Ionization Energies and Entropies of Cycloalkanes. Kinetics of Free Energy Controlled Charge-Transfer Reactions

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Enthalpies and entropies of ionization (ΔH°_{ion} and ΔS°_{ion}) of alkylcyclohexanes, as well as cycloheptane, cyclooctane, and *trans*-Decalin, have been determined by charge-transfer equilibrium measurements. Values of ΔH_{ion}, in units of kcal mol^{-1} (or eV), range from 229.6 (9.96) for cycloheptane to 210.7 (9.14) for *trans*-Decalin. A major effect of alkyl substitution is observed following substitution at a site α to a tertiary hydrogen atom (as from methylcyclohexane to 1,2-dimethylcyclohexane), or following replacement of a tertiary hydrogen atom (as from methylcyclohexane to 1,1-dimethylcyclohexane). In both cases, ΔH°_{ion} decreases by ca. 5 kcal mol^{-1}. Entropies of ionization are near zero for alkylcyclohexanes but range up to 5 cal deg^{-1} mol^{-1} for nonsubstituted cycloalkanes (cyclooctane). The charge-transfer reactions involving the cycloalkanes are shown to be fast processes; i.e., the sum of the reaction efficiencies ($r = k/k_{collision}$) of the forward and reverse processes is near unity. The efficiencies of these processes appear to be determined uniquely by the overall free energy change (or equilibrium constant K). Specifically, the reaction efficiencies are defined, within a factor of 2 by the relation $r = K/(1 + K)$, which can be justified by using transition-state theory applied to the decomposition of a collision complex over surfaces lacking energy barriers. These reactions are defined as intrinsically fast processes in that they are slowed only by the overall reaction thermochemistry and not by any properties or reactions of the intermediate complex.

Introduction

Recently we reported a mass-spectrometric study of the gas-phase cationic charge-transfer equilibria occurring in the normal alkanes as a function of temperature.[1] Adiabatic ionization energies (ΔH_{ion}) were determined to within ±0.7 kcal mol^{-1} for a variety of molecules up to a chain length of 11 (undecane), and the effects of isotopic labeling and methyl substitution were also evaluated in a number of cases. The surprising result was the observation of large negative entropies of ionization (ΔS_{ion}) in C_7 and longer-chain alkanes, up to -13.9 cal deg^{-1} mol^{-1} in undecane. It was suggested that the negative (ΔS_{ion}) values were due to constrained cyclic conformations in the larger flexible molecular ions resulting from noncovalent intramolecular bonding. Similar effects had been observed previously in the protonation of diamines[2] and the ionization of diphenylalkanes.[3]

As an extension of that study, we decided to determine ΔH_{ion} and ΔS_{ion} for various alkylcyclohexanes. This class of compounds was chosen because the molecular ions are known[4] to be stable with respect to ring opening or isomerization, and little, if any, information concerning the thermochemistry of ionization is available since the thresholds obtained by photoionization/photoelectron spectroscopy are diffuse and difficult to interpret. The measurements were extended to cycloheptane and cyclooctane as well.

In addition to the thermochemical measurements we also determined the rate constants for many of the present charge-transfer reactions. With cyclic reactants steric inhibition should be minimal, and it should be possible to clearly assess the relation between thermochemistry and

kinetics. Previously[5] we observed that similar charge-transfer reactions were intrinsically fast; i.e., the efficiencies were affected only by the overall reaction thermochemistry, and the reactions were not inhibited by any properties of the reaction complex. It was found that the relation $r \approx K/(1 + K)$ between the reaction efficiencies and equilibrium constant applied for such reactions over a wide range of r and K, for a variety of reactions with different enthalpy and entropy changes. The present reactions were examined in the context of such intrinsically fast kinetics.

Experimental Section

Equilibrium measurements were carried out by using both the NBS high-pressure photoionization and pulsed ion cyclotron resonance (ICR) mass spectrometers, which have been described in detail elsewhere.[6,7] Materials used were of the highest purity commercially available, usually >99%, and were of the trans configuration. When the high-pressure instrument was used, mixtures for study were prepared by liquid volumetric dilution and then syringe-injected and vaporized into a 3-L reservoir interfaced to the reaction chamber by a micrometering valve and an associated vapor inlet system. Mixture composition was independently verified by GC analysis. Temperatures were adjusted to ensure that the ion source, the inlet system, and the sample reservoir were all within ±2 °C of the chosen temperature, although substantial changes in the reservoir temperature had a negligible effect on the observed equilibrium ion ratios. Ionization of the cycloalkanes was induced by photoionization at 123.6 and 116.5 nm (mixed radiation at 10.0 and 10.6 eV) provided by a microwave-powered krypton resonance lamp. Since the high-pressure instrument is not operated in a pulsed mode, all of the checks described in detail previously were per-

(1) Meot-Ner (Mautner), M.; Sieck, L. W.; Ausloos, P. *J. Am. Chem. Soc.* **1981**, *103*, 5342.

