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Reactivity at Low Temperature of Carbon Suboxide (C_3O_2) with Amorphous Surface of HCl Hydrates Monitored by FTIR Spectroscopy

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An experimental study, monitored by FTIR spectroscopy, of the spontaneous reaction of C_3O_2 with HCl on the acid hydrate surface has been performed at low temperature. The first appearing reaction product at 85 K was assigned to chloroformylketene while the second, appearing at 145 K, to malonyl dichloride by comparison with previously reported data in matrix isolation spectroscopy. C_3O_2 was deposited at 80 K over an amorphous surface of HCl hydrates mainly formed from ionic species ($H_3O^+(H_2O)_{n-1}Cl^-$; $n = 1-3, 4, 6$), prepared by codeposition of a H_2O:HCl gaseous mixture at 80 K. The reactions were promoted by warming the substrate from 80 to 200 K. Experiments showed that monohydrate $H_3O^+Cl^-$ was more reactive than higher hydrates by easier C_3O_2 protonation. Reactions are described by an ionic mechanism catalyzed by ice water and occurring on the surface. Spectral evidence of HCl amorphous hydrates, chloroformylketene, and malonyl dichloride are reported.

Introduction

Water in microporous ice of high adsorbent capacity[1,2] can play the role of catalyst in heterogeneous reactions occurring between trapped impurities in stratospheric[3−6] or interstellar middles.[7−9] The more typical example of ice-catalyzed reaction is the formation of gaseous chlorine (Cl_2) and solid nitric acid (HNO_3) from chlorine nitrate ($ClONO_2$) reacting with hydrogen chloride (HCl).[10,11] The FTIR observations of Sodeau et al.[12,13] demonstrate that the mechanism by which HCl may interact with a second partner, adsorbed at low temperature on the ice surface, is through its ionic dissociation. The activation energy barrier seems to be reduced by solvation of the intermediate species.

We report in this paper final experiments in which water in amorphous ice of HCl hydrates catalyzes the reaction occurring between carbon suboxide (C_3O_2) and HCl in the 80−200 K temperature range. This reaction has been chosen as a model of a possible heterogeneous reaction on the ice surface of the Halley comet on which the presence of C_3O_2, H_3O^+, or H^+ has been identified during its last observation.[14−16] In a previous study, we showed by matrix isolation infrared spectroscopy that interaction between C_3O_2 and HCl in the gas phase, at room temperature, led only to the formation of a T-shaped molecular complex, identified by vibrational analysis[17,18] and presented in Figure 1. In argon matrix, this complex was perfectly stable at low temperature (10−35 K) and remained unreactive, over days, whatever the experimental conditions (gas mixture concentration in the vessel at room temperature or temperature of the matrix). Nevertheless, this result, as those of Allen et al.,[19] suggests that, under required conditions leading to the HCl ionization, the C_3O_2 could be protonated on its central carbon atom, due to its negative charge density (Figure 1), rather than on an oxygen atom. Then this bisacylium ion, stabilized by resonance, could react with an ion as for instance Cl^- to produce chloroformylketene (ClC(O)−HC═C═O). HCl ionization can be realized either by HCl adsorption on amorphous water ice surface, at temperature above 60 K, or by codeposition of HCl:H_2O vapor mixture on a cold infrared window held at low temperature (15−130 K).[20] We opted for this last procedure, and following the chosen HCl:H_2O molar ratio, we obtained HCl amorphous hydrates as defined by Delzeit, Rowland, and Devlin.[20] These hydrates are mainly referred to as $H_3O^+(H_2O)_{n-1}Cl^-$ with $n = 1-3, 4, 6$. Crystal structures of these hydrates have been determined from X-ray diffraction.[21−24] The monohydrate $H_3O^+Cl^-$ ($n = 1$) exists as a symmetric pyramidal configuration whereas the dihydrate ($n = 2$), trihydrate ($n = 3$), tetrahydrate ($n = 4$), and hexahydrate ($n = 6$) can be illustrated as a H_3O^+ core solvated by H_2O groups. Their infrared spectra, already reported in the literature,[20,25,26] have been used in this study to identify the hydrates and follow their evolutions with increasing temperatures.

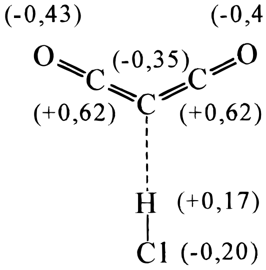

Figure 1. Structure of the C_3O_2:HCl complex[17,18] with the atomic charges reported in parentheses.

