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Reactions of iodine oxide and iodine oxoacid anion species with nitric acid

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Abstract

Results of studies of the reactivity of anions of iodine oxides and iodine oxoacids with nitric acid are reported, including bimolecular reaction rate constants and the observed ion products. Based on this new information, these reactions are evaluated in terms of the elaborate chemistry observed. The potential relevance to atmospheric chemistry, including applications for active chemical ionization mass spectrometry, is also discussed. (Int J Mass Spectrom 179/180 (1998) 327–335) © 1998 Elsevier Science B.V.

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1. Introduction

Overall interest in iodine oxide and iodine oxoacid chemistry is widespread. For example, knowledge of iodine chemistry is necessary for the development of analytical methods for the determination of iodide and iodate in seawater [1]. In another context, gas-phase conversion of radioactive iodine to solid iodine oxides is being explored for application in nuclear facilities [2]. Also, in other laboratories, studies are being conducted to elucidate the sorption of iodide and iodate onto andosols [3]. The structural parameters of hydration of the iodate ion have been calculated to obtain information on glass formation in iodate systems [4]. There is also interest in iodine chemistry in the atmosphere; reactions involving formation of OI and HOI (DOI) are being explored in order to shed light on the thermochemical properties of these species for incorporation into atmospheric models [5,6]. Active chemical ionization mass spectrometry (ACIMS) utilizing iodide as the primary ion, requires information on the reactivity and product formation of iodine as well as iodine oxides with atmospherically relevant reactants [7]. Also, there is an increasing interest in the possible role of iodine containing species in ozone chemistry [8,9], specifically the reactivity of free radical iodine oxides [10].

In general, there is a paucity of data on the bimolecular rate constants of iodine containing anion species. There are limited values reported for the bare iodine anion, I^-, with several reactants, and also some data [11] on the dimer anion I_2^-. Most recently, a study involving gas-phase reactions of hydrated halides with chlorine has been reported in the literature

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Dedicated to Professor Fulvio Cacace honoring his 40 years of contribution to the field of ion chemistry.

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[12]. However, the present study is the first, of which we are aware, dealing with the reactivity of the oxide and oxoacid anion species.

Methyl iodide is a highly abundant naturally occurring halomethane and several studies have focused on the transport of methyl iodide from its tropospheric sources to the upper atmosphere [13–19]. Our present understanding of the role that anthropogenic source halogens play in atmospheric chemistry brings to the forefront questions regarding “natural” fluctuations in atmospheric composition prior to and perhaps after mankind’s loading the atmosphere with ozone depleting compounds. However, there is a paucity of information as to the reaction products of naturally prevalent halogens, such as iodine species, in regard to atmospherically relevant chemical transformations.

Nitric acid has an important role in the atmosphere. It is a temporary reservoir for both OH and NO_2 species involved in reactions relevant to the ozone budget in the stratosphere [20–22]. HNO_3 is also a significant component of type I polar stratospheric clouds [23,24]. In light of the importance of nitric acid in the atmosphere, several studies of its reactions with ionic species have been made previously. Comparisons can be made to the reaction rates measured for other anion species by the groups of Fehsenfeld et al. [25], Viggiano et al. [26], Mohler and Arnold [27], Amelynck et al. [28], Huey et al. [29], Huey and Lovejoy [30], Huey [31], and Wincel et al. [32].

2. Experiment

2.1. General procedures

The fast-flow reactor employed in the present study has been described in detail previously [33,34]. A continuous flow of 7000 sccm (standard cubic centimeters per minute) helium buffer gas is employed to transport the ions into the flow tube, which is maintained at a selected monitored pressure of a few tenths torr. The helium also serves to thermalize the ions. A neutral reactant gas is introduced approximately 30 cm downstream and is allowed to react for a few milliseconds before a small fraction of the flow mixture is sampled through an orifice. The actual reaction time is determined by an electric pulsing technique that yields a direct measure of the ion residence time in the reaction zone of the flow tube under each specific reaction condition employed in a given experiment [35]. Reactant ion intensity is monitored by mass selection with a quadrupole mass spectrometer and detection with a channeltron electron multiplier (CEM).

