must be directed toward C_2 of the diene system (i.e., must be an interior methyl H). This would result in a through-space interaction of the C_3 p(π) orbital and, more importantly, the C_2 p(π) orbital with a hydrogen 1s orbital (or orbitals) which would account for the observed destabilization of ψ_4^*. The major interaction is illustrated in Figure 6 for conformation **4b**, although there are clearly an infinite number of conformations with interior out-of-plane methyl hydrogens which would account for this observation. (The occurrence of such conformations can be rationalized on the basis of an interaction between the eclipsed methyl hydrogen and H_2 in conformation **4a.**) A similar through-space interaction accounts for the *relative* stabilization of ψ_3^* in **4** and **5** compared to **2** and **3**, respectively. Indeed the agreement of the *relative* trans–cis shifts of *both* ψ_3^* and ψ_4^* with the foregoing through-space interaction is an important factor in support of this analysis.

The long-wavelength electronic-absorption band for the negative ions of **1**, **3**, and **4**, prepared by γ-irradiation in methyltetrahydrofuran glasses at −196 °C, has been attributed to a transition between ψ_3^* and ψ_4^*.[14] The energies of these transitions (2.18, 2.16, and 2.20 eV, respectively) are in the same relative order as are the values of $AE_2 - AE_1$ (2.02, 1.65, and 2.21 eV, respectively), but the differences are greatly attenuated. This observation might be attributed to a substantial amount of diffuse character in these negative ion states which is greatly diminished in condensed phases.[15,16]

Summary. The key findings of the present investigation are (a) that significant through-space methyl-π interactions exist in the ψ_3^* and ψ_4^* negative ion states of **4** and **5**, (b) the this interaction in ψ_4^*, and probably also in ψ_3^*, primarily involves the hydrogen 1s (π) rather than the carbon p(π) orbital of the methyl group, and (c) that conformations with interior out-of-plane methyl hydrogens make a significant (but as yet unspecified) contribution to the distribution of conformations in **4**. Similar considerations also apply to **5**. We believe that the electron-transmission technique may prove to be quite powerful in probing certain conformational questions. This will serve to greatly expand its already recognized importance in providing electron affinities and attachment energies of complex molecules.

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Thermoneutral Isotope Exchange Reactions of Cations in the Gas Phase

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Abstract: Rate constants have been measured for reactions of the type $AD_2^+ + MH \rightarrow MD + ADH^+$, where AD_2^+ is CD_3CND^+, CD_3CDOD^+, $(CD_3COCD_3)D^+$, or $(C_2D_5)_2OD^+$ and the MH molecules are alcohols, acids, mercaptans, H_2S, AsH_3, PH_3, or aromatic molecules. Rate constants are also presented for the reactions $Ar_HD^+ + D_2O \rightarrow Ar_DD^+ + HDO$, where Ar_HD^+ is a deuteronated aromatic molecule and Ar_DD^+ is the same species with a D atom incorporated on the ring. In all but two cases, the competing deuteron transfer is sufficiently endothermic that it cannot be observed under the conditions of the ICR experiments at 320–420 K. The efficiencies of the isotope exchange reactions are interpreted in terms of estimated potential surface cross sections for the reactions $AD_2^+ + MH \rightarrow [AD_2^+{\cdot}MH] \rightarrow [AD{\cdot}MHD^+] \rightarrow [ADH^+{\cdot}MD] \rightarrow ADH^+ + MD$. When the formation of the $[AD{\cdot}MHD^+]$ complex is estimated to be thermoneutral or slightly endothermic, the isotope exchange process is inefficient (probability of a reactive collision < 0.1) or does not occur. The most efficient isotope exchange reactions are observed for those systems for which it is estimated that the transformation $[AD_2^+{\cdot}MH] \rightarrow [AD{\cdot}MHD^+]$ is exothermic. For most of the systems, trends in reaction efficiency appear to be related to factors such as dipole moments of reactant species (or for aromatic compounds, the electron-donating or -withdrawing properties of ring substituents) which influence the relative orientation of the two reactant species in the complex.

In 1975, Freiser, Woodin, and Beauchamp[1] reported the observation of isotope exchange reactions involving protonated (deuteronated) aromatic molecules and D_2O. The sequence:

$$C_6H_6D^+ + D_2O \rightarrow C_6H_5D_2^+ + HDO \quad (1a)$$

$$C_6H_5D_2^+ + D_2O \rightarrow C_6H_4D_3^+ + HDO \quad (1b)$$

and analogous sequences involving other aromatic species were seen to continue until all H atoms on the aromatic ring were replaced by D atoms. They proposed that ring protonation was a necessary condition for exchange, and suggested that the mechanism involved the occurrence of a proton transfer to D_2O *in the complex*, followed by dissociation of the complex to form HDO, since formation of separated HD_2O^+ is endothermic for these reactions.

Martinsen and Buttrill[2] investigated such isotope exchange reactions involving protonated (deuteronated) aromatic species and D_2O in a high-pressure mass spectrometer, and reported observations and conclusions essentially in agreement with those of the ion cyclotron resonance study.[1]

More recently, Hunt and collaborators[3] have examined such reactions in conjunction with work on chemical ionization mass

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spectrometry. Their extensive study[3a] of exchange reactions with D_2O and C_2H_5OD uses the occurrence of such reaction sequences as a method for counting hydrogen atoms in specific organic structural environments. These authors have observed[3b] that "the extent of exchange is dependent on the exothermicity of the ion–molecule reaction involved" (i.e., the corresponding proton transfer reactions, since the isotope exchange reactions themselves are essentially thermoneutral). When proton transfer between the reactant pair is endothermic by more than about 20–25 kcal/mol, the H/D exchange reaction is not observed, suggesting that the intermediate state is inaccessible to the reactants for energetic reasons.[3]

It has also been shown[1-3] that isotope exchange is observed only when the reactant molecule has a H(D) at the site in the molecule at which proton transfer would occur. These observations lend support to the suggestion that the transition state for isotope exchange is the same as the transition state for proton (deuteron) transfer[1] and point up the value of these reactions as a transition state probe.

