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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Dioxolane[1]

BY WILLIAM B. GUENTHER[2] AND W. D. WALTERS

The homogeneous thermal decomposition of dioxolane has been investigated over the temperature range 455–525° and at initial pressures from 50 to 400 mm. On the basis of (a) aldehyde analyses, (b) mass spectrometric analyses of the gaseous products during and at the end of the decomposition, and (c) measurement of the ratio of the final to the initial pressure, the following decompositions seem to occur: (1) $C_3H_6O_2 \rightarrow CH_2O + CH_3CHO$ and (2) $C_3H_6O_2 \rightarrow CO_2 + C_2H_4 + H_2$ with (1) and (2) occurring at approximately equal rates; the subsequent reactions of the substances formed in (1) and (2) yield the final products, 2CO, H_2, CH_4, CO_2 and C_2H_6. Experiments at different initial pressures indicate an apparent order of reaction of 1.3. The rate of pressure increase is markedly inhibited by the addition of either nitric oxide or propylene, and accelerated by the addition of ethylene oxide.

Introduction

Of the decompositions of cyclic compounds investigated thus far the decomposition of the cyclic ether dioxane appears to be one of the few reactions inhibited by nitric oxide.[3] The very marked inhibition indicates that dioxane decomposes chiefly by a chain reaction. On the other hand in two previous investigations[4,5] of five-membered ring compounds no appreciable inhibition by nitric oxide was observed. It was of interest, therefore, to examine the five-membered cyclic formal dioxolane to ascertain whether its homogeneous decomposition would be a chain reaction similar to that for dioxane. For dioxolane no detailed investigation has been reported. Bilger and Hibbert[6] have pyrolyzed dioxolane in a flow system at 474° in the presence of carbon dioxide. They observed that two of the important products are ethylene and an acid, the yield of the acid being about 35% of that of ethylene. Catalytic pyrolysis of substituted dioxolanes in a flow system has been carried out by Neish, Haskell and MacDonald.[7] They reported that these compounds decompose, presumably by the way of free radicals, to form chiefly carbonyl compounds and, to a lesser extent, unsaturated hydrocarbons.

Experimental

Materials.—The samples of 1,3-dioxolane were kindly donated by the Carbon and Carbide Chemicals Corporation and the du Pont Company. The dioxolane was usually treated with potassium hydroxide pellets and Drierite before vacuum fractionation. For the experiments to determine the order of the reaction, the dioxolane was dried as above and then treated with sodium before it was fractionated under vacuum three times. For the samples used in the present study, the boiling points, read after short boiling times, were within the range 74.6° at 747 mm. to 74.8° at 753 mm. The value of Legault and Lewis[8] is 75.0–75.2° at 760 mm. The index of refraction of the purified dioxolane was found to be $n^{21}\text{D}$ 1.3997. Clarke[9] reports $n^{20}\alpha$ 1.39736 and $n^{20}\gamma$ 1.40734. By means of the color tests mentioned in a later section it was found that the dioxolane after purification did not contain formaldehyde or acetaldehyde. Likewise peroxides were absent from the purified dioxolane which had been vacuum-fractionated and stored under vacuum.

Nitric oxide prepared earlier by the method described by Klute and Walters[10] was employed after removal of any impurities non-volatile at −78°. C.P. propylene, 99.5%, from the Ohio Chemical and Manufacturing Company was employed after degassing at −196°. A sample of purified propylene prepared from *n*-propyl alcohol was also used. The ethylene oxide was a specially purified sample from the Dow Chemical Company and was supplied to us by Dr. D. R. Stull. Biacetyl was obtained from the Eastman Kodak Company.