The average pressure within the reaction region of the flow tube is monitored halfway between the reactant gas inlet and the sampling orifice. The flow rate of reactant gas is regulated by a 1–200 sccm range flow controller. The desired flows of typically less than 2 sccm of reactant are achieved by making a dilution of reactant neutral in helium, within a ballast tank. Mixtures are heated modestly from below to enhance convection and ensure a homogeneous concentration; the mixture is allowed to cool to room temperature prior to use.

2.2. Ion source

The experiments are performed using a fast-flow reactor affixed with a high pressure ion source as depicted in Fig. 1. A pressure differential is maintained between the source and the flow reactor, by forcing all gas flow through a 3 mm orifice. The source pressure has been measured to be 20 Torr, with the flow tube maintained at 0.3 Torr. Ions are formed in the source via discharge ionization of a mixture of helium buffer gas and methyl iodide. D_2O vapor is added downstream of the discharge, but still in the high pressure source region. Heavy water is used in place of light water in order to increase the mass separation of reactant ions and to minimize mass overlap with proton transfer reactions involving HNO_3. The resulting distribution of reactant ions is carried by flowing helium from the ion source into the flow tube.

In the absence of D_2O, the presence of an electric discharge in the high pressure source region generates a considerable amount of I^-. The addition of D_2O under these conditions forces consideration of several different bonding possibilities (i.e. $[D–O–I]^-$ or

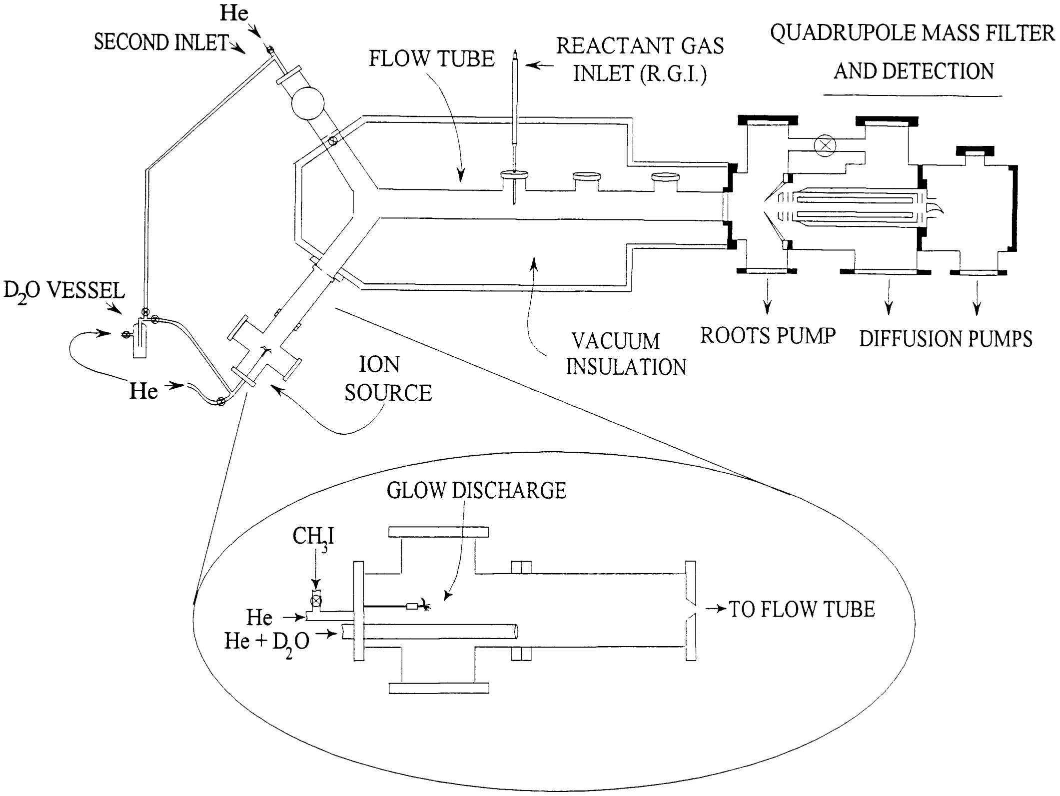

Fig. 1. Schematic diagram of the fast-flow apparatus.

