5. The isomeric methoxypropanols can be characterized by their 3,5-dinitrobenzoates and α-naphthyl urethans.

6. Each of the isomeric methoxypropanols forms an azeotrope with water.

COLLEGE PARK, MARYLAND RECEIVED APRIL 14, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE PITTSBURGH PLATE GLASS CO., COLUMBIA CHEMICAL DIVISION]

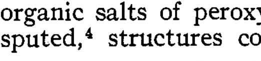
Esters of Peroxycarbonic Acids

BY F. STRAIN, W. E. BISSINGER, W. R. DIAL, H. RUDOFF,[1] B. J. DEWITT, H. C. STEVENS AND J. H. LANGSTON[2]

Diethyl peroxydicarbonate (I, R = C_2H_5), obtained in impure form by Wieland, vom Hove and Borner, is described[3] as an explosive oil of extreme instability, decomposing at moderate temperatures, and possessing the sharp ozone-like odor of volatile acyl peroxides. The preparative method consisted of the reaction of ethyl chloroformate in chloroform solution with powdered sodium peroxide, promoted by a drop or two of water added to the dry reagents. Control of the reaction was difficult. The instability of the compound, under the conditions of preparation and attempted purification by distillation, probably accounted for their failure to obtain a product of greater than 88% purity.

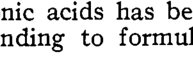
Our preliminary experiments confirmed this description, and further demonstrated that the diethyl and other esters of peroxydicarbonic acid could be prepared readily by the careful reaction of chloroformates with aqueous sodium peroxide solutions, and that the products were effective polymerization catalysts for several ethenoid monomers. A series of the esters was therefore prepared for further observation of their properties.

While the present paper is concerned chiefly with the aforementioned esters of peroxydicarbonic acid (Type I), illustrative preparations of the related esters of monoperoxycarbonic acid (Type II) and of diperoxycarbonic acid (Type III), derived from the reactions of a chloroformate and phosgene, respectively, with *t*-butyl hydroperoxide in the presence of acid acceptors are also included. Although the identity of some of the inorganic salts of peroxycarbonic acids has been disputed,[4] structures corresponding to formulas of Types I, II and III have been assigned.[5] Preparation of esters of these three types tends to support further the plausibility of the assigned structures of these salts.



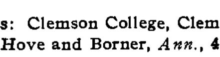
$$RO-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-OR$$

I



$$RO-\overset{O}{\overset{\|}{C}}-O-OR$$

II



$$RO-O-\overset{O}{\overset{\|}{C}}-O-OR$$

III

Esters of Type I.—The ready availability of many chloroformates from the alcohols and phosgene affords access to a variety of the dialkyl and substituted dialkyl peroxydicarbonates. Some of the chloroformates used were prepared by the common procedure of passing phosgene into the cooled alcohol,[6a,b] but a number were obtained by an improved method in which the alcohol was added to an established pool of the chloroformate containing some phosgene, which refluxed and served to cool the reaction mixture. The latter method enabled maintenance of an excess of phosgene throughout the reaction without the necessity for handling large quantities[7a,b] of liquid phosgene. This improved procedure also gave increased yields, and often a chloroformate of higher purity than the simpler method. Chloroformates employed in this investigation included a number previously unreported. These are listed in Table I, along with hitherto unreported characterizing data upon the isopropyl and allyl compounds.

The preparative procedure for the esters of Type I consisted of careful addition of cold aqueous sodium peroxide solutions (or slurries) to the cooled chloroformate[8] with efficient mixing. Due to the high degree of thermal instability and danger of violent decomposition observed for a number of the esters at temperatures only slightly above the temperature (0–10°) of preparation, special care was required in temperature control in all of the operations of preparation and purification. The chief impurity present in the crude esters was the alcohol formed by hydrolysis of the chloroformate. Since this impurity was easily removed from the crude lower alkyl esters by washing with cold water to give a product of high

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(3) Wieland, vom Hove and Borner, *Ann.*, **446**, 46 (1926).

(4) Tanatar, *Ber.*, **32**, 1544 (1899); Wolffenstein and Peltner, *ibid.*, **41**, 280–297 (1908); Le Blanc and Zellerman, *Z. Elektrochem.*, **29**, 179, 192 (1923); Kamtikar and Husain, *J. Osmania Univ. Coll.*, **2**, 39 (1934).

(5) F. Ephraim, "Inorganic Chemistry," Fourth Edition revised, Nordeman Publishing Co., Inc., New York, N. Y., 1943, p. 842.

(6) (a) See Dyson, *Chem. Revs.*, **4**, 149–150 (1927), for a review of early literature references to the preparation of chloroformates from alcohols and phosgene; (b) see Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, index pp. 1420–1421, and text indicated for references and reported properties on many of the chloroformates used.

(7) (a) Ashburn, Collett and Lazzell, THIS JOURNAL, **60**, 2933 (1938); (b) Slimowicz and Degering, *ibid.*, **71**, 1043 (1949).

(8) F. Strain, U. S. Patent 2,370,588, Feb. 27, 1945.

TABLE I

PREPARATION AND PROPERTIES OF CHLOROFORMATES

Chloroformate	Scale of prepn., theoret. moles	Yield, %	B. p., °C.	B. p., Mm.	n^{20}_{D}	Analyses, % Cl Calcd.	Analyses, % Cl Found
Isopropyl[a]	5.0[b]	83	47	100	1.3981[c]	29.0	28.8
Neopentyl	0.4[b]	83	52	27	1.4091	23.5	23.4
Allyl[d]	10.0	90	56	97	1.4223[e]	29.4	29.2
Tetrahydrofurfuryl	0.5	54	94–97	19	1.4522	21.5	21.4
2-Carbamyloxyethyl	0.5[b]	100	....	...	1.4640[f]	21.2	21.1
2-Nitrobutyl	0.5[b]	81	....	...	1.4472	19.5	19.1
2-Nitro-2-methylpropyl	1.0[b,g]	88	....	...	1.4453	19.5	18.8
Dodecyl	0.2[h]	84	....	...	1.4408	14.3	14.1
Ethylene-bis-[i]	5.0[b]	77	113	25	1.4498	37.9	37.9
2,2′-Oxydiethylene-bis-[j]	5.0[b]	95	122	4	1.4542	30.7	30.7

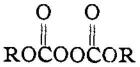
[a] Ref. 27; ref. 6b, page 1034. [b] Preparative Procedure B was employed. [c] d^{20}_{4} 1.076. [d] Fierz-David and Müller, *J. Chem. Soc.*, **125**, 26 (1924); Schving and Sabetay, *Bull. soc. chim.*, [4] **43**, 858 (1928). [e] d^{20}_{4} 1.136. [f] d^{20}_{4} 1.421; mol. ref. calcd. for $H_2NCOOC_2H_4OCOCl$: 32.22; found: 32.52. [g] Dioxane, 100 cc., was employed as a solvent in the reaction mixture. [h] Ether was added as a solvent to maintain a liquid reaction mixture and to assist in washing of the crude product. [i] d^{20}_{4} 1.465; Oesper, Broker and Cook, THIS JOURNAL, **47**, 2609 (1925); F. Strain, U. S. Patent 2,397,630, Apr. 2, 1946. [j] d^{20}_{4} 1.389, m. p. 5–6°; I. E. Muskat and F. Strain, U. S. Patent 2,370,568, Feb. 27, 1945.

purity, and because of the great instability of these esters, it was considered impracticable to attempt distillation. The preparations of esters of Type I are summarized in Table II. Attempts to prepare a diaryl (diphenyl) peroxydicarbonate failed, no compound containing active oxygen being obtained.

