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Studies of the binary reactions of H_3O^+ (H_2O)_{0,1,2} ions and their deuterated analogues with D₂O, H₂O, and NH₃

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The rate coefficients and product ion distributions for the binary reactions of H_3O^+ (H_2O)_{0,1,2} and D_3O^+ (D_2O)_{0,1,2} ions with D_2O and H_2O , respectively, and with NH_3 have been studied at 300 K using a selected ion flow tube (SIFT) apparatus. The ions were created in a flowing afterglow ion source and after mass filtering were injected at low energy into the SIFT. All the reactions proceeded at or near the gas kinetic limit. In the D_2O and H_2O thermoneutral isotopic exchange reactions, the distribution of H and D amongst the product ions and neutrals was seen to be purely statistical. This implies that these reactions proceed via the formation of an intermediate long-lived association ion in which total randomization of the H and D atoms takes place prior to unimolecular decomposition. No appreciable isotopic exchange occurred in the exothermic NH_3 reactions which apparently proceeded via the simpler mechanisms of D^+ (or H^+) or D_3O^+ (or H_3O^+) transfer. The differing mechanisms for the H_2O and D_2O reactions compared to the NH_3 reactions are rationalized in terms of the thermicities of the reactions and the lifetimes of the respective intermediate ions.

INTRODUCTION

Hydrated hydronium ions, i.e., $H_3O^* \cdot (H_2O)_n$, have received considerable attention in recent years since they are invariably present in moist ionized gases, since they dominate the positive-ion composition of the Earth's lower atmosphere and since they are important species in aqueous solutions. These so-called cluster ions can grow to be very large in the gas phase ($n \approx 100$) by sequential third-body (M) stabilized reactions of the kind

$$H_3O^* \cdot (H_2O)_n + H_2O + M - H_3O^* \cdot (H_2O)_{n+1} + M$$
 (1)

The recognition by Kebarle¹ that it was not only possible to produce solvated ions in the gas phase but that with suitable control their thermodynamic properties could be measured has stimulated great interest in the comparative study of the properties of solvated ions in the gas phase and in solution.^{2,3} Insight into the effect of selective ion solvation on ion-molecule reaction rates has come from the flowing afterglow technique, initially by Bohme⁴ and in the extensive studies by Ferguson and his associates⁵: For example, this has led to the formulation of a model for the production of the water cluster ions, the dominant positive ions in the middle and upper atmosphere. The difficulty of measuring product ion distributions for these solvated-ion reactions in the flowing afterglow⁶ has hindered mechanistic studies of the role of the solvent molecules. The selected ion flow tube (SIFT), a technique developed recently by two of us, can produce such data and this paper consists of our first application of the technique to study solvent participation in ion-molecule reactions.

There is considerable evidence from experiments involving isotopic labeling that asymmetric proton-transfer reactions $AH^* + B \rightarrow A + BH^*$ involve the discrete transfer of a proton^{7,8} and the plausible inference is that this proceeds through an intermediate proton-bound dimer.^{9,10} Where these reactions are appreciably excergic they are found to proceed at the gas-kinetic limit.¹¹ For those asymmetric proton-transfer reactions which are close to thermoneutral¹¹ and for those symmetric protontransfer reactions (distinguished by a single isotopic label) which are essentially thermoneutral, ^{7,8} the rate coefficients are reduced below the gas-kinetic limit and approximate the value predicted from the statistical decomposition of a proton-bound intermediate. Such considerations would predict the following mechanism for the system considered here:

$$\begin{array}{c} H & H & H & H \\ I & I & I & I \\ H - O - H + O - H - H - O + H - O - H \\ \end{array}$$

a mechanism which is supported strongly by bulk properties of liquid water, specifically the anomalous equivalent conductivity of the proton in aqueous solution. By extension, therefore, the comparable thermoneutral reactions of the hydrated hydronium ions may be viewed as proceeding via the discrete transfer of an $H_3O^*(H_2O)_{n-1}$ moiety, but perhaps more simply as the discrete addition of a water molecule to the ion followed by the immediate ejection of another:

$$H_{3}O^{*} \cdot (H_{2}O)_{n} + H_{2}O - H_{2}O + H_{3}O^{*} \cdot (H_{2}O)_{n}$$
 (3)

Such a mechanism would be the gas-phase analog for the mechanism established in aqueous solution for a series of asymmetric proton-transfer reactions, in which one, two, or more water molecules are shown by NMR techniques to be kinetically involved in the rate-determining step.¹² In this paper, however, we present the results of a study which clearly indicate that, at least for small clusters, the simple transfer processes (2) and (3) are not a proper description of the interactions. This study involves the reactions of the ions $H_3O^* \cdot (H_2O)_{0,1,2}$ and their partially and totally deuterated analog with D_2O and H_2O as appropriate.

