ORGANIC SECTION

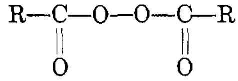
Synthesis and Thermal Decomposition of Series of Acyl Peroxides

DELOS R. BYRNE,[1] STEPHEN R. BURTON,[2] ANDREW CHIU,[3] FREDERICK KABBE,[4] and FRED M. GRUEN[5]
Department of Chemistry, Olivet College, Olivet, Mich. 49076

ROBERT D. SCHUETZ
Institute of Biology and Medicine, Michigan State University, East Lansing, Mich. 48823

The present paper describes the effect of various systems (carbocylic, as well as heterocyclic), on the decomposition rates of acyl peroxides. Systems studied include benzoyl-, 1-naphthoyl-, 2-naphthoyl-, 2- and 3-thenoyl-, and 2- and 3-furoyl. A total of 16 peroxides were prepared of which 12 have not previously been described. Rate studies were performed on the various compounds at 3 to 7 temperatures ranging from approximately 60–100°C. Rates were determined by infrared spectroscopy. Activation energies were computed for all compounds studied. Further investigation, involving compounds which bear substituents on the various aromatic groups, appears to be indicated before any overall conclusions on the effect of structure on decomposition rate can be made.

Due to the relative weakness of the oxygen to oxygen bond (36 kcal mol^{-1}), the decomposition of organic peroxides has been the subject of study for an extended period. Up to roughly 10 years ago dibenzoyl peroxide and several of its derivatives have been the only acyl peroxides which have been studied in detail, especially in relation to their rates of decomposition. Earlier work (*1*) in these laboratories and at Michigan State University had been limited to symmetrical thenoyl peroxides (*7*, *8*), but more recently a few unsymmetrical peroxides of the thiophene series containing also the benzoyl group were studied by Gruen et al. (*2*). The present paper is concerned with the study of the influence of various ring systems (both heterocylic and carbocylic) on the decomposition rates of acyl peroxides of the general formulation:



$$R{-}\underset{\parallel}{\overset{}{C}}{-}O{-}O{-}C{-}R' \quad (\text{C}{=}\text{O at both carbons})$$

where R and R′ include 1- and 2-naphthoyl-, benzoyl-, 2- and 3-furoyl-, and 2- and 3-thenoyl groups. Most of the compounds considered in the present work are unsymmetrical peroxides (R differs from R′), but a few symmetrical compounds are included for comparison. Of the 16 compounds studied, 12 have not been previously reported in the literature. Analyses of the new compounds prepared were performed by Spang Micro Analytical Laboratories, Ann Arbor, Mich., and percentages of elements found corresponded well with values calculated for the appropriate formulas.

EXPERIMENTAL

The preparation of one peroxide is shown in detail as an example for the method used in the synthesis of all unsymmetrical peroxy compounds. For the steps leading to the preparation of symmetrical peroxides of this type, previous publications (*2*, *7*, *8*) should be consulted.

Sodium-2-perfuroate. The procedure of Milas and MacAlevy (*6*) was used. In a 250-ml Erlenmeyer flask, cooled by means of an ice–salt bath and fitted with a drying tube containing 55 ml. of acetone-free methanol, 15 grams (0.07 g-atom) of sodium metal were dissolved. At the same time 13.55 grams (0.06 mole) of bis-2-furoyl peroxide were dissolved in 410 ml of anhydrous ether in a 1000-ml Erlenmeyer flask. The resulting solution was cooled to −5°C. The methoxide solution was cooled to 0°C and added cautiously to the vigorously stirred peroxide solution. The resulting mixture was agitated for 4–5 min. It was then washed twice with 50 ml of cold, spectroscopically pure chloroform to extract any methyl-2-furoate. The aqueous solution was then used directly for the preparation of the unsymmetrical peroxide.