(2) (a) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1978**, 95, 3504. (b) Meot-Ner (Mautner), M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *Ibid.* **1980**, *102*, 6393.

(3) Meot-Ner (Mautner), M.; Hunter, E. P.; Hamlet, P.; Field, F. H.; Ausloos, P.; Sieck, L. W., presented at the 28th Annual Conference of the American Society for Mass Spectrometry, New York, 1980.

(4) Borchers, F.; Levsen, K.; Schwarz, H.; Wesdemiotis, C.; Wolfschutz, R. *J. Am. Chem. Soc.* **1977**, *99*, 1716.

(5) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.*, submitted for publication.

(6) (a) Sieck, L. W.; Searles, S. K.; Ausloos, P. *J. Am. Chem. Soc.* **1969**, *91*, 7627. (b) Sieck, L. W.; Searles, S. K. *Ibid.* **1970**, *92*, 2937.

(7) (a) Lias, S. G.; Ausloos, P.; Horvath, Z. *Int. J. Chem. Kinet.* **1976**, *8*, 725. (b) Lias, S. G.; Eyler, J. R.; Ausloos, P. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 219.

TABLE I: Equilibrium Constants, Rate Constants, and Reaction Efficiencies for Charge-Transfer Reactions $A^+ + B \rightleftarrows B^+ + A$ As Measured by ICR Mass Spectrometry

reaction no.	A	B	K^a	r_f^b	r_r^b	k_f^c	k_r^c	$\Delta G°$ d,e	$\Delta H°$ d,f	$\Delta S°$ f,g
1	c-C$_7$H$_{14}^+$	n-C$_6$H$_{14}$	0.026	0.029	0.89	0.35	11.1	2.4	0.6	−5.2
2	c-C$_6$H$_{11}$C$_2$H$_5$	c-C$_6$H$_{11}$CH$_3$	0.027	0.025	0.98	0.32	12.1	2.4	2.1	−0.7
3	c-C$_6$H$_{11}$-t-C$_4$H$_9$	C$_6$H$_5$F	0.061	0.065	1.0	0.79	12.0	1.9		
4	1,4-c-C$_6$H$_{10}$(CH$_3$)$_2$	c-C$_6$H$_{11}$CH$_3$	0.088	0.065	0.84	0.75	10.4	1.7	1.7	−0.1
5	c-C$_6$H$_{11}$-n-C$_3$H$_7$	c-C$_6$H$_{11}$C$_2$H$_5$	0.10	0.071	1.0	1.1	12.8	1.5	1.9	0.9
6	c-C$_8$H$_{12}$	c-C$_7$H$_{14}$	0.12	0.096	0.96	1.2	11.1	1.4	3.1	5.6
7	c-C$_8$H$_{12}$	c-C$_7$H$_{14}$	0.24^a	0.19^a	0.62^a	2.5^a	10.9^a	1.1^a	3.1	5.6
8	c-C$_8$D$_{12}$	c-C$_7$H$_{14}$	0.26	0.15	0.58	1.8	6.5	1.1	2.4	4.9
9	c-C$_8$D$_{12}$	c-C$_7$H$_{14}$	0.43^a	0.26^a	0.65^a	3.2^a	7.3^a	0.7^a	2.4	4.9
10	c-C$_6$H$_{11}$-sec-C$_4$H$_9$	1,2-C$_6$H$_4$F$_2$	0.34	0.20	0.73	2.8	9.3	0.7	1.3	1.8
11	c-C$_6$D$_{12}$	n-C$_7$D$_{16}$	0.67	0.25	0.28	2.9	3.3	0.3	−1.5	−5.7
12	c-C$_6$D$_{12}$	n-C$_7$D$_{16}$	0.38^a	0.12^a	0.49^a	2.0^a	5.2^a	0.6^a	−1.5	−5.7
13	C$_6$HF$_5$	c-C$_6$H$_{11}$CH$_3$	0.88	0.31	0.27	3.3	2.8	0.1	0.2	0.3
14	c-C$_6$H$_{11}$C$_2$H$_5$	1,2,3,4-C$_6$H$_2$F$_4$	0.77					0.2	−0.2	−1.0
15	c-C$_6$H$_{11}$C$_2$H$_5$	1,2,3,5-C$_6$H$_2$F$_4$	1.0					0.0	−0.3	−1.0
16	c-C$_8$H$_{16}^+$	n-C$_8$D$_{18}$	0.15	0.17	0.78	1.4	9.5	1.2	−1.1	−7.0

