A Study of the Heterogeneous Reaction between Dinitrogen Pentaoxide and Chloride Ions on Low-Temperature Thin Films

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When low-temperature thin films of either ionic or covalent dinitrogen pentaoxide, N_2O_5, are exposed to gaseous HCl and water, the only products observed in the solid phase by reflection−absorption infrared spectroscopy (RAIRS) are molecular nitric acid and the oxonium ion. Nitryl chloride, $ClNO_2$, is not detectable. When dinitrogen pentaoxide is co-deposited with hydrogen chloride and water at 85 K and annealed to 140 K, the resultant RAIR spectra indicate that the film is composed of $H_3O^+Cl^-$, N_2O_5, HNO_3, and D_{2h}-N_2O_4. When nitryl chloride is co-deposited with either water or HCl/water mixtures, infrared spectra indicative of solid D_{2h}-N_2O_4 are measured, as well as peaks corresponding to nitrate ions and *cis*-ClONO (chlorine nitrite). Reaction between $ClNO_2$ and its isomer, *cis*-ClONO, is proposed as an explanation for the formation of dinitrogen tetraoxide in both systems. The proposed reaction mechanism for this hydrolysis is extended to the $N_2O_5/H_2O/HCl$ deposits in order to explain the lack of observable $ClNO_2$ in such thin films.

Introduction

The chemical composition of the troposphere is influenced by reactions occurring in both the gas phase and at the interfaces between the gas, solid, and/or liquid phase. Compared to homogeneous chemical processing, the role of heterogeneous chemistry within the atmosphere is not well understood. This problem is due to the compounded difficulty of both monitoring and categorizing the huge variety of interfacial surfaces that are present and then predicting the reactions that can take place on/within them.[1]

One of the primary effects of heterogeneous chemistry on the atmosphere is the removal of trace constituents by interaction with particles and aerosols. For example, the adsorption of nitric acid on tropospheric surfaces leads to a reduction of daytime NO_2 concentration. However, it is the heterogeneous potential for the *formation* of unexpected gaseous compounds from surfaces that is currently least understood in models of atmospheric composition. For instance, a number of reactions are known to occur between atmospheric trace gases and sea salt aerosols but their kinetomechanistic pathways are not understood.[2−6] The most important contributing surface reactions are those involving chloride ions or HCl, and so the current state of knowledge for the chemistry associated with the processes is outlined below.

A deficiency of chloride ions on particles collected in or near urban areas compared to those found in seawater has often been observed.[7−9] This reduction in Cl^- concentrations has been attributed to a number of ion-exchange reactions between atmospheric trace gases and the halide surface as follows:

$$N_2O_5\,(g) + NaCl\,(s\text{ or }aq) \rightarrow ClNO_2\,(g) + NaNO_3\,(s\text{ or }aq) \quad (1)$$

$$HNO_3\,(g) + NaCl\,(s\text{ or }aq) \rightarrow HCl\,(g) + NaNO_3\,(s\text{ or }aq) \quad (2)$$

$$H_2SO_4\,(g) + 2NaCl\,(s\text{ or }aq) \rightarrow 2HCl\,(g) + Na_2SO_4\,(s\text{ or }aq) \quad (3)$$

$$2NO_2\,(g) + NaCl\,(s\text{ or }aq) \rightarrow ClNO\,(g) + NaNO_3\,(s\text{ or }aq) \quad (4)$$

All of these reactions are significant in atmospheric chemistry as they serve to convert inert solid or aqueous chloride to gas-phase “active” chlorine compounds. In particular, reactions 1 and 4 produce the highly photolabile gas-phase compounds ClNO and $ClNO_2$ that subsequently go on to form Cl and NO_x radicals when exposed to solar radiation.[10,11]

The product halogen radicals can go on to abstract hydrogen atoms from hydrocarbons and hence initiate the chain reactions that lead to photochemical smog. Indeed, it has been suggested that Cl radicals are responsible for 20−40% of the nonmethane hydrocarbon oxidation in marine environments.[12]

The most well-studied of the above four reactions is the one involving the important trace species, dinitrogen pentaoxide, which acts as a temporary reservoir for nitrogen oxides. This surface process is important because the product, nitryl chloride, ($ClNO_2$) is sufficiently reactive to form secondary products, which are potentially relevant to atmospheric chemical composition. For example, experimental studies show that $ClNO_2$ reacts with aromatic organic compounds known to be present in the troposphere. Specifically, flow tube observations indicate that the nitration of phenols is observed after exposure to gaseous $ClNO_2$.[6] Furthermore, environmental chamber measurements have shown that chlorinated organic compounds are formed upon exposure to $ClNO_2$.[13] It can also react heterogeneously with ionic anions, including bromide,[14] iodide,[15] and nitrite[14] to form a variety of gas-phase halogenated products.

The NO_x radicals produced as a consequence of $ClNO_2$ formation can go on to take part in catalytic chain reactions, which cause a *net* increase in tropospheric ozone. Reactions 1 and 4 are especially important in this respect because they lead to a regeneration of gas-phase NO_x that would otherwise have been removed from the atmosphere by the deposition of N_2O_5. As mentioned above, nitryl chloride is also extremely photolabile: it dissociates in a facile manner when exposed to visible light below 870 nm[11,16] as indicated by reaction 5

$$ClNO_2\,(g) + h\nu\,(\lambda < 870\text{ nm}) \rightarrow Cl\,(g) + NO_2\,(g) \quad (5)$$

Reaction 1 can occur with chloride ions that are either in a solid form[5,17] or in aqueous solution.[6,15] In fact, droplet-train measurements have established that the reactive uptake of N_2O_5 occurs

