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Multiple Proton Transfers within Long-Lived Ion–Molecule Complexes

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Abstract: Gas-phase hydrogen–deuterium exchange reactions involving a series of 2-substituted propenes and the corresponding allylic anions ($CH_2{=}C(R)CH_3$ and $CH_2{=}C(R)CH_2^-$, R = H, OCH_3, $CH{=}CH_2$, F, CHO, CN) have been examined in order to characterize the multiple hydrogen exchanges which may occur within a long-lived collision complex of an anionic base and a neutral acid. In exchange reactions between the substituted allyl anions and D_2O, comparison of the observed and statistical deuterated carbanion product distribution indicates that although more than one H–D exchange per D_2O collision may occur in some cases, complete scrambling of the two deuteriums among the carbanion and water is not evident. In proton-transfer reactions between DO^- and the substituted propenes, the carbanion products exhibited varying degrees of deuterium incorporation which were always less than the calculated statistical limit. The unified results for the two types of experiments have been rationalized in terms of the effects of the relative acidities of the propenes and the relative ion–dipole attractive forces on the lifetimes of the intermediate anion–molecule collision complexes.

The reaction of an ion with a neutral species in the gas phase often proceeds with the intermediacy of a long-lived collision complex.[2,3] Examples of this mechanism can be found among many different kinds of ion–molecule reactions as studied by a variety of experimental methods.[4-6] Long-lived complexes are frequently postulated to account for the emergence of particular products from an ion–molecule collision. Thus, the ability of a "loosely bound" ion and neutral to undergo several successive bond reorganizations during the course of a single encounter is a prevalent theme in the ion chemistry literature.[7-11] Persistent complexes are commonly invoked to explain the appearance of ion–molecule cluster species under conditions of relatively low pressure.[2,3,12,13]

Though the a priori interposition of long-lived complexes is now a common practice, and Brauman's "multiple-well potential" model for ion–molecule reactions[14] has achieved general acceptance, we still know very little about these important intermediates. Reliable means for the determination of their structures and energies remain

$$R\bar{C}H_2 + D_2O \rightleftharpoons \begin{bmatrix} R\bar{C}H_2 \\ D_2O \end{bmatrix} \rightleftharpoons \begin{bmatrix} RCH_2D \\ DO^- \end{bmatrix} \rightleftharpoons \begin{bmatrix} R\bar{C}HD \\ HOD \end{bmatrix} \rightleftharpoons R\bar{C}HD + HOD \tag{1}$$

$$RH^+ + D_2O \rightleftharpoons \begin{bmatrix} RH^+ \\ D_2O \end{bmatrix} \rightleftharpoons \begin{bmatrix} R \\ D_2OH^+ \end{bmatrix} \rightleftharpoons \begin{bmatrix} RD^+ \\ HOD \end{bmatrix} \rightleftharpoons RD^+ + HOD \tag{2}$$

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(1) (a) Purdue University. (b) University of Colorado.

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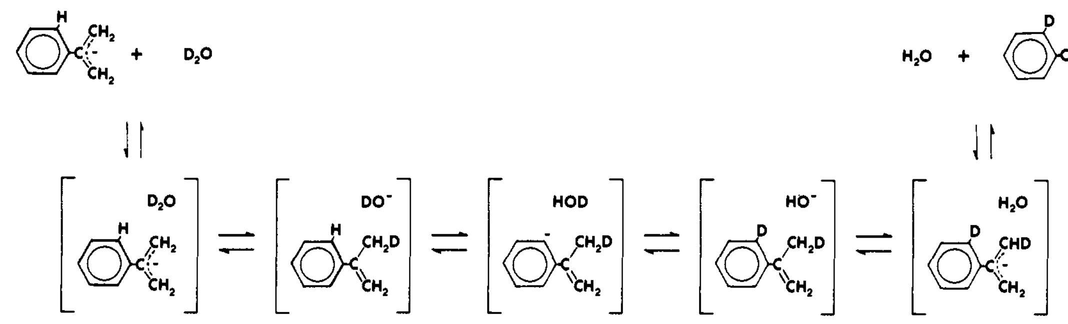

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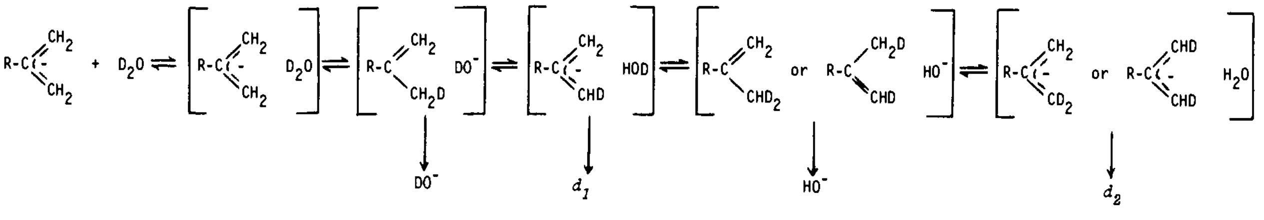

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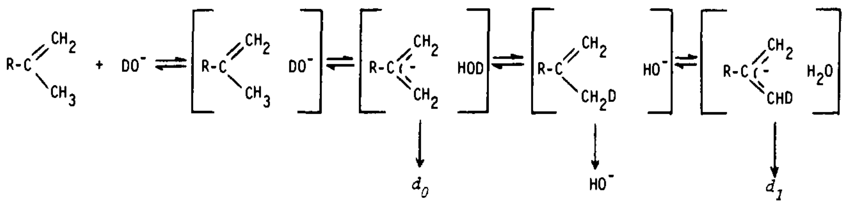
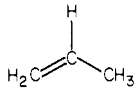


(5)

few in number and the crucial question as to how long a given collision complex may survive is exceedingly difficult to answer. In a few studies, collision lifetimes ranging from picoseconds to a few milliseconds have been inferred from experimental data.[3,12,15-17] However, many lifetime measurements must be considered crude at best.

From a mechanistic standpoint, perhaps an equally pertinent and experimentally more tractable parameter than a collision lifetime would be a measure of the number of discrete chemical steps occurring within a complex during its lifetime. In this paper we report the results of our flowing afterglow studies of multiple proton transfers occurring during a gas-phase encounter of an anionic base and an acidic neutral. That multiple proton transfers may occur within an ion-molecule complex has been known for some time. For example, the present view of the mechanism for gas-phase hydrogen-deuterium exchange between carbanions[5a,7a,18-20] or protonated neutrals[20-22] and D_2O involves at least two proton transfers per exchange (eq 1 and 2). We more recently reported[4b] on the apparent "double-exchange" reaction between D_2O and certain carbanions possessing several different types of hydrogens (eq 3). In this example, not only do the allylic hydrogens exchange but also the weakly acidic aryl protons. At least four proton transfers, and probably many more, must occur during a single encounter in order to achieve the observed ring deuteration.

