[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Reactions Involving Free Alkyl Groups. II. The Photo-oxidation of Gaseous Ethyl Iodide[1]

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In a previous investigation it was shown that the photo-reaction which methyl iodide undergoes in the presence of oxygen is essentially the oxidation of free methyl groups.[2] A similar reaction with ethyl iodide should yield the same data for ethyl groups and the present work concerns itself with an attempt to compare the reactions of the two different alkyl groups. Bates and Spence have already found that the products of the ethyl iodide–oxygen reaction are iodine, acetaldehyde and ethyl alcohol, which are analogous to the products of the methyl iodide reaction. More recently Thompson and Kelland[3] attempted a similar study by studying the oxidation of zinc diethyl. There was ample evidence, however, that free ethyl groups were not intermediates in this reaction.

Experimental Method

The experimental arrangement consisted of a quartz reaction vessel joined by capillary tubing to a mercury manometer and oil pump. The vessel was clear fused quartz, 50 mm. in diameter, 150 mm. in length and having a volume of 268 cc. with two plane, circular, polished windows fused into either end. This was fitted into a metal tank in such a way that one window was flush with the outer side of the tank. As the vapor pressure of ethyl iodide at 0° is too low to give a workable range of pressures, it was necessary to work at a higher temperature. This was accomplished by circulating water, thermostatically regulated at 17 ± 0.3°, into the tank so the vessel was completely covered. The iodine condensed on the sides rather than the window illuminated. Its vapor pressure is 0.158 mm. at 17° as calculated from the equation given by Giauque.[4] Ethyl iodide was first treated with sodium bisulfite solution to remove the iodine, separated from the aqueous layer, and dried with calcium chloride before distillation. Only the colorless portion boiling between 72–73° was reserved which was redistilled, *in vacuo*, into a storage bulb and kept under its own pressure as a practically colorless liquid. Tank oxygen, dried by calcium chloride, was kept in a large bulb from which it could be introduced into the reaction vessel. A mercury vapor lamp of the Kromayer type was the source of illumination, arranged so that after tilting to start the arc, it could be returned to the same place each time.

The Action of Light on Ethyl Iodide Vapor in the Absence of Oxygen.—When pure ethyl iodide vapor is illuminated for long periods of time no decrease in pressure is observed and only a small amount of iodine is liberated. As an illustration, 120 mm. of the vapor, upon being illuminated for seven hours, showed no pressure decrease, yet a residual gas pressure of approximately 8 mm. remained when the trap of the vessel was immersed into a carbon dioxide–ether mixture. The iodine liberated was equivalent to a decrease of 8.1 mm. of ethyl iodide.

The Action of Light on Ethyl Iodide in Presence of Oxygen.—With the presence of oxygen there is a pressure decrease which is sufficiently rapid to permit kinetic measurements. The iodine liberated was titrated and the pressure decrease was calculated on the basis of the all-over reaction

$$2C_2H_5I + O_2 \longrightarrow CH_3CHO + C_2H_5OH + I_2$$

in which the initial pressure is decreased by one third. Table I shows the experimental decrease and that calculated on the basis of the above equation from the iodine liberated.

TABLE I

C_2H_5I, mm.	O_2, mm.	0.121 *N* $Na_2S_2O_3$, cc.	$-\Delta P$ obs.	$-\Delta P$ calcd.
53	304	2.03	9.0	8.10
50	300	1.51	6.2	6.79
50	293	1.72	8.4	7.97
50	13.8	1.00	4.8	4.05
55	12.4	1.04	4.8	4.21
50	23.4	0.81	3.6	3.25
50	27.0	1.07	4.6	4.33
52	156	0.97	4.8	4.0
52	157	.96	4.2	4.0

Variations of Ethyl Iodide and Oxygen Concentrations.—An endeavor to maintain uniform light intensity for each series of experiments, and constant conditions for all the series were made in every one of the kinetic measurements. The uniformity of light intensity was checked by repeating one of the experiments chosen as a reference point, and if no change in rate was observed, it was assumed that the light intensity had remained constant. When there was an appreciable deviation, that series was discarded. Manometer readings were made at one, two or three minute intervals for about seven to ten minutes duration. After ten to fifteen minutes, depending upon concentrations, the rate would decrease appreciably, so measurements were made for that part that gave a linear relationship between pressure decrease and time. At the beginning of each run a small expansion, known as the Budde effect, similar to that shown by methyl iodide and

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[1] The material in this paper comprises a portion of a thesis presented by Loren T. Jones to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1934.