We have complemented our study of the symmetric thermoneutral reaction between hydrated hydronium ions

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and water with a comparable study of the asymmetric exoergic reaction of these ions with ammonia: Here the reaction mechanisms are found to differ significantly from those established for the symmetric reactions with H_2O and D_2O .

EXPERIMENTAL

The SIFT technique has been described in detail elsewhere. $^{13-15}$ It is a very versatile technique for the study of ion-neutral reactions and has been used to date to study a wide variety of positive ion/molecule reactions, ¹⁶⁻¹⁸ excited ion reactions, ^{19,20} ternary association reactions, ^{21,22} and doubly charged ion reactions.^{23,24} In essence, the technique involves the injection of a massselected ion beam at low kinetic energy into a relatively high pressure flowing gas and the reactions of the ions are studied by introducing controlled amounts of reactant gas into the flowing gas downstream of the ion injection point. Thus, the rate coefficients and product ion distributions can be determined at thermal energies for the reactions of any ionic species which can be injected at sufficiently high currents into the flow tube without significant collisional fragmentation.

The present study was carried out using a new SIFT apparatus (described briefly in Ref. 15) possessing many more features than the basic SIFT with which most of the previous work has been carried out. The essential new feature for the purpose of the present study was the integral flowing afterglow ion source which was used to generate the hydrated hydronium ions. The details of this ion source will be discussed elsewhere²⁵ but briefly it consists of a Pyrex glass flow tube in which a flowing afterglow plasma can be established by the combined action of a continuous microwave discharge in helium at pressures in the range 0.1 to 5 Torr and of a small Roots blower pump. The addition of water vapor downstream of the microwave discharge and thus into the afterglow plasma resulted in the production of H_3O^+ ions initially and then the hydrated species via reactions of the kind described by Eq. (1). By judicious variation of the partial pressures of the water vapor and helium, the current of the particular ion required from the source could be optimized. The addition of D₂O vapor downstream of the H₂O injection port resulted in the partial or total deuteration of the $H_3O^* \cdot (H_2O)_n$ ions according to the relative concentration of H_2O to D_2O . Obviously, the relative positions of H₂O and D₂O injection into the flowing afterglow could be reversed and thus selective hydrogenation of the $D_3O^{+}(D_2O)_n$ ions could also be accomplished.

The current of the cluster ions exiting from the flowing afterglow ion source is severely reduced by the very rapid recombination of the ions with the plasma electrons, the recombination coefficients for such reactions being very large.²⁶ An effective solution to this problem was apparent from the work carried out in our laboratories on positive ion-negative ion recombination^{27,28} which has shown that ion-ion recombination coefficients at thermal energies are some two orders of magnitude smaller than the electron recombination coefficients of water cluster ions. Thus, the addition of small traces of SF₆ into the afterglow, insufficient to disturb the positive ion chemistry yet sufficient to convert the plasma electrons to SF₆ (with some SF₅), resulted in a vast improvement in the efficiency of the ion source.

It is in the nature of the technique that the higher the energy of the ions at the point of entry into the main flow tube (the SIFT) the larger is the fraction of the ion current which passes into the flowing gas and is convected down the flow tube. However, the center-of-mass energy $E_{\rm c.m.}$ of the injected ion/carrier gas atom must be sufficiently small such that collisional breakup of the ions is insignificant, a problem considerably alleviated by the use of a helium carrier gas

$$E_{\rm c.m.} = \frac{M_{\rm He}}{M_{\rm He} + M_{\rm ion}} E_{\rm lab} \ . \label{eq:Ec.m.}$$

This problem becomes more acute as the degree of hydration of the hydronium ion increases due to the corresponding reduction the binding energy of the water molecules to the core ion.¹ Additionally, the study of the trihydrate was not possible at 300 K because thermal decomposition of the ion in the He carrier gas occurred at a sufficiently high rate so that all of the trihydrate ions had been effectively dissociated to the dihydrates in their passage along the flow tube to the reaction region. This latter problem can in principle be overcome by operating at lower temperature, but this was not done in these studies.

