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PROTON TRANSFER REACTIONS OF HCO^+ AT 298 K

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ABSTRACT

Rate constants measured with the flowing afterglow technique at 298 ± 2 K are reported for the proton transfer reactions of HCO^+ 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 channels were observed with C_2H_5OH and 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 of possible sites of protonation and in terms of the energetics and mechanisms of various modes of dissociation.

INTRODUCTION

Laboratory studies of the chemistry of the formyl ion, HCO^+, have not been extensive. The only systematic investigation of HCO^+ reactions which has been reported previously is that of Pritchard and Harrison [1]. These authors, as part of a general study of ion—molecule reactions postulated to occur in hydrocarbon flames, determined rate constants for reactions of HCO^+ which occurred when this ion was produced from various oxygenated molecules exposed to ionizing electrons in the ion source of a medium-pressure mass spectrometer at approximately 100°C and an ion exit energy of either 2.4 or 3.4 eV. The few flowing afterglow studies of HCO^+ reactions which have been reported previously were largely incidental to investigations directed towards systematic assessments of classical theories of ion—molecule collisions [2—5] and determinations of the kinetic energy dependence of proton-transfer rate constants [6]. We report here an extensive flowing afterglow study of the kinetics of reactions involving HCO^+ which was undertaken primarily in response to the renewed interest in this ion which has recently been expressed in several diverse areas of chemistry. Formyl ion, HCO^+, has been proposed to play a pivotal role in models of the ion chemistry believed to occur in dense interstellar clouds [7,8]. Recent observations which have confirmed the presence of HCO^+ in these clouds attest to the relevance of its reactions in these environments [9]. Current investigations of the in situ chemical ionization proceeding in atmospheric-pressure hydrocarbon flames have indicated a need for further kinetic information for HCO^+ reactions which are postulated to dominate the upstream ion chemistry proceeding in these flames [10]. The formyl ion has also been implicated as an important intermediate in solution chemistry although it has, as yet, not been observed even in "favorable" super acid media at low temperatures in spite of several serious attempts to detect it [11]. Finally, this general importance of HCO^+ has also inspired several extensive theoretical studies of its structures and properties [12,13].

EXPERIMENTAL

The majority of the measurements were made in a conventional flowing plasma mass spectrometer (flowing afterglow) system which has been described previously [14]. Hydrogen was used as the carrier gas. A few of the measurements were made with the apparatus in the selected ion flow tube (SIFT) configuration modelled after the original design reported by Adams and Smith [15]. In this configuration a differentially pumped quadrupole mass filter was interposed between the ion production and ion reaction regions. The HCO^+ ions, after being produced in the conventional manner from the reaction of H_3^+ with CO, were extracted from the ion production region through a 1-mm diameter orifice into the quadrupole mass filter which communicated with the flow tube through a 5-mm diameter gas entrainment orifice. After injection into the flow tube at ca. 40 eV, the HCO^+ ions were allowed to thermalize by collision before they entered the reaction region 106 cm downstream. In this way one could avoid the introduction of ion types other than HCO^+ into the reaction region, although some H_3O^+ was produced prior to the reaction zone as a result of the reaction of HCO^+ with the H_2O impurity in the H_2 carrier gas. This procedure also eliminated CO, the parent gas of HCO^+, from the reaction region.

The reactant neutral species were added into the reaction region as vapours either in their pure form or diluted with helium. The determination of their flows required separate viscosity measurements, as has been described [16]. Rate constants were determined in the usual manner from measurements of the *m/z* 29 signal as a function of addition of vapour into the reaction region. Product ion signals were measured concomitantly. The operating conditions in these experiments encompassed total gas pressures, P, in the range 0.301—0.713 torr, average gas velocities, $\bar{v}$, in the range $(7.5-8.1) \times 10^3$ cm s^{-1}, effective reaction lengths, L, of 60 and 85 cm and a gas temperature, T, of 298 ± 2 K.

The vapours 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)). Formaldehyde was prepared by the low pressure distillation of paraformaldehyde (Fisher Scientific, Purified Grade) by an adaptation of the method of Spence and Wild [17]. 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 [18,19]. 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 vapour. The infrared spectrum of a sample of ketene vapour was recorded over a period of several days and was compared to those of the ketene monomer [20,21] and dimer [22]. Over the range of pressure and storage time of our experimental gas samples, the mole fraction of dimer in the vapour phase appeared to be negligible.

