An Extended Form of the Evans–Polanyi Equation: a Simple Empirical Relationship for the Prediction of Activation Energies for Hydrogen-atom Transfer Reactions

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An empirical approach has been used to devise a simple relationship [eqn. (B)] between the activation energy for an elementary hydrogen-atom transfer reaction (A) and ground state properties

$$A^{\bullet} + H\text{–}B \longrightarrow A\text{–}H + B^{\bullet} \qquad (A)$$

$$E_a = E_0 f + \alpha\Delta H^{\circ}(1 - d) + \beta\Delta\chi^2_{AB} + \gamma(s_A + s_B) \qquad (B)$$

of the reactants and products. The role of polar effects, which operate in the transition state, is emphasised and described quantitatively in terms of the difference in Mulliken electronegativities ($\Delta\chi_{AB}$) of the radicals $A^{\bullet}$ and $B^{\bullet}$. Eqn. (B) reproduces the activation energies for 65 reactions, taken from the literature, within a standard error of ± 2.0 kJ mol^{-1} and with a correlation coefficient of 0.988. Reactions of widely differing types are included and no distinction is made between gas-phase reactions and those which take place in non-polar solvents. Examples of hydrogen-atom transfer reactions which are not treated satisfactorily by eqn. (B) are discussed.

The hydrogen-atom transfer reaction (1) is of fundamental importance in several areas of chemistry and the understanding and prediction of the rates of such processes are worthwhile goals. The rate constant for reaction (1) can be expressed in terms of the Arrhenius eqn. (2), in which E_a is the activation

$$A^{\bullet} + H\text{–}B \longrightarrow A\text{–}H + B^{\bullet} \qquad (1)$$

$$k_1 = A \exp(-E_a/RT) \qquad (2)$$

energy and A is the Arrhenius pre-exponential factor. The A-factor for H-atom transfer, which reflects the entropy of activation as understood in terms of transition-state theory,[1] can usually be estimated to within $10^{\pm 0.5}$ dm^3 mol^{-1} s^{-1},[2,3] and thus knowledge of the activation energy for a particular abstraction permits calculation of the corresponding rate constant.

Over 50 years ago, Evans and Polanyi[4] showed that, within a series of closely related atom-transfer reactions, the activation energies depended linearly on the reaction enthalpies. Evans–Polanyi (E–P) relationships, which are usually written in the form of eqn. (3) where E_0 and α are constants, were later

$$E_a = E_0 + \alpha\Delta H^{\circ} \qquad (3)$$

shown to apply to many different types of atom transfer reaction. For example, the hydrogen abstraction reactions of methyl and of trifluoromethyl radicals with alkanes conform individually to eqn. (3), but the values of E_0 and α are different for the two radicals.[5,6] Methyl radicals are less reactive than $CF_3^{\bullet}$ and, since $(A_{CF_3^{\bullet}}/A_{CH_3^{\bullet}})$ is *ca.* 1, the difference derives mainly from a difference in activation energies of *ca.* 5–15 kJ mol^{-1}.[7] The smaller activation energies for abstraction by $CF_3^{\bullet}$ can be attributed partly to 'enthalpic' effects, because the C–H bond is stronger in CF_3H than in CH_4, but other factors, especially polar effects which operate in the transition state,[8] must also play a role.

Numerous attempts have been made to extend the E–P eqn. (3) and to establish empirical and semi-empirical relationships between E_a and various ground-state properties of the reactants and products for reaction (1).[3,9–18] The complexity of these relationships varies considerably, as do the insights they provide into the factors that govern activation energies for hydrogen-atom transfer.

In recent years, it has become feasible to carry out high-level *ab initio* molecular orbital calculations to obtain reliable geometries and energies of the transition states (structures)[18] for reactions of the type (1) and to compute the corresponding activation energies.[19–25] While this approach is generally very successful in the quantitative sense, it often does not provide direct insight into the various effects which influence the height of the barrier to a particular reaction. Thus, even in the age of the supercomputer, the practitioner of radical chemistry still resorts to rather qualitative arguments when challenged to predict the rate of an elementary reaction. In the case of the single-step hydrogen-atom transfer reaction (1), factors other than the overall enthalpy change ΔH° will generally need to be considered. These factors may be classified[26] as (*i*) polar effects, (*ii*) steric (van der Waals) effects and (*iii*) stereoelectronic effects, which operate in the transition state to influence its energy in relation to that of the separated reactants. Furthermore, when estimating the activation energy for reaction (1), it is necessary to consider the differences in the structures of the moieties A and B in the radicals $A^{\bullet}$ and $B^{\bullet}$ and in the transition state $[A\cdots H\cdots B]^{\bullet}$.[27] Finally, the extent to which any stabilisation of $B^{\bullet}$, by delocalisation of the unpaired electron, is available in the transition state $[A\cdots H\cdots B]^{\bullet}$ will need to be taken into account.

The purpose of the present work was to determine whether this qualitative empirical approach to the estimation of E_a for reaction (1) can be quantified and summarised in the form of a simple algorithm. The basis for our quantitative empirical treatment was suggested in an earlier paper.[28]

Results and Discussion

Reactions which are subject to steric and/or stereoelectronic control are best considered on an individual basis and are excluded at this stage. Activation energies for a wide variety of hydrogen-atom transfer reactions have been collected from the literature (see Table 1); the values of E_a range 1–59 kJ mol^{-1} and no distinction has been made between gas-phase reactions and those proceeding in non-polar solvents. All reactions are considered in the exothermic direction and ΔH° varies from zero (thermoneutral) to -129 kJ mol^{-1}: where the available experimental data refer to the reverse (endothermic) reaction, the activation energy in the exothermic direction was calculated using eqn. (4).

$$E_a(\text{exothermic}) = E_a(\text{endothermic}) + \Delta H^\circ \qquad (4)$$

Consideration of those factors which, together with ΔH°, control the activation energy for the thermoneutral or exothermic reaction (1) leads us to propose eqn. (5) as a logical extension of the simple E–P eqn. (3). The term f is defined in eqn. (6); the quantities D_{AH}, D_{BH} and D_{H_2} are the bond dissociation enthalpies for AH, BH and H_2, respectively. The term $\Delta\chi_{AB}$ is the difference in electronegativities of A$^\bullet$ and B$^\bullet$, the structural parameters s_A and s_B are characteristic of the radicals A$^\bullet$ and B$^\bullet$, and d is the delocalisation term for the radical B$^\bullet$. The parameters E_0, α, β and γ are constants, obtained from multiple regression analysis of the experimental data. Justification for and explanation of each of the terms in eqn. (5) are given in detail below.