The lower aliphatic esters of Type I were obtained as oily liquids or low-melting solids possessing a characteristic odor similar to that of the lower acyl peroxides. As the size of the aliphatic radical is increased, especially if polar groups are contained therein, solid compounds tend to result and the characteristic odor is diminished. The esters were found to be soluble in a wide range of organic solvents, but only slightly or negligibly soluble in water. They exhibit the common reactions of organic peroxides such as liberation of iodine from acidified solutions of potassium iodide, decomposition on contact with concentrated sulfuric acid, deflagration on contact with flame, and in some cases explosive decomposition on being subjected to heat, friction or shock. With few exceptions the peroxydicarbonates prepared tended to decompose spontaneously at normal room temperatures. The heating resulting from this decomposition tended to produce an autoaccelerated explosive decomposition of the lower alipha-

TABLE II

PREPARATION AND PROPERTIES OF PEROXYDICARBONATES, TYPE I,



$RO\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}R$

R	Scale of preparation, moles[a]	Yield, %	n^{20}_{D}[b]	Gross decompn., temp., °C., method[c] T	C	Anal., active O, % Calcd.	Found
Methyl	0.10	6	.....	55–60, expl.		10.66	10.50
Ethyl	5.0	81	1.4017	28–35		8.98	8.88
n-Propyl	0.5	81	.....	32–36		7.76	7.67
Isopropyl	0.5–6.0	81–89	1.4034[d]	35–38	47–51	7.76	7.68
Isobutyl	1.3	75	1.4148[e]	40–45		6.83	6.79
Neopentyl	0.08	67[f]	[g]		54–56	6.10	6.03
Cyclohexyl	.15	72[f]	[h]		65–70	5.59	5.57
Allyl	.05	46	1.434	Expl.		7.91	7.13
Tetrahydrofurfuryl	.05	...	.....	10–20		5.51	5.51
Benzyl	.03	90	[i]		101–102	5.29	5.22
β-Methoxyethyl	.1	28	1.4250	34, expl.		6.72	6.52
α-Carbethoxyethyl	.25	27	1.4266	....		4.96	4.81
2-Chloroethyl	.10	79[f]	1.4582	40–45		6.48	6.44
2-Carbamyloxyethyl	.05	58	[j]		99–100	5.40	5.25
2-Nitrobutyl	.10	85[f]	[k]		94	4.93	4.89
2-Nitro-2-methylpropyl	.4	78[l]	[m]	101	101	4.93	4.90[n]

[a] Theoretical yield of peroxydicarbonate. [b] Melting points indicated by footnotes *d*, *g-k* and *m* in this column are uncorrected. [c] Minimum temperature ranges required for steady gas evolution, observed in 4-ml. test-tubes (T) or m. p. capillaries (C); see Experimental. [d] M. p. 8–10°; mol. wt. calcd. for $C_8H_{14}O_6$: 206.18; found (cryoscopic in ethylene dibromide), 206; $d^{15.5}_{4}$ 1.080. [e] d^{4}_{4} 1.060. [f] Ether was employed as a solvent in this preparation. [g] M. p. 45°. [h] M. p. 46°. [i] M. p. 101–102°. [j] Compound was a solid at room temperature. [k] M. p. 50°. [l] Ethyl acetate was employed as a solvent in this preparation. [m] M. p. 100.5–101°. [n] *Anal.* Calcd. for $C_{10}H_{16}O_{10}N_2$: C, 37.0; H, 4.97; N, 8.64, Found (by Dr. C. Tiedcke, Laboratory of Microchemistry, Teaneck, N. J.): C, 36.4; H, 4.72; N, 7.52.

tic esters. Quantities of more than a few grams of the pure diethyl and diisopropyl esters, for example, were found to be hazardous for this reason at temperatures above 10°, although kilogram or larger quantities were kept with negligible decomposition when adequately refrigerated. In smaller masses with highly efficient heat transfer, the tendency for the decomposition to become violent could be suppressed up to temperatures of 40–50°. As the size of the aliphatic radical is increased, the tendency for spontaneous heating with violent decomposition is moderated at normal temperatures, resulting in a sudden-to-mild effervescence on exposure to slightly elevated temperatures. When subjected to impact or explosive shock, the dimethyl and diethyl esters appeared more sensitive than benzoyl peroxide. Several of the other lower esters also were exploded easily, but as the transition was made to the higher aliphatic esters, these became much less sensitive to such shocks than benzoyl peroxide. The peroxydicarbonates prepared from the bis-chloroformates of ethylene and diethylene glycols were polymeric solids or gums possessing stability characteristics similar to those of the monomeric esters.

Decomposition of most of the higher aliphatic and substituted aliphatic esters which were solids (Table II, footnotes *g-k* and *m*) proceeded at rates of 1–2% per day at 25–30°, but was retarded by refrigeration. The bis-(2-nitrobutyl) and bis-(2-nitro-2-methylpropyl) esters were notable exceptions (see following discussion) in that these compounds could be kept for weeks or months at ordinary temperatures with but little (1–2% or less) decomposition.

Evidence that chain reactions of the radical type are involved in the decompositions of the esters of Type I was provided by the observation that the tendencies for autoaccelerated decomposition are susceptible to moderation or inhibition by small additions (1–5%) of a variety of compounds, the most effective being known inhibitors of chain reactions, including polyhydroxy- and nitroaromatics, certain unsaturated compounds, oxygen (or air) and iodine.[9] As shown by the data given in Table III, the inhibiting compounds largely suppressed the normal autoaccelerated decomposition of diisopropyl peroxydicarbonate occurring at room temperature, but some decomposition continued at different rates with the different additives. An induction period was often observed in the presence of these inhibitors, the length of which depended upon the amount of the inhibitor. Apparently the consumption of the inhibitor terminated this induction period after which the autoaccelerated decomposition occurred.

TABLE III

INHIBITION OF DECOMPOSITION OF DIISOPROPYL PEROXYDICARBONATE

Peroxydicarbonate, g.	Inhibitor	%	Time, hr.	Temp., °C.	Assay loss, av. % per hr.[a]
300.0	Iodine	1	288[b]	8–16	0.04[c]
50.0	Iodine	1	72[b]	25–30	.12
50.0	Iodine	1	258[b]	25–30	.12[d]
5.0	Trinitrobenzene	5	23	30	.32
1.0	Trinitrobenzene	1	23	30	.33
20.0	Acetanilide	1	18	30	.53[e]
10.0	Nitromethane	5	45	25–30	.54
1.0	Ethyl acetoacetate	1	24	30	.60
5.0	Phenol	5	27	30	.63
5.0	Phenol	1	27	30	.86
5.0	Tetralin	5	18	25–30	.91
1.0	None	..	1.00	25.0–27.3	6.8

[a] Av. per cent. of original assay lost per hr. [b] Samples were stored in darkness. [c] A loss in wt. of 23.2 g. occurred during this test. [d] Extensively decomposed solutions containing iodine exploded violently on several occasions, especially if stored at higher temperatures (30–45°). [e] Violent decomposition occurred after forty-two hours.

The decomposition rates of the esters of Type I in solutions were strongly influenced by the nature of the solvent. This was illustrated by the losses in peroxydicarbonate assay values of approximately 30% solutions of the diisopropyl ester in solvents containing different constituent (ethenoid, aromatic, ester, carbinol) groups. For example, losses of the original assay values in diethyl maleate, tricresyl phosphate and dibutyl phthalate after seven days (one hundred and sixty-eight hours) at 25 ± 1° amounted to 28.5, 34.8 and 91.2%, respectively. In isopropyl alcohol as solvent, the diisopropyl ester was highly unstable, decomposing with violent ebullition of the solution after twenty-five minutes. The order of activity of a number of the compounds tested in retarding or promoting the decomposition of the diisopropyl ester (including acceleration by some amines, see Experimental), when added in small amounts or when used as solvents, was similar to the order of activity of the same or like compounds in influencing the rate of decomposition of benzoyl peroxide when these are added to its solutions or used as solvents for this peroxide.[10a–c,11a] Some exceptions[11b] were noted, however.

The kinetic data given in Table IV, and represented in Figs. 1 and 2 show that esters of Type I, even though differing greatly in gross stability in pure form, decompose in dilute solutions at nearly identical rates conforming quite closely to first order kinetics. These rates are approximately thirty times the rates of decomposition reported for benzoyl peroxide in many solutions in the

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(9) H. C. Stevens, U. S. Patent 2,415,971, Feb. 18, 1947.

(10) (a) Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946); (b) Bartlett and Nozaki, *ibid.*, **69**, 2299 (1947); (c) Cass, *ibid.*, **68**, 1976 (1946).

(11) (a) Barnett and Vaughan, *J. Phys. Coll. Chem.*, **51**, 926, 942 (1947); (b) for example phenol tended to inhibit the decomposition of the diisopropyl ester (see Table III and Experimental) but appears to promote the decomposition of benzoyl peroxide when used as solvent (ref. 10b).