RESULTS AND DISCUSSION

Protonation of CO

Protonation of CO was conveniently accomplished in the H_2 buffer gas through the rapid proton transfer

$$H_3^+ + CO \rightarrow HCO^+ + H_2 \qquad (1a)$$

the H_3^+ itself being established by the rapid reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (2)$$

We have remeasured the rate constant for the reaction of H_3^+ with CO and found it to be $(2.0 \pm 0.4) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, somewhat higher than the value of $(1.4 \pm 0.4) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} previously reported by Burt et al. [23]. Some ambiguity exists regarding the structure of protonated CO prepared in this manner. Ab initio molecular orbital calculations 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 [12]. Consequently, it appears that two isomers are energetically accessible in the protonation of CO by H_3^+ according to reactions (1a) and (1b)

$$H_3^+ + CO \rightarrow COH^+ + H_2 \qquad (1b)$$

which would be 42 and 24 kcal mol^{-1} exothermic, respectively, given a proton affinity of 142.6 ± 1.0 kcal mol^{-1} for the carbon site [24] and a proton affinity for H_2 of 101 ± 1 kcal mol^{-1} [25]. The experiments reported here do not provide any information regarding the extent of initial formation of the COH^+ isomer. Should such formation be proceeding and the COH^+ not isomerize to HCO^+, either unimolecularly or by collision with H_2 buffer molecules, one would nevertheless expect the HCO^+ form to be preferred ultimately as a result of the proton transfer

$$COH^+ + CO \rightarrow HCO^+ + CO \qquad (3)$$

which would be 18 kcal mol^{-1} exothermic and would be promoted under our experimental conditions by the presence of the CO parent gas.

Several observations were made which were consistent with these expectations. The rate constant and branching ratio for observed product ions determined for the reaction of the m/z 29 ion with C_2H_5OH were found to be independent of the mode of production of this ion when it was generated either by reaction (1) or reaction (4)

$$CH_5^+ + CO \rightarrow HCO^+ + CH_4 \qquad (4)$$

which is only 11 kcal mol^{-1} exothermic, assuming a proton affinity for CH_4 of 131.5 ± 2.2 kcal mol^{-1} [26]. The formation of COH^+ by reaction (4) should therefore be precluded on energetic grounds, given the 18 kcal mol^{-1} difference in energy between COH^+ and HCO^+ predicted by the molecular orbital calculations. Furthermore, in several SIFT experiments in which the m/z 29 ion was produced by reaction (1), this ion was observed to transfer a proton to N_2O with a rate constant in agreement with the value of 3.5×10^{-12} cm^3 molecule^{-1} s^{-1} for the endothermic proton transfer reaction

$$HCO^+ + N_2O \rightarrow N_2OH^+ + CO \qquad (5)$$

which can be deduced from our equilibrium measurements for this reaction [27]. There was no evidence for a significant contribution to the observed m/z 29 decay by the corresponding reaction involving the COH^+ isomer which would be ca. 14 kcal mol^{-1} exothermic and therefore expected to proceed rapidly.

Kinetics of proton transfer from HCO^+

Table 1 summarizes the rate constants determined at 298 ± 2 K for the ten reactions of HCO^+ with oxygenated bases investigated in this study and several others which have been observed previously here. The majority of these reactions appeared to proceed simply by the transfer of a proton unaccompanied by further decomposition of the protonated product, but followed by its solvation either with the parent base or, as was the case with $C_2H_3^+$, the H_2 buffer gas. For example, as is evident from Fig. 1, the reaction of HCO^+ with $(CH_3)_2O$ produced $(CH_3)_2OH^+$ as the only primary product ion which then reacted further with $(CH_3)_2O$ by solvation to form the cluster ion $(CH_3)_2OH^+ \cdot (CH_3)_2O$ presumably via the three-body association reaction

$$(CH_3)_2OH^+ + (CH_3)_2O + H_2 \rightarrow (CH_3)_2OH^+ \cdot (CH_3)_2O + H_2 \qquad (6)$$

TABLE 1

Proton transfer energetics and measured rate constants (in units of 10^{-9} cm^3 molecule^{-1} s^{-1} at 298 K) for reactions of HCO^+ with molecules, M

M	$PA^\circ_{298}(M)$ [a]	Ref.	$-\Delta H^\circ_{298}$ [b]	k_{FA} [c]	Ref.	k_{MS} [d]	k^e_{ICR}
C_2H_2	153 ± 3 [f]		10 ± 4	1.4 ± 0.4	5		
H_2O	166.4 ± 2.4	31	23 ± 3	3.2 ± 0.8	3	$1.2_8 \pm 0.1$	
CH_2O	170.9 ± 1.2	31	28 ± 2	3.3 ± 0.8 (4)		2.0_6	0.61
HCN	171.0 ± 1.7	31	28 ± 3	3.0 ± 0.6	4		1.14 ± 0.07
HCOOH	178.1 ± 2	32	35 ± 3	1.8 ± 0.5 (3)		$1.3_2 \pm 0.1$	
CH_3NO_2	181 ± 3	33	38 ± 4	3.3 ± 0.8	33		
CH_3OH	181 ± 3	33	38 ± 4	2.7 ± 0.7 (4)		$1.7_5 \pm 0.2$	
CH_3CHO	185.4 ± 2	32	42 ± 3	3.4 ± 0.9 (3)		$2.4_5 \pm 0.2$	
C_2H_5OH [g]	186.8 ± 2	32	44 ± 3	2.2 ± 0.6 (8)			
CH_3COOH [g]	187.4 ± 2	32	44 ± 3	2.5 ± 0.8 (2)			
CH_3CN	187.4 ± 2	32	44 ± 3	4.1 ± 1.0	4		
$HCOOCH_3$	187.8 ± 2	32	45 ± 3	2.9 ± 0.7 (8)			
$(CH_3)_2O$	190.1 ± 2	32	47 ± 3	2.1 ± 0.5 (3)		$1.5_5 \pm 0.2$	
$(CH_3)_2CO$	193.6 ± 1	34	51 ± 3	2.7 ± 0.6 (2)			
CH_2CO	194.1 ± 1	34	51 ± 3	1.8 ± 0.5 (3)			
NH_3	200.4 ± 2	32	57 ± 3	2.4 ± 0.5	2		2.6 ± 0.1
				2.1	6		