Apparatus and Method.—The furnace and method of temperature regulation for the static experiments were similar to those already described.[5] The temperature was measured with a standardized[11] platinum, platinum–13% rhodium thermocouple connected to a Leeds and Northrup Type K-2 potentiometer. In most of the experiments a heated stopcock lubricated with Myvacene-S was used next to the reaction vessel. Tests showed that this lubricant did not absorb a manometrically measurable amount of dioxolane under the conditions of the experiments. Moreover, for comparison, a mercury cut-off was employed in place of the above stopcock for a number of runs, but no appreciable difference in the pressure–time curves was observed. The remainder of the vacuum system for the static experiments was of the usual type. With added nitric oxide or propylene, the gas to be added was introduced into the reaction vessel before the dioxolane. With ethylene oxide or biacetyl a known amount of the added material was condensed in a cold finger (−78°) prior to the condensation of the dioxolane. Then the entire mixture was vaporized into the reaction vessel. The effect of surface was tested by installing a reaction bulb packed with lengths of smooth glass tubing which increased the surface to volume ratio by a factor of approximately 35. The apparatus for the flow experiments was similar to that used by Rice and Haynes.[12]

Analyses.—Formaldehyde and acetaldehyde were identified as intermediate products in the decomposition of dioxolane in three ways: (a) by solid derivatives, (b) by color reactions, and (c) by their polarographic half-wave potentials. The flow system was used to obtain sufficient quantities of products for the identification of the aldehydes by means of derivatives. The dioxolane was allowed to flow rapidly at about 15 mm. pressure through a furnace held at approximately 800°. The products which condensed at −196° were dissolved in water and a water solution saturated at 100° with methone (dimedon) was added in ex-

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[1] This work was supported by the Office of Naval Research under Contract N6onr-241, Task Order I, with the University of Rochester.

[2] Abstracted from the M.S. thesis of William B. Guenther.

[3] L. Küchler and J. D. Lambert, *Z. physik. Chem.*, **B37**, 285 (1937).

[4] C. H. Klute and W. D. Walters, THIS JOURNAL, **68**, 506 (1946).

[5] D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948).

[6] E. M. Bilger and H. Hibbert, *ibid.*, **58**, 823 (1936).

[7] A. C. Neish, V. C. Haskell and F. J. MacDonald, *Can. J. Research*, **25B**, 266 (1947).

[8] R. R. Legault and D. C. Lewis, THIS JOURNAL, **64**, 1354 (1942).

[9] H. T. Clarke, *J. Chem. Soc.*, **101**, 1788 (1912).

[10] C. H. Klute and W. D. Walters, THIS JOURNAL, **67**, 550 (1945).

[11] W. F. Roeser and H. T. Wensel, *J. Research Natl. Bur. Standards*, **14**, 247 (1935).

[12] F. O. Rice and W. S. Haynes, THIS JOURNAL, **70**, 964 (1948).

cess.[13,14] From the products both the alkali-soluble methylene bis-methone which indicated the presence of formaldehyde and an alkali-insoluble xanthene derivative which served to identify acetaldehyde could be prepared and separated. The former after crystallization from alcohol melted at about 190° compared with published values from 189 to 191.4° for the formaldehyde derivative. The other derivative melted at about 176° in agreement with the literature values for the acetaldehyde derivative which range from 173 to 176.5°. Mixed melting points with derivatives prepared from formaldehyde and acetaldehyde showed no depression.

For the color tests the products of three static runs, in which about 1/4 of the dioxolane had decomposed, were condensed at −196° and then dissolved in 10 ml. of water. This solution gave positive color changes in the Lebbin resorcinol test[14] for formaldehyde and in the Lewin test[15] for acetaldehyde.

The polarographic analysis for the aldehydes was performed by a method adapted from previous work.[16] The products were removed from the reaction vessel and the aldehydes were dissolved in water. The current–voltage curve of the aqueous solution of aldehydes (containing lithium hydroxide–lithium chloride) was obtained with a Fisher Elecdropode. By comparison of the wave heights with those of a standard solution of formaldehyde and acetaldehyde the concentrations could be obtained. The method of recovery and analysis of acetaldehyde was tested twice by placing a known quantity of gaseous acetaldehyde in the reaction vessel at 350°. Removal and analysis in the usual manner showed that the accuracy was about 5%. By consideration of the various errors involved, it is estimated that the pressures of aldehydes given in Table I are accurate to within ±10%.

