yielded mixtures of oxygen compounds containing alcohols, aldehydes, ketones and acids.[14]

Assuming that the formation of hydrocarbons from ketene proceeded step-wise in the following manner

(a) $CH_2CO \longrightarrow CH_2 + CO$

(b) $CH_2 + CH_2CO \longrightarrow CH_3CH{=}C{=}O$

(c) $CH_3CH{=}C{=}O \longrightarrow CH_2{=}CH_2 + CO$

(d) $CH_2 + CH_3CH{=}C{=}O \longrightarrow$
$CH_3CH_2CH{=}C{=}O \longrightarrow CH_3CH{=}CH_2 + CO$, etc.

a reaction mechanism for the Fischer–Tropsch synthesis may be formulated from the above reactions by providing a source of methylene radicals. Such a source might be the usual one from metal carbide and hydrogen or that postulated by Eidus.[7]

(14) Fischer and Tropsch, *J. Inst. Fuel*, **10**, 10 (1936).

Summary

Ketene in the presence of hydrogen reacts on a Co–ThO_2–kieselguhr catalyst to yield hydrocarbons and oxygenated compounds which are similar to the products of the Fischer–Tropsch synthesis. The possibility that ketene is an intermediate in the Fischer–Tropsch synthesis is discussed.

PITTSBURGH, PA. RECEIVED MARCH 25, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Studies in Organic Peroxides. XII. Molecular Refractivity and the Structure of Organic Peroxides

BY NICHOLAS A. MILAS, DOUGLAS M. SURGENOR[1] AND LLOYD H. PERRY[2]

Enough pure liquid organic peroxides have now been synthesized in this Laboratory and elsewhere to justify a study of the influence of molecular refraction on the structure of this class of organic compounds. The molecular refraction of pure hydrogen peroxide[3] and of water[4] have been determined very accurately. By simply subtracting the observed molecular refraction of water from that of hydrogen peroxide, a value of 2.19 is obtained, which represents the atomic refraction of the peroxidic oxygen (O*). This value has been used as the basis for the calculations of the molecular refractions of all of the liquid peroxides listed in Table I. By merely adding this value to the calculated molecular refraction of the oxygen analog (Column 6) of a given peroxide, a value is obtained which is compared with the observed molecular refraction (Column 2). A large deviation between the observed and the calculated molecular refraction would indicate an abnormality in the structure of the peroxide.

Rieche[5] has proposed two different values for the molecular refraction of the peroxide group (—O—O—): 4.04 for the dialkyl peroxides and 3.7 for the alkyl hydroperoxides. These values are somewhat inconvenient and much less useful than the single value adopted in the present investigation. Besides, by subtracting 1.643, the atomic refractivity of oxygen in ethers, from 4.04, and, similarly, 1.525, the atomic refractivity of oxygen in alcohols, from 3.70, values of 2.40 and 2.17 respectively are obtained which agree rather well with the atomic refractivity of the peroxidic oxygen.

Discussion

The value of the atomic refractivity of the peroxidic oxygen is, within the limits of experimental error, almost identical with that of the carbonyl oxygen (2.211). It is therefore conceivable that hydrogen peroxide and the simple aliphatic alkyl hydroperoxides and dialkyl peroxides may have the unsymmetrical oxo-oxide structures (Ia, b, c) rather than the normal peroxide structures (IIa, b, c). The bulk of experimental evidence, however, is certainly not in favor of the oxo-oxide structure.

H—O—H ‖ O	R—O—H ‖ O	R—O—R ‖ O
Ia	Ib	Ic
H—OO—H	R—OO—H	R—OO—R
IIa	IIb	IIc

For example, the dissociation of hydrogen peroxide under the influence of ultraviolet light into free hydroxyl radicals,[6] and the thermal decomposition of simple aliphatic peroxides are more in accord with the normal structures. This is particularly true in the case of ditertiary alkyl peroxides[e,f,g] in which the carbon–oxygen bond seems to be much stronger than the oxygen–oxygen bond. The extraordinary stability of these peroxides is probably due to this relationship.

With only a few exceptions, the small exaltations which exist in the simple aliphatic alkyl hydroperoxides, dialkyl peroxides and hydroxyalkyl peroxides are probably due to experimental

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(3) Maass and Hatcher, THIS JOURNAL, **42**, 2548 (1920).

(4) "Landolt-Börnstein Physikalisch-chemische Tabellen," nos. 182, 184, 5. Aufl., Berlin, 1926.

