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LABORATORY STUDIES OF SOME ION-ATOM REACTIONS RELATED TO INTERSTELLAR MOLECULAR SYNTHESIS

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ABSTRACT

The rate coefficients and product ions have been determined for reactions involving C^+, CH^+, $CH_2{}^+$, $CH_3{}^+$, $CH_5{}^+$, $C_2{}^+$, C_2H^+, $C_2H_2{}^+$, D^+, OH^+, and H_2O^+ ions with N and O atoms and NO molecules at 300 K. The values obtained for the rate coefficients are generally substantial fractions of the collision-limiting values, indicating that ion-atom reactions can be important steps in the synthesis of some of the molecules observed in interstellar clouds, in accordance with previous models.

Subject headings: interstellar: molecules — laboratory spectra — molecular processes

I. INTRODUCTION

It is now generally accepted that positive-ion–neutral reactions play an important role in the synthesis of some of the molecules observed in interstellar clouds (see reviews by Herbst and Klemperer 1976; Watson 1976; Black and Dalgarno 1977). Laboratory studies have provided many of the rate coefficients required to model interstellar ion chemistry (see Sinnott 1973; Ferguson 1973; Sieck and Lias 1976; Huntress 1977; Albritton 1978; Sieck 1979). For example, recent investigations (Smith and Adams 1977, 1978) have determined the rate coefficients for the reactions of several of the astrophysically important $C_nH_m{}^+$ ions with H_2, which is the most abundant molecular species in such regions. However, most of the ion-chemical models, particularly those of diffuse clouds where the atom-to-molecule ratio is relatively high, include ion-atom reactions, which are a class of ion-neutral reactions for which the relevant data are still somewhat sparse. There have been some laboratory studies of astrophysical ion-atom reactions (e.g., Fehsenfeld and Ferguson 1972; Fehsenfeld 1976; Karpas, Anicich, and Huntress 1979), which have shown that the rate coefficients of such reactions can often be fast, thus reinforcing the importance of including such reactions in interstellar ion-chemical models and the need for further laboratory measurements.

The predominant reactive atomic species present in diffuse interstellar clouds are H, C, N, and O atoms (Black and Dalgarno 1977). The reaction of these atoms with the "chain-initiating" ions like CH^+ could be competitive with the reactions of these ions with molecular hydrogen. These atoms might also exist in significant concentrations even in the shielded regions of dense clouds (Iglesias 1977), where they would be able to react with the more complex positive ions, especially the "chain-terminating" ions like $CH_5{}^+$, which react only slowly, if at all, with molecular hydrogen. Furthermore, while the importance of the atom reactions with the more complex ions clearly depends on the reaction rates and the atom concentrations, it is not inconceivable that they could compete with the radiative-association reactions with H_2, which have been suggested by Smith and Adams (1977, 1978).

Thus, there is a clear need for further laboratory studies of ion-atom reactions of interstellar interest. The present work contributes in that regard by reporting the measurement of the thermal-energy rate coefficients of the reactions of several C- and H-containing positive ions with N and O atoms. The reactions of these ions with NO were also examined. While these were a by-product of the ion-atom reaction investigation, these NO data are not without astrophysical interest, since this neutral has recently joined the list of observed interstellar molecules (Liszt and Turner 1978).

II. EXPERIMENTAL APPARATUS AND TECHNIQUES

The measurements were carried out at the National Oceanic and Atmospheric Administration (NOAA) laboratories in Boulder using a selected-ion flow tube (SIFT) (Adams and Smith 1976*a*) modified for reactant-atom addition and shown schematically in Figure 1. The principles of the SIFT technique and its applications have been reviewed recently (Smith

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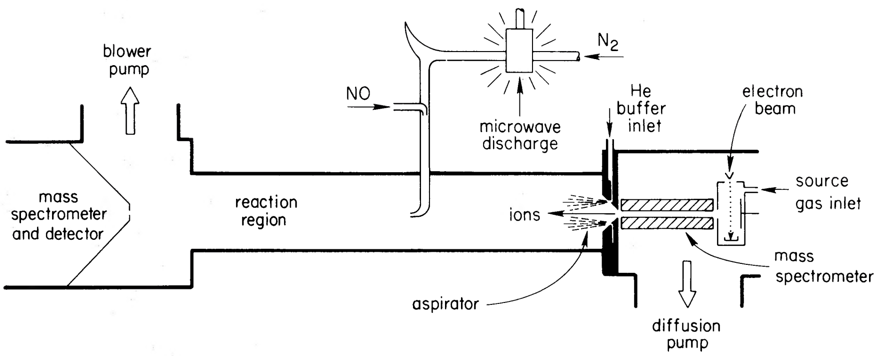

FIG. 1.—Schematic representation of the selected-ion flow tube and atomic neutral reactant source

and Adams 1979); hence, its features need only be summarized here, reserving the detailed description for the modifications necessary for the present measurements.

