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

# Photochemical Studies. XLVIII. The Reactions of Methyl Radicals with Oxygen[1]

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Exposure of mixtures of mercury dimethyl and oxygen and of methyl iodide and oxygen to radiation from the Alpine burner leads to different relative amounts of products than exposure of mixtures of acetone and oxygen. Since methyl radicals formed photochemically in these systems start chains of events which lead to secondary production of different radicals, it is difficult to isolate uniquely the reactions of methyl radicals. It is concluded that both carbon monoxide and carbon dioxide result ultimately from reaction of methyl radicals with oxygen. The reaction of methyl radicals with mercury dimethyl to give ethane may not proceed as a simple one-step process. The question of "hot" radicals in these systems is discussed.

## I. Introduction

The photochemical reaction of acetone with oxygen at low oxygen pressures (less than 2 mm.) has already been studied.[2] A mechanism consistent with most of the facts was presented, but proof for the various steps in the mechanism was not conclusive. According to this mechanism the reaction $CH_3 + O_2 = HCO + H_2O$ was followed either by $HCO = H + CO$ or $HCO + O_2 = CO_2 + OH$. The photochemical oxidation of formaldehyde, which presumably proceeds *via* the formyl radical,[3] leads mainly to carbon monoxide. However, formaldehyde seems to act as an inhibitor in the acetone–oxygen system[4] so that formaldehyde oxidation may not afford conclusive proof against the previously presented mechanisms. Other mechanisms will undoubtedly account also for the facts in the acetone–oxygen system.

In any of these oxidation reactions secondary radicals, such as acetonyl, are produced by hydrogen abstraction. The reactions of these radicals with oxygen lead to products which complicate the elucidation of the methyl radical–oxygen reaction. The present studies with mercury dimethyl and with methyl iodide were undertaken to attempt to obtain additional information about the reactions of methyl radicals with oxygen.

## II. Experimental

The preparation of mercury dimethyl has already been described.[5] The methyl iodide was that used in a previous study.[6]

Oxygen was prepared by heating solid potassium permanganate and dried by passage through a trap immersed in liquid nitrogen.

A Hanovia Type SH "Alpine" burner was used as a source of radiation. The radiation was made parallel with a quartz lens and passed through a thickness of 3.0 mm. of Corning No. 9863 Purple Corex glass. The beam was approximately 2.0 cm. in diameter and passed centrally down a quartz reaction cell 5.0 cm. in diameter and 8.5 cm. long with fused quartz windows. The main wave lengths absorbed by both gases are 2537 and 2654 Å. Since absorptions for these wave lengths for both gases are high, wall effects were not completely obviated, especially with mercury dimethyl which could not be used at high pressures because of its low vapor pressure at room temperature.

Since oxygen was not added during the course of the runs, the partial pressure of oxygen did not remain constant. The gases were circulated with a magnetically driven stirrer to avoid depletion of oxygen in the reaction zone.

Gaseous products were separated and determined by methods previously described.[2] A fraction determined to

TABLE I

MERCURY DIMETHYL–OXYGEN

Cell diameter, 5.0 cm.; cell length, 8.5 cm.; Hanovia "Alpine" burner; diameter of light beam, 2 cm.; Corning 9863 filter. Products are given in molecules formed per second. Time of runs, 100 min. unless otherwise stated; pressure of mercury dimethyl, 5.0 mm. unless otherwise stated; volume of reaction cell plus tubing to cut-offs and stirrer, 486 ml.