(5) Rieche, "Alkyl Peroxyde und Ozonide," Theodor Steinkoff, Dresden, 1931, pp. 98–100.

(6a) Urey, Dawsey and Rice, THIS JOURNAL, **51**, 1371 (1929); (b) Milas, Kurz and Anslow, *ibid.*, **59**, 543 (1937); (c) Davis and Ackerman, *ibid.*, **67**, 486 (1945).

TABLE I

COMPARISON OF THE MOLECULAR REFRACTION OF LIQUID PEROXIDES WITH THAT OF THEIR NORMAL OXYGEN ANALOGS

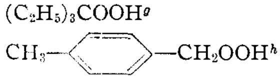
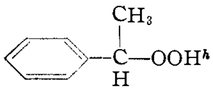
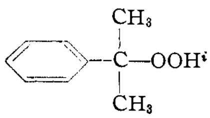
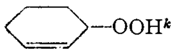
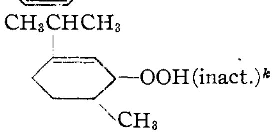
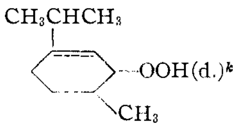
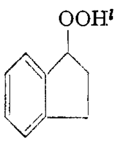
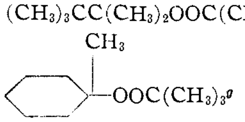
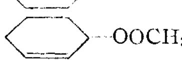
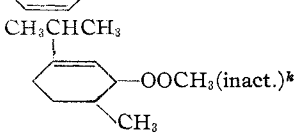
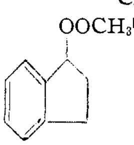
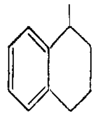
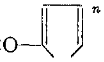
Peroxide	Hydrogen peroxide			Water		
	MR_D (obs.)	MR_D (calcd.)	Exaltation	MR_D (obs.)	MR_D (calcd.)	Exaltation
HOOH[a]	5.90	5.90	0.00	3.71[p]	3.73	−0.02
	Organic hydroperoxides			Alcohol analogs		
CH_3OOH[b]	10.74	10.53	0.21	8.23[c]	8.34	−0.11
C_2H_5OOH[b]	15.17	15.15	.02	12.89[c]	12.96	− .07
i-C_3H_7OOH[d]	20.01	19.77	.34	17.67[c]	17.58	.09
t-C_4H_9OOH[e]	24.42	24.39	.03	22.22[p]	22.20	.02
t-$C_5H_{11}OOH$[f]	28.95	29.01	− .02	26.72[p]	26.82	− .10
$(C_2H_5)_3COOH$[g]	37.90	38.34	− .44	...	36.15	....
 [h]	39.93	39.26	.67	...	37.07	....
 [h]	39.51	39.26	.25	37.08[c]	37.07	.01
 [i]	44.42	43.88	.54	...	41.69	....
 [k]	30.75	30.95	− .20	...	28.76	....
 (inact.)[k]	50.17	49.43	.74	...	47.24	....
 (d.)[k]	50.00	49.43	.57	...	47.24	....
 [l]	42.31	41.68	.63	...	39.49	....
	Dialkyl peroxides			Ether analogs		
CH_3OOCH_3[b]	15.40	15.27	0.13	...	13.08	....
$C_2H_5OOCH_3$[b]	20.09	19.89	.20	...	17.70	....
$C_2H_5OOC_2H_5$[b]	24.74	24.51	.23	22.47[c]	22.32	0.15
t-C_4H_9OO-t-C_4H_9[e]	43.36	42.97	.39	40.68[m]	40.78	.10
t-$C_5H_{11}OO$-t-C_5H_{11}[f]	52.53	52.21	.32	...	50.02	....
$(CH_3CH_2)_3COOC(CH_2CH_3)_3$[g]	68.80	70.68	−1.88	...	68.49	....
$(CH_3)_3CC(CH_3)_2OOC(CH_3)_3$[g]	56.80	56.90	−0.10	...	54.71	....
 [g]	55.10	54.61	.49	...	52.42	....
 [k]	35.95	35.69	.26	...	33.50	....
 (inact.)[k]	54.74	54.16	.58	...	51.97	....
 [l]	47.35	46.41	.94	...	44.22	....

