# 328. *The Kinetics of the Photolysis of Acetaldehyde. Part I. The Determination of Ethane and Hydrogen in the Reaction Products by the Use of a Mass Spectrometer.*

By C. J. Danby, A. S. Buchanan, and I. H. S. Henderson.

Ethane and hydrogen have been determined in the products of the high-temperature (300°) photolysis of acetaldehyde by the use of a mass spectrometer. The influence of acetaldehyde pressure and of temperature on their formation has been studied.

The photolysis of acetaldehyde by ultra-violet light at about 300° takes place by a chain process of considerable chain length. It is probable that methyl radicals are the chain-propagating particles and that chain-termination occurs by the recombination of two methyl radicals to form ethane according to the scheme :

$$CH_3{\cdot}CHO + h\nu = CH_4 + CO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$CH_3{\cdot}CHO + h\nu = CH_3{\cdot} + {\cdot}CHO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$CH_3{\cdot} + CH_3{\cdot}CHO = CH_3{\cdot} + CH_4 + CO \quad . \; . \; . \; . \; . \; . \quad (3)$$

$$CH_3{\cdot} + CH_3{\cdot} = C_2H_6 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

(cf. Leermakers, *J. Amer. Chem. Soc.*, 1934, **56**, 1537; Akeroyd and Norrish, *J.*, 1936, 890).

This mechanism does not take into account any subsequent reaction of the formyl radicals produced in reaction (2). Haden and Rice (*J. Chem. Physics*, 1942, **10**, 445) have suggested the following chain reaction :

$${\cdot}CHO + CH_3{\cdot}CHO = CH_4 + CO + {\cdot}CHO \quad . \; . \; . \; . \; . \quad (5)$$

$$CH_3{\cdot} + {\cdot}CHO = CH_3{\cdot}CHO \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

This requires that the formyl radical should be fairly stable at high temperatures.

An alternative process is :

$${\cdot}CHO = H + CO \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

$$H + CH_3{\cdot}CHO = CH_4 + CO + H \quad . \; . \; . \; . \; . \; . \quad (8)$$

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

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

Experiments on the photolysis of methyl iodide (West and Schlesinger, *J. Amer. Chem. Soc.*, 1938, **60**, 961), dimethylmercury (Gomer, *J. Chem. Physics*, 1950, **18**, 998), and acetone (Trotman-Dickenson and Steacie, *ibid.*, p. 1097) have shown that the bimolecular association of two methyl radicals to form ethane occurs readily.

The participation of reaction (4) and of reactions (7)—(10) in the high-temperature photolysis of acetaldehyde can only be established by analysis of the reaction products for ethane and hydrogen. From the known chain length of the reaction, however, the concentrations of ethane and hydrogen to be expected are about 1% of the reaction products. The unambiguous detection of concentrations of this order is hardly practicable by normal methods of gas analysis.

By the use of a mass spectrometer it has now been found possible not only to detect ethane and hydrogen in the products of the photolysis of acetaldehyde at temperatures between 212° and 340° but also to measure the changes in concentration produced by changes in initial aldehyde pressure and temperature.

*The Principles of Gas Analysis by the Use of the Mass Spectrometer.*—Although the general principle of the mass spectrometer is familiar the practical application of the instrument to the analysis of mixtures of organic compounds is perhaps neither obvious nor well known and a short summary will be given here. Organic molecules are dissociated when bombarded by electrons of adequate energy to form a variety of positive ions. In a mass spectrometer these ions are resolved according to their ratio of charge to mass, and their relative abundances determined as deflections of an indicating or recording instrument. In general, the mass spectrum of an organic molecule is fairly complex. In addition to the positive ion corresponding to the undissociated molecule there will also be ions due to fragments produced by the dissociation of the molecule in almost all possible ways. Doubly charged ions may also be present. The relative abundances of these different ions may differ by several powers of ten.

The use of the mass spectrometer for the analysis of mixtures of organic compounds depends on the fact that under carefully controlled conditions the *relative abundance* of the different ions produced by a given molecule remains constant. This pattern may therefore be used to identify the molecule. At the same time the *absolute abundance* of the ions is proportional to the partial pressure of the substance in the ionisation chamber of the instrument. Both the mass spectrum and the relation between ion abundance and partial pressure (the " sensitivity ") have to be determined empirically for each possible component of a mixture by separate experiments with pure samples.