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

[b] Standard enthalpy change for proton transfer based on PA°_{298} (CO) = 143 ± 1 kcal mol^{-1} [24].

[c] The mean value together with the estimated accuracy of the measurements at 298 ± 2 K. The number of measurements is given in parentheses. The precision of the measurements was observed to be better than ±15%.

[d] Medium-pressure mass spectrometer results reported by Pritchard and Harrison [1].

[e] Ion cyclotron resonance mass spectrometer results [28,29].

[f] Based on the appearance potential of $C_2H_3^+$ from C_2H_4 [30].

[g] Accompanied by partial or nearly complete dissociation of MH^+.

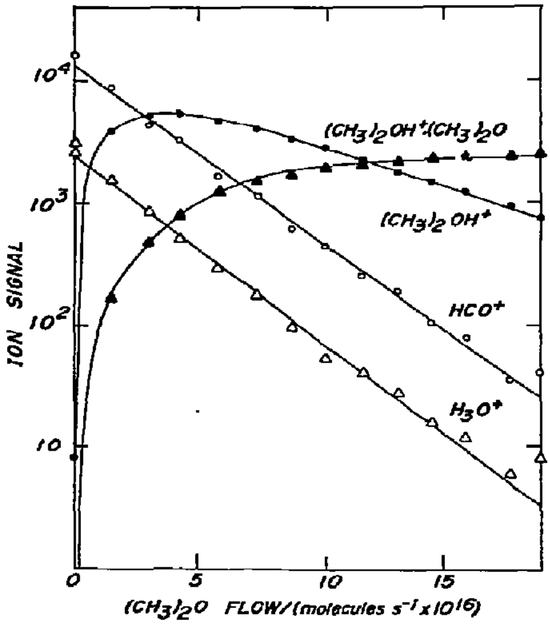


Fig. 1. The variation of the major positive ions observed upon the addition of $(CH_3)_2O$ into a flowing CO—H_2 plasma in which HCO^+ is initially a dominant ion. The decay of HCO^+ provides a rate constant of 2.3×10^{-9} cm^3 $molecule^{-1}$ s^{-1}. $T = 298$ K, $P = 0.311$ torr, $\bar{v} = 7.7 \times 10^3$ cm s^{-1}, and $L = 84$ cm.

Table 1 also includes comparisons with the rate constants reported by Pritchard and Harrison [1] and several practitioners of the ion-cyclotron-resonance technique [28,29]. The agreement with the latter results is of varying quality. The values reported by Pritchard and Harrison [1] are all lower, by as much as a factor of 2.5 in the case of H_2O, than those obtained in the present study. However, such a systematic difference is qualitatively in accord with expectations, given the flow-drift tube measurements reported by Lindinger et al. [6] which show that the rate constants for exothermic proton transfer reactions generally exhibit a gradual decrease with increasing ion kinetic energy. For example, for the one proton transfer reaction involving HCO^+ which was studied by these authors, viz. the reaction of HCO^+ with NH_3, the rate constant declined from a value of 2.1×10^{-9} cm^3 $molecule^{-1}$ s^{-1} at 300 K to ca. 1.3×10^{-9} cm^3 $molecule^{-1}$ s^{-1} at a center-of-mass kinetic energy of 1 eV. The medium-pressure mass spectrometer measurements of Pritchard and Harrison [1] were made at an ion source temperature approximately 75 K higher than our operating temperature and also a constant repeller field corresponding to an ion exit energy of either 2.4 or 3.4 eV. The observed systematic difference in the two sets of rate constants may also, in part, be attributable to possible differences in the internal state of excitation of the HCO^+ which was generated in two distinctly different ways: via the dissociative ionization of oxygen bases by electron impact in

