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# Photochemical Oxidations. II. Methyl Iodide

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The room-temperature photo-oxidation of methyl iodide (0.2 to 3.0 mm.) in oxygen (0.030 to 10 mm.) with continuous ultraviolet radiation above 2200 Å. has been studied by the method outlined in article I of this series: observations were made by leaking the reaction mixture directly into the electron beam of the mass spectrometer during photolysis. The principal products of reaction were $I_2$, $H_2CO$, $CH_3OH$ and under some conditions $CH_3OOH$; minor products were $H_2O$, $CO_2$, HCOOH, $CH_3OOCH_3$ and $CH_3OI$. Because of the cracking pattern of the reactants and major products and the background air peaks, it was impossible to establish the presence or absence of $CH_4$, CO and HI. There are conflicting claims in the literature as to whether methyl radicals react with oxygen according to $CH_3 + O_2 (+ M) \rightarrow CH_3O_2(+ M)$ (followed by the Vaughn mechanism) or $CH_3 + O_2 \rightarrow H_2CO + HO$ (followed by HO attack on loosely bound hydrogen atoms). This study indicates *both* processes do occur, with the first being more important under conditions used here. Furthermore, it seems probable that oxygen molecules abstract hydrogen atoms from $CH_3O$ radicals to produce $H_2CO$ and $HO_2$. A fairly complete and internally consistent mechanism is developed for the initial reaction, typically the reaction of about $10^{-4}$ or $10^{-3}$ of the methyl iodide. As the reaction progresses, inhibition caused by $CH_3 + I_2 \rightarrow CH_3I + I$ becomes very pronounced, radicals abstract from $H_2CO$, a large number of other secondary reactions seem to occur, and the mechanism proposed is regarded as exemplary rather than established. In terms of the relatively simple initial reaction, many ratios of rate constants are evaluated.

## Introduction

For convenience in reference, all mechanistic steps considered in this article are presented here

$$CH_3I + h\nu \longrightarrow CH_3 + I \qquad \text{(a)}$$

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M \qquad \text{(b)}$$

$$I + I + M \longrightarrow I_2 + M \qquad \text{(c)}$$

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad \text{(d)}$$

$$2CH_3O_2 \longrightarrow 2CH_3O + O_2 \qquad \text{(e)}$$

$$2CH_3O \longrightarrow CH_3OH + CH_2O \qquad \text{(f)}$$

$$2CH_3O \longrightarrow CH_3OOCH_3 \qquad \text{(g)}$$

$$CH_3O_2 + CH_3O \longrightarrow CH_3OOH + CH_2O \qquad \text{(h)}$$

$$CH_3O + I + M \longrightarrow CH_3OI + M \qquad \text{(i)}$$

$$CH_3O + I \longrightarrow CH_2O + HI \qquad \text{(j)}$$

$$CH_3OOH \xrightarrow{\text{surface}} CH_2O + H_2O \qquad \text{(l)}$$

$$CH_3OI + H_2O \xrightarrow{\text{surface}} CH_3OH,\ \text{adsorbed oxides of I} \qquad \text{(m)}$$

$$CH_3O + HI \longrightarrow CH_3OH + I \qquad \text{(p)}$$

$$CH_3 + O_2 \longrightarrow CH_2O + HO \qquad \text{(q)}$$

$$HO + CH_3O \longrightarrow CH_2O + H_2O \qquad \text{(r)}$$

$$HO + CH_3OO \longrightarrow H_2O + CH_2OO\ (\rightarrow CO_2,\ CO,\ HCOOH) \qquad \text{(s)}$$

$$HO + CH_2O \longrightarrow H_2O + CHO \qquad \text{(t)}$$

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$$CH_3O + CH_2O \longrightarrow CH_3OH + CHO \qquad \text{(u)}$$

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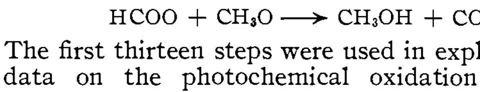
$$CH_3O + O_2 \longrightarrow CH_2O + HO_2 \qquad \text{(v)}$$

$$CH_3O_2 + HO_2 \longrightarrow CH_3O_2H + O_2 \qquad \text{(w)}$$

$$CHO + O_2 \longrightarrow OH + CO_2 \qquad \text{(x)}$$

$$CHO + O_2 \longrightarrow HO_2 + CO \qquad \text{(y)}$$



$$CHO + O_2 + M \longrightarrow M + H{-}C\begin{smallmatrix} O \\ OO \end{smallmatrix} \longrightarrow HCOO\ldots \longrightarrow HCOOH \qquad \text{(z)}$$

$$HCOO + CH_3O \longrightarrow CH_3OH + CO_2 \qquad \text{(f')}$$

The first thirteen steps were used in explaining the data on the photochemical oxidation of ethyl iodide in article I of this series,[1] and these steps will be re-examined in the present case. Also in ref. 1 there were given key references to the literature of methyl radical oxidation. This mechanism represents addition of molecular oxygen to the free radical to form peroxy radicals and the subsequent products of these radicals. The direct bimolecular reaction of oxygen with methyl radicals to produce hydroxyl radicals, step q, was proposed long ago by Bates and Spence[2] and directly demonstrated by McKellar and Norrish[3] at 140°. Steps r to t and in part x to z indicate the products expected to follow from step q. The other steps are proposed on a more or less *ad hoc* basis to discuss various minor products or secondary effects in the data, and these steps will be discussed later.

## Experimental

The apparatus and experimental procedures have been described in article I of this series.[1]

Eight series of runs were made with variation of the oxygen pressure and methyl iodide pressure (and thus the absorbed intensity). The incident intensity and spectral distribution of the radiation were the same for all runs. The incident radiation passed through a Corning 9-54 glass before entering the reaction cell to remove all radiation below 2200 Å. The various products were analyzed in series, with some drift in the instrument and some variation in reproducing the initial chemical composition. Duplicate series were run in some cases. The final values of initial rates, half-lives and steady-state pressures of products (relative to diffusion through the pinhole) are estimated to have a standard deviation of about 10 to 15% except for the unfavorable cases (*e.g.*, water). Though this error is large, it must be remembered that the steady-state pressure of products was between 0.01 and 20$\mu$, or the order of magnitude of 0.01 to 30 millionths of an atmosphere.

Matheson tank oxygen was used, and impurities were 0.3 % argon and 0.7 % nitrogen. Eastman Kodak Co. white-label methyl iodide was used. The cracking pattern of a methyl iodide–oxygen mixtures is given in Table I. Impurity peaks occur at *m/e* 41, 43 and 254 in amounts of less than one part in 1000 compared to the 142 peak. The 254 peak belongs to molecular iodine which is present in one part of $I_2$ to 4000 ± 700 parts of methyl iodide. The peaks at *m/e* 121 and 135 have not been identified, but they are probably unstable ion peaks rather than impurities.

As the runs progressed, products appeared at a large number of mass numbers. The mass spectra and sensitivity relative to oxygen were determined from the literature, from calibrations performed in this Laboratory, and estimated by analogy for the unstable products. Only in the case of $CH_3OOH$ did the cracking pattern have to be estimated. Only two cracking peaks of this compound were of

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[1] J. Heicklen and H. S. Johnston, *J. Am. Chem. Soc.*, **84**, Nov. 20 (1962).

[2] J. R. Bates and R. Spence, *ibid.*, **53**, 1689 (1931); *Trans. Faraday Soc.*, **27**, 468 (1931).

[3] J. F. McKellar and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A263**, 51 (1961).

TABLE I

MASS SPECTRUM OF $CH_3I$–$O_2$; $CH_3I$ = 3.0 MM.; $O_2$ = 10.0 MM.

| *m/e* | Rel. height | Identification | Remarks | *m/e* | Rel. height | Identification | Remarks |
|---|---|---|---|---|---|---|---|
| 12 | 1.19 | $C^+$ | | $63^1/_2$ | 0.04 | $I^{++}$ | |
| 13 | 2.82 | $CH^+$ | | 70 | .14 | ... | In $CH_3I$ |
| 14 | 7.2 | $CH_2{}^+$ | | 71 | .36 | $CH_3{}^{++}$ | |
| 15 | 81 | $CH_3{}^+$ | | 96 | .02 | ... | Background in mass spec. |
| 16 | ... | $O^+$ | | 97 | .01 | ... | Background in mass spec. |
| 17 | ... | $OH^+$ | $H_2O$ in mass spec. | 121 | .32 | ... | Unstable ion in $CH_3I$ |
| 18 | 0.07 | $H_2O^+$ | $H_2O$ in mass spec. | 127 | 40.5 | $I^+$ | |
| 28 | 3.3 | $N_2{}^+$ | Air in mass spec. | 135 | 0.80 | ... | Unstable ion in $CH_3I$ |
| $30^1/_3$ | 1.81[a] | .. | Unstable ion in $O_2$ | 139 | 5.21 | $CI^+$ | |
| 32 | 170 | $O_2{}^+$ | | 140 | Shoulder | $CHI^+$ | |
| 34 | 1.09 | .. | | 141 | Shoulder | $CH_2I^+$ | |
| 40 | 0.68 | $Ar^+$ | In $O_2$ | 142 | 100.0 | $CH_3I^+$ | |
| 41 | .03 | .. | In $CH_3I$ | 254 | 0.03[b] | $I_2{}^+$ | $I_2$ in $CH_3I$ |
| 43 | .06 | .. | In $CH_3I$ | | | | |
| 44 | .04 | $CO_2{}^+$ | In $O_2$ | | | | |
| 45 | 0–0.05 | .. | | | | | |

[a] The ratio of *m/e* $30^1/_3$:32 diminishes rapidly with $O_2$ pressure and is essentially unobservable below $O_2$ pressures of 1 mm.; [b] The ratio of $CH_3I$ and $I_2$ pressures is 4000 ± 700.

