5342 J. Am. Chem. Soc. 1981, 103, 5342-5348

Ionization of Normal Alkanes: Enthalpy, Entropy, Structural, and Isotope Effects

M. Meot-Ner (Mautner),* L. W. Sieck, and P. Ausloos

Contribution from the Chemical Thermodynamics Division, National Bureau of Standards, Washington, DC 20234. *Received February 2, 1981*

Abstract: Enthalpies and entropies of ionization (ΔH_i°, ΔS_i°) of C_4 to C_{11} normal alkanes were determined from charge-transfer equilibrium measurements between 300 and 420 K by using photoionization high-pressure mass spectrometry. Large negative ΔS_i° values are observed in C_7 and larger *n*-alkanes, from -4.7 cal mol^{-1} K^{-1} (-19.6 J mol^{-1} K^{-1}) in heptane to -13.9 cal mol^{-1} K^{-1} (-58.1 J mol^{-1} K^{-1}) in undecane; in contrast, ΔS_i° of C_4–C_7 *n*-alkanes is negligible. ΔH_i° values range from 10.35 eV (997.6 kJ mol^{-1}) (butane) to 9.45 eV (910.9 kJ mol^{-1}) (undecane); the incremental ΔH_i° values also suggest the occurrence of an effect that stabilizes C_7 and higher but not the lower molecular ions. Analogy with disubstituted alkanes suggests that the negative ΔS_i° values and the excess stabilization in C_7 and higher alkane ions are due to constrained cyclic conformations which result from noncovalent intramolecular bonding between the terminal $-C_2H_5$ groups in the large, flexible molecular ions. These effects are more pronounced in *n*-alkanes than in 2-methylalkanes. Isotope effects on ΔH_i° as measured by the equilibrium constant K_{290} for $n\text{-}C_mD_{2m+2}^+ + n\text{-}C_mH_{2m+2} \rightleftarrows n\text{-}C_mH_{2m+2}^+ + n\text{-}C_mD_{2m+2}$ are significant for ethane ($k_{291} = 4.5$) but decrease with increasing m: in propane $K_{290} = 3.2$ and in hexane and octane $K_{291} = 1.0$. However, the isotope effects in cyclic alkanes are much larger than in corresponding normal alkanes: in cyclohexane, $K_{321} = 3.3$ compared with that in *n*-hexane, where $K_{320} = 1.0$.

Equilibrium studies of ion–molecule reactions have been used extensively in the last decade to measure gas-phase ion thermochemical properties, especially the intrinsic proton affinities and acidities of organic molecules.[1] More recently, studies of charge-transfer reactions in substituted benzenes[2,3] and polycyclic aromatics[4] showed that adiabatic ionization energies can be determined by equilibrium measurements to within accuracies better than ±1 kcal/mol. This indicates that equilibrium techniques should be useful in measuring ionization energies of molecules in those cases where adiabatic ionization energies (ΔH_i°) cannot be measured accurately by other methods. One such group of compounds is normal alkanes larger than *n*-butane; in these molecules the photoionization onset is so diffuse that accurate adiabatic ionization energies have not been determined. The value of charge-transfer equilibrium in measurements for linear alkanes was demonstrated in an earlier study from this laboratory,[5] which determined differences in free energies of ionization for several alkanes at a single temperature (~330 K).

In addition to ionization energies, temperature studies of charge-transfer equilibria also yield the entropy changes involved in the charge-transfer reactions. In the case of rigid structures such as substituted benzenes it was shown that the entropy changes can be accounted for by changes in rotational symmetry and electronic multiplicity upon ionization.[3] In contrast, in flexible molecules such as diphenylbutane[6] or polyfunctional amines[7] entropy changes up to ≈−17 cal mol^{-1} deg^{-1} have been observed upon protonation, indicating that ionization can lead to substantial geometry changes in flexible structures. It is therefore also of interest to examine the entropy changes upon ionization of *n*-alkanes to determine whether ionization induces structural changes in this class of flexible molecules as well.

Experimental Section

(1) General Data. The measurements were performed on the NBS high-pressure photoionization mass spectrometer.[8] In most experiments the ionizing radiation was supplied by a Kr resonance lamp (mixed 10.0- and 10.6-eV photons); a few measurements were also made by using an Ar lamp (11.7 eV). The ion source, which has been described previously,[8] was equipped with a cartridge heater. Thermocouples placed at various points of the source and the stainless-steel inlet line (separately heated) showed that the temperature was always homogenous to within ±3 K. The gas was admitted to the inlet line and source from a heated 3-L bulb; control experiments verified that the bulb temperature did not affect the measured equilibrium constants.

All spectra were corrected for the fact that (i) the quadrupole ion injection energy was maintained at a constant value of 10 eV, (ii) mass discrimination may exist in the quadrupole analyzer depending upon the resolution setting, and (iii) the detector exhibits a subtle mass-dependent gain. These combined effects never require a correction of more than 10% in the observed ion intensity ratios.

Materials used were high purity commercial samples. Liquid mixtures of the reactants for each equilibrium measurement were prepared and injected to the heated bulb in small quantities to assure complete vaporization. The composition and purity of each mixture were determined by gas chromatography. The purity of the reactants was also verified by the absence of significant impurity peaks in the mass spectra of the reaction mixtures.

(2) Tests of Equilibrium. The present measurements were performed by using continuous, time-resolved ionization and ion extraction from the source; therefore, the approach to equilibrium as a function of reaction time cannot be directly observed. It was therefore essential to perform thorough checks to confirm that equilibrium was indeed obtained in the charge-transfer reactions.

(a) Pressure Studies. At very low source pressures the number of reactive collisions of the ion in the source is negligible and the relative intensities of ion signals are determined by the partial pressures of the reactants and their relative photoionization cross sections. Increasing source pressure increases both the number densities of the neutral reactants and the residence times of the ions in the source; therefore, the number of reactive collisions increases according to $N_c \alpha P^2$. The progress of the electron-exchange reaction $A^+ + B \rightleftarrows B^+ + A$ can then be followed as I_{B^+}/I_{A^+} changes with increasing pressure until a constant ratio is obtained. This occurs when the pressure is sufficiently high to reach equilibrium within the ions residence time in the source (Figures 1 and 2).

Each equilibrium constant (K) in this study was measured at several different source pressures. The result was accepted only if K was found constant over a pressure range in which the number of reactive collisions

---

(1) For recent reviews see: Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445; "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979.

(2) Meot-Ner, M.; Field, F. H. *Chem. Phys. Lett.* **1976**, *44*, 484.

(3) Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1978**, *100*, 6027.

(4) Meot-Ner, M. *J. Phys. Chem.*, in press.

(5) Lias, S. G.; Ausloos, P.; Horvath, Z. *Int. J. Chem. Kinet.* **1976**, *8*, 725.

(6) Meot-Ner (Mautner), M.; Hunter, E. P.; Hamlett, Pr.; Field, F. H.; Ausloos, P.; Sieck, L. W. 28th Annual Conference of the American Socity for Mass Spectrometrists, New York, 1980.

(7) (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.

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

(9) Ikuta, S.; Yoshihara, K.; Shiokawa, T.; Jinno, M.; Yokoma, Y.; Ikeda, S. *Chem. Lett.* **1978**, 1237.

(10) Raymonda, J. W. *J. Chem. Phys.* **1972**, *56*, 3912.

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

(12) Brehm, B. *Z. Naturfursch., A* **1966**, *21A*, 196.

(13) Recommended values from: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. No. 1.

