[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Synthesis and Thermal Decomposition of Some Bis(2-thenoyl) Peroxides[1,2]

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A new series of symmetrical 5,5′-disubstituted bis(2-thenoyl) peroxides was prepared, with the substituents chloro, bromo, methyl, *t*-butyl, and nitro groups. The unsymmetrical 5-methylbis(2-thenoyl) peroxide and two new 4,4′-disubstituted bis-(2-thenoyl) peroxides, the 4,4′-dimethyl and 4,4′-dibromo compounds were also prepared. The thermal decomposition products of bis(2-thenoyl) peroxides in carbon tetrachloride are 2-thenoic acid (20 mole per cent), carbon dioxide (20 mole per cent), and a polymeric material (46 per cent by weight of initial peroxide). In the presence of the free radical scavenger 3,4-dichlorostyrene, a polymer was isolated which contained 2.95% sulfur. The rates of spontaneous thermal decomposition of the thenoyl peroxides in carbon tetrachloride were determined by conducting their decompositions in the presence of the efficient free radical scavenger, 3,4-dichlorostyrene. In all cases studied, with the exception of bis(5-nitro-2-thenoyl) peroxide, the decomposition rates followed strict first-order kinetics. In the absence of a free radical scavenger the rate of decomposition of bis(2-thenoyl) peroxide is much greater. The rate constants (75°) show that electron-donating substituents on the thiophene rings accelerate the rate of decomposition, while electron-withdrawing substituents have the opposite effect. The Hammett equation was found applicable to the spontaneous decomposition of the substituted bis (2-thenoyl)peroxides.

The initial cleavage in the thermal decomposition of benzoyl peroxide has been shown to occur at the oxygen-oxygen bond to yield two benzoyloxy radicals.[3] The rate of decomposition of benzoyl peroxide is greater than first-order to an extent which varies with the solvent, indicating that in addition to the initial cleavage to benzoyloxy radicals, some induced decomposition occurs. The induced decomposition is thought to involve a chain reaction in which the benzoyloxy radicals (or phenyl radicals formed by loss of carbon dioxide) attack benzoyl peroxide molecules to produce further decomposition, or alternatively these radicals may attack solvent molecules forming solvent radicals which in turn are capable of attacking benzoyl peroxide molecules.[4-6]

Swain, Stockmayer, and Clarke[7] employed the efficient free radical scavenger, 3,4-dichlorostyrene, to inhibit completely the induced decomposition of substituted benzoyl peroxides.

This scavenger was employed in the present study to obtain the first-order rate constants for the thermal decomposition of a series of bis(2-thenoyl) peroxides in carbon tetrachloride solution. The symmetrical sulfur heterocyclic peroxides were prepared from the corresponding thenoyl chlorides and aqueous sodium peroxide.[8] The unsymmetrical 5-methylbis(2-thenoyl) peroxide was synthesized by the reaction of 5-methyl-2-thenoyl chloride with sodium perthenoate.[7-9] The rates of decomposition were determined iodometrically[4] using the dead-stop method[10] to determine the titration end point.

RESULTS AND DISCUSSION

The bis(2-thenoyl) peroxides prepared, the solvents used for their recrystallization, the solvent used for recrystallization of their corresponding acid chlorides, their yields, melting points, and purity as determined by iodometric titration and analysis are listed in Table I. The 5-methylbis(2-thenoyl) peroxide partially decomposed and took on a slight yellow coloration after storage in a vacuum desiccator, at 0°, for several months. Under the same storage conditions, the other peroxides remained colorless and showed no decomposition after several months.

The products isolated from the decomposition of bis(2-thenoyl) peroxide in carbon tetrachloride in the absence of a free radical scavenger were 2-thenoic acid (20 mole per cent), carbon dioxide (20 mole per cent), and polymeric material (46 per cent by weight of initial peroxide.[11] The formation of 2-thenoic acid as a major product, together with the low yield of carbon dioxide, suggest that the initially formed 2-thenoyloxy radicals react by abstraction of a hydrogen atom from either peroxide molecule or from the accumulating polymeric material, as well as by loss of carbon dioxide. In contrast, bis(3-thenoyl)peroxide was found to yield 55 mole per cent carbon dioxide, indicating the 3-thenoyloxy radical is less stable towards decarboxylation than the 2-thenoyloxy radical. In the presence of 3,4-dichlorostyrene bis(2-thenoyl) peroxide decomposed to yield a polymer containing 2.95% sulfur.

