# Gas-phase proton-transfer reactions of the hydronium ion at 298 K

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Rate constants measured with the flowing afterglow technique at 298 ± 2 K are reported for the proton-transfer reactions of $H_3O^+$ with $CH_2O$, $CH_3CHO$, $(CH_3)_2CO$, HCOOH, $CH_3COOH$, $HCOOCH_3$, $CH_3OH$, $C_2H_5OH$, $(CH_3)_2O$, and $CH_2CO$. Dissociative proton-transfer was observed only with $CH_3COOH$. The rate constants are compared with the predictions of various theories for ion–molecule collisions. The protonation is discussed in terms of the energetics and mechanisms of various modes of dissociation.

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On rapporte les constantes de vitesse à 298 ± 2 K, mesurées grâce à la technique de lueur d'écoulement, pour les réactions de transfert de proton de $H_3O^+$ avec $CH_2O$, $CH_3CHO$, $(CH_3)_2CO$, HCOOH, $CH_3COOH$, $HCOOCH_3$, $CH_3OH$, $C_2H_5OH$, $(CH_3)_2O$ et $CH_2CO$. On a observé la réaction de transfert dissociatif de proton que dans le cas du $CH_3COOH$. On compare les constantes de vitesse avec les valeurs prédites par diverses théories pour les collisions ion–molécule. On discute de la protonation en termes des énergies et des mécanismes de divers modes de dissociation.

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## Introduction

Experimental studies of the gas-phase chemistry of the hydronium ion have not been extensive since its first observation in 1940 (1). This is somewhat surprising, particularly in view of the history of this ubiquitous ion in solution chemistry. The gas-phase measurements have generally been restricted to the kinetics and equilibria of three-body association reactions of the hydronium ion with $H_2O$ molecules (2, 3). They were undertaken primarily to provide insight into fundamental aspects of the step-wise hydration of this ion, particularly as it is believed to proceed in and below the D-region of the earth's ionosphere (4, 5). The few measurements concerned with two-body reactions of $H_3O^+$ which have been reported were largely incidental to investigations directed towards the determination of the gas-phase proton affinity of $H_2O$ (6), the systematic assessment of classical theories of ion–molecule collisions (7–9), and the identification of ion–molecule reactions which represent a sink for chlorofluoromethanes in the troposphere and stratosphere (10). We report here an extensive flowing afterglow study of the room-temperature kinetics and energetics of proton-transfer reactions of $H_3O^+$ which was undertaken primarily to provide a 'benchmark' for the solution chemistry of the hydronium ion and to set the stage for further gas-phase measurements designed to elucidate the influence of step-wise hydration on the chemical behaviour of $H_3O^+$ (11). Proton-transfer reactions of $H_3O^+$ are also of interest in several other diverse areas of chemistry including chemical ionization mass spectrometry (12), flame ion chemistry (13), and the ion chemistry of moist atmospheres (5).

## Experimental

The majority of the measurements was carried out in a conventional flowing plasma mass-spectrometer (flowing afterglow) system which has been described previously (14). The reactant $H_3O^+$ ions were established in either a flowing helium or a flowing hydrogen plasma. Distilled water vapor was added to the helium upstream of the ion production region. In this mode the $H_2O^+$, $OH^+$, and $H^+$ ions produced, either directly by electron impact, or indirectly by reactions of helium ions and excited neutral atoms, undergo further reactions with $H_2O$ to eventually produce $H_3O^+$. In a flowing hydrogen plasma $H_3O^+$ is established primarily by the fast proton-transfer reaction

$$[1] \qquad H_3^+ + H_2O \rightarrow H_3O^+ + H_2$$

with $k = (4.3 \pm 1) \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (15). In this case the distilled water vapor was added downstream of the ionizer in amounts sufficient to ensure the completion of reaction [1] prior to the reaction region further downstream.

