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indicates that approximately 25% of the m/z 29 is HOC^+. At this pressure an average of 10 collisions with CO are expected to occur before HOC^+ exists the ion source. The nascent product distributions resulting from reactions 5–8 are not known and subsequently more than 25% HOC^+ could be formed initially. However, the observed increase in the C^+/CH^+ ratio suggests that reaction 3 occurs with a rate substantially less than the collision rate, which contradicts the suggestions of Nobes and Radom.[1] Experiments designed to study the catalytic conversion of HOC^+ to HCO^+ (reaction 3) as well as reactions 5–8 were not successful due to a large $^{13}CO^+$ contribution to the main beam.

Conclusion

Both HCO^+ and HOC^+ have been detected confirming the predictions of ab initio calculations[1-3] which concluded that both of these structures should be experimentally observable. The reaction between H_3^+ and CO appears to produce 6 ± 5% HOC^+ and thus may be one of the major pathways leading to this ion in interstellar space. In addition, HOC^+ does not appear to be rapidly converted to HCO^+ by reaction with CO as previously thought.

Acknowledgment. The support of the National Science Foundation under Grant CHE80-20464 and partial support by the California Space Institute are gratefully acknowledged. One of us (M.F.J.) wishes to acknowledge the Science and Engineering Research Council (U.K.) for a NATO/SERC fellowship.

Registry No. CO, 630-08-0; HCO^+, 17030-74-9; HOC^+, 60528-75-8; CD_3OH, 1849-29-2; CH_3COOH, 64-19-7; CH_3OH, 67-56-1; CH_3OCH_3, 115-10-6; $HCOOCH_3$, 107-31-3; H_2CO, 50-00-0.

Gas-Phase Hydrogen–Deuterium Exchange Reactions of HO^- and DO^- with Weakly Acidic Neutrals

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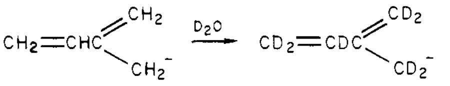
Abstract: Rate constants for hydrogen–deuterium exchange reactions between HO^- and DO^- and a series of weakly acidic neutrals, both organic and inorganic, have been measured in the gas phase by using the selected ion flow tube (SIFT) technique. The reaction efficiencies are discussed in terms of the initial ion–dipole complex energies, the relative acidities of the neutrals, and the change in solvation energy accompanying proton transfer; the effect of these energies on transition-state properties profoundly influences the outcome of the reactions. Exchange occurs rapidly between hydroxide and most aromatic and vinyl compounds but is relatively inefficient for hydrogen. The efficiency for exchange with ammonia is intermediate. Ethylene, dimethyl ether, and methane do not exhibit exchange.

Proton transfer is one of the most fundamental of chemical processes and so it is not surprising that it has been the subject of many investigations in the field of gas-phase ion–molecule chemistry. By combining the results obtained from a wide variety of experimental techniques, including ion cyclotron resonance spectroscopy, high-pressure mass spectrometry, and the flowing afterglow method, Bartmess and McIver[1] and Aue and Bowers[2] have compiled extensive tabulations of gas-phase acidities and basicities. Brauman and co-workers[3] and more recently Lias and co-workers[4] have shown how the kinetics of proton transfer can be useful in probing the nature of the potential energy surfaces for ion–molecule reactions. Indeed most groups active in the field of gas-phase ion–molecule chemistry have studied one aspect or another of proton-transfer processes.

Our own interest in this area arose from our discovery of the facile hydrogen–deuterium exchange reactions between carbanions and D_2O in the gas phase. Using a flowing afterglow apparatus, we found that carbanions, for example, the allylic anions obtained by proton abstraction from 1-pentene, will exchange protons for deuterium when allowed to react in the gas phase with D_2O (eq 1).[5] Less basic anions, for example, those stabilized by two double bonds or adjacent to carbonyl or other electron-withdrawing groups, do not exchange with D_2O but do so with stronger gas-phase acids (CH_3OD or CF_3CH_2OD).[6] More recently we showed that protons less acidic than those in water (e.g., vinyl or aryl protons) can also be exchanged with D_2O provided they are incorporated within anions that are less basic than HO^- (eq 2).[7]

$$CH_3CH_2\bar{C}HCH{=}CH_2 \xrightarrow{D_2O} C_5D_9^-,\ C_5D_8H^- \ldots \qquad (1)$$


(2)

These exchange reactions are useful in probing ion structure since isomeric ions will often exchange different numbers of protons. This method has also been applied to negative-ion chemical ionization mass spectrometry.[8]

A general, qualitative picture of the process by which H–D exchange is thought to occur is summarized in eq 3. A carbanion

$$RCH_2^- + D_2O \rightleftarrows \underset{\text{I}}{[RCH_2^-{\cdot}D_2O]} \rightleftarrows \underset{\text{II}}{[RCH_2D{\cdot}DO^-]} \rightleftarrows \underset{\text{III}}{[RCHD^-{\cdot}HOD]} \rightleftarrows RCHD^- + HOD \qquad (3)$$

attracts D_2O by ion–dipole and ion-induced dipole forces and they enter into a relatively long-lived reaction complex I that contains

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excess energy. This same amount of energy is required to separate the ion and neutral after exchange. Part of this energy may be used to carry out an otherwise endothermic deuteron transfer to form a new complex II with insufficient energy to separate. This energy is regained by exothermic proton transfer to form complex III. Dissociation of III and subsequent reaction of the carbanion with other molecules of D_2O leads to further exchange. In the process of proton addition and reabstraction, double-bond migration may occur so that eventually each proton in the anion may be allylic and hence susceptible to exchange.

While this scheme accounts in a general way for the exchange, there remain a number of anomalies. For example, the acetonitrile anion $N{\equiv}CCH_2^-$ (PA = 372 kcal mol^{-1}) exchanges fairly readily with D_2O (ΔH°_{acid} = 391 kcal mol^{-1}), while the more basic acetylide ion $HC{\equiv}C^-$ (PA = 375 kcal mol^{-1}) will not exchange with D_2O or with CH_3OD (ΔH°_{acid} = 379 kcal mol^{-1}). Obviously more is involved in the exchange process than simply the relative basicities of the separated ions: electrostatic interactions within the complexes I, II, and III must also play crucial roles. In order to unravel the nature and role of these interactions, kinetic studies of the exchange reactions are necessary.

