A room-temperature study of the kinetics of protonation of formaldehyde

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Rate constants measured with the flowing afterglow technique at 297 ± 2 K are reported for the protonation of CH_2O by H_3^+, N_2H^+, CH_5^+, HCO^+, $C_2H_5^+$, H_3O^+, H_3S^+, and $HCNH^+$ and for the subsequent deprotonation by NH_3. The rate constants are compared with predictions of various theories for ion–molecule collisions. The protonation was observed to proceed in the absence of competing channels and further decomposition and is discussed in terms of the energetics of the two sites of protonation and the energetics and mechanism of H_2 elimination. The rate measurements provide evidence for the room-temperature conversion of the adduct $C_2H_3^+ \cdot H_2$ to the more stable isomer derived from the direct protonation of C_2H_4.

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Opérant à 297 ± 2 K et faisant appel à la technique de lueur d'écoulement résiduelle, on a mesuré les constantes de vitesse pour la protonation de CH_2O par H_3^+, N_2H^+, CH_5^+, HCO^+, $C_2H_5^+$, H_3O^+, H_3S^+ et $HCNH^+$ et la déprotonation subséquente par NH_3. On compare les constantes de vitesse avec celles que l'on peut prédire à l'aide de diverses théories relatives aux collisions ion–molécule. On a observé que la protonation se produit même s'il n'existe pas d'autres chemins en compétition et d'autres décompositions et on en discute en termes des énergies des deux sites de protonation et de l'énergie et du mécanisme d'élimination de H_2. Les mesures de vitesse fournissent des preuves à l'effet de la transformation, à température ambiante, de l'adduit $C_2H_3^+$ en son isomère plus stable dérivé de la protonation directe de C_2H_4.

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Introduction

Ion-molecule reactions of gaseous formaldehyde have been receiving an increasing amount of attention in the past few years. This is especially evident from the recent incorporation of formaldehyde into models of the ion chemistry proceeding in such diverse chemical environments as dense interstellar clouds (1), hydrocarbon flames (2), and planetary atmospheres, particularly the earth's stratosphere (3, 4). However, quantitative information on the rates of such reactions is still rather sparse. Here we present the results of a flowing afterglow study of the room-temperature kinetics of ion–molecule reactions which lead to the protonation of formaldehyde. Such reactions play an integral part in these chemical models. Their study also provides further fundamental insight into the kinetics of proton-transfer reactions in general.

Experimental

The measurements were carried out in a conventional flowing plasma mass-spectrometer (flowing afterglow) system in a manner which has been described previously (5).

Monomeric formaldehyde was prepared from paraformaldehyde (Fisher Scientific, Purified Grade) by an adaption of the method developed by Spence and Wild (6). Paraformaldehyde was distilled at low pressures at ~370 K. The formaldehyde was then dried by passing it through a cold trap at 195 K and frozen out at liquid nitrogen temperatures. A gaseous mixture of ~5% formaldehyde was used in these studies and the partial pressure of formaldehyde was maintained below 7 Torr to avoid polymerization. The monomer could be stored at these partial pressures for several days with negligible polymerization. It was introduced into the flowing afterglow sufficiently downstream of the ion production region to ensure that the reactant ions were thermalized by collisions with H_2 carrier gas molecules to the ambient temperature of 297 ± 2 K prior to reaction. The total pressure in the reaction region ranged from 0.29 to 0.68 Torr and the effective reaction length had values of 59 and 85 cm.

The gases used were hydrogen (Linde, Very Dry Grade, 99.95% H_2), methane (Matheson, Ultra High Purity, 99.97% CH_4), ethylene (Matheson, C.P. Grade, 99.5% C_2H_4), acetylene (Matheson, Purified Grade, 99.6% C_2H_2), carbon monoxide (Matheson, Coleman Grade, 99.99% CO), and nitrogen (Matheson, Prepurified Grade, 99.998% N_2).