$$E_a = E_0 f + \alpha\Delta H^\circ(1 - d) + \beta\Delta\chi_{AB}^2 + \gamma(s_A + s_B) \qquad (5)$$

$$f = (D_{AH}D_{BH}/D_{H_2}^2) \qquad (6)$$

(*a*) *The* f-*Term.*—The E–P eqn. (3) predicts that for a series of thermoneutral abstractions the activation energy will be constant and equal to E_0. Clearly this will not be true in general and E_a will depend not only on ΔH° but also on the strengths of the bonds A–H and B–H being formed and broken in the transition state. For a series of thermoneutral identity reactions (A$^\bullet$ + AH), the activation energy would be expected to decrease as the strength of the A–H bond decreases. The f-term is included to provide a measure of the energetic cost of stretching the A–H and B–H bonds to their respective lengths in the transition state. The product[*] $D_{AH}D_{BH}$ is divided by $D_{H_2}^2$ simply to make f a dimensionless quantity in the region of unity.

(*b*) *The* d-*Term.*—The activation energy for hydrogen-atom transfer would be expected to decrease as the abstraction becomes more exothermic. However, for some types of reactant B–H, stabilisation of B$^\bullet$ by conjugative delocalisation of the unpaired electron may not develop linearly along the reaction coordinate and consequently may not be 'felt' proportionately in the transition state.[8,14b] For example, in abstraction from toluene, because of the pyramidal structure of the benzylic moiety in the transition state, little stabilising effect of delocalisation onto the benzene ring may be available unless the transition state occurs very late along the reaction coordinate. For simplicity, the delocalisation term d is set equal to a single average value a if B$^\bullet$ is a three-coordinate carbon-centred radical in which the unpaired electron is conjugatively delocalised onto an α-substituent (*e.g.* an aryl, cyano, acyl, oxy or amino group, see Table 1). The term d is set equal to zero for all other reactions listed in Table 1, because any stabilisation of B$^\bullet$ as a result of unpaired electron delocalisation should be felt proportionately in the transition state. It is important to note that this division into two classes depends only on the structures of the radicals B$^\bullet$ and is independent of the statistical treatment of the experimental data.

(*c*) *Polar Effects.*—The important role played by polar factors in influencing the reactions of uncharged radicals is well-recognised.[8,26–29] Polar effects can be understood in terms of the perturbational interactions between the frontier molecular orbitals of the reacting partners,[30] but the early explanation[31,32] based on the consideration of charge-transfer interactions in the transition state, using a valence-bond model, represents a valid (and in some ways preferable) alternative, which attempts to give a simple picture of the transition state itself.

Pauling's pioneering work to quantify the concept of electronegativity was based on the observation that the bond between two unlike atoms in a molecule A–B is stronger than the (geometric) mean strength of the bonds in the homopolar molecules A–A and B–B.[33] In Pauling's model, this extra bond strength was identified with the additional ionic resonance energy of the A–B bond, which increases with the electronegativity difference between A and B. If the molecule A–B is represented as a hybrid of the canonical structures **1a–c**, then the additional resonance energy arises because of the increased contribution to the hybrid from one or other of the ionic structures **1b** or **1c** which occurs when the electronegativities of A and B differ. In Pauling's definition, the difference in the electronegativities of the atoms A and B ($\Delta\chi_{AB}$) is related to the bond strengths (in kJ mol^{-1}) for A–A, B–B and A–B by eqn. (7).[33]

$$\underset{\mathbf{1a}}{[\mathrm{A{-}B}]} \longleftrightarrow \underset{\mathbf{1b}}{[\mathrm{A}\!:^{-}\ \mathrm{B}^{+}]} \longleftrightarrow \underset{\mathbf{1c}}{[\mathrm{A}^{+}\ :\!\mathrm{B}^{-}]}$$

$$D_{AB} = (D_{AA}D_{BB})^{\frac{1}{2}} + 125.5\,\Delta\chi_{AB}^2 \qquad (7)$$

In the same way that the strength of the bond between A and B is increased by ionic resonance when these two atoms or groups differ in electronegativity, so the transition state for hydrogen-atom abstraction from B–H by A$^\bullet$ should be subject to increasing stabilisation as $\Delta\chi_{AB}$ increases.[†] The extents to which **2c** and **2d** contribute to the hybrid structure of the transition state, and thus the degree to which the transition state is stabilised by ionic resonance will depend on $\Delta\chi_{AB}$. It can be argued that ionic structures of the type **2c** and **2d** cannot really make a significant contribution to the hybrid transition state, because they must be much less stable than **2a** and **2b** on account of the small coulombic energy of the ion pair at the separation in the transition state. Even when account is taken of the relative weakness of the long A–H and B–H bonds in **2a** and **2b** as compared with the corresponding bonds in the ground state molecules A–H and B–H, this assertion is still likely to be true and, instead of **2c** and **2d**, structures which involve one- and three-electron bonds are probably more appropriate. For example, **2c** should be replaced by **3a** and **3b**. Even so, the electronegativity difference between A$^\bullet$ and B$^\bullet$ should remain a

$$\underset{\mathbf{2a}}{[\mathrm{A}^{\bullet}\ \mathrm{H{-}B}]} \longleftrightarrow \underset{\mathbf{2b}}{[\mathrm{A{-}H}\ {}^{\bullet}\mathrm{B}]} \longleftrightarrow \underset{\mathbf{2c}}{[\mathrm{A}\!:^{-}\ \mathrm{H}^{\bullet}\ \mathrm{B}^{+}]} \longleftrightarrow \underset{\mathbf{2d}}{[\mathrm{A}^{+}\ \mathrm{H}^{\bullet}\ :\!\mathrm{B}^{-}]}$$

$$\underset{\mathbf{3a}}{[\mathrm{A}\dot{-}\mathrm{H}^{-}\ {}^{+}\mathrm{B}]} \longleftrightarrow \underset{\mathbf{3b}}{[\mathrm{A}\!:^{-}\ \mathrm{H}{\cdot}\mathrm{B}^{+}]}$$

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[*] Use of the sum ($D_{AH} + D_{BH}$) in place of the product gives less good agreement between E_a(calc.) and E_a(expt.).