TABLE IV

RATES OF DECOMPOSITION OF DIALKYL PEROXYDICARBONATES IN DILUTE SOLUTIONS

Peroxydicarbonate	Initial concn., m./l.	Solvent	Apparent k, hr.$^{-1}$ 40.0°[c]	50.0°[c]	60 0°[c]
Diethyl	0.210[a]	[b]	0.025	0.103	0.46
Diisopropyl	.144	Toluene	...	.109	..
	.152[a]	[b]	0.023	.082	0.34
Dibenzyl	.053	Toluene	...	.105[13]	..
Bis-(2-NO_2-2-MePr)	.118	Toluene	...	.080	..

[a] Concentration, m./kg. [b] 2,2'-Oxydiethylene bis-(allyl carbonate). [c] ±0.2°.

concentration range represented, at temperatures of 40–60°.[12a,b,13] The over-all activation energies for the decomposition of the diethyl and diisopropyl esters in the dilute solutions, 30.4 and 28.1 kcal. per mole, respectively, are sufficiently close to the values of 29–31 kcal. reported for benzoyl peroxide[12a] in solutions of similar concentration to indicate that the primary rate controlling step is the same for the peroxydicarbonates as for benzoyl peroxide, *viz.*, dissociation into acyloxy radicals.[14a–c] For the esters of peroxydicarbonic acid this step is represented by equation 1 (R = H or alkyl, R' = alkyl or substituted alkyl)

$$(RR'CH—O—\overset{O}{\overset{\|}{C}}—O)_2 \xrightarrow{k_1} 2RR'CH—O—\overset{O}{\overset{\|}{C}}—O— \quad (1)$$

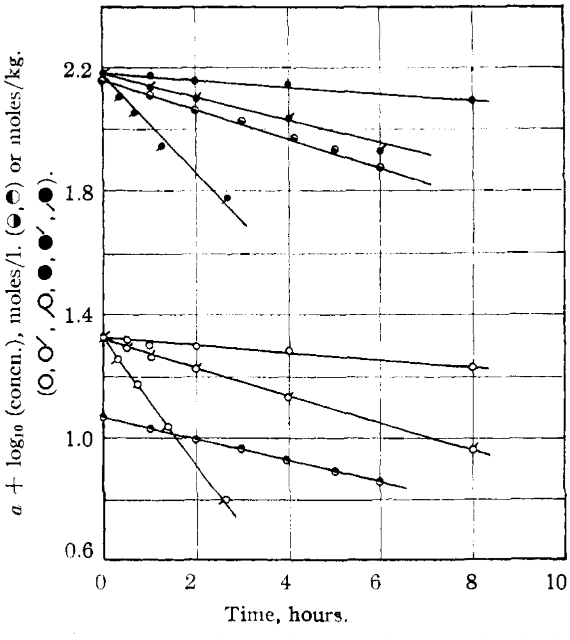

Fig. 1.—Decomposition of esters of peroxydicarbonic acid diethyl ester: O,O',⁄O, 0.210 mole/kg. in 2,2'-oxydiethylene bis-(allyl carbonate) at 40.0, 50.0 and 60.0°, respectively (a = 2); diisopropyl ester: ◐, 0.144 mole/l. in toluene at 50.0° (a = 3); ●,●',⁄●, 0.152 mole/kg. in 2,2'-oxydiethylene bis-(allyl carbonate) at 40,0, 50.0 and 60.0°, respectively (a = 3); bis-(2-nitro-2-methylpropyl) ester: ◓, 0.118 mole/l. in toluene at 50.0° (a = 2).

Acceleration or inhibition effects upon the decompositions by accumulated decomposition products, such as have been observed in the decomposition of benzoyl peroxide in solvents,[10a,b] apparently were largely avoided in these rate measurements, probably due to the limited extents (15–60%) to which the decompositions were allowed to proceed. The conformity of the data to first order kinetics, when considered in conjunction with the inordinately high rates of decomposition of the lower alkyl peroxydicarbonates in pure form[15] and in some of their concentrated solutions,

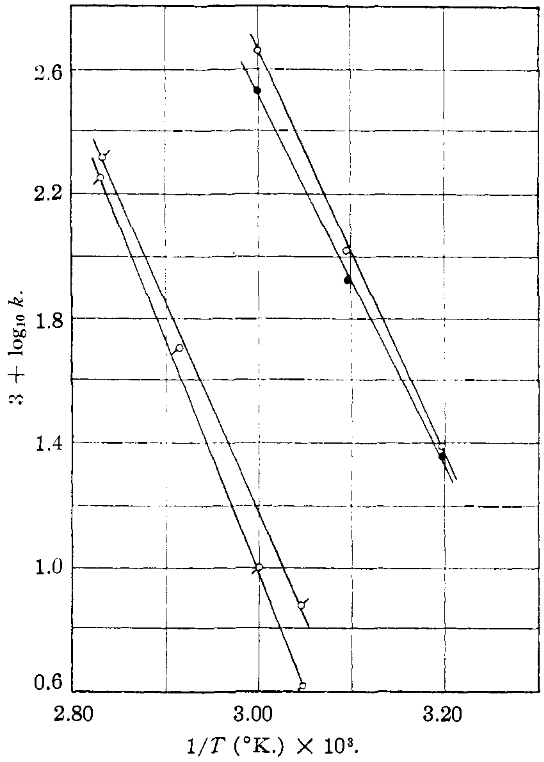

Fig. 2.—Decomposition of esters of peroxydicarbonic acid and benzoyl peroxide in solvents, effect of temperature: O = diethyl ester, ● = diisopropyl ester, 0.210 and 0.152 mole/kg., respectively, in 2,2'-oxydiethylene bis-(allyl carbonate); O' = benzoyl peroxide, 0.18–0.19 mole/kg. in allyl acetate[12b]; ⁄O = benzoyl peroxide, 0.07–0.10 mole/kg. in benzene[11a].

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(12) (a) Refs. 10a, b, c, 11a and earlier references cited therein; (b) Bartlett and Nozaki, THIS JOURNAL, **68**, 1497 (1946).

(13) Prof. P. D. Bartlett and Dr. R. Altschul, private communication.

(14) (a) See refs. 10a, b, c and 11a; (b) Bartlett and Altschul, THIS JOURNAL, **67**, 813, 819 (1945); (c) Price and Kell, *ibid.*, **63**, 2800 (1941).

(15) Extrapolation of the curve for diisopropyl peroxydicarbonate in Fig. 1 indicates values for k at 25 and 30°, respectively, of 0.003 and 0.006 hr.$^{-1}$. The decomposition data for the pure ester at 25.0–27.3° (last entry, Table III) show the decomposition in the latter case to be at least twenty times as rapid as would be predicted on the basis of these extrapolated values of k.

shows that reactions of higher than first order are involved in the chain decompositions. The nearly identical over-all decomposition rates of the esters of widely differing gross stabilities in pure form (Table IV) further show that the differing specific chain decomposition reactions responsible for these differing gross stabilities have been reduced to minor roles in the decompositions due to dilution in the solvents[10a–c,11a] used. It is probable that at the apparent over-all first order decomposition rates (Table IV), containing the contributions from the true unimolecular dissociation (k_1, equation 1) still include appreciable contributions from the higher order chain reaction (which may involve the solvent) analogous to the higher order contribution (k_i)[10a] reported for the chain decomposition of benzoyl peroxide in solvents.

The products recovered from the thermal decomposition of pure diethyl and diisopropyl peroxydicarbonates by slow passage of the esters through a steam-heated tube contributed further evidence that these decompositions involve free radicals. Ethyl alcohol and acetaldehyde (recovered as paraldehyde) were identified as decomposition products of the ethyl ester, while a more complete analysis of the liquid and gaseous products recovered from decomposition of the diisopropyl ester gave the results summarized in Table V.

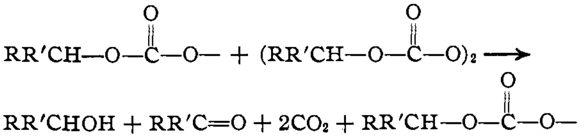
TABLE V

THERMAL DECOMPOSITION PRODUCTS OF DIISOPROPYL PEROXYDICARBONATE

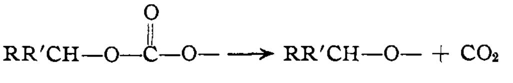
Product	Moles per mole of peroxydicarbonate
Acetaldehyde	[a]
Acetone	0.42
Isopropyl alcohol	0.91
Carbon dioxide	1.61
Ethane[b]	0.41
Other gases[c]	0.11

[a] Since some loss of acetaldehyde occurred, the initial experiment was in part duplicated giving 0.45 mole of acetaldehyde, 0.43 mole of acetone and 0.61 mole of isopropyl alcohol per mole of peroxydicarbonate. [b] Saturated hydrocarbon, mol. wt. 26.4; ethane qualitatively confirmed by chlorination to hexachloroethane. [c] Oxygen, carbon monoxide and olefins.

