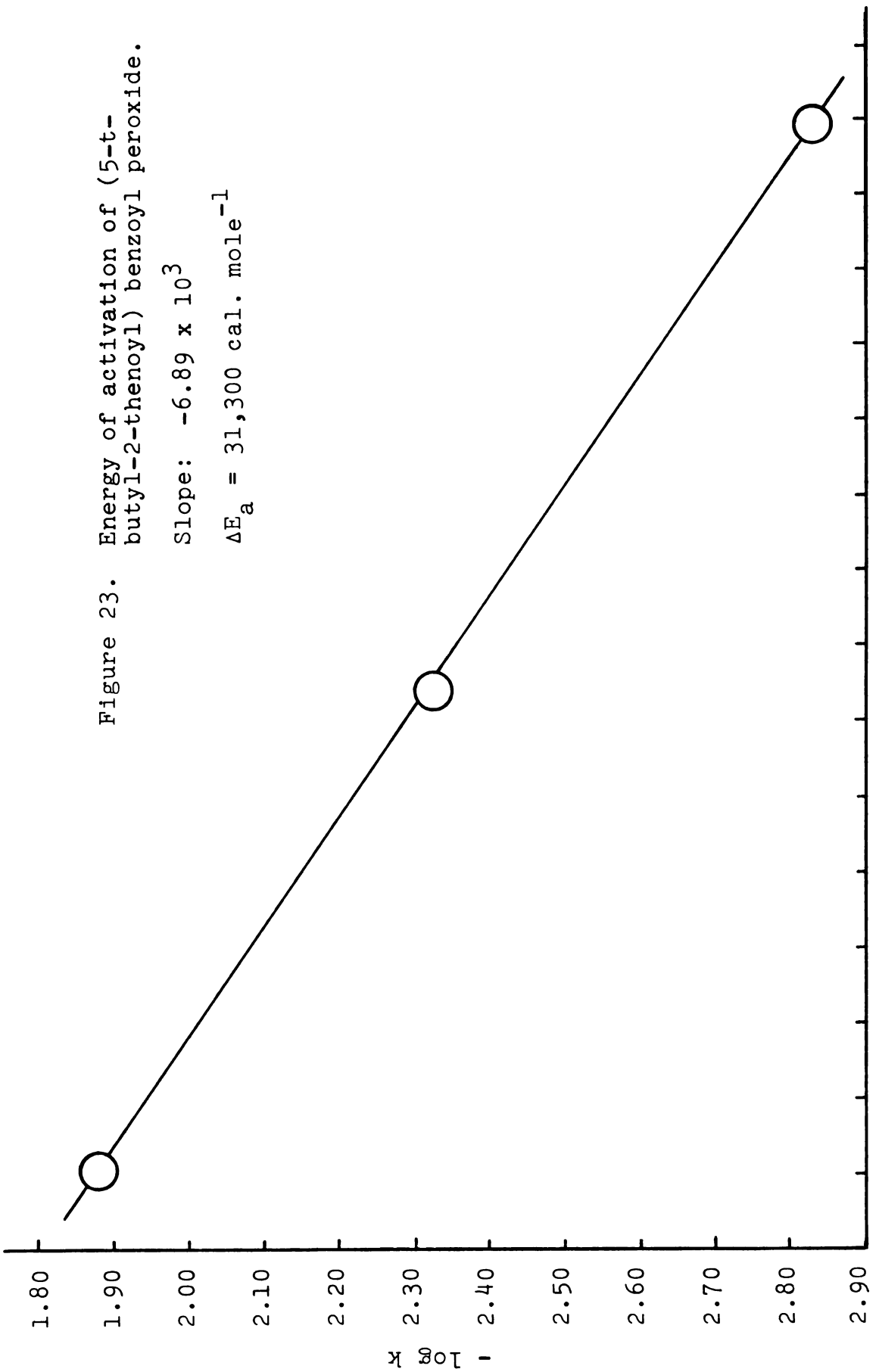

Figure 23. Energy of activation of (5-t-butyl-2-thenoyl) benzoyl peroxide.

Slope: -6.89×10^3

$\Delta E_a = 31{,}300$ cal. $mole^{-1}$