Activation Energies from Bond Energies. A Modification

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Abstract: Activation energies and transition state bond lengths are accurately calculated for H-atom transfer reactions by reevaluating the parameters previously employed in the bond energy-bond order (BEBO) method of Johnston and Parr. The changes made are (1) substituting the recently measured rare gas intermolecular potentials for the Lennard-Jones potentials, (2) using a modified Pauling bond distance-bond order relationship, and (3) using a zero-point energy correction. Over 100 examples are presented.

The bond energy-bond order (BEBO) method of Johnston and Parr[1,2] has been widely used and extended[3-10] for calculating energies of activation, E_a, of atom transfer reactions. Until recently the method was believed to calculate energies of activation to an accuracy of ±2 kcal/mol. When experimental results for the intermolecular potentials of rare gases were employed in place of the previously used Lennard-Jones potentials, Jordan and Kaufman[11] found a substantial decline in the predictive ability of BEBO. This paper demonstrates that the predictive ability of BEBO can be restored by also employing other, more recent, results.[12]

The BEBO method employs empiricism entirely outside the field of chemical kinetics. With the substitution of measured intermolecular rare gas potentials, the method becomes entirely empirical. The method is based upon the assumption that the path of lowest energy from reactants to products is given, for hydrogen atom transfer, eq 1, when the sum of the bond orders for the breaking and the incipient bonds is unity,[13] eq 2. The method employs empirical relationships to calculate bond energies of fractional bonds.

$$\mathrm{A{-}H} + \mathrm{B} \rightarrow \mathrm{A} + \mathrm{H{-}B} \tag{1}$$

$$n_{\mathrm{AH}} + n_{\mathrm{HB}} = 1 \tag{2}$$

Pauling has given a relationship for relating bond lengths to bond orders. Lide[15] has given an accurate, consistent set of bond lengths for C-C, C=C, and C≡C of 1.526, 1.335, and 1.206 Å. Using these values to redetermine the constant in the Pauling relationship, we obtain

$$R_n = R_s - 0.28 \ln n_{xy} \tag{3}$$

where R_n is the bond length in Ångstrom units of bond X-Y of order n, and R_s is the single bond length ($n = 1$). Equation 3 becomes the definition of bond order. Johnston[13] has given an expression relating bond energy to bond length where E_n and E_s are the bond energies of bond X-Y of bond order n and of a single bond in kcal/mol, and p is an empirical parameter:

$$D_n = D_s n^p \tag{4}$$

Combining eq 3 and 4 gives an expression for p.

$$p = 0.28 \ln (D_s/D_n)/(R_n - R_s) \tag{5}$$

To evaluate p using eq 5, we use R_n as the internuclear bond distance for a rare gas diatomic cluster and D_n as the depth of the attractive well, ϵ. Both have now been measured by Lee;[16-17] the values are given in Table I. To evaluate p for any bond H-X, the single bond length and energy must be known and used with ϵ and R_n of the rare gas pair He-Y, where X and Y are from the same row of the periodic table. Some values of p found this way follow: H-H, 1.069; H_3C-H, 1.050; HO-H, 1.037; Cl-H, 0.948. The bonding energy of a bond of order n, D_n, can then be calculated using eq 4.

Table I. Location and Depth of Well for He-Rare Gas Pairs[a]

System	ϵ, cal/mol	r_m, Å
He-He	21.0	2.97
He-Ne	28.4	3.21
He-Ar	48.3	3.54
He-Kr	49.1	3.75
He-Xe	50.1	4.15

[a] Values from ref 16 and 17.