$[O–I–D]^-$) as well as the likelihood of a solvated ion isomer $D_2O \cdot I^-$ versus $[D–O–I–D]^-$. These, among other cases, are addressed specifically in the following sections.

Experiments were also conducted under conditions that allow distributions to be analyzed to provide a greater understanding of the nature of the reactant ions. Oxygen was added to the helium buffer gas prior to the electric discharge in the ion source, producing a distribution of iodine oxides. Furthermore, in selected experiments, ions were produced by adding D_2O through a second source, such that the initial encounter with the iodine ion or iodine oxide ion took place in the low pressure region of the flow tube far from the electric discharge.

2.3. Neutral gas

The preparation technique for nitric acid has been discussed in previous work [35]. A vessel is prepared with one part nitric acid and two parts sulfuric acid, which is employed for drying purposes. This vessel is placed in liquid nitrogen, evacuated at this temperature, and warmed to room temperature repeatedly to ensure that the nitric acid vapor remains.

2.4. Data analysis

The details for determination of the kinetics of an ion molecule reaction in a fast-flow reactor have been extensively covered elsewhere [36]. Briefly, consider a bimolecular reaction expressed by

$$A^+ + B \rightarrow C^+ + D, \qquad (1)$$

where A^+ represents the ion species, B designates the neutral reactant, and C^+ and D represent the products. The integrated reaction rate of Eq. (4) can be written with standard pseudofirst order assumptions:

Table 1
Bimolecular rate constants

Reaction	k_{det}[a]	k_{cal}[b]	$k_{\mathrm{det}}/k_{\mathrm{cal}}$
$OI^- + HNO_3 \rightarrow$ products	1.63 (±0.3)	1.75	0.93
$DOI^- + HNO_3 \rightarrow$ products	1.74 (±0.05)	1.74	1.00
$D_2OI^- + HNO_3 \rightarrow$ products	1.59 (±0.06)	1.74	0.91
$O_2I^- + HNO_3 \rightarrow$ products	1.70 (±0.06)	1.72	0.99
$DO_2I^- + HNO_3 \rightarrow$ products	1.63 (±0.17)	1.72	0.95
$D_2O_2I^- + HNO_3 \rightarrow$ products	1.72 (±0.11)	1.71	1.01
$D_3O_2I^- + HNO_3 \rightarrow$ products	1.72 (±0.04)	1.71	1.00
$O_3I^- + HNO_3 \rightarrow$ products	0.98 (±0.06)	1.70	0.58
$DO_3I^- + HNO_3 \rightarrow$ products	1.72 (±0.06)	1.70	1.01
$D_2O_3I^- + HNO_3 \rightarrow$ products	1.69 (±0.09)	1.69	1.00
$D_3O_3I^- + HNO_3 \rightarrow$ products	1.62 (±0.13)	1.69	0.96
$D_4O_3I^- + HNO_3 \rightarrow$ products	1.71 (±0.08)	1.69	1.01

[a] Rate constant determined in this work in units of 10^{-9} cm^3/s.