^{a} At $T = 335$ K, except reactions 7, 9, and 12, where $T = 400$ K. ^{b} $r_f = k_f/k_{ADO}$ and $r_r = k_r/k_{ADO}$, where k_{ADO} are collision rate constants calculated from ADO theory. Subscripts f and r refer to the forward reaction, i.e, as given in the table, and the reverse reaction, respectively. ^{c} In units of 10^{-10} cm^3 s^{-1}. ^{d} In units of kcal mol^{-1}. Also see note footnote a. ^{e} Obtained from $\Delta G° = -RT \ln K$, using ICR equilibrium constants. ^{f} From van't Hoff plots obtained by the high-pressure measurements, except for reaction 11, where $\Delta H°$ and $\Delta S°$ are obtained from ICR measurements at 335 and 400 K. ^{g} In units of cal mol^{-1} K^{-1}.
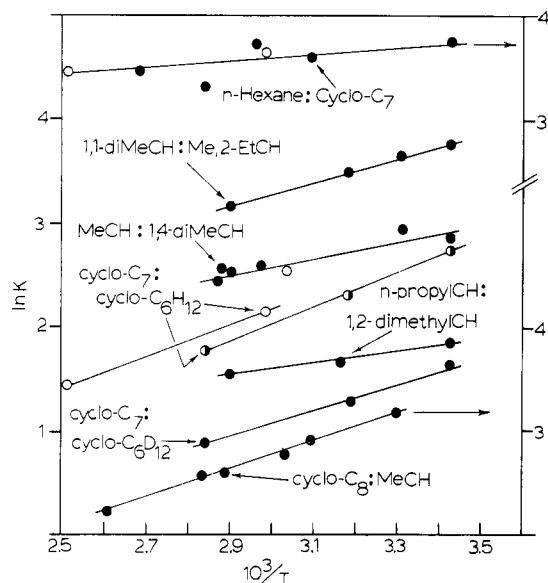

Figure 1. van't Hoff plots for selected reaction pairs. Each line designated as A:B, corresponding to the equilibrium $A^+ + B \leftrightarrow B^+ + A$. ICR data indicated by open circles.

Figure 2. van't Hoff plots for selected reaction pairs. Each line designated as A:B, corresponding to the equilibrium $A^+ + B \leftrightarrow B^+ + A$. ICR data indicated by open circles.

formed in order to verify that the ion ratio observed in a given measurement actually reflected the true charge-transfer equilibrium value. In order for values at a given temperature to be acceptable, the ion ratios were required to be insensitive to (i) changes in total pressure over a factor of at least 5, (ii) lamp intensity, (iii) mixture composition, and (iv) possible reaction with either photochemically generated neutral degradation products or impurities originally present in the starting material. When dissociative charge transfer was observed, even at very low levels, the value was also rejected. With very few exceptions, the cycloalkanes proved to be extremely clean systems in that they exhibited little primary fragmentation, achieved equilibrium rapidly, and showed little, if any, impurity involvement.

Unless otherwise noted, measurements involving the pulsed ICR instrument were taken at 335 K. The methodology involved in determining equilibrium constants, as well as rate constants for forward and reverse reactions,
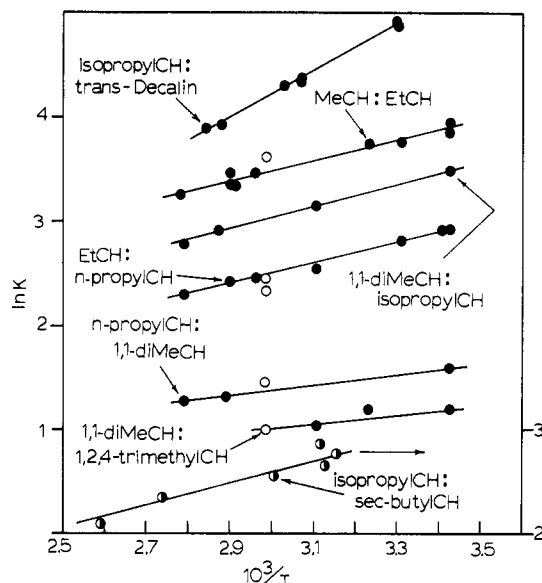
has been described elsewhere.[7]

Results and Discussion

Composite van't Hoff plots, containing results from both the high-pressure and ICR instruments, are given in Figures 1 and 2 (ICR values are displayed as open circles). Considering the vast differences in experimental conditions (pressure, reaction time, ion detection method, etc.), the agreement between the two techniques is essentially quantitative. For some systems only ΔG was determined vs. a reference compound at a single temperature. Those results, as well as measurements of k_f and k_r for certain reaction pairs, are given in Table I.