[2] Bates and Spence, THIS JOURNAL, **53**, 1689 (1931); *Trans. Faraday Soc.*, **27**, 414 (1931).

[3] Thompson and Kelland, *J. Chem. Soc.*, 756 (1933).

[4] Giauque, THIS JOURNAL, **53**, 507 (1931).

chlorine upon illumination was observed. Figure 1 contains results obtained upon varying the concentrations of ethyl iodide and constant oxygen. The results for varying the oxygen concentrations and constant ethyl iodide are given in Fig. 2.

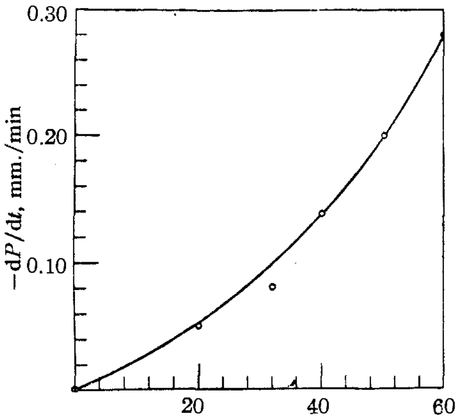
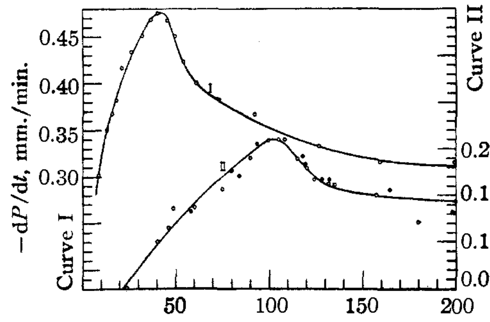


Fig. 1.



I $[C_2H_5I]$ = 75 mm., II $[C_2H_5I]$ = 50 mm.

Fig. 2.

Theoretical Discussion

Decomposition of Ethyl Iodide.—The decomposition of ethyl iodide in the absence of oxygen is quite similar to that of the methyl compound. The slowness of the reaction may be accounted for on the same basis. The ethyl groups, once formed, react for the most part with iodine, regenerating the iodide.

$$C_2H_5 + I_2 \longrightarrow C_2H_5I + I$$

Some few apparently react according to the equation

$$C_2H_5 + C_2H_5 \longrightarrow C_2H_6 + C_2H_4$$

There is thus no resulting pressure change, which would be the case were they to combine to form butane.

Their reaction with disproportionation is further indicated by the results of Emschwiller,[5] who found in the liquid photo-reaction ethylene and ethane, but neither butane nor hydrogen. This is also analogous to the reaction suggested to explain the reaction of hydrogen atoms with oxygen and other molecules[6] where the intermediate HO_2 molecules react for the most part with disproportionation.

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$

Ethyl Iodide and Oxygen.—The change in the rate of the oxidation reaction with oxygen and with ethyl iodide concentrations is entirely unlike the methyl group oxidation. The appearance of the maximum rate with increasing oxygen concentration (Fig. 2) and the very rapid increase in rate with increasing ethyl iodide concentration (Fig. 1) indicate that the simple mechanism postulated for the methyl group cannot be applied here. It is evident that only through a peroxide intermediate will it be possible to obtain the maximum in the rate–oxygen curve. Another fact which is apparent from an inspection of the curves in Fig. 2 is that at high oxygen concentrations an asymptote greater than zero is approached. This removes the possibility of explaining the results with the simpler of the peroxide mechanisms

$$\begin{array}{rll}
C_2H_5I + h\nu \longrightarrow & C_2H_5 + I & I_{abs.} \\
C_2H_5 + I_2 \longrightarrow & C_2H_5 + I & k_1 \\
C_2H_5 + O_2 \longrightarrow & C_2H_2O_2' & k_2 \\
C_2H_5O_2' + C_2H_5I \longrightarrow & CH_3CHO + C_2H_5OH + I & k_3 \\
C_2H_5O_2' + O_2 \longrightarrow & C_2H_5O_2 + O_2 & k_4 \\
C_2H_5O_2 + I_2 \longrightarrow & C_2H_5I + O_2 + I & k_5
\end{array}$$

where $C_2H_5O_2'$ represents the energy rich peroxide upon formation. This yields as a rate expression

$$-\frac{d\,[C_2H_5I]}{dt} = \frac{2I_{abs}k_2k_3\,[C_2H_5I]\,[O_2]}{(k_1[I_2] + k_2[O_2])\,(k_3\,[C_2H_5I] + k_2[O_2])}$$

which contains an $[O_2]^2$ term in the denominator and gives a maximum, with appropriate choice of constants. However, at high $[O_2]$ the curve will approach zero, which does not coincide with experiment.