[†] Use of $\Delta\chi_{AB}$ in place[34] of $\Delta\chi_{AB}^2$ in eqn. (5) gives less good agreement (R = 0.959) between E_a(calc.) and E_a(expt.).

Table 1 Experimental activation energies and those calculated using eqns. (3) and (5)

Entry	$A^{\bullet}$	BH	E_a(expt.)/ kJ mol^{-1}	Ref.	$\Delta H°$/ kJ mol^{-1}	f	d	$\Delta\chi^2_{AB}$/ eV^2	$s_A + s_B$	E_a(3)/ kJ mol^{-1}	E_a(5)/ kJ mol^{-1}	$\Delta E(5)^a$/ kJ mol^{-1}
1	$Bu^{t\bullet}$	$PhCH_3$	43.2	*b*	−34	0.778	0.44	0.53	5.0	30.5	41.1	−2.1
2	$Bu^{t\bullet}$	$HCCl_3$	34.0	*c*	−1	0.848	0.00	4.08	3.2	38.3	34.8	0.8
3	$Bu^tO^{\bullet}$	$PhCH_3$	17.7	*d*	−72	0.852	0.44	8.18	3.1	21.5	16.5	−1.2
4	$Bu^tO^{\bullet}$	c-C_5H_{10}	14.5	*e*	−40	0.926	0.00	11.29	3.1	29.1	13.1	−1.4
5	$Bu^tO^{\bullet}$	Bu^tOCH_3	12.6	*f*	−51	0.900	0.44	13.18	3.1	26.5	11.0	−1.6
6	$Bu^tO^{\bullet}$	PhOH	11.7	*g*	−84	0.824	0.00	1.72	1.2	18.7	11.4	−0.3
7	$Bu^tO^{\bullet}$	Et_3SiH	11.0	*h*	−52	0.898	0.00	9.12	2.8	26.2	12.4	1.4
8	$Bu^tO^{\bullet}$	$O(CH_2)_4$	10.5	*i*	−55	0.891	0.44	13.18	3.1	25.5	10.1	−0.4
9	c-$C_6H_{11}^{\bullet}$	Bu_3SnH	16.6	*j*	−90	0.652	0.00	0.58	4.7	17.3	17.6	1.0
10	$CCl_3^{\bullet}$	$HSiCl_3$	36.7	*k*	−19	0.806	0.00	0.02	2.9	34.0	36.1	−0.6
11	$CCl_3^{\bullet}$	Me_3SiH	36.4	*l*	−13	0.818	0.00	2.10	2.9	35.4	33.7	−2.7
12	$CCl_3^{\bullet}$	Et_3SiH	33.7	*l*	−13	0.818	0.00	2.10	2.9	35.4	33.7	0.0
13	$CF_3^{\bullet}$	MeH	45.6	*m*	−7	1.030	0.00	0.32	2.5	36.9	45.6	0.0
14	$CF_3^{\bullet}$	H_2	39.7	*n*	−10	1.023	0.00	0.25	0.0	36.1	36.2	−3.5
15	$CF_3^{\bullet}$	EtH	33.7	*o*	−25	0.988	0.00	2.34	2.5	32.6	35.4	1.7
16	$CF_3^{\bullet}$	Me_2CO	32.3	*m*	−61	0.903	0.44	0.04	2.5	24.1	34.6	2.3
17	$CF_3^{\bullet}$	Me_2O	28.4	*p*	−57	0.913	0.44	5.06	2.5	25.1	25.3	−3.1
18	$CF_3^{\bullet}$	Pr^iH	27.2	*q*	−35	0.964	0.00	3.92	2.5	30.3	28.8	1.6
19	$CF_3^{\bullet}$	c-C_5H_{10}	25.9	*r*	−46	0.938	0.00	4.67	2.5	27.7	23.6	−2.3
20	$CF_3^{\bullet}$	$HSiCl_3$	25.9	*l*	−64	0.896	0.00	0.10	2.2	23.4	25.8	−0.1
21	$CF_3^{\bullet}$	$HCCl_3$	25.4	*m*	−45	0.941	0.00	0.04	0.7	27.9	27.3	1.9
22	$CF_3^{\bullet}$	$PhCH_3$	24.1	*m*	−78	0.863	0.44	2.19	2.5	20.1	26.3	2.2
23	$CF_3^{\bullet}$	c-C_6H_{12}	23.5	*m*	−46	0.938	0.00	4.67	2.5	27.7	23.6	0.1
24	$CF_3^{\bullet}$	Me_3SiH	23.3	*s*	−58	0.910	0.00	2.69	2.2	24.8	22.5	−0.8
25	$CF_3^{\bullet}$	HCl	21.8	*t*	−15	1.011	0.00	7.78	0.0	35.0	19.1	−2.7
26	$CF_3^{\bullet}$	Bu^tH	20.3	*q*	−44	0.943	0.00	4.88	2.5	28.1	23.8	3.5
27	$Cl^{\bullet}$	EtH	1.1	*u*	−10	0.955	0.00	18.58	2.5	36.1	4.6	3.5
28	$Et^{\bullet}$	$HCCl_3$	39.4	*v*	−20	0.888	0.00	1.80	3.2	33.8	36.3	−3.1
29	$Et^{\bullet}$	$PhCH_3$	38.9	*w*	−53	0.815	0.44	0.00	5.0	26.0	41.0	2.1
30	$Et^{\bullet}$	Bu_3SnH	15.9	*j*	−111	0.687	0.00	0.00	4.7	12.3	14.9	−1.0
31	$H^{\bullet}$	EtH	40.6	*x*	−15	0.966	0.00	1.06	2.5	35.0	39.7	−0.9
32	$H^{\bullet}$	H_2	38.5	*y*	0	1.000	0.00	0.00	0.0	38.5	38.3	−0.2
33	$H^{\bullet}$	Pr^iH	34.7	*x*	−25	0.943	0.00	2.19	2.5	32.6	34.0	−0.7
34	$H^{\bullet}$	Bu^tH	29.3	*x*	−34	0.922	0.00	2.92	2.5	30.5	29.5	0.2
35	$H^{\bullet}$	HCl	14.2	*z*	−5	0.989	0.00	10.76	0.0	37.3	14.6	0.4
36	$H^{\bullet}$	HBr	2.6	*aa*	−70	0.839	0.00	6.60	0.0	22.0	1.3	−1.3
