Rate of Recombination of Ethyl Radicals in the Gas Phase

By R. M. Marshall* and J. H. Purnell
(*Department of Chemistry, University College of Swansea, Swansea* SA2 8PP)

Summary Recent experimental measurements of the rate constant, k_1, of ethyl radical recombination which yield $k_1 = 10^{11.6}$ cm^3 mol^{-1} s^{-1}, are confirmed by analysis of literature data for some reactions involving ethyl.

The rate constant for the mutual recombination of ethyl radicals has long been assumed to be $k_1 = 10^{13.3}$ cm^3 mol^{-1} s^{-1} and to be temperature independent. This value,

$$2C_2H_5 \rightleftharpoons n\text{-}C_4H_{10} \qquad (1, -1)$$

measured by the difficult sector technique,[1] is identical with the value for the corresponding reaction of methyl and this has buttressed the commonly held view that most, if not all, alkyl radicals mutually recombine with a rate constant of about this magnitude.

However, two recent determinations by techniques different from each other and from the above suggest a much lower value for k_1. Hiatt and Benson,[2] using a new experimental technique, in the temperature range 350—410 K, have measured $k_1 = 10^{11.6}$ cm^3 mol^{-1} s^{-1}, with zero activation energy. We have measured[3] the initiation rate of n-butane pyrolysis at 951 K and hence k_{-1}, which, *via* a thermochemical calculation of the equilibrium constant, K_1, leads to $k_1 = 10^{11.5}$ cm^3 mol^{-1} s^{-1}, in agreement with the determination of Hiatt and Benson.

It is important that we decide whether the 'high' or the 'low' value of k_1 is the more reliable not only because of its intrinsic interest but also because most absolute values of rate constants, k, quoted in the literature for reactions of ethyl have been evaluated from measurements of $k/k_1^{\frac{1}{2}}$ using the assumed 'high' value for k_1. We show here that data are at present available which make such a decision possible.

Consider the reactions (2) and (−2). The most recent

$$C_2H_5 + H_2 \rightleftharpoons C_2H_6 + H \qquad (2, -2)$$

and comprehensive experimental determinations, at temperatures around 550 K, give[4] $k_{-2} = 10^{14.0} \exp(-9300 \text{ cal mol}^{-1}/RT)$ cm^3 mol^{-1} s^{-1} and [5] $k_2/k_1^{\frac{1}{2}} = 10^{6.0} \exp(-13700 \text{ cal mol}^{-1}/RT)$ cm$^{3/2}$ mol$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$.

The equilibrium constant at 550 K, K_2, may be calculated from the values $\Delta H_2 = 5900$ cal mol^{-1} and $\Delta S_2 = -8{\cdot}6$ cal mol^{-1} K^{-1}, derived using the data of Benson *et al.*[6] and standard A.P.I. values.[7]

Combination of the experimental k_{-2} and the calculated K_2 leads to $k_2 = 10^{12.1} \exp(-15{,}200 \text{ cal mol}^{-1}/RT)$ cm^3 mol^{-1} s^{-1} and hence, using the experimental $k_2/k_1^{\frac{1}{2}}$, we estimate $k_1 = 10^{12.2} \exp(-3000 \text{ cal mol}^{-1}/RT)$ cm^3 mol^{-1} s^{-1}. From consideration of the possible errors both in the thermochemistry and in the experimental Arrhenius parameters (though not in the measured rates), we conclude that these calculated Arrhenius parameters for k_1 are not reliable and, in particular, that the activation energy is not significantly different from zero. However, the absolute value of k_1 derived for 550 K should be reliable within the error limits placed upon it by the thermochemistry. We therefore conclude $k_1 = ca.\ 10^{11.0}$ cm^3 mol^{-1} s^{-1} at 550 K.

A similar calculation based on reactions (3) and (−3) provides another independent estimate of k_1. Experimentally, it is found that k_3 and k_{-3} are pressure dependent