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more rapidly on sodium chloride solution than on pure water.[18] The reaction is of primary importance in the marine troposphere due to the high concentration of sea-salt, but it has also been proposed that it may occur in the stratosphere after volcanic eruptions.[19] Such a hypothesis is borne out by the observation of NaCl particles in the lower stratosphere after the El Chichon volcanic eruption in 1982; this event was accompanied by an increase in the HCl column density of around 40% relative to background levels.[20,21] Thus, reaction 1 can also produce active chlorine species in the lower stratosphere if sodium chloride particles are present, although it will be competing with the direct production of hydrogen chloride due to their reaction with gas-phase nitric acid[22] as follows:

$$HNO_3\ (g) + NaCl\ (s\ or\ aq) \rightarrow HCl\ (g) + NaNO_3\ (s\ or\ aq) \quad (2)$$

The reaction between hydrogen chloride and dinitrogen pentaoxide occurs in a manner analogous to the reaction of N_2O_5 with a chloride ion surface:

$$N_2O_5\ (g) + HCl\ (s\ or\ aq) \rightarrow ClNO_2\ (g) + HNO_3\ (s\ or\ aq) \quad (6)$$

In the stratosphere, reaction 6 does not occur to any significant degree in the gas-phase.[23] However, if polar stratospheric clouds (PSC's) are present, this heterogeneous reaction would lead to a reactivation of chlorine from the HCl reservoir species.[24] The process also effectively couples the odd-nitrogen/odd-chlorine catalytic cycles and can lead to denitrification of the stratosphere by the production of solid-phase nitric acid.[25]

The important, competing reaction for N_2O_5 in both the troposphere and stratosphere is the following heterogeneous hydrolysis reaction:

$$N_2O_5\ (g) + H_2O\ (s\ or\ l) \rightarrow 2HNO_3\ (s\ or\ aq) \quad (7)$$

Numerous experimental measurements of this reaction have been reported, involving a variety of techniques including flow-tube studies,[26] droplet-train,[18,27] and water clusters.[28] RAIR spectroscopic investigations of the solid-state interaction between co-deposited N_2O_5 and water−ice show that no reaction occurs at temperatures between 85 and 160 K, even after holding the film for a period of several hours. However, when N_2O_5 is deposited onto a solid water−ice film at 140 K, products from the gas−solid reaction are observed, although not when water is deposited onto frozen N_2O_5.[29,30] In the stratosphere, reaction 7 leads to denitrification, which in turn affects the ambient ozone level as less gas-phase NO_x becomes available to sequester active chlorine.

As shown above, the occurrence and balance between reactions 1, 6, and 7 have potentially important impacts on "active" chlorine release into the troposphere. The surface changes in terms of reaction intermediates, associated with these reactions have not been monitored directly before. Therefore, the purpose of the current experiments is to observe the effects of the interactions in N_2O_5/HCl/chloride ion/H_2O low-temperature thin films of varying composition using reflection−absorption infrared spectroscopy (RAIRS). By this means, it is hoped to ascertain whether the main implication drawn from kinetics investigations, i.e., that $ClNO_2$ is the primary product of the surface reaction between N_2O_5 and chloride ions, is always valid for the system.

Experimental Section

The RAIR spectroscopy experiments were performed utilizing a UHV stainless steel vacuum chamber, which was optically coupled to a Digilab FTS-60A spectrometer with aluminum mirror transfer optics. Vacuum-compatible KBr windows were used in conjunction with mirrors to focus the IR beam onto the sample position at a grazing angle of incidence (ca. 75°). The reflected beam was detected by a HgCdTe detector cooled to 77 K. The polycrystalline gold foil used as a substrate was mounted between a pair of tungsten supports which were in thermal contact with a liquid nitrogen reservoir. The substrate temperature was measured using a chromel/alumel thermocouple directly spot-welded to the gold foil; it could be varied between 80 and 1000 K with a stability of ±0.5 K. Inside the chamber, the gases were directed onto the substrate by glass guidance tubes. The total exposure of the substrate was measured by a cold cathode ionization gauge (MKS).

Ultrathin films of dinitrogen pentaoxide and hydrogen chloride hydrates ($H_3O^+Cl^-\cdot nH_2O$) were produced by effusive deposition on to the cold gold substrate. N_2O_5 was synthesized/purified according to the method of Davidson et al.[31] No impurities were observable in its gas-phase IR spectrum. The water was purified prior to deposition; HCl gas was obtained from BDH (99.6% purity), and no impurities were observed in either its gas-phase infrared or mass spectra. The compounds were either simultaneously deposited via separate glass dosing lines, or the acid mixtures were deposited onto a prepared N_2O_5 surface. The mixtures were monitored where possible using quadrupole mass spectrometry and reaction sequences were followed in the temperature range 85−170 K.

Nitryl chloride was prepared from the room-temperature reaction between 50 mbar N_2O_5 and 100 g dry sodium chloride in a darkened bulb to prevent photolysis of the product.[5] The $ClNO_2$ was transferred to a blackened glass reservoir and was found to be stable for 24 h. The main decomposition (impurity) products are N_2O_4 and ClNO as evidenced in the IR spectra as will be discussed. Hence, freshly prepared samples of $ClNO_2$ were deposited on to the cold gold substrate either in pure form or with water or with HCl/water mixtures.

Dinitrogen tetroxide was prepared by the deposition of gaseous NO_2 (BDH, 99.5%) onto the cold gold-foil surface. No impurities were detectable from the RAIR spectra obtained.

In all cases, RAIR spectra of the resulting submicrometer films were recorded at a resolution of 4 cm^{-1} by the co-addition of 256 double-sided interferograms.