[b] Calculated collision rate by Su-Chesnavich parameterized trajectory calculation modification of Langevin collision rate theory. A dipole polarizability of 4.5×10^{-24} cm^3 is estimated for nitric acid.

$$\ln (I/I_0) = -k[\mathrm{B}]t, \qquad (2)$$

where t is the residence time of the ion in the reaction region of the flow tube, measured by pulsing experiments, [B] is the concentration of reactant neutral, calculated directly from the flow through a calibrated mass flow controller, and I and I_0 denote the intensities of the monitored reactant ion species, with and without the added reactant gas, detected by the CEM. The reaction rate constant k is derived from the slope of the plot of $\ln (I/I_0)$ versus [B] as

$$k = -\mathrm{slope}/t \qquad (3)$$

3. Results

The bimolecular reaction rate constants, based on the disappearance of reactant ion intensity, are presented in Table 1. Experiments were conducted at room temperature over a range of pressures (0.2–0.8 Torr) and no pressure dependence was observed for any of the reactions. This precludes termolecular association reactions being invoked to account for the various ion products. The reactant ion distribution depicted in Fig. 2 follows the general pattern O_nI^-, DO_nI^-, $D_2O_nI^-$ . . . terminating with $D_{n+1}O_nI^-$. Only the ion products can be observed in this experiment; therefore, these are given primary consideration. Some consideration as to the probable neutral products is also presented. However, it should be clearly noted that neutral products cannot be observed in this type of experiment, and assignment of neutral products is made exclusively by inference when the ion products are observed.

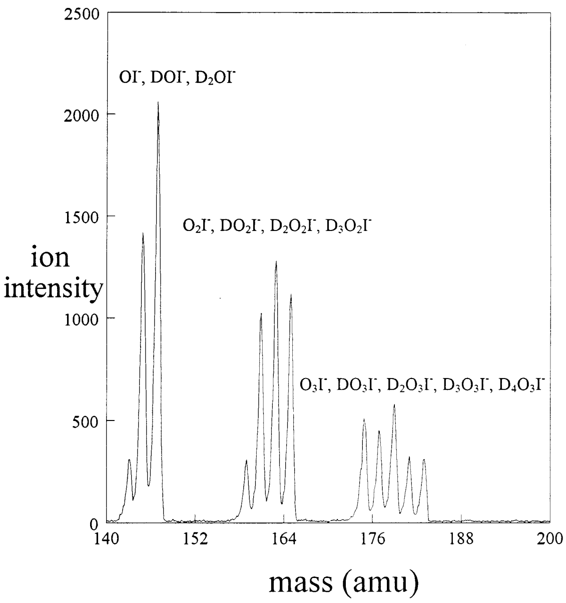

Fig. 2. Mass spectrum of the reactant ion distribution.

The addition of nitric acid to the distribution of reactant ions depicted in Fig. 2 immediately results in formation of products corresponding to: NO_3^-, $HINO_3^-$, INO_4^-, $HINO_4^-$, $DINO_4^-$, INO_5^-, $HINO_5^-$, $DINO_5^-$, $DHINO_5^-$, $D_2INO_5^-$, $D_2HINO_5^-$, INO_6^-, $DINO_6^-$, and $D_3INO_6^-$ (these species denote composition, not the structural arrangements). Initially, it appeared that the product analysis would be of such a complex nature that the experiment must proceed by adapting the selected ion flow tube (SIFT) source sometimes employed by this group to generate the ions of desired composition. A literature search of those employing SIFT technology for similar experiments revealed that resolution of the order necessary for unambiguous assignment (2 u) may not be feasible, while still producing the range of iodine oxides and oxoacids we wish to study [37]. Furthermore, experimental evidence suggests that in some cases, with this source configuration, ions of the same mass to charge ratio represent two or more distinct species which undergo completely different reactions. However, we recognize that valuable information for probing the reactions we discuss may well be gained by employing a SIFT in future studies, and we are currently modifying the SIFT employed by our group in order to produce the range of ions of interest and study some of them individually.