The interaction of A and B of eq 1 has been shown to be of considerable importance.[1,2,18,19] For simultaneous bonding of H to A and B, the three electrons each must have spin functions of α or β. For simultaneous bonding the spins must be α- - -β- - -α or β- - -α- - -β. The electrons on the end atoms must have parallel spins and, therefore, be repulsive by a triplet interaction. The triplet repulsive term due to Sato is employed to obtain the energy of A- - -B interaction:

$$^{3}E_{\mathrm{AB}} = fD_e[(1 + e^{-\beta(R_{\mathrm{AB}_n} - R_{\mathrm{AB}_s})})^2 - 1] \tag{6}$$

(In this modified anit-Morse curve, the value of f originally used by Sato[20] and used by Johnston and Parr[1] was taken as 0.5. More recently, Zavitsas[18] has shown that $f = 0.45$ gives a value for $^{3}E_{\mathrm{AB}}$ more consistent with the value obtained by Kolas and Roothaan[21] using a variational calculation. We have adopted this value.) The "spectroscopic" constant β used in eq 6 is given by eq 7 where ω_0 is the equilibrium vibrational frequency of the bond in cm^{-1} (the observed frequency is frequently used), μ is the reduced mass in amu of the two interacting atoms, and D_0 is the observed dissociation energy in kcal/mol multiplied by 350 to convert to cm^{-1}. The D_e in eq 6 is obtained by adding the zero-point energy, $0.00143\omega_0$, to D_0, eq 8. For a linear transition state R_{AB} in eq 6 can be expressed in terms of bond orders and single bond lengths as in eq 9.

$$\beta = 0.1218\omega_0(\mu/350D_0)^{1/2} \tag{7}$$

$$D_e = D_0 + 0.00143\omega_0 \tag{8}$$

$$R_{\mathrm{AB}} - R_{\mathrm{AB}_s} = R_{\mathrm{AH}_s} + R_{\mathrm{HB}_s} - R_{\mathrm{AB}_s} - 0.28 \ln n_{\mathrm{AH}}n_{\mathrm{HB}} = \Delta R_s - 0.28 \ln n_{\mathrm{AH}}n_{\mathrm{HB}} \tag{9}$$

Using the above assumptions, a "classical" value for the activation energy can be obtained from the locus of the line of minimum energy between reactants and products on the R_{AH}-R_{HB} plane. This locus is obtained in terms of one progress variable n_{AH} and spectroscopic parameters where q is the index for bond H-B (obtained using eq 5), and Z is 0.45 $\exp(-\beta\Delta R_s)$. Taking the minimal potential energy of the re-

Table II. Experimental[a] and Calculated Activation Energies (kcal/mol)