Unfortunately obtaining good kinetic data for the exchange process between carbanions and D_2O is extremely difficult. There are several reasons for this: most carbanions contain several different types of hydrogen atoms that exchange at different rates; there can be multiple exchanges within a single D_2O–carbanion encounter; clustering occurs between many anions (particularly those containing oxygen and nitrogen) and D_2O. Kinetic analysis becomes much simpler if the exchange is reversed and the conversion of HO^- to DO^- is examined by using deuterated compounds less acidic than water as the exchange reagent. For example, hydroxide ion is readily converted to deuteriooxide ion in the presence of deuteriobenzene (eq 4). Field and co-workers[9] were

$$HO^- \xrightarrow{C_6D_6} DO^- \tag{4}$$

the first to measure rates for this type of reaction when they studied exchange between HO^- and D_2 and ND_3 in a high-pressure mass spectrometer. However the extension of such studies to a wide variety of neutrals in a flowing afterglow would require the preparation of many perdeuterated compounds. A more attractive approach is to measure rates of conversion of DO^- to HO^- in the presence of unlabeled neutral substrates (eq 5). These experi-

$$DO^- \xrightarrow{C_6H_6} HO^- \tag{5}$$

ments must be performed in the absence of D_2O since it would rapidly reconvert HO^- to DO^-. In a conventional flowing afterglow, the generation of DO^- without D_2O as precursor requires large amounts of CD_4 and is prohibitively expensive. We have recently constructed a newer, modified version of the flowing afterglow, known as a selected ion flow tube (SIFT).[10] In a SIFT, DO^- can be produced by direct electron impact on D_2O in a low-pressure ion source outside of the flow tube and injected into the flow tube in the absence of D_2O and other ions. In this paper we report our studies of H–D exchange of 20 compounds, organic and inorganic, and show how these studies may be used to shed light on the factors that determine the potential energy surfaces for gas-phase proton-transfer reactions.

Experimental Section

The experiments were performed with the selected ion flow tube (SIFT) recently constructed in our laboratory. In essence, the SIFT technique allows one to inject a mass-analyzed ion beam into a multiple-collision reaction region where the reaction is carried out at thermal energies. The reactant anions must be produced at sufficiently low energies to prevent collisional detachment or fragmentation upon exiting the low-pressure ion source region and entering the higher pressure flow tube and with high enough current to allow accurate measurements. In addition to satisfying these two conditions, the SIFT circumvents several problems. The SIFT excludes from the reaction region (i) other primary ions, (ii) the neutral precursors of the reactant ion, and (iii) sources of continuing ionization such as electrons or metastables. Once ions are produced and injected into the flow tube, reactions are studied in the same manner as in the conventional flowing afterglow.

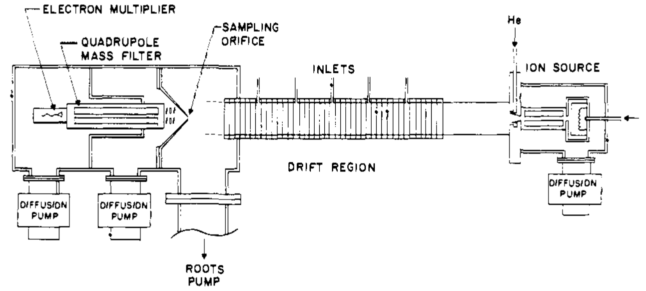

Figure 1. Selected ion flow tube apparatus.

The apparatus, shown schematically in Figure 1, is a flow reactor[11] employing the mass-selected Venturi-inlet ion injection system of Smith and Adams.[10] Ions are produced by electron impact in a low-pressure Brinks-type ion source that is remote from the flow/reaction tube. For example, D_2O^+, DO^+, O^+, DO^-, and O^- are produced from D_2O by using 50-eV electrons from a 0.25-mm-diameter tungsten wire operated at 25 W. The ions are extracted from the ion source via a 5-mm-diameter orifice and are directed toward the entrance of a 10-cm quadrupole mass filter, which focuses only the mass-selected ion component onto the 2-mm Venturi-inlet orifice leading to the flow tube. The pressure in the injection mass spectrometer chamber is typically 2×10^{-4} torr, while the pressure in the ion source itself is somewhat higher. The flow tube is at ground potential, and the low-energy (~20 V) passage of the ions from low to high pressure is made possible by the expansion of the helium gas into the flow tube through a narrow annulus (0.4 mm in width and 2.1 cm in diameter) surrounding the orifice. Through this annulus helium flows of typically 150 STP cm^3 s^{-1} are admitted, which establishes flow tube pressures of about 0.4 torr. The effect of this inlet is to reduce the helium pressure at the ion-entrance orifice. The helium carries the ions downstream at ~80 m s^{-1} in the 7.30-cm i.d., 100-cm-long flow tube. Pumping is accomplished with a 755 l s^{-1} Roots blower backed by a 71 l s^{-1} mechanical pump. Helium pressure is monitored with a capacitance manometer while the helium flow is maintained with a calibrated mass flow controller. The ions are collisionally relaxed in the first 30 cm, after which they pass through the reaction region that contains seven equally spaced neutral gas inlets. These inlets allow radial addition of the neutral reagent gas through 17 pinholes evenly spaced around the flow tube perimeter. The flow of the neutral is measured just prior to and immediately after each kinetic run by monitoring a pressure change in a calibrated volume.

At the end of the reaction region, the ionic population is sampled through a 1-mm orifice in a molybdenum plate mounted on the blunt tip of a 120° nose cone into a differentially pumped quadrupole mass spectrometer detection system. The ions are mass analyzed and counted via standard techniques under either manual or computer control. Either positive or negative ions may be injected, sampled, analyzed, and detected by appropriate choices of the polarities of the necessary voltages.

For these experiments, the reactant ions were formed in two ways: electron impact on D_2O (H_2O) to give DO^- (HO^-) or electron impact on a mixture of nitrous oxide and cyclohexane-d_{12} (n-butane) to give O^-, which rapidly abstracts a D (H) atom to give DO^- (HO^-). The formation of DO^- or HO^- by these secondary reactions was useful since diffusion of D_2O (H_2O) from the ion source into the flow tube was occasionally sufficient to reconvert some of the product ion to reactant ion, causing curvature in the kinetic plots at long reaction times. Slight leakage of the hydrocarbons (C_6D_{12} or C_4H_{10}) probably also occurs, but these molecules do not undergo isotope exchange with DO^- or HO^-.

Gas purities were as follows: helium (99.995%), methane (99.0%), ammonia (99.997%), ammonia-d_3 (99%), ethylene (98.5%), hydrogen (99.999%), deuterium (99.5%), butadiene (99.0%), methyl vinyl ether (99.5%), dimethyl ether (99.5%), methylamine (98.0%), and dimethylamine (99.0%). HD was prepared by reaction of $LiAlH_4$ with D_2O and was dried by passing through dry ice and liquid nitrogen traps. Helium buffer gas was purified by passage through 10 m of 1.9-cm o.d. copper tubing packed with 4-Å molecular sieves and immersed in liquid nitrogen. H_2 and D_2 were dried during use by passage through 4 m of 6.4-mm o.d.

