[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photolysis of Simple Alkyl Esters

BY J. K. ROYAL AND G. K. ROLLEFSON

In this paper are presented some studies on the photolysis of methyl formate and methyl acetate. The work is in two parts: first, tests for radicals and hydrogen atoms by mirror methods; second, a detailed study of the decomposition products of methyl formate.

Experiments with Mirrors

The esters were treated with magnesium amalgam and with phosphorus pentoxide and distilled. The fractions which were used distilled at 32.0–32.1° (methyl formate) and 57.2–57.3° (methyl acetate). The acetone for comparison experiments distilled at 56°. Air was removed from the liquids by alternately freezing and melting and finally distilling in vacuum. Hydrogen was prepared from zinc and sulfuric acid and given a suitable purification. J. T. Baker bismuth and Kahlbaum tellurium were used for the mirrors.

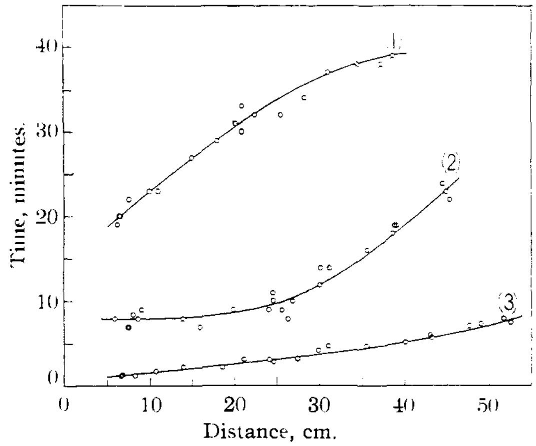

Fig. 1.—Time of removal of bismuth mirrors at various distances from the irradiated zone: (1) methyl formate, (2) methyl acetate, (3) acetone.

The apparatus was essentially the same as that described by Burton[1] and the mirrors were prepared in the manner described by Rice.[2] It was found to be advantageous to use a gas-air rather than a gas-oxygen flame to prepare the mirrors, probably because the hotter flame causes the formation of silicates which are not attacked by radicals. From time to time the tube was cleaned with hot nitric acid and distilled water and then flushed with hydrofluoric acid and distilled water.

During a run a 4.8-cm. portion of the quartz tube, about 23 cm. from the end at which the vapors entered, was exposed to the light from a capillary mercury arc. The tube was 115.5 cm. long with an average internal diameter of 0.66 cm. Both the arc and exposed portion of the tube were cooled with running water. The results obtained are shown in Fig. 1. Since no analysis of the organo-metallic compounds was made, the formulas of the fragments removing the mirrors cannot be stated. Acetone was used for comparison purposes since it has been studied previously.[1,3] Since the concentration of radicals is inversely proportional to the time required to remove the mirrors it is apparent that acetone gives the greatest and methyl formate the least concentration of radicals in our experiments. It is to be noted, however, that the radicals may not be the same in the three reactions.

The time required for a radical to reach any given point along the tube was calculated by means of the following equation given by Paneth and Lautsch.[4]

$$t = \frac{X_2 - X_1}{V} - \frac{aX_2^2 - X_1^2}{2VP}$$

The streaming velocities, V, at the pressures, P, were obtained from the data shown in Fig. 2 in which the time required for a mole of vapor to pass through the tube is plotted against the pressure. The streaming velocities at

