liquid cyclopropene and the solution stirred at room temperature for 15 min. On evaporation to dryness 250 mg (100%) of **14** was obtained as a microcrystalline material: colorless needles (methanol); mp 161–162° dec; nmr ($CDCl_3$) δ 3.96 (s, 6), 1.93 (dd, J = 3.7 and 7.4 Hz, 4), 0.56 (9, $J \approx$ 7.2 Hz, 2), 0.13 (dt, J = 3.7 and 6.8 Hz, 2). The simplicity of the nmr spectrum indicates a highly symmetrical structure.

Anal. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.22. Found: C, 57.62; H, 5.76; N, 11.32.

Reaction of 10a with Water. When 2 drops of water was added to a slurry of 210 mg (1.00 mmol) of **10a** in 2 ml of dioxane, the yellow solid rapidly dissolved on shaking, resulting in a colorless solution, from which **15** was isolated in quantitative yield: colorless prisms (ethyl acetate); mp 132–133°dec; ir (KBr) 3300 (OH, NH), 1735, 1707, 1610 cm^{-1}; nmr (pyridine-d_5) δ 7.2 (broad singlet, 1), 3.79 (s, 3), 3.73 (s, 3), 2.5 (m, 2), 1.5 and 1.15 (AB part of an ABCD pattern).

Anal. Calcd for $C_9H_{12}N_2O_5$: C, 47.37; H, 5.30; N, 12.28. Found: C, 47.37; H, 5.28; N, 12.14.

1-Methyl-2,5-dicarbomethoxy-3,4-diazanorcaradiene (10b). Reaction of 1-methylcyclopropene with **6** in the manner described for the preparation of **10a** produced **10b** in 60% yield: mp 77–79° dec; ir (KBr) 3095, 1750, 1725, 1530 cm^{-1}; nmr ($CDCl_3$) δ 3.96 (s, 6) 1.49 (s, 3), ABC pattern at −32.8° (see Table I).

Anal. Calcd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39; N, 12.50. Found: C, 53.40; H, 5.46; N, 12.46.

7-Methyl-2,5-dicarbomethoxy-3,4-diazanorcaradiene (10c). Prepared in 75% yield from **6** and 3-methylcyclopropene: mp 113–115°dec; ir (KBr) 1735, 1710 cm^{-1}; nmr ($CDCl_3$) δ 3.99 (s, 6) and broad signals in the range from δ 3.0 to 0.5 at room temperature; at −30° two sharp doublets were discernible at δ 1.52 and 0.54 in the approximate intensity ratio of 65:35, superimposed on a complex pattern; a value for $\Delta G^{\ddagger}$ was calculated at 55°, using formulas described in the literature.[35,51]

Anal. Calcd for $C_{10}H_{12}N_2O_4$; C, 53.57; H, 5.39; N, 12.50. Found: C, 53.59; H, 5.28; N, 12.29.

7,7-Dimethyl-2,5-dicarbomethoxy-3,4-diazanorcaradiene (10e) was prepared in 59% yield from **6** and 3,3-dimethylcyclopropene: mp 98–100°; ir (KBr) 1740, 1710 cm^{-1}; nmr ($CDCl_3$) δ 3.96 (s, 6), 2.88 (s, 2), at −20° two singlets of relative intensity 3 at δ 1.55 and 0.59, which coalesced at 66°.

Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.45; H, 5.92; N, 11.76. Found: C, 55.07; H, 5.85; N, 11.74.

1-Methyl-2,5-diphenyl-3,4-diazanorcaradiene (9b). To a solution of 1-methylcyclopropene, generated from 4 g (0.1 mol) of sodium amide and 10.0 g (0.11 mol) of methallyl chloride, in 5 ml of chloroform was added **5**[52] in 100-mg portions. After each addition the solution was shaken until the yellow color had disappeared; 3.0 g (12.7 mmol) of **5** could thus be brought to react. The solvent was removed under reduced pressure and the remaining oil crystallized from ethyl acetate–petroleum ether to yield 3.28 g (99%) of **9b**: mp 100–102°; nmr ($CDCl_3$) δ 8.2–7.3 (m, 10), 1.34 (s, 3), ABC pattern with δ_A 2.30, δ_B 1.94, δ_C 0.53.

Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 83.33; H, 6.38; N, 10.57.

2-Carbomethoxy-6,7-diphenyl-4*H*-azepine (13a). A gaseous stream of cyclopropene was passed through a stirred suspension of 1.46 g (5.0 mmol) of **11a**[26,53] in 20 ml of dry ether for 15 min, after which time a homogeneous solution resulted. The oil remaining after removal of the solvent yielded 1.40 g (92%) of **13a** upon crystallization from methanol: mp 75–79°; ir (KBr) 1715 cm^{-1}; nmr ($CDCl_3$) δ 8–7 (m, 10), 3.85 (s, 3), ABXY pattern at −26.7° (see Table I).

Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.18; H, 5.65; N, 4.62. Found: C, 79.29; H, 5.73; N, 4.71.

2,6,7-Tricarbomethoxy-4*H*-azepine (13b) was prepared in analogy to **13a** from **11b**[26] in 77% yield: mp 94–95°; ir (KBr) 1730, 1705, 1620, 1575 cm^{-1}; nmr ($CDCl_3$) δ 7.06 (t, 1), 6.55 (t, 1), 3.94 (s, 3), 3.85 (s, 3), 3.75 (s, 3), 2.57 (t, 2).

Anal. Calcd for $C_{12}H_{13}NO_6$: C, 53.93; H, 4.90; N, 5.24. Found: C, 53.82; H, 5.07; N, 5.25.

2-Carbomethoxy-7-phenyl-4*H*-azepine (13c) was prepared in analogy to **13a** from **11c**[54] in 82% yield: mp 61–62°; ir (KBr) 1710, 1620, 1595 cm^{-1}; nmr ($CDCl_3$) δ 8.2–7.3 (m, 5), 6.37 (dt, J = 0.7 and 7.1 Hz, 1), 6.35 (d, J = 9.9 Hz, 1), 6.05 (ddt, J = 0.7, 9.9, and 6.6 Hz, 1), 3.80 (s, 3), 2.33 (t, J = 6.9 Hz, 2).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.88; H, 5.72; N, 6.42.

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Activation Energy Requirements in Hydrogen Abstractions. Quantitative Description of the Causes in Terms of Bond Energies and Infrared Frequencies

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Abstract: The energy of the three-body system in the transition state for hydrogen abstraction reactions can be obtained by the combination of three Morse curves. The calculated energies of activation are accurate to better than 1 kcal/mol for $\Delta H < \pm 15$ kcal/mol. Forty reactions of wide variety are treated successfully. Examples are given for the use of the method in assigning bond dissociation energies from energies of activation. The method describes the "polar effect" quantitatively. It is found that the energy of activation primarily serves to overcome antibonding between the terminal groups in the transition state. In addition to bond strengths, bond lengths and vibrational stretching frequencies are found to affect the energy of activation significantly.

The empirical Arrhenius expression (eq 1) has been found to provide a reasonably accurate

$$k = Ae^{-E_a/RT} \qquad (1)$$

description of the temperature dependence of rate constants over wide temperature ranges. More theoretical approaches, such as collision models, transition-state theory, and thermodynamic and detailed quantum mechanical theory, lead to expressions of essentially the same form. The *a priori* calculation of rate constants has been an area of interest and has received considerable attention for many years; the benefit of success would be immense. Preexponential terms are often predictable to a good approximation for various reaction types, and much progress has been made toward their estimation from reasonable assumptions concerning the structure of the transition state.[1,2] The energy term, however, still cannot be estimated with any reasonable accuracy; this term describes the sensitivity of the rate constant to changes in temperature and is generally considered to be a measure of the minimum amount of energy required for reaction to occur, the activation energy.

