Use of Buckingham Potentials in Engineering Approximations for Chemical Kinetics

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Previous investigators have often used the Polanyi relationship to correlate activation barriers for series of reactions. The correlations often work, but a different Polanyi relationship is needed for each class of reactions. As a result, the correlations are difficult to extrapolate to new situations. In this article, we suggest new correlations that show greater capability to correlate rate data. Quantum mechanical calculations are done which indicate that the main barriers to ligand exchange reactions are associated with getting the reactants close enough to react. The energy to get the reactants close enough to react can be calculated from a united-atom Buckingham potential and correlated to rate data. The additional correlating parameter allows the activation energies for a series of hydrocarbon reactions to be collapsed onto a single line. The root-mean-square error of the line is 2 kcal/mol compared to 7 kcal/mol with the Polanyi relationship alone. This shows that our new correlating parameter will be useful in engineering approximations in kinetics.

Introduction

In the recent literature, Klein and coworkers (Boock and Klein, 1993; Fake et al., 1994; Watson et al., 1997; Watson and Klein, 1997), Broadbelt and coworkers (Broadbelt et al., 1996; Klinke and Broadbelt, 1997; Broadbelt et al., 1994), and Lee and Masel (Masel and Lee, 1997; Lee and Masel, 1995, 1996) have developed a number of engineering approximations for chemical kinetics. The idea behind the method is that one uses an approximation to estimate the activation energy and preexponential for all of the steps in a mechanism. One then does a simulation to calculate overall rates.

In many cases the results of these calculations have had reasonable agreement with experiments. Still, there has been some reluctance to accept the methods in the literature. For example, Schmidt (1998) cautions: "If someone claims to have a general correlation of reaction rates, the prudent engineer should be suspicious." Clearly, additional work is needed.

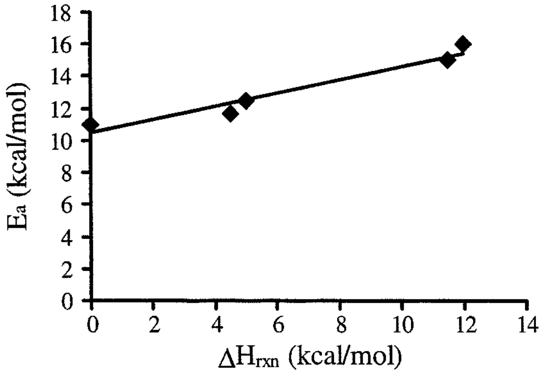

Figure 1. Activation energy as a function of the heat of reaction for $CH_3 + H - R \rightarrow CH_4 + R$ (Boock and Klein, 1993).

One area of concern is that a correlation calculated for a limited data set often does not carry over to a wider data set. For example, Figure 1 shows a correlation for a series of hydrogen transfer reactions of the form

$$CH_3 + H - R \rightarrow CH_4 + R \qquad (1)$$

with $R = CH_3$. Boock and Klein (1993) fit this data to the Polanyi relationship (Evans and Polanyi, 1936)

$$E_a = E_a^o + \gamma_P \Delta H_r \qquad (2)$$

where E_A is the activation barrier, E_a^o is the intrinsic barrier, ΔH_r is the heat of reaction, and γ_P is the transfer coeffi-

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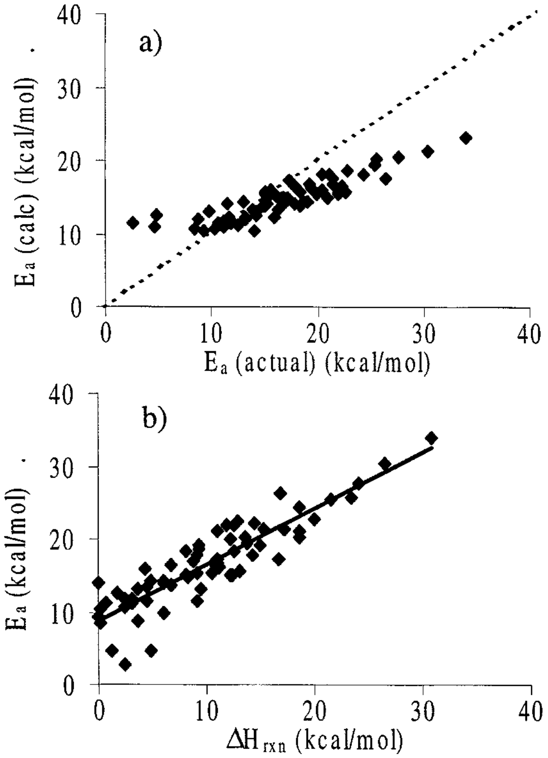

Figure 2. (a) Calculated activation energy vs. activation energy for reactions of the form: $R' + HR \rightarrow R'H + R$ using Klein's fit; (b) calculated activation energy vs. activation energy using an empirical fit to Steel's data.

The dashed line in 2a was calculated for E_a (calc) = E_a (actual). The solid line in 2b is the least-squares fit to the data.

cient. Figure 1 shows that the Polanyi relationship fits the data quite well. Unfortunately, the correlation does not extrapolate to new data well.

For example, Figure 2a compares the experimental activation barriers for a number of hydrogen transfer reactions of the form

$$R' + H - R \rightarrow R'H + R \qquad (3)$$

to those calculated from Boock and Klein's fits of the data in Figure 1. The specific reactions are listed in Table 1. Notice that the correlation shows errors as large as 30 kcal/mol. One can improve the correlation by fitting Eq. 2 to all of the rate data in Table 1. Figure 2b compares the experimental activation barriers for the hydrogen transfer reactions given in Table 1 to those calculated by fitting Eq. 2 to the data. One finds a better correlation. However, the errors are still as large as 20 kcal/mol.