2-Furoyl-3-thenoyl Peroxide. The sodium-2-perfuroate solution was introduced into a 300-ml, three-necked, standard taper flask, fitted with mechanical stirrer and a dropping funnel, the third neck being left open to the atmosphere. The vessel was cooled to 0°C by means of an ice–salt bath. To the vigorously stirred solution there was introduced a solution of 3.5 grams (0.023 mole) of 3-thenoyl chloride (*3*) in 20 ml of dry cyclohexane (warmed to keep the acid chloride dissolved). The system was stirred at −5–0°C for an additional hour. The white, fluffy, extremely hydrophobic solid was separated by filtration on a sintered glass funnel and washed with several 50-ml portions of ice-cold water. The yield was 0.75 gram of peroxide (0.0031 mole, 13.5% based on thenoyl chloride). The melting point was 73–74°C. *Anal.* Calcd for $C_{10}H_6SO_5$: C, 50.42; H, 2.54; S, 13.46. Found: C, 50.21; H, 2.34; S, 13.39.

Product Analysis. A 0.2-gram quantity of each of the peroxides was dissolved in a 25-ml volume of spectrograde chloroform which was 0.2*M* in styrene.

Samples of each of the peroxide solutions were sealed in 3-ml ampuls, and the peroxide decomposed overnight on a steam bath or in an oven at 70°C.

Gas chromatography of the decomposition mixtures revealed no new peaks, indicating that no volatile products were formed.

Thin-film chromatography of the decomposition mixtures

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[1] Present address, Department of Chemistry, Wayne State University, Detroit, Mich. 48202

[2] Present address, School of Medicine, The University of Michigan, Ann Arbor, Mich. 48104

[3] Present address, Department of Pharmacology, University of Virginia, Charlottesville, Va. 22901

[4] Present address, Department of Chemistry, Central Michigan University, Mount Pleasant, Mich. 48858

[5] To whom correspondence should be addressed.

