The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **56**, 2427 (1972); doi: 10.1063/1.1677551
View online: http://dx.doi.org/10.1063/1.1677551
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/56/5?ver=pdfcov
Published by the AIP Publishing

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THE JOURNAL OF CHEMICAL PHYSICS VOLUME 56, NUMBER 5 1 MARCH 1972

Proton Affinity of Water*

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(Received 30 August 1971)

By employing elevated pressures in the ion source of a quadrupole mass filter, it is shown that D_3S^+ does not transfer a deuteron to D_2O and that D_3O^+ transfers a deuteron to D_2S. Studies were carried out in most instances under conditions where the reactant ion undergoes 30–60 collisions before reacting. Thus, most excess energy should have been removed. The transfer of deuteron from D_3O^+ to D_2S appears to go to equilibrium with an equilibrium constant of 14.4 which corresponds to a heat of reaction of 1.8 kcal/mole. From this we deduce the proton affinity of water to be 168 kcal/mole.

INTRODUCTION

Because of its implications for solution chemistry, the proton affinity of water or its equivalent, $\Delta H_f(H_3O^+)$, has been the subject of several investigations. Van Raalte and Harrison[1] and Munson and Franklin[2] deduced values of about 152 and 167 kcal/mole, respectively, for $PA(H_2O)$ from the appearance potentials of H_3O^+ from several organic compounds. Values of 171[3] and 187[4] kcal/mole have been determined from measurements of crystal lattice energies, and values from 136 to 253 kcal/mole[5–9] have been obtained in various theoretical studies. Chupka and Russell[10] have employed photoionization of ethanol; Haney and Franklin[11] employed electron impact on ethanol with corrections for excess energy; and several workers[12,13] have deduced values from ion–molecule reactions. References 10–13 found heats of formation of H_3O^+ in the neighborhood of 142 kcal/mole corresponding to a proton affinity of 165 kcal/mole. In a recent investigation, DePas, Leventhal, and Friedman,[14] employing a molecular beam method, determined the threshold for the decomposition of H_3O^+ and from this deduced a value of the proton affinity of water of 182 kcal/mole. Long and Munson[15] subsequently redetermined the proton affinity of water by examining mixtures of water with several compounds to ascertain which would transfer a proton to water and which would receive a proton from H_3O^+. Their experiments were carried out at moderate pressures (0.04–0.1 torr) but at variable retention time so that the ions would undergo several collisions in the hope of removing any excitation from the reactant ion. They concluded that their results supported a value of 164±4 kcal/mole for $PA(H_2O)$.

In view of the large discrepancy between the results of DePas *et al.*[14] and other workers, we also considered it worthwhile to attempt a further determination at least with a view to fixing limits to the proton affinity of water. With this in mind, we have attempted to determine whether the reaction

$$H_3O^+ + H_2S \rightleftarrows H_3S^+ + H_2O \tag{1}$$

proceeds in the forward or reverse direction.

The proton affinity of H_2S and the heat of formation of H_3S^+ have been variously determined. The fact that the H_2S^+ ion reacts with H_2S gives an upper limit to $\Delta H_f(H_3S^+)$ of 197 kcal/mole. Haney and Franklin[11] determined the heat of formation of H_3S^+ by measuring its appearance potential and excess energy from ethane thiol and thiopropane finding an average value of 191 kcal/mole for the heat of formation and the corresponding value of 170 kcal/mole for the proton affinity of H_2S. If the proton affinity of water is less than that of H_2S then H_3O^+ should transfer a proton to H_2S. If it is greater than that of H_2S then the reverse should be the case and H_3S^+ should transfer a proton to water. However, to avoid errors that might arise from excess energy retained in the H_3O^+ or H_3S^+ reactant, resulting from the exothermicity of the reaction by which they were formed, the reactions were carried out at as high a pressure as possible in order to remove translational and vibrational excitation. Our method differed from that of Long and Munson[15] in that considerably higher pressures were employed in an effort to be certain that the reacting ions were in their ground states. As will be shown, this was sufficiently effective to permit Reaction (1) to attain equilibrium.