Roberts and Steel (1994) did an empirical fit to the data in Table 1. They found they could fit all of the data with a complicated equation, provided they added a correction factor for each R and R′ group. Such a correlation works reasonably well. However, the correction factors are not known *a priori*. As a result, these correlations have limited utility.

Another approach, suggested by Klein and coworkers (Boock and Klein, 1993; Fake et al., 1994; Watson et al., 1997;

Table 1. Reactions Considered in Figure 3

$C_4H_9 + C_6H_5CH_3 \rightleftarrows C_4H_{10} + C_6H_5CH_2$
$C_4H_9 + HCCl_3 \rightleftarrows C_4H_{10} + CCl_3$
$C_4H_9O + C_6H_5CH_3 \rightleftarrows C_4H_9OH + C_6H_5CH_2$
$C_4H_9O + c\text{-}C_5H_{10} \rightleftarrows C_4H_9OH + c\text{-}C_5H_9$
$C_4H_9O + C_4H_9OCH_3 \rightleftarrows C_4H_9OH + C_4H_9OCH_2$
$C_4H_9O + C_6H_5OH \rightleftarrows C_4H_9OH + C_6H_5O$
$C_4H_9O + (C_2H_5)_3SiH \rightleftarrows C_4H_9OH + (C_2H_5)_3Si$
$C_4H_9O + Oc\text{-}(CH_2)_4 \rightleftarrows C_4H_9OH + c\text{-}O(C_2H_2)_3CH$
$c\text{-}C_6H_{11} + (C_4H_9)_3SnH \rightleftarrows C_6H_{12} + (C_4H_9)_3Sn$
$CCl_3 + HSiCl_3 \rightleftarrows HCCl_3 + SiCl_3$
$CCl_3 + (CH_3)_3SiH \rightleftarrows HCCl_3 + (CH_3)_3Si$
$CCl_3 + (C_2H_5)_3SiH \rightleftarrows HCCl_3 + (C_2H_5)_3Si$
$CF_3 + CH_4 \rightleftarrows HCF_3 + CH_3$
$CF_3 + H_2 \rightleftarrows HCF_3 + H$
$CF_3 + C_2H_6 \rightleftarrows HCF_3 + C_2H_5$
$CF_3 + (CH_3)_2CO \rightleftarrows HCF_3 + CH_3COCH_2$
$CF_3(CH_3)_2O \rightleftarrows HFC_3 + CH_3OCH_2$
$CF_3 + PrH \rightleftarrows HFC_3 + Pr$
$CF_3 + c\text{-}C_5H_{10} \rightleftarrows HFC_3 + c\text{-}C_5H_9$
$CF_3 + HSiCl_3 \rightleftarrows HCF_3 + SiCl_3$
$CF_3 + HCCl_3 \rightleftarrows HCF_3 + CCl_3$
$CF_3 + C_6H_5CH_3 \rightleftarrows HCF_3 + C_6H_5CH_2$
$CF_3 + c\text{-}C_6H_{12} \rightleftarrows HCF_3 + c\text{-}C_6H_{11}$
$CF_3(CH_3)_3SiH \rightleftarrows HCF_3 + (CH_3)_3Si$
$CF_3 + HCl \rightleftarrows HCF_3 + Cl$
$CF_3 + C_4H_{10} \rightleftarrows HCF_3 + C_4H_9$
$Cl + C_2H_6 \rightleftarrows HCl + C_2H_5$
$C_2H_5 + HCCl_3 \rightleftarrows C_2H_6 + CCl_3$
$C_2H_5 + C_6H_5CH_3 \rightleftarrows C_2H_6 + C_6H_5CH_2$
$C_2H_5 + (C_4H_9)_2SnH \rightleftarrows C_2H_6 + (C_4H_9)_3Sn$
$H + C_2H_6 \rightleftarrows H_2 + C_2H_5$
$H + H_2 \rightleftarrows H_2 + H$
$H + PrH \rightleftarrows H_2 + Pr$
$H + C_4H_{10} \rightleftarrows H_2 + C_4H_9$
$H + HCl \rightleftarrows H_2 + Cl$
$H + HBr \rightleftarrows H_2 + Br$
$H_2N + H_2 \rightleftarrows NH_3 + H$
$H_2N + C_2H_6 \rightleftarrows NH_3 + C_2H_5$
$H_2N + PrH \rightleftarrows NH_3 + Pr$
$H_2N + C_4H_{10} \rightleftarrows NH_3 + C_4H_9$
$HO + HCF_3 \rightleftarrows H_2O + CF_3$
$HO + H_2 \rightleftarrows H_2O + H$
$HO + C_2H_6 \rightleftarrows H_2O + C_2H_5$
$HO + HCCl_3 \rightleftarrows H_2O + CCl_3$
$CH_3 + CH_4 \rightleftarrows CH_4 + CH_3$
$CH_3 + C_2H_6 \rightleftarrows CH_4 + C_2H_5$
$CH_3 + H_2 \rightleftarrows CH_4 + H$
$CH_3 + CH_3CN \rightleftarrows CH_4 + CH_2CN$
$CH_3 + CH_3OH \rightleftarrows CH_4 + CH_3O$
$CH_3 + (CH_3)_2O \rightleftarrows CH_4 + CH_3OCH_2$
$CH_3 + c\text{-}C_6H_{12} \rightleftarrows CH_4 + c\text{-}C_6H_{11}$
$CH_3 + (CH_3)_2CO \rightleftarrows CH_4 + CH_3COCH_2$
$CH_3 + PrH \rightleftarrows CH_4 + Pr$
$CH_3 + C_6H_5CH_3 \rightleftarrows CH_4 + C_6H_5CH_2$
$CH_3 + c\text{-}C_5H_{10} \rightleftarrows CH_4 + c\text{-}C_5H_9$
$CH_3 + HCCl_3 \rightleftarrows CH_4 + CCl_3$
$CH_3 + C_4H_{10} \rightleftarrows CH_4 + C_4H_9$
$CH_3 + (CH_3)_3SiH \rightleftarrows CH_4 + (CH_3)_3Si$
$CH_3 + (C_4H_9)_3SnH \rightleftarrows CH_4 + (C_4H_9)_3Sn$
$CH_3O + CH_4 \rightleftarrows CH_3OH + CH_3$
$CH_3O + C_2H_6 \rightleftarrows CH_3OH + C_2H_5$
$CH_3O + C_4H_{10} \rightleftarrows CH_3OH + C_4H_9$
$C_6H_5CH_2 + (C_4H_9)_3SnH \rightleftarrows C_6H_5CH_3 + (C_4H_9)_3Sn$
$Pr + HCCl_3 \rightleftarrows PrH + CCl_3$
$Pr + (C_4H_9)_3SnH \rightleftarrows PrH + (C_4H_9)_3Sn$
$Cl + PrH \rightleftarrows HCl + Pr$
$C_4H_9O + C_4H_9OH \rightleftarrows C_4H_9OH + C_4H_9O$
$C_6H_5CH_2 + C_6H_5SH \rightleftarrows C_6H_5CH_3 + C_6H_5S$
$C_4H_9 + C_6H_5SH \rightleftarrows C_4H_{10} + C_6H_5S$
$HO + CH_4 + H_2O + CH_3$