A few of the measurements were carried out with the apparatus in the Selected Ion Flow Tube (SIFT) configuration modelled after the original design reported by Adams and Smith (16). In this configuration a differentially pumped quadrupole mass filter was interposed between the ion production and ion reaction regions. The $H_3O^+$ ions, after being produced in the conventional manner described above, were extracted from the ion production region through a 1 mm diameter orifice into the quadrupole mass filter which communicated

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TABLE 1. Energetics and measured rate constants (in units of $10^{-9}$ $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$) at $298 \pm 2$ K for proton-transfer reactions of $H_3O^+$ with molecules, M

| M | $\mathrm{PA_{298}(M)}$[a] | Ref. | $-\Delta H_{298}^0$[b] | $k$[c] | Ref. |
|---|---|---|---|---|---|
| $H_2S$ | 170.2±1.8 | 6 | 3.8±0.6 | 1.9±0.4 | 6 |
| $CH_2O$ | 170.9±1.2 | 6 | 4.5±1.1 | 3.4±0.9(14) | |
| HCN | 171.0±1.7 | 6 | 4.7±0.5 | 3.5±0.7 | 6 |
| HCOOH | 178.1±2 | 24 | 12±5 | 2.7±0.8(12) | |
| $CH_3CHCH_2$ | 180±2 | 9 | 14±5 | 1.5±0.3 | 25 |
| $CH_3NO_2$ | 181±3 | 9 | 15±6 | 4.1±1.0 | 9 |
| $CH_3OH$ | 181±3 | 9 | 15±6 | 2.8±0.7(7) | |
| $CH_3CHO$ | 185.4±2 | 24 | 19±5 | 3.6±0.9(12) | |
| $C_2H_5OH$ | 186.8±2 | 24 | 20±5 | 2.8±0.7(4) | |
| $CH_3COOH$ | 187.4±2 | 24 | 21±5 | 3.0±0.9(7) | |
| $CH_3CN$ | 187.4±2 | 24 | 21±5 | 4.7±0.7 | 8 |
| $HCOOCH_3$ | 187.8±2 | 24 | 21±5 | 3.3±0.8(3) | |
| $(CH_3)_2O$ | 190.1±2 | 24 | 24±5 | 2.7±0.7(5) | |
| $(CH_3)_2CO$ | 193.6±1 | 26 | 27±4 | 3.9±1.0(7) | |
| $CH_2CO$ | 194.1±1 | 26 | 28±4 | 2.0±0.5(3) | |
| $NH_3$ | 200.4±2 | 24 | 34±5 | 2.4±0.5 | 7 |

[a] Proton affinity (in kcal $\mathrm{mol^{-1}}$) corresponding to the formation of the lowest energy tautomer.

[b] Standard enthalpy change for proton transfer based on $\mathrm{PA_{298}(H_2O)} = 166.4 \pm 2.4$ kcal $\mathrm{mol^{-1}}$ or direct equilibrium constant measurement (6).

[c] The mean value together with the estimated accuracy of the measurement. The number of measurements is given in parentheses. The precision of the measurements was observed to be better than ±15%.

with the flow tube through a 5 mm diameter gas entrainment orifice. After injection into the flow tube at ca. 40 eV, the $H_3O^+$ ions were allowed to thermalize by collision before they entered the reaction region 106 cm further downstream. In this way we could avoid the introduction of ion types other than $H_3O^+$ into the reaction region. This procedure also eliminated $H_2O$, the parent gas of $H_3O^+$, from the reaction region.

The reactant neutrals were added into the reaction region as vapors either in their pure form or diluted with helium. The determination of their flows required separate viscosity measurements as has been described (17). Rate constants were determined in the usual manner from measurements of the $m/e = 19$ signal as a function of addition of vapor into the reaction region (14). Product ion signals were measured concomitantly. The operating conditions in these experiments encompassed total gas pressures, $P$, in the range 0.258 to 0.509 Torr, average gas velocities, $\bar{v}$, in the range 6.7 to $8.2 \times 10^3$ cm $\mathrm{s^{-1}}$, effective reaction lengths, $L$, of the order of 60 and 85 cm and a gas temperature, $T = 298 \pm 2$ K.

