Hydrogen Abstractions by Free Radicals. Factors Controlling Reactivity[1]

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Abstract: Hydrogen abstractions by free radicals are simulated accurately by a model constructed of two Morse curves and an antibonding curve. Reactivity is controlled to a large extent by antibonding interactions, which are described quantitatively in terms of familiar parameters, i.e., ir stretching frequency, bond dissociation energy, bond length, and masses. Over 100 examples are presented.

In an effort to understand the factors controlling reactivity in free radical reactions, we formulated a method for calculating energies of activation in terms of generally familiar chemical concepts and quantities;[2,3] utilizing Morse curves, in what is generally classified as a semiempirical approach, we were successful with hydrogen atom transfer reactions of ΔH limited in the range of +15 to −15 kcal/mol. That method was one of the most accurate available.[4,5]

Now we report a modified approach which is also applicable to very exothermic and endothermic reactions and which is equally as simple and accurate. Basically, our approach is straightforward: a reasonable model for the transition state is postulated and its energy is estimated. Parameters that must be adjusted with every reaction are not used.

In reactions such as depicted by eq 1, we assume that at

$$\mathrm{X{-}H} + \mathrm{Y}\cdot \longrightarrow \begin{array}{ll} \mathrm{X{-}{-}{-}H{-}{-}{-}Y} & \text{(I)} \\ \mathrm{X} : \mathrm{H} \quad \mathrm{Y}\cdot & \text{(II)} \\ \cdot\mathrm{X} \quad \mathrm{H} : \mathrm{Y} & \text{(III)} \\ \dot{\mathrm{X}} \quad \dot{\mathrm{H}} \quad \dot{\mathrm{Y}} & \text{(IV)} \end{array} \longrightarrow \mathrm{X}\cdot + \mathrm{H{-}Y} \qquad (1)$$

the transition state the complex is linear and that the partial bonding in X–H is equal to the partial bonding in H–Y, i.e., that the two canonical forms II and III are of equal energy. Since this will result in maximum resonance stabilization for the odd electron, the assumption is reasonable and also has been proposed previously by others.[6] Therefore, the total bonding energy in the transition state will be the average bonding energy of canonical structures II and III (which is the bonding energy of either one of them, e.g., ${}^1E_{XH}{}^{\ddagger}$), augmented by the resonance energy of the delocalization of one odd electron over three atoms, $E_R{}^{\ddagger}$. In addition, the simultaneous bonding of H to both X and Y (structure I) requires that the electron spins in IV be either $\uparrow\downarrow\uparrow$ or $\downarrow\uparrow\downarrow$, indicating repulsion (antibonding) between X and Y, ${}^3E_{XY}{}^{\ddagger}$.[2,7] Thus the total transition state energy of the system is given by eq 2.

$$E_{tot}{}^{\ddagger} = E_{XH}{}^{\ddagger} + E_R{}^{\ddagger} + E_{XY}{}^{\ddagger} \qquad (2)$$

The most straightforward method for estimating bond energies of stretched bonds is the semiempirical Morse equation,[8] eq 3.

$${}^1E = D_e\{(1 - e^{-\beta(r-r_e)})^2 - 1\} \qquad (3)$$

Antibonding can be estimated by the Sato modification of the Morse equation,[9] as we have shown,[2] eq 4.

$${}^3E_{XY} = 0.45D_e\{(1 + e^{-\beta(r-r_e)})^2 - 1\} \qquad (4)$$

The symbols in eq 3 and 4 denote the following: D_e is the Morse curve dissociation energy, (D_0) plus the zero-point energy in kcal/mol, $D_e = D_0 + 0.00143\omega_0$; r_e is the equilibrium internuclear distance of the bond in ångströms; r is the distance at which the energy is being evaluated; and β is the "spectroscopic" constant given by

$$\beta = 0.1218\omega_0\{\mu/(350D_0)\}^{1/2} \qquad (5)$$

ω_0 is the equilibrium vibrational stretching frequency of the bond in reciprocal centimeters (often approximated by the observed frequency); μ is the reduced mass in atomic mass units of the two bonded atoms; D_0 is multiplied by 350 to convert to reciprocal centimeters.

The value of $E_R{}^{\ddagger}$ must be estimated either from chemical intuition, or it can be regarded as an adjustable parameter to be set by comparison of the results of the calculation with well established energies of activation for a large variety of reactions. From the resonance energy of the allyl radical, we estimate $E_R{}^{\ddagger}$ = 10–11 kcal/mol for the delocalization of one odd electron over three atoms; we find that a value of 10.6 is of general applicability and this is the value adopted for all reactions. Therefore, the data required for the calculation are those needed for the Morse functions, i.e., bond dissociation energies (BDE), ir stretching frequencies, bond lengths, and masses for X–H, H–Y, and X–Y of reaction 1.

The transition state is obtained by evaluating the total energy of the three body system at increasingly stretched r_{XH} distances, always satisfying the "equibonding" criterion (for details see the Appendix). As r_{XH} is increased, $E_{tot}{}^{\ddagger}$ diminishes, reaches a minimum, and then increases again. Clearly, the minimum is the most stable arrangement that satisfies the "equibonding" criterion, i.e., the transition state.

The "classical" energy of activation is the difference between $E_{tot}{}^{\ddagger}$ and D_e(X–H). A small and very approximate correction can be applied for zero-point energy (ZPE) effects via eq 6, to give our calculated energy of activation, to be denoted E^*.

$$\mathrm{ZPE}^{\ddagger} = 0.5(\mathrm{ZPE}_{XH} + \mathrm{ZPE}_{HY}) \qquad (6)$$

The derivation is based on two simple assumptions about the transition state: (1) that the two stretched bonds are of equal energy; and (2) that the most stable linear arrangement satisfying condition 1 is the transition state. The approximations made are: (1) that bonding and antibonding Morse curves can describe the energy of stretched bonds adequately; and (2) that the resonance energy of delocalization of the odd electron over three atoms is independent of the type of X and Y atoms involved and is equal to 10.6 kcal/mol. This last approximation is probably the most questionable. Nevertheless, the calculated activation energies are sufficiently accurate in a large variety of systems to indicate that both our assumptions and approximations are reasonable, even though it is not feasible to exclude the possibility of some fortuitous cancellation of errors.

