Kinetic Data for Coupling of Primary Alkyl Radicals with a Stable Nitroxide

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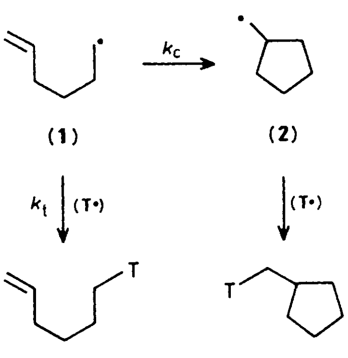
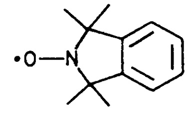
Rate constants and Arrhenius parameters have been determined for coupling of a nitroxide radical with two primary alkyl radicals (**1**) and (**5**).

Coupling of carbon-centred radicals with stable nitroxides has recently been extensively applied to the trapping and identification of radicals formed as intermediates under typical conditions for vinyl polymerisation, or by the reaction of hydroxy, t-butoxy, or other radicals with organic substrates.[1] The utility of the method would be considerably enhanced if the rate constants for coupling with various types of radical were known, because it would then be possible to deduce the rates of competing processes. Although it has sometimes been assumed that such reactions occur under diffusion control, a recent compilation[2] gives values of rate constants at *ca.* 25 °C ranging from 3×10^7 to 8×10^8 $\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$. In order to

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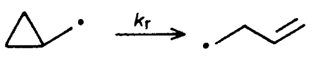

(5) (6)

obtain accurate values over a range of temperatures we have now employed two previously calibrated 'radical clocks'[3] to determine the rate constants for coupling of a cyclic nitroxide ($T^\bullet$)[4] with typical primary radicals.

Accurate kinetic data for the ring closure of hex-5-enyl radical (**1**) to give cyclopentylmethyl radical (**2**) are available.[5] When the former is generated in the presence of the nitroxide ($T^\bullet$), coupling to give the substituted hydroxylamine (**3**) competes with ring closure, the occurrence of which is reflected in the formation of the hydroxylamine derivative (**4**). Steady state analysis shows that when the nitroxide ($T^\bullet$) is in large excess, $k_t/k_c = [(T^\bullet)]^{-1}\cdot\{[(3)]_f/[(4)]_f\}$, where k_t and k_c are the rate constants for trapping by nitroxide and cyclisation respectively, $[(T^\bullet)]$ is the mean concentration of the nitroxide, and $[(3)]_f$ and $[(4)]_f$ are the final concentrations of products.

In a typical experiment,† a solution (6.01×10^{-3} M) of the nitroxide ($T^\bullet$) in cyclohexane containing 3×10^{-4} mmol ml^{-1} of dihept-6-enoyl peroxide was heated at 80 °C for 20 h, then analysed by h.p.l.c. on a reversed phase column with aqueous methanol as elutant. Integration of peaks detected by u.v. absorption at 270 nm gave the relative yields of the products $[(3)]_f:[(4)]_f$ as 4.86:1. The total yield was *ca.* 70%; other products mainly arise by dimerisation and disproportionation within the solvent cage. Application of the integrated rate equation with $[(T^\bullet)] = 6.01 \times 10^{-3}$ M gave the value of k_t/k_c as 809 mol^{-1} dm^3. Each experiment was conducted in triplicate and five different concentrations of the nitroxide ranging from 6.3×10^{-4} to 1.202×10^{-2} M were used. The mean value of k_t/k_c so obtained was 809 ± 23 mol^{-1} dm^3.

Similar experiments were conducted over a range of temperatures. The values of k_t/k_c were: 1450 ± 103 mol^{-1} dm^3 at 50 °C; 1120 ± 104 mol^{-1} dm^3 at 60.1 °C; 630 ± 32 mol^{-1} dm^3 at 99.7 °C; and 541 ± 31 mol^{-1} dm^3 at 111.1 °C. Linear regression of $\log(k_t/k_c)$ against $1/T$ gave a straight line plot (correlation coefficient, 0.994) from which the differences in Arrhenius parameters were obtained: $\log(A_t/A_c) = 0.49 \pm 0.34$ and $E_t - E_c = -3.93 \pm 0.28$ kcal mol^{-1} (1 kcal = 4.184 kJ). Since the parameters for ring closure of the hex-5-enyl radical are[5]‡ $\log A_c = 10.34 \pm 0.32$ and E_c 6.78 ± 0.42 kcal mol^{-1}, those for k_t must be $\log A_t = 10.84 \pm 0.47$ and $E_t = 2.88 \pm 0.57$ kcal mol^{-1}. These give a calculated value of the rate constant, k_t, at 60 °C of 8.9×10^8 mol^{-1} dm^3 s^{-1}.

In a second series of experiments involving bis(cyclopropylacetyl) peroxide (below 80 °C) and t-butyl cyclopropylperacetate (above 80 °C) the competition between ring opening of the cyclopropylmethyl radical (**5**) to give but-3-enyl radical (**6**) and trapping of the former with the nitroxide ($T^\bullet$) was determined. As before the value of k_t/k_r, where k_r is the rate constant for ring opening of the cyclopropylmethyl radical, was found to be independent of concentration. The values of k_t/k_r obtained were: 4.12 mol^{-1} dm^3 at 40 °C; 3.10 mol^{-1} dm^3 at 60 °C; 2.30 mol^{-1} dm^3 at 80 °C; 1.72 mol^{-1} dm^3 at 100 °C; and 1.53 mol^{-1} dm^3 at 120 °C. They give $\log(A_t/A_r) = -1.59 \pm 0.28$ and $E_t - E_r = -3.16 \pm 0.31$ kcal mol^{-1}. These data, when combined with those available[6] for k_r ($\log A_r = 12.48 \pm 1.25$, and $E_r = 5.95 \pm 0.81$ kcal mol^{-1}) give $\log A_t = 10.89 \pm 1.28$, $E_t = 2.79 \pm 0.87$ kcal mol^{-1}, and a calculated value of $k_t = 1.1 \times 10^9$ mol^{-1} dm^3 s^{-1} at 60 °C.

In all of the above calculations we have made no allowance for the amount of nitroxide consumed during the reaction. Since about 30% of the radicals generated from peroxide are consumed in cage processes, the actual mean value of $[(T^\bullet)]$ during the reaction is about 96% of $[(T^\bullet)]_i$, but the resultant correction to the kinetic data would be well within experimental error.

The excellent agreement between the two sets of data strongly suggests that the reactions of the nitroxide ($T^\bullet$) with other unhindered primary alkyl radicals will conform to similar kinetic parameters. Also, since the observed rate constants are very close to those calculated in the usual way[7] for diffusion controlled reactions, it seems likely that they will be relatively insensitive to substituent effects and will therefore be useful as kinetic standards in competition experiments.

Added in proof: Dr K. U. Ingold has recently informed us that the Arrhenius parameters for ring opening of (**5**) may be in error. However, as the kinetic data for cyclisation of (**1**) is considered to be highly reliable we believe our values of k_t to be correct.

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† Satisfactory microanalytical and spectroscopic data were obtained for all new compounds. All of the *o*-alkyl hydroxylamines prepared had $\lambda_{max.}$ at 270 nm ($\log \varepsilon$, 2.92).

‡ Further experimental results have been collected in these laboratories leading to a slight revision of the Arrhenius coefficients presented in ref. 5.