The only serious attempts to carry out a theoretical evaluation of activation energies have centered on the simple atom transfer reaction (eq 2) between a hydrogen molecule and a hydrogen atom; recent approaches have been both classical and quantum mechanical.[3-9] The older work has been reviewed.[10]

$$\text{A–B} + \text{C}\cdot \longrightarrow \text{A}\cdot + \text{B–C} \tag{2}$$

The quantum mechanical calculations are often quite elaborate and are not always free of adjustable parameters of an empirical nature. Considering that they refer only to the simplest of chemical reactions, the outlook is not favorable for extensions of the theoretical treatment to more complex systems and other types of reactions in the immediate future. SCF–MO and extended Hückel calculations are better suited to calculations of relative stabilities of various conformations and heats of formation of stable molecules than activation energies.[11-14] These approaches often involve adjustable or calibration parameters, are quite complex, and occasionally fail badly even with stable molecules.[15] For this reason semiempirical approaches to the problem retain their significance.

Most semiempirical approaches are based on the London equation (eq 3) where A, B, and C denote the

$$E = A + B + C - \{{}^1/_2((\beta - \alpha)^2 + (\gamma - \beta)^2 + (\gamma - \alpha)^2)\}^{1/2} \tag{3}$$

Coulombic energy in molecules A–B, B–C, and A–C of eq 2, respectively, and α, β, and γ are the corresponding exchange energies. The equation was derived to give the total energy of the three-body system in the hydrogen exchange reaction and assumes orthogonal orbitals, thus disregarding the overlap integral.[16]

Equation 3 has been applied to a variety of systems.[10] The usual approach is to assume that the most stable transition state is linear, as indicated by the theoretical treatments, and to use Morse functions[17] to describe bonding (eq 4) and antibonding[18] (eq 5) energies in

$${}^1E = D_e\{(1 - e^{-a(r-r_e)})^2 - 1\} \tag{4}$$

$${}^3E = fD_e\{(1 + e^{-a(r-r_e)})^2 - 1\} \tag{5}$$

A–B, B–C, and A–C as a function of distances. ${}^1E$ and ${}^3E$ denote the energies of each diatomic molecule at a distance r in ångströms, r_e is the equilibrium internuclear distance, f was originally given the value of 0.5;[18] the "spectroscopic" constant a is given by eq 6,

$$a = 0.1218\omega_o\{\mu/(350D_o)\}^{1/2} \tag{6}$$

where ω_o denotes the equilibrium vibrational frequency of the bond in cm^{-1} (often approximated by the observed frequency), μ denotes the reduced mass in amu, and D_o is the observed dissociation energy in kcal/mol multiplied by 350 to convert to cm^{-1}. D_e in eq 4 and 5 denotes the observed dissociation energy in kcal/mol plus the zero-point energy, *i.e.*, $D_o + 0.00143\omega_o$.

In the London–Eyring–Polanyi approximation ${}^1E$ from eq 4 is set equal to $A + \alpha$, $B + \beta$, and $C + \gamma$, and the ratios A/α, etc., are approximated to be invariant with r and are set equal to approximately 0.2[19] Potential energy surfaces may thus be constructed by evaluating E of eq 3 at various $r_{\text{A–B}}$ and $r_{\text{B–C}}$ combinations. Although the value used for the above ratios is not too different from what might reasonably be expected[3,20] at the distances of transition states, its constancy and some features of the potential energy surfaces obtained by this method have been questioned.[10] Most important is the fact that the value of the ratio of the coulombic to the exchange energy is found to not be constant from reaction to reaction, so that the method cannot be expected to give reliable predictions concerning activation energies. Instead, the ratio is used as an adjustable parameter to "normalize" the potential energy surface obtained to the experimentally observed activation energy, and then the curvature of the surface is used to obtain detailed information concerning the structure of the activated complex and to calculate the preexponential term in eq 1.[21]

Sato obtained the values of coulombic and exchange energies by setting eq 4 equal to $A + \alpha$, etc., and eq 5 equal to $A - \alpha$, etc.[18] Equation 3 is then evaluated at various combinations of distances and the results are multiplied by a factor of 0.85, to correct for the neglect of the overlap integral. The correction factor again is not constant from reaction to reaction; its value is considerably larger than actual overlap integrals would suggest[22] and leads to potential energy surfaces of questionable validity.[23] The adjustable parameter has been used to normalize the potential energy surface to experimental activation energies, and the curvature of the normalized surface has been

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used to obtain detailed information concerning the structure of the transition state.[24]

The only method that can be used to predict activation energies with some reliability has been developed by Johnston and Parr.[25] It applies to hydrogen-transfer reactions and uses a bond energy–bond order correlation. It is postulated that the sum of the bond orders of the bonds being broken and being made remains equal to 1.0; Pauling's correlation of bond length and bond order[26] is used along with the rule that bond energy can be correlated with single bond energy by eq 7, where n denotes the bond order and p

$$D = D_s n^p \tag{7}$$

is a constant obtainable from equilibrium internuclear separations and bond energies in noble gas diatomic clusters. Antibonding in A–C is estimated from eq 5 with $f = 0.25$. The energy of the three-body system of reaction 2 is evaluated subject to the bond order constancy restriction. The method does not depend on any parameters adjustable with every reaction, and it has been successful in estimating activation energies for hydrogen abstraction reactions by simple radicals from alkanes, hydrogen halides, H_2, and CF_3H. Calculated activation energies are within about 3 kcal/mol of experimental values, often better, and never much worse with the above compounds. Potential energy surfaces are not obtained, but a reaction coordinate type chart can be made. To our knowledge there is no consistently superior method for the *a priori* calculation of activation energies in any type of reaction.

We propose a method that is accurate and simple, and which allows a clear insight into the causes for often unexpected variations in energies of activation of hydrogen abstraction reactions.

For reaction 8, the transition state can be considered

$$\mathrm{X{:}H} + \mathrm{Y}\cdot \longrightarrow \mathrm{X}\cdot + \mathrm{H{:}Y} \tag{8}$$

as a stable molecule in the classical approach, and resonance structures I and II can be written for it (eq 9). It can be seen that, for simultaneous bonding

$$\underset{\mathrm{I}}{\mathrm{X{:}H\ Y}\cdot} \longleftrightarrow \underset{\mathrm{II}}{\cdot\mathrm{X\ H{:}Y}} \tag{9}$$

of H to X and Y, the spins of the three electrons involved must be either $\uparrow\downarrow\uparrow$ or $\downarrow\uparrow\downarrow$; either way there is antibonding between the terminal atoms X and Y. Resonance structures I and II each contribute 50%, since the classical triatomic molecule is about equally unstable in either direction, and the bonding energy of the three-body system will be the average of the bonding energies in I and II, *i.e.*, $0.5({}^1E_{XH} + {}^1E_{HY})$; in addition since the odd electron is not localized, certain bonding energy due to resonance I ↔ II must be added. For one odd electron delocalized over three atoms the simplest allylic system may serve as a rough model: in propane the primary C–H bond dissociation energy (BDE) is 98 kcal/mol, whereas in propylene it is 88, indicating a resonance stabilization in the allyl radical of about 10 kcal/mol or about 10% of the C–H BDE in the saturated molecule.[27] As a first approximation the total bonding energy in the transition state for reaction 8 will be $0.55({}^1E_{XH} + {}^1E_{HY})$. The antibonding energy can be approximated by ${}^3E_{XY}$ (eq 5). Thus in this approximation the total energy of the three-body system in the transition state will be given by eq 10.

$$E = 0.55({}^1E_{XH} + {}^1E_{HY}) + {}^3E_{XY} \tag{10}$$

Recent detailed calculations on H_2 have shown that the standard Morse curve (eq 4) gives a sufficiently accurate approximation of the bonding energy of H_2 up to about 1.5 Å, or twice the equilibrium length of the bond.[3,28,29] We employed eq 4 to estimate the ${}^1E$ terms since distances in the transition state are not expected to be larger than twice r_e.