Entirely analogous isotope exchange reactions involving intracomplex proton transfer mechanisms have been observed for negative ions.[3-8]

Although such isotope exchange reactions are potentially useful for probing the details of ion–molecule reaction mechanisms and understanding the potential energy surfaces associated with these reactions, only a few quantitative results of the kinetics of isotope exchange processes have been reported.[9] We report such results here for the reactions (such as (1)) involving protonated (deuteronated) aromatic species with D_2O, as well as similar isotope exchange reactions of CD_3CND^+, CD_3CDOD^+, $(CD_3COCD_3)D^+$, and $(C_2D_5)_2OD^+$ with various organic and inorganic compounds.

Experimental Section

The experiments were performed using the NBS pulsed ion cyclotron resonance spectrometer, which has been described before.[10] The experimental and computational procedures followed in deriving rate constants have also been described previously.[11] The pressures used in these experiments were in the range of 10^{-7}–10^{-5} Torr, and the temperature was 330 ± 5 K, except where otherwise specified. The ions were observed at times in the range 10^{-3} to 0.5 s. Rate constants were determined, in each case, in premixed mixtures, and also by introducing the gases separately through two different inlets; differences between the measurements made by the two techniques were within the error limits of either set of determinations. Each rate constant reported represents the average of three to five separate determinations. The error limits cited in the tables are the standard deviation of the measurements. The accuracy of the measurements is estimated to be ±20%. Determinations were made at a magnetic field strength of 1.25–1.35 T. In each case, the reactant ion was observed independently in the absence of the reactive molecule to ascertain the rate of unreactive ion loss; this was negligible in most cases, but corrections were made routinely whenever any decay was observed on the time scale of the experiments.

Results

Table I lists rate constants for isotope exchange reactions involving CD_3CND^+, $(C_2D_5)_2OD^+$, CD_3CDOD^+, and $(CD_3COCD_3)D^+$ ions with a variety of organic and inorganic molecules. The reactant ions were formed in mixtures in which small concentrations (<10%) of reactant molecule, MH, were added to bulk CD_3CN, $(C_2D_5)_2O$, CD_3CDO, or CD_3COCD_3. The reactant ions were generated through self-deuteronation reactions of the parent ions:

$$AD^+ + AD \rightarrow AD_2^+ + A \quad (2)$$

(where AD is CD_3CN, $(C_2D_5)_2O$, CD_3CDO, or CD_3COCD_3). In every instance, proton (deuteron) transfer from AD_2^+ to the additive molecule is sufficiently endothermic that it does not occur under the conditions of these experiments.

Table I. Rate Constants at 331 K for the Isotope Exchange Reaction: $AD_2^+ + MH \rightarrow ADH^+ + MD$

AD_2^+	MH	$k \times 10^{10}$, cm^3/molecule·s	k/Z[a]	ΔG[b] (D^+ transfer), kcal/mol[c]
CD_3CND^+	CH_3CHO	0.0		+1.8
	C_6H_6	11.3 ± 0.4	0.81	+4.9
	CH_3OH	8.8 ± 0.4	0.50	+5.6
	AsH_3	3.8 ± 0.3	0.40	+7.7
	H_2S	2.0 ± 0.2	0.16	+14.5
$(CD_3COCD_3)D^+$	CH_3COOH	4.5 ± 0.4	0.31	+5.6
	C_2H_5SH	3.5 ± 0.3	0.23	+5.3
	C_2H_5OH	5.1 ± 0.2	0.33	+7.6
	CH_3SH	3.2 ± 0.3	0.22	+8.9
	CH_3CHO	0.0		+9.8
	CH_3OH	4.1 ± 0.3	0.26	+13.6
	AsH_3	0.0		+15.7
CD_3CDOD^+	C_6H_6	6.6 ± 0.3	0.49	+3.1
	CH_3OH	3.1 ± 0.4	0.18	+3.8
	AsH_3	1.6 ± 0.3	0.17	+5.9
	H_2S	0.69 ± 0.17	0.053	+14.6
$(C_2D_5)_2OD^+$	C_2H_5SH	1.6 ± 0.2	0.12	+8.4
	n-C_3H_7SH	2.0 ± 0.3	0.14	+8.6
	C_2H_5OH	2.9 ± 0.3	0.21	+11.8
	CH_3SH	0.90 ± 0.20	0.071	+12.0
	CH_3OH	1.3 ± 0.2	0.090	+16.7

[a] Reaction efficiency. Z is the estimated ion–molecule collision rate constant (ref 21). [b] Experimental results from ref 12 and 13. [c] 1 kcal/mol = 4.184 kJ/mol.

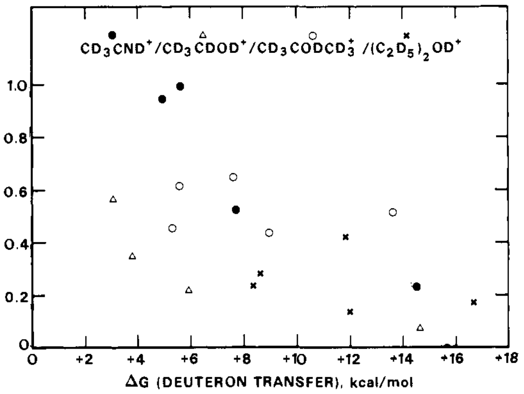

Figure 1. The statistically corrected relative efficiencies of the H/D transfer reaction ($AD_2^+ + MH \rightarrow AHD^+ + MD$) (data from Table I) as a function of the ΔG of the corresponding deuteron-transfer reaction ($AD_2^+ + MH \rightarrow MHD^+ + AD$).

