A Novel Reaction of Hydrogen Atoms

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MOST of the reactions[1] of H atoms with saturated organic molecules appear to take place *via* an initial hydrogen abstraction of the type

$$H + RH = H_2 + R.$$

The reaction with acetaldehyde has not been investigated fully, although various products have been suggested in connection with certain overall mechanisms.[2] This reaction has therefore been studied mass spectrometrically at room temperature and at 2·38 mm. Hg, in a microwave discharge–flow system.[3] The major products were methane (identified by its fragmentation at m/e = 14, 15, 16) and carbon monoxide in approximately equal amounts, together with a substance yielding m/e = 43 ions. Minor products were glyoxal and formaldehyde (identified by their 56/68 and 29/30 fragmentations, respectively) and a small amount of a substance yielding ions at m/e = 86. The formation curves for all these products, with the exception of the last, are shown in Figures 1 and 2.

Methane formation was strictly first-order in acetaldehyde, and it is clear from Figure 1 that the reaction forming CO is distinct from that which leads to CH_4. It is suggested that the main course of the reaction is

$$H + CH_3{\cdot}CHO = CH_4 + CHO \qquad (1)$$

$$CHO + CH_3{\cdot}CHO = CO + H_2 + CH_2{\cdot}CHO \qquad (2)$$

Reaction (1) probably occurs by a Walden-inversion type process, as this would presumably involve the transition state of lowest energy. It is noteworthy that Steacie and Philips[4] obtained evidence that the corresponding reaction with ethane occurred rapidly at room temperature. A reaction similar to (2), but leading to the formation of acetyl radicals, has been suggested by Blacet and Blaedel.[5] However, recent work in this laboratory[6] using $CH_3{\cdot}CDO$ has shown that the reaction of formyl radicals with acetaldehyde leads almost exclusively to removal of the methyl hydrogen, and that the competing reaction

$$CHO + CH_3{\cdot}CHO = CO + H_2 + CH_3{\cdot}CO \qquad (3)$$

is only of minor importance.

This sequence also explains the ion at m/e = 43 which is identified as originating from $CH_2{\cdot}CHO$. Electron delocalisation in this radical ($\dot{C}H_2CH{=}O \longleftrightarrow CH_2{=}CH\dot{O}$) would account for the relatively low reactivity which it must possess in order to have been detected with the present apparatus. Further evidence for the low reactivity of $CH_2{\cdot}CHO$ with respect to recombination is provided by the complete absence of succinaldehyde from the products; this substance gives an ion of high abundance at m/e = 18. The small increment at m/e = 86 may have been due to acetoacetaldehyde formed by

$$CH_3{\cdot}CO + CH_2{\cdot}CO = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CHO$$

Hydrogen formation could not be studied due to the large amount of H_2 carrier gas in this system.

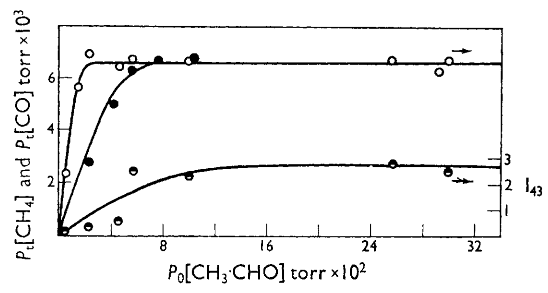

FIGURE 1. *Partial pressure of* CH_4(○) *and* CO(●) *and also ion beam intensity due to product at* m/e = 43 (◓) *for a particular residence time* (0·079 sec.) *as a function of the initial acetaldehyde partial pressure; Pressure of hydrogen* = 2·36 torr.

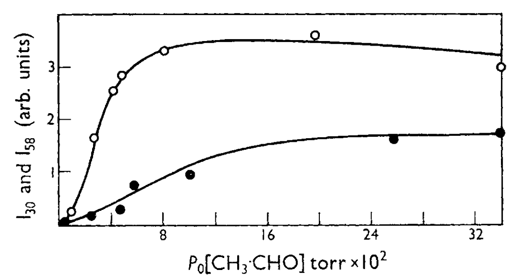

FIGURE 2. *Ion beam intensities for* m/e = 30 (formaldehyde, ○) *and* m/e = 58 (glyoxal, ●) *as a function of initial acetaldehyde partial pressure. The intensity units have been normalised so that the graphs represent truly the relative amounts of the two substances. Residence time*: 0·079 sec.; *Pressure of hydrogen* 2·36 torr.

Glyoxal formation may be explained by the reaction

$$CHO + CHO + M = (CHO)_2 + M \qquad (4)$$

but it has been shown[6] that the reaction

$$CHO + CHO = CH_2O + CO$$

is not a source of formaldehyde in this kind of system. This product probably arises by

$$H + CHO + M = CH_2O + M \qquad (5)$$

The combined yields of glyoxal and formaldehyde were never greater than about 0·1% of the methane formed.

An estimate was made of the rate constant of (1) k_1, by measuring the amount of methane formed after a known reaction time. The mean of ten such experiments carried out under varying conditions was

$$k_1 = 5{\cdot}2 \pm 1{\cdot}2 \times 10^{10}\ \text{mole}^{-1}\text{cm.}^3\text{sec.}^{-1} \text{ at } 297^\circ\text{K}.$$

However, this result involves some uncertainty since the calculation requires a knowledge of the initial H-atom concentration. For this purpose it was assumed that the limiting CH_4 yield, produced by addition of a large excess of acetaldehyde, was equivalent to the initial atom concentration at the point of injection of the organic compound.

In order to obtain some idea of the usefulness of this scavenging method for the estimation of hydrogen atoms, it was employed to study the homogeneous recombination of H, a reaction whose rate constant is known.[7] Apparent atom concentrations were measured at different points along the reactor over a tenfold range of pressure. The resulting third-order rate constants for the reaction:

$$H + H + H_2 = H_2 + H_2$$

showed that the methane yield under these conditions was not a good measure of atom concentration, but underestimated it by a factor of about two. This effect is probably due to concurrent removal of H by reactions other than that leading to CH_4. Thus it is possible that CHO radicals catalyse the recombination of H, in a manner entirely analogous to the NO catalysis, by reaction (5) followed by

$$CH_2O + H = H_2 + CHO \qquad (6)$$

In addition, the reaction

$$H + CH_2{\cdot}CHO = CH_3{\cdot}CHO \qquad (7)$$

might also be expected to remove hydrogen atoms. Some evidence for the occurrence of (7) comes from the observation that the yield of $CH_2{\cdot}CHO$ is considerably less than would be expected in the absence of this reaction.[6] Because of the error introduced by these competing reactions, the value for k_1 given above may be too large by a factor of three or four.

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