Eq 5 as proposed by Sato with $f = 0.5$[18] appears to overestimate ${}^3E$ for H_2 when compared to more detailed calculations.[30-33] Values lower than 0.5 have been used;[3,25,34] we employed $f = 0.45$ to be consistent with the results of Kolos and Roothaan[31] as discussed in a later section.

The energy of the three-body system, as given by eq 10, for a linear transition state deduced from detailed calculations,[10] is a function of two variables: the X–H internuclear distance, r^*_{XH}, and the H–Y distance, r^*_{HY}. In the transition state, the rough approximation can be made that the ratio r^*_{XH}/r^*_{HY} will be equal to the corresponding ratio of the equilibrium distances in the stable molecules. This approximation would be expected to hold better with reactions which have relatively symmetrical potential energy diagrams (small $\pm\Delta H$) than with very skew situations (large $\pm\Delta H$). Subject to this expected limitation, r^*_{HY} can be expressed as a function of r^*_{XH} (eq 11)

$$r^*_{HY} = r^*_{XH} r_{HY}/r_{XH} \tag{11}$$

so that eq 10 involves only one variable, r^*_{XH}. Obviously the transition state occurs when $dE/dr^*_{XH} = 0$; r^*_{XH} can be evaluated at that point and used in eq 4 and 5 to obtain the energy of the three-body system at the transition state. The "classical" energy of activation will be the difference between E calculated at r^*_{XH} and D_e(X–H). A correction can be applied for zero-point energy (ZPE) effects by the approximation of eq 12.

$$\mathrm{ZPE}^* = 0.5(\mathrm{ZPE}_{XH} + \mathrm{ZPE}_{HY}) \tag{12}$$

Since our approach considers only a three-body system, only the characteristics of the reacting bonds are involved in evaluating the Morse functions and ZPE effects and only the masses of the three atoms directly involved in the reactions have been used in the calculation of μ values.

In this derivation the most obvious first approximations have been made in order to obtain the simplest

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possible function (eq 10). As with all approximations, their justification is a successful outcome of the calculation. The energies of activation calculated by methods such as ours have been described as akin to $\Delta H^\dagger$ (the enthalpy of activation in the transition-state theory approach to reaction-rate theory) rather than to E_a, the Arrhenius activation energy.[35] However, uncertainties in the experimental values and approximations in our method make such differences insignificant for our purposes. E^* will denote our calculated values.

Results

The results of our calculations for gas-phase hydrogen abstractions of known energies of activation and for which all the necessary molecular data appear to be well established are tabulated in Table I. The data used to calculate the E^* values given in Table I are given in Table II; a few of the values deserve some comment and this is given in the section on Data.

Table I. Gas-Phase Hydrogen-Abstraction Reactions

Reaction	Calcd E^*, kcal/mol	Exptl E_a, kcal/mol
$H–H + CH_3\cdot$	11.7	10–13
$CH_3–H + CH_3\cdot$	13.7	13.8–14.8
$CH_3CH_2–H + CH_3\cdot$	11.0	10–12
$(CH_3)_2CH–H + CH_3\cdot$	10.3	9–10.5
$(CH_3)_3C–H + CH_3\cdot$	7.6	6.6–9
$c\text{-}C_6H_{11}–H + CH_3\cdot$	9.3	8.3–9.5
$(CH_3)_3CCH_2–H + CH_3\cdot$	10.9	10–11
$CH_3OCH_2–H + CH_3\cdot$	8.9	8.4–10
$CH_3O–H + CH_3\cdot$	10.0	6.5–9
$HOCH_2–H + CH_3\cdot$	8.7	8–10
$Br–H + CH_3\cdot$	1.7	1–2
$CCl_3–H + CH_3\cdot$	6.4	5.8–6.8
$HO–H + CH_3\cdot$	20.3	20–25
$SiH_3–H + CH_3\cdot$	7.1	7
$H–H + H\cdot$	9.3	7–9.4
$CH_3–H + H\cdot$	11.5	5–13.5
$CH_3CH_2–H + H\cdot$	7.0	6.8–10
$Br–H + H\cdot$	0.7	0.9
$CH_3–H + CH_3O\cdot$	10.4	7–11
$CH_3CH_2–H + CH_3O\cdot$	7.4	7
$(CH_3)_2CH–H + CH_3O\cdot$	6.1	5.2
$(CH_3)_3C–H + CH_3O\cdot$	4.2	4.1
$(CH_3)_3CCH_2–H + CH_3O\cdot$	7.7	7.3
$H–H + Br\cdot$	17.4	18–20
$CH_3–H + Br\cdot$	18.2	17.3–18.3
$(CH_3)_3C–H + (CH_3)_3CO\cdot$	3.3	4
$CH_3–H + HO\cdot$	5.3	5–7
$H–H + CH_3CH_2\cdot$	13.2	11.3–15.9
$CH_3CH_2–H + CH_3CH_2\cdot$	14.2	14.1

There have been many investigations of the abstraction by methyl radicals from H_2, and the results show some scatter. Values of $E_a = 10 \pm 0.5$[36–38] as well as higher values of 13 ± 2[39] and 13.5 ± 1[40] have been reported; with $CD_3\cdot$, a value of 11.1 has been given.[36] For abstraction from D_2, $E_a = 11.8$,[36,37] 12 ± 1,[40,41]

Table II. Data Used for Table I

Molecule and bond	D_0,[a] kcal/mol	r_e,[b] Å	ν,[c] cm^{-1}
$H–H$	104.2	0.742	4395.2
$CH_3–H$	104	1.09	2967[d]
$CH_3–CH_3$	88	1.54	993
$CH_3CH_2–H$	98	1.09	2952[d]
$CH_3CH_2–CH_3$	85	1.54	960[d]
$(CH_3)_2CH–H$	94.5	1.09	2890[d]
$(CH_3)_2CH–CH_3$	84	1.54	920[e]
$(CH_3)_3C–H$	91	1.09	2890[f]
$(CH_3)_3C–CH_3$	80	1.54	900[g]
$(CH_3)_3CCH_2–H$	99[h]	1.09	2952[i]
$(CH_3)_3CCH_2–CH_3$	84	1.54	960[j]
$c\text{-}C_6H_{11}–H$	94	1.10[k]	2898[d]
$c\text{-}C_6H_{11}–CH_3$	83[l]	1.54	920[m]
$CH_3OCH_2–H$	93.3	1.09	2906
$CH_3OCH_2–CH_3$	83.3	1.54	937[n,p]
$CH_3O–H$	103.6	0.96	3682
$CH_3O–CH_3$	81.5	1.43	1015[d]
$HOCH_2–H$	93.5	1.09	2924[d]
$HOCH_2–CH_3$	83.5	1.54	946[n]
$Br–H$	87.5	1.414	2649.7
$Br–CH_3$	69.2[o]	1.92	717[n]
$CCl_3–H$	95.6	1.095	3020[p]
$CCl_3–CH_3$	84	1.55[q]	1075[r]
$HO–H$	119	0.96	3704[d]
$HO–CH_3$	91.5	1.43	1034
$SiH_3–H$	94[s]	1.48[t]	2188[t,d]
$SiH_3–CH_3$	87[c,t]	1.87[w]	800[f]
$CH_3CH_2–OCH_3$	81.5	1.43[u]	1031
$(CH_3)_2CH–OCH_3$	82	1.43[u]	1023[n]
$(CH_3)_3C–OCH_3$	81.5	1.43[u]	1030[u]
$(CH_3)_3CCH_2–OCH_3$	81.5	1.43[u]	1031[u]
$(CH_3)_3CO–H$	105.3	0.96	3682[u]
$(CH_3)_3C–OC(CH_3)_3$	81.5	1.43[u]	1030[u]
$F–H$	135.8	0.92	4138
$F–CH_3$	109[o]	1.42	1100[f]
$CH_2CHCH_2–H$	88.4	1.09	2895
$CH_2CHCH_2–CH_3$	74.5	1.55	850[v]
$CH_3CH_2–CH_2CH_3$	82	1.54	927[u]