EXPERIMENTAL

In this study a quadrupole mass filter furnished with a high-pressure source capable of operating at pressures up to about 1 torr, was employed. The operation of the instrument and the techniques employed have been described previously.[16] In most of the experiments one component was present in large concentration and the other added in small increments. In two experiments, unreactive materials such as helium or argon were added in order to raise the pressure and to provide an inert means of removing any vibrational excitation from the reactant ion.

In most instances, D_2O and D_2S were employed rather than H_2O and H_2S. Several attempts were made to employ D_2O with H_2S but isotope exchange seemed to occur so rapidly that the data were almost impossible to interpret. The D_2O was employed without further purification. The D_2S was purified by condensation in liquid nitrogen and revaporization. Research-grade helium and argon were employed without further purification.

RESULTS AND DISCUSSION

In a further attempt to set an upper limit to the proton affinity of H_2S, which we assume to be the same as the deuteron affinity of D_2S, we introduced D_2S at 400 μ into the ion source at which point almost all of the D_2S^+ and DS^+ ions were converted to D_3S^+. At this pressure, D_3S^+ should undergo a large number of collisions in drifting through the ion source and should be essentially in the ground vibrational state. Formic acid was added to this in small increments up to a maximum of 7 μ pressure. The addition of the 7 μ of formic acid resulted in the disappearance of approximately three-fourths of the D_3S^+ ion and the formation of an equivalent amount of $HCOOHD^+$. This shows conclusively that the proton affinity of formic acid is greater than that of H_2S if we may assume that the deuteron affinity and the proton affinity are essentially equal. Haney and Franklin[17] have determined the proton affinity of formic acid to be 179 kcal/mole by determining the appearance potential and excess energy of $HCOOH_2^+$ from ethyl formate. This result shows that H_2S must have a lower proton affinity than formic acid and so is further support for the conclusion that the proton affinity of H_2S is well below that determined by DePas *et al.*[14] for the proton affinity of H_2O.

In a further experiment, D_2S was introduced into the ion source at a pressure of 265 μ at which point essentially all of the DS^+ and D_2S^+ ions were converted to D_3S^+. Small amounts of water were added in amounts up to 9 μ with no significant alteration in the intensity of the D_3S^+ ion. No H_2DO^+ and only a faint trace of H_3O^+ ions were observed and thus it is evident that there is no deuteration of water by D_3S^+ under these conditions.

Having demonstrated that D_3S^+ does not transfer D^+ to D_2O, it remains to demonstrate that the D_3O^+ does transfer D^+ to D_2S. This is a considerably more difficult problem because of the rapid addition of further water molecules to D_3O^+. In pure D_2O the maximum intensity of D_3O^+ with minimal intensities of D_2O^+ and $D_3O^+ \cdot D_2O$ was attained at 0.117 torr. When small increments of D_2S were added, the D_3O^+ ion decreased rapidly in intensity and D_3S^+ was formed at a corresponding rate. However, very little collisional deactivation of D_3O^+ could occur at these conditions. In order to have a maximum of D_3O^+, while also providing for collisional deactivation of the D_3O^+, we employed mixtures of D_2O with helium and with argon. The proportions were adjusted to give maximum intensities of D_3O^+ at pressures of 362 μ in the case of helium and 480 μ in the case of argon. When D_2S was added in small increments, the D_3O^+ decreased in intensity and the D_3S^+ increased indicating that D_2S has a greater deuteron affinity and presumably a greater proton affinity than does water.

The number of collisions that the reactant ion (D_3O^+ or D_3S^+) undergoes in passing from the electron beam to the exit port is given in Table I. The number of collisions was calculated as follows: The number of collisions that an ion makes in traversing the distance l from the electron beam to the ion exit port while drifting through a gas at a concentration of M molecules/cubic centimeter is

$$Z = \sigma M l, \tag{2}$$

where σ, the collision cross section, is given by[18]

$$\sigma = (2\pi e/v)(\alpha/\mu)^{1/2}. \tag{3}$$

Here α is the polarizability; μ the reduced mass; e the unit electric charge; and v the velocity of the ion. We will take v as the drift velocity which is given by

$$v_d = KE, \tag{4}$$

where K is the mobility and E the field strength. Since the mobility is not known for any of the systems employed in these studies, it is necessary to estimate them by employing the equation[19a]

$$K_0 = 13.8/(\alpha\mu)^{1/2}, \tag{5}$$

where K_0 is the mobility at standard conditions. Combining Eqs. (2)–(5) and making appropriate correc-

TABLE I. Reaction rates.