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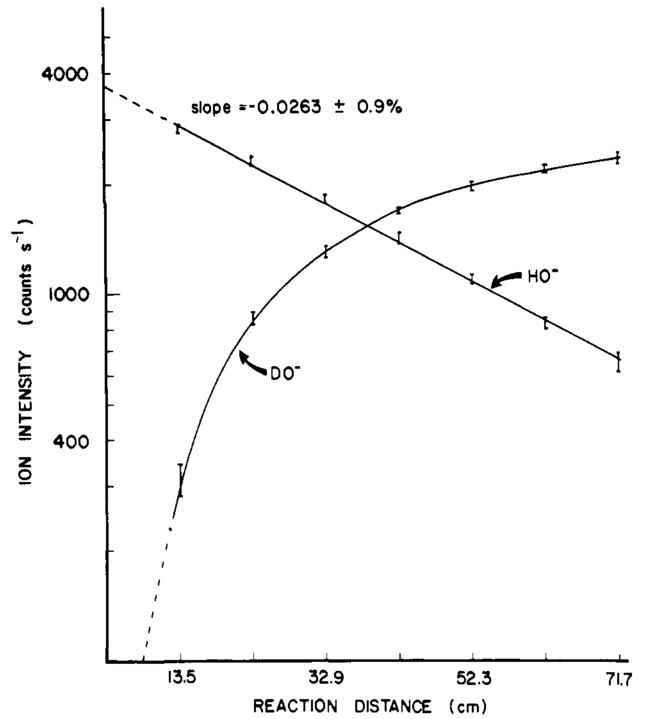

Figure 2. Kinetic data for the reaction $HO^- + C_6D_6 \rightarrow DO^- + C_6D_5H$. Flow of helium = 145 STP cm^3 s^{-1}, pressure of helium = 0.350 torr, flow of benzene-d_6 = 5.47×10^{-3} STP cm^3 s^{-1} and T = 298 K. $k = 8.01 \times 10^{-10}$ cm^3 particle^{-1} s^{-1}.

stainless steel tubing immersed in liquid nitrogen. CH_4 was purified by passage through this same trap immersed in a slush of dry ice-isopropanol. NH_3, ND_3, H_2O, D_2O, ethylene, and dimethylamine were used without further purification. Benzene, benzene-d_6 (99%), *tert*-butylbenzene, and dimethyl ether were dried over $LiAlH_4$. Norbornadiene and *tert*-butylethylene were distilled prior to use and then dried with $LiAlH_4$. Butadiene, methyl vinyl ether, and methylamine were passed through a 5-m-long 9.5-mm o.d. copper tube, packed with ~50% $CaSO_4$, ~50% 3-Å molecular sieve mixture. All liquid samples were purified by several freeze-pump-thaw cycles.

Data analysis is straightforward and is analogous to that described in detail elsewhere.[11] Briefly, for an ion-molecule reaction of the type in eq 4, standard kinetic analysis for pseudo-first-order conditions gives eq 6, where $\bar{v}$ is the average buffer gas velocity, z is the reaction distance,

$$k = -\frac{d(\ln [HO^-])}{dz} \frac{\alpha \bar{v}}{[C_6D_6]} \tag{6}$$

and α = 1.6 converts the average flow velocity to the average transport velocity of the ions. Reducing eq 6 to a form containing the experimentally determined parameters yields eq 7, where r = 3.65 cm is the

$$k\left(\frac{\text{cm}^3}{\text{particle s}}\right) = - \frac{d(\ln [HO^-])}{dz \text{ (cm)}}\left[\frac{F_{He}{}^2\left(\frac{\text{STP cm}^3}{\text{s}}\right)^2 T(\text{K})\ \alpha}{P_{He}{}^2\ (\text{torr})^2\ F_{C_6D_6}\left(\frac{\text{STP cm}^3}{\text{s}}\right) r^2\ (\text{cm})^2}\right] 2.72 \times 10^{-17} \tag{7}$$

flow tube radius. The flow and pressure of helium are easily measured, as is the flow of the neutral reactant. Ion intensities, as measured by the mass spectrometer, are of arbitrary units directly proportional to the true ion concentration and are plotted vs. the reaction distance as in Figure 2. Substituting the slope of Figure 2 into eq 7, with F_{He} = 145 STP cm^3 s^{-1}, P_{He} = 0.350 torr, $F_{C_6D_6} = 5.47 \times 10^{-3}$ STP cm^3 s^{-1}, and T = 298 K gives a rate constant of 8.01×10^{-10} cm^3 particle^{-1} s^{-1}. Figure 2 also shows the behavior of the product ion, DO^-.

Table I. Rate Constants for Hydrogen-Deuterium Exchange Reactions at 299 (± 1) K

base	neutral	k_{obsd}[a]	reaction[b] efficiency	$\Delta[\Delta H^\circ_{acid}]$,[c] kcal mol^{-1}	ΔH_{rxn},[d] kcal mol^{-1}
HO^-	D_2	0.68	0.060	9.6	−0.6
DO^-	H_2	0.38	0.024	9.6	+0.8
HO^-	HD	0.35	0.027	9.6	−0.8
DO^-	HD	0.15[e]	0.012[e]	9.6	+0.6
HO^-	ND_3	2.7	0.13	12.8	+0.5
DO^-	NH_3	3.8	0.18	12.8	−0.5
HO^-	D_2O	12	0.50	0	+0.3
DO^-	H_2O	18	0.74	0	−0.1
HO^-	C_6D_6	7.5	0.38	<12.8	−0.5
DO^-	C_6H_6	6.6	0.34	<12.8	+0.5

[a] In units of 10^{-10} cm^3 particle^{-1} s^{-1}. [b] Reaction efficiency = k_{obsd}/k_{ADO}, ref 13. [c] Reference 1. [d] Reference 14. [e] This rate constant is calculated from an equilibrium constant for $HO^- + D_2 \rightleftarrows DO^- + HD$ (K = 4.6) derived from thermodynamic data and our measured forward rate constant.