The gaseous products were analyzed on the mass spectrometer at the National Bureau of Standards under the direction of Dr. F. L. Mohler. The products given in the last four columns of Table II are only those readily volatile at −78°. The products from several runs carried to about 35% decomposition were tested for acid constituents. After the products had been brought into contact with water, as described previously,[17] the water solution was boiled a short time to remove carbon dioxide (but not formic or acetic acid). The solution was titrated with 0.05 normal base. The limit of detection of an acid constituent was considered to be 0.005 meq. which would correspond to a pressure of 1% of the amount of dioxolane decomposed. The amount of acidic material, such as formic acid or acetic acid which would have been formed from ketene, did not exceed this limit.

Although the presence of water as a product appeared unlikely, the reaction products were passed over anhydrous cobalt chloride to test for water. No water was detected.

Results and Discussion

Products.—The results of the polarographic analyses for acetaldehyde and formaldehyde during the decomposition of dioxolane at various temperatures and pressures are summarized in Table I. Acetaldehyde and formaldehyde appear to be present in approximately equivalent amounts throughout the decomposition. The change in total aldehyde content as the decomposition proceeds at 475° is shown as curve 1 in Fig. 1. The aldehyde content rises to a maximum of 20 mm. aldehydes/100 mm. initial dioxolane at about 80% pressure increase. Curve 1 in Fig. 1 is the type expected for substances which are intermediate products in a reaction. From an inspection of the results in Table I it appears that for a given per cent. pressure increase the amounts of aldehydes present do not change appreciably over the ranges of temperatures and pressures used.

Table I

Aldehyde Content During the Decomposition of Dioxolane

P/P_0 = ratio of pressure at time of removal to the initial pressure; P_F and P_A = pressures of formaldehyde and acetaldehyde; $P_{Ald.}$ = total pressure of aldehydes

P_0, mm.	P/P_0	P_F/P_0	P_A/P_0	$P_{Ald.}/P_0$
Temp. 475 ± 1°				
114	1.21	0.048	0.043	0.09
104	1.37	.079	.065	.14
102	1.37	.077	.066	.14
74	1.38	.072	.068	.14
79	1.40	.081	.074	.16
101	1.47	.078	.077	.16
102	1.47	.088	.080	.17
100	1.48	.100	.088	.19
101	1.75	.098	.096	.19
103	1.76	.113	.099	.21
105	2.05	.100	.100	.20
106	2.05	.104	.097	.20
102	2.04	.102	.100	.20
113	2.44	.067	.068	.14
106	2.43	.063	.070	.13
Temp. 455°				
103	1.35	0.073	0.069	0.14
101	1.32	.071	.060	.13
Temp. 465°				
103	1.36	0.079	0.067	0.15
128	1.40	.074	.071	.15
Temp. 495°				
130	1.75	0.106	0.097	0.20
96	1.70	.105	.094	.20
57	1.70	.112	.096	.21
Temp. 506°				
100	1.89	0.101	0.114	0.22
Temp. 475°, 4 mm. NO added				
103	1.33	0.057	0.069	0.13
104	1.36	.060	.071	.13
Temp. 455°, 3.5 mm. biacetyl added				
105	1.80	0.093	0.094	0.19
Temp. 475°, packed bulb				
116	1.90	0.14	0.14	0.28

The gaseous products, as determined by mass spectrometric analysis, are shown in Table II. The results indicate that over the temperature range 475–525° the composition of the gaseous products remains almost constant. It may be noted that the 2:1 relationship of carbon monoxide to methane is that which would be predicted if the methane and carbon monoxide were formed from an equimolar mixture of formaldehyde and acetaldehyde. In the experiments carried to nearly complete decomposition the percentage of carbon dioxide is approximately equal to the sum of the percentages of ethane and ethylene. A comparison

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(13) D. Vorlaender, *Z. anal. Chem.*, **77**, 241 (1929); E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, pp. 44 and 50.

(14) J. F. Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1944, pp. 246, 263.

(15) L. Lewin, *Ber.*, **32**, 3388 (1899).

(16) G. C. Whitnack and R. W. Moshier, *Ind. Eng. Chem., Anal. Ed.*, **16**, 496 (1944); P. J. Elving and E. Rutner, *ibid.*, **18**, 176 (1946); P. J. Elving, B. Warshowsky, E. Shoemaker and J. Margolik, *ibid.*, **20**, 25 (1948).