The vapors were derived from the following liquids: $CH_3OH$, HCOOH, and $(CH_3)_2CO$ (BDH chemicals, Analytical Reagent Grade), $C_2H_5OH$ (Consolidated Alcohols, Absolute), $CH_3CHO$ (BDH chemicals, Laboratory Reagent Grade, 99.0% min.), $HCOOCH_3$ (BDH chemicals, 98%), $CH_3COOH$ (Anachemia Chemicals, Glacial, 99.7%), and $(CH_3)_2O$ (Matheson, 99.8% (typical)). $CH_2O$ was prepared by the low pressure distillation of paraformaldehyde (Fisher Scientific, Purified Grade) by an adaptation of the method of Spence and Wild (18). Ketene was prepared by the pyrolysis of acetone at ca. 800 K. The monomeric gas was purified by passing it through a cold trap at 250 K ($CCl_4$ slush) and collecting it as a liquid at 144 K (pentane slush).

The flows of formic acid and acetic acid were corrected for dimerization using the dissociation equilibrium constants $K_p$ (Torr) = 2.704 and 0.5458 respectively, at 299 K (19, 20). This correction was based on the reasonable assumption that the dimers were present in their equilibrium amounts both in the storage bulbs and prior to their entry into the reaction region. A separate experiment was performed to determine the extent of dimerization in ketene vapor. The infrared spectrum of a sample of ketene vapor was recorded over a period of several days and was compared to those of the ketene monomer (21, 22) and dimer (23). Over the range of pressure and storage time of our experimental gas samples, the mole fraction of dimer in the vapor phase appeared to be negligible.

## Results and Discussion

### *Kinetics of Proton Transfer*

The rate constants measured in this study for the reactions of $H_3O^+$ with oxygen bases are given in Table 1 along with several others which have been determined previously in this laboratory. The majority of these reactions appeared to proceed simply by the transfer of a proton without concomitant decomposition of the protonated product but followed by its solvation, primarily with the parent base. For example, as is evident from Fig. 1, the reaction of $H_3O^+$ with HCOOH produced $HCOOH_2^+$ as the only primary product ion which then reacted further by solvation to form the proton-bound formic acid dimer, $HCOOH_2^+ \cdot HCOOH$, presumably via three-body association according to the reaction

$$[2] \quad HCOOH_2^+ + HCOOH + M \rightarrow HCOOH_2^+ \cdot HCOOH + M$$

where M is a stabilizing third body which is primarily $H_2$ in these experiments. The rise in the hydrated ion $HCOOH_2^+ \cdot H_2O$ may be attributed primarily to the reaction of the hydrated $H_3O^+$ with HCOOH (11).

Proton transfer was observed to proceed in all cases with the rate constants spanning a range in

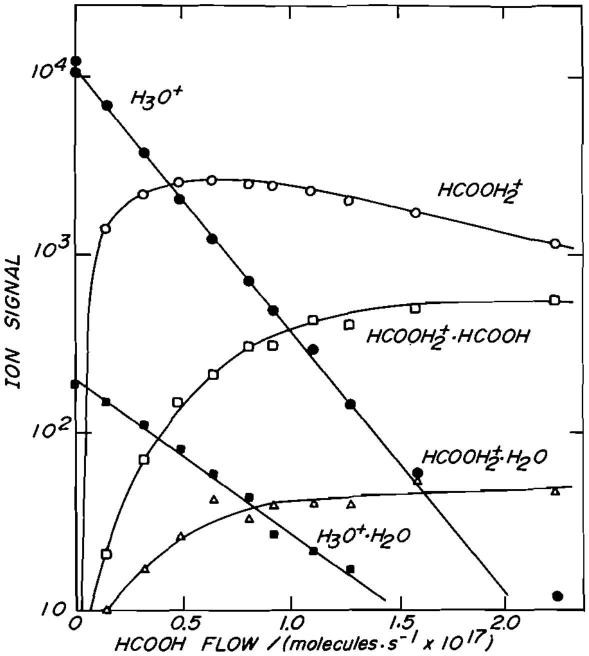


FIG. 1. The variation of the major positive ions observed upon the addition of formic acid vapor into a flowing $H_2O$–$H_2$ plasma in which $H_3O^+$ is initially a dominant ion. This decay of the $H_3O^+$ signal provides a rate constant of $2.4 \times 10^{-9}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. $T = 298$ K, $P = 0.414$ Torr, $\bar{v} = 8.0 \times 10^3$ cm $s^{-1}$, and $L = 85$ cm.