The reactant ions are generated in an appropriate source, mass-selected, and injected into the flow tube through a venturi-type aspirator inlet, whence they are carried downstream past the reactant-atom inlet and are detected by a mass spectrometer sampling system. The rate coefficient for the selected ion-atom reaction is determined from the decline of the ion signal as a function of reactant-atom addition (Ferguson, Fehsenfeld, and Schmeltekopf 1969). As described below, the presence of more than one reactive neutral species in the flow tube limited the usual quantitative determination of production branching ratios (Adams and Smith 1976*b*).

Two types of ion sources were employed. The majority of the measurements were made using an electron impact source. At low pressures, D^+ was produced from D_2; C^+, CH^+, $CH_2{}^+$, $CH_3{}^+$, and $CH_4{}^+$ from CH_4; and $C_2{}^+$ and C_2H^+ from CH_3CN; and OH^+ and H_2O^+ from H_2O. At higher CH_4 pressures, $CH_5{}^+$ was formed in the source by the fast binary reaction of $CH_4{}^+$ with CH_4. The second source employed was a hollow-cathode discharge (Howorka 1978), used here principally to produce $C_2H_2{}^+$ from a discharge in CH_4.

The inlet mass spectrometer is a 10 cm quadrupole. The details of the concentric-annulus aspirator-injector inlet are given by Howorka, Fehsenfeld, and Albritton (1979). The carrier gas was helium for all of these measurements, except for some of the reactions involving $CH_5{}^+$. To test for the role of possible structural forms of $CH_5{}^+$, for reasons discussed below, these ions were made in a variety of ways. In addition to those described above, $CH_5{}^+$ was produced from the termolecular reaction of injected $CH_3{}^+$ ions with the H_2 carrier gas and similarly by the bimolecular reaction of injected $CH_4{}^+$ ions with H_2.

The reactant atoms are introduced at the beginning of the reaction region, having been formed in the following way. Nitrogen atoms are generated in a Pyrex side tube by a microwave discharge in either pure N_2 or a mixture of He and N_2. The fractional dissociation of N_2 is small, but sufficient, and can be varied up to about 0.5%, depending on the N_2 flow rate and/or the power expended by the discharge. The N atoms and the N_2 carrier molecules enter the flow tube on-axis. Vibrationally excited N_2 molecules are largely relaxed by collisions before leaving the side arm (Schmeltekopf, Ferguson, and Fehsenfeld 1968), and no evidence has been found to suggest that the N atoms are in other than their ground electronic state, $^4S^o{}_{3/2}$. A light horn prevents energetic photons from the discharge from entering the flow tube, where photoionization could cause spurious ion signals. The surface of the side tube was coated with boric acid to reduce the loss of atoms by surface recombination.

Ground-state O atoms were produced by reacting the N atoms with NO, $N + NO \rightarrow O + N_2$, the NO being added in measured flow rates into the side tube through a port downstream of the microwave discharge. The flow time is sufficiently long such that all of the neutral reactions occur in the side tube. For each NO molecule reactively lost, one N atom is replaced by one O atom. Hence, the known NO flow rate can yield both the N and O atom flow rates, which are required to deduce the ion-atom reaction rate coefficients. Specifically, the endpoint of the N + NO reaction, i.e., the NO flow rate at which *all* of the N atoms reactively lost, is easily observable, as noted below. Since the endpoint NO flow is equal to the original N atom flow rate and since any NO flow rate less than this rate is equal to the number of N atoms lost and number of O atoms produced, the atom flow rates are established. Other details of the production and use of N and O atoms as reactants are given by Fehsenfeld and Ferguson (1972).

Thus, depending on whether the discharge and NO flow are on or off, the flow out of the side tube may contain N_2, N, O, and/or NO. The N_2 carrier gas is not bimolecularly reactive with most non–rare-gas ions (Albritton 1978), and, in particular, is not reactive with the ions considered here (Smith and Adams 1977). Reactions can, however, occur simultaneously with the remaining three species and examples are given here to show how the separate rates are obtained.

