Temperature dependencies of the reactions of CO−3(H2O)0,1 and O−3 with NO and NO2

Susan T. Arnold, Robert A. Morris, and A. A. Viggiano

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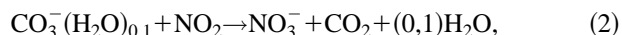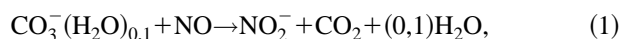
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We have measured temperature dependencies of the rate constants for CO_3^- and O_3^- reacting with NO and NO_2. In addition, the temperature dependence of the $CO_3^-(H_2O)$ reaction with NO was determined, and a 196 K rate constant was measured for the reaction of $CO_3^-(H_2O)$ with NO_2. The reactions with NO all proceed by O^- transfer to produce NO_2^-. The temperature dependencies of the rate constants for the reactions of CO_3^- and O_3^- with NO are represented as $1.5\times10^{-7}*T^{-1.64}$ and $4.4\times10^{-7}*T^{-2.15}$ cm^3 s^{-1}, respectively, and agree very well with previous measurements. The rate constant for the reaction of $CO_3^-(H_2O)$ with NO is $4.1\times10^{-5}*T^{-2.72}$ cm^3 s^{-1}. Previous measurements of the rate constants for CO_3^-, $CO_3^-(H_2O)$, and O_3^- reacting with NO_2 appear to be in error; our measured rate constants for the first two reactions are represented as $2.6\times10^{-5}*T^{-2.38}$ and $9.1\times10^{-9}*T^{-0.79}$ cm^3 s^{-1}, respectively. The rate constant for the reaction $CO_3^-(H_2O)$ with NO_2 is 7.9×10^{-11} cm^3 s^{-1} at 196 K. The reactions of CO_3^- and $CO_3^-(H_2O)$ with NO_2 proceed by O^- transfer, producing NO_3^-. While the reaction of O_3^- with NO_2 proceeds mainly by charge transfer at room temperature, about half the reactivity at 200 K is due to charge transfer with the remainder arising from O^- transfer. Atmospheric implications of the present results are discussed. © *1995 American Institute of Physics.*

INTRODUCTION

Recently, Arnold and co-workers have reported a chemical ionization technique for deriving NO and NO_2 concentrations in the atmosphere, particularly in the plumes of aircraft where the concentrations of these compounds are relatively large.[1,2] The technique involves producing $CO_3^-(H_2O)_{0,1}$ reactant ions in a flow tube which samples the atmosphere and monitoring the product ions NO_2^-, NO_3^-, and their hydrates. The important reactions are

$$CO_3^-(H_2O)_{0,1}+NO\rightarrow NO_2^-+CO_2+(0,1)H_2O, \quad (1)$$

$$CO_3^-(H_2O)_{0,1}+NO_2\rightarrow NO_3^-+CO_2+(0,1)H_2O, \quad (2)$$

where hydration of the product ion is also possible. Derivation of NO and NO_2 concentrations requires a knowledge of the rate constants for the above reactions at the temperatures of interest, namely those at airplane cruise heights, i.e., 200–220 K.

Rate constants for these reactions have previously been measured at room temperature only,[3,4] except for the reaction of CO_3^- with NO for which temperature and kinetic energy dependencies were measured at the NOAA laboratory in a flowing afterglow.[5] Since these reactions are inefficient and such reactions generally have temperature dependent rate constants, we have performed a temperature dependence study of these reactions. In general, we have studied the reactions from 100 to 500 K. However, for experimental reasons, the reaction of NO_2 with $CO_3^-(H_2O)$ could only be studied at 200 K, a temperature close to that at airplane cruise altitudes. The present measurements were made in a selected ion flow tube, which allows for a more accurate determination of product ions than in the flowing afterglow measurement. In this study, we have also examined the temperature dependence for the reactions of O_3^- with NO and NO_2, reactions which play a minor role in atmospheric ion chemistry.[6]

EXPERIMENT

The measurements were made in a variable temperature selected ion flow tube. The apparatus has been described in detail previously,[7,8] and only details pertinent to the present experiments are presented here. The ions CO_3^- and O_3^- were formed in an electron impact ion source from CO_2 and O_2 source gases, respectively, while $CO_3^-(H_2O)$ was produced from a mixture of CO_2 and H_2O vapor.