TABLE II

INITIAL RATES OF FORMATION OF PRODUCTS

| Series | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8[b] |
|---|---|---|---|---|---|---|---|---|
| $[O_2]$, mm. | 9.4 | 2.0 | 9.5 | 9.4 | 2.9 | 0.90 | 0.27 | 0.030 |
| $[CH_3I]$, mm. | 0.19 | 0.19 | 0.75 | 2.8 | 2.9 | 2.8 | 2.9 | 3.0 |
| $R_i \times 10^6/[CH_3I]$, sec.$^{-1}$ | | | | | | | | |
| $H_2O$ | .. | .. | 21 | 8 | 9 | 4.0 | .. | .. |
| $CH_2O$ | .. | 70 | 78 | 61 | 66 | 29.3 | 24.1 | 10.8 |
| $CH_3OH$ | 73 | 48 | 47 | 45 | 40 | 19.0 | 18 | 5.5 |
| $CO_2$ | $\sim$7 | .. | <1.6 | 1.0 | <1.0 | 0.61 | 0.54 | 0.58 |
| HCOOH | .. | .. | .. | 0.45 | 0.07 | .. | .. | .. |
| $CH_3OOH$ | 31.5 | 10 | 18.6 | 15.7 | 10.8 | 3.2 | 3 | 0.7 |
| $CH_3OOCH_3$ | 8.6 | 4.5 | 5.4 | 4.6 | 4.5 | 2.05 | $\gtrsim$0.8 | .. |
| $CH_3OI$ | 6.3 | .. | 6.3 | 7.5 | 5.5 | .. | .. | .. |
| $I_2$ | 75 | 68 | 67 | 55 | 70 | 29.7 | 21 | 11.9 |
| *m/e* 43 | .. | .. | 0.0 | 0.0 | 0.0 | .. | .. | .. |
| *m/e* 240[a] | .. | .. | .. | 0.46 | .. | .. | .. | .. |

[a] Unidentified product due to impurity in vacuum line. If mixture 4 is allowed to stand overnight in vacuum line, 240 peak is much larger. [b] Did not find $C_2H_6$ or $CH_3OCH_3$ in this run.

interest, those at *m/e* 30 and 31. By combining the information obtained from the photolysis of $CH_3I$, $CH_3COCH_3$ and $CH_3CHO$, accurate cracking patterns could be obtained. At the steady-state, relatively small amounts of $CH_3OOH$ were present, so that its cracking pattern would have little effect on the values of $CH_2O$ and $CH_3OH$. Thus, $P_{ss}(CH_2O)$ and $P_{ss}(CH_3OH)$ were known quite accurately, and in the $CH_3CHO$ and $CH_3COCH_3$ systems $R_i(CH_2O)$ and $R_i(CH_3OH)$ could then be accurately computed from eq. 34 of article I. The results indicated that for $CH_3OOH$ the ratios of *m/e* 30/48 and 31/48 were 0.0 ± 0.1 and 0.50 ± 0.1, respectively.

Because of the background cracking peaks, analyses could not be made for HI(128), CO(28) and $CH_4$(16).

## Results

During irradiation product peaks were observed at *m/e* 17, 18, 28–31, 43–48, 62, 63-1/2, 158, 240 and 254. All of the peaks, except those at *m/e* 43 and 240, could be assigned to $H_2O$, $CH_2O$, $CH_3OH$, $CO_2$, HCOOH, $CH_3OOH$, $CH_3OOCH_3$, $CH_3OI$ and $I_2$. The 240 peak was extremely small and found in only one run. It was due to the reaction of I atoms with some impurity which degases from the storage bulb. The 43 peak was never identified but apparently was a true product peak. However, it appeared only after a long induction period and never became large. The absolute pressures of the products were estimated from the calibrations values. However, it is reemphasized that calibrations for some of the products were not made on our mass spectrometer, and thus some of the calibration values may be in error by as much as 30 or 40%.

The following compounds were not found as products: $CH_2I_2$, $CH_3OOI$, HCOI, $O_3$ and $H_2O_2$. The first three compounds would have been easily detected if they were present in amounts exceeding 0.01% of methyl iodide; IO and $IO_2$ may be present in free radical concentrations. The analysis for $H_2O_2$ is considerably less sensitive because its mass is identical with $O^{16}O^{18}$. The mass peak at 48 was present as a product peak. At first thought this might be $O_3$. However, $CH_3OOH$ has the same mass as $O_3$. Furthermore it is the only product which has a cracking peak at *m/e* 47. In the studies reported here, the ratio of the 47 and 48 mass peaks was invariant at 0.90 ± 0.1 to all changes in conditions and time of irradiation. Furthermore, this ratio is identical with that found for $CH_3OOH$ at the National Research Council of Canada. Conse-

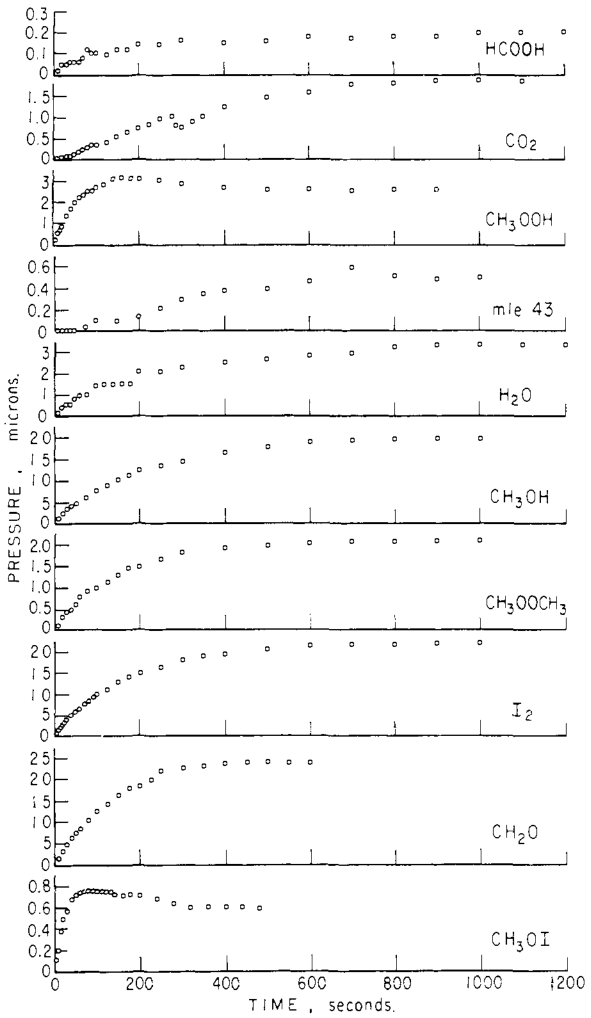

Fig. 1.—Formation of the various products as a function of time for series 4.

quently, it was concluded that ozone was not present to any measurable extent in this system.

The experimental results are listed in Tables II-IV. For all of the products there are listed the initial rates, $R_i$; the steady-state partial pressure, $P_{ss}$; the maximum pressure and irradiation time for this maximum if the product passes through a maximum value; the half-time of build-up to the maximum value, $\tau_L$ (or steady-state pressure if there is no maximum); and the half-time of decay from the steady-state value after the light was turned off, $\tau_D$. The steady-state is reached when the rate of formation of the product equals its rate of removal, both by chemical processes and effusion through the pinhole into the mass spectrometer. For the series 4, the detailed growth curves are presented in Fig. 1.

The results can be summarized in phenomenological terms, using the classification of the appendix of article I, with no reference to mechanism: (1) The initial measured products were $H_2O$, $CH_2O$, $CH_3OH$, $CO_2$, $CH_3OOH$, $CH_3OOCH_3$, $CH_3OI$, $I_2$ and possibly HCOOH.