The accuracy of quantitative kinetic studies with the new apparatus was demonstrated by measuring the rate coefficients for two well-known ion-molecule reactions. We studied the reaction of $He^+ + N_2$ by adding a constant flow of nitrogen to a helium plasma and monitoring the He^+ signal as the reaction distance was varied (i.e., as nitrogen was added through different radial inlets). We obtain as an average of six experiments, $k = 1.20$ ($\sigma = \pm 0.13$) $\times 10^{-9}$ cm^3 particle^{-1} s^{-1} in exact agreement with previous determinations.[12] For $Ar^+ + O_2$, an average of eight experiments gave $k = 4.55$ ($\sigma = \pm 0.46$) $\times 10^{-11}$ cm^3 particle^{-1} s^{-1} in good agreement with the literature value[12] of 4.9×10^{-11} cm^3 particle^{-1} s^{-1}. We estimate the accuracy of our reported rate constants to be ±20%.

The reported rate constants for hydrogen-deuterium exchange reactions are the average of five or more independent observations, with the exceptions of $DO^- + H_2O$ (four measurements) and DO^- with CH_4, C_2H_4, and CH_3OCH_3 (two measurements each). In a series of rate coefficient measurements the flow and pressure of helium and the flow of the neutral were varied to insure that these reactions are pseudo-first-order.

Results

For a few molecules, hydrogen, ammonia, benzene, and water, deuterated derivatives are readily obtainable, so that H-D exchange reactions can be studied from two directions and the effect of isotopic substitution on rate can be determined. Results for these compounds are collected in Table I. It is usually not sufficient in gas-phase ion-molecule chemistry merely to compare absolute rates of reaction because molecules with dipole moments or high polarizabilities collide more frequently with ions than do nonpolar, weakly polarizable molecules. We have therefore included in Table I the reaction efficiency, that is, the probability of reaction per collision. The rate of collision between an ion and a molecule was calculated by using the average dipole orientation (ADO) theory of Su and Bowers.[13] As an example of the importance of this correction, a hydrogen molecule, which has no dipole moment and only a low polarizability, collides with HO^- only two-thirds as frequently as does NH_3. In the same table we have included the difference in acidity between the neutral and water and the enthalpy change of the overall reaction.

One value in Table I, the rate of exchange of DO^- with HD, is calculated rather than measured. The HO^- produced in this reaction undergoes back exchange with HD at a faster rate than that by which it is formed. However a rate constant for this reaction can be calculated from the reverse rate constant and the reaction equilibrium constant determined from thermodynamic data.[14]

In Table II are collected the rates of exchange of ten organic neutrals with DO^-. Acid dissociation enthalpies for most of these compounds are not known. However, all that exchange are more acidic than ammonia because M-1 ions are produced from each upon reaction with H_2N^-. Only the very weak acids, methane, dimethyl ether, and ethylene, exhibit no exchange. In a qualitative

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Table II. Rate Constants for the Isotope Exchange Reactions $DO^- + MH \rightarrow HO^- + MD$ at 299 (± 1) K

MH	k_{obsd}[a]	reaction[b] efficiency	$\Delta[\Delta H^\circ_{acid}]$, kcal mol^{-1}
$H_2C{=}CHCH{=}CH_2$	9.6	0.56[c]	<12.8
$H_2C{=}CHOCH_3$	10	0.55[c]	<12.8
norbornadiene	10	0.50[c]	11.2[d]
$C_6H_5C(CH_3)_3$	19	0.78[c]	<12.8
$H_2C{=}CHC(CH_3)_3$	1.1	0.053[c]	<12.8
CH_3NH_2	5.7	0.28	12.4[e]
$(CH_3)_2NH$	7.5	0.38	5.6[e]
CH_4	≤0.002	≤0.0002	25.8[e]
CH_3OCH_3[f]	≤0.003	≤0.0002	>12.8
$H_2C{=}CH_2$	≤0.002	≤0.0002	>12.8
$H_2C{=}O$	exchange observed		<12.8

[a] In units of 10^{-10} cm^3 particle^{-1} s^{-1}. [b] Reaction efficiency = k_{obsd}/k_{ADO}, ref 13. [c] Polarizabilities have been calculated from refractive index data. Dipole moments have been estimated by analogy to other compounds. [d] Reference 15. [e] Reference 1. [f] No reaction of any sort (including displacement to form CH_3O^-) is observed.

experiment we observed that formaldehyde readily exchanges with DO^-. We did not measure a rate constant for this reaction because of potential contamination of our radial inlets by polymerization. An M-1 ion has been reported from the reaction of formaldehyde with H_2N^-.[16]

Discussion

The first obvious conclusion from the data in Tables I and II is that H–D exchange rates show only a weak correlation with the relative acidities of the exchange reagent and water. For example, H_2 is more acidic than NH_3, yet it exchanges more slowly with DO^-, both in absolute rate and in the probability of reaction per collision (reaction efficiency). Among the amines the trend in exchange rates, $(CH_3)_2NH > CH_3NH_2 > NH_3$, is in the direction expected on the basis of relative acidities, but the differences in rate are quite small considering the large changes in ΔH°_{acid}. Unfortunately the acidities of the organic molecules are not accurately known. On the basis of inductive and resonance effects, butadiene and methyl vinyl ether are expected to be more acidic than *tert*-butylethylene, and this is in accord with the qualitative observation that it is easy to obtain large signals of M-1 ions from these compounds with H_2N^- but difficult to do so from *tert*-butylethylene. Labeling experiments have shown that the hydrogen at the 2-position in butadiene and that adjacent to oxygen are abstracted from butadiene and methyl vinyl ether, respectively. Labeling studies have not been performed with *tert*-butylethylene, but presumably it is the hydrogen on C-2 that is abstracted. Exchange studies with ND_3 have shown that the methyl hydrogens are not involved. The C-2 hydrogen in *tert*-butylethylene would be expected to be more acidic than that in ethylene since the *tert*-butyl group should stabilize an adjacent charge. For the same reason *tert*-butylbenzene can reasonably be assumed to be somewhat more acidic than benzene itself. The vinyl protons in norbornadiene are known to be relatively more acidic in solution than normal for vinyl protons, probably due to strain effects, and this should carry over into the gas phase. With the exception of *tert*-butylethylene, all of the compounds in Table II that lie between ammonia and water in acidity exchange rapidly. Thus while relative acidity obviously plays a role in exchange reactions, it is not the only important factor.