The NO reactant gas was added into the system through a molecular sieve trap which was cooled to 205 K to remove minor NO_2 and HNO_3 impurities. The NO_2 reactant was added directly into the flow tube. However, to prevent the NO_2 from freezing in the reactant gas inlet, it was necessary to heat the inlet lines when cooling the flow tube. This technique has been described previously.[9] Even when heating the inlet lines, freezing prevented our working with NO_2 at temperatures significantly below 200 K.

There were particular experimental difficulties associated with studying reactions of $CO_3^-(H_2O)$. For example, $HCO_3^-(H_2O)$ and HCO_4^- ions were produced more easily in the ion source than was $CO_3^-(H_2O)$ under the same conditions. Thus, high mass resolution was required on the upstream quadrupole, which significantly reduced the ion signal. The identity of the ion could be ascertained because breakup on injection yielded CO_3^-. Only very mild injection

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FIG. 1. Rate constants for the reactions of CO_3^- and O_3^- reacting with NO as a function of temperature. The present data are shown as solid circles and squares, respectively. Previous data from the NOAA laboratory (Refs. 3 and 5) are shown as open circles and squares, respectively. Power law dependencies for the present data are shown as dashed lines. The power law dependence for the O_3^- reaction does not include the highest temperature data point (see text).
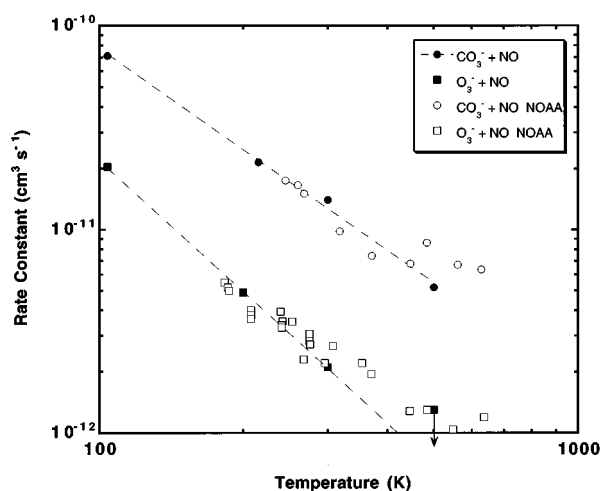

FIG. 2. Rate constants for the reactions of CO_3^- and O_3^- reacting with NO$_2$ as a function of temperature. The present data are shown as solid circles and squares, respectively. Previous data from the NOAA laboratory (Refs. 3 and 4) are shown as open circles and squares, respectively. Power law dependencies for the present data are shown as dashed lines.

conditions resulted in a large percent of the ion signal remaining as $CO_3^-(H_2O)$.

In addition, $CO_3^-(H_2O)$ could not be studied at temperatures much above 200 K, due to thermal dissociation of the $CO_3^-(H_2O)$ ions at higher temperatures.[9] Measurements involving $CO_3^-(H_2O)$ ions also required the use of a hydrogen buffer gas, which yields a lower center-of-mass collision energy for the same laboratory ion injection energy. This results in less dissociation from the initial collisions of the ions with the buffer.[10] Despite these difficulties, it was still possible to obtain several hundred counts per second of this ion at 200 K.