Reaction	Exptl mean	BEBO original	Zavitsas III	This work
$H_2 + CH_3$	11.2	12.4	11.6	12.5
$CH_4 + CH_3$	14.1	16.1	14.1	14.4
$CH_3CH_3 + CH_3$	11.1	12.2	10.6	10.9
$(CH_3)_2CH_2 + CH_3$	10.0	10.9	9.9	9.6
$(CH_3)_3CH + CH_3$	7.8	9.2	8.0	7.9
$C(CH_3)_4 + CH_3$	11.1	12.7	11.3	11.4
$c\text{-}C_6H_{12} + CH_3$	8.7	10.9	9.7	9.6
$CH_3COCH_3 + CH_3$	9.6	11.7	9.7	10.4
$CH_2{=}CHCH_3 + CH_3$	7.8	8.6	7.3	7.4
$C_6H_5CH_3 + CH_3$	8.4	8.4	7.4	7.1
$CCl_3H + CH_3$	6.8	9.1	6.0	8.1
$HOCH_3 + CH_3$	9.2	10.5	9.3	9.2
$CH_3OH + CH_3$	7.7	10.5	9.9	9.7
$CH_3OCH_3 + CH_3$	9.7	9.9	8.6	8.7
$SiH_4 + CH_3$	7.1	7.9	7.8	7.4
$CH_3SH + CH_3$	4.1	4.8	5.4	4.2
$HCHO + CH_3$	6.4	6.2	3.7	5.2
$CH_3CHO + CH_3$	7.5	6.3	5.5	6.2
$ClH + CH_3$	2.8[b]	8.7	12.8	8.5
$BrH + CH_3$	1.4[b]	3.3	2.9	2.7
$IH + CH_3$	2.2[b]	2.8	1.6	2.1
$HSH + CH_3$	3.0[b]	6.1	7.4	5.6
$NH_3 + CH_3$	9.9	12.0	10.1	11.2
$CH_3NH_2 + CH_3$	5.7	8.1	5.8	7.3
$H_2NNH_2 + CH_3$	5.0	7.5	5.0	6.7
$SiH_4 + CH_3$	6.9[b]	7.4	6.9	7.0
$H_2 + CH_3CH_2$	12.0[c]	14.5	13.7	14.9
$CH_3CH_3 + CH_3CH_2$	13.4	14.7	13.4	13.4
$c\text{-}C_6H_{12} + CH_3CH_2$	10.4	12.3	10.6	11.0
$(CH_3)_3CH + CH_3CH_2$	8.9	10.3	8.9	9.1
$CH_2{=}CHCH_3 + CH_3CH_2$	8.2	10.0	8.9	8.7
$C(CH_3)_4 + CH_3CH_2$	12.6	15.1	13.7	13.8
$C_6H_5CH_3 + CH_3COCH_2$	9.3	9.5	8.8	8.3
$CH_2{=}CHCH_3 + C_6H_5H_2$	14.0	13.1	12.0	12.0
$C_6H_5CH_3 + C_6H_5CH_2$	17.0	12.3	11.3	11.2
$H_2 + C_6H_5$	6.5	10.6	9.7	10.5
$H_2 + F$	1.7	1.5	1.8	1.5
$CH_4 + F$	1.2	3.4	6.0	2.8
$CH_3CH_3 + F$	0.3	2.5	4.4	1.9
$(CH_3)_2CH_2 + F$	0.0	2.0	3.5	1.6
$H_2 + Cl$	5.7	6.5	11.0	7.9
$CH_4 + Cl$	3.9	10.4	14.5	10.2
$ClH + Cl$	6.0	0.2	5.1	0.5
$CCl_3H + Cl$	4.4	2.7	6.5	3.2
$H_2 + Br$	19.0	18.9	20.4	19.1
$CH_4 + Br$	18.0	20.6	20.2	20.0
$CF_3H + Br$	22.1	21.4	20.2	20.8
$CH_3CH_3 + Br$	13.7	14.6	14.9	14.0
$(CH_3)_2CH_2 + Br$	10.3	11.0	11.5	10.4
$(CH_3)_3CH + Br$	7.5	7.5	8.2	7.0
$C_6H_5CH_3 + Br$	7.6	6.0	8.3	5.4
$CH_3COCH_3 + Br$	14.0	15.0	15.8	14.3
$C(CH_3)_4 + Br$	14.3	15.6	15.8	15.0
$H_2 + I$	33.7	33.7	32.4	33.7
$CH_4 + I$	34.2	36.3	35.1	35.6
$CH_3CH_3 + I$	27.9	30.1	29.8	29.3
$(CH_3)_2CH_2 + I$	25.3	26.2	26.2	25.5
$(CH_3)_3CH + I$	21.4	22.4	22.2	21.7
$H_2 + OH$	4.9	3.9	4.0	4.1
$CH_4 + OH$	7.2	6.8	8.7	6.3
$CH_3CH_3 + OH$	5.5	4.8	6.1	4.0
$(CH_3)_2CH_2 + OH$	2.9	3.5	4.2	2.9
$(CH_3)_3CH + OH$	2.8	2.5	2.6	2.0
$ClH + OH$	2.4	1.6	2.8	1.6
$BrH + OH$	1.1	0.8	0.4	0.5
$CH_4 + CH_3O$	11.0	11.3	10.7	10.5
$CH_3CH_3 + CH_3O$	7.1	7.5	7.7	6.7
$(CH_3)_2CH_2 + CH_3O$	5.2	5.9	6.7	5.2
$(CH_3)_3CH + CH_3O$	4.1	4.4	5.4	3.8
$(CH_3)_4C + CH_3O$	7.3	8.2	8.6	7.4
$HCHO + CH_3O$	4.0	2.8	3.4	2.3
$CH_3CH_3 + (CH_3)_3CO$	6.5	7.2	7.5	6.5
$(CH_3)_2CH_2 + (CH_3)_3CO$	5.5	5.6	6.3	5.0
$(CH_3)_3CH + (CH_3)_3CO$	4.4	4.4	5.3	3.7
$C_6H_5CH_3 + (CH_3)_3CO$	4.3	3.6	4.3	3.0
$(CH_3)_3COH + (CH_3)_3CO$	2.6	4.6	1.4	4.7
$H_2 + H$	8.2	9.5	9.4	11.2
$CH_4 + H$	9.3	13.0	12.2	13.1
$CH_3CH_3 + H$	9.7	8.6	7.8	9.0
$CH_3COCH_3 + H$	8.0	8.4	7.5	8.8
$HCHO + H$	3.2	3.9	3.2	4.3
$H_2NNH_2 + H$	2.3	4.4	2.8	5.2
$NH_3 + H$	10.0	9.4	8.2	10.0
$CH_3SH + H$	3.0	2.3	3.4	2.7
$HOH + H$	19.0	18.9	19.0	19.1
$BrH + H$	2.6[d]	2.2	3.7	2.4
$H_2 + CF_3$	9.8	11.8	10.7	11.9
$CH_4 + CF_3$	10.7	13.9	10.7	12.7
$CH_3CH_3 + CF_3$	7.9	10.2	7.1	9.1
$(CH_3)_2CH_2 + CF_3$	5.3	8.4	5.2	7.4
$(CH_3)_3CH + CF_3$	3.9	6.6	3.1	5.7
$ClH + CF_3$	5.2[b]	9.2	13.7	8.9
$BrH + CF_3$	2.8[b]	2.9	1.7	2.3
$HSH + CF_3$	4.1[b]	5.4	6.0	5.0
$NH_3 + CF_3$	8.1[b]	10.4	6.9	9.7
$SiH_4 + CF_3$	5.0[b]	7.2	6.7	6.8
$H_2 + CCl_3$	11.3	15.2	13.9	15.6