Data from Roberts and Steel (1994).

Table 2. The Reactions Considered Here

$H + CH_3OH \rightleftarrows CH_4 + OH$
$H + CH_3OH \rightleftarrows H_2 + CH_2OH$
$H^1 + CH_3OH \rightleftarrows H + CH_2H'OH$
$H + CH_3CH_2CH_3 \rightleftarrows H_2 + CH_2CH_2CH_3$
$H + CH_3CH_2NH_2 \rightleftarrows H_2 + CH_2CH_2NH_2$
$H + CH_3CH_2CF_3 \rightleftarrows H_2 + CH_2CH_2CF_3$
$H + CH_3CH_2CN \rightleftarrows H_2 + CH_2CH_2CN$
$H + CH_3CH_2C_6H_5 \rightleftarrows H_2CH_2CH_2C_6H_5$
$H + CH_3CH_3 \rightleftarrows CH_4 + CH_3$
$H + CH_3CH_2CH_3 \rightleftarrows CH_4 + CH_2CH_3$
$H + CH_3CH_2NH_2 \rightleftarrows CH_4 + CH_2NH_2$
$H + CH_3CH_2CF_3 \rightleftarrows CH_4 + CH_2CF_3$
$H + CH_3CH_2CN \rightleftarrows CH_4 + CH_2CN$
$H + CH_3CH_2C_6H_5 \rightleftarrows CH_4 + CH_2C_6H_5$
$H' + CH_4 \rightleftarrows CH_3H' + H$

Watson and Klein, 1997), is to divide the reactions in Table 1 into groups and then fit a separate Polanyi relationship to each group of reactions. Again, that approach works, but the results are limited because one needs a new correlation every time a new type of reaction is considered.

It would be very useful if one could find a way to correlate a wide range of rate data to a single correlation. That way, one might not have to do a new fit each time one considers a new type of reaction.

In this article, an attempt is made to develop some better models for chemical kinetics that can be more reliably extrapolated to a wide data set. Our approach will be to consider the 30 reactions in Table 2 and use *ab-initio* quantum mechanical methods to examine the key interactions. We will then use the information obtained from the *ab-initio* calculations to construct parameters that should correlate to barriers. Tests will be done to see how well the approximations work.

The reactions in Table 2 were chosen because they are typical of reactions of hydrocarbons. There are C-H bond scissions, C-O bond scissions, hydrogen transfer reactions, and hydrogen exchange reactions. This set of reactions does not have the full complexity that Klein has considered in his extensive models. Still, it does provide a wide enough data set to ask whether a general correlation is possible.

Methods

The quantum mechanical calculations were done using the Gaussian 92 suite of programs. The geometries and vibrational frequencies were calculated at the PMP2(full)/6-31G* level. Transition states were verified to have only one negative eigenvalue in the Hessian matrix, proving that the structures are first-order saddle points. All stable products and reactants were also verified. QCISD(T)/6-311G** calculations were done at the stationary points as a further check of the results. Additional details of the calculations appear elsewhere (Blowers, 1998).

Results

Table 3 shows the heats of reaction and activation barriers calculated at the PMP2(full)/6-31g* level for each of the reactions in Table 2, while Figure 3 shows a plot of the activation barriers for the reaction vs. the heat of reaction. Generally, the activation barriers to reaction increase as the heat of reaction increases. Still, if one tries to fit the data to a single line, the line deviates significantly from the data. A least-

