J. Am. Chem. Soc. **1983**, *105*, 2562–2565

Experimental Investigation of Gaseous Ionic Structures of Interstellar Importance: HCO^+ and HOC^+

A. J. Illies, M. F. Jarrold, and M. T. Bowers*

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. *Received October 22, 1982*

Abstract: Collision-induced dissociation (CID) fragmentation patterns for ions originating from different precursors are consistent with two structures for m/z 29 (HCO^+ and HOC^+). These results are in agreement with the predictions of recent ab initio calculations which indicate that two stable structures should be experimentally observable. The structure of protonated CO formed by the reaction between H_3^+ and CO was investigated since it has been suggested that both HCO^+ and HOC^+ are formed. The experimental data indicates that the product is predominantly the most stable isomer, HCO^+; however, 6 ± 5% of the less stable HOC^+ isomer is produced.

Introduction

Recent ab initio calculations[1-3] on the isomeric species HCO^+ and HOC^+ predict that HCO^+ is 157 kJ mol^{-1} more stable than HOC^+ with a barrier to rearrangement from the less stable HOC^+ structure of 150 kJ mol^{-1}. These results suggest that the isomeric species HCO^+ and HOC^+ should be experimentally observable. Establishing if these predicted structures are stable is important because these ions play an important role in the chemistry of interstellar clouds.[4-6] HCO^+, for example, has been referred to as the "cornerstone of the ion-molecule chemistry in outer-space."[7] Herbst, Klemperer, and co-worker[7,8] proposed that formation of the formyl ion in interstellar space occurs primarily via the reaction

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

and that isoformyl ion, HOC^+, may be produced in a similar manner

$$H_3^+ + CO \rightarrow HOC^+ + H_2 \qquad (2)$$

These ideas are supported by the more recent calculations of Nobes and Radom.[1]

HCO^+ is well-known in the laboratory,[9] and its presence in interstellar clouds has been confirmed by detection of microwave emission.[6,10] Less is known about HOC^+; however, during the course of this work we learned that Woods[11] has assigned some of the lines in the spectrum from a discharge through a CO and H_2 mixture to HOC^+. Using this information, Irvine[12] has found evidence for HOC^+ in an interstellar dust cloud. He estimates that HOC^+ is 300 times less abundant than HCO^+ in the same interstellar cloud. The existence of the isoformyl ion in interstellar clouds has important consequences with regard to the modeling of the chemistry in these clouds since proton transfer from HOC^+ is approximately 157 kJ mol^{-1} more exothermic than from HCO^+.[1] Hence the subsequent reactions of HOC^+ may be very different from those of HCO^+. For example, proton transfer to CH_4 is exothermic for HOC^+ but endothermic for HCO^+.

On the basis of their calculations, Nobes and Radom[1] suggested that HOC^+ could react with CO with no activation barrier to produce HCO^+, i.e.

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

Hence CO may catalyze isomerization to the more stable structure. This could explain why no evidence for the existence of HOC^+ was found in the flowing afterglow experiments of Tanner et al.[13] and suggests that experiments designed to detect the high-energy isomer should be carried out under conditions of trace or no CO.

In this study we have used collision-induced dissociation (CID) to investigate whether the high energy but theoretically stable isomer can be experimentally observed. This work complements the previous theoretical work on these ions.[1-3] We have also investigated the structure of the protonated CO ion formed in the reaction between H_3^+ and CO to determine if the HOC^+ ion should be considered in the modeling of interstellar chemistry. A preliminary account of this work has been given.[14]

Experimental Section

Experiments were performed with a reverse geometry mass spectrometer (VG Micromass ZAB-2F) fitted with a combined EI/CI temperature-variable ion source constructed at the University of California, Santa Barbara (UCSB). Ion source pressures were either measured directly with a capacitance monometer (MKS Baratron 170 M) or with an ionization gauge calibrated with a capacitance manometer. Ions were formed using 70–150-eV electron impact. The ion source temperature was ~50 °C for all studies. Both analog and pulse-counting detection methods were employed.