[a] Average value, taken from ref 19 unless otherwise noted. [b] Reference 7. [c] Reference 9. [d] Reference 22.

acting molecule A-H as the origin, the function $E^*_{\rm Cl}$, eq 10, is evaluated point by point for values of $n_{\rm AH}$ from 1 to 0 and the maximum value of $E^*_{\rm Cl}$ is the activation energy.

$$E^*_{\rm Cl} = E_{\rm bond} + {}^3E_{\rm AB} = D_{\rm eAH} - D_{\rm eAH}n^p_{\rm AH} - D_{\rm eHB}(1 - n_{\rm AH})^q + ZD_{\rm eAB}[n_{\rm AH}(1 - n_{\rm AH})]^{0.28\beta} \times \{1 + Z[n_{\rm AH}(1 - n_{\rm AH})]^{0.28\beta}\} \quad (10)$$

The "classical" energy of activation can be corrected naively for zero-point energy (ZPE) effects as has been pointed out.[18] Rather than use the proposed correction of Zavitsas,[18] i.e., the average ZPE of bond A-H and of H-B, we have chosen to use a weighted average given by

$$\text{ZPE}^* = 0.00143n_{\rm AH}\omega_{\rm AH} + 0.00143(1 - n_{\rm AH})\omega_{\rm HB} \quad (11)$$

Equation 12 was used to calculate the activation energies, E^*, in the following work by point-by-point evaluation.