Results and Discussion

The measurements were performed in H_2 carrier gas in which a variety of protonating agents with proton affinities intermediate between H_2 and CH_2O could be conveniently prepared upstream of the reaction region. This was accomplished for X = N_2, CO, CH_4, C_2H_4, H_2O, H_2S, and HCN through rapid proton transfer reactions of the type

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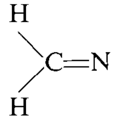
[1] $H_3^+ + X \rightarrow XH^+ + H_2$

the H_3^+ itself resulting from the reaction

[2] $H_2^+ + H_2 \rightarrow H_3^+ + H$

After their formation, the H_3^+ and XH^+ ions were allowed to undergo many thousands of collisions in the H_2 buffer gas upstream of the reaction region in order to establish Maxwell–Boltzmann energy distributions prior to reaction. Some ambiguity exists about the structure of the protonated heteroatomic species CO and HCN for which there are two possible sites of protonation. *Ab initio* molecular orbital calculations reported to date indicate that the proton affinity of the carbon site in the CO molecule is only ca. 18 kcal mol^{-1} higher than that of the oxygen site and that both the HCO^+ and COH^+ systems prefer a linear arrangement of nuclei in their ground states at equilibrium (7, 8). In the case of protonated HCN, calculations predict that the linear acetylene-like isomer, $H{-}C{\equiv}N^+{-}H$, lies ca. 70 kcal mol^{-1} lower in energy than the formaldehyde-like isomer,  $H_2C{=}N^+$ (9). Consequently, it appears that two isomers are energetically accessible in the protonation of CO and HCN by H_3^+ according to reactions [3] and [4], where the exothermicity is given in kcal mol^{-1}. The experiments

[3] $H_3^+ + CO \rightarrow HCO^+ + H_2 + 42$
$\rightarrow COH^+ + H_2 + 28$

[4] $H_3^+ + HCN \rightarrow HCNH^+ + H_2 + 70$
$\rightarrow H_2CN^+ + H_2 + 0$

reported here do not provide any information about the extent of initial formation of the high energy isomer in either case. However, should such formation be occurring to any significant extent, we can expect isomerization to proceed to the low energy form, if not unimolecularly or by collision with H_2 carrier molecules, then by the proton transfer reactions

[5] $COH^+ + CO \rightarrow HCO^+ + CO + 18$

[6] $H_2CN^+ + HCN \rightarrow HCNH^+ + HCN + 70$

which would be encouraged to proceed by the presence of CO and HCN, respectively, upstream of the reaction region. Evidence for the ultimate preferential formation of the HCO^+ isomer under our experimental operating condition is given elsewhere (10). The $C_2H_5^+$ ions were prepared in two ways, either directly by proton transfer to C_2H_4 or indirectly through H_2 association

[7] $C_2H_3^+ + H_2 + M \rightarrow C_2H_5^+ + M$

preceded by proton transfer from H_3^+ to C_2H_2 (11).

Rate constants were measured in separate experiments in each of which the desired protonating agent was established as the major positive ion present in the flowing plasma. Figure 1 shows the decays of H_3^+, HCO^+, and H_3O^+ observed upon the addition of CH_2O into the reaction region under conditions of only partial conversion of H_3^+ to HCO^+ (relatively small additions of CO upstream). H_3O^+ results from proton transfer to H_2O impurity. The concomitant rise in the $m/e = 31$ signal is a manifestation of the production of protonated formaldehyde to which we have assigned the structure CH_2OH^+ (*vide infra*). The initial signal at $m/e = 31$ is accounted for by the ^{18}O isotope of HCO^+. No other primary product ions were observed. CH_2OH^+ appears to react further with CH_2O to form the cluster ion $CH_2OH^+ \cdot CH_2O$ presumably by three-body association. There was no evidence for the association of