[a] Values given in ref 1, and D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969), and S. W. Benson *et al.*, *ibid.*, **69**, 279 (1969), or calculated from ΔH_f° values given therein, unless otherwise indicated. [b] Values from L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, and from "International Tables of X-Ray Crystallography," as quoted in "Handbook of Chemistry and Physics," 47th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967, unless otherwise indicated. [c] Values from T. Shimanouchi, "Tables of Molecular Vibrational Frequencies," NSRDS-NBS 6, 11, 17, National Bureau of Standards, Washington, D. C., 1968; G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, Van Nostrand, New York, N. Y., 1950; and G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1945, unless otherwise indicated. [d] Average of symmetric and asymmetric stretching vibrations. [e] H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952). [f] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958. [g] Recommended average value for complex molecules in footnote *c*. [h] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [i] By analogy from ethane. [j] By analogy from propane. [k] B. Beagley, D. P. Brown, and J. J. Monaghan, *J. Mol. Struct.*, **4**, 233 (1969). [l] Estimated. [m] By analogy from isobutane. [n] See discussion in text. [o] S. Furuyama, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 7564 (1969). [p] "Sadtler Standard Spectra," Sadtler, Philadelphia, Pa. [q] By interpolation from $H_3C–CH_3$, $r_e = 1.54$, and $Cl_3C–CCl_3$, $r_e = 1.56$ Å. [r] K. S. Pitzer and J. L. Hollenberg, *J. Amer. Chem. Soc.*, **75**, 2219 (1953). [s] W. C. Steele, L. D. Nichols, and F. G. A. Stone, *ibid.*, **84**, 4441 (1962). [t] G. R. Wilkinson and K. M. Wilson, *J. Chem. Phys.*, **44**, 3867 (1966). [u] By analogy from similar simpler compounds. [v] N. Sheppard, *J. Chem. Phys.*, **17**, 74 (1949). [w] R. E. Wilde, *J. Mol. Spectrosc.*, **8**, 424 (1962).

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14.2 ± 0.6,[40] 12.7 ± 0.5,[42] 12.1 ± 0.6,[43] 11.9,[44] and 12.0 ± 0.7[45] have been obtained. The compilation of Trotman-Dickenson[46] recommends $E_a = 10$, but a recent critical evaluation of all kinetic data for the forward and the reverse reaction and the deuterated analogs, using recent values of bond strengths, concludes that $E_a = 12.2$;[47] our calculated value of 11.7 is in agreement.

Abstraction by $CD_3\cdot$ from CH_4 has been reported to occur with $E_a = 14.1$[48] and with $\Delta H^\dagger = 13.8$.[49] Abstractions by $CD_3\cdot$ have often been considered to occur with the same E_a as those by $CH_3\cdot$, although the former might be expected to be a little more facile.[50] We calculate $E^* = 13.7$ in good agreement with the experimental values.

Abstraction by methyl radicals from ethane has been reported to occur with $E_a = 12$,[51] 10 ± 1,[52] 10.4 ± 0.4,[53] and $\Delta H^\dagger = 11.2 \pm 0.3$.[54,55] Abstractions from the deuterated analogs are consistent with a value near 11;[56] our calculated $E^* = 11.0$ is in agreement.

Abstraction of a secondary hydrogen from propane by methyl radicals has been reported with $\Delta H^\dagger = 9.7$.[57] Abstractions of a secondary deuterium from propane[58,59] and *n*-butane[60] have been reported with $E_a = 11.7$; since abstraction of deuterium in this type of reaction requires an activation energy about 1.5 kcal/mol greater than abstraction of hydrogen,[57] it appears that a value near 10.2 is indicated for this reaction. We obtain $E^* = 10.3$.

Abstraction of a tertiary hydrogen from isobutane by methyl radicals has been reported with $\Delta H^\dagger = 7.6$ and the results with deuterated analogs are in agreement.[57] These results agree with the concensus[61] that for tertiary hydrogens $E_a = 7.5 \pm 0.5$. We obtain $E^* = 7.6$.

The most recent value of E_a for hydrogen abstraction from cyclohexane by methyl radical is 9.5,[62] higher than two older values of 8.3 ± 0.3.[63,64] We calculate $E^* = 9.3$.

For abstraction by methyl radicals from neopentane $E_a = 10$,[53] 10.4,[63] and 10.8[65] have been reported. We obtain $E^* = 10.9$.

For abstraction by methyl radicals from dimethyl ether $E_a = 10$,[66] 9.5,[64] and 8.4[67] have been reported; $E^* = 8.9$.

Abstractions by methyl radicals from methanol have been reported to occur with $E_a = 8.2$,[64] 8.7,[68] and 8.4[69] from the whole molecule. Agreement is less satisfactory when a distinction between the hydroxylic and the methyl hydrogens was attempted. One investigation reported $E_a = 6.4$ for abstraction of the hydroxylic hydrogen and 10.4 for abstraction of the methyl hydrogens (11.7 for abstraction of methyl-*d*).[68] The reverse order of reactivity was found in another work; abstraction of the hydroxylic hydrogen is reported with $E_a = 9$ and of the methyl hydrogens with $E_a = 8.1$ (9.3 for methyl-*d*).[69] Additional data indicate that abstraction occurs preferentially from the methyl group, but the values of E_a found for various isotopically substituted alcohols are not self-consistent; the overall study appears to indicate $E_a = 8$–10 for methyl hydrogen abstraction.[70] We obtain $E^* = 10.0$ for the hydroxylic hydrogen and 8.7 for the methyl hydrogens. This agrees with many reports that $HOCH_2\cdot$ is observed during abstractions of hydrogen by radicals from methanol, and not $CH_3O\cdot$.[71] Our results are compatible with the values for the whole molecule and with the apparent concensus as to the relative reactivity of the two types of hydrogen in methanol, but also point out that the difference is not very large despite a difference of 10 kcal/mol in the exothermicity of the two abstractions.

Hydrogen abstraction from H–Br by methyl radicals has been reported to occur with $E_a = 1.5$[72] and 1.4;[73] we obtain $E^* = 1.7$.

Abstraction of hydrogen from chloroform by methyl radicals has been reported with $E_a = 5.8$[74] and 6.8;[75] reservations have been expressed for the lower value.[76] We calculate $E^* = 6.4$.

Abstraction of hydrogen from water by methyl radicals apparently has not been studied directly but $E_a = 24.7$ has been used at high temperatures.[77] From

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the reverse reaction[78,79] E_a = 20–21 can be estimated. We obtain E^* = 20.3.

Abstraction from silane by methyl radicals has been reported with $E_a = 7.0 \pm 0.6$,[80] and 6.9.[81] We calculate E^* = 7.1, in good agreement.

The system H_2 + H· has received considerable attention; recent experimental values for E_a have been 7.6 for D· + H_2 and 9.4 for H· + D_2.[82] When a tunneling factor is included in the expression describing the temperature dependence of the experimental rate constant, the activation energy is found to be 9.2 for H· + H_2 and 9.4 for D· + H_2.[83] The need for taking tunneling into account is evident in the above four cases; plots of log k_{exp} *vs.* $1/T$ show curvature below 450°K, most pronounced with the data for H· + H_2, as might be expected. Activation energies for different isotopic species have been described as being quite similar,[84] although tunneling will differ substantially. Extensive calculations by the variation method have shown that experimental rate constants can be described by assuming an activation energy of 9.35.[84,85] A "classical" barrier height of 9.13 has been used to describe the temperature dependence of the rate constant in a calculation which results in an observable E_a of 7.4 in a plot of log k *vs.* $1/T$; the discrepancy arises from the complex temperature dependence of the model which includes all angles of approach.[5] All earlier experimental evidence is also consistent with an "observable" Arrhenius activation energy of 8.0 ± 0.5,[22,86] for H· + H_2 and the recent theoretical and experimental work indicates a "classical" energy barrier near 9.2. Our calculated E^* = 9.33 is the "classical" barrier height, since our ZPE correction (eq 12) is zero for symmetrical reactions such as this.