Results

Table I lists calculated energies of activation, E^*, for a large variety of gas phase reactions and reported experimental values of E_a. Our choice of reactions in Table I has been guided by the availability of relatively reliable data for each case. Even for these reactions, the molecular data used are not always completely unequivocal and a more detailed discussion is given in the Data section. The experimental values of E_a have been taken from our previous compilation[2] and from that of Trotman-Dickenson and Milne,[10] unless otherwise indicated; these values are presented generally in chronological order (earliest work first) and their accuracy seldom is better than ±0.5 kcal/mol, usually ±1.

A general inspection of Table I shows that the calculated values of E^* are remarkably accurate, particularly for reactions among simple species where the molecular data are good and the energies of activation well known. Very exothermic and endothermic reactions are simulated well, unlike our previous method[2] which would not be applicable to such extreme cases. This limitation was due to the approximation that, in the transition state, the lengths of the two stretched bonds were in the same ratio as their equilibrium distances. This appears to be valid for reactions that are symmetrical in terms of thermochemistry, but fails for skewed cases.

Discussion

The general accuracy of the method as demonstrated in Table I guarantees that our results are not fortuitous and that the assumptions and approximations made in the derivation of eq 2 are reasonable. The major factors controlling reactivity in gas phase hydrogen abstractions are being taken into account by the calculation, and the conclusions that can be reached regarding their importance reinforce our previous findings.[2,3]

In all cases the repulsion term, ${}^3E_{XY}{}^{\ddagger}$, calculated in the transition state exceeds the value of the activation energy. This repulsion is overcome partially by the resonance energy gained by the delocalization of the odd electron and partially by the energy of activation.

The importance of the antibonding term is best illustrated by a closer examination of a series of nearly thermoneutral reactions in which the influence of ΔH is minimal. Table II shows a series of such reactions arranged in order of decreasing energy of activation. Whereas there is not a similar trend in the BDE of the bonds being broken and made, the calculated repulsion terms closely follow a decreasing trend. Therefore, the properties of molecule X–Y are of importance even though it is never formed in the reaction. A strong X–Y bond will increase the energy of activation, and vice-versa. In addition, factors that broaden the X–Y Morse curve will result in higher repulsion at a given distance and higher E_a; these factors are lower stretching frequency and greater bond length. The stretching frequency increases with BDE and with the dipole moment of the bond, and decreases as the masses increase. Thus, parameters not usually considered by free radical chemists as relevant to reactivity, e.g., bond lengths and masses, can be of major importance.

The idea that repulsive forces are a factor in radical reactions is not novel.[11] However, the concept, as used in free radical work, was highly qualitative, not unequivocal, and of little use with actual systems.[12] This method of calculation places the concept of repulsion on a quantitative basis, simply and accurately.

The calculation does not make any special provision for charge separated structures, such as X^+HY^-, as the "polar effect" is commonly depicted in radical reactions.[11,13] Nevertheless, many reactions in which polar effects would be expected to play a role ($CH_4 + CCl_3\cdot$, $CH_4 + CH_3O\cdot$, $H_2 + F\cdot$, $C_6H_5CH_3 + Br\cdot$, etc.) are simulated accurately, apparently in terms of the effect of dipoles on the ir stretching frequency, the BDE, and the bond length of the X–Y bond.

Reactivity reversals are generally explained in terms of the "polar effect". For instance, in terms of the energy of activation, H_2 is more reactive than CH_4 by about 3 kcal/mol in hydrogen abstractions by H·; when the attacking radical is $CF_3\cdot$, the two energies of activation are comparable. The calculation simulates this effect quite accurately (Table I). Gas phase abstractions by $CH_3\cdot$ from methanol exhibit nearly the same activation energy for attack on the methyl or the hydroxy hydrogens, even though abstraction of the methyl hydrogen is considerably more exothermic (about 10 kcal/mol). This demonstration of a polar effect also is simulated accurately by our calculation (Table I). Thus the qualitative concept of the polar effect is placed on a quantitative basis and the influence of dipoles (e.g., on stretching frequencies) can be distinguished clearly from the effects of bond dissociation energies.

The idea that atoms react faster than multiatomic radicals because the latter require energy for structural reorganization (rehybridization) has been expressed repeatedly.[14] The results of Tables I and II show no evidence supporting such a conclusion about energy requirements.

In terms of the overall utility of our method, it has been pointed out that, since about 90% of all reported gas phase, exothermic, atom abstractions have activation energies of 8 ± 3 kcal/mol, it is going to take a fairly sophisticated rule to have much predictive value.[15] Even though our calculation is not particularly sophisticated, it seems to be reliable enough to be worth the effort of carrying *it* out.

Applications

The calculation can be helpful in many current problems and we provide a few examples as an illustration.

Reactions of Alkoxy Radicals with Alcohols. Abstractions of hydroxylic hydrogen by alkoxy radicals have not attracted much attention; in fact they have been thought to be very slow processes.[16] For the identity reaction $(CH_3)_3COH$ + $(CH_3)_3CO\cdot$, we calculate a very low energy of activation (Table I). Griller and Ingold very recently established experimentally the rapid nature of the reaction and its low activation energy.[17] The fact that reactions such as these, which are not exothermic, proceed with very low energies of activation can be understood only in terms of the very low X–Y repulsion.