(17) W. D. Walters, This Journal, **62**, 880 (1940).

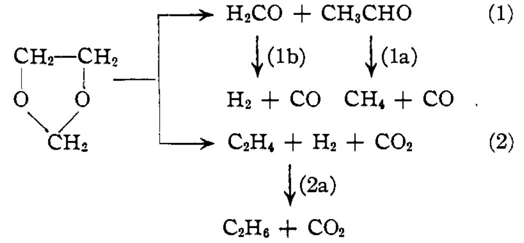
TABLE II

PRODUCTS BY MASS SPECTROMETRIC ANALYSIS IN MOLE PER CENT.

Temp., °C.	525	475	475	476	475	475
P_0, mm.	83	101	62	111	96	89
P/P_0			1.64	1.61	1.81	1.78
	End products 3.8 hr.	 10.2 hr.	P. B.[a]	P. B.		4 mm. NO
CO	30.2	28.7	19.1	16.1	17.9	23.9
CH_4	15.0	14.0	9.0	8.2	9.2	9.3
CO_2	17.0	17.8	18.2	22.0	19.2	16.9
C_2H_6	15.9	17.1	5.3	6.9	8.0	8.7
C_2H_4	1.5	1.2	18.4	15.4	15.4	13.2
H_2	19.8	20.1	29.6	29.6	29.2	26.4
NO	...	...	....	....	....	0.9
CH_2CO[d]	...	...	1[c]	0.3	0.2	0.1
Remain.[b]	0.6	1.1	0.4	1.8	1.1	0.7

[a] P.B. denotes packed bulb. [b] Remain. designates small amounts of acetaldehyde and undecomposed dioxolane. [c] A trace of formic acid, less than 0.1%, was indicated. In the last four experiments any formic acid present would be almost completely removed by the −78° trap. [d] The analyses for ketene are somewhat uncertain.

of the final products with those after partial decomposition indicates that the percentage of ethylene decreases whereas that of ethane increases as the reaction continues. The products in Table II, as well as the intermediate aldehydes, may be explained by the over-all reactions



If these reactions are correct, the composition of the final products indicates that about 45% of the dioxolane decomposes to give carbon monoxide, methane and hydrogen as end products, whereas 55% seems to give carbon dioxide and ethane (or ethylene and hydrogen). The ratios for the final pressure to the initial pressure for the experiments at 525° and 475° (first two columns of data in Table II) were 3.0 and 2.9, respectively; corrections for "dead space" raise these values to 3.1 and 3.0. These values indicate that the first reaction is approximately as important as the second reaction. Material balances were calculated on the basis of the two experiments mentioned above, and the amounts of carbon, oxygen and hydrogen in the products usually agreed within 2–4% with the amounts present in the original dioxolane. Therefore, it appears that the final products shown in Table II account for nearly all of the dioxolane which decomposes.

The yields of aldehydes for the various pressure increases up to about half reaction were calculated and the plot of the results is shown as curve 2 in Fig. 1. By extrapolation to the start of the decomposition it appears that initial yield of aldehydes is about 42%. In view of the close agreement between the yield of aldehydes (42%) and the percentage of dioxolane molecules forming carbon monoxide and methane as end products (45%), it appears that most of the carbon monoxide and methane and part of the hydrogen result from the 40–45% of the dioxolane molecules which decompose into aldehydes.

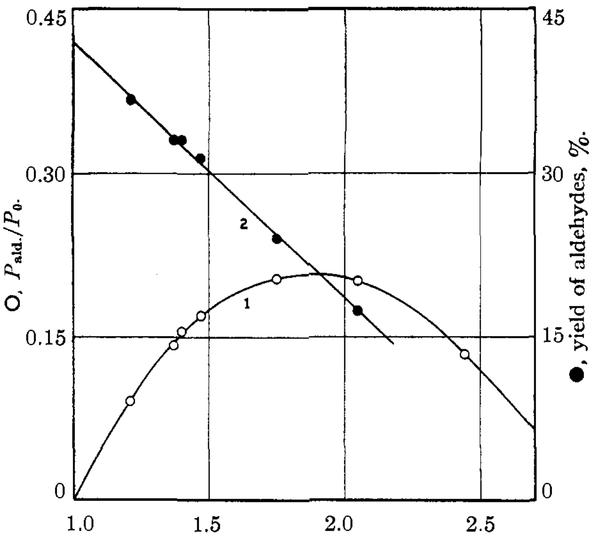


Fig. 1.—Aldehydes present during the decomposition of dioxolane at 475°.