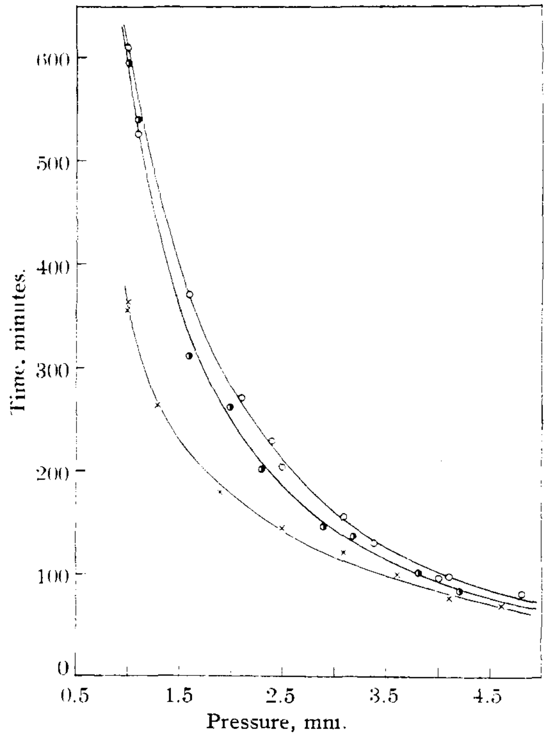

Fig. 2.—Time required for 1 mole of substance to flow through tube at various pressures: ×, acetone; O, methyl acetate; ◑, methyl formate.

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[1] Burton, THIS JOURNAL, **58**, 1645 (1936).

[2] Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins University Press, Baltimore, Md., 1935.

[3] Pearson, *J. Chem. Soc.*, 1718 (1934); 115 (1935).

[4] Paneth and Lautsch, *Ber.*, **64**, 2708 (1931)

the beginning of the constricted portion with a pressure of 0.28 cm. were calculated to be 17.7 × 10^2 cm. per sec. for methyl acetate, 19.9 × 10^2 cm. per sec. for methyl formate and 24.5 × 10^2 cm. per sec. for acetone.

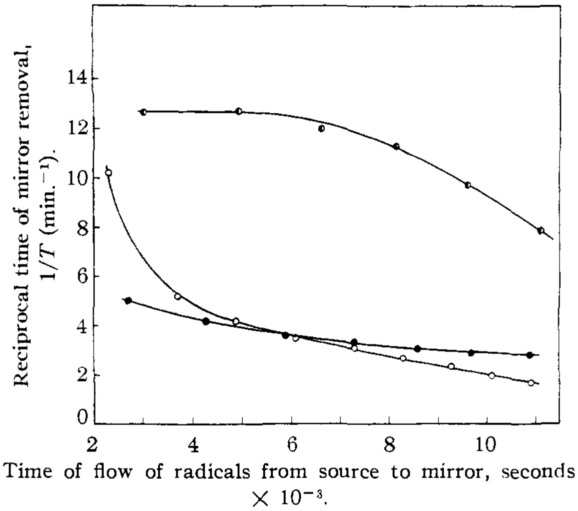

Fig. 3.—Effect of time on concentration of free radicals: $1/T \times 10^{-2}$ for CH_3COOCH_3 and $HCOOCH_3$; $1/T \times 10^{-1}$ for CH_3COCH_3; ◐, methyl acetate; ●, methyl formate; O, acetone.

Figure 3 indicates the manner in which the concentration of free radicals diminishes with time. It was found that the rate of disappearance of the fragments did not follow equations of either the first or second order very exactly, especially in the case of methyl acetate. Free radicals from methyl formate were found to have a half-life of 6–8 × 10^{-3} second and in the case of acetone the fragments had a half-life of 2–3 × 10^{-3} second. Methyl acetate gave results of the same order of magnitude. The constants used in making the calculations for methyl formate and acetone were computed using equations of the first order. The value for the half-life of the radicals obtained from methyl formate agreed closely with the value of 5.8 × 10^{-3} second obtained by Paneth and Hofeditz[5] in their work on the pyrolysis of lead tetramethyl carried by a stream of hydrogen. The half-life of the radicals from acetone agreed with the value of 0.55–2.8 × 10^{-3} second obtained by Rice, Johnston and Evering[6] for the radicals formed in the thermal decomposition of acetone.

Tests were made for hydrogen atoms by Burton's guard mirror method using bismuth for the guard and tellurium as the detector. In the runs made, no hydrogen atoms could be detected after exposures up to ninety-five minutes and sixty-three minutes in the case of methyl formate and methyl acetate, respectively. Tellurium mirrors of far greater density, placed at the same distances from the source were removed in twenty-four minutes by methyl formate and eleven minutes by methyl acetate in the absence of a bismuth guard mirror. The failure to detect hydrogen atoms by this method may be due to the rapid removal of them by secondary reactions in the vapor.

