513. *The Kinetics of the Photolysis of Acetaldehyde. Part II.* The Rate of Production of Methyl Radicals.*

By A. S. Buchanan.

The rate of production of ethane in the high-temperature photolysis of acetaldehyde has been calculated from data on the rate of formation of methyl radicals. These results have been compared with the ethane in the reaction products as determined by analysis.

In conjunction with direct determinations of the ethane produced in the high-temperature photolysis of acetaldehyde (Danby, Buchanan, and Henderson, *J.*, 1951, 1426) determinations have been made of the rate of production of methyl radicals in the system undergoing photolysis. Such data enabled calculations of the ethane which would be produced if all the methyl radicals associated to give this substance. Comparison of the calculated values with the actual production of ethane should give a measure of the efficiency of the latter reaction.

The experimental method was that first used by Gorin (*Acta Physiochim. U.R.S.S.*, 1938, **9**, 681), and subsequently repeated and extended by Blacet and his co-workers (Blacet and Heldman, *J. Amer. Chem. Soc.*, 1942, **64**, 889; Blacet and Loeffler, *ibid.*, p. 893). Acetaldehyde is illuminated in the presence of iodine, and the methyl radicals, as they are produced, form methyl iodide which may be estimated. In addition, the formyl radicals may also react with iodine, *e.g.*, $CHO + I_2 = HI + CO + I$. Some evidence for the latter reaction was obtained by Gorin but the amounts of hydrogen iodide produced were very small, being only 1/10th to 1/100th of the methyl iodide production. Blacet was unable to detect hydrogen iodide in measurable amount and suggested that it probably reacts with acetaldehyde to give polymers.

Experimental.

The experimental arrangements were the same as those described by Danby, Buchanan, and Henderson (*loc. cit.*). The required pressure of iodine was vaporized into the reaction vessel, and the acetaldehyde then admitted. The vessel was isolated by a magnetically operated ground-glass valve. After illumination, the reaction products were pumped slowly (with a Töpler pump) over a large area of mercury on the walls of the tube, to remove excess of iodine. The products were then compressed in the absorbing section of the apparatus, which consisted of a U-tube containing potassium hydroxide pellets and a tube containing a measured volume of sodium ethoxide solution. The former was intended to remove hydrogen iodide, but the amount detected was always negligible and, since the potassium hydroxide sometimes absorbed appreciable amounts of methyl iodide, the use of this tube was dispensed with in most cases. After being sealed, the sodium ethoxide tube was heated at 130° for several hours, and the sodium iodide produced was determined.

Results.

In the first instance a survey of the method was made, *i.e.*, determination of the methyl-radical production with variation in acetaldehyde pressure, time of illumination, pressure of iodine, and temperature.

Fig. 1(*a*) shows the amount of methyl iodide produced as the pressure of aldehyde increases at 60 minutes' illumination and approximately 5 mm. of iodine. Above about 3×10^{-4} mole of acetaldehyde per 105 c.c., the production of methyl iodide ceases to increase with pressure, remaining constant thereafter. To ensure that this effect was not due to lack of iodine (since the methyl iodide might decompose if excess of iodine was not present) a similar curve but with double the iodine pressure, was prepared [Fig. 1(*b*)]. There are apparently no significant differences in the curves; the fact that the plateau occurs at a somewhat higher value in the latter is almost certainly to be ascribed to experimental error. Halving the exposure time to 30 minutes gave a curve with much the same characteristics [Fig. 1(*c*)]. The slope of the initial proportional region is just half that for the 60-minute curve and the plateau value is slightly over half. The beginning of the plateau in each case occurred at an aldehyde concentration of about 3—4×10^{-4} mole per 105 c.c. The evidence thus suggested that the appearance of the plateau was due to complete utilisation of the light entering the cell, and this was confirmed by arranging a reflector behind the lamp in order to increase the incident intensity, whereupon an increase in methyl iodide production of 30% was observed.

The influence of time of exposure on methyl-radical production was investigated at 120° and 200° (Fig. 2). A concentration of aldehyde sufficiently high to secure full light utilisation was used throughout. It can be seen that, initially, the formation of methyl iodide is proportional to the time of exposure, but after about 20—30 minutes it begins to fall off. This is probably to be attributed to the effects of secondary reactions of unknown nature. However, it is clear that only results obtained with short

---

* Part I, *J.*, 1951, 1426.

times of exposure are unambiguous (*i.e.*, up to about 10 minutes). The initial rate of production of methyl radicals is about $0{\cdot}53 \times 10^{-6}$ and $0{\cdot}55 \times 10^{-6}$ mole per 105 c.c. per minute at 120° and 200°, respectively. This result appears to be in agreement with the generally accepted notion that radical production by photolysis should be temperature independent. At 300° an appreciable "dark" reaction occurred, apparently leading to the formation of methyl iodide; experiments at this temperature therefore were discontinued.

FIG. 1.

Production of CH_3I *with varying* $CH_3{\cdot}CHO$ *pressure*: (*a*) 5—6 *mm. of iodine*; 60 *mins.' exposure*; 120°. (*b*) 10—11 *mm. of iodine*; 60 *mins.' exposure*; 120°. (*c*) 5—6 *mm. of iodine*; 30 *mins.' exposure*; 120°.