Table 3. Thermodynamic Data for the Reactions Considered in This Work*

Reaction	ΔH_{rxn}	E_a
$H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$	8.39	20.11
$H + CH_3CH_2CH_3 \rightarrow H_2 + CH_2CH_2CH_3$	9.11	20.25
$H + CH_3CH_2NH_2 \rightarrow H_2 + CH_2CH_2NH_2$	9.16	20.22
$H\_CH_3CH_2CN \rightarrow H_2 + CH_2CH_2CN$	10.50	23.96
$H + CH_3CH_2CF_3 \rightarrow H_2 + CH_2CH_2CF_3$	10.05	21.37
$H_2 + CH_2CH_3 \rightarrow H + CH_3CH_3$	−8.34	11.72
$H_2 + CH_2CH_2CH_3 \rightarrow H + CH_3CH_2CH_3$	−9.11	11.14
$H_2 + CH_2CH_2NH_2 \rightarrow H + CH_3CH_2NH_2$	−9.16	11.06
$H_2 + CH_2CH_2CN \rightarrow H + CH_3CH_2CN$	−10.50	13.46
$H_2 + CH_2CH_2CF_3 \rightarrow H + CH_3CH_2CF_3$	−10.05	11.32
$H + CH_3OH \rightarrow H_2 + CH_2OH$	−3.02	16.92
$H + CH_3OH \rightarrow H_2 + CH_3O$	8.27	22.69
$H + CH_3OH \rightarrow H + CH_2H'OH$	0	50.66
$H + CH_3OH \rightarrow H + CH_3OH'$	0	41.00
$H_2 + CH_2OH \rightarrow H + CH_3OH$	3.02	15.55
$H_2 + CH_3O \rightarrow H + CH_3OH$	−8.27	15.01
$H + CH_3CH_3 \rightarrow CH_4 + CH_3$	−6.22	46.55
$H + CH_3CH_2CH_3 \rightarrow CH_4 + CH_2CH_3$	−5.65	45.23
$H + CH_3CH_2NH_2 \rightarrow CH_4 + CH_2NH_2$	−13.04	42.53
$H + CH_3CH_2CN \rightarrow CH_{45} + CH_2CN$	−1.64	4.48
$H + CH_3CH_2CF_3 \rightarrow CH_4 + CH_2CF_3$	−0.40	44.98
$CH_4 + CH_3 \rightarrow H + CH_3CH_3$	6.22	52.77
$CH_4 + CH_2CH_3 \rightarrow H + CH_3CH_2CH_3$	5.65	50.88
$CH_4 + CH_2NH_2 \rightarrow H + CH_3CH_2NH_2$	13.04	55.62
$CH_4 + CH_2CN \rightarrow H + CH_3CH_2CN$	1.64	45.12
$CH_4 + CH_2CF_3 \rightarrow H + CH_3CH_2CF_3$	0.40	45.38
$H + CH_3OH \rightarrow CH_4 + OH$	−23.0	41.69
$H + CH_3OH \rightarrow CH_3 + H_2O$	−10.98	34.17
$H + CH_4 \rightarrow CH_4 + H$	0	46.6
$CH_3 + H_2O \rightarrow H + CH_3OH$	10.98	48.74
$CH_4 + OH \rightarrow H + CH_3OH$	23.09	48.44

*All energies are in kcal/mol.

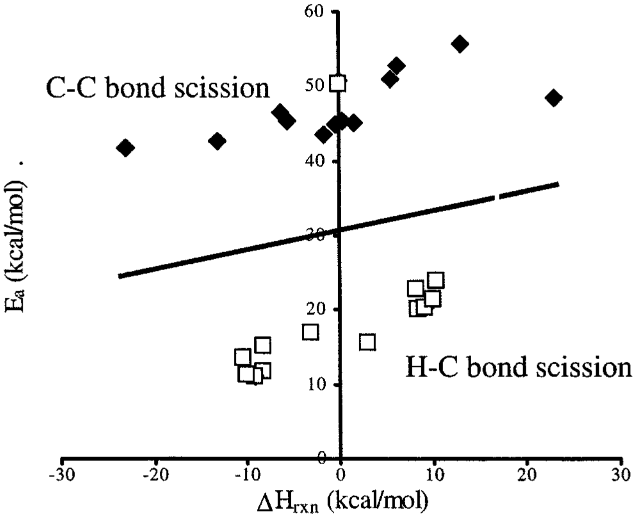

Figure 3. Activation energy as a function of the heat of reaction for the reactions considered in this work.

All energies in kcal/mol. The open squares are H-C bond scission reactions. The closed triangles are C-C bond scission reactions.

squares fit to the data gives a root mean-square error of 7 kcal/mol. This is certainly a significant deviation.

In the literature, people often try to reduce these errors by grouping sets of points. For example, one set of points might be reactions of the form

$$H + CH_3R \rightarrow H_2 + CH_2R \qquad (4)$$

while another grouping might be reactions of the form

$$H + CH_3R \rightarrow CH_4 + R \qquad (5)$$

Figure 4 shows a plot of those sets of points. Generally, the Polanyi plots look much better when this is done. However, there are still a few significant deviations. The maximum error is 30 kcal/mol, which is clearly unacceptable.

A Bond Search for Better Correlations

The objective of this article is to find a way to reduce the errors in the correlation of the data in Figure 4. The approach will be to do *ab-initio* calculations to identify the key factors that cause reactions to be activated. Then, the results of the calculations will be used to develop more robust models for chemical kinetics.

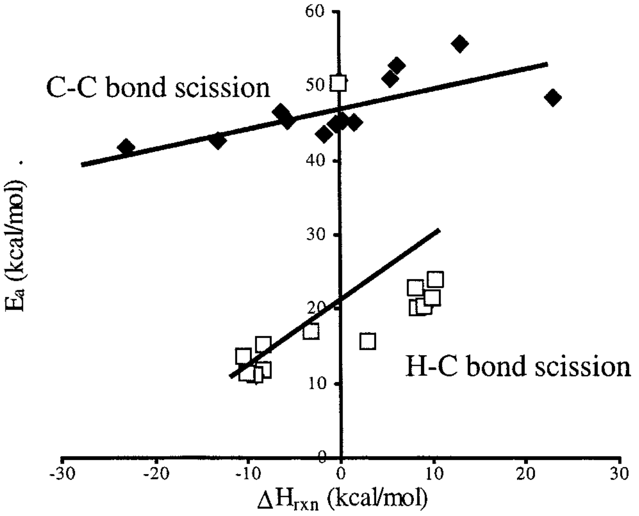

Figure 4. Activation energy as a function of the heat of reaction with two Polanyi fits.

$E_a = 4.71 + 0.26\ \Delta H_{rxn}$ for group transfer reactions; $E_a = 16.8 + 0.48\ \Delta H_{rxn}$ for atom transfer reactions. All energies are in kcal/mol.

