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The Parabolic Transition State Model and Resultant Nonlinear Correlations for the Kinetics of Free Radical Reactions

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The transition state of a radical reaction may be treated as the point of intersection of two undisturbed potential curves, each of which characterises the energy of vibration of the atom attacked in either the initial molecule or that formed; a series of nonlinear equations of correlation has been derived for the dependence of the activation energy of a free radical abstraction reaction on the heat of reaction, the energy of triplet repulsion and the electronegativities of the atoms.

Analysis of the factors that influence the reactivity of reagents and determine the values of rate constants is important in chemical kinetics. Evans and Polany suggested a linear dependence of activation energy on heat of reaction.[1] Important stages in this study include the Marcus equation,[2] the BEBO method of Johnston[3] and Bell's analysis of this problem in chemistry.[4,5] This communication presents a study of experimental data on the activation energies of free radical reactions using nonlinear equations, derived on the basis of a parabolic model of the transition state.

$$\mathrm{R_f\cdot + H{-}R_i \longrightarrow R_f{-}H + R_i\cdot}$$

In a reaction of this type, the R_i—H bond is being broken and the R_f—H bond is being formed. According to the theory of absolute rates,[6] the reaction may be treated as a translation of the hydrogen atom along the reaction coordinate from an initial position at $x=0$ with potential energy $U_i(0)=0$ to its final position at $x=r_e$ and $U_f(r_e)=\Delta_i H_e$, where $\Delta_i H_e$ is the reaction enthalpy, with zero energies taken into account, so $\Delta_i H_e = U_f(r_e) - U_i(0) = D_{ei} - D_{ef}$; $D_{ei} = D_i + 0.5h\nu_i L$ and $D_{ef} = D_f + 0.5h\nu_f L$, where D_i and D_f are the dissociation energies of the R_i—H and R_f—H bonds, ν_i and ν_f are their vibration frequencies, h is Planck's constant and L is Avogadro's number. Let us consider the vibration of atoms along the R_i—H and R_f—H bonds to be harmonic, so that $U_i^{1/2} = b_i x$ and $U_f^{1/2} = b_f(r_e - x)$, $b_i = \pi\nu_i(2\mu_i)^{1/2}$, $b_f = \pi\nu_f(2\mu_f)^{1/2}$, where μ_i and μ_f are the reduced masses of the atoms. The transition state is proposed to be represented by the point of intersection of two undisturbed potential curves at $x = r^{\ddagger}$, when $E_{ei} = U_i(r^{\ddagger}) = U_f(r_e - r^{\ddagger}) - \Delta_i H_e$. The activation energy E_{ei} is related to the observed E_i by the equation $E_{ei} = E_i + 0.5(h\nu_i L - RT)$.

The important characteristic of the transition state is the distance r_e, which may be estimated in the form $b_i r_e$ using eqn. (1), where $\alpha = b_i/b_f = \nu_i \nu_f^{-1}(\mu_i/\mu_f)^{1/2}$.

$$b_i r_e = \alpha(E_{ei} - \Delta_i H_e)^{1/2} + E_{ei}^{1/2} \tag{1}$$

The activation energy of the thermoneutral reaction in the given series may be calculated using eqn. (2),

$$E_{eo} = (b_i r_e)_0^2 (1+\alpha)^{-2} \tag{2}$$

where $(b_i r_e)_0 = b_i r_e$ at $\Delta_i H_e = 0$. The parameter $b_i r_e$ allows us to calculate E_{ei} for any reaction using eqn. (3).

$$E_{ei}^{1/2} = \frac{b_i r_e}{1-\alpha^2}\left\{1 - \alpha\left[1 - \frac{1-\alpha^2}{(b_i r_e)^2}\Delta_i H_e\right]^{1/2}\right\} \tag{3}$$

Eqn. (3) takes its simplest form when $\Delta_i H_e \ll (b_i r_e)^2(1-\alpha^2)^{-1}$ [eqn. (4)].

$$E_{ei}^{1/2} = \frac{b_i r_e}{1+\alpha} + \frac{\alpha}{2b_i r_e}\Delta_i H_e \tag{4}$$

Experimental data on the activation energies of reactions of free radicals and atoms were analysed using this model.

The parameter $b_i r_e$ was calculated for 30 reactions of type (5).

$$\mathrm{CH_3\cdot + R_iH \longrightarrow CH_4 + R_i\cdot} \tag{5}$$

Values of E_i were taken from ref. 7 and those of the bond dissociation energies from ref. 8; $b_i r_e$ was found to depend on $\Delta_i H_e$ [eqn. (6)].