RESULTS AND DISCUSSION

Rate constants for the reactions of CO_3^- and O_3^- reacting with NO are shown in Fig. 1 as a function of temperature. Both reactions are inefficient and proceed exclusively by O^- transfer to produce NO_2^-. The rate constant for CO_3^- is approximately 5 times larger than that for O_3^-. Power law dependencies, excluding the highest temperature point for the O_3^- reaction, are shown as dashed lines in the figure. The highest temperature point for the O_3^- reaction is plotted as an upper limit since we could not be sure whether a small impurity in the NO reactant gas was affecting the measured rate constant. This point lies slightly above the power law dependence given by the other data points. Also plotted in Fig. 1 are the previous results from NOAA.[5] There is excellent agreement between the present measurements and those from NOAA, the data being essentially indistinguishable, except possibly for the 500 K point for CO_3^-.

The temperature dependencies of these two reactions are similar. For atmospheric purposes (temperatures of 300 K and below), we recommend the following power law expressions for the rate constants:
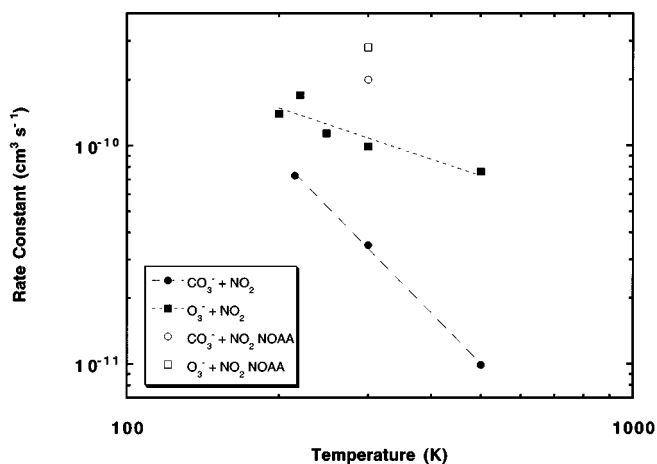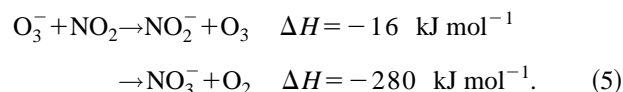
$$k_{CO_3^-+NO}=1.5\times10^{-7}*T^{-1.64}, \qquad (3)$$

$$k_{O_3^-+NO}=4.4\times10^{-7}*T^{-2.15}. \qquad (4)$$

All power law expressions in this paper contain an extra digit in the exponent to prevent roundoff error, i.e., only the first digit following the decimal point is significant. The O_3^- expression excluded the highest temperature data point. The low temperatures data ($\leq$300 K), which correspond to the important temperature range for the atmosphere, follow the power law very well. Thus, it is inconsequential for atmospheric applications whether or not the highest temperature data point is affected by impurities.

Rate constants for the reactions of CO_3^- and O_3^- reacting with NO$_2$ are shown in Fig. 2 as a function of temperature. Power law dependencies are shown as dashed lines. As was the case for NO, the reactions with NO$_2$ are also inefficient. However, in contrast to the NO reactions, in which CO_3^- reacts faster than O_3^-, the reaction of O_3^- with NO$_2$ is several times faster than the reaction of CO_3^- with NO$_2$. A likely explanation for this is that the CO_3^- reaction proceeds exclusively by O^- transfer to produce NO_3^-, whereas the O_3^- reaction proceeds both by O^- transfer and by charge transfer, forming NO_3^- and NO_2^-, respectively,

$$O_3^-+NO_2\rightarrow NO_2^-+O_3 \quad \Delta H=-16 \text{ kJ mol}^{-1}$$

$$\rightarrow NO_3^-+O_2 \quad \Delta H=-280 \text{ kJ mol}^{-1}. \qquad (5)$$

The thermochemistry is from Lias et al.[11] except for the electron affinity of NO$_2$, which was taken from Ervin et al.[12]

