

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BUCKNELL UNIVERSITY]

Studies on Oxygen Absorption Induced by Ether Linkages. Rates of Oxygen Absorption by Dioxolane and Methyl-dioxolane

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Numerous studies have been made on the formation, structure, and decomposition of ether peroxides.^{1,2,3,4} However, there has been no direct measurement on the rate of oxygen absorption and its relation to the hydrolytic and thermal stability of the respective ether. A preliminary investigation, in which we examined a large number of simple and complex ethers, disclosed that a study of dioxolane and its derivatives might be useful for the evaluation of the aforementioned factors. The dioxolanes are readily hydrolyzed and pyrolyzed and, furthermore, they absorb oxygen at measurable rates, even at room temperature.

Experimental

A Barcroft-Warburg type of apparatus⁵ was used for the measurement of oxygen consumption; the volume of the reaction flasks was approximately fifty ml. Complications due to the diffusion of water vapor from the manometers to the reaction flasks were avoided by substituting dibutyl phthalate for the conventional Brodie manometer fluid. Optimum reaction rates were obtained with a vibration rate of 68 oscillations per minute at an amplitude of 2 cm. It is probable that the vibration and amplitude values are dependent on the viscosity of the liquid under investigation. For example, Johnston and Frey⁶ found 110 oscillations per minute at an amplitude of 3 cm. as optimum for the oxidation of fatty oils. The precision⁶ of the measurements is within 5%. All measurements were made at 25° ($\pm 0.05^\circ$).

Reaction flasks were cleaned by removing grease from the ground joints, and residues from previous runs with petroleum ether, then by immersion in a chromic acid bath for about six hours followed by rinsing in five baths of distilled water. After drainage the flasks were dried in a vacuum desiccator over calcium chloride.

The dioxolanes⁶ were dried over *c. p.* potassium hydroxide pellets and then slowly distilled through a 150 × 12 mm. Vigreux column. The use of longer columns was found objectionable due to the more prolonged heating and subsequent decomposition of the dioxolane. Distillation at reduced pressure did not appreciably affect the quality of the products judged on the basis of boiling range and rates of oxygen absorption. The boiling range of dioxolane

(CH₂OCH₂CH₂O) was 75.0–75.2° (cor.) at 760 mm. and methyl-dioxolane (CH₃CHOCH₂CH₂O) 85.3–85.5° (cor.) at 760 mm.

The oxygen was passed through a purification train composed of red hot cupric oxide followed successively by concentrated sulfuric acid, soda lime, and fine glass wool. The conventional method of first charging the reaction flasks with the liquids and then flushing with oxygen was reversed in order to avoid evaporation losses that are appreciable for substances of high vapor pressure. Thus, the empty flasks were attached to the manometers and swept with a stream of oxygen gas at a pressure of about 5 cm. of dibutyl phthalate for five minutes, then 1.00-ml. samples of dioxolanes were added and the flasks quickly stoppered. In cases where accelerators or inhibitors were studied, these substances were dissolved in the dioxolane and 1.00-ml. samples of the respective solutions were added to the reaction flasks.

The apparatus was placed in a dark room to facilitate control of illumination. For experiments conducted *in the light*, a 12-inch, 60-watt fluorescent lamp was fixed above and midway between the two parallel banks of reaction flasks. Thus, the most direct rays travelled through 6 in. of air space and 4 in. of water before impinging on the Pyrex reaction flasks. Although this method of illumination was not without certain objections, simplicity of operation and reproducibility of results were its justification.

In control experiments it was found that neither the ground joint lubricant⁷ nor the manometer fluid absorbed appreciable amounts of oxygen in the course of eighteen hours in the dark or in the light.

Although the dried and distilled dioxolanes were stored in the dark, discrepancies in the rate of oxygen absorption appeared on comparison of the data of successive runs. In the dark, freshly distilled samples of methyl-dioxolane and dioxolane absorbed no oxygen in five hours. Under the same conditions, samples of dioxolane that had aged for five and eight days absorbed 167 and 217 cmm. of oxygen, respectively. Peroxide tests on samples that had aged for five days showed positive for methyl-dioxolane, but were negative for dioxolane. (The ferrous ion-thiocyanate ion method was used for the tests.) On standing for longer periods, dioxolane gave positive peroxide tests.