Figure 2 gives the data for the reaction of $CH_5{}^+$ ions with O atoms, which represents a relatively simple reactive situation since $CH_5{}^+$ does not react with

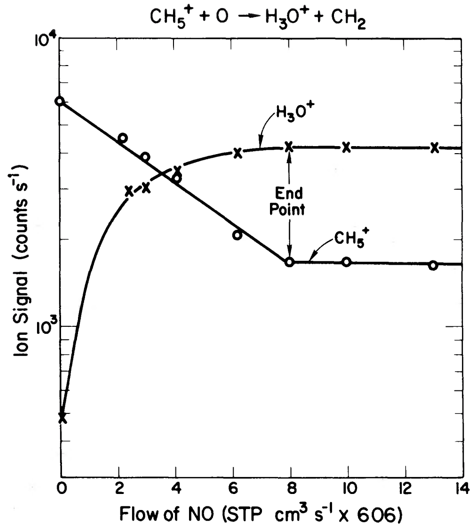

FIG. 2.—Data for the reaction of CH_5^+ with O. Only the major product ion, H_3O^+, is shown.

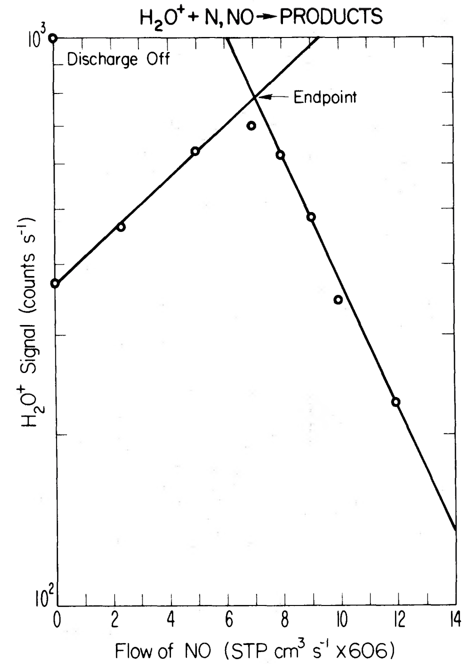

FIG. 3.—Data for the reactions of H_2O^+ with N and NO

N or NO. With the microwave discharge on, the CH_5^+ ion signal decreases as a function of increasing NO flow into the side tube, which is equal to the O atom flow into the flow tube. The slope of this initial decline yields the $CH_5^+ + O$ rate coefficient in the usual way (Ferguson, Fehsenfeld, and Schmeltekopf 1969). At the endpoint, all of the N atoms produced by the discharge are destroyed by the NO. Further increases in the NO flow, therefore, produce no additional O atoms in the side tube and hence no additional loss of the CH_5^+ ions in the flow tube, as Figure 2 demonstrates. The loss of CH_5^+ ions is approximately balanced by the appearance of H_3O^+ ions, which is the principal product channel of this reaction. A small (approximately 2%) CH_3O^+ product signal is not shown.

Figure 3 gives an example that is essentially the opposite of the previous one, in that H_2O^+ reacts with N atoms, but not O atoms. The point in the upper left corner of the figure is the H_2O^+ signal with both the discharge and the NO flow off, i.e., no reactive neutral species. When the discharge is struck, the N atoms enter the flow tube and the H_2O^+ signal drops accordingly. Then as NO is added, N atoms are reactively lost in the side tube and the H_2O^+ signal increases. At the end point, the H_2O^+ signal returns very nearly to its initial value, indicating little, if any, reaction between H_2O^+ and O atoms. The rate coefficient for the reaction of H_2O^+ with N atoms is straightforwardly determined from the increasing H_2O^+ signal prior to the end point. At larger NO flows, NO molecules enter the flow tube and react with the H_2O^+ ions, as indicated. The slope of this decline gives the rate coefficient of the $H_2O^+ + NO$ reaction in the usual way.

Figure 4 gives a general example, namely, CH^+ reacting with N, O, and NO. The rate coefficients for the separate reactions are deduced in the following way. The difference in the CH^+ signal with the discharge on and off and with zero NO flow is due to the loss arising from the $CH^+ + N$ reaction. The endpoint NO flow rate and the magnitude of the CH^+ signal decline establish this rate coefficient. As NO is then added, the decline of the CH^+ signal is due to a combination of a decreasing loss reflecting the N atom reaction and an increasing loss reflecting the O atom