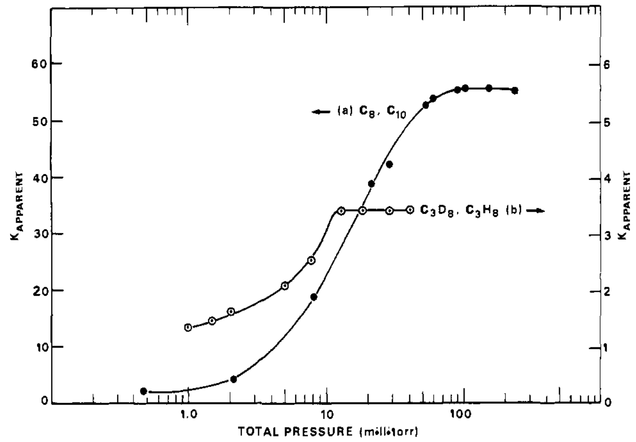

Figure 1. Change of the apparent equilibrium constant *K* apparent = ($I_B + P_A$)/($I_A + P_B$) for the reaction $A^+ + B \rightleftharpoons B^+ + A$ as a function of total pressure of the reactants in the ion source: (a) A = *n*-octane, B = *n*-decane, P_A/P_B = 10.9 *T* = 344 K; (b) A = C_3D_8, B = C_3H_8, P_A/P_B = 1.12, *T* = 291 K.

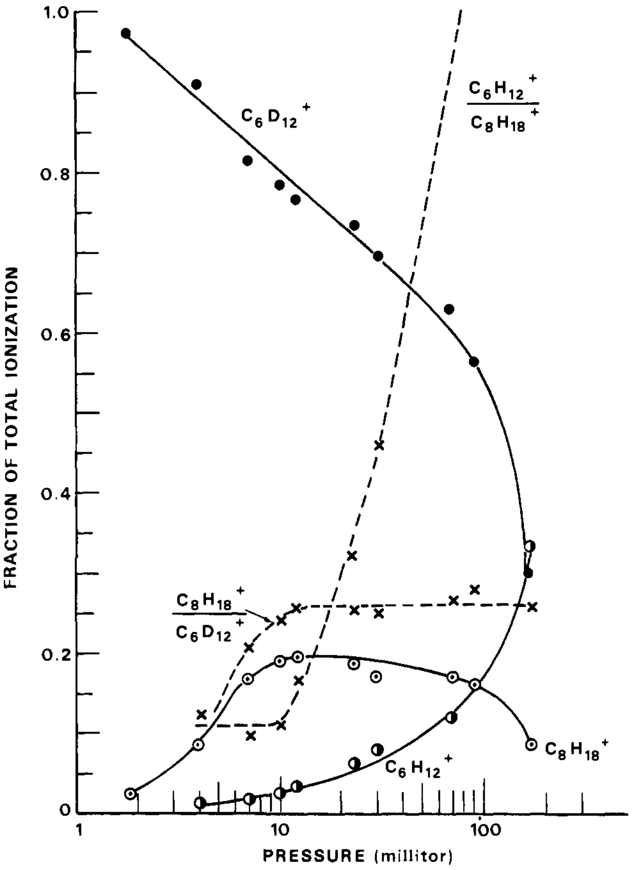

Figure 2. Relative ion intensities as a function of pressure in a mixture of 95.4% c-C_6D_{12} and 4.6% *n*-C_8H_{18}, at 371 K. The $C_8H_{18}^+$:$C_6D_{12}^+$ ratio represents approach to equilibrium in the c-$C_6D_{12}^+$ + *n*-C_8H_{18} ⇄ *n*-$C_8H_{18}^+$ + c-C_6D_{12} reaction. The $C_6H_{12}^+$:$C_8H_{18}^+$ ratio reflects the formation the $C_6H_{12}^+$ fragments in the course of the charge-transfer reaction.

in the source varied by at least a factor of 2.5.

(b) Kinetic Calculations. To further verify that equilibrium can be reached in the source during ion residence, we carried out numerical calculations by using the usual kinetic equations associated with the reversible reaction (1). Here k_f and k_r are the pseudo-first-order rate

$$A^+ + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B^+ + A \qquad (1)$$

constants; i.e., $k_f = k_{(A^+,B)}N_b$, where $k_{(A^+,B)}$ is the second-order rate constant for the forward, exothermic charge-transfer process. For several of the reactions $k_{(A^+,B)}$ can be obtained or estimated from the results of Lias et al.[5] For example, for the reaction of octane$^+$ + decane, we estimate $k_{(A^+,B)}$ to be similar to $k_{(A^+,B)}$ for octane$^+$ + nonane system, i.e., 2.5×10^{-10} cm^3 s^{-1}. Using this value and the measured equilibrium constant at 344 K, we then obtain $k_{(B^+,A)}$. Using standard kinetic equations, we can then calculate the time, τ_{99}, at which the ion ratio B^+/A^+ reaches 99% of its equilibrium value, starting with the initial ion ratios as determined by P_A, P_B, and the relative photoionization cross sections. For the reaction system in Figure 1a at 100 mtorr, we obtain τ_{99} = 135 μs. This is well within the average ion residence time (τ_{res}), which we calculate as 300 μs. Indeed, we can calculate the lowest pressures (P_{eq}) at which equilibrium is just obtained within the ion residence time, i.e., where $\tau_{99} = \tau_{res}$. For this system, we find P_{eq} = 67 mtorr, in very (probably fortuitously) good agreement with the curve of Figure 1a.

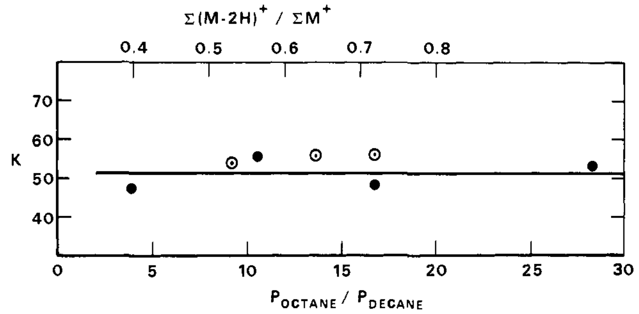

Figure 3. Equilibrium constant for octane$^+$ + decane ⇄ decane$^+$ + octane, at 344 K, measured at various neutral reactant ratios (●) and lamp intensities (⊙). Increased lamp intensity caused increase in $(M-2H)^+$- vs. M^+-type ions as indicated on upper ordinate.

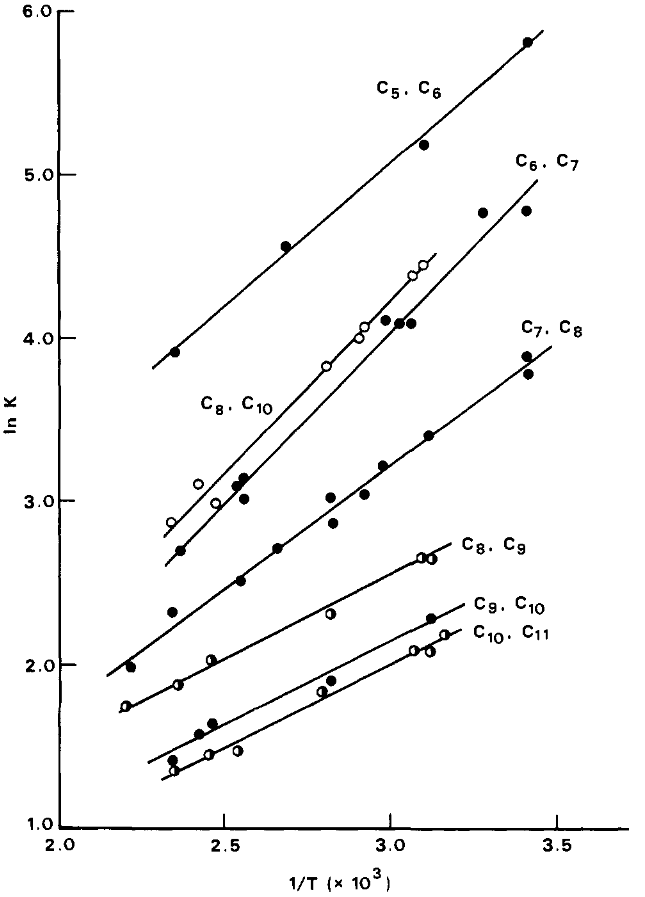

Figure 4. van't Hoff plots for charge-transfer equilibria between normal alkanes $C_nH_{2n+2}^+$ + C_mH_{2m+2} ⇄ $C_mH_{2m+2}^+$ + C_nH_{2n+2} (*n* and *m* as indicated).