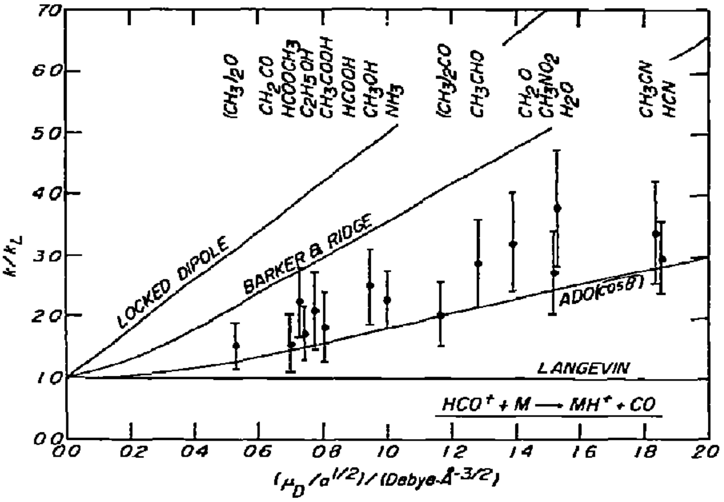


Fig. 2. A comparison of measured rate constants with capture rate constants predicted by various theories of collision for proton transfer reactions of HCO^+ with polar molecules. The solid bars represent the estimated accuracy of the measurements. k_L is the collision rate constant determined from the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

the ion source experiments, and via the protonation of CO by ion—molecule reaction in the flowing afterglow experiments.

Figure 2 compares all the proton-transfer rate constants given 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 [35], the average-dipole-orientation (ADO) theory (the $\cos\theta$ model) [36], the theory of Barker and Ridge [37], and the locked-dipole limit [38]. The permanent dipole moments, μ_D, were all taken from the compilation of Nelson et al. [39]. The polarizabilities, α, for H_2O, CH_2O, HCN, CH_3OH, $(CH_3)_2CO$, and NH_3 were taken from existing compilations [40—42]. The mean polarizabilities of the remaining molecules were calculated from bond and group polarizabilities [41] 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 the proton transfer to these molecules from HCO^+ proceeds with essentially unit probability, in concert with the behavior reported previously for other analogous systems [43]. 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 here previously for other proton transfer reactions. Barker and Ridge [37] 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.

Site(s) of protonation

Many of the molecules investigated in this study contain more than one potential site of protonation, albeit the measurements reported here do not provide any direct evidence for the site(s) actually protonated by HCO^+. Some insight into the availability of the various potential sites to the protonation by HCO^+ may be gained from thermodynamic considerations made possible by recent molecular orbital calculations [44—46] and ionization energy correlations [47] which have provided estimates of the intrinsic proton affinities of various sites in many of these molecules. The proton affinities listed in Table 1 are derived from experiment and should refer to the site of highest proton affinity, viz. the formation of the lowest energy tautomer, since they are based on step-wise equilibrium constant measurements for series of nearly thermoneutral reactions. The exothermicities quoted in Table 1 should therefore refer to the lowest energy route of protonation and thus be a measure of the maximum excess energy made available by reaction with HCO^+. A particular higher-energy site of protonation will then be available to HCO^+ only if this excess energy exceeds the difference in energy (or proton affinity) between the high-energy and ground-state tautomers. The extent to which this is the case for the compounds investigated in this study will now be considered in turn.

HCN, CH_3CN. The high-energy tautomer resulting from protonation on the cyano carbon atom should not be accessible at room temperature for ground-state reactants. In the case of HCN, according to the theoretical difference of 71 kcal mol^{-1} in the proton affinities of the two sites [44] and the maximum excess energy of only 28 kcal mol^{-1} made available by reaction with HCO^+, protonation on carbon should be endothermic by 43 kcal mol^{-1} and consequently highly unfavorable.

CH_2O, CH_3CHO, $(CH_3)_2CO$. Molecular orbital calculations predict an energy difference of at least 40 kcal mol^{-1} between the two tautomers of CH_2O corresponding to carbon and oxygen atom protonation [44]. This energy is higher than the maximum 28 kcal mol^{-1} available from the reaction of CH_2O with HCO^+ which is consequently expected to protonate preferentially at the oxygen site. Similar theoretical predictions for the energy difference between the tautomers corresponding to carbonyl carbon and oxygen protonation are not available for CH_3CHO and $(CH_3)_2CO$, although protonation at oxygen in CH_3CHO has been shown to lead to two isomers corresponding to a *syn* (or *cis*) and *anti* (or *trans*) arrangement of the proton to the carbonyl hydrogen only 1.2 kcal mol^{-1} apart in energy, the former being more stable. Both of these isomers should be accessible to the reaction of HCO^+ with CH_3CHO.

$HCOOH$, CH_3COOH. Molecular orbital calculations indicate that the high-energy form corresponding to protonation on the hydroxy oxygen in HCOOH lies 25 kcal mol^{-1} above the lowest of three conformers which can result from protonation on the carboxyl group [45]. The ionization energy

correlations of Benoit and Harrison [47] predict a similar energy difference of 26 ± 3 kcal mol^{-1} in the case of HCOOH and a difference of 27 ± 3 kcal mol^{-1} in the case of CH_3COOH. Protonation by HCO^+ at the hydroxy oxygen position in these two carboxylic acids should therefore be exothermic by ca. 9 and 17 kcal mol^{-1}, respectively.

$HCOOCH_3$. Molecular orbital calculations are not available in this case. The ionization energy correlations [47] indicate that the proton affinity of the methoxy oxygen is only ca. 22 kcal mol^{-1} less than that of the carbonyl oxygen. This means that the 45 ± 3 kcal mol^{-1} available from the reaction with HCO^+ is sufficient to protonate both sites even if only one-half of the exothermicity appears as internal excitation.