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(1) Abstracted in part from the doctoral thesis of D. M. Teller, 1959.

(2) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September 1961.

(3) G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950).

(4) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

(5) P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **69**, 2299 (1947).

(6) W. E. Cass, *J. Am. Chem. Soc.*, **68**, 1976 (1946).

(7) C. G. Swain, W. T. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

(8) C. C. Price and E. Krebs, *Org. Syntheses*, **23**, 65 (1943).

(9) G. Braun, *Org. Syntheses*, **Coll. Vol. I.**, 431 (1956).

(10) E. W. Abrahamson and H. Linschitz, *Anal. Chem.*, **24**, 1355 (1952).

(11) M. C. Ford and D. MacKay, *J. Am. Chem. Soc.*, 4620 (1957).

TABLE I

BIS(2-THENOYL) PEROXIDES

Peroxide[a]	Solvent for Recrystallization	Yield, %	M.P.[c]	Purity,[d] %	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found
Bis(2-thenoyl)	Chloroform-cyclohexane	40	100–101	98.9	47.23	47.52	2.38	2.40	25.22	25.43
Bis(5-methyl-2-thenoyl)	Pet. ether[e]	35	104	99.2	51.05	51.12	3.57	3.62	22.72	22.58
Bis(4-methyl-2-thenoyl)	Benzene–pet. ether[e]	54	113	99.6	51.05	51.26	3.57	3.49	22.72	22.56
Bis(3-thenoyl)[b]	Cyclohexane	52	120	100	47.23	47.41	2.38	2.22	25.22	25.19
Bis(5-bromo-2-thenoyl)	*n*-Butyl ether–chloroform	44	130	99.5	29.14	28.98	0.98	1.10	15.56	15.56
Bis(5-chloro-2-thenoyl)	Pet. ether[e]	48	110	100	37.16	37.48	1.25	1.66	19.84	19.84
Bis(5-*t*-butyl-2-thenoyl)	Pet. ether[e]	24	93	99.2	58.99	59.16	6.05	6.00	17.50	17.56
Bis(4-bromo-2-thenoyl)	Pet. ether[e]	23	126	100	29.14	29.16	0.98	1.07	15.56	15.47
Bis(5-nitro-2-thenoyl)	Chloroform–pet. ether[e]	34	120–122	98.9	34.88	34.78	1.17	1.31	18.63	18.81
5-Methylbis(2-thenoyl)	Chloroform–pet. ether[e]	22	78–80	98.0	49.24	49.31	3.01	3.21	23.90	23.70

[a] With the first four peroxides listed toluene was used as a solvent for the acid chloride, with the next four peroxides cyclohexane was used as the solvent and with the nitro peroxide benzene was used as the solvent. [b] Although it is not structurally a bis(2-thenoyl) peroxide, this peroxide was prepared and studied for purposes of comparison. [c] All melting points are uncorrected. [d] Purity after one recrystallization. [e] Pet. ether (b.p. 30–60°).

The kinetic determinations were carried out in a carbon tetrachloride solution containing 0.20*M* of 3,4-dichlorostyrene. The initial peroxide concentrations varied from 0.009*M* to 0.025*M*. With the exception of bis(5-nitro-2-thenoyl) peroxide, the decomposition rates were found to obey the first-order rate equation. In the absence of a free radical scavenger the rate of decomposition of bis(2-thenoyl) peroxide is much greater than first-order. Integration of the first-order rate equation gives: $k = 2.303/t \log C_0/C$, where C is the concentration of peroxide at time t, C_0 is the initial concentration of peroxide and k is the first-order rate constant. The rate constants were calculated from the slope of the plots of log C *vs.* t, the slope in each case being determined by the method of least squares. The rate constants, determined at 75°, are listed in Table II, with the rate constants for some substituted benzoyl peroxides determined at 80° in dioxane solution with 3,4-dichlorostyrene as the free radical scavenger[7] for comparison.

Examination of the rate constants for the bis(2-thenoyl) peroxides shows that electron-donating substituents on the heterocyclic ring increase the rate of decomposition of the peroxide, while electron-withdrawing substituents have the opposite effect. This effect parallels that found for the benzoyl peroxides (Table II).[7] There is a close parallel in rate constants, both in absolute values and the relative order for the corresponding thenoyl and benzoyl peroxides, if the reasonable assumption is made that the 5-substituted thenoyl peroxides are analogous to the *para*-substituted benzoyl peroxides. As the rate constants for the benzoyl peroxides were determined at 80° while those for the thenoyl peroxides were determined at 75°, a better comparison between the two series of peroxides can be made by doubling the recorded rate constants for the thenoyl peroxides, since in the latter case the rate constant doubles, roughly, for each five degrees rise in the decomposition temperature.