We sought a more systematic way in which to study multiple proton transfers within long-lived complexes and were led to an examination of the negative ion chemistry of the series of 2-substituted propenes shown below (**1**–**6**). Multiple exchange can be studied in two ways. In a conventional flowing afterglow we can prepare the corresponding allylic carbanions by reaction of the propylenes with H_2N^- and allow them to exchange with D_2O. By studying deuterium incorporation as a function of D_2O flow or the reaction time and extrapolating to zero D_2O flow or zero time, we can determine the amount of single and double incorporation occurring in a single encounter (eq 4). In a set of related experiments we can use our selected ion flow tube (SIFT)[23,24] to inject DO^- into the flow tube in the absence of other ions or D_2O. We can then examine the incorporation of deuterium into the allyl anion which is generated by proton abstraction (eq 5). The appearance of a deuterated carbanion from the reaction provides a conveniently monitored indicator for multiple proton transfer within the intermediate complex. Using these two complementary techniques we can form the same ion-dipole complex from different anion-neutral sources. In some cases the complex formed in these two different ways will have quite different energies. For example, when transfer of a proton from a substituted propene to hydroxide is exothermic, the complexes which result will contain more internal energy than those that are formed by simple ion-neutral association. This variation in the amount of energy present within the ion-dipole complex can have a significant influence on the extent of multiple proton exchanges which occur. In this paper we show how we can establish an empirical "count" of the number of proton exchanges occurring during a single anion-neutral collision and how this information may be used in assessing the effects of internal energy on the relative lifetimes of the ion-molecule complexes.



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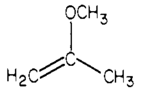

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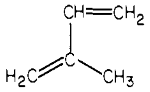

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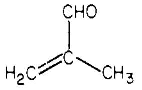

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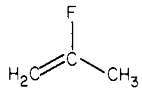

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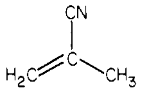

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Experimental Section

The hydrogen-deuterium exchange reactions between D_2O and the series of 2-substituted allylic anions were carried out in a conventional

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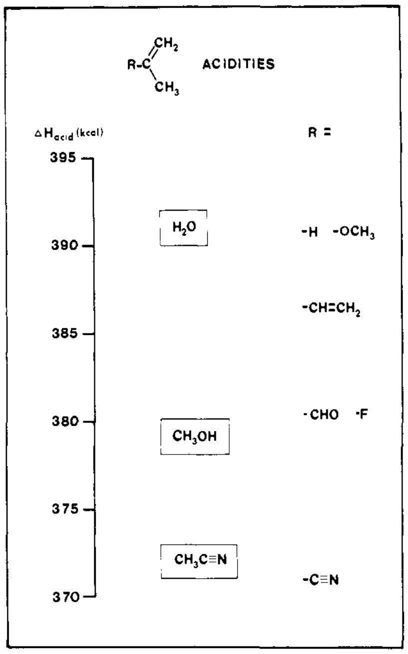


Figure 1. Gas-phase acidity scale for 2-substituted propenes. Taken from ref 26 and this work.

flowing afterglow (FA) system described in detail previously.[4a] The helium buffer gas (99.995%, liquid nitrogen trap) was maintained at a pressure of 0.3 torr and the bulk flow rate was 140 STP cm^3 s^{-1}. D_2O was added to the flow system through a moveable ring inlet which permits variation of the reaction distance (z) over a range of approximately 60 cm of the overall 100 cm long flow tube. Flow rates of all neutral reactants were measured either by monitoring the corresponding pressure increase with time in a calibrated volume or by using a mass flow meter calibrated for use with the particular reactant. All of the allylic anions (**1a**–**6a**) were generated from the parent substituted propenes (**1**–**6**) via proton abstraction by amide or hydroxide ion. These two primary ions were in turn produced in the upstream source region by electron bombardment on NH_3 (Matheson, 99.999%) or dissociative electron capture by N_2O (Matheson, 99.0%, 240 K trap) followed by hydrogen atom abstraction from CH_4 (Matheson, 99.0%, 210 K trap), respectively.

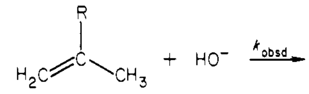
All experiments employing DO^- as a primary reactant ion were carried out in our recently completed selected ion flow tube (SIFT).[23,24] DO^- was generated in a low-pressure Brinks-type ion source by 70-eV electron bombardment on D_2O ($P_{D_2O} \approx 10^{-3}$ torr). Ions of m/z 18 were selected by a quadrupole mass filter and injected into the flow tube through a Venturi inlet. In the SIFT system the helium buffer gas pressure and flow rate were typically 0.4 torr and 170 STP cm^3 s^{-1}, respectively. Neutral reactants were added to the flow tube through fixed radial inlets and the flows were measured by monitoring a pressure change in a calibrated volume.

The 2-substituted propenes (**1**–**6**) were all obtained from commercial sources. Propene (Matheson, 99.7%) was dried by passage through a 1.5 m × 6 mm copper tube packed with $CaSO_4$ and molecular sieves which was immersed in an ice-salt mixture at 260 K. Each of the liquid samples (**2**, **3**, **4**, **6**) were distilled before use and placed over an appropriate drying agent ($LiAlH_4$ or $CaCl_2$). The 2-fluoropropene (98%) was used without further purification. All experiments were carried out at 298 ± 2 K.

Results

Gas-Phase Acidities of the Substituted Propenes. The gas-phase acidities of the propenes **1**–**6** span a range of about 20 kcal/mol as shown diagramatically in Figure 1. Most of the values for $\Delta H°_{acid}$ were obtained from a recent ion cyclotron resonance (ICR) study of 2-substituted propenes by Bartmess and Burnham.[26] We have modified some of the reported values on the basis of our experience with these compounds in the flowing afterglow. For example, whereas Bartmess and Burnham report an acidity for 2-methoxypropene (**2**) of 385 ± 5 kcal/mol and calculate (MNDO)[27] a value of 384 kcal/mol, we favor a value closer to that for water (390.7 kcal/mol)[28] since a significant amount of DO^- is formed in the reaction of **2a** with D_2O.