Although molecular reactions (1b) and (2a) are probably not fast in the temperature range employed in the present study, there is evidence that reactions (1a),[18] (1b)[19] and (2a)[20] will probably occur readily in the presence of hydrogen atoms or radicals. As will be discussed in a later section, free radical or atomic reactions are probably occurring in the decomposition of dioxolane; therefore, reactions (1a), (1b) and (2a) appear to be possible. However, Küchler and Lambert[3] have suggested that in the dioxane decomposition ethane is formed by the reaction

$$C_2H_4 + H_2CO \longrightarrow C_2H_6 + CO \tag{3}$$

If this reaction accounts entirely for the disappearance of formaldehyde in the dioxolane decomposition, the percentage of hydrogen as the decomposition proceeds should not exceed either the percentage of carbon dioxide or the sum of the percentages of ethylene and ethane. The results in Table II show that during the decomposition the percentage of hydrogen is greater than that for carbon dioxide and also greater than the sum of ethylene and ethane. This finding gives evidence that at least an appreciable amount of hydrogen is formed by the decomposition of formaldehyde (1b).

Since the amount of ethane present at complete decomposition is equal to or greater than the amount of formaldehyde produced in the decompo-

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(18) (a) A. O. Allen and D. V. Sickman, THIS JOURNAL, **56**, 2031 (1934); (b) C. J. M. Fletcher and G. K. Rollefson, *ibid.*, **58**, 2135 (1936).

(19) In this Laboratory Mr. J. E. Longfield has found that formaldehyde undergoes a radical sensitized decomposition in the range 380–490°.

(20) H. S. Taylor and D. G. Hill, *ibid.*, **51**, 2922 (1929); E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 262.

sition, and since part of the formaldehyde seems to yield hydrogen and carbon monoxide by a reaction in which ethane is not produced, there must be a reaction other than (3) for producing ethane. Presumably this is the reaction of hydrogen and ethylene (2a). Although it appears that reactions (1b) and (2a) are of importance, the present results do not rule out the occurrence of reaction (3) to a significant extent.

Small amounts of ketene and a trace of formic acid were reported in the mass spectrometric analyses. From the titration of aqueous solutions of the products it appears that the quantity of acid constituents present in the products does not exceed 1% of the decomposed dioxolane. If formic acid were formed and then decomposed rapidly into hydrogen and carbon dioxide, it might be of greater importance than the instantaneous concentration would indicate. Therefore, the possibility that formic acid is an intermediate in the decomposition cannot be excluded. However, it does not seem that a significant fraction of the decomposition proceeds through ketene as an intermediate since the amounts of the various gaseous products would not be in agreement with the products formed in reactions involving ketene as an intermediate.[21]

Kinetics.—To determine the order of the reaction, experiments were carried out at 465° with initial pressures from 94 to 391 mm. The time (in minutes) necessary to attain 30% increase in pressure, or about 18% decomposition, was chosen as a measure of the rate. Since the percentages of aldehydes after a given time (Table I) and the analyses for the gaseous products (Table II) did not appear to change significantly with the initial pressure, it was assumed that the use of the time for 30% pressure increase was satisfactory for the comparison of rates of decomposition at different initial pressures. The variation of log t_{30} with log P_0 is shown in Fig. 2. The slope of the line is about -0.3 indicating that the order is 1.3. Approximately the same value was obtained for the order by the use of either the initial rate of pressure rise or the time for 10% pressure increase as a measure of the rate. Likewise for experiments at 475° a plot similar to Fig. 2 indicated a value of 1.3.