Experimental Section

Amorphous films of HCl hydrates were prepared by co-condensation of HCl and water vapors at various ratios onto the CsBr infrared window held at 80 K under the basic pressure of a cryostat (10^{-6} Torr). To probe the surface reactivity, we shall report in this paper different results mainly obtained with 1:1 ratio but also with more diluted hydrates.

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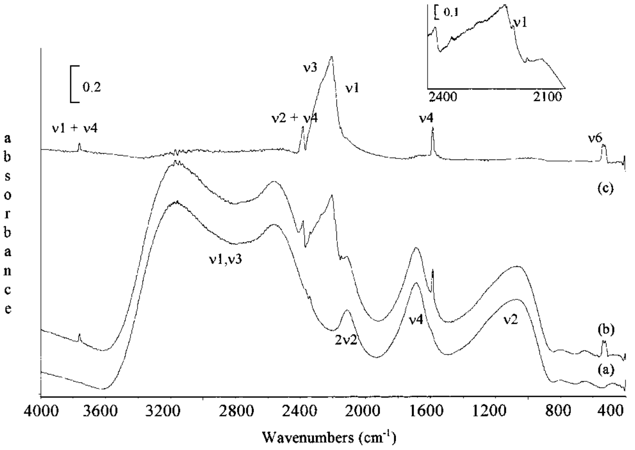


Figure 2. Infrared spectra of carbon suboxide C_3O_2 deposited on amorphous surface of HCl hydrates prepared by a codeposit at 80 K of gaseous mixture for a ratio $HCl:H_2O = 1:1$ (a) bare HCl hydrates film at 80 K where the vibrational modes of $H_3O^+Cl^-$ have been reported; (b) HCl hydrates film after C_3O_2 deposition at 80 K; (c) C_3O_2 spectrum at 80 K resulting of the (b) − (a) difference spectra. Spectra have been offset for clarity in this figure as in the following. The inset displays the ν_1 mode in the Figure 2, curve c.

Ultimately, about 40 μmol of carbon suboxide, prepared by the thermal dehydration of malonic acid in the presence of the drying agent P_2O_5 as described by Long et al.,[27] is deposited at 80 K (3 mmol/h) over the amorphous surface of HCl hydrates previously prepared. Thermal activation of the sample was realized by progressive warming of the CsBr window (from 80 to 200 K), using increments of 5 K and a heating rate of 0.5 K/min.

Due to the poor smoothing of the surfaces, it was impossible to measure accurately the film thickness by interference spectra. Nevertheless, all samples were realized with an equivalent deposited molar quantity.

For each temperature, infrared spectra of the sample were recorded on a Nicolet 7199 FTIR spectrometer equipped with a liquid N_2 cooled detector, a germanium coated KBr beam splitter, and a globar source. One hundred interferrograms were accumulated, and the resolution was set to 1 cm^{-1} without apodization.

Results and Discussion

A. Deposition of Carbon Suboxide over Amorphous Surface of HCl Hydrates ($HCl:H_2O = 1:1$). The spectrum of the substrate at 80 K, presented in Figure 2, curve a, is consistent with that previously reported for the ionic HCl monohydrate ($H_3O^+Cl^-$)[28] in its amorphous phase. The two broad peaks at 2560 and 3157 cm^{-1} were assigned to the symmetric (ν_1) and antisymmetric (ν_3) OH stretching modes, and the two lowest frequency peaks around 1065 and 1685 cm^{-1} were respectively ascribed to the symmetric (ν_2) and antisymmetric (ν_4) bending of the monohydrate. The vibrational band at 2112 cm^{-1} was assigned to the $2\nu_2$ mode. However, knowing that 1:1 water HCl complex in N_2 matrix absorbs at 2540 cm^{-1},[29,30] it is possible that the 2560 cm^{-1} band also contains a component of this complex. Then the existence of such a species within the 1:1 hydrate is not excluded.

