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Preparation and Thermal Decomposition of Certain

Substituted Bis-(thenoyl) Peroxides (1)

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The effect of various substituents on the rates of thermal decomposition of substituted bis-(thenoyl) peroxides has been investigated. Nine unreported peroxides were prepared, including derivatives of 2- and 3-thenoic acids. The thermal decomposition rates of these peroxides were examined, in the presence of styrene as a free radical scavenger. First order kinetics were observed in all cases studied. In general it was found that electron releasing substituents increase, while electron withdrawing groups decrease, the decomposition rate; the only exception being bis-(5-nitro-3-thenoyl) peroxide. Entropies and energies of activation were determined and found to be linearly related for the peroxides studied.

Organic peroxides have been and are of theoretical and practical interest to chemists. The oxygen-oxygen bond, being relatively weak (bond energy 36 kcal. $mole^{-1}$), is capable of easy fission, by thermal or photochemical methods. It has been reported that while di-t-butyl peroxide decomposes thermally according to a strictly first order rate law, the similar decomposition of benzoyl peroxide was considerably more complex. Brown (4), as well as Erlenmeyer and Schonauer (5), have demonstrated that two processes were involved in the thermal decomposition of aromatic acyl peroxides; one of the reactions, thermal oxygen-oxygen fission, followed strictly first order kinetics, while the other, a free radical induced oxygen-oxygen fission, followed a higher order.

Swain, Stockmeyer, and Clark (6) reported that free radical scavengers such as 3,4-dichlorostyrene and methyl methacrylate suppress the free radical induced reaction sufficiently to make the overall reaction rate essentially identical to the rate of spontaneous cleavage of the oxygen-oxygen bond. Inhibitors of this type were also used by Blomquist and Buselli (7) in their study of the rates of decomposition of substituted benzoyl peroxides, and 3,4-dichlorostyrene was similarly employed by Schuetz and Teller (8) in an analogous investigation involving derivatives of bis-(2-thenoyl) peroxides. In the present investigation, as part of a continuing study of heterocyclic peroxides in these laboratories, styrene was used exclusively as a free radical scavenger, and good first order kinetics were observed in an examination of the decomposition rates of eight new symmetrical heterocyclic peroxides. These were prepared from the corresponding acid chlorides by interaction with aqueous sodium peroxide (8). The present investigation differed from the earlier report (8) by including the following types of peroxides, derivatives of mono-substituted 3-

thenoic acids; di-substituted 3-thenoic acids; 2-thenoic acids having structures capable of exerting steric hindrance during their decomposition; and a phenyl derivative of 2-thenoic acid, which could show unusual properties due to resonance interaction between the phenyl and thiophene rings. Iodometric analytical titration procedures (9) were employed to ascertain the purity of the peroxides investigated (Table I).

The decomposition rates were determined by infrared spectroscopy using a Perkin Elmer 21 Infrared spectrometer. Spectroscopically pure (8) carbon tetrachloride was employed as the decomposition medium for the kinetic examinations, with the exception of bis-(5-nitro-3-thenoyl) peroxide where chloroform had to be used as a reaction solvent since this peroxide was only very slightly soluble in carbon tetrachloride. A ninth, heretofore un-
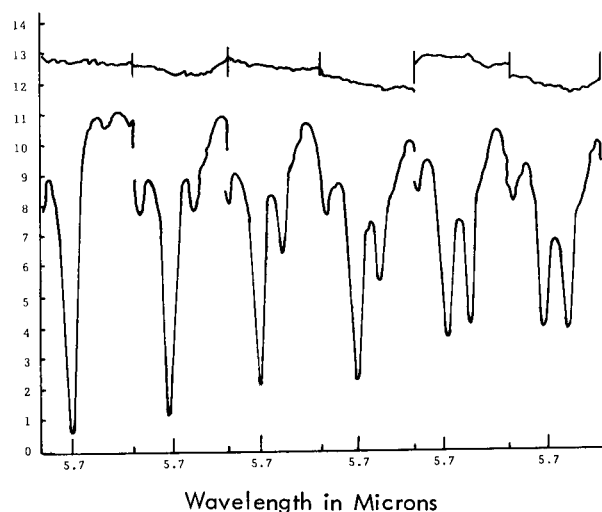

