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Energies of Activation. The Paradigm of Hydrogen Abstractions by Radicals

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Abstract: Energies of activation are calculated for hydrogen abstractions by radicals, using bonding and antibonding Morse curves. The model is not parametric. Forty seven reactions are treated, including many involving abstractions from silicon, sulfur, germanium, and tin hydrides. The overall average deviation between experimental and calculated values is less than 1 kcal/mol. For X−H + •Y to give X• + H−Y, the calculation requires the following input data for X−H, H−Y, and X−Y: bond dissociation energy, bond length, and infrared stretching frequency. The model indicates that the properties of the X−Y bond have a major effect on the energy of activation. The importance of repulsive forces is highlighted. Several puzzling patterns of known reactivities are explained satisfactorily. From the rules established, reasonable predictions can be made without actually carrying out the calculation.

In considering the factors that influence the rate of chemical reactions, it appears that we have a better understanding of the entropy term than we have of the energy of activation. While most reactions used in synthesis are of the ion−molecule type, the vast majority of those studied are in solution, where solvent effects have such a major influence that it becomes difficult to separate out of observed energies of activation the effect of solvent from the effect of molecular structure of reactant and product molecules *per se*. In contrast, free radical and Diels−Alder type reactions often exhibit similar energies of activation in the gas phase as in nonpolar solvents. There is a wealth of information on hydrogen abstractions by radicals, and we focused on this class of reaction in an effort to understand the factors that influence energies of activation. Gaps in our understanding are revealed in pondering Table 1, which lists identity hydrogen abstractions studied experimentally, X−H + •X → X• + H−X. Despite a common heat of reaction of $\Delta H = 0$, Arrhenius energies of activation (E_a) differ by at least 13 kcal/mol and their ordering bears no relation to bond dissociation energies, BDE(X−H). It is the aim of this work to identify the major factors controlling energy barriers for hydrogen abstractions. A model is presented that identifies these factors and provides insight into the fundamental, but generally not asked, question of why there is an energy barrier even for very exothermic hydrogen abstractions.

Since the publication of our nonparametric model for calculating energies of activation for hydrogen abstractions,[1] many more reactions have been studied and values of the bond properties required as input to the calculation have been determined more accurately (BDE, bond lengths, etc.). This work examines more recently studied hydrogen abstractions primarily from thiols, silanes, stannanes, and germanes in an effort to understand some puzzling aspects of observed reactivity patterns and because of the importance of these reagents to synthetic applications.

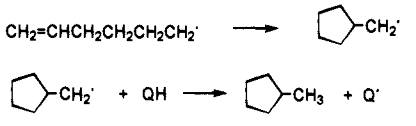
Table 1. Identity Hydrogen Abstractions (Experimental E_a and BDE(X−H) in kcal/mol)

X−H + •X	E_a	BDE(X−H)
$H_3Si{-}H + {}^{\bullet}SiH_3$	>15	91.6
$H_3C{-}H + {}^{\bullet}CH_3$	14.5	104.9
$CH_3CH_2{-}H + {}^{\bullet}CH_2CH_3$	13.5	100.6
$H{-}H + {}^{\bullet}H$	9.6	104.2
$RCH_2S{-}H + {}^{\bullet}SCH_2R$	5.2	87.8
$Cl{-}H + {}^{\bullet}Cl$	4.8	103.2
$(CH_3)_3CO{-}H + {}^{\bullet}OC(CH_3)_3$	2.6	105.1

The majority of radical reactions of interest to synthetic chemists are chain processes, particularly reductions of a variety of functional groups and formation of carbon−carbon bonds (intermolecularly or intramolecularly).[2] Reducing agents QH (such as stannanes,[3] silanes,[4] and thiols[5]) are used in both types of reactions, reactions 1−4. The value of the rate constant for the reduction of an alkyl radical, reaction 2, is crucial in selecting the appropriate reducing agent, at the proper concentration, to maximize the yield of the desired product. The ratio of cyclized to uncyclized product depends on the relative rates of reactions 2 and 3. The range of rate constants for reaction 2 is very wide: 7.2 × 10^2 M^{-1} s^{-1} for abstraction from Et$_3$SiH to 1.4 × 10^8 from PhSH at 25 °C.[6] Thiols are excellent hydrogen donors for alkyl radicals, and glutathione is considered a major

$$CH_2{=}CHCH_2CH_2CH_2CH_2Br + Q^{\bullet} \longrightarrow CH_2{=}CHCH_2CH_2CH_2CH_2^{\bullet} + QBr \quad (1)$$

$$CH_2{=}CHCH_2CH_2CH_2CH_2^{\bullet} + QH \longrightarrow CH_2{=}CHCH_2CH_2CH_2CH_3 + Q^{\bullet} \quad (2)$$



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participant in the "repair reaction" of carbon radicals in biological systems.[7] The reduction of some types of carbon radicals can be highly diasterioselective.[8]

The reactivity patterns of some of these hydrogen donors are not easy to rationalize. Hydrogen abstraction by methyl radicals from silane proceeds with an energy of activation about 3 kcal/mol higher than abstraction from hydrogen sulfide in the gas phase. However, the bond dissociation energies of the two are essentially the same: BDE(HS−H) = 91.2 kcal/mol and BDE(H_3Si−H) = 91.6. An analogous situation exists for hydrogen abstraction from tri-*n*-butylstannane compared to thiophenol, in the liquid phase. Even though the R_3Sn−H bond is weaker than the PhS−H bond by at least 3 kcal/mol, primary alkyl radicals abstract from the stannane with an E_a that is greater by 2 kcal/mol.

We examined these interesting results, where hydrogen abstractions of comparable exothermicities proceed with quite different E_a. Focusing on the comparison of H_2S to SiH_4, the explanation often given, explicitly or implicitly, for this type of phenomenon is the polar effect, i.e., structures such as $HS^-\text{- - -}H^\bullet\text{- - -}{}^+CH_3$ stabilize the transition state (TS) and cause lower energies of activation than otherwise would have been the case.[7,9] While the polar effect explanation may appear reasonable and is certainly convenient, we are not convinced of its validity in this case for the following reasons:

In a reaction $X{-}H + Y^\bullet \rightarrow X^\bullet + H{-}Y$, the polar effect in the TS can be written as either $X^-\text{- - -}H^\bullet\text{- - -}Y^+$ or $X^+\text{- - -}H^\bullet\text{- - -}Y^-$. Which one is appropriate should depend on the relative electronegativities of X and Y. In the case of hydrogen abstraction from sulfur by methyl radicals, the electronegativities of sulfur and carbon are identical, 2.5 in Pauling's scale.[10] Therefore, polar effects would not be expected to make significant contributions to the TS. Other electronegativity scales or criteria also do not provide unequivocal guidance for the direction of the dipole, if any. Group electronegativities placed on Pauling's scale have $-CH_3$ at 2.30 and −SH at 2.25.[11] The ionization potential of $^\bullet CH_3$ is 9.84 eV, and those of $CH_3S^\bullet$, $CH_3CH_2S^\bullet$, and $(CH_3)_3CS^\bullet$ are 8.1, 8.2, and 9.6, respectively;[5] this criterion would require the positive end of the dipole on sulfur at the TS. The sum of ionization potential plus electron affinity is proportional to electronegativity;[10] the sum is 9.96 eV for $CH_3S^\bullet$ and 9.92 for $H_3C^\bullet$; this criterion offers little guidance. Also, BDE(CH_3−SH) = 74.7 kcal/mol is near the geometric mean of BDE(H_3C−CH_3) and BDE(HS−SH), $(89.9 \times 64.5)^{1/2} = 76.1$, indicating small electronegativity difference.[10] Finally, the C−S stretching vibration is a weak absorbance in the infrared, consistent with a small dipole.