(2) At high oxygen pressures the initial rates of the products, except $CH_3OOH$ and probably $H_2O$, are proportional to the $CH_3I$ pressure (*i.e.*, the absorbed intensity). The $CH_3OOH$ increases significantly with the oxygen pressure. On the basis of one series, the $H_2O$ is relatively larger at lower $CH_3I$ pressures.

(3) As the oxygen pressure diminishes, so does the initial rate of formation of all the products.

(4) The product at *m/e* 43 appears with an induction period and is an example of case 3 of article I.

(5) The curves of growth and steady-state pressures of the products all show marked inhibition, and thus all fall into case 5 of article I.[4] The $CH_3OOH$ and $CH_3OI$ pass through maxima. However, after the inhibition is corrected for (see Table VIII) then the products can be classed as: $H_2O$, case 1, 2 or 4; $CH_2O$ case 1; $CH_3OH$ case 4; $CO_2$, case 4; HCOOH, case 1, 3 or 4; $CH_3OOH$, case 2; $CH_3OOCH_3$, case 1; $CH_3OI$, case 2; $I_2$, case 2; *m/e* 43, case 3. Thus the mechanism of reaction at the steady-state which corresponds to less than 4% decomposition in all cases is considerably different from the initial mechanism.

The carbon-iodine and carbon-hydrogen mass balance data, shown in Table V both for the initial rates and at the steady state, is satisfactory for the initial rates as is the carbon-hydrogen balance at the steady-state. The data are somewhat scattered but the discrepancy is random and never more than 20% (except for series 8). The hydrogen deficiency and iodine excess in series 8 may be due to the formation of $CH_4$, since $C_2H_6$ and $CH_3OCH_3$ were not found. On the other hand, there is a marked deficiency of iodine in all the series at the steady state. This is due to the deposition of some iodine product (probably a polymer of iodine and oxygen) on the gold foil. After the experiments were performed, a purple deposit was observed on the gold foil. Furthermore, the photo-oxidation of acetone or acetaldehyde produced trace amounts of $CH_3I$ as a product if the photolysis was performed after photo-oxidizing $CH_3I$ or $C_2H_5I$ and before cleaning the gold foil.

## Discussion

**Over-all Quantum Yields and Inhibition by Iodine.**—The primary photochemical process is taken to be step a, the production of methyl radicals and iodine atoms. Oxidation of the methyl radicals by step b or step q leads to the products of reaction, but methyl radicals are reconverted to methyl iodide by step d. The total reaction rate may be measured as the sum of all products containing carbon

$$R(\Sigma C) = R(CH_2O) + R(CH_3OH) + R(CH_3OOH) + 2R(CH_3OOCH_3) + R(CH_3OI) + R(CO_2) + R(HCOOH) + R(\text{other C cmpd.}) \quad (1)$$

or the total reaction rate may be measured as the sum of all products containing iodine

$$R(\Sigma I) = 2R(I_2) + R(CH_3OH) + R(\text{other I compd.}) \quad (2)$$

In the present system the mass spectrometer is

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(4) The five cases discussed in article I are: 1, initial product is unaffected as irradiation proceeds; 2, initial product decomposes or is attacked; 3, product forms with an induction period; 4, initial product is also produced from another product; 5, the formation of the initial product is inhibited as the irradiation proceeds.

TABLE III

STEADY STATE PRESSURES OF PRODUCTS

| Series | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| $[O_2]$, mm. | 9.4 | 2.0 | 9.5 | 9.4 | 2.9 | 0.90 | 0.27 | 0.030 |
| $[CH_3I]$, mm. | 0.19 | 0.19 | 0.75 | 2.8 | 2.9 | 2.8 | 2.9 | 3.0 |
| $10^3 P_{ss}/[CH_3I]$ | | | | | | | | |
| $H_2O^a$ | .. | .. | 3.0 | 1.2 | 1.0 | 0.71 | .. | .. |
| $CH_2O$ | 20.2 | 9.6 | 15.2 | 8.6 | 6.4 | 3.3 | 2.2 | 1.22 |
| $CH_3OH$ | 11.8 | 8.2 | 10.3 | 7.1 | 6.5 | 2.30 | 1.71 | 0.96 |
| $CO_2^a$ | 1.8 | .. | 1.1 | 0.66 | 0.42 | 0.28 | 0.28 | 0.21 |
| HCOOH | .. | .. | .. | .07 | .04 | .. | .. | .. |
| $CH_3OOH$ | 1.92 | $0.2^b$ | 1.8 | $.94^c$ | $.16^d$ | $.044^e$ | $.05^f$ | ~ .02 |
| $CH_3OOCH_3$ | 1.51 | 0.63 | 1.1 | .74 | .41 | .22 | (.05) | .. |
| $CH_3OI$ | 0.20 | .. | 0.24 | $.21^g$ | $.056^h$ | .. | .. | .. |
| $I_2^a$ | 16 | 8.5 | 11.8 | 7.8 | 6.3 | 2.79 | 1.65 | .66 |
| $m/e$ $43^{a,i}$ | .. | .. | Present | 0.19 | 0.13 | .. | .. | .. |
| $m/e$ $240^j$ | 0.0 | 0.0 | 0.0 | 0.085 | .. | 0.0 | 0.0 | .. |

[a] Does not include background value. [b] Maximum value of 0.4 at 50–90 sec. [c] Maximum value of 1.10 at 150–190 sec. [d] Maximum value of 0.29 at 70–90 sec. [e] Maximum value of 0.14 at 100–130 sec. [f] Maximum value of 0.08 at 70–130 sec. [g] Maximum value of 0.27 at 60–130 sec. [h] Maximum value of 0.074 at 10–30 sec. [i] Unidentified product. [j] Product caused by impurity in vacuum line.

TABLE IV

HALF-LIVES OF PRODUCTS

| Series | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| $[O_2]$, mm. | 9.4 | 2.0 | 9.5 | 9.4 | 2.9 | 0.90 | 0.27 | 0.030 |
| $[CH_3I]$, mm. | 0.19 | 0.19 | 0.75 | 2.8 | 2.9 | 2.8 | 2.9 | 3.0 |
| $\tau_D$, sec. | | | | | | | | |
| $H_2O$ | ... | ... | 390 | 280 ± 50 | 300 ± 40 | 250 ± 50 | ... | ... |
| $CH_2O$ | 175 ± 30 | 200 ± 20 | 260 ± 20 | 215 ± 10 | 215 | 240 ± 20 | 250 ± 30 | 260 ± 20 |
| $CH_3OH$ | 200 ± 20 | 220 ± 20 | 195 ± 15 | 220 ± 20 | 235 ± 20 | 280 ± 15 | 260 ± 20 | 280 ± 20 |
| $CO_2$ | ... | ... | ... | 240 ± 40 | ... | ... | ... | 300 ± 20 |
| HCOOH | ... | ... | ... | 260 ± 50 | ... | ... | ... | ... |
| $CH_3OOH$ | 80 ± 20 | 90 ± 30 | 82 ± 10 | 130 ± 10 | 70 ± 20 | 100 ± 50 | ... | ... |
| $CH_3OOCH_3$ | 170 ± 20 | 200 ± 40 | 195 ± 15 | 190 ± 10 | 240 | 285 ± 20 | 230 ± 60 | ... |
| $CH_3OI$ | 30 ± 5 | ... | 29 ± 3 | 34 ± 3 | 25 ± 5 | ... | ... | ... |
| $I_2$ | 220 ± 20 | 370 ± 20 | 210 ± 10 | 220 ± 10 | 305 ± 10 | 350 ± 20 | 350 ± 30 | 330 ± 20 |
| $m/e$ 43 | ... | ... | ... | ... | ... | ... | ... | ... |
| $m/e$ 240 | ... | ... | ... | 240 ± 20 | ... | ... | ... | ... |
| $\tau_E$, sec. (to max. value) | | | | | | | | |
| $H_2O$ | ... | ... | 200 ± 50 | 190 ± 20 | 230 ± 30 | 200 ± 10 | ... | ... |
| $CH_2O$ | 145 ± 15 | 90 ± 10 | 125 ± 10 | 100 ± 10 | 80 | 85 ± 5 | 68 ± 5 | 60 ± 20 |
| $CH_3OH$ | 130 ± 10 | 125 ± 10 | 155 ± 20 | 140 ± 20 | 115 | 85 ± 5 | 80 ± 10 | 75 ± 10 |
| $CO_2$ | 225 ± 25 | ... | 350 ± 50 | 260 ± 40 | 250 ± 30 | 320 ± 40 | 320 ± 30 | 310 ± 30 |
| HCOOH | ... | ... | ... | 250 ± 50 | 250 | ... | ... | ... |
| $CH_3OOH$ | 45 ± 15 | 18 ± 5 | 46 ± 4 | 38 ± 4 | 15 ± 3 | 22 ± 3 | 25 ± 5 | ... |
| $CH_3OI$ | 20 ± 10 | ... | 22 ± 3 | 15 ± 2 | 7 | ... | ... | ... |
| $I_2$ | 168 ± 5 | 145 ± 10 | 132 ± 5 | 117 ± 10 | 100 ± 10 | 110 ± 5 | 110 ± 5 | 75 ± 15 |
| $m/e$ 43 | ... | ... | ... | 305 ± 30 | 300 | ... | ... | ... |
| $m/e$ 240 | ... | ... | ... | 100 ± 20 | ... | ... | ... | ... |

unable to measure CO, $CH_4$ and HI. These are the non-observable $R$(other compounds) in eq. 1 and 2. The discussion will proceed on the assumption that these products are negligible, and the assumption will be evaluated later.

