THE PREPARATION AND RATES OF DECOMPOSITION OF VARIOUS 2 AND 3-BENZO (B) THENOYL PEROXIDES

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ABSTRACT

THE PREPARATION AND RATES OF DECOMPOSITION OF
VARIOUS 2 AND 3-BENZO [b] THENOYL PEROXIDES

by Ralph Leslie Wisner

The purpose of this investigation was to prepare some 3 or 2-substituted, 2 or 3-benzo [b] thenoyl peroxides and determine their rates of decomposition at several temperatures.

In the presence of a radical scavenger, the decomposition rates were all first order. However, in the absence of a scavenger, the decompositions were higher than first order and increased with increasing peroxide concentration. The rates of decomposition of the 3 or 2-substituted, 2 or 3-benzo [b] thenoyl peroxides were much faster than the unsubstituted peroxides.

-benzo [b] thenoyl peroxide	Relative rate at 80°
2-	1.00
3-bromo, 2-	10.00
3-methyl,2-	66.80
3-	0.70
2-bromo, 3-	27.9
2-methyl,3-	365.0

The enhanced rate of decomposition of the substituted peroxides was attributed to a combination of a steric and inductive effect of the substituent.

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Ralph Leslie Wisner

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INTRODUCTION AND HISTORICAL

The thermal decomposition of diacyl peroxides has been the subject of numerous investigations during the past three decades. The decomposition of benzoyl peroxide provides a classic example of the thermal dissociation of an organic molecule into reactive free radicals. That a free radical mechanism was involved was demonstrated by Hey and Waters in 1937 (1). The decomposition of substituted benzoyl peroxides was investigated both by Swain, Stockmayer and Clark (2), in dioxane as the solvent medium using 3,4-dichlorostyrene to inhibit induced decomposition; and by Blomquist and Burelli (3) in acetophenone as the solvent. A good correlation of the decomposition rate of the various meta and para symmetrically substituted benzoyl peroxides with Hammett sigma values was obtained. Schuetz and Teller (4), similarly, found a good correlation with Hammett's sigma-rho plot for 4 or 5 substituted 2-thenoyl peroxides. Both these investigators found that electron-donating substitutents increased the rate of decomposition of the peroxides, whereas electron-withdrawing groups decreased the decomposition rate. Schuetz and Shea (21) observed a similar effect of substitutents in substituted t-butyl perthenates.

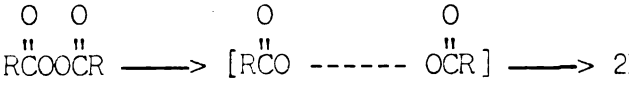
The present investigation was undertaken because of the continued interest in these laboratories in the chemistry of sulfur heterocyclics. The more specific objective of this thesis was to prepare 2 or 3 substituted 3 or 2-benzo [b] thenoyl peroxides and to examine their rates of decomposition.

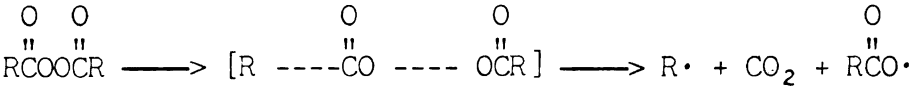
Several textbooks contain excellent reviews of diacyl peroxide decompositions (18,19,20). In general, the decomposition of benzoyl peroxide is first order, although the rate constants generally increase with increasing initial concentration and are affected by the solvent medium in which the decomposition occurs.

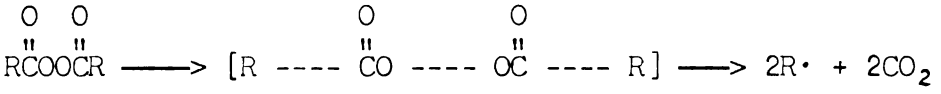
These facts suggested that uni-molecular cleavage of the peroxide is accompanied by a higher order reaction, which appeared to be a radical-induced attack on the peroxide (5,2). The induced decomposition can be effectively eliminated by the use of radical traps (2,6) which inhibit the induced process by converting the radical from a species that attacks the peroxide linkage to a radical which will not. Another method of separating the normal rate of decomposition from the induced is by a kinetic analysis of the rate data (5,9).

Even in the absence of induced decomposition, the rate still varies with the solvent medium indicating some polar character during the decomposition. That is, it is known that the primary step involved when benzoyl peroxide decomposes is the simple rupture of the oxygen-oxygen bond. This was shown by observing that essentially all of the initial peroxide is converted to benzoic acid when the decomposition is conducted in the presence of iodine in moist carbon tetrachloride (7). On the other hand, phenylacetyl peroxide (10) decomposed at a considerably faster rate than benzoyl peroxide under the same conditions and suggested a concerted decomposition mechanism was operative allowing the resonance energy of the benzyl radical to decrease the energy level of the transition state.

The thermal decomposition of diacyl peroxides may then be envisioned as occurring by any or all of the paths indicated below:

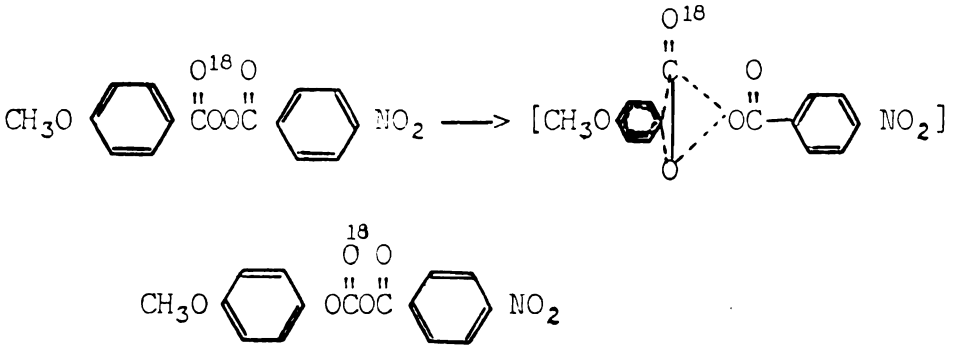




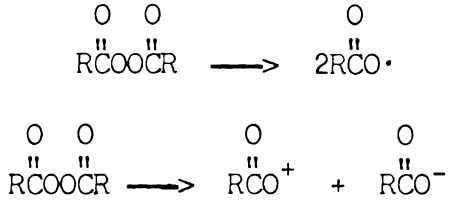


Bartlett and Hiatt (11) reported that in a series of tertiary butyl peresters, the rates of decomposition could be correlated with the stability of the incipient R radical. Hart and Wyman (12), likewise, found that in a series of cycloalkaneformyl and cycloalkaneacetyl peroxides that the faster decomposition rate of the cycloalkaneformyl peroxides was in agreement with the expected greater stability of the secondary radical over that of the primary radical.

Leffler (13), in his studies of the decomposition of the unsymmetrical 4-methoxy-4'-nitrobenzoyl peroxide, observed that it decomposed at about the same rate as benzoyl peroxides in nonpolar solvents. In polar solvents, however, the decomposition rate was considerably enhanced with the rate being proportional to the acidity constant of the acid. That the decomposition does not involve simple heterolytic rupture of the oxygen-oxygen bond was demonstrated by Denney (14) using isotopic tracer techniques. Using oxygen^{18}, he determined that the oxygens do not equilibrate indicating that the ions are not free. Denney postulated a mechanism consistent with this data for Leffer's unsymmetrical peroxide



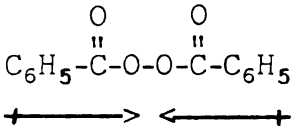
Thus, it can be concluded that the decomposition of diacyl peroxides occurs by two different routs. One route in which bond breaking occurs by a homolytic process to yield two neutral products (radicals) and another route by a heterolytic process to produce ions.



In the heterolytic mode of decomposition, the transition may vary from slight polarization of the oxygen-oxygen bond to complete dissociation into ions. If the decomposition is carried out in dilute solution with a solvent of low polarity, the homolytic process is favored.

The reason the solvent would be expected to affect the rate of decomposition by the homolytic process is understandable from the studies of the effect of substituents (2,3) mentioned previously. These investigators found that electron releasing substituents in the meta or para positions increase the rate of decomposition; whereas electron withdrawing substituents decrease the rate of decomposition

compared to the unsubstituted benzoyl peroxide. Swain et. al.(2) proposed structure (I) which was consistent with their observations. In I, the two benzoate groups in the benzoyl peroxide are dipoles oriented in a manner to repel one another.



(I)

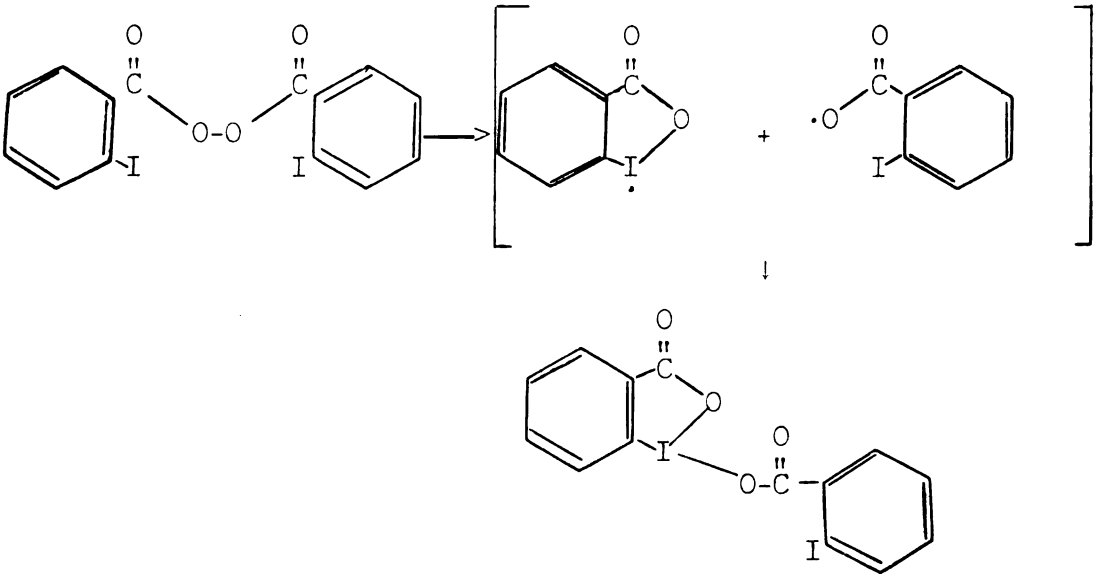
The effect of ortho substituents on the rate of decomposition of benzoyl peroxides were studied by Blomquist and Buselli(3) and the rates of decomposition of these are summarized in Table I along with their results on meta and para substituted benzoyl peroxides.

The faster rate of decomposition of the ortho substituted peroxides was consistent with lower energy of activation and higher entropy of activation noted. These in turn were attributed to field effects and coulombic interactions of the substituents.

Some ortho substituents have been found to greatly accelerate the rate of decomposition of some diacyl peroxides and peresters. Thus Leffler and Petropoules (15) found that ortho-iodobenzoyl peroxide decomposed at a rate of 1.86×10^{-3} min.$^{-1}$ at 22°C in chloroform. Whereas, Cooper (17) had shown previously that the meta and para isomers were not much different than the other halo substituted peroxides. This enhanced rate was attributed to a stabilization of the intermediate acyloxy-radical and the iodine.

Table I. Rates of decomposition of substituted benzoyl peroxides at 80°C.