Table I. Experimental Data for Reaction of HO^- with Substituted Propenes



no.	R	k_{obsd}[a]	reaction efficiency[b]	primary products
1	-H	9.1	0.54	$(M-H)^-$, 100%
2	$-OCH_3$	9.5	0.40	$(M-H)^-$, 90% $CH_3COCH_2^-$, 10%
3	$-CH=CH_2$	12	0.57	$(M-H)^-$, 100%
4	-CHO	44	1.4	$(M-H)^-$, 100%
5	-F	32	1.4	$(M-H)^-$, 75% $(F^- \cdot H_2O)$, 18% F^-, 7%
6	-CN	57	1.4	$(M-H)^-$, 98% CN^-, 2%

[a] In units of 10^{-10} cm^3 molecule^{-1} s^{-1}. [b] Reaction efficiency = k_{obsd}/k_{ADO}, reference 33.

In addition, we have adjusted the reported values of $\Delta H°_{acid}$ for 2-fluoropropene (**5**) (378 ± 3 kcal/mol) and methacrolein (**4**) (374 ± 3 kcal/mol) to be slightly greater than that for methanol (379.2 kcal/mol)[28] since the corresponding carbanions **4a** and **5a** yield mostly methoxide ion upon reaction with CH_3OD. Though these discrepancies are minor ones, they do underscore the utility of H–D exchange reactions for estimating gas-phase acidities.

Reactions of 1–6 with Hydroxide Ion. All members of the series except propene (**1**) and 2-methoxypropene (**2**) are significantly more acidic than water; therefore proton abstraction from these neutrals by HO^- is exothermic. As would be expected for exothermic or thermoneutral proton transfers, the rates of reaction of **1**–**6** with HO^- are fast and the reaction efficiencies are high. Table I gives a summary of the measured rate constants and efficiencies along with the primary product distributions. In all cases the carbanion is the major product. In addition, the reaction of hydroxide with methacrylonitrile (**6**) yields 2% CN^- while hydroxide with 2-fluoropropene (**5**) gives 25% fluoride, products of what are most likely base-promoted elimination reactions. Roughly 10% of the reaction between HO^- and 2-methoxypropene (**2**) results in the acetone enolate ion (m/z 57) by S_N2 displacement on the methyl group. In addition to these primary products, the anions from **4** and **6** were observed to undergo reaction with their parent neutrals, probably by Michael addition, to produce ions of m/z 139 and 133, respectively.[29] These ions could be minimized by working with low propylene concentrations. Similar product distributions from these reactants were observed in an ICR by Bartmess and co-workers.[26]

Hydrogen-Deuterium Exchange in the Anions. Reaction of D_2O with the allyl anions **1a**–**6a** ultimately results in exchange of up to four hydrogens for deuterium. At higher D_2O flow rates the isoprene anion (**3a**) exchanges all seven of its hydrogens for

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(28) Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

(29) Anionic condensations of this type as well as even more extensive gas-phase teleomerizations have been observed by McDonald and Chowdhury: McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 2675–2676.

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Scheme I

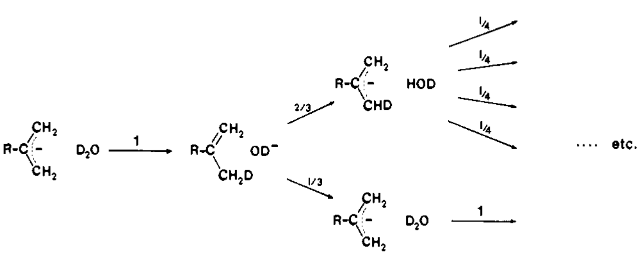
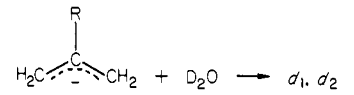


Table II. Calculated Deuterated Carbanion Product Distributions for a Single Encounter of an Allylic Anion with D_2O



no. of exchanges per encounter	d_1 (%)	d_2 (%)	d_2/d_1
1	100.0	0.0	0.00
2	80.0	20.0	0.25
3	68.7	31.3	0.45
4	62.9	37.1	0.59
5	60.0	40.0	0.67
6	58.6	41.4	0.71
.	.	.	.
.	.	.	.
∞[a]	57.1	42.9	0.75

[a] Complete scrambling.

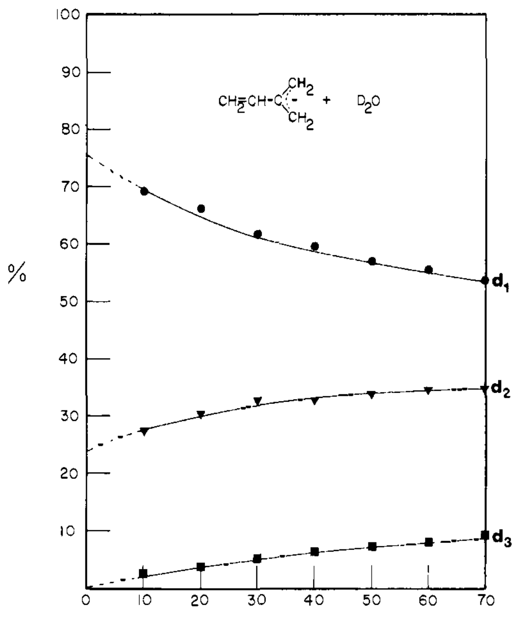


Figure 2. Normalized deuterated carbanion product distribution vs. reaction distance z for reaction of D_2O with isoprene anion (**3a**).