Whereas a steady-state treatment of the entire mechanism is overwhelmingly complicated, one can readily carry out a steady-state analysis for methyl radicals and the over-all rate, eq. 1 or 2. The total rate of product formation is

$$R(\Sigma C) = k_a(h\nu)[CH_3I] - k_d[CH_3][I_2] \qquad (3)$$

The steady-state relation for methyl radicals is

$$d[CH_3]/dt = 0 = k_a(h\nu)[CH_3I] - [CH_3]\{k_b[M][O_2] + k_q[O_2] + k[I_2]\} \qquad (4)$$

Solving eq. 4 for $[CH_3]$ and substituting in eq. 3, one finds

$$\frac{k_a(h\nu)[CH_3I]}{R(\Sigma C)} = 1 + \frac{k_d[I_2]}{\{k_b[M] + k_q\}[O_2]} \qquad (5)$$

The ratio of total reaction rate to rate of light adsorption is a quantum yield (not measured absolutely against an actinometer but rather in relative terms in this system), and one defines

$$\Phi(C) = R(\Sigma C)/k_a(h\nu)[CH_3I] \qquad (6)$$

$$\Phi(I) = R(\Sigma I)/k_a(h\nu)[CH_3I] \qquad (7)$$

The value of $k_a(h\nu)$ in this system is found by extrapolating $\Phi^{-1}$ against $1/[O_2]$ to zero. Values of total initial rates, total steady-state rates, initial quantum yield and steady-state quantum yields are given in Table V.

TABLE V

MASS BALANCE DATA

| Series | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| $[O_2]$, mm. | 9.4 | 2.0 | 9.5 | 9.4 | 2.9 | 0.90 | 0.27 | 0.030 |
| $[CH_3I]$, mm. | 0.19 | 0.19 | 0.75 | 2.8 | 2.9 | 2.8 | 2.9 | 3.0 |
| $R_i\ (\Sigma I) \times 10^6/[CH_3I]$, sec.$^{-1}$ | 156 | ~142 | 139 | 118 | 145 | ~62 | ~44 | 24 |
| $R_i\ (\Sigma C) \times 10^6/[CH_3I]$, sec.$^{-1}$ | . . . | 145 | 162 | 140 | 133 | 65 | 48 | 19 |
| [a] | >105 | >58 | 107 | 77 | 69 | 31 | ~24 | ~7 |
| [b] | . . . | ~80 | 83 | 64 | 69 | 31 | 26 | 12.6 |
| $10^3P_{ss}(\Sigma I)/[CH_3I]$ | 32 | 17 | 24 | 15.8 | 12.7 | 5.6 | 3.3 | 1.32 |
| $10^3P_{ss}(\Sigma C)/[CH_3I]$ | 39 | 20 | 31 | 18.8 | 14.4 | 6.4 | 4.4 | 2.4 |
| $10^6R_{ss}(\Sigma I)/[CH_3I]$, sec.$^{-1}$ | 99 | 32 | 79 | 50 | 15 | 11.1 | 6.5 | 2.8 |
| $10^6R_{ss}(\Sigma C)/[CH_3I]$, sec.$^{-1}$ | 140 | 66 | 97 | 59 | 45 | 17 | 12.0 | 6.1 |
| [c] | >13.7 | >8.4 | 18.1 | 10.4 | 8.8 | 3.8 | >1.8 | $\gtrsim$1.0 |
| [d] | 25.6 | >9.6 | 18.5 | 10.4 | 7.6 | 4.1 | 3.0 | 1.85 |
| $\Phi_i(C)$, eq. 6 | . . . | ~0.94 | 1.05 | 0.91 | 0.86 | ~0.42 | ~0.31 | 0.123 |
| $\Phi_i(I)$, eq. 7 | 1.01 | .92 | 0.90 | .77 | .94 | .40 | .29 | .156 |
| $\Phi_{ss}(C)$, eq. 6 | 0.91 | .44 | .63 | .38 | .29 | .11 | .078 | .040 |
| $\Phi_{ss}(I)$, eq. 7 | 0.64 | .21 | .51 | .32 | .10 | .072 | .042 | .018 |

[a] $10^6[2R_i(H_2O) + R_i(CH_3OH) + R_i(CH_3OOH)]/[CH_3]$, sec.$^{-1}$. [b] $10^6[R_i(CH_2O) + 3R_i(CO_2) + R_i(HCOOH)][CH_3I]$, sec.$^{-1}$. [c] $10^3[2P_{ss}(H_2O) + P_{ss}\ (CH_3OH) + P_{ss}(CH_3COOH)]/[CH_3I]$. [d] $10^3[P_{ss}(CH_2O) + 3P_{ss}(CO_2) + P_{ss}(HCOOH)/[CH_3I]$. [a] *vs.* [b] gives hydrogen carbon balance for initial rates; [c] *vs.* [d] gives same information under steady-state conditions.

The quantum yields are plotted in Fig. 2 against the ratio $[CH_3I]/[O_2]$ for all series for both initial rates and steady-state (with respect to leak through pin-hole) rates. The initial quantum yields based on carbon are in excellent agreement with those based on iodine, and this result indicates that non-observed products ($CH_4$, CO, HI) are negligible (perhaps excepting series 8) or that CO and HI, for example, are produced at equal rates. The initial-rate quantum yield decreases with decreasing oxygen and is far below unity for the last three series. The steady-state quantum yields are far below those for the initial rate, as one expects from the competition of step d with steps b and q. The quantum yield at steady state based on all carbon compounds is substantially greater than that based on all iodine compounds. Thus at the steady state a significant amount of iodine is not observed; either HI or (more probably) the purple deposit is noted on the gold foil. Thus the analysis of steady-state data is based on the yield of carbon, not iodine.

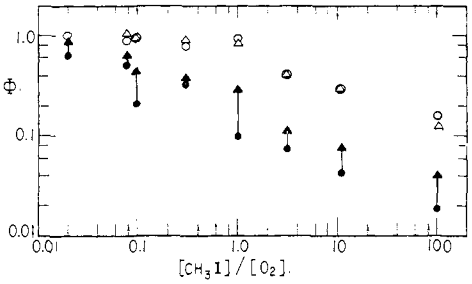

Fig. 2.—Relative quantum yield as a function of ratio of reactant pressures: ○, based on initial rate of formation of all products containing iodine; ●, based on steady-state rate of all products containing iodine; △, initial rates of carbon-containing compounds; ▲, steady-state rates of carbon-containing compounds.

Equation 5 can be re-written as

$$\frac{1}{\Phi_{ss}(C)} = 1 + \left\{\frac{k_b[M]}{k_d} + \frac{k_q}{k_d}\right\}^{-1} \frac{[I_2]_{ss}}{[O_2]} \qquad (8)$$

Christie[5] evaluated the ratio of rate constants, $k_b/k_d$, 0.55 × $10^4$ cc./mole at room temperature. The relative efficiency of $CH_3I$ and $O_2$ as foreign gases can be estimated from the boiling point correlation found for reaction *c* by Russell and Simons,[6] and the equivalent pressure of methyl iodide is given in Table VI by

$$[M]_e = [CH_3I] + 0.037[O_2] \qquad (9)$$

In these experiments the pressures of oxygen and methyl iodide were known by synthesis, and steady-state pressure of iodine was measured in the mass spectrometer. Thus every term in eq. 8 is known except the ratio of rate constants, $k_q/k_d$. This ratio was assumed to be zero, and curve A in Fig. 3 was prepared. It is seen that the calculated curve is in serious disagreement with experiment. Next it was assumed that $k_q/k_d$ is: 0.5 × $10^{-3}$, curve B; 1.0 × $10^{-3}$, curve C; 2.0 × $10^{-3}$, curve D.