The observation reported before that isotope exchange does not occur when there is no H atom at the site of proton transfer in the neutral molecule[1-3] is confirmed. No reaction is observed when the neutral reactant species is a carbonyl compound (Table I).

Figure 1 shows the probability of a reactive H/D exchange encounter for these deuteronated ions as a function of the Gibbs free-energy change of the (endoergic) deuteron transfer reaction:[12,13]

$$AD_2^+ + MH \rightarrow MHD^+ + AD \quad (3)$$

The results shown in the figure have been statistically corrected

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Table II. Rate Constants for Proton Transfer and Deuteron Exchange Reactions Occurring in Competition

		cm³/molecule·s × 10^{10}					
	T	k_f	Z_f	k_r	Z_r	K_{eq}	ΔG, kcal/mol
$CH_3SH_2^+ + CH_3CN \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CH_3CN\ H^+ + CH_3SH$	323	19.9 ± 0.5	30.4	3.6 ± 0.4 9.8[a]	15.7	5.5	−1.1
	390			5.1 ± 0.3	15.2		
	414	17.2 ± 0.5	27.6	5.5 ± 0.4 10.6[a]	15.0	3.1	−0.9
$CH_3CN\ H^+ + PH_3 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} PH_4^+ + CH_3CN$	323	3.4 ± 0.2 10.6 ± 0.3[b]	12.2	5.9 ± 0.3	31.9	0.49	+0.45
	390	2.9 ± 0.3 10.7 ± 0.3[b]	12.1	7.8 ± 0.4	29.6	0.37	+0.77
	423	3.1 ± 0.2 10.8 ± 0.3[b]	12.0	8.4 ± 0.4	28.8	0.37	+0.84

[a] Rate constant for disappearance of CD_3CND^+ by reaction with CH_3SH through deuteron transfer and isotope exchange. [b] Rate constant for disappearance of CD_3CND^+ by reaction with PH_3 through deuteron transfer and isotope exchange.

Table III. Rate Constants at 331 K for the Reactions $Ar_DH^+ + D_2O \rightarrow Ar_DD^+ + HDO$ and $Ar_DH^+ + Ar_H \rightarrow Ar_HH^+ + Ar_D$

Ar	$k_4 \times 10^{10}$, cm³/molecule·s	k/Z[d]	ΔG,[b] (proton transfer), kcal/mol[c]	$k_5 \times 10^{10}$, cm³/molecule·s
p-$C_6H_4F_2$	5.3 ± 0.3 [f][a]	0.3	+12.6	0.50 ± 0.15
o-$C_6H_4F_2$	4.4 ± 0.4 [f][a]	0.3	+13.1	0.60 ± 0.20
m-$C_6H_4F_2$	0.44 ± 0.2 [m][a]	0.03	+13.2	0.16 ± 0.10
C_6H_5F	1.8 ± 0.2 [f][a]	0.1	+13.3	0.38 ± 0.12
C_6H_6	2.7 ± 0.3 [f][a]	0.2	+13.5	2.2 ± 0.20
$CH_3C_6H_5$	0.3 [m][a]		+19.7	1.1 ± 0.20

[a] Results from ref 1: [f] = "fast" and [m] = "medium fast". [b] Experimental results from ref 22 and 23. [c] 1 kcal/mol = 4.184 kJ/mol. [d] Reaction efficiency. Z is the estimated ion–molecule collision rate constant (ref 21).

for the relative number of H(D) atoms at the site of deuteron transfer.

Data have also been obtained in two systems (CD_3CN–PH_3 and CD_3CN–CH_3SH) for which the proton transfer reactions are close to thermoneutral. In both systems, proton transfer reactions occur for both the exothermic and endothermic channels, and when CD_3CN is replaced by CH_3CN, an equilibrium is established in the ion cyclotron resonance ion source. Isotope exchange processes are also seen to occur in both these systems. Table II gives the rate constants for the exothermic and endothermic proton transfer reactions (obtained using the double resonance technique) at several temperatures, the corresponding equilibrium constants, and the rate constants for loss of CD_3CND^+ through H/D transfer plus deuteron-transfer reactions.

Isotope exchange sequence 1 and analogous sequences involving C_6H_5F, o-, m-, and p-$C_6H_4F_2$, and $C_6H_5CH_3$ were also examined:

$$Ar_DH^+ + D_2O \rightarrow Ar_DD^+ + HDO \qquad (4)$$

(where Ar_D denotes an aromatic ring containing or associated with one or more D atoms). In every case examined, the sequence was seen to continue until all the ring hydrogens had been replaced by D atoms. The rate constants for the first steps in these sequences were estimated in mixtures of small amounts of aromatic compound in D_2O and are listed in Table III. Accurate determinations of these rate constants are difficult because of the occurrence of the competing reactions:

$$Ar_DH^+ + Ar_H \rightarrow Ar_HH^+ + Ar_D \qquad (5)$$

as well as reactions which regenerate the Ar_DH^+ reactant ion, such as:

$$Ar_HH^+ + D_2O \rightarrow Ar_DH^+ + HDO \qquad (6)$$

$$Ar_DD^+ + ArH \rightarrow Ar_DH^+ + Ar_D \qquad (7)$$

The rate constants for reaction 5 were measured in mixtures of the aromatic compounds with CD_4; the Ar_DH^+ ion was formed by deuteron transfer to Ar_H from CD_5^+. (Correction had to be made for slow, $k < 10^{-12}$ cm³/molecules, isotope exchange reactions involving Ar_DH^+ and CD_4.) The rate constants for reactions 4 were estimated by keeping the concentraton of the aromatic compound low enough that reaction 5 constituted less that 10% of the reaction of Ar_DH^+ in the D_2O mixture. Under these conditions, most of the product ions of reaction 5 will undergo reaction 6 to regenerate Ar_DH^+, and reaction 7 will also be unimportant. The estimated rate constants for the first steps in the sequence of reaction 4, as well as the rate constants measured for reactions 5, are given in Table III. The trends are in agreement with the qualitative results reported by Freiser, Woodin, and Beauchamp.[1] The m-$C_6H_3DF_2H^+$ ion, reported by those authors to undergo only the first step in the reaction sequence, indeed reacts with D_2O much more slowly that do any of the other isomeric ions, although, as reported by Martinsen and Buttrill, all the H atoms in the molecule are sequentially replaced by D atoms.

