Engineering Approximations for Activation Energies in Hydrogen Transfer Reactions

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Previous investigators have often used the Polanyi relationship, extensions due to Seminov, or the BOC-MP/UBI-QEP relationship to estimate activation barriers in complex reaction networks. However, these relationships are not accurate for many reactions. In this article, a new engineering approximation for the estimate of activation barriers is presented. The approximation allows one to estimate barriers analytically, using known heats of reaction and one adjustable parameter, the intrinsic barrier. The equation was fit to the recommended values of activation energies for all 151 independent hydrogen transfer reactions in the NIST tables. All but nine of the reactions are fit within ± 4 *kcal/mol. Of the nine failures, seven of the data points came from previous estimates, and may not be accurate. By comparison, Seminov's relationship fails for 47 of the reactions even though the Seminov relationship has three adjustable parameters compared to one in our approximation. The BOC-MP/UBI-QEP method gives errors of more than 10 kcal/mol for all 151 reactions and errors of more than 30 kcal/mol for many of the reactions. These results show that the new approximation is a significant improvement over the approximations that are currently in use.*

Introduction

The objective of this article is to describe a new way to estimate activation barriers for hydrogen transfer reactions. In recent years many investigators have attempted to develop microkinetic models of complex chemical processes (Broadbelt et al., 1994a,b; 1995a,b, 1996; Klinke et al., 1997; Susnow et al., 1997; Truong, 1999; Virk, 1999). Typically, these models need hundreds of rate constants as inputs, many of which are unknown. Engineering approximations are used to estimate the rate constants in cases where no kinetic data exists (Herron et al., 1969; Boock and Klein, 1994; Cohen, 1991a,b; Kapoor, 1997; Neurock and Klein, 1993; Watson et al., 1996).

The most popular engineering approximation for estimating the unknown rate constants is called *the Polanyi relationship* (Evans and Polanyi, 1936; Polanyi et al., 1969; Polanyi, 1972):

$$E_a = E_a^0 + \gamma_p \Delta H_r. \tag{1}$$

In Eq. 1, E_a is the activation barrier, ΔH_r is the heat of reaction, and E_a^0 and γ_p are constants fit to data. E_a^0 is called the *intrinsic barrier* and γ_p is called the *transfer coefficient.* In practice people often fit the Polanyi equation to a series of reactions and then use the values of E_a^0 and γ_p to estimate rate constants for other ''similar'' reactions (Boock, 1994; Neurock, 1993; Watson et al., 1996). Another approach is to treat E_a^0 and γ_p as adjustable parameters that can be fit to the process being simulated (Susnow et al., 1997; Klinke et al., 1997). It has been common in the literature to use a different value of γ_p for exothermic and endothermic reactions. Sometimes multiple values of γ_p are used to represent different reaction sets.

Equation 1 has a practical advantage in that the activation energies can be calculated from a property that is easily estimated: the heat of reaction. While there are other approximations that could, in principle, be used to estimate activation barriers, so far none of the other approximations in the literature use parameters that are known or easily estimated for a wide variety of reactions.

The disadvantage of the Polanyi relationship, though, is that its accuracy is not as good as one might like. For exam-

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ple, Figure 1 shows experimental data for the activation energy of 302 reactions (Westley, 1980) of the form

$$R + HR' \rightarrow RH + R. \tag{2}$$

The reactions are listed in Table 1. Generally, activation barriers show nonlinear behavior with ΔH_r. One can fit individual parts of the data with the Polanyi relationship, but one cannot fit a wide range of data accurately with a single line.

There are several alternative equations in the literature. Denisov (1995, 1999) has proposed using the Marcus equation,

$$E_a = E_a^0\left(1+\frac{\Delta H_r}{8E_a^0}\right)^2 \tag{3}$$

to calculate properties. The Marcus equation, however, fails for very endothermic or very exothermic reactions, as shown in Figure 1.

There are extensions of the Polanyi method due to Roberts and Steele (1994), Zavitsas et al. (1996), Zavitsas (1998). Those methods add many additional parameters, which limits the utility of the methods in practice.

There is an alternative method called the BOC-MP method, or more recently the UBI-QEP method. Shustorovich (1991) derived the method by assuming that the intermolecular potential was given by a sum of Morse potentials, and imposing bond-order conservation during the reaction. Under this approximation, the activation barrier is given by

$$E_a = \frac{(w_B)^2}{w_B + w_F}, \tag{4}$$

where w_B and w_F are the bond dissociation energies of the bonds that break and form during the reaction. Equation 4 has the correct qualitative behavior in that it goes to the right limits when the heat of reaction is very large. Further, Shustorovich showed that Eq. 4 gives reasonable agreement with experiments for surface reactions. However, Eq. 4 is not as good for gas-phase reactions. For example, Eq. 4 predicts that reaction $H + H_2 \rightarrow H_2 + H$ has an activation barrier for 52 kcal/mol compared to an experimental value of 8.6 kcal/mol. Figure 1 compares the trends via Eq. 4 using typical values of bond strengths to those from the data. Notice that in the gas phase, Eq. 4 is not close to the data. There is some improvement if the actual bond strengths are substituted into Eq. 4. Still, the average error for the reaction set in Figure 1 is 40.2 kcal/mol; further, all of the reactions show errors of 14.9 kcal/mol or more. That is too large an error to be useful.

There are other older approximations, including an approximation of Johnston and Parr (1963) and Berces and Dombi (1980). None of these approximations fit a wide range of data.

The objective of this article is to provide an extension of the Polanyi equation that shows the correct nonlinear behavior. We will then fit that approximation to data for hydrogen transfer reactions to derive a better approximation for the calculation of activation barriers.

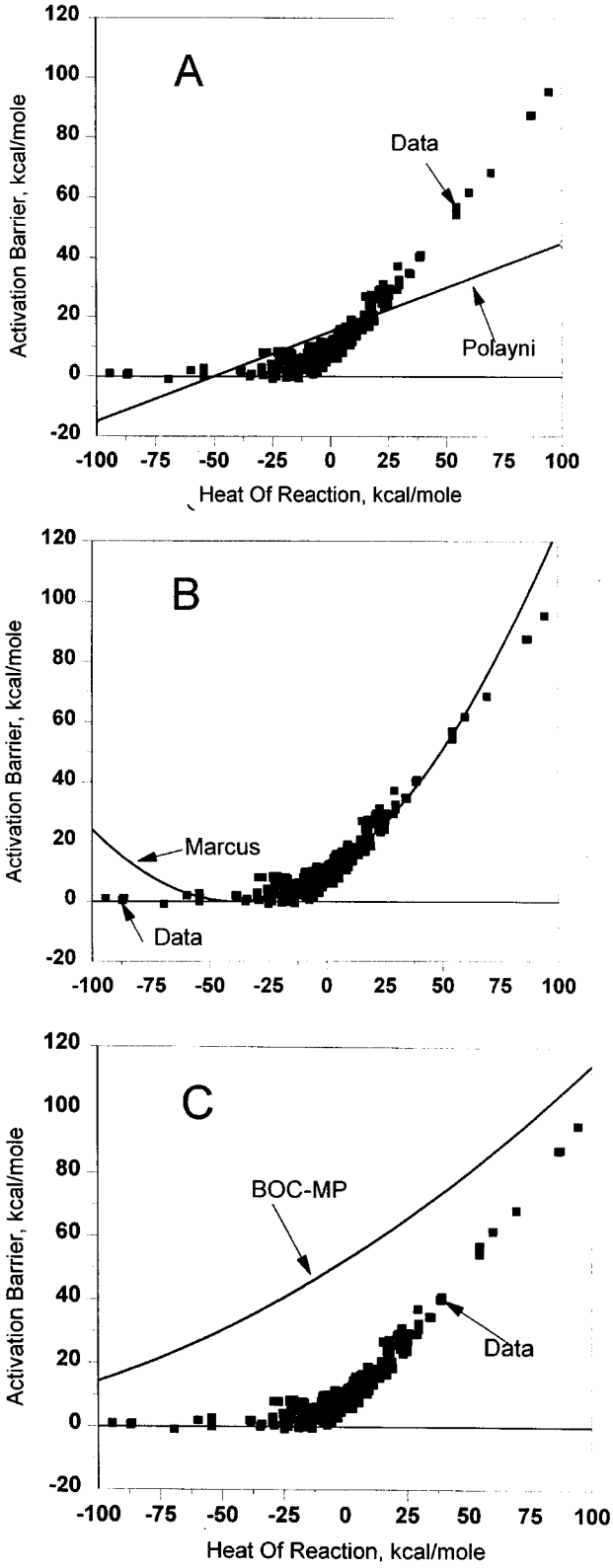

Figure 1. Activation barriers for the reactions in Table 1 as a function of the heat of reaction to the following.