The experimental methods used in CID studies have been reported previously[15] and will only be briefly reviewed here. After exiting the ion source, the ions are accelerated to 8 kV, mass analyzed by the magnet, and focused into the collision cell located at the focal point between the magnet and electrostatic analyzer (ESA). Helium was added to the collision cell until the main beam intensity was reduced by 50%. The CID fragmentation pattern was then obtained by scanning the ESA.

High resolution mass spectra (>10 000 fwhm) were measured for the main beam to ensure that the intensities of other ions at the same nominal mass were small. For m/z 29 impurity peaks were N_2H^+, $C_2H_5^+$, and $^{13}CO^+$. The $C_2H_5^+$ and $^{13}CO^+$ ions were present at less than 1%, while N_2H^+ was present at a few percent in the majority of the work. The N_2H^+ ion does not have CID peaks at m/z 12, 13, 16, and 17 and so does not significantly interfere with the CID pattern of either HOC^+ or HCO^+. In the studies on the reaction of H_3^+ with CO, N_2H^+ was present

---

[1] Nobes, R. H.; Radom, L. *Chem. Phys.* **1981**, *60*, 1.

[2] Bruna, P. J.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys.* **1975**, *10*, 323.

[3] Forsen, S.; Ross, B. *Chem. Phys. Lett.* **1970**, *6*, 128.

[4] Smith, D.; Adams, N. G. *Astrophys. J.* **1977**, *217*, 741.

[5] Watson, W. D. *Astrophys. J.* **1977**, *217*, 741.

[6] Snyder, L. E.; Hollis, T. M.; Lovas, F. J.; Ulich, B. L. *Astrophys. J.* **1976**, *209*, 67.

[7] Herbst, E.; Norbeck, J. M.; Certain, P. R.; Klemperer, W. *Astrophys. J.* **1976**, *207*, 110.

[8] Herbst, E.; Klemperer, W. *Astrophys. J.* **1973**, *185*, 505.

[9] Woods, R. C.; Dixon, T. A.; Sackally, R. J.; Szanto, P. G. *Phys. Rev. Lett.* **1975**, *35*, 1269.

[10] Klemperer, W. *Nature (London)* **1970**, *227*, 1230.

[11] Gudeman, C. S.; Woods, R. C. *Phys. Rev. Lett.* **1982**, *48*, 1344.

[12] Irvine, W. *Chem. Eng. News* **1982**, *60* (11), 19. See also: Woods, R. C.; Gudeman, C. S.; Dickman, R. L.; Goldsmith, P. F.; Huguenin, G. R.; Irvine, W. M.; Hjalmarson, Å.; Nyman, L.-Å.; Olofsson, H. *Astrophys. J.*, in press.

[13] Tanner, S. D.; MacKay, G. I.; Hopkinson, A. L.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *29*, 153; Tanner, S. D.; MacKay, G. I.; Bohme, D. K. *Can. J. Chem.* **1979**, *57*, 2350.

[14] Illies, A. J.; Jarrold, M. F.; Bowers, M. T. *J. Chem. Phys.* **1982**, *77*, 5847.

[15] See for example: "Collision Spectroscopy", Cooks, R. G., Ed.; Plenum Press: New York, 1978. Nibbering, N. M. M.; Nishishita, T.; Van de Sande, C. C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1978**, *70*, 45; Illies, A. J.; Liu, S.; Bowers, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 5674.