A series of experiments were designed in order to probe the specific reactivity of the various ion species that could be generated by the source described above. The reactivity of I^- with HNO_3 has been explored in previous work [25], and its association with HNO_3 could be observed simply by reacting I^-, generated within the source in the absence of D_2O, with nitric acid. The behavior of $I^- \cdot D_2O$ was studied by adding D_2O through a separate inlet (Fig. 1), away from the electric discharge, such that I^- and D_2O collided in the low pressure region of the flow tube. Employment of this method resulted in exclusive generation of an association product. This species was then exposed to HNO_3 added through the reactant gas inlet (RGI) and a switching reaction was observed which led to the water molecule being replaced by nitric acid. Oxygen was then added in the ion source, generating the iodine oxides, IO^-, IO_2^-, and IO_3^-; each of these species produce NO_3^- when allowed to react with HNO_3. Addition of D_2O to these iodine oxide species, introduced through the second inlet shown in Fig. 1, produced $IO^- \cdot D_2O$ and $IO_2^- \cdot D_2O$. These reactant ions generated products with masses corresponding to switching reactions when exposed to HNO_3.

Various reactive experiments conducted during the course of the investigation provide key information as to the origin of the following product ions (once again, note: neutral species cannot be determined in these experiments; however, the most likely neutral products are presented and set apart in parentheses):

$$NO_3^-: \quad OI^- + HNO_3 \rightarrow NO_3^- \ (+\ HOI), \tag{4}$$

$$O_2I^- + HNO_3 \rightarrow NO_3^- \ (+\ HI + O_2) \tag{5}$$

$$O_3I^- + HNO_3 \rightarrow NO_3^- \ (+\ HOI + O_2) \tag{6}$$

$$HINO_3^-: \quad [I \cdot D_2O]^- + HNO_3 \rightarrow [I \cdot HNO_3]^- \ (+\ D_2O) \tag{7}$$

$$HINO_4^-: \quad [OI \cdot D_2O]^- + HNO_3 \rightarrow [OI \cdot HNO_3]^- \ (+\ D_2O) \tag{8}$$

$$HINO_5^-: \quad [O_2I \cdot D_2O]^- + HNO_3 \rightarrow [O_2I \cdot HNO_3]^- \ (+\ D_2O) \tag{9}$$

This leaves INO_4^-, $DINO_4^-$, INO_5^-, $DINO_5^-$, $D_2INO_5^-$, $DHINO_5^-$, $D_2HINO_5^-$, INO_6^-, $DINO_6^-$, and $D_3INO_6^-$ to be explained by examining the remaining chemical transformations which were observed in the experiments.

Analogous switching reactions for reactant ions $[DO_2I \cdot D_2O]^-$, $[D_2O_2I \cdot D_2O]^-$, can be invoked to account for the appearance of the following product ions:

$$DHINO_5^-: \ [DO_2I \cdot D_2O]^- + HNO_3 \rightarrow [DO_2I \cdot HNO_3]^- \ (+\ D_2O) \tag{10}$$

$$D_2HINO_5^-: \ [D_2O_2I \cdot D_2O]^- + HNO_3 \rightarrow [D_2O_2I \cdot HNO_3]^- \ (+\ D_2O) \tag{11}$$

The remainder of the ion products observed can be explained by formation of molecular hydrogen in the form of HD, leaving the iodine oxide (oxoacid) bound to NO_3^- as in

$$INO_4^-: \ DOI^- + HNO_3 \rightarrow OINO_3^- \ (+ HD) \quad (12)$$

$$DINO_4^-: \ D_2OI^- + HNO_3 \rightarrow DOINO_3^- \ (+ HD) \quad (13)$$

$$INO_5^-: \ DO_2I^- + HNO_3 \rightarrow O_2INO_3^- \ (+ HD) \quad (14)$$

$$DINO_5^-: \ D_2O_2I^- + HNO_3 \rightarrow DO_2INO_3^- \ (+ HD) \quad (15)$$

$$D_2INO_5^-: \ D_3O_2I^- + HNO_3 \rightarrow D_2O_2INO_3^- \ (+ HD) \quad (16)$$

$$INO_6^-: \ DO_3I^- + HNO_3 \rightarrow O_3INO_3^- \ (+ HD) \quad (17)$$

$$DINO_6^-: \ D_2O_3I^- + HNO_3 \rightarrow DO_3INO_3^- \ (+ HD) \quad (18)$$

$$D_3INO_6^-: \ D_4O_3I^- + HNO_3 \rightarrow D_3O_3INO_3^- \ (+ HD) \quad (19)$$