$$E^* = E^*_{\rm Cl} - (\text{ZPE})_{\rm AH} + \text{ZPE}^* \quad (12)$$

Results

Table II lists energies of activation calculated by the original BEBO method of Johnston and Parr,[1] a related Morse curve approach of Zavitsas and Melikian,[19] and the values obtained using eq 12 described above, along with the mean of reported experimental values of a large variety of gas-phase reactions. These 97 reactions for which experimental activation energies are available are used to compare the three methods of calculation. The BEBO method in its original form gives an average error of 1.54 kcal/mol with a standard deviation (s) of 2.04. The Zavitsas and Melikian calculation gives an average error of 1.46 kcal/mol and s of 2.39. The method described

Table III. Calculated Activation Energies (kcal/mol)

Reaction	BEBO original	Zavitsas III	This work
FH + F	5.3	0.2	5.7
$CH_2{=}CHCH_3$ + Br	6.7	8.4	6.1
c-C_6H_{12} + Br	10.9	11.2	10.3
BrH + Br	0.1	3.0	0.1
c-C_5H_{10} + I	26.7	26.7	26.0
$C(CH_3)_4$ + I	31.2	30.8	30.4
HOH + OH	7.7	6.3	7.5
H_2 + CH_3O	6.9	5.5	7.8
c-C_6H_{12} + CH_3O	5.9	6.6	5.2
CH_4 + $(CH_3)_3CO$	11.0	10.6	10.1
C_6H_6 + $(CH_3)_3CO$	13.7	11.5	13.1
ClH + $(CH_3)_3CO$	1.3	1.4	1.8
$(CH_3)_2CH_2$ + H	6.5	5.7	6.9
$(CH_3)_3CH$ + H	5.0	4.1	5.4
$HOCH_3$ + H	6.3	5.3	6.7
CH_3OH + H	5.7	5.3	7.6
$C_6H_5CH_3$ + H	3.7	2.3	4.1
HNO_3 + H	5.5	4.3	6.4
HSH + H	2.7	4.4	3.3
SiH_4 + SiH_3	14.7	21.5	14.7
NH_3 + NH_2	10.4	10.1	9.7

Table IV. Comparison of Minimum Energy Paths Obtained by BEBO and by CI Calculations for H_2 + H[a] and H_2 + F[b]

BEBO			CI		
R_1, Å	R_2, Å	E^*, kcal/mol	R_1, Å	R_2, Å	E^*, kcal/mol
			H_2 + H		
0.745	1.917	1.67	0.744	1.890	1.30
0.747	1.836	2.01	0.745	1.837	1.54
0.751	1.680	2.90	0.748	1.687	2.49
0.755	1.580	3.65	0.752	1.572	3.32
0.767	1.415	5.27	0.762	1.414	4.88
0.780	1.312	6.55	0.773	1.309	6.11
0.800	1.206	8.06	0.791	1.204	7.39
0.831	1.102	9.59	0.820	1.103	8.59
0.877	1.008	10.77	0.867	1.008	9.48
0.898	0.997	11.02	0.898	0.965	9.73
0.935	0.935	11.17	0.930	0.930	9.80
			H_2 + F		
0.745	2.092	0.81	0.751	2.117	0.25
0.754	1.784	1.33	0.757	1.799	0.75
0.763	1.641	1.50	0.762	1.588	1.61
0.767	1.590	1.52	0.767	1.535	1.66
0.781	1.482	1.37	0.783	1.482	1.59
0.793	1.412	1.06	0.794	1.392	1.18
0.843	1.248	−1.00	0.847	1.249	−2.15
0.977	1.073	−8.34	0.953	1.074	−12.30
1.165	0.986	−17.11	1.164	0.953	−25.30
1.323	0.953	−22.21	1.323	0.942	−29.15
1.580	0.930	−27.14	1.588	0.937	−32.19

[a] Reference 25. [b] Reference 26.

above affords an average error of 1.29 kcal/mol and *s* of 1.87. Additional values of calculated activation energy are given in Table III for comparison with results obtained from the earlier BEBO method and with the results obtained using the Zavitsas-3[19] approach. All data used in the calculations reported in Tables II and III were those of Zavitsas and Melikian[19] supplemented only as needed by the data given by Arthur et al.[5-9] Both the "BEBO original" and "Zavitsas-III" values were recalculated using this consistent set of data.