In order to examine what other factors are important, let us consider a typical H–D exchange reaction, for example, that between DO^- and a hydrocarbon MH, in terms of the potential energy diagram given in Figure 3a, which reflects the mechanism of eq 8. Lias and co-workers[4] have used similar diagrams to explain the efficiency of isotope exchange in the reactions of

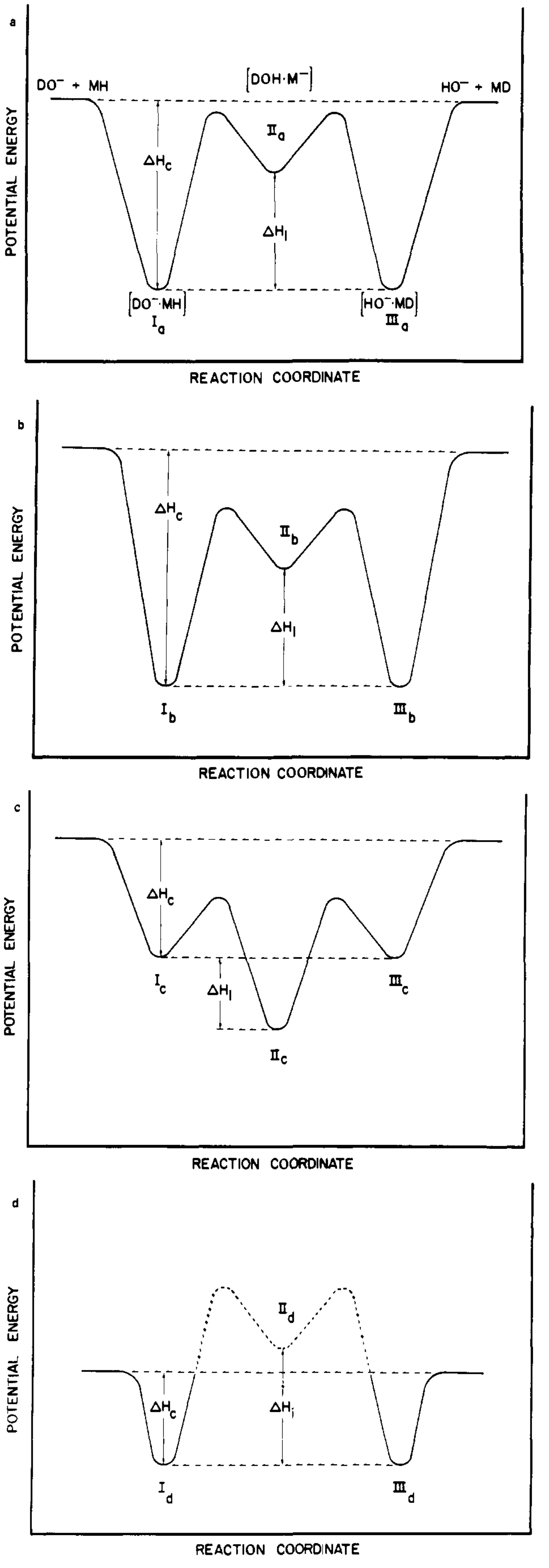

Figure 3. Schematic potential energy diagrams for isotope exchange. In each case the total energy of the system, as given by the upper dashed lines, remains constant throughout the reaction. I and III represent stable ion–dipole complexes of the reactants and products, respectively. II represents a reaction intermediate resulting from proton transfer from the neutral reagent. The relative energies of I, II, and III depend upon acidity and solvation differences. See text for detail.

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$$\mathrm{DO^- + MH} \underset{}{\overset{\Delta H_c}{\rightleftharpoons}} \underset{\mathrm{I_a}}{[\mathrm{DO^-{\cdot}MH}]} \overset{\Delta H_i}{\rightleftharpoons} \underset{\mathrm{II_a}}{[\mathrm{DOH{\cdot}M^-}]} \rightleftarrows \underset{\mathrm{III_a}}{[\mathrm{HO^-{\cdot}MD}]} \rightleftarrows \mathrm{HO^- + MD} \quad (8)$$

cations. For simplicity, Figure 3 considers only the gross energetics of these processes and ignores isotope effects. The hydrocarbon and DO^- enter into a reactive ion–dipole complex in which the ion-induced dipole energy is given by ΔH_c. This energy remains within the complex during reaction and is lost when the products separate. Part of this energy can be used to convert the initially formed complex I_a into a new complex II_a by proton transfer. In order for this to occur, the energy of the transition state leading to II_a must be less than the total energy of the system, given by the dashed line. Thus the activation energy for the conversion of I_a to II_a must be less than ΔH_c.

The decomposition of complexes such as I_a has been described by RRKM theory and applied to ion–molecule reactions by Brauman and co-workers.[17] The exchange rate depends upon the relative rates of decomposition of an activated "molecule" (in this case the ion–dipole complex I_a) with sufficient energy to proceed along several different reaction coordinates. In the case of I_a, the exchange efficiency will depend upon the relative rates of conversion to II_a vs. dissociation to DO^- and MH. Since there is sufficient energy in the complex to accomplish either of these reactions, the problem is one of entropy rather than energy. In RRKM terminology the relative rates in the two directions, that is, the relative flux through the different transition states, depends upon the sum of states in the two directions. This in turn depends only on the structure and energy of the transition states. The well depths along the reaction coordinate influence the outcome of the reaction by affecting the transition-state properties. Throughout the following discussion the energies of complexes I, II, and III are discussed since these can be readily quantified; however, it is not these energies directly but rather their mapping onto the transition-state energies that determines reactivity.

Consider the two exchanging systems represented by Figures 3a and 3b. In Figure 3b, the ion-complex interaction energy is increased relative to that in Figure 3a, so that the energies of I, II, and the transition state separating them are all lowered by a constant value relative to the energy of the reactants. In general a dissociation channel will have a high density of states since the separated particles have more degrees of freedom. However, in the first case where ΔH_c is small, there will be relatively few states available along the exchange pathway, between the top of the barrier and the total energy of the system (dashed line). The transition state for exchange requires the localization of almost all of ΔH_c into reaction energy. Thus the reaction probability will greatly favor dissociation.

If the interaction energy is increased, as shown in Figure 3b, the lifetime of the complex will increase because of the larger number of states available to complex I_b as compared to I_a. The number of states available for dissociation will not change; however, the number of states available for exchange will increase greatly, since the absolute energy of the transition state separating I and II is lowered and the density of states increases rapidly with distance above a potential barrier. Thus, relative to dissociation, the rate of exchange will increase.

The enthalpy difference between complexes I and II, ΔH_i, is determined in part by the relative basicity of DO^- and M^-. This contributes an endothermic term to ΔH_i. A second important factor is the relative ion complex energies of I and II. In complex I DO^- is "solvated" by MH; in complex II M^- is "solvated" by DOH. If this ion-complex energy ("solvation" energy) is similar in I and II, then ΔH_i (and hence, by assumption, ΔH^* for I → II) will be dominated by the difference in proton affinities between DO^- and M^-. Figures 3a and 3b both represent this situation.

