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The formation and destruction of H_3O^-

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We report the first measurements of rate constants for formation and reaction of the hydrated-hydride ion H_3O^-. We studied the Kleingeld–Nibbering reaction [Int. J. Mass Spectrom. Ion Phys. **49**, 311 (1983)], namely, dehydrogenation of formaldehyde by hydroxide to form hydrated-hydride ion and carbon monoxide. The $OD^- + H_2CO$ reaction is about 35% efficient at 298 K, with OD^-/OH^- exchange occurring in about half the reactions. H_3O^- was observed to undergo thermal dissociation in a helium carrier gas at room temperature with a rate constant of 1.6×10^{-12} $cm^3\ s^{-1}$. We also studied a new reaction in which H_3O^- is formed: The association of OH^- with H_2 in a He carrier gas at low temperatures. The rate coefficient for this ternary reaction is 1×10^{-30} $cm^6\ s^{-1}$ at 88 K. Rate coefficients and product branching fractions were determined for H_3O^- reactions with 19 neutral species at low temperatures (88–194 K) in an H_2 carrier. The results of ion-beam studies, negative-ion photoelectron spectroscopy, and ion-molecule reaction data allow us to specify the hydride–water bond energy $D^0_{298}(H^- - H_2O) = 14.4 \pm 1.0$ kcal mol^{-1} (0.62 ± 0.04 eV). The heat of formation of H_3O^-, -37.5 ± 1.0 kcal mol^{-1}, and the proton affinity of H_3O^-, 386.0 ± 1.0 kcal mol^{-1}, are derived from these results. Dissociation of H_3O^- into OH^- and H_2 requires 4.5 ± 1.0 kcal mol^{-1} energy.

I. INTRODUCTION

In 1982, Paulson and Henchman[1] reported the first observations of the negative ion H_3O^-. Some 15 years earlier, the hydrated-hydride ion had been predicted by Richie and King[2] (on the basis of *ab initio* electronic structure calculations) to be a stable member of a small class of weakly bound hydrides. However, other calculations made just prior to the experimental observation of H_3O^- indicated that the ion was *not* stable, by as much as 70 kcal mol^{-1}.[3]

It happens that H_3O^- is the reactive intermediate in the first negative ion-molecule reaction ever reported,[4]

$$H^- + H_2O \rightleftharpoons [H_3O^-] \rightarrow OH^- + H_2, \tag{1}$$

where the square brackets denote a collision complex. Reaction (1) is known to be exothermic since H_2O is more acidic than H_2, by 9.9 ± 0.1 kcal mol^{-1} (0.429 ± 0.004 eV),[5,6] and proton transfer is thus energetically allowed. There have been several calculations of the structure and energy of the transition state for this reaction.[7–9] Hydrated hydride is also a reactive intermediate proposed[10,11] to explain isotopic exchange in reaction (2),

$$\begin{aligned} OH^- + D_2 &\rightleftharpoons [HO^- \cdots D_2] \rightleftharpoons [HOD \cdots D^-] \\ &\rightleftharpoons [DOH \cdots D^-] \rightleftharpoons [DO^- \cdots HD] \\ &\rightarrow OD^- + DH. \end{aligned} \tag{2}$$

The discovery of H_3O^- came about in a deliberate experiment to form it, but an unusual feature was observed. Henchman and Paulson[11] used a tandem mass spectrometer to examine the ionic products of the endothermic reaction

$$OH^- \cdot H_2O + H_2 \rightarrow H_3O^- + H_2O \tag{3}$$

as a function of relative kinetic energy. They found that the cross section for the production of H_3O^- exhibited resonant behavior, i.e., the cross section appeared to be significant only in an extremely narrow range of collision energies about a center-of-mass energy of 1.1 ± 0.2 eV (25 ± 5 kcal mol^{-1}). The resonant behavior of the cross section for this process remains unexplained. Deuteration of the projectiles and/or the target hydrogen provided unambiguous identification of the composition of the product ion in reaction (3). Differences in threshold energies for the formation of H_3O^-, OH^-, and H^- ion products implied that (a) the most stable form of H_3O^- is $H^- \cdot H_2O$; (b) the bond energy $D(H_2O - H^-)$ is 0.75 ± 0.15 eV (17 ± 4 kcal mol^{-1}); and (c) dissociation of H_3O^- to $OH^- + H_2$ requires 0.3 ± 0.15 eV (7 ± 4 kcal mol^{-1}) energy. One might think that in an $H^- \cdot H_2O$ complex, proton transfer analogous to that shown in reaction (1) for the separated reactants might take place, resulting in an anion with the structure $OH^- \cdot H_2$. Not surprisingly, water is a sufficiently better ligand[10,12] than H_2 so that the $H^- \cdot H_2O$ structure is lower in energy.

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In 1983, a second major advance in the understanding of H_3O^- came about when Kleingeld and Nibbering,[13] using a Fourier-transform ion cyclotron resonance mass spectrometer, observed an exothermic reaction in which H_3O^- is produced via the dehydrogenation of formaldehyde by OH^-. Deuteration and reaction studies indicated that the reaction proceeds in two steps, proton transfer followed by hydride transfer:

$$OH^- + H_2CO \rightleftharpoons [HOH\cdots HCO^-] \rightarrow HOH\cdot H^- + CO. \tag{4}$$

Proton transfer to yield separated $HOH+HCO^-$ is 3.0 kcal mol^{-1} endothermic.[5] Hydride transfer from HCO^- to H_2O is 7.8 kcal mol^{-1} exothermic,[5] so the overall process is 4.8 kcal mol^{-1} exothermic. Interestingly, no isotopic scrambling occurs between the hydride and the water constituents of the ion product that results from deuteration of either of the reactants. Kleingeld and Nibbering also demonstrated both hydride-transfer and hydroxide-transfer reactions of H_3O^-:

$$H_3O^- + H_2CO \begin{cases} \rightarrow H_3CO^- + H_2O & (5a) \\ \rightarrow OH^-\cdot H_2CO + H_2, & (5b) \end{cases}$$

$$H_3O^- + H_2O \rightarrow OH^-\cdot H_2O + H_2. \tag{6}$$

Reaction (6) is the inverse of reaction (3), in which H_3O^- was first observed. Kleingeld and Nibbering's study of reaction (4) using partially deuterated primary ions showed that the H^- can migrate to either end of the water molecule, that is, the ion product $H^-\cdot HDO$ was found to consist of 50% $H^-\cdot HOD$ and 50% $H^-\cdot DOH$.