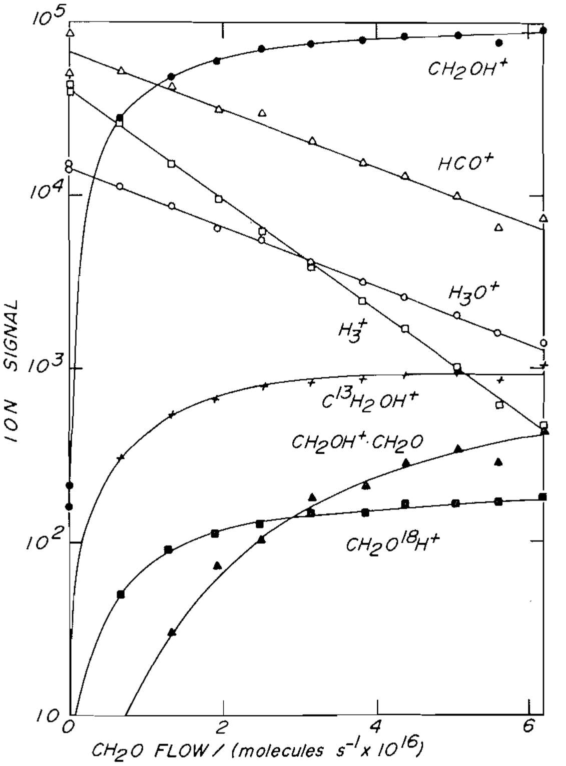


FIG. 1. The variation in the dominant ion signals recorded upon the addition of formaldehyde into a H_2–CO plasma in which HCO^+, H_3^+, and H_3O^+ are initial major ions: $T = 297$ K, $P = 0.421$ Torr, $v = 7.8 \times 10^3$ cm s^{-1}, $L = 60$ cm, and the flow of CO $= 3.12 \times 10^{16}$ molecules s^{-1}.

TABLE 1. Rate constants at 297 ± 2 K (in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}) for reactions of the type $XH^+ + CH_2O \rightarrow CH_2OH^+ + X$

XH^+	k_{expt}[a]	k_{AADO}[b]	k_{expt}/k_{AADO}	$-\Delta H_{298}^{0}$[c]
H_3^+	6.3±1.6(4)	6.68	0.94	70 ±2
N_2H^+	3.3±0.8(3)	2.87	1.1	54 ±2
CH_5^+	4.5±1.1(3)	3.35	1.3	40 ±3
HCO^+	3.3±0.8(4)	2.87	1.1	28 ±2
$C_2H_5^+$[d]	3.1±0.8(4)	2.87	1.1	12 ±4
H_3O^+	3.4±0.9(14)	3.23	1.1	5.1±0.8[e]
H_3S^+	2.2±0.6(3)	2.74	0.80	1.4±0.5[e]
$HCNH^+$	≥1.6	2.90	≥0.6	−0.1±0.4[e]

[a] The mean value together with the estimated accuracy of the measurements. The number of measurements is given in parentheses.

[b] The collision rate constant calculated using the angular momentum conserved-average dipole orientation theory with $C = 0.257$ (16), $\alpha = 2.81$ $Å^3$ (17), $\mu_D = 2.33$ D (18), and $I = 2.16 \times 10^{-39}$ g cm^2 (19).

[c] Standard enthalpy change based on $PA(CH_2O) = 170.9 \pm 1.2$ kcal mol^{-1} (15, 20) and $PA(H_2, N_2, CH_4, CO, C_2H_4) = 101 \pm 1$ (21), 117 ± 1 (unpublished results from this laboratory), 131 ± 2 (unpublished results from this laboratory), 143 ± 1 (23), and 159 ± 3 (24) kcal mol^{-1}, respectively.

[d] Derived from $H_3^+ + C_2H_4$ or $C_2H_3^+ + H_2 + M$.

[e] Standard enthalpy change based on equilibrium constant measurements performed in this laboratory (15).