The percentage of NO_3^- produced in reaction (5) is shown in Fig. 3 as a function of temperature. While the reaction proceeds almost entirely by charge transfer at 500 K, roughly half of the product ions at 200 K are NO_3^- demonstrating a rather strong dependence of the branching ratio on temperature. A power dependence is shown as the dashed line in Fig. 3 and is represented as
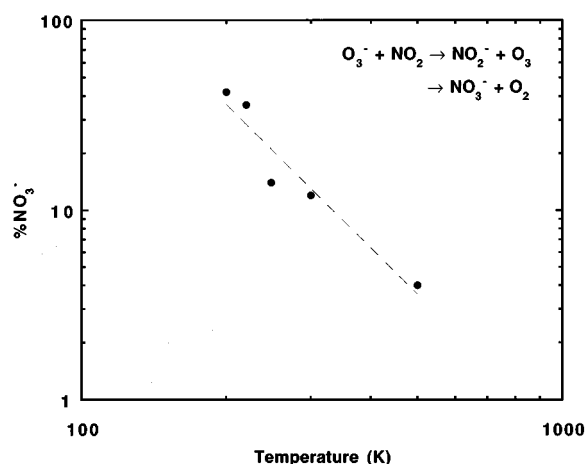
FIG. 3. Percentage of NO$_3^-$ product formed in the reaction of O$_3^-$ with NO$_2$ as a function of temperature. A power law dependence of the data is shown as a dashed line.

$$\%\text{NO}_3^- = 2.3 \times 10^7 \times T^{-2.52}. \tag{6}$$

The scatter in the data is attributed to low signal levels.

The mechanism of reaction (5) is likely to involve initial charge transfer which is then followed by an intracomplex rearrangement. The percentage of the observed NO$_3^-$ product ion increases with decreasing temperature, where the complex lifetime becomes longer and more time is available for rearrangement. The temperature dependence of the branching ratio is approximately what is expected for the temperature dependence of the complex lifetime.[13]

Thermal rate constants for the reactions of CO$_3^-$ and O$_3^-$ with NO$_2$ were measured previously at the NOAA laboratory,[3,4] and these are plotted in Fig. 2 as open points. The agreement is not very satisfactory, only within about a factor of 3–5 which is quite unusual. Data from our laboratory usually agree very well with data taken at the NOAA laboratory, e.g., the data shown in Fig. 1 and those reported elsewhere.[7,14,15] However, the NOAA group reported NO$_3^-$ as the exclusive product of the reaction of O$_3^-$ with NO$_2$. At room temperature we find that NO$_3^-$ accounts for only 12% of the reactivity. The NOAA group looked specifically for the charge transfer product, as they attempted to bracket the electron affinity of NO$_2$, and the fact that they observed only NO$_3^-$ indicates some unknown chemistry probably interfered in their flowing afterglow measurements, possibly from O atoms or O$_3$ formed in the ion source. The NOAA flowing afterglow measurements discussed here were performed using a pure oxygen buffer gas. For this reason, we repeated our measurements using an oxygen buffer but found no significant difference from the data taken using a helium buffer.

A previously reported beam study[16] of the reaction of O$_3^-$ with NO$_2$ also yielded a rate constant larger than the present value and in satisfactory agreement with the NOAA results. However, Lifschitz et al.[16] found that the majority of the reactivity is due to charge transfer, as reported in the present study. They also found that the charge transfer contribution increases with increasing collision energy. The percentage of NO$_3^-$ production found in their experiment is in

relatively good agreement with the data shown in Fig. 3, especially considering that the two techniques have differing energy distributions. The lowest kinetic energy in their experiments corresponds to a temperature of about 400 K.

In general, thermal rate constants measured in a SIFT are more reliable than those measured in either a flowing afterglow or a beam apparatus. Beam data suffer from collection efficiency problems and nonthermal energy distributions, especially at low energy. The flowing afterglow, although similar to a SIFT, has the disadvantage of having multiple gases and multiple ions present in the flow tube at the same time.