Similarly, $k_{(A^+,B)}$ for the hexane–heptane system is given by Lias et al.[5] as 2.7×10^{-10} cm^3 s^{-1}. Using this value and the above methods, we find P_{eq} = 51 mtorr at 336 K. Pressure studies showed that the $C_7H_{16}^+/C_6H_{14}^+$ ratio reached a constant value between 80 and 110 mtorr, in reasonable agreement with the calculated value.

The octane–decane and hexane–heptane systems are some of the most extreme in this study in that the equilibrium constants in these systems

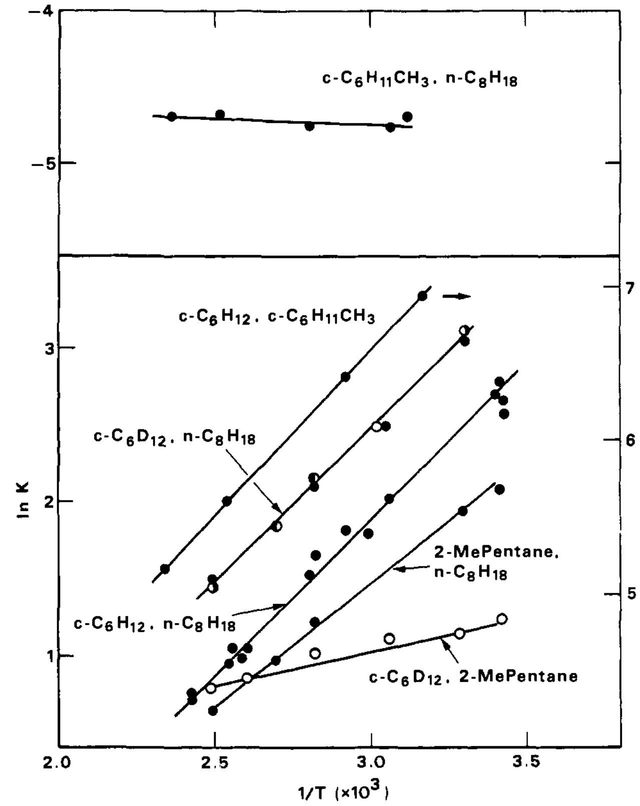

Figure 5. van't Hoff plots for charge-transfer equilibria $A^+ + B \rightleftarrows B^+ + A$, involving cyclohexane, methylcyclohexane, and octane. A and B are as indicated. Point indicated by ○ for the c-C_6D_{12}-octane reaction from ICR results of Lias et al.[5]

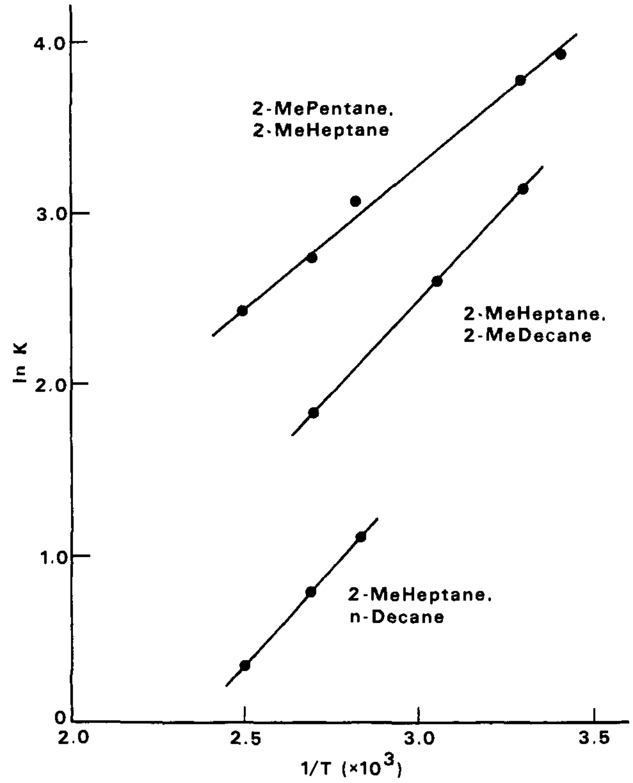

Figure 6. van't Hoff plots for charge-transfer equilibria involving 2-methylalkanes.

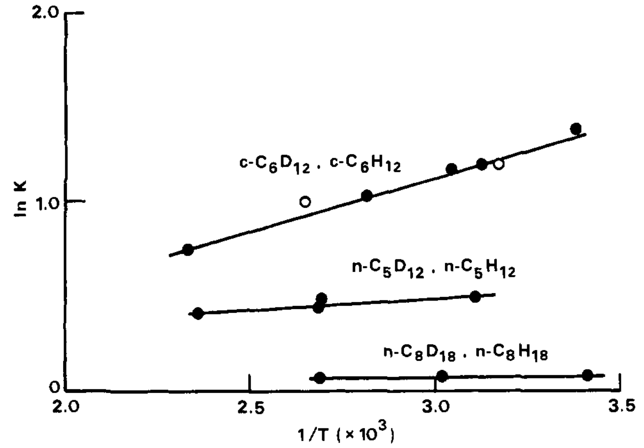

Figure 7. van't Hoff plots for charge-transfer eequilibria $A^+ + B \rightleftarrows B^+ + A$ between cyclohexane, normal pentane, normal octane, and their perdeuterated analogues. A and B are as indicated in figure. Points indicated by open circles were obtained by time-resolved ICR.

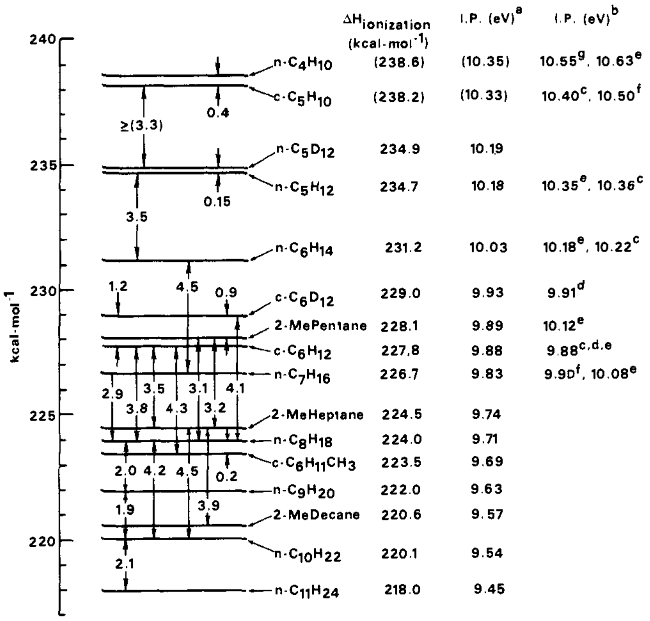

Figure 8. Interlocking ladder of ionization enthalpies (ΔH_i°) (absolute values are related to $\Delta H_i^\circ(c\text{-}C_6H_{12})$ = 9.88 eV as reference): (a) present results; (b) literature values; (c) ref 9; (d) ref 10; (e) ref 11; (f) ref 12; (g) ref 13. Values for n-C_4H_{10} and c-C_5H_{10} are lower limits.

are some of the highest and therefore τ_{99} is the largest. In comparison, for example, the C_3H_8–C_3D_8 system already reaches equilibrium at 12 mtorr (Figure 1). The calculations therefore demonstrate that equilibrium can indeed be reached within the ionic residence time in the mass spectrometer source and support the experimental results of the pressure studies which show attainment of equilibrium at moderate pressures.

