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ADDITIONAL FLOWING AFTERGLOW MEASUREMENTS OF NEGATIVE ION REACTIONS OF *D*-REGION INTEREST

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Abstract—Some additional negative ion reactions of possible *D*-region importance have been measured in the ESSA flowing afterglow system at 300°K. It has been found that NO_3^- does not react with atomic oxygen or atomic nitrogen with a rate constant as large as 10^{-11} cm^3/sec. The electron affinity of NO_3 is found to be greater than that of NO_2 by more than 0·9 eV. It is pointed out that conversion of O_2^- to O_4^- followed by subsequent reactions of the O_4^- may play an important role in *D*-region negative ion chemistry. Rate constants for the reaction of O_4^- with NO, CO_2 and O are reported. The reaction of O_4^- with CO_2 produces CO_4^-. Rate constants for the reactions of CO_4^- with NO and O are reported.

INTRODUCTION

A number of rate constants for reactions between negative ions and neutrals of atmospheric importance have previously been reported from this laboratory (Fehsenfeld *et al.*, 1967; Fehsenfeld and Ferguson, 1968). The available laboratory data on negative ion processes have recently been reviewed (Phelps, 1969; Ferguson, 1969). Some additional measurements have now been made and are reported here. The flowing afterglow technique for ion–molecule reaction rate constant measurements used in this laboratory has been described in the earlier papers and has recently been described in considerable detail (Ferguson *et al.*, 1969).

NEGATIVE ION REACTIONS

Negative ion chemistry is initiated in the *D*-region by the three-body attachment of electrons to O_2 to form O_2^-. In our first paper (Fehsenfeld *et al.*, 1967), we described a sequence of reactions which led predominantly to NO_2^-. In a subsequent paper (Fehsenfeld and Ferguson, 1968) we reported that the reaction

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2 \tag{1}$$

has a rate constant $1{\cdot}8 \times 10^{-11}$ cm^3/sec at 300°K and suggested that this could lead to NO_3^- being a dominant negative ion in the *D*-region.

The question as to whether the NO_3^- produced in (1) can undergo further reaction is therefore an important one. The first possibility investigated was reaction of NO_3^- with atomic oxygen:

$$NO_3^- + O \rightarrow NO_2^- + O_2 \tag{2a}$$
$$\rightarrow NO_2 + O_2^- \tag{2b}$$
$$\rightarrow NO_2 + O_2 + e \tag{2c}$$
$$\rightarrow NO + O_3^-. \tag{2d}$$

No reaction of NO_3^- with O was observed and it was possible to set an upper limit of 10^{-11} cm^3/sec to the sum of all possible channels, i.e. $k_2 < 10^{-11}$ cm^3/sec. The failure to observe an ion–neutral reaction with a rate constant larger than 10^{-11} cm^3/sec often (although not always) implies that the reaction is endothermic. This does not seem likely to be the case for the most energetically favored channel (2a) however. Reaction (2a) is exothermic unless the electron affinity of NO_3 exceeds that of NO_2 by more than 2·9 eV. The electron affinities of neither NO_2 nor NO_3 are known. However, the electron affinity of NO_2 exceeds that of OH (1·78 eV) since the reaction

$$OH^- + NO_2 \rightarrow NO_2^- + OH \qquad (3)$$

is known to proceed with a large (10^{-9} cm^3/sec) rate constant (Ferguson *et al.*, 1969). This would require that $EA(NO_3) > 4{\cdot}7$ eV in order for (2a) to be endothermic and this is a larger electron affinity than any molecule fo far is known to have. Calculated values of the electron affinities are $EA(NO_2) = 1{\cdot}6$ eV and $EA(NO_3) = 3{\cdot}9$ eV (Pritchard, 1953), however these values (from lattice energy calculations) cannot be relied upon. The other branches of reaction (2) are probably endothermic. Reaction (2b) requiring only that $EA(NO_3) > 3{\cdot}3$ eV, (2c) that $EA(NO_3) > 2{\cdot}9$ eV and (2d) that $EA(NO_3) > 2{\cdot}7$ eV to be endothermic. The (2d) estimate assumes $EA(O_3) = 1{\cdot}9$ eV, which is also rather uncertain (Wood and D'Orazio, 1965).

For most important purposes reaction (2a) would be of little significance, since conversion of NO_3^- to NO_2^- would be followed by the reconversion reaction (1). Reactions (2b), (2c) and (2d) however would all enhance electron detachment in the *D*-region and thus play an important role in determining the electron density if they did occur.

Since nitric oxide appears to be fairly abundant in the *D*-region (Pearce, 1969), we have examined the reaction

$$NO_3^- + NO \rightarrow NO_2^- + NO_2. \qquad (4)$$

No reaction was observed, and an upper limit to k_4 was determined to be 10^{-12} cm^3/sec. Indeed reaction (4) appears to be endothermic as the reverse reaction

$$NO_2^- + NO_2 \rightarrow NO_3^- + NO \qquad (5)$$

was observed to occur, somewhat indirectly in the flowing afterglow system. The ratio of NO_2^-/NO_3^- was found to decrease with NO_2 concentration in the afterglow. A rate constant, $k_5 \simeq 4 \times 10^{-12}$ cm^3/sec was deduced from this effect. With increased NO_2 concentrations the dimer $NO_2^- . NO_2$ or $NO_3^- . NO$ was also observed but its concentration was small compared to that of NO_3^-. The occurrence of reaction (5) gives some useful data on the NO_3 electron affinity. For (5) to be exothermic,

$$\Delta E_5 = D(NO_2\text{–}O) - D(NO\text{–}O) + EA(NO_3) - EA(NO_2) > 0$$

or (6)

$$EA(NO_3) > EA(NO_2) + 0{\cdot}9 \text{ eV}.$$

Since we know $EA(NO_2) > 1{\cdot}8$ eV, it follows that $EA(NO_3) > 2{\cdot}7$ eV. This in turn implies that only wavelengths shorter than 4600 Å could be effective in photodetachment of NO_3^- in the *D*-region. Since it unlikely that $EA(NO_2)$ is just barely greater than that of OH, and that reaction (5) is just barely exothermic, it is probable that $EA(NO_3)$ is significantly greater than 2·7 eV and that ultraviolet light will be required for photodetachment.