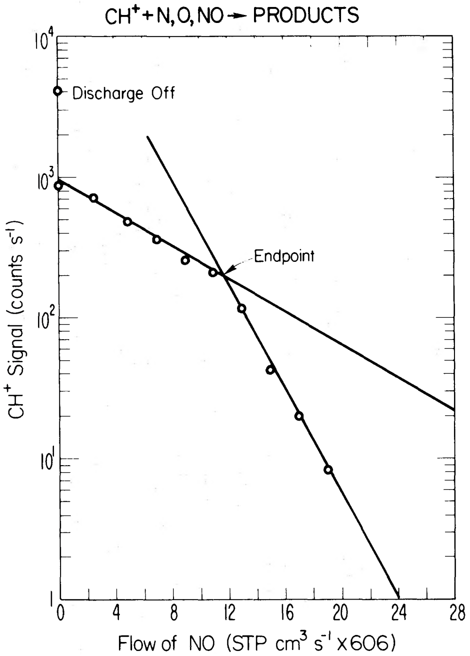

FIG. 4.—Data for the reactions of CH^+ with N, O, and NO.

reaction, the latter being predominant here. Since the $CH^+ + N$ rate coefficient has been established, that for the $CH^+ + O$ reaction can be deduced. For NO flows beyond the endpoint, there are no N atoms entering the flow tube and the O atom flow rate is unchanged; thus, the observed decline in the CH^+ signal reflects the loss due to the $CH^+ + NO$ reaction.

The rate coefficients determined using these techniques are considered accurate to ±50%. The principal factor in this estimate is the uncertainty in determining the atom concentration and the larger ion-signal instabilities that accompany measurements involving atoms, these instabilities being presumably due to changes in the ion sampling efficiencies arising from atom-surface reactions in the vicinity of the mass spectrometer sampling aperture.

III. RESULTS AND DISCUSSION

Table 1 contains the results obtained in the present study. The listed rate coefficients refer to the total rate into all possible product channels. The product ratios, where they could be determined, are the percentages of the total rate that correspond to each channel. Even when the product ratios could not be quantified, the product ions could be identified and these are given. The listed product neutrals are inferred from the energetics of the reaction. The ratio of the measured total rate constant to the collision-limiting value (Gioumousis and Stevenson 1958; Su and Bowers 1973) is given as a percentage. Where other measurements exist for these reactions, the values are listed for comparison. The agreement with

TABLE 1

RATE COEFFICIENT MEASURED FOR THE REACTIONS OF LIKELY INTERSTELLAR IONS WITH N AND O ATOMS AND NO MOLECULES AT 300 K

Reaction	Rate Coefficient (present study) ($cm^3\ s^{-1}$)	Product Ratio (%)	k/k_c[a] (%)	Rate Coefficient (other studies) ($cm^3\ s^{-1}$)
	N Atom Reactions			
1. $CH^+ + N \rightarrow CN^+ + H$	1.9×10^{-10}	...	20	
$\rightarrow H^+ + CN$				
2. $CH_2^+ + N \rightarrow CN^+ + H_2$	2.2×10^{-10}	...	23	
$\rightarrow HCN^+ + H$				
3. $CH_5^+ + N \rightarrow$ products	$\leq 1 \times 10^{-11}$	...	≤ 1	
4. $C_2^+ + N \rightarrow C^+ + CN$	$\leq 4 \times 10^{-11}$	...	≤ 5	
5. $C_2H^+ + N \rightarrow CH^+ + CN$	9.0×10^{-11}	...	11	
6. $C_2H_2^+ + N \rightarrow CH^+ + HCN$	2.5×10^{-10}	~10	30	
$\rightarrow HC_2N^+ + H$		~60		
$\rightarrow C_2N^+ + H_2$		~30		
7. $H_2O^+ + N \rightarrow HNO^+ + H$	1.9×10^{-10}	...	21	
$\rightarrow NO^+ + H_2$				
8. $CH^+ + O \rightarrow CO^+ + H$	3.5×10^{-10}	...	45	
$\rightarrow H^+ + CO$				
9. $CH_5^+ + O \rightarrow CH_3O^+ + H_2$	2.2×10^{-10}	~2	31	
$\rightarrow H_3O^+ + CH_2$		~98		
10. $C_2^+ + O \rightarrow C^+ + CO$	3.1×10^{-10}	...	47	
$\rightarrow CO^+ + C$				
11. $C_2H^+ + O \rightarrow C^+ + CHO$	3.3×10^{-10}	...	50	
$\rightarrow CH^+ + CO$				
$\rightarrow HCO^+ + C$				
$\rightarrow CO^+ + CH$				
12. $C_2H_2^+ + O \rightarrow HCO^+ + CH$	1.7×10^{-10}	~50	26	
$\rightarrow HC_2O^+ + H$		~50		
13. $D^+ + O \rightarrow O^+ + D$	2.8×10^{-10}	...	18	
14. $H_2O^+ + O \rightarrow O_2^+ + H_2$	$\leq 4 \times 10^{-11}$	...	≤ 6	
15. $C^+ + NO \rightarrow NO^+ + C$	5.2×10^{-10}	...	50	8.5×10^{-10} (1)
16. $CH^+ + NO \rightarrow NO^+ + CH$	7.6×10^{-10}	...	75	
17. $CH_2^+ + NO \rightarrow NO^+ + CH_2$	4.2×10^{-10}	...	42	
18. $CH_3^+ + NO \rightarrow NO^+ + CH_3$	1.0×10^{-9}	...	102	9.4×10^{-10} (2)
				1×10^{-9} (3)
19. $CH_5^+ + NO \rightarrow$ products	$\leq 3 \times 10^{-12}$	...	≤ 1	$\leq 1 \times 10^{-11}$ (4)
20. $C_2^+ + NO \rightarrow NO^+ + C_2$	3.4×10^{-10}	...	40	
21. $C_2H^+ + NO \rightarrow NO^+ + C_2H$	1.2×10^{-10}	...	14	
22. $C_2H_2^+ + NO \rightarrow NO^+ + C_2H_2$	1.2×10^{-10}	...	15	3×10^{-11} (3)
23. $OH^+ + NO \rightarrow NO^+ + OH$	6.7×10^{-10}	...	71	1.30×10^{-9} (5)
24. $H_2O^+ + NO \rightarrow NO^+ + H_2O$	3.6×10^{-10}	...	39	1.16×10^{-9} (5),
				4.4×10^{-10} (6)