Enthalpies of Ionization. The van't Hoff plots may be used to establish a thermodynamic ladder of relative enthalpies of ionization (ΔH_{ion}) for the various reaction pairs. This ladder can then be converted to an absolute scale by interlocking the ladder with reference compounds having reasonably well-established ionization potentials (IP's). In

a previous article we chose cyclohexane as a reference molecule since it has been studied by several spectroscopic techniques and the values from various laboratories seem consistent; IP = 9.88 ± 0.01 eV, ΔH_{ion} = 227.8 ± 0.2 kcal mol⁻¹, and ΔS_{ion} = 0.0 (assumed). The substituted cyclohexanes studied here could then be tied to cyclohexane through methylcyclohexane, for which ΔH_{ion} was previously determined to be 223.5 ± 0.7 kcal mol⁻¹ (9.69 ± 0.03 eV). As an independent test of the validity of the absolute scale based on cyclohexane, values of ΔG for charge transfer at 335 K were determined by using the ICR instrument for the following reaction pairs (see Table I); pentafluoro-benzene vs. methylcyclohexane, 1,2,3,4- and 1,2,3,5-tetra-fluorobenzene vs. ethylcyclohexane, and 1,2-difluoro-benzene vs. sec-butylcyclohexane. The ΔG values (Table I), taken with the recommended values for ΔH_{ion} of the fluorobenzenes[8] and the experimentally determined ΔS_{ion} of the alkylcyclohexanes (see below), give the following values for ΔH_{ion} (in kcal mol⁻¹): methylcyclohexane, 222.3; ethylcyclohexane, 220.1; and sec-butylcyclohexane, 212.8; all with error limits of ±0.2 kcal mol⁻¹, which is the uncertainty in the recommended values for the fluoro-benzenes (these values assume that the entropies of ionization of the fluorobenzenes are zero, which is expected for molecules of very low symmetry). The disparity between the two absolute values for ΔH_{ion} of methylcyclohexane is somewhat puzzling (223.5 ± 0.7 kcal mol⁻¹ based on cyclohexane and 222.3 ± 0.2 kcal mol⁻¹ based on pentafluorobenzene). In general, however, we have found that the IP's of paraffinic hydrocarbons determined by photoionization/photoelectron spectroscopy are slightly higher than the values obtained by charge-transfer equilibrium measurements. This is ascribed to the fact that the photoionization onsets for these types of molecules are usually diffuse, which makes it difficult to accurately define the threshold associated with the adiabatic IP's. Recognizing that the literature values for the IP of cyclohexane may represent an upper limit to the true value, we have chosen to relate the enthalpy ladder for the cycloalkanes to the reference values derived from the fluorobenzene equilibrium measurements. The resultant absolute scale is given in Figure 3.

The overall consistency between the relative enthalpy ladder established by the high-pressure measurements and the differences in absolute values derived from the fluorobenzene measurements is excellent. For methyl- vs. ethylcyclohexane the difference in ΔH_{ion} from the ladder is 2.1 kcal mol⁻¹ compared with 2.2 kcal mol⁻¹ when each is measured separately against the appropriate fluoro-benzene (methyl- vs. pentafluoro- and ethyl- vs. 1,2,3,4- and 1,2,3,5-tetrafluoro-). Furthermore, the sequence ethyl- to propyl- to 1,1-dimethyl- to isopropyl- to sec-butyl-cyclohexane gives an overall enthalpy change of 7.2 kcal mol⁻¹ between ethyl- and sec-butylcyclohexane, whereas the difference indicated by the fluorobenzene measurements is 220.1 – 212.8 (from sec-butyl- vs. 1,2-difluoro-benzene) or 7.3 kcal mol⁻¹. Consequently, over the entire range covered by the methyl- to sec-butyl ladder, the two sets of measurements differ by only 0.2 kcal mol⁻¹ (9.3 vs. 9.5), or less than 0.01 eV.