Table III. Comparison of Calculated and Experimental Solvation Energies

	μ_D, debye	α, 10^{-25} cm^3	r,[a] 10^{-8} cm	ΔH_{solv^-} (calcd),[b] kcal mol^{-1}	ΔH_{solv^-} (exptl),[c] kcal mol^{-1}
$Cl^-{\cdot}H_2O$	1.85	14.44	3.14	−15	−13
$HO^-{\cdot}H_2O$	1.85	14.44	2.70	−22	−25
$Cl^-{\cdot}HOC_6H_5$	1.45	108[d]	3.14	−29	−27
$Cl^-{\cdot}HOCH_3$	1.70	32.2	3.14	−17	−14

[a] See text. [b] Equation 9. [c] Reference 18. [d] Estimated by the method described in ref 19.

Next consider a case in which the "solvation" energy in II exceeds that in I. This will not be unusual since water has a high dipole moment and polarizability whereas MH may have little or no dipole moment and may only be weakly polarizable. Under these circumstances the increase in energy due to basicity differences on going from I to II will be offset by a gain in "solvation". An energy diagram for the case in which the gain in solvation exceeds the loss in proton affinity is shown in Figure 3c.

Finally, there will be cases in which "solvation" in II will be less than that in I; the change in solvation and in proton affinity will be in the same endothermic direction. Figure 3d represents such a situation in which the result is that the energy required for proton transfer exceeds the initial ion-complex energy ΔH_c and no exchange will be observed.

As yet there is little experimental data on the ion–neutral bond strengths in $[DO^-{\cdot}MH]$ and $[DOH{\cdot}M^-]$ for most of the systems we have examined. Therefore, in order to discuss the potential energy diagrams for these systems, we must estimate the relative ion–molecule complex energies. A rigorous calculational solution to this problem, while desirable, is beyond the scope of this paper. However, we can use the classical equation[13] describing the potential between an ion and a molecule at relatively long distances (eq 9). While this potential is inexact because it ignores the

$$V(r) = -\frac{\alpha q^2}{2r^4} - \frac{q\mu_D}{r^2}\cos\bar{\theta}(r) + \frac{1}{2}\mu v^2\frac{b^2}{r^2} \quad (9)$$

short-range repulsive forces, it can serve as a first approximation of relative solvation energies. In eq 9, α is the gross molecular polarizability, q is the electronic charge on the ion, μ_D is the dipole moment of the neutral, $\bar{\theta}$ is the average angle between the line of centers of the ion and the neutral, v is the average collision velocity, μ is the reduced mass of the ion and neutral, b is the impact parameter, and r is the distance of separation between the ion and neutral. Although one can obtain an estimate of $\bar{\theta}$ by knowing μ_D and α, we chose to set $\bar{\theta} = 0$ in order to compute the energy of the complex at the bottom of the well. In addition, since we are interested in the interaction energy of rotationally and translationally relaxed complexes, the last term of eq 9 is not necessary (i.e., $b = 0$). One of the most difficult aspects of using this equation is determining the appropriate distance parameter, r. We have assumed that a linear configuration ($DO^-{\cdots}HM$ or $DOH{\cdots}M^-$) best represents the reaction coordinate for proton transfer. We then estimate the distance of separation, using van der Waal radii and bond lengths, between the center of the atom containing the greatest part of the negative charge and the atom on the neutral that contains the orbitals that are most important in polarizability effects. For benzene this atom is the closest carbon atom, for water it is the oxygen atom, and so forth. The usefulness of this calculation is shown in its ability to reproduce roughly some measured solvation energies as summarized in Table III. Table IV lists the parameters used and the resulting energies of the complexes for some of the reactions examined in this paper.

From Table IV it is evident that the case of DO^- exchange with ammonia is exemplified by Figure 3a or 3b. Both ammonia and water form strong ion complexes so that ΔH_i is primarily determined by the differences in basicity of DO^- and H_2N^- (12.8 kcal mol^{-1}). ΔH_c is expected to be larger than that, so that

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(17) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993–5999. Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219–4228.

(18) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445–476.

(19) Miller, K. J.; Savchik, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206–7213.

Table IV. Enthalpy Changes for the Steps in the Mechanism

$$\mathrm{DO^- + MH} \underset{}{\overset{\Delta H_c}{\rightleftarrows}} \underset{\mathrm{I}}{[\mathrm{DO^-{\cdot}MH}]} \overset{\Delta H_i}{\rightleftarrows} \underset{\mathrm{II}}{[\mathrm{DOH{\cdot}M^-}]} \rightleftarrows \underset{\mathrm{III}}{[\mathrm{HO^-{\cdot}MD}]} \rightleftarrows \mathrm{HO^- + MD}$$

				[DO$^-$·MH]		[DOH·M$^-$]			
MH	ΔH°_{acid},[a] kcal mol^{-1}	μ_D, debye	α, 10^{-25} cm^3	r,[b] 10^{-8} cm	ΔH_{solv},[c] kcal mol^{-1}	r,[b] 10^{-8} cm	ΔH_{solv},[d] kcal mol^{-1}	ΔH_i,[e] kcal mol^{-1}	$\Delta H_c + \Delta H_i$,[f] kcal mol^{-1}
H_2	400.4	0	7.9	2.1	−7	2.6	−24	−7	−14
NH_3	403.6	1.47	22.6	2.7	−21	2.6	−24	+10	−11
H_2O	390.8	1.85	14.44	2.7	−22	2.7	−22	0	−22
C_6H_6	399	0	103.2	2.8	−28	2.6	−24	+12	−16
CH_3NH_2	403.2	1.31	40.1	2.8	−22	2.6	−24	+10	−12
CH_4	416.6	0	26.0	2.8	−7	2.6	−24	+9	+2
C_2H_4	>404	0	40.97	2.8	−11	2.6	−24	>0	>−11

[a] Reference 1. [b] See text. [c] The enthalpy change for the reaction $DO^- + MH \rightarrow [DO^-{\cdot}MH]$; this quantity equals ΔH_c, that is, the energy of complex I relative to reactants. [d] The enthalpy change for the reaction $DOH + M^- \rightarrow [DOH{\cdot}M^-]$. [e] ΔH_i is the difference in energy between complexes I and II; this quantity includes both the difference in acidity between DOH and MH as well as the difference in solvation energy for the two complexes relative to their separate components. [f] $\Delta H_c + \Delta H_i$ represents the energy of complex II relative to the reactants.

exchange occurs on one out of every five collisions. The kinetic isotope effect is in the expected direction, $k_H > k_D$, that is, exchange of DO^- with NH_3 is faster than exchange of HO^- with ND_3 since the N–H bond is weaker than the N–D bond. Methyl- and dimethylamine are more acidic than ammonia, and exchange is more rapid.