Considerations of relative electronegativities of $^\bullet SH$ and $^\bullet CH_3$ are not only inconclusive: they are half the picture. In comparing relative reactivities of H-abstraction by carbon radicals from sulfur and from silicon, consistency requires that polar effects be considered for both reactions. In considering polar effects in the TS for hydrogen abstraction from silicon, there is no ambiguity. The electronegativity of silicon, 1.8 in Pauling's scale, is considerably lower than that of carbon. BDE(H_3C−SiH_3) = 89.2 kcal/mol is greater than the geometric mean of BDE(H_3C−CH_3) and BDE(H_3Si−SiH_3), $(89.9 \times 76.7)^{1/2} = 83.0$, as expected from the electronegativity difference. The C−Si stretching is intense in the IR. Polar structures such as $H_3Si^+\text{- - -}H^\bullet\text{- - -}{}^-CH_3$ are reasonable and should be of greater importance in stabilizing the TS compared to polar structures for abstraction from H_2S. Therefore, in this case, *a priori* consistent application of the qualitative polar effect approach would lead to the expectation that H-abstraction by methyl radicals from silane would be subject to greater polar effects and lower E_a. The opposite is observed. How can these effects be understood?

We believe that a better understanding of such reactivities is obtained from a more quantitative approach. Energies of activation in hydrogen abstractions have been treated by means of the following model.[1a] For the reaction $X{-}H + Y^\bullet \rightarrow X^\bullet + H{-}Y$, the TS is described by four canonical forms:

$$X{\uparrow}{\downarrow}H\cdots Y{\uparrow} \qquad {\uparrow}X\cdots H{\downarrow}{\uparrow}Y \qquad X{\uparrow}\cdots H{\downarrow}\cdots Y{\uparrow} \qquad [X\cdots H{-}{-}Y]^\bullet$$

I **II** **III** **IV**

X and Y are atoms or groups. In the TS of this three-electron system, residual bonding in the breaking X−H bond is assumed to be equal to bonding in the forming H−Y bond for maximum resonance; i.e., **I** and **II** are assumed to be of equal energy. **III** gives rise to triplet repulsion (antibonding) between X and Y, since the three electron spins must be either up-down-up or down-up-down, placing parallel spins on X and Y. The minimum energy path is assumed to be linear, and the total energy is given by the average of the bonding energies of **I**, ^1E(X−H), and **II**, ^1E(H−Y), plus the triplet repulsion between X and Y of **III**, ^3E, plus the resonance energy for delocalization of one electron over three atoms in **IV**, E_R.

$$E_{tot} = 0.5[{}^1E(X{-}H) + {}^1E(H{-}Y)] + {}^3E(X{-}Y) + E_R \quad (5)$$

Bonding at different bond extensions is calculated by the Morse equation and antibonding by a variant of the Sato equation.[1]

$$^1E = D_e[\exp(-2\beta x) - 2\exp(-\beta x)] \quad (6)$$

$$^3E = 0.45D_e[\exp(-2\beta x) + 2\exp(-\beta_x)] \quad (7)$$

D_e = BDE + $0.00143\omega_e$ kcal/mol; $x = r - r_e$ Å, where r_e is the equilibrium and r the stretched bond length. The equilibrium stretching frequency is $\omega_e = \nu + 0.00143\nu^2/(\text{BDE})$ cm^{-1}, where ν is the infrared stretching frequency of the bond.[12] The "spectroscopic constant" is given by eq 8, where μ is the reduced

$$\beta = (2\pi^2 c\mu\omega_e{}^2/hD_e)^{1/2} = (6.51 \times 10^{-3})\omega_e[\mu/(D_e)]^{1/2} \quad (8)$$

mass in amu. of the directly bonded atoms. E_R was set to −10.6 kcal/mol as an estimate of the delocalization energy of one electron over three atoms, approximately the difference in BDE of a primary C−H bond in propane and in propylene.

For a given distance r(X−H) the value of r(H−Y) is found that satisfies the equibonding criterion, ^1E(X−H) = ^1E(H−Y). Since r(X−H) + r(H−Y) = r(X−Y), ^3E(X−Y) can be calculated. A small correction is made for zero point energy effects. The X−H bond length is increased incrementally, and E_{tot} is calculated by eq 5. This produces a series of possible transition states from very "tight" to very "loose". The procedure is equivalent to sliding Morse curves for X−H and H−Y past each other (subject to the equibonding criterion) and calculating the total energy by eq 5 at their intersections. This

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is not a reaction coordinate. The energy change as a function of r(X−H) is an approximation to a cut through the col of the potential energy surface and gives the shape of the "saddle" or "pass" between the "valleys" of reactants and products. The energy falls to a minimum and then increases again. The most stable combination of r(X−H) and r(H−Y), the minimum, is the TS. There are no empirical parameters to be changed for each X or Y. The input data are those required for the construction of Morse curves for X−H, H−Y, and X−Y: BDE r_e, ν, and masses of the bonded atoms.

This approach proved to be successful with a large variety of more than 80 hydrogen abstractions. Most of the gas phase data available at the time pertained to X and Y from the first two rows of the periodic table (H, C, O, N) and to the halogens.[1] In an evaluation of the method by others with 87 abstractions, calculated values of the energy of activation were reported to agree with experimental E_a with an average discrepancy of 1.46 kcal/mol.[13] This was quite good, considering that some of the BDE values used at the time are now known to have had uncertainties of about 2 kcal/mol; also, absolute uncertainties in experimental E_a are seldom less than 1 kcal/mol, even though reported precision may be smaller.

It is remarkable that the calculation was successful despite its minimalist approach: Complex reacting molecules are reduced to a three-electron system. Morse curves are not always accurate.[12] The Sato equation is a rough approximation of antibonding. Tunneling is neglected. The calculation gives TS distances somewhat shorter than those obtained from quantum mechanical estimates.[14] Applied to abstractions of halogen atoms, the calculation invariably produces low values. Also, the approximation that delocalization of one electron over three atoms provides 10.6 kcal/mol of resonance stabilization, independent of the nature of X and Y, cannot be exactly valid in all cases. Over the last 20 years, the calculation has been used with many hydrogen abstractions both in the gas and liquid phase.[15]

For abstraction by methyl radicals from H_2S, the previous version of the method[1a] results in a calculated energy of activation, denoted by E^*, which is 3 kcal/mol lower than for abstraction from SiH_4, consistent with the difference in the experimental values of E_a. However, the absolute values of E^* are both too high by about 2 kcal/mol.

Results

Since the original calculation was published, measurements became available involving elements of the third and higher rows, *e.g.*, X or Y = S, Si, Sn, Ge, etc. It became evident that, with higher row X or Y, calculated E^* values are consistently greater than measured values of E_a. An examination of tables of the values of "overlap integrals"[16] for p orbitals of elements of the third and higher rows shows that they reach a maximum at longer distances and remain higher at TS distances for hydrogen abstractions than those involving first and second row elements.[17] This trend can be taken into account by increasing the value of the resonance stabilization term in our calculation. For hydrogen abstractions involving X or Y with atomic numbers greater than 11 (fluorine), the odd electron is delocalized over a larger area and a resonance term of $E_R = -12$ kcal/mol is more appropriate for estimating experimental values of E_a. We modified the original method to automatically change E_R from −10.6 to −12.0 kcal/mol, when either X or Y is beyond fluorine.[18]

With the less reliable values of bond properties of 20 years ago the calculation appeared less accurate than it does today, when we apply it to the previously[1] treated reactions. Therefore, an approximation made for the sake of simplicity by using observed BDE and ν in calculating β is no longer justified; "equilibrium" values are now used as shown in eq 8. This refinement usually affects E^* by 0.3 kcal/mol or less.