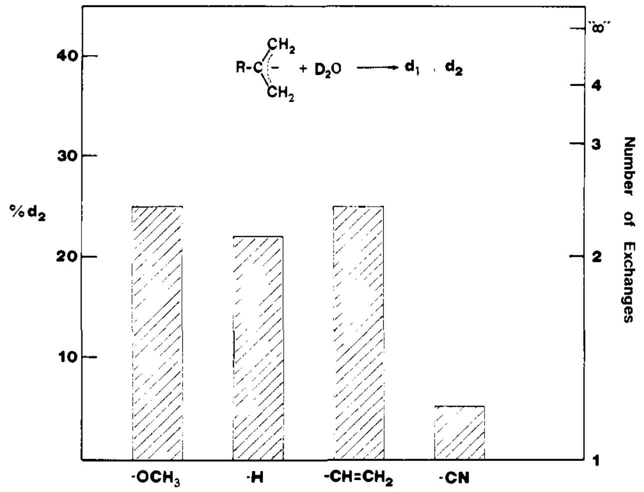


Figure 3. Bar graph summary of results for allylic anion–D_2O experiments showing percentage of d_2 carbanion arising from a single D_2O encounter. Corresponding number of exchanges shown at right.

deuterium.[4b] In a single encounter of an allylic anion with D_2O several ionic products may emerge from a long-lived complex. As shown in eq 4, one exchange of H for D may occur yielding the d_1 anion and, in principle, both deuteriums may incorporate into the carbanion to give a d_2 species.[4b] Further, if the basicity of the carbanion is close to that of HO^-, as in **1a** and **2a**, both DO^- and/or HO^- may also appear as primary products. We have focussed our attention on the primary deuterated carbanion product distributions as an indicator for the number of exchanges occurring during a single collision.[30] In order to count the proton transfers within an anion–D_2O complex, we first must consider the statistical factors which are inherent in the mechanism for H–D exchange. Scheme I depicts a generalized allylic anion and D_2O undergoing proton/deuteron transfers back and forth within a long-lived complex. Assignment of the simple statistical factors to the branching ratios for each of the ion–molecule pairs as shown permits a calculation of the relative amounts of the d_0, d_1, and d_2 carbanions present as a function of the number of exchanges. An "exchange" is defined here as the conversion of one carbanion to the next via a propene/hydroxide intermediate. This simple treatment allows a determination of the deuterated carbanion product distribution which occurs in discrete steps as the system approaches complete scrambling of the labels among the various sites in the carbanion and water.[31] Table II summarizes the calculated distributions as a function of the number of exchanges. The relative percentages of the d_1 and d_2 anions which correspond to complete scrambling are rapidly approached; after five or six exchanges the values are essentially equal to the statistical limit. Because of competing side reactions with D_2O in the cases of the methacrolein anion (**4a**) and the 2-fluoropropene anion (**5a**) we were unable to obtain reliable quantitative exchange data for these species. For the remaining ions, normalized deuterated carbanion product distributions have been plotted vs. the reaction distance z. A sample plot of this type is shown for the isoprene anion (**3a**) in Figure 2. Here, the ordinate indicates the percentage that each deuterated carbanion represents of the sum of the deuterated carbanions (i.e., $100\, d_i/\sum d_i$). Extrapolation of the smooth curve to the zero distance (time) value defines the primary product distribution.[30] Therefore, for the isoprene anion reacting with D_2O, 75% of the primary product is the d_1 species and 25% is the d_2 species; as expected, the d_3 species is not a primary product. The decrease in d_1 and the corresponding increase in d_2 and d_3 at longer reaction times indicates that the d_1 ion reacts further with D_2O to form d_2 and d_3. From plots of this type, percentages for the d_2 species formed as primary products are **1a** (22%), **2a** (25%), **3a** (25%), and **6a** (5%). Due to uncertainty in the actual reaction time which corresponds to a given z value ("inlet end effects"), the extrapolations should be interpreted with some caution. Indeed, small non-zero y intercepts for the d_3 species seen in some cases indicate the error limits in this approach. However, it is clear that the three ions **1a**–**3a** yield between 20 and 30% of a d_2 product from a single encounter with D_2O whereas the methacrylonitrile anion (**6a**) yields essentially none. Figure 3 summarizes the results for these experiments in the form of a bar graph

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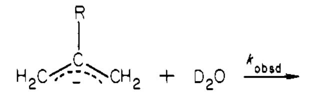
(31) Imposition of a slight bias for hydrogen transfer relative to deuterium transfer (normal primary isotope effect) does not significantly alter either the intermediate distributions of deuterated products or the statistical distributions which are calculated. The overall differential isotope effects in the exchange reactions are probably small and we have ignored their influence in our analysis. Experiments to support this hypothesis are currently in progress.

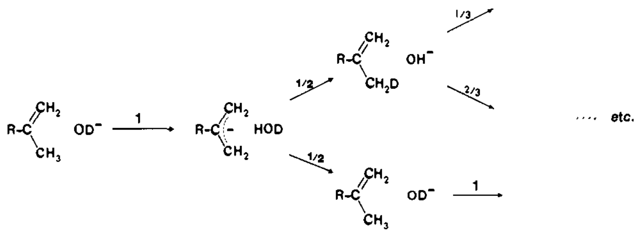
Table III. Rate Constants for Reaction of Substituted Allylic Anions with D_2O



no.	R	k_{obsd}[a]	reaction efficiency[b]
1a	-H	(4.0)[c]	(0.21)[c]
2a	$-OCH_3$	9.6	0.53
3a	$-CH{=}CH_2$	1.3	0.72
5a	-F	7.3	0.40
6a	-CN	0.05	0.003

[a] Rate constant for disappearance of allylic anion in units of 10^{-10} cm^3 molecule^{-1} s^{-1}. [b] Reaction efficiency = k_{obsd}/k_{ADO}, reference 33. [c] Significant curvature of pseudo-first order rate plot indicates equilibration of the ion with DO^-/D_2O.

Scheme II



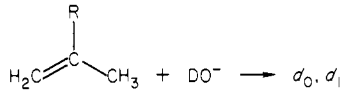
where the left-hand ordinate represents the normalized percentage of the d_2 species and the right-hand ordinate is the corresponding number of exchanges. We conclude from this plot that anions **1a**–**3a** give essentially the same result and undergo 2–3 exchanges in the course of a collision with D_2O. The methacrylonitrile anion (**6a**) behaves quite differently, yielding only one exchange per encounter. These results indicate that although more than one exchange can occur within the complexes, complete scrambling of hydrogens (deuterons) among the available sites is not evident.

Addition of D_2O to an allylic anion results in a decrease in the d_0 ion concentration as the H–D exchange reaction proceeds. The relative rates of the d_0 signal falloff as a function of D_2O flow or reaction time serve as an indication of the relative rates of H–D exchange for the carbanions of the series. An analysis of this type has been carried out and the results are summarized in terms of reaction efficiencies in Table III. A wide variation in the D_2O reaction efficiencies was found, spanning more than two orders of magnitude. In the case of propene we observed significant curvature in the allyl anion falloff plot indicating extensive back reaction (equilibration) between DO^- and the propene present in the system.[32] The reaction between methacrylonitrile anion (**6a**) and D_2O is exceedingly slow (eff ~ 0.003) and the probability for incorporation of two deuteriums in the carbanion is correspondingly low.