CH_2OH^+ with the H_2 carrier gas molecules to form either the adduct $H_2COH^+ \cdot H_2$ or protonated methanol, $CH_3OH_2^+$. The observed rise in the $m/e = 33$ signal is completely accounted for by the ^{18}O isotope of CH_2OH^+. Our failure to observe $CH_2OH^+ \cdot H_2$ is consistent with the equilibrium constant measurements reported by Hiraoka and Kebarle (12) which suggest that this ion is stable only at low temperatures. Also, according to a recent study of the metastable decomposition of $CH_3OH_2^+$ (13), the formation of $CH_3OH_2^+$ from $CH_2OH^+ + H_2$ has an activation energy of 31 kcal mol^{-1}. The ^{18}O isotope also rules out significant formation (<0.2%) of $CH_3OH_2^+$ by the two-body reaction [8]

[8] $CH_2OH^+ + CH_2O \rightarrow CH_3OH_2^+ + CO$

which is 33 ± 4 kcal mol^{-1} exothermic and which appears to have been observed previously in the ion-cyclotron double resonance (ICR) experiments of Karpas and Klein (14). The CH_3O^+ in the ICR experiments was generated at relatively low pressures in CH_2O from CH_2O^+ and CHO^+ and was observed to produce not only CH_5O^+ but also a variety of $C_2H_xO_y^+$ ions. In fact, a number of these channels are endothermic so that it is necessary to surmise, as Karpas and Klein have done, that excited CH_3O^+ ions were present under their experimental conditions.

Table 1 summarizes the rate constants determined in this laboratory for the reactions of seven XH^+ ions with CH_2O. Measurements associated with the reactions of H_3S^+ and $HCNH^+$ with CH_2O have been reported previously in the context of a determination of their equilibrium constants (15). Very few other measurements appear to be available for comparison. Fehsenfeld and co-workers (4) have recently reported a flowing afterglow value of (2.2 ± 0.9) × 10^{-9} cm^3 $molecule^{-1}$ s^{-1} for the reaction of H_3O^+ with CH_2O at room temperature which is somewhat lower than the value determined here, but there is agreement within the overall uncertainties of the two sets of measurements. Recent SIFT measurements in which HCO^+ was produced from CH_2O at low pressures indicated a rate constant of (3.2 ± 1.0) × 10^{-9} cm^3 $molecule^{-1}$ s^{-1} which is in good agreement with the present result (25). Karpas and Klein (14) have reported a value of 6.1 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} for the same reaction proceeding under the less well defined conditions of their ICR cell.

Figure 2 compares the measured rate constants with capture rate constants predicted by various ion–molecule collision theories: the Langevin theory which ignores the influence of the permanent dipole moment of CH_2O (26), the angular momentum-conserved average dipole orientation (AADO) theory (16), and the locked-dipole limit (27, 28). It is encouraging that the AADO theory predicts rate constants for the reactions studied here which are essentially within the uncertainty of the experimental measurements.

All of the reactions in Table 1 appeared to proceed predominantly by proton transfer unaccompanied by other competing channels and further decomposition of the protonated product. The isotopic labelling studies of Karpas and Klein (14) have shown that proton transfer and not H_2 transfer is responsible for the conversion of HCO^+ to CH_2OH^+. Some ambiguity exists regarding the actual site of protonation. Molecular orbital calculations have predicted an energy difference of at least 40 kcal mol^{-1} between the two tautomers corresponding to C and O protonation, viz. CH_3O^+ and CH_2OH^+ (9). Consequently it appears that two isomers may be energetically accessible in the protonation of CH_2O by H_3^+, N_2H^+, and possibly CH_5^+. For each of these ions the proton transfer reaction exothermicity

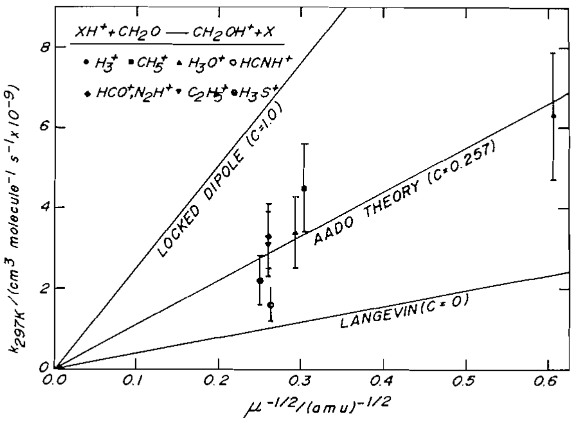


FIG. 2. A comparison of the measured rate constants with capture rate constants predicted by classical theories of collision for proton-transfer reactions with formaldehyde at 297 ± 2 K. The solid bars represent the estimated accuracy of the measurements.