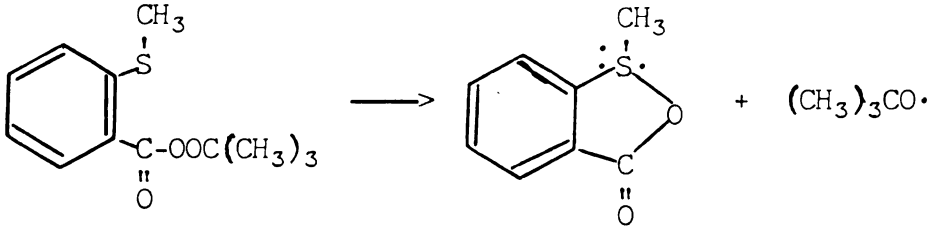
Substituent	$k \times 10^3$ ($min.^{-1}$)	E K Cal $mole^{-1}$	ΔS Cal $degree^{-1}$ $mole^{-1}$
Bis-(p-methoxy)	9.35	28.7	3.0
Bis-(m-methoxy)	3.85	28.9	2.0
Bis-(o-methoxy)	129.0	27.2	3.8
Bis-(p-methyl)	3.55	29.9	4.3
Bis-(m-methyl)	2.82	30.2	4.7
Bis-(o-methyl)	18.8	30.2	8.7
Unsubstituted	0.691	30.2	4.5
Bis-(p-chloro)	2.30	30.4	5.2
Bis-(m-chloro)	1.71	30.7	5.3
Bis-(o-chloro)	23.3	29.4	6.7
Bis-(p-cyano)	1.46	31.2	6.4
Bis-(p-nitro)	2.60	30.3	8.4
Bis-(m-nitro)	2.28	30.2	4.2
Bis-(o-phenoxy)	30.0	29.0	6.0



(A)

Compound A was found to be the principle product of decomposition.

Martin and Drew (16), also, found that a methylthio group accelerated the rate of decomposition of t-butylperbenzoate by a factor of 2 x 10^4 (at 20^0). An acceleration most easily explained by postulating the participation of the neighboring sulfur in the decomposition step.



RESULTS AND DISCUSSION

Rates of Decomposition of the Benzo [b] Thenoyl Peroxides

The decomposition rate of the various benzo [b] thenoyl peroxides were followed by determining the residual peroxide concentration iodometrically at definite time intervals following initiation of the reaction.

The decomposition rate of the peroxides containing no added radical scavenger were found to increase with increasing peroxide concentration; indicating that some induced decomposition, normally associated with diacyl peroxide decomposition, was occurring. The radical scavenger, o-chlorostyrene, was used in all decompositions which followed a first order kinetic rate law. The data for the respective kinetic determinations are summarized in the appendix.

The experimental technique employed in determining the rates of decomposition involved the preparation of a solution of the peroxide at 0° in purified chlorobenzene. Then, o-chlorostyrene was added as a radical scavenger while purging the peroxide solution with purified nitrogen. Aliquots of the peroxide solution were, then, transferred to ampoules which had been previously purged with nitrogen. The ampoules were, next, placed in a dry ice-isopropanol slurry to freeze the contents. The vapor space was purged with nitrogen; and the ampoules were sealed with an air torch under a nitrogen atmosphere. The ampoules and their contents were warmed to approximately 0° and immersed in a constant temperature bath controlled to ±0.05°. Three minutes were allowed for the contents to reach thermal equilibrium

with the bath. The ampoules were withdrawn at definite time intervals; and the contents frozen by storing the ampoules in a dry ice-isopropanol slurry until completion of the kinetic run. The tips of the ampoules were, then, broken and the contents transferred to a 250 ml. boiling flask. The peroxide concentration was determined iodometrically by the procedure described in the experimental section of this report.

Vigorous exclusion of oxygen from the sample during preparation of the peroxide solution and in subsequent handling operations was mandatory to obtain first order kinetics. This was particularly important with respect to the substituted benzo [b] thenoyl peroxides. If the peroxide solutions were contaminated with oxygen, results similar to those in Table II were observed.

Table II. Effect of oxygen contamination on the kinetics of the decomposition of 2-methyl-3-benzo [b] thenoyl peroxide at 40°C.

Time	0	30	60	91	115	169
C x 10^3	2.105	2.025	1.108	0.950	0.784	0.510
log C	0.3232	0.3065	0.0444	-0.0223	-0.1057	-0.2924
k x 10^3		1.28	10.7	8.73	8.59	8.40

The rate constant observed for the 2-methyl-3-benzo [b] thenoyl peroxide at 40° was 13.4 x 10^{-3} min.$^{-1}$ and first order when oxygen was excluded from the reaction system. Very probably the oxygen was reacting to form a fairly stable peroxide at this temperature which would give rise to the induction period and the slow decomposition

finally observed. This peroxide could well have been o-chlorostyrene polyperoxide.

The rate of decomposition of benzoyl peroxide in chlorobenzene at 75° was determined to establish the accuracy and reproducibility of the experimental technique and the ability of the o-chlorostyrene as a radical scavenger in repressing induced decomposition. The rate constant was found to be 1.02×10^{-3} min.$^{-1}$ in good agreement with previous literature values in benzene (22).

The rates of decomposition at several temperatures and the activation parameters determined for the benzo [b] thenoyl peroxides are summarized in Table III.

The data indicate that the ortho substitutents increase the decomposition rates of the respective peroxides by lowering the activation energy or raising the entropy of activation in a manner similar to that observed by Blomquist and Buselli (3) for the ortho substituted benzoyl peroxides. However, the ortho substituents were found to exert a greater effect in the benzo [b] thenoyl peroxide series than had been reported for the ortho substituted benzoyl peroxide series.

The relative rates of decomposition at 80° of the benzo [b] thenoyl peroxides and thenoyl peroxides as compared to benzoyl peroxides as compared to benzoyl peroxide are summarized in Table IV.

The faster rate of decomposition of the unsubstituted benzo [b] thenoyl peroxides than either benzoyl or thenoyl peroxides may be attributable to the greater aromaticity of the thionaphthene group. The 2-benzo [b] thenoyl peroxide was found to decompose faster than

Table III. Rate constants and activation parameters for the benzo [b] thenoyl peroxides in chlorobenzene.

Peroxide -benzo [b] thenoyl	Temp. °C.	k x 10^3 $min.^{-1}$	E_a k Cal/mole	$S^{\ddagger}$ e.u.
2-	65	1.38	31.2	10.6
	70	2.87		
	75	5.67		
3-	65	1.01	30.1	6.8
	70	2.18		
	75	4.23		
3-methyl-2-	30	1.60	25.7	3.4
	35	3.05		
	40	5.54		
2-methyl-3-	30	3.38	25.9	6.1
	35	8.06		
	40	14.15		
2-bromo-3-	45	2.05	29.2	11.0
	50	4.50		
	55	9.00		
3-bromo-2-	50	2.31	28.8	8.5
	55	4.88		
	60	8.77		

Table IV. Relative rate of decomposition of several diacyl peroxides at 80°.

Peroxide	Relative Rate
Benzoyl	1.00
p-chlorobenzoyl	0.89
o-chlorobenzoyl	9.00
p-methylbenzoyl	6.50
o-methylbenzoyl	7.25
2-thenoyl	1.028
3-thenoyl	0.996
2-benzo [b] thenoyl	4.63
3-benzo [b] thenoyl	4.24
3-bromo-2-benzo [b] thenoyl	46.3
2-bromo-3-benzo [b] thenoyl	129.0
3-methyl-2-benzo [b] thenoyl	324.0
2-methyl-3-benzo [b] thenoyl	1690.

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the corresponding 3-analog, similar to the results reported by Schuetz and Teller (4) for the 2-and 3-thenoyl peroxides. This may be due to a inductive effect of the sulfur in increasing the electron density on the oxygen-oxygen bond in the transition state rather than the greater stability of the 2-benzo [b] thienyl radical compared to the corresponding 3-radical. That is, if the decomposition is proceeding by a concerted mechanism in which both the oxygen-oxygen bond and the carbon-carbon bonds are stretched in the transition state, then the 3-benzo [b] thenoyl peroxide would be expected to decompose more rapidly since this leads to a benzylic radical. In fact, carbon dioxide measurements indicate that the 3-benzo [b] thenoyloxy radicals decarboxylate more readily (38%) than the 2-benzo [b] thenoyloxy radicals (25%).

In contrast to the unsubstituted benzo [b] thenoyl peroxide, the 2-substituted-3-benzo [b] thenoyl peroxides decompose more rapidly than the 3-substituted-2-benzo [b] thenoyl peroxides.

Blomquist and Buselli (3) in their investigations of ortho substituted benzoyl peroxides indicated that there were three methods by which the substituent might affect the stability of the peroxide bond: inductive effect, coulombic field effect and inhibition of resonance.

That is, in addition to the inductive effect of the substituent which would be expected to be similar to the para analog, they observed that certain substituents increased the rate of decomposition of the benzoyl peroxide even more. For instance, while the nitro group in the para position decreased the rate of decomposition of

the peroxide, a nitro group in the ortho position increased the decomposition rate. They attributed this to repulsive coulombic forces between the two groups. This effect would be expected to be greatest for substituents which are capable of charge separation, due to resonance.

Inhibition of resonance was postulated to explain the slower rate of decomposition of the o-phenoxybenzoyl peroxide compared to that of the methoxy derivative.

Finally, there is the possibility of a steric effect of the substituent on the stability of the peroxide bond. Such effects may be greater in the case of the benzo [b] thenoyl peroxide than in the benzoyl peroxide series. Indeed molecular models indicate a greater crowding in the case of the ortho substituted benzo [b] thenoyl peroxide than with the ortho substituted benzoyl peroxides.

With the limited data available at present, it is difficult to ascertain whether the bromo substituents increase the decomposition rate of the benzo [b] thenoyl peroxides due to a steric effect or because of a coulombic field effect. Molecular models suggest that a substituent in the 2-position may have a greater steric effect than in the 3-position which parallels our results with the peroxide.

If steric effects of the substituent were the only important factor operating; then, since the size of the bromo and methyl groups are approximately the same (36), the rate of decomposition of the methyl benzo [b] thenoyl peroxides would have been anticipated to be about equal to the bromo analogs. However, the methyl derivatives were found to decompose faster by a factor of 6.7 and 13 for the

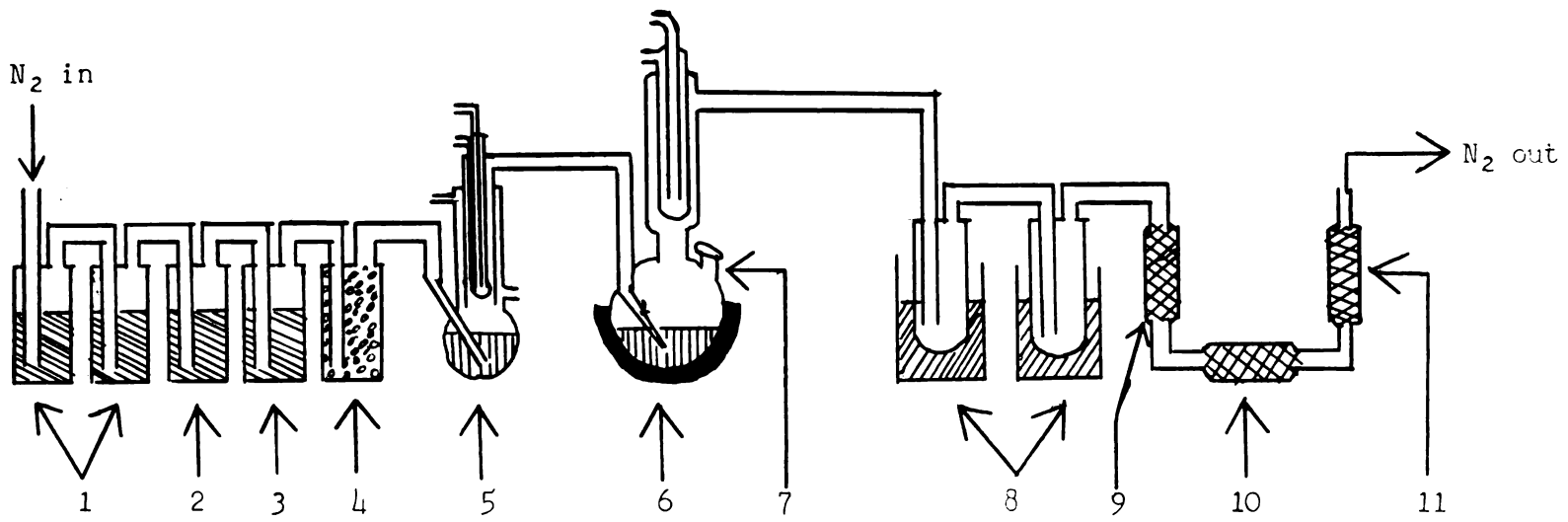
2 and 3 substituted peroxide, respectively, compared to the bromo analogs. The increased rate might be expected to be due to the electron donating effects of the methyl substituents.