| Av. $P_{O_2}$, mm. | $-\Delta O_2$, molecules sec.$^{-1}$ $\times 10^{-13}$ | $CO_2$ molecules sec.$^{-1}$ $\times 10^{-13}$ | CO, molecules sec.$^{-1}$ $\times 10^{-13}$ | $CH_4$, molecules sec.$^{-1}$ $\times 10^{-13}$ | $CO_2$/CO |
|---|---|---|---|---|---|
| | | | Temp. = 200° | | |
| 0.22 | 31.8 | 6.07 | 7.15 | 0.57 | 0.85 |
| .27 | 28.5 | .... | 5.67 | .47 | .. |
| .45 | 34.9 | 8.66 | 7.08 | .. | 1.23 |
| .58 | 29.8 | .... | 5.15 | .60 | .. |
| .64 | 33.2 | 5.44 | 4.75 | .60 | 1.14 |
| .76 | 17.9 | 2.89 | 1.43 | .43 | 2.02 |
| .77 | 26.2 | 9.74 | 5.02 | .63 | 1.94 |
| 1.12 | 29.5 | .... | 4.38 | .60 | .. |
| 2.07[a] | 31.8 | 5.71 | 7.01 | .53 | 0.82 |
| 0.55[b] | 79.4 | (7.97) | 11.11 | 1.07 | (0.72) |
| .68[c] | 74.6 | 11.95 | 5.42 | 4.25 | 2.20 |
| .12[d] | 8.7 | .... | 2.93 | 0.52 | .. |
| .14[d] | 8.3 | .... | 3.18 | .58 | .. |
| .59[d] | 3.5 | .... | 1.25 | .27 | .. |
| | | | Temp. = 150° | | |
| 0.19 | 19.9 | 1.96 | 3.56 | 0.28 | 0.55 |
| .28 | 17.6 | 3.15 | 3.15 | .27 | 1.00 |
| .51[e] | 13.3 | 2.24 | 2.52 | .47 | 0.89 |
| .69[e] | 11.9 | 2.02 | 1.74 | .32 | 1.16 |
| .55[f] | 76.0 | 7.11 | 8.04 | .72 | 0.88 |
| | | | Temp. = 100° | | |
| 0.64[g,h] | 38.2 | 3.24 | 3.46 | 0.41 | 0.93 |

[a] A run without oxygen immediately following this run and under otherwise identical conditions gave $N_{C_2H_6} = 5.64$ and $N_{CH_4} = 0.80 \times 10^{13}$ molecules/sec. To a first approximation $CO + CO_2 = 2C_2H_6 + CH_4$. [b] $P(Hg(CH_3)_2) = 20$ mm., $CO_2$ probably low. [c] $P(Hg(CH_3)_2) = 58$ mm.; time = 60 min. [d] Cell, 20.0 cm. long; 1.8 cm. diameter; $P(Hg(CH_3)_2) = 5.3$ cm.; time = 300 min. Light beam filled cell. [e] 120 min. [f] $P(Hg(CH_3)_2) = 55.0$ mm.; time = 120 min. [g] $P(Hg(CH_3)_2) = 51.0$ mm.; time = 120 min. [h] A run without oxygen immediately following this run and under otherwise identical conditions gave $N_{C_2H_6} = 10.2$, $N_{CH_4} = 0.33 \times 10^{13}$ molecules/sec. In this case $CO + CO_2 < 2C_2H_6 + CH_4$.

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[1] This work was supported in part by a contract between the Office of Naval Research, United States Navy, and the Department of Chemistry, University of Rochester.

[2] F. B. Marcotte and W. A. Noyes, Jr., *Discs. Faraday Soc.*, **10**, 236 (1951); THIS JOURNAL, **74**, 783 (1952).

[3] E. C. A. Horner, Ph.D. thesis, King's College, London, 1951. (Work performed under the direction of Dr. D. W. G. Style.)

[4] Results obtained by Dr. D. E. Hoare at the University of Rochester and to be published in the near future.

[5] R. Gomer and W. A. Noyes, Jr., THIS JOURNAL, **71**, 3390 (1949); see H. Gilman and R. E. Brown, *ibid.*, **52**, 3314 (1930).

[6] J. T. Dubois and W. A. Noyes, Jr., *J. Chem. Phys.*, **19**, 1512 (1951).

be formaldehyde by mass spectrographic analysis[4] was separated in some instances by the Ward still at −130°.

Prepurified tank nitrogen was passed through a liquid nitrogen trap and over heated copper turnings. Tank carbon dioxide was degassed at −160°.

The reaction cell was placed in a furnace and the temperature maintained and read by customary procedures.

## III. Results

Table I presents results obtained in mixtures of mercury dimethyl and oxygen. Ethane was not found among the products when oxygen was present. The oxygen was always determined at the end of a run, and in no case was it completely used up.

The amount of methane was too small to permit good accuracy in its determination. It was always found even when oxygen was present.

Table II shows results obtained with methyl iodide. In this case it was found impossible to use temperatures higher than about 120° because of thermal reaction with the oxygen.

