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# LABORATORY MEASUREMENTS OF SELECTED D-REGION REACTIONS

National Oceanic & Atmospheric Administration  
Aeronomy Laboratory  
Environmental Research Laboratories  
Department of Commerce  
Boulder, Colorado 80302

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The flowing afterglow and flow-draft instrumental laboratory capabilities have been applied during the past year to the experimental investigation of the kinetics and thermochemistry of important D-region atomic and molecular ions. The information obtained will be used to redefine the atmospheric ionic composition and the processes by which this ionic composition may be modified.			

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20. ABSTRACT (Continued)

The positive ion chemistry below 80 km is dominated by the reactions that convert  $O_2^+$  to  $(H_3O^+ \cdot nH_2O)$ . Interactions of  $CO_2$ ,  $O_3$ , and  $CH_4$  with  $O_2^+$ ,  $(O_2^+ \cdot O_2)$  or  $(O_2^+ \cdot H_2O)$  could alter this conversion process, but the end product of the altered reaction scheme will still be  $(H_3O^+ \cdot nH_2O)$ .

Current models predict  $(H_3O^+ \cdot nH_2O)$  as the terminal positive ions below 80 km. However, below 60 km ions other than  $(H_3O^+ \cdot nH_2O)$  are observed as the terminal ions. To understand this conversion, the reaction of  $(H_3O^+ \cdot nH_2O)$  with  $H_2CO$  or  $CH_3OH$ , both of which are present in the atmosphere, has been investigated. We conclude that, if present,  $CH_3OH$  will destroy the hydronium ions, while  $H_2CO$  will not.

The unstable neutral  $N_2O_5$  was found to react rapidly with  $NO^+$ ,  $H_3O^+$ ,  $(H_3O^+ \cdot H_2O)$  and  $(H_3O^+ \cdot 2H_2O)$ . These reactions have important implications for the neutral, as well as the ion, chemistry in this region.

In other positive ion studies, ground state  $S^+$  ions are found to react with  $O_2$  and  $NO$ . This indicates that the positive ions observed in the mesosphere at mass 32 and 34 cannot be  $S^+$ . In addition metastable  $NO^+$  (a  $^3\Sigma^+$ ) ions are found to react rapidly with  $N_2$ . This reaction is important in F-region ion chemistry under disturbed conditions.

In the negative ion studies,  $CO_3^-$ ,  $Cl^-$ ,  $I^-$ , and  $F^-$  are found to react rapidly with  $N_2O_5$  to produce  $NO_3^-$ . These reactions indicate that  $NO_3^-$  will be the terminal negative ion in the middle-atmospheric ion chemistry.

Flow drift tube measurements have been used to measure the mobilities of  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$  in He and Ar. These data are of great use in the modeling of rare-gas halide lasers.

Finally, significant progress has been made toward the development of a selected ion source to be used in conjunction with the flowing afterglow and flow-drift systems and will greatly increase the species of ions that can be studied.

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ANNUAL PROGRESS REPORT

Atmospheric Collision Processes Laboratory

Aeronomy Laboratory

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Boulder Colorado 80302

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During the past year, the program for measuring ion-molecule reaction rate constants and ion thermochemical values has been involved with a number of current problems of atmospheric ion chemistry pertaining to both normal and disturbed conditions. The present investigations include studies carried out as a function of relative kinetic energy in the flow-drift system and as a function of temperature in the variable-temperature flowing afterglow, as well as room-temperature measurements in the conventional flowing afterglow. Several reaction studies involving unstable neutral reactants were carried out in the flowing afterglow, which remains the chief source of information concerning these reactions. Some specific results are listed below.

1. The conversion of  $O_2^+$  to  $H_3O^+$  and  $[H_3O^+ \cdot H_2O]$  plays an important role in the production of  $[H_3O^+ \cdot nH_2O]$ ,  $n = 0, 1, 2, \dots$ , which are observed to be the dominant ions in the lower mesosphere and upper stratosphere. As a consequence, any reaction that could alter this process would be important to the ion chemistry below 80 km. In this connection, the reactions of  $O_2^+$  and  $[O_2^+ \cdot O_2]$  with  $CH_4$ ,  $CO_2$ , and  $O_3$  and the reaction of

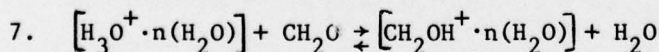
$[O_2^+ \cdot O_3]$  with  $H_2O$  have been investigated using the variable-temperature flowing afterglow and the flow-drift tube.