The only decomposition product of the benzo [b] thenoyl peroxides that was measured quantitatively was carbon dioxide. The experimental procedure involved decomposing the peroxide in purified chlorobenzene for a minimum of ten half-lives at 90° while purging the reaction system with purified nitrogen. The carbon dioxide was absorbed on ascarite and weighed directly. A description of the apparatus used is given in Figure 1, and the results of the carbon dioxide determinations are summarized in Table V.

Table V. Yields of carbon dioxide evolved during the decomposition of benzo [b] thenoyl peroxides in chlorobenzene.

Peroxide	Yield
2-benzo [b] thenoyl	25
3-bromo-2-benzo [b] thenoyl	26
3-methyl-2-benzo [b] thenoyl	40
3-benzo [b] thenoyl	38
2-bromo-3-benzo [b] thenoyl	20
2-methyl-3-benzo [b] thenoyl	26

The results indicate that the unsubstituted benzo [b] thenoyloxy radical decarboxylates more rapidly than the corresponding 2 analog suggesting that the benzylic radical is more stable than the 2-benzo [b] thenoyl radical. The 2- and 3-bromo substituted benzo [b] thenoyl



1. Fieser's Solution to remove oxygen.
2. Saturated lead acetate in water, to remove sulfur compounds.
3. Concentrated sulfuric acid, to dry nitrogen.
4. Potassium hydroxide, to remove sulfuric acid.
5. Flask equipped with condenser and containing chlorobenzene to saturate nitrogen.
6. Heating mantle maintained at desired temperature.
7. Reaction vessel.
8. Dry ice traps.
9. Tared ascarite-anhydrone tube.
10. Protective ascarite-anhydrone tube.
11. Protective drierite tube.

Figure 1. Apparatus used in the determination of carbon dioxide.

peroxides both decarboxylate to the same extent within experimental limits. The methyl groups reverse the order noted in comparison to the unsubstituted peroxides.

EXPERIMENTAL

I. Reagents

A. Chlorobenzene

The chlorobenzene was purified according to the method of Bartlett and Hiatt (11). Two liters of chlorobenzene from Fisher Scientific Company were extracted with small portions (approximately 100 ml.) of concentrated sulfuric acid until the acid extracted was colorless. The chlorobenzene was the rinsed twice with 200 ml. of water, 200 ml. of 10% sodium bicarbonate solution and again rinsed twice with water. It was dried with calcium chloride and distilled from phosphorus pentoxide using a 12 inch column packed with glass helices. The fraction distilling between 130.0-130.5° was collected and used in the kinetic determinations.

B. Styrene

Dow Chemical Company Styrene, purity +99.8%, was fractionated using a column packed with glass helices and that material with a boiling point of 143-144° was used in the present investigation. The styrene was stored in an amber bottle under a nitrogen atmosphere at -13°.

C. o-Chlorostyrene

Ortho-chlorostyrene obtained from the Dow Chemical Company was purified by vacuum distillation using an 18 inch semi-micro horizontal

vigreaux column. The fraction distilling at 29-30°/1.0 mm. was used in this study. The monomer was stored in an amber bottle under nitrogen atmosphere at 13°.

D. Standardization of sodium thiosulfate solution.

In a typical standardization procedure, four liters of approximately 0.01 or 0.002 N sodium thiosulfate solution were prepared a minimum of two days prior to its standarization and stabilized by adding approximately 0.25 g. of sodium carbonate. In the standardization of the thiosulfate solution, a sample of previously dried, reagent grade potassium iodate was weighed directly into a 50 ml. volumetric flask, dissolved and diluted to the volumetric mark with water. Several 5 ml. aliquots were transferred to a 250 ml. boiling flask and 25 ml. of a 10% solution of glacial acetic acid in isopropyl alcohol was added, followed by 10 ml. of a saturated solution of sodium iodide in isopropanol. The resulting solution was refluxed for 15 minutes, 10 ml. of water was added to it and the liberated iodine was titrated with the sodium thiosulfate solution to a colorless endpoint. The normality of the standard thiosulfate by the procedure was 9.90 (±0.05) x 10^{-3}. Standardization by indentical procedure using recrystallized benzoyl peroxide, gave a normality of 9.95 (±0.05) x 10^{-3}.

E. Standardization of n-butyllithium.

The procedure of Gilman and Haubein (23) was utilized in estimating the concentration of the n-butyllithium solution, used in this

study. The procedure depends upon determining first the total alkalinity (due to both lithium hydroxide and the alkyl lithium) and then allowing the alkyl lithium to interact with benzyl chloride and determining the alkalinity due to the lithium hydroxide. The difference in alkalinity represents the n-butyllithium concentration. In a typical procedure, 3 ml. of the n-butyllithium reagent (prepared as described later) was pipetted into a 125 ml. iodine flask containing 10 ml. of water. Titration with standard hydrochloric acid, using phenolphthalein as the indicator, gave the total alkalinity. A second 3 ml. aliquot was added to 10 ml. of freshly distilled benzyl chloride, shaken for a minute, diluted with 10 ml. of water and titrated as before. The difference in the titers represents the n-butyllithium concentration.

II. Preparation of Benzo [b] thenoyl Peroxides

A. Preparation of the sulfur heterocyclic acids.

1. Preparation of n butyllithium. In a three necked liter round bottom flask fitted with a stirrer, dropping funnel and a bulb reflux condenser equipped with a drying tube, was placed 10 g. (1.443 moles) of lithium sand (prepared by heating lithium metal to 200-210° in paraffin oil in a 250 ml. iodine flask and shaking until cool) and 200 ml. of anhydrous ethyl ether. The flask was immersed in a dry ice-acetone bath, cooled to -10°, and approximately 5 ml. of a solution containing 90 g. (0.657 mole) of n-butylbromide in 100 ml. of anhydrous ether was added dropwise to the lithium dispersion. If reaction did not initiate immediately as evidenced by the formation of

a white precipitate and a brightening of the surface of the lithium, the flask was warmed gently until the reaction commenced and then cooled to -10°. The remainder of the n-butylbromide solution was added during approximately 30 minutes while maintaining the reaction temperature at -10°. Folowing the addition of the alkyl halide the flask was warmed to 0° and stirred for an additional two hours. The reaction was conducted in an atmosphere of dry nitrogen. The n-butyllithium solution was decanted thru a glass wool plug into a previously dried bottle and stored at 0° until used. The concentration of the n-butyllithium solution was determined by the procedure of Gilman and Haubein (2) just prior to use. Yields of greater than 90% were realized via this procedure.

2. Preparation of 2-benzo [b] thenoic acid. In a three-necked liter flask fitted with a stirrer, dropping funnel and reflux condenser was placed 0.2 mole of n-butyllithium solution. After cooling the flask and its contents to 0°, a solution containing 24.1 g. (0.180 mole) of thianaphthene in 100 ml. of anhydrous ether was added dropwise, while maintaining the reaction temperature between 0 and 10°. After adding the thianaphthene solution, the reaction temperature was raised to the reflux temperature of the reaction mixture and held there for 45 minutes. The reaction solution was then poured over a slurry of dry ice and ether. After allowing the excess dry ice to sublime, 100 ml. of water was added to the ether solution, and the water layer was separated. The ether layer was extracted twice with water, and the combined water extracts were acidified with concentrated

hydrochloric acid. The crude 2-benzo [b] thenoic acid was recovered by filtration and dried over night, at 105°. Recrystallization of the crude acid from methanol yielded 32.0 g. (0.18 mole, 58.8%) of white solid acid melting at 243-244°. Literature value (24): melting point 243-244°.

3. Preparation of 2-bromo-thianaphthene. In a three-necked liter flask equipped with a stirrer, dropping funnel and a drying tube, was placed 36.0 g. (0.268 mole) of thianaphthene, 36.5 g. of anhydrous sodium acetate and 110 ml. of chloroform. A solution containing 14 ml. (0.273 mole) of bromine in 35 ml. of chloroform was added dropwise during 15-20 minutes to the thianaphthene solution. Some external cooling of the reaction mixture was necessary to control the rate of bromination. The mixture was stirred for an additional hour to complete the reaction, and then 100 ml. of water was added to dissolve the inorganic salts. The chloroform layer was separated, washed first with 100 ml. of water, secondly with 50 ml. of a five percent caustic solution, next with 100 ml. of water and finally with 100 ml. of a saturated sodium chloride solution. The washed solution was, then, slowly filtered through anhydrous sodium sulfate and distilled using a 12 inch vigreaux column. Pure 3-bromothianaphthene, 42.0 g. (0.197 mole, 73.5%) as a light yellow colored liquid boiling at 118-128°/7mm. was obtained. Literature value (25): 90-105°/1.5 mm.

The halothianaphthene turned red on being set aside for a period of time and was redistilled just prior to use.

4. Preparation of 3-benzo [b] thenoic acid. In a three-necked flask, fitted with a stirrer, dropping funnel and reflux condenser was placed 3.2 g. (0.132 mole) of magnesium turnings and 150 ml. of anhydrous ether. To the magnesium suspension was added dropwise, a solution containing 27.3 g. (0.128 mole) of 3-bromothianaphthene in 100 ml. of anhydrous ether. The Grignard reaction was initiated by adding approximately a ml. of 1,2-dibromoethane. After the reaction had started, the 3-bromothianaphthene solution was added at a rate sufficient to maintain gentle refluxing of the reaction solution. When the halothianaphthene solution had been added, the reaction mixture was heated at its reflux temperature for approximately five hours and then it was poured over a slurry of dry ice and ether. The dry ice was allowed to evaporate and 100 ml. of water was added to the ether solution. After heating it gently to break the emulsion, the water layer was separated. This procedure was repeated twice. The combined extracts were acidified with concentrated hydrochloric acid and the crude 3-benzo [b] thenoic acid recovered by filtration. This was dissolved in base and reprecipitated with hydrochloric acid, filtered, washed with water and dried overnight at 105°. The acid, on recrystallization from benzene-acetone, yielded 8.3 g. (0.0466 mole, 36.5%) of a slightly pink colored product melting at 178.8-180.0°. Literature value (25): melting point, 179-180°.