Possible modes of chain decomposition for the dialkyl peroxydicarbonates capable of accounting for the available data, with initiation by radicals resulting from the initial dissociation (equation 1) and analogous to formulations proposed for the chain decomposition of benzoyl peroxide,[10a–c] are

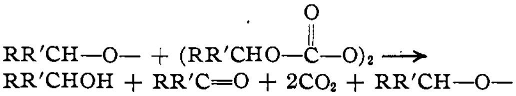


$$\mathrm{RR'CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}} + \mathrm{(RR'CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}O)_2} \longrightarrow \mathrm{RR'CHOH} + \mathrm{RR'C{=}O} + 2\mathrm{CO_2} + \mathrm{RR'CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}} \qquad (2)$$



$$\mathrm{RR'CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}} \longrightarrow \mathrm{RR'CH{-}O{-}} + \mathrm{CO_2} \qquad (3)$$

The alkoxy radicals resulting from reaction 3, lacking a capacity for resonance stabilization in contrast to the strong resonance possible in the alkylcarbonate radicals, may be especially reactive in attacking the peroxydicarbonate (equation 4) or other molecules formed as decomposition



$$\mathrm{RR'CH{-}O{-}} + \mathrm{(RR'CHO{-}\overset{\overset{O}{\|}}{C}{-}O)_2} \longrightarrow \mathrm{RR'CHOH} + \mathrm{RR'C{=}O} + 2\mathrm{CO_2} + \mathrm{RR'CH{-}O{-}} \qquad (4)$$

products, or may decompose further, *e. g.*, by loss of an alkyl fragment[16a,b] or hydrogen atom, to form a carbonyl compound, *i. e.*

$$\mathrm{RR'CHO{-}} \longrightarrow \mathrm{R{-}} + \mathrm{R'CH{=}O} \qquad (5)$$

The recovery of acetaldehyde along with the saturated hydrocarbon gas consisting largely of ethane (Table V) as products of the decomposition of diisopropyl peroxydicarbonate constitutes evidence for the formation of isopropoxy radicals (equation 3) followed by their decomposition according to equation 5, as well as for the possible chain terminating combination of the (methyl) radicals,[16b] *i. e.*

$$2\mathrm{R{-}} \longrightarrow \mathrm{R{-}R} \qquad (6)$$

The products of the decompositions of both the diethyl and diisopropyl esters suggest, furthermore, that, as an additional chain terminating step, disproportionation of the alkoxy radicals (equation 3) may occur as follows

$$2\mathrm{RR'CH{-}O{-}} \longrightarrow \mathrm{RR'CHOH} + \mathrm{RR'C{=}O} \qquad (7)$$

The wide differences in stability observed among the different esters of Type I in pure form are thus clearly due to the different extents to which the specific radicals produced in the respective decompositions attack the peroxydicarbonate molecules (equations 2, 4 and other similar possible reactions of radicals derived from the decomposition products with the peroxydicarbonate), and thereby propagate the chain decomposition. While dilution with solvents, *i. e.*, reduction of the concentration of the peroxydicarbonate, would be expected to reduce the proportion of the decomposition occurring by the higher order chain mechanism (see preceding text), the profound influence of solvent character on decomposition rate must be attributed to participation of the solvent in the chain reaction. This may involve transfer, propagation or termination reactions, in a manner analogous to those observed upon decomposition of benzoyl peroxide in different solvents.[10a–c,11a] In the sense that these influences associated with solvents are provided by and vary with the differing structures of the alkyl groups of the peroxydicarbonates, the compounds themselves may be regarded as their own solvents. It is of interest in this connection to

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[16] (a) This has been suggested for ethoxy radicals, see Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corporation, New York, N. Y., 1946, p. 141; (b) compare similar decompositions found for tertiary alkoxy radicals: Milas and Surgenor, THIS JOURNAL, **68**, 205, 643 (1946); Raley, Rust and Vaughan, *ibid.*, **70**, 88, 1336 (1948); Rust, Seubold and Vaughan, *ibid.*, **70**, 95 (1948).

note the increasing gross stability with increasing size of the alkyl group above ethyl (Table II), as well as the correlation of the high stabilities of the bis-(2-nitro-2-methylpropyl) and dibenzyl esters with the improved stability of the unstable diisopropyl ester in the presence of small amounts of nitromethane, toluene and the bis-(2-nitro-2-methylpropyl) ester itself (Experimental).

As illustrated by isopropyl peroxydicarbonate (Experimental), many of the esters listed in Table II were effective catalysts for polymerization of typical ethenoid monomers at moderate temperatures.[17,18] Some of the esters, notably the bis-nitroalkyl and dibenzyl esters, although active catalysts, produced somewhat less polymerization in allyl esters[18] per active oxygen equivalent consumed than the others, indicating either some wastage[19] in reactions not producing polymerization or some concurrent inhibiting action resulting from use of these particular peroxydicarbonates.

Esters of Types II and III.—Reaction of isopropyl chloroformate and phosgene, respectively, with *t*-butyl hydroperoxide in the presence of acid acceptors readily produced examples of the esters of Types II[20] and III, namely, OO-*t*-butyl O-isopropyl peroxycarbonate in the first case and di-*t*-butyl diperoxycarbonate in the second. These compounds were stable at room temperature, appearing to be comparable in stability to the similar reported *t*-butyl peroxyesters of organic carboxylic acids.[21] The ester of Type II was much less sensitive to impact than that of Type III. The gross thermal stabilities of the pure esters of Types II and III, as indicated by minimum temperatures required for steady gas evolution (104–106° and 86–88°, respectively)[22] were much greater than for the pure unsubstituted alkyl esters of Type I (see Table II). Dilution with nitrobenzene (concentrations 1.00 *M*) also affected (increased) these minimum temperatures for the compounds of Types II and III less than for an unsubstituted dialkyl ester of Type I (respective temperatures 117–118°, 85–86° and 63–65° for diisopropyl peroxydicarbonate),[23] indicating that the tendencies for chain decomposition in the pure compounds of Types II and III were less than in the pure unsubstituted ester of Type I.

The compounds of both Types II and III were also active polymerization catalysts for typical ethenoid monomers.[24]

Experimental

Preparation of Chloroformates.—The alcohols employed for the preparation of the corresponding chloroformates, except for neopentyl alcohol and 2-hydroxyethyl carbamate described below, were Eastman Kodak Co. white or yellow label chemicals, or technical products if available; they were used directly if a check of physical constants indicated high purity; if not they were redistilled before use.

Neopentyl alcohol was prepared by the action of formaldehyde upon *t*-butylmagnesium chloride.[25] The reaction mixture was poured into ice-water, the resulting solution acidified with dilute sulfuric acid, and extracted with ether. After washing and drying over sodium sulfate the extract was distilled, giving 27% of the theoretical of neopentyl alcohol, b. p. 109–114°.

2-Hydroxyethyl carbamate was obtained by allowing a mixture of 88 g. (1.0 mole) of ethylene carbonate[26] and 80 ml. (1.2 moles) of concentrated aqueous ammonia to stand overnight at room temperature. After heating to constant weight on a steam-bath at 3-mm. pressure, there remained a 98-g. residue (93% yield) of liquid product; n^{20}_{D} 1.4626, d^{20}_{4} 1.289; mol. refraction: calcd. for 2-hydroxyethyl carbamate, $C_3H_7O_3N$: M^{20}_{D} 21.5; observed: M^{20}_{D} 22.4.

Methyl, ethyl, *n*-propyl and isobutyl chloroformates were the Eastman Kodak Co. white or yellow label chemicals. Procedure A, following, was employed for preparation of cyclohexyl,[6b] benzyl,[6b] methoxyethyl,[6b] α-carbethoxyethyl[27] and 2-chloroethyl[6b] chloroformates and for the remaining chloroformates listed in Table I, except for those in which the somewhat more efficient Procedure B was followed, as noted in the Table.