CH_2CO. Molecular orbital calculations indicate that the energies of the oxygen-protonated ketene and the α-carbon protonated isomer lie 29 and 65 kcal mol^{-1}, respectively, above that of the acetyl ion, CH_3CO^+ [46]. The reaction of ketene with HCO^+ is 51 ± 3 kcal mol^{-1} exothermic so that protonation at oxygen is energetically feasible.

Dissociative proton transfer

Although the majority of the reactions of HCO^+ studied in this investigation appeared to proceed simply by proton transfer to form predominantly (>99%) MH^+, the primary product spectrum observed with C_2H_5OH and CH_3COOH included substantial amounts of ions other than MH^+ with lower values of *m/z*. Evidently the transfer of a proton to these molecules caused substantial dissociation of MH^+ according to

$$HCO^+ + M \rightarrow [MH^+]^* + CO \qquad (7)$$

$$\hookrightarrow \text{products} \qquad (7a)$$

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 is 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. Dissociative proton transfer is also thermodynamically feasible for the reactions of HCO^+ with CH_3OH, $(CH_3)_2O$, CH_2O, CH_3CHO, $(CH_3)_2CO$, $HCOOCH_3$ and HCOOH. These will be considered in the section following, together with the two reactions for which some dissociative proton transfer was actually observed. The excess energy available in the form of reaction exothermicity is given by the difference in the proton affinity of CO and M which is included in Table 1. Auxiliary thermochemical information was taken from the recent compilation of Rosenstock et al. [48].

CH_3OH, C_2H_5OH. The exclusive formation of protonated methanol observed for the reaction of HCO^+ with CH_3OH is readily understood in terms

of the energetics of the unimolecular decomposition of this ion recently inferred from the results of investigations of the reaction of CH_3OH with H_3^+ done in a conventional ICR mass spectrometer [49], a tandem—ICR mass spectrometer [50], and a high-pressure chemical ionization source [51]. These investigations have suggested that, in the limit of complete collisional deactivation, H_3^+ ions react with CH_3OH at near-thermal kinetic energies to produce $CH_3OH_2^+$ ions and of these a significant fraction have sufficient energy to decompose either by cleavage of the C—O bond to produce CH_3^+ or by vicinal H_2 elimination to produce CH_2OH^+ according to

$$H_3^+ + CH_3OH \rightarrow [CH_3OH_2^+]^* + H_2 + 80 \tag{8}$$

$$\hookrightarrow CH_3^+ + H_2O - 64 \tag{8a}$$

$$\hookrightarrow CH_2OH^+ + H_2 - 32 \tag{8b}$$

where standard enthalpy changes have been indicated in kcal mol^{-1}. The validity of this interpretation was established from the results of investigations of analogous reactions involving D_3^+ [49,50]. The direct production of CH_2OH^+ by exothermic hydride ion abstraction

$$H_3^+ + CH_3OH \rightarrow CH_2OH^+ + 2H_2 + 48 \tag{9}$$

was observed to be restricted to highly excited H_3^+ ions [49,50]. In contrast, the observations reported here indicated no detectable decomposition (<0.1%) when CH_3OH was protonated with HCO^+, nor any evidence for the occurrence of hydride abstraction according to

$$HCO^+ + CH_3OH \rightarrow CH_2OH^+ + H_2CO + 6 \tag{10}$$

In this case the energetics for dissociative proton transfer are as follows

$$HCO^+ + CH_3OH \rightarrow [CH_3OH_2^+]^* + CO + 38 \tag{11}$$

$$\hookrightarrow CH_3^+ + H_2O - 64 \tag{11a}$$

$$\hookrightarrow CH_2OH^+ + H_2 - 32 \tag{11b}$$

The 38 ± 4 kcal mol^{-1} excess energy in the form of reaction exothermicity is much less than the 80 ± 4 kcal mol^{-1} available from the reaction with H_3^+. In fact, C—O cleavage is very endothermic so that it is not expected to occur, whereas H_2 elimination has remained exothermic by 6 kcal mol^{-1}. However, this latter fragmentation is also expected to be unfavorable, in this case because of the presence of a kinetic barrier which has been established from observations of the metastable decomposition of $[CH_3OH_2^+]^*$ generated from H_3^+ [51]. The kinetic energy release calculated for the metastable H_2 elimination from this ion amounts to a barrier height for the inverse association of CH_2OH^+ with H_2 of >21 kcal mol^{-1} which is more than sufficient to account for our failure to observe the formation of CH_2OH^+ via reaction (11b).