(c). Comparison with ICR Measurements. As a check on the thermochemical scale obtained from our equilibrium measurements, we investigated the equilibrium c-$C_6D_{12}^+$ + n-C_7D_{16} $\rightleftarrows$ n-$C_7D_{16}^+$ + c-C_6H_{12}, using the NBS pulsed ICR mass spectrometer at 317 K and 402 K. The ICR results gave for this reaction $\Delta H^\circ = -1.6$ kcal mol^{-1} and $\Delta S^\circ = -5.7$ cal mol^{-1} K^{-1}, in good agreement with the values of -2.3 kcal mol^{-1} K^{-1} and -6.1 cal mol^{-1} K^{-1}, respectively, which are obtained from the thermochemical scales of Figures 8 and 9. (For the present purposes we equate n-C_7D_{16} with n-C_7H_{16}, which is justified by the isotope effect results below.) We also measured by ICR the reaction c-$C_6H_{12}^+$ + n-C_8D_{18} $\rightleftarrows$ n-$C_8D_{18}^+$ + c-C_6H_{12}. We found $\Delta H^\circ = -4.4$ kcal mol^{-1} and $\Delta S^\circ = -9.0$ cal mol^{-1} K^{-1} in good agreement with $\Delta H^\circ = -3.8$ kcal mol^{-1} and $\Delta S^\circ = -7.7$ cal mol^{-1} K^{-1} from the thermochemical scales of Figures 8 and 9.

Several ICR measurements of equilibria involving c-$C_6H_{12}^+$ also gave results in good agreement with the van't Hoff plots obtained by the high-pressure technique (Figures 5 and 7).

(d) Mixture Composition. True equilibrium constants should be independent of mixture composition. We investigated this thoroughly in the octane–decane and cyclohexane–octane systems. In the octane–decane system at 340 K, we determined K at octane:decane pressure ratios of 4.1, 17.4, and 30.0. The measured values of K were 52.0, 51.7, and 57.4, respectively. In the c-C_6H_{12}-n-C_8H_{18} system at 412 K we measured K at cyclohexane:octane pressure ratios of 3.3 and 44.7 and obtained K

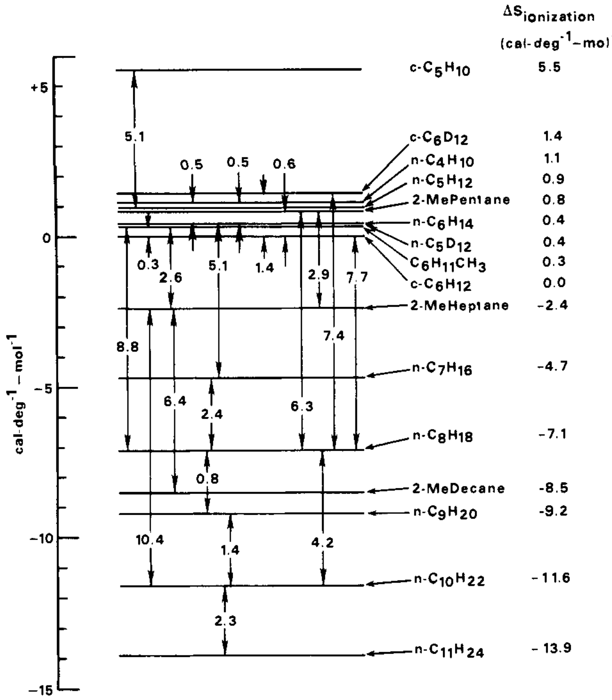

Figure 9. Interlocking ladder of ionization entropies ($\Delta S_i°$). Absolute values are related to $\Delta S_i°(c\text{-}C_6H_{12}) = 0.0$ cal mol^{-1} K^{-1}.

= 2.1 and 2.0, respectively. In the c-C_6D_{12}–n-C_8H_{18} system the equilibrium constant was checked in several mixtures throughout the temperature range. (See points on the van't Hoff plot in Figure 5).

Also, in reactions involving the C_8–C_{11} alkanes measurements were taken in mixtures composed only of the reactants, as well as in the presence of a large excess of cyclohexane. In the first case ions are generated directly and in the second case mostly by charge-transfer chemical ionization involving c-$C_6H_{12}^+$. Results obtained by the two techniques were identical.

(e) **Lamp Intensity.** Photolysis of the reactant mixtures produces olefins, which in turn react with the molecular ions to produce $(M - 2H)^+$-type ions. These side reactions occur concurrently with the approach to equilibrium and continuously reduce the concentration of the molecular ions. To establish that the equilibrium constants measured in the presence of these side reactions are the true equilibrium constants, we determined K by using several different lamp intensities under otherwise identical conditions. We found no effect on K even though the relative concentrations of $(M - 2H)^+$ vs. M^+ type ions increased with lamp intensity (Figure 3).

Results and Discussion

van't Hoff plots for charge-transfer equilibria from C_n to C_{n+1} normal alkanes are presented in Figure 4 and for other equilibria in Figures 5–7. The network of $\Delta H°$ values is presented in Figure 8 and of $\Delta S°$ values in Figure 9.

(a) Error Estimates; Effects of Ion Decomposition and Rearrangement. The internal consistency of the network of thermochemical cycles may be examined by following alternate paths in the thermochemical ladder between the same two compounds. The most extensive network is for charge transfer from c-$C_6H_{12}^+$ to n-C_8H_{18}, where we can trace the following routes: the reaction c-C_6H_{12}–n-C_8H_{18} directly, the route c-C_6H_{12}–c-C_8D_{12}–n-C_8H_{18}, the route c-C_6H_{12}–c-C_6H_{12}–2-methylpentane–n-C_8H_{18}, and the route c-C_6H_{12}–c-$C_6H_{11}CH_3$–n-C_8H_{18}. For these routes we get respectively $\Delta H° = -4.3, -2.9, -3.1$, and -4.1 kcal mol^{-1} and $\Delta S° = -7.7, -5.6, -6.4$, and -8.5 cal mol^{-1} K^{-1}. For another comparison we can trace $\Delta H°$ for charge transfer from c-C_6H_{12} to n-$C_{10}H_{22}$ through the following routes: c-C_6H_{12}–n-C_8H_{18}–n-$C_{10}H_{22}$; c-C_6H_{12}–n-C_8H_{18}–n-C_9H_{20}–n-$C_{10}H_{22}$; c-C_6H_{12}–2-methylheptane–n-$C_{10}H_{22}$; c-C_6H_{12}–c-C_6D_{12}–2-methylheptane–n-$C_{10}H_{22}$. We obtain, respectively, $\Delta H° = -7.7, -7.7, -7.4$, and -8.0 kcal mol^{-1} and $\Delta S° = -11.7, -9.3, -13.0$, and -12.5 cal mol^{-1} K^{-1}. From the standard deviation of these sets of results we estimate the error in our $\Delta H°$ values as ±0.7 kcal mol^{-1} and in $\Delta S°$ as ±1.3 cal mol^{-1} K^{-1}.