37	$H_2N^{\bullet}$	H_2	35.5	*ab*	−13	1.030	0.00	1.08	0.5	35.4	35.8	0.3
38	$H_2N^{\bullet}$	EtH	29.9	*ab*	−28	0.994	0.00	4.28	3.0	31.9	32.7	2.8
39	$H_2N^{\bullet}$	Pr^iH	25.7	*ab*	−38	0.971	0.00	6.35	3.0	29.5	25.1	−0.6
40	$H_2N^{\bullet}$	Bu^tH	20.5	*ab*	−47	0.950	0.00	7.56	3.0	27.4	19.6	−0.9
41	$HO^{\bullet}$	HCF_3	24.2	*ac*	−53	1.171	0.00	3.88	0.6	26.0	25.9	1.7
42	$HO^{\bullet}$	H_2	17.5	*ad*	−63	1.144	0.00	6.10	0.6	23.7	17.8	0.3
43	$HO^{\bullet}$	EtH	10.5	*ad*	−78	1.105	0.00	12.25	3.1	20.1	8.6	−1.9
44	$HO^{\bullet}$	$HCCl_3$	9.4	*z*	−98	1.053	0.00	4.67	1.3	15.4	11.0	1.6
45	$Me^{\bullet}$	MeH	58.6	*ae*	0	1.014	0.00	0.00	5.0	38.5	55.9	−2.7
46	$Me^{\bullet}$	EtH	48.7	*ae*	−18	0.972	0.00	0.92	5.0	34.3	48.0	−0.7
47	$Me^{\bullet}$	H_2	44.0	*af*	−3	1.007	0.00	0.00	2.5	37.8	46.4	2.4
48	$Me^{\bullet}$	MeCN	42.3	*ae*	−50	0.898	0.44	0.66	5.0	26.7	43.2	0.9
49	$Me^{\bullet}$	CH_3OH	41.8	*ae*	−46	0.908	0.44	1.88	5.0	27.7	41.7	−0.1
50	$Me^{\bullet}$	Me_2O	41.8	*ae*	−50	0.898	0.44	2.82	5.0	26.7	38.8	−3.0
51	$Me^{\bullet}$	c-C_6H_{12}	41.0	*ae*	−39	0.924	0.00	2.53	5.0	29.3	37.7	−3.3
52	$Me^{\bullet}$	Me_2CO	40.6	*ae*	−54	0.889	0.44	0.14	5.0	25.8	43.4	2.8
53	$Me^{\bullet}$	Pr^iH	40.3	*ae*	−28	0.949	0.00	1.99	5.0	31.9	42.4	2.1
54	$Me^{\bullet}$	$PhCH_3$	39.7	*ae*	−71	0.850	0.44	0.83	5.0	21.8	38.1	−1.6
55	$Me^{\bullet}$	c-C_5H_{10}	39.3	*ae*	−39	0.924	0.00	2.53	5.0	29.3	37.7	−1.6
56	$Me^{\bullet}$	$HCCl_3$	36.8	*v*	−38	0.926	0.00	0.14	3.2	29.5	36.7	−0.1
57	$Me^{\bullet}$	Bu^tH	33.8	*ag*	−37	0.928	0.00	2.69	5.0	29.8	38.0	4.2
58	$Me^{\bullet}$	Me_3SiH	32.6	*ae*	−51	0.896	0.00	1.14	4.7	26.5	35.4	2.8
59	$Me^{\bullet}$	Bu_3SnH	13.5	*j*	−129	0.716	0.00	0.85	4.7	8.1	9.9	−3.6
60	$MeO^{\bullet}$	MeH	42.4	*m*	−1	1.016	0.00	3.24	3.1	38.3	42.6	0.2
61	$MeO^{\bullet}$	EtH	29.7	*ah*	−19	0.974	0.00	7.62	3.1	34.0	27.6	−2.1
62	$MeO^{\bullet}$	Bu^tH	10.1	*ai*	−38	0.930	0.00	11.83	3.1	29.5	12.6	2.5
63	$PhCH_2^{\bullet}$	Bu_3SnH	23.4	*aj*	−58	0.600	0.00	0.00	4.7	24.8	24.7	1.3
64	$Pr^{i\bullet}$	$HCCl_3$	34.3	*v*	−10	0.867	0.00	3.20	3.2	36.1	35.1	0.8
65	$Pr^{i\bullet}$	Bu_3SnH	14.5	*j*	−101	0.670	0.00	0.24	4.7	14.7	16.3	1.8
66	$Cl^{\bullet}$	Pr^iH	0.0	*ah*	−20	0.932	0.00	22.66	2.5	33.8	−7.1	−7.1
67	$Bu^tO^{\bullet}$	Bu^tOH	—	—	0	1.018	0.00	0.00	1.2	38.5	43.1	—
68	$PhCH_2^{\bullet}$	PhSH	15.9	*aj*	−25	0.664	0.00	2.25	3.1	32.6	25.2	9.3
69	$Bu^{\bullet}$	PhSH	7.3	*aj*	−78	0.760	0.00	2.40	3.1	20.1	15.5	8.2
70	$HO^{\bullet}$	MeH	15.1	*ak*	−60	1.152	0.00	6.45	3.1	24.4	26.7	11.6

[a] $E_a(5) - E_a$(expt.). [b] Ref. 54, assuming an *A*-factor of $10^{8.18}$ dm^3 mol^{-1} s^{-1} as determined for the reaction shown in entry 2 (ref. 55). [c] Ref. 55. [d] Ref. 56. [e] Ref. 57. [f] Ref. 58. [g] Ref. 59. [h] Ref. 60. [i] Ref. 61. [j] Ref. 62. [k] Ref. 63. [l] Ref. 64. [m] Averaged data from ref. 65. [n] Ref. 66. [o] Ref. 7. [p] Ref. 67. [q] Ref. 68. [r] Ref. 69. [s] Ref. 70. [t] Ref. 71. [u] Ref. 72. [v] Ref. 73. [w] Ref. 74. [x] Ref. 75. [y] Refs. 10 and 38(*a*). [z] Ref. 76. [aa] Ref. 77. [ab] Ref. 78. [ac] Ref. 79. [ad] Ref. 80. [ae] Ref. 81. [af] Ref. 82. [ag] Ref. 83. [ah] Ref. 65. [ai] Ref. 84. [aj] Ref. 50. [ak] Ref. 85.