The data for the reaction of hydrogen atoms with methane show wide scatter; much of the information comes from ignition techniques, with which it is difficult to obtain quantitative data for the calculation of activation energies.[61] Available data include the following values for E_a: 6.6,[87] 4.5,[88] 11.5,[89] 7.4,[90] 13.5,[91] 8.5,[45]and a recommended value of 9.6.[46] The most recent value of E_a = 11.8[92] agrees with a recent review giving 11.9.[47] Our value of E^* = 11.5 is in good agreement.

The data for the reaction of hydrogen atoms with ethane also exhibit large scatter with values of E_a = 6.8[93] 9.0,[94] 9.7,[95] 9.0,[96] and 6.5 for abstraction by D·;[45] using data from the reverse reaction,[97] a value of 5.1 can also be calculated. E^* = 7.04 is compatible with the available data.

Attack by a hydrogen atom on HBr has been reported to proceed with E_a = 0.9 for hydrogen abstraction.[61,98] E^* = 0.7.

Data for the abstraction of hydrogen by methoxy radicals do not appear to be available for methane, but from the reverse reaction E_a = 7–11 can be estimated.[68,69] Table I lists data for hydrogen abstractions by methoxy radicals from other hydrocarbons; these are single experiments pertaining to the whole molecule.[99,100] Our calculated E^* is in good agreement.

Abstractions by bromine atoms from H_2 have been investigated several times; critical reviews have appeared recommending E_a = 17.8[101] and 19.7 at higher temperatures.[2] Our calculated E^* = 17.4 is in agreement. Results with various isotopic combinations of hydrogen also support this value.[46]

For abstraction from methane by bromine reported values include $E_a = 18.2 \pm 0.5$,[102] 18.3,[103] and 17.3.[104] We obtain E^* = 18.2, only as an estimate because of uncertainty in the value of the proper C–Br stretching vibration (see Data).

Abstractions by the *tert*-butoxy radical have not been studied extensively in the gas phase. There is a value of E_a = 4 for abstraction from isobutane.[105] Since the radical is known to be quite selective,[106] the value for the whole molecule can be assumed to be a little higher than for the tertiary hydrogen. We calculate E^* = 3.3, in good agreement despite the relative complexity of the molecules involved.

Data on abstractions by hydroxy radicals from methane are rather scattered,[46] but recent values include E_a = 7.4[107] and a review giving 5 ± 1.[79] We calculate E^* = 5.3

Abstraction by ethyl radicals from H_2 has been reported with E_a = 11.5[108] and 11.3;[97] a survey of the data for the forward and the reverse reaction recommends 15.9.[46] We obtain E^* = 13.2. Abstraction from ethane also agrees well.[109,110]

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Evaluation and Additional Cases

In all the above cases the agreement between our calculated values of E^* and the generally accepted experimental values of activation energy is excellent. In fact, the values are in such good agreement that this success would be considered fortuitous were it not for the variety of reactions treated. The above reactions were chosen because the necessary data (bond dissociation energies, lengths, and stretching frequencies) are known rather accurately, which is not the case in general. We find that the approximation made in eq 11 holds quite well, probably reflecting the fact that in calculations of bond energies in stable molecules the energy is not very sensitive to the equilibrium separation used in the model.[111] Equation 11 fails as expected when ΔH becomes large. We find that for $\Delta H > \pm 15$, the calculation becomes unreliable. Table I generally lists reactions within these limits. Some examples of reactions outside this range of ΔH are as follows (experimental E_a in parentheses): $CH_3\cdot + CH_2CHCH_2\text{–}H$, $E^* = 6.1$ (7.5 ± 1),[46] $\Delta H = -16$; $CH_3\cdot + C_6H_5CH_2\text{–}H$, $E^* = 4.5$ (7–9),[46] $\Delta H = -19$; $HO\cdot + CH_3CH_2\text{–}H$, $E^* = 2.2$ (4–7),[46] $\Delta H = -21$; $F\cdot + H\text{–}H$, $E^* = 26.5$ (?), $\Delta H = -32$. However, for $F\cdot + CH_3\text{–}H$, $E^* = 1.4$ (1.2 ± 0.8),[112] $\Delta H = -32$; also abstractions by bromine (Table I, $\Delta H = +17$) appear to be calculated accurately. It should be noted that, when the approximation does fail because of a very skew potential energy diagram, it predicts activation energies that are invariably too low; *i.e.*, the failure is predictable and in the expected direction.

In abstractions by chorine atoms from hydrogen and hydrocarbons, this method predicts activation energies that are too high. It does not appear that it is a question of electronegativity; bromine atoms and oxy radicals do not present any difficulty. Significantly, the BEBO method also predicts high in such cases.[25,34]

Within the limitations outlined above, we have not encountered any failures in cases for which molecular data and activation energies are well established. Some of the most interesting cases treated involve reactions within the acceptable range of ΔH but yielding apparently erroneous calculated activation energies. Some of these are discussed below.

Hydrogen abstraction from ammonia by methyl radicals is known to occur with an activation energy near 10; $E_a = 9.8 \pm 0.9$,[113] 10.0 ± 0.2,[114] and 10.0 ± 0.4.[64] The stretching frequencies needed for the calculation are well known (Table III); using the accepted[1,115–117] values of $D_0(H_2N\text{–}H) = 103$ and $D_0(H_2N\text{–}CH_3) = 79$, we calculate a low value of $E^* = 8.5$. Recent preliminary data from very low pressure pyrolysis (VLPP) work indicate that bonds to nitrogen are often stronger than were thought heretofore.[118] We will employ our calculation to assign BDE values to several bonds to nitrogen; this type of approach has been used often with Polanyi-type relations.[116] However, whereas the Polanyi relation is applicable only to reactions of some radicals with a series of compounds of the same class,[119] usually alkanes, our method should be more useful in this application since it has been shown to apply equally well to quite different classes of compounds with a variety of radicals.

Table III. New Assignments and Additional Data

Molecule and bond	D_0, kcal/mol	r_e,[b] Å	ν,[c] cm^{-1}
$NH_2\text{–}H$	105[a]	1.01	3390[d]
$NH_2\text{–}CH_3$	81[a]	1.48	1044[e]
$CH_3NH\text{–}H$	97[a]	1.01	3320[d,f]
$CH_3NH\text{–}CH_3$	78[a]	1.48	1030[a,d,g]
$NH_2NH\text{–}H$	96[a]	1.01	3330[d]
$NH_2NH\text{–}CH_3$	78[a]	1.48	1027[h]
$C_6H_5CH_2\text{–}H$	85[i]	1.09	2895[d]
$C_6H_5CH_2\text{–}Br$	56.7[i]	1.92	602[j]
$CH_3COCH_2\text{–}H$	96[a]	1.09	2981[d]
$CH_3COCH_2\text{–}CH_3$	83[a]	1.54	946[g]
$CH_3COCH_2\text{–}Br$	62[a]	1.92	660[k]
$CF_3\text{–}H$	104[l]	1.10	3031[m]
$CH_3S\text{–}H$	89[n]	1.33	2575[o]
$CH_3S\text{–}CH_3$	74.5[i,n]	1.82	717[d,p]
$Cl\text{–}H$	103[i]	1.275	2990
$Cl\text{–}Cl$	57.8[i]	1.99	565