To start, it is useful to examine the role of bond stretching on barriers to chemical reactions. In the previous literature, Cohen and Marcus (1968), Szabo and Berces (1968), Mitchell et al. (1985), Johnston (1966) and Glasstone (1941) have suggested that bond stretching plays an important role in barriers to reactions. Generally stronger bonds are harder to break. Consequently, it has been supposed that there is a correla-

Table 4. Activation Energies Compared to Bond Strengths, Energies to Stretch Reactants to the Transition-State, Energies to Distort the Reactants to the Transition State, and the Energies to Bring the Reactants Together*

Reaction	Bond Strength	*E* Stretch	*E* Distort	*E* Pauli	E_a
$H + CH_3 + CH_3 \rightarrow H_2CH_2CH_3$	101.06	22.53	22.96	27.40	20.11
$H + CH_3CH_2CH_3 \rightarrow H_2 + CH_2CH_2CH_3$	101.78	23.5	23.38	27.54	20.25
$H + CH_3CH_2NH_2 \rightarrow H_2 + CH_2CH_2NH_2$	103.17	24.39	23.13	27.63	20.22
$H + CH_3CH_2CN \rightarrow H_2 + CH_2CH_2CN$	103.17	22.47	22.03	31.97	23.96
$H + CH_3CH_2CF_3 \rightarrow H_2 + CH_2CH_2CF_3$	102.72	28.91	24.39	28.95	21.37
$H_2 + CH_2CH_3 \rightarrow H + CH_3CH_3$	92.67	7.65	8.5	21.34	11.72
$H_2 + CH_2CH_2CH_3 \rightarrow H + CH_3CH_2CH_3$	92.67	7.46	8.18	22.28	11.14
$H_2 + CH_2CH_2NH_2 \rightarrow H + CH_3CH_2NH_2$	92.67	7.53	8.23	22.01	11.06
$H_2 + CH_2CH_2CN \rightarrow H + CH_3CH_2CN$	92.67	6.46	7.46	28.6	13.46
$H_2 + CH_2CH_2CF_3 \rightarrow H + CH_3CH_2CF_3$	92.67	6.93	7.91	21.65	11.32
$H + CH_3OH \rightarrow H_2 + CH_2OH$	94.03	17.47	18.71	24.23	16.92
$H + CH_3OH \rightarrow H_2 + CH_3O$	100.35	24.79	25	27.71	22.69
$H + CH_3OH \rightarrow H + CH_2H'OH$	94.03	12.67	39.92	68.37	50.66
$H + CH_3OH \rightarrow H + CH_3OH'$	100.35	11.21	13.39	44.83	41.00
$H_2 + CH_2OH \rightarrow H + CH_3OH$	92.67	9.91	4.91	24.44	15.55
$H_2 + CH_3O \rightarrow H + CH_3OH$	92.67	5.64	25	20.12	15.01
$H + CH_3CH_3 \rightarrow CH_4 + CH_3$	96.49	25.28	36.88	53.2	46.55
$H + CH_3CH_2CH_3 \rightarrow CH_4 + CH_2CH_3$	97.11	25.15	35.78	53.28	45.23
$H + CH_3CH_2NH_2 \rightarrow CH_4 + CH_2NH_2$	89.67	24.26	38.86	49.60	42.53
$H + CH_3CH_2CN \rightarrow CH_4CH_2CN$	101.12	26.2	33.42	56.52	4.48
$H + CH_3CH_2CF_3 \rightarrow CH_4 + CH_2CF_3$	102.37	29.29	22.48	51.15	44.98
$CH_4 + CH_3 \rightarrow H + CH_3CH_3$	102.77	14.1	44.47	80.67	52.77
$CH_4 + CH_2CH_3 \rightarrow H + CH_3CH_2CH_3$	102.77	21.53	42.98	71.46	50.88
$CH_4 + CH_2NH_2 \rightarrow H + CH_3CH_2NH_2$	102.77	24.87	52.38	72.22	55.62
$CH_4 + CH_2CN \rightarrow H + CH_3CH_2CN$	102.77	18.68	39.17	96.59	45.12
$CH_4 + CH_2CF_3 \rightarrow H + CH_3CH_2CF_3$	102.77	20.21	42.92	74.69	45.38
$H + CH_3OH \rightarrow CH_4OH$	95.89	18.13	29.3	52.21	41.69
$H + CH_3OH \rightarrow CH_3 + H_2O$	95.89	16.91	17.21	40.54	34.17
$H + CH_4 \rightarrow CH_4 + H$	102.77	21.35	34.93	58.51	50.33
$CH_3 + H_2O \rightarrow CH_3OH$	110.47	20.78	24.99	59.95	48.74
$CH_4 + OH \rightarrow H + CH_3OH$	102.77	17.54	39.77	66.88	48.44

*All energies are in kcal/mol.

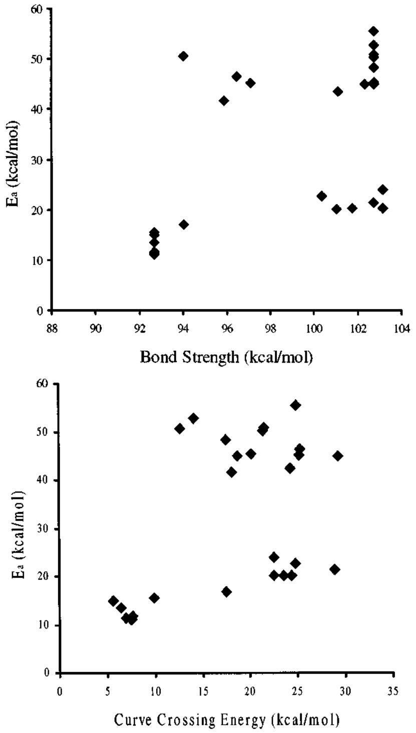

Figure 5. Activation energy vs. bond strength and the curve crossing energy.