Table I. Hydrogen Isotope Effects on Ionization Energies of Alkanes as Measured by the Equilibria $A^+ + B \rightleftarrows B^+ + A$

A	B	K_T	$\Delta G°_T$, kcal mol^{-1}	$\Delta G°_T$, eV	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} K^{-1}
C_2D_6	C_2H_6	4.5_{291}	−0.88	−0.038		
C_3D_8	C_3H_8	3.2_{291}	−0.68	−0.029		
n-C_4D_{10}	n-C_4H_{10}	2.7_{293}	−0.58	−0.025	−0.80	−0.80
n-C_5D_{12}	n-C_5H_{12}	1.7_{296}	−0.31	−0.013	−0.15	+0.5
n-C_6D_{14}	n-C_6H_{14}	1.0_{332}	−0.00	0.000	−0.02	0.0
n-C_8D_{18}	n-C_8H_{18}	1.1_{294}	−0.06	−0.003	−0.07	−0.1
CH_3CD_3	C_2H_6	2.4_{291}	−0.51	−0.022	−0.90	+1.4
c-C_5D_{10}	c-C_5H_{10}	3.2_{293}	−0.68	−0.029	−0.82	+0.92
c-C_6D_{12}	c-C_6H_{12}	3.3_{321}	−0.77	−0.033	−1.20	−1.4

As for systematic errors or artifacts, the principal problems may arise from ion decomposition and/or rearrangement. We examined the question of ion decomposition in c-C_6D_{12}–n-C_8H_{18} as a model system at a high (371 K) and low (292 K) temperature. In this system the cyclohexane ion is stable and the lowest threshold fragment ion from octane is $C_6H_{12}^+$. Indeed, the $C_6H_{12}^+$ ion is observed in the mass spectrum with increasing pressure and the other olefinic type ions $C_6D_{10}^+$ and $C_8H_{16}^+$ also grow in. The latter may be, at least in part, products of reactions of the fragment ion $C_6H_{12}^+$ with the neutral reactants; they may also be associated with the presence of olefinic impurities or neutral photoproducts. Also, $C_6H_{12}^+$ can, in principle, be formed by unimolecular thermal decomposition of n-$C_8H_{18}^+$. The possible reactions in this system are therefore given by (2)–(8).

$$c\text{-}C_6D_{12}^+ + n\text{-}C_8H_{18} \rightarrow n\text{-}C_8H_{18}^+ + c\text{-}C_6D_{12} \tag{2}$$

$$c\text{-}C_6D_{12}^+ + n\text{-}C_8H_{18} \rightarrow C_6H_{12}^+ + \text{neutrals} \tag{3}$$

$$n\text{-}C_8H_{18}^+ + c\text{-}C_6D_{12} \rightarrow c\text{-}C_6D_{12}^+ + n\text{-}C_8H_{18} \tag{4}$$

$$C_6H_{12}^+ + \text{impurities} \rightarrow C_6D_{10}^+,\ C_8H_{18}^+ \tag{5}$$

$$c\text{-}C_6D_{12}^+ + \text{impurities} \rightarrow C_6D_{10}^+,\ C_8H_{18}^+ \tag{6}$$

$$n\text{-}C_8H_{18}^+ + \text{impurities} \rightarrow C_6D_{10}^+,\ C_8H_{18}^+ \tag{7}$$

$$n\text{-}C_8H_{18}^+ \rightarrow C_6H_{12}^+ + C_2H_6 \tag{8}$$

All of the reactions follow first-order or pseudo-first-order kinetics. The equilibrium ion ratio of interest is $K_{2,4}$

$$K_{2,4} = (C_8H_{18}^+/C_6D_{12}^+)_{eq} = k_2/k_4 \tag{9}$$

where k_2 and k_4 denote the pseudo-first-order rate constants. The presence of the dissociative charge-transfer channel (3) and the complicating reactions 5–8 may lead to a steady-state ion ratio $K_{2,4}$ which will be invariant with reaction time, pressure, or mixture composition, yet different from the true equilibrium ion ratio. The effect of such an artifact may be substantial. For example, eq 11 (see below) shows that under certain conditions, i.e., when $K \gg 1$, the presence of 22% fragmentation at high temperature and none at low temperature would introduce an error of −1 kcal mol^{-1} in $\Delta H°$ and −3 cal mol^{-1} in $\Delta S°$, both of which are significant compared with the overall $\Delta H°$ and $\Delta S°$ effects measured in this study.

To check the importance of decomposition reactions, we examined the pressure dependence of ion intensity ratios in a c-C_6D_{12}–n-C_8H_{18} mixture at 371 K (Figure 2). We first note that at least 98% of the primary ionization produces c-$C_6D_{12}^+$ as is evident from the ion distribution at the lowest pressure. As the pressure is raised up to 10 mtorr the primary reactions 2 and 3 increase the relative intensities of $C_8H_{18}^+$ and $C_6H_{12}^+$. In this range the C_6H_{12}:$C_8H_{18}^+$ ion ratio remains constant at ~0.11 and the olefinic ions $C_8H_{18}^+$ and $C_6D_{10}^+$ are smaller by at least a factor of 5 even than $C_6H_{12}^+$. These results indicate (a) that $C_6H_{12}^+$ and $C_8H_{18}^+$ are formed in parallel by (3) and (2), (b) that the rate at which $C_8H_{18}^+$ is depleted by (8), if at all, is slow compared with the rates of formation, i.e., $k_8 \ll k_2$, k_2, and that (c) the side reactions 5–7 are much slower than the primary reactions, i.e., $k_2, k_3, k_4 >> k_5, k_6, k_7, k_8$.

We then have to consider to what extent will the steady-state ion ratio $K'_{2,4}$ be different from $K_{2,4}$ due to reaction 3. To do so we note that at high pressures the ion ratio $(C_8H_{18}^+):(C_6D_{12}^+)$ reaches a steady-state value $K'_{2,4}$, although the intensity of both ions is depleted via reaction 3. Therefore

$$d(C_8H_{18}^+)/dt = K'_{2,4}[d(C_6D_{12}^+)/dt] \qquad (10)$$

Using eq 10 and the kinetic scheme presented by reactions 2–4, we obtain

$$K'_{2,4}/K_{2,4} = 1 + K'_{2,4}(k_3/k_2)/(K'_{2,4} + 1) \qquad (11)$$

In the present system, with $K'_{2,4} = 0.24$ and $k_3/k_2 = 0.11$, eq 11 yields $K_{2,4}/K'_{2,4} = 1.02$; i.e., the steady-state ion ratio is larger than the true equilibrium value by only 2%. Similar experiments at 292 K show that $k_3/k_2 = 0.5$ and $K_{2,4}/K'_{2,4} = 1.01$ at this temperature. The presence of (3) causes an error of -0.04 kcal mol^{-1} in $\Delta H°$ and -0.12 cal mol^{-1} K^{-1} in $\Delta S°$. Both errors are negligible. We have observed similar behavior in the c-C_6H_{12}–2-methylheptane system, where, at 393 K, we observed $k_4/k_2 = 0.09$, which leads to a 2% deviation from the true equilibrium ion ratio. In a similar manner we examined the octane–decane system at 378 K in a mixture of n-C_8D_{18}:n-$C_{10}H_{22}$ = 20.1. Low-pressure observations gave an upper limit of 3% for the dissociative channel (if any) in the exothermic charge transfer. Since the other reactions we investigated are less exothermic and/or involve lower molecular weight reactants than the cyclohexane–octane and octane–decane system, fragmentation is even less likely. Therefore, even though as little as 20% fragmentation upon charge transfer could create a significant error, in the present systems fragmentation does not affect the results.

In order to ascertain whether normal alkane cations retain their structure under thermal conditions, a series of closed-system experiments were carried out in which a cyclohexane–n-octane–nitric oxide (100:20:1) mixture was exposed to argon resonance radiation (104.8–106.7 nm). After exposure the reaction mixture was analyzed by GC for octane isomers. It was found that over the pressure range from 0.5 to 10 torr and a 0.1 to 0.5% conversion of the cyclohexane, no branched octane could be detected. Taking a photoionization quantum yield of 0.5 at 104.8–106.7 nm, the detection limit of the GC, and the rate constants for the charge exchange reactions (c-$C_6H_{12}^+$ + n-C_8H_{18} → n-$C_8H_{18}^+$ + c-$C_6H_{12}^+$ and n-$C_8H_{18}^+$ + NO → NO^+ C_8H_{18}), we conclude that no more than 0.5% of the $C_8H_{18}^+$ ions produced by charge exchange could isomerize at 300 K.