The calculation, with the modifications described above, designated ESTAR, version 4, is now applied to a series of hydrogen abstractions by radicals from sulfur, silicon, tin, and germanium compounds, and the results are shown in Table 2 along with experimental values of the Arrhenius energy of

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Table 2. Experimental[a] Arrhenius Energies of Activation and Calculated E^* for Hydrogen Abstractions (kcal/mol)

reaction	E_a	E^*
$HS{-}H + {}^{\bullet}H$	2.7, 2.8, 1.7, 1.7, 0.7, 4.9[b]	4.0
$HS{-}H + {}^{\bullet}CH_3$	2.6, 2.0, 1.8, 2.9, 4.1,[c] 4.1[d]	4.7
$HS{-}H + {}^{\bullet}SH$		7.4
$CH_3S{-}H + {}^{\bullet}H$	2.6[e]	2.0
$(CH_3)_2CHS{-}H + {}^{\bullet}H$	3.2[e]	2.8
$CH_3S{-}H + {}^{\bullet}CH_3$	4.1, 3.1, 4.1, 4.1,[f] 4.1[d]	3.6
$CH_3S{-}H + {}^{\bullet}CH_2CH_3$		4.7
$CH_3S{-}H + {}^{\bullet}CH(CH_3)_2$		5.0
$CH_3S{-}H + {}^{\bullet}C(CH_3)_3$		5.6
$CH_3CH_2S{-}H + {}^{\bullet}CH_2CH_3$		4.6
$PhS{-}H + {}^{\bullet}CH_3$		1.0
$PhS + {}^{\bullet}CH_2CH_3$	1.7,[g,h] 1.8[g,h]	2.2
$PhS{-}H + {}^{\bullet}CH(CH_3)_2$	1.7[g,h]	2.0
$PhS{-}H + {}^{\bullet}C(CH_3)_3$	1.5,[g,h] 1.7[g,h]	2.7
$PhS{-}H + {}^{\bullet}CH_2Ph$	3.8[g,h]	4.3
$CH_3S{-}H + {}^{\bullet}SCH_3$		5.8
$CH_3CH_2S{-}H + {}^{\bullet}SCH_2CH_3$	5.2[g,i]	5.1
$PhS{-}H + {}^{\bullet}SCH_2CH_3$	4.2[g,i]	3.8
$H_3Si{-}H + {}^{\bullet}CH_3$	7.0, 6.9, 6.2, 7.5, 7.0,[c] 7.0[j]	7.3
$H_3Si{-}H + {}^{\bullet}CH_2CH_3$	7.3, 8.9[k]	8.1
$(CH_3)_3Si{-}H + {}^{\bullet}CH_3$	7.0, 7.8, 8.3, 7.8,[c] 7.2[j]	8.3
$(CH_3)_3Si{-}H + {}^{\bullet}CH_2CH_3$	8.0[g,l]	8.8
$(CH_3)_3Si{-}H + {}^{\bullet}CH(CH_3)_2$		9.1
$(CH_3)_3Si{-}H + {}^{\bullet}OCH_3$	2.1,[m] 2.6,[g,n] 2.8[g,o]	2.5
$(CH_3)_3C{-}H + {}^{\bullet}CH_3$	7.9, 12.9, 9.5, 7.9[c]	9.0
$(CH_3)_3C{-}H + {}^{\bullet}OCH_3$	4.1, 4.8,[p] 4.3, 5.7[q]	5.5
$((CH_3)_3Si)_3Si{-}H + {}^{\bullet}CH_2CH_3$	4.5[g,r]	5.4
$H_3Si{-}H + {}^{\bullet}SiH_3$	>15[s]	17.1
$CH_3{-}H + {}^{\bullet}CH_3$	14.1, 14.5, 14.1, 14.0, 14.5[j]	14.5
$(CH_3)_3Sn{-}H + {}^{\bullet}CH_3$	3.2[g,t]	3.2
$(CH_3)_3Sn{-}H + {}^{\bullet}CH_2CH_3$	3.7,[g,t] 3.8,[g,t] 2.7[g,u]	3.9
$(CH_3)_3Sn{-}H + {}^{\bullet}CH_2Ph$	5.6[g]	7.3
$(CH_3)_3Sn{-}H + {}^{\bullet}C_6H_5$	1.7[g,v]	1.7
$(CH_3)_3Ge{-}H + {}^{\bullet}CH_2CH_3$	4.7[g,w]	5.6
$(CH_3)_3CO{-}H + {}^{\bullet}OC(CH_3)_3$	2.6[g,x]	2.6
$H{-}H + {}^{\bullet}H$	9.8,[y] 9.6[y]	9.8[y]
$CH_3CH_2{-}H + {}^{\bullet}CH_2CH_3$	14.1,[z] 12.6[aa]	13.8
$(CH_3)_3C{-}H + {}^{\bullet}CH_3$	7.9, 12.9, 9.5, 7.9[c]	9.0
$Cl{-}H + {}^{\bullet}Cl$	6.6, 5.4,[bb] 2.6[cc]	3.9
$H{-}H + {}^{\bullet}Br$	18.3, 19.2, 19.7, 19.2, 19.7	19.3
$NH_2{-}H + {}^{\bullet}CH_3$	11.1, 9.8, 10.0, 10.2[c]	10.1
$CH_3COCH_2{-}H + {}^{\bullet}CH_3$	9.6, 9.8, 9.2, 9.6, 9.5, 9.7[c]	9.8
$CH_3COCH_2{-}H + {}^{\bullet}H$	6.4	5.6
$CH_3CO{-}H + {}^{\bullet}CH_3$	6.2, 6.8, 7.9, 7.2, 8.2	6.2
$CH_3CO{-}H + {}^{\bullet}H$	3.3	3.1
$CH_3{-}H + {}^{\bullet}OOH$	18.6[dd]	18.3
$CH_3CH_2{-}H + {}^{\bullet}OOCH_3$	14.9[ee]	15.2

[a] Gas phase from ref 19, unless otherwise indicated. Generally in chronological order, more recent last. [b] Reference 20. [c] Evaluated, ref 19. [d] Recommended, ref 21. [e] Reference 22. [f] Critical review, ref 23. [g] Liquid phase. [h] Reference 24. [i] Reference 25. [j] Recommended, ref 26. [k] Reference 27. [l] Triethylsilane and $PhCMe_2CH_2^{\bullet}$, ref 28. [m] *tert*-Butoxyl radicals, ref 29. [n] Triethylsilane and *tert*-butoxyl radicals, ref 30a. [o] Triethylsilane and *tert*-butoxyl radicals, ref 30b. [p] *tert*-Butoxyl radicals. [q] *tert*-Butoxyl radicals, ref 31. [r] Abstraction by hex-5-enyl radical, ref 32. [s] Reference 33. [t] Ethyl and *tert*-butyl radical and tri-*n*-butylstannane, ref 34a. [u] Neopentyl radical, ref 34b. [v] Tri-*n*-butylstannane, ref 34b. [w] Tri-*n*-butylgermane, ref 35. [x] Reference 36. [y] "Exact" *ab initio* classical barrier at 0 K, ref 37. E^* value of classical barrier using BDE values also at 0 K. [z] Reference 38. [aa] Reference 39. [bb] Reference 40. [cc] Reference 41. [dd] Reference 42. [ee] Reference 43.

activation, E_a, when available. Reactions in which polar effects in the TS would be expected to be important are also treated. Identity hydrogen transfers address the general question of radical reactivity, unencumbered by enthalpic changes, and X−Y dipoles. Not included in Table 2 are some reactions involving complex silane derivatives (e.g., $(MeS)_3SiH$, $(Me_3Si)_3SiMe_2H$, etc.) and abstractions by perfluoro-*n*-alkyl radicals, acyl radicals, etc., because reliable input data are not available and could not be estimated with a fair degree of confidence from closely related compounds.

The results of Table 2 demonstrate excellent overall agreement between experimental and calculated energies of activation. For all entries, the average deviation between each calculated E^* and the average corresponding experimental E_a is 0.6 kcal/mol. The largest such deviation is 1.8 kcal/mol for abstraction by methyl radicals from H_2S; nevertheless, E^* differs by only 0.6 kcal/mol from the recommended E_a for this reaction. By comparison, experimental values also differ overall from their respective averages by 0.6 kcal/mol, when three or more values are available in Table 2. In the text below all E_a and E^* values are in kcal/mol.

Several gas phase measurements exist for hydrogen abstraction from H_2S by $H^{\bullet}$, and Table 2 shows that the calculated E^* is within the range of reported values of E_a. Abstractions by $H^{\bullet}$ from methanethiol and isopropyl thioalcohol are also calculated well, within 0.6 and 0.4, respectively. For abstraction from H_2S by methyl radicals, E^* is 0.6 greater than the recommended value of E_a. Such deviations should be judged in the context of the expected uncertainties in experimental values of E_a and of uncertainties in the input data. For example, an uncertainty of 1.0 kcal/mol in the heat of formation $\Delta H_f(HS^{\bullet})$ leads to BDE uncertainties that result in ±0.6 in E^*.