All energies in kcal/mol.

tion between the bond strength and the activation barrier for a reaction.

It would be interesting to see if one can get better correlations if one explicitly includes the energy to stretch the bond as a correlating parameter. For the purposes of discussion, we have computed two different measures of the bond strength: E_{Bond} the total bond energy of the bond that breaks during the reaction, and E_{stretch}, which is the amount of energy needed to stretch the bonds which break to the transition state geometry. Details of the calculations are given by Blowers et al. (1998). The numerical values E_{Bond} and E_{stretch} are given in Table 4.

Figure 5 shows plots of the activation energy for the reactions in Table 2 as a function of E_{Bond} and E_{stretch}. Little correlation is evident. Statistical analysis shows that there is a weak correlation between the energy to stretch bonds and the activation barriers. However, the calculations do not indicate that bonds that are easier to stretch are necessarily easier to break.

Another idea in the literature is that bond distortions play a key role in the barriers. The idea is that when a reaction happens, part or all of the molecules distort to new geometries. This bond distortion is thought to lead to barriers to reaction.

Again, one can use the quantum mechanical calculations to quantify this effect. We calculated E_{Distort}, the energy to distort the bonds in the reactants to the transition state. Details are given by Blowers et al. (1998) and the numerical values are given in Table 4.

Figure 6 shows a plot of the activation energy for the reactions in Table 2 vs. the bond distortion energy for the reactions. Again, little correlation is evident. Statistical analysis shows that there is a weak correlation between the bond distortion energy and the activation barriers. However, there is no indication that bonds that are easier to bend are more reactive.

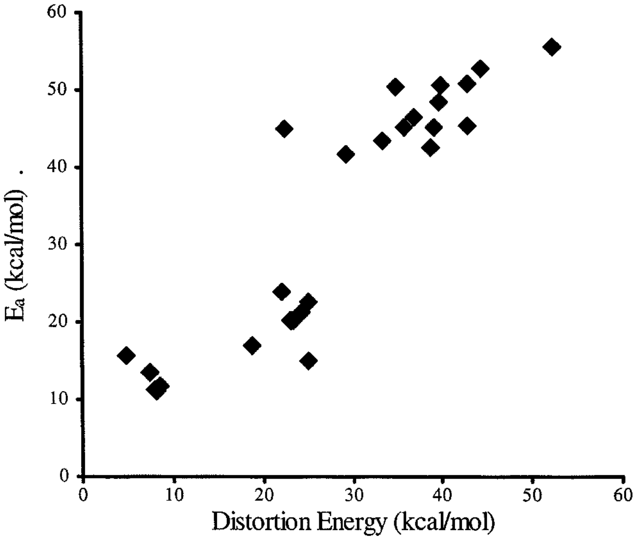

Figure 6. Activation energy as a function of the bond distortion energy.

All energies in kcal/mol.

At this point, we have found that the key factors that people discuss in the literature only have a weak correlation to the activation barriers to the reactions in Figure 2. Therefore, there is a need to go back and use the quantum mechanical calculations to get a better picture of the barriers.

One of the details in the quantum mechanical calculations is that accurate activation barriers were obtained only when "diffuse functions" were included in the basis set. The diffuse functions are large orbitals. When bonds stretch, the diffuse functions couple into the wavefunction. The diffuse functions had the largest coupling when there are significant orbital distortions during the reaction. Therefore, we decided to explore the orbital distortions in more detail.

Figure 7 shows some of the orbital distortions observed in the quantum mechanical calculations for the reaction

$$H + CH_3CH_3 \rightarrow H_2 + C_2H_5 \tag{6}$$

Notice the large orbital distortions. The hydrogen approaches the C−H bond and pushes into the orbitals on the methyl hydrogen. That causes the orbitals to compress. The energy rises in response to the compression. Eventually, the incoming hydrogen pushes the C−H bond off the methyl hydrogen, causing the C−H bond to break. Then a hydrogen-hydrogen bond forms to complete the reaction.

Figure 7 looks quite different from what was expected based on the previous literature. In the past, people have noted that bonds break during reaction and assumed that the main barriers to reaction are associated with the bond scission process. Notice, however, that there are significant orbital distortions when the reactants are separated by 2.0 Å. The bond lengths and angles in the reactants have hardly changed at

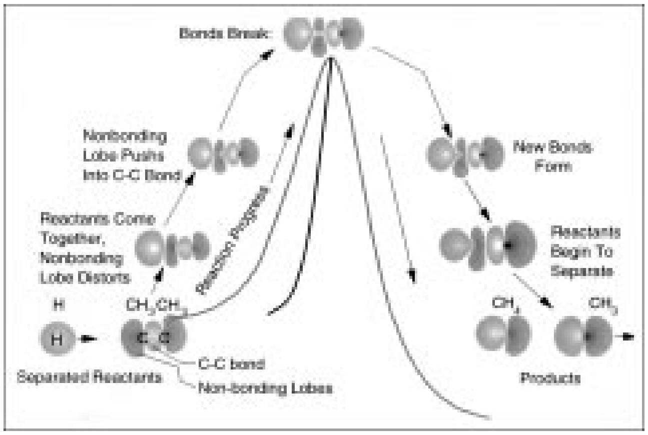

Figure 7. Orbital distortions for $H + CH_3CH_3 \rightarrow H_2 + C_2H_5$ at the PMP2/6-31g* level.

that point, but the energy of the system has gone up. Therefore, it would seem that orbital distortions are significant before there are significant bond distortions and that the orbital distortions can cause the energy to rise.

Next, we want to consider how the orbital distortions affect the barriers to reaction. In order to quantify the effect, we have calculated how much energy it takes to push the reactants together without distorting any bonds. Details of the calculations are given in Blowers (1998). The numerical results are given in Table 4.