Ethylene, we believe, represents a neutral that does not exchange, primarily because ΔH_c, the initial complexation energy, is too small. Ethylene is less acidic than ammonia, but it must be only slightly so since all substituted ethylenes, including *tert*-butylethylene, are more acidic. We have observed slow production of the vinyl anion from the reaction of amide with ethylene in SIFT experiments. In addition, we have shown earlier that primary vinylic hydrogens in isoprene will exchange with D_2O with $k = 1 \times 10^{-11}$ (eq 2). Because ethylene has no dipole moment and is only slightly polarizable, ΔH_c is small, and the potential energy diagram for exchange is given by Figure 3d. ΔH_i for ethylene may be no larger than that for ammonia, but ΔH_c is much smaller. Although this figure places complex II above the energy of the reactants, the lack of exchange only strictly requires that the barrier between I and II lies above this value. In contrast to ethylene, *tert*-butylethylene exchanges in 1 of 20 collisions. The highly polarizable *tert*-butyl group will increase ΔH_c, thus converting Figure 3d into Figure 3a. The *tert*-butyl group is also expected to increase the acidity at C-2.

The lack of exchange between DO^- and methane arises from two factors. The initial ion-complex energy is small, in analogy with ethylene. But additionally, methane is so weakly acidic that complex II must lie well above the energy of the reactants as represented by Figure 3d. Similarly, dimethyl ether is less acidic than ammonia and no exchange is observed with DO^-.

With the exception of ethylene and *tert*-butylethylene, exchange occurs rapidly for the unsaturated compounds studied. For these compounds the definition of reaction efficiency is less clear. Suppose a reacting system reaches II_a (Figure 3a) at each collision. This would amount to reaction at every collision, but half the time II_a will return to I_a and dissociate to reactants. The maximum apparent reaction efficiency will be 50% of the calculated collision rate.[20]

We know, however, that for some systems there can be multiple exchanges within a single complex. In the system represented by Figure 3b, complex I_b has a long lifetime (large ΔH_c) and ΔH_i is much smaller than ΔH_c. If II_b is reached several times in a single collision, hydrogens and deuteriums become scrambled. Under these circumstances the reaction efficiency can exceed 0.5. In fact we believe that the large reaction efficiency for *tert*-butylbenzene in Table II (0.78) is indicative of multiple exchange; the potential energy diagram for this reaction would be expected to be given by Figure 3b.

As a final case we consider exchange with hydrogen. This is a system that can be studied by using H_2, D_2, and HD as substrates and DO^- and HO^- as bases. In addition, all the thermodynamic parameters (heats of formation (ΔH_f), bond dissociation energies, entropies) are known. The large *inverse* isotope effect is striking and most surprising; D_2 exchanges with HO^- twice as fast as H_2 exchanges with DO^-. This cannot be understood in terms of relative acidities, since D_2 is slightly less acidic than H_2. The values under the anions and molecules in eq 10–13 refer to the ΔH_f values in kcal mol^{-1}.

$$\underset{-35.1}{DO^-} + \underset{0}{H_2} \rightarrow \underset{-58.6}{DOH} + \underset{33.2}{H^-} \tag{10}$$

$$\Delta H = +9.7 \text{ kcal mol}^{-1}$$

$$\underset{-34.4}{HO^-} + \underset{0}{D_2} \rightarrow \underset{-58.6}{DOH} + \underset{34.1}{D^-} \tag{11}$$

$$\Delta H = +9.9 \text{ kcal mol}^{-1}$$

A possible clue is given by the thermochemistry[14] of the overall reaction, where we see that exchange of D_2 is exothermic (and exoergic) whereas exchange of H_2 is endothermic (and endoergic).[21] However we are dealing with a kinetic rather than an equilibrium problem, since only 1 in 17 (for D_2) or 1 in 42 (for H_2) encounters lead to reaction. We also must explain why reaction occurs at all, since the ion complex energy (ΔH_c) between HO^- and D_2 or DO^- and H_2 is expected to be exceedingly small.

$$\underset{-35.1}{DO^-} + \underset{0}{H_2} \rightarrow \underset{-34.4}{HO^-} + \underset{0.1}{HD} \tag{12}$$

$$\Delta H = +0.8 \text{ kcal mol}^{-1};\ \Delta G = +0.3 \text{ kcal mol}^{-1}$$

$$\underset{-34.4}{HO^-} + \underset{0}{D_2} \rightarrow \underset{-35.1}{DO^-} + \underset{0.1}{HD} \tag{13}$$

$$\Delta H = -0.6 \text{ kcal mol}^{-1};\ \Delta G = -0.9 \text{ kcal mol}^{-1}$$

We believe that all of our results can be explained satisfactorily if H_2 and D_2 exchange on a potential energy surface of the type represented by Figure 3c. The details for these two reactions are shown in Figure 4. HO^- and D_2 enter a very weakly bound ion complex that would not contain enough energy for deuterium transfer if the reaction were controlled by the relative proton affinities of HO^- and D^-. However, as deuterium transfer occurs

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(20) A referee has noted that a theoretical treatment of this situation has been published (Chesnavich, W. J.; Bass, L.; Su, T.; Bowers, M. T. *J. Chem. Phys.* **1981**, *74*, 2228–2246). A reaction efficiency of one-half is obtained if the fluxes through the transition states in the entrance and exit channels are identical and all intermediate transition-state fluxes are very much larger than the entrance/exit fluxes. Isotope effects will clearly alter this situation.

(21) For reaction 12, tabulated values of $\Delta H_f°_{298}$ and $S°_{298}$ lead to $\Delta G_{calcd} = +0.3$ kcal mol^{-1}, while our measured forward and reverse rate constants (Table I) give $\Delta G_{obsd} = -0.05$ kcal mol^{-1}. This is within the error limits of the calculated value because the ΔH values are known only to ±1 kcal mol^{-1} and therefore $\Delta G_{calcd} = +0.3$ (± 2) kcal mol^{-1}. If we assume the maximum 20% error in the absolute values of the rate constants (that is, the measured k_f is 20% too high and the measured k_r is 20% too low), then $\Delta G_{obsd} = +0.2$ kcal mol^{-1}.