Table IV gives the rate constants for the isotope exchange reactions of CD_3CND^+ and CD_3CDOD^+ ions with various halogenated aromatic compounds. Unlike the reactions of the same ions shown in Figure 1, there are wide variations in the probability

Table IV. Rate Constants at 331 K for the Reactions $CD_3CND^+ + Ar_H \rightarrow CD_3CNH^+ + Ar_D$ and $CD_3CDOD^+ + Ar_H \rightarrow CD_3CDOH^+ + Ar_D$

Ar	$k \times 10^{10}$ (CD_3CND^+ + Ar), cm³/molecule·s	k/Z[a]	$k \times 10^{10}$ (CD_3CDOD^+ + Ar), cm³/molecule·s	k/Z[a]
C_6H_6	7.9 ± 0.3	0.56	8.6 ± 0.3	0.63
C_6H_5F	7.6 ± 0.3	0.45		
m-$C_6H_4F_2$	4.8 ± 0.3	0.29	3.9 ± 0.3	0.24
o-$C_6H_4F_2$	0.60 ± 0.15	0.031	0.60 ± 0.12	0.032
C_6H_5Cl	4.2 ± 0.4	0.23	2.2 ± 0.2	0.13
1,3,5-$C_6H_3F_3$	1.8 ± 0.2	0.14	1.4 ± 0.3	0.11
p-$C_6H_4F_2$	0.0		<~0.2	<0.013
1,2,4-$C_6H_3F_3$	0.085 ± 0.04	0.006		
1,2,3,4-$C_6H_2F_4$	0.5 ± 0.2	0.03		

[a] Reaction efficiency. Z is the estimated ion–molecule collision rate constant (ref 21).

Table V. Enthalpy Changes Estimated[a] for Steps in the Mechanism: $AD_2^+ + MH \rightarrow [AD_2^+{\cdot}MH] \rightarrow [AD{\cdot}MHD^+] \rightarrow [ADH^+{\cdot}MD] \rightarrow ADH^+ + MD$

						~ΔH, kcal/mol[b]		
	AD	μ_D	MH	μ_D	k/Z[e]	formation of $[AD_2^+{\cdot}MH]$[c]	formation of $[AD{\cdot}MHD^+]$[d]	$[AD_2^+{\cdot}MH] \downarrow [AD{\cdot}MHD^+]$
A	CD_3CN	3.96	C_6H_6	0.0	0.81	−3	−8	−5
B	CD_3CN	3.96	CH_3OH	1.70	0.50	−7	−10	−3
C	CD_3CDO	2.72	C_6H_6	0.0	0.49	−3	−7	−4
D	CD_3CN	3.96	AsH_3	0.16	0.40	−3	−8	−5
E	CD_3COCD_3	2.89	C_2H_5OH	1.70	0.33	−8	−5	+3
F	CD_3COCD_3	2.89	CH_3COOH	1.74	0.31	−7	−5	+2
G	CD_3COCD_3	2.89	CH_3OH	1.70	0.26	−8	−2	+6
H	CD_3COCD_3	2.89	C_2H_5SH	1.58	0.23	−8	−5	+1
I	CD_3COCD_3	2.89	CH_3SH	1.26	0.22	−7	−4	+3
J	$(C_2D_5)_2O$	1.15	C_2H_5OH	1.70	0.21	−11	−3	+8
K	CD_3CDO	2.72	CH_3OH	1.70	0.18	−7	−7	0
L	CD_3CDO	2.72	AsH_3	0.16	0.17	−4	−4	0
M	CD_3CN	3.96	H_2S	0.92	0.16	−6	−3	+3
N	$(C_2D_5)_2O$	1.15	n-C_3H_7SH	~1.6	0.14	−12	−3	+9
O	$(C_2D_5)_2O$	1.15	C_2H_5SH	1.58	0.12	−11	−3	+8
P	$(C_2D_5)_2O$	1.15	CH_3OH	1.70	0.090	−13	0	+13
Q	$(C_2D_5)_2O$	1.15	CH_3SH	1.26	0.071	−12	+1	+13
R	CD_3CDO	2.72	H_2S	0.92	0.053	−6	+1	+8
S	CD_3COCD_3	2.89	AsH_3	0.16	0.00	−3	+2	+5

[a] Estimated from eq 10; see Discussion. [b] 1 kcal/mol = 4.184 kJ/mol. [c] Estimated enthalpy change for formation of $[AD_2^+{\cdot}MH]$ complex from separated $AD_2^+ + MH$. [d] Estimated enthalpy change for formation of $[AD{\cdot}MHD^+]$ complex from separated $AD_2^+ + MH$ (from overall endothermicity of proton transfer reaction and estimated well depth for formation of complex from separated $AD + MHD^+$ reactants). [e] Reaction efficiency of the isotope exchange reaction from Table I.

of H(D) exchange reactions involving a given ion even through the endothermicities of the corresponding proton (deuteron) transfer reactions are all approximately the same. For example, no reaction occurs between CD_3CND^+ and p-$C_4H_4F_2$ (ΔG(proton transfer) = +6.5 kcal/mol), the efficiency of exchange with o-$C_6H_4F_2$ is only 0.03 (ΔG(proton transfer) = +6.0 kcal/mol), and the probability of a reactive exchange with m-$C_6H_4F_2$ is 0.29 (ΔG(proton transfer) = +5.9 kcal/mol).