The following results were obtained:

1.  $O_2^+ + CH_4 \rightarrow CH_3O_2^+ + H$   $k_1 = 7.5 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$
2.  $[O_2^+ \cdot O_2] + CH_4 \rightarrow O_2^+ \cdot CH_4 + O_2$   $k_2 = 3 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$  at 130K
3.  $[O_2^+ \cdot O_3] + CH_4 \rightarrow \text{products}$   $k_3 \leq 5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$  at 260K
4.  $[O_2^+ \cdot O_3] + H_2O \rightarrow O_2^+ \cdot H_2O + O_3$   $k_4 = 1.2 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$  at 260K
5.  $[O_2^+ \cdot O_2] + CO_2 \rightleftharpoons O_2^+ \cdot CO_2 + O_2$   $\Delta H_{273}^{\circ}(5) = 0.31 \pm 1.0 \text{ kcal mole}^{-1}$   
 $\Delta S_{273}^{\circ}(5) = 4.3 \pm 3.0 \text{ cal mole}^{-1} \text{ K}^{-1}$
6.  $[O_2^+ \cdot O_2] + O_3 \rightleftharpoons O_2^+ \cdot O_3 + O_2$   $-\Delta H_{273}^{\circ}(6) = 3.3 \pm 1.0 \text{ kcal mole}^{-1}$   
 $\Delta S_{273}^{\circ}(6) = 4.5 \pm 4.0 \text{ cal mole}^{-1} \text{ K}^{-1}$

The above equilibrium constants indicate that the concentration of  $[O_2^+ \cdot CO_2]$  will be negligibly small relative to  $[O_2^+ \cdot O_2]$  in the atmosphere, while the concentration of  $[O_2^+ \cdot O_3]$  relative to  $[O_2^+ \cdot O_2]$  will depend strongly on the  $O_3$  to  $O_2$  mixing ratio and temperature. However, since reactions (1), (2), and (3) are slow and in contrast reaction (4) is fast, the conversion of  $O_2^+$  to  $[H_3O^+ \cdot nH_2O]$  will not be altered.

2. Current atmospheric models predict significant concentrations of  $CH_2O$  in the stratosphere as by-products of the oxidation of methane. For this reason the reactions



have been studied for  $n = 0, 1, 2, 3$ , in the variable-temperature flowing afterglow. From these measurements thermochemical values for reactions (7) have been obtained. The results are as follows.

Reactions	$\Delta H_T^\circ$ (kcal/mole)	$\Delta S_T^\circ$ (cal/mole·K)	Mean Temperature (K)
7a. $H_3O^+ + CH_2O \rightarrow CH_2OH^+ + H_2O$	$-5.2 \pm 0.8$	$2.2 \pm 3.0$	470
7b. $[H_3O^+ \cdot H_2O] + CH_2O \rightarrow [CH_2OH^+ \cdot H_2O] + H_2O$	$-0.41 \pm 0.29$	$2.6 \pm 2.5$	400
7c. $[H_3O^+ \cdot 2H_2O] + CH_2O \rightarrow [CH_2OH^+ \cdot 2H_2O] + H_2O$	$0.58 \pm 0.43$	$2.3 \pm 2.8$	400
7d. $[H_3O^+ \cdot 3H_2O] + CH_2O \rightarrow [CH_2OH^+ \cdot 2H_2O] + H_2O$	$1.1 \pm 0.6$	$4.1 \pm 2.0$	325
8. $[CH_3O^+ \cdot H_2O] + CH_2O \rightarrow [CH_2OH^+ \cdot CH_2O] + H_2O$	$-0.80 \pm 0.13$	$-0.71 \pm 2.2$	400

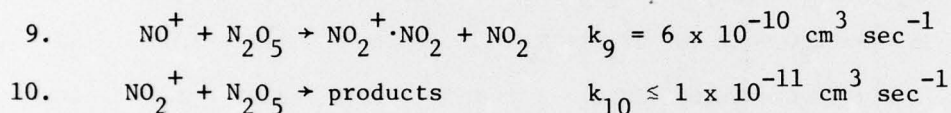
These measurements imply that the reactions of the hydrated hydronium ions with  $CH_2O$  in the stratosphere will not produce significant  $CH_2OH^+$  and its clusters because of the small equilibrium constants and the large  $H_2O / H_2CO$  ratio.

3. In addition to  $CH_2O$ , atmospheric models suggest the possibility of large concentrations of  $CH_3OH$ . The reactions of  $[H_3O^+ \cdot nH_2O]$ ,  $n = 0, 1, 2, 3$  have been studied in the flowing afterglow and the flow-drift system. The reactions are fast at all energies studied and proceed predominately by proton transfer. Since  $CH_2OH^+$  and its cluster ions are not observed in the stratosphere above 30 km where  $[H_3O^+ \cdot nH_2O]$  dominant, the present results indicate that the  $CH_3OH$  concentration in this region is less than  $10^6$  molecules  $cm^{-3}$ , i.e., a mixing ratio of less than  $10^{-11}$ .