0002-7863/83/1505-2562$01.50/0

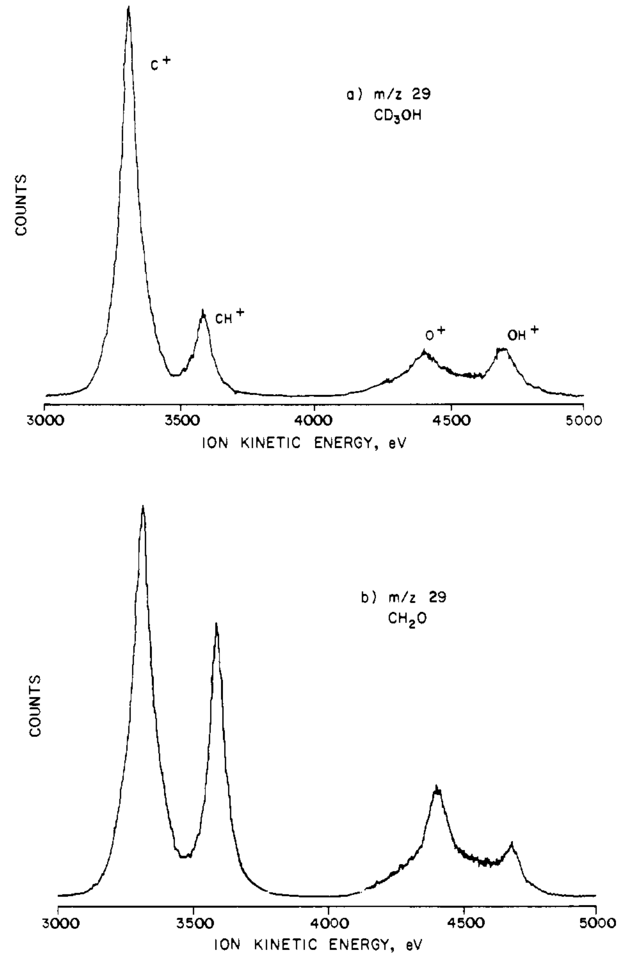


Figure 1. CID fragmentation pattern from *m/z* 29 derived from electron impact of (a) methanol-d_3, and (b) formaldehyde. Note the bimodal energy release in the O^+ peak at *m/z* 16 (4400 eV).

at 30% of the main beam intensity at the lowest CO pressure used. Since the N^+ and CH^+ peaks were not completely resolved, the N_2H^+ background CID spectrum was deconvoluted from the CID spectrum. This resulted in a change of less than 3% in the C^+/CH^+ ratio at the lowest CO pressure used.

In the first set of experiments, CID spectra were recorded for *m/z* 29 ions resulting from electron impact on a number of neutral precursors. To ensure that changes observed in the CID spectra were due to structural differences and not internal energy effects,[16] a number of experiments were performed using He CI. Under these conditions, ions were produced predominantly by charge transfer or dissociative charge transfer and undergo a large number of stabilizing collisions prior to leaving the source.

The structure of the product of the proton transfer reaction between H_3^+ and CO was investigated by measuring the CID fragmentation pattern as a function of CO pressure in an H_2/CO mixture under CI conditions. The CO pressure was varied over the range 4×10^{-5} to 3×10^{-2} torr with an H_2 pressure of 0.1 torr. The probability of *m/z* 29 undergoing a collision with CO can be estimated from the average ion source residence time and CO pressure assuming a Langevin collision rate. The average ion source residence time for *m/z* 29 was determined from the ion source residence time distribution (RTD) which was measured by pulsing the ionizing electron beam and measuring the ion arrival time at the detector using the method of Sroka et al.[17]

All samples were obtained from commercial sources and were not further purified except for several freeze-pump-thaw cycles. The CO (Research purity), H_2 (Ultra-High purity), He (99.995%), and dimethyl ether (99%) were supplied by Linde. The H_2CO was obtained by depolymerizing paraformaldehyde (Aldrich) by heating. CH_3OH (AR grade) and CH_3COOH (AR grade) were both obtained from Malinckrodt. The $HCOOCH_3$ was obtained from Aldrich, and the CD_3OH (99 atom % D) from Merck Sharp & Dohme.