Wavelength in Microns

Figure 1. Quantitative infrared spectra of the decomposition of bis(3-methyl-2-thenoyl)peroxide
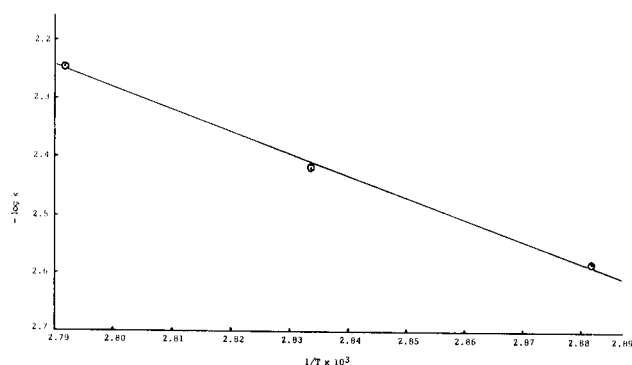
Figure 2. Energy of Activation of bis-(2,5-dimethyl-3-thenoyl)peroxide,.   Slope: -3.76×10^3

known, peroxide, bis(4,5-dibromo-2-thenoyl) peroxide, though prepared, was not kinetically investigated, as it was insoluble in solvents compatible with infrared techniques.

RESULTS AND DISCUSSION

The bis(thenoyl) peroxides prepared and characterized in this study are summarized, together with some of their properties, in Table I.
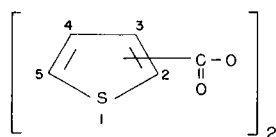
Some difficulties were encountered in the synthesis of the parent thenoic acids from which the peroxides investigated were in turn obtained. 3-Thenoic acid was prepared from 3-bromothiophene by two different methods, namely, through the butyl-lithium procedure as originally suggested by Zabik (10), and through the 3-thenonitrile as developed by Imoto and

his coworkers (11). The 3-bromothiophene itself was prepared from commercially available 2,5-dibromothiophene by its bromination to 2,3,5-tribromothiophene and subsequent removal of the alpha bromines with zinc dust in acetic acid. The yield of the 3-bromothiophene was doubled from that originally reported (12). At present, efforts in these laboratories have been unsuccessful in obtaining 3-thenoyl peroxides with a single electron releasing substituent in the heterocyclic ring. Attempts to convert 3-bromo-2-ethyl thiophene to 2-ethyl-3-thenoic acid through the lithium derivative of the former compound gave, only 5-ethyl-4-bromo-2-thenoic acid in poor yield. Thus it was decided that some information about the decomposition rates of such structures could be gained by a study of thenoic acids having the carboxyl group in the 3-position and bearing two additional substituents in the alpha positions of the heterocyclic ring. The acids, 2,5-dichloro- and 2,5-dimethyl-3-thenoic acids were easily prepared from 2,5-dichloro- and 2,5-dimethylthiophenes, respectively, as the latter materials are commercially available. The 2,5-dichloro- and 2,5-dimethylthiophenes were readily acetylated in the 3-position (13,14) and the ketones obtained were easily oxidized to the corresponding acids using hypochlorite.

In the kinetic determinations, the decomposition rates of the peroxides were followed by infrared spectrometery as suggested by Schuetz and Shea (9). The carbonyl absorption, typical for acyl peroxides at 5.7 microns was used to determine the peroxide concentration, and the absorption coefficient, A, equal to $\log I/I_0$ was calculated, where I is the linear distance of the "peroxide peak" from an arbitrary-zero-line, and I_0 is the distance of the base line from the same zero position (Figure 1, is a typical

TABLE I

Bis (Thenoyl) Peroxides

| Position of Substituents | | | | Peroxide | Formula | Yield, % | M.p., °C (i) | Purity, % (j) | Carbon | | Hydrogen | | Sulfur | |
2	3	4	5						Calcd.	Found	Calcd.	Found	Calcd.	Found
			Br	3 (a) (e)	$C_{10}H_4Br_2S_2O_4$	44	102-103	98.0	29.14	28.98	0.978	1.10	15.56	15.56
			Cl	3 (b) (e)	$C_{10}H_4Cl_2S_2O_4$	58	72-73	99.5	37.16	37.43	1.25	1.66	19.84	19.84
			NO₂	3 (c) (f)	$C_{10}H_4S_2N_2O_8$	80	153-154	98.9	34.78	35.02	1.16	1.21	18.61	18.57
	CH₃			2 (d) (f)	$C_{12}H_{10}S_2O_4$	35	92-93	97.5	51.05	51.12	3.75	3.62	22.72	22.58
Cl			Cl	3 (b) (e)	$C_{10}H_2Cl_4S_2O_4$	70	92-93	94.7	30.61	30.51	0.51	0.71	16.33	16.28
		Br	Br	3 (e)	$C_{10}H_2Br_2S_2O_4$	59	158-159 (decomp.)	97.5	21.05	20.96	0.35	0.31	11.23	10.67
			C₆H₅	2 (c) (f)	$C_{22}H_{14}S_2O_4$	80	81 (decomp.)	98.3	65.0	65.0	3.4	3.42	15.80	15.98
		Br	C₂H₅	2 (b) (e)	$C_{14}H_{12}Br_2S_2O_4$	82	98-102	99.9	35.89	35.36	2.56	2.62	13.68	13.29
CH₃			CH₃	3 (b) (g)	$C_{14}H_{12}S_2O_4$	82		96.7	54.19	53.94	4.82	4.52	20.65	20.17