For $HS{-}H + {}^{\bullet}SH$ we obtain $E^* = 7.4$; there is only an *ab initio* estimate of 5.2 kcal/mol.[25]

For the gas phase H-abstraction by methyl radicals from methanethiol, E^* is within the range of experimental values. For abstraction by ethyl radicals from ethanethiol, $E^* = 4.6$. There exists one liquid phase value for the related abstraction by primary alkyl radicals from *tert*-butyl thioalcohol, $E_a = 2.0$,[6] but accurate data are not available for calculating E^* for this reaction. For abstractions from alkyl thioalcohols by primary, secondary, and tertiary alkyl radicals, E_a is not available; however, it has been noted that these reactions have similar rates, which has been thought surprising in view of the substantially different exothermicities.[5] E^* for abstractions from methanethiol is not very sensitive to the nature of the alkyl radical, consistent with the rate measurements.

Liquid phase values of E_a exist for abstraction from thiophenol by primary, secondary, and tertiary alkyl and benzyl radicals. Agreement of the calculated values is satisfactory in all cases. E_a is not very sensitive to the nature of the alkyl radical, and the E^* values duplicate this behavior, showing a spread of only 0.5.

Liquid phase values exist for abstraction from hexanethiol by octylthiyl radicals, essentially an identity reaction with $E_a = 5.2 \pm 0.4$; $E^* = 5.1$ for $EtS{-}H + {}^{\bullet}SEt$. Abstraction by ${}^{\bullet}SEt$ from thiophenol is calculated to proceed with $E^* = 3.8$, compared to a liquid phase value of $E_a = 4.2 \pm 0.3$ for the equivalent abstraction by octylthiyl radicals. Agreement is excellent in both cases.

For abstractions from silane, there is good agreement between calculated and measured values. For abstraction by methyl radicals in the gas phase, E_a values range from 6.2 to 7.5; $E^* = 7.3$. Gas phase abstraction by ethyl radicals is also treated satisfactorily, with E^* falling between the two reported values. Gas phase abstraction by methyl radicals from trimethylsilane is also in good agreement, with E^* matching the highest of the five available E_a values. One liquid phase value exists for abstraction from triethylsilane by primary alkyl (neophyl) radicals, $E_a = 8.0 \pm 0.9$; for the similar reaction between ethyl radicals and trimethylsilane, $E^* = 8.8$.

In comparing abstractions by methyl radicals from H_2S and SiH_4, E^* is lower with H_2S by 2.6 kcal/mol, even though ΔH

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(43) Mims, C. A.; Mauti, R.; Dean, A. M.; Rose, K. D. *J. Phys. Chem.* **1994**, *98*, 13357−13372.

is essentially the same. The recommended E_a values differ by 2.9 kcal/mol.

For abstraction by methoxyl radicals from trimethylsilane, we calculate $E^* = 2.5$, a value between the one gas phase measurement of $E_a = 2.1$ and liquid phase measurements of 2.6 and 2.8 for abstraction by *tert*-butoxyl from trialkylsilane. Gas phase values exist for abstraction by methoxyl radical from isobutane ($E_a = 4-5$); a gas phase value for the similar abstraction by *tert*-butoxyl radical is $E_a = 5.7$. $E^* = 5.5$ for abstraction by methoxyl radical. By comparison, for the equally exothermic H-abstraction by methyl radicals, $E^* = 9.0$, which also is in the range of reported experimental values.

Isotopic studies have shown that silyl radicals do not give detectable products of hydrogen abstraction from silane,[33,44] while the equivalent identity reaction with methyl radicals and methane is well-known, $E_a = 14.5$. Instead of the thermoneutral reaction, displacement is the preferred path, $SiH_4 + H_3Si^\bullet \rightarrow H_3SiSiH_3 + H^\bullet$, despite a ΔH of 15 kcal/mol. E^* for the identity hydrogen abstraction is 17.1; evidently hydrogen abstraction is slower than the displacement reaction, even though abstraction is 15 kcal/mol more exothermic.

"Exact" quantum mechanical calculations yield a "classical barrier" height of 9.6 at 0 K for the $H_2 + {}^\bullet H$ exchange. This benchmark for calculations is also treated satisfactorily, $E^* = 9.8$.

Abstraction from tris(trimethylsilyl)silane by primary alkyl radicals is also treated well, despite some uncertainty in the BDE values (see Data section). $E_a = 4.5 \pm 0.9$ in the liquid phase; $E^* = 5.4$.

The calculation also is successful in describing H-abstraction from trialkylstannanes by carbon radicals. $E^* = 3.2$ for methyl radicals, while the liquid phase E_a value is 3.2 ± 0.3. $E^* = 3.9$ for abstraction by ethyl radicals, while liquid phase $E_a = 3.8 \pm 0.6$ for abstraction by ethyl radicals and 3.7 ± 0.4 for abstraction by *n*-butyl radicals. $E_a = 1.7 \pm 0.3$ has been reported for abstraction by phenyl radicals,[34c] but there were some complications caused by possible concurrent abstraction by benzoyloxyl radicals; we obtain $E^* = 1.7$. For abstraction by benzyl radicals, E^* is 1.7 kcal/mol greater than the one available liquid phase value of E_a. For trialkylgermane and primary alkyl radicals, E^* is 0.9 kcal/mol higher than the single available value of E_a. Such agreement with stannanes and germanes is surprising, since the available BDE values for these carbon to metal bonds have uncertainties of 3−4 kcal/mol.

Table 2 includes five entries for species for which BDE values have been revised substantially after publication of the previous version of this calculation. Using a forerunner of the present model,[1b] we found that much too low values of E^* were calculated with the BDE(X−H) in common use at the time (values in parentheses) for abstractions from ammonia (103 kcal/mol), from acetone (92.0), from acetaldehyde (77.0),[1a] etc. Therefore, we ventured to propose higher values for all these bonds. With the higher current values, E^* now is consistent with experimental E_a values involving these bonds.

Discussion

Why is there an energy of activation, even for very exothermic hydrogen abstractions? While this question is not asked often, the explanation occasionally given is that bond making lags behind bond breaking in the TS. Accurate *ab initio* calculations for the $H_2 + H^\bullet$ exchange have shown that the TS is symmetrical; the energy lost in stretching one bond is exactly the same as that gained by making the other. This does not mean that total bonding energy remains unchanged, because the starting state must change its geometry in order for the system to attain resonance **I** ↔ **II**. A very "loose" TS (at the extreme, three separated atoms) will have very little residual bonding; the reverse will be true with a "tight" TS. Our model assumes that the energy of the isolated bond being broken is equal to the energy of the bond being made in all cases, independent of the ΔH.

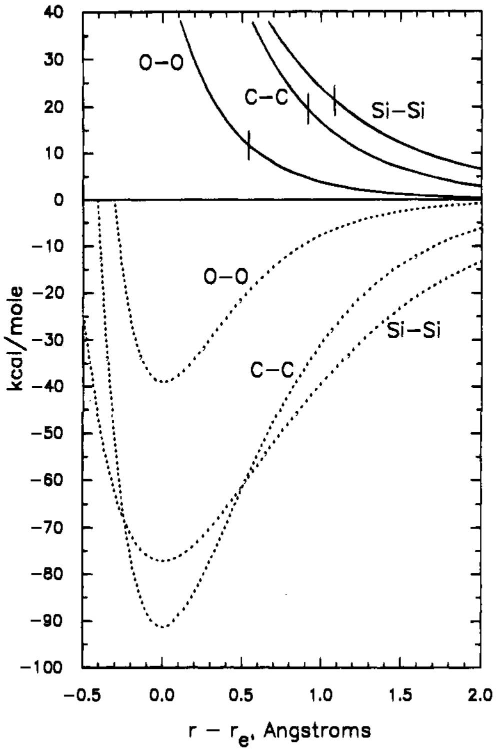

Figure 1. Antibonding energy (solid lines) *vs* distance for $(CH_3)_3CO-OC(CH_3)_3$, H_3C-CH_3, and $H_3Si-SiH_3$. The bonding Morse curves (dashed lines) are also shown as a familiar reference. The TS is shown by the short vertical line on the antibonding curves. The curves have been shifted so that their respective bond lengths (r_e) coincide, for easier visual comparison.