Notice that there is a quantitative correlation between the energy to move the reactants together and the activation barriers for reaction. Therefore, the orbital distortion energy is playing a key role in determining the barrier to reaction.

Figure 8 shows a plot of the activation energy for the reactions in Table 2 vs. the energy to move the reactants together. One finds that the results seem to collapse to a line. Therefore, it seems that the energy to move the reactants together might be a good correlating parameter for rate data.

Buckingham Potentials

The problem with using the energy to move the reactants together as a correlating parameter is that without doing the quantum mechanical calculations, one will not know the energy to bring the reactants together for a given reaction. Therefore, we decided to see if we could find a way to estimate the energy to bring the reactants together and use that estimate in a correlation for chemical kinetics.

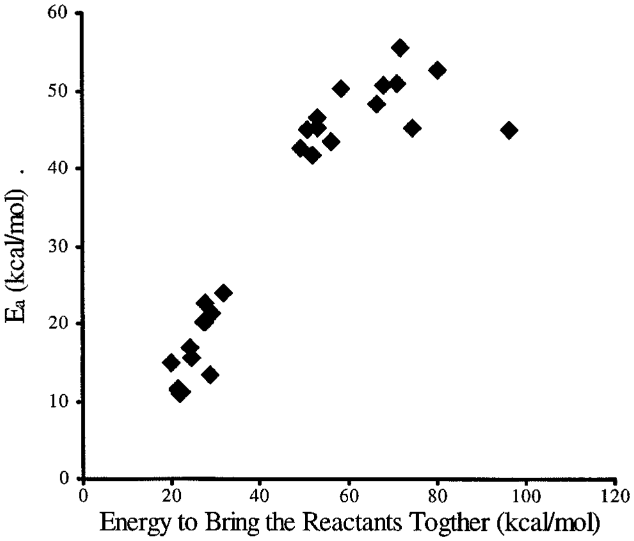

Figure 8. Activation energy as a function of the energy to bring the reactants together.

Our approach will be to build on what is known about the interaction of molecules from the molecular dynamics (MD) literature (Amaee and Brown, 1993; Hill, 1997; Metzger et al., 1997; Gianturco et al., 1992). In MD, one needs to describe the forces between molecules in order to do any calculations. At short distances, the forces are often exponential in the intermolecular distance, while at long distances, a $1/R^6$ dependence is often seen. People have found that a so-called united-atom Buckingham potential is often a good approximation to the intermolecular potential at short and long distances. In the united-atom approach, each CH_X group in a hydrocarbon is fit to an empirical potential. The forces on a group are calculated as a sum of the united-atom potentials. In our work we only considered the united-atom potential for a CH_3 group, and fit the potential to a Buckingham potential given by

$$V(R) = w\frac{6\exp\left[\alpha(1 - R/R_m)\right] - \alpha\left(\frac{R_m}{R}\right)^6}{\alpha - 6} \tag{7}$$

where V is the energy at some separation R, and w is the depth of the energy well at the minimum located at R_m. α indicates the steepness of the exponential repulsion term.

It is useful to see if Buckingham potentials can be used to estimate the energy to bring the reactants together. At present, there are no Buckingham potentials for the interaction between the various species in Table 2. However, one can calculate the potentials using quantum mechanical methods.

We have calculated a Buckingham potential for the reaction

$$H' + CH_3R \rightarrow H'H + CH_2R \tag{8}$$

at the PMP2/6-31g* and G-2 levels of theory.

Figure 9 shows the PMP2/6-31g* results. There is a minimum in the potential curve that is located at $R = 4$ Angstroms. However, this minimum energy is only 0.02 kcal/mol lower than the energy of the separated ethane molecule and hydrogen atom. As the hydrogen atom approaches the C-atom or ethane, the energy rises sharply at shorter distances. The data was fit to the exp-6 form of the Buckingham potential in Eq. 7 to give

$$V(R) = -0.02987\left(\exp\left[0.656\left(\frac{1 - R_x}{4}\right)\right] - 0.656\left(\frac{4}{R_x}\right)^6\right) \tag{9}$$

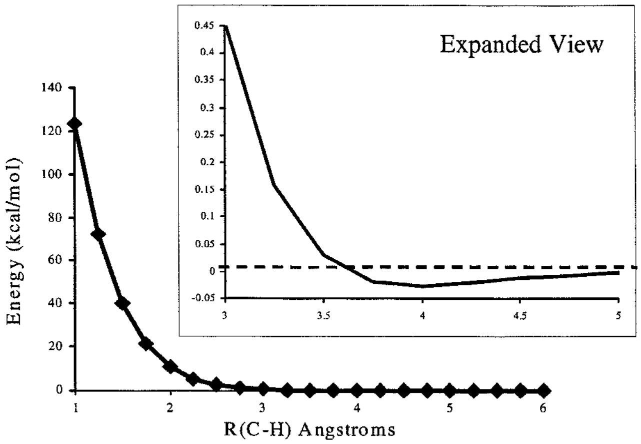

Figure 9. PMP2/6-31g* Buckingham potential for the interaction between hydrogen and ethane along the carbon-carbon bond.

All energies in kcal/mol.

Correlations Between Buckingham Potentials and Activation Barriers

Next, it is interesting to see if one can use the average Buckingham potentials to get some better approximations for chemical kinetics. The idea is to use the Buckingham potential to estimate the energy to bring the reactants together, and then try to correlate that energy to the barriers to reaction. In actual practice, one needs a value of R in Eq. 9 to calculate the energy to bring the reactants together. In a future article we will show that transition state bond lengths are approximately 25% bigger than equilibrium bond lengths. Consequently, we calculated R_x by multiplying the experimental bond lengths in the product structures by 1.25. We only considered the forward reactions in Table 2, since, if we know the results for the forward reactions, we can calculate the energies for the reverse reactions via microscopic reversibility.