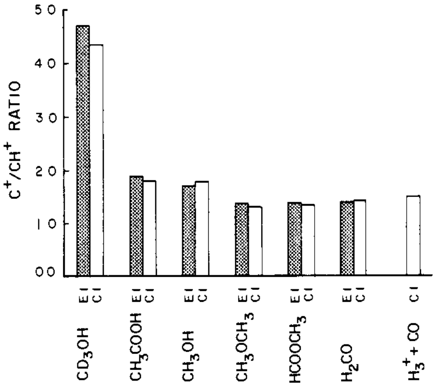


Figure 2. A bar graph showing the collision-induced C^+/CH^+ ratio resulting from CID on *m/z* 29 formed by electron impact and chemical ionization of various precursor neutral molecules and by reaction of H_3^+ with CO.

Results and Discussion

Figure 1 shows part of the CID spectrum resulting from the *m/z* 29 fragment ion from electron impact on (a) CD_3OH and (b) H_2CO. The peak at *m/z* 28 was not used for structure elucidation. As will be discussed in more detail below, we assign the CID fragmentation pattern of *m/z* 29 from CD_3OH EI as arising mainly from HOC^+, and that due to *m/z* 29 from H_2CO EI as arising mainly from HCO^+. This assignment is supported by the larger CH^+ intensity in the *m/z* 29 from H_2CO spectrum and the larger OH^+ intensity in the *m/z* 29 from CD_3OH spectrum. Note in Figure 1b the bimodal kinetic energy release associated with the production of O^+. The larger release component makes a quantitative determination of the OH^+ intensity difficult; therefore we have concentrated on the relative intensities of the C^+ and CH^+ peaks for determining the isomeric content.

Figure 2 summarizes our results for the C^+/CH^+ ratio determined from the CID spectra of the *m/z* 29 ion derived from electron impact and He CI on a number of precursors. The C^+/CH^+ ratio for *m/z* 29 from $HCOOCH_3$, CH_3OCH_3 and H_2CO are similar. The C^+/CH^+ ratio is larger for *m/z* 29 from CH_3OH, CH_3COOH and CD_3OH suggesting that at least some of the *m/z* 29 ions from these precursors have the less stable HOC^+ structure. The similarity between the electron impact data and He CI data suggests that the differences in the C^+/CH^+ intensity ratio are not due to internal energy effects. The observation that CH_3OH produces some HOC^+, and that CD_3OH produces larger amounts of HOC^+ is consistent with the suggestions of Berkowitz.[18] He performed a photoionization study of isotopically labeled methanol and suggested that 10% of the *m/z* 29 peak from CH_3OH was due to HOC^+.

To determine if both HCO^+ and HOC^+ are produced in the proton transfer reaction between H_3^+ and CO, the CID fragmentation pattern was measured as a function of CO pressure in an H_2/CO mixture.[19] Figure 3 shows a plot of the C^+/CH^+ ratio against CO pressure. By use of the *m/z* 29 ion source residence times measured by pulsing the electron beam and assuming a Langevin collision rate, the CO pressure scale has been transformed to a scale showing the average collision probability between HCO^+/HOC^+ and CO. The C^+/CH^+ ratio remains

---

(16) Jarrold, M. F.; Illies, A. J.; Kirchner, N. J. Bowers, M. T. *Org. Mass Spectrom.*, in press.

(17) Sroka, G.; Chang, C.; Meisels, G. G. *J. Am. Chem. Soc.* **1982**, *94*, 1052.

(18) Berkowitz, J. *J. Chem. Phys.* **1978**, *69*, 3044.

(19) Numerous experiments were carried out with EI on dimethyl ether and formaldehyde and with CI on H_2/CO mixtures (using a CO partial pressure which lies on the flat region in Figure 3) in order to determine if the difference noted in the C^+/CH^+ ratio were due to the formation of small amounts of HOC^+ (<10%) or if they were simply due to the scatter in our data. Since the C^+/CH^+ ratio is sensitive to the He collision gas pressure, comparisons could not be made between sets of data that were taken if the collision gas pressure had changed. However, numerous experiments were carried out without changing any instrumentation parameters. The results of these experiments always show that the C^+/CH^+ ratio from *m/z* 29 resulting from the reaction between H_3^+ and CO is higher than the ratio determined from formaldehyde and dimethyl ether.