Table I. Rate Constants and Half-Lives

Temp, °C	k(sec.$^{-1}$) × 10^5	$T_{1/2}$ sec
Benzoyl-2-thenoyl Peroxide		
59.18 ± 0.08	0.36 ± 0.00	192,600 ± 2700
72.90 ± 0.05	2.02 ± 0.02	34,380 ± 2664
80.65 ± 0.06	5.68 ± 0.0	12,180 ± 4
82.17 ± 0.02	7.40 ± 0.03	9,360 ± 430
90.35 ± 0.05	19.8 ± 0.3	3,492 ± 50
99.35 ± 0.06	51.3 ± 0.5	1,350 ± 13
99.35 ± 0.06	54.7 ± 0.3	1,266 ± 7
Benzoyl-3-thenoyl Peroxide		
59.18 ± 0.08	0.29 ± 0.01	238,800 ± 5280
72.90 ± 0.05	1.85 ± 0.08	37,440 ± 1680
82.17 ± 0.02	6.03 ± 0.10	11,460 ± 168
90.35 ± 0.05	18.0 ± 1.2	3,852 ± 244
99.43 ± 0.8	42.5 ± 0.5	1,632 ± 222
Bis-2-naphthoyl Peroxide		
79.90 ± 0.10	4.90 ± 0.10	14,160 ± 294
89.30 ± 0.10	15.0 ± 0.2	4,602 ± 46
100.10 ± 0.05	51.8 ± 0.6	1,338 ± 18
1-Naphthoyl-benzoyl Peroxide		
63.00 ± 0.05	5.62 ± 0.17	12,360 ± 282
70.00 ± 0.10	14.2 ± 0.2	4,602 ± 74
79.90 ± 0.10	42.2 ± 0.3	1,644 ± 16
90.00 ± 0.10	118.0 ± 2.0	587 ± 10
2-Furoyl-2-thenoyl Peroxide—Run 1		
59.83 ± 0.05	0.66 ± 0.01	105,000 ± 2520
69.80 ± 0.10	2.05 ± 0.06	33,780 ± 1044
80.65 ± 0.06	1.01 ± 0.16	6,900 ± 138
89.35 ± 0.05	23.0 ± 0.3	3,012 ± 34.8
99.35 ± 0.05	69.3 ± 0.5	1,002 ± 9.6
2-Thenoyl-3-thenoyl Peroxides		
59.18 ± 0.08	0.47 ± 0.10	148,200 ± 3000
69.80 ± 0.10	1.77 ± 0.08	39,960 ± 1632
80.65 ± 0.05	7.22 ± 0.30	9,600 ± 378
89.85 ± 0.05	20.5 ± 0.7	3,378 ± 114
99.45 ± 0.06	62.5 ± 0.5	1,104 ± 7
2-Furoyl-3-thenoyl Peroxide		
60.07 ± 0.10	0.57 ± 0.13	122,400 ± 3120
69.50 ± 0.10	1.90 ± 0.02	36,480 ± 420
80.75 ± 0.07	7.58 ± 0.05	9,120 ± 360
90.00 ± 0.05	22.3 ± 0.3	3,102 ± 64
99.70 ± 0.10	62.0 ± 1.2	1,116 ± 21
2-Naphthoyl Benzoyl Peroxide		
70.00 ± 0.10	1.17 ± 0.08	59,460 ± 3810
79.90 ± 0.10	4.28 ± 0.05	16,200 ± 210
89.90 ± 0.10	13.2 ± 0.05	5,250 ± 21
99.80 ± 0.05	41.7 ± 0.7	1,662 ± 26
2-Naphthoyl-2-furoyl Peroxide		
80.95 ± 0.05	7.83 ± 0.08	8,820 ± 60
90.00 ± 0.10	23.0 ± 0.0	3,012 ± 3
89.90 ± 0.10	22.3 ± 0.0	3,102 ± 2
100.00 ± 0.10	68.5 ± 9.2	1,014 ± 121
2-Naphthoyl-3-thenoyl Peroxide		
70.00 ± 0.10	1.85 ± 0.02	37,440 ± 426
79.90 ± 0.10	4.97 ± 0.23	13,980 ± 642
89.40 ± 0.10	14.6 ± 0.1	4,728 ± 19.8
99.95 ± 0.05	47.5 ± 0.2	1,458 ± 4.8
1-Naphthoyl-2-naphthoyl Peroxide		
63.00 ± 0.05	7.42 ± 0.18	9,360 ± 234
70.00 ± 0.05	16.4 ± 0.3	4,224 ± 82
79.40 ± 0.10	47.7 ± 0.3	1,452 ± 8
89.60 ± 0.10	128 ± 1	540 ± 2
2-Furoyl-benzoyl Peroxide		
59.18 ± 0.06	0.39 ± 0.03	177,000 ± 178
70.00 ± 0.10	2.20 ± 0.25	31,500 ± 2772
75.00 ± 0.10	4.63 ± 3.05	14,970 ± 9860
80.00 ± 0.10	6.53 ± 0.24	10,200 ± 374
80.65 ± 0.06	6.17 ± 0.25	11,460 ± 464
90.00 ± 0.10	26.2 ± 1.07	2,646 ± 108
99.35 ± 0.06	53.7 ± 0.10	1,290 ± 2
Bis-2-furoyl Peroxide		
70.00 ± 0.10	2.99 ± 0.26	23,200 ± 1980
75.00 ± 0.10	5.98 ± 0.48	11,580 ± 929
80.00 ± 0.10	12.0 ± 2.0	5,916 ± 986
90.00 ± 0.10	39.8 ± 0.1	1,740 ± 4
100.00 ± 0.10	141.5 ± 39.5	490 ± 137
Bis-3-furoyl Peroxide		
61.00 ± 0.10	0.283 ± 0.083	244,800 ± 106,300
65.20 ± 0.10	0.530 ± 0.173	130,750 ± 40,060
71.20 ± 0.10	1.002 ± 0.118	69,160 ± 8130
80.00 ± 0.10	3.62 ± 1.50	19,100 ± 7930
90.00 ± 0.10	15.9 ± 2.6	4,358 ± 713

