A value of $\lambda^{\circ}_{UO_2^{++}} = 39$ was obtained from uranyl sulfate data[2] corrected only for the conductance of hydrogen ions.

Values for the dissociation constant, K, given in Table II were calculated from the corrected conductance data using theoretical activity coefficients and assuming that the dissociation reaction was represented by

$$UO_2F_2 \rightleftarrows UO_2F^+ + F^-$$

Although the constancy of the K values at the lower concentrations is believed to be of significance, the dissociation of uranyl fluoride is most probably more complex than was assumed. The agreement may be largely fortuitous.

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The Heterogeneous Carbon Monoxide–Ozone Reaction on Silver[1]

BY DAVID GARVIN

RECEIVED DECEMBER 11, 1953

Both the efficient decomposition of ozone by silver (and silver oxide)[2] and the reduction of silver oxide by carbon monoxide are well known.[3] We have observed that carbon dioxide is produced during the decomposition of ozone in mixtures of CO, O_3, O_2 and N_2 upon passage through beds of ascarite, potassium hydroxide or precipitated silver.[4] Of these, only silver is capable of producing as much as one CO_2 molecule per ozone molecule decomposed.

The figure summarizes some experiments with various CO, O_3, O_2, N_2 mixtures on precipitated silver at 0° and atmospheric pressure. Contact times ranged from 0.03 to 0.1 second, CO mole fractions from 0.036 to 0.5, and ozone mole fractions from 0.002 to 0.02. Carbon monoxide was in excess in all cases, and the ozone was completely decomposed. No carbon dioxide production was observed in the absence of ozone. At room temperature and above the decomposition of ozone was favored over the production of carbon dioxide.

Empirically the experiments are well correlated by the plot shown, but not by plots of CO_2 or CO_2/O_3 *vs.* CO. The fact that the carbon dioxide produced is limited by the ozone decomposed, and that ozone decomposes completely on silver suggests a primary process such as

$$O_3 + Ag \longrightarrow O\text{ (bound)} + O_2 \qquad \text{(I)}$$

where the surface oxygen may be an oxide or be chemisorbed. The amount of carbon dioxide produced relative to ozone decomposed suggests that competitive processes consume the surface oxygen. One set, consistent with catalytic oxidation of CO, and with our scant knowledge of the ozone decomposition on silver, is

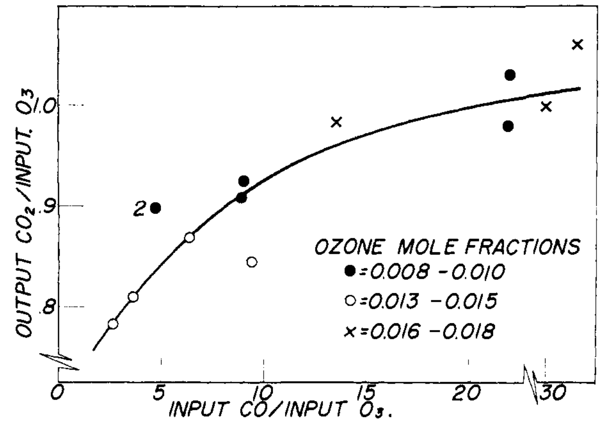

Fig. 1.—Production of carbon dioxide in $CO–O_2–O_3–N_2$ mixtures on precipitated silver.

$$O_3 + O\text{ (bound)} \longrightarrow Ag + 2O_2 \qquad \text{(II)}$$

$$CO + O\text{ (bound)} \longrightarrow Ag + CO_2 \qquad \text{(III)}$$

When the data are analyzed according to this mechanism, they indicate that k_2 and k_3 are of the same magnitude.

These arguments indicate a close relation between this rapid, low temperature oxidation and that of CO on silver at higher temperatures. In the latter, a higher temperature (100° or more) is required for the rate of activated adsorption of O_2 to be appreciable. In the former, ozone serves as an efficient source of oxygen, permitting subsequent reaction at 0°. Thus, this work indicates the correctness of Benton's[5] conclusion that the activated adsorption of oxygen is the slow step in CO oxidation on silver.

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(1) This research was supported by the United States Air Force under Contract No. AF33(038)-23976 monitored by the Office of Scientific Research.

(2) W. Manchot and W. Kampschulte, *Ber.*, **40**, 2891 (1907); J. W. Strutt, *Proc. Roy. Soc.* (*London*), **87**, 302 (1912).