[a] Ratio of measured rate coefficient to the collision-limiting rate coefficient.

REFERENCES.—(1) Anicich *et al.* 1976. (2) Huntress 1977. (3) Sieck and Futrell 1968. (4) Roche *et al.* 1971. (5) Karpas and Huntress 1978. (6) Dotan *et al.* 1980.

these other measurements is generally within the respective uncertainties, except for the comparison with the ion-cyclotron-resonance study of Karpas and Huntress (1978), for which the relatively large difference is not understood. Two other important interstellar ions were considered for inclusion in this study, HCO^+ and H_3O^+, but examination of the energetics showed that no exothermic channels are available for their reactions with N and O atoms. The compilations cited in § I are sources for other ion-atom studies of astrophysical interest.

The measured rate coefficients are, for the most part, smaller than the collision-limiting values. It has been observed that the occurrence of such ratios is rather strongly correlated with a negative temperature dependence (Ferguson *et al.* 1969), i.e., rate coefficients that decrease with increasing temperature. Therefore, many of the reactions in Table 1 may have rate coefficients that are larger at interstellar cloud temperatures than at 300 K.

A general feature of the reactions in Table 1 is the strong tendency to form C–N and C–O bonds. Indeed, where such bonds are energetically possible, they seem to invariably occur. The notable exception is the reaction of CH_5^+ with O, which preferentially forms the least-exothermic H_3O^+ product ion, rather than the most-exothermic H_3CO^+ product ion. Furthermore, the exothermic $CH_3^+ + H_2O$ product channel is totally absent, which is somewhat unexpected, since the CH_5^+ ion is considered to involve a three-centered bond between CH_3^+ and H_2 (Pople 1976). Because of these unusual features, this reaction was examined using different CH_5^+ sources to explore whether different structural forms of this ion might exist. The rate coefficients obtained were virtually independent of the mode of ion production, however. These tests also precluded that the injected ion with $m/e = 17$ and interpreted as CH_5^+ could have been OH^+, which has the same m/e ratio.

In Figure 5, the ion-atom reactions examined in the present study are placed into the context of interstellar ion chemistry. For clarity, the simple model depicted is an abridgment of the features that have appeared in many previous models that were much more complete and complex (see the reviews cited in § I and references therein). The rate coefficients presented here are slightly smaller than those that had been adopted in some of the model studies and thus could influence some of the quantitative aspects of those calculations.