Results

RAIR Spectroscopy of N_2O_5/HCl/H_2O Low-Temperature Films. Figure 1 shows the RAIR absorbance spectra produced before (a) and after (b) dosing HCl (ca. 5×10^{-7} mbar) and a small amount of water (ca.1×10^{-8} mbar) on top of N_2O_5 films grown and maintained at 135 K. This temperature was chosen because in this regime N_2O_5 exists in its ionic form, i.e., nitronium nitrate, $NO_2^+NO_3^-$. Some water was included in the dosing mixture to promote the probability of adsorption, because molecular HCl alone will not stick to the substrate, as has been discussed previously.[32] The difference spectrum between Figure 1a and Figure 1b is shown as Figure 1c. Loss peaks are observed for the $NO_2^+NO_3^-$ reactant, while simultaneous growth peaks at 1670, 1310, and 956 cm^{-1} are observed, which can be assigned to molecular nitric acid by comparison both with literature values and an authentic sample shown as Figure 2b.[33,34] The peaks correspond to the antisymmetric NO_2 stretch, the symmetric NO_2 stretch, and the NO stretching mode, respectively. The broad features observed in parts b and c of Figure 1 centered on 1700 and 1200 cm^{-1} are due to the formation of H_3O^+ ions.[35] A clear and direct comparison between the

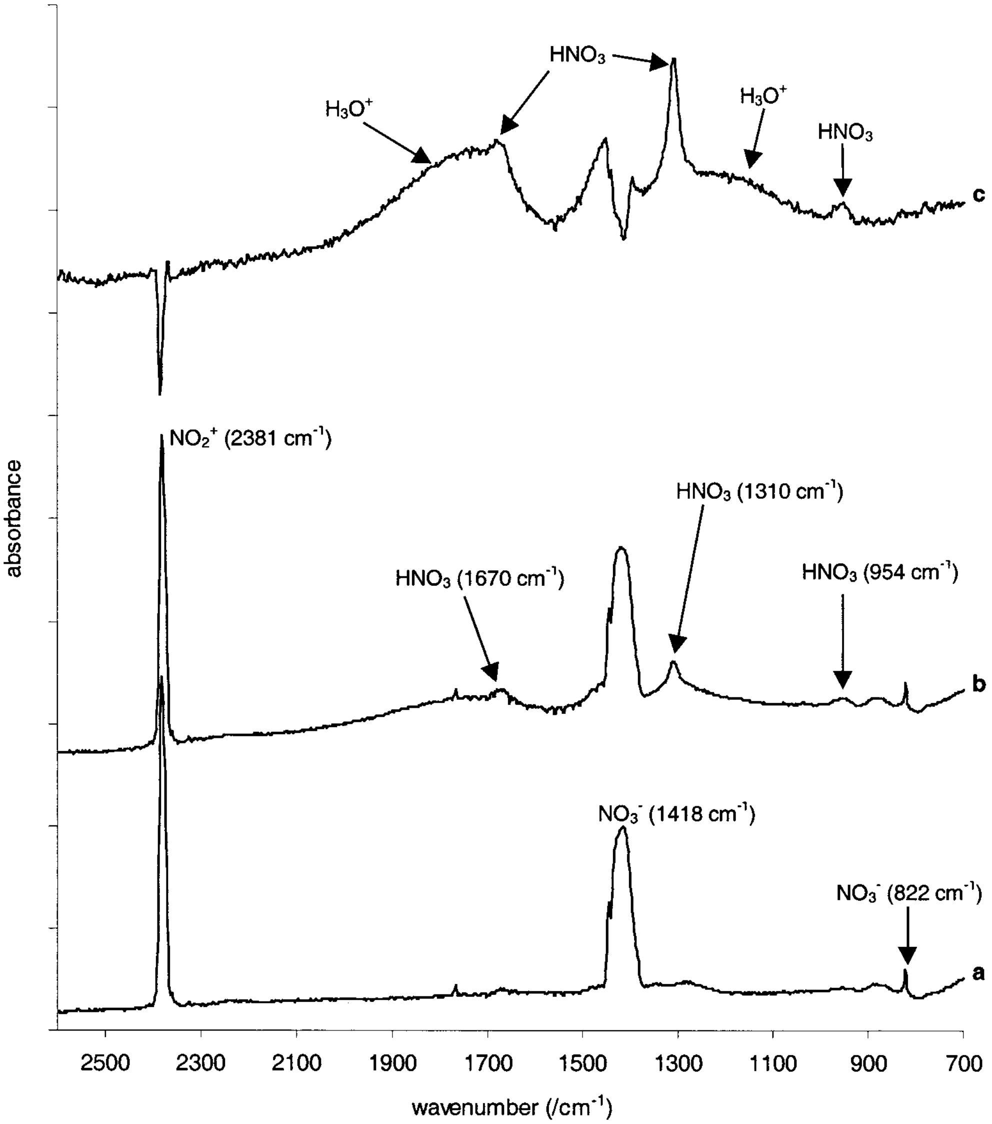

Figure 1. Reaction of a thin film of nitrosonium nitrate with HCl at 135 K: (a) RAIR spectrum of a thin film of $NO_2^+NO_3^-$; (b) RAIR spectrum of thin film of $NO_2^+NO_3^-$ following dosing of HCl/H_2O; (c) RAIR difference spectrum of spectra b and a.

$NO_2^+NO_3^-$/HCl spectrum and the HNO_3 spectrum obtained in the RAIRS apparatus is shown as parts a and b of Figure 2. Identical results were obtained when the experiments were performed on surfaces held at 85 K, i.e., when N_2O_5 is present exclusively in its amorphous covalent form.[29]

Thus, it appears that when HCl/H_2O is dosed on to either amorphous, covalent, or ionic dinitrogen pentaoxide, the only identifiable solid-phase products are molecular nitric acid along with H_3O^+ ions. For both the ionic and covalent starting materials, reaction stops once a layer of molecular acid has built up thereby “poisoning” the surface.