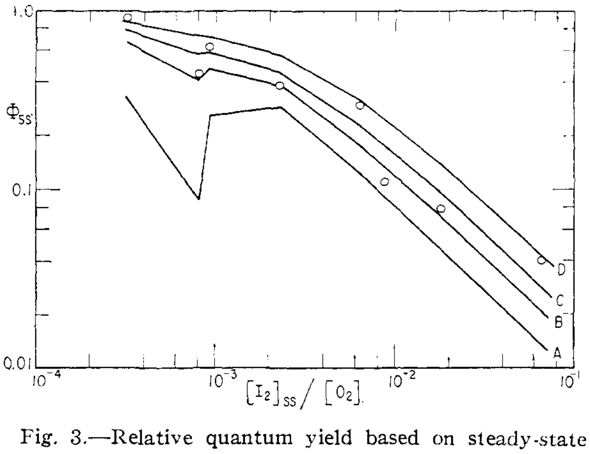

Fig. 3.—Relative quantum yield based on steady-state rate of formation of all products containing carbon, eq. 8, for various assumed values of $k_q/k_d$: A, 0; B, 0.5 × $10^{-3}$; C, 1 × $10^{-3}$; D, 2 × $10^{-3}$. The irregularity in the curves arises from the effect of the independently varied total effective pressure, *M*.

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(5) M. I. Christie, *Proc. Roy. Soc.* (*London*), **244A**, 411 (1958).

(6) K. E. Russell and J. Simons, *ibid.*, **217A**, 271 (1953).

TABLE VI

INTERPRETATION OF INITIAL RATE DATA

| | Series | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $[O_2]$, mm. | 9.4 | 2.0 | 9.5 | 9.4 | 2.9 | 0.90 | 0.27 | 0.030 |
| 2 | $[CH_3I]$, mm. | 0.19 | 0.19 | 0.75 | 2.8 | 2.9 | 2.8 | 2.9 | 3.0 |
| 3 | $R_i(CH_3OH)/R_i(CH_3OOCH_3)$ | 8.5 | 10.7 | 8.7 | 9.8 | 8.9 | 9.3 | $\lesssim 22$ | .. |
| 4 | of $\times 10^6/[CH_3I]$, sec.$^{-1}$ | 110 | 65 | 74 | 64 | 57 | 26 | 23 | 6.5 |
| 5 | l.h.s.,[a] eq. 16 | 0.43 | 0.18 | 0.32 | 0.29 | 0.23 | 0.147 | 0.147 | 0.12 |
| 6 | $[O_2]^{1/2}$ of (mm.-sec.)$^{1/2}$ | 2000 | 570 | 1280 | 710 | 230 | 108 | 33 | 6.8 |
| 7 | l.h.s., eq. 18, mm.$^{-1}$ | .. | .. | 9 | 6 | 5 | 5.5 | .. | .. |
| 8 | $[O_2]/[CH_3I]$ | 50 | 10.5 | 12.7 | 3.4 | 1.0 | 0.32 | 0.093 | 0.010 |
| 9 | $[M]_c$. mm., eq. 9 | 0.54 | 0.26 | 1.10 | 3.15 | 3.01 | 2.84 | 2.91 | 3.00 |
| 10 | l.h.s., eq. 19, mm.$^{-1/2}$ | 0.33 | .. | 0.158 | 0.092 | 0.061 | | | |

[a] l.h.s. means left-hand side.

Curve A predicts quantum yields too low everywhere, and curve D gives quantum yields too high in all cases. The scatter of data is such that it is difficult to choose between curve B and C. Each gives a fairly good representation of the data. Thus one concludes that reaction q certainly occurs in this system and that the value of $k_q/k_d$ is between $0.5 \times 10^{-3}$ and $1.0 \times 10^{-3}$. From the distribution of products (see below) the lower figure is to be preferred.

The quantum yield based on initial rates falls off at low oxygen, Fig. 2, for series 6, 7 and 8. For these runs, the yield of products is small, the background noise in the instrument is as great as ever, and a re-examination of the data shows the "initial rates" not to be truly initial, after all. The true initial rate is

$$R_i = \lim dx/dt \text{ as } t \rightarrow 0 \qquad (10)$$

where $x$ is the pressure of a product. The small yields of products and the noise level are such as not to support the detailed analysis of eq. 10. The observed "initial rates" are

$$\text{"}R_i\text{"} = (x - x_0)/(t - t_0) \qquad (11)$$

In the last three series, significant amounts of iodine had built up during the time over which eq. 11 was applied. The data in series 6, 7 and 8 are average rates over an early portion of the reaction; the distribution of products inside each series is a valid datum, but no comparisons of initial rates between series 6–8 and series 1–5 may be made. The constancy of quantum yield over the wide variation of conditions in series 1–5 indicates that trends from one series to another may be considered here.

**Initial Reaction.**—The mechanism proposed for the initial reaction in the photo-oxidation of ethyl iodide does not account for all the products. It predicts that $CH_2O$ equals the sum of $CH_3OH$ and $CH_3OOH$ with no initial $H_2O$ or $CO_2$. In fact the following important differences are observed in the $CH_3I$–$O_2$ system: (1) $H_2O$ and $CO_2$ are definitely initial products; (2) $R_i(CH_3OH) + R_i(CH_3OOH) < R_i(CH_2O) < R_i(CH_3OH) + R_i(CH_3OOH) + 2R_i(H_2O)$ in all cases: (3) the relative amount of $CH_3OOH$ increases markedly with the oxygen pressure.

Water is formed from HO radicals produced by reaction q, and thus the initial products are in agreement (at least qualitatively) with the conclusion reached above that reaction q is important in this system. Hydroxyl radical is particularly reactive, and step t, abstraction of hydrogen from formaldehyde, may be important as well as disproportionation reactions such as r. On the other hand, methanol is a very important product in this system, reaction q does not lead to methanol, and reaction b and its sequels also occur. The simultaneous occurrence of reaction b and reaction q, with the sequence of products formed in each case, is consistent with fact 2 above.

The third fact is most easily explained by adding steps v and w. The $HO_2$ radical might also donate its hydrogen to $CH_2O$, I, OH or another $HO_2$. However, an *easily* abstracted hydrogen will go to the most abundant, not the most active radical; thus it seems reasonable that w is the most important reaction of $HO_2$. At first thought it might appear that the $HO_2$ radical might also produce $H_2O$. However, this possibility must be ruled out for the following reasons: (1) the relative rate of water formation does not increase with the oxygen pressure; (2) to form water the $HO_2$ radical would have to produce $H_2O_2$ as an intermediate. No $H_2O_2$ was found. Even if $H_2O_2$ were present, water could not be an initial product from this source unless the heterogeneous decay rate of $H_2O_2$ was so fast that it reached its steady state value within about 10 or 20 seconds.

Because of the good mass balances found for the initial rates, reactions j and thus p, are regarded as unimportant in this system, unlike the case for ethyl iodide.

The free radicals reach their steady state very fast (estimated half-lives of $10^{-4}$ to $10^{-2}$ second) compared to the steady state of products relative to diffusion through the pinhole (200–3000 seconds). Thus the steady-state analysis with respect to radicals can be applied to the initial-rate data of the products. As in article I, the rate constant for reaction **b**, for example, will be written as $k_b$; but the rate of the reaction will be abbreviated by use of the symbol **b**, that is:

$$\mathbf{b} = k_b[CH_3][O_2][M] \qquad (12)$$

In these terms the initial rates of formation of products are

$$R_i(CH_2O) = \mathbf{f} + \mathbf{h} + \mathbf{q} + \mathbf{r} + \mathbf{v}$$

$$R_i(CH_3OH) = \mathbf{f}$$

$$R_i(CH_3OOH) = \mathbf{h} + \mathbf{w}$$

$$R_i(H_2O) = \mathbf{q}$$

$R_i(CH_3OOCH_3) = g$

$R_i(CH_3OI) = i$

$R_i(I_2) = c$

$R_i(CO_2) \leq s$

Other minor initial products, such as HCOOH, are omitted, since these may be rapidly-appearing secondary products (when present in very small amounts it is extremely difficult to establish whether a product is truly "initial"). Making the steady-state assumption of zero net rate for formation of each radical, one finds

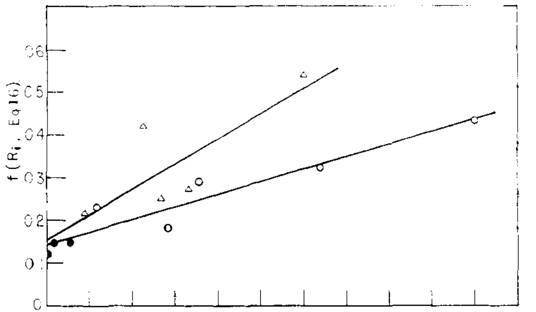

Fig. 4.—Test of eq. 16 and the evaluation of the ratios of rate constants; slope, $k_v/k_f^{1/2}$; intercept, $k_h/(k_f k_0)^{1/2}$: ○, series 1–5; ●, series 6–8; Δ, data of $C_2H_5I–O_2$ system; lower curve, $CH_3I–O_2$; upper curve, $C_2H_5I–O_2$.

