The Rate of the Reaction between Hydrogen Atoms and Ethylene

By J. M. BROWN, P. B. COATES, and B. A. THRUSH
(*Department of Physical Chemistry, University of Cambridge*)

THERE have been several studies of the relative rates of hydrogen atom addition to olefins.[1] The absolute rate constants are less easily determined,[2] and estimates for the reaction $H + C_2H_4$ vary between 10^{10} and 10^{12} cm.^{3} mole^{-1} sec.$^{-1}$.

We have used electron spin resonance to measure the rate of removal of hydrogen atoms by ethylene in a discharge-flow system. The reaction was first order in atomic hydrogen over at least three half-lives and its rate was independent of total pressure over the range 1·6—3·1 mm. Hg. The measured rate constant for hydrogen atom removal was $k_{obs} = (3{\cdot}07 \pm 0{\cdot}15) \times 10^{11}$ cm.^{3} mole^{-1} sec.$^{-1}$ at 298°K. The absence of a pressure-dependence is not surprising, since analytical studies of the reaction[3,4] show that the pressures used in our work would give rate constants close to the limiting second-order value.

To obtain a value of k_1 from the rate constant

$$H + C_2H_4 = C_2H_5 \qquad (1)$$

for hydrogen atom removal, the overall stoicheiometry of the reaction must be known. Experiments at low ethylene concentrations showed that at least three hydrogen atoms are removed per ethylene molecule. This contrasts with conventional photochemical studies at high pressures where ethyl radicals are removed by mutual combination and disproportionation,[5] and giving $k_{obs} = k_1$ and 0·88 ethylene molecules removed per hydrogen atom reacted.

In our experiments, where the initial concentrations are $[Ar] \gg [H] > [C_2H_4]$, ethyl radicals are removed mainly by reaction (2), since $k_2 \gg k_1$ (ref. 5) and the steady-state concentration

$$H + C_2H_5 \rightarrow C_2H_6^* \rightarrow CH_3 + CH_3 \qquad (2)$$

of ethyl radicals is therefore very much lower than that of hydrogen atoms. In the presence of an excess of hydrogen atoms, methyl radicals will yield methane by reaction (3) rather than ethane by reaction (4).

$$CH_3 + H\ (+M) = CH_4\ (+M) \qquad (3)$$

$$CH_3 + CH_3\ (+M) = C_2H_6\ (+M) \qquad (4)$$

This mechanism is supported by Toby and Schiff's analytical studies[6] of the reaction of deuterium atoms with ethylene in an argon carrier under conditions almost identical with ours. For the lowest ethylene pressures used in our work ($[H]_0 > 5\ [C_2H_4]_0$), methane was virtually the sole product, giving $k_{obs} = 4\ k_1$ and the stoicheiometry $\Delta[H] = 4\Delta[C_2H_4]$. At our highest ethylene pressures they found 40% of ethane, [^{2}H]ethylenes, C_3 and C_4 hydrocarbons giving $k_{obs} = 3{\cdot}2\ k_1$ and $\Delta[H] = 3{\cdot}6\,\Delta[C_2H_4]$. Their data agree well with our observation that $\Delta[H] > 3\Delta[C_2H_4]$, and taking $k_{obs} = (3{\cdot}5 \pm 0{\cdot}5)k_1$ we obtain $k_1 = (8{\cdot}8 \pm 1{\cdot}6) \times 10^{10}$ cm.^{3} mole^{-1} sec.$^{-1}$ at 298°K.

Toby and Schiff found that the ratio of methane to ethane increased with total pressure. This indicates that reaction (3) is in its pressure-dependent region and that ethane is formed mainly in reaction (4) which competes with (3) for methyl radicals. Significant stabilisation of the excited ethane which is an intermediate in reaction (2) would decrease the methane to ethane ratio at higher pressures. Such a process should not be important since H + C_2H_5 yields excited ethane with 13 kcal./mole more energy than does CH_3 + CH_3. On this basis, our value of k_1 and published values of k_4 can be used to estimate k_3. The values obtained from their product analyses[6] are 2 × 10^{12} or 4 × 10^{12} cm.^{3} mole^{-1} sec.$^{-1}$ for an argon carrier at 1·3 mm. pressure, depending on whether k_4 is taken to be 5·5 × 10^{12} cm.^{3} mole^{-1} sec.$^{-1}$ on the basis of the pressure- and temperature-dependences found by Ingold, Henderson, and Lossing,[7] or the normal second-order limiting value[8] of $k_4 = 2{\cdot}2 \times 10^{13}$ cm.^{3} mole^{-1} sec.$^{-1}$.

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[1] R. J. Cvetanović, *Adv. Photochem.*, 1963, **1**, 115.
[2] B. A. Thrush, *Progr. Reaction Kinetics*, 1965, **3**, 63.
[3] B. S. Rabinowitch, D. H. Dills, W. H. McLain, and J. H. Current, *J. Chem. Phys.*, 1960, **32**, 493.
[4] C. A. Heller and A. S. Gordon, *J. Chem. Phys.*, 1962, **36**, 2648.
[5] A. H. Turner and R. J. Cvetanović, *Canad. J. Chem.*, 1959, **37**, 1075.
[6] S. Toby and H. I. Schiff, *Canad. J. Chem.*, 1955, **34**, 1061.
[7] K. U. Ingold, I. H. Henderson, and F. P. Lossing, *J. Chem. Phys.*, 1953, **21**, 1135, 2239.
[8] A. Shepp, *J. Chem. Phys.*, 1956, **24**, 939.