(A) Those predicted with the Polanyi relationship with $E_a^0 = 7.95$ kcal/mol, $\gamma_p = 0.15$, (B) those predicted with the Marcus equation with $E_a^0 =$ kcal/mol; (C) those predicted with the BOC-MP relationship (Eq. 4) with $w_o = 105$ kcal/mol.

Table 1. Reactions Considered

$O + H \leftrightharpoons OH + H$	$O + CH_4 \leftrightharpoons OH + CH_3$
$O + D_2 \leftrightharpoons OD + D$	$O + CHO \leftrightharpoons OH + CO$
$O + OH \leftrightharpoons OH + O$	$O + HCHO \leftrightharpoons OH + CHO$
$O + H_2O \leftrightharpoons OH + OH$	$O + CH_3CH_3 \leftrightharpoons OH + CH_2CH_2$
$O + SH \leftrightharpoons OH + S$	$O + CH_3CH_2CH_2CH_3 \leftrightharpoons OH + CH_3CH_2CH_2CH_2$
$O + NH \leftrightharpoons OH + N$	$O + CH_3CH_2CH_2CH_3 \leftrightharpoons OH + CH_3CH_2CH(\cdot)CH_3$
$O + NH_3 \leftrightharpoons OH + NH_2$	$O + CH_3CH_2CH_2CH_2CH_3 \leftrightharpoons OH + CH_3CH_2CH_2CH_2CH_2$
$O + CH \leftrightharpoons OH + C$	$O + CH_3(CH_2)_4CH_3 \leftrightharpoons OH + CH_3(CH_2)_4CH_2$
$O + CH_2 \leftrightharpoons OH + CH$	$O + CH_3(CH_2)_5CH_3 \leftrightharpoons OH + CH_3(CH_2)_5CH_2$
$O + CH_3(CH_2)_6CH_3 \leftrightharpoons OH + CH_3(CH_2)_6CH_2$	$H + H_2 \leftrightharpoons H_2 + H$
$H + D_2 \leftrightharpoons DH + D$	$D + H_2 \leftrightharpoons DH + H$
$H + OH \leftrightharpoons H_2 + O$	$H + HO_2 \leftrightharpoons OH + OH$
$H + H_2O_2 \leftrightharpoons H_2 + HO_2$	$H + H_2S \leftrightharpoons H_2 + SH$
$H + NH \leftrightharpoons H_2 + N$	$H + NH_2NH_2 \leftrightharpoons H_2 + NH_2NH$
$H + HNO \leftrightharpoons H_2 + NO$	$H + CH \leftrightharpoons H_2 + C$
$H + CH_2 \leftrightharpoons H_2 + CH$	$D + CH_4 \leftrightharpoons DH + CH_3$
$H + HCHO \leftrightharpoons H_2 + CHO$	$H + CH_3CH_3 \leftrightharpoons H_2 + H_2 + CH_3CH_2$
$H + CH_3CH_2CH_2CH_3 \leftrightharpoons H_2 + CH_3CH_2CH(\cdot)CH_3 + CH_3CH_2CH_2CH_2$	
$D_2 + O \leftrightharpoons D + OD$	$H_2 + H \leftrightharpoons H + H_2$
$H_2 + D \leftrightharpoons H + HD$	$D_2 + H \leftrightharpoons D + DH$
$H_2 + OH \leftrightharpoons H + H_2O$	$D_2 + OH \leftrightharpoons D + DHO$
$H_2 + N \leftrightharpoons H + NH$	$H_2 + C \leftrightharpoons H + CH$
$H_2 + CH_3 \leftrightharpoons H + CH_4$	$H_2 + CD_3 \leftrightharpoons H + CD_3H$
$DH + CH_3 \leftrightharpoons H + CH_3D$	$DH + CH_3 \leftrightharpoons D + CH_3D$
$H_2 + CN \leftrightharpoons H + HCN$	$H_2 + CH_3CH_2 \leftrightharpoons H + CH_3CH_3$
$OH + D_2 \leftrightharpoons DHO + D$	$OH + O \leftrightharpoons O + OH$
$OH + H_2O_2 \leftrightharpoons H_2O + HO_2$	$OH + H_2S \leftrightharpoons H_2O + HS$
$OH + HNO \leftrightharpoons H_2O + NO$	$OH + NH \leftrightharpoons H_2O + N$
$OH + CO \leftrightharpoons H + CO_2$	$OH + CH_2 \leftrightharpoons O + CH_3$
$OH + CH_2 \leftrightharpoons H_2O + CH$	$OH + CH_3 \leftrightharpoons H_2O + CH_2$
$OH + CH_4 \leftrightharpoons H_2O + CH_3$	$OH + CN \leftrightharpoons O + HCN$
$OH + CN \leftrightharpoons O + HCN$	$OH + HCN \leftrightharpoons H_2O + CN$
$OH + CH{\equiv}CH \leftrightharpoons H_2O + CH{\equiv}C$	$OH + CH_2{=}CH_2 \leftrightharpoons H_2O + CH_2{=}CH$
$OH + CH_3CH_3 \leftrightharpoons H_2O + CH_3CH_2$	$HO_2 + H_2 \leftrightharpoons H_2O_2 + H$
$HO_2 + HCHO \leftrightharpoons H_2O_2 + CHO$	$HO_2 + CH_3 + CH_3 \leftrightharpoons H_2O_2 + CH_3CH_2$
$HO_2CH_3CH_2CH_3 \leftrightharpoons H_2O_2 + (CH_3)_2CH$	$HO_2 + CH_3CH_2CH_2CH_3 \leftrightharpoons H_2O_2CH_3CH_2CH(\cdot)CH_3$
$S + SH \leftrightharpoons SH + S$	$S + CH \leftrightharpoons SH + C$
$S_2 + H \leftrightharpoons S + SH$	$SH + N \leftrightharpoons S + NH$
$SH + S \leftrightharpoons S + SH$	$SH + C \leftrightharpoons S + CH$
$N + CH \leftrightharpoons NH + C$	$N + HNO \leftrightharpoons NH + NO$
$N + CHO \leftrightharpoons NH + CO$	$N + CH_2 \leftrightharpoons CH + NH$
$N_2O_4 \leftrightharpoons NO_2 + NO_2$	$NO + CHO \leftrightharpoons HNO + CO$
$NH + CN \leftrightharpoons N + HCN$	$NH + N \leftrightharpoons N + NH$
$NH_3 + CH_3 \leftrightharpoons NH_2 + CH_4$	$NH_2NH_2 + H \leftrightharpoons NH_2NH + H_2$
$ND_2ND_2 + CH_3 \leftrightharpoons ND_2ND + CH_3D$	$HN_3 + CH_3 \leftrightharpoons N_3 + CH_4$
$HNO + H \leftrightharpoons NO + H_2$	$HNO + N \leftrightharpoons NO + NH$
$CO + CH_3 \leftrightharpoons CH_2 + CHO$	$CH + O \leftrightharpoons C + OH$
$CH + CH_4 \leftrightharpoons CH_2 + CH_3$	$CH + C \leftrightharpoons C + CH$
$CH + HCHO \leftrightharpoons CH_2 + CHO$	$CH + CHO \leftrightharpoons CH_2 + CO$
$CH_2 + CH_2 \leftrightharpoons CH + CH_3$	$CH_2 + H_2 \leftrightharpoons CH_3 + H$
$CH_2 + HCHO \leftrightharpoons CH_3 + CHO$	$CH_2 + N \leftrightharpoons CH + NH$
$CH_2 + CN \leftrightharpoons CH + HCN$	$CH_2 + CHO \leftrightharpoons CH_3 + CO$
$CH_3 + NH_3 \leftrightharpoons CH_4 + NH_2$	$CH_3 + H_2S \leftrightharpoons CH_4 + SH$
$CH_3 + ND_2ND_2 \leftrightharpoons CH_3D + ND_2ND$	$CH_3 + NH_2NH_2 \leftrightharpoons CH_4 + NH_2NH$
$CH_3 + HCHO \leftrightharpoons CH_4 + CHO$	$CH_3 + HN_3 \leftrightharpoons CH_4 + N_3$
$CH_3 + CH_3OH \leftrightharpoons CH_4 + CH_3O$	$CH_3 + CH_3OH \leftrightharpoons CH_4 + CH_2OH$
$2CH_3 + 2CH_3OH \leftrightharpoons 2CH_4 + CH_3O + CH_2OH$	$CH_3 + CN \leftrightharpoons CH_2 + HCN$
$CH_3 + CH_3NH_2 \leftrightharpoons CH_4 + CH_2NH_2$	$CH_3 + CH{=}CH \leftrightharpoons CH_4 + CH{=}C$
$CH_3 + CH_2{=}CH_2 \leftrightharpoons CH_4 + CH_2{=}CH$	$CH_3 + CH_3CH_3 \leftrightharpoons CH_4 + CH_3CH_2$
$CH_3 + CH_3CHO \leftrightharpoons CH_4 + CH_3C(O)$	$CH_3 + CH_3OCH_3 \leftrightharpoons CH_4 + CH_3OCH_2$
$CH_3 + CH_3CN \leftrightharpoons CH_4 + CH_2CN$	$CH_3 + CH_3CH = CH_2 \leftrightharpoons CH_4 + [C_3H_5]$
$CH_3 + CH_3CH_2CH_3 \leftrightharpoons CH_4 + (CH_3)_2CH$	$CH_3 + CH_3CH_2CH_2CH_3 \leftrightharpoons CH_4 + CH_3CH_2CH(.)CH_3$
$CH_3 + CH_3CH_2CH_2CH_3 \leftrightharpoons CH_4 + CH_3CH_2CH(\cdot)CH_3 + CH_3CH_2CH_2CH_2$	$CH_3 + (CH_3)_3CH \leftrightharpoons CH_4 + (CH_3)_3C + (CH_3)_2CHCH_2$
$CH_3 + (CH_3)_3CH \leftrightharpoons CH_4 + (CH_3)_3C$	$CH_3 + CH_3CH_2CH_2CH_2CH_3 \leftrightharpoons CH_4 + CH_3CH_2CH_2CH_2CH_2$
$CH_3 + (CH_3)_2CHCH_2CH_3 \leftrightharpoons CH_4 + (CH_3)_2C(\cdot)CH_2CH_3$	$CH_3 + (CH_3)_2CHCH_2CH_3 \leftrightharpoons CH_4 + (CH_3)_2CHCH(\cdot)CH_3$
$CH_3 + CH_3(CH_2)_6CH_3 \leftrightharpoons CH_4 + CH_3(CH_2)_6CH_2$	$CH_3 + (CH_3)_2CHCH(CH_3)CH(CH_3)_2 \leftrightharpoons CH_4 + [C_8H_{17}]$
$CH_4 + CN \leftrightharpoons HCN + CH_3$	$CHO + CH \leftrightharpoons CO + CH_2$
$CHO + N \leftrightharpoons CO + NH$	$HCHO + CH \leftrightharpoons CHO + H_2O_2$
$CHO + CH_2 \leftrightharpoons CO + CH_3$	$HCHO + CH_2 \leftrightharpoons CHO + CH_3$
$HCHO + CH \leftrightharpoons CHO + CH_3$	$HCHO + CN \leftrightharpoons CHO + HCN$
$HCHO + CH_3 \leftrightharpoons CHO + CH_4$	$CH_3OD + CD_3 \leftrightharpoons CH_2OD + CD_3H$
$CH_3OD + CD_3 \leftrightharpoons CH_3O + CD_4$	$CD_3OH + CH_3 \leftrightharpoons CD_3O + CH_4$
$CN + NH \leftrightharpoons HCN + N$	$CN + CH_2 \leftrightharpoons HCN + CH$
$CN + CH_3 \leftrightharpoons HCN + CH_2$	$CN + CH_4 \leftrightharpoons HCN + CH_3$