Effect of Substitution. The thermodynamic scale given in Figure 3 may be used to derive quantitative information concerning the relationship between the site of methyl substitution and the enthalpy of ionization. The most dramatic and consistent effect is the decrease in ΔH_{ion} which occurs when a methyl group is substituted in a position α to a tertiary hydrogen atom. For example, the
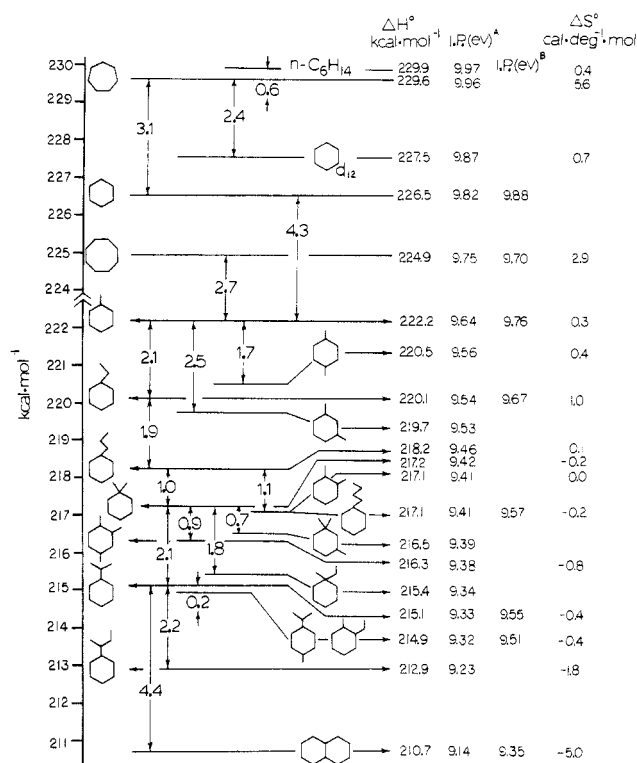

Figure 3. Enthalpy and entropy scale: (A) present data; (B) literature values (ref 13).

following pairs give $\Delta(\Delta H_{ion})$ values (in kcal mol⁻¹) for this type of α substitution on the ring system: methyl to 1,2-dimethyl, -5.1; ethyl to 1-methyl, 2-ethyl, -5.2; and 1,4-dimethyl to 1,2,4-trimethyl, -4.2. The same reduction occurs when substituting in the α position on the alkyl side chain; i.e., the ethyl to isopropyl and n-propyl to sec-butyl pairs given $\Delta(\Delta H_{ion})$ values of -5.0 and -5.3 kcal mol⁻¹, respectively. On this basis we conclude that methylation at a secondary site adjacent to a position having a tertiary hydrogen atom results in a reduction in the ionization potential of ~5 kcal mol⁻¹ (0.22 eV). β substitution has a much smaller effect (only -2.5 kcal mol⁻¹ in the methyl to 1,3-dimethyl pair) and γ the least (-1.7 kcal mol⁻¹ in the methyl to 1,4-dimethyl pair). A similar large decrease in ΔH_{ion} is apparently also associated with the substitution of a methyl group for a tertiary hydrogen to give a quaternary carbon atom. This occurs in the methyl to 1,1-dimethyl and ethyl to 1-methyl, 1-ethyl pairs, where the $\Delta(\Delta H_{ion})$ values are -5.9 and -4.7 kcal mol⁻¹, respectively.

Corroborative data pertinent to the α-methyl and quaternary carbon effects is sparse. The only systematic measurements are those of Watanabe et al.,[9] who derived photoionization values for the IP's of the isomeric butanes, pentanes, and hexanes. Although, as pointed out earlier, their absolute values may be high, all of the thresholds were interpreted in the same manner, so that the differences are probably reasonably reliable. They obtain an IP difference of 0.30 eV between 2-methyl- and 2,3-di-methylbutane, which is a decrease of 6.9 kcal mol⁻¹ associated with α-methyl substitution. For the conversion to quaternary carbon, they report a 0.22-eV (5.1 kcal mol⁻¹) difference between isobutane and neopentane, and a 0.26-eV (6.0 kcal mol⁻¹) difference between 2-methylbutane and 2,2-dimethylbutane. These are to be compared with the values of approximately 5 kcal mol⁻¹ for both substitutions suggested by the present measurements.

(8) Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1978**, *100*, 19.

(9) Watanabe, K.; Nakayame, T.; Mottl, J. *J. Quant. Spectrosc. Radiat. Transfer* **1962**, *2*, 369.

