Determination of unimolecular rate data from reaction mid-point temperatures derived from EPR spectra

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The activation energies of unimolecular homolytic reactions (E_r) are predicted to correlate linearly with the mid-point temperatures (T_{mid}) defined as the temperature at which the rearranged and unrearranged species are of equal concentration, for photochemically initiated processes under EPR conditions. A linear relationship (E_r/kcal mol^{-1} = $0.044T_{mid} + 0.22$) has been demonstrated from experimental data and shown to hold for a range of solvents and instrumental configurations. The relationship will facilitate the determination of kinetic parameters, particularly for processes where the spectra of the intermediates are of low intensity.

Introduction

Rate constants for many unimolecular homolytic reactions such as β-scissions, ring closures and group migrations have been determined by steady state EPR spectroscopic techniques.[1,2] These methods rely on photochemical initiation in solution, combined with simultaneous measurements of the concentrations of the unrearranged and rearranged radicals deduced from their individual EPR spectra. Rate constants covering more than seven orders of magnitude from, for example, 59 s^{-1} for the neophyl rearrangement[3,4] to 1.3×10^8 s^{-1} at 298 K for the cyclopropylmethyl to but-3-enyl rearrangement[5] have been obtained with this technique. In several cases the reliability of EPR-derived rate constants and Arrhenius parameters has been confirmed by independent measurements using conventional product analysis methods.[6–8] Due to rapid termination steps, the stationary concentrations of radicals which can be obtained with conventional light sources is usually $10^{-(7\pm1)}$ mol dm^{-3}, which is close to the detection limit of the current generation of EPR spectrometers. Consequently, signal-to-noise ratios are low (often <10), double integration of the spectra, needed for concentration measurements, is rendered problematic and the useful temperature range is therefore narrow (30 ± 10 K). These factors have limited the range of applicability of the method and have made it difficult to extrapolate out reliable Arrhenius pre-exponential factors. This paper describes a simplified way of treating the data which can be used with spectra too weak for accurate integration.

Results and discussion

A variety of photochemical methods have been employed for generation of the unrearranged free radicals $U^\bullet$, which convert to the rearranged species $R^\bullet$ in competition with termination steps, under EPR conditions, see Scheme 1.

$$\begin{gathered}
\text{Precursor} \xrightarrow{h\nu} U^\bullet \\
U^\bullet \xrightarrow{k_r} R^\bullet \\
2U^\bullet \xrightarrow{2k_{UU}} \text{non-radical products} \\
U^\bullet + R^\bullet \xrightarrow{k_{UR}} \text{non-radical products} \\
2R^\bullet \xrightarrow{2k_{RR}} \text{non-radical products}
\end{gathered}$$

Scheme 1

Small transient radicals terminate at about the diffusion-controlled limit, *i.e.* $2k_t$ is independent of the fine details of structure.[2,3] Making this approximation, and assuming steady-state conditions, leads to eqn. (1) and eqn. (2) can be derived from this.

$$d[R^\bullet]/dt = k_r[U^\bullet] - 2k_t[U^\bullet][R^\bullet] - 2k_t[R^\bullet]^2 = 0 \qquad (1)$$

$$k_r/2k_t = [R^\bullet]\{[R^\bullet]/[U^\bullet] + 1\} \qquad (2)$$

The experimental technique usually relies on a series of measurements of $[U^\bullet]$ and $[R^\bullet]$ at different temperatures. The mid-point of the rearrangement may be defined by the temperature (T_{mid}) at which $[U^\bullet]$ and $[R^\bullet]$ become equal. Usually this is about the middle of the temperature range over which $U^\bullet$ and $R^\bullet$ can be observed, but exceptions occur when the two radicals have very different linewidths or multiplicities. Substituting into eqn. (2) gives: $k_r/2k_t = 2[R^\bullet]$ and, on introduction of the Arrhenius functions (A_r, E_r for the rearrangement and $2A_t$, E_t, for the termination) and rearranging, eqn. (3), which will apply at the mid-point, is obtained.