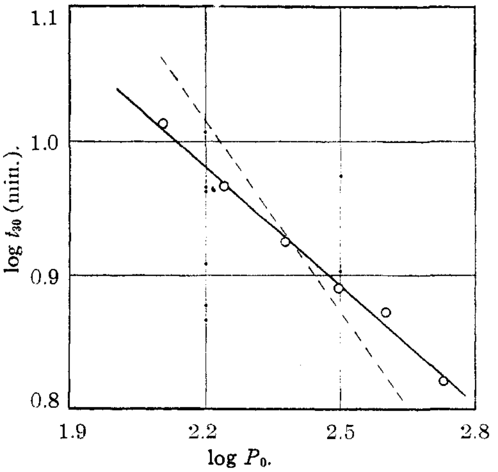

Fig. 2.—Dependence of the time for 30% pressure increase at 465° upon the initial pressure. Broken line represents the behavior of 1.5 order reaction.

A representative pressure–time curve is shown as curve 1 in Fig. 4. The pressure–time curve does not exhibit a marked induction period, but there is an indication that the rate of pressure increase during the first minute or two is not quite as great as the subsequent rate. In this connection it is to be noted that at the start of the reaction the intermediate aldehydes are building up. A plot of the logarithm of the pressure of undecomposed dioxolane (calcd.) *vs.* time during a run showed that until about 80% pressure increase (~44% decomposition) the deviation from a straight line is small, but later the rate is slower than the first order straight line would indicate.

The data obtained from experiments at initial pressures of 93–108 mm. at temperatures from 455 to 524° are summarized graphically in Fig. 3. The results at 455, 465 and 475° represent averages of three or more experiments. A small correction was applied to bring each result to 100-mm. pressure. If the change of t_{30} with temperature were represented by an Arrhenius-like function, $1/t_{30} = Ae^{-E/RT}$, the value of E would be 53 ± 3 kcal.

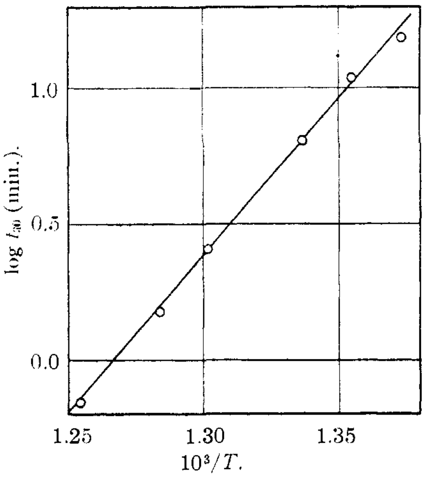

Fig. 3.—Change in t_{30} of the dioxolane decomposition with temperature; initial pressure, 100 mm.

Added Substances.—In a series of experiments at 475° it was observed that the rate of the decomposition of dioxolane is decreased by the addition of nitric oxide or propylene, both of which are known to inhibit many free radical chain reactions.[22,23] As shown in Fig. 4, the results indicate that about 80% of the reaction can be inhibited by either nitric oxide or propylene. Thus these experiments give evidence that a large fraction of the decomposition proceeds by a free radical chain reaction. Since for a given pressure increase the analyses for aldehydes, as well as the gaseous products, are not greatly altered when the reaction is inhibited by nitric oxide (Tables I and II), it seems

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(21) A. T. Williamson, THIS JOURNAL, **56**, 2216 (1934); C. D. Hurd and J. W. Williams, *ibid.*, **58**, 962 (1936).

(22) L. A. K. Staveley and C. N. Hinshelwood, *Proc. Roy. Soc* (*London*), **154A**, 335 (1930); **159A**, 192 (1937); *J. Chem. Soc.*, 1568 (1937).

(23) F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938), L. S. Echols and R. N. Pease, THIS JOURNAL, **61**, 1924 (1939).

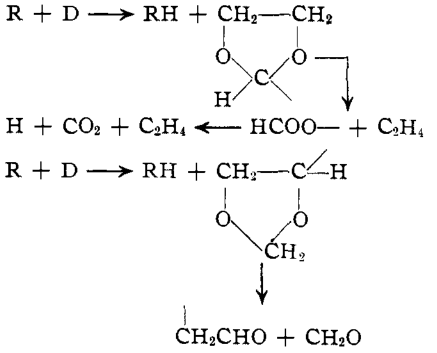
that both reactions (1) and (2) are chain reactions which are inhibited to approximately the same extent.