The enthalpy of reaction and X−Y dipoles (polar effects) can be removed as factors by examining the order of experimental E_a for the thermoneutral identity hydrogen exchanges of Table 1, as described in detail in Table 2. For $X-H + {}^\bullet X$, the lack of correlation between the ordering of E_a and BDE(X−H) may appear surprising, but the BDE factor would be expected to cancel out if the isolated bond breaking and making parts contributing to the total energy are equal at the TS, as we have postulated. The same conclusion was also reached in a recent high-level theoretical study of identity S_N2 exchanges in the gas phase, $X^- + CH_3X \rightarrow XCH_3 + X^-$.[45] The ordering of calculated X−X antibonding (${}^3E$, kcal/mol) in the TS of the radical identity exchanges duplicates the ordering of E_a: X = silyl (21.3) > methyl (19.5) > ethyl (19.0) > H (16.4) > thiyl (13.8) > Cl (12.8) > alkoxyl (11.4). Energies of activation are always lower than ${}^3E$, indicating that partial bonding at the TS plus the resonance stabilization of delocalizing the odd electron offset some of the antibonding between the terminal atoms of the three-body system. Our model indicates that the energy of activation is needed to overcome this repulsion.

Figure 1 compares antibonding in three identity reactions: $H_3Si-H + {}^\bullet SiH_3$, $CH_3-H + {}^\bullet CH_3$, and $(CH_3)_3CO-H + {}^\bullet OC(CH_3)_3$, with $E^* = 17.1$, 14.5, and 2.6, respectively. The

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[44] Pollock, T. L.; Sandhu, H. S.; Jordan, A.; Strausz, O. P. *J. Am. Chem. Soc.* **1973**, *95*, 1017−1024.

[45] At the G2(+) level of theory: Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1995**, *117*, 2024−2032.

antibonding species X−Y are $H_3Si{-}SiH_3$, $CH_3{-}CH_3$, and $(CH_3)_3CO{-}OC(CH_3)_3$, and their potential energy curves are drawn with r_e shifted to a common minimum for easier visual comparison; the bonding curves (not used in the calculation) are shown only as a more familiar reference. Compared to ethane, the low antibonding in the peroxide is due to its low BDE. The high E^* for the silyl identity exchange is not caused by a particularly high BDE(X−Y) in disilane, compare BDE($H_3C{-}CH_3$) = 89.9 and BDE($H_3Si{-}SiH_3$) = 76.6 kcal/mol. The silyl identity reaction has to overcome high antibonding (21 kcal/mol at the TS, the highest of the reactions of Table 2) because of a wide X−Y Morse curve (antibonding persisting at long distances). This is caused primarily by the low stretching frequency of 432 cm^{-1} in $H_3Si{-}SiH_3$, compared to 995 cm^{-1} for $H_3C{-}CH_3$. The major factor for the much lower frequency (and the wider Morse curve) is the greater mass of silicon. In the simplest terms, the high E_a here is a mass effect on the shape of the antibonding curve of X−Y, causing high antibonding at long distances between Si and Si, despite a lower BDE(X−Y) compared to the methane/methyl exchange. The identity reactions $H_3Ge{-}H + {}^{\bullet}GeH_3$ and $H_3Sn{-}H + {}^{\bullet}SnH_3$ have not been reported, and we expect that they would have high E_a because of the low stretching frequencies of 268 cm^{-1} in Ge−Ge and 192 cm^{-1} in Sn−Sn. Mass and size effects of this kind are not usually considered in trying to rationalize radical reactivities in hydrogen abstractions. Our model reproduces the known facts about the all the symmetrical H-exchange reactions available, spanning a range of 15 kcal/mol in energies of activation.

In comparing abstractions by methyl radicals from SiH_4 and from H_2S, reactions of about equal ΔH, the principal reason for the lower E_a with H_2S is the weaker BDE(X−Y): BDE($HS{-}CH_3$) = 74.7 kcal/mol and BDE($H_3Si{-}CH_3$) = 89.2. The X−Y values of r_e, ν, and μ are similar (see Data section). Postulating polar effects for abstraction by carbon radicals from sulfur is not justified by the calculation. The concept of "polarity reversal" does not appear necessary to explain the elegant method of using thiols as catalysts for the effective reduction of alkyl halides by trialkylsilanes;[9] unfortunately data on S−Si bonds is not available for calculating E^* for abstraction by thiyl radicals from silanes and thus modeling all three reactions involved.

In comparing abstractions by primary alkyl radicals from thiophenol and from trialkylstannane, ΔH favors the stannane by at least 3 kcal/mol. E^* is lower by 1.6 for abstraction from thiophenol, consistent with the experimental $\Delta E_a = 2.0$. Here BDE(X−Y) is about the same: BDE($PhS{-}CH_2CH_3$) = 64.7 kcal/mol, BDE($R_3Sn{-}CH_2CH_3$) = 63.1. However, antibonding at the TS is 12.9 and 13.5, respectively. The higher repulsion with the tin demonstrates the effect of the X−Y bond length and frequency, in a pattern that we found common to all H-abstractions. All else being equal, the longer r_e produces higher antibonding at the TS: $r_e(PhS{-}CH_2CH_3) = 1.817$ Å, $r_e(R_3Sn{-}CH_2CH_3) = 2.148$ Å. Also, all else being equal, the lower ν produces the higher antibonding: $\nu(PhS{-}CH_2CH_3) = 655$ cm^{-1}, $\nu(R_3Sn{-}CH_2CH_3) = 504$.

It is evident that our model is equally successful, whether or not polar effects are expected at the TS. A classic demonstration of a polar effect is a comparison of H-abstraction from isobutane by methyl and by alkoxyl radicals. The reaction ΔH is about the same, but E_a for alkoxyl is 4.8 kcal/mol lower; we obtain $\Delta E^* = 4.5$, in excellent agreement. The polar effect is even more intensely demonstrated in comparing abstractions by methyl and by alkoxyl radicals from trialkylsilanes. Despite equal ΔH, E_a for alkoxyl is 5.1 kcal/mol lower; we obtain $\Delta E^* = 5.8$. The model has no provision specifically for calculating polar effects at the TS, i.e., the electronegativities of X and Y are not required as input data. The success of the method in describing polar effects accurately, when they exist, is due to the fact that electronegativity differences between X and Y, if any, are reflected in the X−Y bond properties: bond strength, length, and stretching frequency. The contribution of any dipolar structures at the TS is not neglected but is built into the X−Y bond data that must be input to the calculation. By its nature, our model incorporates the qualitative concept of polar effects, as originally envisioned for radical additions to alkenes by Mayo and Walling,[46] and places it on a quantitative and unequivocal basis.

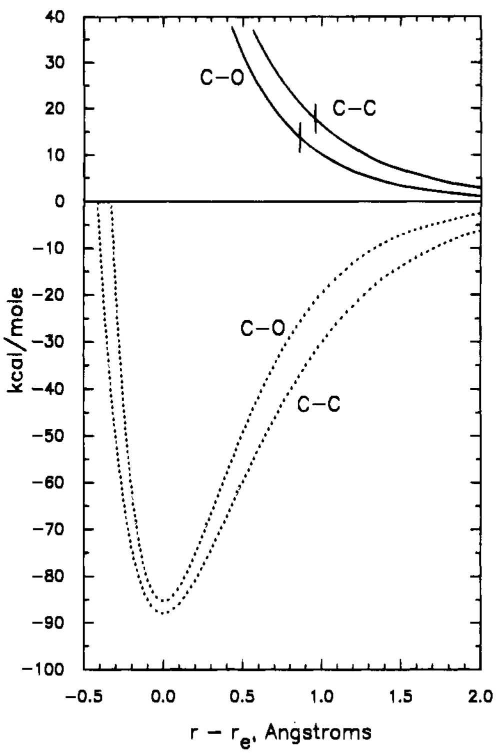

Figure 2. Antibonding energy (solid lines) *vs* distance for $(CH_3)_3C{-}CH_3$ and $(CH_3)_3C{-}OCH_3$. The bonding Morse curves (dashed lines) are also shown as a familiar reference. The TS is shown by the short vertical line on the antibonding curves. The curves have been shifted so that their respective bond lengths (r_e) coincide, for easier visual comparison.