To test the efficiency of distillation as a means of removing peroxides, a sample of methyl-dioxolane that had stood for eight days and which gave a strong peroxide test, was redistilled at atmospheric pressure through the 150 × 12 mm. Vigreux column. In five hours, the distillate, which gave no peroxide test, absorbed no oxygen in the dark, whereas the residue, which gave a strong peroxide test, absorbed 560 cmm. Similar results were obtained with redistilled samples of dioxolane.

Further proof of the accelerative influence of peroxides

(1) Clover, *THIS JOURNAL*, **44**, 1107 (1922).

(2) Wieland and Wingler, *Ann.*, **431**, 301 (1923).

(3) Rieche, *Z. angew. Chem.*, **44**, 896 (1931).

(4) Liebhaufsky and Sharkey, *THIS JOURNAL*, **62**, 190 (1940).

(5) For equipment and technique, see Dixon, "Manometric Methods," The Macmillan Co., New York, N. Y., 1934; also, Johnston and Frey, *Ind. Eng. Chem., Anal. Ed.*, **13**, 479 (1941).

(6) Generously furnished by the Carbide and Carbon Chemical Corp.

(7) Lutrisal, sold by A. H. Thomas, Philadelphia, Pa.

is offered by the fact that 0.1 mole % of benzoyl peroxide added to freshly distilled samples of dioxolane and methyl-dioxolane led to an oxygen absorption of 615 and 372 *cm.*, respectively, over a five hour period in the dark. The high oxygen consumption in cases where benzoyl peroxide was added is made more significant by the fact that this peroxide did not induce oxygen absorption when dissolved in dibutyl phthalate. Thus, benzoyl peroxide probably accelerates the absorption of oxygen by the dioxolanes in the dark.

In Table I are presented data illustrating the effects of light and of inhibitors. The samples of dioxolane and methyl-dioxolane used for this run were free of peroxides at the start.

TABLE I
CENTIMETERS OXYGEN ABSORBED, IN THE LIGHT

Time, hr.	Dioxolane ^a				Methyldioxolane ^a			
	○	●	⊙	⊗	○	●	⊙	⊗
2.0	133	54	38	0	0	0	0	0
4.0	269	96	63	.	0	0	0	.
6.0	456	168	104	.	18	7	13	.
9.0	724	262	174	.	46	13	34	.
11.0	904	327	228	0	67	23	52	0
12.0	1005	364	248	.	77	31	66	.
21.0	1873	668	435	.	189	73	180	.
24.0	2150	774	501	.	228	75	196	.
26.5	2460	892	581	0	296	97	261	0
28.5	2700	978	647	.	353	122	320	.
30.5	2915	1051	702	.	400	134	368	.
34.5	3356	1214	828	.	535	179	493	.
45.0	4641	1660	1186	0	1075	323	970	0
48.0	4821	1773	1272	.	1225	366	1108	.
54.0	5610	2055	1488	.	1746	522	1415	.
58.8	6141	2240	1688	.	2120	644	1676	.
72.0	7760	2838	2289	78	3360	1241	2055	0
76.2	8142	2961	2432	.	3720	1424	2191	.
78.2	8330	3022	2513	.	3908	1514	2285	.
82.4	8811	3169	2732	.	4375	1790	2527	.
94.0	10060	3710	3372	118	5700	2630	3232	18
97.4	10425	3884	3588	.	6105	3019	3460	.
100.4	10720	4010	3768	.	6450	3156	3646	.
105.5	11200	4250	4069	.	7055	3590	3949	.
107.0	11340	4340	4178	127	7231	3740	4045	53
117.2	12210	4840	4815	.	8419	4656	4640	.
120.2	12460	5009	5030	.	8771	4932	4821	.
122.2	12640	5119	5180	.	9000	5135	4950	.
124.2	12790	5220	5306	.	9205	5307	5055	.
128.2	13080	5435	5560	151	9680	5636	5281	78
130.0	13270	5558	5721	.	9921	5745	5431	.
141.2	14190	6220	6490	284	11165	6815	5685	210

^a ○, no addition; ●, plus 2 mole % water; ⊙, plus 2 mole % ethanol; ⊗, plus 2 mole % hydroquinone.