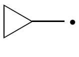
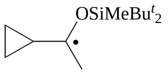
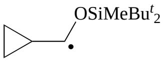
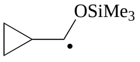
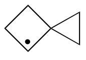
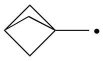
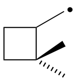
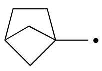
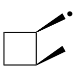
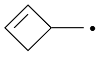
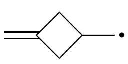
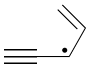
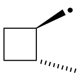
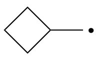
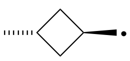
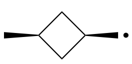
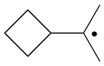
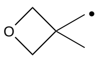
$$E_r = 2.3RT_{mid}\log\{A_r/2[R^\bullet] \times 2A_t\} + E_t \qquad (3)$$

The termination steps are diffusion controlled and hence depend largely on the solvent viscosity. For small transient radicals in the same solvent A_t and E_t should be constant from one rearrangement to another. Many unimolecular reactions, including β-scissions, ring-fissions, group migrations and conformational changes (but not cyclisations) have about the same $\log(A_r/s^{-1})$ value, *i.e.* 13 ± 1. Thus, E_r is predicted to be linearly related to T_{mid} for a substantial range of rearrangements.

A list of Arrhenius parameters, obtained from concentration measurements using eqn. (2), together with the corresponding mid-point temperatures, is given in Table 1 for a set of unimolecular radical rearrangements examined with the St. Andrews' EPR equipment. All were ring fissions, except for one conformational change. Column 3 confirms that to within the large experimental errors (>±1.5) the A_r values are constant. The activation energies span more than 8 kcal mol^{-1} and the temperature mid-points range across nearly 200 K so that these data provide a good test for eqn. (3). Fig. 1 shows that there is a good linear relationship between E_r and T_{mid} as predicted by eqn. (3). Linear regression gave eqn. (4) with a correlation coefficient of $r^2 = 0.977$. Fig. 1 shows data for reactions conducted in *tert*-butylbenzene or cyclopropane together with isolated

$$E_r/\text{kcal mol}^{-1} = T_{mid}(0.0441 \pm 0.0017) + (0.22 \pm 0.38) \qquad (4)$$

Table 1 Arrhenius parameters and EPR mid-point temperatures for unimolecular radical rearrangements

Radical rearrangement	Solvent	log A_r[a]/s^{-1}	E_r[d]/kcal mol^{-1}	T_{mid}/K	Ref.
	*n*-Propane	[13.0]	6.0	130	9
	Cyclopropane	[13.0]	7.2	150	10
	Cyclopropane	[13.0]	6.9	150	10
	Cyclopropane	[13.0]	7.4	155	10
	Cyclopropane	12.5	7.2	160	11
	Cyclopropane	12.3	7.1	170	8
	Cyclopropane	12.4	8.8	205	6
	Bu^{t}Ph	12.0	9.3[b]	210	8
	Bu^{t}Ph	12.4	11.1[b]	235	6
	MePh	12.2	10.2	240	12
	Bu^{t}Ph	12.9	11.5[b]	245	7
 [c]	Isopentane	13.2	11.4	245	13
	Bu^{t}Ph	12.5	11.9[b]	265	6
	MePh	13.0	11.9[b]	280	14
	Bu^{t}Ph	12.6	12.8[b]	290	6
	Bu^{t}Ph	12.7	12.8[b]	290	6
	Bu^{t}Ph	13.6	13.9	300	14
	Bu^{t}Ph	13.5	14.6	320	15

[a] Assumed values are given in brackets. [b] Values confirmed by product ratio kinetics with organotin hydrides. [c] Bond rotation. [d] 1 cal = 4.18 J.

points for a few other solvents. According to eqn. (3) the gradient and intercept of the correlation are related to the Arrhenius parameters of the termination reactions. Because termination is diffusion controlled these parameters will depend on viscosity and are therefore expected to change in different solvents. However, Fig. 1 shows that variations arising from this source lie within the scatter.