Discussion

It has been pointed out before[3] that the efficiency of isotope exchange reactions diminishes with increasing endothermicity of the corresponding proton transfer reaction. The results from Table I, plotted in Figure 1, demonstrate the existence of such a trend for the reactions studied here, although the overall scatter in the data is very wide. The fact that such trends are seen, and that when the corresponding proton transfer reaction is more endothermic than about 20 kcal/mol the isotope exchange process is not observed, suggests that the mechanism of the isotope exchange reaction is the occurrence of a proton transfer reaction *in the complex*, as suggested before:[1]

$$AD_2^+ + MH \underset{k_{-1}}{\overset{Z}{\rightleftarrows}} [AD_2^+{\cdot}MH] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [AD{\cdot}MDH^+] \underset{k_2'}{\overset{k_{-2}'}{\rightleftarrows}} [ADH^+{\cdot}MD] \xrightarrow{k_{-1}'} ADH^+ + MD \quad (8)$$

An additional piece of evidence suggesting reaction 8 as the mechanism for the isotope exchange processes is the fact that isotope exchange is not observed when MH is a molecule (such as CH_3COCH_3, CH_3CHO, or CH_3CN) which does not have an H atom at the site where proton transfer would be expected to occur. The overall trends in the efficiency of these processes with energy suggest[3] that the occurrence of the proton transfer *in the complex* eventually becomes energetically unfavorable when the overall proton transfer reaction becomes sufficiently endothermic. That is, the enthalpy change of proton (deuteron) transfer *in the complex*:

$$AD_2^+ + MH \rightarrow [AD_2^+{\cdot}MH] \rightarrow [AD{\cdot}MHD^+] \quad (9)$$

may be exothermic in most cases, even though the dissociation of $[AD{\cdot}MHD^+]$ to form the separated products ($AD + MHD^+$) is prohibited because of the overall endothermicity of the deuteron transfer reaction from AD_2^+ to MH. However, formation of $[AD{\cdot}MHD^+]$ from ($AD_2^+ + MH$) may in some cases be endothermic, accounting for some of the low efficiencies of isotope exchange listed in Table I. Cross sections of potential surfaces illustrating these two possible situations are given in Figure 2.

In order to evaluate the results in terms of the energetic requirements of reaction 9, it is necessary to estimate the relative potential well depths of the "loose" ion-molecule complexes, $[AD_2^+{\cdot}MH]$ and $[AD{\cdot}MHD^+]$. At short ranges, the ion-molecule potentials contain attractive and repulsive interactions determined largely by valence forces, and can only be calculated by quantum mechanics. Since such calculations are not within the scope of this work, it is necessary to use an approximate approach to obtain some idea, however inexact, of the overall shapes of the potential surface cross sections for the reactions of interest. One possible first approximation would be to evaluate the classical potential of interaction between an ion and a molecule at a distance corresponding approximately to the collision diameter:

$$V(r) = -q\mu_D(\cos\theta)/r^2 - q^2\alpha/2r^4 \quad (10)$$

(where q is the electronic charge, μ_D is the dipole moment, α is the polarizability of MH, θ is the angle between the line of centers of AD_2^+ and MH, and r is the separation between them). To test whether such a procedure gives even an approximate estimate of the well depth of an ion-molecule complex, we carry out such a calculation for several polyatomic ion-molecule complexes for which experimentally determined values of the potential well depths are available (taking as the collision diameter, 85% of the value estimated from van der Waals radii): $[NH_4^+{\cdot}NH_3]$, calcd −23 kcal/mol compared with −27 kcal/mol, exptl;[14] $[H_3O^+{\cdot}H_2O]$, calcd −28 kcal/mol compared with −36 kcal/mol, exptl;[15] $[C_6H_6^+{\cdot}c\text{-}C_6H_{12}]$, −6 kcal/mol compared with −9.9 kcal/mol, exptl;[16] and $[C_6H_6^+{\cdot}CS_2]$, −11 kcal/mol, compared with −12.2 kcal/mol, exptl.[16] Clearly, eq 10 underestimates the maximum values of the well depths but does seem to reproduce in an ap-

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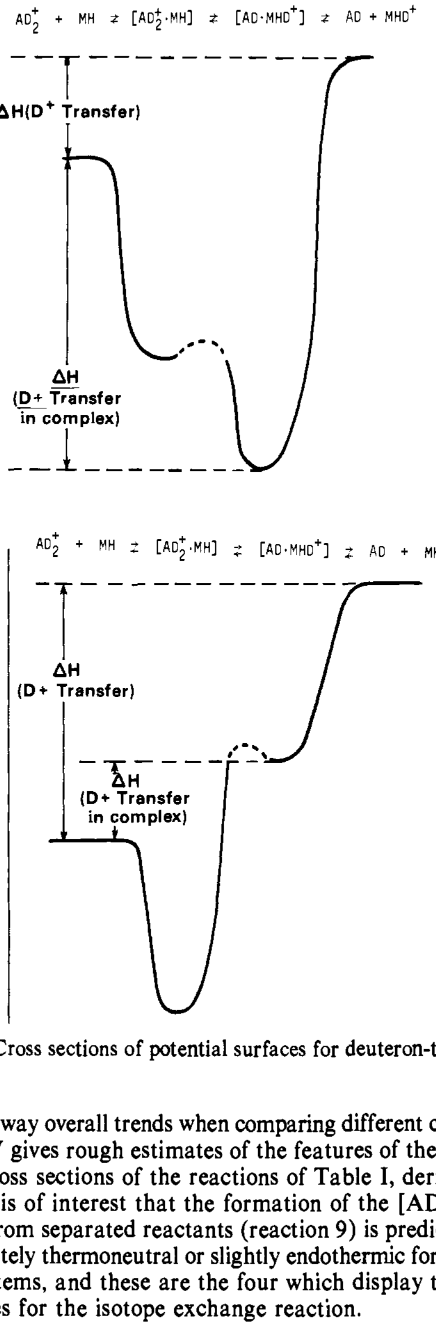

Figure 2. Cross sections of potential surfaces for deuteron-transfer reactions.

proximate way overall trends when comparing different complexes.