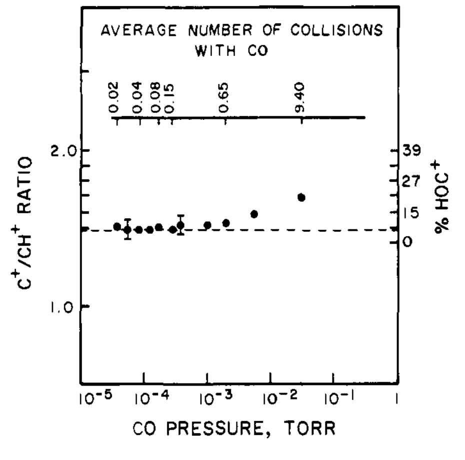


Figure 3. A plot of the collision-induced C^+/CH^+ ratio for m/z 29 formed in an H_2/CO mixture as a function of CO partial pressure in the ion source. The top scale shows the average number of collisions between m/z 29 and CO assuming a Langevin collision rate. The scale on the right gives the percent HOC^+ when the curve in Figure 4 is used.

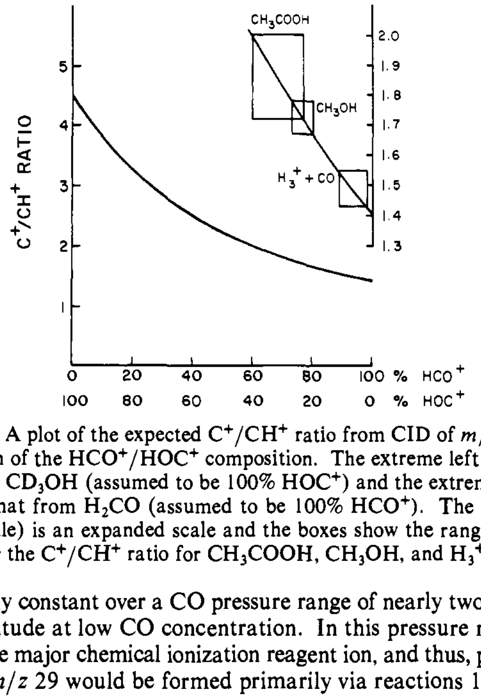


Figure 4. A plot of the expected C^+/CH^+ ratio from CID of m/z 29 as a function of the HCO^+/HOC^+ composition. The extreme left point is that from CD_3OH (assumed to be 100% HOC^+) and the extreme right point is that from H_2CO (assumed to be 100% HCO^+). The top line (right scale) is an expanded scale and the boxes show the range determined for the C^+/CH^+ ratio for CH_3COOH, CH_3OH, and H_3^+ + CO.

essentially constant over a CO pressure range of nearly two orders of magnitude at low CO concentration. In this pressure regime, H_3^+ is the major chemical ionization reagent ion, and thus, product ions at m/z 29 would be formed primarily via reactions 1 and 2. Extrapolating the data shown in Figure 3 to zero CO partial pressure yields 1.49 ± 0.06 for the C^+/CH^+ ratio. This ratio may be compared with the ratio 1.41 ± 0.03 determined from EI on formaldehyde (Figure 2).