$$R_i(I) = 0 = a - 2c - i \qquad (13)$$

$$R_i(CH_3) = 0 = a - b - q$$

$$R_i(CH_3OO) = 0 = b - 2e - h - w$$

$$R_i(CH_3O) = 0 = 2e - 2(f + g) - h - i - r - v$$

$$R_i(HO) = 0 = q - r - s$$

$$R_i(HO_2) = 0 = v - w$$

The rates of reaction in terms of products and rate constants are

$$a = R_i(\Sigma C) = R_i(\Sigma I) \qquad (14)$$

$$b = R(\Sigma C) - R_i(H_2O)$$

$$c = R_i(I_2)$$

$$e = R_i(CH_3OH) + R_i(CH_3OOCH_3) + {}^1/_2[R_i(CH_3OOH) + R_i(CH_3OI) + R_i(H_2O) - R_i(CO) - R_i(CO_2)]$$

$$f = R_i(CH_3OH)$$

$$g = R_i(CH_3OOCH_3)$$

$$h = \{k_h/k_e^{1/2}k_f^{1/2}\}e^{1/2}\{R_i(CH_3OH)\}^{1/2}$$

$$i = R_i(CH_3OI)$$

$$q = R_i(H_2O)$$

$$v = w = R_i(CH_3OOH) - h$$

$$s = R_i(CO_2) + R_i(CO)$$

$$r = R_i(H_2O) - R_i(CO_2) - R_i(CO)$$

The mechanism predicts the constancy of several ratios of constants. The division of products between f and g should be constant if g is second order, not dependent on [M]. The ratio

$$R_i(CH_3OH)/R_i(CH_3OOCH_3) = k_f/k_g \qquad (15)$$

is entry 3 of Table VI. Except for the unreliable value for series 7, the ratio varies only from 8.5 to 10.7 indicating that f and g are the only sources of $CH_3OH$ and $CH_3OOCH_3$, respectively. Furthermore, this value is close to the value of 12 ± 1 found for the ethyl system.[1]

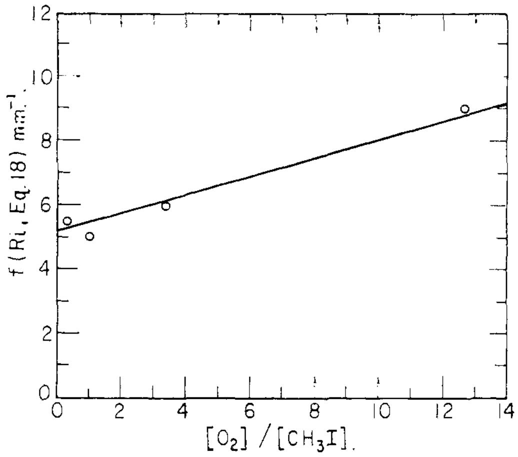

Fig. 5.—Test of eq. 18 and the evaluation of the ratio $K_h/K_q$ from the intercept and the relative efficiency of $O_2$ and $CH_3I$ as catalysts for reaction b.

The competition between reactions f and v gives the relationship

$$\frac{R_i(CH_3OOH)}{\{R_i(CH_3OH)e\}^{1/2}} = \frac{k_y[O_2]}{k_f^{1/2}e^{1/2}} + \frac{k_h}{k_f k_e^{1/2}} \qquad (16)$$

where **e** is given in eq. 14. Ignoring the term in CO which could not be measured, **e** can be computed and is listed as entry 4 of Table VI. The left-hand side of 16 is listed as entry 5 and the ratio $[O_2]/\mathbf{e}^{1/2}$ is listed as entry 6 of Table VI. Equation 16 predicts that a plot of $R_i(CH_3OOH)/\{R_i(CH_3OH)\mathbf{e}\}^{1/2}$ *versus* $[O_2]/\mathbf{e}^{1/2}$ should be linear. Figure 4 is such a plot, and the expectation is verified. The intercept gives $k_h/(k_f k_e)^{1/2} = 0.14$ and the slope gives $k_v/k_f = 1.44 \times 10^{-4}$ (mm.-sec.)$^{-1/2}$ or 0.59 (cc./mole-sec.)$^{1/2}$. (The $C_2H_5I$ data of article I are shown on the same plot; in this case the data are badly scattered owing to the difficulty in analyzing the $C_2H_5OOH$.) The correlation shown in Fig. 4 is the principal evidence in favor of step v, the abstraction of a hydrogen atom from a free radical by molecular oxygen.

In the section above on over-all quantum yield, the relative efficiency of oxygen to methyl iodide as an M gas for reaction b was taken to be 0.037, from the relative efficiencies for reaction c as found by Russell and Simons. The data obtained here give a direct estimate of the relative efficiency of oxygen and methyl iodide for reaction b and also for reaction i. Instead of eq. 9, one can write

$$[M]_b = [CH_3I]\ \{1 + \alpha_b\ [O_2]/[CH_3I]\} \qquad (17)$$

Competition between reactions b and q gives the relation

$$\frac{R_i(\Sigma C) - R_i(H_2O)}{[CH_3I]\ R_i(H_2O)} = \frac{k_b}{k_q}\left\{1 + \alpha_b \frac{[O_2]}{[CH_3I]}\right\} \qquad (18)$$

Entry 7 of Table VI lists for the left-hand side of eq. 18. These values are plotted against $[O_2]/[CH_3I]$ in Fig. 5. The ratio of slope to intercept for step b gives a value of 0.06 for $\alpha_b$, in fair agreement with 0.037 from Russell and Simons. The intercept yields a value of 5.0 mm.$^{-1}$ for $k_b/k_q$ or $1.0 \times 10^8$ cc./mole. By combining this value

TABLE VII

INTERPRETATION OF STEADY-STATE DATA

| Entry no. | Series | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $[O_2]$, mm. | 9.4 | 2.0 | 9.5 | 9.4 | 2.9 | 0.90 | 0.27 | 0.030 |
| 2 | $[CH_3I]$, mm. | 0.19 | 0.19 | 0.75 | 2.8 | 2.9 | 2.8 | 2.9 | 3.0 |
| 3 | $k_l \times 10^3$ sec.$^{-1}$ | 5 | 4.5 | 5 | 2.6 | 7 | 4 | .. | .. |
| 4 | $\frac{10^3(R_i' - R_{ss})}{P_{ss}(CH_3OOH)}$, sec.$^{-1}$ | ~10 | 20 | 2.7 | 4.3 | 20 | 16 | ~13 | ~10 |
| 5 | $k_m \times 10^3$, sec.$^{-1}$ | 19 | .. | 21 | 17 | 24 | .. | .. | .. |
| 6 | $\frac{10^3(R_i' - R_{ss})}{P_{ss}(CH_3OI)}$, sec.$^{-1}$ | 20 | .. | 12 | 12 | 30 | .. | .. | .. |

TABLE VIII

COMPARISON OF STEADY STATE RATES WITH CORRECTED INITIAL RATES

| Series 1 | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| $[O_2]$, mm. | | 9.4 | 2.0 | 9.5 | 9.4 | 2.9 | 0.90 | 0.27 | 0.030 |
| $[CH_3I]$, mm. | | 0.19 | 0.19 | 0.75 | 2.8 | 2.9 | 2.8 | 2.9 | 3.0 |
| $R \times 10^6/[CH_3I]$, sec.$^{-1}$ | | | | | | | | | |
| $H_2O$ | $R_{ss}$ | .. | .. | 5.4 | 3.0 | 2.3 | 2.0 | .. | .. |
| | $R_i'$ | .. | .. | 12.5 | 3.1 | 3.0 | 1.05 | .. | .. |
| $CH_2O$ | $R_{ss}$ | 80 | 33 | 40 | 28 | 21 | 8.2 | 6.1 | 3.2 |
| | $R_i'$ | .. | 32 | 47 | 26 | 22 | 7.7 | 6.0 | 3.4 |
| $CH_3OH$ | $R_{ss}$ | 41 | 26 | 37 | 22 | 19 | 5.7 | 4.6 | 2.4 |
| | $R_i'$ | ~60 | 22 | 28 | 19 | $13^1/_2$ | 5.0 | 4.5 | 1.8 |
| $CO_2$ | $R_{ss}$ | (6.2)[a] | .. | (3.8) | 1.64 | (1.16) | (0.77) | (0.77) | 0.49 |
| | $R_i'$ | ~6 | .. | <1.0 | 0.42 | <0.34 | 0.16 | 0.14 | 0.19 |
| HCOOH | $R_{ss}$ | .. | .. | .. | 0.13 | (0.08) | .. | .. | .. |
| | $R_i'$ | .. | .. | .. | 0.14 | <0.02 | .. | .. | .. |
| $CH_3OOH$ | $R_{ss}$ | (6.6) | (0.7) | (6.2) | (2.6) | (0.44) | (0.122) | (0.14) | (~0.05) |
| | $R_i'$ | ~25 | 4.6 | 11.1 | 6.6 | 3.6 | 0.84 | 0.8 | ~0.2 |
| $CH_3OOCH_3$ | $R_{ss}$ | 6.1 | 2.2 | 3.9 | 2.5 | 1.19 | 0.52 | >0.15 | .. |
| | $R_i'$ | ~6 | 2.1 | 3.2 | 1.95 | 1.5 | 0.54 | >0.2 | .. |
| $CH_3OI$ | $R_{ss}$ | (0.69) | .. | (0.83) | (0.58) | (0.16) | .. | .. | .. |
| | $R_i'$ | ~5 | .. | 3.8 | 3.2 | 1.85 | .. | .. | .. |
| $I_2$ | $R_{ss}$ | 50 | 16 | 39 | 25 | 14.4 | 5.5 | 3.3 | 1.39 |
| | $R_i'$ | ~60 | 31 | 40 | 23 | 24 | 7.8 | 5.0 | 3.8 |