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(4) S. Dondes, A. J. Hogan, P. Harteck and H. M. Clark, Report SO-3251 (Chemistry) Rensselaer Polytechnic Institute, March, 1953, have recently reported carbon dioxide production on silver foil in the presence of ozone.

(5) A. F. Benton and R. T. Bell, THIS JOURNAL, **56**, 501 (1934).

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The Decomposition of Benzoyl Peroxide in Glacial Acetic Acid

BY MATTHEW T. GLADSTONE[1]

RECEIVED OCTOBER 15, 1953

Acetyl peroxide, when decomposed in glacial acetic acid, gives a high yield of succinic acid.[2] Kharasch, Jensen and Urry,[3] however, found that no succinic acid is formed when benzoyl peroxide is slowly added to boiling acetic acid. Gelissen and Hermans[4] used a somewhat different technique. They added benzoyl peroxide to acetic acid and the whole was heated for 5 hours at about 90°. They isolated biphenyl, benzene, phenyl benzoate, benzoic acid and *p*-phenylbenzoic acid, but the main product was a resinous mass soluble in alkali.

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(1) Technical Department, Behr-Manning Corp., Troy, N. Y.

(2) M. S. Kharasch and M. T. Gladstone, THIS JOURNAL, **65**, 15 (1943).

(3) M. S. Kharasch, E. V. Jensen and W. Urry, *J. Org. Chem.*, **10**, 386 (1945).

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The work reported here is a repetition of that of Gelissen and Hermans. However, in addition to the products isolated by these authors, a substantial amount of homophthalic and homoterephthalic acids has been isolated. The products obtained in this study are indicated in Table I.

TABLE I

DECOMPOSITION OF BENZOYL PEROXIDE IN ACETIC ACID AT 75°

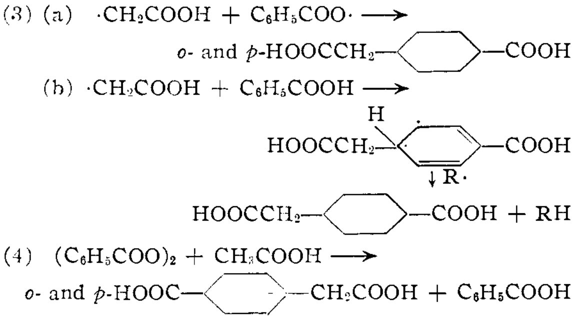
	Grams	Moles	Moles/mole peroxide
Reactants			
Benzoyl peroxide	48.4	0.2	1
Acetic acid	440	7	35
Products			
Homoterephthalic acid	3.3	0.018	0.09
Homophthalic acid	2.5	.014	.07
Benzoic acid	2.9	.024	.12
p-Phenylbenzoic acid	4.2	.021	.11
Carbon dioxide	8.4	.19	.95
Benzene	5.5	.07	.35
Biphenyl	0.34	.002	.01
Resinous residue	6.7	...	...

No succinic acid was found in the reaction mixture. The resinous material had a neutral equivalent of 131 and was alkali soluble. It is possibly a mixture of higher molecular weight acids formed by further reaction of the initial products. A complete radical balance sheet cannot be given since the composition of the residue is unknown and there is a lack of material balance of peroxide fragments.

The formation of the reaction products can be accounted for by the schematic representation

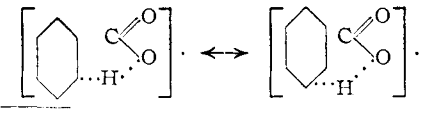
(1) $(C_6H_5COO)_2 \longrightarrow 2C_6H_5COO\cdot$[5]

(2) $C_6H_5COO\cdot$ (or $C_6H_5\cdot$) + $CH_3COOH \longrightarrow$ C_6H_5COOH(or C_6H_5H + CO_2) + $\cdot CH_2COOH$



Reaction 4, the direct bimolecular reaction is a possibility which has not as yet been eliminated. The mechanism for the formation of the other products of the reaction are similar and have been covered in the literature.