The Decomposition of Methyl Formate in a Static System.—Methyl formate was purified, degassed and stored by the method described. Formaldehyde was prepared by heating Eastman Kodak Co. trioxymethylene at 110–120° over an oil-bath and collecting the gas in a two-liter bulb. Nitric oxide was obtained from Mr. K. Atwood of this Laboratory. It was prepared by the method of Johnston and Giauque.[7]

The apparatus consisted essentially of a cylindrical quartz vessel, 5 cm. long and 5.5 cm. in diameter. A click gage[8] separated the vessel from a mercury and a sulfuric acid manometer. The reaction vessel was connected to the click gage by means of capillary tubing in order to minimize the "dead" space. The volume of the vessel and adjoining tubing was 114 cc. A Toepler pump was employed to pump off the gases for analysis. Two tubes, separated by three-way stopcocks, connected the reaction vessel to the Toepler pump. One of the tubes contained phosphorus pentoxide. The other contained a copper gauze heavily coated with the oxide, and was surrounded by an electric furnace which heated the gauze to approximately 430° when desired. A small flask, equipped with a ground glass joint and a stopcock, was placed at either end of the two glass tubes at points between the three-way stopcock and the reaction vessel in one case; and between the three-way and the Toepler pump in the second case. By this means, gases which were condensable in liquid air could be distilled back and forth either through the tube containing the copper oxide or through the tube containing phosphoric anhydride by a suitable manipulation of a liquid-air bath around the two small flasks. All the stopcocks in contact with the substances under investigation were lubricated with Apiezon grease.

The horizontal arc employed in the mirror experiments was replaced by a more powerful arc designed by K. Atwood.[9]

In a typical run the quartz reaction vessel was cooled by running a stream of water over it. The methyl formate was introduced to the desired pressure and the temperature of the cell and pressure were recorded. Runs made with the arc at different distances from the reaction vessel showed no difference in the products formed hence no special precautions were taken to maintain the light intensity constant. When a suitable pressure increase had been attained, the illumination was discontinued, and the products analyzed.

The reaction vessel was immersed in liquid air and the pressure noted. This pressure multiplied by an empirical freeze-out factor (3.51) served as a rough measure of the products non-condensable in liquid air. These gases were pumped out by means of a Toepler pump and were analyzed by the methods developed by Blacet, Leighton, and others.[10] The substances which remained in the reaction vessel were warmed to the original temperature and the pressure noted. The difference between this reading and the pressure at the end of the illumination period was

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(5) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929).

(6) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932).

(7) Johnston and Giauque, *ibid.*, **51**, 3194 (1929).

(8) Smith and Taylor, *ibid.*, **46**, 1393 (1924).

(9) K. Atwood, Ph. D. thesis, University of California, 1940.

(10) Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 766 (1931); Blacet, MacDonald and Leighton, *ibid.*, **5**, 272 (1933). Blacet and MacDonald, *ibid.*, **6**, 334 (1934); Blacet and Volman, *ibid.*, **9**, 44 (1937).

taken as the accurate measure of the total amounts of non-condensable gases.

Next, a partial separation of the condensable products was effected by immersing the reaction vessel in a mixture of acetone and solid carbon dioxide at −80°. Any formaldehyde, the presence of which was shown by Schiff reagent, would also appear in this fraction. However, tests showed the amount of formaldehyde present at any time to be negligible. A portion of this mixture was analyzed by absorbing the carbon dioxide with a potassium hydroxide bead and the residue was shown to be ethane by a combustion.