Procedure A.—An excess (10–20% over the theoretical) of phosgene was introduced with vigorous stirring into the alcohol, maintaining the temperature somewhat above the b. p. of phosgene (at 10–15°) by adjustment of the rate of phosgene introduction and by use of an ice-salt-bath, with some cooling by reflux of phosgene from a Dry Ice–acetone cooled reflux condenser. The cooling bath was then removed and stirring continued for one-half to one and one-half hours while allowing the temperature to rise to that of the room. Hydrogen chloride and phosgene remaining were removed by blowing dry air through the mixture, exit gases being absorbed in methanol–sodium hydroxide traps. With the less volatile chloroformates this was followed by heating to 65° at 9–15 mm. pressure for approximately fifteen minutes. The products were usually washed several times with cold water to remove alcohol, and dried over calcium chloride. They were then distilled for final purification unless analysis showed high purity, or unless a product of lower purity tended to result due to some decomposition on distillation. Boiling point data are included in Table I.

Procedure B.—A small pool of liquid phosgene was condensed in a reaction flask after which the alcohol was introduced slowly with vigorous stirring while continuing the phosgene addition at such a rate that some excess phosgene continued to reflux from a Dry Ice–acetone cooled reflux condenser through which hydrogen chloride was vented. Cooling was thus effected by the refluxing phosgene, the temperature of the reaction mixture soon rising above the boiling point of pure phosgene and being maintained in

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(17) A. Pechukas, U. S. Patent 2,464,056, Mar. 8, 1949; F. Strain, U. S. Patent 2,464,062, Mar. 8, 1949.

(18) Unpublished observations, this Laboratory. Experiments show that in many cases polymerization in the presence of equimolar concentrations of peroxydicarbonate or benzoyl peroxide proceeds at approximately equal rates if the temperature is about 25° lower in the peroxydicarbonate solution than in the benzoyl peroxide solution, *i. e.*, if the rates of decomposition of the peroxy catalysts are approximately equal (compare data given in Fig. 2).

(19) Ref. 14b p. 820; ref. 10a p. 1691; ref. 10b p. 2300; Cohen, THIS JOURNAL, **67**, 19 (1945); Redington, *J. Polymer Sci.*, **3**, 504 (1948).

(20) F. Strain, U. S. Patent 2,374,789, May 1, 1945.

(21) Milas and Surgenor, THIS JOURNAL, **68**, 642 (1946).

(22) Observed in 4-ml. test-tubes; see Experimental.

(23) The corresponding temperature observed for a 1.00 *M* solution of benzoyl peroxide in nitrobenzene was 87–89°. In the absence of solvent crystalline benzoyl peroxide exploded at 105°.

(24) Unpublished observations, this Laboratory. This catalytic activity was developed at somewhat higher temperatures than for benzoyl peroxide as suggested by the thermal stability data (see also ref. 23). The ester of Type II possessed high catalytic efficiency in the polymerization of allyl esters but that of Type III was less efficient; see refs. 18 and 19.

(25) Conant, Webb and Mendum, THIS JOURNAL, **51**, 1246 (1929).

(26) Nemirowsky, *J. prakt. Chem.*, [2] **28**, 439 (1883).

(27) Thiele and Dent, *Ann.*, **302**, 245 (1898).

the range of 10–20°. Stirring was continued in the presence of some excess (refluxing) phosgene for one-half to one and one-half hours while gradually allowing this excess of phosgene to escape and the reaction mixture to warm to room temperature. The reaction mixture was then degassed by blowing with dry air and heating under reduced pressure as in Procedure A, after which the crude products were purified by distillation, or used directly as in Procedure A.

Except where noted in Table I the chloroformates were analyzed for chloroformate chlorine by dissolving a weighed sample (0.2–0.5 g.) contained in a small vial into 20 ml. of a freshly prepared aqueous reagent solution containing 2.5% sodium hydroxide and 10% pyridine by weight. After agitation of the solution for approximately twenty minutes, or until all of the chloroformate phase had disappeared, the solution was acidified with dilute nitric acid and the chloride ion determined by the Volhard method.

Phenyl chloroformate, formed readily by the reaction of phenol with phosgene only at elevated temperatures,[28a] was prepared more conveniently by the addition of dimethylaniline,[28b] 12.6 g. (0.10 mole), to a stirred solution of 9.4 g. (0.10 mole) of phenol and 9.9 g. (0.10 mole) of phosgene in 40 g. of benzene at 5 to 10°. The oily product obtained by dilution of the reaction mixture with cold water was washed with dilute hydrochloric acid, water, and dried over calcium chloride. Distillation gave 9.0 g. (58% yield) of phenyl chloroformate, b. p. 74–75° (13 mm.), $n^{20}\mathrm{D}$ 1.5131.

Anal. Calcd. for $C_7H_5O_2Cl$: Cl, 22.6. Found: Cl, 21.4.

Esters of Peroxydicarbonic Acid.—The esters listed in Table II were prepared by a general procedure consisting of careful addition of a cold solution of aqueous sodium peroxide to the well-stirred and cooled chloroformate. Initial preparations were usually conducted behind safety screens on a scale equivalent to theoretical yields of 0.02–0.10 mole of the peroxydicarbonate in order to observe properties such as stability of the product to heat and shock, without attempting to obtain optimum yields, and in order to evaluate explosion hazards which might be presented by the larger scale preparations. Details of the preparative procedure, essentially the same for the smaller scale as for the larger preparations, are illustrated by the following preparation of diisopropyl peroxydicarbonate:

A sodium peroxide solution was prepared by adding 68.2 g. (0.55 mole) of 27.4% hydrogen peroxide (Albone, analyzed iodometrically immediately before use) to a cooled solution of 44.0 g. (1.10 moles) of C. P. sodium hydroxide in 300 ml. of water, keeping the temperature in the range of 10–15°. Some solid sodium peroxide octahydrate separated out but was easily suspended by stirring the solution. This procedure for preparation of the sodium peroxide solution superseded one employed in the earlier preparations involving a solution of A. R. sodium peroxide in water, and avoided the greater care required in the latter method to prevent overheating, some decomposition and formation of large crystal masses of difficultly dispersible octahydrate.

The sodium peroxide solution[29] containing some suspended octahydrate was then added slowly through a dropping funnel to 122.6 g. (1.0 mole) of vigorously stirred isopropyl chloroformate, cooling with an ice-salt mixture and adjusting the rate of addition so that the reaction temperature was maintained at 6 to 10°, but never allowed to rise higher. Lower temperatures tended to cause solidification of the oily product suspended in the reaction mixture while danger of thermal decomposition of this product was present at higher temperatures. Stirring was continued for one-half hour after all of the sodium peroxide solution had been added. The oily product was then separated,[30] and washed with cold distilled water at 5 to 10° until free from chloride ion,[31] then dried by addition of cold anhydrous sodium sulfate. Cooling was applied as necessary to maintain the temperature in this range. After filtration from the drying agent, the diisopropyl peroxydicarbonate was obtained as a clear, colorless oil weighing 83–92 g. (81–89%). The liquid diisopropyl ester froze readily on cooling (m. p. 9–10° when pure), and was stored conveniently in the frozen state (Dry Ice). When melted carefully, in the presence of some solid, it could be handled readily without appreciable thermal decomposition. Spontaneous heating could be observed in a mass of the liquid ester if allowed to warm toward room temperature, and unless strong cooling was applied danger of an uncontrollable, violent, exothermic decomposition was present.

In cases in which the chloroformate or percarbonate was a solid, a volatile organic solvent, preferably one which could be washed out of the product by cold water or removed by vacuum evaporation, such as ether or ethyl acetate, was added as necessary to the reaction mixture before or during the preparations to maintain it in the liquid state.

Following the above indicated procedure 3.1 g. (0.02 mole) of phenyl chloroformate gave a solid product, 0.15 g., m. p. 74–75°, which contained no active oxygen but was diphenyl carbonate; mixed m. p. with an authentic sample of diphenyl carbonate (m. p. 78°) was 74°. A similar preparation from dodecyl chloroformate gave an impure waxy peroxydicarbonate containing dodecanol which could not be removed by washing. The wax liquefied on warming and decomposed with effervescence at 60–65°.