Our general approach is to

- Do high-level calculations of transition state properties.
- Use what is learned from those calculations to derive engineering approximations for transition-state properties.
- Fit the models to available data.
- Test to see how well the correlations fit a wide data set.

Ab Initio Calculations

The first part of the work involved *ab initio* calculations to determine the relative contributions of the various forces to bond activation. We have considered several types of forces, and used *Gaussian 98* (Frisch et al., 1993, 1998) to estimate properties. Generally geometries are calculated at the MP2/6-31G(d) or MP2/6-311++G(d,p) level, while energies are calculated at the MP2/6-31G(d), G-2 (Curtiss, 1991) or G-3 level (Curtiss, 1998). In some cases full geometry optimizations at the CCSD(T)/aug-cc-pvtz level were also done. Here we consider reactions where the MP2 geometries were only weakly dependent on basis set size, and there is little difference between the MP2 and CCSD(T) geometries. Cases where the geometries vary more strongly with basis set size are described elsewhere. Further details about the computational methods and results are described in Blowers (Blowers et al., 1998; Blowers and Masel, 1998, 1999a,b,c).

Ab Initio Results

In previous articles (Blowers et al., 1998; Blowers and Masel, 1998), we used the *ab initio* calculations to examine the relative contributions of bond stretching, Pauli repulsions, bond distortions, curve crossing, and other factors on the series of reactions in Table 2. Blowers et al. calculated the total energy to bring the reactants to the transition state, with full geometric optimizations. Blowers et al. also calculated the energy by doing the geometric optimization in stages, where the reactants were brought together without allowing any bonds to distort, then allowing the active bonds to stretch, and finally allowing all of the other bonds in the molecule to relax.

Table 2 shows the results. In the table E_{Pauli} is the energy to bring the reactants together without distorting any bonds, $E_{\text{StretchClose}}$ is the energy change when we allow the bonds to stretch the adsorbate bonds to the transition state geometry when the reactants are in close proximity, E_{Bend} is the energy to distort all of the bonds away from the active bonds, $E_{\text{StretchFar}}$ is the energy change when we allow the bonds to stretch the adsorbate bonds to the transition state geometry when the reactants are far apart, and E_a is the activation barrier.

Notice that E_{Pauli} is large and positive. The implication of this result is that the energy to bring the reactants together is a large portion of the activation barrier. $E_{\text{StretchClose}}$ is large, but negative. The fact that it is large implies that the bond energy is important to the barriers, but the fact that the energy is negative implies that there is no net barrier to bond stretching; that is, more energy is gained by forming new bonds than is lost by stretching old bonds.