Table V gives rough estimates of the features of the potential surface cross sections of the reactions of Table I, derived from eq 10. It is of interest that the formation of the [AD·MHD$^+$] complex from separated reactants (reaction 9) is predicted to be approximately thermoneutral or slightly endothermic for only four of the systems, and these are the four which display the lowest efficiencies for the isotope exchange reaction.

In the interpretation of the efficiencies of ion-molecule reactions, an approach often used is to assume that the energy of the complex is completely randomized over certain degrees of freedom, and to treat its reaction or dissociation back to separated reactant molecules in terms of standard statistical theory. Recent treatments of proton transfer reactions:[6,17]

$$AH^+ + B \underset{k_{-1}}{\overset{Z}{\rightleftarrows}} [AH^+ \cdot B] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [BH^+ \cdot A] \xrightarrow{k_3} BH^+ + A \qquad (11)$$

have explained lower-than-unity reaction efficiencies for the production of separated products from reactants in terms of the competition between the two unimolecular channels −1 and 2. The overall forward rate constant associated with this mechanism is:

$$k_f = \frac{Zk_2k_3}{(k_{-1} + k_2)k_3 + k_{-2}k_{-1}} \qquad (12)$$

Under the assumption that when [AH$^+$·B] has been converted to [A·BH$^+$], formation of (BH$^+$ + A) always results (i.e., $k_{-2} = 0$), the efficiency of reaction is given by:

$$\frac{k_f}{Z} = \frac{k_2}{(k_{-1} + k_2)} \qquad (13)$$

The procedure then has been to make appropriate assumptions about the vibrational frequencies and moments of inertia for the transition states associated with channels −1 and 2, and evaluate the corresponding sums of states. In treatments published to date,[17] the height of a barrier in the reaction channel corresponding to transition state 2 has been taken as an arbitrary variable parameter. In order to apply this model to the results of Table I, we apply the steady-state treatment to mechanism 8. If we make the simplifying assumption that isotope effects on unimolecular rate constants associated with this mechanism will be minimal, then $k_{-1} \simeq k_{-1}'$, $k_2 \simeq k_2'$, and $k_{-2} \simeq k_{-2}'$, and we obtain for the efficiency of the isotope exchange process an expression identical with eq 13. (Experimental results[17,18] indicate that isotope effects on proton transfer reactions are negligible except when there is significant steric hindrance.[17]) That is, just as in the case of proton transfer reactions, the reaction efficiency is predicted to depend on the competition between channels −1 and 2 (mechanisms 8 and 11), that is, between dissociation of the [AD$_2^+$·MH] complex to (AD$_2^+$ + MH) and reaction to form [AD·MHD$^+$]. A treatment of these data through statistical unimolecular theory would necessarily be highly speculative in view of the complete lack of quantitative information about the details of the potential surface in the region of the transition state for channel 2. It is more instructive to examine the experimental results for clues about factors which influence the competition between channels −1 and 2.

It is first of interest to examine whether the unimolecular conversion of [AD$_2^+$·MH] to [AD·MHD$^+$] is predicted to be endothermic or exothermic on the basis of the estimated potential surface cross sections given in Table V. It is seen that this channel is estimated to be clearly exothermic for only four reactant pairs, and these are the four systems which exhibit the most efficient isotope-exchange reactions. For all other systems, the transformation [AD$_2^+$·MH] → [AD·MHD$^+$] may be endothermic; i.e., there may well be a barrier in the reaction coordinate having at least the height of the endothermicity of this transformation. However, as long as the overall reaction leading from separated reactants to the [AD·MHD$^+$] complex is exothermic, there is no apparent relationship between the relative energy requirements of channels −1 and 2 and the efficiency of the reaction. Such a relationship might, however, be revealed if a more accurate estimation of the relevant potential surfaces were available.

If we compare series of reactons for which it is predicted that the features of the potential surface having to do with the competition between channels −1 and 2 are very similar, it would seem that the probability of exchange is enhanced, the greater the dipole moment of the MH molecule. Compare, for example, reactions E, F, H, I, and M, or reactions J and O in Table V. Kollman[19] and Allen[20] have carried out theoretical analyses of the potential surfaces associated with complexes which (like those complexes discussed here) are not covalently bonded. Kollman[19] concludes that the most favorable structures of such complexes can be rationalized from the electrostatic potentials of the molecules, and for complex molecules can sometimes be predicted from such parameters as dipole moments and electronegativities. Thus, the observed dipole moment dependence suggests that the unimolecular rate constant associated with the proton transfer in the complex, channel 2, is increased by factors which aid in bringing about a particular alignment of the two reactant species in the [AD$_2^+$·MH] collision complex. This conclusion is supported by the results given in Tables III and IV having to do with reactions involving aromatic species, as will be discussed below.

Efficient isotope exchange processes compete with proton transfer reactions when the proton transfer reactions are close to

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thermoneutral, as shown by the data given in Table II. For the reactant pair ($CH_3CNH^+ + CH_3SH$), about one-fourth or one-third of the collisions result in the occurrence of the endothermic proton transfer reaction between the two at 323 and 414 K, respectively. When CH_3CNH^+ is replaced by CD_3CND^+, however, the observed rate constant for loss of this reactant ion demonstrates that, in fact, in this system, every collision does lead to reaction:

323 K: k(proton transfer) $= 3.6 \times 10^{-10}$ cm^3/molecule·s
k(statistically corrected isotope exchange) $= (9.8\text{-}3.6) \times 2 \times 10^{-10}$ cm^3/molecule·s
k(total) $= 16. \times 10^{-10}$ cm^3/molecule·s
Z(collision) $= 15.9 \times 10^{-10}$ cm^3/molecule·s

414 K: k(proton transfer) $= 5.5 \times 10^{-10}$ cm^3/molecule·s
k(statistically corrected isotope exchange) $= (10.6\text{-}5.5) \times 2 \times 10^{-10}$ cm^3/molecule·s
k(total) $= 15.9 \times 10^{-10}$ cm^3/molecule·s
Z(collision) $= 15.2 \times 10^{-10}$ cm^3/molecule·s

(where Z is the predicted ion-molecule collision rate constant[21]). As would be expected for a reaction in which an energy barrier must be overcome, it is seen that the rate constant for the endothermic proton transfer reaction increases with temperature at the expense of the isotope exchange process, although the probability of forming the [$CD_3SHD^+{\cdot}CD_3CN$] complex remains unity over the temperature range examined here.