Table 2 Data for the radicals $A^{\bullet}$ and $B^{\bullet}$ involved in the hydrogen-atom transfer reaction (1)

Radical ($X^{\bullet}$)	D_{HX}/kJ mol^{-1}	IE^a/eV	EA^a/eV	χ_X/eV	s_X
$NC\dot{C}H_2$	389[b]	10.0[c]	1.54[c]	5.77	2.5
$MeC(O)\dot{C}H_2$	385[d]	8.8[e]	1.86[c]	5.33	
$Me^{\bullet}$	439[f]	9.84[c]	0.08[c]	4.96	
$Ph\dot{C}H_2$	368[g]	7.20[c]	0.90[c]	4.05	
$Et^{\bullet}$	421[f]	8.38	−0.39	4.00	
$HO\dot{C}H_2$	393[b]	7.56[c]	−0.38[h]	3.59	
$Pr^{i\bullet}$	411[f]	7.57	−0.48	3.55	
c-$C_6H_{11}^{\bullet}$	400[g]	7.21[i]	−0.48[j]	3.37	
c-$C_5H_9^{\bullet}$	400[g]	7.21[c]	−0.48[j]	3.37	
$Bu^{t\bullet}$	402[f]	6.93	−0.30	3.32	
$Bu^tO\dot{C}H_2$	389[k]	6.94[l]	−0.38[m]	3.28	
$MeO\dot{C}H_2$	389[b]	6.94[c]	−0.38[m]	3.28	
$\overline{O[CH_2]_3\dot{C}}H$	385[b]	—	—	3.28[l]	
$F_3C^{\bullet}$	446[b]	9.25	1.8	5.53	0.0
$Cl_3C^{\bullet}$	401[b]	8.78	1.90	5.34	0.7
$Cl_3Si^{\bullet}$	382[b]	7.92	2.50	5.21	2.2
$Me_3Sn^{\bullet}$	310[g]	7.10[c]	0.97[n]	4.04	
$Bu_3Sn^{\bullet}$	310[o]	7.10[p]	0.97[n]	4.04	
$Me_3Si^{\bullet}$	388[q]	6.81[r]	0.97[s]	3.89	
$Et_3Si^{\bullet}$	388[q]	6.81[m]	0.97[n]	3.89	
$H_2N^{\bullet}$	449[g]	11.40	0.74	6.07	0.5
$HO^{\bullet}$	499[g]	13.17	1.83	7.50	0.6
$Bu^tO^{\bullet}$	440[b]	11.9[t]	1.91[c]	6.91	
$MeO^{\bullet}$	440[b]	11.9[e]	1.62[c]	6.76	
$PhO^{\bullet}$	356[u]	8.85	2.35	5.60	
$PhS^{\bullet}$	343[g]	8.63	2.47	5.55	
$F^{\bullet}$	570[g]	17.42	3.40	10.41	0.0
$Cl^{\bullet}$	431[g]	13.01	3.62	8.32	
$Br^{\bullet}$	366[g]	11.84	3.36	7.60	
$H^{\bullet}$	436[g]	13.59	0.74	7.17	

[a] Data from ref. 35 unless otherwise noted. [b] Ref. 86. [c] Ref. 87. [d] Ref. 88. [e] Ref. 89. [f] Ref. 90. [g] Ref. 91. [h] Ref. 92. [i] Value for c-$C_5H_9^{\bullet}$. [j] Value for $Pr^{i\bullet}$. [k] Value for $MeOCH_2$–H. [l] Value for $MeO\dot{C}H_2$. [m] Value for $H_2\dot{C}OH$. [n] Value for $Me_3Si^{\bullet}$. [o] Value for Me_3Sn–H. [p] Value for $Me_3Sn^{\bullet}$. [q] Taken as the mean of the recent value for D_{Me_3SiH} (ref. 93) and the previously accepted value (ref. 94), which agrees with the value reported for D_{Et_3SiH} (377 kJ mol^{-1}, ref. 95). [r] Ref. 96. [s] Ref. 97. [t] Value for $MeO^{\bullet}$. [u] Ref. 98.

good indicator of both the direction of charge transfer in the transition state and the extent of stabilisation of the latter by ionic resonance. In this context, the Mulliken-type electronegativity[35] of the radical $X^{\bullet}$, defined in eqn. (8) as the mean of

$$\chi_X = (IE_X + EA_X)/2 \qquad (8)$$

the vertical ionisation energy and the vertical electron affinity of $X^{\bullet}$, appears to be the most appropriate. Literature data for the radicals $A^{\bullet}$ and $B^{\bullet}$, and for the molecules A–H and B–H are given in Table 2.

As pointed out by Pauling,[36] the Mulliken electronegativity of $H^{\bullet}$ (7.17) is anomalously large, both in relation to the value of χ_H on the Pauling scale and in terms of the polarity of the bonds which hydrogen forms to other elements. In noting this, Pauling comments that hydrogen 'with its unique electronic structure might be expected to misbehave!' The value of χ_H used here was chosen to give the best correlation between E_a(calc.) and E_a(expt.); the value obtained in this way (5.03) is very close to χ for the methyl radical (4.96), which lends confidence to our general approach as expressed by eqn. (5).