Proton Abstraction from the Propenes by DO^- Except for a small equilibrium isotope effect (<1 kcal/mol), an H–D exchange reaction between a carbanion and D_2O is thermoneutral. In order to test for multiple hydrogen exchanges during an exothermic proton transfer, we have examined proton abstraction from the 2-substituted propenes, **1**–**6**, by DO^-.

DO^- was generated in the SIFT apparatus as described previously.[24] Downstream addition of a neutral propene (M) resulted in rapid disappearance of the DO^- signal and a product mass spectrum containing signals for the $(M-H)^-$ anion, a monodeuterated carbanion $(M - 2H + D)^-$, and, in some cases, the hydroxide ion (eq 5). The intensities of the signals for each of the reactant and product species were monitored as a function of the flow rate of the hydrocarbon. For these experiments, an inlet port 43 cm from the detector was used for the neutral additions.

Table IV. Calculated Product Distributions for a Single Encounter of a Substituted Propene with DO^-



no. of exchanges per encounter	d_0 (%)	d_1 (%)	d_1/d_0
1	100.0	0.0	0.0
2	66.7	33.3	0.5
3	50.0	50.0	1.0
4	41.7	58.3	1.4
5	37.5	62.5	1.7
6	35.4	64.6	1.8
.	.	.	.
.	.	.	.
.	.	.	.
∞[a]	33.3	66.7	2.0

[a] Complete scrambling.

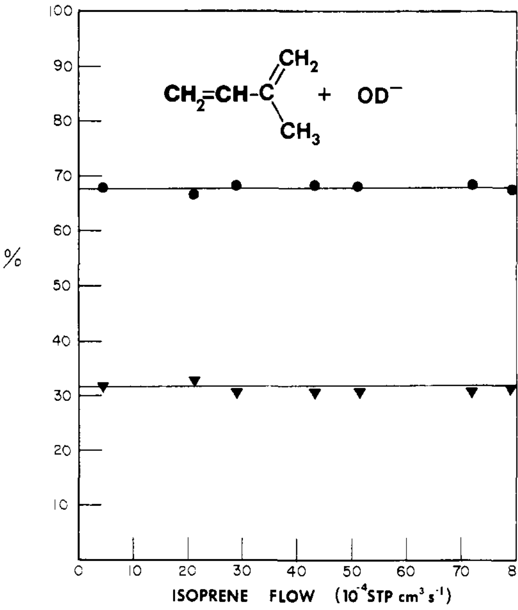


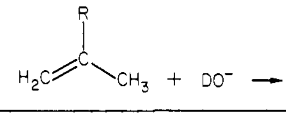
Figure 4. Normalized product distribution vs. neutral flow rate for reaction of DO^- with isoprene (**3**).

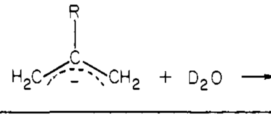
Again, in order to establish how many hydrogen exchanges correspond to an observed product distribution for this reaction, we must determine the statistical branching ratios for the detailed mechanism and propagate them to the "complete scrambling" values. Scheme II outlines the relevant proton/deuteron transfers as before. Table IV summarizes the calculation, showing the percentages of the d_0 and d_1 carbanions which are present as a function of the number of exchanges.[31] Also shown in the table are the d_1/d_0 ratios. The limiting value of this ratio must obviously be 2.0 since there are four available sites for a deuterium in the carbanion and two sites in water.

A sample data set for the reaction between DO^- and isoprene (**3**) is shown in Figure 4. Here, the normalized distribution of the d_0 and d_1 carbanion (m/z 67 and m/z 68, respectively) is plotted vs. the flow rate of added isoprene. Extrapolating these data back to zero flow provides the single-collision product distribution. Reaction branching ratios derived from neutral flow rate variance are more reliable than those determined from variation of the reaction distance z since absolute flow rates are more easily determined than absolute reaction distances; the latter are complicated by inlet end effects. Thus, in the case of isoprene, 68% of the carbanions emerging from the encounter with DO^- are undeuterated and 32% of them possess the label. The independence of the product distribution on flow of the neutral reagent indicates that neither d_0 nor d_1 react further with isoprene.

A bar graph analogous to Figure 3 summarizing the results for the series is shown in Figure 5. The left ordinate is the d_1/d_0

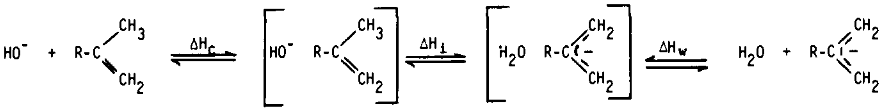
Table V. Summary of Results for Multiple Exchange Experiments





no.	R	$\Delta\Delta H^\circ_{acid}$[a]	reaction efficiency[b]	d_1/d_0	exchanges per encounter	reaction efficiency[c]	% d_2 species	exchanges per encounter
1	-H	0	0.54	0.36	1.7	(0.21)	22	2.2
2	$-OCH_3$	0	0.40	1.1	3.2	0.53	25	2.4
3	$-CH{=}CH_2$	−5	0.57	0.47	1.9	0.72	25	2.4
4	-CHO	−11	1.4	0.64	2.3	*d*	*d*	*d*
5	-F	−11	1.4	0.06	1.1	0.40	*d*	*d*
6	-CN	−19	1.4	0.16	1.3	0.003	5	1.3

[a] Difference in acidity between substituted propene and water in kcal/mol. [b] Efficiency for reaction of substituted propene with HO^-. [c] Reaction efficiency for overall disappearance of the allylic anion upon reaction with D_2O. [d] Parameters indeterminable due to dominant side reactions.



(6)

ratio and the right is the corresponding number of exchanges derived from Table IV.

For a one-step exothermic proton abstraction by DO^- the value of the d_1/d_0 ratio is, of course, zero. We have found significant amounts of the monodeuterated product anion ($d_1/d_0 > 0$) for most propenes studied. In the case of propene (**1**) and 2-methoxypropene (**2**), HO^- was a significant primary product of the reaction with DO^-. Most of the reactants exhibited d_1/d_0 ratios which suggest 1–2 exchanges per encounter. 2-Methoxypropene (**2**) gave the largest ratio, 1.1, which corresponds to 3–4 exchanges per DO^- collision. The least reactive member of the series was 2-fluoropropene (**5**) with a d_1/d_0 value only slightly above zero. A summary of experimental results for both types of exchange reactions is given in Table V.