Upon comparison of the above measurements with previously published work, no IR absorption bands due to nitryl chloride appear to be formed in our experiments at either temperature condition. This fact is surprising in view of the well-documented reaction 6 discussed above,

$$N_2O_5\ (g) + HCl\ (s\ or\ aq) \rightarrow ClNO_2\ (g) + HNO_3\ (s\ or\ aq) \quad (6)$$

To confirm this fact, an authentic sample of $ClNO_2$ was prepared and a fresh deposit made on to the gold foil surface held at 80 K. The comparison is shown as parts a and c of Figure 2; the strong 810 cm^{-1} absorption band for $ClNO_2$ is clearly absent in Figure 2a. Comparison could not be made at 135 K because nitryl chloride desorbs before this temperature is reached. The implications are that, in the reaction experiments, the $ClNO_2$ product has either desorbed from the substrate surface or undergone further reaction. Although the former is likely in the case of reaction with nitronium nitrate at 135 K, it should not occur in the case of covalent nitrogen pentaoxide maintained at 85 K.

Complementary experiments in which N_2O_5, HCl, and H_2O were *simultaneously* deposited via separate glass dosing lines onto the cold substrate were also performed. Figure 3 shows the resulting RAIR spectrum after deposition at 85 K, and then after annealing the mixed film to a variety of temperatures.

The spectrum of the initial film held at 85 K (Figure 3a) is complicated. It indicates that a small amount of reaction has occurred because it comprises mainly a mixture of amorphous covalent N_2O_5, amorphous HCl monohydrate, molecular nitric acid, plus some of the so-called “low-temperature” form of dinitrogen tetraoxide previously discussed elsewhere.[36] Upon annealing the film to 140 K (Figure 3b), bands due to amorphous N_2O_5 disappear, while a new set appears at 1766, 1740, 1271, 764, and 741 cm^{-1}. These features correspond to the high-

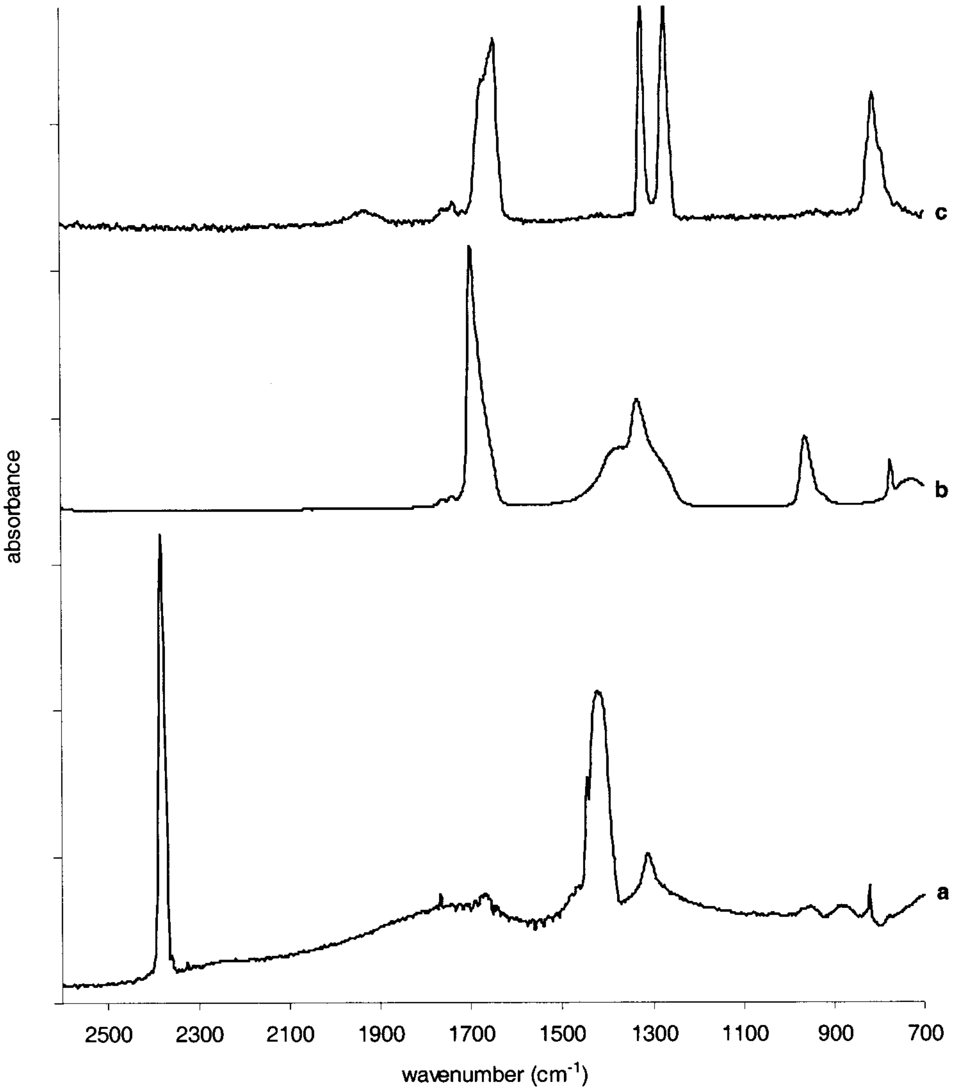

Figure 2. Comparison spectra for nitrosonium nitrate HCl reactions in a frozen thin film: (a) RAIR spectrum of thin film of $NO_2^+NO_3^-$ following reaction with HCl at 135 K; (b) RAIR spectrum of thin film of HNO_3 at 85 K; (c) RAIR spectrum of thin film of $ClNO_2$ at 85 K.

temperature form of amorphous/crystalline D_{2h}-dinitrogen tetraoxide.[36−39] For comparison, an authentic sample of N_2O_4 was prepared by the deposition of NO_2 onto the cold gold-foil surface; the resulting spectrum is shown as Figure 4. In Figure 3b, a small peak at 800 cm^{-1} also appears, which may correspond to the antisymmetric NO_2 deformation mode of $ClNO_2$ or of the nitrite ion.