Entropy of Ionization. Entropies of ionization (ΔS_{ion}) derived from the van't Hoff plots are also listed in Table I. The values are referenced to a ΔS_{ion} for cyclohexane of zero. With the exception of cycloheptane, cyclooctane, *sec*-butylcyclohexane, and *trans*-Decalin, all of the cycloalkanes were found to exhibit values within ± 1 cal deg^{-1} mol^{-1} of zero, which may be assumed to be the actual value for these molecules. Furthermore, it has been independently verified[10] that there is no overall entropy change associated with the equilibrium $C_6F_5H^+$ + methylcyclohexane $\leftrightarrow$ methylcyclohexane$^+$ + C_6F_5H. Since it is expected that there should be no entropy change associated with the ionization of C_6F_5H due to its low symmetry, it follows that ΔS_{ion} for methylcyclohexane is also zero, in agreement with the scale based on cyclohexane.

Kinetics of the Charge-Transfer Reactions. The kinetics of the present reactions are characterized by two related and somewhat novel features: they are intrinsically fast, i.e., the sum of the forward and reverse efficiencies is about unity; and the reaction efficiency in each direction is determined uniquely by the equilibrium constant through the simple relation $r = K/(1 + K)$. In this section we shall present and discuss these kinetic features.

Many exothermic gas-phase ion–molecule charge-transfer reactions are known to proceed at near unit efficiency, where the reaction efficiency r is defined by eq I. Evidently, such reactions are not inhibited by any

$$r = k/k_{collision} \qquad (I)$$

unfavorable properties of the transition complex, and they are usually called fast processes. The most simple scheme for such reactions may be written as

$$A^+ + B \underset{k_b}{\overset{k_d}{\rightleftarrows}} (A \cdot B)^{+*} \underset{k_{cr}}{\overset{k_p}{\rightleftarrows}} B^+ + A \qquad (II)$$
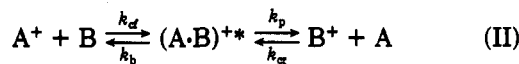
The overall forward and reverse rate constants are then given by

$$k_f = k_{cf}k_p/(k_b + k_p) \qquad (III)$$

$$k_r = k_{cr}k_b/(k_b + k_p) \qquad (IV)$$

Here k_{cf} and k_{cr} represent the collision rate constants in the forward and reverse reactions, respectively; $(A \cdot B)^{+*}$ is the reaction complex. The corresponding reaction efficiencies are given by

$$r_f = k_p/(k_b + k_p) \qquad (V)$$

$$r_r = k_b/(k_b + k_p) \qquad (VI)$$

Adding eq V and VI yields

$$r_f + r_r = 1 \qquad (VII)$$

Therefore, in reactions that proceed by the simple mechanism II involving *one intermediate* which is common to the forward and reverse reaction, *the sum of the forward and reverse efficiencies is unity. This relation may serve as a general condition for intrinsically fast reactions.* Equation I is consistent with a one-intermediate, one-minimum surface (Figure 5b), rather than the double-well surfaces usually associated with slow ion–molecule reactions (Figure 5a). Equation I (and therefore surface 5b) applies to the present reactions (Table I).

For all of the present reactions the forward and reverse capture collision rate constants, as calculated from Lan-

gevin or ADO theory, are equal within 15%. For the present purposes we shall therefore use $k_{cf} = k_{cr}$. Equations III and IV can then be divided and rearranged to yield

$$r_f = K_f/(1 + K_f) \qquad (VIII)$$

$$r_r = K_r/(1 + K_r) \qquad (IX)$$

where K_f and K_r are the equilibrium constants for reaction II written in the forward and reverse directions, respectively; i.e., $K_r = 1/K_f$. Equations VIII and IX show that the efficiencies of intrinsically fast reactions, as defined by eq II and VII, are determined entirely by the equilibrium constant, i.e., by the equilibrium thermochemical properties of the reactants and products. Such reactions are different from the great majority of other thermal chemical processes, including slow ion–molecule reactions, where reaction efficiencies are determined by the enthalpy and entropy barriers associated with the transition complex.

Table I and Figure 4 show the relation between the experimental reaction efficiencies and the prediction of eq VIII. Over a range of more than 3 orders of magnitude variation in K, eq VIII is satisfied within at least a factor of 2. Within this limit, the present reactions therefore satisfy the criteria for intrinsically fast reactions as given by eq VII–IX.