Several other observations also suggest that rearrangement is not important. First, we note that in the equilibrium systems we are studying ions that are produced by charge-transfer processes with internal energies generally at most 4 kcal mol^{-1} above thermal. Observations in the literature[14] suggest that rearrangements of n-alkane ions (e.g., n-butane$^+$) require higher activation energies. Indeed, Levsen and co-workers observed that n-$C_8H_{18}^+$ molecular ions retain their original structure[15] and that this conclusion applies to n-alkane ions at least up to dodecane.[16] They suggest that for radical cations the activation energies for rearrangement are higher than for decomposition. Therefore in our systems, where decomposition is negligible, rearrangement should also be so. In fact, the minor decomposition channels we do observe yield primarily the $(M - C_2H_6)^+$ olefinic ions. If rearrangement to branched structure did occur prior to decomposition, we would expect fragments corresponding to loss of C_3, C_4, C_5 alkanes.[17]

The internal consistency of the thermochemical cycles also suggests the absence of rearrangements. If rearrangements occurred, our observed equilibrium constants would be in fact the ratios of rate constants of unrelated (not forwards and reverse) processes. In general, the ratios of such "steady-state constants" do not have to fulfill the same relations as true equilibrium constants. However, our equilibrium constants show excellent consistency. For example, we checked the systems: (I) c-C_6D_{12}–2-methylpentane; (II) 2-methylpentane–octane; (III) c-C_6D_{12}–octane. At 303 K, $K_IK_{II} = 21.3$, compared with $K_{III} = 21.2$; at 410 K, $K_IK_{II} = 4.04$, compared with $K_{III} = 4.08$. Similarly, for the systems (IV) c-C_6H_{12}–octane, (V) octane–c-$C_6H_{11}CH_3$, and (VI) c-C_6H_{12}–c-$C_6H_{11}CH_3$, at 393 K, we get $K_{IV}K_V = 2.74 \times 103.2 = 283$, compared with $K_{VI} = 274$. Only by a very high degree of fortuitous circumstances could steady-state ion ratios give such consistency if they did not represent true equilibrium constants.

(b) Thermochemistry of Ionization. The enthalpies of ionization of normal alkanes are listed in Figure 8. Our measurements yield, of course, only relative values. To convert these to absolute values, we use the ionization energy of cyclohexane as reference, since this value is established by several consistent spectroscopic and photoionization values as 227.8 kcal mol^{-1} (9.88 eV). The absolute values of $\Delta H_i°$ give ionization energies at 300 K. As it was discussed previously by Lias and Ausloos,[3] these values are expected to be within 1 kcal mol^{-1} of ionization energies at 0 K, i.e., adiabatic ionization potentials, if the differences between ionic and neutral heat capacities are negligible. However, we should note that for the higher alkanes there appears to be less conformational freedom available to the ions than to the neutral molecules (see below). Therefore some internal rotations may be converted to low-frequency vibrations upon ionization. This would make the heat capacity of the ions lower than the neutrals and it would decrease the value of $\Delta H_i°$ (300 K) compared with the true adiabatic IP, i.e., $\Delta H_i°$(0 K). Nevertheless, we can estimate that even in the alkanes where negative $\Delta S_i°$ indicates conformation changes upon ionization, the effects of transforming rotors to oscillators on $\Delta H_i°$ will be negligible.

For example, $\Delta S_i°$ of n-C_7H_{16} is -4.7 cal mol^{-1} K^{-1} (Figure 8). This can be compared with the total entropy of the six internal rotors in n-C_7H_{16}, $S°_{\mathrm{int\,rot\,300}}$. To estimate this value, we consider the fully extended, i.e., all trans, conformation of n-C_7H_{16} and a barrier of 3 kcal mol^{-1} to each rotor. Using the methods of Benson,[24] we obtain $S°_{\mathrm{int\,rot\,300}} = 31$ cal mol^{-1} K^{-1}. Evidently, only a fraction of this entropy is lost when the ion assumes a constrained conformation since $\Delta S_i°$ is only -4.7 cal mol^{-1} K^{-1}. Therefore ca. 26 cal mol^{-1} K^{-1} is regained from the entropy of the low-frequency oscillators that are formed from the rotors. With use of the values of Benson,[24] this corresponds to the formation of six new oscillators each of $\bar{\nu} = 75$ cm^{-1}. (Actually, a set of oscillators with a distribution of frequencies will be formed). Now the contribution of the rotors to $\Delta H_f°$ of n-C_7H_{16} at 300 K, using the same model, is $H°_{\mathrm{int\,rot\,300}} = 3.1$ kcal mol^{-1}. The loss of this enthalpy will be almost exactly compensated for by $H°_{\mathrm{vib\,300}}$ of the six oscillators, which is 3.2 kcal mol^{-1}. In other words, even though the larger alkanes appear to assume loosely constrained structures upon ionization, the enthalpies of ionization measured at 300 K still approach the true adiabatic ionization potentials within a few tenths of 1 kcal mol^{-1}.

Literature values of ionization energies are available for some of the compounds except C_8 and higher n-alkanes (Table I). The photoionization values for n-alkanes are usually inaccurate, however, because the onsets are diffuse and the adiabatic threshold cannot be usually established. The most accurate value appears to be 228.3 kcal mol^{-1} (9.90 eV) for n-C_7H_{16}.[12] This agrees well with our value of 226.7 kcal mol^{-1} (9.83 eV).

The other literature values are all high by ca. 0.15 eV, which is to be expected for nonadiabatic IP's. We note that the literature IP's of c-C_5H_{10}, n-C_4H_{10}, n-C_5H_{12}, n-C_7H_{16}, and c-$C_6H_{11}CH_3$ constitute a scale which is displaced from our scale by a constant value of 0.15 ± 0.05 eV; i.e., all the PI IP's are displaced from the adiabatic value by a constant difference.

Relative entropies of ionization are given in Figure 9. Since absolute values of $\Delta S_i°$ are not known for any of the compounds,

---

[14] Wolkoff, P.; Holmes, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 7346.

[15] Levsen, K.; Heinbrecht, J. *Org. Mass Spectrom.* **1977**, *12*, 131.

[16] Levsen, K.; Heimbach, H.; Shaw, G. J.; Milne, G. W. A. *Org. Mass Spectrom.* **1977**, *12*, 663.

[17] In 2-Meheptane$^+$ we observed three very minor fragmentation processes, the loss of $CH_3\cdot$, CH_4, and C_3H_8.

[18] Sieck, L. W.; Moet-Ner (Mautner), M.; Ausloos, P. *J. Am. Chem. Soc.*, in press.