[a] Assigned in this work; see Discussion in text. [b] Footnote *b*, Table II. [c] Footnote *c*, Table II. [d] Footnote *d*, Table II. [e] Footnote *f*, Table II. [f] J. R. Durig, S. F. Bush, and F. G. Baglin, *J. Chem. Phys.*, 49, 2106 (1968). [g] Footnote *p*, Table II. [h] Average of skeleton stretching vibrations at 1246 and 808 cm^{-1}: J. R. Durig, W. C. Harris, and D. W. Wertz, *J. Chem. Phys.*, **50**, 1449 (1969). [i] Footnote *a*, Table II. [j] N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964. [k] G. A. Crowder and B. R. Cook, *J. Chem. Phys.*, **47**, 367 (1967). [l] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965). [m] S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **21**, 1129 (1953). [n] L. Batt and S. W. Benson, *ibid.*, **36**, 895 (1962); T. F. Palmer and F. P. Lossing, *J. Amer. Chem. Soc.*, **84**, 4661 (1962). [o] N. Sheppard, *J. Chem. Phys.*, **17**, 79 (1949). [p] J. R. Alkins and P. J. Hendra, *Spectrochim. Acta*, **22**, 2075 (1966).

We assign $\Delta H_f°(H_2N\cdot) = 42$,[120] compared to older values of 40 ± 2[1] and 41.[121] This assignment leads to $D_0(H_2N\text{–}H) = 105$ and $D_0(H_2N\text{–}CH_3) = 81$ when combined with the heats of formation of the stable molecules.[115] With the above BDE values we obtain $E^* = 10.2$ for the reaction between methyl radicals and ammonia.

For the reaction $H\cdot + H_2NNH_2 \rightarrow H_2 + H_2NNH\cdot$, only one value exists, $E_a = 2$.[122] With an assigned value of $D_0(H_2NNH\text{–}H) = 96$, we obtain $E^* = 2.16$. From $\Delta H_f° = 22.8$[115] and the above value of BDE, we obtain $\Delta H_f°(H_2NNH\cdot) = 66.7$; from $\Delta H_f°(H_2NNH\text{–}CH_3) = 22.3$ and $\Delta H_f°(CH_3\cdot) = 34$.[115] we obtain $D_0(H_2NNH\text{–}CH_3) = 78$. The two values of BDE thus obtained may be tested as data in the reaction $CH_3\cdot + H_2NNH_2 \rightarrow CH_4 + H_2NNH\cdot$; we obtain $E^* = 5.4$, in agreement with the single available measurement of $E_a = 5$.[113] Such agreement is a significant indication of consistency in the new assignments which are tested further below.

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For the reaction $CH_3\cdot + CH_3NH_2 \rightarrow CH_4 + CH_3NH\cdot$, $E_a = 5.7 \pm 0.4$[123] and 6.0 ± 0.5[124] have been reported. Using the accepted values of $D_0(CH_3NH\text{-}H) = 92$ and $D_0(CH_3NH\text{-}CH_3) = 73$,[116] we obtain $E^* = 3.3$ in obvious disagreement with experiment. Assigning $D_0(CH_3NH\text{-}H) = 97$ and correspondingly $D_0(CH_3NH\text{-}CH_3) = 78$, we obtain $E^* = 6.0$. Thus $\Delta H_f{}^\circ(CH_3NH\cdot) = 39.4$, compared with an existing estimate of 34.5.[1,116] Combining $\Delta H_f{}^\circ$ for the amino and the methylamino radicals with the heat of formation of methylhydrazine,[115] we obtain $D_0(CH_3NH\text{-}NH_2) = 59.1$ compared to 52 that can be calculated from the older data.[115-117] VLPP also has indicated higher values for N-N BDE's in hydrazines than were reported heretofore.[118] Also from $\Delta H_f{}^\circ(CH_3NHNHCH_3) = 21.6$,[115] we calculate $D_0(CH_3NH\text{-}NHCH_3) = 52.7$ compared to the accepted value of 47.[116]

For the reaction $Br\cdot + C_6H_5CH_3 \rightarrow HBr + C_6H_5CH_2\cdot$, using the data given in Table III, we obtain $E^* = 8.4$. One investigation reported $E_a = 7.2$ and 8.0 from two series of experiments differing in light intensity used for the gas-phase photobromination of toluene.[125] Our calculated value appears to be within the expected accuracy of the method from the high value. The photobromination study has been criticized;[126-128] nevertheless, both the experimental and the calculated values of the energy of activation predict roughly comparable reactivities for toluene and 2,3-dimethylbutane (for which $E_a = 7.5 \pm 0.2$)[103] toward $Br\cdot$, especially since the preexponential term would be expected to favor the primary hydrogen of toluene. Indeed such has been found to be the case (about 3:1 in favor of toluene, per hydrogen) in competitive brominations in the liquid phase.[128,129]

The reaction $CH_3COCH_3 + CH_3\cdot \rightarrow CH_4 + CH_3COCH_2\cdot$ has been studied extensively and is an important standard; $E_a = 9.6 \pm 0.2$ satisfies the numerous reported values.[43,130-135] $D_0(CH_3COCH_2\text{-}H) = 92$ has been used[116] until recently when values of 98 ± 2.7[136] and 98.3 ± 1.8[119] were reported. From the accepted heats of formation[115] of the compounds we obtain $D_0(CH_3COCH_2\text{-}H) - D_0(CH_3COCH_2\text{-}CH_3) = 12.8$. Using the older BDE values we obtain $E^* = 6.3$, a clear indication that these values are too low; on the other hand, use of the latest value of 98 leads to $E^* = 11.5$, an indication that this value may be too high. $E^* = 9.7$ is calculated with $D_0(CH_3COCH_2\text{-}H) = 96$ and we have assigned this value for acetone (Table III). Actually the agreement between the two different approaches may be better than indicated. The value of 98.3 ± 1.8 for acetone was based on a series of measurements of the rate constant for the reaction $CH_3COCH_3 + Br\cdot \rightarrow HBr + CH_3COCH_2\cdot$ at six temperatures between 261.8 and 345.0°; $E_a = 13.9 \pm 0.6$ was found. However, the rate expression for the reaction was found to become complex at 251° or lower. If the observations at 261.8° are excluded as being too close to the doubtful region (6 out of 51 total reported observations), a least-squares fit to the remaining points gives $E_a = 12.85$ which leads to $D_0(CH_3COCH_2\text{-}H) = 97.3 \pm 1.8$, in good agreement with the value deduced from our method.

Although energies of activation for hydrogen abstractions from acetone by other radicals are available, the necessary BDE values and particularly the vibrational frequency assignments for $CH_3COCH_2\text{-}X$ are not well known so that it is not possible to simulate many of these reactions with confidence. However, a further check on the value of 96 proposed above for the BDE in acetone can be performed with a simulation of the reaction $Br\cdot + CH_3COCH_3 \rightarrow HBr + CH_3COCH_2\cdot$, for which $E_a = 13\text{-}14$.[119] $D_0(CH_3COCH_2\text{-}Br)$ is not known well but $\nu = 660\ cm^{-1}$ has been reported for the gas-phase stretching vibration of the bond.[137] From BDE values of C-Br in similar compounds, we estimate $D_0(CH_3COCH_2\text{-}Br) = 62$; the use of this value in the calculation leads to $E^* = 13.7$, a reasonable estimate.