TABLE II

METHYL IODIDE–OXYGEN

Conditions as in Table I except $P(CH_3I)$ = 141 mm.

| Time, min. | Av. $P_{O_2}$, mm. | $-\Delta O_2$, molecules sec.$^{-1}$ $\times 10^{-13}$ | $CO_2$, molecules sec.$^{-1}$ $\times 10^{-13}$ | CO, molecules sec.$^{-1}$ $\times 10^{-13}$ | $CH_4$, molecules sec.$^{-1}$ $\times 10^{-13}$ | $CO_2$/CO |
|---|---|---|---|---|---|---|
| | | | Temp. = 35° | | | |
| 120 | 0.0 | 0.0 | ($C_2H_6$ = 19.1) | | 2.82 | |
| 120 | .68 | 18.2 | 2.37 | 0.94 | 2.48 | 2.5 |
| 120 | .99 | 12.4 | 2.75 | 1.42 | 1.72 | 1.9 |
| | | | Temp. = 120° | | | |
| 60 | 0.35 | 64.7 | 5.58 | 7.07 | 1.16 | 0.79 |
| 120[a] | 0.68 | 66.0 | 7.70 | 9.91 | 2.54 | .78 |
| 120 | 1.10 | 72.6 | 6.90 | 10.30 | 1.96 | .67 |
| 120[b] | 1.18 | 68.7 | 6.07 | 9.85 | 1.44 | .63 |
| 90 | 1.86 | 128.2 | 13.78 | 9.70 | 3.39 | 1.42 |

[a] Immediately preceding this run a run was made without oxygen but under otherwise identical conditions. $N_{C_2H_6} = 20.5$; $N_{CH_4} = 2.85 \times 10^{13}$ molecules/sec. Hence $CO + CO_2 << 2C_2H_6 + CH_4$. [b] Immediately following this run a run was made without oxygen but under otherwise identical conditions. $N_{C_2H_6} = 33.1$; $N_{CH_4} = 3.55 \times 10^{13}$ molecules/sec. Hence $CO + CO_2 << 2C_2H_6 + CH_4$.

Certain experiments were performed with addition of inert gases to test wall effects. Unfortunately no good inert gas could be found which would permit simultaneous determination of carbon monoxide and of carbon dioxide. With added nitrogen analyses could be made for carbon dioxide. With added carbon dioxide analyses could be made for carbon monoxide. Table III shows side by side runs made for comparison purposes.

TABLE III

METHYL IODIDE–OXYGEN WITH INERT GAS

Conditions same as for Table II (temp. = 120°) unless otherwise stated.

| Time, min. | Av. $P_{O_2}$, mm. | Foreign gas and pressure, mm. | $-\Delta O_2$, molecules sec.$^{-1}$ $\times 10^{-13}$ | $CO_2$, molecules sec.$^{-1}$ $\times 10^{-13}$ | CO, molecules sec.$^{-1}$ $\times 10^{-13}$ | $CH_4$, molecules sec.$^{-1}$ $\times 10^{-13}$ |
|---|---|---|---|---|---|---|
| 120 | 0.48 | $CO_2$ (126) | 71.9 | .. | 9.70 | 0.35 |
| 120 | .47 | $N_2$ (150) | .. | 5.88 | .. | .. |
| 240 | .61[a] | $N_2$ (134) | .. | 1.32 | .. | .. |
| 240 | .57[b] | $N_2$ (305) | .. | 1.64 | .. | .. |
| 240 | .58[c] | None | 8.6 | 1.00 | 1.23 | 0.12 |
| 240 | .61 | $CO_2$ (135) | 16.3 | .. | 3.74 | 0.28 |

[a] $P(CH_3I)$ = 5.5 mm. [b] $P(CH_3I)$ = 6.0 mm. [c] $P(CH_3I)$ = 5.0 mm.