The mass spectrum of a mixture is the sum of the spectra of the constituents, each multiplied by the sensitivity for that constituent and by its partial pressure. These mass spectra will inevitably overlap, *i.e.*, ions of the same mass will appear in the spectra of many of the components. The observed abundance at many mass numbers in the spectrum of the mixture will hence be the sum of contributions from a number of constituents.

There are several ways in which the composition of the mixture may be calculated from the data of the mass spectrometer. In general, we obtained a set of linear simultaneous equations of the form :

$$\begin{aligned} a_p k_a + b_p k_b + c_p k_c + \ldots &= m_p \\ a_q k_a + b_q k_b + c_q k_c + \ldots &= m_q \\ a_r k_a + b_r k_b + c_r k_c + \ldots &= m_r \\ \text{etc.} & \end{aligned}$$

where $a_p, a_q, a_r, \ldots$ are the ion abundances at mass numbers $p, q, r, \ldots$ given by unit partial pressure of substance A; $b_p, b_q, b_r, \ldots$ and $c_p, c_q, c_r, \ldots$ being the corresponding data for for substances B and C. The ion abundances at the same mass numbers given by unit amount of the mixture are $m_p, m_q, m_r, \ldots$. This set of equations must be solved for the coefficients $k_a, k_b, k_c, \ldots$ which are the proportions of A, B, C . . . in the mixture.

With relatively simple mixtures it is sometimes possible to find a mass number in the mixture spectrum which appears in the mass spectrum of only only of the constituents. This greatly simplifies the calculation as the abundance of this ion can be related immediately to the partial pressure of the substance producing it by means of the data of the calibration experiments. This was possible in the present work.

## EXPERIMENTAL.

The acetaldehyde was photolysed in a silica vessel of about 100 ml., having plane windows and kept at the required temperature in a temperature-controlled furnace. It was connected to storage vessels for reagents, manometer, Töpler device for removing samples of the reaction product, and the usual system of pumps. The light source was a 500-w. mercury lamp radiating principally at 3600 A., the output being kept constant by manual control of the current. Acetaldehyde was purified by neutralisation of free acid followed by distillation and storage under nitrogen. Before use it was redistilled *in vacuo*.

Samples of reaction products were passed repeatedly through moist sodium hydrogen sulphite on pumice (which reduced the aldehyde concentration to a value undetectable by the mass spectrometer), dried by solid potassium hydroxide, and transferred to the mass spectrometer in small vessels fitted with a tap and standard ground joint.

A Metropolitan-Vickers mass spectrometer Type M.S.2 was used. This is a Nier-type instrument fitted with a pen recorder. In all experiments an ionising electron energy of 70 ev. was used. The gas samples were measured in terms of pressure in a constant-volume gas pipette of about 3-ml. volume and were then allowed to expand into a 5-l. vessel communicating with the ionisation chamber through a small leak. The temperatures of the gas pipette and the reservoir were measured and corrections applied to allow for any changes.

The pressure of gas in the ionisation chamber is proportional to the rate of flow through the leak and hence to the pressure in the reservoir (the pressure in the ionisation chamber being negligible compared with this). The pressure in the reservoir is determined by the amount of gas admitted to it, hence the pressure of the gas sample in the gas pipette may be taken as a measure of the pressure in the ionisation chamber.

The amount of gas taken for an analysis is less than 0·5 ml. at N.T.P. and of this only about 1% is actually consumed.