Figure 2 illustrates our model's quantitative description of the polar effect for abstraction from isobutane by methoxyl and by methyl radicals. The lower antibonding in the ether is due primarily to its narrower curve, caused by the higher frequency, 1116 cm^{-1} in X−Y = $(CH_3)_3C{-}OCH_3$ *vs* 964 in X−Y = $(CH_3)_3C{-}CH_3$ (see Data section). The ether's higher frequency is due to the electronegativity difference, $\Delta\chi$, between C and O. BDE(X−Y) for the ether is only 3% weaker and r_e(X−Y) 6% shorter. The greatest difference is in the stretching frequencies, where ν(C−O) is 16% greater than ν(C−C). Taking the methane/methyl exchange as a standard, an arbitrary increase of 5% in BDE(X−Y) causes a 12.5% increase in E^*; a 5% increase in r_e, a 19.9% increase; and an increase of 5% in ν and 11% decrease in E^*. The interplay is subtle, changes in bond properties being not independent of each other. In comparing abstractions from trimethylsilane by methoxyl and by methyl radicals, again ΔH is the same and the greatest difference in the corresponding X−Y bond properties is in the stretching frequencies, where ν(Si−O) is 27% higher than ν-

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(46) Mayo, F. R.; Walling, C. *Chem. Rev.* **1950**, *46*, 192.

(C−O), due to the greater $\Delta\chi$ in the former. The calculation shows that structures such as $(CH_3)_3C^+$- - -H•- - -$^-$OR and R_3-Si^+- - -H•- - -$^-$OR are justifiably written to qualitatively describe the TS stabilization resulting from the $\Delta\chi$ of X and Y in these cases.

This calculation yields E^* values that are too high by 2−5 kcal/mol for abstraction by F• and Cl• atoms from alkanes. We have no specific explanation for the larger deviations in these cases, except to note that abstractions by Br• and I• are described well. It is possible that there is something special about F• and Cl• abstractions from alkanes, where $\Delta\chi$ is particularly large; also it has been shown that the Morse equation describes HF and HCl particularly poorly.[12] Calculated E^* for abstractions by •OH cannot be compared to Arrhenius E_a because of high curvatures found in plots of ln k vs $1/T$ for such reactions. The calculation[1a] was reported to fail for abstractions by alkylperoxyl radicals from hydrocarbons,[47] but the last two entries in Table 2 indicate that this may not be the case.

It has been found that the low energy of activation for RO−H + •OR is accompanied by a low Arrhenius pre-exponential term of $A = 10^{6.4}\ M^{-1}\ s^{-1}$, compared to $10^{8.5\pm1.0}$ for H-abstractions from carbon, and it was noted that our calculation provides a good rationale for the low pre-exponential term, since low antibonding allows a tight TS for hydrogen transfer between alkoxy groups.[36] Our model finds that the two oxygen atoms at the TS are only 0.55 Å away from their equilibrium value, r_e, in X−Y = RO−OR. For hydrogen transfer between methyl groups, the two carbons are 0.92 angstroms from $r_e(H_3C{-}CH_3)$, and for transfer between silyl groups 1.09 from $r_e(H_3Si{-}SiH_3)$, as shown in Figure 1. In terms of "looseness" or "tightness" of the TS, the silane/silyl exchange has the loosest and the alcohol/alkoxyl exchange the tightest TS in the series of identity reactions discussed. The combined bonding and resonance terms contributing to the total energy of the TS are always greater (more stable) than the energy of the starting X−H bond in the reactions examined. Relative to the starting state, bonding and resonance contributions to the TS are ($^3E-E^*$): X = silyl, −4.2; methyl, −5.0; ethyl, −5.2; H, −6.6; thiyl, −8.6; Cl, −8.9; alkoxyl, −8.8 kcal/mol. This is essentially the same order as experimental E_a values and shows that the loosest TS (silyl) gains the least in bonding/resonance and the tightest TS gains the most. At the same time, the loosest TS has the greatest X−Y triplet repulsion and the tightest the least. The combined effects give the tightest TS the lowest energy of activation.

Figure 3 shows that, in addition to the tight TS, the calculated shape of the "pass" on the potential energy surface is narrower for H-transfer between alkoxy groups compared to methyls. Low pre-exponential terms of $A = 10^{6.5\pm0.5}$ have been found for abstractions by peroxyl radicals from α- and β-naphthol,[15a] and even lower values have been reported for abstractions by tri-*tert*-butylphenoxyl from various monosubstituted phenols.[48] A hydrogen bonded complex formed prior to H-transfer has, occasionally, been invoked as an explanation for the low E_a and low A terms; electron transfer prior to H-transfer has also been postulated for the same reasons. While such processes may be operative, our model shows that they are not needed simply to explain the low E_a and low A factors.

Since the model is successful with the varity of reactions in Table 2, as well as with the many reactions previously treated,[1] it is highly unlikely that agreement with experiment is fortuitous. Despite its shortcomings, the model must reflect the essential reasons for the existence of an energy barrier between reactants and products and must be based on reasonable assumptions and approximations. This provides the confidence to formulate some rules that go beyond the broad statement that, in a series of closely related reactions, the most exothermic one usually has the lowest energy of activation:

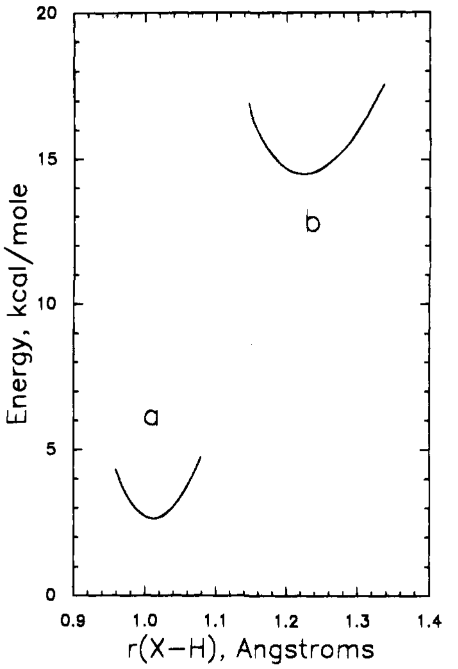

Figure 3. Energy *vs* X−H bond extension in the symmetrical reactions: (a) $(CH_3)_3CO{-}H$ + $•OC(CH_3)_3$ and (b) $CH_3{-}H$ + $•CH_3$. The lowest energy value is E^*, 2.6 and 14.5, respectively. The experimental Arrhenius pre-exponential terms are $A(a) = 10^{6.4}$ and $A(b) = 10^{8.6}$.

In addition to ΔH in hydrogen abstractions by radicals, another major factor affecting the energy of activation is X−Y antibonding (^3E) at the TS. Low antibonding leads to low E_a. The X−Y bond properties affect antibonding as follows: (a) Weak BDE leads to low ^3E. (b) High stretching frequency leads to low ^3E. (c) Short bond length leads to low ^3E. All three properties are affected by the X−Y dipole; the stretching frequency is affected also by the reduced mass of X−Y.

Antibonding effects on E_a often can be estimated qualitatively without actually carrying out the calculation, but by looking at the properties of X−Y, the molecule never made. We provide two examples:

(1) *tert*-Butoxyl radicals abstract hydrogen from amines $(RCH_2)_2NH$ exclusively from the nitrogen, even though abstraction form the α-carbon would be more exothermic.[49] This was described as "a bit of mystery", but it was noted that hydrogen transfers between heteroatoms often have low energies of activation. Our rules allow the qualitative prediction that abstraction from the nitrogen would have a low energy of activation because X−Y antibonding would be low as a result of the weak X−Y bond, BDE($RCH_2N{-}OR$) = 30−40 kcal/mol.

(2) It is well-known that phenols are good antioxidants, and one of the reasons for this is the pronounced preference shown for H-abstraction from phenol by ROO• radicals, the chain propagating species in autoxidations.[50] In comparing phenol

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[47] Mahoney, L. R.; DaRooge, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 4722−4731.

[48] Mahoney, L. R.; DaRooge, M. A. *J. Am. Chem. Soc.* **1970**, *92*, 890−899.

[49] Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 328−331.