Adequate currents of H_3O^* , $H_3O^* \cdot (H_2O)$, and $H_3O^* \cdot (H_2O)_2$ and their partially or totally deuterated analogs were individually introduced into the main flow tube and their rate coefficients and product ion distributions determined in the usual way in reaction with H_2O and D_2O (as appropriate) and with NH_3 . Known flow rates of the H_2O and D_2O vapors were introduced into the SIFT using prepared mixtures of H_2O and D_2O vapor of known partial pressures in helium. All measurements were carried out at 300 K.

RESULTS

Reactions of $H_3O^+ \cdot (H_2O)_{0,1,2}$ and $D_3O^+ \cdot (D_2O)_{0,1,2}$

with D_2O and H_2O , respectively

The essential features of the data are best illustrated with reference to the simplest reactions studied, viz, the $H_3O^+ + D_2O$ and the $D_3O^+ + H_2O$ reactions. As an example, the raw data for the latter reaction is given in Fig. 1(a), in which the count rates of the primary reactant ion D_3O^+ and the product ions, as detected by the downstream mass spectrometer/multiplier/detection system, are plotted as a function of the flow rate of H₂O into the SIFT. The rate coefficient for the reaction is obtained from the slope of the linear semilogarithmic decay curve. The ions generated as a result of the interaction are the successively hydrogenated ions D_2HO^+ , DH_2O^* and H_3O^* . Clearly, H_3O^* cannot be a primary product of the $D_3O^* + H_2O$ reaction and must be a secondary product resulting from the further reaction of the D_2HO^* and DH_2O^* with H_2O ; such can be seen to occur [Fig. 1(a)] by the reducing count rate of these two ions with increasing H₂O flow following their initially increasing count rate. The important question is whether one



FIG. 1. Variation with H_2O flow rate of (a) the primary and product ion counts (10 s sampling period) and (b) the percentages of the ionized products for the H/D exchange reaction $D_3O + H_2O$ studied in a SIFT at ~ 300 K.

or both of the ions D_2HO^+ and DH_2O^+ are products of the primary reaction. This is simply resolved by plotting the relative count rates for these two possible product ions as a function of the H₂O flow rate, as indicated in Fig. 1(b), from which it can clearly be seen that at essentially zero H₂O flow, finite percentages of both $D_2HO^{+}(\sim 65\%)$ and $DH_2O^{+}(\sim 35\%)$ are evident. In cases where it is deemed necessary to define the product ion distribution very accurately, additional data points can, of course, be readily obtained at low reactant gas flow rates. By this simple procedure the product ion distribution of the primary reaction is determined.¹⁴ As can be seen, the relative ion currents are dependent on the H₂O flow rate as a result of secondary reactions of the ions with H₂O, and thus the relative currents at any finite H₂O flow do not indicate the true primary product distribution.

So both D_2HO^* and DH_2O^* are primary products of the reaction which proceeds thus:

$$D_3O^* + H_2O - D_2HO^* + DHO (65\%)$$
, (4a)

$$\rightarrow DH_2O^* + D_2O \quad (35\%) ,$$
 (4b)

$$(- D_3 O^* + H_2 O)$$
, (4c)