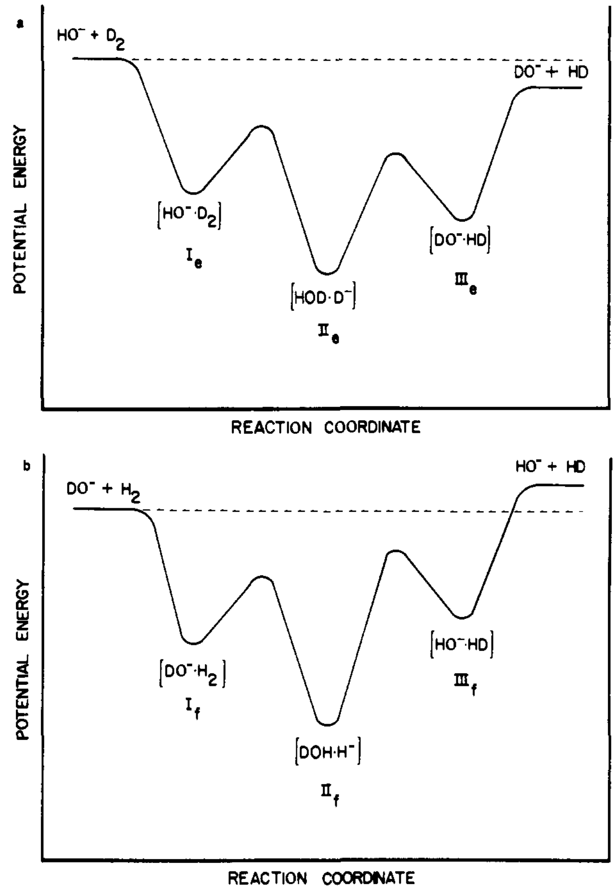

Figure 4. Schematic potential energy diagram for isotope exchange between HO^- and D_2 and DO^- and H_2. The effects of isotopic substitution on the energetics of the exchange are explicitly considered. In order to explain the inverse isotope effect, we propose that the most stable form of the complex is II, in which hydride is solvated by water, rather than I or III, in which hydroxide is solvated by hydrogen.

the solvating species is converted from the poorly solvating D_2 to the much better solvating HOD and the gain in solvation energy compensates for the loss of energy in converting a weaker to a stronger base. This idea is supported by recent ab initio calculations of Squires.[22] Once in the initial complex (I_e or I_f) a barrier must be surmounted to form II_e or II_f. Since ΔH_c is small, the lifetime of the complex will be short. Moreover, since the barrier will be high there will be relatively few states available at the transition state and the probability of reaction will be relatively small in either case. There may well be a small normal ($(k_H/k_D) > 1$) kinetic isotope effect in this step. However, the overall isotope effect is determined by the return to separated products from II_e and II_f. From II_e the favored exothermic pathway will be on to III_e and then to $DO^- + HD$ (overall exchange from $HO^- + D_2$). From II_f the favored pathway will be back to $DO^- + H_2$ via I_f (reaction without exchange). In fact, since overall exchange is endothermic, only a portion of the incoming molecules will have sufficient energy above threshold to give exchange. Note that the favored pathway from both II_e and II_f is one with a *normal* isotope effect (i.e., abstraction of H from HOD). The net result, however, is that $HO^- + D_2$ tends to go on to exchange and $DO^- + H_2$ tends to go back to nonexchange.[23]

With the ideas we have developed from these studies of exchange of DO^-, the anomalies in rates of exchange of carbanions with D_2O as described in the introduction now become understandable. Consider the examples of the acetonitrile anion, which

$$N{\equiv}CCH_2^- \xrightarrow{D_2O} N{\equiv}CCD_2^- \quad (14)$$

$$HC{\equiv}C^- \xrightarrow{D_2O} \text{no exchange} \quad (15)$$

exchanges with D_2O even though it is 19 kcal mol^{-1} less basic than HO^-, and the acetylide ion, which does not exchange with D_2O even though it is only 15 kcal mol^{-1} less basic than hydroxide ion. In the former case deuterium transfer leads to DO^- "solvated" by CH_2DCN. Acetonitrile has a large dipole moment and is highly polarizable so that the ion-complex energy may in fact be larger after deuterium transfer than before. A gain in ion-complex energy could well compensate for part of the 19 kcal mol^{-1} loss from basicity differences. Deuterium transfer from D_2O to acetylide is only 15 kcal mol^{-1} endothermic, but transfer leads to $[DO^-{\cdot}D{-}C{\equiv}CH]$. Acetylene, with no dipole moment and a low polarizability, is expected to form extremely weak ion complexes. The loss in ion-complex energy will augment the loss in energy due to proton transfer so that no exchange is observed. Similar but less dramatic effects are seen with dienes and other hydrocarbon anions, for which the neutral reagent is expected to form weak complexes.

Conclusion

In summary, we have identified three primary factors that determine the rates of gas-phase H-D exchange reactions in anions. The first of these is the magnitude of the initial ion-molecule complex energy (ΔH_c). Everything else being equal, molecules with large dipole moments and/or polarizabilities will exchange more rapidly with DO^- than those without. Rates of proton transfer within a complex are determined primarily by two factors, the relative basicity of the two anions (DO^- and M^-) and the relative ion-molecule attractive energies of the two complexes $[DO^-{\cdot}HM]$ and $[DOH{\cdot}M^-]$. Examples are given where these two energies are essentially the same, so that exchange rates are determined mainly by the basicity differences (e.g., $DO^- + NH_3$), where an increase in complex interaction energy compensates for an increase in basicity (e.g., $DO^- + H_2$) and where deuterium transfer leads to a decrease in complex interaction energy so that no exchange occurs although exchange would be expected on the basis of basicity differences alone (e.g., $HC{\equiv}C^- + D_2O$).

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Registry No. HO^-, 14280-30-9; DO^-, 17693-79-7; $C_6H_5C(CH_3)_3$, 98-06-6; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3; CH_4, 74-82-8; CH_3OCH_3, 115-10-6; Cl^-, 16887-00-6; H_2, 1333-74-0; NH_3, 7664-41-7; H_2O, 7732-18-5; C_6H_6, 71-43-2; butadiene, 106-99-0; methyl vinyl ether, 107-25-5; norbornadiene, 121-46-0; *tert*-butylethylene, 558-37-2; ethylene, 74-85-1; formaldehyde, 50-00-0.

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(22) Squires, R. R., private communication.

(23) It is interesting to note that the intermediate in this reaction, H_3O^-, has recently been detected by Nibbering and co-workers using Fourier transform ICR and by Paulson and co-workers using ion beam techniques; presented at the NATO Advanced Study Institute, Chemistry of Ions in the Gas Phase, Vimeiro, Portugal, Sept 1982.