5. Preparation of 2-methyl-thianaphthene. In a three-necked flask fitted with a stirrer, dropping funnel and reflux condenser was placed 0.20 mole of n-butyllithium as an ether solution. After cooling the alkyl-lithium solution to 0°, a second solution containing

24.1 g. (0.18 mole) of the thianaphthene in 100 ml. of anhydrous ether was added dropwise to the alkyl lithium solution. The reaction mixture was stirred for an additional 45 minutes while maintaining its temperature at 0°. Following metallation of the thianaphthene, a solution containing 22.7 g. (0.18 mole) of dimethylsulfate in 100 ml. of anhydrous ether was cautiously added dropwise, while maintaining the reaction temperature at 0-10°. Caution: A very vigorous reaction occurs at this point. Following the addition of the dialkylsulfate, the mixture was heated at its reflux temperature for a half hour and then set aside overnight. The reaction mixture was treated with 50 ml. of water; followed by 100 ml. of 10% sodium hydroxide. After refluxing the mixture for two hours, the ether layer was separated and dried by dripping it slowly through anhydrous sodium sulfate. The majority of the ether was removed on a steam bath and the 2-methylthianaphthene was fractionated using an 18 inch semi-micro vigreaux column, to obtain 26.6 g. (0.168 mole, 85%) of 2-methylthianaphthene, boiling at 84-86°/3.5 mm. It melted at 48-50°. Literature value (27): melting point, 51-52°.

6. Preparation of 2-methyl-3-iodothianaphthene. In a three-necked flask fitted with a stirrer, reflux condenser and a thermometer, was placed 18.6 g. (0.1255 mole) of 2-methylthianaphthene and 150 ml. of benzene. The solution was heated to 60° and small portions of a mixture of 32.0 g. (0.126 mole) of iodine and 19.2 g. (0.089 mole) of yellow mercuric oxide were added during an hour. The reaction mixture was stirred for another four hours maintaining its temperature at 60°, cooled and filtered. The filtrate was washed with 100 ml. of

saturated sodium thiosulfate solution, 100 ml. of water and dried over calcium chloride. The benzene was removed by distillation at atmospheric pressure and the residue was distilled under reduced pressure, to obtain 20.0 g. (0.0704 mole, 58.2%) of a yellow liquid boiling at 105-107°/0.5 mm. Literature value 105-107°/0.5 mm.(28).

7. Preparation of 2-methyl-3-benzo [b] thenoic acid. In a three-necked 500 ml. flask equipped with stirrer, reflux condenser and dropping funnel was placed 2.0 g. (0.0823 mole) of magnesium turnings and 100 ml. of anhydrous ether. To this suspension was added dropwise, a solution containing 20.0 g. (0.073 mole) of 2-methyl-3-iodothianaphthene in 75 ml. of anhydrous ether. After a few milliliters of the 2-methyl-3-iodothianaphthene solution had been added, approximately a ml. of 1,2-dibromoethane was added to initiate the Grignard reaction. The remainder of the 2-methyl-3-iodothianaphthene solution was added at a sufficient rate to maintain the reaction at its reflux temperature for approximately an hour. Following the additions of the alkylhalothianaphthene, the reaction mixture was heated at its reflux temperature for an additional two hours; and, then, poured over a slurry of dry ice and anhydrous ether. After allowing the dry ice to evaporate, 100 ml. of water was added and the mixture was heated gently to break the emulsion. The water layer was separated and the ether extracted twice with water. The combined water extracts were acidified with hydrochloric acid. The crude 2-methyl-3-benzo [b] thenoic acid was recovered by filtration and dried overnight at 105°. Recrystallization of the crude acid

from acetone-benzene yielded 9.6 g. (0.050 mole, 68.5%) of a white product melting at 194-195°. Literature value (29): melting point 195.5-196.4°.

8. Preparation of 3-methyl-thianaphthene. In a three-necked 500 ml. flask fitted with a stirrer, reflux condenser and dropping funnel was placed 10.5 g. (0.432 mole) of magnesium turnings in 100 ml. of anhydrous ether. A solution containing 50 g. (0.235 mole) of 3-bromothianaphthene in 100 ml. of anhydrous ether was added dropwise to the magnesium suspension. After approximately five milliliters of the 3-bromothianaphthene solution had been added, a milliliter of 1,2-dibromoethane was added to initiate the Grignard reaction, after which the remainder of the 3-bromothianaphthene solution was added at a rate sufficient to maintain the reaction solution at its reflux temperature. The mixture was refluxed for three hours cooled, and a solution containing 59.2 g. (0.47 mole) of dimethylsulfate in 100 ml. of anhydrous ether was then added to the thianaphthene Grignard, dropwise, at such a rate as to maintain the reaction solution at its reflux temperature. The mixture was refluxed for an additional hour and set aside overnight. Unreacted dimethylsulfate was removed by washing the ether solution with 50 ml. of 50% base (vigorous reaction when the base is added). After the water and base had been added, the mixture was refluxed to break the emulsion. The ether layer separated and the water solution was extracted twice with ether. The combined ether extracts were dried over anhydrous sodium sulfate, filtered, the ether was removed by evaporation and the residue was fractionated using an 18 inch vigreaux column under

vacuum, to obtain 17.0 g. (0.108 mole, 48.9%) of 3-methylthianaphthene boiling at 54-56°/0.3 mm. Literature value (30): boiling point 108-109°/12 mm.

9. Preparation of 3-methyl-2-benzo [b] thenoic acid. In a three-necked 500 ml. flask fitted with a stirrer, reflux condenser and a dropping funnel was placed 0.124 mole of n-butyllithium in 125 ml. of anhydrous ether. A solution containing 17.0 g. (0.115 mole) of 3-methylthianaphthene in 50 ml. of anhydrous ether was added dropwise to the n-butyllithium solution while holding the temperature at 0-10°. Following the addition of the thianaphthene solution, the mixture was heated at its reflux temperature for an hour, cooled and poured over a slurry of dry ice and ether. Following evaporation of the dry ice, 100 ml. of water was added to the residual solution. The water layer was separated and the ether layer was extracted twice with water, using a slight amount of base in the second extraction. The combined extracts were acidified and the organic acid produced was recovered by filtration and washed with water. The acid was dried overnight at 105°. Recrystallization of the acid from benzene-acetone yielded 10.0 g. (0.0521 mole, 45.2%) of a light yellow colored acid, melting at 244-246°. Literature value (30): melting point 244-244.5°.

10. Preparation of 2,3-dibromothianaphthene. In a three-necked 500 ml. flask fitted with a stirrer, dropping funnel and a drying tube was placed 26.8 g. (0.2 mole) of thianaphthene and 150 ml. of chloroform. A solution containing 22 ml. (0.4 mole) of bromine

in 50 ml. of chloroform was added dropwise to the thianaphthene solution. The solution was stirred at ambient conditions (20-30°) for 12 hours. The chloroform solution was extracted with 100 ml. of 10% sodium hydroxide solution, 100 ml. of water and dried by dripping it thru anhydrous sodium sulfate. The majority of the chloroform was removed on a steam bath, the last traces being removed under vacuum. Recrystallization of the residue from methanol yielded 58.5 g. (0.200 mole, 58.5%) of pure product in the form of white (turned pink on standing) needles, melting at 58.5°. Literature value (31): melting point 59°.

11. Preparation of 3-bromo-2-benzo [b] thenoic acid. In a three-necked 500 ml. flask, fitted with a stirrer, dropping funnel, thermometer and condenser, was placed 0.08 mole of n-butyllithium in approximately 100 ml. of ether. A solution containing 18.0 g. (0.0617 mole) of 2,3-dibromothianaphthene in 100 ml. of anhydrous ether was added dropwise to the n-butyllithium solution while maintaining the temperature of the reaction solution at 0-5°. The mixture was stirred for an additional three hours while maintaining its temperature at 0°. It then was poured over a dry ice slurry. When the dry ice had evaporated, 100 ml. of water was added and the mixture was heated on a steam bath to break the emulsion. The water layer was separated and the ether layer extracted twice with dilute base. The combined water extracts were acidified with hydrochloric acid and the crude 3-bromo-2-benzo [b] thenoic acid was removed by filtration, and dried overnight at 105°. Recrystallization of the

crude acid from benzene-acetone yielded 10 g. (0.0389 mole, 63%) of white needles, melting at 274-275°. Literature value (31): melting point, 274-275°.

12. Preparation of 3-carboxy-2-benzo [b] thienyllithium, lithium salt. In a two-necked 100 ml. flask, equipped with a stirrer and thermometer was placed 0.06 mole of n-butyllithium in approximately 10 ml. of anhydrous ether. A solution containing 0.5 g. (0.00281 mole) of 3-benzo [b] thenoic acid in approximately 25 ml. of anhydrous ether was added rapidly to the n-butyllithium solution. The reaction mixture was stirred for an hour while maintaining its temperature at -50 to -70°. It was then poured over a slurry of dry ice and ether. After sublimation of the dry ice, the acid was extracted with water and reprecipitated by acidifying the alkali extract with concentrated hydrochloric acid. Sublimation of the crude product at approximately 200°/5 mm. yielded 0.25 g. (0.00113 mole, 40.2%) of a light yellow product melting at 250-251°. Literature value (29): melting point 249.5-251.5°.

Attempted preparation of the 3-carboylate-2-benzo [b] thienyllithium at 0° or 30° gave only an oily product upon carbonation and subsequent product isolation.

13. Preparation of 2-bromo-3-benzo [b] thenoic acid. In a three-necked 500 ml. flask fitted with a stirrer, dropping funnel and thermometer was placed 0.05 mole of n-butyllithium in 50 ml. of anhydrous ether. After cooling the alkyl-lithium solution to 60° by immersion in a dry ice-acetone bath, a solution containing 5.2 g. (0.0292 mole)

of 3-benzo [b] thenoic acid in 200 ml. of anhdrous ether was added dropwise to it. After stirring the reaction mixture an hour at -60°, 1.5 ml. (0.0584 mole) of bromine in 10 ml. of anhydrous benzene was added rapidly. Following a reaction period of a half hour the reaction temperature was raised to -20° and 10 ml. of water was added causing the temperature of the mixture to raise above zero and then an additional 20 ml. of water added. The water layer was separated and the ether layer was extracted with two additional quantities of water. The combined water extracts were acidified with hydrochloric acid and the crude acid was recovered by filtration, and dried overnight at 105°. Recrystallization of the crude product from acetone-benzene mixture yielded 4.25 g. (0.0165 mole, 56.7%) of white needles melting at 214-216.5°. Elemental analysis: Carbon, calculated - 42.04, found 42.32; hydrogen, calculated - 1.96, found 2.01; sulfur, calculated - 12.47, found 12.29; bromine, calculated-31.08, found 30.80.

B. Preparation of Acid Chlorides

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

In a typical preparation, a 100 ml. round-bottomed flask fitted with a reflux condenser and drying tube was charged with 5.2 g. (0.0292 mole) of 3-benzo [b] thenoic acid, 20 ml. of dry chloroform and 10 g. (0.084 mole) of thenoyl chloride. The mixture was heated cautiously to initiate the reaction, the heat being removed immediately until the vigorous reaction subsided. It was then heated at its reflux

temperature three and one half hours, cooled and distilled. The chloroform and unreacted thenoyl chloride were removed at atmospheric pressure, to obtain 5.2 g. (0.0265 mole, 90.7%) of 3-thianaphthene carbonylchloride, boiling at 114-115°/0.5 mm. and melting at 50-52°. Literature value (32): melting point 53-54°; boiling point 296-298°/758 mm.

For the product yields, and the physical constants of the acid chlorides prepared in the course of this investigation see Table VI.

Table VI. Data on preparation of benzo [b] thenoyl chlorides.