In the case of the other reaction given in Table II:

$$CH_3CNH^+ + PH_3 \rightleftarrows PH_4^+ + CH_3CN \qquad (14)$$

the proton transfer involving the pair corresponding to those undergoing the isotope exchange:

$$CD_3CND^+ + PH_3 \rightleftarrows PH_2D + CD_3CNH^+ \qquad (15)$$

is actually exothermic, although in the temperature range of these experiments, the Gibbs free energy change of reaction is positive. Again, an analysis of the rate constants for loss of CD_3CND^+ reveals that every collision results in the formation of a transition state for proton transfer, even though only a fraction separate as $PH_4^+ + CH_3CN$ (or $PH_3D^+ + CD_3CN$) products.

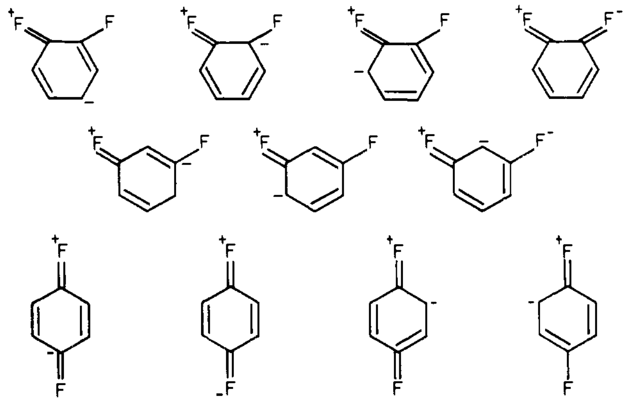
323 K: k(proton transfer) $= 3.4 \times 10^{-10}$ cm^3/molecule·s
k(statistically corrected isotope exchange) $= (10.6\text{-}3.4) \times 4/3 \times 10^{-10}$ cm^3/molecule·s
k(total) $= 13.0 \times 10^{-10}$ cm^3/molecule·s
Z(collision) $= 12.2 \times 10^{-10}$ cm^3/molecule·s

390 K: k(proton transfer) $= 2.9 \times 10^{-10}$ cm^3/molecule·s
k(statistically corrected isotope exchange) $= (10.7\text{-}2.9) \times 4/3 \times 10^{-10}$ cm^3/molecule·s
k(total) $= 13.3 \times 10^{-10}$ cm^3/molecule·s
Z(collision) $= 12.1 \times 10^{-10}$ cm^3/molecule·s

423 K: k(proton transfer) $= 3.1 \times 10^{-10}$ cm^3/molecule·s
k(statistically corrected isotope exchange) $(10.8\text{-}3.1) \times 4/3 \times 10^{-10}$ cm^3/molecule·s
k(total) $= 13.3 \times 10^{-10}$ cm^3/molecule·s
Z(collision) $= 12.0 \times 10^{-10}$ cm^3/molecule·s

It is of interest to examine the rate constants of these two proton transfer reactions in terms of mechanism 11 and eq 12 and 13. In the case of reaction 14, the isotope exchange evidence suggests that every collision leads to the formation of a [$CH_3CN{\cdot}PH_4^+$] complex, but only a fraction of these, about one-fourth, separate to form products. Since $e^{\Delta S/R}$ for the overall reaction is equal to 0.40, it would seem that the barrier to separaton of the products in this case is entropic. In the case of the ($CH_3CNH^+ + CH_3SH$) reactants, the results also indicate that every collision leads to the formation of the ion-molecule complex corresponding to the product species, [$CH_3CN{\cdot}CH_3SH_2^+$]. Here the barrier to separation to products is the endothermicity of the proton transfer reaction in this direction. In both systems, those complexes which are unable to separate to products return to form the original reactant species with a statistical distribution of H/D labeling in the isotopically labeled experiments. For these two reactions, at least, it must be concluded that k_{-2} in mechanism 11 is not zero (as is assumed in the simplification of eq 12 to eq 13).

Reactions Involving Aromatic Species. In the H/D exchange reactions of protonated aromatic molecules with D_2O (Table III) and CD_3CND^+ and CD_3CDOD^+ with aromatic molecules (Table IV), the overall shapes of the relevant potential surfaces are predicted to be similar for all reactant molecules. Yet, as pointed out above, there are wide variations in the efficiency of the isotope exchange reactions. This is not surprising if, as suggested above, the determining factors for reaction efficiency are those which have to do with influencing the relative orientation of the two reactant species in the complex. The orientation of a positive ion with respect to an aromatic ring will, of course, be governed by the electron-donating or -withdrawing properties of substituents on the ring. For these halogen-substituted compounds, the electron density of the ring is decreased and that of the halogen atom increased by σ-withdrawal, while at the same time, electron donation through the π system exerts an opposing effect. In monosubstituted compounds, the π donation predominates, and the ortho and para positions are activated to attack by positively charged species. With increasing halogen substitution, the σ-withdrawal effect begins to predominate over the π-donation effect. Thus, the proton affinities of halogen-substituted benzenes decrease somewhat with increasing substitution.[22,23] For a consideration of the thermoneutral H/D transfer, remembering that exchange occurs only when the ion attacks at a site bearing an H atom, one must estimate the probability that attack of the positive ion will be directed to the (nonreactive) halogen site. For example, in *o*-, *m*-, and *p*-difluorobenzene, the resonance structures below can be drawn to illustrate the effects of the π-donating effect. In the case of the ortho and para compounds, half of the structures favor attack by a positively charged species at an F atom or an F-substituted C atom; σ-withdrawal would amplify this tendency, and it would be predicted that the H/D exchange reaction with a deuteronated ion would be less efficient for these compounds than for the meta isomer, for which the π-donating effect activates only sites bearing an H atom. This is indeed what is observed for both CD_3CND^+ and CD_3CDOD^+ reactant ions (Table IV). Similarly, if one considers the efficiencies of H/D exchange reactions with 1,3,5-$C_6H_3F_3$ and 1,2,4-$C_6H_3F_3$, one sees that the reaction with the 1,3,5 isomer is much more efficient than reaction with the 1,2,4 isomer, although neither multiply substituted ring undergoes a highly efficient exchange. Again, in the 1,3,5 isomer, σ-donation activates only sites bearing H atoms, while in the 1,2,4