The major portion of Figure 5 pertains to diffuse-cloud ion chemistry and has been divided (somewhat artificially) into two reaction chains. The CH_n^+ series connects C^+ to CH_3^+ via reactions with H_2 and is the predominant series. All of these ions are subject to photodissociation in diffuse clouds, thereby producing smaller radical species, which, because of their relatively low ionization potentials, can be photoionized to produce the smaller ions in the chain. Thus, a constant recycling along the ion chain occurs. The reactions of the CH_n^+ ($n \geq 1$) ions with N and O atoms, however, yield product ions containing C–N and C–O bonds, which are much less readily dissociated by ultraviolet radiation. These ions then react with H_2 to produce HCO^+ and H_2CN^+ ions, which are unreactive with H_2 and hence are relatively stable. These ions may then undergo electron-ion recombination to produce the neutral species CO, CN and HCN (and/or HNC) (Herbst 1978), which have been observed in interstellar clouds.

The $C_2H_n^+$ series also involves reactions with H_2. The reaction of these ions with O atoms eventually leads to the production of HCO^+ ions, as in the CH_n^+ series. However, the reactions with N atoms produce C_2N^+ and HC_2N^+ ions, which are not products in the CH_n^+ series. Electron-ion recombination involving these ions would probably produce CN.

In the dense, dark interstellar clouds, the ultraviolet photon flux is reduced and the ratio of electron density to H_2 density is lower; thus, the reaction sequence C^+ to CH_3^+ proceeds with less competition from photodissociation and electron-ion recombination. As a

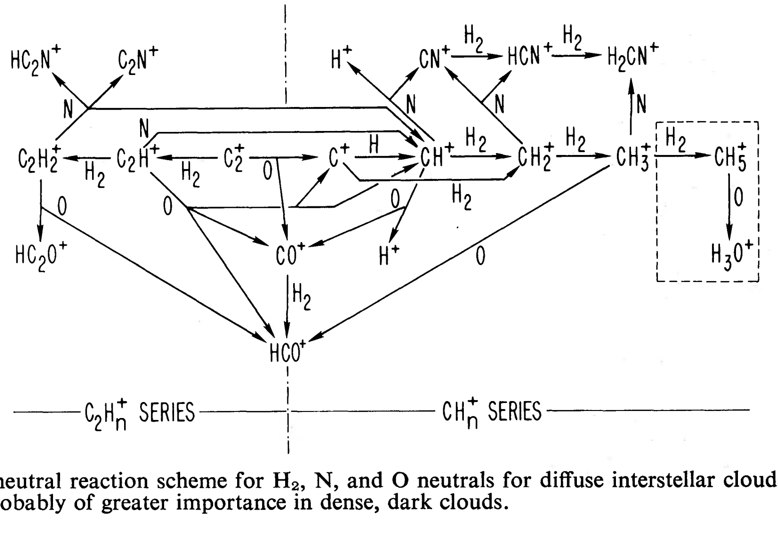

FIG. 5.—Limited ion-neutral reaction scheme for H_2, N, and O neutrals for diffuse interstellar clouds. The reactions enclosed by the dashed line are probably of greater importance in dense, dark clouds.

consequence, CH_3^+ reactions become relatively more important in these clouds. The role of these ions with molecular species has been discussed in detail by Smith and Adams (1978), who stressed the likely importance of radiative-association reactions. Such a reaction with H_2 can form CH_5^+, as indicated within the dashed portion of Figure 5, which pertains specifically to low-temperature, dense clouds. The reaction of CH_5^+ with O atoms has, therefore, a special significance under these circumstances.

The H_2O^+ ion (not shown in Fig. 5) must exist as a transient species in interstellar clouds, being formed in diffuse clouds in the sequence,

$$H^+ \xrightarrow{O} O^+ \xrightarrow{H_2} OH^+ \xrightarrow{H_2} H_2O^+ \xrightarrow{H_2} H_3O^+ ,$$

and in dense clouds in the sequence

$$H_2^+ \xrightarrow{H_2} H_3^+ \xrightarrow{O} OH^+ \xrightarrow{H_2} H_2O^+ \xrightarrow{H_2} H_3O^+ \xrightarrow{O} H_2O^+ \xrightarrow{H_2} H_3O^+ .$$

Therefore, the reactions of H_2O^+ with N and O atoms were included in this study. The reaction with N atoms is particularly interesting since electron-ion recombination involving the HNO^+ product ion would presumably produce NO, a recently observed interstellar species. Recombination of the NO^+ product and the O_2^+ product of the $H_2O^+ + O$ reaction would simply regenerate N and O atoms. The presence of significant concentrations of NO in molecular clouds could be an important factor in the ion chemistry because of its low ionization energy and hence its great propensity to participate in charge-transfer reactions.

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