In each of these cases, we consider the possibility that the D atom that leaves with the H atom is the one bound directly to the iodine, making it susceptible to attack by the HNO_3. Although, we cannot be absolutely certain that the neutral product in reactions (13), (15), (16), (18), and (19) is exclusively HD, there is a definite bias toward a significant fraction of the ion products which contain solely heavy hydrogen as accounted for by the reaction schemes described herein. Again, the presence of H atom containing product ions, which we have assigned to other reaction schemes [reactions (7)–(11)] precludes our being able to state conclusively that these neutral products are HD, but the evidence points in that direction. This is one of the areas where SIFT technology will help us clarify some lingering questions in future studies of this system.

The remaining reactant ion signal depletion/product ion appearance is accounted for by a series of proton/charge transfer reactions analogous to reactions (4)–(6), all producing NO_3^-.

$$NO_3^-: \ DOI^- + HNO_3 \rightarrow NO_3^- \ (+ DHO + I) \quad (20)$$

$$NO_3^-: \ DO_2I^- + HNO_3 \rightarrow NO_3^- \ (+ DH + O_2 + I) \quad (21)$$

$$NO_3^-: \ D_3O_2I^- + HNO_3 \rightarrow NO_3^- \ (+ D_2O + HDO + I) \quad (22)$$

$$NO_3^-: \ DO_3I^- + HNO_3 \rightarrow NO_3^- \ (+ HDO + O_2 + I) \quad (23)$$

$$NO_3^-: \ D_3O_3I^- + HNO_3 \rightarrow NO_3^- \ (+D_2 + HDO + O_2 + I) \quad (24)$$

A detailed "charge balance" was calculated for each of these reactions. The depletion of reactant ions was tallied along with the appearance of product ions under conditions where a low initial flow of HNO_3 was established. This procedure was employed in order to not further complicate matters with secondary processes. Because of mass discrimination effects, where one mass may be more efficiently detected than another, this type of accounting process is often not very successful when applied to a quadrupole mass filter detection system. However, using the reaction schemes described above and depicted in Table 2 in the present case, and employing a careful selection of settings to avoid mass discrimination effects, we were able to make an account for 93% of the reactant ion loss to product formation.

4. Discussion

Many of the values necessary for a thorough thermodynamic analysis of these reaction schemes are not available. Therefore, we limit our discussion to a preliminary analysis using those values that are in the literature, which do provide some foundation for further consideration [38,39].

First, it is instructive to note that the reaction [25] $Cl^- + HNO_3 \rightarrow NO_3^- + HCl$ proceeds rapidly. The analogous I^- reaction is not observed. Electron affinity considerations [40], 3.615 and 3.0591 eV for Cl and I, respectively, and 3.937 eV for NO_3, at first might be thought to suggest that the I^- reaction should take place. However, the driving force of the reaction is the formation of the neutral product;

Table 2
Account of the proposed structural (bond order) formulae along with the ion product assigned to each species