(*d*) *The* s-*Factors*.—The structures of the groups A and B in the transition state $[A\cdots H\cdots B]^{\bullet}$ will, in general, differ from their structures in the radicals $A^{\bullet}$ and $B^{\bullet}$, unless the latter are atoms. Since the ionisation energies, electron affinities and enthalpies of formation (*via* the bond dissociation enthalpies D_{XH}) used in eqn. (5) relate to the free radicals $A^{\bullet}$ and $B^{\bullet}$, a structure factor s_X, which is assumed to be a constant for the radical $X^{\bullet}$, is included to reflect any such structural differences. Thus, s_X should be zero if $X^{\bullet}$ is an atom. The s-factor for the planar methyl radical would be expected to be relatively large, because the geometry of the CH_3 moiety in the radical is significantly different from that in the tetrahedral methane. The equilibrium geometries of the higher acyclic alkyl radicals are somewhat non-planar, but their time-averaged structures still differ significantly from the near-tetrahedral geometries of the alkyl moieties in the corresponding hydrocarbons. Alkyl radicals which carry an α-unsaturated substituent (*e.g.* an aryl, acyl or cyano group) are more rigidly planar at C_α. For simplicity and generality, we have assumed that all simple alkyl radicals (including the cyclopentyl and cyclohexyl radicals) and monosubstituted alkyl radicals have the same s-factor; further refinement may prove justified in the future. In contrast, the s-factor for the trifluoromethyl radical should be very small, because $CF_3^{\bullet}$ is strongly and rigidly pyramidal,[37] and therefore similar in structure to the CF_3 group in CF_3H. The classification of radicals according to their s-factor is given in Table 2.

The extent to which the structure of the A moiety in the transition state differs from that in $A^{\bullet}$ should increase with the distance of the transition state along the reaction coordinate, whereas the later the transition state the more closely the structure of the B moiety will resemble that in $B^{\bullet}$. If the exothermicity of the abstraction is used as a measure of the distance of the transition state along the reaction coordinate, then it might be thought that the final term in eqn. (5) could take a form such as $\gamma[rs_A + (2 - r)s_B]$, where r is given by eqn. (9) in which λ is a constant. The value of r will vary from

$$r = 1/(1 - \lambda\Delta H^{\circ}) \qquad (9)$$

unity for a thermoneutral reaction to approach zero for highly exothermic reactions. However, for all values of λ the simple form given in eqn. (5) gave better agreement between E_a(calc.) and E_a(expt.), until λ was reduced to zero when the two forms become identical.

Corresponding attempts to modify the second term in eqn. (5) $[\alpha\Delta H^{\circ}(1 - d)]$, to take account of the variable position of the transition state along the reaction coordinate, resulted in only an insignificant improvement in the fit of E_a(calc.) to E_a(expt.) at the expense of a substantial increase in complexity.

Analysis of Data.—Except for the prototypical hydrogen-atom transfer reaction of $H^{\bullet}$ with H_2 (entry 32), quantum mechanical tunnelling is thought to have rather little influence on the measured activation energies in the experimental temperature ranges.[9,38] The 'classical barrier' (*i.e.* the barrier estimated on the assumption that there is no tunnelling) to the reaction of $H^{\bullet}$ with dihydrogen is believed to be close to 38.5 kJ mol^{-1},[10,38a] and this is the value given in Table 1. Data for the first 65 reactions listed in Table 1 were fitted to eqns. (3) and (5) using multiple linear regression methods (Quattro Pro™ and Excel™); the coefficients and statistical parameters are given in Table 3.

Not surprisingly, the correlation between E_a(calc.) and E_a(expt.) obtained using the simple E–P eqn. (3) is very poor (correlation coefficient, $R = 0.544$) and these results are presented graphically in Fig. 1. However, using eqn. (5), the correlation is dramatically improved ($R = 0.988$), as is immediately apparent from Fig. 2. The best fit to eqn. (5) was obtained by iteratively optimising the values of s_X (±0.1) to give the highest value of R. Each radical $A^{\bullet}$ and $B^{\bullet}$ was placed in

Table 3 Results from multiple regression analysis of the data presented in Table 1[a]

	Eqn. (3)[b]	Eqn.(5)[b]
E_0/kJ mol^{-1}	38.501 (2.335)	38.337 (0.677)
α	0.2356 (0.0457)	0.2472 (0.0088)
β/kJ mol^{-1} eV^{-2}	—	-2.048 (0.064)
γ/kJ mol^{-1}	—	3.412 (0.154)
Std. error in E_a(calc.)/kJ mol^{-1}	10.5	2.0
R	0.544	0.988

[a] Data for the first 65 reactions were included. [b] Standard errors are shown in parentheses.

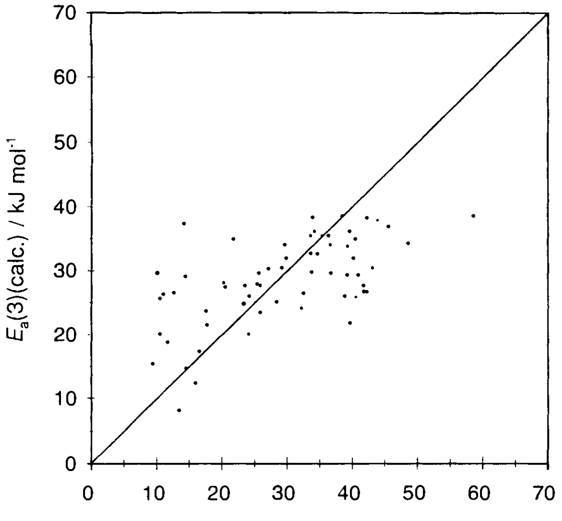

Fig. 1 Plot of the experimental activation energies against those calculated using eqn. (3) for the first 65 reactions listed in Table 1. The straight line corresponds to E_a(calc.) = E_a(expt.).