Discussion

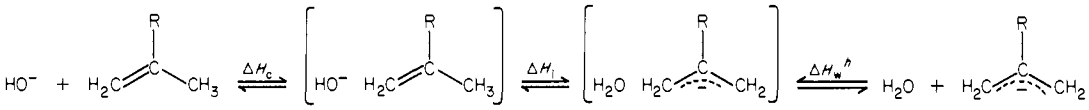
In an earlier study of gas-phase hydrogen–deuterium exchange reactions of DO^- with various neutral acids,[24] we identified several variables which are important in determining reaction rates. As we shall demonstrate, these same factors may be applied in interpreting the extent of multiple proton transfers determined in the present study. The first of these, and the most obvious, is the difference in gas-phase acidity between the acid and H_2O. Since H–D exchange involves one or more formally endothermic proton transfers,[18-22] the magnitude of this energy difference is expected to play a role. While important, this cannot be the sole factor since DO^- exchanges more slowly with H_2 than it does with NH_3,[24] despite the fact that the former is closer in acidity to water than the latter.[28] As is obvious from the summary in Table V, the extent of multiple exchange during a single collision is also a function of more than simply the difference in acidity between the propylenes and water. For example, in reactions with DO^- a larger d_1/d_0 ratio is seen for methacrylonitrile (**6**) than for 2-fluoropropene (**5**). The larger ratio suggests more exchange during ionization of **6** despite a much greater exothermicity in the proton abstraction reaction as compared to that of **5**. On the other hand, 2-methoxypropene (**2**) gives evidence for undergoing substantially more exchange than does propene (**1**), even though they are roughly equal in acidity.

A second important factor is the magnitude of the attractive energy in the initially formed ion–dipole complex. In an ion–molecule reaction the reactants are attracted to one another and the extent of the attraction depends upon the size of the dipole moment and polarizability of the neutral partner. It is these attractive forces which fuel the intermediate endothermic proton transfers that give rise to H–D exchange. If they facilitate small, as for instance in the complex between DO^- and H_2, then the exchange reaction will ordinarily be slower than if they are larger, as in $[DO^-{\cdot}NH_3]$.[24] An influence of ion–dipole energy on the extent of multiple exchange is also evident. While propene (**1**) and 2-methoxypropene (**2**) have about equal acidities, the energy of association with DO^- is greater for **2** since it possesses a larger dipole moment (μ_D = 1.2 D) and a larger polarizability (α = 9.3 Å^3) than does **1** (μ_D = 0.36 D; α = 6.1 Å^3). Consequently, we find that 2-methoxypropene undergoes "three" exchanges per DO^- collision and propene undergoes less than "two". This same trend appears in comparing methacrolein (**4**) with 2-fluoropropene (**5**). These neutrals transfer a proton to DO^- with about the same exothermicity, but a greater number of exchanges per collision are found for the more polar and more polarizable **4** (μ_D = 2.7 D; α = 8.6 Å^3) than for **5** (μ_D = 1.6 D; α = 6.4 Å^3). The data for the D_2O–allylic anion experiments are consistent with this interpretation. The ion–dipole energy present within complexes of D_2O and any of the substituted allylic anions must be similar since it is mainly the dipole moment and polarizability of the D_2O which determines the attractive forces. Therefore, it might be expected that the relative extent of double deuterium incorporation in a single D_2O encounter would largely depend upon the magnitude of the deuteron abstraction endothermicity. That this is the case is shown by our data. The first three propenes of the series **1**–**3** are very close to water in acidity and their corresponding anions **1a**–**3a** all yield about the same amount of primary d_2 product. Methacrylonitrile anion (**6a**) gives essentially no double exchange in keeping with a high endothermicity for the deuteron abstraction from D_2O.

We can illustrate the interplay of the factors which govern the observed multiple exchange variations by using a semiquantitative description of the proton-transfer energy surface which we developed in the previous study.[24] Our discussion will consider the proton-transfer mechanism depicted in eq 6 which presumes a double-well potential model for the exchange reactions.[4b,14c] Here, ΔH_c represents the complexation energy of the reactants, ΔH_i is the energy of interconversion of complexes I and II, and ΔH_w represents the solvation energy of the carbanion by water. Factors which facilitate the interconversion of the intermediate complexes I and II will increase the extent of multiple exchange.

Defining a complete potential energy surface for proton-transfer reactions involving large molecules and ions such as in this study is, of course, not yet practical. However, with a knowledge of the relative acidities of the neutral species plus estimates of the relative ion–neutral bond energies in I and II, we can construct qualitative potential energy diagrams for each of the exchange reactions. Good estimates of the gas-phase acidities of all the neutrals examined in this study are available (vide supra). Unfortunately, there are no experimental data on the relative energies of complexes like I and II. However, approximate values may

Table VI. Calculated Enthalpy Changes for Proton-Transfer-Reaction Profiles



no.	R	μ_D[a] (Debye)	α[b] ($Å^3$)	$\Delta H°_{acid}$[c,i]	$\Delta\Delta H°_{acid}$[i]	ΔV_I[d,i]	ΔH_c[e,i]	ΔV_{II}[f,i]	ΔH_i[g,i]
1	-H	0.364	6.07	391	0	0	−10.0	−3.5	−3.5
2	$-OCH_3$	1.20	9.25	391	0	−5.7	−15.7	2.2	2.2
3	$-CH=CH_2$	0.260	10.3	386	−5	−2.3	−12.3	−1.2	−6.2
4	-CHO	2.68	8.62	380	−11	−11.7	−21.7	8.2	−2.8
5	-F	1.61	6.37	380	−11	−5.6	−15.6	2.1	−8.9
6	-CN	3.69	8.58	372	−19	−16.0	−26.0	12.5	−6.5
	H_2O	1.86	1.45	391					

[a] Reference 35. [b] References 36 and 37. [c] Reference 26 and this work. [d] Difference in ion-dipole interaction potential (eq 8) between the 2-substituted propene and propene. [e] Calculated enthalpy change for $RC(CH_3)CH_2 + HO^- \rightarrow [RC(CH_3)CH_2 \cdot HO^-]$ using estimated value for (R = H) of −10 kcal/mol; $\Delta H_c = -10 + \Delta V_I$. [f] Difference in interaction potential between $[RC(CH_3)CH_2 \cdot HO^-]$ and $[RC(CH_2)_2^- \cdot H_2O]$. [g] Calculated enthalpy change for the reaction $[RC(CH_3)CH_2 \cdot HO^-] \rightarrow [RC(CH_2)_2^- \cdot H_2O]$; $\Delta H_i = \Delta V_{II} + \Delta\Delta H°_{acid}$. [h] Constant value for hydration of 2-substituted allylic anion; $\Delta H_w = -13.5$ kcal/mol. [i] kcal/mol.