The results in Table 2 are quite important. Recall that the Polanyi relationship is derived by assuming that the energy

Table 2. Activation Barriers and Other Properties Estimated from MP2/6-31G(d) Calculations

Reaction	E_a (kcal/mol)	E_{Pauli} (kcal/mol)	$E_{\text{StretchClose}}$ (kcal/mol)	E_{Bend} (kcal/mol)	$E_{\text{StretchFar}}$ (kcal/mol)
$H_2 + CH_2CH_2NH_2 \rightarrow H + CH_3CH_2NH_2$	11.06	22.01	−10.9	−0.05	8.23
$H_2 + CH_2CH_2CH_3 \rightarrow H + CH_3CH_2CH_3$	11.14	22.28	−11.1	−0.04	8.18
$H_2 + CH_2CH_2CF_3 \rightarrow H + CH_3CH_2CF_3$	11.32	21.65	−10.3	−0.03	7.91
$H_2 + CH_2CH_3 \rightarrow H + CH_3CH_3$	11.72	21.34	−9.6	−0.02	8.5
$H_2 + CH_2CH_2CN \rightarrow H + CH_3CH_2CN$	13.46	28.60	−15.1	−0.04	7.46
$H_2 + CH_3O \rightarrow H + CH_3OH$	15.01	20.12	−5.1	−0.01	25
$H_2 + CH_2OH \rightarrow H + CH_3OH$	15.55	24.44	−8.9	0.01	4.91
$H + CH_3OH \rightarrow H_2 + CH_2OH$	16.92	24.23	−8.3	0.99	18.71
$H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$	20.11	27.40	−7.3	0.01	22.96
$H + CH_3CH_2NH_2 \rightarrow H_2 + CH_2CH_2NH_2$	20.22	27.63	−7.4	−0.01	23.13
$H + CH_3CH_2CH_3 \rightarrow H_2 + CH_2CH_2CH_3$	20.25	27.54	−7.3	−0.01	23.38
$H + CH_3CH_2CF_3 \rightarrow H_2 + CH_2CH_2CF_3$	21.37	28.95	−7.6	0.02	24.39
$H + CH_3OH \rightarrow H_2 + CH_3O$	22.69	27.71	−5	−0.02	25
$H + CH_3CH_2CN \rightarrow H_2 + CH_2CH_2CN$	23.96	31.97	−8	−0.01	22.03
$H + CH_3OH \rightarrow CH_3 + H_2O$	34.17	40.54	−6.3	−0.07	17.21
$H + CH_3OH \rightarrow H + CH_3OH'$	41.00	44.83	−3.7	−0.13	13.39
$H + CH_3OH \rightarrow CH_4 + OH$	41.69	52.21	−10.6	0.08	29.3
$H + CH_3CH_2NH_2 \rightarrow CH_4 + CH_2NH_2$	42.53	49.60	−6.7	−0.37	38.86
$H + CH_3CH_2CN \rightarrow CH_4 + CH_2CN$	43.48	56.52	−12.6	−0.44	33.42
$H + CH_3CH_2CF_3 \rightarrow CH_4 + CH_2CF_3$	44.98	51.15	−5.7	−0.47	22.48
$CH_4 + CH_2CN \rightarrow H + CH_3CH_2CN$	45.12	96.59	−51.5	0.03	39.17
$H + CH_3CH_2CH_3 \rightarrow CH_4 + CH_2CH_3$	45.23	53.28	−8	−0.05	35.78
$CH_4 + CH_2CF_3 \rightarrow H + CH_3CH_2CF_3$	45.38	74.69	−28.9	−0.41	42.92
$H + CH_3CH_3 \rightarrow CH_4 + CH_3$	46.55	53.2	−6.3	−0.35	36.88
$H + CH_4 \rightarrow CH_4 + H$	46.6	58.51	−11.7	−0.21	34.93
$CH_4 + OH \rightarrow H + CH_3OH$	48.44	66.88	−18.2	−0.24	39.77
$CH_3 + H_2O \rightarrow H + CH_3OH$	48.74	59.95	−11	−0.21	24.99
$H + CH_3OH \rightarrow H + CH_2H'OH$	50.66	68.37	−17.7	−0.01	39.92
$CH_4 + CH_2CH_3 \rightarrow H + CH_3CH_2CH_3$	50.88	71.46	−20.7	0.12	42.98
$CH_4 + CH_3 \rightarrow H + CH_3CH_3$	52.77	80.67	−27.7	−0.2	44.47
$CH_4 + CH_2NH_2 \rightarrow H + CH_3CH_2NH_2$	55.62	72.22	−16.6	0	52.38

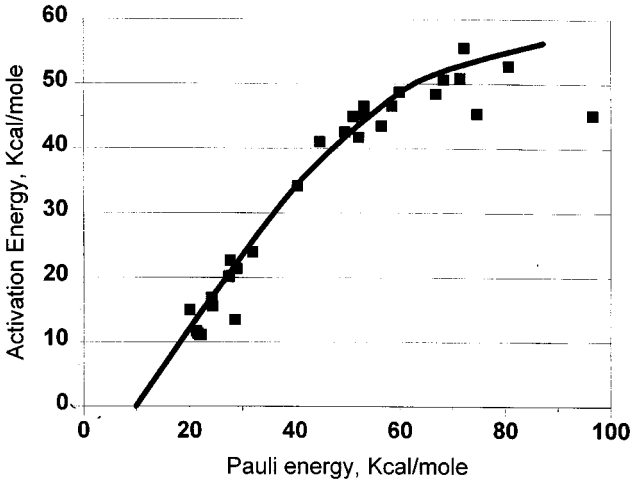

Figure 2. Activation barrier for the reactions in Table 2 as a function of the Pauli repulsion energy for the reactions.

needed to bring the reactants together is negligible, and that most of the barrier is associated with the energy to stretch bonds. Our *ab initio* calculations show that this assumption is in error. The energy to bring the reactants together is quite important.

Figure 2 shows a plot of the activation barrier for the reactions in Table 2 as a function of the Pauli repulsion energy for the reactions. Notice that the variations in the activation barriers track the changes in E_{Pauli}. Therefore, it seems that the Pauli repulsions are controlling the activation barriers for reaction as the reactants come together.

Similarly BOC-MP/UBI-QEP is derived by assuming that bond order is conserved and that E_{Pauli} was negligable. If bond order were conserved, $E_{\text{StretchClose}}$ would be positive and not negative. More detailed calculations show that in the types of reactions considered here, there is a net gain in the bond order when the reactants approach the transition state. BOC-MP/UBI-QEP does not allow there to be enough net bonding in the transition state, which is why BOC-MP/UBI-QEP overestimates the barriers in Figure 1.

Another assumption in BOC-MP/UBI-QEP is that the energy to stretch the bonds is the same whether the reactants are far apart or close together. Table 2 gives values for $E_{\text{StretchFar}}$, the energy change when we allow the bonds to stretch the adsorbate bonds to the transition-state geometry when the reactants are far apart, and $E_{\text{StretchClose}}$, the energy change when we allow the bonds to stretch the adsorbate bonds to the transition-state geometry when the reactants are close together. Clearly, the two values are not the same.

The results in Table 2 imply that the Polanyi relationship fails in Figure 1 because it assumes that the energy to bring the reactants together is negligible. That clearly is an incorrect assumption. Bond order conservation fails because there is a net gain in the bond order as the reactants approach the transition state and because it ignores the energy to bring the reactants together.

The results in Table 2 also imply that the key forces determining activation barriers are the energy to bring the reactants together without distorting bonds, and the energy to stretch bonds near the active site.

An Improved Model

Next it is useful to derive a new model that has the correct physical interactions between species. We will assume that the key energies are the energy to move the reactants together without distorting any bonds, and the energies to distort bonds around the reactive site. We will ignore the energy associated with the distortions away from the reactive site, since Table 2 shows that those energies are small. We will then derive a new model and see how well it fits data.

Much of the derivation follows a recent paper of Blowers and Masel (1999a). Blowers and Masel's premise was that $V(R)$, the potential energy surface for the reaction $A + BC \rightarrow AB + C$, could be written as

$$V(R) = V_{AB} + V_{BC} + V_I, \tag{5}$$

In Eq. 5 V_{AB} is the potential for the AB interaction, V_{BC} is the potential for the BC interaction, and V_I is an interaction potential. There are no assumptions in Eq. 5; if one knows the potential energy surface and the potentials for each of the reactants, one can always calculate a function V_I to fit the potential energy surface exactly. The hard part is to find appropriate forms for V_I, V_{AB}, and V_{BC}.