Discussion of Results

Comparison of the rate curves for dioxolane and methyl-dioxolane, Fig. 1, brings out a striking difference in their respective induction periods. Evidently, the dioxolane-oxygen reaction is immediately accelerated by light whereas the methyl-dioxolane-oxygen reaction is not as light sensitive and requires a longer induction period during which a catalyst is probably formed. The characteristic decreases in rate can hardly be ascribed to diminishing dioxolane or methyl-dioxolane concentration since the decreases appear when less

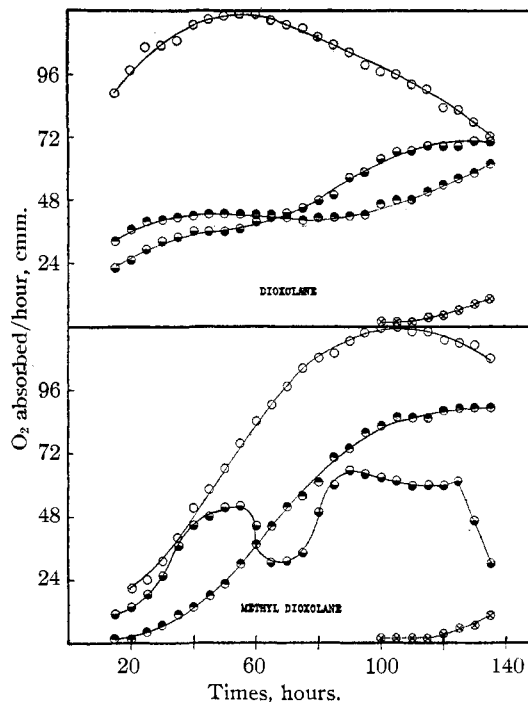


Fig. 1.—Time-rate curves: rates determined graphically on 25 × 30 *cm.* coordinate paper; symbols have same significance as in Table I.

than 5% of the theoretical amount (based on a 1:1 dioxolane-oxygen ratio) of oxygen has been absorbed. On the other hand, the decrease in rate might be ascribed to the influence of peroxide decomposition products. Assuming that these peroxides are of the same type as the ordinary ether peroxides, their decomposition into aldehydic and alcoholic reagents^{1,2,3} would undoubtedly affect the rate of oxygen absorption. It has been reported that aldehydes catalyze the rate of peroxide formation¹; we have attempted to measure their influence on oxygen absorption but experimental difficulties involved in the preparation of peroxide-free aldehydes led us to a temporary abandonment of the attempt. However, the retarding influence of an alcohol is clearly demonstrated by the data of Table I and by the curves, Fig. 1. The data at hand do not permit an accurate explanation of the peculiar shape of the rate curves for the alcohol and water inhibited reactions. But, if we reason from the postulates of Clover¹ and of Wieland and Wiegler,² it appears probable that alcoholysis of the peroxides is an important phase of the alcohol inhibition process. Similarly, the inhibitory action of water, Fig. 1, can be associated with the hydrolysis of the peroxide. The interpretation of the rate decrease on

the basis of peroxide decomposition is supported by the results of peroxide tests performed at the end of runs in the light. Thus, after 141 hours methyl dioxolane had acquired a greater rate and gave a stronger peroxide test than did dioxolane, even though the latter had absorbed a total of approximately 25% more oxygen. In conclusion, it must be emphasized that these considerations are tentative and that further work is required before a clear understanding of the ether peroxidation reaction can be acquired. However, it is believed that our results prove the importance of oxygen absorption measurements in a study of the peroxides of compounds containing ether linkages.