The C_3O_2 deposition over the amorphous surface of HCl hydrate at 80 K (Figure 2, curve b) leads to the emergence of new bands in close agreement with those observed by Smith and Leroi[31] for C_3O_2 solid, indicating that the substrate is completely covered by the solid phase. The more characteristic vibrational bands at 530 cm^{-1}, 1585 cm^{-1}, and the very strong one at 2218 cm^{-1} have been assigned respectively to the C=C=O bending antisymmetric, C=C stretching, and antisymmetric C=O stretching modes labeled respectively ν_6, ν_4, and ν_3 for clarity in Figure 2, curve c. As for our study[18] in matrix isolation spectroscopy, the observation of a weak and narrow peak at 2182 cm^{-1}, relative to the ν_1 symmetric C=O stretching mode, suggests the existence of a nonlinear structure when the molecule interacts with its environment. The others bands at 2380 and 3761 cm^{-1} result from the ($\nu_2 + \nu_4$) and ($\nu_1 + \nu_4$) combination modes. After C_3O_2 deposition at 80 K, no reaction was detected.

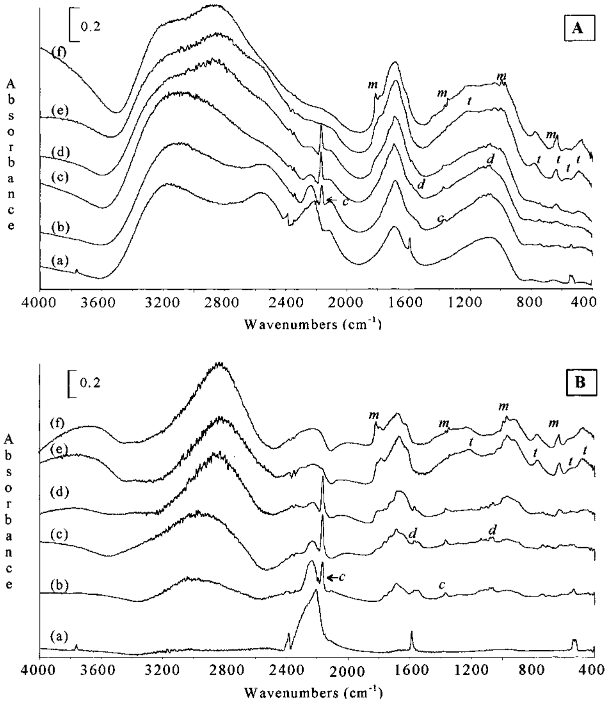


Figure 3. Successive infrared spectra (A) and difference spectra (B) relative to a progressive warming (0.5 K/min) of the C_3O_2 deposited on a hydrate film of HCl at 80 K. The spectra (B) are presented as the differences between the spectra reported in (A) and the spectrum of the amorphous surface of HCl hydrates at 80 K (Figure 2, curve a). (a) 80, (b) 130, (c) 145, (d) 150, (e) 170, (f) 190 K. The ionic di- and trihydrate species have been respectively labeled *d* and *t*. Upon temperature increase the growing bands of chloroformylketene and malonyl dichloride have been labeled *c* and *m*.

B. Thermal Activation of the Sample. The experimental results are reported in Figure 3 under two forms: the first one (A) as the spectra recorded during the experiments without modifications and the second one (B) as the differences between the spectra reported in Figure 3A and that of the amorphous surface of HCl hydrates at 80 K (Figure 2, curve a). When the sample was warmed from 80 to 145 K (Figure 3, curves a and c), we observed a decrease and a narrowing of the antisymmetric C=O stretching mode of C_3O_2 which completely disappeared above 150 K (Figure 3, curve d). This effect is induced both by sublimation of physisorbed C_3O_2 and by reaction of C_3O_2 with HCl monohydrates. Indeed, we observed the increase of two peaks, a strong and narrow peak at 2164 cm^{-1} (fwhm ≈ 16 cm^{-1}) and a weaker one at 1367 cm^{-1} (labeled c in Figure 3, curve b), due to the emergence of the new product. Correlatively, we observed a decrease of the monohydrate $H_3O^+Cl^-$ characteristic bands at 2560 and 2112 cm^{-1}. The two new arising absorption bands measured at 2164 and 1367 cm^{-1} are respectively assigned, by comparison with spectra in an argon matrix, to the C=C=O stretching and C=C−H bending modes of chloroformylketene (ClC(O)−HC=C=O).[32] The