TABLE II

RATE CONSTANTS FOR THE DECOMPOSITION OF SUBSTITUTED BIS(2-THENOYL) PEROXIDES AT 75°

Peroxide	$k \times 10^3$ (Min.$^{-1}$)	$\sigma_1 + \sigma_2$
Bis(5-methyl-2-thenoyl)	2.54	+0.340
Bis(5-*t*-butyl-2-thenoyl)	2.43	+0.394
5-Methylbis(2-thenoyl)	1.79	+0.170
Bis(4-methyl-2-thenoyl)	1.76	+0.138
Bis(2-thenoyl)	1.33	0.000
Bis(3-thenoyl)	1.29	—
Bis(5-chloro-2-thenoyl)	0.95	+0.454
Bis(5-bromo-2-thenoyl)	0.92	+0.464
Bis(4-bromo-2-thenoyl)	0.69	+0.782
Bis(*p*-methyl)benzoyl)	3.68	+0.340
Bis(*p*-*t*-butylbenzoyl)	3.65	+0.394
Bis(*m*-methylbenzoyl)	2.64	+0.138
Bis(benzoyl)	2.52	0.000
Bis(*p*-chlorobenzoyl)	2.17	+0.454
Bis(*p*-bromobenzoyl)	1.94	+0.464
Bis(*m*-bromobenzoyl)	1.54	+0.782

When the values of log k/k_0 for the bis(2-thenoyl) peroxides [where k_0 is the rate constant for bis(2-thenoyl) peroxide] were plotted against $(\sigma_1 + \sigma_2)$, where σ_1 and σ_2 are the substituent constants for the two groups on the thiophene rings of the substituted thenoyl peroxides a fairly good straight line resulted for the 4- and 5-substituted thenoyl peroxides studied (Fig. 1). The assumption was made that the ρ values derived from the ionization constants of the substituted benzoic acid are reasonably applicable to the corresponding thiophene analogs.

The value of the reaction constant, ρ, is equal to -0.38 for the benzoyl peroxides. The small magni-

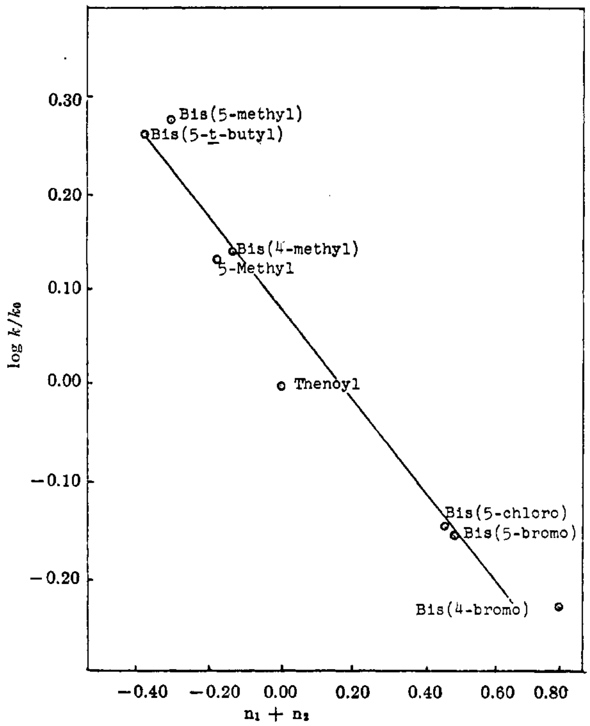

Fig. 1. Hammett relationship for the bis(2-thenoyl) peroxides

tude of this value shows that the electronic effect of the substituents has only a very small influence on the rate of decomposition of the benzoyl peroxides. The reaction constant, ρ, for the bis(2-thenoyl) peroxides is -0.44, approximately equal to the ρ value for the substituted benzoyl peroxides.

EXPERIMENTAL

Preparation of the acid chlorides. All of the thenoyl chlorides were prepared from the corresponding acids by reaction with thionyl chloride.