The essential mechanistic feature of these processes (eq II) is that the reaction complex is formed by every capture collision of A^+ with B or B^+ with A and it dissociates to $B^+ + A$ or $A^+ + B$ according to the equilibrium ratio of $[B^+][A]/([A^+][B])$. The latter reaction can be obtained by dividing III by eq IV, which gives

$$k_p/k_b = (k_f k_{cr})/(k_r k_{cf}) \approx k_f k_r = K \qquad (X)$$

The most simple potential energy surface consistent with eq X is one where no barriers exist to the formation (or decomposition) of $(A \cdot B)^{+*}$ from (or to) $A^+ + B$ or $B^+ + A$ and where the transition states for these decompositions are similar to $A^+ + B$ or $B^+ + A$, respectively. Then, the relation $k_p/k_b = K$ can be obtained by applying transition-state-theory (TST) arguments to the dissociation of $(A \cdot B)^+$. For either dissociation eq XI applies with Q^* representing the partition function for the transition state in the appropriate channel.

$$k = \frac{k_b T}{h} \frac{Q^*}{Q(A \cdot B)^+} \exp[E^*_0 - E_0(A \cdot B^+)]/RT \qquad (XI)$$

If the only barrier to the dissociation of $(A \cdot B)^+$ is just the overall energy change associated with the dissociation (see Figure 5b), the transition states for dissociation to $B^+ + A$ or $A^+ + B$ may be taken at points on the potential energy surface where the relative energies of the transition states are equal to those of $B^+ + A$ or A^+B, respectively. For ion–molecule reactions, the transition states correspond to well-separated entities.[12] The ratio of the partition functions of the transition states is therefore also similar to the ratio of the partition functions of $B^+ + A$ and $A^+ + B$, respectively. Therefore

$$\frac{k_p}{k_b} =$$

$$\frac{Q(B^+ + A)}{Q(A^+ + B)} \exp\{-[E_0(B^+ + A) - E_0(A^+ + B)]/RT\} = K$$

$$(XII)$$

(10) Lias, S. G., private communication.

(11) For example, $E_{internal}$ of the reactants in reaction 2 is 12.4 kcal mol^{-1} at 335 K as obtained from $E_{internal} = (H^\circ - H^\circ_0) - {}^3/_2RT$ for each reactant. Values of $H^\circ - H^\circ_0$ from: Rossini, F. D., et al. "Selected Values of Properties of Hydrocarbons"; National Bureau of Standards: Washington, DC, 1947; NBS Circular C461.

(12) (a) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. (b) Jasinski, J. M.; Brauman, J. I. *Ibid.* **1980**, *102*, 2906.

(13) Levin, R. D.; Lias, S. G. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)*, in press.

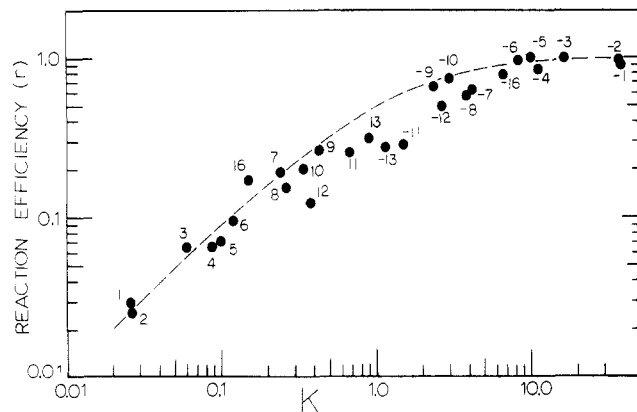**Figure 4.** Relation between the reaction efficiency $r = k/k_{collision}$ and the equilibrium constant in charge-transfer reactions. Numbers refer to reactions in Table I. Negative numbers refer to the reverse reactions. Solid line fitted to experimental points. Broken line shows r calculated as $r = K/(1 + K)$.
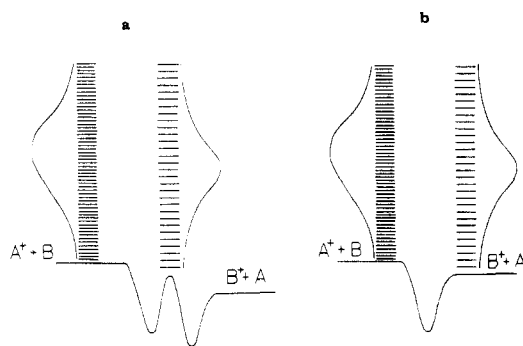

Figure 5. Potential energy diagrams for double-well (a) and single-well (b) surfaces. See text for explanation.