De Lange and Nibbering[14] later showed that collision-induced dissociation of H_3O^- yields OH^- ionic product. Thus, the dissociation proceeds exclusively along the lowest energy pathway.

Grabowski, DePuy, and Bierbaum[10] used a selected ion flow tube to study isotopic transfer in the reaction OD^-+H_2CO. Although they could not observe DH_2O^- product directly under their operating conditions, they estimated H_2–DO^- and H_2O–H^- bond enthalpies to be 7 and 24 kcal mol^{-1}, respectively. Combining these numbers with the gas-phase acidities of H_2 and H_2O leads to a relative enthalpy of 7 kcal mol^{-1} between the two configurations. The estimates of bond enthalpies were based upon classical polarization potentials, and calibrated using known bond enthalpies.

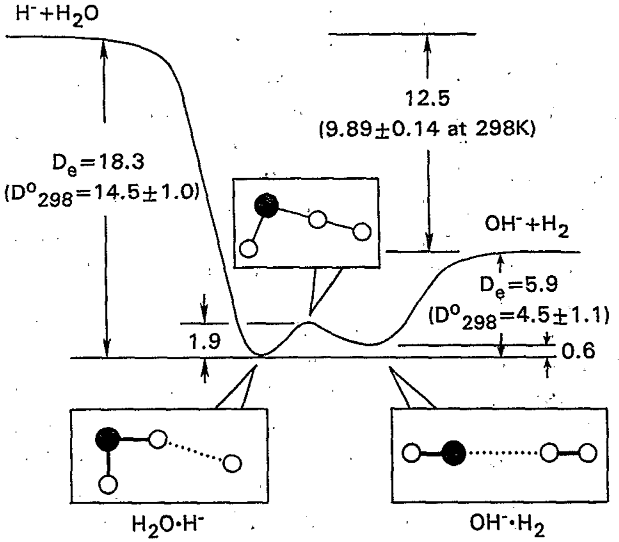


FIG. 1. Sketch of the potential surface for $H^-+H_2O\rightarrow OH^-+H_2$. Energies are theoretical values from Ref. 9 and are given in kcal mol^{-1}. Experimental energies are given in parentheses; the D^0_{298} values are from the present paper, and the asymptotic energy difference is from Ref. 5. Adapted from Dunning *et al.*, Ref. 9.

In 1985, Miller *et al.*[15] reported the results of a photoelectron spectroscopy (PES) study of H_3O^- and its deuterated and partially deuterated analogs, as produced by reaction (4) in a flowing afterglow ion source. The shape of the H_3O^- photodetachment spectrum suggests a bound-free transition from H_3O^- ground state to the repulsive part of the $H\cdot H_2O$ van der Waals surface. The vertical electron detachment energy was found to be 1.53 eV (35 kcal mol^{-1}). This figure is consistent with the hydrated-hydride structure for H_3O^-, but rules out the $OH^-\cdot H_2$ form for the ion, since the latter must have a higher electron detachment energy than does OH^-, 1.83 eV (42 kcal mol^{-1}).[16] Further evidence for the hydrated-hydride structure of H_3O^- is found in the photoelectron spectrum in that some of the transient neutral H_3O is seen to be excited by an amount equal to one quantum of stretching vibration in H_2O. A normal mode analysis of the photoelectron spectrum indicated an O–H equilibrium bond length change of 0.03 Å in going from the negative ion to the neutral.[15] The photoelectron result places an upper bound of 0.78 eV (18 kcal mol^{-1}) on $D^0_{298}(H^-–H_2O)$, being the difference between the vertical detachment energy and EA(H). The adiabatic electron detachment energy for H_3O^- cannot be determined unambiguously from the photoelectron spectrum. The photoelectron spectrum implies that the threshold for photodetachment from H_3O^- is 1.40 eV (32 kcal mol^{-1}). If there is little vibrationally excited H_3O^- in the PES experiment, then the adiabatic electron detachment energy for H_3O^- is ≤1.40 eV, and a more restrictive upper bound results, $D^0_{298}(H^-–H_2O)\leq 0.65$ eV (15 kcal mol^{-1}). Significant vibrational excitation is not expected in room temperature H_3O^-; the lowest vibrational frequency would only be populated at the 7% level.[7]

A number of *ab initio* electronic structure calculations have been carried out on weakly bound hydrides, including H_3O^-, by Squires,[12] by Cremer and Kraka,[8] by Chalasinski, Kendall, and Simons,[7] by Ortiz,[17] and by Xantheas and Dunning.[9] All of these theoretical results for the structure and energetics of H_3O^- are in conformity with the experimental research quoted above. A sketch of the potential energy surface for reaction (1) is given in Fig. 1, which also shows structures and energies of the stable and transition states for the H_3O^- complex, according to the calculations of Xantheas and Dunning.[9] The equilibrium bending angle $\measuredangle$HOH is calculated to be a few degrees smaller than in isolated H_2O, probably due to the electrostatic attraction between H^- and the most distant H atom in the molecule.[8] One of the OH bond lengths is hardly changed (shortened by

0.002 Å) from that of isolated H_2O, while the OH bond nearest the companion hydride is lengthened by 0.073 Å (7.5%).[7] The water deformation contributes about -3 kcal mol^{-1} to the H_3O^- binding energy.[7] Chalasinski, Kendall, and Simons[7] and Ortiz[17] have calculated the vibrational frequencies of H_3O^-. Three frequencies (1657, 2473, and 3824 cm^{-1}) are associated with vibrations within the water molecule, and three frequencies (532, 647, and 1005 cm^{-1}) are associated primarily with relative motions of the hydride–water units.

