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ION REACTIONS WITH ATOMIC OXYGEN AND ATOMIC NITROGEN OF ASTROPHYSICAL IMPORTANCE

F. C. FEHSENFELD
Aeronomy Laboratory, NOAA Environmental Research Laboratory, Boulder, Colorado

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ABSTRACT

The rate constants for the reaction of H_3^+ and CH_3^+ with O and CH_3^+ with N have been measured at 300 K, using a flowing afterglow technique. These reactions are thought to play important roles in interstellar ion chemistry.

Subject headings: interstellar molecules — molecular processes

Various chemical schemes involving ion-molecule reactions have been proposed to account for the formation of interstellar molecules (Herbst and Klemperer 1973; Dalgarno 1975; Watson 1974). In dense interstellar clouds, there are presumed to be relatively large abundances of atomic nitrogen and atomic oxygen, $N/H_2 \sim O/H_2 \sim 10^{-4}$ (Herbst and Klemperer 1973), and O and N are thought to play important roles in the interstellar ion chemistry. In this article, rate constants for the reaction of H_3^+ and CH_3^+ with O and CH_3^+ with N are reported.

The present results were obtained in a room-temperature flowing afterglow which has been described at length (Ferguson, Fehsenfeld, and Schmeltekopf 1969; Fehsenfeld 1975). In this system, ions of interest are produced by secondary reactions in ionized helium and reacted with atomic oxygen and atomic nitrogen. A discussion of the use of atomic oxygen and atomic nitrogen as reactant may be found elsewhere (Fehsenfeld 1977). The method used to produce these atomic reactants requires the measurements to be made in the presence of N_2 in the case of N, and either N_2 or O_2 in the case of O, with the molecular concentration several times larger than the atom concentration. Consequently, it is only feasible to measure rate constants for atomic nitrogen reactions with ions which do not react with N_2, while atomic oxygen reaction-rate constants can only be determined for ions which do not react either with N_2 or O_2. The measured reactions, along with their calculated exothermicities (Franklin *et al.* 1969; Beauchamp 1975; Stull and Prophet 1975) are summarized in Table 1. The rate constants are for reaction into all available channels. The uncertainties in these rates are ± 50 percent due principally to the estimated uncertainty in the atomic oxygen and atomic nitrogen concentrations. There are additional uncertainties associated with the assignment of the reaction channels due to secondary reactions of the product ions with the various components of the gas mixture. These uncertainties are detailed in the discussion of the individual reactions.

The H_3^+ ions used as reactant ions in the present experiment were produced as described in a recent study (Fehsenfeld, Lindinger, and Albritton 1975). In the reaction of H_3^+ with O, there are two exothermic channels leading to the formation of OH^+ (1*a*) and H_2O^+ (1*b*). From the present measurements, it was not possible to determine the relative importance of these channels, since both OH^+ and H_2O^+ were rapidly converted to H_3O^+ in the experimental apparatus by reaction with H_2, the source gas for the H_3^+.

The CH_3^+ ion was generated by reacting small quantities of CH_4 with He^+ and $He(2^3S)$, producing CH^+, CH_2^+, CH_3^+, and CH_4^+. Sufficient H_2 was then added to convert CH^+ and CH_2^+ rapidly to CH_3^+ and CH_4^+ to CH_5^+. By using small amounts of CH_4, the reaction of CH_3^+ with CH_4 to produce $C_2H_5^+$ (Beauchamp 1971) was minimized, leaving sufficient quantities of CH_3^+ for the reaction studies. Under typical operating conditions, the relative concentration of $CH_3^+/CH_5^+/C_2H_5^+$ was approximately 0.2/1.0/0.4.

In the reaction of CH_3^+ with O, there are three exothermic channels leading to the formation of COH^+(2*a*), H_3^+(2*b*), and CH_2O^+(2*c*). The last channel, 2*c*, has been suggested as a possible source of observed interstellar CH_2O (Dalgarno 1975). Of these ions, however, only COH^+ was actually

TABLE 1

SUMMARY OF MEASURED REACTIONS

Reaction	Exothermicity (eV)	Rate (10^{-10} cm³ s⁻¹)
$H_3^+ + O$:		
$\xrightarrow{a} OH^+ + H_2$.......	0.6	8.0
$\xrightarrow{b} H_2O^+ + H$.......	4.0	
$CH_3^+ + O$:		
$\xrightarrow{a} COH^+ + H_2$.....	5.3	4.4
$\xrightarrow{b} H_3^+ + CO$.......	3.5	
$\xrightarrow{c} COH_2^+ + H$.....	1.9	
$CH_3^+ + N$:		
$\xrightarrow{a} HCN^+ + H_2$.....	1.0	0.67
$\xrightarrow{b} H_2CN^+ + H$.....	4.0	

observed as a reaction product. Because of possible secondary reactions that would destroy H_3^+, reaction (1), and reaction with CH_4, it is not possible to preclude channel 2*b* from contributing (~20 percent) to the reaction. In like fashion, neither CH_2O^+ nor CH_3O^+, produced by reaction of CH_2O^+ with H_2, was observed. In the case of either CH_2O^+ or CH_3O^+, the presence of CH_4 should not interfere, since both the simple proton transfers or charge transfers from these ions to CH_4 are strongly endothermic (Beauchamp 1975; Franklin *et al.* 1969). However, if there are fast reactions ($k \sim 10^{-9}$ cm^3 s^{-1}) between either CH_2O^+ or CH_3O^+ and O to produce COH^+, H_2O^+, or H_3O^+, then CH_2O^+ production by reaction (2*c*) as large as 10 percent could be masked.

The reaction of CH_3^+ with N was about 7 times slower than with O. The observed product of the reaction was H_2CN^+. It is possible that HCN^+, (3*a*), was produced and converted to H_2CN^+ by reaction with H_2. The measured rate for this reaction implies a reaction probability of about 0.05 per collision between CH_3^+ and N at 300 K. Reactions which occur with low efficiency often exhibit strong temperature dependencies. For exothermic reactions such as this, the rate constants are generally found to increase with decreasing temperature.

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F. C. FEHSENFELD: Aeronomy Laboratory, NOAA Environmental Research Laboratory, Boulder, CO 80302