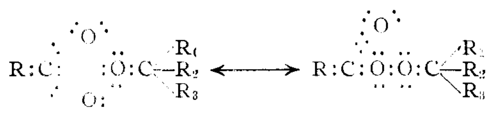
TABLE I (*Concluded*)

Peroxide	Dialkyl peroxide MR_D (obs.)	MR_D (calcd.)	Exaltation	Water MR_D (obs.)	MR_D (calcd.)	Exaltation
$OOCH_3$[k] 	51.83	51.05	.80	...	48.84	....
	Hydroxyalkylperoxides			Hemiacetal analogs		
$HOCH_2OOCH_3$[c]	16.95	16.79	0.16	...	14.60	....
$CH_3CH(OH)OOCH_3$[c]	21.35	21.41	− .06	...	19.22	....
$C_2H_5OOCH_2OH$[c]	21.56	21.41	.14	...	19.22	....
$C_2H_5OOCH(OH)CH_3$[c]	25.17	26.03	− .86	...	23.84	....
	Peresters			Ester analogs		
t-$C_4H_9OOCOC_6H_5$[n]	54.84	53.24	1.60	51.86[o]	51.05	0.81
t-$C_5H_{11}OOCOC_6H_5$[n]	59.16	57.86	1.30	...	55.67	....
t-C_4H_9OOCO—  [n]	47.46	46.11	1.35	...	43.92	....
t-$C_4H_9OOCOCH{=}CHCH_3$[n]	43.85	42.52	1.33	...	40.33	....
t-$C_4H_9OOCO[CH_2]_8CH{=}CH_2$[n]	75.72	74.85	0.87	...	72.66	....

[a] Ref. 3. [b] Ref. 5. [c] Lange, "Handbook of Chemistry," Sandusky, Ohio, 1937, pp. 734–837. [d] Medwedewa and Alexejewa, *Ber.*, **65B**, 133 (1932). [e] Milas and Surgenor, THIS JOURNAL, **68**, 205 (1946). [f] Milas and Surgenor, *ibid.*, **68**, 643 (1946). [g] Milas and Perry, *ibid.*, **68**, Sept. (1946). [h] Hock and Lang, *Ber.*, **76B**, 169 (1943). [i] Hock and Lang, *ibid.*, **77B**, 257 (1944). [j] Criegee, Pilz and Flygare, *ibid.*, **72**, 1799 (1939). [k] Hock and Lang, *ibid.*, **75B**, 300 (1942). [l] Hock and Lang, *ibid.*, **75B**, 1051 (1942). [m] Erickson and Ashton, THIS JOURNAL, **60**, 2434 (1938). [n] Milas and Surgenor, *ibid.*, **68**, 642 (1946). [o] Norris and Rigby, *ibid.*, **54**, 2098 (1932). [p] Ref. 4.

error or to lack of absolute purity. Real exaltations, however, appear in hydroperoxides, dialkyl peroxides and peresters which contain the aromatic nucleus or carbon–carbon double bonds usually attached to the molecule in positions beta to the peroxidic oxygen. In these cases the peroxide group seems to behave like an unsaturated group in conjugation with the carbon–carbon double bond.

The peresters show an exaltation almost equivalent to an additional oxygen atom. Since the normal esters also show small but real exaltations, the increased exaltation in the peresters must be attributed to the peroxide group. To account for the high exaltation shown by the peresters, structure III of the perester group is postulated in which the two oxygen atoms attached to the same carbon atom are equivalent, as in the case of the carboxylic acids, and the oxygen attached to the tertiary carbon atom is bound to the two oxygen atoms by single electron bonds. Such a hybrid structure should be in



III IV

resonance with the normal structure IV. If the peresters have structure III, they would be expected to show abnormal properties. This has actually been found to be the case with all of the t-alkyl peresters so far synthesized.[f]

Acknowledgment.—The authors wish to thank the Union Bay State Chemical Company for financial support in carrying out this investigation.

Summary

1. A simple method for the calculation of the molecular refraction of organic liquid peroxides has been proposed. This method is based on the addition of 2.19, the atomic refractivity of the peroxidic oxygen, to the calculated molecular refractivity of the normal oxygen analog of a given peroxide.

2. The molecular refractivities of 13 alkyl hydroperoxides, 12 dialkyl peroxides, 4 hydroxyalkyl peroxides and 5 peresters have been calculated and the values obtained compared with the observed values.

3. A hybrid structure of the peresters has been postulated to account for their abnormal exaltations.

CAMBRIDGE 39, MASS. RECEIVED MAY 1, 1946