[b] thenoyl chloride	Yield(%)	b.p. (pres.)	m.p.
2-benzo	83.4	106-108(0.5 mm.)	88.0-88.5
3-methyl, 2-benzo	84.6	124-126(0.5 mm.)	106
3-bromo, 2-benzo	66.0	171-174 (1.3 mm.)	138-139
3-benzo	90.7	114-115(0.5 mm.)	50-52
2-methyl, 3-benzo	87.3	119-121(0.5 mm.)	73-75.5
2-bromo, 3-benzo	87.0	144(0.5 mm.)	68-70

C. Preparation of Benzo [b] thenoyl peroxides

The benzo [b] thenoyl peroxides were prepared from the respective acid chlorides by the method of Price and Krebs (33).

In a typical preparation, a three-necked 100 ml. flask, fitted with a stirrer, thermometer and dropping funnel was charged with 50 ml. of water and 1.25 g. (0.016 mole) of reagent grade sodium peroxide. The vigorously stirred peroxide solution was cooled to approximately

0° and a solution containing 3g. (0.0152 mole) of 2-benzo [b] thenoyl chloride in 20 ml. of anhydrous toluene was added dropwise, to it. A white insoluble product started to form in the solution during the first 15 minutes of addition of acid chloride solution. The reaction mixture was stirred for an additional two hours at 0° to complete the reaction. The product was recovered by filtration, washed with ice water and dried overnight under vacuum at -13°. Recrystallization of the crude product from a chloroform-hexane solution gave 1.0 g. (37.1%) of a light yellow colored product with a purity of 99+%.

For a summary of data pertaining to the additional peroxides prepared during the course of the present study, see Table VII.

Table VII. Data on preparation of benzo [b] thenoyl peroxides

[b] thenoyl peroxide	Yield	Purity	m.p.	Recrystallization Solvent
2-benzo	37.1	99.	123(decomp.)	$CHCl_3$-hexane
3-methyl-2-benzo	40.1	93.4	105(decomp.)	acetone
3-bromo-2-benzo	37.6	98.2	139(decomp.)	$CHCl_3$
3-benzo	36.	98.6	118(decomp.)	$CHCl_3$-MeOH
2-methyl-3-benzo	47.8	99.	101(decomp.)	acetone
2-bromo-3-benzo	45.2	98.7	119(decomp.)	$CHCl_3$-acetone

Table VIII. Elemental analyses of the benzo [b] thenoyl peroxides

[b] thenoyl peroxide	Carbon		Hydrogen		Sulfur		Bromine	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
2-benzo	61.05	61.26	2.83	2.83	18.08	17.70	--	--
3-benzo	61.05	61.17	2.83	2.80	18.08	18.39	--	--
3-bromo-2-benzo	42.20	42.52	1.56	1.46	12.50	12.55	31.30	31.05
2-bromo-3-benzo	42.20	44.1	1.56	1.60	12.50	12.94	31.30	34.9
3-methyl-2-benzo	62.80	62.48	3.67	3.41	16.75	16.45	--	--
2-methyl-3-benzo	62.80	62.96	3.67	3.69	16.75	16.49	--	--

III. Kinetic Method for Determination of the Decomposition Rate of the Peroxides

The rates of decomposition of the peroxides were determined by measureing the concentration of undecomposed peroxide at various time intervals employing the iodometric method of Mair and Graupner (34).

The peroxide solutions for the kinetic determination were contained in 5 ml. ampoules supplied by the Will Corporation Laboratories Supplies, Rochester, New York.

The ampoules were cleaned prior to the kinetic analysis as follows: They were filled with a warm cleaning solution, set aside for a half hour, rinsed with water, filled with a dilute solution of ammonium hydroxide and again set aside for a half hour, then were rinsed with water, then with acetone and dried at 105° for 24 hours.

The following experimental procedure was used in a typical kinetic run. The chlorobenzene solution of peroxide, 0.01 to 0.0002 M in peroxide and 0.01 M in o-chlorostyrene, was cooled to 0° and purged with nitrogen for 15 minutes. Using a syringe and needle, 5 ml. of the peroxide solution was transferred to a previously nitrogen purged ampoule. The vapor space was purged with nitrogen for one-half minute, and the ampoule capped with a medicine dropper bulb. The contents were frozen by immersion of the ampoule in a dry ice-isopropanol bath. The vapor space was again purged with nitrogen. The ampoules were sealed at -70° using an oxygen gas torch under a nitrogen atmosphere. After the contents had melted, the ampoules were placed in a constant temperature oil bath controlled within 0.05°. The zero time, the time for the contents to come to

thermal equilibrium, was estimated to be three minutes. The initial sample was withdrawn from the bath after zero time and immersed in a dry ice-isopropanol bath. The remainder of the samples were removed from the constant temperature bath at various time intervals and the decomposition of the peroxide quenched by cooling in a dry ice-isopropanol bath. The chlorobenzene was melted and tips of the ampoule broken. The contents were transferred into a 250 ml. boiling flask, rinsed thoroughly with purified chlorobenzen and 25 m. of a 10% solution of glacial acetic acid in isopropanol and 10 ml. of a saturated solution of sodium iodide in isopropanol were added. After refluxing the mixture for 15 minutes, approximately 10 ml. of water was added and the liberated iodine titrated with standard sodium thiosulfate solution using the yellow to clear endpoint. The rate constants were calculated from the slope of the line of a log C versus time plot using the method of least squares. It is apparent from the plots of log C versus time for each peroxide (see Appendix) that all decompositions obeyed a first order rate law. The decompositions were determined for at least one-half life and several for over three-half lives of their decomposition periods.

The energies of activation were calculated from a plot of the log of rate constants versus the reciprocal of the absolute temperature employing the method of least squares to determine the slopes. The entropies of activation were calculated by the method of Foster, Cope and Daniels (35).

IV. Quantitative Determination of the Carbon Dioxide Evolved During the Thermal Decomposition of the Peroxides.

Using the apparatus illustrated in Figure 1, 50 to 80 mg. of peroxide dissolved in 100 ml. of purified chlorobenzene was placed in the reaction flask. The latter was cooled by immersion in an ice-water bath and the system was purged with nitrogen for an hour. The absorption tube, packed with a 2:1 mixture of ascarite and anhydrous magnesium perchlorate, was removed, weighed and replaced in the system. The reaction flask was immersed in a constant temperature bath controlled at $90(\pm 1)^{0}$, for at least ten half-lifes of the peroxides decomposition period, while purging the system continuously with nitrogen. The reaction flask was removed from the constant temperature bath and the dry ice traps set aside at room temperature for a half hour. The absorption tube was reweighed and the gain in weight taken as the amount of carbon dioxide liberated by the peroxide during its decomposition. The results of carbon dioxide evolution for the thermal decomposition of the peroxides examined during the course of this study are tabulated in Table V.

SUMMARY

1. Six new peroxides, derived from 2 or 3-benzo [b] thenoic acids and their 3 or 2-methyl and bromo derivatives, were prepared and their rates of decomposition in chlorobenzene measured.
2. The rates of decomposition of the benzo [b] thenoyl peroxides were all first order in the presence of a radical scavenger, o-chlorostyrene.
3. Substituents in the 2-position effect the rate of decomposition of the 3-benzo [b] thenoyl peroxide greater than do 3- substituents affect the stability of 2-benzo [b] thenoyl peroxide. A methyl substituent accelerates the decomposition rate greater than does a bromo group.
4. One new substituted thianaphthene acid was prepared.

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APPENDIX

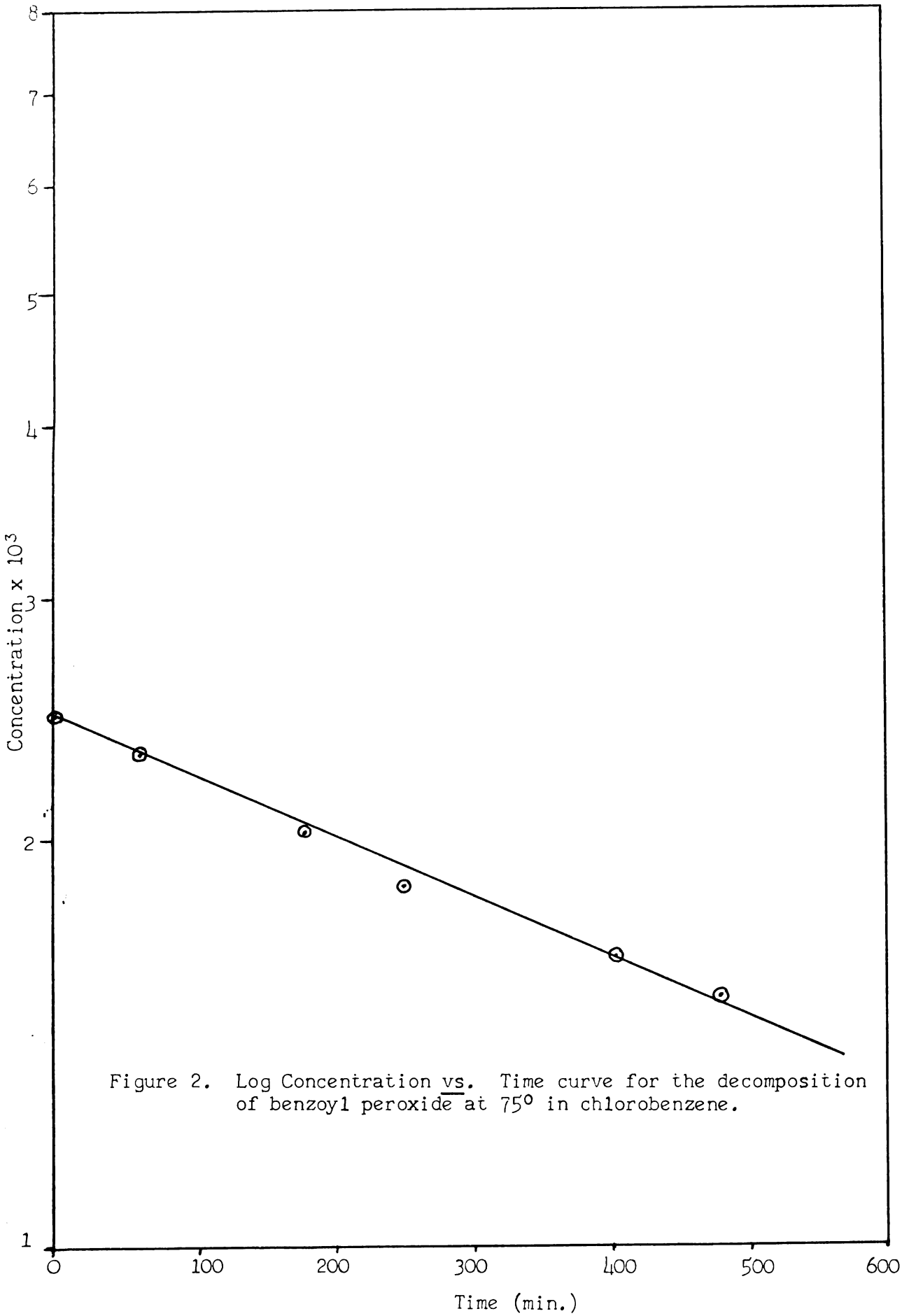


Figure 2. Log Concentration vs. Time curve for the decomposition of benzoyl peroxide at 75° in chlorobenzene.