Figure 4 shows the calculated C^+/CH^+ ratios as a function of isomeric composition determined assuming that the CID fragmentation pattern of pure HCO^+ is given by that of m/z 29 from formaldehyde EI and the CID fragmentation pattern of pure HOC^+ is given by that of m/z 29 from EI on CD_3OH.[20] The calculated C^+/CH^+ ratio is given by

$$\frac{C^+}{CH^+} = \frac{fI^{C^+}_{HOC^+} + (1-f)I^{C^+}_{HCO^+}}{fI^{CH^+}_{HOC^+} + (1-f)I^{CH^+}_{HCO^+}} \tag{4}$$

where f is the fraction of HOC^+ isomer and I^n_m is the intensity of fragment ion n arising from isomer m normalized to the main beam intensity. It is important that fragment intensities normalized to the main beam intensity are used since, if a simple intensity ratio were used, the calculated C^+/CH^+ ratio would be a straight line and the calculated isomeric composition would be in error.

The boxes in Figure 4 represent the outer limits of both the spread and the statistical errors in our data. The graph indicates that 33 ± 7% of the m/z 29 ion from EI on CH_3COOH is HOC^+ and 25 ± 3% of the m/z 29 ion from EI on CH_3OH is HOC^+. Berkowitz[18] estimated that 10% of the m/z 29 peak from CH_3OH was due to HOC^+ on the basis of a photoionization study of isotopically labeled methanol. When CO is protonated with H_3^+, Figure 4 shows that 6 ± 4% HOC^+ is produced. Including the uncertainty in the C^+/CH^+ ratio for m/z 29 from EI on formaldehyde yields a value of 6 ± 5%. In other experiments carried out under slightly different conditions,[19] the C^+/CH^+ ratio was always higher for the m/z 29 produced in the reaction between H_3^+ and CO than that determined from m/z 29 resulting from EI and He CI on formaldehyde and dimethyl ether. These results all indicate that at least some HOC^+ is produced in reaction 2. On the basis of simple dynamical considerations, we might expect the H_3^+ to approach the O and C ends of the CO molecule with equal probability leading to equal proportions and HCO^+ and HOC^+. However, a low-energy encounter between an ion and molecule may not be a single-collision event.[21] Multiple collisions might be expected to lead to formation of products in proportion to the number of available product states and hence the product would be predominantly HCO^+, as observed.

Figure 3 shows that as the CO partial pressure is raised above ~0.001 torr the C^+/CH^+ ratio begins to increase. The increase is probably brought about by the formation of HOC^+ by a different set of reactions. Possibilities are[22,23]

$$CO^{+}\cdot + H_2 \rightarrow HCO^+ + H\cdot \quad (\Delta H = -200\ \text{kJ mol}^{-1}) \tag{5}$$

$$CO^{+}\cdot + H_2 \rightarrow HOC^+ + H\cdot \quad (\Delta H \sim -43\ \text{kJ mol}^{-1}) \tag{6}$$

and

$$H_2^{+}\cdot + CO \rightarrow HCO^+ + H\cdot \quad (\Delta H = -336\ \text{kJ mol}^{-1}) \tag{7}$$

$$H_2^{+}\cdot + CO \rightarrow HOC^+ + H\cdot \quad (\Delta H = -179\ \text{kJ mol}^{-1}) \tag{8}$$

Smith and Adams[4] have reported a rate constant of 2×10^{-9} mol^{-1} cm^3 s^{-1} for the reaction between $CO^{+}\cdot$ and H_2. Kim and Huntress[24] have studied the reaction between $H_2^{+}\cdot$ and CO. They reported a total rate constant of 2.8×10^{-9} mol^{-1} s^{-1} and the product branching ratio was 77% proton transfer and 23% charge transfer. These reactions might be expected to generate more HOC^+ than proton transfer from H_3^+ because they are more exothermic. The enthalpy change for proton transfer from ground state H_3^+ to generate HCO^+ is $\Delta H = -169$ kJ mol^{-1} and for HOC^+ is $\Delta H \simeq -12$ kJ mol^{-1}.[23] Another possibility is that the reactant H_3^+ ions may be vibrationally excited at large CO partial pressures. Nascent H_3^+ formed from reaction of $H_2^{+}\cdot$ with H_2 is known to have an average internal energy of 250 kJ/mol,[25] and the reaction of vibrationally excited H_3^+ may result in the formation of more HOC^+.