The formation of products *via* reaction 3a is quite reasonable if one postulates a transition state for the benzoxy radical



which reacts with the $\cdot CH_2COOH$ or phenyl radical to give the observed products. This is similar to the equilibrium postulated for the naphthoxy radical by Kharasch and Dannley.[6] In the decomposition of α-naphthoyl peroxide in carbon tetrachloride they found α-naphthoic acids substituted in the 4-position by CCl_3 and α-naphthoxy groups. This appears to be a more reasonable hypothesis than the addition as in reaction 3b.

To determine the effect of higher temperatures benzoyl peroxide was decomposed in acetic acid at 90°. Table II gives the pertinent data.

TABLE II

DECOMPOSITION OF BENZOYL PEROXIDE IN ACETIC ACID AT 90°

	Grams	Moles acid	Moles/mole peroxide
Reactants			
Benzoyl peroxide	48.4	0.2	1
Acetic acid	440	7	35
Products			
Homoterephthalic acid	1.3	0.0071	0.036
Carbon dioxide	9.2	.21	1.1
Benzene	6.6	.084	.42
Biphenyl	0.1	.0009	.0045
Benzoic acid	3.4	.028	.14
p-Phenylbenzoic acid	0.63	.0032	.016
Residue	24	....	.....

A comparison of Tables I and II shows that at the higher temperature, the yield of homophthalic acids is somewhat lower, perhaps due to the greater instability of the free radical $(C_6H_5COO)\cdot$ at higher temperatures.

Experimental

Materials.—Commercial benzoyl peroxide was purified as described by Cass[7] and assayed 99.5–99.7% by iodometric titration using the method of Kokatnur and Jelling.[8] The benzoic acid was an analytical grade. The glacial acetic acid was purified as described by Kharasch and Hobbs.[9]

Procedure.—The benzoyl peroxide was placed in a three-neck flask fitted with a thermometer, stirrer and reflux condenser, and suspended in the acetic acid by stirring. An absorption train described previously[2] was attached to the condenser. The mixture was heated at the desired temperature by means of a Glas-Col heating mantle until no more peroxide could be demonstrated in the solution.

The reaction mixture was then distilled through a column, the first fraction containing some benzene which had not been removed during the reaction. The residue remaining after distillation was steam distilled to remove any biphenyl and benzoic acid. From the aqueous layer remaining after the steam distillation, *o*- and *p*-homophthalic acids were obtained by cooling and concentration and separated by fractional crystallization from water. The remaining residue on extraction with acetone–water mixture gave *p*-phenylbenzoic acid. Various organic solvents were tried, but no further crystalline materials could be isolated.

Identification of Products.—Carbon dioxide was determined by the increase in weight of the soda-lime tubes, benzene by odor and boiling point, and benzoic acid and diphenyl by melting point and mixed melting point with authentic samples. The identity of the homophthalic and *p*-phenylbenzoic acids was established by analysis and derivatives.

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		Acid		
		Homoterephthalic	Homophthalic	*p*-Phenylbenzoic
M.p., °C.	Found	234–236	175–177	215–218
	Liter.	237–238	175–177	216–218
Neut. equiv.	Found	97	89	214
	Calcd.	90	90	198
Carbon, %	Found	60.5	60.6	78.7
	Calcd.	60.0	60.0	78.4
Hydrogen, %	Found	4.7	4.5	5.45
	Calcd.	4.5	4.5	5.43
Oxidation		Terephthalic acid[a]	Phthalic acid[b]	Methyl ester[c]

[a] Shown by m.p. of dimethyl ester and mixed m.p.'s with authentic sample. [b] Formed anhydride by heat, m.p. 139–140°. [c] M.p. 110–113°, lit. m.p. 117°.

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The Quantum Yields during Mercury Dimethyl Decomposition

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Received December 5, 1953

The photochemical decomposition of mercury dimethyl has been used as a source of methyl radicals during several recent investigations. Some disagreement exists, however, between various authors as to the steps in the decomposition of this molecule in the absence of foreign gas. This work reports quantum yields of ethane and of methane formation; the data provide evidence concerning certain steps which have been suggested by various authors for the mechanism.

Experimental

The mercury dimethyl was prepared by the method of Gilman and Brown[2] and purified by the method previously described.[3]

Acetone vapor at a temperature of 150° and diethyl ketone vapor at a temperature of 100° were used as actinometers. The quantum yields of carbon monoxide formation from both of these substances are unity under these conditions.[4,5] Radiation from an Hanovia Alpine burner was collimated by a quartz lens and passed through both a chlorine filter and a solution of iodine dissolved in potassium iodide. The effective radiation consisted of wave lengths at 2600 ± 200 Å.