values from 1.5 to $4.1 \times 10^{-9}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. Surprisingly few other measurements are available for comparison. Interest in tropospheric and stratospheric ion chemistry prompted Fehsenfeld and co-workers to determine and report rate constants for the reaction of $H_3O^+$ with $NH_3$ for which (27) $k = (2.1 \pm 0.6) \times 10^{-9}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 296 K, and with $CH_2O$ and $CH_3OH$ for both of which (28) $k = (2.2 \pm 0.9) \times 10^{-9}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at room temperature. These values are systematically lower than the corresponding values in Table 1, albeit there is agreement within the overall uncertainties reported for the two sets of measurements. The larger uncertainties associated with the reactions involving $CH_2O$ and $CH_3OH$ are attributed by these authors to the uncertainties associated with the measurement of the flow of these substances as vapors when derived from the liquid phase. The reaction of $H_3O^+$ with $NH_3$ has also been investigated with the ion cyclotron resonance technique by Huntress who reported (29) a value of $(2.20 \pm 0.12) \times 10^{-9}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. The remaining rate constants in Table 1 appear not to have been determined previously by other workers.

Figure 2 compares the proton-transfer rate constants listed in Table 1 with the capture rate constants predicted by various ion–molecule collision theories: the Langevin theory which ignores the influence of the permanent dipole moment of the molecule (30), the average-dipole-orientation (ADO) theory (the $\overline{\cos\theta}$ model) (31), the theory of Barker and Ridge (32), and the locked-dipole limit (33). The permanent dipole moments, $\mu_D$, were all taken from the compilation of Nelson *et al.* (34). The polarizabilities, $\alpha$, for $H_2S, CH_2O, HCN, CH_3CHCH_2, CH_3OH, (CH_3)_2CO$, and $NH_3$ were taken from existing compilations (35–37). The mean polarizabilities of the remaining molecules were calculated from bond and group polarizabilities (36) to be 3.09, 5.2, 4.40, 5.17, 5.03, 4.56, 5.90, 6.04, and 4.12 Å$^3$ for HCOOH, $CH_3NO_2, CH_3CHO, C_2H_5OH, CH_3COOH, CH_3CN$, $HCOOCH_3$, $(CH_3)_2O$, and $CH_2CO$, respectively. It is apparent from Fig. 2 that proton transfer to these molecules from $H_3O^+$ proceeds with essentially unit probability, in concert with the behaviour reported previously for other analogous systems (38). The small deviation of the measured proton-transfer rate constants from the calculated capture rate constants which is evident from Fig. 2 is reminiscent of similar deviations observed previously in our laboratory for other proton-transfer reactions. Barker and Ridge (32) have also discussed the implications of these deviations. No new substantial insight is evident from the comparison reported here, but the results do provide an additional useful data base for the assessment of any future developments in theories of ion–molecule collision and reaction.

*Dissociative Proton Transfer*

Most of the reactions of $H_3O^+$ listed in Table 1 appeared to proceed simply by proton transfer to form predominantly (>99%) $MH^+$. Only with $CH_3COOH$ did the primary product spectrum include substantial amounts of ions other than $MH^+$ with lower values of *m*/*e*, evidently because of the dissociation of $MH^+$ according to

$$[3] \qquad H_3O^+ + M \rightarrow [MH^+]^* + H_2O$$

$$[3a] \qquad [MH^+]^* \rightarrow \text{products}$$

where the internal energy required for the unimolecular decomposition of $[MH^+]^*$ is provided by the deposition of a substantial fraction of the excess energy which is in the form of reaction exothermicity. The extent to which this decomposition may be moderated under our experimental conditions by collisional stabilization of $[MH^+]^*$ is uncertain; the influence of the $H_2$ bath pressure on the primary product spectrum was not investigated systematically. The excess energy available in the form of reaction exothermicity is given by the difference in the proton affinity of $H_2O$ and M which is included in Table 1. It is possible, therefore, using thermo-