Similar considerations appear to apply for the reaction of HCO^+ with the

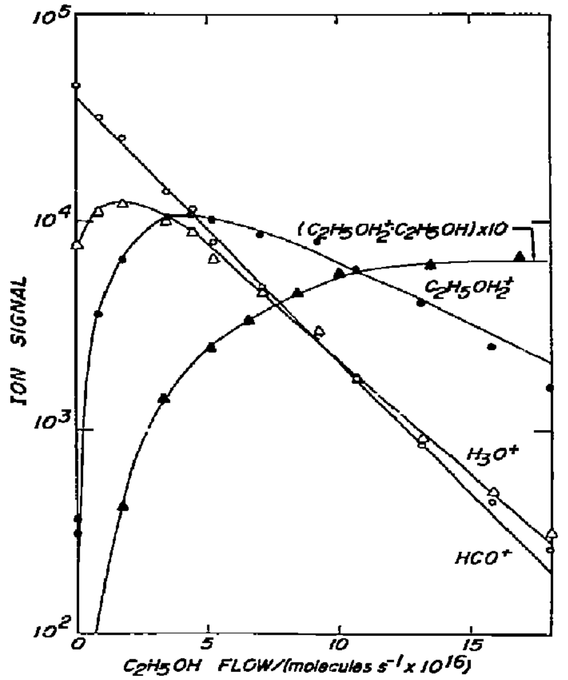


Fig. 3. The variation of the major positive ions observed upon the addition of C_2H_5OH into a flowing $CO—H_2$ plasma in which HCO^+ is initially a dominant ion. The decay of HCO^+ provides a rate constant of 2.2×10^{-9} cm^3 $molecule^{-1}$ s^{-1}. $T = 298$ K, $P = 0.442$ torr, $\bar{v} = 8.0 \times 10^3$ cm s^{-1}, and $L = 85$ cm.

next member in the homologous series, C_2H_5OH, for which the energetics are as follows

$$HCO^+ + C_2H_5OH \rightarrow [C_2H_5OH_2^+]^* + CO + 44 \qquad (12)$$

$$\rightarrow C_2H_5^+ + H_2O - 37 \qquad (12a)$$

$$\rightarrow C_2H_4OH^+ + H_2 - 18 \qquad (12b)$$

where $C_2H_4OH^+$ has been assumed to be protonated acetaldehyde. Our measurements indicated no evidence (<1%) for H_2 elimination to form a *m/z* 45 ion either by the decomposition (12b) which, by analogy with CH_3OH, is likely to have a kinetic barrier, or the hydride abstraction

$$HCO^+ + C_2H_5OH \rightarrow C_2H_4OH^+ + H_2CO + 25 \qquad (13)$$

Figure 3 shows that H_3O^+ was the only primary product ion observed apart from $C_2H_5OH_2^+$. The extent of C—O bond scission to produce $C_2H_5^+$ could not be ascertained since this ion could not be distinguished with our mass spectrometer from the reactant HCO^+ ion. Consequently the rate constant determined in this study from the decay of the *m/z* 29 ion may only be a lower limit. The observed H_3O^+ variation, corrected for mass discrimination, was fitted to provide a branching probability of 0.45 ± 0.1 for H_3O^+ production and thus 0.55 ± 0.1 for $C_2H_5OH_2^+$ production. These probabilities were not monitored over a large range in H_2 pressure and may both only be upper limits if some $C_2H_5^+$ is indeed produced and if it reacts further with C_2H_5OH to form H_3O^+. We propose that the observed production of H_3O^+ may be reasonably viewed to result from C—O bond scission in $[C_2H_5OH_2^+]^*$ with synchronous or near-synchronous proton transfer from $C_2H_5^+$ to H_2O prior to separation into products.

$(CH_3)_2O$. Only 47 ± 3 kcal mol^{-1} is available as excess energy in the form of reaction exothermicity in the protonation of dimethyl ether by HCO^+. This is not enough energy to bring about the C—O rupture of $[(CH_3)_2OH^+]^*$ into CH_3^+ and CH_3OH which requires 79 kcal mol^{-1}. Other conceivable decomposition channels which are allowed on thermodynamic grounds are

$$(CH_3)_2OH^+ \rightarrow CH_3CHOH^+ + H_2 - 9 \tag{14a}$$

$$\rightarrow CH_2OH^+ + CH_4 - 19 \tag{14b}$$

$$\rightarrow H_3O^+ + C_2H_4 - 23 \tag{14c}$$

These appeared not to be favorable, presumably because of the elaborate chemical redisposition which must be involved.

CH_2O, CH_3CHO, $(CH_3)_2CO$. Not unexpectedly, reaction with HCO^+ was observed in all of these cases to result in simple protonation of the molecule with no subsequent decomposition under our experimental conditions. The least endothermic routes of decomposition of the protonated aldehydes correspond to vicinal H_2 elimination according to

$$CH_2OH^+ \rightarrow HCO^+ + H_2 - 28 \tag{15}$$

$$CH_3CHOH^+ \rightarrow CH_3CO^+ + H_2 - 20 \tag{16}$$

Other studies have shown that CH_2OH^+ undergoes symmetry-forbidden 1,2-elimination of H_2 only in a reaction requiring at least 61 kcal mol^{-1} [52]. This is evident from Fig. 4 which shows the reaction coordinate for