Reaction	Pressure (torr)					No. Collisions	Rate const (cm^3/molecule·sec)	
	D_2O	D_2S	HCOOH	He	Ar		10^9k^-[a]	10^9k^+[b]
$D_3S^+ + HCOOH \rightarrow HCOOHD^+ + D_2S$	···	0.4	0.007[c]	···	···	66	1.88	1.80
$D_3S^+ + H_2O \rightarrow DH_2O^+ + D_2S$	0.025[d]	0.265	···	···	···	29	None detected	
$D_3O^+ + D_2S \rightarrow D_3S^+ + D_2O$	0.117	0.113[c]	···	···	···	···	1.2[e]	0.8[e]
$D_3O^+ + D_2S \rightarrow D_3S^+ + D_2O$	0.045	0.148[c]	···	0.317	···	3	1.8	1.88
$D_3O^+ + D_2S \rightarrow D_3S^+ + D_2O$	∼0.012	0.047[c]	···	···	0.48	44	1.1	···
$HD_2O^+ + D_2S \rightarrow HD_2S^+ + D_2O$	∼0.012	0.047[c]	···	···	0.48	44	1.2	···
$D_2O^+ + D_2S \rightarrow D_3S^+ + OD$	∼0.012	0.047[c]	···	···	0.48	44	1.0	···

[a] Determined from the decay of the reactant ion.

[b] Determined from the buildup of the product ion.

[c] Maximum pressure employed. Rate constants determined from measurements at pressures below 0.2 torr.

[d] H_2O rather than D_2O employed. Pressure is of H_2O.

[e] Free fall time of ion in the electric field employed.

tions for pressure and temperature gives

$$Z=115.5p^2\alpha, \tag{6}$$

where p is in torr and α in cubic angstroms. In computing the constant in Eq. (6), the source temperature was taken as 340°K and the field strength as 11.6 V/cm. The distance l in our source is 0.26 cm. The polarizabilities employed[19b] were He, 0.206; Ar, 1.64; H_2O, 1.45; H_2S, 3.61, all in cubic angstroms.

It will be observed in Table I that when water alone or water plus helium was employed the total number of deactivating collisions is very small. However, in the presence of argon the total number of deactivating collisions was about 44 and presumably this should be sufficient to remove any vibrational energy from D_3O^+. In all three cases, however, there was no question that the D_3O^+ transferred a deuteron to D_2S. It thus seems clear that the proton or deuteron affinity of water is less than that of H_2S or D_2S and, in our opinion, must then be less than about 170 kcal/mole.

TABLE II. Measurement of the equilibrium constant of Reaction (1).

Press (torr)		Intensity, % of total ionization		
D_2O	D_2S	D_3O^+	D_3S^+	K_{eq}
0.115	0.224	2.77	67.9	12.6
0.201	0.215	3.44	62.3	16.9
0.201	0.398	1.55	53.3	17.4
0.234	0.359	2.11	50.0	15.4
0.190	0.176	5.44	58.1	11.5
0.190	0.235	3.20	57.3	14.5
0.190	0.360	1.94	46.8	12.7
0.190	0.420	1.33	42.2	14.4
0.190	0.442	0.94	36.3	16.6
0.190	0.490	0.69	21.7	12.2
				$K_{Av}=14.4$

REACTION KINETICS

In several of the experiments it has been possible to calculate rate constants. These were computed from semilog plots of the decay of the intensity of the reactant ion (D_3O^+ or D_3S^+) and in some cases from the increase in intensity of the product ion with addition of the reactant molecule. In all but one instance it was necessary to estimate the time from mobility considerations, thus,

$$t=l/v_d=l/KE. \tag{7}$$

Since K had not been independently determined for any of the systems studied, it was estimated by the use of Eq. (5) with corrections for the conditions existing in our source as discussed above. It should be emphasized that these experiments were not primarily directed toward measurements of rate constants but the results given in Table I appear reasonable. In most instances the agreement among the various constants is that to be expected. All of the reactions appear to be quite fast.