In the previous literature, Johnston and Parr (1963), Shusturovich (1990), Shusturovich and Sellers (1998), and others have assumed that V_{AB} and V_{BC} are represented by Morse potentials. We have fit our *ab initio* calculations to both Morse potentials and parabolas, and both fit reasonably well in the transition-state region. However, the algebra in the derivation will be easier if we use Morse potentials.

There is some question in the literature about what form to use for V_I. Shustorovich ignores V_I in his derivation, and instead assumes that bond order is conserved. The resultant model predicts activation barriers that are 14–50 kcal/mol too high, as indicated in Figure 1C. Johnston and Parr assumed that V_I is given by an anti-Morse potential. Johnston and Parr then assumed that bond order was conserved to derive a result with a barrier that was very high. They showed that they could adjust the findings by adding on an empirical attractive potential. However, this procedure still gives significant errors.

Our approach is to use the *ab initio* calculations to find suitable forms for V_I. No bond order conservation assumption will be made since the *ab initio* calculations show that bond order is not conserved. Instead, an analytical expression for the saddle-point energy in the potential will be derived and that the expression will be used to estimate properties.

Next, it is useful to consider an appropriate form for V_I. Recently Blowers and Masel calculated V_I for the interaction of a hydrogen atom with an ethane molecule (1999b). Figure 3 shows the potential obtained at different levels of theory. Notice that the potential is largely independent of the computational method for all of the methods shown. Instead, there is always a rapid rise in energy as the reactants come together. The figure is a computation for the hydrogen approaching along the C–C axis, but Blowers and Masel also considered the hydrogen approaching along the C–H bond, and the potential was very similar to those in Figure 3.

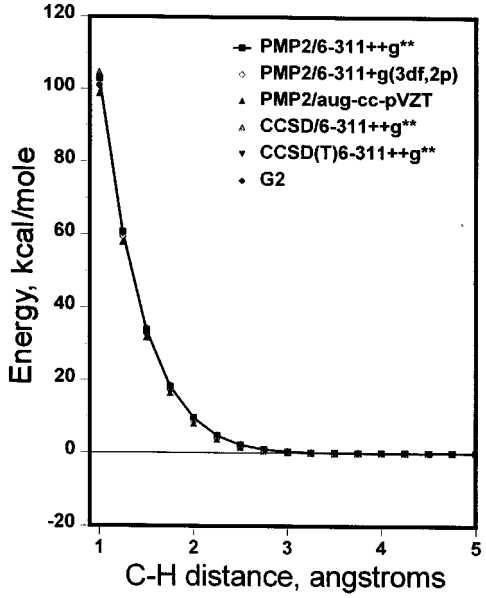

Figure 3. Potential for the interaction of a hydrogen atom with an ethane molecule for interactions along the C–C bond.

The points are calculations done at different levels of theory. The line is a fit to the data using Eq. 6 with $V_o = 9{,}580$ kcal/mol and $\alpha = 2.25$/Å. Results of Blowers and Masel.

Figure 3 also shows a plot of a line calculated via the expression:

$$V_I = V_o \exp(-\alpha_1 r_{\mathrm{AC}}). \tag{6}$$

In Eq. 6, r_{AC} is the distance from the incoming hydrogen to the carbon atom on the ethane, and V_o and α_1 are parameters. Notice that the potential is largely independent of the calculational method in the region of interest ($r_{\mathrm{AC}} < 3$ Å). Further, the results are easily fit to the expression in Eq. 6.

A Model Potential Energy Surface

Next we assume that the interaction potential always can be represented by Eq. 5, that V_{AB} and V_{BC} can be presented by Morse potentials, as indicated in our *ab initio* calculations, and that the bonds are linear at the transition state. We will then provide an equation for the potential energy surface and the activation barrier.

If the transition state is linear,

$$r_{\mathrm{AC}} = r_{\mathrm{AB}} + r_{\mathrm{BC}}. \tag{7}$$

one can then write the potential as

$$V(R) = w_B\left(\left\{\exp\left(\alpha_B\left[r_{\mathrm{BC}} - r_{\mathrm{BC,equ}}\right)\right] - 1\right\}^2 - 1\right) + w_F\left(\left\{\exp\left(\alpha_F\left[r_{\mathrm{AB}} - r_{\mathrm{AB,equ}}\right)\right] - 1\right\}^2 - 1\right) + V_I \exp\left[\alpha_1(r_{\mathrm{AB}} + r_{\mathrm{BC}})\right]. \tag{8}$$

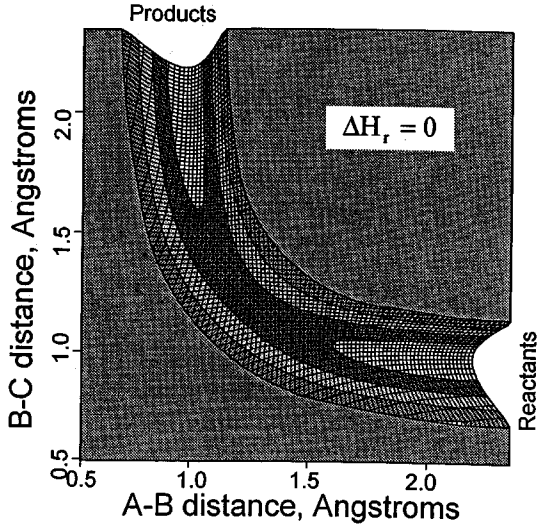

Figure 4. Potential given by Eq. 6 for $V_o = 9{,}580$ kcal/mol and $\alpha = 2.25$/Å, $r_{\mathrm{equ}} = 0.815$ Å, $w_o = w_F = w_B = 105$ kcal/mol, $\Delta H_r = 0$.

In Eq. 8 w_B is the bond energy for the B–C bond that breaks, w_F is the bond energy for the new A–B bond that forms, r_{BC} and r_{AB} are the lengths of the AB and BC bond at any point during the collision, $r_{\mathrm{BC,equ}}$ and $r_{\mathrm{AB,\,equ}}$ are the equilibrium bond lengths, and α_B, α_F, and α_1 are parameters.

Figure 4 shows a plot of the potential given by Eq. 8 for some typical values of the parameters. Notice that the potential has a saddle point between the reactants and products and looks just like the potential energy surface calculated for $H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$.

In other work Blowers and Masel (1999a,b) found there will be a saddle point in the potential energy surface when $-4E_a^0 < \Delta H_r < 4E_a^0$, but the reaction will be barrierless for very exothermic reactions that is, when $\Delta H_r < -4E_a^0$. The activation barrier will equal the heat of reaction when $4E_a^0 < \Delta H_r$ where E_a^0 is given by

$$E_a^0 = \frac{\left(\frac{w_B + w_F}{2}\right)\left\{V_1 \exp\left[-\alpha_1(r_{\mathrm{AB,equ}} + r_{\mathrm{BC,equ}})\right] - w_B - w_F\right\}^2}{(V_1)^2 \exp\left[-2\alpha_1(r_{\mathrm{AB,equ}} + r_{\mathrm{BC,equ}})\right] - (w_B + w_F)^2}. \tag{9}$$

Physically, E_a^0 is called the intrinsic barrier to reaction. One can show that the activation barrier will equal the intrinsic barrier when $\Delta H_r = 0$.