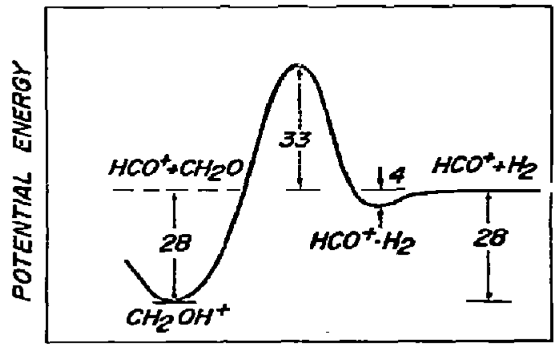


Fig. 4. Reaction coordinate vs. potential energy for the CH_2OH^+ system formed by reaction of ground-state HCO^+ ions with CH_2O. All energies are in kcal mol^{-1}.

the decomposition of CH_2OH^+ into HCO^+ and H_2, including the weakly bound intermediate $HCO^+ \cdot H_2$. Figure 4 has been constructed from previously reported low-temperature equilibrium studies of the reverse association [53] and measurements of the kinetic energy release in metastable decomposition [54]. The excess energy available to CH_2OH^+ from HCO^+ is only 28 ± 2 kcal mol^{-1}, well below the required 61 kcal mol^{-1}. Similar considerations should apply to the elimination of H_2 from CH_3CHOH^+ for which a maximum of 42 ± 3 kcal mol^{-1} of excess energy is available for deposition from HCO^+. However, a second route of decomposition may now become exothermic, viz.

$$CH_3CHOH^+ \rightarrow HCO^+ + CH_4 - 38 \qquad (17)$$

This decomposition involves a 1,3-shift of a hydrogen atom, a process thermally forbidden for the isoelectronic propene [55] and also shown to have a high barrier for the interconversion of vinyl alcohol and acetaldehyde [56]. In view of these high barriers it is unlikely that this mode of decomposition would occur. Again, hydride transfer is exothermic and is not observed to compete with the proton transfer in CH_3CHO. In the case of CH_2O, production of HCO^+ by hydride transfer would lead to an anomalously low rate constant.

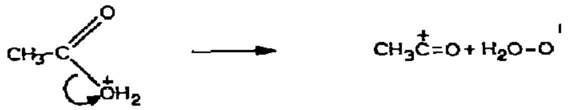
In the reaction with $(CH_3)_2CO$, sufficient excess energy (51 ± 3 kcal mol^{-1}) is conceivably available from HCO^+ to allow the following two modes of decomposition

$$(CH_3)_2COH^+ \rightarrow CH_3CO^+ + CH_4 - 22 \qquad (18a)$$

$$\rightarrow CH_2 \mathrel{\overset{\cdots}{-}} \overset{+}{C}H \mathrel{\overset{\cdots}{-}} CH_2 + H_2O - 46 \qquad (18b)$$

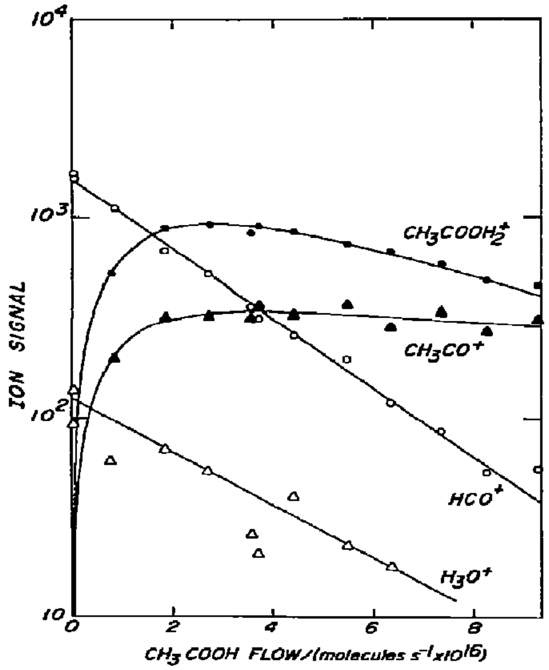
Neither of these products were observed. Again high barriers are likely to be associated with their formation as they both involve 1,3 hydrogen-atom shifts from and to the oxygen atom, respectively.

HCOOH, CH_3COOH, $HCOOCH_3$. For these molecules proton transfer was again the predominant reaction channel. However some dissociation of MH^+ was evident for CH_3COOH and $HCOOCH_3$ as indicated in Figs. 5 and 6. These observations can most reasonably be explained in terms of C—O fission corresponding to the $A_{Ac}1$ mechanism commonly invoked for the cleavage of esters, amides, and carboxylic acids in concentrated acid solutions [57]. For acetic acid this mechanism is



(19)

and requires protonation at the hydroxy oxygen. As discussed earlier, sufficient excess energy is available with HCO^+ to protonate this site. Alternatively, this tautomer may be achieved indirectly through carbonyl protonation