Molecular formula	Proposed structural formula	Reaction	Products
OI^-	$[O–I]^-$	$+ HNO_3 \rightarrow$	NO_3^- (+ HOI)
DOI^-	$[O–I–D]^-$	$+ HNO_3 \rightarrow$	$OINO_3^-$ (+ DH)
	$[D–O–I]^-$	$+ HNO_3 \rightarrow$	NO_3^- (+ DHO + I)
D_2OI^-	$[D–O–I–D]^-$	$+ HNO_3 \rightarrow$	$DOINO_3^-$ (+ DH)
	$[I \cdot D_2O]^-$	$+ HNO_3 \rightarrow$	$[I \cdot HNO_3]^-$ ($+D_2O$)
O_2I^-	$[O–I–O]^-$	$+ HNO_3 \rightarrow$	NO_3^- ($+HI + O_2$)
DO_2I^-	$[O_2I–D]^-$	$+ HNO_3 \rightarrow$	$O_2INO_3^-$ (+ DH)
	$[D–O–I–O]^-$	$+ HNO_3 \rightarrow$	NO_3^- ($+DH + O_2 + I$)
$D_2O_2I^-$	$[DO_2I–D]^-$	$+ HNO_3 \rightarrow$	$DO_2INO_3^-$ (+ DH)
	$[IO \cdot D_2O]^-$	$+ HNO_3 \rightarrow$	$[IO \cdot HNO_3]^-$ ($+ D_2O$)
$D_3O_2I^-$	$[D_2O_2I–D]^-$	$+ HNO_3 \rightarrow$	$D_2O_2INO_3^-$ (+ DH)
	$[DOI \cdot D_2O]^-$	$+ HNO_3 \rightarrow$	NO_3^- ($+ D_2O +$ HDO + I)
O_3I^-	$[O_3I]^-$	$+ HNO_3 \rightarrow$	NO_3^- (+ HOI $+ O_2$)
DO_3I^-	$[O_3I–D]^-$	$+ HNO_3 \rightarrow$	$O_3INO_3^-$ (+ DH)
	$[D–O_3I]^-$	$+ HNO_3 \rightarrow$	NO_3^- (+ HDO $+ O_2 +$ I)
$D_2O_3I^-$	$[DO_3I–D]^-$	$+ HNO_3 \rightarrow$	$DO_3INO_3^-$ (+ DH)
	$[IO_2 \cdot D_2O]^-$	$+ HNO_3 \rightarrow$	$[IO_2 \cdot HNO_3]^-$ ($+ D_2O$)
$D_3O_3I^-$	$[DO_2I \cdot D_2O]^-$	$+ HNO_3 \rightarrow$	$[DIO_2 \cdot HNO_3]^-$ ($+ D_2O$)
	$[DO_3I]^-$	$+ HNO_3 \rightarrow$	NO_3^- ($+ D_2 +$ HDO $+ O_2 +$ I)
$D_4O_3I^-$	$[(DO)_3I–D]^-$	$+ HNO_3 \rightarrow$	$(DO)_3INO_3^-$ (+ DH)
	$[(DO)_2I \cdot D_2O]^-$	$+ HNO_3 \rightarrow$	$[(DO)_2I \cdot HNO_3]^-$ ($+ D_2O$)

indeed, considering HCl (ΔH_f° −22.06 kcal/mol) and HI (ΔH_f° +6.3 kcal/mol) supports this argument:

$$Cl^- + HNO_3 \rightarrow NO_3^- + HCl,$$

$$\Delta H_r^0 = -7.84 \text{ kcal/mol} \quad (25)$$

$$I^- + HNO_3 \rightarrow NO_3^- + HI,$$

$$\Delta H_r^0 = +11.12 \text{ kcal/mol} \quad (26)$$

While unambiguous determination of neutral products is not possible in this experiment, one can infer that $D_{n+1}O_nI^- + HNO_3$ will produce DHO (ΔH_f^0 −58.63 kcal/mol) or D_2O (ΔH_f^0 −59.56 kcal/mol [38], thus providing sufficient energy release making these reactions sufficiently exothermic to proceed spontaneously, which we have referred to as "driving force" above. This type of reaction product is considered as likely for a number of these reactions.