Next it is useful to obtain an analytical expression for the energy of the saddle point. The expression will be obtained by differentiating Eq. 8 with respect to r_B and r_F, and solving for the case where the derivatives are zero. It will also be assumed α_B, follow Badger's rule:

$$\frac{\alpha_F}{\alpha_B} = \frac{r_{\mathrm{AB,equ}}}{r_{\mathrm{BC,equ}}},$$

The assumption that bond order is not conserved will not be made. The result is a simple expression for the activation barrier:

$$E_a = \begin{cases} 0 & \text{for } \Delta H_r < -4E_a^0 \\ \Delta H_r & \text{for } \Delta H_r > 4E_a^0 \\ \dfrac{\left(\dfrac{w_B + w_F + \Delta H_r}{2}\right)(V_P - w_B - w_F + \Delta H_r)^2}{V_p^2 - (w_B + w_F)^2 + \Delta H_r^2}, & \text{otherwise.} \end{cases} \tag{10}$$

The inequalities in Eq. 10 arise because there is no saddle point for very exothermic or very endothermic reactions. In Eq. 10, ΔH_r is the heat of reaction, w_B is the bond dissociation energy of the bond which breaks, w_F is the bond dissociation energy of the new bond which forms, E_a^0 is the intrinsic barrier, and V_P is a parameter related to the intrinsic barrier by

$$V_P = (w_B + w_F)\frac{(w_B + w_F + 2E_a^0)}{(w_B + w_F - 2E_a^0)}. \tag{11}$$

Equations 10 and 11 differ from the equations in Blowers and Masel (1999a), but they are equivalent to our earlier results.

Equations 10 and 11 provide a simple expression for the activation barrier in terms of properties that are easy to estimate (that is, ΔH_r, w_B, and w_F) and one adjustable parameter E_a^0. (Note the α dependence drops out of the equation.)

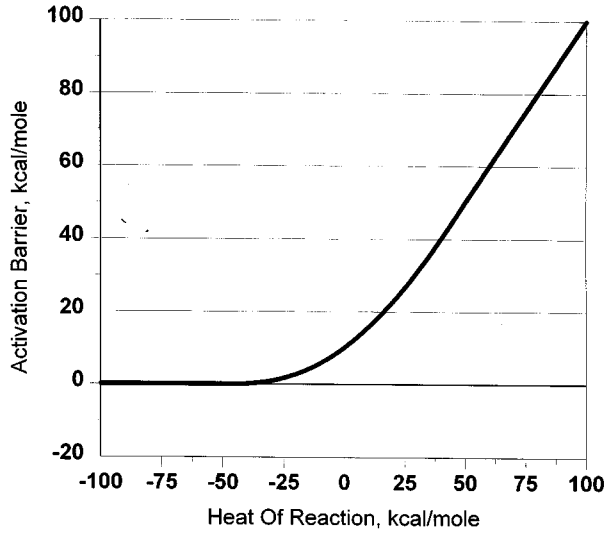

Figure 5. Activation barriers calculated from Eq. 10 with $E_a^0 = 10$ kcal/mol and $w_o = 80$, 100 and 120 kcal/mol.

There are three lines in the figure, but they are all equivalent on the scale shown.

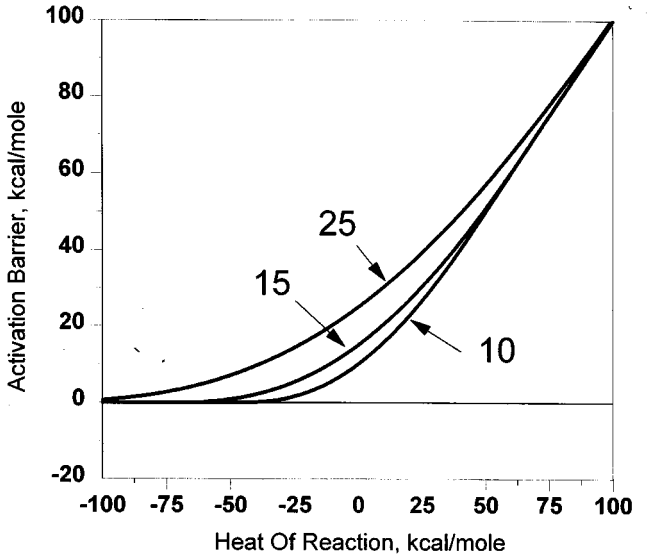

Figure 6. Activation barriers calculated from Eq. 10 with $E_a^0 = 10$, 15, 25 kcal/mol and $w_o = 105$ kcal/mol.

Figure 5 shows a plot of the activation barriers calculated from Eq. 9 with $E_a^0 = 10.0$ kcal/mol and $w_o = 80$, 100, and 120 kcal/mol, where w_o is given by

$$w_o = \frac{w_B + w_F}{2}. \tag{12}$$

There are three lines in the figure, but all three are indistinguishable on the scale shown. Notice that unlike the Polanyi relationship, the trends that are predicted by Eq. 10 follow the trends in the data in Figure 1. Further, the predicted activation barriers are almost independent of w_o, so one can use Eq. 10 even if one does not know accurate bond dissociation energies.

Figure 6 shows a plot of the activation energy calculated from Eq. 10 for several typical values of E_a^0. Notice that the predicted barriers increase as E_a^0 increases and are largely independent of w_o. Therefore E_a^0 could be a useful correlating parameter.

Fitting Eq. 10 to Data

Next it is useful to see how well Eq. 10 fits actual experimental data. In order to do so we have taken all of the hydrogen transfer reactions listed in the NIST tables (Westley, 1980), and looked up the heats of reaction. Data were available for the 151 reactions in Table 1. We also considered the activation barriers for the reverse reactions. That gave us a data set of 302 reactions that could be fit to data.

We choose Westley's compilation over more modern tabulations because Westley reports activation energies. More modern compilations would require us to fit the data to Arrhenius's law.

Figure 7 shows a comparison of the data in Figure 1 to the predictions of Eq. 10 with E_a^0 10 kcal/mol. The plot was calculated with $w_o = 105$ kcal/mol, but an indistinguishable plot would be obtained for any value of w_o between 90 and 120 kcal/mol. Notice that the plot goes through the center of the data and shows all of the correct trends. A more detailed analysis shows that if one assumes that $E_a^0 = 10$ kcal/mol, the predictions of the model are within ± 4 kcal/mol for most of the reaction in Table 1. There are 9 reversible reactions (out of 151) with errors greater than 4 kcal/mol. Those reactions are listed in Table 3.

Next it is useful to compare the errors in Eq. 10 to those from the Polanyi relationship. Figure 8 and Table 4 compare the data to the predictions of the Polanyi relationship. In the table we have included errors in both the forward and reverse reactions, so each of the reactions in Table 3 has been counted twice. We did this because the Polanyi relationship does not satisfy macroscopic reversibility, so it can give poor predictions on the forward reaction but not the reverse reaction or vice versa.

Table 4 shows that the Polanyi relationship does not fit the data very well. R.M.S. errors are about 5 kcal/mol, and there are 85 reactions with errors of 4 kcal/mol or more. That is not accurate enough for most kinetic modeling applications.

Semenov (1958) suggested that one could get a better correlation if one arbitrarily assumes that γ_p changes from 0.3 to 0.7 at $\Delta H_r = 0$. Table 4 shows how well Semenov's approximation fits. Generally, when 10 kcal/mol $> \Delta H_r > -10$ kcal/mol, Semenov's approximation makes little error. However, there are sizable deviations at larger values of ΔH_r. There are 92 reactions with errors of ± 4 kcal/mol or more and 16 with errors greater than ± 10 kcal/mol. That is too large an error for accurate calculations.

We have tried optimizing Semenov's parameters, and find that we can reduce the total number of examples where the error barrier is greater than ± 4 kcal/mol using the parameters in Table 4. However, there are still 72 reactions with errors greater than ± 4 kcal/mol.

Next we tried fitting the E_a vs. ΔH_r curve with a series of line segments. We divided the data into a series of ranges of ΔH_r and fit each range of values to a line. We find that if we empirically break the E_a vs. ΔH_r curves into four line segments and optimize the line segments, we can get a different approximation that has a reasonable average error. However, the curve has eight adjustable parameters. (The slopes, intercepts, and points where the slope changes were all optimized.)