Upon further warming to 160 K (Figure 3c), the majority of the D_{2h}-N_2O_4 desorbs, along with the HCl, as evidenced by the loss of broad peaks corresponding to the hydrated oxonium ion at 2580, 2125, 1720, and 1140 cm^{-1}. Only molecular nitric acid and water remain, along with some amorphous $H_3O^+NO_3^-$, as revealed by the increased intensity of the nitrate antisymmetric stretching mode at 1445 cm^{-1}. Finally, heating to 170 K (Figure 3D) results in the desorption of much of the molecular nitric acid and water, accompanied by the formation of peaks due to crystalline nitric acid dihydrate.[35] At no point was nitronium nitrate observed.

The production of large amounts of D_{2h} dinitrogen tetraoxide in the spectra displayed in Figure 3, as well as the fact that no nitryl chloride product is observed are surprising features. Therefore, a further set of experiments involving pure $ClNO_2$ were undertaken in order to clarify the mechanism.

RAIR Spectroscopy of $ClNO_2$/H_2O Low-Temperature Films. Figure 5 shows the RAIR spectrum produced after 3 min dosing of a freshly prepared sample of $ClNO_2$ at a pressure of 1×10^{-7} mbar on to the clean gold substrate held at 85 K.

Absorption peaks at ~1660, 1274, and ~810 cm^{-1} correspond to the ν_4 antisymmetric stretch, ν_1 symmetric stretch, and ν_2 deformation modes of the NO_2 group, respectively. The absorption at 1323 cm^{-1} is due to the overtone band $2\nu_6$, which has high intensity due to Fermi resonance with the ν_1 stretching mode.[40] Modes are blue-shifted from the values obtained using transmission infrared spectroscopy due to the observation of longitudinal optical modes rather than transverse optical modes, as expected for RAIR spectra. Finally, small peaks observed at ca.1750 and 1930 cm^{-1} are due to N_2O_4 and ClNO impurities, respectively. From IR analysis of authentic samples of these materials on low-temperature surfaces, the levels of impurity typically present in the main experiments are assessed as <1%. The above assignments are summarized in Table 1.

Figure 6 shows the result of co-depositing $ClNO_2$ at a pressure of 1×10^{-7} mbar with water at a pressure of 1×10^{-6} mbar for 30 s. By comparison with Figure 5 (pure nitryl chloride), it is clear that a new strong peak has appeared at 1743 cm^{-1}. This feature is accompanied by an apparent increase in intensity of the ν_1 modes of $ClNO_2$, which have shifted slightly to 1271 cm^{-1}. Furthermore, the ν_2 mode at 810 cm^{-1} broadens, increases in intensity, and grows a "sideband" feature centered at 760

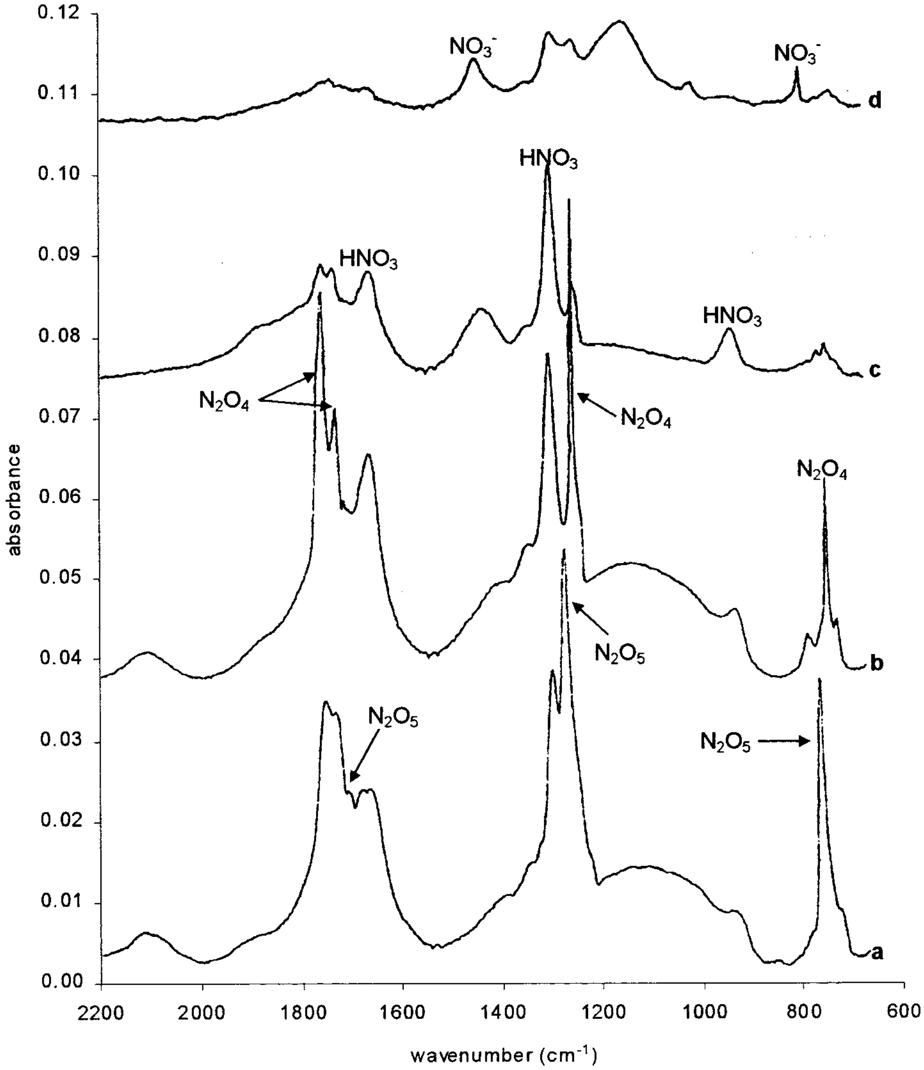

Figure 3. RAIR spectra of (a) mixed $N_2O_5/HCl/H_2O$ film at 80 K, then annealed to (b) 140 K, (c) 160, or (d) 170 K.