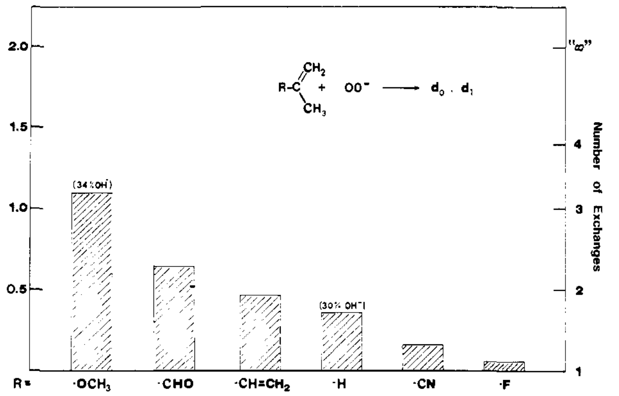


Figure 5. Bar graph summary of results for substituted propene–DO⁻ experiments showing the d_1/d_0 ratio for product carbanions. Corresponding number of exchanges per encounter shown at right. Hydroxide ion was also a primary ionic product in the case of propene (**1**) and 2-methoxypropene (**2**).

be calculated by using an effective radial potential describing the interaction of an ion with a polar molecule (eq 7).[33] In spite of

$$V(r) = -\frac{\alpha q^2}{2r^4} - \frac{q\mu_D}{r^2} \tag{7}$$

its neglect of short-range repulsive forces, we find that this potential can give good first approximations for solvation energy differences.[24] Other examples of the successful application of this approach have been noted by Hunter and Lias.[25] The first term gives the ion–induced dipole contribution and the second is the ion–permanent dipole term with the dipole locked in its lowest energy configuration. Here α is the molecular polarizability, q is the electronic charge on the ion, μ_D is the dipole moment of the neutral, and r is the ion–neutral separation distance (collision diameter). With the assumption of a constant r value, the difference in interaction energy between two ion–neutral complexes is given by eq 8. For type-I complexes (eq 6) we have computed

$$\Delta V(r) = V_2(r) - V_1(r) = -\frac{q^2(\alpha_2 - \alpha_1)}{2r^4} - \frac{q(\mu_D(2) - \mu_D(1))}{r^2} \tag{8}$$

ΔV_I as the difference between interaction of hydroxide ion with the substituted propenes **2**–**6** and propene itself. The absolute values of ΔV_I are obviously sensitive to the choice of the ion–neutral separation distance r. However, a plot of ΔV_I vs. r shows that the relative ordering of values for our series remains constant over a wide range of separation distances. Since repulsive forces are neglected in the potential an unusually large r value would be necessary to produce "reasonable" absolute magnitudes of ΔV_I. Recognizing this fact along with the insensitivity of the ΔV_I ordering to the exact choice of r, we have used a value of r = 4 Å in our calculations. In order to determine the relative energies for the type-II complexes, we have calculated ΔV_{II} as the difference in interaction potential between each type-II complex and the corresponding type-I complex. Thus, ΔV_{II} represents the change in ion–dipole attractive forces which accompany proton transfer from a propene to hydroxide. Again, the order of ΔV_{II} values calculated in this fashion is not sensitive to the choice of r and a separation distance of 4 Å was used. Using an estimated value of −10 kcal/mol for the $[HO^- \cdot CH_2{=}CHCH_3]$ solvation energy,[34] we can now calculate the energies of each of the complexes. The results of our calculations along with the parameters used are summarized in Table VI. We have constructed a family of proton-transfer potential energy diagrams from these data and these are shown in Figure 6.

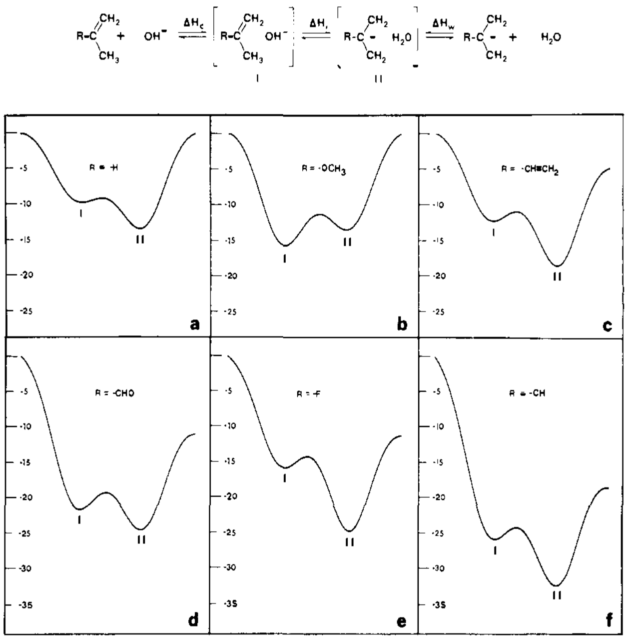


Figure 6. Schematic potential energy diagrams for proton transfer from substituted propenes **1**–**6** to hydroxide ion (energies in kcal/mol).

Following the reaction profiles starting from the left, HO⁻ and the propene enter into a reactive type-I complex for which the ion–dipole well depth is given by ΔH_c. Proton transfer from the propene to HO⁻ interconverts I and II and the energy for this process is given by ΔH_i which is the sum of the water–propene

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(32) Mackay, G. I.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Can. J. Chem.* **1978**, *56*, 131–140.

(33) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347–356.

acidity difference plus the change in solvation energy (ΔV_{II}). The ion–dipole attractive energy in the type-II complexes with respect to the carbanion and water is a constant value for the series $\Delta H_w = -13.5$ kcal/mol.

The potential energy diagrams provide insight into the origins of the multiple exchange variations. For pairs of propenes of similar acidity such as **1** and **2** or **4** and **5**, the one with the greater ΔH_c (**2** or **4**) exhibits the most deuterium incorporation (i.e., undergoes more exchanges) upon reaction with DO^-. Furthermore, for a pair of propenes with similar ΔH_c values such as **2** and **5**, the one lying closer in acidity to water (**2**) also exhibits more exchange. We can see from the diagrams that both an increase in the depth of the initial ion–dipole well (ΔH_c) and a decrease in the proton-transfer exothermicity ($\Delta\Delta H^\circ_{\mathrm{acid}}$) will serve to decrease the energy difference between I and II, thus facilitating their interconversion.