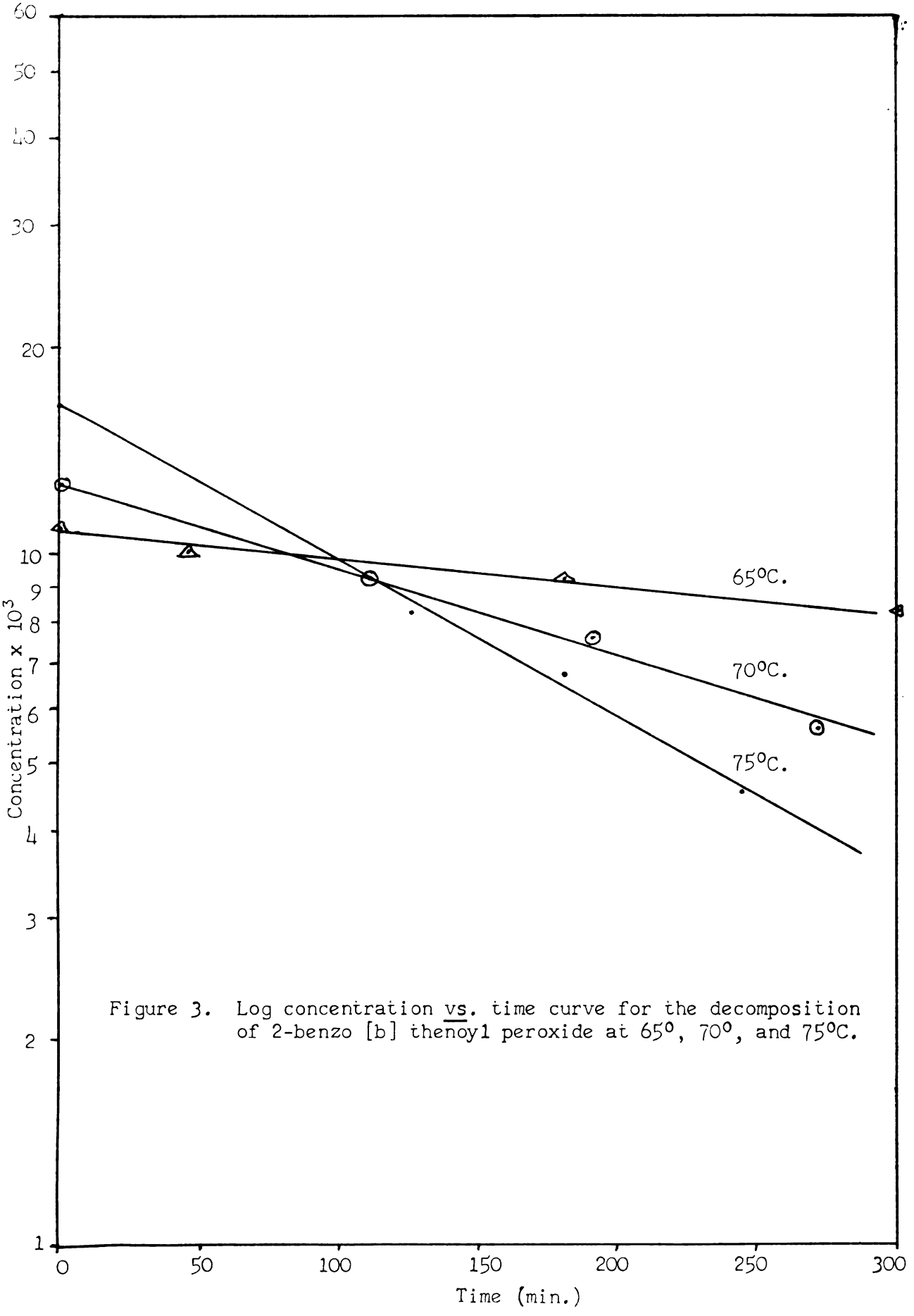
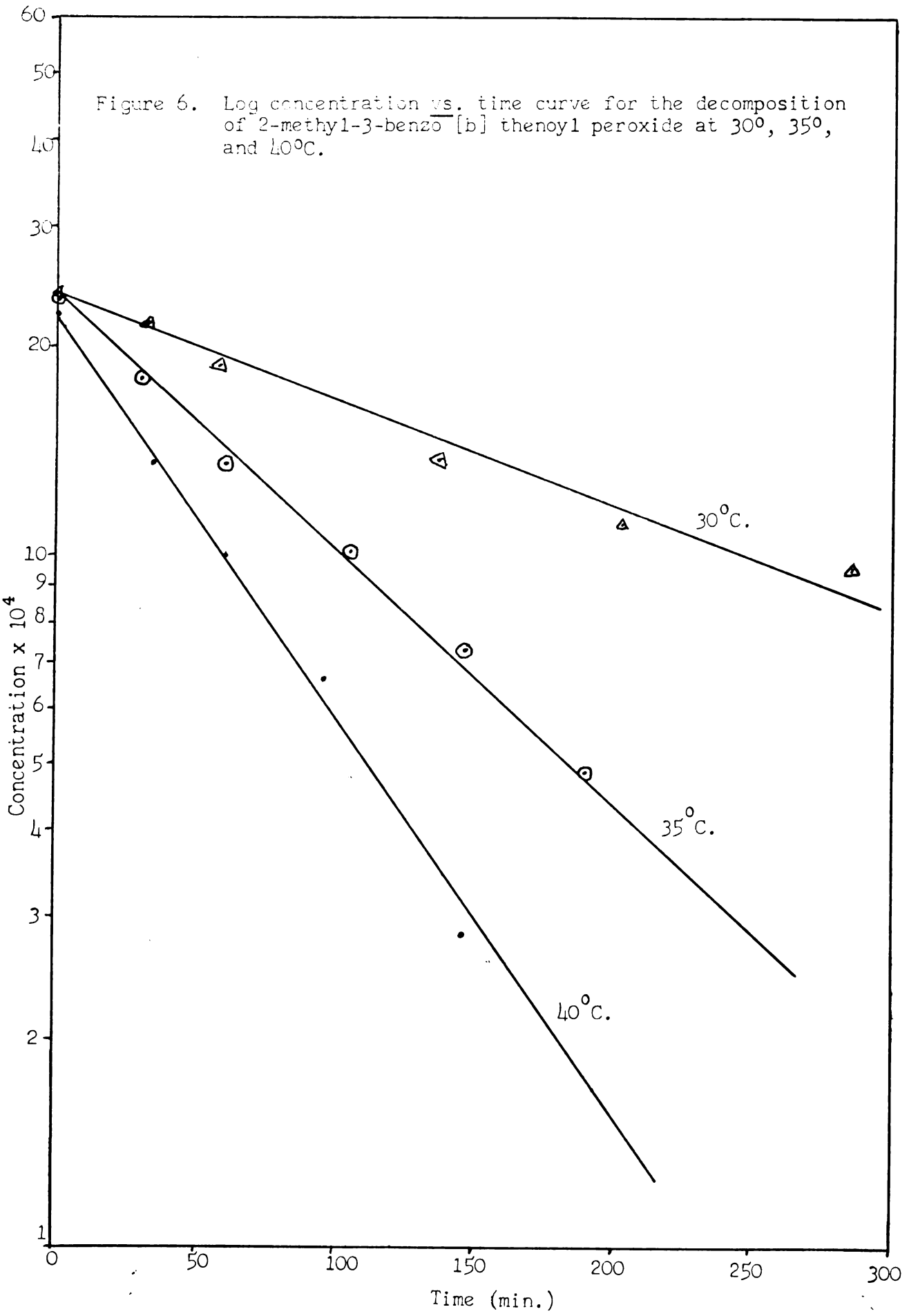


Figure 3. Log concentration vs. time curve for the decomposition of 2-benzo [b] thenoyl peroxide at 65°, 70°, and 75°C.

Figure 6. Log concentration vs. time curve for the decomposition of 2-methyl-3-benzo [b] thenoyl peroxide at 30°, 35°, and 40°C.



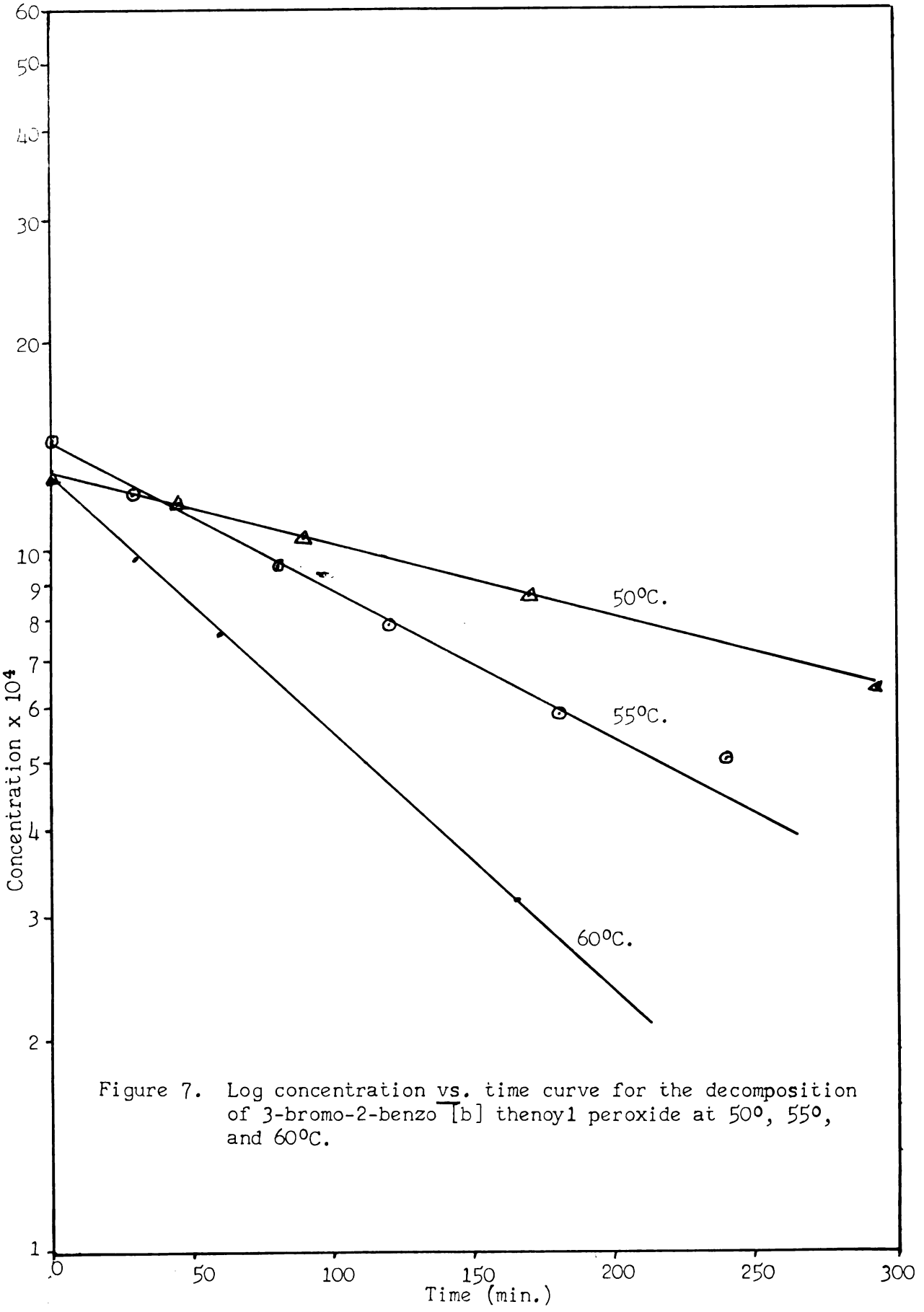


Figure 7. Log concentration vs. time curve for the decomposition of 3-bromo-2-benzo [b] thenoyl peroxide at 50°, 55°, and 60°C.