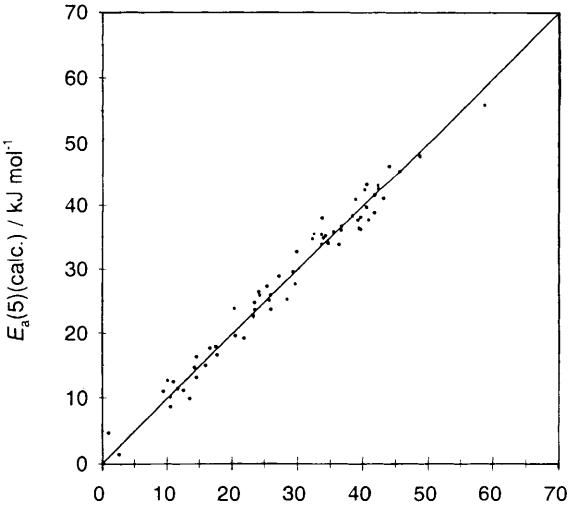

Fig. 2 Plot of the experimental activation energies against those calculated using eqn. (5) for the first 65 reactions listed in Table 1. The straight line corresponds to E_a(calc.) = E_a(expt.).

one of seven categories; (*i*) alkyl and mono substituted alkyl ($s = 2.5$), (*ii*) $CF_3^•$ ($s = 0.0$), (*iii*) $CCl_3^•$ ($s = 0.7$), (*iv*) $X_3Si^•$ and $X_3Sn^•$ ($s = 2.2$), (*v*) $X_2N^•$ ($s = 0.5$), (*vi*) $XO^•$ and $XS^•$ ($s = 0.6$), or (*vii*) an atom ($s = 0.0$).* Silyl and stannyl radicals both have pyramidal equilibrium geometries[39] and, at this stage, both types of radical are placed in the same s-factor class. The value of a ($d = a$ or zero, see before) was optimised (±0.01) to 0.44 and, as discussed above, the value of χ_H was iteratively optimised (±0.01) to 5.03.

Using eqn. (5), the standard error on E_a(calc.) is ±2.0 kJ mol^{-1}, within the error limits associated with most recent experimental determinations.

The simplest of all the empirical correlations between E_a and ΔH° is the general relationship proposed by Semenov [eqn. (10)].[40] It was suggested that this equation applies approximately for a wide variety of exothermic atom-transfer reactions

$$E_a = E_o + 0.25\,\Delta H^\circ \qquad (10)$$

and that E_o is about 48 kJ mol^{-1}. Although this relationship is clearly a gross over-simplification (see Fig. 1), it is of interest that the scaling factor (0.25) in the Semenov equation is very close to the value found for α both in the simple E–P eqn. (3) and in our extended eqn. (5), by regression analysis of the data given in Table 1. It is also noteworthy that the value obtained for E_o in eqn. (3) is effectively the same as that found for E_o in eqn. (5), which is (and should be) very close to E_a(expt.) for $H^• + H_2$ (entry 32).

It is obvious from its mathematical form that eqn. (5), like the E–P eqn. (3), is capable of predicting negative activation energies for single-step reactions. However, since eqn. (5) is successful in predicting even quite small activation energies to within experimental accuracy, we do not see this as a major failing. Reactions for which eqn. (5) predicts a negative activation energy should proceed essentially without barrier in the gas phase and at the diffusion-controlled encounter rate in solution.

Exothermic abstraction of hydrogen from hydrocarbons by chlorine atoms is extremely rapid. For example, eqn. (5) predicts the activation energy for reaction (11) (Table 1, entry 27) to be

$$Cl^• + EtH \longrightarrow HCl + Et^• \qquad (11)$$

4.6 kJ mol^{-1}, although this is still greater than the currently preferred experimental value (*ca.* 1 kJ mol^{-1}). However, $\Delta\chi_{AB}$ is large for this reaction and charge transfer in the transition state is evidently very important. Considering its simplicity, eqn. (5) is very successful in predicting this low activation energy and, in fact, only a small increase in the value of $\Delta\chi_{AB}$ from 4.31 to 4.51 eV would be necessary to reduce the value of E_a(calc.) to 1 kJ mol^{-1}. For reaction (12), which proceeds

$$Cl^• + Pr^iH \longrightarrow HCl + Pr^{i•} \qquad (12)$$

without measurable barrier in the gas phase, eqn. (5) predicts a negative activation energy of −7.1 kJ mol^{-1} (entry 66) (the radical chain reaction of propane with molecular chlorine in the liquid phase is evidently a complex process[41]). Eqn. (5) also predicts negative activation energies for hydrogen transfer to fluorine atoms from H_2 and from all alkanes.

A few reactions for which the experimental activation energies deviate markedly from the predictions of eqn. (5) merit individual consideration. Griller and Ingold have reported that *tert*-butoxyl radicals rapidly abstract the hydroxylic hydrogen atom from alcohols, provided that the latter are not strongly associated by intermolecular hydrogen bonding.[42] Similar

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* While the relative values of s_x are significant, their absolute magnitudes are, of course, arbitrary and may be adjusted at will within the constraint that the product $\gamma(s_A + s_B)$ must remain constant for each reaction. For example, if each s-value were twice as large, the value of the constant γ would be half that given in Table 3.

results have been reported by Elson and Kochi.[43] Griller and Ingold estimated an approximate rate expression [eqn. (14), $\theta = 2.303RT$ kJ mol^{-1}] for reaction (13); corresponding hydrogen abstraction from hydrogen-bonded alcohols is much slower.[42–44] In accord with this experimental result, a very low

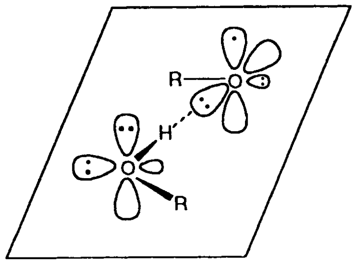
$$\mathrm{Bu^tO^{\bullet} + Bu^t{}_3COH \longrightarrow Bu^tOH + Bu^t{}_3CO^{\bullet}} \tag{13}$$

$$\log_{10}(k_{13}/\mathrm{dm^3\,mol^{-1}\,s^{-1}}) \simeq 6.4 - 10.9/\theta \tag{14}$$

activation energy (*ca.* 8 kJ mol^{-1}) is predicted[42] for the identity reaction (15), using the procedure devised by Zavitsas[10] which