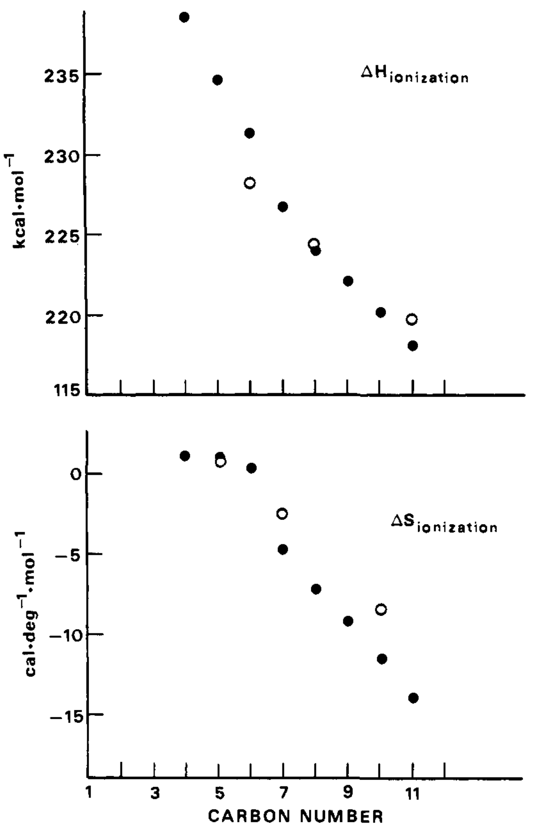

Figure 10. Variation of ionization enthalpies and entropies of normal alkanes n-C_nH_{2n+2} with n. Values for three 2-methylalkanes are also shown (open circles). $\Delta H_i°$ values of 2-methylalkanes are compared with n-alkanes of the same total number of carbon atoms, while $\Delta S_i°$ values of 2-methylalkanes are compared with n-alkanes of the same chain length.

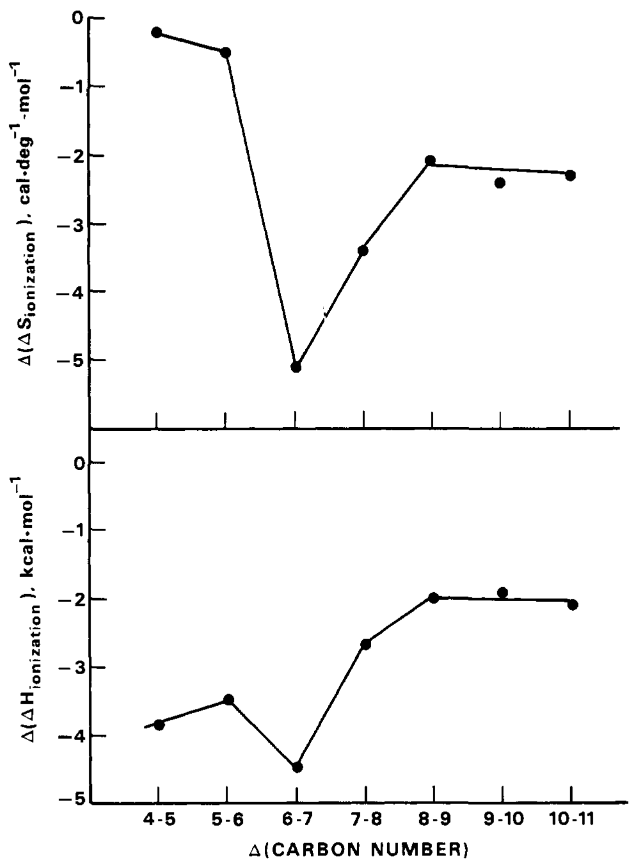

Figure 11. Incremental values of ionization enthalpies and entropies $(-\Delta\Delta P_i°(n,n+1) = \Delta P_i°(n\text{-}C_nH_{2n+2}) - \Delta P_i°(n\text{-}C_{2n+4})$ where $P = H$ or S).

we chose c-C_6H_{12} as zero for reference. This is an arbitrary value, and we note that Jahn–Teller distortion could decrease the symmetry number of c-C_6H_{12} from 6 to 1 upon ionization resulting in a +3.5 cal mol^{-1} K^{-1} contribution to $\Delta S_i°$. Nevertheless, we find indications that ΔS_i of c-C_6H_{12} is indeed very small, as follows. We note that ΔS_i(c-C_6H_{12}) is very close to ΔS_i(c-$C_6H_{11}CH_3$) where such symmetry contributions should not occur. Moreover, we note that ΔS_i of most of the smaller compounds is grouped within ±1.3 cal mol^{-1} K^{-1} of c-C_6H_{12}. These compounds include the C_4–C_6 normal alkanes and 2-methylpentane. Of the present set, these are the compounds with the most rigid structures (cyclics) or least conformational flexibility. The ionization entropies of such molecules are expected to be small. The results show that they all lie within experimental error of the same value. This common value is most likely to be zero.

One cylcic compound, c-C_5H_{10}, shows a positive $\Delta S_i°$ significantly different from zero. This may be an artifact due to the isomerization of some of the $C_5H_{10}^+$ ions to an olefinic structure at high temperatures. On the other hand, further measurements showed[29] a similar positive $\Delta S_i°$ in cycloheptane, where ring opening is absent, and $\Delta S_i°$ is due to the release of ring strain upon ionization. Therefore the measured ΔS_i of cyclopentane may indeed be real and also due to ring-strain release.

The most unexpected result in the present work is the observation of large negative $\Delta S_i°$ values for the n-alkanes C_7 and higher. This effect is discussed below.

(c) The Relation between Ionization Thermochemistry and Molecular Structure. The variation of $\Delta H_i°$ and $\Delta S_i°$ with molecular size in the normal alkanes n-C_nH_{2n+2} is shown in Figure 10. As anticipated, $\Delta H_i°$ decreases with increasing molecular size. However, a discontinuity occurs at heptane, as is evident in the incremental enthalpies, i.e., in $\Delta(\Delta H_i°)$ (Figure 11). Charge transfer from hexane to heptane is more exothermic by about 1.5 kcal mol^{-1} than expected from interpolation from other $\Delta(\Delta H_i°)$ values in this series. This suggests the onset of some stabilizing effect in n-$C_7H_{16}^+$. The abrupt change at heptane is even more pronounced in the $\Delta S_i°$ plot; whereas $\Delta S_i°$ values of C_4–C_6 n-alkanes are negligible, $\Delta S_i°$ values of the C_7 and higher alkanes are significantly negative, reaching −13.5 cal mol^{-1} K^{-1} in undecane.

To interpret these results, we recall that negative entropy changes of comparable magnitude were recently observed upon the ionization of other flexible molecules and that these effects occurred only for molecules above a certain limiting size.[6,7,19] In the case of diamines, entropy changes of −14.7 and −17.1 cal mol^{-1} K^{-1} were observed upon the protonation of diamino propane and butane, while a smaller entropy change of −8.0 cal mol^{-1} K^{-1} occurred in diaminoethane.[7] Enthalpies of protonation showed that these effects are due to the formation of constrained cyclic structures which also stabilize the ions; however, this stabilization is weakened substantially in diamino ethane by strain in the smaller ring. Similarly, intramolecular solvation of the charge leads to an entropy of protonation of −11.9 cal mol^{-1} K^{-1} in 3-aminopropanol, but the effect was absent in 2-aminoethanol.

The thermochemistry of ionization of diphenylalkanes, which are more closely related to the present systems, was investigated by Meot-Ner et al.[6] Analogous to the present results, the behavior of 1,2-diphenylethane was substantially different from the larger, more flexible 1,4-diphenylbutane as observed in charge transfer from a rigid reference ion.

$$1,2\text{-}C_6H_4(CH_3)_2^+ + C_6H_5(CH_2)_2C_6H_5 \rightarrow C_6H_5(CH_2)_2C_6H_5^+ + 1,2\text{-}C_6H_4(CH_3) \quad (12)$$

$$\Delta H = -0.8 \text{ kcal mol}^{-1} \quad \Delta S = -0.2 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$1,2\text{-}C_6H_4(CH_3)_2^+ + C_6H_5(CH_2)_4C_6H_5 \rightarrow C_6H_5(CH_2)_4C_6H_5^+ + 1,2\text{-}C_6H_4(CH_3)_2 \quad (13)$$

$$\Delta H = -5.6 \text{ kcal mol}^{-1} \quad \Delta S = -7.5 \text{ cal mol}^{-1} \text{ K}^{-1}$$

---

(19) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 3504.