## IV. Discussion

It is significant that small amounts of methane were produced by irradiation of mercury dimethyl and of methyl iodide under all experimental conditions studied even when oxygen was present. In a previous study and in agreement with earlier work by other authors[7] it was found to be probable that two methods of ethane formation must be considered: (a) $CH_3 + CH_3 = C_2H_6$; (b) $CH_3 + Hg(CH_3)_2 = C_2H_6 + (HgCH_3)$. The second of these reactions could only be treated as written at sufficient intensity and mercury dimethyl pressures. To explain all of the facts it appeared necessary to write this reaction in steps.

$$CH_3 + Hg(CH_3)_2 \rightleftarrows X \qquad (1)$$

$$CH_3 + X = C_2H_6 + (Hg(CH_3)_2) \qquad (2)$$

The second of these reactions may or may not regenerate methyl radicals. There is no real evidence for a chain photochemical decomposition of mercury dimethyl up to 200°.[7] If this method of ethane formation were a simple reaction and methane were produced solely by

$$CH_3 + Hg(CH_3)_2 = CH_4 + CH_2HgCH_3 \qquad (3)$$

it would be possible to calculate from earlier data[5,8] the ratio of ethane produced in this way to methane. This calculation shows that in the present experiments measurable amounts of ethane should always have been found with the methane. This was definitely not the case with added oxygen in the present experiments.

If one assumes a reasonable activation energy and a reasonable steric factor for the reaction[9]

$$CH_3 + CH_3I = CH_4 + CH_2I \qquad (4)$$

one can calculate the amount of ethane which should be formed if the rate of methane formation is known. There is a definite discrepancy between calculation and results. More specifically $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ is too high ($R$ stands for rate).

Thus with both mercury dimethyl and with methyl iodide, oxygen at low pressures suppresses ethane without suppressing methane to the expected extent. Two explanations of these facts seem possible: (a) a wall reaction which favors methane formation; (b) "hot" radicals formed in the primary process.[10] Since the activation energies for (3) and (4) are higher than for

$$CH_3 + CH_3 = C_2H_6 \qquad (5)$$

the effect of wall catalysis would almost certainly be to increase the rate of methane formation relative to ethane formation. The results with added inert gas in the methyl iodide experiment tend to show but do not prove that (a) is not the correct explanation. Explanation (b) may be explored further.

If 2600 Å. is taken as the absorbed wave length, and if it is assumed that all energy in excess of that

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[7] H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, **33**, 874 (1937).

[8] See also R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

[9] *Cf.* A. F. Trotman-Dickenson and E. W. R. Steacie, *ibid.*, **19**, 163 (1951); also F. A. Raal and E. W. R. Steacie, *ibid.*, **20**, 578 (1952).

[10] For an excellent discussion of the "hot" radical problem see W. H. Hamill, R. R. Williams, Jr., H. A. Schwarz and E. E. Voiland, March 1, 1951, Radiation Chemistry Project Report, University of Notre Dame, AECU-1321.

required to dissociate the carbon–iodine bond appears as kinetic energy, one can show that

$$E_1\left(1 + \frac{M_1}{M_2}\right) = 109000 - D_{\text{C-I}} \qquad (6)$$

where $E_1$ is the kinetic energy of the methyl radical, $M_1$ and $M_2$ are the molecular weights of the methyl radical and of the iodine atom, respectively, and $D_{\text{C-I}}$ is the energy required to break the carbon–iodine bond. If the latter is taken as 54000 cal.,[11] $E_1 \sim 47000$ cal. If the iodine atom is formed in a $^2P_{1/2}$ state, the kinetic energy would be 30000 cal. This energy is in excess of the approximate 9000 cal. activation energy of (4), and each "hot" radical may be expected to undergo 10 to 50 collisions before having its kinetic energy reduced to that figure. If the steric factor is $10^{-3}$ for methane formation, the "hot" methyl radicals will have a probability from 0.01 to 0.05 of forming methane before being reduced essentially to thermal radicals. The assumption of $10^{-3}$ for the methane forming reaction[9] may not be justified, but no adequate theory exists for treating the pre-exponential term in a rate equation as a function of kinetic energy. Actually it is assumed that aside from entropy effects this pre-exponential term is constant for a given reaction.

The order of magnitude of formation of methane in the presence of oxygen is, therefore, compatible with simple theory. The chance of forming methane this way will be roughly proportional to the mole fraction of the methyl iodide. The trend with inert gases and with oxygen is approximately correct, but the data are not precise enough to afford a quantitative check. In the absence of oxygen the effect due to "hot" radicals will exceed experimental error only under conditions such that the thermal reaction (4) is unimportant (*i.e.*, high intensities or low temperatures or both).