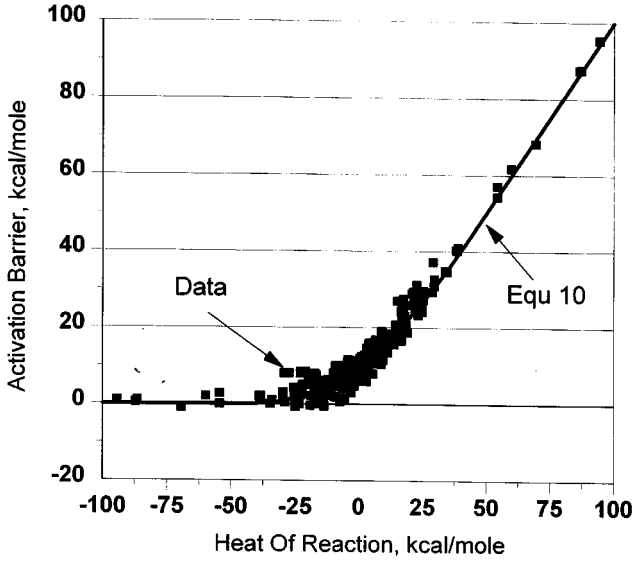

Figure 7. Data in Figure 1 vs. predictions of Eq. 10 with $E_a^0 = 10$ kcal/mol and $w_o = 105$ kcal/mol.

We have some doubt whether an eight-parameter fit is reasonable.

We have also tried BOC-MP/UBI-QEP (Shustorovich, 1990, 1998) and Denisov's (1995, 1999) version of the Marcus equation. BOC-MP/UBI-QEP fails for all of the reactions in our data set. All 302 reactions have errors of ± 14.9 kcal/mol or more, and 254 reactions have errors of ± 40 kcal/mol or more. The Marcus equation does fairly well for most of the reactions, but there are 42 reactions where the errors are larger than ± 4 kcal/mol and 12 where the errors are greater than ± 10 kcal/mol.

The implications of Figure 8 and Table 4 are that the Polanyi relationship, the extension of the Polanyi relationship due to Semenov, and the BOC-MP/UBI-QEP method do not do a good job of fitting the data. We can get a reasonable fit by using four line segments. However, there is no theoretical justification for using four line segments, except that the model then fits the data. Equation 10, on the other hand, we justified theoretically, and fits the data well with only one adjustable parameter. Therefore, Eq. 10, with $E_o^0 = 10$ kcal/mol, seems to be a substantial improvement compared to Polanyi's model.

Table 3. Reactions Where Predictions of Eq. 9 Differ from the Westley Data by More Than 4 kcal/mol

Reaction	E_a, Westley (kcal/mol)	Westley's Source	E_a, Eq. 9 (kcal/mol)
$H + CH \leftrightharpoons H_2 + C$	8	Estimate	2.04
$O + NH \leftrightharpoons OH + N$	8	Estimate	2.33
$O + CH \leftrightharpoons OH + C$	8	Estimate	2.44
$O + SH \leftrightharpoons OH + S$	8	Estimate	3.34
$H + NH \leftrightharpoons H_2 + N$	8	Estimate	0.96
$CH + CH_4 \leftrightharpoons CH_2 + CH_3$	6 ± 5	Kinetic Model	11.5
$HO_2 + CH_3CH_2CH_2CH_3 \leftrightharpoons H_2O_2 + CH_3CH_2CHCH_3$	7.9	Kinetic Model	15.0
$O + NH_3 \leftrightharpoons OH + NH_2$	6	Data	10.8
$CH_3 + (CH_3)_3CH \leftrightharpoons CH_4 + (CH_3)_3C$	7.8 Undeuterated 11.5 Deuterated	Data	13.0

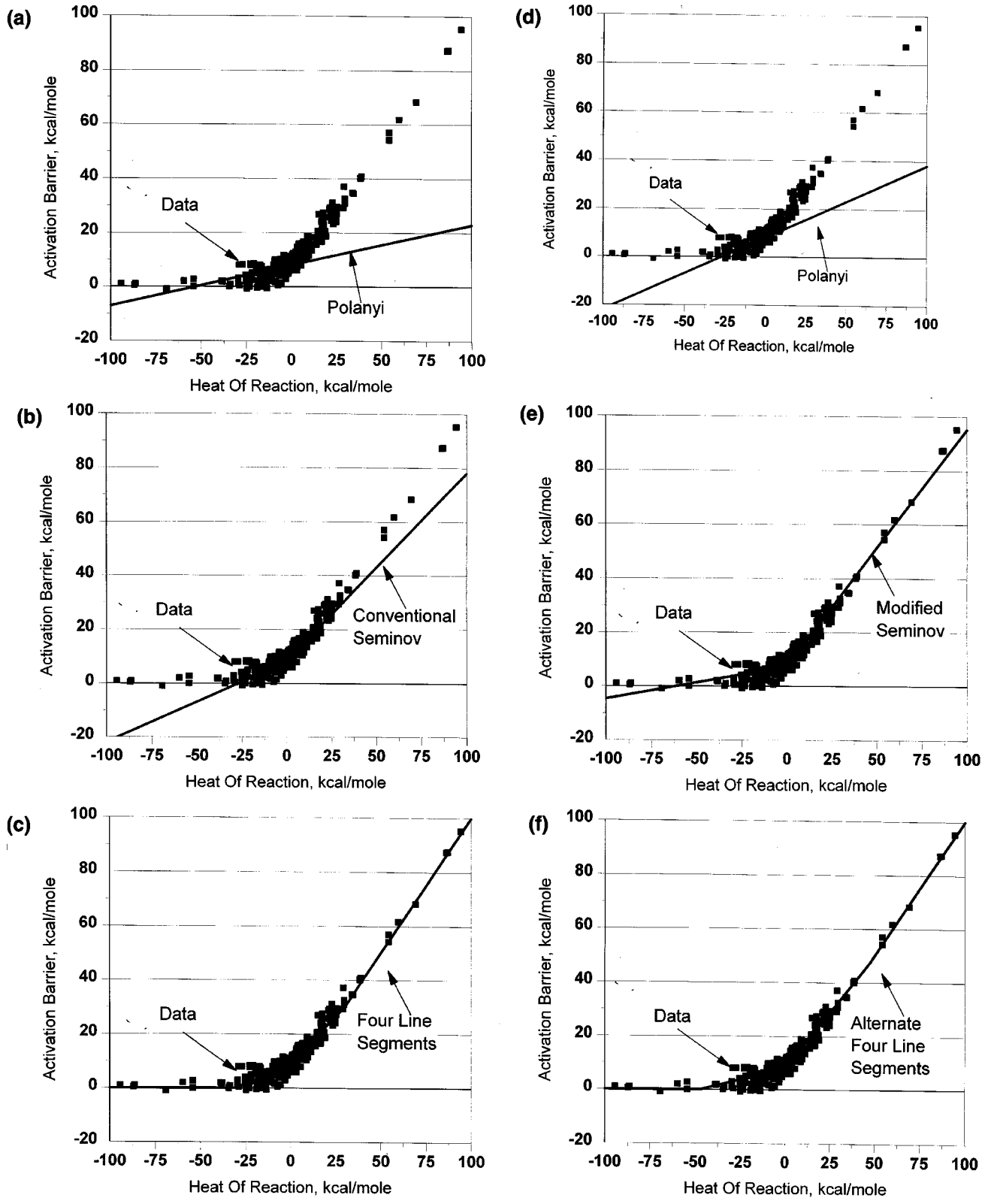

Figure 8. Data in Figure 1 vs. predictions of the Polanyi relationship .