The peroxydicarbonates in most cases were analyzed for active oxygen by solution of 0.1–0.4 g. in 50 ml. of absolute acetone, addition of 5 ml. of 20% aqueous acetic acid containing 2 g. of dissolved potassium iodide, and after five minutes standing with occasional shaking, titration of the liberated iodine with standard sodium thiosulfate solution. Some samples were also analyzed employing a different procedure,[32] without significant alteration of the results.

Peroxydicarbonates of Bis-chloroformates.—Following the general procedure employed for preparation of the esters listed in Table I, 2,2′-oxydiethylene bis-chloroformate (*i. e.*, diethylene glycol bis-chloroformate) gave a white polymeric solid peroxydicarbonate which was only partially soluble in acetone and which decomposed slowly forming a gummy mass on warming to room temperature. A similar product was also obtained from ethylene bis-chloroformate. A solid polymeric peroxydicarbonate prepared as follows from a mixture of ethylene bis-chloroformate and ethyl chloroformate was mostly, but not completely, soluble in acetone:

To a mixture of 15.0 g. (0.080 mole) of ethylene bis-chloroformate and 5.00 g. (0.046 mole) of ethyl chloroformate was added with vigorous stirring a cold solution of 9.0 g. (0.11 mole) of sodium peroxide in 105 ml. of cold water, keeping the temperature near 0°. The resulting suspension was then stirred for one-half hour, the solid filtered off and washed several times with cold distilled water. The white solid after drying overnight in air at approximately 20°, weighed 6.9 g., equivalent to a 43% yield of product on the basis of the formula $C_2H_5OCOO(OCOOC_2H_4OCOO)_xOCOOC_2H_5$ assuming the average value of x to be 3.5, the theoretical value which would result from complete reaction of the two chloroformates.

Anal. Calcd. for $C_{20}H_{24}O_{27}$: active O, 10.34. Found: active O, 10.42.

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(28) (a) Kempf, *J. prakt. Chem.*, [2] **1**, 403 (1870); (b) Oesper, Broker and Cook, THIS JOURNAL, **47**, 2609 (1925); German Patent 251,805 (1912).

(29) A slight (*e. g.*, 5–10%) excess of sodium peroxide was desirable in the preparation in order to assure complete reaction of the chloroformate.

(30) It was frequently desirable to make certain of complete reaction of the chloroformate before making this separation by addition of a sample of the filtered and washed oily product to cold 20% aqueous pyridine followed by acidification with nitric acid and qualitative test for chloride ion.

(31) In some preparations traces of unreacted chloroformate made this difficult; one or more washes with cold, dilute (*e. g.*, 5%) aqueous pyridine were then employed for removal followed by additional washes with cold distilled water.

(32) Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

OO-*t*-Butyl O-Isopropyl Peroxycarbonate.—A mixture of 63.8 g. of 58% *t*-butyl hydroperoxide (0.41 mole, analysis by titanous chloride procedure outlined below) (Union Bay State Co.) and 50.9 g. (0.41 mole) of isopropyl chloroformate was cooled to −5°. A cold solution of 17.2 g. (0.43 mole) of sodium hydroxide in 160 cc. of water was then added dropwise with vigorous stirring and cooling to maintain the temperature at −5 to 0°. After stirring the mixture for thirty minutes the upper oily layer was separated, washed with distilled water until free from chloride ion, then dried over sodium sulfate. Distillation in three portions through a 1 × 8-cm. Vigreux column gave 58.5 g. (81%) of colorless OO-*t*-butyl-O-isopropyl peroxycarbonate, b. p. 52–55° (1 mm.), $n^{20}{}_D$ 1.4050, $d^{20}{}_4$ 0.966. The product was analyzed for active oxygen using standard 0.03 *N* titanous chloride reagent, employing glacial acetic acid to maintain homogeneity of the solution of peroxide in the aqueous reagent, and heating at 60–65° in a carbon dioxide atmosphere for ten to twenty minutes before back titration of unused reagent with standard ferric alum solution.

Anal. Calcd. for OO-*t*-butyl O-isopropyl peroxycarbonate, $C_8H_{16}O_4$: active O, 9.08; $M^{20}{}_D$ (peroxide O = 2.19[33]), 44.65. Found: active O, 9.05; $M^{20}{}_D$, 44.52.

Di-*t*-butyl Diperoxycarbonate.—Phosgene, 0.080 mole, was introduced at a rate of six millimoles per minute into a stirred solution of 18.0 g. of 71% *t*-butyl hydroperoxide (0.14 mole) and 16.6 g. (0.21 mole) of pyridine in 40 ml. of ether, cooling to keep the temperature at 3-5°. The resulting mixture was allowed to stand in the cold for forty-five minutes after the phosgene addition was complete, then diluted with 100 ml. of ice-water. The ether layer was separated, washed once with cold water, twice with cold 5% aqueous hydrochloric acid, then again with cold water until free from chloride ion. The ether solution was then dried over sodium sulfate, filtered, and evaporated to constant weight at 20-mm. pressure. The yield of colorless di-*t*-butyl diperoxycarbonate remaining was 11.0 g., 76%; $n^{20}{}_D$ 1.4106. The b. p. of the product was above 95° (4 mm.); decomposition with gas evolution occurred under these conditions which prevented satisfactory distillation. In one experiment a partially decomposed sample being heated at 135–140° exploded with violence.

Anal. Calcd. for $C_9H_{18}O_5$: active O, 15.5. Found: active O (titanous chloride method; *cf.* preceding preparation), 14.9.

Stability of Peroxycarbonate Esters.—The gross thermal stability of the liquid peroxydicarbonate esters was observed by raising the temperature of 1 ml. of the ester in a 4-ml. (10 × 75-mm.) test-tube (behind a protective screen) at a rate of approximately one degree per minute using a water-bath with a thermometer immersed in the ester. The minimum temperature range in which bubbling of the liquid with gas evolution became readily observable and steady was determined. This temperature range depended upon the efficiency of heat transfer and rate of heating, nevertheless, was quite narrow and reproducible for the different compounds under these standardized conditions. This temperature range is recorded as the gross decomposition temperature in Table II. In many cases the autoaccelerated exothermic decomposition soon raised the temperature above the minimum values given; for example, in one case the temperature recorded by the thermometer quickly reached 124° in a test using diethyl peroxydicarbonate. The decompositions, especially of the lower aliphatic esters, thus tended to become explosive. In a few cases, indicated in the table, sharp explosions occurred at the temperatures noted.

Decomposition temperatures for crystalline peroxydicarbonates melting above room temperature (25°) and recorded in Table II were observed in the m. p. capillary tubes (Kimble Glass No. 34505) on continuing to raise the temperature at a rate of approximately one degree per minute after melting had occurred. Decomposition temperature ranges observed in this manner were usually higher, by up to 10-15°, than those observed in 4-ml. test-tubes as described above, the temperature observed in a capillary for diisopropyl peroxydicarbonate being for example 47-51° (Table II).

The extent of decomposition on standing of samples of peroxydicarbonates which were solids at room temperature was determined by iodometric assay for active oxygen. Samples, a few grams in size, of each of the following peroxydicarbonates were stored at 25-30° (except at 10° where indicated) in loosely-closed glass bottles; initial assay values, in per cent. of the theoretical active oxygen for each ester, are followed by the assay values found after the different respective periods of standing: dineopentyl 98.4, one day 96.0; dicyclohexyl 99.5, three weeks 40–50, one week (10°) 98.0; dibenzyl 98.0, one day 96.5[13]; bis-(2-carbamyloxyethyl) (a) 88.9, four weeks 51.3, (b) 92.4, eight weeks (10°) 88.9; bis-(2-nitrobutyl) 99.1, twelve weeks at 10° followed by two weeks 97.4; bis-(2-nitro-2-methylpropyl) (a) 98.6, five weeks 98.6, (b) 99.4, one year (10)° 97.0.

A preliminary indication of the sensitivity of the peroxycarbonate esters to impact was obtained by placing a few drops or crystals of the compound on a clean flat steel plate followed by striking blows of increasing force with a steel hammer. Dimethyl peroxydicarbonate was easily exploded in this manner, and the diethyl compound with more difficulty, but the higher esters gave less evidence of sensitivity, and were much less sensitive to such impacts than benzoyl peroxide. OO-*t*-Butyl O-isopropyl peroxycarbonate likewise exhibited little sensitivity to such shocks, but di-*t*-butyl diperoxycarbonate could be exploded easily in this manner.