The application of equation (6) to mercury dimethyl is less easy because of lack of full knowledge about the primary process. Presumably one methyl dissociates off photochemically and the second thermally. Thus only one of the two methyls would be "hot." If $D_{\text{Hg-C}} \sim 51000$ cal.,[12] $E_1 \sim 54000$ cal. at 2537 Å. Thus while the "hot" methyls might be more effective than with methyl iodide in producing methane, only half of those produced will be "hot," and the net effect should be smaller. Comparison of the data in the tables at comparable rates of oxygen consumption shows this to be the case.

"Hot" radical effects have been suggested previously for both of these molecules,[13,14] and these results with oxygen confirm the fact that this possibility must be considered. With acetone at 3130 Å. and $D_{\text{C-C}} \sim 70000$ cal., $E_1 \sim 13000$ cal., any effect due to "hot" radicals will be noticeable only at low temperatures and high light intensities. This does afford an explanation of the discrepancy between low and high temperature apparent activation energies for hydrogen abstraction.[15]

The reactions of methyl radicals with oxygen as proposed in the literature almost all start with

$$CH_3 + O_2 = CH_3O_2 \qquad (7)$$

The radical $CH_3O_2$ may last long enough either to combine with atoms and/or radicals or to abstract hydrogen atoms to give methyl hydroperoxide.[16] Peroxy-alkyl radicals are, however, unstable, and various possibilities for their reactions have been suggested.

$$CH_3O_2 = HCHO + OH^{17} \qquad (8)$$

$$= CHO + H_2O^{2} \qquad (9)$$

$$CH_3O_2 + CH_3O_2 = 2CH_3O + O_2^{18} \qquad (10)$$

Reaction (10) could only occur if radical concentrations were very high.

Inspection of the data in Tables I–III, and comparison with the acetone–oxygen work reveals important differences as follows.

1. The $CO_2$–CO ratio is not very dependent either on oxygen pressure or on temperature in the cases of dimethyl mercury and methyl iodide whereas it increases in general with oxygen pressure and decreases with increase in temperature in the case of acetone.

2. Formaldehyde is found in the acetone case.[4] With methyl iodide–oxygen mixtures at room temperature, formaldehyde seems to be one of the principal products.[19] With mercury dimethyl at temperatures over 100°, it does not seem to be a principal product. For these and other reasons[4] considerable doubt exists as to whether (8) is the principal reaction. On the other hand, it is unsafe to assume that (9) is the principal reaction in the absence of more complete information.

The data on the behaviors of secondary radicals, such as $CH_2COCH_3$, $CH_2I$ and $CH_2HgCH_3$ are at present too incomplete to warrant postulating a complete mechanism for any of these oxygen reactions. Reaction (8) is analogous to one which appears very probable for $C_2H_5$ radicals.[20] On the other hand, the variation of the $CO_2/CO$ ratio in acetone–low oxygen mixtures requires some radical or series of reactions such that this ratio is proportional to oxygen pressure if correction is made for CO formed in the primary process. While the HCO radical might meet these requirements, the data for $CH_3I$ and $(CH_3)_2Hg$ cast some doubt on whether the intermediate, whatever it is, is formed from $CH_3$ radicals. More data are needed on this point.

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[11] C. T. Mortimer, H. O. Pritchard and H. A. Skinner, *Trans. Faraday Soc.*, **48**, 220 (1952).

[12] K. Hartley, H. O. Pritchard and H. A. Skinner, *ibid.*, **46**, 1019 (1950).

[13] M. K. Phibbs and B. de B. Darwent, *ibid.*, **45**, 541 (1949).

[14] R. D. Schultz and H. A. Taylor, *J. Chem. Phys.*, **18**, 194 (1950); see R. R. Williams and R. A. Ogg, Jr., *ibid.*, **15**, 696 (1947), who seem to have mentioned these effects first.

[15] A. J. C. Nicholson, THIS JOURNAL, **73**, 3981 (1951).

[16] *Cf.* J. A. Gray, *J. Chem. Soc.*, 3150 (1952).

[17] A. D. Walsh, *Trans. Faraday Soc.*, **43**, 297 (1947); B. Lewis and G. von Elbe, "Combustions, Flames and Explosions," Academic Press, Inc., New York, N. Y., 1951.

[18] J. H. Raley, L. M. Porter, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **73**, 15 (1951).

[19] J. R. Bates and R. Spence, *ibid.*, **53**, 1689 (1931).

[20] A. Finkelstein and W. A. Noyes, Jr., *Disc. Faraday Soc.*, **49**, 76 (1953).