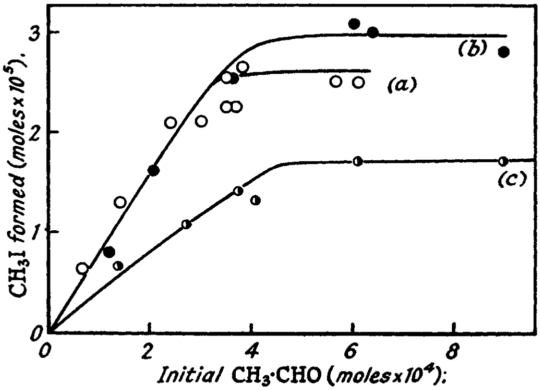
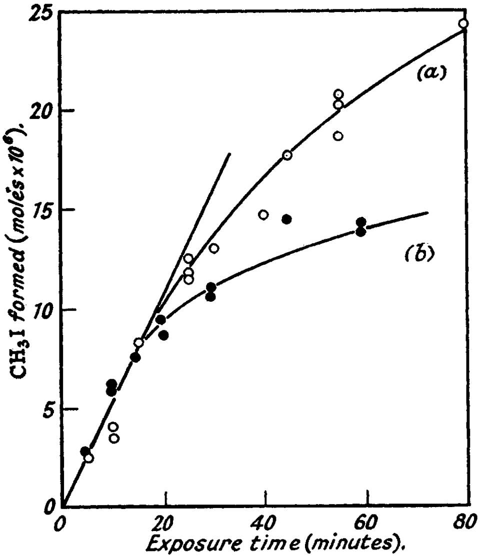


FIG. 2.

Production of CH_3I *with varying exposure time*: (*a*) *at* 120°; (*b*) *at* 200°.



To permit of a calculation of ethane production in the region of chain reaction, it is necessary to know the rate of methyl-radical formation over a range of pressures, since the aldehyde pressure rapidly diminishes during the course of an experiment. A series of pressures was therefore selected, and the initial rates of methyl iodide formation determined (Fig. 3). This curve was determined at 200°, and for use at other temperatures the reasonable assumption was made that radical production was independent of temperature. To apply it, aldehyde pressures are first reduced to values at 200°.

The method of calculation of ethane production was as follows. The period of the reaction was divided into a number of short time intervals (such that the change of aldehyde pressure was not more than about 2%), the rate of formation of methyl radicals for the mean pressure of the interval read off from Fig. 3, and the total of methyl radicals produced during the interval obtained in this way. The sum of all these gave the total over the period of the reaction, and half this quantity represented the expected amount of ethane. For short time divisions, the errors of this method cancel, since the rate of formation of methyl radicals is greater at the beginning and less at the end of each interval, than the value for the mean pressure.

FIG. 3.

Initial rates of production of CH_3I *with varying* $CH_3{\cdot}CHO$ *pressure at* 200°.

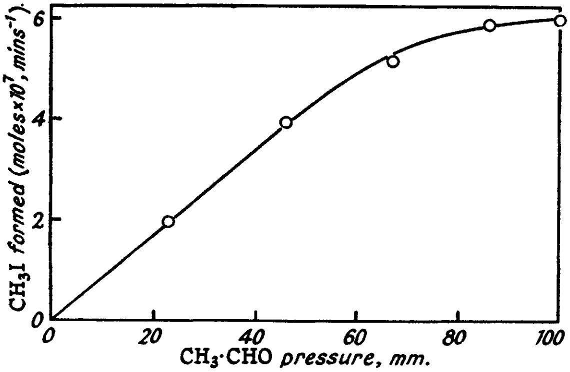


FIG. 4.

Variation in the ratio C_2H_6 *to* CH_4 *with change in* $CH_3{\cdot}CHO$ *pressure. Open circles : from mass-spectrometer analysis. Full circles : calculated from rate of formation of methyl radicals.*

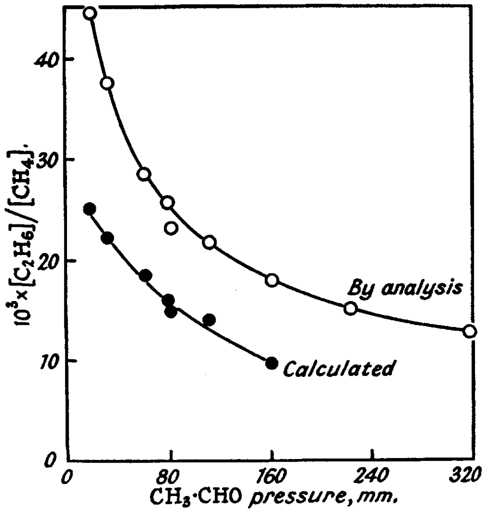
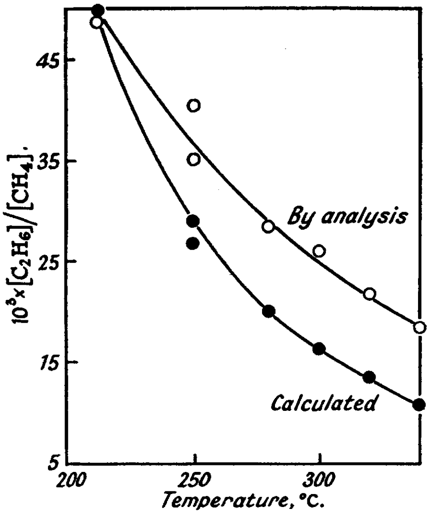


FIG. 5.