>40 kcal mol^{-1} (see Table 1). The least endothermic route of decomposition of the CH_2OH^+ isomer corresponds to a symmetry-forbidden vicinal H_2 elimination which is ca. 28 kcal mol^{-1} endothermic and requires an excess energy of at least ca. 61 kcal mol^{-1} according to measurements of the kinetic energy release in the metastable decomposition of CH_2OH^+ (29). Such an excess energy is not available from any of the XH^+ ions used in this study except perhaps H_3^+:

[9*a*] $H_3^+ + CH_2O \rightarrow CH_2OH^+ + H_2 + 70$

[9*b*] $\hookrightarrow HCO^+ + H_2 - 28$

Also, Bowen and Williams have reported measurements which appear to indicate that the high energy CH_3O^+ tautomer loses H_2 in an exothermic symmetry-allowed reaction with a small activation energy (30). A second route of dissociative proton transfer can therefore be envisaged for the stronger acids H_3^+, N_2H^+, CH_5^+, e.g.,

[10*a*] $H_3^+ + CH_2O \rightarrow CH_3O^+ + H_2 + 30$

[10*b*] $\hookrightarrow HCO^+ + H_2 + 12$

Careful measurements of the $m/e = 29$ signal in the H_3^+ experiments, although complicated by the presence of N_2 and (or) CO impurities, provided an upper limit of ca. 1% to the occurrence of dissociation either via reaction [9*b*] or reaction [10*b*] under our experimental operating conditions.

The rate constant determined for the reaction of $C_2H_5^+$ with CH_2O was observed to be independent of the chemical history of this ion and there was no evidence for the formation of either CH_5O^+ or $C_3H_5O^+$ which may be conceived to proceed via "solvated" proton transfer according to

[11] $C_2H_3^+ \cdot H_2 + CH_2O \rightarrow CH_2OH^+ \cdot H_2 + C_2H_2$

or a switching reaction of the type

[12] $C_2H_3^+ \cdot H_2 + CH_2O \rightarrow C_2H_3^+ \cdot CH_2O + H_2$

Apparently the hydrogen adduct, $C_2H_3^+ \cdot H_2$, formed by the association of $C_2H_3^+$ with H_2 rearranges its structure at room temperature into that corresponding to the more stabler isomer derived from the direct protonation of C_2H_4 with H_3^+. This is in complete analogy with the behaviour proposed by Hiraoka and Kebarle for the corresponding isomers of $C_2H_7^+$ (31). These authors were able to characterise a loose hydrogen adduct, $C_2H_5^+ \cdot H_2$, approximately 8 kcal mol^{-1} less stable than the protonated ethane structure, $C_2H_7^+$. It was observed only at temperatures sufficiently low (−130 to −160°C) to prevent the interconversion which has a small activation energy. The facile formation at room temperature of the ethyl ion from $C_2H_3^+ + H_2$ is also in accord with observations of a small or negligible release of kinetic energy in what is conceived to be a concerted 1,1-elimination of H_2 from the ethyl cation to the vinylium ion (32). Theoretical treatments of the structures and relative energies of the ethyl and vinylium ions and possible transition states associated with their interconversion have recently been discussed and summarized by Dewar and Rzepa (33).

The reactions of protonated formaldehyde itself were not investigated in great detail. The recent SIFT measurements of Adams *et al.* (25) have shown that this ion is unreactive towards H_2, O_2, CO_2, COS, and CH_4 and reacts by proton transfer with NH_3 and CH_3OH which have proton affinities greater than that of CH_2O. We have studied the proton transfer reaction with NH_3 in these investigations and have determined a rate constant of $(1.7 \pm 0.4) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} which compares favorably with the SIFT value (2.0 ± 0.4), a previous flowing afterglow value (≃2), and an ICR value $(2.3 \pm 0.1) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} (22, 34).

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