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compound, one would predict that both π-donation and σ-withdrawal should activate attack at F atoms, thus lowering the efficiency of the transfer reaction.

On the other hand, when one starts with the deuterated halobenzene ions as reactants with neutral D_2O (Table III), the trends in reactivity for the chemical species described above are reversed: *o*-$C_6H_4F_2D^+$ and *p*-$C_6H_4F_2D^+$ undergo efficient H/D transfer reactions, while *m*-$C_6H_4F_2D^+$ reacts with an efficiency of only 0.03. This would suggest that proton (deuterons) associated with a halogen atom are more readily transferred than are $H^+(D^+)$ species on the ring. However, in these reactions, the occurrence of successive exchange steps analogous to those written in eq 1, demonstrates that rearrangement of the H^+/D^+ species within the ion does occur.

Absolute Heats of Formation for Gas-Phase Cations

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Abstract: The relationship between $\Delta H_f{}^\circ{}_{298}(A^+)$ and the appearance energy for the process $AB + h\nu \rightarrow A^+ + B + e^-$ is examined. A general-purpose expression is derived and applied to the measurement of absolute 298 K enthalpies of formation for some simple alkyl cations. If a stationary electron convention is adopted for $\Delta H_f{}^\circ{}_{298}(A^+)$, the following values are obtained: $CH_3^+ = 261.3 \pm 0.4$ kcal mol^{-1}; $C_2H_5^+ = 216.0 \pm 0.5$ kcal mol^{-1}; *s*-$C_3H_7^+ = 191.8 \pm 0.4$ kcal mol^{-1}; *t*-$C_4H_9^+ \lesssim 166.2 \pm 0.8$ kcal mol^{-1}. Absolute proton affinities are calculated for ethylene, propene, and isobutene. From a consideration of other studies, a value of 34.4 ± 0.7 kcal mol^{-1} is recommended for the methyl radical heat of formation.

The precise determination of heats of formation for cations in the gas phase has assumed considerable importance in recent years. With the development of experimental techniques for the measurement of equilibrium constants associated with proton-transfer reactions among positive ions, extensive networks of relative gas-phase basicities and proton affinities have been compiled.[1] The assignment of absolute proton affinities relies on the use of suitable reference standards which are usually derived from heats of formation for positive ions. However, these are still not firmly established, with uncertainties in appearance energies, ionization energies, and supplementary thermochemical data giving rise to values over ranges of several kilocalories per mole.[2] A recent study of proton-transfer reactions involving alkyl ions and alkenes[3] has produced a set of relative ionic heats of formation which may assist in their absolute determination.

The most precise ionic heats of formation have been obtained from variable-temperature photoionization experiments.[4] These can lead to reliable 0 K values, provided that the auxiliary thermochemical data at 0 K is available or can be estimated; in most cases this is the major source of uncertainty in $\Delta H_f{}^\circ{}_0$ (ion). Extrapolation of data from experiments performed at temperatures very much above room temperature is of limited application because of possible thermal decomposition effects; there is also the likelihood of errors being introduced as a result of extrapolation over a large temperature range.[5] The best technique is to perform low-temperature experiments, although these are not always practicable due to problems with sample condensation and reduced sample pressure. It would thus be useful if a method could be developed to enable ionic heats of formation to be accurately estimated from room-temperature photoionization measurements.

In this paper we examine the relationship between $\Delta H_f{}^\circ{}_{298}(A^+)$ and the appearance energy (AE) for the general process

$$AB + h\nu \rightarrow A^+ + B + e^- \tag{1}$$

with particular application to the enthalpies of formation, at 298 K, for some simple alkyl cations.

Experimental Section

The computer-controlled photoionization mass spectrometer employed in this study has been described in detail elsewhere.[6] The source of photons used was the hydrogen many-line spectrum, and the band-pass of the monochromator in the present experiments was 1.25 Å. The absolute energy scale was calibrated with known atomic emission lines and found to be accurate to better than ±0.005 eV. All compounds used were commerical samples of research grade which showed no impurities of significance in their mass spectra. The measurements were carried out with sample pressures in the range 10^{-6}–10^{-5} torr.

Results and Discussion

Convention for Cationic Heats of Formation. In order to obtain absolute heats of formation for positive ions in the gas phase, it is necessary to adopt a standard state convention for the electron ejected in the ionization process. This can be readily demonstrated by considering the standard gas-phase heat of formation for a proton, $\Delta H_f{}^\circ(H^+)$, which refers to the enthalpy change for the reaction

$$^1/_2H_2(g) \rightarrow H^+(g) + e^-(g)$$

At 0 K, the heat of reaction is the adiabatic ionization energy (IE) and corresponds to the formation of a proton and an electron with zero translational energy, i.e., at rest. For the reaction at a temperature *T*, it is possible to consider $\Delta H_f{}^\circ{}_T$ with reference to the production of either a proton and an electron, each with $^3/_2RT$

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