One run was made at 30° by use of two cells in series. By use of the following series of experiments data could be obtained for a quantum yield calculation: (a) cell I empty, cell II filled with acetone; (b) cell I and cell II filled with acetone (this and the previous run give data for window corrections); (c) cell I filled with mercury dimethyl and cell II with acetone. From the three runs one can calculate the fraction of the radiation absorbed by the mercury dimethyl and the amount of radiation entering cell I. With mercury dimethyl at a pressure of 21.6 mm., 2.1×10^{12} quanta absorbed per cc. per second (about 25% of the incident radiation was absorbed, light beam filled the cell), and temperature 30°, $\Phi_{C_2H_6}$ was 1.14 and Φ_{CH_4} was too small to measured with any accuracy.

For most of the runs the percentage of radiation absorbed was determined by the malachite green leucocyanide actinometer.[6] It was not feasible to meet all of the conditions for use of this actinometer and hence corrections were made by use of acetone and of diethyl ketone used as internal actinometers. Results with the two ketones agreed to better than 5%.

Rates (in molecules per cubic centimeter per second) are calculated on the assumption that they are uniform throughout the vessel. This assumption may be approximately valid at 30° where about 25% of the incident radiation was absorbed, but the validity at 175° where the absorption was more than twice as great is doubtful.

The results are given in Table I.

Table I

Quantum Yields during Mercury Dimethyl Decomposition

Concentration, 6.9×10^{17} molecules/cc.; cell length, 200 mm.; cell diameter, 18 mm.; light beam fills vessel, wave length 2600 ± 200 Å.

$T = 30°$

Quanta absorbed/cc./sec. $\times 10^{-10}$	31.7	17.3	16.9	6.7	6.3	3.8	1.6
$\Phi_{C_2H_6}$	0.9	0.9	1.0	1.3	1.2	1.4	1.3
Φ_{CH_4}	(Negligible)						

$T = 175°$

Quanta absorbed/cc./sec. $\times 10^{-10}$	119	66.8	39.8	20.6	10.1
$\Phi_{C_2H_6}$	1.0	1.2	1.1	0.9	1.3
Φ_{CH_4}	0.35	0.47	0.54	0.7	1.0
$R_{CH_4}/(R_{C_2H_6})^{1/2}$ molecules$^{1/2}$/cc.$^{1/2}$/sec.$^{1/2}$ $\times 10^{-5}$	3.8	3.5	3.3	3.3	2.8

The average values of $\Phi_{C_2H_6}$ are 1.14 ± 0.16 at 30° and 1.10 ± 0.12 at 175°. There seems to be, therefore, little or no change with temperature. The trend with intensity at 30° is probably not real but might possibly be due to a small amount of back reaction, such as $CH_3 + HgCH_3 = Hg(CH_3)_2$. The trends of Φ_{CH_4} both with temperature and with intensity are undoubtedly real.

Discussion

It is not necessary at this point to enter upon a detailed discussion of reaction mechanism. Rebbert and Steacie,[7] in a series of articles have shown that to all intents and purposes ethane may be considered to be formed by the reaction

$$CH_3 + CH_3 = C_2H_6 \quad (1)$$

and methane by the reaction

$$CH_3 + Hg(CH_3)_2 = CH_4 + CH_2HgCH_3 \quad (2)$$

We will discuss only two points: (a) the possibility of a second ethane producing reaction; (b) the question of "hot" radicals.

Failure to obtain a linear plot of $R_{C_2H_6}/R_{CH_4}$ *vs.* R_{CH_4} at constant pressure and temperature but variable intensity[3] should lead also to failure to obtain a linear plot for $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ *vs.* (DM) where (DM) is the concentration of mercury dimethyl. Reasons for failure to obtain correct values of $k_2/k_1{}^{1/2}$ have been discussed.[8] Due to the high absorption coefficient of mercury dimethyl and the fact that its vapor pressure at room temperature precludes the use of high enough pressures to ensure the absence of wall effects, it is difficult to be sure that the effective "volume" for the reaction is constant and independent of conditions.

The trend in $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ at 175° in Table I is

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[1] National Science Foundation Predoctoral Fellow, 1953–1954.

[2] H. Gilman and R. E. Brown, This Journal, **52**, 3314 (1930).

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