An interesting aspect of this reaction is the low value found for the preexponential term of the Arrhenius expression, log $A = 6.4$ (units of l./(mol sec)); this is much lower than the values usually recommended for hydrogen abstractions, log $A = 8.5 \pm 0.5$.[18] Similarly low log A values have been reported for hydrogen transfer between phenoxy radicals[19] and peroxy radicals with hindered phenols and with aromatic amines.[20] To explain the low A values, the suggestion has been made that a hydrogen bonded free radical–reactant complex is formed first, followed by hydrogen transfer within the complex.[20] However, recent results for the reaction of *tert*-butylperoxy radicals with nonhindered phenols, amines, and thiophenols are not compatible with the hydrogen bonded complex proposal.[21] Our calculations indicate that, in reactions with very weak antibonding (X–Y = O–O, O–N, O–S, etc.), the transition state is very tight. For the *tert*-butyl alcohol–*tert*-butoxy exchange, the X–H and H–Y bonds are stretched only 0.06 Å; for the ROO·–phenol exchange, the two O–H bonds are within 0.05 Å of their equilibrium value. These distances can be compared with those of the methane–methyl exchange

Table I. Gas Phase Hydrogen Abstraction Reactions

Reaction[a]	Calcd E^*, kcal/mol	Exptl E_a, kcal/mol
$\mathrm{H_2 + CH_3\cdot}$	11.6	9.9, 10.0, 13.0, 13.2, 10.0, 10.2, 12.2, 10.9[b]
$\mathrm{CH_4 + CH_3\cdot}$	14.1	13.8, 14.6, 13.8, 14.1
$\mathrm{CH_3CH_3 + CH_3\cdot}$	10.6	10.4, 9.9, 11.5, 11.2, 11.4, 12.0
$\mathrm{(CH_3)_2C}\mathit{H}_2 + \mathrm{CH_3\cdot}$	9.9	9.7, 10.2
$\mathrm{(CH_3)_3C}\mathit{H} + \mathrm{CH_3\cdot}$	8.0	7.6, 7.4, 6.6, 9.0, 7.7, 8.2
$\mathrm{C(CH_3)_4 + CH_3\cdot}$	11.3	10.0, 10.4, 10.8, 12.0,[c] 11.5,[d] 11.7[e]
$\mathrm{c\text{-}C_6H_{12} + CH_3\cdot}$	9.4	8.3, 8.3, 9.5
$\mathrm{CH_3COCH_3 + CH_3\cdot}$	9.7	9.6, 9.7, 9.8, 9.5, 9.6
$\mathrm{CH_2{=}CHC}\mathit{H}_3 + \mathrm{CH_3\cdot}$	7.3	7.7, 7.3, 8.0, 8.2
$\mathrm{C_6H_5C}\mathit{H}_3 + \mathrm{CH_3\cdot}$	7.4	7.3,[f] 8.3,[f] 9.6
$\mathrm{CCl_3H + CH_3\cdot}$	6.5	6.8
$\mathrm{C}\mathit{H}_3\mathrm{OH + CH_3\cdot}$	9.3	10.4, 8.1, 9.0
$\mathrm{CH_3O}\mathit{H} + \mathrm{CH_3\cdot}$	9.9	6.4, 9.0
$\mathrm{CH_3OCH_3 + CH_3\cdot}$	8.6	10.0, 8.4, 9.5, 10.8
$\mathrm{SiH_4 + CH_3\cdot}$	7.8	6.9, 7.0, 7.5[e]
$\mathrm{CH_3S}\mathit{H} + \mathrm{CH_3\cdot}$	5.3	4.1
$\mathrm{HCHO + CH_3\cdot}$	3.7	6.2, 6.6[g]
$\mathrm{CH_3C}\mathit{H}\mathrm{O + CH_3\cdot}$	5.5	7.9, 6.5, 6.8, 8.5, 8.7, 7.6, 6.8[g]
$\mathrm{NH_3 + CH_3\cdot}$	9.8	10.0, 9.8, 10.0
$\mathrm{CH_3N}\mathit{H}_2 + \mathrm{CH_3\cdot}$	5.8	5.7
$\mathrm{H_2NNH_2 + CH_3\cdot}$	5.0	5.0
$\mathrm{CH_3CH_3 + CH_3CH_2\cdot}$	13.4	14.1, 12.6[h]
$\mathrm{c\text{-}C_6H_{12} + CH_3CH_2\cdot}$	10.6	10.4
$\mathrm{(CH_3)_3C}\mathit{H} + \mathrm{CH_3CH_2\cdot}$	8.9	8.9
$\mathrm{CH_2{=}CHC}\mathit{H}_3 + \mathrm{CH_3CH_2\cdot}$	8.9	7.6, 8.7
$\mathrm{C(CH_3)_4 + CH_3CH_2\cdot}$	13.6	12.6
$\mathrm{C_6H_5C}\mathit{H}_3 + \mathrm{CH_3COCH_2\cdot}$	8.8	9.3[i]
$\mathrm{CH_2{=}CHC}\mathit{H}_3 + \mathrm{C_6H_5CH_2\cdot}$	11.4	≅14[j]
$\mathrm{C_6H_5C}\mathit{H}_3 + \mathrm{C_6H_5CH_2\cdot}$	11.3	≅17[k]
$\mathrm{H_2 + C_6H_5\cdot}$	9.7	6.5
$\mathrm{H_2 + F\cdot}$	1.8	1.7
$\mathrm{CH_4 + F\cdot}$	5.9 ± 2.5	1.2
$\mathrm{CH_3CH_3 + F\cdot}$	4.4 ± 2.5	0.3
$\mathrm{(CH_3)_2C}\mathit{H}_2 + \mathrm{F\cdot}$	3.8 ± 2.5	0.0
$\mathrm{FH + F\cdot}$	0.0	
$\mathrm{H_2 + Cl\cdot}$	11.0	6.1, 5.5, 5.5
$\mathrm{CH_4 + Cl\cdot}$	12.8	3.9
$\mathrm{ClH + Cl\cdot}$	5.1	6.6, 5.4[jj]
$\mathrm{CCl_3H + Cl\cdot}$	6.5	3.3, 6.5, 3.3
$\mathrm{H_2 + Br\cdot}$	20.3	19.4, 17.6, 18.6, 19.8, 17.8, 18.3, 19.7, 19.4, 20.4[l]
$\mathrm{CH_4 + Br\cdot}$	20.1	18.3, 18.2, 17.3, 18.2
$\mathrm{CF_3H + Br\cdot}$	20.7	23.0, 21.1
$\mathrm{CH_3CH_3 + Br\cdot}$	14.9	13.6, 13.4, 14.0[m]
$\mathrm{(CH_3)_2C}\mathit{H}_2 + \mathrm{Br\cdot}$	11.5	10.1, 10.2, 10.7[n]
$\mathrm{(CH_3)_3C}\mathit{H} + \mathrm{Br\cdot}$	8.2	7.5
$\mathrm{C_6H_5C}\mathit{H}_3 + \mathrm{Br\cdot}$	8.3	7.2, 8.0[o]
$\mathrm{CH_2{=}CHC}\mathit{H}_3 + \mathrm{Br\cdot}$	8.6	
$\mathrm{CH_3COCH_3 + Br\cdot}$	15.8	14
$\mathrm{C(CH_3)_4 + Br\cdot}$	15.8	14.3
$\mathrm{c\text{-}C_6H_{12} + Br\cdot}$	11.2	
$\mathrm{BrH + Br\cdot}$	3.0	
$\mathrm{H_2 + I\cdot}$	33.0	33.9, 33.5
$\mathrm{CH_4 + I\cdot}$	35.1	33.5, 34.1, 35.0
$\mathrm{CH_3CH_3 + I\cdot}$	29.8	27.9
$\mathrm{(CH_3)_2C}\mathit{H}_2 + \mathrm{I\cdot}$	26.2	25.5, 25.0
$\mathrm{(CH_3)_3C}\mathit{H} + \mathrm{I\cdot}$	22.2	21.4
$\mathrm{c\text{-}C_5H_{10} + I\cdot}$	26.7	
$\mathrm{C(CH_3)_4 + I\cdot}$	30.8	
$\mathrm{H_2 + HO\cdot}$	4.0	5.5,[p] 5.1,[p] 3–6;[r] 4.0[s]
$\mathrm{CH_4 + HO\cdot}$	8.7	8.3, 9.0, 6.5, 7.4, 5.0,[p] 9—4[p]
$\mathrm{CH_3CH_3 + HO\cdot}$	6.0	7.3, 3.6[p]
$\mathrm{(CH_3)_2C}\mathit{H}_2 + \mathrm{HO\cdot}$	4.2	2.9[q]
$\mathrm{(CH_3)_3C}\mathit{H} + \mathrm{HO\cdot}$	2.6	2.8[q]
$\mathrm{ClH + HO\cdot}$	2.8	2.1–2.6[t]
$\mathrm{BrH + HO\cdot}$	0.4	1.1[t]