[a] Note: Parentheses indicate that lifetime used for the computation was not measured directly.

with Christie's value $0.55 \times 10^4$ cc./mole for $k_b/k_d$, one finds the ratio $k_q/k_d$ to be $0.55 \times 10^{-4}$, rather much lower than the value estimated from Fig. 3.

The relative efficiency $\alpha_i$ for step i is found from the relation

$$\frac{[M]_c^{1/2} R_i(CH_3OI)}{[CH_3I][R_i(I_2)\, R_i(CH_3OH)]^{1/2}} = \frac{k_i}{(k_f k_c)^{1/2}} \left\{ 1 + \alpha_i \frac{[O_2]}{[CH_3I]} \right\} \quad (19)$$

where $[M]_c$ is given by eq. 9 and entry 9 of Table VI. The left-hand side of eq. 19 is entry 10 of Table VI, and it is plotted against $[O_2]/[CH_3I]$ in Fig. 6. The intercept $k_i/(k_f k_c)^{1/2}$ is 0.09 mm.$^{-1/2}$ and the ratio of slope to intercept gives the relative efficiency $\alpha_i = 0.055$. The term $k_i/(k_f k_c)^{1/2}$ in the ethyl iodide system is about 4 or 5 times as great as the value found here. Thus for all three reactions involving foreign gas effects, the relative efficiency of oxygen to methyl iodide is: $\alpha_b$, 0.06: $\alpha_c$, 0.037; $\alpha_i$, 0.055.

**Other Subsequent Reactions.**—As the other products build up they also enter the reaction. For example, the half-life data clearly show that both $CH_3OOH$ and $CH_3OI$ decay even in the dark. The reactions are regarded as l and m, although these are probably oversimplifications of more complicated decays. Reaction l is known to occur on stainless steel,[7] and both l and m are undoubtedly heterogeneous decays in our system. The decay constants can be computed by the methods outlined in the appendix of article I, and they are listed as entries 3 and 5 in Table VII. The value for $k_l$ is $5 \pm 1 \times 10^{-3}$ sec.$^{-1}$, and for $k_m$ is $18 \pm 6 \times 10^{-3}$ sec.$^{-1}$.

The net steady-state rates of formation of products can be compared to the initial rates corrected for the inhibition to see what additional processes occur. The observed net steady-state rates can be obtained from

$$R_{ss} = 0.69 P_{ss}/\tau_0 \quad (20)$$

as shown in article I, where $\tau_0$ is the diffusion half-life of the pinhole. The initial rates corrected for inhibition are computed from

$$R_i'(x) = R_i(x)\, R_{ss}(\Sigma C)/R_i(\Sigma C) \quad (21)$$

where $R_i'(x)$ is the corrected initial rate. Both $R_{ss}$ and $R_i'$ are listed in Table VIII for all products.

From the data in Table VIII, it is immediately apparent that both $CH_3OOH$ and $CH_3OI$ decay. The decay constants can be computed from

$$k = [R_i' - R_{ss}]/P_{ss} \quad (22)$$

These quantities are listed for $CH_3OOH$ and $CH_3OI$ as entries 4 and 6, respectively, of Table VIII.

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[7] M. Shanin and K. O. Kutschke, *J. Phys. Chem.*, **65**, 189 (1961).

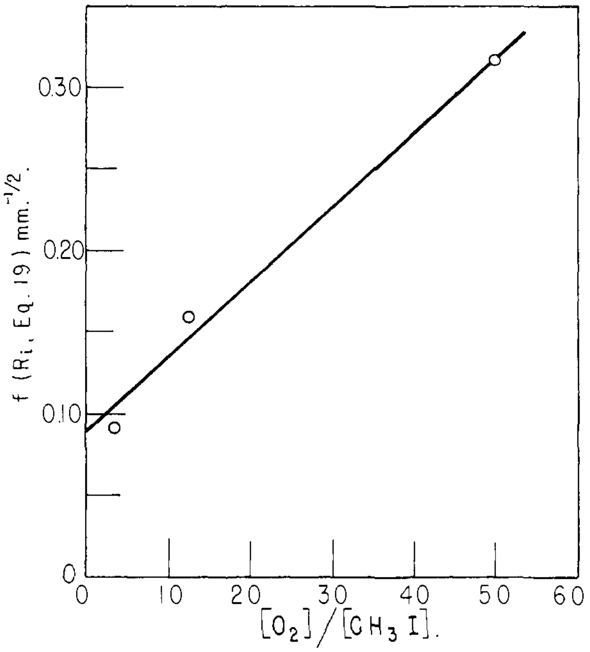

Fig. 6.—Test of eq. 19 and the evaluation of the ratio $k_l/(k_t k_c)^{1/2}$ and the relative efficiency of $O_2$ and $CH_3I$ as catalysts for reaction *i*.

For $CH_3OI$ the decay constant, identical with that in the dark, is thus associated with $k_m$. However, for $CH_3OOH$ the decay constant varies by a factor of eight and is somewhat larger than $k_l$. If the discrepancy is real, an additional gas-phase free radical attack on $CH_3OOH$ must occur.

Table VIII shows that the net rate of formation of $CH_2O$ is approximately the same as the initial corrected rate. Since additional $CH_2O$ is formed by l and m, the formaldehyde must be removed by some other process to compensate for the gain. Step t is suggested although methoxy radical may also be involved, step u.

The detailed fate of the HCO radical is not clear. However, in every investigation of methyl radical oxidations, HCOOH has been produced, often as a major product. The HCOOH undoubtedly is produced from HCO by reactions analogous to the production of $CH_3OH$ from methyl radical oxidation, starting with reaction z. In this system HCOOH is not an important product and can be neglected in the subsequent analysis. Hanst and Calvert[8] have studied the photo-oxidation of azomethane at room temperature and have shown that CO is a significant product as have Kutschke and his co-workers[9] at elevated temperatures. Under their conditions a reasonable reaction that could produce major amounts of CO is step y, and this reaction should also occur in our system. Table VIII shows that $R_{ss}(CO_2)$ is considerably greater than $R_i(CO_2)$. Probably the excess $CO_2$ results from HCO oxidation, but there are at least two possible routes, x and f′. Hanst and Calvert did not find $CO_2$ in their experiments. This is to be expected as z would be favored over f′ and x for their conditions of high pressure, whereas the reverse would be true here.

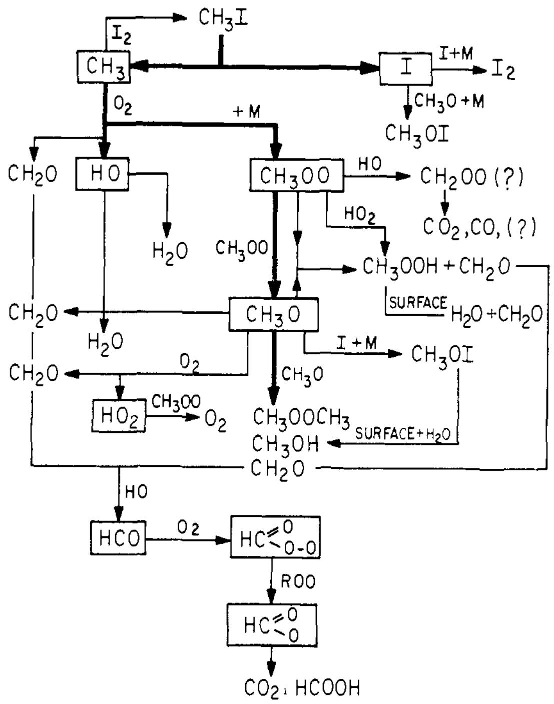

Fig. 7.—Flow chart showing source and fate of free radicals (in square boxes) and source of products in the proposed complex mechanism.