The increase in the C^+/CH^+ ratio apparent in Figure 3 raises a question concerning the catalytic conversion of HOC^+ to HCO^+ by CO (reaction 3). At ~0.03 torr CO, the C^+/CH^+ ratio

---

(20) Both theory[1] and experiment[18] indicate the threshold for formation of HCO^+ from CD_3OH should be substantially lower than the threshold for formation of HOC^+. Formation of HCO^+ from CD_3OH takes substantial rearrangement, however, and the $k(E)$ vs. E curve should rise relatively slowly above threshold. The formation of HOC^+, on the other hand, is a mechanistically simple process and hence $k(E)$ vs. E should rise relatively rapidly above threshold. Hence, for energies substantially above threshold, such as those employed here, the HOC^+ isomer should comprise essentially 100% of the m/z 29 intensity.

(21) Wolf, F. A. In "Interactions between Ions and Molecules"; Ausloos, P., Ed.; Plenum Press: New York, 1975.

(22) In principle, it is also possible that the reactions leading to m/z 29 result in excited electronic or vibronic state(s) resulting in a different C^+/CH^+ ratio; however, since these experiments were carried out under CI conditions, it is more likely that the higher C^+/CH^+ ratio is due to the formation of HOC^+.

(23) Thermochemical values were derived using data given in ref 1; in Walder, R.; Franklin, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 85; and in Rosenstock; H. M., Draxl, K. Steiner, B. W.; Herron, J. T. *J. Chem. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. No. 1 (Energetics of Gaseous Ions).

(24) Kim, J. K.; Huntress, W. T., Jr. *J. Chem. Phys.* **1975**, *62*, 2820.

(25) Bowers, M. T.; Chesnavich, W. J.; Huntress, W. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 357.

indicates that approximately 25% of the m/z 29 is HOC^+. At this pressure an average of 10 collisions with CO are expected to occur before HOC^+ exists the ion source. The nascent product distributions resulting from reactions 5–8 are not known and subsequently more than 25% HOC^+ could be formed initially. However, the observed increase in the C^+/CH^+ ratio suggests that reaction 3 occurs with a rate substantially less than the collision rate, which contradicts the suggestions of Nobes and Radom.[1] Experiments designed to study the catalytic conversion of HOC^+ to HCO^+ (reaction 3) as well as reactions 5–8 were not successful due to a large $^{13}CO^+$ contribution to the main beam.

Conclusion

Both HCO^+ and HOC^+ have been detected confirming the predictions of ab initio calculations[1-3] which concluded that both of these structures should be experimentally observable. The reaction between H_3^+ and CO appears to produce 6 ± 5% HOC^+ and thus may be one of the major pathways leading to this ion in interstellar space. In addition, HOC^+ does not appear to be rapidly converted to HCO^+ by reaction with CO as previously thought.

Acknowledgment. The support of the National Science Foundation under Grant CHE80-20464 and partial support by the California Space Institute are gratefully acknowledged. One of us (M.F.J.) wishes to acknowledge the Science and Engineering Research Council (U.K.) for a NATO/SERC fellowship.

Registry No. CO, 630-08-0; HCO^+, 17030-74-9; HOC^+, 60528-75-8; CD_3OH, 1849-29-2; CH_3COOH, 64-19-7; CH_3OH, 67-56-1; CH_3OCH_3, 115-10-6; $HCOOCH_3$, 107-31-3; H_2CO, 50-00-0.