The remaining condensable gases consisted of unchanged methyl formate and any products condensable at −80°. In order to avoid loss of these substances all of the ethane and carbon dioxide was not removed before the procedure to be described was carried out. First it was necessary to establish that under the experimental conditions methyl formate vapor consists of single molecules. This was done first, by vapor density measurements, and second, by oxidizing the vapor to carbon dioxide and water by passing it over hot copper oxide. The formation of two moles of carbon dioxide per mole of vapor proved that only single molecules were present. Next the condensable gas mixture was put through the same treatment. The increase in pressure was taken to correspond to the sum of the ethane and methyl formate and from the data previously obtained for ethane the methyl formate could be calculated. The sum of the pressures of ethane, methyl formate, and carbon dioxide obtained by these procedures was found to be considerably less than the total pressure measured for the substances condensable in liquid air. This fact requires the addition of another product which contains only one carbon atom per molecule and is condensable at −80°. It was found that if this product were assumed to be methyl alcohol the carbon, hydrogen, and oxygen ratios calculated for the sum of the products was in good agreement with the proportions for methyl formate. Additional evidence for the selection of methyl alcohol as a product is found in the fact that on prolonged illumination it was found that the carbon monoxide and hydrogen in the products increased and the methyl alcohol decreased. This behavior is in accord with the known decomposition of methyl alcohol into carbon monoxide and hydrogen at the short wave lengths which are present in the unfiltered light from the arc.

The results of the analyses are summarized in Table I. The data were obtained from experiments in which the initial pressure of methyl formate was ~ 2 cm. of mercury. Some experiments were performed at an initial pressure of about 10 cm. of mercury but in these a considerable amount of an unidentified high boiling product was obtained. Since we are primarily concerned with a study of the action of light on the methyl formate molecule, we confined our experiments to the conditions under which the secondary reactions were reduced to a minimum as is indicated by relatively simple products.

In order to secure some information as to which products were obtained by a free radical mechanism some experiments were performed in which initially about seven times as much nitric oxide was present as methyl formate. Under these conditions the only non-condensable product was found to be carbon monoxide. The increased complexity of the condensable products prevented a complete analysis of them but it was ascertained that there was no ethane present.

Some evidence was also obtained that some of the nitric oxide was reduced to nitrous oxide. Similar results have been obtained in other experiments in this Laboratory.[11] The failure to find ethane and methane in the products when nitric oxide is present indicates that free radicals are responsible for their formation. The absence of hydrogen suggests that this gas must be formed either from radicals or hydrogen atoms.

TABLE I

PRODUCTS OF THE PHOTOLYSIS OF METHYL FORMATE EXPRESSED AS MOLE PER CENT.

$HCOOCH_3$ dec.	CO	H_2	CH_4	CO_2	C_2H_6	CH_3OH
32.7	37.9	15.8	5.8	10.7	4.6	25.0
40.8	37.6	16.1	5.4	12.9	4.2	23.4
57.2	38.2	19.8	7.9	7.0	3.2	23.8
57.6	38.2	19.5	6.6	8.7	2.7	24.4
73.1	38.0	18.7	5.5	8.9	2.9	26.0
86.0	37.6	17.8	6.1	10.0	2.6	26.2
88.1	38.6	19.5	6.1	8.7	2.9	26.4
~100.0	41.7	25.2	6.7	9.3	2.7	14.8
~100.0	42.4	26.2	7.2	9.4	3.1	11.8

One of the possible mechanisms for the formation of hydrogen which we considered was a split of the methyl formate molecule into formaldehyde molecules followed by the decomposition of the formaldehyde into hydrogen and carbon monoxide. The positive test for aldehyde with Schiff reagent is in favor of such a mechanism. Since it is possible that under some conditions formaldehyde may decompose directly into carbon monoxide and hydrogen[12] experiments were performed with mixtures of formaldehyde and nitric oxide to see if any hydrogen would be produced when illuminated as in our experiments. It was found that with a nitric oxide–formaldehyde ratio of 7.2 the carbon monoxide–hydrogen ratio was 2.3 and with the former 13.7 the latter increased to 6.5. Therefore we concluded that in experiments such as ours with methyl formate and nitric oxide in which the nitric oxide–formalde-

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(11) Anderson and Rollefson, THIS JOURNAL, **63**, 816 (1941).

(12) Burton and Rollefson, *J. Chem. Phys.*, **6**, 816 (1938).

hyde ratio was at least 70 no appreciable amount of hydrogen could be expected in the products whether it was produced from formaldehyde or by some other process involving free radicals or hydrogen atoms.