An estimate of the gradient can be made from the 'reasonable' values of A_r and [R$^\bullet$] noted above together with $2A_t$, experimental values of which are *ca.* 10^{10} dm^3 mol^{-1} s^{-1} for small radicals in low viscosity solvents.[16] Substituting into the first term on the RHS of eqn. (3) gives 0.049 which is in extremely good agreement with the gradient obtained in eqn. (4). Experimental values of E_t are known to be approximately

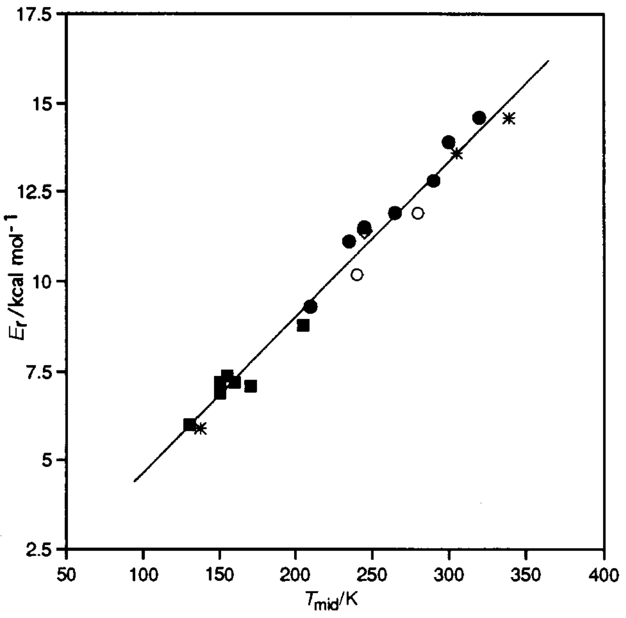


Fig. 1 Correlation of the activation energies of unimolecular reactions (E_r) with their mid-point temperatures as determined by EPR spectroscopy: (■) in cyclopropane or *n*-propane (rows 1–7 of Table 1), (●) in *tert*-butylbenzene, (○) in toluene, (▽) in isopentane, (*) data from the Ottawa laboratory (see text)

equal to the E_η values for each hydrocarbon solvent, which are obtained from Andrade plots of the dynamic viscosities *vs.* reciprocal temperature.[16] The viscosity data for cyclopropane[17] lead to $E_\eta = 0.56$ kcal mol^{-1} which is reasonably close to the 'average' E_t (0.22 kcal mol^{-1}) obtained as the intercept of eqn. (4). Analogous viscosity data for *tert*-butylbenzene is lacking, but other alkylbenzenes all give E_η values close to 3 kcal mol^{-1}, *i.e.* significantly greater than the 'average' E_t. Linear regression analysis of just the set of T_{mid} data for rearrangements in *tert*-butylbenzene yields the same gradient but a slightly larger E_t value of 0.36 kcal mol^{-1} from the intercept. The difference between this and E_η(Bu^{t}Ph) is not much greater than the experimental errors plus the errors inherent in the approximations underlying eqn. (3) and the diffusional control model. A second possible source of scatter lies in the statistical factors of the rearrangements. The data in Table 1 have not been corrected for the fact that some of the ring-fissions have two identical reaction channels and one has three. The main influence of this will be in the A_r values which, as noted above, can rarely be measured accurately enough to reveal effects of this size. It is noteworthy, however, that the ring-fission of the bicyclo-[1.1.1]pentylmethyl radical (row 7), which has three equivalent modes, lies furthest from the correlation line.

Mid-point temperatures of EPR tractable rearrangements can often be estimated by visual inspection of spectra or, where the linewidths or multiplicities of the two species are grossly different, with the aid of computer simulations. The use of eqn. (4) then avoids problematic double integrations, as well as the need for absolute concentration measurements. Activation energies can be obtained much more rapidly even when good quality spectra are available, but the most important benefit will be that Arrhenius data of reasonable quality can still be derived when only very low intensity spectra can be recorded. Eqn. (4) relates to measurements made with the St. Andrews' EPR spectrometer and light train. In general, [R$^\bullet$] will change with the incident light intensity and experimental configuration. Published data from the Ottawa laboratory of Ingold and co-workers for the cyclopropylmethyl ring-opening,[5] for the 1,2-migration of the 3-*tert*-butylphenyl group in the 2-(3-*tert*-butylphenyl)-2,2-dimethylethyl radical,[4] and for migration of the 2-*tert*-butylethynyl group in the corresponding 2,2-dimethylethyl radical,[18] are also plotted in Fig. 1. It is evident that although there are substantial differences in the two experimental set-ups, eqn. (4) still applies and hence may have some general applicability, although universal suitability is not expected. Calibration of individual spectrometers can be simply accomplished by means of observations with a few known unimolecular rearrangements.

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