THERMODYNAMICS

As was mentioned above, in the comparatively low pressure experiment in which D_2S was added in small increments to pure D_2O, it appeared that equilibrium in Reaction (1) was being approached. It seemed of interest to pursue this and, consequently, a number of mixtures of D_2O and D_2S in various proportions and at various pressures from 339 to 680 μ were introduced into the instrument and the intensities of D_3O^+ and D_3S^+ determined. In Table II the results are given along with equilibrium constants computed from the data. It appears that equilibrium is reached with an average value of K_{eq} of 14.4±1.9. Taking the source temperature to be 340±5°K, we compute $-\Delta G$ to be 1.8±0.1 kcal/mole. The entropy change in the reaction can reasonably be taken as zero. However, allowing a possible error of ±1 eu, the heat of reaction becomes 1.8±0.44 kcal/mole. Insofar as we have been able to determine, $\Delta H_f(D_2S)$ and $\Delta H_f(D_3S^+)$ are not known and, hence, an exact computation of $\Delta H_f(D_3O^+)$ from these data is impossible. However, it is reasonable to assume that $-\Delta H_r$ for Reaction (1) will be the same as that for the reaction,

$$D_3O^+ + D_2S \rightleftarrows D_3S^+ + D_2O, \qquad (8)$$

which we have measured. Haney and Franklin[11,17] have determined $\Delta H_f(H_3S^+)$ to be 191±3 kcal/mole. Combining this with our value for the heat of Reaction (8) and assuming the heat of Reaction (1) to be the same as that of (8), we compute $\Delta H_f(H_3O^+)$ to be 139.8±3.4 kcal/mole and the proton affinity of water to be 168.2±3.4 kcal/mole.

Beauchamp and Buttrill[20] have found that CH_2OH^+ does not protonate water. Rafaey and Chupka[21] have determined the appearance potential of CH_2OH^+ from ethanol by photoionization to be 11.25 eV from which $\Delta H_f(CH_2OH^+)$ is computed to be 170 kcal/mole. The fact that this ion does not protonate water sets a lower limit to $\Delta H_f(H_3O^+)$ of 140 kcal/mole, corresponding to a maximum proton affinity of water of 168 kcal/mole. Further, Long and Munson[15] have found the proton affinity of water to be 164±4 kcal/mole. Thus our value may be taken as in agreement with these. Although we have set the error limits of our value of $PA(H_2O)$ rather wide, it is evident that these are largely attributable to the uncertainty in $\Delta H_f(H_3S^+)$. If a more precise value for $\Delta H_f(H_3S^+)$ is determined, a corresponding improvement in $\Delta H_f(H_3O^+)$ and $PA(H_2O)$ will result.

The proton affinity of water was determined by DePas *et al.*[14] to be 182±7 kcal/mole. Thus the upper limit of our value and the lower limit of theirs differ by some 3 kcal/mole. Thus the two values may be taken as nearly in agreement or in serious disagreement, depending upon whether one focuses upon the error limits or upon the most probable values of the two determinations. In view of the fact that our value depends upon a rather precise determination of the equilibrium constant of Reaction (8), we are confident that our measurement gives a value for $PA(H_2O)$ that is correct within the accuracy of $PA(H_2S)$.

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* This work was sponsored by Project SQUID which is supported by the Office of Naval Research, Department of the Navy, under Contract N00014-67-A0226-0005, NR-098-038. Reproduction in full or in part is permitted for any use of the United States Government. One of us (R.A.M.) would like to express his appreciation to the Rice University Chemistry Department Undergraduate Research Participation Program for the Summer of 1971 for financial support.

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