## ANALYTICAL PROCEDURE.

Although the mass spectrum of a molecule and the sensitivity are, in principle, constant under controlled conditions, these conditions are not yet attainable in practice. In spite of precautions there are still uncontrolled and largely unknown variables which can cause changes in mass spectra. These phenomena are not faults in the particular instrument used but arise to a greater or lesser extent with all mass spectrometers at the present time. Changes in the *relative* ion abundances given by a substance are usually small and errors from this cause may be practically eliminated by carrying out frequent calibration experiments. More serious are changes in sensitivity which are often large. These changes can be detected and corrections applied by the use of an internal standard reference gas. In the present work neon has been used for this purpose. None of the substances present in the acetaldehyde photolysis products gives rise to ions of masses 20 or 22. Ions at these mass numbers were therefore unambiguously due to neon. A measured partial pressure of pure neon was added to all gas samples and the recorded neon ion abundances compared with a standard value. The actual sensitivity of the instrument during the tracing of each mass spectrum was thus determined, and the appropriate corrections could be applied to the measured abundances to bring them all to a standard level of sensitivity.

The reaction products of the photolysis consist largely of carbon monoxide and methane, the unchanged acetaldehyde having been removed chemically. The relative abundances of the more important positive ions in the mass spectra of the possible constituents are given in Table I.

TABLE I.

*Mass spectra of possible constituents of the reaction products.*

Relative positive ion abundances.

| Mass no. | $CH_3\cdot CHO$. | $C_2H_6$. | $CH_4$. | CO. | Mass no. | $CH_3\cdot CHO$. | $C_2H_6$. | $CH_4$. | CO. |
|---|---|---|---|---|---|---|---|---|---|
| 12 | 1·5 | 0·6 | 1·3 | 1·2 | 27 | 5·9 | 108·6 | — | — |
| 13 | 6·9 | 1·5 | 4·1 | — | 28 | 7·1 | 360·0 | — | 100·0 |
| 14 | 20·2 | 7·0 | 9·5 | — | 29 | 156·0 | 83·5 | — | 1·2 ($^{13}C^{16}O$) |
| 15 | 59·3 | 9·7 | 79·5 | — | 30 | 1·8 | 100·0 | — | 0·2 ($^{12}C^{18}O$) |
| 16 | 8·6 | — | 100·0 | 0·3 | 42 | 16·1 | — | — | — |
| 25 | 5·1 | 11·0 | — | — | 43 | 57·3 | — | — | — |
| 26 | 10·5 | 72·5 | — | — | 44 | 100·0 | — | — | — |

In this table the ions corresponding to the undissociated molecules have been taken as having an abundance of 100·0. Only the more abundant ions have been included.

From this Table it is evident that it is not practicable to use the abundance of the $C_2H_4^+$ ion to determine small amounts of ethane in the reaction products because carbon monoxide, which is present in very large amount, gives an ion of the same mass ($CO^+$). The same is true to a lesser extent with masses 29 and 30 where there are contributions from carbon monoxide ions containing the heavy isotopes of carbon and oxygen. Ethane was therefore determined from the abundance of the ion of mass 27 which appears in the ethane spectrum only. The contribution of ethane at mass 15 was then calculated and subtracted from the observed abundance at this mass, leaving the contribution due to methane, from which the methane pressure was calculated.

Hydrogen was estimated from the mass 2 ion abundance. With the positive ion beam focussing potentials set at the optimum values for ions of masses between 12 and 50 the sensitivity of the instrument at mass 2 is small. The precision of the estimation of hydrogen is therefore considerably less than that for ethane.

## RESULTS.

Table II gives the analytical results for a series of reaction product samples obtained by varying the initial aldehyde pressure at a constant temperature (300°). Table III gives the corresponding results for the photolysis of the same initial pressure of aldehyde at different temperatures.

Duplicate analyses were made on two of the reaction product samples after a lapse of several days during which the ion source of the mass spectrometer was dismantled and a new filament fitted. These analyses (which are shown in Table II) show that the estimation of ethane when present to the extent of 0·5—1% is reproducible to about 1·5% of this value.

Blacet (*J. Phys. Chem.*, 1948, **52**, 540), using a mass spectrometer, was unable to detect ethane in the products of the low-temperature acetaldehyde photolysis. The results in

Table II show that the proportion of ethane is increasing with decreasing temperature down to about 200°. It would appear that either a different mechanism of reaction is predominant at lower temperatures, or that the previous analytical work was not sufficiently sensitive to detect the ethane.