The sensitivity to explosive shock of diethyl and diisopropyl peroxydicarbonates was observed[34] by exploding no. 6 electric detonating caps (containing 1.5 g. of mercury fulminate) in hollow chambers on the interior of frozen (estimated temperatures −20 to −50°) 0.25-lb. charges of these esters contained in open metal cans, 2⁵/₈ in. in diameter by 4 in. high. The report produced by the diethyl ester was audibly sharper than that produced by an equal amount of benzoyl peroxide (Lucidol) (temperature approx. 10°), while the report produced by the diisopropyl ester, which was only partially exploded was milder than that produced by benzoyl peroxide.

Inhibition and Acceleration of Decomposition of Diisopropyl Peroxydicarbonate.—When enough liquid pure diisopropyl peroxydicarbonate was placed in small (4 to 15-ml.) test-tubes to occupy about one-third of the volume of the test-tube and allowed to stand at 25-30° free from drafts, the ester heated spontaneously and decomposed with violent effervescence after a period of ten to thirty minutes. Various added chemicals, in the amounts indicated as follows based on the ester, (a) affected but little, (b), (c) lengthened, or (d) shortened this period:

(a) Chemicals affecting period before decomposition but little (five to fifty minutes): water 1%, acetone 1%, methyl alcohol 1%, ethyl alcohol 1%, isopropyl alcohol 1%, *t*-butyl alcohol 1%, acetic acid 1%, propionaldehyde 1%, benzyl alcohol 1%, ethyl acetate 1%, acetamide 1%, diisopropyl ether 1%, dioxane 1%, diethyl malonate 1%, acetylacetone 1%, triacetin 1%, benzene 5%, pyridine 1%, benzoyl peroxide 1%, 10% aqueous hydrochloric acid 1%, nitrogen bubbled continuously through liquid, carbon dioxide bubbled continuously through liquid.

(b) Chemicals extending period before decomposition to one to ten hours: toluene 1%, cyclohexene 2%, allyl alcohol 1%, dicyclopentadiene 5%, β-phenylethyl alcohol 1%, phenetole 1%, salicylic acid 1%, naphthalene 5%, 30% aqueous hydrogen peroxide 1%, lead tetraethyl 0.4%, nickel carbonyl 5%, sulfur 1%, sulfur dioxide bubbled through liquid for thirty minutes, bis-(2-nitro-2-methylpropyl) peroxydicarbonate 2%.

(c) Chemicals extending period before decomposition to twenty hours or longer: phenol 1%, hydroquinone 1%, resorcinol 1%, pyrogallol 1%, tetralin 1%, diphenyl ether

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[33] Milas, Surgenor and Perry, This Journal, 68, 1617 (1946).

[34] Tests conducted with the assistance of Mr. R. H. Fredenburg.

5%, ethyl acetoacetate 1%, acetanilide 1%, phenetole 5%, salicylic acid 5%, nitromethane 2%, trinitrobenzene 1%, iodine 1%, air or oxygen bubbled continuously through liquid.

(d) Chemicals shortening period before decomposition (to respective times indicated): aniline 1%, 5–10 sec.; dimethylaniline 1%, instant (explosion); ethylenediamine 1%, instant; potassium iodide 1%, instant; 10% aqueous potassium hydroxide, less than 60 sec.

To quantities of liquid diisopropyl peroxydicarbonate (assay 98.0–99.8%) were added small amounts of some of the more efficient inhibiting compounds listed above, after which the solutions were stored in loosely stoppered glass bottles in diffuse light at room temperature, unless otherwise indicated (Table III). Samples were withdrawn after different periods of time for assay of the liquid for peroxydicarbonate by iodometric analysis for active oxygen. A 1.00-g. sample of the diisopropyl ester containing no inhibitor was allowed to decompose in a 9-ml. (13 × 100-mm.) test-tube immersed in a water-bath kept at 25 ± 0.1°. Air was displaced from this tube using carbon dioxide, and the tube was closed by a clean cork stopper carrying a thermometer with bulb immersed in the ester. A small groove was filed in the cork for release of pressure developing in the test-tube. The temperature of the inhibitor-free ester, brought rapidly from 10 to 25.0° at the start of the experiment as the tube was immersed in the bath, reached 25.5° within four minutes, and rose gradually to 27.3° at the end of 1.00 hr. Small bubbles of gas were evolved slowly after approximately fifteen minutes. The peroxydicarbonate content of the liquid was determined by iodometric analysis at the beginning and end of the experiment; respective assays were 98.0 and 91.3%. Table III summarizes the results.

Decomposition of Peroxycarbonates in Solvents.—The gross stabilities of the peroxycarbonate esters of the three different types in 1.00 *M* nitrobenzene solutions were observed by raising the temperature of 1.0-ml. samples in 4-ml. test-tubes, observing the minimum temperature range in which bubbling of the solutions due to gas evolution resulting from decomposition became steady in the same manner as described previously for observation of the gross stabilities of the pure esters of peroxydicarbonic acid. The corresponding temperature ranges for pure OO-*t*-butyl O-isopropyl peroxycarbonate and di-*t*-butyl diperoxycarbonate were observed in the same manner.

Ten-gram quantities of solutions containing approximately 30% by weight of diisopropyl peroxydicarbonate in several solvents were stored in loosely stoppered glass containers in air at 25 ± 1°. The peroxydicarbonate contents of the solutions were determined by withdrawal of weighed samples for iodometric assay at the beginning of the storage period, and after periods of twenty-four and one hundred and sixty-eight hours. Initial, twenty-four-hour and one hundred and sixty-eight-hour assay values, respectively, for the different solvents were as follows: diethyl maleate, 27.7, 27.5, 20.0; tricresyl phosphate 27.6, 25.6, 18.0; tetralin 29.4, 23.7, 8.6; tetrachloroethylene, 30.6, 28.5, 7.0; dibutyl phthalate 28.8, 24.6, 2.5; bis-2-(2-butoxyethoxy)-ethyl maleate, 26.2, 15.1, 0.4. Although a solution in isopropyl alcohol decomposed violently after twenty-five minutes, a solution in tricresyl phosphate–isopropyl alcohol (1:1) mixture gave the following respective assay values: 29.8, 13.2, 0.4. Addition of 1% of (a) iodine or (b) hydroquinone to the diethyl maleate solution gave as respective assay values: (a) 29.2, 25.0, 17.9; (b) 27.0, 21.1, 12.6.

For the decomposition rates of the diethyl, diisopropyl and bis-(2-nitro-2-methylpropyl) esters in more dilute solutions (Table IV, Figs. 1 and 2), redistilled toluene and 2,2′-oxydiethylene bis-(allyl carbonate) prepared as described in the following section were used as solvents. Two-ml. samples of the toluene solutions or 2-g. samples of the bis-(allyl carbonate)[35] solutions of the peroxydicarbonates were heated in a nitrogen atmosphere in individual, closed, Pyrex tubes (10 mm. × 75 mm.) using a water-bath controlled at 50.0° by a thermostat. Separate tests using a thermocouple showed that the temperature within the tubes did not differ from that of the bath by more than 0.1°. Tubes were removed after different lengths of time, cooled, opened and the total peroxydicarbonate remaining in each determined iodometrically by the same procedure as used in analysis in preparation of the esters. Insoluble polymer gels from the diallyl compound were crushed and extracted with 50 ml. of absolute acetone for at least two hours in the dark at 10°. Undissolved gel particles were then filtered off and washed with a small amount of acetone which was combined with the filtered extract for analysis.

Thermal Decomposition Products of Peroxydicarbonates.—Diethyl and diisopropyl peroxydicarbonates were decomposed by dropping slowly from an ice-water-cooled, jacketed dropping funnel into an adapting tube attached to an inclined West-type condenser steam-heated at approximately 100°. A collection train attached to the end of the heated condenser for collecting the decomposition products consisted of an ice-water-cooled trap, a Dry Ice-acetone-cooled trap and a gasometer for collecting uncondensed gases over saturated aqueous sodium sulfate solution. Liquid products were separated by fractional distillation, while gaseous products were analyzed by the Orsat method.

Decomposition of 5.0 g. (0.028 mole) of diethyl peroxydicarbonate in the above indicated manner, without collection of uncondensed gases, gave 2.3 g. of distilled liquid product which consisted of approximately equal parts of ethyl alcohol (b. p. 78–80°) and paraldehyde (dinitrophenylhydrazone m. p. 143°, mixed m. p. with an authentic sample of the hydrazone from paraldehyde of m. p. 145° remained at 145°).

