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A New Series of Unsymmetrical Acyl Peroxides (1a)

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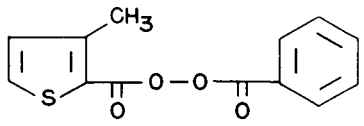
Our interest in studying the decomposition rates of substituted acyl peroxides of various heterocyclic series has prompted us to prepare some unsymmetrical peroxides containing the phenyl group as well as heterocyclic ring systems.



Bis-2-thenoyl- (4), bis-2-furoyl (5), bis-3-thenoyl (6) peroxides as well as derivatives of these compounds carrying various substituents (6, 7, 8) have been prepared and the influence of the substituents on their decomposition rates have been investigated. The only unsymmetrical peroxy compound reported before the present work is 5-methyl-bis-(2-thenoyl) peroxide (6).

The compounds were prepared by the reaction of the heterocyclic acid chloride with sodium perbenzoate, employing the procedure originally used by Braun (9). Kinetic studies involving the rates of thermal decomposition of the peroxy compounds into free radicals by the homolytic scission of the oxygen-oxygen bond were conducted as previously described for symmetrical compounds (8). So far studies in this series were conducted on only one compound (3-methyl-2-thenoyl)benzoyl peroxide, whose structure is shown above. The kinetics have been described in a previous publication (8).

Just as for the previously described (8) symmetrical compounds rate constants calculated fitted the first-order rate law. They were calculated from infrared data obtained for three temperatures (7, 8). The absorption peak employed in these studies is the carbonyl absorption peak at 5.7 microns, typical for this type of peroxy compound (6, 7, 8).

EXPERIMENTAL

A typical preparation of an unsymmetrical peroxide follows:

3-Thenoyl Benzoyl Peroxide.

A sodium peroxybenzoate solution was prepared as described in the literature (8), introduced into a 500 ml. flask fitted with stirrer and cooled by a dry-ice 2-propanol bath to maintain the temperature at -5°. Twelve and seven-tenths g. (0.086 mole) of 3-thenoyl chloride (6) was dissolved in approximately 50 g. of dry cyclohexane, a slight excess of solvent had to be used, as some difficulty was encountered in dissolving the solid acid chloride. The acid chloride solution was added slowly through a dropping funnel to the aqueous solution of sodium peroxybenzoate. The mixture was then stirred at -5° for an additional hour, after which the white solid was filtered off, washed several times with ice-cold water and dried *in vacuo* to yield 14.3 g. (0.057 mole, 66%) of peroxide, m.p. 102-102.3°. After melting the material turned red, but did not detonate.

A Beckmann IR-5 Spectrophotometer was employed for the kinetic studies, the samples being prepared in glass ampoules in solution in spectroscopically pure carbon tetrachloride.

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TABLE I

Peroxides Prepared

Peroxide	Yield %	M.P. °C	Analysis (%) Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found
2-Furoyl-benzoyl-	28	57.5-58	62.07	61.96	3.42	3.58	-----	-----
2-Thenoyl-benzoyl-	83	92-92.5	58.06	57.44	3.23	3.20	12.90	12.84
3-Thenoyl-benzoyl-	66	102-102.3	58.06	57.90	3.23	3.24	12.90	12.98
(3-Methyl-2-thenoyl-) benzoyl	53	49.5-50	59.53	59.44	3.84	3.84	12.22	12.24

TABLE II

Rates and Activation Energy
for the Thermal Decomposition of
(3-Methyl-2-thenoyl) Benzoyl Peroxide

Temp. °C	k (min^{-1}) x 10^3	E_a# cal. $mole^{-1}$
73.2 ± 0.1	1.34 ± 0.13	
80.9 ± 0.1	2.94 ± 0.05	24,990
85.2 ± 0.1	4.51 ± 0.00	

obtained by plotting log k against 1/T and multiplying by 2.303 R

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