Perhaps the most serious failing of the BEBO method is for the hydrogen exchange reaction of hydrogen halide and halogen atom.[19,20] The reaction F-H + F · was predicted to give an energy barrier of 5.5-6 kcal/mol using the original BEBO procedure.[1-23] The Zavitsas-III method[19] affords an even lower barrier of 0.2 kcal/mol using our data. Using our computational approach gives a barrier height of 5.7 kcal/mol. While experimental values for this reaction are not available, ab initio calculations give a value >18.[24] For the reaction of Cl-H + Cl·, the original BEBO method predicts a Cl-H-Cl species stable by 1.4 kcal/mol[19] relative to isolated reactants. The approach described here predicts an E^* of 0.53 kcal/mol with an unsymmetrical structure, r_1 = 1.34 Å, r_2 = 1.73 Å, and a very flat surface from n_1 = 0.15 to 0.85 with a Cl-H-Cl structure 0.01 kcal/mol more stable than the activated complex. The Zavitsas calculation gives a symmetrical barrier of 5.1, close to the experimental value.[19] Our method predicts a barrier of 0.1 kcal/mol and a symmetrical intermediate stable by 0.6 for the reaction Br-H + Br·. The experimental value is not available but Zavitsas calculates a barrier of 3.0.[19] A second criticism of the BEBO method has been made by Endo and Glass,[22] who report that the transition state for Br-H + H predicted by the original BEBO method lies too far into the entrance valley of the H- - -H-Br system, $r_{H\text{-}H}$ = 1.43 Å, $r_{H\text{-}Br}$ = 1.44 Å, E^* = 2.41 kcal/mol, and yields kinetic isotope effects much smaller than they measured. The new BEBO method corrects this somewhat, $r_{H\text{-}H}$ = 1.37 Å, $r_{H\text{-}Br}$ = 1.45 Å, E^* = 2.41 kcal/mol, but does not reach the values of the LEPS surface of Parr and Kuppermann of $r_{H\text{-}H}$ = 1.15 Å, $r_{H\text{-}Br}$ = 1.49 Å, and E^* = 1.6 kcal/mol reported by Endo and Glass to more accurately predict measured kinetic isotope effects.[22]

A remarkable success of the original BEBO method was the accuracy with which not only the barrier height but also the position of the minimum-energy path were predicted for the reactions of H and of F with H_2.[25] Bond lengths on the minimum energy path for the reaction of H· + H_2 are compared in Table IV with those obtained by Liu[25] using a CI calculation. A similar comparison is also made for the BEBO results for the reaction of F· + H_2 with the results of a CI calculation obtained by Bender, O'Neil, Pearson, and Schaefer[26] is also given in Table IV. For both of these ab initio minimum-energy paths, the BEBO method agrees everywhere within 0.055 Å. It should be recognized that the BEBO minimum-energy path does not contain a reference to a specific coordinate system, a situation that has been shown to lead to an uncertainty of at least 0.04 Å.[10,27]

The method for calculating activation energies describe above is far easier than ab initio methods, being easily carried out with a calculator. The results appear to be equal to or better than those obtained by the Zavitsas-3 method of calculating activation energies and much closer than their method to ab initio values for transition state bond lengths. Zavitsas and Melikian report 0.85 Å for the bond lengths in the H_2 + H· reaction and 0.78 Å for H-H and 1.20 Å for H-F in the H_2 + F reaction;[19] cf. Table IV. Our results also suggest that a modified triplet term as has been proposed[7] is not necessary.