In recent years, theoretical work on "double Rydberg" systems (those with a closed-shell core and two diffuse, Rydberg-like valence electrons) has appeared.[18] This work focuses upon a pyramidal H_3O^- structure which is found to be locally stable. There is no evidence for this structure in the beam experiments,[1,11] in the photoelectron spectrum,[15] or in the present reaction data on H_3O^-. However, a double-Rydberg tetrahedral form of NH_4^- has been predicted[18] and observed[19] in the photoelectron spectra in addition to the solvated H^- structure, $H^- \cdot NH_3$.

Thus, it may be said that the *structure* and *energetics* of H_3O^- are relatively well understood. However, the kinetics of formation reaction (4) and chemical reactivity and kinetics of this intriguing ion are virtually unexplored. Below, we discuss these kinetics and reactivity, surmounting the difficulties arising from the facts that (a) H_3O^- is found to undergo thermal decomposition in buffer gases, and (b) there are competing reactions which limit the efficiency of reaction (4) in producing H_3O^- in a high pressure ion source. In the present work we have studied 22 ion-molecule reactions associated with the formation and destruction of H_3O^- and in the process have utilized a new—albeit very simple—synthesis of the ion via the ternary reaction

$$OH^- + 2H_2 \rightarrow H_3O^- + H_2. \tag{7}$$

As a final note, it is interesting to compare reaction (4) with reaction (8):[15]

$$HCO^- + H_2O \rightarrow OH^- + H_2CO, \tag{8}$$

in which proton transfer takes place instead of hydride transfer, even though the latter is more exothermic. HCO^- is a good hydride donor and will produce H_3O^- in the reaction complex of (4) but fails to create H_3O^- in the isolated reaction (8). The difference is that the collision complex of (4) has had 3 kcal mol^{-1} of energy removed from it by an initial proton transfer (from H_2CO to OH^-) before the hydride transfer takes place. It is possible that too great an exothermicity is unfavorable for the production of H_3O^-. The ion NH_4^-, which has a structure ($H_2NH \cdot H^-$) analogous to that of H_3O^-($HOH \cdot H^-$), can be made from the nearly thermoneutral reaction (9):[20]

$$HCO^- + NH_3 \rightarrow NH_4^- + CO. \tag{9}$$

Another weakly bound hydride, a long-lived SiH_5^- ion, has been produced in reaction of alkylsilyl hydride ions with SiH_4.[21]

II. EXPERIMENT

The measurements reported here were carried out using a variable-temperature selected ion flow tube (SIFT) which has been described in detail previously.[22] This type of experiment and associated techniques are well established and have been reviewed by Smith and Adams.[23] Briefly, mass-selected ions created in an electron-impact ion source were injected into a fast flow (3–9 std. l min^{-1}) of helium or hydrogen carrier gas at pressures of 0.13–0.60 torr, and the exponential attenuation of the primary ion signal was measured as a function of the concentration of neutral reactant over known reaction distances. The ion velocity in the reaction zone was measured directly in order to express the attenuation as a reaction rate coefficient. Neutral reaction products listed in the text and tables were not detected but were inferred from the mass balance and energetics of the reactions. A reactive electron detachment channel was identified by noting a drop in total ion current measured at the end of the flow tube both on the ion sampling aperture plate and in the sum of the mass-analyzed ion signals detected with the particle multiplier. Since electrons diffuse rapidly to the walls of the flow tube the current to the aperture plate is essentially entirely due to negative ions.

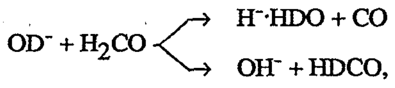
OH^- (or OD^-) was made from a 4:1 mixture of N_2O and NH_3 (or ND_3) in the ion source. We were unable to find a gas combination that would allow us to create usable amounts of H_3O^- in the high pressure ion source. Too high a pressure of H_2CO led to reaction of H_3O^- with H_2CO inside the ion source, and too low a pressure left too few ions. In addition, we found that H_3O^- thermally decomposes at room temperature.[24] For the study of reactions of H_3O^-, the ion was formed from OH^- in a cold (88–194 K) H_2 carrier gas in the flow tube, as described below. All of the reactant gases were commercially available and handled without further purification. Formaldehyde vapor was created by heating paraformaldehyde to 100 °C. The gas feedlines were not heated, however, so some polymerization of formaldehyde may have occurred, and the measured reactant concentrations and reaction rate coefficients may not be as accurate as usual.[22] The problem of measuring the formaldehyde flow rate is discussed more fully in Ref. 24. A helium carrier was used for reactions involving formaldehyde. All other gases were used in cold (88–194 K) H_2 carrier. Reaction rates for OH^- carried out both in He and H_2 carriers agreed within 10%. The accuracy of the rate coefficients reported here is estimated to be ±35%. Branching fractions for multiple products are accurate to within ten percentage points.

III. RESULTS AND DISCUSSION

A. Formation of H_3O^-

1. Dehydrogenation of H_2CO by OH^-

Reaction rate coefficients and branching fractions for



$$OD^- + H_2CO \rightarrow H^- \cdot HDO + CO \tag{10a}$$
$$OD^- + H_2CO \rightarrow OH^- + HDCO, \tag{10b}$$

were measured in a helium buffer at 298 K. The results for (10) and for isotopic variations are given in Table I. In a

TABLE I. Rate coefficients for reactions involved in the formation of H_3O^- (and isotopic variants), and the thermal decomposition of H_3O^- and D_3O^-. The rate coefficients are accurate within 35% except for the final two values (thermal decomposition), which are correct within a factor of 2.