TABLE 1: Observed Infrared Frequencies (cm^{-1}) and Vibrational Assignments for Solid Nitryl Chloride

normal mode	RAIRS[a]	transmission[b]
ν_4 (NO_2 asym stretch)	1675 m, sh	1657 s
	1648 s	1633 s
$2\nu_6$	1323 s	1320 s
		1316 s
$\nu1$ (NO_2 sym stretch)	1274 s	1261 s
		1256 s
ν_2 (NO_2 bend)	811 m	804 m
	791 m, sh	786 m
ν_6(NO_2 out-of-pl bend)	653 w	654 sh
		652 m

[a] This work, Figure 5. [b] From ref 40.

cm^{-1}. As shown in Figure 4, a spectrum with concurrently growing absorbances at 1740, 1270, and 760 cm^{-1} corresponds to the production of amorphous D_{2h}-N_2O_4. The ν_4 mode of $ClNO_2$ is still observable as a single absorption centered around 1665 cm^{-1}. A broad peak at ca. 850 cm^{-1} is also present due to the lattice mode of amorphous water−ice. Small peaks at 1925 and 1400 cm^{-1} correspond to nitrosyl chloride and nitrate impurities, respectively.

The most important feature is a new, sharp peak at 1717 cm^{-1}, which is most readily assigned to the strong ν_1 N=O stretching mode of the cis isomer of chlorine nitrite, ClONO as measured by three other research groups.[41−43] The same product spectrum as shown in Figure 6 is observed when $ClNO_2$ and HCl are co-deposited with water.

Effusive deposition of a water layer on top of solid $ClNO_2$ maintained at 85 K showed no reactant loss or N_2O_4 formation.

Discussion

Isomerization of $ClNO_2$ to ClONO on a Low-Temperature Surface. The reaction between dinitrogen pentaoxide and hydrogen chloride is expected to produce both nitric acid and nitryl chloride as discussed above.

$$N_2O_5\ (g) + HCl\ (s\ or\ aq) \rightarrow ClNO_2\ (g) + HNO_3\ (s\ or\ aq) \quad (6)$$

From parts b and c of Figure 2, it can be seen that the infrared frequencies of nitryl chloride overlap to an extent with those of molecular nitric acid. However, if $ClNO_2$ is present, it should be readily identifiable by the appearance of its ν_2 NO_2 bending mode at around 810 cm^{-1}. This feature is not observed in the spectra displayed as parts b and c of Figure 1. Hence, only the nitric acid product of reaction 6 is identified in the solid phase. Its origin is not due to a simple stoichiometric reaction with water as given in reaction 7 because it has been shown previously that N_2O_5 does not hydrolyze when water is deposited

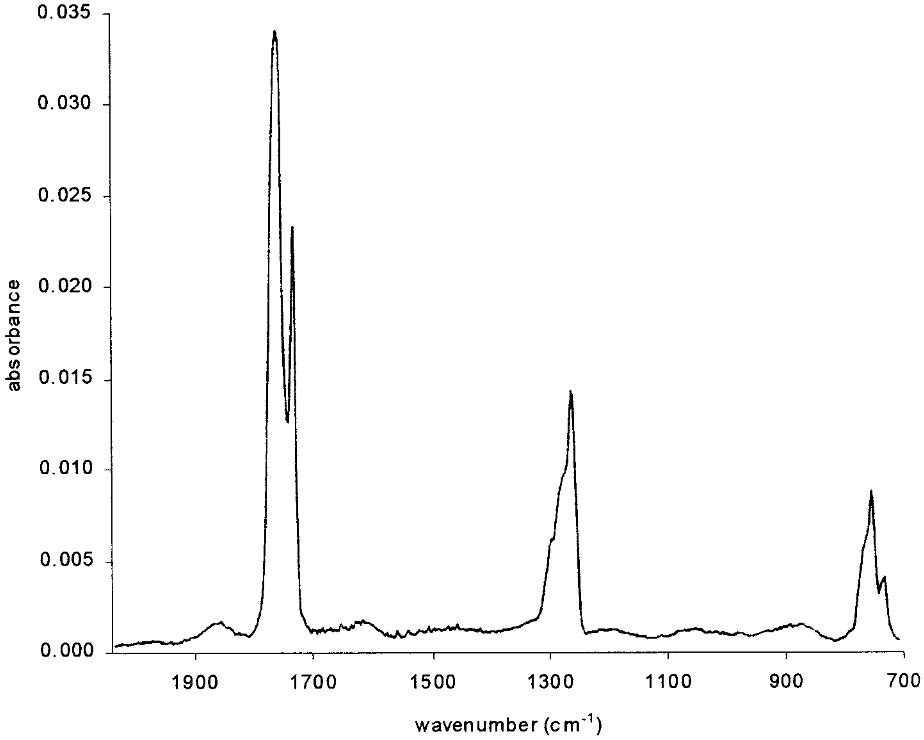

Figure 4. RAIR spectrum of D_{2h}-N_2O_4 formed after the deposition of gaseous NO_2/N_2O_4 on to the gold substrate held at 120 K.