$$\mathrm{RO^{\bullet} + ROH \longrightarrow ROH + RO^{\bullet}} \tag{15}$$

emphasises the antibonding interaction between the oxygen atoms in the transition state [RO ··· H ··· OR]$^{\bullet}$ and, in this treatment, the low calculated value of E_a parallels the weakness of the O–O bond in a dialkyl peroxide. However, eqn. (5) predicts a large activation energy (43.1 kJ mol^{-1}) for reaction (15) (entry 67), because $\Delta H^\circ = \Delta\chi_{AB} = 0$ and the RO–H bond in an alcohol is relatively strong. Although eqn. (5) contains no term which relates to any possible antibonding interaction between the groups A and B in the transition state, it is nevertheless generally successful in predicting E_a for the first 65 reactions listed in Table 1. As noted by Griller and Ingold,[42] and emphasised by ourselves,[28] the low *A*-factor and low activation energy for reaction (13) could alternatively be a consequence of hydrogen bonding prior to H-atom transfer.[45,*] Indeed, hydrogen bonding to RO$^{\bullet}$, as well as full protonation of the latter, do significantly affect the reactions of these radicals.[46] If the reaction proceeds in a single step, our empirical method would not take account of the stabilising contribution from hydrogen bonding in the symmetrical transition state [RO ··· H ··· OR]$^{\bullet}$, which might well reduce the value of E_a as calculated by eqn. (5) to *ca.* 10–15 kJ mol^{-1}. Alternatively, the reaction can be envisaged as proceeding by a two-step mechanism involving intramolecular transfer of a single π-electron[47] over 2.5–3 Å from one oxygen to the other in a preformed hydrogen-bonded complex[48] of the type **4**.[†]



4

The activation energy of 25.2 kJ mol^{-1} calculated by eqn. (5) for reaction (16) (entry 68) is 9.3 kJ mol^{-1} larger than the

$$\mathrm{PhCH_2{}^{\bullet} + PhSH \longrightarrow PhCH_3 + PhS^{\bullet}} \tag{16}$$

experimental value, which is recent and apparently reliable.[50] Similarly, the calculated barrier to abstraction of hydrogen from thiophenol by the butyl radical is 8.2 kJ mol^{-1} greater than the experimental value.[50] Other data in the literature for abstraction of hydrogen from thiols or $\mathrm{H_2S}$ by alkyl radicals also indicate that eqn. (5) underestimates the activation energies of such reactions. Radical addition to divalent sulfur to give a sulfuranyl radical $\mathrm{X_3S^{\bullet}}$ is well known, particularly when the addendum radical is electrophilic,[51] and we suggest that abstraction of hydrogen from a thiol (even by a nucleophilic radical) may involve an assisting interaction between the attacking radical and the polarisable sulfur atom, which is not accounted for by eqn. (5). It is also possible that a two-step process could be involved, with prior addition of the carbon-centred radical to sulfur. Abstraction of hydrogen from HBr, HI and (perhaps) from HCl by alkyl radicals is now believed to be a complex process, involving an intermediate adduct of the alkyl radical to the hydrogen halide.[52,53] This complex mechanism is thought to be responsible for the negative activation energies measured for the overall abstraction of hydrogen from HI and HBr by alkyl radicals.[53]

In some cases, it is not clear whether a deviation from the prediction of eqn. (5) should be attributed to a defect in the latter or to uncertainty in the value of E_a(expt.). For example, although the activation energies for abstraction of hydrogen by HO$^{\bullet}$ from $\mathrm{HCF_3}$, dihydrogen, ethane or $\mathrm{HCCl_3}$ are reproduced well by eqn. (5) (see Table 1, entries 41–44), the predicted value of E_a for abstraction from methane (entry 70) is 26.7 kJ mol^{-1}, appreciably larger than the most recent experimental value (15.1 kJ mol^{-1}, in the temperature range 223–420 K). However, recent theoretical work[99] has indicated that quantum mechanical tunnelling may be important in this reaction and theArrhenius plot appears to show appreciable curvature.[99]

Conclusions

Eqn. (5) is generally successful in reproducing the experimental activation energies for a wide range of hydrogen-atom transfer reactions in gas and liquid phases. Although the experimental data are undoubtedly subject to error, because a large number and variety of reactions are considered, the predictions and insights which eqn. (5) provides should prove of some value. It is necessary only to know D_{AH}, D_{BH} and $\Delta\chi_{AB}$, along with the simple structural classification of A$^{\bullet}$ and B$^{\bullet}$, and whether or not B$^{\bullet}$ is an α-conjugated alkyl radical, in order to be able to predict the value of E_a for hydrogen-atom transfer. The form of eqn. (5) focuses attention on the various factors that govern the rate of reaction (1) and the particular role played by polar effects is emphasised and quantified. In future, it may prove possible to generalise this type of empirical approach to include most classes of atom and group transfer reactions (*cf.* ref. 40).

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[*] Such acid–base complex formation prior to atom transfer is closely related to our proposal that $\mathrm{S_H2}$ displacement of R$^{\bullet}$ from the Lewis-acidic $\mathrm{R_3B}$ by Lewis-basic $\mathrm{R_2N^{\bullet}}$ proceeds in a stepwise manner *via* an intermediate aminyl–borane complex $\mathrm{R_2\dot{N}{\rightarrow}BR_3}$.[49] Similar mechanistic conclusions apply to homolytic dealkylation by RO$^{\bullet}$ or RS$^{\bullet}$ at boron or other Lewis-acidic metalloidal (metallic) centres.

[†] In view of these possible complications, hydrogen-atom transfer from phenol to Bu^{t}O$^{\bullet}$ (entry 6) should probably be excluded from the correlation, although in this instance the agreement between calculated and experimental activation energies is actually very good. Similar difficulties arise for H-atom transfer from phenols to other oxyl radicals,[45] notably the *tert*-butylperoxyl radical.[45b,c] Hydrogen-atom abstraction by peroxyl radicals from C–H groups would not be subject to complications arising from hydrogen bonding, but data for such reactions have been excluded at this stage because neither ionisation energies nor electron affinities for alkylperoxyl radicals appear to be available in the literature. [Such abstractions are usually endothermic and the activation energies for the reverse reactions (R$^{\bullet}$ + ROOH) would have to be estimated using eqn. (4).] When rough estimates of *IE* and *EA* for ROO$^{\bullet}$ are used along with $d = 0.44$ in conjunction with eqn. (5), the calculated activation energies are significantly smaller than the experimental values, unless an anomalously large value of *s* is used for the peroxyl radical. There is clearly a need to examine the data for these reactions in more detail in future work.

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