To account for the differences between our measurements and those made previously, we have considered the possibility that there were dimers or other impurities in the NO$_2$ reactant gas. To discount the possibility of interference by NO$_2$ dimers, we made measurements using a dilute gas mixture, in which the partial pressure of NO$_2$ in the sample reservoir was kept low (10–30 Torr). We found no measurable difference between neat NO$_2$ and the dilute mixture. We do not feel that other impurities should be a problem in our results either. We synthesized a sample of NO$_2$ (from NO and O$_2$) in order to check for a problem with our source of NO$_2$. Our two data sets agree within experimental uncertainty, except for the CO$_3^-$ reaction at 500 K, i.e., for the smallest rate constant measured for NO$_2$ in this study. We attribute the slightly larger rate constant observed to a small ($\sim$1%) HNO$_3$ impurity in the synthesized NO$_2$. For an impurity in our sample to be the cause of the discrepancy between our results and the previous measurements, the impurity must be nonreactive and make up over 80% of the sample. (A fast reacting impurity will yield larger rather than smaller rate constants.) This scenario seems highly unlikely. The good agreement between the branching ratios measured in the present and beam experiments indicates that impurities were probably not a problem in the beam experiment either. Likely causes for the discrepancy in rate constants are calibration errors in the beam apparatus pressure measurement or differing energy distributions.

For these reasons, we recommend the following power law expressions for the rate constants based exclusively on the present results:

$$k_{\text{CO}_3^- + \text{NO}_2} = 2.6 \times 10^{-5} * T^{-2.38}, \tag{7}$$

$$k_{\text{O}_3^- + \text{NO}_2} = 9.1 \times 10^{-9} * T^{-0.79}. \tag{8}$$

An additional measurement of these rate constants is warranted to help resolve the discrepancy.

Rate constants for the reactions of CO$_3^-$(H$_2$O) with NO and NO$_2$ are shown in Fig. 4. Data from the NOAA laboratory are also included in the figure. As discussed previously, these reactions were examined in the present study at temperatures of $\leqslant$200 K only, while the NOAA workers studied the reactions at room temperature only. [The NOAA researchers were able to perform the experiments at room temperature because water was present in the flow tube, so that CO$_3^-$ and CO$_3^-$(H$_2$O) were in equilibrium.] Our low temperature rate constant measurements for the reaction of CO$_3^-$(H$_2$O) with NO, together with the NOAA room tem-
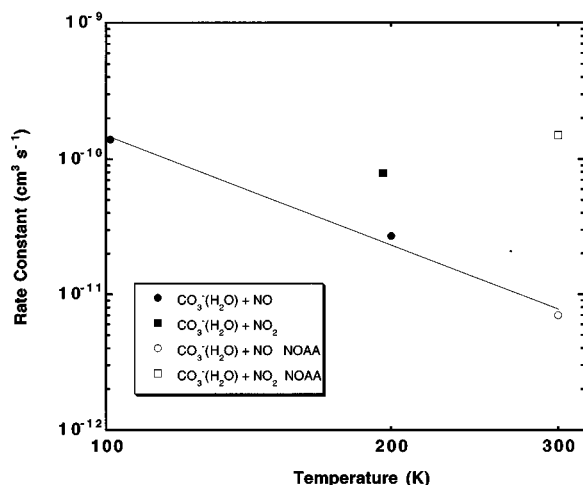
FIG. 4. Rate constants for the reactions of $CO_3^-(H_2O)$ reacting with NO and NO_2 as a function of temperature. The present data are shown as solid circles and squares, respectively. Previous data from the NOAA laboratory (Ref. 3) are shown as open circles and squares, respectively. A power law dependence for the NO data is shown as a solid line.

perature measurement, fit nicely to a power law. Thus, we recommend the following expression for the rate constant for $CO_3^-(H_2O)$ reacting with NO:

$$k_{CO_3^-(H_2O)+NO} = 4.1 \times 10^{-5} * T^{-2.72}. \qquad (9)$$

The reaction produces mainly NO_2^-, with $NO_2^-(H_2O)$ comprising less than 8% of the total product ion signal at 100 K and a negligible amount at 200 K. In the atmosphere, an equilibrium between NO_2^- and $NO_2^-(H_2O)$ is quickly established.