with a rate coefficient at 300 K of 2.0×10^{-9} cm³ s⁻¹ which should be compared with the collisional rate coefficient of 2.23×10^{-9} cm³s⁻¹ (calculated using the ADO theory^{29,30}). Therefore, deuterium/hydrogen exchange occurs at essentially every collision and, as Reaction (4a) indicates, in the majority of the collisions one hydrogen atom is apparently exchanged for one of the deuterium atoms in the D_3O^* ion and the neutral molecule HDO is generated. So although Reaction (4b) can be considered as a simple deuteron transfer reaction, the overall reaction in this case cannot be as simple as has been generally assumed.^{7,8} In fact, the mechanism which is clearly indicated by these data and strongly supported by the larger body of data relating to the D₂O and H₂O reactions given in Table I is one in which the ion and molecule come together as a complex which exists long enough for total scrambling of the deuterium and hydrogen atoms to occur before the ion and molecule separate. Accordingly, the distribution of D and H amongst the product ions and neutrals should be statistical, as is seen to be the case in Table I, in which the experimentally obtained percentages, given in round brackets, and those based on simple probability, given in square brackets, are essentially equal. Omitted from the data in Table I is the "nonreactive channel" exemplified by Reaction (4c) which recognizes the finite probability (in this case 1/10) that reactants and products can be identical and therefore undetectable in the experiment. This means, therefore, that the measured reaction rate should be smaller than the actual collision rate by this small factor. As can also be seen from Table I, within experimental error, an identical result is obtained for the $H_3O^* + D_2Q$ reaction. This identity establishes the absence of significant kinetic isotope effects at 300 K and the point is further emphasized by the similarity of the two rate coefficients. Accordingly, we may conclude that, at the temperature of these experiments, zeropoint-energy differences are significantly less than kT, such that both Reactions (4) and the mirror-isotope reaction $(H_3O^* + D_2O)$ may be considered as being thermoneutral. It is worth stressing that such a clear picture of these interactions could not have been obtained in systems containing both H₂O and D₂O since forward and back reactions which essentially occur with the same rate coefficient would confuse the situation, i.e.,

$$H_3O^* + D_2O \rightleftharpoons isotopically mixed ions \rightleftharpoons D_3O^* + H_2O.$$
(5)

Complications due to such back reactions are excluded in the SIFT since the molecules from which the primary ions are derived are absent from the reaction zone.

It is a necessary consequence of this simple scrambling statistical mechanism for these reactions that the partially hydrogenated ions D_2HO^+ and DH_2O^+ will effectively react more slowly with H_2O . That this requirement is met is indicated by the rate of decline of the count rate of these ions with H_2O flow shown in Fig. 1(a). TABLE I. Rate coefficients (cm³ s⁻¹) and product-ion distributions (percentage in round brackets) for the reactions indicated as determined using a SIFT at 300 K. The corresponding ADO theoretical values^{29,30} for the rate coefficients and the product-ion distributions, calculated assuming that the distribution of H and D amongst the products is purely statistical,^a are given in square brackets following the experimentally determined values. The rate coefficients are accurate to $\pm 20\%$ for the reactions with NH₃ and $\pm 30\%$ for those with H₂O and D₂O.

$H_3O^+ + D_2O \rightarrow DH_2O^+ + DHO$ (70%) [6 $\rightarrow D_2HO^+ + H_2O$ (30%) [33	7%] $D_3O^* + H_2O - D_2HO^* + DHO$ (65%) [67%] %] $- DH_2O^* + D_2O$ (35%) [33%]
2.2(-9) [2.27(-9)]	2.0(-9) [2.23(-9)]
$\begin{array}{c} \mathrm{H_3O}^{\bullet}(\mathrm{H_2O}) + \mathrm{D_2O} \rightarrow \mathrm{DH_4O_2^{\bullet}} + \mathrm{DHO} & (50) \\ \rightarrow \mathrm{D_2H_3O_2^{\bullet}} + \mathrm{H_2O} & (50) \end{array}$	%) [50%] $D_3O^*(D_2O) + H_2O \rightarrow D_3H_2O_2^* + D_2O$ (55%) [50%] %) [50%] $\rightarrow D_4HO_2^* + DHO$ (45%) [50%]
1.8(-9) [1.96(-9)]	1.7(-9) [1.98(-9)]
$H_3O^{+}(H_2O)_2 + D_2O \rightarrow \text{products}$	$D_3O^{+}(D_2O)_2 + H_2O \rightarrow \text{products}$
2.2(-9) [1.85(-9)]	1.7(-9) [1.88(-9)]
$D_2HO^* + H_2O \rightarrow DH_2O^* + DHO$ $\rightarrow H_3O^* + D_2O$	
1.5(-9) [2.24(-9)]	
$DH_2O^* + H_2O \rightarrow H_3O^* + DHO$	
7.3(-10) [2.28(-9)]	
$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$	$D_3O^* + NH_3 \rightarrow NH_3D^* + D_2O$
2.2(-9) [2.14(-9)]	2.2(-9) [2.07(-9)]
$H_3O^{+}(H_2O) + NH_3 \rightarrow NH_4^{+} + 2H_2O$	$D_3O^{\bullet}(D_2O) + NH_3 \rightarrow NH_3D^{\bullet} + 2D_2O$
2.2(-9) [1.88(-9)]	2.0(-9) [1.85(-9)]
$H_3O^{\bullet}(H_2O)_2 + NH_3 \rightarrow NH_4^{\bullet}(H_2O) + 2H_2O$	$D_3O^{\bullet}(D_2O)_2 + NH_3 \rightarrow NH_3D^{\bullet}(D_2O) + 2D_2O$
2.3(-9) [1.78(-9)]	1.9(-9) [1.76(-9)]