One of the few reaction schemes that can be explored with recently assessed values [39,41] is $OI^- + HNO_3$ [see reaction (4)]. Given the thermodynamic evaluation of the $I^- + HNO_3$ reaction, it is not surprising that $I^- \cdot D_2O + HNO_3$ undergoes a switching reaction. It was, however, unexpected that $OI^- \cdot D_2O$ would be a switching product, namely $OI^- \cdot HNO_3$ [reaction (8); also see reaction (4)] as our results suggest. Using the conservative $\Delta H_f^0(HOI) = -9$ kcal/mol value yields $\Delta H_r^0 = -38.2$ kcal/mol which is evaluated as energetically favorable, and accounts for the experimental findings. In view of the large exothermicity, we propose that the products of this reaction are indeed NO_3^- and HOI, but that they remain associated, with the D_2O carrying off the excess energy. Thus, a potential energy surface corresponding to the bound complex is made accessible by the dynamics of the switching reaction. This type of formation mechanism could also explain the $[IO_2 \cdot HNO_3]^-$ product ion, actually having the form of

$NO_3^- \cdot HIO_2$; however we are unaware of available thermodynamic values by which to evaluate this suggestion.

The reactant ions containing at least two D atoms and one O atom appear to undergo switching reactions, where a D_2O is replaced by HNO_3 [see reactions (7)–(11)], with one exception. In the case of $D_3O_2I^-$, depletion of the reactant ion is partly accounted for by the formation of $D_2O_2INO_3^- + HD$ ~20% [see reaction (16)]. The remaining 80% of reactant ion depletion is attributed to NO_3^- formation, and this is in excellent agreement with the charge balance previously described. It might appear surprising however, that no switching product is observable, as in

$$[DOI \cdot D_2O]^- + HNO_3 \rightarrow [DOI \cdot HNO_3]^- \ (+\ D_2O) \quad \text{(not observed)} \qquad (27)$$

The reaction dynamics of the possible ligand switching reaction may be such that the potential energy surface corresponding to the bound complex is not accessible in this case.

5. Conclusions

The reactivity of iodine oxide and iodine oxoacid anion species with nitric acid has been studied, including a determination of their bimolecular reaction rate constants and ion products. Experiments were conducted such that a range of species were generated in the high pressure ion source. Further studies were designed to assist in the assignment of the product ion species. Future studies will involve determination of the detailed mechanisms of these reactions, experiments and calculations aimed at gaining structural insight in regard to a number of these species which exhibit remarkable reactivity as well as study of the reactivity of these ions with other reactant neutral species.

This information may find immediate application regarding ACIMS involving iodine as the primary ion, selected to produce characteristic secondary ions from ion–chemical reactions with the neutral gases of interest [7]. Studies of atmospheric nitric acid levels involving the use of a balloon borne mass spectrometer affixed with a discharge ion source producing iodine anion species, have raised several questions regarding the reaction rates and products of certain iodine oxide and iodine oxoacid anion species [42]. What are the possible origins of the numerous iodine oxide species concurrently generated by the ion source? What reactivity can be expected from these iodine oxide species? What are reaction rate constants for these species with nitric acid? Some answers to these questions are now available, along with explanations for species observed in the mass spectra taken in those experiments.

Interest in the role of iodine chemistry on ozone depletion has been fueled by a desire to obtain a more complete picture of the reactivity of all the halogen species present in the atmosphere. The fact that iodine is the most prominent biogenic-source halogen has not been overlooked. The exploration of the potential impact of iodine has been limited because of the fact that neutral iodine tends to be far less reactive than its fluorine, chlorine, and bromine counterparts. However, the present study demonstrates that reactions of iodine oxide and iodine oxoacid anion species with nitric acid, proceed at near collisional rates. The approach of using ion clusters to model aqueous phase ion sites including those on polar stratospheric clouds has long been of interest in this research group [43,44]. As more information about the complex chemistry of the atmosphere is unraveled, ionization and solvation mechanisms for neutral halide species are being postulated [45,46]. Considering the magnitude of the rate constants determined herein, as well as the product distributions for the various iodine containing reactant ions, reactivities analogous with certain species such as Cl^-, O_2^-, O_3^-, and NO_2^-, are found. This fact provides motivation for further consideration of iodine ion levels in atmospheric models.

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