Reaction			Rate coefficient ($cm^3\ s^{-1}$)	*T* (K)
OH^-+H_2CO	→	H_3O^-+CO	7.6×10^{-10}	300
OD^-+D_2CO	→	D_3O^-+CO	5.7×10^{-10}	300
OH^-+D_2CO	→ →	OD^-+HDCO (~50%) HD_2O^-+CO (~50%)	1.3×10^{-9}	300
OD^-+H_2CO	→ →	OH^-+HDCO (~50%) H_2DO^-+CO (~50%)	1.3×10^{-9}	300
OH^-+H_2+He	→	H_3O^-+He	3.3×10^{-14} [a]	88
H_3O^-+He	→	OH^-+H_2+He	1.6×10^{-12}	300
D_3O^-+He	→	OD^-+D_2+He	1.1×10^{-12}	300

[a] Equivalent binary rate coefficient, measured at a helium number density of $3.3\times10^{16}\ cm^{-3}$. The ternary rate coefficient is $1\times10^{-30}\ cm^6\ s^{-1}$.

flowing-afterglow study, Bohme, Mackay, and Tanner[25] reported that OH^- associates with H_2CO in a helium afterglow and measured a ternary rate coefficient for the process. Our work and that of Kleingeld and Nibbering[13] indicate that the product ion Bohme *et al.* observed, $CH_3O_2^-$ (along with CH_3O^-), is a secondary ion formed in collisions of H_3O^- with H_2CO, reaction (5), but we cannot rule out a small fraction of $CH_3O_2^-$ being due to association. Kleingeld and Nibbering[13] observed $CH_3O_2^-$ with gas pressures too low for collisional association reactions to be observed. A small signal (1%–2% of the total product ion intensity) of HCO_2^- (or DCO_2^-) is observed in our work. We cannot pinpoint the source of the HCO_2^-; the ion was not observed by Kleingeld and Nibbering.[13] Bohme, Mackay, and Tanner[25] measured a reaction rate coefficient of $3.1\times10^{-10}\ cm^3\ s^{-1}$ (which we verified) for $O^-+H_2CO\rightarrow HCO_2^-+H$, but we do not have significant O^- in our injected ion current. The HCO_2^- could arise from OH^- reaction with an impurity [such as $(H_2CO)_2$ or HCOOH] in the H_2CO.

A mass spectrum for the reaction OH^-+D_2CO is given in Fig. 2. Grabowski, DePuy, and Bierbaum[10] reported that OD^- readily undergoes isotopic exchange with H_2CO, but no rate coefficient was measured, and $H^-\cdot HDO$ was not observed. Indeed, our mass spectra (Fig. 2, for example) implied that isotopic exchange (10b) was by far the major reaction channel—with a branching fraction approaching 95%. This first impression turns out to be incorrect; we have found that the H_3O^- product (and its isotopic analogs) thermally dissociates in the flow tube, generating the hydroxide ion. Determining the true branching fraction for OH^-/OD^- exchange involves simultaneous measurement of the collisional dissociation rate for H_3O^-.

Reaction attenuation plots for OH^-+H_2CO and OD^-+D_2CO, where no isotopic exchange occurs, show curvature due to regeneration of the primary ion (OH^- or OD^-) in the reaction zone, with eventual decline due to secondary reactions. Identical curvature for the hydroxide–formaldehyde reactions was earlier noted by Paulson, Viggiano, and Dale.[26] In the present work on this reaction, a scavenger technique was used to remove the H_3O^- (and analogs) from the reaction zone before it had a chance to dissociate thermally, thereby eliminating the curvature problem. CO was chosen as the scavenger because it does not react with OH^- at room temperature (a fact we verified) but was

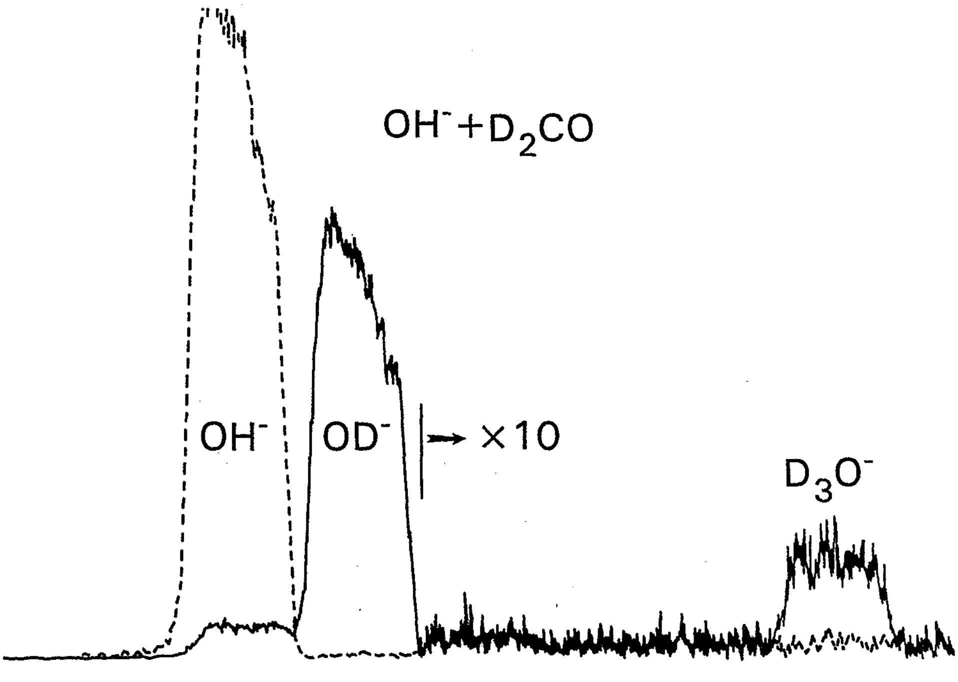


FIG. 2. Low-resolution mass spectra for the reaction OH^-+D_2CO in 0.4 torr He buffer at 300 K. The dashed line shows the injected OH^- with no reactant gas present. The full line shows the mass spectrum after reaction with $1.1\times10^{12}\ cm^{-3}$ D_2CO with 2.9 ms reaction time. At this time, some of the total ion current has been converted into higher masses by the secondary reaction (5).