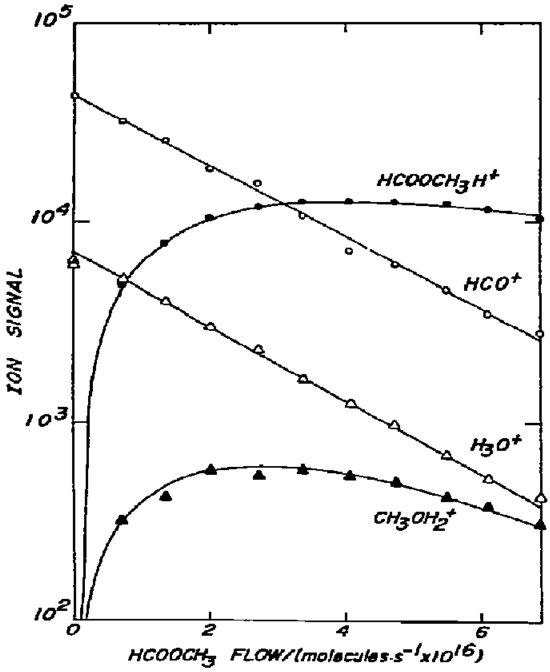
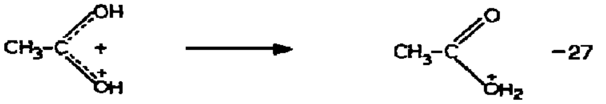


Fig. 5. Variation of ion signals recorded upon the addition of CH_3COOH into the reaction region in the SIFT configuration. Buffer gas = H_2, $T = 300$ K, $P = 0.356$ torr, $\bar{v} = 7.8 \times 10^3$ cm s^{-1}, and $L = 59$ cm.

Fig. 6. The variation in the major positive ions observed upon the addition of $HCOOCH_3$ into a flowing CO—H_2 plasma in which HCO^+ is initially a dominant ion. The decay of HCO^+ provides a rate constant of 2.8×10^{-9} cm^3 $molecule^{-1}$ s^{-1}. $T = 299$ K, $P = 0.367$ torr, $\bar{v} = 7.6 \times 10^3$ cm s^{-1}, and $L = 85$ cm.

followed by a 1,3 hydrogen shift according to



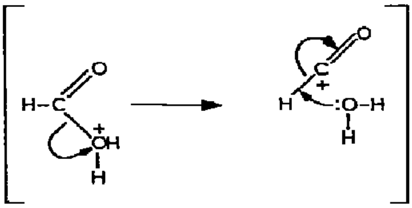
(20)

However, this route seems more improbable as barriers to 1,3 hydrogen shifts in similar systems are known to be high [56,58]. The results plotted in Fig. 5 indicate that about 20% of the protonated acetic acid acquires sufficient energy under our experimental conditions to decompose ultimately into CH_3CO^+ and H_2O.

The analogous decomposition of $HCOOH_2^+$ into HCO^+ and H_2O is 7 kcal mol^{-1} endothermic and therefore not expected to occur. However, in this case an alternate route of decomposition becomes exothermic, viz.

$$HCOOH_2^+ \rightarrow H_3O^+ + CO - 18 \qquad (21)$$

which can also be viewed as an $A_{Ac}1$ cleavage, albeit accompanied by the synchronous transfer of the proton from the carbon atom:



(22)

H_3O^+ was not observed to be a product indicating perhaps that too small a fraction of the 35 kcal mol^{-1} of excess energy is available to overcome the overall barrier to C—O cleavage, which is at least 25 kcal mol^{-1} [45,47]. Independent measurements performed here, which will be reported elsewhere [59], have established that this mode of decomposition does occur to an appreciable extent with the much stronger acid H_3^+.

The small production (3 ± 1%) of $CH_3OH_2^+$ shown in Fig. 6 which apparently arises from the reaction of HCO^+ with $HCOOCH_3$ could again be explained in terms of the modified $A_{Ac}1$ mechanism in which the proton from the carbon atom is transferred synchronously to the developing methanol molecule. This channel is exothermic by 28 kcal mol^{-1} while the formation of the products HCO^+ + CH_3OH via the $A_{Ac}1$ mechanism without concomitant proton transfer is 10 kcal mol^{-1} endothermic. However, a purity check with conventional gas chromatograph—mass spectrometer techniques indicated that the methyl formate contained 2 ± 1% methanol which is sufficient to account for the bulk of the observed increase in the $CH_3OH_2^+$ signal. As previously noted, HCO^+ rapidly transfers a proton to methanol. Other dissociative proton transfer channels can be envisaged, e.g.

$$HCOO(CH_3)H^+ \rightarrow CH_3CO^+ + H_2O - 7 \quad (23a)$$

$$\rightarrow H_3O^+ + CH_2CO - 36 \quad (23b)$$

but these were not observed, probably because considerable skeletal rearrangement would be required to achieve them. It is evident from Fig. 6 that the $CH_3OH_2^+$ reacts further with $HCOOCH_3$ by proton transfer. The H_3O^+ ion present initially as a result of H_2O impurities in the flowing plasma also reacts with $HCOOCH_3$ in a manner similar to that of HCO^+, as will be reported elsewhere [60], but does not contribute significantly to the rise in the $CH_3OH_2^+$ signal shown in Fig. 6.

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