Summary

The use of the Barcroft-Warburg apparatus for the measurement of oxygen absorption by dioxolane and methyl dioxolane has been described. The rates of oxygen absorption by the dioxolanes in the dark and in the light have been reported. The accelerative action of the peroxides and the inhibitory action of ethanol and water have been discussed. The inhibitory action of hydroquinone has been reported. Some factors that may account for the complexities of the dioxolane and methyl dioxolane-oxygen reactions have been suggested.

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Hydrogen Fluoride as a Condensing Agent. XVI. Reactions of Carbon Monoxide

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Carbon monoxide is known to react with numerous organic substances in the presence of catalysts. It has, for instance, been known for a long time that carbon monoxide reacts with aromatic hydrocarbons in the presence of aluminum chloride to produce aromatic aldehydes.² More recently it has been shown to react with chlorobenzene using active carbon and cuprous chloride to form a small amount of benzoic acid.³ Its reactions have also been studied with the higher alcohols, olefins, and methyl alcohol, using active carbon impregnated with phosphoric acid as a catalyst.^{4,5}

In this situation it has seemed worth while to study the possible reaction of carbon monoxide in the presence of hydrogen fluoride with various organic compounds.

It was found that alcohols reacted to form aliphatic acids, and that alkyl halides reacted in the presence of water or methanol to form acids. Attempts to prepare an ester from diethyl ether, benzoic acid from phenol, and an aldehyde from toluene all resulted in the formation of tarry products. The last mentioned indicates that the Gattermann and Koch reaction occurred but that the aldehyde product polymerized under the influence of the catalyst. Benzaldehyde has been

found in this Laboratory to polymerize under the conditions used, and toluene to be unaffected.

First Procedure.—To a mixture of 1 to 2.5 moles of anhydrous hydrogen fluoride and 0.5 to 0.67 mole of an organic material in a cold copper bomb of 150-cc. capacity, 0.5 to 1 mole of 90% formic acid was added, the bomb then sealed and heated to 100–160° for one to two days. Carbon monoxide was generated in the mixture and at the end of the reaction period was vented through a small hole in the cap of the cold bomb. The product formed was poured over ice, made alkaline with sodium carbonate, filtered, extracted with ether to remove non-acidic material, and the aqueous layer acidified with hydrochloric acid. The resulting solution was then extracted with ether, the ethereal solution dried over calcium chloride, and the ether evaporated.

Isopropyl alcohol thus treated gave rise to a tar, but no acidic product. *n*-Propyl alcohol gave 16 g. (28%) of isobutyric acid identified by its b. p. 148–149° and its anilide, m. p. 105–106°. *n*-Amyl bromide gave some high-boiling material, some tar, and 14 g. (19%) of recovered amyl bromide, a very small amount of alkali-soluble material being obtained which with difficulty yielded an anilide in amount insufficient to purify. *s*-Amyl bromide gave 6 g. (11%) of acidic material, b. p. 185–187°, identified as a six-carbon acid by its neutralization equivalent 121 (calcd. 116).

In a variation of this procedure, nickel carbonyl (42 g.) was used in place of the formic acid. Six moles of hydrogen fluoride (120 g.), 40 g. of isopropyl chloride and 20 g. of water were used. No reaction resulted after one day of heating at 109°, but 8 g. (20%) of isobutyric acid was obtained after one and one-half days of heating at 150°.

Second Procedure.—Instead of using formic acid, carbon monoxide was added under pressure to the mixture of hydrogen fluoride and organic material in a copper pressure

(1) For the previous paper of this series see THIS JOURNAL, **63**, 1921 (1941).

(2) Gattermann and Koch, *Ber.*, **30**, 1622 (1897).

(3) Marecek, *Chem. Obzor.*, **7**, 171 (1932).

(4) Krase and Singh, *Ind. Eng. Chem.*, **27**, 909 (1935).

(5) Hardy, *J. Chem. Soc.*, 358 (1936).