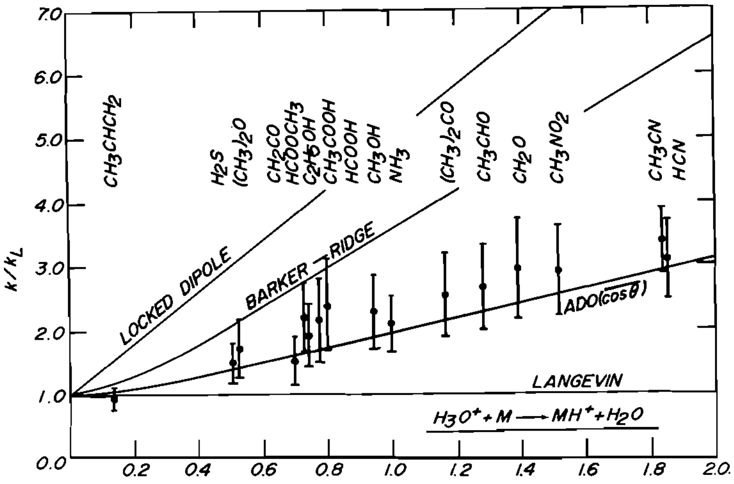


FIG. 2. A comparison of measured rate constants with capture rate constants predicted by various theories of collision for proton transfer reactions of $H_3O^+$ with polar molecules. The solid bars represent the estimated accuracy of the measurements. $k_L$ is the collision rate constant determined from the Langevin expression.

TABLE 2. Energies (in kcal/mol) and energetically possible dissociative pathways

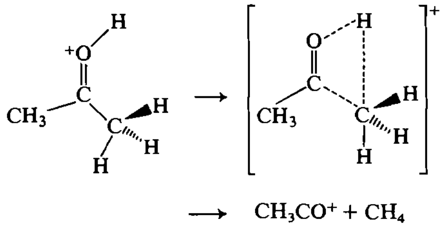
| Molecule | Maximum excess energy available on protonation by $H_3O^+$ | Possible dissociation reaction | | |
|---|---|---|---|---|
| $C_2H_5OH$ | 20±4 | $C_2H_5OH_2^+$ | $\rightarrow C_2H_4OH^+ + H_2$ | −18 |
| $(CH_3)_2O$ | 24±5 | $(CH_3)_2O^+H$ | $\rightarrow CH_3CHOH^+ + H_2$ | −9 |
| | | | $\rightarrow CH_2OH^+ + CH_4$ | −19 |
| | | | $\rightarrow H_3O^+ + C_2H_4$ | −23 |
| $(CH_3)_2CO$ | 27±4 | $(CH_3)_2C^+OH$ | $\rightarrow CH_3CO^+ + CH_4$ | −22 |
| $CH_3COOH$ | 21±5 | $CH_3COOH_2^+$ | $\rightarrow CH_3CO^+ + H_2O$ | 0 |
| $HCOOH$ | 12±5 | $HCOOH_2^+$ | $\rightarrow HCO^+ + H_2O$ | −41 |
| | | | $\rightarrow CO + H_3O^+$ | −18 |
| $HCOOCH_3$ | 22±5 | $HCOO(CH_3)H^+$ | $\rightarrow HCO^+ + CH_3OH$ | −54 |
| | | | $\rightarrow CH_3OH_2^+ + CO$ | −16 |
| | | | $\rightarrow CH_3CO^+ + H_2O$ | −8 |

chemical data from the recent compilation of Rosenstock *et al.* (39), to calculate what dissociation reactions are feasible for each protonated base. The energetically possible dissociation pathways are listed in Table 2.

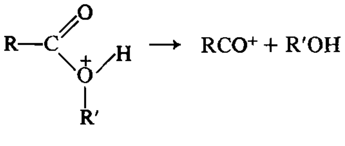
$H_2$ elimination from $C_2H_5OH_2^+$ to yield $C_2H_4OH^+$ (assumed to be protonated acetaldehyde) is, by analogy with vicinal elimination of $H_2$ from $CH_3OH_2^+$ (40), likely to have a kinetic barrier of approximately 20 kcal/mol and would therefore not be expected to occur. Furthermore, this mode of decomposition is not observed with the stronger acid $HCO^+$ (41).

