New Technique for Investigation of the Thermochemistry of Free Radicals; the n-Propyl Radical

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Summary A new technique involving the establishment of an equilibrium between two radicals and an olefin is described for the investigation of the thermochemistry of gas-phase free radicals and is exemplified by results for n-propyl which show a discrepancy with presently accepted values.

In recent years, it has become clear that there are serious discrepancies between measured values of the rate constants for recombination of alkyl radicals other than methyl and values calculated from kinetic data using thermochemical parameters (entropies and enthalpies of formation) for the alkyl radicals involved. Because of the relative paucity of directly measured recombination rates and because of the apparent reliability of the thermochemistry it was assumed that, in fact, the directly measured values were in error and that the 'low' values calculated using the currently accepted thermochemistry were the correct values. In this way, values close to $10^{11\cdot6}$ cm^3 mol^{-1} s^{-1} were calculated for the rate constants of mutual recombination of ethyl[1] and of isopropyl,[2] and even lower values were found for the recombination of t-butyl.[3]

Recently, however, new methods have been used to measure directly the rates of recombination of ethyl, isopropyl, and t-butyl and values much higher than the thermochemically calculated ones have been obtained.[4–6] It appears, therefore, that the thermochemical properties of alkyl radicals are not as reliable as at first thought and thus experiments which can provide information about them are of considerable interest.

We report here a new method in which an equilibrium is set up between two alkyl radicals and the relative rates of recombination of the two radicals are measured. Equilibrium (1) is set up, and the recombination reactions (2) and (3) are measured. Thus, the ratio of the measured yields of ethane and n-butane is given by equation (4), always assuming that reactions (1) and (−1) are at true chemical equilibrium and where k_2 is the rate constant for reaction (2) and K_1 the equilibrium constant for reactions (1) and (−1).

$$CH_3 + C_2H_4 \rightleftharpoons n\text{-}C_3H_7 \qquad (1)$$

$$2\,CH_3 \rightarrow C_2H_6 \qquad (2)$$

$$CH_3 + n\text{-}C_3H_7 \rightarrow n\text{-}C_4H_{10} \qquad (3)$$

$$\frac{Y(C_2H_6)}{Y(C_4H_{10})} = \frac{k_2}{k_3}\frac{[CH_3]}{[n\text{-}C_3H_7]} = \frac{k_2}{k_3}\frac{1}{K_1[C_2H_4]} \qquad (4)$$

Briefly, our experiments consist of pyrolysing at *ca* 600—650 K a few Torr of azomethane (a source of methyl) in the presence of a few Torr of ethene, the total pressure being made up to *ca.* 300 Torr with argon. The total pressure was kept high to ensure that reaction (2) was in its high-pressure region. Reaction conditions were chosen so as to minimise the importance of products other than ethane and butane and thus we believe that there are no significant sources of ethane and butane other than reactions (2) and (3), respectively. The Table shows typical results for the function $[C_2H_4]Y(C_2H_6)/Y(C_4H_{10})$ $(=k_2/(k_3K_1))$ as a function of reaction conditions. No time of reaction is quoted since the measured function was shown to be independent of reaction time. Furthermore, the concentration of ethene was essentially constant during any single experiment.

Table. Some experimental values for 620 K

[Azomethane]/Torr	3·55	2·59	2·01	1·71	3·99	3·40
[Ethene]/Torr ..	3·65	2·66	6·77	5·77	1·39	1·18
Total Pressure/Torr	344	250	281	239	298	254
$k_2/(k_3K_1)$/Torr ..	18·4	17·6	16·9	16·3	15·5	14·8

The constancy of the measured values over a fairly wide range of conditions (a factor of 10 variation in the ratio of azomethane to ethene) leads us to believe that we have achieved true chemical equilibrium and that we are measuring $k_2/(k_3K_1)$. A more complete set of results gives a mean value $k_2/(k_3K_1)$/Torr = 16·55 ± 0·72, where the errors are the 95% confidence limits.

It seems likely that $k_2 = k_3$ very nearly, an equality implying, *via* the geometric mean rule, and assuming that k_2/cm^3 mol^{-1} s^{-1} = $10^{13\cdot4}$, that the rate constant for n-propyl recombination is $10^{12\cdot8}$ cm^3 mol^{-1} s^{-1}, a value close to that recently measured for ethyl[4] and for isopropyl.[5] The assumption, $k_2 = k_3$, is probably correct to within better than a factor of two when the quoted error limits for the recombination rate constants of methyl, ethyl, and isopropyl are considered. Thus, making this assumption, we conclude that $K_1 = 0\cdot0604$ Torr^{-1} $\equiv 2\cdot3 \times 10^6$ cm^3 mol^{-1} at 620 K.

Current thermochemistry[7] gives the results for temperatures around 600 K, ΔH_1/kJ mol^{-1} = − 108 and ΔS_1 (standard state 1 mol cm^{-3})/J mol^{-1} K^{-1} = − 39 and hence, K_1/cm^3 mol^{-1} = $1\cdot1 \times 10^7$ at 620 *K*, *i.e.* a factor of five greater than the presently obtained value. This discrepancy implies either a breakdown in the assumption $k_2 = k_3$, which, in the light of recent results seems unlikely, or an error in the thermochemistry of n-propyl. If all the error is assumed to be in the enthalpy, then the enthalpy of formation of n-propyl needs to be raised by *ca.* 8 kJ mol^{-1}. In this context it is of interest to note that the experimental value for the enthalpy of formation of n-propyl due to Knox and Musgrave[8] is *ca.* 8 kJ mol^{-1} higher than the group additivity value used here as the current thermochemistry, although these authors think that their value is too high. Alternatively, the entropy of n-propyl needs to be reduced by *ca.* 13 J mol^{-1} K^{-1}. Of course, some combination of adjustments to the enthalpy and entropy may be necessary. The necessary adjustments to the thermochemistry are being investigated, and details will be given elsewhere.

In conclusion we note that the approach outlined in this communication can be used for any system involving a source of free radicals and an olefin in which the appropriate equilibrium can be set up. It is therefore of quite general application.

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[1] D. G. Hughes, R. M. Marshall, and J. H. Purnell, *J.C.S. Faraday I*, 1974, **70**, 594, and references therein; R. M. Marshall and J. H. Purnell, *J.C.S. Chem. Comm.*, 1972, 764.

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

[3] D. F. McMillen, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 1972, **94**, 4403.

[4] D. M. Golden, K. Y. Choo, M. J. Perona, and L. W. Piszkiewicz, *Internat. J. Chem. Kinetics*, 1976, **8**, 381.

[5] D. M. Golden, L. W. Piskiewicz, M. J. Perona, and P. C. Beadle, *J. Amer. Chem. Soc.*, 1974, **96**, 1645;

[6] D. A. Parkes and C. P. Quinn, *Chem. Phys. Letters*, 1975, **33**, 483.

[7] A.P.I. 44 Tables, Selected Values of Properties of Hydrocarbons and Related Compounds (Thermodynamics Research Centre, Texas A. & M. University, 1971); H. E. O'Neal and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 221.

[8] J. H. Knox and R. G. Musgrave, *Trans. Faraday Soc.*, 1967, **63**, 2201.