Small amounts of either ethylene oxide or biacetyl which presumably act as sources of free radicals[18b,24] were found to accelerate the decomposition of dioxolane at 455°. Ethylene oxide produces a considerably greater effect than biacetyl; the addition of 4 mm. of ethylene oxide to 102 mm. of dioxolane decreases the time for 30% pressure increase to one-eighth its normal value at 455°.

In connection with the study of dioxolane, an experiment with dioxane and another experiment with dioxane plus biacetyl were carried out at 491°. These preliminary results indicated that about 5% added biacetyl accelerates the decomposition of dioxane at least sixfold.

Effect of Surface.—The slower rate in the packed bulb (curve 2, Fig. 4) indicates that free radical chains are probably present and that the added surface increases the rate of recombination or destruction of atoms or radicals. Moreover, it appears that the amount of the decomposition which could occur as a surface-catalyzed reaction in the unpacked vessel is not important. In the packed bulb the composition of the gaseous products is approximately the same as the composition in the unpacked vessel (Table II), but the analysis for aldehydes gives some indication that the pressure of aldehydes during the decomposition may be slightly higher (Table I). The ratio of the final to the initial pressure for an experiment at 526° with 87 mm. of dioxolane was found to be 3.1, or with "dead space" correction 3.2.

Mechanism.—To explain the two paths of decomposition suggested by the products, the following reactions



(4)

(5)

seem satisfactory, where R may be either H or $-CH_2CHO$ and D = dioxolane.

Since the products show that both paths of decomposition are of about equal probability, any radical (or atom), R, may be assumed to produce reaction (4) or (5) with equal frequency. Thus the hydrogen atoms of the methylene group between the oxygen atoms appear to be twice as reactive as those on the other two methylene groups. That an oxygen atom will affect the ease of removal of the hydrogen atoms on an adjacent carbon atom has been observed previously.[25] The quantities of formic acid and ketene which may be present might be explained by assuming other reactions for the $HCOO-$ and $-CH_2CHO$ radicals. As the decomposition proceeds the intermediate products acetaldehyde, formaldehyde and ethylene will participate in the free radical processes.

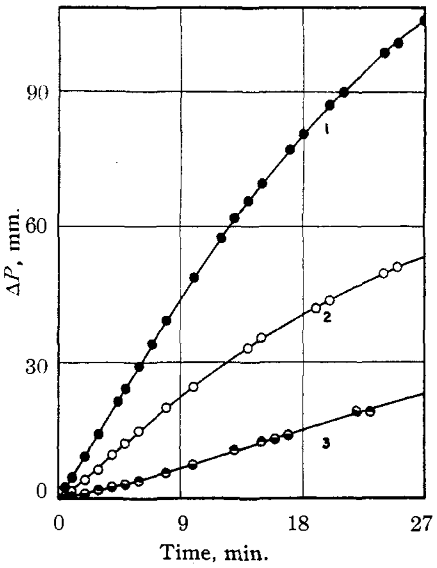


Fig. 4.—Decomposition of dioxolane (curve 1), in the presence of added nitric oxide or propylene (curve 3), or increased surface (curve 2): ●, 104 mm. dioxolane at 475°; ◓, 96 mm. dioxolane and 4 mm. nitric oxide at 477°; ◒, 109 mm. dioxolane and 53 mm. propylene at 476°; ○, 104 mm. dioxolane at 476° in packed bulb, 35-fold increase in *S*/*V* (other runs in unpacked vessel).

With reasonable reactions for the chain-initiating and the chain-breaking steps one can account for an order from 1.5 to 1 for the early portion of the decomposition. However, the experimental evidence available at present concerning this rather complex chain decomposition is not sufficient to establish a complete mechanism.

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[24] L. S. Echols and R. N. Pease, THIS JOURNAL, **58**, 1317 (1936); F. O. Rice and W. D. Walters, *ibid.*, **63**, 1701 (1941).

[25] S. J. Magram and H. A. Taylor, *J. Chem. Phys.*, **9**, 755 (1941).