^aThe number of ways of producing a molecule H_xD_y via the statistical decomposition of an intermediate complex H_vD_w is simple given by $[v !/(v-x)!x!] \cdot [w!/(w-y)!y!]$.

However, to determine the rate coefficients for these two reactions, the D_2HO^+ and DH_2O^+ ions were formed in the flowing afterglow ion source, separately injected into the SIFT and the rate coefficients for their reaction with H_2O determined in the usual way. According to the model, the reactions should be as follows:

$$D_2 HO^* + H_2 O - DH_2 O^* + DHO$$
(6a)

$$- H_3O^* + D_2O \qquad) \qquad (10\%), \qquad (6b)$$

$$(-D_2 HO^* + H_2 O)$$
 (30%), (6c)

 $DH_2O^* + H_2O \rightarrow H_3O^* + DHO$ (40%), (7a)

$$(- DH_2O^* + H_2O)$$
 (60%). (7b)

So the observable reactive channels (6a), (6b), and (7a) and hence the net rate coefficients for Reactions (6) and (7) should be in the ratio 70:40. The measured rate coefficients (Table I) are seen to be in the ratio 2:1, which to within error is in good agreement with the statistical prediction. As can also be seen, the actual rate coefficients are the expected fraction of the ADO theoretical value as predicted by the statistical model.

It is however important to consider these results for the reactions (6) and (7) within the context of the protonbound-dimer model. Thus, for Reactions (6), this model predicts that 50% of the collisions should follow Reactions (6a) and (6b), while the remaining 50% should follow the channel (6c). The experimental results of 67% and 33%, respectively, clearly favor the statistical model. The predictions for the branching ratios (6a):(6b) are 6:1 for the statistical model and 2:1 for the proton-bound-dimer model: The experimental value was 5:1. We therefore see that both the results for Reactions (4) and (6) allow a clear decision to be made between the two models. The same does not hold for Reaction (7), where the percentages for channels (7a) and (7b) are 33% and 67%, respectively, for the protonbound-dimer model and 40% and 60% for the statistical model, to be compared with the values of 32% and 68%. respectively, deduced from the ratio of the measured net rate coefficient of Reactions (7) and the ADO collisional rate coefficient. The startling conclusion therefore emerges that, had we too restricted ourselves to an examination of the singly deuterated reaction (7), we too probably would have used our data as supporting evidence for the general validity of the proton-bound-dimer model.^{7,8}

This very convincing evidence for the scrambling/ statistical picture is further reinforced by the reactions of the $H_3O^* \cdot (H_2O)$ and $D_3O^* \cdot (D_2O)$ ions with D_2O and H_2O , respectively, the experimental data showing that again the product ion distribution is statistical and that the reaction rates are gas kinetic [in these cases reaction channels analogous to Reaction (4c) would be < 5% of the collision rate]. A similar result was obtained for the dihydrate and its deuterium analogue although de-

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FIG. 2. The usually envisaged structures for the intermediate ions formed in the reactions of (a) $H_3O^{**}(H_2O)$ with D_2O and (b), (c) $H_3O^{**}(H_2O)_2$ with D_2O .⁶

tailed product distributions were not obtained in these cases.