4. The reactions of  $S^+$  with  $O_2$  and  $NO$  have been investigated as a function of ion kinetic energy in the flow-drift system. In the present studies, extensive checks were made to insure that the  $S^+$  were not

excited. The present results are in good agreement with those results previously reported by this laboratory (F. C. Fehsenfeld, J. Geophys. Res. 78, 1966, 1973). These results indicated that the positive ions observed in the mesosphere at mass 32 and mass 34 cannot be  $S^+$ .

5. The investigation of the ion chemistry of  $N_2O_5$  has been started. We find  $N_2O_5$  reacts rapidly with  $CO_3^-$ ,  $Cl^-$ ,  $I^-$ , and  $F^-$ . In the case of the positive ions, we find



In addition the  $N_2O_5$  reactions with  $H_3O^+$ ,  $H_3O^+ \cdot H_2O$  and  $H_3O^+ \cdot 2H_2O$  will be studied. Since  $N_2O_5$  is an important stratospheric neutral involved in the odd nitrogen cycle, the reactions of  $N_2O_5$  with hydrated ions may have important consequences for the neutral, as well as the ion, chemistry of the stratosphere.

6. The metastable  $NO^+(a^3 \ ^+)$  ion may be formed in the ionosphere by primary ionization of NO or as a product of ion-molecule reactions. The reaction of  $NO^+(a^3 \ ^+)$  with  $N_2$  has been studied as a function of ion kinetic energy in the flow-drift system between 0.063 eV and 1.6 eV. The reaction rate constant is large at all energies and is  $7 \pm 3.5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$  at 0.063 eV. This reaction will provide the major removal mechanism for  $NO^+(a^3 \ ^+)$  in the atmosphere. Future studies of this metastable ion will include the assesment of the relative roles of quenching and reaction. Furthermore, the reactions with other neutrals, like  $O_2$ , will be examined.

7. The flow-drift tube has been used to measure the mobilities of the halogen negative ions  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$  in helium and argon buffer gases. The measurements covered a wide range of ratios of electric field strengths to buffer gas number densities. Since no values were previously available, these data will be of great use in the modeling of the rare-gas halide lasers, which previously had to rely only on approximations of these mobilities.

8. Ions produced in a low pressure ion source have been injected at low energy (i.e. K.E.  $\leq 10$  eV) into the flowing afterglow in sufficient concentration to give usable signal levels after passage through the flowing afterglow and mass analysis. This confirms the feasibility of this technique and will serve as the basis for a selected ion flowing afterglow and flow-drift measurements. This new ion source will extend the laboratory's capabilities by greatly increasing the species of ions that can be studied.

#### SUMMARY

The flowing afterglow and flow-drift capabilities have been applied during the past year to the experimental investigation of the kinetics and thermochemistry of aeronomically important atomic and molecular ions. The information obtained from these studies is used to understand the chemistry that shapes the atmospheric ionic composition and the processes by which this ionic composition may be modified.

The positive ion chemistry below 80 km is dominated by the reactions that convert  $O_2^+$  to  $[H_3O^+ \cdot nH_2O]$ . Because the concentration of  $CO_2$ ,  $O_3$ , and  $CH_4$  approach or exceed the concentration of  $H_2O$ , reactions of these compounds with  $O_2^+$ ,  $[O_2^+ \cdot O_2]$  or  $[O_2^+ \cdot H_2O]$  could alter this conversion process. The present studies have shown that, although the conversion process is altered by these reactions, the end product of the altered reaction scheme is still  $[H_3O^+ \cdot nH_2O]$ .

Current models would predict  $[H_3O^+ \cdot nH_2O]$  as the terminal positive ions below 80 km. However, below 60 km ions other than  $[H_3O^+ \cdot nH_2O]$  are observed as the terminal ions. To understand this conversion, the reaction of  $[H_3O^+ \cdot nH_2O]$  with  $H_2CO$  and  $CH_3OH$ , both of which are present in the atmosphere as a by-product of the oxidation of methane, have been studied. We conclude that, if present,  $CH_3OH$  will destroy the hydronium ions, while  $H_2CO$  will not. In addition, the unstable neutral  $N_2O_5$ , which is an important product of the odd-nitrogen chemistry in the middle atmosphere, is found to react rapidly with  $NO^+$ ,  $H_3O^+$ ,  $[H_3O^+ \cdot H_2O]$  and  $[H_3O^+ \cdot 2H_2O]$ . These reactions have important implications for the neutral, as well as the ion chemistry in this region.

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Finally, significant progress has been made toward the development of a selected ion source to be used in conjunction with the flowing after-glow and flow-drift systems and will greatly increase the species of ions that can be studied.