Table I (*Continued*)

Reaction[a]	Calcd E^*, kcal/mol	Exptl E_a, kcal/mol
$\mathrm{HOH + HO\cdot}$	6.3	
$\mathrm{H_2 + CH_3O\cdot}$	5.5	
$\mathrm{CH_4 + CH_3O\cdot}$	10.7	11.0[u]
$\mathrm{CH_3CH_3 + CH_3O\cdot}$	7.7	7.1
$\mathrm{(CH_3)_2C}H_2\mathrm{ + CH_3O\cdot}$	6.7	5.2
$\mathrm{(CH_3)_3C}H\mathrm{ + CH_3O\cdot}$	5.4	4.1
$\mathrm{(CH_3)_4C + CH_3O\cdot}$	8.6	7.3
$\mathrm{c\text{-}C_6H_{12} + CH_3O\cdot}$	6.6	
$\mathrm{HCHO + CH_3O\cdot}$	3.3	≅4
$\mathrm{CH_4 + (CH_3)_3CO\cdot}$	10.6	
$\mathrm{CH_3CH_3 + (CH_3)_3CO\cdot}$	7.5	6.5[v,w]
$\mathrm{(CH_3)_2C}H_2\mathrm{ + (CH_3)_3CO\cdot}$	6.3	5.5[w]
$\mathrm{(CH_3)_3C}H\mathrm{ + (CH_3)_3CO\cdot}$	5.3	4.0, 4.8[w]
$\mathrm{C_6H_5C}H_3\mathrm{ + (CH_3)_3CO\cdot}$	4.3	4.3[x]
$\mathrm{C_6H_6 + (CH_3)_3CO\cdot}$	11.6	
$\mathrm{ClH + (CH_3)_3CO\cdot}$	1.4	
$\mathrm{(CH_3)_3CO}H\mathrm{ + (CH_3)_3CO\cdot}$	1.4	2.6[y]
$\mathrm{H_2 + H\cdot}$	9.4	6.7, 7.5, 8.0, 9.2, 9.4[z]
$\mathrm{CH_4 + H\cdot}$	12.1	7.8, 7.0, 6.6, 4.5, 9.0, 8.0, 9.6, 11.5, 15.1, 11.1, 7.4, 11.9, 11.8
$\mathrm{CH_3CH_3 + H\cdot}$	7.7	9.0, 6.8, 9.0, 12.0, 12.2, 9.0, 9.7
$\mathrm{(CH_3)_2C}H_2\mathrm{ + H\cdot}$	5.7	
$\mathrm{(CH_3)_3C}H\mathrm{ + H\cdot}$	4.1	
$\mathrm{C}H_3\mathrm{OH + H\cdot}$	5.3	
$\mathrm{CH_3O}H\mathrm{ + H\cdot}$	5.3	
$\mathrm{CH_3COCH_3 + H\cdot}$	7.5	≅8[aa]
$\mathrm{C_6H_5C}H_3\mathrm{ + H\cdot}$	2.3	
$\mathrm{HCHO + H\cdot}$	3.2	2.6, 3.2, 3.8[bb]
$\mathrm{H_2NNH_2 + H\cdot}$	2.8	2.0, 2.5[cc]
$\mathrm{NH_3 + H\cdot}$	8.1	≅10[dd]
$\mathrm{CH_3S}H\mathrm{ + H\cdot}$	3.4	≅3
$\mathrm{HOH + H\cdot}$	19.0	19.0[ee]
$\mathrm{HNO_3 + H\cdot}$	4.2 ± 2.5	
$\mathrm{HSH + H\cdot}$	4.4	
$\mathrm{H_2 + CF_3\cdot}$	10.6	8.8, 9.5, 11[ff]
$\mathrm{CH_4 + CF_3\cdot}$	10.7	10.3, 9.5, 10.6, 11.0, 11.3, 11.0, 11.2[gg]
$\mathrm{CH_3CH_3 + CF_3\cdot}$	7.1	7.5, 8.3[hh]
$\mathrm{(CH_3)_2C}H_2\mathrm{ + CF_3\cdot}$	5.2	5.5, 5.3, 5.1
$\mathrm{(CH_3)_3C}H\mathrm{ + CF_3\cdot}$	3.1	4.7, 3.0[u]
$\mathrm{SiH_4 + SiH_3\cdot}$	21.5	
$\mathrm{NH_3 + NH_2\cdot}$	10.1	
$\mathrm{H_2 + CCl_3\cdot}$	14.4	11.3[ii]