Discussion.—The products obtained in the photolysis of methyl formate show that several reactions occur in the system. The results may be expressed by a suitable combination of the net reactions

$$\begin{aligned} HCOOCH_3 &\longrightarrow CO + CH_3OH & (1)\\ HCOOCH_3 &\longrightarrow 2CO + 2H_2 & (2)\\ HCOOCH_3 &\longrightarrow CO_2 + CH_4 & (3)\\ 2HCOOCH_3 &\longrightarrow C_2H_6 + H_2 + 2CO_2 & (4) \end{aligned}$$

From Fig. 4, which is a plot of the data in Table I, it is apparent that only small changes occur in the composition of the products until the reaction is essentially complete when the decomposition of the alcohol occurs. There is a definite decrease in the percentage of ethane produced and a slight increase in the methane. This change is consistent with the view that these gases are formed from free radicals as is indicated by their absence from the products when nitric oxide is present. The concentration of free radicals in the reaction mixture would be higher in the early stages of the reaction and therefore the chance of forming ethane under those conditions by the combination of two methyl radicals is greater than in the later stages of the reaction. The net effect would be that the fourth reaction given above decreases in importance and the third increases slightly in the course of the reaction. If we take the points on the curves in Fig. 4 which correspond to 50% of the methyl formate decomposed the relative importance of the four net reactions may be calculated. It is found that 61% of the methyl formate decomposes according to (1), 16% by (2), 15% by (3) and 8% by (4). In making this calculation the weight of the analytical errors was thrown entirely on reaction (4), which is the least important.

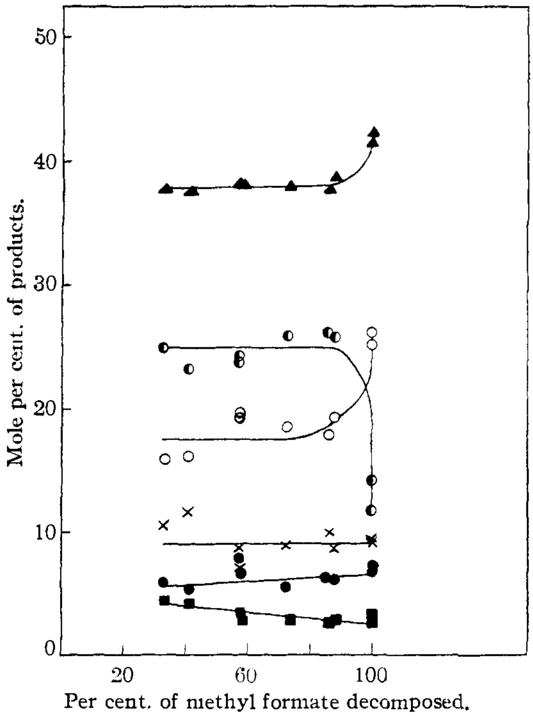

Fig. 4.—Relation between mole per cent. of products and per cent. of methyl formate decomposed: ▲, CO; ◐, CH_6OH; ○, H_2; ×, CO_2; ●, CH_4; ■, C_2H_6.

The mechanisms for these reactions cannot be determined completely from our observations but a number of conclusions can be drawn. Evidence has already been cited for the assumption of free radical mechanisms for (3) and (4). The most probable primary step which will account for these products is a rupture of the ester into methyl and formate radicals. No decision can be made concerning the various possible secondary reactions except that the decrease in the formation of ethane in the later stages of the reaction suggests that this gas is formed at least partially by the combination of two methyl radicals. A free radical mechanism might be assigned to (2) on the grounds that no hydrogen was found when nitric oxide was present in the reaction mixture. However, a mechanism which we consider more probable in view of the positive test obtained for the presence of aldehyde is that a hydrogen atom shifts from the methyl to the carboxyl carbon and the molecule splits into two formaldehyde molecules. These molecules decompose into carbon monoxide and hydrogen. Our control experiments with mixtures of formaldehyde and nitric oxide have shown that with relatively high nitric oxide pressures no hydrogen will be formed. The alternative free radical mechanisms are too numerous to record. Reaction (1), which accounts for the major portion of the methyl formate decomposed, is most readily accounted for by the shift of the formate hydrogen with the resultant splitting of the molecule into methyl alcohol and carbon monoxide. Such a mechanism differs from the one given for (2) above only in that in one case one of the methyl hydrogens shifts, in the other it is the formate hydrogen.