Decomposition of 46.1 g. (0.224 mole) of diisopropyl peroxydicarbonate gave a total of 22.7 g. of liquid collected in the two traps and 12.3 liters of uncondensed gas, measured at 34° and 741 mm. Most of the liquid product (19.2 g.) was distilled at 741 mm. using a 0.7 × 33-cm. column packed with 6-mesh carborundum to give the following fractions: (a) 0.5 g., plus some loss, b. p. to 35°, n^{20}D 1.3383–1.3434; (b) 4.6 g., b. p. 47–58°, n^{20}D 1.3584–1.3620; (c) 10.3 g., b. p. 75–81°, n^{20}D 1.3709–1.3776; (d) 1.7 g. of tarry residue. Fraction (a) gave a dinitrophenylhydrazone, m. p. 143–144°; mixed m. p. with an authentic derivative prepared from acetaldehyde (of m. p. 146–147°) was 144–145°. Although most of fraction (b) boiled at 56°, preparation of a pure dinitrophenylhydrazone proved difficult, probably due to the presence of some acetaldehyde (positive fuchsin-aldehyde test); the dinitrophenylhydrazone was finally obtained in pure form from a corresponding fraction in a duplication of part of this experiment (see below), however, by three recrystallizations from absolute alcohol containing a trace of hydrochloric acid, m. p. 124.5–125.5°; a mixed m. p. with an authentic derivative prepared from acetone of m. p. 124.5–125.5° exhibited no depression. Fraction (c) gave a 3,5-dinitrobenzoate, m. p. 120°; mixed m. p. with a known sample of isopropyl 3,5-dinitrobenzoate (m. p. 120°) was not depressed. An Orsat analysis of the uncondensed gaseous product of the decomposition showed this to be composed of the following constituents (% by volume): carbon dioxide 75.9%, oxygen 2.8%, carbon monoxide 1.4%, ethylene 0.0%, higher olefins as propylene 0.8%, saturated hydrocarbon (apparent mol. wt. 26.4) 19.1%. In the aforementioned duplication of the experiment,[36] the acetaldehyde, acetone and isopropyl alcohol fractions from the total product weighed 4.46 g., 5.61 g. and 8.23 g., respectively. Also, the presence of substantial quantities of ethane in the saturated hydrocarbon fraction of the gaseous product was confirmed by chlorination to hexachloroethane at 480–500° using excess chlorine. The product, after recrystallization from absolute ethanol, sublimed entirely in a melting point capillary at 185–187°. The sublimation temperature was un-

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(35) Experiments using this solvent performed by Mr. John O. Punderson.

(36) Performed by Dr. W. A. Strong.

changed on admixture with an authentic sample of hexachloroethane.

Anal. Calcd. for C_2Cl_6: Cl, 89.9. Found: Cl, 89.4.

Catalysis of Polymerization of Ethenoid Monomers by Peroxydicarbonates.—Monomeric styrene, vinyl acetate and methyl methacrylate from commercial sources were redistilled before use.

2,2'-Oxydiethylene bis-(allyl carbonate), *i. e.*, the bis-(allyl carbonate) of diethylene glycol,[37] was prepared[38] by the addition of 1326 g. (11.0 moles, 10% excess) of allyl chloroformate to an efficiently stirred mixture of 531 g. (5.0 moles) of diethylene glycol and 949 g. (12.0 moles) of pyridine, cooling to keep the reaction mixture at 5-10°. After the addition was complete, the reaction mixture was allowed to warm to room temperature, diluted with an equal volume of water and neutralized to the methyl orange end-point using dilute hydrochloric acid. The crude oily ester was separated, washed with an equal volume of cold 2% aqueous hydrochloric acid, once with an equal volume of cold 2% aqueous sodium hydroxide then twice further with cold water. The crude product was dried over sodium sulfate, and purified by distillation with a small stream of carbon dioxide passing through the ester. The yield was 1030 g. (75%) of colorless 2,2'-oxydiethylene bis-(allyl carbonate), b. p. 160° (2 mm.), n^{20}_D 1.4503, d^{20}_4 1.143.

Anal. Calcd. for $(C_3H_5OCOOC_2H_4)_2O$, $C_{12}H_{18}O_7$: C, 52.5; iodine number,[39] 185.1. Found: C, 52.2; iodine number, 185.1.

A loss of about 15% due to polymerization during distillation was avoided in other preparations by heating the crude ester at 150° *in vacuo* (5-10 mm.) for removal of volatile impurities, the product obtained being 97-99% pure by unsaturation analysis.

Diisopropyl peroxydicarbonate was dissolved in these monomers in the following percentages by weight, based on the monomer: styrene 0.5%, vinyl acetate 0.1%, methyl methacrylate 0.2%, 2,2'-oxydiethylene bis-(allyl-carbonate) 3.0%. Two-ml. samples of the solutions were heated under nitrogen in closed test-tubes (10 mm. × 75 mm.) for three days at 45° then cooled to room temperature. Hard, colorless, solid polymers were obtained in all cases.

Summary

1. Dialkyl and substituted dialkyl peroxydicarbonates (Type I peroxycarbonates) may be prepared readily, often in good yields and high purity, from the corresponding chloroformates and sodium peroxide solutions. Most of these esters in pure form are unstable, decomposing, in some cases explosively, at normal temperatures. Appropriate temperature control in preparation and handling is accordingly required.

2. Wide differences in thermal stability in pure form are observed among esters of Type I, depending upon the alkyl or substituted alkyl group. Similarly wide differences in stability are observed in solutions of a given ester depending upon the nature of the solvent used. The thermal decomposition of the more unstable esters is retarded by known inhibitors of chain reactions, and yields a complex mixture of products characteristic of chain decompositions. In dilute solutions in selected solvents the wide differences in decomposition rates are no longer observed, and the decompositions conform closely to first order kinetics. The thermal decomposition of the different esters is thus shown to consist of a spontaneous unimolecular decomposition, with the formation of free radicals which induce concurrent chain decomposition reactions of the esters to different extents depending upon the particular ester and solvent involved. These chain decompositions are similar to those known to occur in benzoyl peroxide solutions.

3. Examples of the related esters of monoperoxycarbonic acid (Type II) and of diperoxycarbonic acid (Type III) have also been prepared; these esters are more stable than the esters of Type I.

4. Many of the esters of Type I are effective free radical type catalysts for polymerization of typical ethenoid monomers at moderate temperatures.

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[37] Muskat and Strain, U. S. Patent 2,370,565, Feb. 27, 1945.

[38] Muskat and Strain, U. S. Patent 2,370,567, Feb. 27, 1945.

[39] Hanus method, Jamieson, "Vegetable Fats and Oils," A. C. S. Monograph No. 58, Second Edition, (The Chemical Catalog Co., Inc.) Reinhold Publ. Corp., New York, N. Y., 1943, p. 394.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Heats of Combustion of Some Isomeric Nitrostilbenes[1]

BY CARL M. ANDERSON,[2a] LELAND G. COLE[2b] AND E. C. GILBERT

For a number of years this Laboratory has been interested in energy relations of isomeric organic compounds as obtained from heats of combustion.[3]

Through the courtesy of Prof. Melvin Calvin, it has now been possible to obtain two additional pairs of carefully purified isomers, *cis-* and *trans-*4,4'-dinitrostilbene, and *cis-* and *trans-*4-mononitrostilbene, (unsym. *p*-nitrostilbene). Measurements of the heat of combustion of these four compounds are reported here, and the energies of isomerization in the solid state are indicated.

Experimental

The adiabatic calorimeter has been previously described.[3] The energy equivalent was determined by the combustion of benzoic acid Standard Sample, 39e, from the National Bureau of Standards, by Anderson who obtained 2607.30 cal. deg.$^{-1}$ with a maximum deviation of 1.45 cal. from the mean, a mean deviation of ±0.56 cal., and a root-mean-square deviation of ±0.28 cal. After approximately a year a redetermination by Cole using Standard 39f, gave 2607.34 cal. deg.$^{-1}$ with a mean deviation of

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[3] Corruccini and Gilbert, THIS JOURNAL, **61**, 2925 (1939); Davies and Gilbert, *ibid.*, **63**, 1585, 2730 (1941); Anderson and Gilbert, *ibid.*, **64**, 2369 (1942).