Gas-Phase Hydrogen–Deuterium Exchange Reactions of HO^- and DO^- with Weakly Acidic Neutrals

Joseph J. Grabowski, Charles H. DePuy,* and Veronica M. Bierbaum

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80309. *Received July 19, 1982*

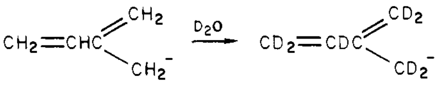
Abstract: Rate constants for hydrogen–deuterium exchange reactions between HO^- and DO^- and a series of weakly acidic neutrals, both organic and inorganic, have been measured in the gas phase by using the selected ion flow tube (SIFT) technique. The reaction efficiencies are discussed in terms of the initial ion–dipole complex energies, the relative acidities of the neutrals, and the change in solvation energy accompanying proton transfer; the effect of these energies on transition-state properties profoundly influences the outcome of the reactions. Exchange occurs rapidly between hydroxide and most aromatic and vinyl compounds but is relatively inefficient for hydrogen. The efficiency for exchange with ammonia is intermediate. Ethylene, dimethyl ether, and methane do not exhibit exchange.

Proton transfer is one of the most fundamental of chemical processes and so it is not surprising that it has been the subject of many investigations in the field of gas-phase ion–molecule chemistry. By combining the results obtained from a wide variety of experimental techniques, including ion cyclotron resonance spectroscopy, high-pressure mass spectrometry, and the flowing afterglow method, Bartmess and McIver[1] and Aue and Bowers[2] have compiled extensive tabulations of gas-phase acidities and basicities. Brauman and co-workers[3] and more recently Lias and co-workers[4] have shown how the kinetics of proton transfer can be useful in probing the nature of the potential energy surfaces for ion–molecule reactions. Indeed most groups active in the field of gas-phase ion–molecule chemistry have studied one aspect or another of proton-transfer processes.

Our own interest in this area arose from our discovery of the facile hydrogen–deuterium exchange reactions between carbanions and D_2O in the gas phase. Using a flowing afterglow apparatus, we found that carbanions, for example, the allylic anions obtained by proton abstraction from 1-pentene, will exchange protons for deuterium when allowed to react in the gas phase with D_2O (eq 1).[5] Less basic anions, for example, those stabilized by two double

$$CH_3CH_2\bar{C}HCH{=}CH_2 \xrightarrow{D_2O} C_5D_9^-, C_5D_8H^- \ldots \qquad (1)$$

bonds or adjacent to carbonyl or other electron-withdrawing groups, do not exchange with D_2O but do so with stronger gas-phase acids (CH_3OD or CF_3CH_2OD).[6] More recently we showed that protons less acidic than those in water (e.g., vinyl or aryl protons) can also be exchanged with D_2O provided they are incorporated within anions that are less basic than HO^- (eq 2).[7]



$$CH_2{=}CHC({=}CH_2)CH_2^- \xrightarrow{D_2O} CD_2{=}CDC({=}CD_2)CD_2^- \qquad (2)$$

These exchange reactions are useful in probing ion structure since isomeric ions will often exchange different numbers of protons. This method has also been applied to negative-ion chemical ionization mass spectrometry.[8]

A general, qualitative picture of the process by which H–D exchange is thought to occur is summarized in eq 3. A carbanion

$$RCH_2^- + D_2O \rightleftarrows \underset{\text{I}}{[RCH_2^-{\cdot}D_2O]} \rightleftarrows \underset{\text{II}}{[RCH_2D{\cdot}DO^-]} \rightleftarrows \underset{\text{III}}{[RCHD^-{\cdot}HOD]} \rightleftarrows RCHD^- + HOD \qquad (3)$$

attracts D_2O by ion–dipole and ion-induced dipole forces and they enter into a relatively long-lived reaction complex I that contains

---

(1) Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979.

(2) Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979.

(3) Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 2906–2913.

(4) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 3641–3647. Hunter, E. P.; Lias, S. G. *J. Phys. Chem.* **1982**, *86*, 2769–2775.

(5) Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650–7653.

(6) DePuy, C. H.; Bierbaum, V. M.; King, G. K.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2921–2922.

(7) Squires, R. R.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 4256–4258.

(8) Hunt, D. F.; Sethi, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 6953–6963.

0002-7863/83/1505-2565$01.50/0