A more detailed explanation may be formulated by considering the decomposition of intermediates I and II in terms of RRKM theory as it has been applied to ion–molecule reactions by Brauman.[38] The extent of multiple exchange will depend upon the relative rates for passage over the barrier between I and II vs. the rates for their dissociation to separated reactants and products, respectively. For deuterium incorporation into the product carbanion in the DO^- reactions, "product" complex II must be able to revert to complex I several times prior to dissociating. In RRKM terms, the competitive branching of II will depend upon the relative densities of states above the centrifugal barrier for dissociation vs. those above the central barrier back to I. For propenes of equal acidity, as ΔH_c increases, the density of states above the central barrier will increase rapidly whereas those available for dissociation of II to products (or of I back to reactants) will not change. Therefore, the lifetime of the ion–dipole complex will increase and more exchange can occur. In a similar manner, when ΔH_c is the same for a pair of reactants but the overall exothermicity for proton transfer differs, the one with the greater reaction exothermicity will have the greater density of states available for dissociation to products. Thus, reversion of complex II to I becomes relatively disfavored and fewer exchanges occur. 2-Fluoropropene (**5**) and methacrylonitrile (**6**) provide an interesting comparison. Whereas the overall proton transfer is 8 kcal/mol more exothermic for the latter, ΔH_c is significantly larger and ΔH_i is slightly smaller. The result is a longer complex lifetime, more facile interconversion of I and II, and increased multiple exchange in methacrylonitrile relative to 2-fluoropropene.

For a d_2 product to appear from a single D_2O–carbanion collision, complexes I and II must interconvert several times. However, the limiting energy for this process is given by the ion–dipole attractive forces present when II is formed from the right-hand side of the potential energy diagrams: $\Delta H_w = -13.5$ kcal/mol. As the top of the central barrier approaches the total energy of the system, interconversion of I and II is slowed by the rapidly decreasing number of available states over the barrier. A sufficient number of states is available above the central barrier for the first three allylic ions; these species all exhibited about 25% double deuterium incorporation. The passage is relatively "narrow" for methacrylonitrile ion, however, and in this case almost no d_2 product was observed. It is unfortunate that reliable data could not be acquired for the pivotal cases 2-fluoropropene (**5**) and methacrolein (**4**). On the basis of our arguments here and inspection of Figure 6, parts d and e, we would predict an appreciable amount of double deuterium incorporation for methacrolein and none for 2-fluoropropene.

An important question remains as to why the scrambling of hydrogens and deuteriums was never complete in any of the cases studied. For the highly exothermic proton abstraction reactions between DO^- and **4**, **5**, and **6** such a result might have been expected since they occur with essentially unit efficiency (cf. Table I). In fact, the appearance of any deuterium-labeled product anion initially came as a surprise to us. We conclude from the incomplete equilibration of hydrogens and deuterium in the near thermoneutral DO^- reactions with **1**, **2**, and **3** that the intermediate ion–dipole complexes are not strongly enough bound to allow a sufficiently long lifetime for complete scrambling.[39] Thus, decomposition of complex II ultimately proceeds faster than its interconversion to I. Adams, Smith, and Henchman recently described an analogous correlation for near thermoneutral isotope exchange reactions in small molecular cations.[40] Complete scrambling of deuterium was observed in the reactions of H_3O^+ with D_2O where the $[H_3O^+{\cdot}D_2O]$ ion–dipole energy (~ -32 kcal/mol)[41] is large. The product distribution was far from statistical for $CH_5^+ + CD_4$ where the complexation energy is small (~ -7 kcal/mol)[41] and $NH_4^+ + ND_3$ ($\Delta H_c \sim -25$ kcal/mol)[41] exhibited intermediate behavior. Since the intermediate ion–molecule complexes presumed for our exchange reactions probably have binding energies in the range ca. $-26 < \Delta H_c <$ ca. -10, the lifetimes may be short relative to that for $[H_3O^+{\cdot}D_2O]$ (~ 2 ns) but long compared to that for $[CH_5^+{\cdot}CD_4]$ (~ 2 ps).[40]

In a recent ion cyclotron resonance study of the reactions of some C_3H_6 isomers with protonated neutrals, Hunter and Lias reported similar conclusions regarding the relationship between ion–molecule complexation energy and isotope exchange efficiency.[25]

Concluding Remarks

In summary, we have determined the primary product distributions for H–D exchange reactions involving a series of 2-substituted propenes. Comparison of the observed and statistical product distributions has provided an empirical count of the number of exchanges occurring during a single ion–neutral encounter. Our data indicate incomplete scrambling of hydrogen and deuterium for all members of the series. We have identified several variables which determine the extent of multiple proton transfer within the intermediate ion–molecule complexes presumed for the reactions. For reactions between a substituted propene and DO^-, those members of the series with larger dipole moments and/or polarizabilities exhibited the greatest amount of multiple exchange. Extensive exchange was found even in cases where the difference in acidity between DO^- and the propene is as large as 19 kcal/mol. Thus, while acidity differences are important in determining the extent of proton shuffling in a gas-phase acid–base reaction, the initial ion–dipole attraction energy of the reactants appears to be the dominant factor. For reactions between 2-substituted allylic anions and D_2O, the extent of multiple exchange is primarily determined by the acidity differences since the initial carbanion–D_2O attractive energy is roughly constant for the series.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant CHE79-09750) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. J.J.G. thanks Proctor and Gamble for a fellowship administered by the Organic Division of the American Chemical Society.

Registry No. 1, 115-07-1; **1a**, 1724-46-5; 2, 116-11-0; **2a**, 86046-88-0; **3**, 78-79-5; **3a**, 78427-90-4; **4**, 78-85-3; **4a**, 86046-89-1; **5**, 1184-60-7; **5a**, 86046-90-4; **6**, 126-98-7; **6a**, 83268-51-3.

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(34) Estimation is for the illustrative purposes of Figure 6 only and is based upon a consideration of the range of known HO^- solvation energies, cf.: Payzant, J. D.; Yamdagni, R.; Kebarle, P. *Can. J. Chem.* **1971**, *49*, 3308–3314. Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7139–7143.

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