[50] Another reason for the good antioxidant properties of phenol, compared to compounds with similar BDE(X−H) such as toluene, is that reaction of phenoxyl radicals with O_2 does not appear to occur and has not been observed; however, the benzyl radical reacts with O_2 to give $PhCH_2$-OO•, which continues the chain. We thank Dr. Cheves Walling for pointing out the relevance of this work to understanding antioxidant properties.

to toluene as another possible ROO• radical trap, we have BDE(PhO−H) = 87−91 kcal/mol[51] and BDE($PhCH_2$−H) = 88. Consideration of polar effects alone leads to the wrong prediction that H-abstractions by ROO• from toluene would have a lower E_a. We cannot calculate E^* precisely for abstraction from phenol by ROO• because BDE(PhO−OOR) is not known, but it is evident that antibonding will be minimal and E_a very low because of the weakness of such a bond, 10−25 kcal/mol, compared to BDE($PhCH_2$−OOR) = 60.7.[52] For abstraction by *tert*-butylperoxyl radicals from 2,6-di-*tert*-butylphenol, a low value of E_a = 0.5 has been reported.[53]

The idea that repulsive energy is a factor in radical reactions is not new; however the concept was highly qualitative and not very useful with actual systems.[54a] For all types of chemical reactions, the importance of repulsions has been noted, but not in any quantitatively useful fashion.[54b] The model presented here for radical reactions places antibonding on a quantitative basis and highlights its importance.

Recent high-level *ab initio* calculations have also quantified repulsive forces for addition of methyl and other radicals to ethylenes. Using the "curve crossing" model for methyl addition, the TS was described by four valence bond configurations contributing to the wave function. They can be written as $H_3C{\uparrow}\text{- - -}{\downarrow}CH_2\text{-}CH_2{\uparrow} \leftrightarrow H_3C{\uparrow}\text{- - -}{\downarrow}CH_2\text{-}CH_2{\downarrow} \leftrightarrow H_3C^-\text{- - -}[CH_2{=}CH_2]^+ \leftrightarrow H_3C^+\text{- - -}[CH_2{=}CH_2]^-$. The location of the TS along the reaction coordinate was near the intersection of repulsive curves for the first and second resonance structures.[55] The first resonance structure, with parallel spins at the terminal carbons, is reminiscent of our resonance form **III**, with parallel spins at the terminal atoms of the three body system, and the "curve crossing" model has similarities with our intersecting potential energy curves.

For comparing our model with other approaches for H-abstractions, we do not find broad systematic attempts to treat a large variety of such reactions by high-level *ab initio* calculations and compare the results with experiment, although examples of relatively small groups exist.[56] Trends in E_a were reproduced in the series H• + hydrogen halides, with accuracies in barrier heights reported as "a few kcal/mole".[56b] At the MP4/6-311G** level, the average deviation between calculated and experimental energy barriers was 1.15 kcal/mol for abstractions of carbon radicals from the hydrogen halides, while for the methane/methyl identity exchange the calculated value was 18.7,[56a] compared to experimental E_a of 14.5 kcal/mol. High values are also obtained by the "fragments in molecules" approach with 6-311++G(df,p), obtaining enthalpies of activation of 8.7 kcal/mol for Cl• + H−Cl and 17.1 for CH_3−H + •CH_3.[44c] We have applied the AM1 method, a commonly used semiempirical molecular orbital calculation, to abstractions by various carbon radicals from tin hydride with successful results but have noted that AM1 is not uniformly successful in modeling hydrogen abstractions, e.g., it simulates the methyl/methane exchange well but yields a negative energy of activation for H−H + •H and too high a value by more than 20 kcal/mol for the RO−H + •OR exchange.[8] Evidently the AM1 calculation has not been uniformly well parametrized for this type of reaction.

Our calculation should not be confused with data-fitting approaches that use known E_a values to obtain different *ad hoc* parameters for different types of X and Y combinations for best agreement.[57] While parametric equations fit well the reactions from which they are derived, they may fail in other cases. For example, a recently proposed algorithm[57b] fails to reproduce the order of E_a with the identity reactions of Table 1, giving the following calculated values of energies of activation: X = silyl, 10.6; methyl, 13.4; ethyl, 12.6; H, 9.2; thiyl, 7.4; Cl, 9.0; and *tert*-butoxyl, 10.3.

Our model is not parametric, but is derived from first principles, based on potential energy curves. It is successful with a very large variety of hydrogen abstractions. Having pointed out shortcomings of our model, we do not wish to leave the reader with the false impression that all those presently engaged in kinetic studies of hydrogen atom transfer reactions should instead devote themselves to spectroscopic and structural studies of X−Y molecules.[47] However, if the primary criterion for judging calculations in chemistry is their ability to reproduce experiment, the present approach passes the test.

Data

The bond properties used as input to the calculation are listed in Table 3. For consistency and wide availability of the data base, we took ref 58 as our primary source. Other sources are given as footnotes to the table. It needs to be said that the result of the calculation cannot be more reliable than the input data. Some of the values used require additional comment to demonstrate the care that must be exercised before observed X−Y infrared frequencies are used for the calculation of force constants for the Morse curves, since they may be coupled to other vibrations in complex molecules. This had been a major problem in using the calculation. We provide now a reliable

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Table 3. Data Used for Calculating E^* of Table 2

bond	BDE,[a] kcal/mol	r_e,[a] Å	ν,[b] cm^{-1}	bond	BDE,[a] kcal/mol	r_e,[a] Å	ν,[b] cm^{-1}
$H-H$	104.2	0.7414	4159[c]	$(CH_3)_3Si-CH_2CH_3$	90.0[g]	1.857[q]	780[e]
CH_3-H	104.9	1.087	2994[d]	$(CH_3)_3Si-CH(CH_3)_2$	88.0[g]	1.857[q]	762[e]
CH_3CH_2-H	100.6	1.094	2951[d]	$H_3Si-SiH_3$	76.6[p]	2.331	432[s]
$(CH_3)_2CH-H$	98.5	1.107	2928[d]	$(CH_3)_3Si-OCH_3$	110.0[e]	1.645	1031[e]
$(CH_3)_3C-H$	95.6	1.122	2890[d]	$(CH_3)_3C-OCH_3$	83.7	1.452	1116[e]
$PhCH_2-H$	88.0	1.111	2934	$((CH_3)_3Si)_3Si-H$	83.0[e]	1.50[g]	2052[t]
$Ph-H$	110.9	1.08	3035	$((CH_3)_3Si)_3Si-CH_2CH_3$	75.0[e]	1.856[u]	638[e]
CH_3O-H	104.4	0.9451	3690	$(CH_3)_3Sn-H$	77.0[e]	1.700	1815
$HS-H$	91.2	1.3356	2621	$(CH_3)_3Sn-CH_3$	65.1[v]	2.144	524[c]
CH_3S-H	87.3	1.340	2610	$(CH_3)_3Sn-CH_2CH_3$	63.1	2.148[g]	504[c]
CH_3CH_2S-H	87.8[e]	1.350	2600	$(CH_3)_3Sn-CH_2Ph$	55.0[e,g]	2.16[g]	414[e,g]
$(CH_3)_2CHS-H$	87.6[e]	1.35[f]	2550	$(CH_3)_3Sn-Ph$	74.0[e,g]	2.14[g]	616[d]
$PhS-H$	80.0[e]	1.36[g]	2597	$(CH3)_3Ge-H$	84.0	1.535	2049[c]
$HS-CH_3$	74.7	1.808[h]	758[e]	$(CH3)_3Ge-CH_2CH_3$	75.0[e]	1.94	601[e]
CH_3S-CH_3	73.6	1.807	746[e]	$(CH3)_3CO-H$	105.1	0.95	3644
$CH_3S-CH_2CH_3$	72.3[i]	1.817	733[e]	$(CH3)_3CO-OC(CH_3)_3$	38.0	1.48	771[w]
$CH_3S-CH(CH_3)_2$	72.7[i]	1.819	737[e]	$Cl-H$	103.2	1.2746	2885[c]
$CH_3S-C(CH_3)_3$	70.4[i]	1.83[g]	714[e]	$Cl-Cl$	58.0	1.9878	554[c]
$CH_3CH_2S-CH_2CH_3$	72.5[k]	1.817	734[e]	$H-Br$	87.6	1.4145	2558[c]
$PhS-CH_3$	66.4[e]	1.789	673[e]	CH_3-CH_3	89.9	1.5351	995[d]
$PhS-CH_2CH_3$	64.7[e]	1.817	655[e]	$CH_3CH_2-CH_2CH_3$	86.6	1.543	965[e]
$PhS-CH(CH_3)_2$	65.6[e]	1.819	665[e]	$(CH_3)_3C-CH_3$	86.5	1.537	964[e]
$PhS-C(CH_3)_3$	63.5[e]	1.83[g]	643[e]	NH_2-H	107.4	1.012	3388[c]
$PhS-CH_2Ph$	55.4[e]	1.817	565[b]	NH_2-CH_3	84.6	1.471	1121[e]
$HS-SH$	64.5[j]	2.055	509[d]	CH_3COCH_2-H	96.5	1.103	2986[d]
CH_3S-SCH_3	65.2	2.029	529	$CH_3COCH_2-CH_3$	84.6[e]	1.535[g]	947[e]
$CH_3CH_2S-SCH_2CH_3$	65.2[l]	2.029[l]	532[e]	CH_3CO-H	89.4[e]	1.128	2822[d]
$PhS-SCH_2CH_3$	59.0[e]	2.06[m]	450[e]	CH_3CO-CH_3	84.4[e]	1.52	945[e]
H_3Si-H	91.6[n]	1.4798	2190[d]	$H-OOH$	88.2	0.96[g]	3599[d]
$(CH_3)_3Si-H$	94.5[o]	1.485	2107	CH_3-OOH	70.1[v]	1.48[g]	993[e]
H_3Si-CH_3	89.2[p]	1.857[q]	770[e]	$H-OOCH_3$	88.2[g]	0.96[x]	3599[x]
$H_3Si-CH_2CH_3$	87.8[g]	1.857[q]	760[e]	$CH_3CH_2-OOCH_3$	72.6[v]	1.48[g]	1018[e]
$(CH_3)_3Si-CH_3$	93.5[p]	1.875	810[r]				