[a] The hydrogen abstracted is shown in italics. [b] J. S. Shapiro and R. E. Weston, Jr., *J. Phys. Chem.*, 76, 1669 (1972). [c] J. A. Kerr and D. Timlin, *J. Chem. Soc. A*, 1241 (1969). [d] E. Furimsky and K. J. Laidler, *Can. J. Chem.*, 50, 1115 (1972). [e] R. E. Berkley, I. Safaric, H. E. Gunning, and O. P. Strausz, *J. Phys. Chem.*, 77, 1734 (1973). [f] R. E. Rebbert and E. W. R. Steacie, *J. Chem. Phys.*, 21, 1723 (1953). [g] These values appear high compared to 5.9 for aldehydic hydrogen abstraction by ethyl radicals and 6.3 by isopropyl radicals: A. F. Trotman-Dickenson, *Adv. Free-Radical Chem.*, 1, 1 (1965). [h] J. A. Kerr, "Free Radicals", J. K. Kochi, Ed., Vol. II, Wiley-Interscience, New York, N.Y., 1973, p 15. [i] Liquid phase: K. Schwetlick and S. Helm, *Tetrahedron*, 22, 793 (1966). [j] M. Szwarc, B. N. Gosh, and A. H. Sehon, *J. Chem. Phys.*, 18, 1142 (1950). [k] For abstraction from $\mathrm{C_6H_5C}D_3$, $E_a = 19.9$: R. A. Jackson and D. W. O'Neill, *Chem. Commun.*, 1210 (1969); this value appears much too high compared to $E_a = 17$ for abstraction by styryl radicals from toluene: G. B. Brandrup, J. Brandrup, and L. J. Young, "Polymer Handbook, II", G. B. Brandrup and E. Immergut, Ed., Interscience, New York, N.Y., 1966, p 77. This value also has been criticized by K. U. Ingold.[4] [l] Calculated from the reverse reaction from the compilation of ref 10. [m] K. D. King, D. M. Golden, and S. I. Benson, *Trans. Faraday Soc.*, 66, 2794 (1970). [n] K. C. Ferguson and E. Whittle, *ibid.*, 67, 2618 (1971). [o] H. R. Anderson, H. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, 21, 1258 (1953). [p] W. E. Wilson, Jr., *J. Phys. Chem. Ref. Data*, 1, 535 (1972). [q] R. R. Baker, R. R. Baldwin, and R. W. Walker, *Trans. Faraday Soc.*, 66, 2812 (1970). [r] A. A. Westenberg and N. DeHaas, *J. Chem. Phys.*, 58, 4061 (1973). [s] R. N. Greiner, *ibid.*, 51, 5049 (1969). [t] Reference 50. [u] P. Gray, R. Shaw, and J. C. J. Thynne, *Prog. React. Kinet.*, 4, 63 (1967). [v] For the primary hydrogens of *n*-butane.[w] [w] J. M. Tedder et al., *Trans. Faraday Soc.*, 66, 2029 (1970). [x] Liquid phase: J. H. T. Brook, *ibid.*, 53, 327 (1957); adjusted with the more recent value of $E_a = 15.6$ for $\mathrm{(CH_3)_3CO\cdot \rightarrow CH_3\cdot + CH_3COCH_3}$.[w] [y] Liquid phase: ref 17. [z] A. A. Westenberg and N. DeHaas, *J. Chem. Phys.*, 47, 1393 (1967). [aa] Steric factor of 1.0 assumed. [bb] A. A. Westenberg and N. DeHaas, *J. Phys. Chem.*, 74, 2213 (1972). [cc] M. Gehring, K. Hoyerman, H. G. Wagner, and J. Wolfrum, *Ber. Bunsenges. Phys. Chem.*. 75, 1287 (1971). [dd] Mechanism unclear; see discussion in text. [ee] D· radicals: N. E. Bibler and R. F. Firestone, *J. Phys. Chem.*, 76, 621 (1972). [ff] C. L. Kibby and R. E. Weston, *J. Chem. Phys.*, 49, 4825 (1968). [gg] R. D. Giles, L. M. Quick, and E. Whittle, *Trans. Faraday Soc.*, 63, 662 (1967). [hh] L. M. Quick and E. Whittle, *ibid.*, 67, 1727 (1971). [ii] Estimated with assumed k_t: R. Foon and K. B. Tait, *J. Chem. Soc., Faraday Trans. 1*, 68, 104 (1972). [jj] R. L. Thommarson and G. C. Berend, *Int. J. Chem. Kinet.*, 5, 629 (1973).