The model which postulates a proton-bound-dimer intermediate for Reactions (4), (6), and (7) makes analogous predictions for the reactions of the monohydrated and dihydrated hydronium ions. For the monohydrate, the intermediate would be a hydronium-ion-bound dimer [Fig. 2(a)] which would lose either H_2O or D_2O statistically but never HDO, necessarily requiring the rate coefficient for the observable channel to be half the gaskinetic limit. For the dihydrate two possibilities arise for the intermediate $H_9O_4^*$: It may either have a linear structure, as illustrated in Fig. 2(b), or the symmetrical structure, wherein each water is held equivalently to the central hydronium ion, as in Fig. 2(c). ^{31,32} Within the framework of the simple proton-bound-dimer model, both intermediates would react by losing either H₂O or D₂O statistically, but never HDO, and the overall rate coefficient would be, respectively, one half or two thirds of the gas-kinetic limit.³²

We note in passing that the proton-bound-dimer model, and its analogs for the hydrated hydronium ions, has an entirely equivalent description in terms of the familiar switching reactions or solvent displacement reactions, during which the integrity of the solvent molecule remains intact. From this perspective, one views the reaction as involving solvent switching about a proton, a hydronium ion, and a monohydrated hydronium ion, respectively.

In conclusion, it is important to distinguish the differing arguments on which the statistical model is advanced here for the hydrated hydronium reactions with water and on which the proton-bound-dimer model has been advanced elsewhere for other symmetric reactions.⁷⁻⁹ Our conclusions are based on experimentally measured branching ratios: In the other case, the conclusion is drawn from a comparison between experimental rate coefficients and theoretical predictions for these.

Collisional-induced dissociation studies

In order to investigate if any preferential disposition of the D and H atoms around the molecule exists in the mixed isotopic cluster ions, these were synthesized in the flowing afterglow ion source and injected individually into the SIFT at a sufficiently high $E_{c.m.}$ to induce the dissociation of one molecule from the ions. Thus, each ion in the mass ranges 37 to 42 amu $[H_3O^* \cdot (H_2O) - D_3O^*$ (D_2O) and 55 to 62 amu $[H_3O^* \cdot (H_2O)_2 - D_3O^* \cdot (D_2O)_2]$ was injected individually into the SIFT and the percentages of the ion fragments of each mass were determined using the downstream mass spectrometer in conjunction with a multichannel scaler to improve the statistics. The data clearly indicated that the distribution of H and D within the fragment ions was quite consistent with the assumption that H and D are randomly distributed within the parent cluster ion.

Reactions with NH₃

We have purposely extended our study of the symmetric reactions of $H_3O^* \cdot (H_2O)_{0,1,2}$ with D_2O and $D_3O^* \cdot (D_2O)_{0,1,2}$ with H_2O , whose thermochemistry has been shown to be essentially thermoneutral at 300 K, to comparable asymmetric reactions with ammonia, whose greater proton affinity makes the reactions appreciably exoergic. This has allowed us not only to consider the possible effect of exoergicity on the reaction mechanisms but, in two cases, to study the competition between different channels of differing exoergicity. These are indicated below as Reactions (8)-(10):

$$H_3O^* + NH_3 - H_2O + NH_4^* + 36$$
, (8)

$$H_{3}O^{*} \cdot (H_{2}O) + NH_{3} -$$
 (9a)

$$L_{+}H_2O + NH_4^{+} \cdot (H_2O) + 21$$
, (9b)

$$\rightarrow 3H_2O + NH_4^+ - 16$$
, (10a)

$$H_3O^* \cdot (H_2O)_2 + NH_3 \longrightarrow 2H_2O + NH_4^* \cdot (H_2O) + 1$$
, (10b)

$$\mapsto$$
 H₂O + NH₄⁺ · (H₂O)₂ + 16 . (10c)

Positive numbers represent reaction excergicities³³ in kcal mol⁻¹ and channel (10a) is closed, being endoer gic. For channels (9a) and (10b), the possibility must be considered that the two water molecules can be formed as a dimer, in which case the excergicity for both should be increased by 4 kcal mol⁻¹.³⁶ Clearly, a similar set of equations can be written involving the D_3O^+ $(D_2O)_{0,1,2}$ ions. Reactions (8)-(10) have been studied in the flowing afterglow by Fehsenfeld and Ferguson,³⁷ who showed that the reactions were rapid but they did not determine the favored channels in Reactions (9) and (10). Thus, we have studied these reactions and those of the deuterium analogs to determine the products of the reactions and to investigate if any significant isotopic scrambling occurred in these excergic reactions. The data are given in Table I and can be summarized quite simply. No measurable isotopic scrambling occurred in any of these reactions; in each case only single reaction channels were observed; and in both cases where competing channels were open (9) and (10), the less excergic channel (9a) and (10b) was followed exclusively

and at the gas-kinetic limit. This last result may be presented in two alternative ways. First, the reaction proceeds via an intermediate complex which always decomposes by ejecting the maximum number of water molecules which are energetically allowed. Second, the reaction proceeds via the discrete transfer of a proton together with the minimum number of water molecules which are energetically allowed. In view of the isotopiclabeling evidence which shows the absence of scrambling, the latter description would seem to be more appropriate although we cannot be sure that this is so.