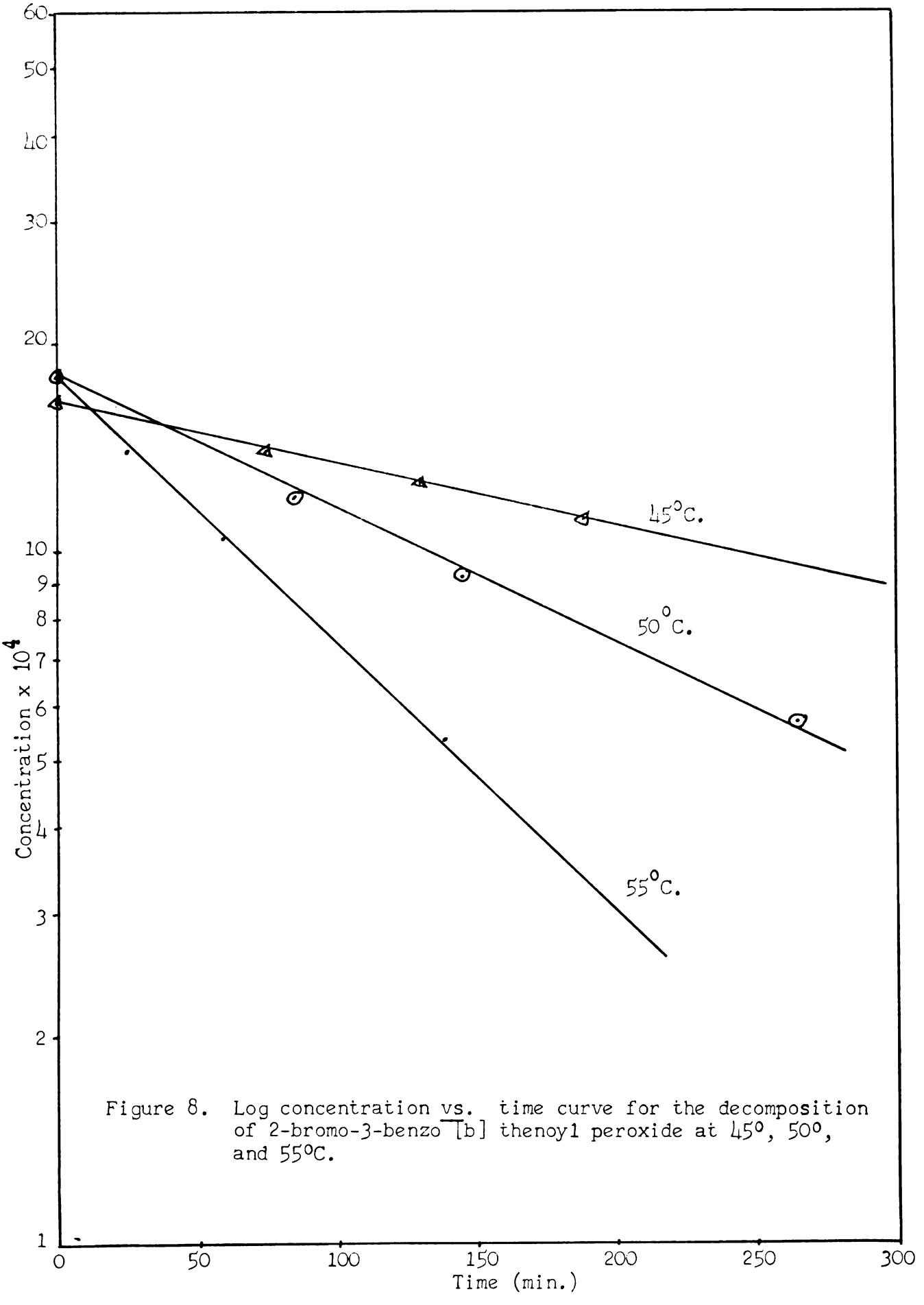


Figure 8. Log concentration vs. time curve for the decomposition of 2-bromo-3-benzo [b] thenoyl peroxide at 45°, 50°, and 55°C.

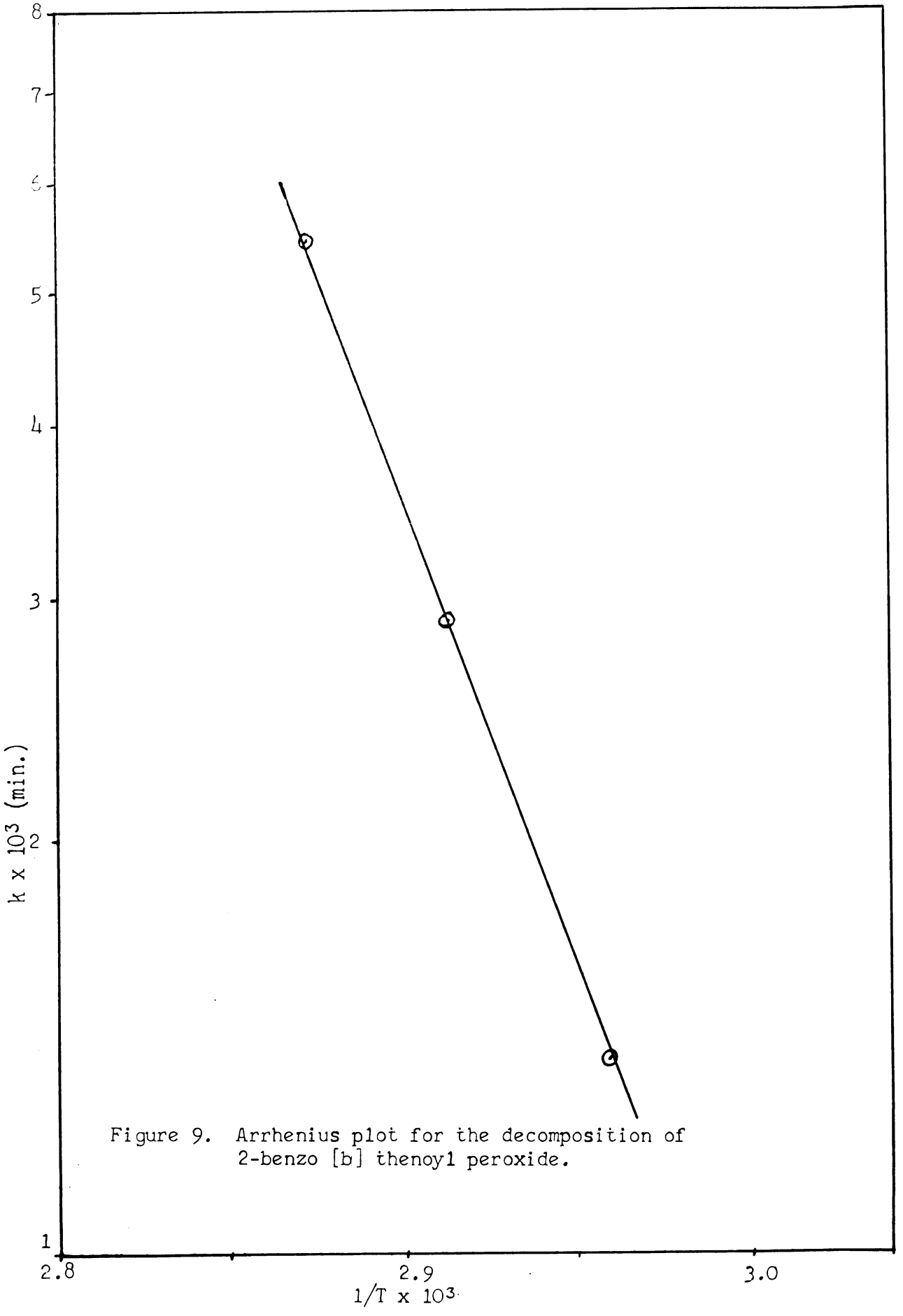


Figure 9. Arrhenius plot for the decomposition of 2-benzo [b] thenoyl peroxide.

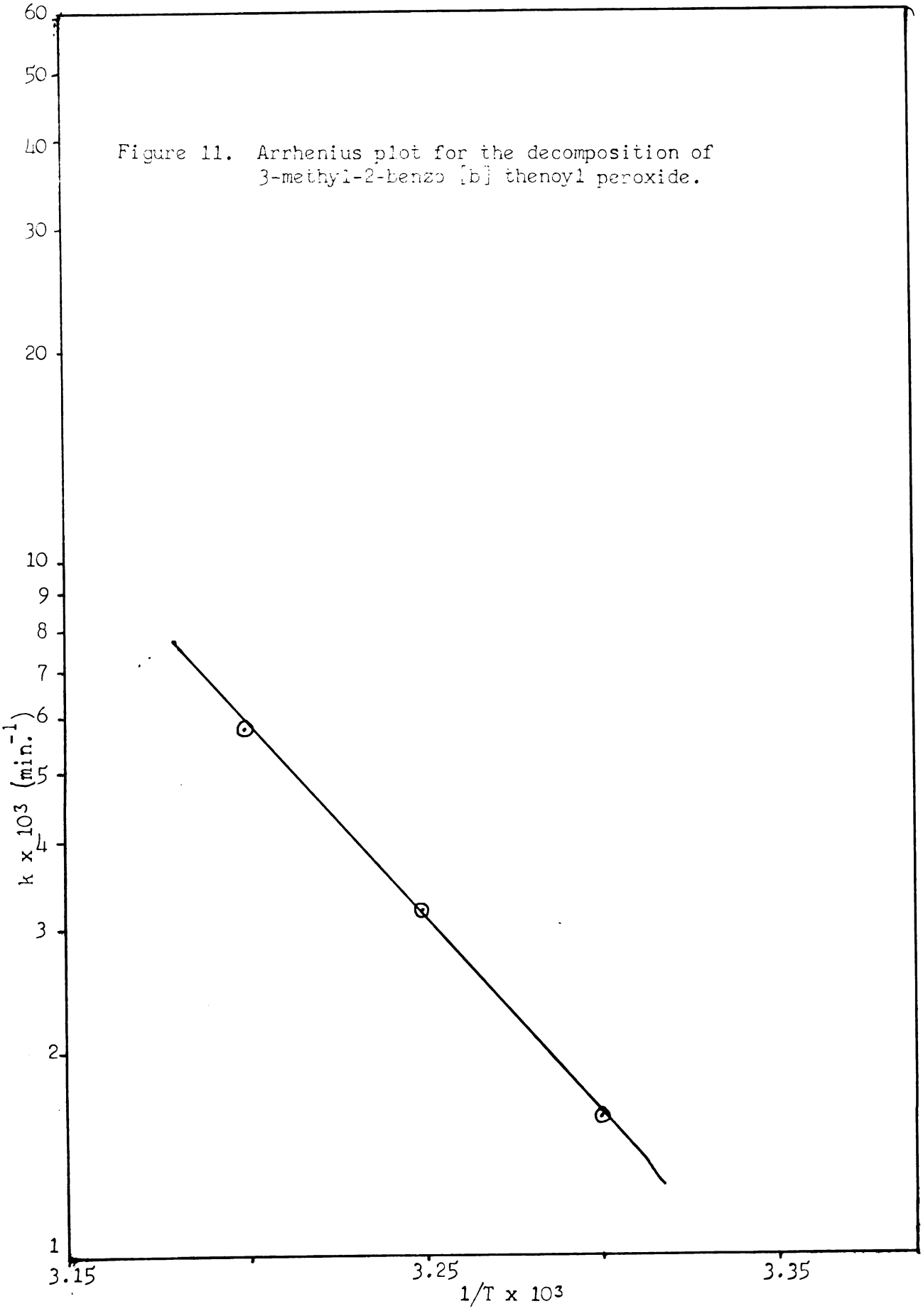


Figure 11. Arrhenius plot for the decomposition of 3-methyl-2-benzo [b] thenoyl peroxide.