Recrystallized from (a) chloroform, n-butyl ether (1:1); (b) petroleum ether (b.p. 30-60°); (c) chloroform; (d) benzene reaction solvent for acid chlorides used in the preparation of the peroxide; (e) cyclohexane; (f) toluene; (g) carbon tetrachloride; (i) all melting points are uncorrected; (j) purity after one recrystallization, except for bis(4,5-dibromo-2-thenoyl) peroxide which could not be recrystallized.

example). A plot of log A against the time in minutes gave a straight line, the slope of which, when multiplied by 2.303 gave the first order rate constant in reciprocal minutes. All peroxides studied were found to follow good first order kinetics; their decomposition rate constants and half lives at 79.6° are summarized in Table II. After preliminary plotting to estimate the magnitude of the rate constants, the final values were determined by the method of least squares, employing a Burroughs B 5,000 computer for the calculations.

The activation energies for the peroxides investigated were determined from a plot of log k versus 1/T (Figure 2 as an example), and the entropies of activation as well as the frequency factors were then calculated by Erying equation (16) (Table III).

TABLE II

Rate Constants and Half Lives for the Decomposition
of Substituted Thenoyl Peroxides at 79.6°

Peroxide	$k \times 10^3$ (min.$^{-1}$)	$T_{1/2}$ (minutes)
Bis-(5-bromo-3-thenoyl)	2.03	341
Bis-(5-chloro-3-thenoyl)	1.87	372
Bis-(5-nitro-3-thenoyl)	5.85	119
Bis-(3-methyl-2-thenoyl)	2.70	257
Bis-(5-ethyl-4-bromo-2-thenoyl)	3.12	222
Bis-(2,5-dichloro-3-thenoyl)	1.68	412
Bis-(5-phenyl-2-thenoyl)	8.50	81
Bis-(2-thenoyl) (a)	2.55	272
Bis-(3-thenoyl) (a)	2.36	294

(a) For comparison (8).

TABLE III

Energies of Activation, Frequency Factors,
and Entropies of Activation

Peroxide	$\Delta E_{act.}$ Kcal mole^{-1}	s $_{-1}$ sec.	$\Delta S_{act.}$ e.u.
Bis-(5-bromo-3-thenoyl-)	24.8	3.09×10^{10}	-8.86
Bis-(5-chloro-3-thenoyl-)	20.1	1.43×10^8	-22.3
Bis-(5-nitro-3-thenoyl-)	30.2	3.57×10^{14}	7.59
Bis-(3-methyl-2-thenoyl-)	29.8	1.63×10^{14}	5.74
Bis-(4-bromo-5-ethyl-2-thenoyl-)	28.7	2.68×10^{13}	2.44
Bis-(2,5-dichloro-3-thenoyl-)	23.1	5.72×10^9	-14.7
Bis-(5-phenyl-2-thenoyl-)	38.1	6.40×10^{19}	29.7
Bis-(2,5-dimethyl-3-thenoyl-)	17.2	2.96×10^6	-30.9

EXPERIMENTAL

3-Bromothiophene.

The method used here differed slightly in detail from that reported by Gronowitz (17); it was initially modified in these laboratories by Dodson (12), but the yields obtained in the present work were improved over those previously reported.

To 2,5-dibromothiophene, 485 g. (2.0 moles), contained in a 1 l. three-necked flask fitted with a condenser, a dropping funnel, and a mechanical stirrer, were added, 332 g. (2.2 moles) of bromine during an hour while cooling the reaction flask by immersion in an ice-bath.

To complete the reaction it was stirred for an additional 3 hours without external cooling. During the addition of the bromine copious quantities of hydrogen bromide were evolved. The reaction solution was set aside at room temperature overnight (16 hours). Methanolic potassium hydroxide (120 g. of potassium hydroxide pellets dissolved in 250 ml. of methanol) was then added to the solution. The alkaline mixture was heated at its reflux temperature for 3 hours and then exhaustively steam distilled to isolate the crude product.