The rate coefficients presented in Table I for Reactions (8)–(10) may be compared with previous results. For Reaction (8), our value of 2.2 (-9) compares favorably with our own previous value of 2.5 (-9), measured on our prototype SIFT machine, ³⁸ the value of 2.4 (-9) from the York flowing afterglow, ^{39,40} and 2.1 (-9) from the NOAA flowing afterglow.³⁷ The NOAA group also reported values of 2.6 (-9) and 1.6 (-9) for Reactions (9) and (10) and the York group 2.0 (-9) and 1.9 (-9)⁶ to be compared with our present values 2.2 (-9) and 2.3 (-9), respectively. In the flowing afterglow experiments, these last two rate coefficients had to be deduced from a complex scheme of competing and consecutive reactions whereas using the present SIFT technique each reaction is studied in isolation.

The absence of any scrambling in the asymmetric exoergic ammonia reactions and the total scrambling in the symmetric (thermoneutral) cases prompted us to examine the interaction of ammonium ions with water molecules, with suitable labeling of one of the reactants. Thus, NH_4^* was synthesized in the flowing-afterglow source, injected into the SIFT, and its reaction with D_2O investigated. The proton-transfer reaction (11) is of course endoergic, being the reverse of Reaction (8):

$$NH_4^+ + D_2O \rightarrow NH_3 + D_2HO^+ - 36 \text{ kcal mol}^{-1}$$
 (11)

but the process of hydrogen-deuterium exchange, according to

$$\operatorname{NH}_{4}^{*} + \operatorname{D}_{2}\operatorname{O}$$
 (12a)

$$\longrightarrow \mathrm{NH}_2\mathrm{D}_2^* + \mathrm{H}_2\mathrm{O} , \qquad (12\mathrm{b})$$

was observed with an overall rate coefficient of $\sim 3 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. The mirror isotope experiment involving ND₄ and H₂O was not performed. It is however clear that our result for Reactions (12) is not the consequence of zero-point-energy differences, since it will be this combination of isotopically labeled compounds which will result in the exchange being excergic. The significance of this interesting result for Reactions (12) and its relationship to the behavior observed for Reactions (4) and (8) will be considered in the discussion below.

DISCUSSION

Our experimental findings may be summarized as follows:

(1) Both the reactions of the hydrated hydronium ions $H_3O^* \cdot (H_2O)_n$ with water and ammonia proceed with essentially unit collision efficiency.

(2) While the reactions with water may be considered as involving the transfer of an $H^* \cdot (H_2O)_{n-1}$ moiety, the actual mechanism at 300 K for $0 \le n \le 2$ involves rapid scrambling of all the hydrogens within the intermediate complex, followed by the loss of one water molecule. Any discussion of the reaction in terms of statistical breakdown of a proton-bound dimer (or equivalently in terms of a solvent-switching reaction) is improperly conceived.

(3) In contrast, the reactions with ammonia proceed by the discrete transfer of a proton (with or without water molecules) from the hydronium ion to the ammonia without any scrambling. Where competing channels are accessible energetically the minimum possible number of water molecules are transferred with the proton.

(4) In collisions of ammonium ions with water molecules, hydrogen scrambling does occur but with a collision efficiency of only ~ 0.001 .