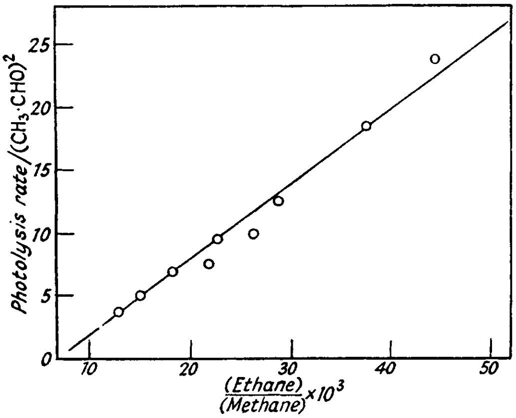

TABLE II.

*Experiments with variable aldehyde pressure at* 300°.

| Initial $CH_3{\cdot}CHO$ pressure, mm. | Initial photolysis rate. | Ethane in total product, moles %. | Moles (%) in product free from $CH_3{\cdot}CHO$. Ethane. | Hydrogen. | Ratio, $\frac{[C_2H_6]}{[CH_4]} \times 10^2$. |
|---|---|---|---|---|---|
| 19·4 | 0·90 | 1·05 | 2·15 | 2·58 | 4·45 |
| 30·8 | 1·75 | 0·96 | 1·83 | — | 3·76 |
| 61·6 | 4·62 | 0·82 | 1·40 | — | 2·86 |
| 80·0 | 6·45 | 0·79 | 1·28 | — | 2·62 |
| 112·0 | 9·20 | 0·67 | 1·07 | — | 2·18 |
| 161·2 | 17·8 | 0·62, 0·63 | 0·90, 0·91 | 1·05 | 1·82 |
| 224·0 | 25·0 | 0·51 | 0·74 | — | 1·50 |
| 317·3 | 38·8 | 0·50, 0·51 | 0·60, 0·61 | 0·70 | 1·29 |

TABLE III.

*Experiments with constant aldehyde pressure at different temperatures.*

| Initial $CH_3{\cdot}CHO$ pressure, mm. | Temp. | Ethane in total product, moles %. | Moles (%) in product free from $CH_3{\cdot}CHO$. Ethane. | Hydrogen. |
|---|---|---|---|---|
| 81·1 | 212° | 0·65 | 2·32 | — |
| 81·3 | 250 | 0·86 | 1·97 | — |
| 82·5 | 250 | 0·74 | 1·63 | 1·81 |
| 83·0 | 280 | 0·76 | 1·42 | — |
| 82·0 | 300 | 0·70 | 1·11 | — |
| 80·0 | 320 | 0·71 | 1·07 | — |
| 80·0 | 340 | 0·68 | 0·93 | — |

If we neglect the aldehyde decomposed in the primary process compared with that reacting by the chain propagation reaction we may write :

$$d[CH_3{\cdot}CHO]/dt = \rho = k_3[CH_3][CH_3{\cdot}CHO]$$

$$[CH_3] = \rho/k_3[CH_3{\cdot}CHO]$$

$$d[C_2H_6]/dt = k_4[CH_3]^2 = k_4\rho^2/k_3^2[CH_3{\cdot}CHO]$$

$$d[CH_4]/dt = \rho$$

Hence

$$\frac{d[C_2H_6]/dt}{d[CH_4]/dt} = \frac{k_4\,\rho}{k_3^2[CH_3{\cdot}CHO]^2}$$

Or, for an early stage of the reaction :

$$[C_4H_6]/[CH_4] \propto \rho/[CH_3{\cdot}CHO]^2$$

The figure shows that this relation is approximately obeyed by the analytical results in Table II. Better agreement would not be expected as the relation only applies strictly to initial rates and concentrations while the analytical data are mean values over appreciable time intervals.

The presence, in the reaction products, of amounts of hydrogen comparable with those of the ethane suggests that reactions of the formyl radical such as reactions (7)—(10) may play an appreciable part. This will be discussed in a subsequent paper.

The mass spectrometer used in this work was provided by the Department of Scientific and Industrial Research to whom we are indebted.

We should like to express our thanks to Professor Sir Cyril Hinshelwood for his help and interest.

PHYSICAL CHEMISTRY LABORATORY, OXFORD UNIVERSITY. [*Received, January* 17*th*, 1951.]