Table II. List of Kinetic Parameters in Order of Increasing Half-Lives at 80°C

Peroxide	k(sec^{-1}) × 10^5	$T_{1/2}$ sec	Ea, kcal-mol^{-1}
1-Naphthoyl-2-naphthoyl	50.88	1,362	26.1 ± 1.7
1-Naphthoyl-benzoyl	42.78	1,620	27.2 ± 2.9
Bis-1-naphthoyl	32.08	2,160	23.2 (*5*)
Bis-2-furoyl-	11.87	5,838	30.9 ± 1.9
2-Furoyl-2-thenoyl	9.31	7,440	29.2 ± 3.1
2-Naphthoyl-2-furoyl-	7.00	9,900	29.8 ± 1.0
2-Furoyl-3-thenoyl-	6.92	10,020	29.4 ± 0.4
2-Furoyl-benzoyl-	6.79	10,200	30.0 ± 3.9
2-Thenoyl-3-thenoyl	6.68	10,380	30.0 ± 1.3
2-Thenoyl-benzoyl-	5.25	13,200	30.9 ± 1.0
2-Naphthoyl-3-thenoyl	5.14	13,800	27.7 ± 4.4
Bis-2-naphthoyl-	4.96	13,980	30.6 ± 1.6
3-Thenoyl-benzoyl-	4.62	15,000	30.9 ± 1.9
2-Naphthoyl-benzoyl-	4.33	16,020	30.3 ± 1.7
Bis-2-thenoyl-	4.25	16,320	29.5 (8)
Bis-3-thenoyl-	3.93	17,640	29.5 (8)
Bis-3-furoyl-	3.68	18,900	33.2 ± 4.1
Bis-benzoyl	3.03	22,860	30.2 (*1*)

showed only spots identified as due to the corresponding carboxylic acids—e.g., 2-furoic, 3-furoic, and benzoic.

Kinetic Experiments. As in the previous work (*2*, *8*), kinetic studies were performed by observing the disappearance of the peak at 5.7 μ (1751 cm^{-1}), typical of the kind of peroxide studied, and, due to the acyl-carbonyl group, modified by the neighboring peroxide (O=C–O–O–). Instead of observing the decomposition rates at only three different temperatures as in previous studies (*2*, *7*, *8*), most of the investigations were done at four, five, and in one case, seven different temperatures, ranging from about 60°C to approximately 100°C. Good first-order kinetics were observed throughout in the presence of styrene as a free radical scavenger known to prevent secondary reactions from occurring (*1*).

The rate constants and half-lives for the peroxides studied are listed in Table I, and the same data, averaged and corrected to 80°C by the Eyring equation (*4*) for all peroxides, are listed in Table II. In the last-mentioned listing, an order of increasing half-lives (decreasing rate constants) is followed to permit comparison of the various compounds and make possible a preliminary conclusion concerning the relationship between structures and reaction rates. The activation energies (Ea) were obtained by plotting (least-square plot by computer) the logarithm of the rate constants against the reciprocal of the absolute temperatures. Computation work was done both at Michigan State University and the University of Michigan (CDC 3600), the work at the latter University having been made possible through the good offices of Milton Tamres of the Department of Chemistry at the University of Michigan.

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Preparation and Properties of Tetrachloroterephthalate Esters

STANLEY H. LANGER, PAUL MOLLINGER, BRUCE M. JOHNSON, and JOHN RUBIN
Chemical Engineering Department, The University of Wisconsin, Madison, Wis. 53706

The preparation and properties of 12 tetrachloroterephthalate esters are reported. Several different types are described. Properties of the di-*n*-alkyl esters are compared with those of the isomeric ortho esters. The tetrachloroterephthalates are higher melting and have less tendency to form molecular complexes with aromatic hydrocarbons. Alkyl tetrachloroterephthalates resist saponification and transesterification. Several synthetic methods are illustrated. Some infrared absorption characteristics are also given.