Table II. Nearly Thermoneutral Reactions

Reaction	E^*, kcal/mol	${}^3E_{XY}{}^\ddagger$, kcal/mol	BDE(X–H), kcal/mol
$SiH_4 + SiH_3\cdot$	21.5	21.9	93.9
$CH_4 + CH_3\cdot$	14.1	19.2	104.8
$CH_3CH_3 + CH_3CH_2\cdot$	13.4	18.5	98.3
$H_2 + CH_3\cdot$	11.6	18.2	104.2
$C_6H_5CH_3 + C_6H_5CH_2\cdot$	11.3	17.8	88.0
$CH_4 + CF_3\cdot$	10.7	17.1	104.8
$CH_4 + CH_3O\cdot$	10.7	16.6	104.8
$H_2 + CF_3\cdot$	10.6	17.7	104.2
$NH_3 + CH_3\cdot$	9.8	16.3	105.0
$H_2 + H\cdot$	9.4	15.7	104.2
$C_6H_5CH_3 + Br\cdot$	8.3	15.2	88.0
$HOH + HO\cdot$	6.3	13.8	119.0
$H_2 + CH_3O\cdot$	5.5	13.0	104.2
$ClH + Cl\cdot$	5.1	12.4	103.0
$BrH + Br\cdot$	3.0	11.0	87.5
$(CH_3)_3COH + (CH_3)_3CO\cdot$	1.4	9.4	105.0
$FH + F\cdot$	0	8.7	136.1

where the C–H bonds being formed and ruptured are 0.14 Å longer than their equilibrium values. The generalization that log $A = 8.5 \pm 0.5$ for atom transfer reactions was based mainly on reactions involving carbon radicals[22] and does not appear to be valid for reactions with very weak X–Y bonds.

Low energies of activation are also predicted for hydrogen abstractions by oxy radicals from halogen acids (Table I), because of the low oxygen-halogen antibonding. The reaction of *tert*-butoxy radicals with HCl is known to be very fast,[23] even though its exothermicity is minimal.

Reactions of Silyl Radicals. The free radical reactions of silane are always complicated by the displacement of hydrogen, eq 7.

$$SiD_3\cdot + SiH_4 \rightarrow D_3SiSiH_3 + H\cdot \qquad \Delta H = 14 \qquad (7)$$

There is no direct evidence for the hydrogen exchange, eq 8.

$$SiD_3\cdot + SiH_4 \rightarrow SiD_3H + SiH_3\cdot \qquad \Delta H \simeq 0 \qquad (8)$$

E.g., in the reaction of hydrogen atoms with mixtures of silane and silane-d_4, the hydrogen exchange is not part of the proposed reaction scheme.[24] In the pyrolysis of mixtures of silane and silane-d_4, eq 8 was postulated to occur even though it is not essential to the explanation of the data, simply because it is 14 kcal/mol more exothermic than reaction 7 which does occur.[25]

Even though one can easily explain reaction 7 in terms of d orbital involvement,[25] it is not at all clear why reaction 8 is not the predominant, if not the exclusive, mode of reaction. The corresponding hydrogen abstraction with the carbon analog compounds has $E_a = 14$, the silane bonds are 10 kcal/mol weaker, and reaction 7 has an activation energy of no less than 14 kcal/mol on thermodynamic grounds. On the basis of these arguments, reaction 8 should, at least, be competitive with 7. However, our calculation shows that Si–Si antibonding is very high (Table II). Since the Si–Si BDE is not particularly high at 81 kcal/mol, the large repulsion is due to the broadness of its Morse curve caused by the low ir stretching frequency (434 cm^{-1}, due to the higher masses) and the longer bond length (2.32 Å). Thus, the energy of activation for the hydrogen exchange, eq 8, is calculated to be well over 14 kcal/mol (Table I).

Reaction of Hydrogen Atoms with Ammonia. An ESR study of the reaction $D\cdot + NH_3$ found that considerable H· is produced; thus, a displacement type of reaction on ammonia was postulated, with $E_a = 10$ kcal/mol. The Arrhenius plot was not quite linear throughout the temperature range examined.[26] Our calculated value of 8.1 kcal/mol for direct abstraction indicates that it should be competitive with the displacement on nitrogen and would explain the curvature of the Arrhenius plot.

Hammett Correlations. Abstractions by radicals from the methyl group of substituted toluenes generally show linear free energy relations of the Hammett type.[11] Unfortunately, it is not possible to simulate such reactions because the molecular data are not available. Nevertheless, the parameters that give rise to such correlations can be identified in terms of the concepts of our calculation. The benzyl C–H BDE in toluenes is probably some function of the substituent, since the percent s character in this bond correlates with Hammett σ's.[27,28] The stretching frequencies of the benzyl-Y bond (where Y is the abstracting species) would also be expected to correlate with σ.[29] The benzyl-Y BDE also would be some function of the substituent.[30] Thus, of necessity, E^* would be a function of σ and the value of the slope, ρ, would depend on the relative importance of these parameters and of ΔH for the overall reaction for each Y·.

C–H BDE in Formaldehyde. The relation between kinetics and thermochemistry has been described.[18,31] The value derived from the recent JANAF Tables for the C–H BDE in formaldehyde is 77 kcal/mol;[32] on the other hand, Benson recommends 87.8.[18] With the lower value, the energy of activation for hydrogen abstraction by H·, $CH_3\cdot$, and $CH_3O\cdot$ is calculated by our method to be negative. The higher value leads to reasonable calculated values of E^* (Table I); our calculation therefore provides strong support for the higher value.

N–H Bond Dissociation Energies. The value derived from the JANAF tables for H_2N–H is 103 kcal/mol.[32] Benson[33] and we[2] have proposed higher N–H values. The values recommended in our previous work (H_2N–H = 105, CH_3NH–H = 97, H_2NNH–H = 95.5)[2] lead to correct predictions of activation energies for hydrogen abstraction from these compounds (Table I).

ROO–H Bond Dissociation Energies. For hydrogen peroxide, BDE(HOO–H) is estimated to be near 90 kcal/mol,[18,32] on the basis of an electron impact measurement and an uncertain value for the heat of formation of HOOH (only an interim table is given in the JANAF compilation[32]). Electron impact measurements can be subject to large uncertainties.[34] Hydrogen abstractions from HOOH by H· and HO· have been reported with activation energies of 4 and 1 kcal/mol, respectively.[35,36] With BDE(HOO–H) = 90, we calculate negative energies of activation for both reactions. A value of 96 kcal/mol is needed to bring the calculated activation energies to 2.2 and near 0, respectively.[37] This higher value is probably a better estimate.