[a] Reference 58; unless otherwise indicated. [b] Reference 59; vapor phase values whenever available. [c] Reference 60; where equilibrium frequencies are given, they were converted to observed frequencies by subtracting $2\omega\chi$. [d] Reference 61. [e] See supporting information. [f] By analogy with EtS−H. [g] Estimated in this work. [h] Average for aliphatic C−SH. [i] From ΔH_f given in reference 62, using the more recent values for ΔH_f of the alkyl radicals and of MeS•, 29.8 kcal/mol.[58] [j] Reference 5, decreased by 1.2 kcal/mol to adjust all RS−R values to the more recent[58] value of BDE(MeS−Me) = 73.6. [k] From the heats of formation of H_2S_2 and •SH, 3.7 and 34.1, respectively.[58] [l] By analogy with MeS−SMe. [m] Average value for CS−SC. [n] Reference 63. [o] Reference 64. [p] From ΔH_f of the silanes derivable from ref 65, with the more recent heats of formation of •SiH_3 and •$SiMe_3$.[63,64] [q] Average for C(sp^3)−Si. [r] Reference 66. [s] Reference 67. [t] Reference 68. [u] Average X-ray value for Me−SiSi from supplementary material of reference 69. [v] Reference 52. [w] Reference 70. [x] By analogy with hydrogen peroxide.

method for estimating uncoupled frequencies for several types of bonds. Most of the data in Table 3 are from standard sources. Some are estimates of ours or of others[52] and are subject to being challenged. The important question is whether such estimates are reasonable and we believe they are.

BDE values in Table 3 are for the gas phase at 298 K. Some needed values were unavailable and estimates were made from similar compounds. A rationale is provided in the supporting information for estimates that are not obvious in the context of other literature values given.

Stretching Frequencies for molecules exhibiting a symmetric and an asymmetric vibration constitute a weighted average.[71]

Difficulties in determining uncoupled X−Y stretching frequencies have been ameliorated by the observation that plots of uncoupled ν *vs* $(\mathrm{BDE})^{1/2}$ are linear and parallel to each other for various types of bonds.[71] Uncoupled frequencies for many normal covalent bonds can be estimated from $\nu = 170(\mathrm{BDE})^{1/2} - c_i$, where the intercept c_i is characteristic of the type of bond. For C−C, c_i = 617 cm^{-1}; for C−N, c_i = 442; for C−O (alcohols, carbonyls, and carbon monoxide), c_i = 550; for C−OG (ethers, esters, peroxides), c_i = 430; for C−Br, c_i = 670; for C−I, c_i = 704. For molecules with symmetric and asymmetric vibrations, the appropriately weighted average ν is obtained. In principle, a single molecule is sufficient for obtaining the appropriate c_i, when the DBE is known and ν is determined to be uncoupled to other vibrations as established by "normal coordinate" analysis, by isotopic substitutions, or by *ab initio* calculation; prudence suggests more than one molecule for confirming a value of c_i. The same c_i is valid for single, double, and triple bonds. For example, uncoupled calculated and observed frequencies (in parentheses) for C−C bonds are 995 ± 9 (995) for ethane; 1128 ± 12 (1196) for C2−C3 in 1,3-butadiene; 1633 ± 12 (1623) for ethylene; and 1966 ± 12 (1974) for acetylene, based on BDE values of 89.8 ± 1, 116.4 ± 1.6, 175.2 ± 2, and 230.9 ± 2, respectively.[58] For C−N bonds, calculated for ν(HCN) = $170(223.1)^{1/2} - 442$ = 2097 cm^{-1} (obsd 2097) and $\nu(\mathrm{Ph{-}NH_2}) = 170(102.6)^{1/2} - 442$ = 1275 cm^{-1} (1274), etc. For C−OG, calculated for ν(*t*-Bu−OMe) = $170(83.7)^{1/2} - 430$ = 1125 (obsd 1116), ν(Ph−OMe) = $170(99.2)^{1/2} - 430$ = 1263 (1249), and $\nu(\mathrm{RCH_2{-}OOH})$ = $170(72.6)^{1/2} - 430$ = 1018 (1024 ± 9 for five *n*-alkyl hydroperoxides). The original equation was in somewhat different form.[71] In this work we established four more such correlations, as described in the supporting information. For C−S bonds, $\nu = 170(\mathrm{BDE})^{1/2} - 712$ cm^{-1}. For S−S bonds, $\nu = 170(\mathrm{BDE})^{1/2} - 856$. For C−Si bonds, $\nu = 170(\mathrm{BDE})^{1/2} - 833$. Tentatively, for C−Sn bonds, $\nu = 170(\mathrm{BDE})^{1/2} - 847$.

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To illustrate the sensitivity of the calculated E^* to uncertainties in ν, an arbitrary increase of the C−S frequency by 30 cm^{-1} results in a decrease of about 0.9 kcal/mol in E^* for HS−H + $^\bullet CH_3$. E^* is much less sensitive to similar uncertainties in the X−H or H−Y stretching frequencies.

Bonds Lengths given in ref 58 were used when available for specific compounds; otherwise recommended average values were used. Some values were estimated by analogy from closely related compounds, guided by the known trend that weaker bonds are longer. The sensitivity of the calculation to uncertainties in X−Y bond lengths is illustrated with MeS−H + Me$^\bullet$: when the MeS−Me bond length is arbitrarily increased by 0.010 Å, E^* increases by 0.3 kcal/mol.

Conclusions

This work demonstrates the importance of X−Y antibonding, in addition to the enthalpy of reaction, for estimating energy barriers to hydrogen abstractions by radicals. For identity hydrogen transfers, we conclude that the strength of the bond being broken and made is not a major factor. When polar effects exist at the TS, our calculation describes them quantitatively.

Computational Aspects

The computer program used, ESTAR.BAS, Version 4, is written in BASIC for IBM PC and compatibles, and it runs under BASIC, BASICA, or QBASIC; it is 161 lines of code, and it runs in a fraction of 1 s. A copy (in ASCII text) may be obtained through e-mail by requesting it from ZAVITSAS@AURORA.LIUNET.EDU. Copies on 3.5 in. diskettes may be obtained by writing to A.A.Z., enclosing a blank diskette. Should a user change the program in any way, we request that the changed version not be identified as ESTAR.

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Supporting Information Available: Text describing BDE data (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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