Interest in the potential application of tetrachloroterephthalate esters as liquid phases for chromatography (*5–7*) led us to investigate the synthesis and properties of a number of the diesters that have not been described previously. A gas chromatographic investigation of the thermodynamics of solution of some of the alkyl diesters, used as liquid phases, has been reported earlier (*5*). Preparations of these diesters and others, some containing aromatic and halogenated aromatic nuclei, are described here. A comparison of properties of many of these compounds with the tetrachlorophthalates (*8*) is of further interest since both classes of materials are potential plasticizers (*10, 12*).

For the preparation of dialkyl diesters, the procedure of Rabjohn and others (*3, 10, 11*) involving direct reaction of tetrachloroterephthaloyl chloride with an excess of primary alcohol was most useful and convenient. While alkyl chlorides were not isolated from reaction of the alcohols with the generated hydrochloric acid, they presumably were formed to some extent. Procedures involving reaction of sodium alkoxides with the tetrachloroterephthaloyl chloride (*8*) and direct reaction of the dichloride with hydroxy compounds in the presence of pyridine were also found to be viable, especially with phenolic compounds. However, in other experiments, to be described at a later date, we found attempted reaction of a tertiary

Table I. Properties of Tetrachloroterephthalate Esters

Compound	Procedure[a]	Formula	Mp, °C	Some characteristic ir absorption wavelengths (see text)				
Di-*n*-propyl[b]	A1, A2	$C_{14}H_{14}O_4Cl_4$	90.0–91.0[c,d]	5.73	6.23	8.08	9.03	12.65 μ
Di-*n* butyl[e]	A1, A2	$C_{16}H_{18}O_4Cl_4$	62.0–63.0	5.73	6.24	8.15	9.08	12.70 μ
Di-*n*-pentyl[e]	A1, A2, C	$C_{18}H_{22}O_4Cl_4$	37.0–38.5	5.75	6.27	8.04	9.04	12.70 μ
Di-*n*-octyl[b,f]	B	$C_{24}H_{34}O_4Cl_4$	51.8–52.8	5.77	6.24	8.08	9.08	12.70 μ
Di-*n*-dodecyl[f]	B	$C_{32}H_{50}O_4Cl_4$	68.7–69.5	5.76	6.27	8.02	8.94	12.70 μ
Bis-cyclohexylmethyl[f,g]	D	$C_{22}H_{26}O_4Cl_4$	174.5–175.2	5.78	6.28	8.06	8.97	12.68 μ
Diphenyl[g]	C	$C_{20}H_{10}O_4Cl_4$	225.0–226.0	5.71	6.25	8.21	9.20	12.83 μ
Bis-3-methylphenyl[g]	C	$C_{22}H_{14}O_4Cl_4$	209.5–210.5	5.69	6.27	8.12	9.18	12.98 μ
Bis-*m*-fluorophenyl[g,h]	C	$C_{20}H_8O_4Cl_4F_2$	222.5–223.0	5.68	6.25	8.22	8.96	12.98 μ
Bis-*p*-fluorophenyl[g,h]	C	$C_{20}H_8O_4Cl_4F_2$	251.0–252.5	5.69	6.28	8.23	9.22	13.00 μ
Bis-pentafluorophenyl[g,h]	C	$C_{20}O_4Cl_4F_{10}$	196.0–197.0	5.57	6.04	8.38	9.03	12.93 μ
Diheptafluoro-1-butyl[b]	C	$C_{16}H_4O_4Cl_4F_{14}$	156.8–157.5	5.68	6.31	8.13	9.03	12.78 μ

[a] Some of procedures used from Experimental indicated; list not exhaustive, procedure may have been slightly modified. Recrystallized from: [b] Ethanol. [c] Reported mp 88.5–89°C, ref. *6*. [d] Boiling point 186–8°C/1 mm. [e] Methanol. [f] Propanol. [g] Benzene. [h] Dioxane.