(a) $E_a^0 = 7.95$ kcal/mol, $\gamma_p = 0.15$; (b) $E_a^0 = 8.1$ kcal/mol, $\gamma_p = 0.30$ for $\Delta H_r < 0$, $E_a^0 = 8.1$ kcal/mol, $\gamma_p = 0.70$ for $\Delta H_r > 0$; (c) $E_a^0 = 8.1$ kcal/mol, $\gamma_p = 0.3$ for $\Delta H_r < 0$, $E_a^0 = 8.1$ kcal/mol, $\gamma_p = 0.7$ for $\Delta H_r > 0$; (d) $E_a^0 = 7.3$ kcal/mol, $\gamma_p = 0.12$ for $\Delta H_r < 0$, $E_a^0 = 7.3$ kcal/mol, $\gamma_p = 0.88$ for $\Delta H_r > 0$; (e) $E_a^0 = 9.1$ kcal/mol, $\gamma_p = 0.30$ for $-30 < \Delta H_r < 0$, $E_a^0 = 9.1$ kcal/mol, $\gamma_p = 0.70$ for $30 > \Delta H_r > 0$, $E_a^0 = 0$, $\gamma_p = 0.0$ for $-30 < \Delta H_r < 0$, $E_a^0 = 0$, $\gamma_p = 1.00$ for $30 > \Delta H_r > 0$; (f) $E_a^0 = 8.0$ kcal/mol, $\gamma_p = 0.17$ for $-47 < \Delta H_r < 0$, $E_a^0 = 8.0$ kcal/mol, $\gamma_p = 0.83$ for $47 > \Delta H_r > 0$, $E_a^0 = 0$, $\gamma_p = 0.0$ for $\Delta H_r < -47$, $E_a^0 = 0$, $\gamma_p = 1.00$ for $\Delta H_r > 47$.

Discussion

The preceding results show that our new model fits data much better than any of the previous models. Westley's data were fit to within ± 4 kcal/mol for 142 of the 151 hydrogen transfer reactions in Table 1. The exceptions are given in Table 3. Of the nine exceptions, seven of the experimental activation energies were theoretical estimates or results of kinetic modeling, not actual data. The other two were from actual measurements, but there are multiple data sources for both reactions. Westley chose to use the values in the table, but if he would have chosen data from a different source, he could have listed a value that better agrees with our model. All of these reactions were dropped from the more recent versions of the NIST tables. We believe that our model fits all of the reliable data in Westley to within ± 4 kcal/mol, which is as good as we can hope for with a one-parameter model.

We have also tested many of the previous models on the same data set. Several of the models do reasonably well for a subset of the data. However, ours is the only one-parameter model that fits the entire range of data.

That is not to imply that there are no opportunities to improve the models. Rather, we believe that this is as close as we are going to get by assuming E_a^0 is constant. In the previous literature, Atkinson et al. (1984), Denisov (1999), Cohen et al. (1991), and Broadbelt et al. (1994b) have shown that it is useful to break reactions into groups, and optimize the parameters for each group. There is some opportunity for similar optimizations here. In particular, Atkinson (1984) showed that the activation barrier for removal of a primary hydrogen atom is slightly different from the activation barrier for removal of a secondary hydrogen atom. We have carefully examined Atkinson's results, and find that we can reproduce them with Eq. 10 only if we assume that E_a^0 is slightly different for removal of a primary hydrogen and removal of a secondary hydrogen.

In other work Blowers and Masel (1999c) showed that E_a^0 is substantially different for hydrogen transfer and methyl transfer reactions. Also, Lee and Masel showed (1997) that E_a^0 is slightly different in the gas phase than on a surface due to the proximity effect.

Physically, the model here implies that the activation energy should only depend on the energy to bring the reactants together, the heat of reaction, and bond energies, and not the details of the reaction. However, Figure 1 shows that there is about a ± 4 kcal/mol variation in the activation barrier under conditions where the heat of reaction and bond energies are nearly constant.

Clearly, then, there is more work to be done. Still, at this point, we have an approximation that is much better than anything proposed previously. We can now estimate activation barriers to within ± 4 kcal/mol using readily available information and one parameter that we fit to data. By comparison, Semenov's extension of the Polanyi relationship often gives errors greater than ± 10 kcal/mol. We have an improvement; perhaps not the final improvement, but still an approximation that is much better than anything that had been proposed before.

Conclusions

In this article we present a new engineering approximation for the activation barriers in hydrogen transfer reactions. The new model is based on the results of our quantum mechanical calculations that indicate that barriers in reactions are determined by a balance between Pauli repulsions and bond

Table 4. Errors in Various Approximations to the Activation Barrier for the Data Set in Table 2

Equation	Parameters	RMS error (kcal/mol)	Avg. Error (kcal/mol)	Median Error (kcal/mol)	Max. Error (kcal/mol)	No. of Reactions with Errors with Errors > 4 kcal/mol
Eq. 10	$E_a^0 = 9.7$ kcal/mol	2.63	2.07	1.78	7.2	20
Eq. 10	$E_a^0 = 10$ kcal/mol	2.63	2.08	1.88	7.1	18
$E_a = E_a^0 + \gamma_p \Delta H_r$	$E_a^0 = 7.95$ kcal/mol, $\gamma_p = 0.15$	4.33	2.78	2.18	26.4	85
$E_a = E_a^0 + \gamma_p \Delta H_r$	$E_a^0 = 8.1$ kcal/mol $\gamma_p = 0.30$ for $\Delta H_r < 0$ $E_a^0 = 8.1$ kcal/mol, $\gamma_p = 0.70$ for $\Delta H_r > 0$ (Seminov's approximation)	3.89	2.72	2.11	21.2	94
$E_a = E_a^0 + \gamma_p \Delta H_r$	$E_a^0 = 7.3$ kcal/mol, $\gamma_p = 0.12$ for $\Delta H_r < 0$ $E_a^0 = 7.3$ kcal/mol, $\gamma_p = 0.88$ for $\Delta H_r > 0$	2.89	2.38	2.19	7.3	72
$E_a = E_a^0 + \gamma_p \Delta H_r$	$E_a^0 = 9.1$ kcal/mol, $\gamma_p = 0.30$ for $-30 < \Delta H_r < 0$ $E_a^o = 9.1$ kcal/mol, $\gamma_p = 0.70$ for $30 > \Delta H_r > 0$ $E_a^0 = 0$, $\gamma_p = 0.0$ for $\Delta H_r < -30$ $E_a^0 = 0$, $\gamma_p = 1.00$ for $\Delta H_r > 30$	2.79	2.14	1.79	7.6	60
$E_a = E_a^0 + \gamma_P \Delta H_r$	$E_a^0 = 8.0$ kcal/mol, $\gamma_p = 0.17$ for $-47 < \Delta H_r < 0$ $E_a^0 = 8.0$ kcal/mol, $\gamma_p = 0.83$ for $47 > \Delta H_r > 0$ $E_a^0 = 0$, $\gamma_p = 0.0$ for $\Delta H_r < -47$ $E_a^0 = 0$, $\gamma_p = 1.00$ for $\Delta H_r > 47$	2.52	2.05	1.92	6.4	30
BOC-MP	none	40.6	40.2	41.5	48.1	302 (All have errors of 14.9 kcal/mol or more)
Marcus	$E_a^0 = 10$ kcal/mol	3.57	2.47	1.98	17.5	36

In the rightmost column, a count of the number of reactions (out of 302 total) with errors greater than 4 kcal/mol is given. Both the forward and back reaction are counted as a separate reaction for this count because the Polayni relationship can be accurate for the forward reaction but not the reverse or vice versa.

production. We find that the new model fits the available data very well. Westley presents recommended values for the activation energy for 151 hydrogen transfer reactions. Of the 151 reactions, 142 are within ± 4 kcal/mol of the model. By comparison, Seminov's extension of the Polanyi relationship often gives errors of ± 10 kcal/mol. The new model only has one adjustable parameter, and the same value was used for all 151 reactions. These results show that the new model is a significant improvement over the approximations that are in use today.

Acknowledgment

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