Table 1

Radical	D_{R-R} /kJ mol^{-1}	$(b_i r_e)_0$ /(kJ mol^{-1})$^{1/2}$	E_{eo} /kJ mol^{-1}
Me·	376	17.06	72.8
Et·	351	16.05	64.4
Pr^n·	347	16.26	66.1
$CH_2{=}CHCH_2$·	257	13.20	43.6

$$(b_i r_e/\mathrm{kJ\ mol^{-1}}) = 17.06 + 1.82(\Delta_i H_e/100)^2 \tag{6}$$

Identical estimations were made for reactions of other radicals. The parameter $(b_i r_e)_0$ was found to change from one radical to another, in accordance with the R—R dissociation energy (Table 1). It can be seen that the lower the R—R bond dissociation energy, the lower are $(b_i r_e)_0$ and E_{eo}. This tendency may be explained by triplet repulsion between two electrons with parallel spins.[3] The energy of repulsion U_T may be expressed as the energy of the R—R bond raised to the power n: $U_T = \mathrm{const}\ D_i^n$. The value of n was found to be 6 [eqn. (7)].

$$(b_i r_e)_0 = 161 + 130(D_i/D_{\mathrm{CH_3CH_3}})^6 \tag{7}$$

The general empirical formula for the reaction of any alkyl radical with a C—H bond of an organic compound was found to be eqn. (8).

$$b_i r_e = [161 + 130(D_i/382)^6]^{1/2} + 4.58(\Delta_i H_e/100)^2 \tag{8}$$

Eqn. (7) was shown to be universal in character. The values of $b_i r_e$ calculated from eqn. (7) and estimated from E_i using eqn. (1) are compared in Table 2. The last two columns show that the values of $b_i r_e$ estimated from eqn. (7) are very close to those calculated from the experimental data.

A similar picture is observed for the reaction of molecules YH = CH_4, NH_3, H_2O with a hydrogen atom [eqn. (9)].[9]

$$(b_i r_e)^2 = 38 + 190(D_e^{\mathrm{HY}}/D_e^{\mathrm{CH_4}})^{1.7} \tag{9}$$

The reactions of hydrogen atoms with HX give evidence of the influence of the electronegativity of X. This effect has been characterised as the nth power of the difference $D_e^{\mathrm{HX}} - \bar{D}_e$, where $\bar{D}_e = 0.5(D_e^{\mathrm{X_2}} + D_e^{\mathrm{H_2}})$ and $U_{EA} = \mathrm{const}(D_e^{\mathrm{HX}} - \bar{D}_e)^n$. The empirical dependence of $b_i r_e$ on the energy of triplet repulsion and on the interaction of atoms with different electronegativity was found to take the form of eqn. (10).

$$b_i r_e = 113 + 120(D_e^{\mathrm{HX}}/D_e^{\mathrm{H_2}})^{1.7} - 2110[(D_e^{\mathrm{HX}} - D_e^{\mathrm{H_2}})/D_e^{\mathrm{H_2}}]^2 \tag{10}$$

Table 2

Reaction	E_{ei}/kJ mol^{-1}	$b_i r_e$ (1)[a]	$b_i r_e$ (7)[b]
$CH_4 + H_2N$·	59.3	14.62	14.68
$C_2H_6 + MeO$·	45.1	13.28	13.53
$RO_2H + RO_2$·	40.5	12.73	12.65
ArOH + ArO·	33.4	11.60	12.60

[a] From eqn. (1). [b] From eqn. (7).

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Table 3

HX	E_{ei} /kJ mol^{-1}	ΔE_H /kJ mol^{-1}	ΔE_T /kJ mol^{-1}	ΔE_{EA} /kJ mol^{-1}
H_2	58.2	0.0	30.0	0.0
HCl	30.6	−6.1	30.8	−24.6
HBr	20.1	−29.2	25.3	−8.3
HI	13.8	−43.7	20.1	−0.06

This formula enables us to estimate the contribution of each physical interaction to the activation energy. The contribution of $\Delta_i H_e$ to E_{ei} may be estimated as $\Delta E_H = E_{ei} - E_{eo}$, that of triplet repulsion as $E_T = 120(1+\alpha)^{-2}(D_e^{HX}/D_e^{H_2})^{1.7}$ and that of the electronegativity of atoms H and X as $\Delta E_{EA} = -2110(1+\alpha)^{-2}[(D_e^{HX} - \bar{D}_e)/D_e^{H_2}]^2$. The results are given in Table 3. The input of $\Delta_i H_e$ is greater for a higher value of $|\Delta_i H_e|$, while that of triplet repulsion is considerably greater (35–52%) and the contribution of electronegativity is at a maximum in the reaction with HCl (−40%).

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