No temperature dependence could be measured for the reaction of $CO_3^-(H_2O)$ with NO_2. The $CO_3^-(H_2O)$ ion thermally dissociates at temperatures much above 200 K, and the NO_2 freezes in the inlet line at temperatures much below 200 K. The rate constant for this reaction at 196 K is 7.9×10^{-11} cm³ s⁻¹. The rate constant reported by NOAA for 300 K is ~1.5×10^{-10} cm³ s⁻¹. As with the other NO_2 reactions discussed previously, the NOAA rate constant for the reaction of $CO_3^-(H_2O)$ with NO_2 is significantly larger than the present value. This is especially true when one takes into account the expected negative temperature dependence of the reactivity. For the same reasons stated earlier, we feel the rate constant determined in the present study is the more reliable value. However, we welcome another measurement to resolve this discrepancy.

The 196 K rate constant reported here for the reaction of $CO_3^-(H_2O)$ with NO_2 is a reasonable first estimate for the rate constants required for atmospheric measurements since the temperature at which reaction (2) is used for trace gas analysis in the atmosphere is approximately 200 K. However, most inefficient ion–molecule reactions have rate constants that decrease with increasing temperature,[17] including those measured in the present study. Slow ion–molecule reactions generally have a weak negative temperature dependence. For reactions like those in the present study a dependence between T^{-1} and T^{-3} is reasonable. The upper range

is approximately what might be expected for the temperature dependence of the complex lifetime.[13] It is estimated that a 10% temperature variation will have a 10%–30% effect on the rate constant. Thus, better estimates for the pertinent atmospheric rate constants may be obtained by applying a temperature dependence to the 200 K value similar to that found for the reaction of $CO_3^-(H_2O)$ with NO, namely $T^{-2.7}$. Since only small extrapolations from 200 K are needed, these two cases, namely T^0 and $T^{-2.7}$, probably give a good bound to the rate constant at other temperatures.

CONCLUSIONS

We have measured temperature dependencies for the rate constants of CO_3^-, $CO_3^-(H_2O)$, and O_3^- reacting with NO and NO_2, except for the reaction of $CO_3^-(H_2O)$ with NO_2 for which only a 200 K rate constant was measured. The present measurements have serious implications for the application of reactions (1) and (2) in deriving NO and NO_2 concentrations in the atmosphere as discussed below.

Previous temperature dependencies of the rate constants for the reactions of CO_3^- and O_3^- with NO are in good agreement with the present measurements. We found that the reaction of $CO_3^-(H_2O)$ with NO is about a factor of 4 faster at 200 K compared with the previous 300 K measurement. This translates into derived NO concentrations that are in error by the same amount since the temperature of the atmosphere is about 200 K in the region where the NO concentration measurements were made.

Previous measurements of the rate constants for NO_2 reacting with CO_3^-, $CO_3^-(H_2O)$, and O_3^- appear to be in error. The discrepancies are large, and in all cases the previously reported rate constant values are too high. Depending on the reaction, errors of factors of 3–6 are found. This has important implications for derivations of NO_2 concentrations using the published chemical ionization mass spectrometric technique.[1,2]

For all these reactions, we recommend temperature dependencies of the rate constants for use in atmospheric chemistry. In all cases except the reaction of $CO_3^-(H_2O)$ with NO_2, these recommendations are based on the present measurements of the rate constants as a function of temperature. For the reaction of $CO_3^-(H_2O)$ with NO_2, we could measure a rate constant at 200 K only, and we assume a temperature dependence for the small extrapolation needed. This assumption should lead to errors no larger than 30%.

ACKNOWLEDGMENTS

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