The differing results for

$$H_3O^* \cdot (H_2O)_n + H_2O \xrightarrow{\text{total}}_{\text{scrambling}} H_2O + H_3O^* \cdot (H_2O)_n , (13)$$

$$H_{3}O^{*} + NH_{3} \frac{\text{little or no}}{\text{scrambling}} H_{2}O + NH_{4}^{*}, \qquad (14)$$

$$NH_4^+ + H_2O \xrightarrow{slight}_{scrambling} NH_4^+ + H_2O$$
(15)

can be readily explained in terms of a simple model. For the scrambling of the hydrogen to be efficient requires that the lifetime of the intermediate complex be long. Such is facilitated by a large excitation energy and a greater atomicity of the intermediate complex and by a small reaction exothermicity. It follows from these requirements that hydrogen scrambling should be most facile for thermoneutral reactions whose intermediates are characterized by deep minima in the hypersurface. Accordingly, one finds for the family of thermoneutral reactions $MH^* + M \rightarrow M + MH^*$ that where the excitation energy is small, e.g., $M = CH_4$ for which the excitation energy is 7.4 kcal mol⁻¹, little or no scrambling is observed, 8,9 but where it is larger, e.g., for reactions of the type (13) for which excitation energies range from 32 to 17 kcal mol⁻¹ as n runs from 0 to 2^{1} (i.e., increasing atomicity of the intermediate), scrambling is complete.

Considering Reactions (14) and (15) in turn, the proton transfer reaction producing NH_4^+ is excergic by 36 kcal and therefore the intermediate complex $H_3O^* \cdot NH_3$ must have a very short lifetime such that scrambling cannot occur in Reaction (14). However, the excited intermediate complex $NH_4^+ \cdot H_2O$ is known to be formed in binary collisions of NH_4^+ with H_2O and can effectively be stabilized by a third body collision.¹ Also, its lifetime against unimolecular decomposition is known to be short but finite and is clearly sufficiently long to allow only slight scrambling of the H atoms to occur in Reaction (15). The observation of hydrogen scrambling within the intermediate of Reaction (13) raises the question of the means whereby the hydrogens can move around the cluster. As a possible mechanism, we may consider the various elements of the cluster $H_3O^* \cdot (H_2O)_n$, viz., H_3O^* and the "n" water molecules, as possessing rotational

energy and being only loosely coupled. Hydrogen as H^* or D^* is exchanged from water molecule to water molecule and scrambling is achieved if there is sufficient time for the H_3O^* species undergoing at least a $2\pi/3$ angular rotation between such exchanges. Double (deuterium and oxygen-18) labeling will allow the testing of such hypotheses. It will also be interesting to explore the rate of hydrogen scrambling as a function of cluster size since the trend is not simple to predict: Increasing the size will increase the lifetime of the intermediate complex and the number of hydrogen sites while maintaining the excitation energy essentially constant.¹

It would be of especial interest to study these isotopic exchange reactions as a function of increasing temperature but perhaps more appropriately up to appreciable energies (~a few eV) and thus, presumably, the lifetime of the intermediate complex would be considerably reduced. It might then be expected that sufficient time would not be available to allow complete randomization between the H and D atoms and as a consequence result in variations in the product distributions with an associated reduction in the reaction rate coefficients. It would be especially valuable to be able to quantitatively relate the complex lifetime to the degree of randomization of the H and D atoms. A SIFT-DRIFT apparatus¹⁵ is nearing completion in our laboratory and will be eminently suited to such studies.

It is hoped that gas-phase studies of the kind described here, and those anticipated experiments alluded to above, will contribute towards an understanding of the challenging problem of how the growth of water clusters in the gas phase leads ultimately to the phase transition resulting in water droplets.⁴¹ They might also contribute in some small degree to the further understanding of charge migration in liquid water.

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- ³²It should be noted that the $H_9O_4^*$ intermediate complex is formed from the thermal reactants $H_2O_3^*$ and H_2O so that it has an excitation energy of 17 kcal mol⁻¹.¹ Under each circumstances one may need to be wary of attempting to ascribe a particular "structure" to the intermediate: Rather than being restricted to a single point in configuration space, it will be free to explore a considerable volume thereof as a consequence of its energy content. Where this volume includes both points corresponding to the structures illustrated in Figs. 2(b) and 2(c), and where both points are sampled in a time scale short compared to the lifetime of the intermediate, the distinction between the two structures has no meaningful kinetic consequence.
- ³³Hydration enthalpies of NH⁴₄ and H₃O⁺ are taken from Kebarle.¹ The matter of the difference in proton affinity between water and ammonia has been a vexatious one and the ICR values continue to change. Recent photoionization studies of Van de Waals dimers^{34,35} have contributed to the growing body of data on the subject.
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