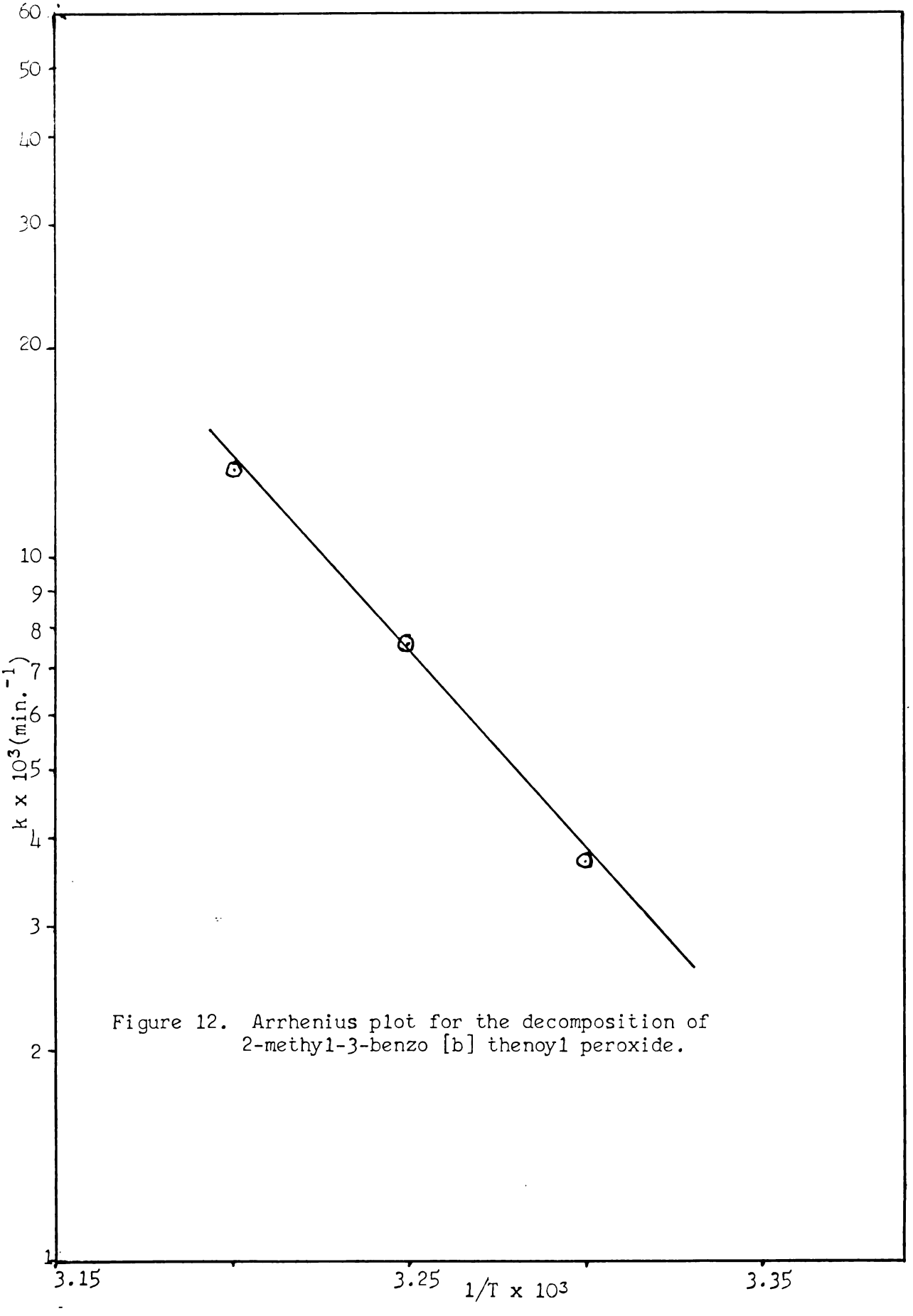


Figure 12. Arrhenius plot for the decomposition of 2-methyl-3-benzo [b] thenoyl peroxide.

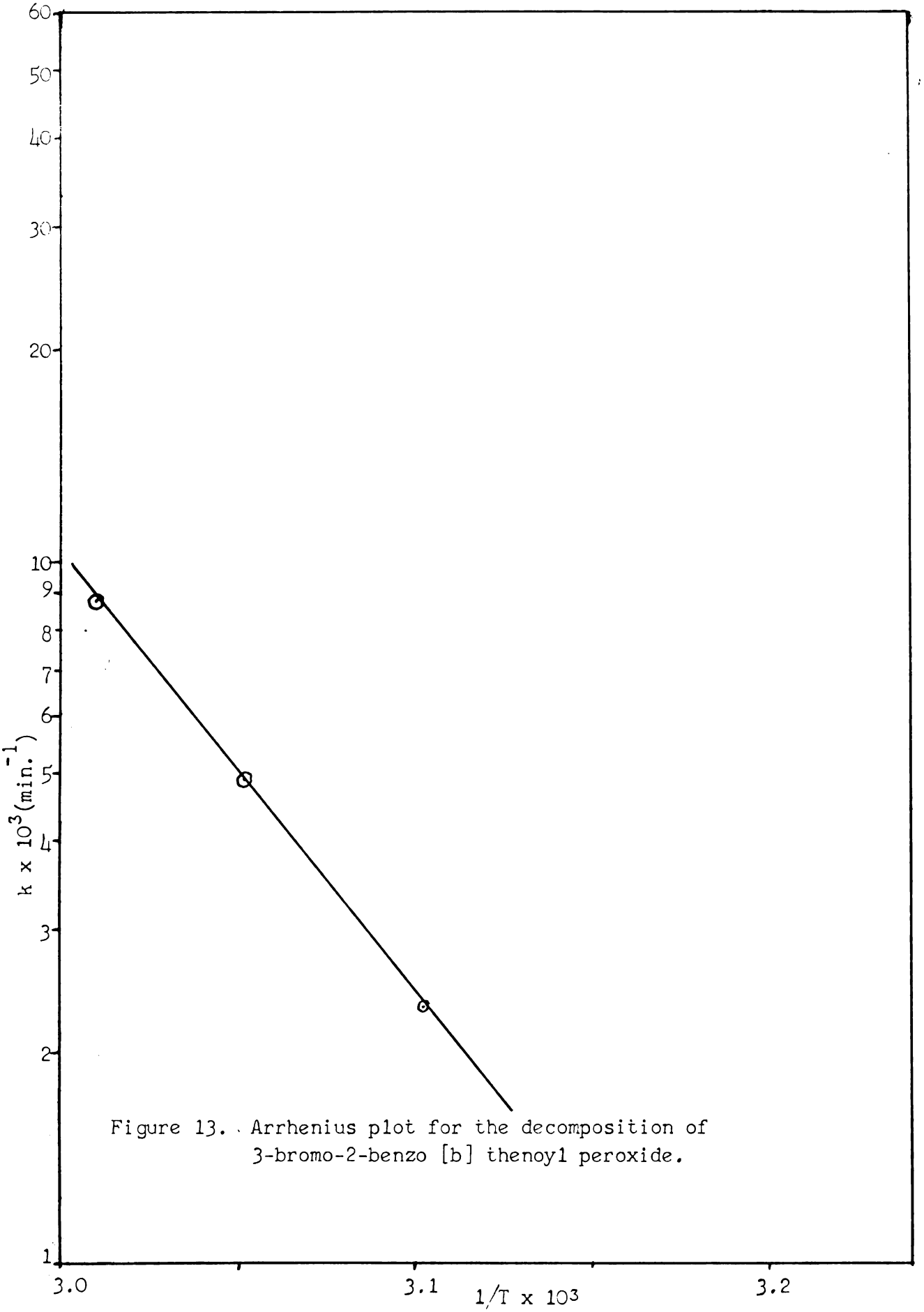


Figure 13. Arrhenius plot for the decomposition of 3-bromo-2-benzo [b] thenoyl peroxide.

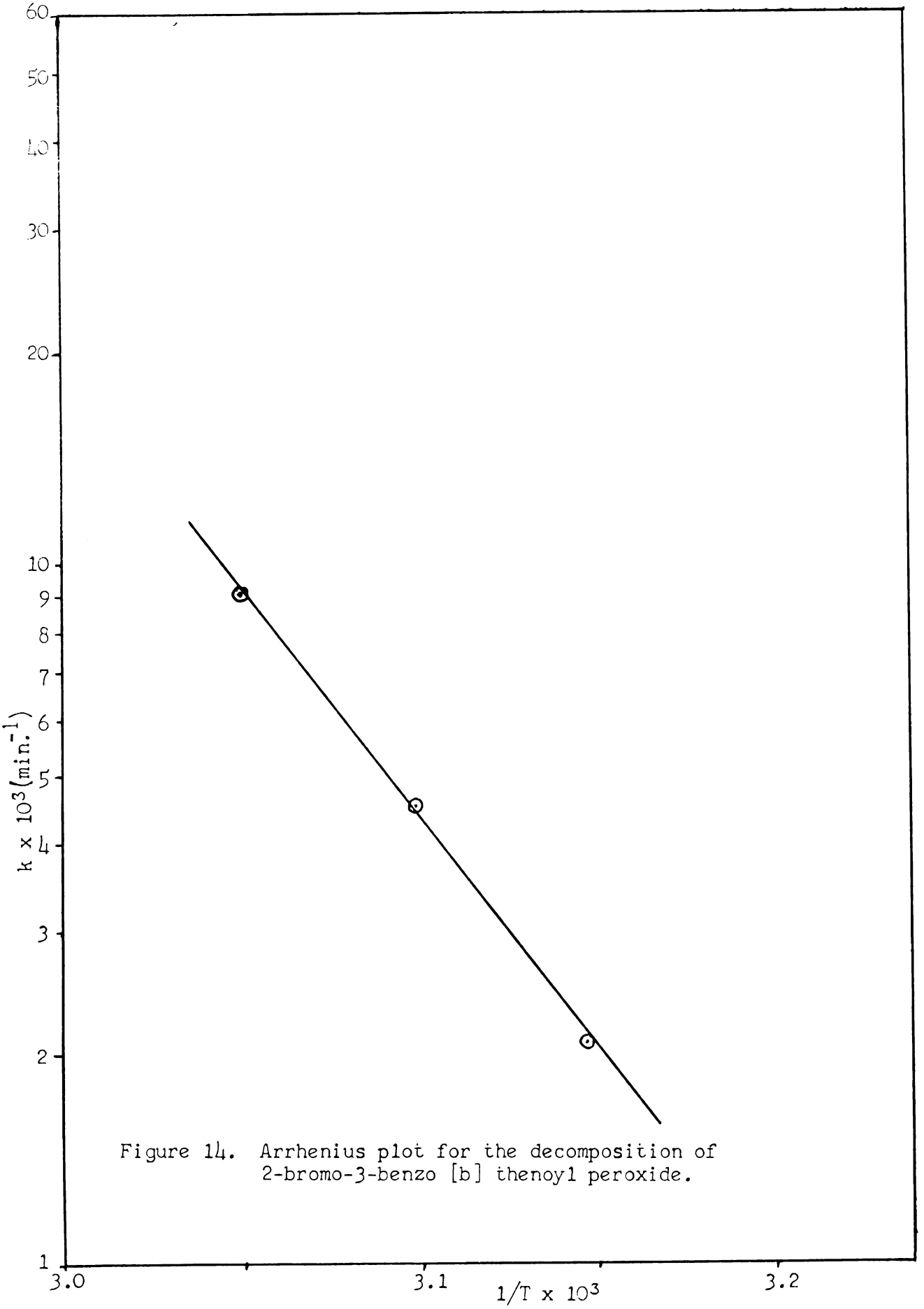


Figure 14. Arrhenius plot for the decomposition of 2-bromo-3-benzo [b] thenoyl peroxide.