The use of this type of calculation to assign BDE values is not novel. This approach has been used often with Polanyi-type relations;[31] however, the Polanyi relation is applicable to very few radicals in reactions with alkanes. Our method should be much more useful in this application, since it has been shown to apply to all hydrogen abstractions by free radicals.

Transition State Distances. The Hammond postulate[38] and Polanyi's similar suggestions[8] are built into this method. Table III shows some results which illustrate transition state distances and their changes with ΔH. Generally, the distances resulting from our calculation are somewhat shorter than those from most other methods. For instance, for the reaction $H_2 + F\cdot$, Bender et al.[39] have performed ab initio rigorous quantum mechanical calculations as follows: (a) a one-configuration self-consistent-field (SCF) wave function and (b) a 214-configuration multiconfiguration wave function. Method (a) results in transition state distances of F–H = 1.06 Å and H–H = 0.81 Å and an energy barrier height of 34.3 kcal/mol; method (b) results in F–H = 1.37 Å and H–H = 0.81 Å, with a barrier height of 5.1 kcal/mol. The experimental value is much lower, $E_a = 1.7$.

Table III. Transition State Distances for X–H + Y· → X· + H–Y[a]

X–H	Y·	ΔH[b]	X–H‡	H–Y‡	X–H[c]	H–Y[c]
H_2	I	32.9	1.17	1.65	0.74	1.61
H_2	Br	16.7	1.02	1.47	0.74	1.41
H_2	Cl	1.8	0.87	1.36	0.74	1.27
H_2	H	0	0.85	0.85	0.74	0.74
H_2	HO	−14.8	0.80	1.16	0.74	0.96
H_2	F	−31.9	0.78	1.20	0.74	0.92
CH_4	CH_3	0	1.23	1.23	1.09	1.09
CH_3CH_3	CH_3	−6.5	1.19	1.28	1.09	1.09
$(CH_3)_2\mathit{CH}_2$[d]	CH_3	−10.3	1.18	1.32	1.09	1.09
$(CH_3)_3\mathit{CH}$[d]	CH_3	−13.8	1.17	1.35	1.09	1.09
$C_6H_5\mathit{CH}_3$[d]	CH_3	−16.8	1.16	1.38	1.09	1.09
CH_4	H	0.6	1.20	0.86	1.09	0.74

[a] All values in Å. [b] In kcal/mol. [c] Distances in the stable molecules. [d] The abstracted hydrogen is in italics.

Muckerman[40] constructed four semiempirical LEPS potential energy surfaces for this reaction and used adjustable parameters to scale the surfaces to the experimental energy barrier height; his distances ranged for F–H = 1.60–1.27 Å and H–H = 0.76–0.82 Å. Our results are not out in line with the above calculations (Table III), but the reliability of transition state distances obtained by methods that predict the wrong barrier height is very questionable. Truhlar has emphasized this point recently.[41]

The reaction of H_2 + H· has been studied for many years; typical examples are an extensive semiempirical calculation which resulted in a symmetrical transition state with distances of 0.90 Å,[42] and a more recent a priori variational calculation which gave 0.93 Å, a barrier height of 11 kcal/mol, and utilized an empirical weight function to improve accuracy.[43] Our value of 0.85 Å is somewhat shorter than these estimates, but we obtain the correct barrier height.

The reaction CH_4 + H· has been simulated using ab initio SCF calculations[44] with minimal (MZ) and double ζ (DZ) basis sets, with and without configurational interaction (CI). The results are as follows for the transition state distances: MZ-SCF, H–H = 0.87 Å, H–CH_3 = 1.37 Å, barrier height = 37.5 kcal/mol; DZ-SCF, H–H = 0.86, H–CH_3 = 1.42; barrier = 35.2; DZ-SCF-CI, H–H = 0.95, H–CH_3 = 1.48, barrier = 18. The experimental E_a is 12 kcal/mol and again it can be seen that the transition state distances change as the calculated energy of activation changes. Our results (Table III) again show somewhat shorter distances and we obtain E^* = 12.1.

Comparison with the BEBO Method. The bond energy bond order method for calculating energies of activation in hydrogen abstractions[7] is another quite successful semiempirical approach, conceptually similar to ours in some respects; often, the calculated energies of activation are nearly the same as ours. There are some differences in the results, however, as illustrated in the following examples (the reaction is followed by the experimental E_a, the BEBO value, and ours in parentheses[45]): CH_4 + CH_3·, 14, 16.1 (14.1); CH_4 + CF_3·, 11, 14.1 (10.7); CH_3COCH_3 + CH_3·, 9.6, 11.9 (9.7); CH_4 + HO·, 5–9, 7.1 (8.7), CH_4 + F·, 1.2, 3.4 ± 2.5 (5.9 ± 2.5), H_2 + Cl·, 5.5, 6.3 (11.0); and CH_4 + Cl·, 4, 10.6 (12.8).

The BEBO method is based on a correlation between energy and bond length that is very different from the Morse curve, as shown by the following results for H_2 (distance, BEBO energy in kcal/mol, Morse energy): 0.80 Å, 86, 109; 0.90 Å, 58, 102; 1.00 Å, 38, 92; 1.10 Å, 26, 81. Extensive quantum mechanical calculations have shown that the standard Morse curve gives quite accurate approximations to the bonding energy of H_2 up to about 1.5 Å.[46] In addition, the BEBO method takes only 55% of the repulsion energy given by eq 4. It is thus somewhat surprising that our method and the BEBO method generally do not give drastically different results, even though BEBO consistently gives slightly greater transition state distances, usually of the order of 0.05 Å.