The TST equations apply rigorously only in the high-pressure limit, where the energy levels of $(A \cdot B)^+$ are populated according to the Boltzmann distribution. This is not true in the present low-pressure ICR measurements, where $(A \cdot B)^{+*}$ can decompose faster than the rate of collisional stabilization, and energy levels below $E_0(B^+ + A)$ are not populated. However, in large charge-delocalized systems, ion–neutral electrostatic interactions are expected to be weak, and the energy well in Figure 5b should be shallow (≈ 5 kcal mol^{-1}). This is much smaller than the internal energy of the reactants (≈ 15 kcal mol^{-1}).[11] Therefore, only the low-energy tail in the population of $(A \cdot B)^+$ is missing and TST is a good approximation. The general agreement between the experimental values of r and the predictions of eq VII–IX supports this argument. In conclusion, the occurrence of intrinsically fast reactions can be attributed either to a barrierless potential energy surface associated with these reactions or to barriers which are small compared with the internal energy contents of the reactants.

For significantly exoergic reactions, i.e., when $\Delta G°$ is significantly negative and $K \gg 1$, then eq VIII reduces to the usual case of fast reactions, i.e., $r_f = 1$. In the reverse of these reactions, where $K \ll 1$, eq VIII reduces to $r = K$; i.e., the reaction efficiency of endoergic, fast reactions is equal to the equilibrium constant. All of the reactions in Table I with $\Delta G°_{340} < -0.5$ kcal mol^{-1}, i.e., $K > 2$, satisfy these relations. For ergoneutral reactions (i.e., when $\Delta G° = 0$ and $K = 1$) eq VIII predicts $r_f = r_r = 0.5$. Indeed, the efficiencies of proton-transfer reactions have been observed to decrease to about 0.5 when approaching thermoneutrality (and ergoneutrality). In some cases, however, the efficiencies decrease somewhat below this value. For ex-

ample, r_f for reactions 11 and 13 is 0.25 and 0.31, respectively, rather than 0.40 and 0.47, respectively, as would be predicted by eq VIII, and $r_f + r_r$ is only 0.53 and 0.58, respectively, rather than 1 as would be predicted from eq II. Thus, these reactions deviate somewhat from the criteria for fast behavior.

For many ion–molecule reactions, such as charge and proton transfer, the entropy change, if any, is small, i.e., $|\Delta S°| \leq 1$ eu. This also applies to most of the present reactions, e.g., reactions 2–5 (Table I). However, in reaction 6 we observe a case which involves a significant entropy change. The endothermicity of this reaction alone would decrease the reaction efficiency to $r = \exp(-\Delta H°/RT) = 0.012$. However, the experimental value is $r_f = 0.096$, in very good agreement with eq VIII, which predicts $r_f = 0.10$. As in this direction the entropy change is positive, it can be said that the entropy change drives this reaction to be faster by a factor of 7.9 than it would be on the basis of the enthalpy change alone. On the other hand, in reaction 1 $\Delta H°$ and $T\Delta S°$ combine in such a manner that, in accordance with eq VIII, the entropy effect slows down the endothermic step. That is, the enthalpy term $\exp(-\Delta H/RT)$ would lead to $r_f = 0.36$; but the experimental value is only 0.029, in agreement with the predicted value of 0.025.

Especially interesting entropy effects arise when $-T\Delta S°$ is larger in magnitude and opposite in sign to $\Delta H°$. In such cases the entropy change can affect significantly the efficiency in both directions. An example is reaction 16, which is an endothermic, but exoergic, reaction. Here the enthalpy factor would reduce the efficiency to 0.20, yet the observed efficiency is 0.78, in good agreement with eq VIII, which predicts 0.87. A similar combination arises in reaction 12, where a positive entropy factor brings the efficiency of an endothermic process near unity. These are therefore instances of fast and endothermic reactions. Other fast endothermic reactions were observed in diamines.[2b]

An analogy can be seen between the entropy effects observed in our reactions and the entropy effects postulated by Brauman and co-workers in slow ion–molecule reactions.[12] The analogy is illustrated in Figure 5, which shows the present, single-interemediate, single-well model and Brauman's double-well model. In our case, dissociation to products (Figure 5b) is analogous to passage over the barrier in Figure 5a. Brauman et al.[12] attribute the low efficiencies of IM reactions to a negative entropy term; in our case we observe experimentally that the negative entropy term slows the reaction. In this sense, the present results provide indirect experimental support for an entropy barrier in slow ion–molecule reactions.

Summary

An extension of the notion of fast reactions is necessary when reactions with significant entropy changes are considered. Here we observed charge-transfer reactions whose efficiencies are entirely determined by the free energy change (or equilibrium constant), regardless of the individual contributions of ΔH and ΔS. All of these reaction efficiencies obey the simple relation $r = K/(1 + K)$. To encompass all of these reactions, *intrinsically fast processes may be defined as reactions whose efficiencies are determined only by the overall reaction thermochemistry and which are not affected by the reactions or properties of the reaction complex.*