$$C_2H_5 \rightleftharpoons C_2H_4 + H \qquad (3, -3)$$

at low pressures. While there have been numerous extrapolated estimates of k^{∞}_{-3}, the most reliable value based on experiments at high pressure is $k^{\infty}_{-3} = 10^{11.9}$ cm^3 mol^{-1} s^{-1} at 298 K.[8] The best available data[9] relating k_3 with k_1 at high pressure give $k^{\infty}_{3}/k_1^{\frac{1}{2}} = 10^{7.8} \exp(-40{,}900$ cal mol$^{-1}/RT)$ cm$^{-3/2}$ mol$^{\frac{1}{2}}$ s$^{-\frac{1}{2}}$ in the range 670—770 K. Although, unfortunately E_{-3} was not measured in these studies, and, moreover, there spective temperature ranges of the measurements of $k^{\infty}_{3}/k_1^{\frac{1}{2}}$ and k^{∞}_{-3} do not overlap, we may use calculated thermochemical quantities for 500 K (approximately midway between the two experimentally used ranges) to estimate a value for E_{-3}. We calculate for 500 K that $\Delta H_3 = 39{,}500$ cal mol^{-1} and $\Delta S_3 = 1{\cdot}3$ cal mol^{-1} K^{-1} (standard state; 1 mol cm^{-3}). Thus, assuming $E_1 = 0$ and $E_3 = 40{,}900$ cal mol^{-1}, $E_{-3} = 2400$ cal mol^{-1}, in excellent agreement with the experimental estimate,[10] $E_{-3} = ca.$ 1900 cal mol^{-1}. Thus we derive $k^{\infty}_{-3} = 10^{13.7}$ exp$(-2400$ cal mol$^{-1}/RT)$ cm^3 mol^{-1} s^{-1} and hence $k^{\infty}_{3} = 10^{13.5}$ exp$(-40{,}900$ cal mol$^{-1}/RT)$s^{-1}. Finally, we calculate $k_1 = 10^{11.4}$ cm^3 mol^{-1} s^{-1}. The error introduced in calculating ΔH_3 *etc.* at 500 K is likely to be small since ΔH_3 and ΔS_3 change respectively by only 1400 cal mol^{-1} and 1·3 cal mol^{-1} K^{-1} over the entire range 300—700 K and, moreover, their variations are to a large extent, self-cancelling.

Thus, the two calculations above both lead to 'low' values for k_1 in excellent agreement with the two 'low' experimental values. Furthermore, if the 'high' value for k_1 is accepted then it must be concluded that the measured rates of reactions (2) and (3) are incompatible with those of (−2) and (−3), respectively, if the thermochemistry above is correct or alternatively, that the thermochemistry is grossly in error. We feel that neither of these conclusions can be justified and hence that the value $k_1 = 10^{11.4}$ cm^3 mol^{-1} s^{-1} in the temperature range 350—950 K is at present the most reliable estimate of this important rate constant.

This conclusion has important repercussions. First, all values of rate constants for ethyl radical reactions derived comparatively on the assumption of the 'high' value for k_1 are too high by a factor of almost 10 and must therefore be corrected accordingly. Secondly, if $k_1 \neq 10^{13.3}$ cm^3 mol^{-1} s^{-1}, it is most unlikely that the rate constants for other, larger, alkyl radical recombination reactions have the same high value, as is almost invariably assumed. Indeed, there is direct experimental evidence on this matter since Benson and his co-workers have recently found that the rate constants for the recombinations of isopropyl[11] and of t-butyl[12] are $10^{11.6}$ cm^3 mol^{-1} s^{-1} and *ca.* $10^{9.5}$ cm^3 mol^{-1} s^{-1}, respectively. Thus, we conclude that many of the rate constants quoted in the literature for alkyl radical reactions (other than methyl) must be in error on this account and that a reconsideration may serve to introduce a substantial degree of consistency in the field of alkyl radical reactions such as we have here illustrated for ethyl.

(*Received*, 9*th May* 1972; *Com.* 795.)

---

[1] A. Shepp and K. O. Kutschke, *J. Chem. Phys.*, 1957, **26**, 1020.

[2] R. Hiatt and S. W. Benson, *J. Amer. Chem. Soc.*, in the press; 1972, **94**, 25.

[3] P. D. Pacey and J. H. Purnell, *Internat. J. Chem. Kinetics*, in the press.

[4] V. V. Azatyan and S. B. Filippov, *Doklady Akad. Nauk. S.S.S.R.*, 1969, **184**, 625.

[5] L. E. Reid and D. J. LeRoy, *Canad. J. Chem.*, 1968, **46**, 3275.

[6] D. M. Golden and S. W. Benson, *Chem. Rev.*, 1969, **69**, 125; H. E. O'Neal and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 221; S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 229.

[7] A. P. I. 44 Tables, Selected Values of Properties of Hydrocarbons and Related Compounds, Thermodynamics Research Centre, Texas A. and M. University, 1971.

[8] M. J. Kurylo, N. C. Peterson, and W. Braun, *J. Chem. Phys.*, 1970, **53**, 2776.

[9] L. F. Loucks and K. J. Laidler, *Canad. J. Chem.*, 1967, **45**, 2795.

[10] K. Yang, *J. Amer. Chem. Soc.*, 1962, **84**, 719.

[11] R. Hiatt and S. W. Benson, *Internat. J. Chem. Kinetics*, 1972, **4**, 151.

[12] D. F. McMillen, D. M. Golden, and S. W. Benson, Abstracts of the 161st Meeting of the American Chemical Society, Los Angeles March 1971, PHYS 63.