TABLE II. Rate coefficients, branching fractions, efficiencies, and enthalpies of reactions of H_3O^- with various molecules, studied in ~0.14 torr H_2 buffer at the temperature *T* indicated.

Reaction		$-\Delta H^a$ (kcal mol^{-1})	Rate Coefficient ($cm^3\ s^{-1}$)	eff^b	T (K)
$H_3O^- + Xe$ →	no reaction	-	$<1 \times 10^{-12}$	0	123
$H_3O^- + N_2$ →	no reaction	-	$<1 \times 10^{-12}$	0	93
$H_3O^- + SF_6$ →	no reaction	-	$<1 \times 10^{-12}$	0	141
$H_3O^- + CH_4$ →	no reaction	-	$<1 \times 10^{-12}$	0	93
$H_3O^- + CF_4$ →	no reaction	-	$<1 \times ^{-12}$	0	93
$H_3O^- + C_2H_6$ →	no reaction	-	$<5 \times 10^{-12}$	0	123
$H_3O^- + C_2H_4$ →	no reaction	-	$<1 \times 10^{-12}$	0	194
$H_3O^- + O_2$ →	$HO_2 + H_2O + e^-$	17	4.5×10^{-11}	0.05	93
$H_3O^- + CO$ →	$HO^- \cdot CO^c + H_2$	18	6.2×10^{-10}	0.60	93
$H_3O^- + HCl$	→ $Cl^- + H_2 + H_2O$ (75%)	52	2.4×10^{-9}	0.94	130
	→ $OH^- \cdot HCl + H_2$ (25%)	18			
$H_3O^- + NO$	→ $HNO + H_2O + e^-$ (80%)	18	6.7×10^{-10d}	0.66	93
	→ $HNO^- + H_2O$ (20%)	25			
$H_3O^- + CO_2$ →	$HCO_2^- + H_2O$	37	8.6×10^{-10}	0.78	141
$H_3O^- + COS$	→ $SH^- + H_2O + CO$ (50%)	32	1.5×10^{-9}	0.74	133
	→ $OH^- \cdot COS + H_2$ (25%)	9			
	→ $HCOS^- + H_2O$ (20%)	53			
	→ $SH^- \cdot H_2O + CO$ (5%)	55			
$H_3O^- + N_2O$	→ $HN_2O^- + H_2O$ (40%)	>8	1.5×10^{-10}	0.13	141
	→ $OH^- + H_2O + N_2$ (35%)	72			
	→ $OH^- \cdot N_2O + H_2$ (25%)	18			
$H_3O^- + BF_3$	→ $HBF_3^- + H_2O$ (>95%)	-	8×10^{-10}	0.72	130
	→ $BF_2O^- + HF + H_2$ (<5%)	7			
$H_3O^- + C_2H_2$	→ $HC_2^- + H_2O + H_2$ (60%)	53	1.5×10^{-9}	1.10	139
	→ $OH^- \cdot C_2H_2 + H_2$ (40%)	18			
$H_3O^- + NH_3$ →	$OH^- \cdot NH_3 + H_2$	18	1.1×10^{-9}	0.32	171
$H_3O^- + CF_3Cl$	→ $CF_3^- + HCl + H_2O$ (80%)	27	1.6×10^{-9}	0.97	141
	→ $OH^- \cdot CF_3Cl + H_2$ (15%)	18			
	→ $CF_3^- \cdot H_2O + HCl$ (5%)	50			
$H_3O^- + CH_3CCH$	→ $CH_3CC^- + H_2O + H_2$ (85%)	4	1.8×10^{-9}	0.83	171
	→ $OH^- \cdot CH_3CCH + H_2$ (15%)	18			

[a] Reaction enthalpies were calculated from heats of formation taken from the present work for H_3O^-, from Ref. 32 for BF_2O^-, and from Ref. 5 for other species. The hydride affinity of COS was taken from Ref. 33. All ionic associations such as $OH^- \cdot CO$ were assumed to have an electrostatic bond energy of 23 kcal mol^{-1} (1 eV) for the purpose of estimating ΔH. The actual structure and formation of these ions are not known.

[b] Reaction efficiencies ("eff") are the ratio of the experimental rate coefficient to a collisional rate coefficient, the latter calculated by the classical trajectory method of Ref. 28, using polarizabilities and dipole moments taken from Refs. 15 and 29; an efficiency >1 implies inaccuracy in one or both of the experimental and calculated rate coefficients.

[c] The $OH^- \cdot CO$ product of this reaction was shown to be different from HCO_2^-; see Sec. III B 2.

[d] An NO_2^- product accounted for as much as 18% of the reactions but is probably due to HNO_3 impurity in the NO gas, as the formation of NO_2^- from H_3O^- is endothermic by 26 kcal mol^{-1}. Therefore, the reaction rate coefficient given above may be as low as 5.5×10^{-10} $cm^3\ s^{-1}$.

found in this work to react with H_3O^- to form $CO \cdot OH^-$ with a rate coefficient (measured at 93 K) of 6.2×10^{-10} $cm^3\ s^{-1}$. The problem of determining branching fractions in the face of a product ion which undergoes thermal dissociation was first discussed quantitatively by Hierl *et al.*,[27] who concluded that the dissociation problem can occur (at room temperature) for ions with bond energies of less than ~15 kcal mol^{-1} (0.65 eV). Details of the curvature problem caused by the thermal dissociation of H_3O^- are given in a separate publication.[24] By modeling the reaction kinetics, we determined rate constants for the thermal decomposition of H_3O^- and D_3O^- in helium at 300 K: 1.6×10^{-12} $cm^3\ s^{-1}$ and 1.1×10^{-12} $cm^3\ s^{-1}$, respectively. These thermal decomposition rate constants are accurate only to within a factor of 2; see Ref. 24.