Abstractions by the trifluoromethyl radical have been intriguing in that they occur with lower energies of activation than the corresponding abstractions by methyl radicals, even though the strength of the C-H bond formed is not much different.[138] There is some doubt concerning $D_0(CF_3\text{-}H)$, with values of 102.6,[121] 104,[117] 105.6,[139] and 106[140] being used; the difficulties of making a choice have been discussed.[116] For $CF_3\cdot + CH_4 \rightarrow CF_3H + CH_3\cdot$, reported values are $E_a = 10.3$,[141] 10.6,[142] 11.0,[143] and 11.3.[144] For the reverse reaction $E_a = 10.4$,[145] which supports the lower values of BDE in fluoroform. For the reaction $CF_3\cdot + H_2$, the use of $D_0(CF_3\text{-}H) = 104$ leads to $E^* = 11.1$ in excellent agreement with the most recent work on various isotopes of hydrogen over a 540° range; $E_a = 11.04$ above 200°.[146] An older value of $E_a = 9.5 \pm 0.7$ was obtained over a narrower temperature range.[147] Unfortunately reliable molecular data are not available for calculations on other reactions of $CF_3\cdot$

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For the reaction $H\cdot + CH_3SH \rightarrow H_2 + CH_3S\cdot$, we calculate $E^* = 2.9$. Direct experimental evidence is not available for comparison, but E_a has been reported to be 0.5 kcal/mol higher than that for $H\cdot + CH_2{=}CH_2 \rightarrow CH_3CH_2\cdot$,[148] implying $E^* = 2.4$ for the latter reaction. This value is in good agreement with the trend to be expected from $E_a = 1.4$ for addition of $H\cdot$ to isobutylene,[149] and $E_a = 2.2$ assumed for addition to propylene.[150]

Data

Table II includes few values that require additional comment.

The value of 717 cm^{-1} used for the C–Br stretching vibration in methyl bromide is based on the recommended[151] value for the average force constant for C–Br (3.13 mdyn/Å). Since R–Br stretching frequencies are extremely variable and depend on the nature of R, the force constant was calculated from stretching, bending, and interaction constants of bromides and other molecules with the same groups.[152] Although the value of 717 cm^{-1} is higher than the frequencies usually observed with simple alkyl bromides, it is consistent with observed C–Br stretching frequencies of 700–750 cm^{-1} in equatorially substituted sterols.[153]

The frequency of 1023 cm^{-1} used for $(CH_3)_3CH$-OCH_3 in Table II is the average of the symmetric and asymmetric stretching frequencies in diisopropyl ether, as we interpret the ir spectrum.

Our method of calculating E^* for a reaction can be useful in making the proper stretching frequency assignment in some cases, specifically when the vibration is uncoupled. The C–C stretching frequency in CH_3–CCl_3 is a typical example, with values of 714,[154] 867,[155] 1005,[156] and 1075[157] cm^{-1} proposed for it at various times. For hydrogen transfer between chloroform and methyl radical, E_a is near 6.5 (Table I); using each of the frequencies above in sequence for the calculation of antibonding forces in the transition state for this reaction, we obtain $E^* = 20$, 13, 8.4, and 6.4, respectively. It is likely therefore that the highest proposed frequency is the correct one and that it is a relatively pure stretching vibration. The assignment is actually not in doubt, having been confirmed on the basis of Raman polarization measurements and other considerations.[158]

All necessary data are available and well established for the simulation of the reaction $CH_3\cdot + CH_3OH \rightarrow CH_4 + \cdot CH_2OH$, except for the C–C stretching frequency in ethanol for which assignments were not found. A value near 950 cm^{-1} is needed to produce an acceptable value for the calculated energy of activation; however, the ir spectrum of ethanol is devoid of any bands in the 900–1000-cm^{-1} region. We concluded that the C–C stretching vibration has shifted from its "inherent" position because of coupling with some other vibration, possibly with an O–H deformation. We therefore prepared CH_3CH_2OD (75% D) and obtained its ir spectrum: the C–C stretch appeared in the predicted region as a weak but well-defined band at 946 cm^{-1}. Confirmation of the assignment is furnished by a report that a series of similar compounds CH_3CH_2X, where X denotes an electronegative atom or group, exhibits the C–C stretching vibration at 970 ± 10 cm^{-1}.[159] Ethyl acetate, diethyl phthalate, ethyl acetoacetate, diethyl ether, etc., also show a characteristic weak absorbance, similar to that of CH_3CH_2OD, between 937 and 965 cm^{-1}, evidently the C–C stretch.

Care must be exercised in the selection and use of vibrational stretching frequencies as data. If the vibration is strongly coupled and its position shifted significantly, the method will appear to fail.

Discussion

The overall success of the method in predicting energies of activation within the expected error of reported experimental values provides adequate support for the approximations made in the derivation. Nevertheless it is of interest to relate some aspects of our procedure to previous work.

Applied to reaction 2, when A = B = C = hydrogen and the transition state is symmetrical, eq 10 simplifies to

$$E = 1.1(^1E_{AB}) + {}^3E_{AC} \qquad (13)$$

For the same case, the London equation (eq 3) simplifies to

$$E = A + (A + \alpha) + (C - \gamma) \qquad (14)$$

We obtain $r_1^* = r_2^* = 0.84$ Å for the transition state distances in this reaction; at this distance the Sugiura integrals give $A/(A + \alpha) = 0.1$.[20] Although other approaches give different values for the ratio above 1 Å, they all substantially agree for smaller distances.[3] It is thus seen that, since $A + \alpha = {}^1E_{AB}$ and $C - \gamma = {}^3E_{AC}$, the London equation reduces to our equation for the transition state of the hydrogen-exchange reaction. Therefore some of the arbitrariness of the choice of the factor 0.55 in eq 10 is removed.

The value of $f = 0.45$ used in eq 5 results in ${}^3E_{AC} = 16.5$ kcal/mol at 1.68 Å, which is the antibonding distance that we find in the transition state for the hydrogen-exchange reaction. The variational calculations of Kolos and Roothaan for this antibonding energy give ${}^3E \simeq 16.2$ at this distance.[31] Therefore both numerical parameters used in our calculation have been given reasonable values. Future refinements in our understanding of chemical reactions may show the method to be strictly an empirical algorithm, but at present the results obtained are of value.

We may now consider in some detail the implications of the results obtained. Table IV lists a series of reactions for which $\Delta H \simeq 0$, in order of increasing E_a. For the last six entries the strengths of the bonds broken and made are all essentially the same, near 104.

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Table IV. Reactions of $\Delta H \simeq 0$. Experimental E_a, Calculated E^*, and Calculated Antibonding Energies ^3E in the Transition State

Reaction	E_a	E^*	^3E
Br· + Br–H		4.4	11.1
HO· + HO–H		4.9	14.5
Cl· + Cl–H	6 6 ± 0.5[a]	5.1	13.0
H· + H–H	9.2	9.3	16.5
CH_3· + CH_3O–H	>9	10.0	17.2
CF_3· + H–H	11.0	11.1	17.6
H· + CH_3–H	11.8	11.5	18.1
CH_3· + CH_3–H	13.8	13.7	19.4

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Table V. E^* on Perturbation[a] of Each Parameter Independently in X–H + Y· → X· + H–Y (Unperturbed $E^* = 15.2$)

Parameter	X–H	H–Y	X–Y
$D_o' = D_o + 10$ kcal/mol	19.7	9.7	19.8
$r_e' = r_e + 0.10$ Å	11.9	11.9	18.9
$\nu' = \nu + 200$ cm^{-1}	15.6	15.5	9.6
$m' = m + 15$ amu	11.4	11.4	6.5[b]

[a] Possible errors in the choice of data would normally be much smaller than the perturbations applied here. [b] Both masses increased.

The activation energies, however, vary substantially, in an essentially unpredictable fashion. Only when antibonding energies are considered do these variations exhibit a reasonable pattern, with E_a reflecting the trend of increasing ^3E. The first two reactions in Table IV involve molecules differing by over 30 kcal/mol in the strengths of the bonds broken and made, but the calculated energies of activation are comparable; data are not available on these two reactions and experimental verification of these predictions will be a most striking way of demonstrating the importance of antibonding energies between terminal groups in the transition state.