Figure 10 shows the activation energy calculated using the Buckingham energy as the fitting parameter. Here, $E_a = 0.35\,E_{\text{Buck}} + 32.09$ when all energies are in kcal/mol. We see that only a few data points lie very far from the expected values.

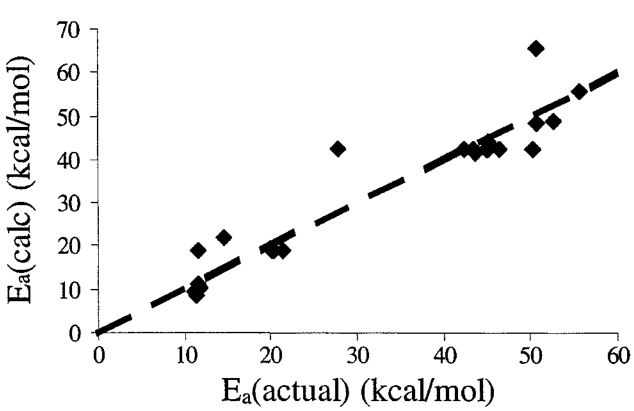

Figure 10. Predicted activation energies vs. the activation energies using the Buckingham energy.

$E_a = 0.35\ E_{\text{Buck}} + 32.09$. All energies are in kcal/mol.

One of the sources of error in Figure 10 is that the calculation ignored that the thermodynamics are more favorable to break a weak bond than a strong one. That could be a significant error.

One can account for that effect, by using a two-parameter fit to the activation barriers

$$E_a = E_O + \gamma_B E_{\text{Buck}} + \gamma_P \Delta Hr \qquad (13)$$

where E_a is the activation energy, E_{Buck} is the energy calculated from the Buckingham potential, ΔHr is the heat of reaction, and E_O, γ_B and γ_P are constants. Figure 11 shows how well this data fits. Notice that the correlation is quite good. The RMS error is only 2 kcal/mol.

Lastly, we have also done statistical analysis on the model

$$E_a = E_O + \gamma_B E_{\text{Buck}} + \gamma_P \Delta Hr + \gamma_S E_{\text{Stretch}} + \gamma_D E_{\text{Distort}} + \gamma_D E_{\text{Bond}} \qquad (14)$$

Statistical analyses were done using Eq. 14 to see if the inclusion of the distortion energy, bond stretching energy, or the bond energy, would improve the results. A standard P-test with confidence intervals of 0.01 and 0.05 was used to show that the inclusion of any or all of the additional terms did not statistically improve the model in Eq. 13.

Discussion

The results in the last section show that one can collapse the activation barriers for a wide group of reactions to a single line by considering two factors: the heat of reaction and the energies to move the reactants together. We also show that one can estimate the energy to move the reactants together using Buckingham potentials. The advantage of this approach is that one can collapse many different reactions

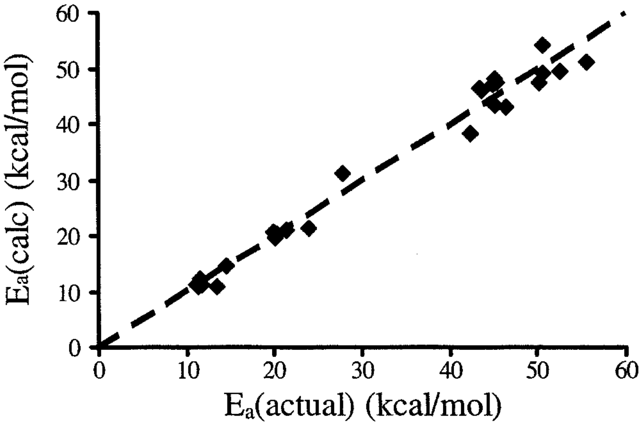

Figure 11. Predicted activation energies vs. the activation energy using the Buckingham energy and heat of reaction.

$E_a = 12.31 + 0.44\ E_{\text{Buck}} + 0.71\Delta H_{\text{rxn}}$. All energies are in kcal/mol.

into a single line. Consequently, one gets a correlation that is robust enough to extrapolate to new situations.

We think that this is an important advance. After all, one of the reasons that people hesitate to use correlations for chemical kinetics is that when one is presented with a new reaction, one does not always know which correlation to use. The advantage of our approach is that we use a single correlation for a wide range of reactions. Consequently, if one considers a new reaction, one can have more confidence that the reaction will fit into the same framework. We also find that the energy to move the reactants together is a new correlating parameter that can be used to improve the accuracy of the correlations for rate data.

The big limitation of the method at present is that one still does not know how to estimate one of the key parameters in the model, the energy to bring the reactants together. However, energies to bring the reactants together are relatively easy to calculate with standard quantum mechanical codes. The calculation takes about 2 min on a workstation compared to several hours to calculate an activation barrier. Further, we have found that we can represent the energies for a wide class of reactions with a single Buckingham potential. Still, the parameters are not yet easily accessible. As a result, there is more work to do before the correlations will have wide applicability.

Conclusions

In summary, we have considered several different correlations for chemical kinetics have been considered. We noted that the standard Polanyi relationships used in current practice are limited, because they are very specific to a given group of reactions and cannot be easily extrapolated to other reactions.

In this article, we provide some new correlations that show greater capability to correlate data. We found that one can collapse the activation barriers for a wide group of reactions to a single line by considering two factors: the heat of reaction and the energies to move the reactants together. We also show that one can estimate the energy to move the reactants together using Buckingham potentials. The advantage of this approach is that one can collapse many different reactions into a single line. Consequently, one gets a correlation that is robust enough to extrapolate to new situations.

Acknowledgment

This work was funded by NSF Grant No. CTS 96-10115.

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Manuscript received Jan. 25, 1999, and revision received May 4, 1999.