We measured a rate coefficient of 1.3×10^{-9} $cm^3\ s^{-1}$ at 298 K for reaction (10). A collisional rate constant of 3.6×10^{-9} $cm^3\ s^{-1}$ may be calculated[28] from the polarizability (2.45×10^{-24} cm^3)[15] and dipole moment (2.332 D)[29] of H_2CO. Thus, the reaction is about 35% efficient. About half of the reactions result in OD^-/OH^- exchange. These results and others are given in Table I.

2. Association of OH^- with H_2

A new synthetic route to H_3O^- was found; the ternary association reaction

$$OH^- + H_2 + He \rightarrow H_3O^- + He. \qquad (11)$$

At 88 K and a helium pressure of 0.3 torr, we measured a rate coefficient of $(1 \pm 0.4) \times 10^{-30}$ $cm^6\ s^{-1}$ for reaction (11). It was not possible to vary the H_2 pressure at 88 K enough to make meaningful tests of the pressure dependence of the reaction. We observed this reaction over the temperature range 88–300 K, though the product H_3O^- was barely perceptible at 300 K. At higher temperatures, the reactant H_2 flow (10 std. $cm^3\ min^{-1}$) required for measuring the reaction rate coefficient caused pickup of enough residual H_2CO from the walls of the inlet lines that reaction (4) dominated the attenuation of the OH^- primary ion signal, preventing a quantitative study of reaction (11) as a function of temperature.

Because the rate coefficient for reaction (11) is so small, we used a pure H_2 carrier gas to generate H_3O^- for the ion-molecule reaction studies:

$$OH^- + 2H_2 \rightarrow H_3O^- + H_2. \qquad (7')$$

Experience[30] normally leads one to expect that the association rate coefficient with a *molecular* third body will be greater than with He (often by a factor of 3). However, Gerlich and Horning[31] have found that H^+ association with H_2 is a factor of 2 *less* efficient in an H_2 buffer relative to a He buffer at 80 K. Thus, at 88 K and 0.13 torr H_2 buffer, the H_3O^- formation rate is between 90–530 s^{-1}, giving a time constant for H_3O^- formation between 2–12 ms, which corresponds to a distance of 17–107 cm in the flow tube at the flow velocity used at 88 K. We found that after a reaction distance of 115 cm (the entire length of the flow tube) the ratio of H_3O^- to OH^- signals was 10:1 at 88 K, consistent with reactions (7,11) having similar rate coefficients (assuming that negligible reverse reaction or thermal dissociation occurs). At 140 K the H_3O^-:OH^- ratio was 7:1; at 170 K it was about 1:1, and at 190 K it was between 0.25:1 and 0.07:1.

B. Reactions of H_3O^-

Measured rate coefficients for H_3O^- reactions are listed in Table II, along with branching fractions, exothermicities [using heats of formation from Ref. 5 except for BF_2O^- (Ref. 32) and H_3O^- (this work), and using the hydride affinity of COS (Ref. 33)], and reaction efficiencies (measured rate coefficient divided by a calculated collisional rate coefficient[28]). We will discuss these results in terms of the types of reactions that take place.

The optimum condition for H_3O^- production is clearly the lowest temperature possible (88 K on this instrument). Therefore, we studied H_3O^- reactions with neutral molecules at as low a temperature as the vapor pressures of the various reactant gases allowed, and did not attempt any measurements above 194 K due to the poor H_3O^-:OH^- ratio, which ruled out the use of many interesting reactant gases. We monitored both the OH^- and H_3O^- attenuations with neutral reactants. The presence of OH^- complicated the determination of branching fractions for products of some of the H_3O^- reactions. In most cases, however, unraveling the branching fractions was straightforward because OH^- is less reactive than H_3O^-, and we could study the OH^- reactions independently in a helium carrier at any desired temperature to determine the products and branching fractions (if any) for the OH^- reactions. The complications from OH^- are more difficult to unravel at higher temperatures (e.g., with C_2H_4 at 194 K) where H_3O^-:OH^-~0.1:1. In the text below and in the tables, approximate branching fractions such as ">95%" result from uncertainty related to the OH^- competition.

H_3O^- ions produced by reaction (7) begin existence as $OH^- \cdot H_2$ clusters. However, proton transfer in the complex is energetically favorable (by 9.9 kcal mol^{-1} for the separated reactants), and we presume that it indeed takes place, either spontaneously or assisted by the third body stabilization, possibly by tunneling. Calculations of the energy difference between the $H^- \cdot H_2O$ and $OH^- \cdot H_2$ structures are not accurate enough to warrant a calculation of an equilibrium constant; values range from 0.6 kcal mol^{-1} to 4 kcal mol^{-1}.[7,9] The maximum value of the equilibrium constant is 0.2 (assuming 0.6 kcal mol^{-1} at 194 K, and that the entropy change makes little contribution). The experimental data, including the present work, cannot be used to infer the energy difference between the two structures.

1. Hydride transfer reactions

H_3O^- will lose its hydride ion at a cost of 14.4 kcal mol^{-1}.[5] Hydride (H^-) transfer may well be the first step taken within the reaction complex with most of the reactant neutrals listed in Table II. A good example for discussion is found in the various reaction channels of $H_3O^- + COS$:

$$H_3O^- + COS \rightarrow [H_2O \cdot H^- \cdot COS] \begin{cases} \rightarrow H_2O + HCOS^- \ (20\%) & \text{(12a)} \\ \rightarrow H_2O + CO + SH^- \ (50\%) & \text{(12b)} \\ \rightarrow H_2O \cdot SH^- + CO \ (5\%) & \text{(12c)} \\ \rightarrow HO^- \cdot COS + H_2 \ (25\%). & \text{(12d)} \end{cases}$$

The multitude of products points to formation of an intermediate complex. Reaction channel (12a) is hydride transfer from H_2O to COS. Channels (12b) and (12c) also appear to begin with hydride transfer within the complex, but different bonds are broken as energy is released. We will comment on channels analogous to (12b) and (12c) below, for all reactions in Table II. Reaction channel (12d) corresponds to OH^- transfer, to be discussed in the subsection below. Overall, about 75% of the channels for the COS reactions may be identified as beginning with hydride transfer, and 25% with OH^- transfer. A similar analysis of all reactions in Table II for which there is more than one product channel leads to much the same fractions for initial H^- and OH^- transfer within the collision complex. There are several cases where both H_2O and H_2 are released, which could result from *either* hydride or hydroxide transfer in the reaction complex.