The yellow oily product was separated from the distillate (approximately 615 g.) and transferred to a 3 l. three-necked flask fitted with a mechanical stirrer and reflux condenser. To the oil were added, 320 ml. of glacial acetic acid, 1,200 ml. of water, and 235 g. of metallic zinc dust. The latter was added carefully in small quantities through a powder addition funnel. An initial spontaneous exothermic reaction occurred, raising the reaction mixture's temperature to its reflux point. This subsided in about 40 minutes and the reaction mixture was held at this temperature for an additional 18 hours, then steam distilled using a 6 inch Vigreaux column until the vapor temperature in the distillation head reached 103°. The light colored oily product was separated, dried with anhydrous calcium chloride, and redistilled at atmospheric pressure to obtain a pure product boiling at 156-160°, n_D^{20} 1.5915, yield, 237.8 g. (1.42 moles, 71%).

3-Thenoic Acid.

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

The first of these suggested by Zabik in these laboratories (10) and also employed by Gronowitz (17) with slight modifications was used in the preparation of approximately half the 3-thenoic acid utilized in this investigation (yield 90% based on 3-bromothiophene). The second method employed in the preparation of 3-thenoic acid was a modification of that reported by Nishimura, Motayama, and Imoto (11), with 3-cyanothiophene as an intermediate (yield 83% based on 3-bromothiophene).

Preparation of 5-Substituted 3-Thenoic Acids.

5-Chloro, 5-bromo, and 5-nitro-3-thenoic acids were prepared following the methods of Campaigne and Bourgeois (18) directly from 3-thenoic acid.

Preparation of acid chlorides.

The acid chlorides were prepared from the parent acids by reaction with thionyl chloride. A typical preparation follows:

5-Bromo-3-thenoyl Chloride.

In a 100 ml. single necked flask with a reflux condenser and a sodium hydroxide trap attached to it, were placed 10 g. (0.0483 mole) of 5-bromo-3-thenoic acid and 25 g. (0.209 mole) of thionyl chloride. A vigorous initial reaction occurred with the evolution of hydrogen chloride gas; when this had subsided the dark colored mixture was heated at its reflux temperature for 4 hours. Excess thionyl chloride was removed by distillation at atmospheric pressure and the residue was distilled at 120-130°/10-15 mm. using a 4 inch Vigreaux column to obtain 12 g. of crude product containing some thionyl chloride. The exact yields of products obtained were not determined as the heterocyclic acid chlorides were not further purified by completely removing the thionyl chloride since its presence offered no experimental difficulties in using the impure acid chlorides to prepare their corresponding heterocyclic peroxides.

Preparation of the Peroxides.

All peroxides were prepared from the corresponding acid chlorides by reaction with aqueous sodium peroxide at 0°. A typical preparation follows:

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

A vigorously stirred 25 ml. volume of water contained in a 300-ml. three-necked reaction flask fitted with a stirrer, thermometer and dropping funnel was cooled to 0° by immersion in an ice-sodium chloride bath and 1.95 g. (0.025 mole) of sodium peroxide was dissolved in it in small portions, care being taken that each portion was completely dissolved, before additional sodium peroxide was added. To the cold peroxide solution, a second solution containing 10.0 g. (0.044 mole) of 5-bromo-3-thenoyl chloride in 35 ml. of dry cyclohexane was added in one portion. A colorless solid precipitated immediately. The mixture was stirred at 0° for an additional 1.5 hours. The colorless, crystalline product was recovered by filtration washed with ice water, and dried at 0°, for 48 hours in a vacuum desiccator. The product was recrystallized from the minimum amount of n-butyl ether, preheated to 50°, and then reprecipitated by the addition of chloroform. The yield of colorless peroxide obtained was

4.0 g. (0.0097 mole, 44%), melting at 102-103°. On melting, the material turned red in color and detonated, after having been maintained at its melting temperature for about 2 minutes.

Anal. Calcd. for $C_{10}H_4Br_2O_4S_2$: C, 29.14; H, 0.99; S, 15.56; Br, 38.65. Found: C, 28.98; H, 1.10; S, 15.56; Br, 38.65.

Kinetics.

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

The peroxide solutions were prepared, using specially purified carbon tetrachloride for all the peroxides except bis(5-nitro-3-thenoyl) peroxide, which was only slightly soluble in carbon tetrachloride. For this peroxide purified chloroform was used as a solvent. The concentration of the peroxide solutions were prepared as closely to 0.01 M as was feasible. They were transferred into ampoules of approximately 1 ml. capacity employing a hypodermic syringe, frozen in dry ice, and immediately sealed with the gas flame torch. The samples were then introduced into the constant temperature bath which had been preheated to the desired reaction temperature. A 3 minute period was allowed for the peroxide solutions to come to thermal equilibrium. Duplicate samples were removed from the thermostatted bath for all determinations at this "zero time". The results of the kinetic determination are shown in Table II.

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