The only thermodynamically possible dissociation products of $(CH_3)_2OH^+$ require generation of carbon bonds. These can only be achieved by large skeletal rearrangements and the large barriers normally accompanying such rearrangements would not be expected to be overcome by the relatively low exothermicity of the initial proton transfer reaction.

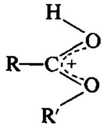
Dissociation of protonated acetone to form methane and the acetyl ion is possible thermodynamically but is mechanistically unlikely as it requires protonation at the methyl carbon (calculation of the exothermicity of the proton-transfer reaction is for protonation at the most basic site, in this case the oxygen atom). Protonation at a saturated carbon is a high energy process, while the alternative process, a 1,3-shift of the proton from the oxygen to the carbon accompanied by synchronous fission of the carbon–carbon bond will also have a high barrier.



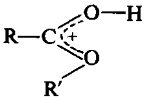
Dissociative proton transfer to formic acid, acetic acid, and methyl formate should result in acylium ions and water or methanol via the $A_{Ac}1$ mechanism.



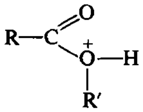
In the case of formyl derivatives subsequent proton transfer between $HCO^+$ and R′OH (R′ = $CH_3$ or H) produces $R'OH_2{}^+$ and CO. However, this mechanism requires protonation at the energetically less accessible ether or hydroxy-oxygen. In solution two



I



II



III

tautomers of $HCOOH_2{}^+$ (42) have been detected by proton nmr but these have been assigned structures **I** and **II**, both rotamers of carbonyl protonated formic acid. Benoit and Harrison (43), using ionization energy correlations, predict that the proton affinities of the hydroxy-oxygens of formic acid and acetic acid will be 26 ± 3 and 27 ± 3 kcal/mol respectively lower than those of the corresponding carbonyl oxygens. *Ab initio* molecular orbital calculations (44) similarly predict hydroxy-protonation of formic acid (**III**, R = R′ = H) to be 25 kcal/mol less stable than the carbonyl-protonated tautomer (structure **I**). The exothermicities listed in Table 2 are for formation of the most stable carbonyl-protonated rotamer and the hydroxy-protonated tautomers, required as intermediates in the $A_{Ac}1$ fission mechanism, can only be attained if the exothermicities of the initial proton transfer are at least 25 kcal/mol. Clearly, then, when the protonating acid is $H_3O^+$ the $A_{Ac}1$ mechanism is not accessible to formic acid and is barely possible, within the error limits, for acetic acid. The observed 5% dissociation of acetic acid and the total lack of dissociation for formic acid are then entirely consistent with this mechanism. Protonation by the stronger acid $HCO^+$ is sufficient to increase the dissociation of acetic acid to 20% but does not cause formic acid dissociation (45). The even stronger acid, $H_3{}^+$, results in complete dissociation of both acetic and formic acids.

Protonation of the methoxy-oxygen of methyl formate, using the ionization energy correlation method (43), only requires ca. 22 kcal/mol more energy than that of the carbonyl group. Hence, in the unlikely event of all the exothermicity appearing as internal energy in the protonated ester, gas-phase protonation by $H_3O^+$ may occur at either oxygen. However, dissociation by the $A_{Ac}1$ mechanism would formally produce $HCO^+$ and $CH_3OH$, a process requiring 54 kcal/mol, and is therefore not possible. The final products from this mode of fission, CO and $CH_3OH_2{}^+$, are within the exothermicity of the initial proton transfer and it is possible to envisage a second proton transfer reaction occurring synchronously with the cleavage of the C—O bond, thereby lowering the overall barrier to the reaction. There is little evidence (46) of such a lowering as the stronger acids $HCO^+$ and $CH_5{}^+$ (reaction exothermicities 45 and 57 kcal/mol, respectively) also do not produce dissociation.

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