The BEBO method has been described as failing seriously in only one known case, F–H + F·, where it predicts an energy barrier of 5.5 kcal/mol.[47] Ab initio calculations give $E_a > 18$.[48] We also obtain a very low E^* for this reaction (Table I), and, since experimental evidence is lacking, we would reserve judgement as to whether the semiempirical methods fail badly in this case. In the very similar reaction Cl–H + Cl·, we obtain E^* = 5.1 which is not far from the experimental value of 6.6;[49] BEBO appears to fail,[50] predicting an unlikely Cl_2H species that is stable by 1.4 kcal/mol compared to isolated reactants. For Br–H + Br·, we obtain E^* = 3.0, and BEBO implies Br_2H stable by 2.8 kcal/mol.

Chlorinations. Our method (and the BEBO method) predicts activation energies that are considerably higher than reported experimental values for abstractions by Cl· from hydrocarbons and from H_2. Since the reactions of other electronegative species are simulated well, it does not appear that the difficulty is related to electronegativity. Either we are faced with a complete breakdown of semiempirical methods, or the criticisms of Benson and Buss[51] concerning the reliability of these measurements have validity, despite the general acceptance of the results.

Data

Obviously the calculated activation energies can be no more accurate than the molecular data used and care was exercised to obtain the best values available.

The data used were obtained from standard reference works, the more recent values being used,[18,32-34,52-58] and from the compilation of ref 2. The JANAF tables were considered the most reliable source.[32] In cases where other sources were used, they are mentioned below. Care must be exercised in the selection and use of vibrational stretching frequencies as data, particularly for complex molecules; if the vibration is strongly coupled to some other mode, its position will shift significantly and its use as data will lead to apparent failure of the method. When it occurs, we used the average of the symmetric and antisymmetric stretch, weighted for degeneracy.

The C–C stretching frequency in CH_3–$C(CH_3)_3$ and CH_3CH_2–$C(CH_3)_3$, for which specific assignments could not be found, was set at 900 cm^{-1}, the average value recommended by Herzberg.[57] A frequency of 1100 cm^{-1} was used for all CF_3–C bonds; this appears to be a good average value.[52] The C–C frequency in $C_6H_5CH_2$–CH_3 was set at 850 cm^{-1} by analogy with $CH_2{=}CHCH_2$–CH_3.[2] The allyl-allyl, ethyl-allyl, and benzyl-benzyl C–C frequencies were obtained by extrapolation of other known values for C–C, utilizing the quantum mechanically required approximate proportionality of stretching frequency to the square root of the BDE.[59] The same type of extrapolation was used for $(CH_3)_3CO$–$CH_2C_6H_5$.

The C–Br stretching frequency in allyl bromide was set at 600 cm^{-1} by analogy from benzyl bromide (602 cm^{-1}).[2] Stretching frequencies for all aliphatic C–Br and C–Cl bonds were set at 725 and 830 cm^{-1}, respectively, from the average force constants recommended by Herzberg.[57] Such frequencies are very much a function of the alkyl group,[58] indicating coupling, and none of the observed frequencies can be assigned principally to a C–halogen stretch, as shown by isotopic shift studies.[60]

The C–Si stretching frequency was set at 800 cm^{-1}, a recommended average value.[58] The observed frequency of 700 cm^{-1} in CH_3SiH_3 is coupled, as shown by D substitution.[52]

Our previous work[2] used a BDE of 96 kcal/mol for CH_3COCH_2–H and a frequency of 946 cm^{-1} for CH_3COCH_2–CH_3. This stretch has now been assigned to a band at 997 cm^{-1};[52] for acetone we used the BDE recommended by Benson (98.3 kcal/mol).[61]

Recent evidence suggests that the benzyl C–H BDE in toluene is greater than the commonly used value of 85 kcal/mol[18] and we used a value of 88 kcal/mol.[62]

The BDE in CF_3–C was set 4 kcal/mol stronger than in the corresponding CH_3–C compounds, following the suggestion of Stefani.[63]

The recent JANAF tables assign large uncertainties of ±7 kcal/mol to C–F BDE's and these affect the calculated E^* for hydrogen abstractions by fluorine atoms from alkanes, as shown in Table I. Uncertainties of ±4 kcal/mol exist in the BDE of S–H bonds[32] and we did not simulate many reactions involving this bond.[64]

The bond length in $C_6H_5CH_2$–$CH_2C_6H_5$ (1.58 Å) was taken from Clark.[65]

A list of all the data used for each reaction will appear in the microfilm edition.

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Appendix

The terms of eq 2 were evaluated as follows: ${}^1E_{XH}{}^{\ddagger}$ is evaluated by eq 3 and the molecular data of X–H, with a distance r(X–H) equal to $r_e + 0.01$ Å. $E_R{}^{\ddagger}$ is always set equal to 10.6 kcal/mol.

${}^3E_{XY}{}^{\ddagger}$ can be evaluated by eq 4 with the molecular data for X–Y, if r(X–Y) is known; since $r(\text{X–Y}) = r(\text{X–H}) + r(\text{H–Y})$, r(H–Y) must be obtained. Therefore, eq 3 must be solved with the molecular data for H–Y, for the value of r(H–Y) which leads to ${}^1E_{HY}{}^{\ddagger} = {}^1E_{XH}{}^{\ddagger}$, to satisfy the equibonding criterion for a possible transition state. This is done, numerically by the Newton-Raphson method. Since the Morse curve will have the same value of energy at two different values of r (at either side of the minimum), care must be exercised to obtain the meaningful solution, $r(\text{H–Y}) > r_e(\text{H–Y})$. Then ${}^3E_{XY}{}^{\ddagger}$ can be evaluated.

The sum of the three terms of eq 2 gives the total energy of this one possible transition state. The process is repeated at 0.01 increments of r(X–H). $E_{tot}{}^{\ddagger}$ decreases to a minimum, then increases again. The minimum in energy is *the* transition state.

A copy of the one-page computer program in Fortran IV with directions for its use is available from the author on request. On an IBM 1130, execution is a few seconds.

Supplementary Material Available. All the data used will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-2757.

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