Summary

The photolysis of methyl formate and methyl acetate has been investigated by means of the mirror method developed by Paneth and others. Free radicals were formed by the esters. No hydrogen atoms were detected. The rates of removal of bismuth mirrors by fragments formed in the decomposition of methyl formate and methyl acetate have been compared with those obtained from acetone. The half-life periods of the free radicals produced by methyl formate and acetone have been computed. The value for the half-life of the fragments from methyl formate was found to be 6–8 × 10^{-3} and from acetone 2–3 × 10^{-3} second. The value for acetone showed good agreement with that obtained by other investigators in the pyrolysis of acetone and the value for methyl formate agreed with the value obtained in the thermal decomposition of lead tetramethyl.

The photolysis of methyl formate in a static system has been studied. The products formed in the decomposition were found to be CO, H_2, CH_4, C_2H_6, CH_3OH, and a minute amount of HCHO. The total reaction can be represented as a combination of four net reactions. These are

$$HCOOCH_3 \longrightarrow CH_3OH + CO \qquad (1)$$
$$HCOOCH_3 \longrightarrow 2CO + 2H_2 \qquad (2)$$
$$HCOOCH_3 \longrightarrow CO_2 + CH_4 \qquad (3)$$
$$2HCOOCH_3 \longrightarrow C_2H_6 + H_2 + 2CO_2 \qquad (4)$$

The products at 50% decomposition of the ester are such that the total reaction may be considered as made up of approximately 61% of (1), 16% of (2), 15% of (3), and 8% of (4). The effect of nitric oxide has been studied. Mechanisms for some of the net reactions have been suggested.

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The Thermal and Photochemical Decomposition of Oxalyl Bromide

BY J. E. TUTTLE AND G. K. ROLLEFSON

In most studies of the photolyses of simple organic molecules the effective wave lengths lie so far in the ultraviolet that the absorbed quanta possess sufficient energy to break the molecule into free radicals. Although some of the molecules which have been studied, such as formaldehyde and acetaldehyde, show some variation in behavior as the wave length is varied, it seems reasonable to expect that more marked effects will be found with substances which absorb at longer wave lengths where free radical formation is either impossible or at least improbable. Oxalyl bromide which has an absorption extending from $\lambda > 4358$ to $\lambda < 2537$ Å. seemed a suitable subject for such an investigation. The results of both the photolysis and pyrolysis of oxalyl bromide are presented in this paper.

Materials.—Oxalyl bromide was prepared by bubbling four times the theoretical amount of dry hydrogen bromide through oxalyl chloride at 0°. The oxalyl chloride was obtained from the Eastman Kodak Co. The conversion to the bromide was apparently quite complete since on distillation practically all of the liquid came over at the boiling point of oxalyl bromide, 106°. The middle portion of this distillate was distilled in vacuum over mercury to remove bromine and the middle portion of this distillate was used for our experiments. The purified compound is yellowish-green in color. In "Beilstein" it is reported that a slow decomposition takes place in the dark with the appearance of bromine. This was not found to be true with our material; after three months no appreciable color of bromine had appeared.

Oxygen was prepared by liquefying tank oxygen and distilling off a considerable amount of the liquid. The gas was admitted to the reaction vessel as needed under its own vapor pressure at liquid air temperatures.

Hydrogen was taken from a cylinder, passed over hot copper to remove oxygen and dried with phosphorus pentoxide.

Hydrogen iodide was prepared by dehydrating hydriodic acid with phosphorus pentoxide and distilling over mercury to remove iodine.

Ethylene was taken from a cylinder, dried over phosphorus pentoxide and distilled in vacuum.

Nitrosyl chloride was obtained from Mr. K. Atwood, who had prepared it in this Laboratory by the direct combination of nitric oxide and chlorine.

Hexane was purified by shaking with concentrated sulfuric acid until the acid layer remained colorless. Next it was shaken with acid potassium permanganate and finally with alkaline permanganate. It was dried by distilling over phosphorus pentoxide.

Absorption Spectrum.—Since no absorption spectrum of oxalyl bromide could be found in the literature, measurements were made of the ab-