Variation in the ratio C_2H_6 *to* CH_4 *with change in temperature. Open circles : from mass-spectrometer analysis. Full circles : calculated from rate of formation of methyl radicals.*



DISCUSSION.

The calculated ratios of ethane to methane in the products are given in the Table, together with the results obtained by the mass-spectrometer analysis. Consideration of the ratio of ethane to methane (col. 3 and Fig. 4) indicates that, as the pressure of aldehyde is increased (at one temperature), the proportion of ethane decreases since the chain length is increased and more methane molecules are produced per methyl radical. The decrease in the proportion of ethane with rising temperature may be explained in the same way, since the chain length is considerably increased on going from 212° to 340°. Further, it will be noted that the calculated ratios of ethane to methane (col. 4 and Figs. 4 and 5) vary in much the same way, suggesting that the formation of ethane takes place by the association of two methyl radicals.

Press. of $CH_3{\cdot}CHO$, mm.	Temp.	Ratio of C_2H_6 to CH_4 in product.		Ratio of actual to calculated C_2H_6.	Ratio of H_2 to C_2H_6 in product.
		Found.	Calc.		
19·4	300°	0·0445	0·0247	1·80	1·20
30·8	300	0·0376	0·0222	1·70	—
61·5	300	0·0286	0·0187	1·53	—
80·0	300	0·0262	0·0161	1·62	—
112·0	300	0·0218	0·0143	1·53	—
161·2	300	0·0182	0·0094	1·94	1·17
224·0	300	0·0150	—	—	—
317·3	300	0·0129	—	—	1·16
81·1	212	0·0487	0·0500	0·98	—
81·3	250	0·0408	0·0298	1·36	—
82·5	250	0·0345	0·0273	1·26	1·11
83·0	280	0·0290	0·0198	1·47	—
82·0	300	0·0227	0·0146	1·55	—
80·0	320	0·0218	0·0136	1·60	—
80·0	340	0·0188	0·0106	1·77	—

Illumination time : 8 minutes.

It is evident, however, that in almost all cases the actual production of ethane is in excess of that calculated from the iodine experiments—the ratio of these quantities varies from 0·98 to 1·94 (col. 5 and Figs. 4 and 5). At about 200°, the actual and calculated amounts of ethane are approximately the same, but as the temperature rises there is a progressive increase in the ratio until at 340° the ethane formed is about 80% in excess of that calculated. This suggests that a proportion (increasing with temperature) of the formyl radicals react to give methyl radicals by a process such as

$$CHO = H + CO \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)^*$$

$$H + CH_3{\cdot}CHO = H_2 + CH_3 + CO \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)^*$$

Each formyl radical yields a molecule of hydrogen by this process. It seems probable that the remainder of the formyl radicals undergo an alternative reaction :

$$CHO = H + CO \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$H + H + (M) = H_2 + (M) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Two formyl radicals are necessary to produce a molecule of hydrogen by the latter mechanism. Analysis for hydrogen showed that, within the limits of accuracy of the analysis, ethane and hydrogen were produced in practically equivalent amounts under a variety of conditions (last col. in table). The simultaneous occurrence of reactions (9) and (10) is quite compatible with this result, since reaction (9), which yields the required extra methyl radicals, also yields additional hydrogen, and it will be found that hydrogen equivalent to ethane is produced whatever the proportion of formyl radicals reacting by the two alternative processes.

Summing up, the reactions occurring in the high-temperature photolysis of acetaldehyde appear to be :

$$CH_3{\cdot}CHO + h\nu = CH_4 + CO \qquad HCO = H + CO$$

$$CH_3{\cdot}CHO + h\nu = CH_3 + CHO \qquad H + CH_3{\cdot}CHO = H_2 + CH_3 + CO$$

$$CH_3 + CH_3{\cdot}CHO = CH_4 + CH_3 + CO \qquad H + H(+M) = H_2(+M)$$

$$2CH_3 = C_2H_6$$

Although these reactions are in accord with the data presented in this paper, it is considered desirable that the investigations be continued at temperatures below 200°, and the results may necessitate modification of the above views.

The author records his appreciation of many helpful discussions with Sir Cyril Hinshelwood, F.R.S., throughout the course of this work, which was carried out whilst on leave from the Chemistry Department, University of Melbourne.

PHYSICAL CHEMISTRY LABORATORY, OXFORD UNIVERSITY. [*Received, January 20th,* 1951.]

---

* Equations are numbered to correspond with those in Part I (*loc. cit.*).