A scheme which gives a fairly satisfactory representation of the data is

$$\begin{array}{rll}
C_2H_5I + h\nu \longrightarrow & C_2H_5 + I & I_{abs.} \\
C_2H_5 + I_2 \longrightarrow & C_2H_5I + I & k_1 \\
C_2H_5 + O_2 \longrightarrow & C_2H_5O_2 & k_2 \\
C_2H_5O_2 \longrightarrow & C_2H_5 + O_2 & k_3 \\
C_2H_5O_2 + O_2 \longrightarrow & C_2H_3CHO + OH + O_2 & k_4 \\
C_2H_5O_2 + C_2H_5I \longrightarrow & CH_3CHO + OH + C_2H_5 + I & k_5 \\
C_2H_5I + OH \longrightarrow & C_2H_5OH + I & k_6
\end{array}$$

$$-\frac{d\,[C_2H_5I]}{dt} = \frac{2I_{abs}[O_2]\,k_2(k_4[O_2] + k_5[C_2H_5I])}{k_2k_4[O_2]^2 + k_1k_4[I_2][O_2] + k_1k_3[I_2] + k_1k_5[C_2H_5I][I_2]}$$

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[5] Emschwiller, *Compt. rend.*, **192**, 799 (1931).

[6] Bates, *J. Chem. Phys.*, **1**, 457 (1933).

This expression will give a curve representing the change in reaction rate with oxygen concentration which is of the same general form as the experimental results. It was, however, found to be impossible to fit the experiments with any degree of exactness. With numerical constants assigned to the constant terms appearing in the theoretically derived expression it was found that an agreement for low oxygen concentrations gave values which were systematically at variance with the portion of the experimental curve representing the results at high concentrations. Comparison is made by using the empirical equation

$$-\frac{d\ C_2H_5I}{dt} = \frac{a\ [O_2]^2 + b\ [O_2]}{[O_2]^2 + C\ [O_2] + d}$$

Values may be assigned to the constants in order to calculate the rate. For the ethyl iodide concentration constant at 50 mm. the values $a = 0.1$, $b = 16$, $c = 7$ and $d = 3{,}700$ gave the best agreement; at 75 mm. the values $a = 0.16$, $b = 60$, $c = 75$ and $d = 1{,}200$ were found best.

The deviations may be due to a systematic error in the experimental results or to the fact that the reaction is more complex than we have considered. We believe that such an error cannot be considered plausible in the light of reproducibility of the results.

The change in rate with ethyl iodide can be seen to be in agreement with this equation when it is remembered that $I_{\text{abs.}}$ is a function of the iodide, thus giving a total dependence of the rate on ethyl iodide of a power lying between one and two, depending upon the value of the absorption coefficient of ethyl iodide.

Although by considering other more complex reaction schemes an expression can be found which fits the results, with an appropriate choice of constants, we feel that the significance of such expressions is defeated by their complexity and therefore prefer to leave the question open, pending either a more simple explanation or a much more extensive investigation.

It may, however, be inferred quite definitely from the results of the present work that a peroxide is an intermediate in ethyl group oxidation, since only by such an assumption may any sort of agreement be obtained with experiment. Such peroxides have been found to be quite generally necessary for the interpretation of oxidation processes involving hydrocarbons as well as other atoms and radicals.[7]

Summary

The photodecomposition of ethyl iodide is extremely slow, resulting after long periods of illumination in an uncondensable gas which is probably ethylene and ethane.

The oxidation is rapid, giving rise to a pressure decrease which indicates acetaldehyde and ethyl alcohol as end-products. The rate of oxidation increases to a maximum, with increasing oxygen content, and then falls off to an asymptotic value greater than zero. The results can be interpreted to a certain degree of exactness by a mechanism involving an intermediate ethyl peroxide, but small deviations from theory indicate a great complexity. A peroxide, however, is the only intermediate which will give even an approximate agreement, which is in accord with other oxidation processes.

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[7] Thompson and Kelland, *J. Chem. Soc.*, 756 (1933): Bodenstein, *Z. physik Chem.*, **B11**, 1516 (1931).