The energy of the photon used to dissociate $CH_3$–I is much greater than the C–I bond energy. This excess energy presumably is carried off mostly by the methyl radical, which is thus said to be "hot." The nature of this energy, translational or vibrational, is not known. The role of the hot radicals in this system is also not known, and its effects may provide an alternative explanation to some of the facts developed here. Further work is under way to clarify this question, which at present is left ambiguous.

**Summary.**—The photo-oxidation of methyl iodide is complicated and a large number of reactions occur. The free radicals in the system are $CH_3$, $CH_3O_2$, $CH_3O$ and $CH_2O_2$, HCO, $\overset{O}{\overset{/}{HC}}{-}OO$, $\overset{O}{\overset{/}{HC}}{-}O$, $HO_2$, and I. The course proposed for these radicals is summarized in the chart, Fig. 7. The initially formed radicals are $CH_3$ and I. The I atoms end up as $I_2$ or $CH_3OI$ or return to $CH_3I$. There are three competing paths for the $CH_3$ radicals, and the last, least important path produces $CH_2O$ and OH radicals, which abstract to form $H_2O$.

The $CH_3OO$ radicals can also follow three paths. By far the most important is a bimolecular dismutation to form $CH_3O$ radicals and $O_2$. However, $CH_3OOH$ is formed by reaction of $CH_3OO$ with $CH_3O$ and $HO_2$. The $CH_2O_2$ radical is formed by the disproportionation of $CH_3OO$ and OH radicals and ultimately yields $CO_2$.

The most important radical in the system is $CH_3O$. It undergoes a large number of reactions,

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[8] P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, **63**, 71 (1959).

[9] G. R. Hoey and K. O. Kutschke, *Can. J. Chem.*, **33**, 496 (1955); F. Wenger and K. O. Kutschke, *ibid.*, **37**, 1546 (1959); M. Shahin and K. O. Kutschke, *ibid.*, **39**, 73 (1961).

TABLE IX

SUMMARY OF RATE CONSTANT DATA

| Rate constant ratio | Reference | Units | Av. value |
|---|---|---|---|
| $k_f/k_g$ | Eq. 15 | None | $9.3 \pm 0.6$ |
| $k_i^2/k_fk_c$ | Eq. 19 and Fig. 6 | Mm.$^{-1}$ | 0.007 |
| $k_i^2/k_fk_c$ | Eq. 19 and Fig. 6 | Cc./mole | $1.2 \times 10^5$ |
| $\alpha_i$ | Eq. 19 and Fig. 6 | None | 0.055 |
| $\alpha_b$ | Eq. 18 and Fig. 5 | None | 0.06 |
| $k_h/k_fk_e^{1/2}$ | Eq. 16 and Fig. 4 | None | 0.14 ($CH_3I$) |
| $k_h/k_fk_e^{1/2}$ | Eq. 16 and Fig. 4 | None | 0.16 ($C_2H_5I$) |
| $k_v/k_f^{1/2}$ | Eq. 16 and Fig. 4 | (Mm.-sec.)$^{-1/2}$ | $1.44 \times 10^{-4}$ ($CH_3I$) |
| $k_v/k_f^{1/2}$ | Eq. 16 and Fig. 4 | (Mm.-sec.)$^{-1/2}$ | $3 \times 10^{-4}$ ($C_2H_5I$) |
| $k_v/k_f^{1/2}$ | Eq. 16 and Fig. 4 | (Cc./mole-sec.)$^{1/2}$ | 0.59 ($CH_3I$) |
| $k_v/k_f^{1/2}$ | Eq. 16 and Fig. 4 | (Cc./mole-sec.)$^{1/2}$ | 1.2 ($C_2H_5I$) |
| $k_b/k_q$ | Eq. 18 and Fig. 5 | Mm.$^{-1}$ | 5 |
| $k_b/k_q$ | Eq. 18 and Fig. 5 | Cc./mole | $1.0 \times 10^8$ |
| $k_l$ | Dark decay | Sec.$^{-1}$ | $5 \pm 1 \times 10^{-3}$ |
| $k_m$ | Dark decay | Sec.$^{-1}$ | $18 \pm 6 \times 10^{-3}$ |

of which disproportionation with other radicals is a very important source of major products. Another reaction of $CH_3O$ is the abstraction of a hydrogen atom from $CH_2O$ to give HCO radicals and $CH_3OH$. The HCO radicals then add $O_2$, the resulting performate radical passes to the formate radical. The formate radical disproportionates with the $CH_3O$ radical yielding $CO_2$ and $CH_3OH$ most of the time, but HCOOH and $CH_2O$ occasionally.

The detailed reactions are given in the text and the ratios of rate constants are summarized in Table IX.

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# Energy Exchange in the 3-Methyl-2-butanone–biacetyl System at 3130 Å.

BY DAVID S. WEIR[1]

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The energy exchange taking place in the 3-methyl-2-butanone–biacetyl system has been studied at 3130 Å. 3-Methyl-2-butanone emits in the same region as acetone and 3-pentanone, and pressure and temperature dependence indicate that the emission is almost certainly composed of both singlet and triplet components. When excited by 3130 Å. radiation, a mixture of 3-methyl-2-butanone and biacetyl shows a very strong green biacetyl emission with maxima at 5120, 5600 and 6000 Å., indicating that an energy transfer mechanism between 3-methyl-2-butanone and biacetyl is important. A preliminary study of the effect of biacetyl pressure on this biacetyl emission suggests that two energy transfer steps are important: one involving triplet state ketone and biacetyl, as it is found in acetone and 3-pentanone, and the other involving singlet state ketone and biacetyl, previously considered unimportant in acetone and 3-pentanone.

The energy exchange taking place in the 3-methyl-2-butanone–biacetyl system has been studied at 3130 Å.

Eastman Kodak Co. methyl isopropyl ketone was used. The ketone was fractionated on a spinning band column and a middle fraction stored over Drierite for several days. The fraction was thoroughly degassed at Dry-Ice temperature in a vacuum line, and the middle fraction retained from a bulb-to-bulb distillation. Vapor phase chromatography gave impurities of less than 1%. Eastman Kodak Co. white-label biacetyl was dried over Drierite, degassed and fractionated in a bulb-to-bulb vacuum distillation. The purity was confirmed by vapor phase chromatography.

The experimental arrangement used for the light emission studies was similar to that used by Weir.[2] Light emissions were photographed on a Hilger quartz prism spectrograph using Eastman Kodak Co. 103–0 plates for the 3-methyl-2-butanone emission and 103-D plates for the excited biacetyl emission. Reflected incident light was removed by a Pyrex filter. The intensity of the biacetyl emission was measured on an R.C.A. WV-84A direct current microammeter connected to an R.C.A. 1P 21 photomultiplier tube. A Corning 3384 filter removed all emission below 5000 Å.

A conventional vacuum line was used.

3-Methyl-2-butanone emits light from about 3500 to about 4700 Å. when excited by 3130 Å. radiation. The emission, although more intense than the very weak emission produced from 3-pentanone, is weak and diffuse, requiring exposures of the order of 22 hours to produce a darkening of the photographic plate. The intensity of the emission is increased by an increase in ketone pressure and decreased 25% when the temperature is raised from 28 to 70°. The spectrum is unaffected by pressure, but the effect of temperature is difficult to assess due to the low intensity of the emission at 70°. The effect of added oxygen was inconclusive due once again to the weakness of the emission and also the restriction of $O_2$ pressures to the range below 4.0 mm., to avoid polymerization. As would be expected, very small amounts of biacetyl are formed during the photolysis of the 3-methyl-2-butanone and over long exposures at 28° a very weak biacetyl emission consisting of three bands with maxima at 5120, 5600 and 6000 Å. can be detected. The biacetyl emission is absent at 70°. The energy exchange between biacetyl and 3-methyl-2-butanone was confirmed by adding 5.6 mm. of biacetyl to 25 mm. of 3-methyl-2-butanone and photographing the very pronounced biacetyl emission. Because of the low intensity of the 3-methyl-2-butanone emission it was impossible to determine whether the addition of biacetyl produced any effect on the intensity or spectrum of this emission.

The effect of biacetyl on the phosphorescence of biacetyl in a 3-methyl-2-butanone–biacetyl mixture is shown in Table I, where the effect is compared to that obtained from the 3-pentanone–biacetyl system.

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[2] D. S. Weir, *J. Am. Chem. Soc.*, **83**, 2629 (1961).