It was also determined that NO_3^- did not react rapidly with N atoms, i.e. the reaction

$$NO_3^- + N \rightarrow \text{products} \qquad (7)$$

had a rate constant $k_7 < 10^{-11}$ cm^3/sec at 300°K. This reaction, to produce $NO_2^- + NO$, is more exothermic by 1·4 eV than reaction (2a).

The implications of the present NO_3^- studies for *D*-region aeronomy bolster our earlier conclusion that NO_3^- should be an important *D*-region negative ion, and probably a 'terminal' one in a chemical sense. That is, NO_3^- may only be lost significantly by ion–ion recombination and/or photodetachment, rather than undergoing further chemical reactions. This is not a firm conclusion however, as we have set only a modest upper limit, $k_2 < 10^{-11}$ cm³/sec and if reactions (2b), (2c), or (2d) should occur with rate constants only as large as 10^{-14} cm³/sec, they would have time constants of only $\sim 10^4$ sec if the calculated O atom concentrations $\sim 10^{10}$ cm^{-3} in the *D*-region are correct (Hesstvedt, 1968).

It is very difficult to measure small rate constants involving negative ions and atomic oxygen so that to establish that $k_2 < 10^{-14}$ cm³ sec experimentally would be very difficult. In this regard it would be most valuable to know $EA(NO_3)$. If, as we suspect, $EA(NO_3) > 3 \cdot 3$ eV, then the reactions (2b), (2c) and (2d), which could lead to electron regeneration in the *D*-region can be dismissed as being endothermic.

CLUSTER ION REACTIONS

A new development in *D*-region negative ion chemistry, which may substantially alter our previous considerations of this subject, is the recent recognition of the importance of three body clustering reactions. For example, we have recently shown qualitatively (Fehsenfeld and Ferguson, 1969) that the positive ion chemistry of the *D*-region is significantly affected by the clustering of O_2^+ with O_2 to form O_4^+. The O_4^+ ion then reacts in a series of binary reactions with H_2O to produce the major positive ion below 80 km, $H_5O_2^+$.

In a similar manner, the clustering of O_2^- with O_2 to form O_4^- may be quite significant in the *D*-region. The cluster ion O_4^- has a bond energy 0·59 eV (Conway and Nesbitt, 1968), significantly more than that of O_4^+ which is 0·42 eV. The rate constant for

$$O_2^- + O_2 + M \rightarrow O_4^- + M \tag{8}$$

is likely to exceed 10^{-30} cm⁶/sec at *D*-region temperatures. This leads to time constants for reaction (8) of less than a second below $\sim$75 km so that association of O_2^- is competitive with any other O_2^- reaction process. Accordingly the fate of O_4^- becomes a matter of critical concern and we have measured the rate constants listed below:

$$O_4^+ + NO \rightarrow NO_3^- + O_2, \quad k_9 = 2 \cdot 5 \times 10^{-10} \text{ cm}^3/\text{sec} \tag{9}$$

$$O_4^- + CO_2 \rightarrow CO_4^- + O_2, \quad k_{10} = 4 \cdot 3 \times 10^{-10} \text{ cm}^3/\text{sec} \tag{10}$$

$$CO_4^- + NO \rightarrow NO_3^- + CO_2, \quad k_{11} = 4 \cdot 8 \times 10^{-11} \text{ cm}^3/\text{sec.} \tag{11}$$

Reaction (8) followed by (9), or followed by (10) and (11) can short circuit the longer reaction chain previously proposed to reach the very stable negative ion NO_3^-.

The cluster ion O_4^- reacts with atomic oxygen,

$$O_4^- + O \rightarrow O_3^- + O_2 \tag{12a}$$

$$\rightarrow O^- + 2O_2 \tag{12b}$$

where $k_{12} = 4 \times 10^{-10}$ cm³/sec. Reaction (12a) is the major channel of (12) but the contribution of (12b) was difficult to evaluate because of further reactions of the product O^- ions under the attainable experimental conditions. The CO_4^- ion also reacts with atomic oxygen,

$$CO_4^- + O \rightarrow CO_3^- + O_2 \tag{13a}$$

$$\rightarrow O_3^- + CO_2 \tag{13b}$$

with $k_{13} = 1{\cdot}5 \times 10^{-10}$ cm^3/sec and (13a) being the major reaction channel. Channel (13b) is again obscured, in this case because of fast reaction with the excess CO_2 in the system to produce CO_3^-.

Finally, it is becoming increasingly apparent that long lived negative (as well as positive) ions can be expected to be hydrated in the lower *D*-region. Thus the properties of ions such as $NO_3^-(H_2O)_n$ may be of considerable importance. A great deal of laboratory study therefore remains to be done. A large impetus will be given to this need when the first successful negative ion composition studies in the *D*-region are carried out.

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