In general, for reaction 8, the stronger the X–Y bond, the higher the value of E_{XY} and of E_a. Equally as important, the higher the stretching frequency, the lower $^3E_{XY}$. Since the width of the potential well given by the Morse equations is governed by the wavelength, short wavelengths lead to narrow potential wells, indicating a rapid decrease in both bonding and antibonding energies as the distance increases. This becomes of major importance at the relatively large distances between X and Y in the transition state.

The "polar effect," often invoked to explain differences in activation energies that cannot be explained in terms of the strengths of the bonds broken and made,[126,160] is an attempt to describe the importance of the polarity of the X–Y bond that we have treated quantitatively in terms of its BDE and its vibrational stretching frequency. The reaction of methyl radicals with the hydroxylic hydrogen of methanol (Table IV) is a typical demonstration of our method's ability to treat the "polar effect" quantitatively. Another notable example is provided by a comparison of the reactions of methyl radicals with ethane and chloroform. The molecular parameters for reactant and product C–H bonds are quite similar in the two reactions (Table II); however, $E_a = 11$ for abstraction from ethane and only about 6.5 for abstraction from chloroform, evidently a demonstration of the "polar effect" creating a difference of 10^4 on the rate at room temperature. The most substantial difference in the molecular data for the two reactions is $\nu_{XY} = 960$ and 1075 cm^{-1} for CH_3-CH_2-CH_3 and for CCl_3-CH_3, respectively; the higher frequency is partially due to the presence of a dipole in the C–C bond of the latter molecule. The change in dipole required for the ir-active vibration in CCl_3–CH_3 thus intensifies the existing charges, and more energy is required for this than would be with a less polar C–C bond. The higher frequency leads to a low value of $^3E = 16.5$ for abstraction from chloroform compared to $^3E = 19.4$ for abstraction from ethane. Thus the "polar effect" is treated quantitatively and the values of E^* calculated for these reactions are in remarkable agreement with experiment.

A striking feature of Table IV is that the antibonding energies are substantially greater than the energies of activation. This implies that net bond making is more extensive than bond breaking (in terms of binding energies) in the transition state, and that the activation energy serves to overcome the antibonding interactions of the terminal groups. This phenomenon is implied for almost all reactions discussed, the H_2 + Br· reaction being a notable exception. If these results are to be taken as meaningful they would conflict with the often expressed notion that "the energy of activation is needed to help break the bond, since in general the stability of the bonds being broken is lost before the new stable bonds are completely formed."[161] It would appear that quite the contrary happens in hydrogen transfer reactions, with resonance I ↔ II causing an increase in the total binding energy in the transition state; usually this increase partially compensates for antibonding in X–Y.

Another common belief regarding variation in E_a in a series of thermoneutral reactions such as shown in Table IV, to the effect that "atoms react faster than multiatomic radicals because bond reorganization occurs in the latter in the transition state,"[160] is clearly not adquate to explain the facts.

The effect of various molecular parameters on E^* is summarized in Table V. For a model reaction of the type shown in eq 8, we obtain $E^* = 15.2$ with the following data: $D_0(\text{X-H}) = D_0(\text{H-Y}) = 90$, $D_0(\text{X-Y}) = 70$; $r_{XH} = r_{HY} = 1.0$, $r_{XY} = 1.5$ Å; $\nu_{XH} = \nu_{HY} = 2800$, $\nu_{XY} = 800$ cm^{-1}; $m_X = m_Y = 15$, $m_H = 1$ amu. When each of the parameters is increased independently by the amounts indicated in Table V, the values of E^* change in the expected direction; the importance of bond lengths and masses, however, is worth noting. Table V also reiterates the major significance of the molecular parameters of X–Y. This independent change of one parameter at a time nevertheless is an unrealistic model; the variations observed also serve as a measure of the influence of possible errors in the choice of data to be used in the calculation.

The calculations were performed on an IBM 1130 computer; the time required is about 1 sec per reaction. A copy of the program in Fortran IV is available on request.

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Effects of Paramagnetic Lanthanide Shift Reagents on the Proton Magnetic Resonance Spectra of Quinoline and Pyridine

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Abstract: Chemical shifts, line broadenings, and longitudinal relaxation rates are reported for CCl_4 solutions of quinoline and pyridine containing the paramagnetic shift reagents $Eu(DPM)_3$ and $Pr(DPM)_3$. It is found that the induced isotropic shifts are stereospecific and therefore likely to be of dipolar pseudocontact origin. The line broadening is a result of the chemical shift difference between the complexed and uncomplexed states of the substrate, whereas the longitudinal relaxation rate is enhanced due to the electron–nuclear dipolar interaction. Evidence is presented for the existence of chemical-exchange spin decoupling in these systems. The dissociation constant of the $Eu(DPM)_3$–quinoline adduct in CCl_4 is estimated to be 0.07 *M* and its mean lifetime 2×10^{-7} sec. The mean lanthanide–nitrogen distance in the adducts is estimated to be 4.0 Å.

The possibility of utilizing specific electron–nuclear interactions with paramagnetic ions to resolve accidental degeneracies in nmr spectra was realized already in 1960 in an oxygen-17 nmr study of cation hydration.[2] Subsequently proton spin–spin coupling constants have been evaluated from the spectra of the paramagnetic nickelous aminotroponeimineates.[3] It was not until recently, however, that paramagnetic shift reagents had an impact on organic nmr spectroscopy following the report by Hinckley that the dipyridine adduct of europium(III) tris(dipivalomethanate), $Eu(DPM)_3$, produces large and stereospecific chemical shifts in the spectrum of cholesterol.[4] Numerous communications reporting work with lanthanide shift reagents of this type have appeared since.[5] At an early stage it was found that the pyridine-free complex is more effective since pyridine competition with the substrate is avoided.[6] While $Eu(DPM)_3$ usually causes shifts toward lower fields,[4,6] the praseodymium (III) complex, $Pr(DPM)_3$, induces upfield shifts.[7]

Two phenomena caused by paramagnetic ions (or complexes) may generally be observed in the nmr spectra of organic molecules: chemical shifts and enhanced relaxation rates.[8] As a result of enhanced longitudinal relaxation of spin–spin coupled nuclei, chemical-exchange spin-decoupling may also occur.[9] The chemical shift arises from two types of interactions. Direct delocalization and/or spin polarization *via* the molecular orbitals places unpaired electron spin density in an atomic s orbital thereby causing a *contact* shift of the nuclear resonance of that atom.[10] For ions with anisotropic *g* tensors, such as the paramagnetic trivalent lanthanides [except for Gd(III)], the electron–nuclear dipolar interaction gives rise to the so-called pseudocontact shift. For a complex of axial symmetry with a tumbling time, τ, much greater than the electron spin relaxation time, T_{1e}, the pseudocontact shift is given by[11]

$$\delta_p/\nu_0 = -K_p F(r,\theta) G(g_\parallel, g_\perp) \qquad (1)$$

where

$$K_p = \beta^2 J(J+1)/45kT$$

$$F(r,\theta) = (3\cos^2\theta - 1)/r^3$$

and

$$G(g_\parallel, g_\perp) = (3g_\parallel + 4g_\perp)(g_\parallel - g_\perp)$$

The symbols in eq 1 are: β = the Bohr magneton, J = the resultant electronic-spin angular momentum (in $\hbar$ units), r = the distance from the metal ion to the nucleus, θ = the angle between the line joining these points and the principal axis of symmetry of the complex, and $g_\parallel$ and $g_\perp$ are the parallel and perpendicular components of the electronic *g* tensor with respect to this axis.

There is no unanimous agreement in the literature regarding the shifts induced by lanthanide shift re-

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