The results imply the formation of constrained structure in the diphenylbutane ion and stabilization of the ion by ca. 4 kcal mol^{-1}, presumably due to interactions of the phenyl π systrems; but this does not occur in the diphenylethane ion. Similar results were obtained in the respective protonated diphenylalkane·H$^+$ ions. Other mass spectrometric observations also indicate intramolecular bonding between the substituents in the 1,3-diarylpropane and 1,4-diarylbutane but not 1,2-diarylethane ions.[20]

To summarize these observations on disubstituted alkanes $X(CH_2)_nX$: (1) ionization involves entropy changes of -5 to -15 cal mol^{-1} K^{-1} and excess stabilization of the ions compared with $CH_3(CH_2)_nX$; (2) these effects are favorable only for alkane chains larger than a critical size, i.e., $n > 2$; (3) these effects are explained by intramolecular bonding $-X-^+-X-$, where the $-X-^+-X-$ bond is strong enough to produce analogous dimer ions (e.g., R_3NH^+--NR_3, $C_6H_6^+$ -C_6H_6).[19,21]

What we wish to point out now is that a complete analogy can be drawn between these observations and the present results. We already noted the negative entropy changes in *n*-alkane ionization and some excess stabilization of the ions in heptane$^+$ and larger alkanes (Figure 11). To complete the analogy, we now suggest that the *n*-alkanes may be viewed as diethylalkanes C_2H_5-$(CH_2)_nC_2H_5$. By analogy with point 3 above, we then note that stable dimer ions $C_2H_6^+$ -C_2H_6 were observed by Sieck.[22] By analogy with point 2 the entropy and stabilization effects are observed for $n > 2$, i.e., heptane and larger alkanes, but not ≤ 2, i.e., hexane and smaller alkanes. The physical interpretation of this analogy suggests that in the C_7 and larger alkane ions bonding between the terminal ethane groups stabilizes a cyclic conformation.

Support for this hypothesis may be found by the examination of molecular models. Space-filling models show that in heptane the two ethane functions can assume a parallel conformation and approach as close as the hydrogen van der Waals radii without imposing steric strain in the rest of the molecule. In this conformation the orbitals derived from the ethane HOMO $1E''$ (Π_{CHO}-type) orbitals can overlap favorably. This will stabilize by delocalization the positive charge and electron spin associated with these orbitals in the *n*-$C_7H_{16}^+$ radical cation in a manner similar to the charge delocalization between overlapping orbitals derived from benzene $^1E_{1g}$ in the diphenylalkane radical cations. Space-filling models show that such a conformation cannot be reached without substantial strain in the hexane ion.

To the extent that the entropy effects in the ionization of alkanes reflect substantial geometry changes, it is interesting to note that large geometry changes also seem to occur in the Rydberg states of *n*-alkanes, as is evidenced by large Stokes shifts in the fluorescence spectra.[25] It is reasonable that removal of an electron to a highly expanded orbital and complete ionization should induce similar geometry changes.

Another interesting, although speculative aspect of the present entropy effect is a possible relation to liquid-phase positive hole conduction in irradiated liquid alkanes. Liquid-phase optical and mobility measurements[26] showed that the positive hole mobility in cyclohexane is more than 10 times greater than the mobility of the cyclohexane ion. The fact that the high-mobility positive holes were only observed in cyclohexane and methyl cyclohexane, and not in normal and branched alkanes, indicates in view of our results that fast resonance charge transfer in the liquid phase will only occur when the geometric configuration of the positive ion and ground-state molecule are similar.

(d) 2-Methylalkanes. The enthalpies and entropies of three 2-methylalkanes are shown in Figures 8 and 9. The results allow some interesting comparisons with the normal alkanes.

While ΔH_i° of isohexane (i.e., 2-methylpentane) is significantly lower than hexane, ΔH_i° of isooctane (2-methylheptane) is higher than that of normal octane. Also, ΔS_i° of 2-methylheptane is just slightly negative, much less so than in *n*-octane or even in the *n*-alkane of the same chain length, i.e., heptane. Both ΔH_i° and ΔS_i° therefore suggest that the stabilization of a folded conformation in the 2-methylheptane ion is less significant than in the heptane ion. Similar comparison applies between the 2-methyldecane and decane or undecane ions, although here we note that ΔS_i° of 2-methyldecane is significantly negative.

The difference between normal and 2-methylalkanes is consistent with the physical model we described above. While bonding between the terminal ethyl groups would be analogous to bonding in symmetric dimer ions, interactions between a terminal ethyl group and a terminal ethyl group substituted by methyl in the 2-position is analogous to an asymmetric dimer. Results in dimer ions of aromatic molecules[21,23] show that bonding in such asymmetric dimers is generally weaker than in symmetric dimer ions.

(e) Isotope Effects on Ionization Energies. In Table I we list the equilibrium constants for the charge-transfer reactions

$$n\text{-}C_nD_{2n+2}^+ + n\text{-}C_nH_{2n+2} \rightleftarrows n\text{-}C_nH_{2n+2}^+ + n\text{-}C_nD_{2n+2} \qquad (14)$$

as well as the isotope effects in cyclohexane and cylopentane. For several reactions ΔH° and ΔS° were also obtained. ΔS° values are zero within experimental error limits; indeed the average of the ΔS° values listed in Table I is only -0.1 cal mol^{-1} K^{-1}, which also suggests that the measured ΔS° values only reflect random scattering about zero. Therefore for isotope effects, i.e., for reaction 17, we can consider $\Delta H^\circ = \Delta G^\circ$.

In the normal alkanes the total number of C–H bonds increases with molecular size while the ratio of C–H to C–C bonds decreases, from 6:1 in ethane to 18:7 in octane. Experimentally we observe that the isotope effect decreases montonically with size, suggesting that as the molecular size increases, ionization increasingly affects C–C- vs. C–H-type orbitals.

Both cyclopentane and cyclohexane show isotope effects much larger than the corresponding normal alkanes. The isotope effect in cyclohexane as obtained from the ΔG° value (0.033 eV) is in excellent agreement with a spectroscopic value of Raymonda (0.032 eV)[10] and in reasonable agreement with a previous equilibrium value obtained by ICR measurements in this laboratory (0.027 eV).[5]

It is interesting to note that isotope effects similar to those observed by us in the gas phase have been observed also in liquid-phase radiolysis. The equilibrium constant for charge transfer from perdeuterated to perhydrogenated alkanes was 3.2 for the gas-phase cyclopentane system, vs. 3.2 in the liquid phase,[27] for cyclohexane 3.3 vs. 3.2,[27] for *n*-butane 2.7 vs. 4.1,[28] and for *n*-pentane 1.7 vs. 2.4.[28]

Acknowledgment. The support of the Office of Basic Energy Sciences, Department of Energy, is gratefully acknowledged.

---

(20) Caluwe, P.; Shimada, K.; Szwarc, M. *J. Am. Chem. Soc.* **1973**, *95*, 1433.

(21) Meot-Ner (Mautner), M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1978**, *100*, 5466.

(22) Searles, S. K.; Sieck, L. W.; Ausloos, P. *J. Chem. Phys.* **1970**, *53*, 849.

(23) Meot-Ner (Mautner), M. *J. Phys. Chem.*, in press.

(24) Benzon, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(25) Hirayama, F.; Lipsky, S. *J. Chem. Phys.* **1969**, *59*, 3676.

(26) Zador, E.; Warman, J. M.; Hummel, A. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 914 and references therein.

(27) Ausloos, P.; Scala, A. A.; Lias, S. G. *J. Am. Chem. Soc.* **1967**, *89*, 3677.

(28) Ausloos, P. *Radiat. Phys. Chem.*, in press.

(29) Sieck, L. W.; Meot-Ner (Mautner), M., unpublished results.