The hydride affinity of BF_3 is apparently not known.[5,33] Observation of hydride transfer (Table II) in this case shows that the hydride affinity of BF_3 must be greater than that of H_2O (14.4±1.0 kcal mol^{-1}; see Sec. III C below).

2. Hydroxide transfer reactions

Only 4.5 kcal/mol of energy is required for H_3O^- to give up hydroxide ion (OH^-), less energy than is required to release either a hydride ion or an electron. We observed OH^- transfer in reactions with CO (100%), NH_3 (100%), C_2H_2 (40%), COS (25%), HCl (25%), N_2O (25%), CF_3Cl (15%), and CH_3CCH (15%), and the overall rate coefficient in each case was essentially collisional. We draw special attention to the ionic product of the reaction $H_3O^- + CO$; this product is written as $OH^- \cdot CO$ rather than the more stable HCO_2^- in Table II because the product ion undergoes a secondary reaction with H_2CO to form $CH_3O_2^-$, whereas HCO_2^- produced in our ion source from formic acid vapor does not react with H_2CO.

3. Electron detachment

H_3O^- requires about 32 kcal mol^{-1} of energy to release an electron. Reactive electron detachment[34] occurs in reac-

TABLE III. Gas-phase acidity data for reference acids, and products of reaction with H_3O^-.

Reactant	$\Delta H^0_{acid,298}$ (kcal mol^{-1})[a]	$\Delta G^0_{acid,298}$ (kcal mol^{-1})[a]	Reaction with H_3O^-	T (K)
CH_3CH_3 ethane	420.1±2.0	412.2±2.3	none	123
CH_4 methane	416.9±1.7	408.8±1.7	none	93
CH_2CH_2 ethylene	409.4±0.6	401.0±0.5	$OH^-\cdot CH_2CH_2$	194
NH_3 ammonia	404.1±0.4	396.5±0.4	$OH^-\cdot NH_3$	171
H_2CO formaldehyde	393.5±0.8	385.6±1.1	$OH^-\cdot H_2CO$, CH_3O^-	298
H_2O water	390.5±0.4	383.9±0.3	$OH^-\cdot H_2O$[b]	298
CH_3CCH methylacetylene	381.1±2.4	373.3±2.0	proton transfer (85%)	171
C_2H_2 acetylene	377.8±0.6	369.8±0.6	proton transfer (60%)	139
HCl hydrochloric acid	333.4±0.2	328.0±0.3	proton transfer (75%)	130

[a] Reference 5, except for ethylene, acetylene, water, and ammonia (Ref. 6).
[b] Reference 9.

tions of H_3O^- with the radicals O_2 (100%) and NO (80%). The first is a slow reaction while the latter is rapid (Table II).

4. Electron transfer

Electron transfer reactions are endothermic between H_3O^- and the reactant neutrals usable at the low temperatures of this experiment. Available neutrals with electron affinities greater than that of $H\cdot H_2O$ all have vapor pressures too low (for $T<194$ K) to provide the flow rates needed in the SIFT experiment.

5. Proton transfer

Proton transfer from a neutral reactant AH to H_3O^- should occur when the proton affinity of H_3O^- is greater than the proton affinity of A^-. An alternative view is that proton transfer will occur when AH is more acidic than is the van der Waals complex $H_2\cdot H_2O$. We observed rapid proton transfer in reactions of H_3O^- with HCl (75%), C_2H_2 (60%), and CH_3CCH (85%). Implications regarding D^0_{298} (H^-–H_2O) and $\Delta_f H^0_{298}(H_3O^-)$ based on these reactions, coupled with information on reactions in which no proton transfer occurred, will be discussed in Sec. III C.

6. Other reactive channels

Reaction of H_3O^- with N_2O produces $OH^-+H_2O+N_2$ with a branching fraction of 35%. Reaction with COS gave the greatest number (4) of ionic products of all reagents studied, including HS^- (50%) and $HS^-\cdot H_2O$ (5%).

In at least two cases (CF_3Cl and COS), it is interesting that both bare and hydrated product ions were observed, for example,

$$H_3O^- + CF_3Cl \begin{array}{l} \nearrow CF_3^- + H_2O + HCl\ (80\%) \quad (13a) \\ \searrow CF_3^-\cdot H_2O + HCl\ (5\%). \quad (13b) \end{array}$$

There are three additional cases (HCl, C_2H_2, and CH_3CCH) where we labeled a product channel straightforwardly as "hydroxide transfer." However, if proton transfer takes place within the complex (converting $OH^-\cdot HCl$ into $Cl^-\cdot H_2O$, for example), then there is a total of five cases where H_2O is found both free and bound in the products.

The presence of both the bare and hydrated product ions forces us to face the question of whether or not the branching fractions might be distorted by thermal dissociation of the solvated product ions. The bond energy D^0_{298} (Cl^-–H_2O) is 13.1 kcal mol^{-1},[32] which is close to that of $H^-\cdot H_2O$—which thermally dissociates at room temperature. However, reaction (12) was studied at 141 K, which reduces the Boltzmann factor for dissociation by many orders of magnitude. The product branching fractions were the same for two different reaction distances, 35 and 50 cm, providing additional evidence for minimal thermal dissociation of the product ions. It thus seems that the branching ratios measured at low temperatures are valid. However, it cannot be ruled out that the hydrated species result from partial stabilization of the intermediate complex.