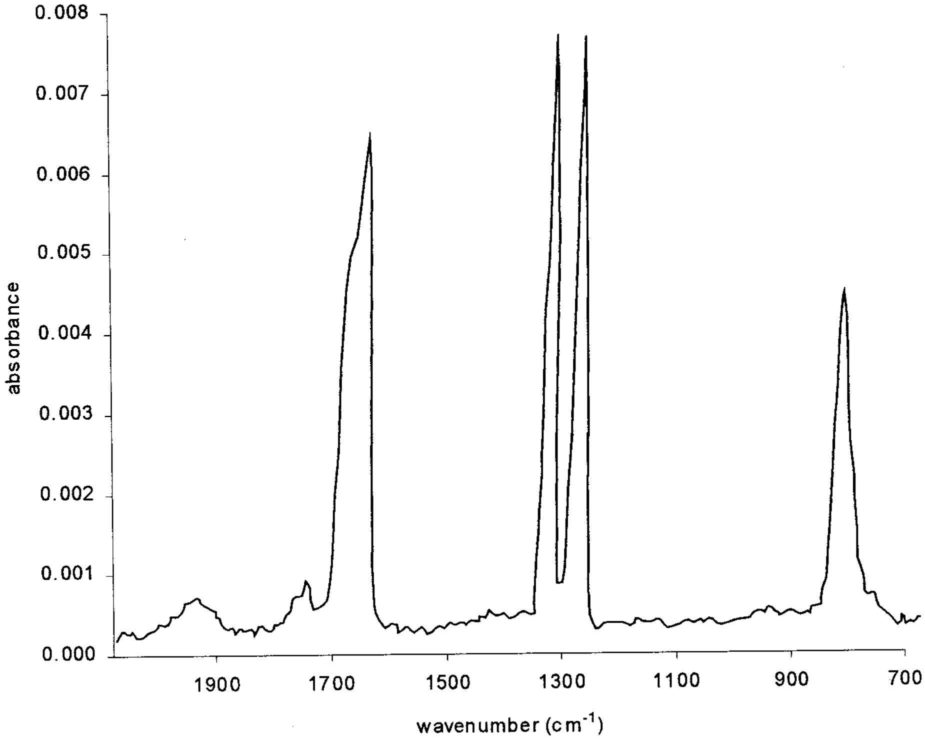

Figure 5. RAIR spectrum of pure nitryl chloride at 85 K.

onto it at any temperature between 80 and 160 K.[29,30]

$$N_2O_5\ (g) + H_2O\ (s\ or\ l) \rightarrow 2HNO_3\ (s\ or\ aq) \qquad (7)$$

The following questions therefore arise from the thin-film observations. (1) What secondary reactions of nitryl chloride can occur in the system? (2) How is the dinitrogen tetraoxide formed? (3) Are the first two questions related?

Production of the dinitrogen tetraoxide occurs when nitryl chloride and water are co-deposited with or without chloride ions present. In the simple two-component system, there are only limited possibilities for the hydrolysis of nitryl chloride. Room-temperature flow-tube experiments by Behnke et al.[6] led them to postulate that the reaction between nitryl chloride and water proceeds via the dissociated, hydrated ionic intermediate $NO_2^+Cl^-$. The overall reaction was described as follows:

$$ClNO_2 + 3H_2O \rightarrow 2H_3O^+ + NO_3^- + Cl^- \qquad (8)$$

However, the well-known absorption spectrum due to the NO_2^+

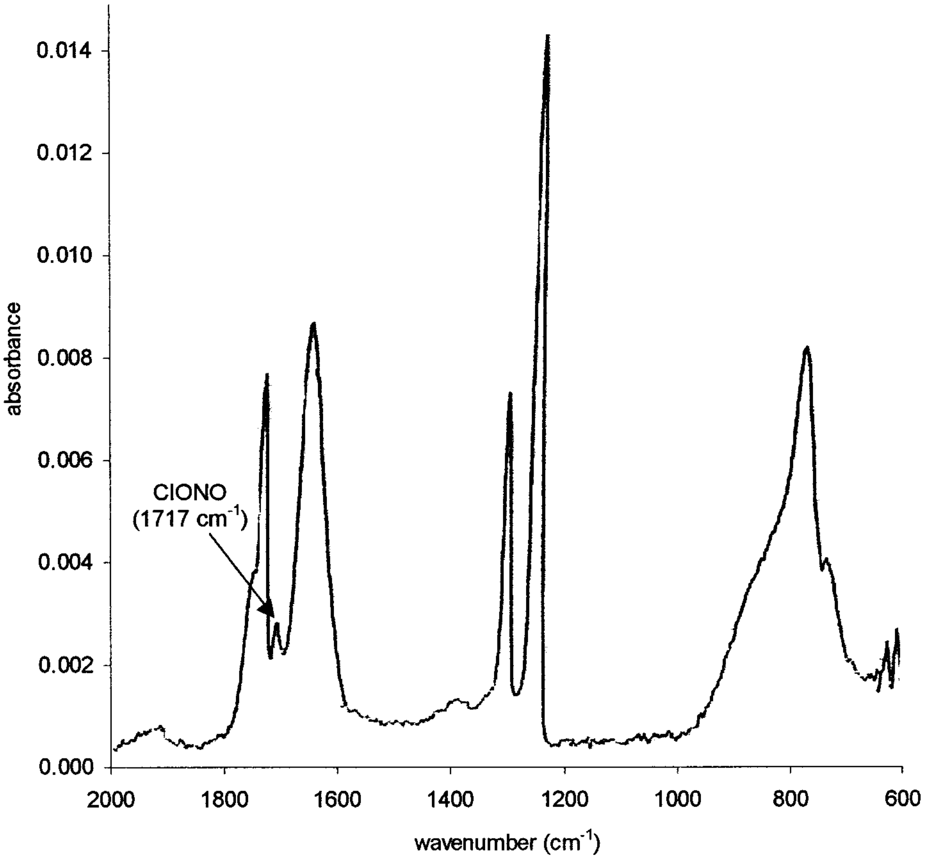

Figure 6. RAIR spectrum of nitryl chloride co-deposited with water at 85 K.

cation was not observed in any of our low-temperature studies of nitryl chloride. Hence, at the very least, it can be concluded that product channel 8 is not dominant in a thin-film.

