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Rate of Hydration of Formaldehyde in Aqueous Solution

By H. C. SUTTON* and T. M. DOWNES

(*Institute of Nuclear Sciences, Department of Scientific and Industrial Research, Lower Hutt, New Zealand*)

Summary Formaldehyde is produced during electron irradiation of aqueous solutions of methanol containing oxygen; the rate of its hydration to methylene glycol has been measured by use of a flow system.

FORMALDEHYDE is hydrated in aqueous solution as in the equilibrium reaction (1). Measurements of the equilibrium

$$HCHO + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_2(OH)_2 \qquad (1)$$

constant $[HCHO]/[CH_2(OH)_2]$ present some difficulty but the value $4{\cdot}4 \times 10^{-4}$ observed at 20 °C[1] is thought to be the most reliable.[2] Bell and Evans have shown that these equilibrated solutions react with excess of aqueous semicarbazide to form semicarbazone in a slow first-order reaction in which the rate-determining step is the dehydration reaction (-1).[2] Evidently formaldehyde (HCHO) reacts rapidly with semicarbazide whilst methylene glycol $[CH_2(OH)_2]$ does not. We have used this criterion to show that some of the formaldehyde produced by the radiolysis of aqueous solutions of methanol containing dissolved oxygen is initially in the unhydrated form, and hence to measure its rate of hydration to methylene glycol.

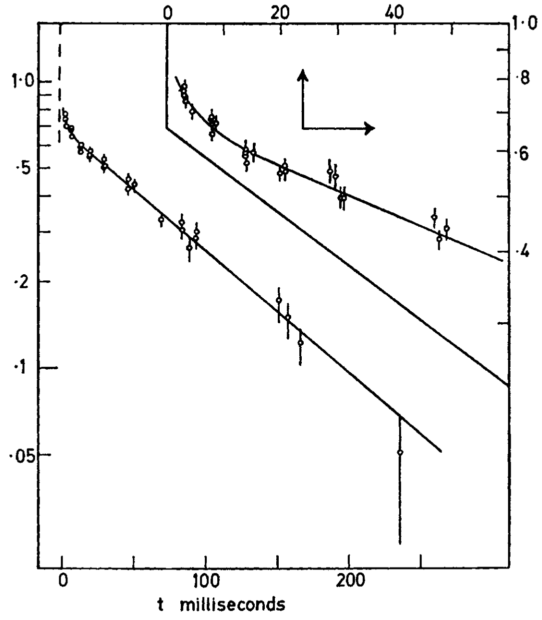

FIGURE *Variation of the fraction* f, *of formaldehyde which reacts immediately with semicarbazide solution with the time,* t, *which elapses between its formation and mixing with this reagent*

Solutions of semicarbazide hydrochloride (2×10^{-3}M) were mixed, in a flow system, with methanol solutions (1×10^{-2}M) saturated with a 4:1 mixture of nitrous oxide and oxygen at time t ms after the methanol had been irradiated with a beam of 2 MeV electrons passing through a defining slit. It was found that semicarbazone was produced from the formaldehyde so formed in two stages. One portion was formed in the slow first-order reaction described by Bell and Evans and is due to formaldehyde formed initially as methylene glycol or hydrated to this form before mixing with semicarbazide. The reaction has a half-life of 2·6 min ($k_{-1} = 4{\cdot}4 \times 10^{-3}\ s^{-1}$) at 22° at pH 4 which agrees with Bell and Evans' measurement of $5{\cdot}2 \times 10^{-3}\ s^{-1}$ at 25° in dilute uncatalysed solutions allowing for the reported activation energy of *ca.* 14·8 kcal mol^{-1}.[3] The remaining portion was formed immediately on mixing with semicarbazide and is due to unhydrated formaldehyde. By extrapolating measurements of the slow reaction to zero time (the first measurement was after 1—1·5 min) the fraction, f, of the total formaldehyde yield which occurred in the fast reacting unhydrated form at the time of mixing with semicarbazide was measured (Figure). The results were independent of (*a*) semicarbazide concentration in the range $0{\cdot}5$—$8 \times 10^{-3}\mathrm{M}$, (*b*) the total formaldehyde concentration produced by irradiation in the range 8—$40 \times 10^{-6}\mathrm{M}$, and (*c*) the pH of the irradiated methanol solution in the range 7—9. Evidently for $t > 20$ ms f diminishes exponentially with a half-life of 70 ± 6 ms. Temperature could not be controlled during irradiation and mixing but was in the range 20—25 °C.

We conclude (*a*) that at least half the formaldehyde produced in this way is initially in the unhydrated form and (*b*) that it hydrolyses in water as in reaction (1) with a half-life of 70 ms, ($k_1 = 9{\cdot}8\ \mathrm{s}^{-1}$) The equilibrium constant $[\mathrm{HCHO}]/[\mathrm{CH_2(OH)_2}] = k_{-1}/k_1 = 4{\cdot}5 \times 10^{-4}$ at 22 °C in agreement with the value mentioned above at 20 °C. So far as we know this is the first direct measurement of k_1.

The initial curvature of the line in the Figure is shown as an insert for greater clarity and indicates the presence of a second short-lived species which decomposes in < 20 ms. This either reacts directly with semicarbazide or is the precursor of an additional yield of formaldehyde in excess of that corresponding to the straight line.

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[3] P. L. Henaff, *Compte rend.*, 1963, **256**, 1752.