7. Nonreactive cases

No reaction of H_3O^- was observed with the reactants N_2, Xe, SF_6, CF_4, CH_4, C_2H_4, and C_2H_6. Upper limits on the reaction rate coefficients are given in Table II.

C. Hydride–water bond energy

Table III presents the results of bracketing the room temperature proton affinity (PA_{298}) of H_3O^-. This matter is significant because the proton affinity can be used to determine $D^0_{298}(H^-–H_2O)$ from the thermochemical relation

$$D^0_{298}(H^-–H_2O)=\Delta H^0_{acid,298}(H_2)-PA_{298}(H_3O^-)+D^0_{298}(H_2–H_2O), \quad (14)$$

where $\Delta H^0_{acid,298}(H_2)$ is the gas-phase acidity of H_2 [equivalently $PA_{298}(H^-)$] and is accurately known (400.399±0.003 kcal mol^{-1}),[35] and the van der Waals bond energy

TABLE IV. Experimental limits on $D^0_{298}(H^-–H_2O)$, in kcal mol^{-1}.

	Lower limit	Upper limit
Beam experiment[a]	13.8	20.8
Photoelectron spectroscopy[b]	···	15.0
Thermal reactions[c]	9.5	21.7
Recommended bond energy[d]	14.4±1.0	

[a] Reference 8.
[b] Reference 12.
[c] This work and Ref. 9.
[d] The stated uncertainty is greater than the limits require, for prudence sake.

$D^0_{298}(H_2–H_2O)$ will be taken as zero since the 0 K value, 0.41 ± 0.04 kcal mol^{-1},[36] is less than kT at room temperature. The results of Table III bracket $PA_{298}(H_3O^-)$ between 378.7 and 390.9 kcal mol^{-1}, where these limits take into account the uncertainties on the ΔH^0_{298} values in Table III. Equation (14) then places $D^0_{298}(H^-–H_2O)$ between 9.5 and 21.7 kcal mol^{-1}. Table IV summarizes this and other experimental limits on $D^0_{298}(H^-–H_2O)$. These data are most consistent with a value for $D^0_{298}(H^-–H_2O)$ of 14.4 ± 1.0 kcal mol^{-1} (0.62 ± 0.04 eV). We emphasize that this bond energy is based on examination of previous experimental work,[11,15] and the present reaction data merely confirm the result. *Ab initio* calculations have yielded 16.6 (Ref. 7), 16 (Ref. 8), 17.4 (Ref. 9), and 19.3 (Ref. 17) kcal mol^{-1} for the equilibrium bond energy. Chalasinski Kendall, and Simons[7] have shown that temperature and zero point energy corrections amount to -0.97 kcal mol^{-1}, so the present value for $D^0_{298}(H^-–H_2O)$ is in reasonable agreement with the theoretical results. One other theoretical bond strength, 15.6 kcal mol^{-1}, was said to be appropriate for 298 K.[12] Comparison may be made with the $F^-\cdot H_2O$ bond strength, 23.2 kcal mol^{-1}, $Cl^-\cdot H_2O$ bond strength, 13.1 kcal mol^{-1}, and the $OH^-\cdot H_2O$ bond strength, 22.5 kcal mol^{-1}.[32,37]

Table IV shows that the beam and PES experiments place a more restrictive limit on $PA(H_3O^-)$ than do the ion-molecule reactions summarized in Table III. Therefore, $PA(H_3O^-)$ is best evaluated from Eq. (14) using $D^0_{298}(H^-–H_2O)$ from Table IV. We calculate $PA(H_3O^-)=386.0\pm1.0$ kcal mol^{-1}.

The heat of formation of H_3O^- may be derived from

$$\Delta_f H^0_{298}(H_3O^-)=\Delta_f H^0_{298}(H)-EA(H) +\Delta_f H^0_{298}(H_2O)-D^0_{298}(H^-–H_2O), \quad (15)$$

using $\Delta_f H$ values from Ref. 5 and EA(H) from Ref. 16. The result is $\Delta_f H^0_{298}(H_3O^-)=-37.5\pm1.0$ kcal mol^{-1}.

IV. CONCLUSIONS

We have carried out the first measurements of reaction rate coefficients for the reactions of H_3O^- with various neutral molecules. We studied the Kleingeld–Nibbering reaction[13] for the dehydrogenation of formaldehyde by hydroxide, forming hydrated hydride, with and without isotopic labeling. We find that the labeled reaction is 35% efficient, with OH^-/OD^- exchange occurring in about half of the reactive collisions. H_3O^- undergoes thermal dissociation in a helium buffer at room temperature with a rate constant of 1.6×10^{-12} cm^3 s^{-1}.

We also studied a new reaction in which H_3O^- is formed: namely, the association of OH^- with H_2, and measured the ternary reaction rate coefficient for the process in a He buffer gas at 88 K. Rate coefficients and product branching fractions were then determined in an H_2 buffer for H_3O^- interacting with 19 neutral species at low temperatures (88–194 K) in an H_2 buffer. A mechanism involving hydride transfer within the collision complex, followed by ejection of one or more neutral molecules or an electron, can explain a majority of the results; hydroxide transfer is also found. Combining the results of ion beam, photoelectron spectroscopy, and ion-molecule reaction experiments allows us to specify the hydride–water bond energy $D^0_{298}(H^-–H_2O)=14.4\pm1.0$ kcal mol^{-1} (0.62 ± 0.04 eV), the proton affinity $PA(H_3O^-)=386.0\pm1.0$ kcal mol^{-1}, and the heat of formation of H_3O^-, $\Delta_f H^0_{298}=-37.5\pm1.0$ kcal mol^{-1}. Dissociation of H_3O^- to OH^- and H_2 requires 4.5 ± 1.0 kcal mol^{-1} energy.

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