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An Empirical Correlation of Activation Energy with Molecular Polarizability for Atom Abstraction Reactions

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Abstract: Activation energies for a homologous series of exoergic atom transfer reactions of the type A· + BC → AB + C· are shown to correlate inversely with molecular polarizability of the reactant BC. A linear relationship between activation energy and reciprocal polarizability provides relatively good agreement with experiment for 13 reaction series comprised of 65 reactions. Activation energies are predicted for the reactions of CH_3·, C_2H_5·, and CF_3· with F_2 using this correlation.

Activation energy is an important property of chemical reactions. For simple exoergic atom transfer reactions differences in activation energy are primarily responsible for the wide variation observed in reaction rates. Although accurate theoretical calculations of activation barriers are not possible in most cases, several empirical and semiempirical formulas for estimating activation energies have been developed. In one approach, activation energies for a series of similar reactions are correlated with molecular properties of the separated reactants and products. If one or two activation energies in the series of reactions are known, the others can be predicted using the correlation. In this paper we discuss three correlation schemes which have been proposed and offer a fourth which yields improved agreement with experiment.

For many series of exoergic reactions of the type A· + BC → AB + C·, activation energy is observed to decrease with increasing exoergicity. Evans and Polanyi first discussed this correlation and analyzed it in terms of intersecting Morse curves.[1,2] They proposed a linear dependence on exoergicity.

$$E_{\text{act}} = E_0 - \gamma q \qquad (1)$$

Here E_0 and γ are empirical parameters and q, the heat of reaction, is positive for exoergic reactions. This relationship was substantiated with a large body of data by Semenov.[3] The correlation with exoergicity has also been expressed in another formula which was derived as part of the bond energy-bond order (BEBO) method for obtaining potential energy parameters of activated complexes.[4-7] This relationship is given by

$$E_{\text{act}} = (D^0{}_{\text{AB}} - q)\left\{1 - \left[1 + \left(1 - \frac{q}{D^0{}_{\text{AB}}}\right)^{1/p-1}\right]^{1-p}\right\} \qquad (2)$$

where p is an empirical parameter and $D^0{}_{\text{AB}}$ is the bond energy of the product molecule. Activation energies and exoergicities for numerous reactions are listed in Table I. Although the exoergicity rule is obeyed in many series of reactions, exceptions are also found in the table. In series A the O + F_2 reaction is the most exoergic but has the highest activation energy. In series B the predicted trend is completely reversed, and in series H the Na + $CHCl_3$ reaction is out of line with the predicted variation. Two other series not listed in the table, CF_3· + CH_3X → CF_3X + CH_3[33] and H· + CH_3X → HX + CH_3[25] (X = halogen atom), also show the reverse trend. These exceptions involve halogen atom abstraction reactions, and they were anticipated in the original analysis of the exoergicity rule.[1,2,39]

Another empirical scheme due to Spirin[8] establishes a relationship between activation energy and both the reaction exoergicity and the polarizabilities of the reacting species. Spirin proposed the expression which is given by

$$E_{\text{act}} = d(0.75D_{\text{AC}} - q)\left(\frac{1}{p_{\text{A}}} + \frac{1}{p_{\text{C}}}\right) \qquad (3)$$

where D_{AC} is the bond energy of molecule AC, q is the exoergicity, and d is an empirical parameter. p_{A} and p_{C} are the polarizabilities of the reactant and product atoms (or radicals), respectively. The dependence on bond strengths is derived from the London formula for the energy of three atoms, and the formula includes a contribution from bonding between the two end atoms in the intermediate complex. The inverse dependence on the polarizability is based on the following reasoning. Attractive dispersion forces lower the interaction energy as reactants approach to distances characteristic of the onset of reaction. These forces are proportional to polarizability among other factors; thus the greater the polarizabilities of the reactants, the less repulsive the approach.[11] In many cases Spirin's