One stoichiometric reaction that would account for the observed formation of the N_2O_4 is the following heterogeneous degradation reaction:[44]

$$2ClNO_2 \rightarrow N_2O_4 + Cl_2 \qquad (9)$$

It is clear from Figure 5 that this reaction does not occur at 85 K as no products are observed; in fact, no such chemistry is observed at any temperature before desorption takes place.

An examination of the enthalpy changes associated with reaction 9 reveals that the reaction is only slightly thermodynamically favorable with a reaction enthalpy of -6 kJ mol^{-1}.[45] However, the overall reaction enthalpy decreases to -48 kJ mol^{-1} if an alternative stoichiometric reaction is considered in which one partner is the less stable isomer, ClONO.[42]

$$ClONO + ClNO_2 \rightarrow N_2O_4 + Cl_2 \qquad (10)$$

This mechanism would represent a plausible explanation for the observed production of N_2O_4 in mixed water/$ClNO_2$ films, as long as it can be shown that the act of surface co-deposition leads to some isomerization from $ClNO_2$ to ClONO. The RAIR results do indeed provide evidence for this process because an absorption band at 1717 cm^{-1} appears, which is most readily assigned to the strong ν_1 N=O stretching mode of the cis isomer of nitryl chloride (ClONO), as previously measured in three other studies.[41-43] The same peak is observed for the co-deposition of $ClNO_2$ with HCl and water at 85 K.

The theory is further borne out by a consideration of the electron distribution for the two isomers. Simple AM1 semi-empirical calculations using the Hyperchem software package (Autodesk Inc., release 3) indicate that while $ClNO_2$ has a negative charge of -0.031 associated with the chlorine atom, the *cis*-ClONO isomer has a substantial $Cl^{\delta+}$ charge of $+0.103$. Reaction 10 may then take place via a concerted reaction analogous to the low-temperature hydrolysis of chlorine nitrate discussed in previously published studies.[46]

Low-Temperature Surface Mechanism for the Reaction between N_2O_5 and HCl. The surprising lack of observable $ClNO_2$ in the *sequential deposition* spectra measured for HCl onto a dinitrogen pentaoxide film (Figure 1) can be readily explained in terms of a mechanism, already published, for the exposure of frozen dinitrogen pentoxide to *acidic* water.[29] It can be summarized by the following sequence:

$$N_2O_5 + H_3O^+ \rightarrow NO_2^+ + H_2O + HNO_3 \qquad (11)$$

$$NO_2^+ + 2H_2O \rightarrow HNO_3 + H_3O^+ \qquad (12)$$

The production of dinitrogen tetraoxide in the presence of a large amount of water within *co-deposited*, mixed $N_2O_5/H_2O/$HCl films (Figure 3) can be explained in relation to the mechanism by which hydrogen chloride reacts with chlorine nitrate on a water–ice surface.[46] Here, the process of reactant surface coadsorption promotes the formation of partially ionized intermediates. Hence if, on a surface, the relatively large chloride ion reactant attacks the more accessible oxygen atoms of dinitrogen pentaoxide rather than either of the two sterically protected nitrogen atoms, then the initial product of the reaction will be the reactive *cis*-ClONO species rather than $ClNO_2$. The following mechanism would than operate in addition to (11) and (12).

$$N_2O_5 + H_3O^+Cl^- \rightarrow {}^{\delta+}ClONO + H_3O^+NO_3^- \quad (13)$$

$${}^{\delta+}ClONO + H_3O^+Cl^- \rightarrow Cl_2 + H_3O^+NO_2^- \quad (14)$$

$$H_3O^+NO_2^- + N_2O_5 \rightarrow N_2O_4 + H_3O^+NO_3^- \quad (15)$$

The net result being

$$2N_2O_5 + 2H_3O^+Cl^- \rightarrow N_2O_4 + Cl_2 + 2H_3O^+NO_3^- \quad (16)$$

The reaction between nitrite ions and dinitrogen pentaoxide to form N_2O_4, i.e., step 15 is well-known and proceeds with a reaction enthalpy of -123 kJ mol^{-1}.[45]

Conclusions

When low-temperature, thin films of either ionic or covalent dinitrogen pentaoxide, N_2O_5, are exposed to gaseous HCl and water, the only products observed in the solid phase by reflection−absorption infrared spectroscopy (RAIRS) are molecular nitric acid and hydrated amorphous ionic nitric acid, $H_3O^+NO_3^-$. Nitryl chloride, $ClNO_2$, is not detectable. When dinitrogen pentaoxide is co-deposited with hydrogen chloride and water at 85 K, the resultant RAIR spectra indicate that the film is composed of $H_3O^+Cl^-$, N_2O_5, HNO_3 and D_{2h}-N_2O_4.

When nitryl chloride is co-deposited with either water or HCl/water mixtures, infrared spectra indicative of solid D_{2h}-N_2O_4 are measured, as well as peaks corresponding to nitrate ions and *cis*-ClONO. Reaction between *cis*-ClONO and its isomer, $ClNO_2$, is proposed as an explanation for the formation of dinitrogen tetraoxide in both systems. The proposed reaction mechanism for this hydrolysis is extended to the N_2O_5/H_2O/HCl deposits in order to explain the lack of observable $ClNO_2$ in such thin films.

Therefore, it appears that the low-temperature, solid-phase chemistry of nitryl chloride isomers differs considerably from room-temperature studies. These results serve to emphasize the mechanistic importance of identifying reaction intermediates by in situ surface measurements as a complement to experimental monitoring of gas-phase reactants and products.

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