Preparation of the peroxides. The following synthesis of bis(2-thenoyl) peroxide illustrates the method used to prepare the symmetrical peroxides. Sodium peroxide, 5.0 g. (0.064 mole) was added to a well stirred quantity of water maintained at 0°. A solution of 14.6 g. (0.10 mole) of 2-thenoyl chloride dissolved in 30 ml. of dry toluene was added dropwise at 0° to the aqueous peroxide solution with vigorous stirring, during a 30 min. period. The colorless, insoluble product began to form immediately after the addition of the acid chloride was complete. The reaction mixture was stirred for an additional 2 hr. at 0°. The product was removed by filtration and washed with ice water. Recrystallization of the dried product from a minimum amount of chloroform by the addition of cyclohexane yielded 5.1 g. (0.020 mole, 40%), of a dense, colorless crystalline solid, melting at 100–101°. See Table I for data on the other peroxides prepared.

Kinetics. The following experimental procedure was used in a typical kinetic determination. A 0.315-g., (0.00124 mole) quantity of bis(2-thenoyl) peroxide and 1.4 ml. (0.010 mole) of 3,4-dichlorostyrene[6] was made up to volume with purified carbon tetrachloride[12] in a 50-ml. volumetric flask. The solution was cooled to 0° and purged of oxygen by bubbling purified nitrogen[13] into the flask for 15 min. The solution was warmed to room temperature and six 5-ml. samples were pipetted into ampoules. The ampoules were sealed at room temperature under a nitrogen atmosphere, placed in a metal rack, and immersed in an electrically heated mineral oil bath maintained at 75° ±0.2°. A period of 3 min. was allowed for the samples to reach the temperature of the bath. Zero time was assumed to be 3 min. after the ampoules were immersed in the bath. At times intervals ampoules were removed from the bath and immediately quenched by immersion in cold water. The contents of the ampoule were emptied into an Erlenmeyer flask, the ampoule was rinsed thoroughly with carbon tetrachloride, and the rinsings were placed in the flask. Several small lumps of Dry Ice were placed in the flask and 10 ml. of analytical reagent grade acetic anhydride and 1 g. of analytical reagent grade sodium iodide were added. The solution was stoppered and stirred for 10 min. with a magnetic stirrer. A volume of 50 ml. of distilled water was added, and the rapidly stirred solution was immediately titrated with standard sodium thiosulfate solution. The dead-stop method[10] was used to determine the end point in the titration, employing a Fisher electropode in conjunction with a pair of platinum electrodes immersed in the vigorously stirred solution. The end point corresponded to the increment of thiosulfate added, after which current failed to register on the galvanometer of the electropode. It was found that no blank was necessary as long as the Dry Ice was added. In the absence of Dry Ice, a positive correction of 0.10 ml. was necessary. Duplicate samples were titrated during several kinetic determinations, and the average deviation varied from 1 to 15 p.p.t. The average deviation usually increased in proportion to the per cent peroxide decomposed.

Several kinetic runs were made in which the initial peroxide concentration was varied by a factor of two. Only a slight decrease in rate was noted on halving the initial concentration of bis(5-methyl-2-thenoyl) peroxide, bis(4-methyl-2-thenoyl) peroxide, and bis(5-chloro-2-thenoyl) peroxide, while with bis(2-thenoyl) peroxide the rate was not affected. Thus, it appears that very little induced decomposition occurred under the experimental conditions employed.

In the presence of 0.20*M* quantities of either styrene or 3,4-dichlorostyrene the rates of decomposition of bis(2-thenoyl) peroxide are the same. This is also true for bis(5-*t*-butyl-2-thenoyl) peroxide. However, the over-all rate of decomposition of bis(5-nitro-2-thenoyl) peroxide, in which a large amount of induced decomposition would be expected to occur,[5] appears to be somewhat slower in 3,4-dichlorostyrene than in styrene, indicating that the former is the more efficient free radical scavenger. With neither inhibitor was the induced decomposition of the nitro peroxide completely eliminated, as evidenced by the nonlinearity of its first-order rate curve.

Product Analyses. The product analyses on bis(2-thenoyl) peroxide were carried out as described by Ford and MacKay[10] for the decomposition of bis(2-thenoyl) peroxide in benzene solution. Carbon dioxide was determined gravimetrically by absorption on ascarite. High vacuum distillation ($< 2 \times 10^{-3}$ mm.) of the tarry brown neutral fraction (*ca.* 10% by weight of starting peroxide) yielded no identifiable products.

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(12) L. F. Fieser, "Experiments in Organic Chemistry," Part II., D. C. Heath and Co., New York, 1941, p. 365.

(13) L. F. Fieser, "Experiments in Organic Chemistry," Part II., D. C. Heath and Co., New York, 1941, p. 395.