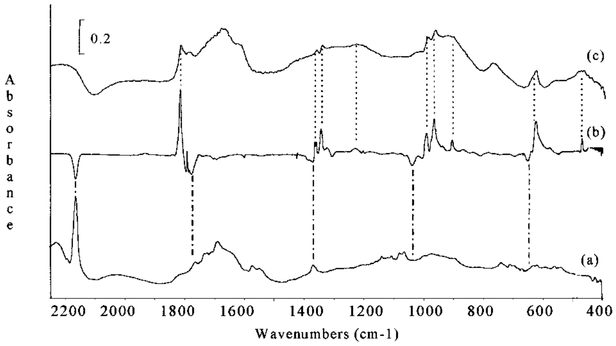


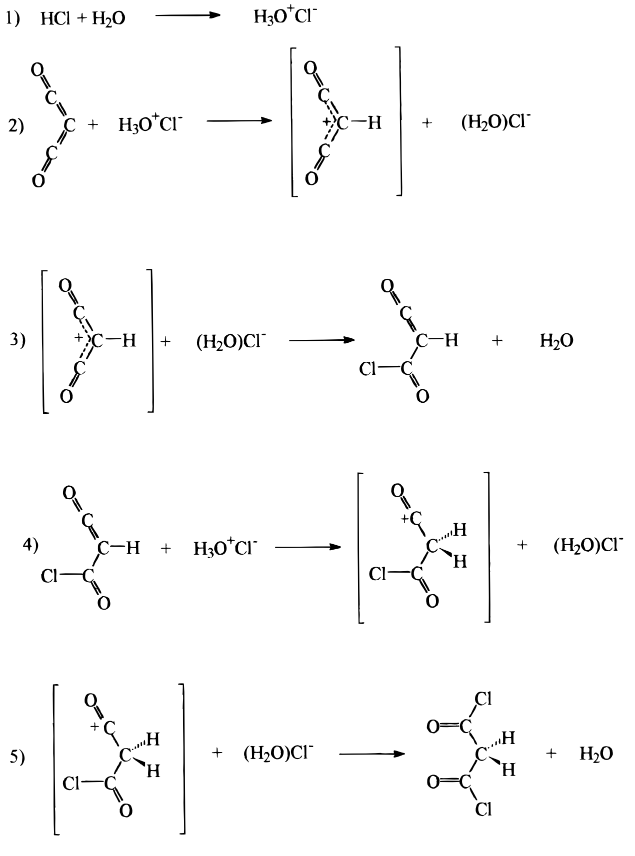
Figure 4. Difference infrared spectra in the 2250−400 cm^{-1} range of (a) chloroformylketene obtained at 145 K from the reaction of C_3O_2 with HCl and (c) malonyl dichloride obtained at 190 K from the reaction of chloroformylketene with HCl on the hydrate surface. Spectra a and c have been already presented in Figure 3B, curves c and f. The chloroformylketene and malonyl dichloride reference spectra are presented in curve b (see text). The positive bands refer to malonyl dichloride and negative bands to chloroformylketene.

weak reduction of the monohydrate's vibrational band at 2560 cm^{-1} observed between 80 and 130 K (Figure 3, curves a and b) is considerably augmented in the 135−145 K (Figure 3, curve c) temperature range where a sublimation of HCl adsorbed on the hydrate film is expected.[33] This observation strongly suggests as mentioned above the presence of a H_2O:HCl complex in the substrate until 145 K. So, the loss of HCl involves a reorganization of the substrate leading to the formation of higher hydrate mixtures. Beside absorption bands relative to the monohydrate, we observed above 145 K the formation of new hydrates as showed clearly by the emergence of a broad band at 2870 cm^{-1}, the increase of the band at 2225 and 1685 cm^{-1}, but also the broadening of that located around 1100 cm^{-1}. All these data, in addition to the appearance of several weak and sharp bands at 1081, 1145, 1553 cm^{-1} (labeled d in Figure 3, curve c) and at 482, 566, 775, 1202 cm^{-1} (labeled t in Figure 3, curve e), are in fair agreement with the respective formation of dihydrate and trihydrate ionic species.[25] So, in this temperature range the substrate is composed as a mixture of mono-, di-, and trihydrate ionic species.

Above 145 K, the most striking spectral behaviors, that we observed, were the progressive decrease of the ketene vibrational bands, which completely vanished at 170 K (Figure 3, curve e), the appearance of a shoulder around 1815 cm^{-1}, on the left side of the peak located at 1685 cm^{-1}, and the emergence of weak vibrational bands at 632, 971, 992, 1341, and 1362 cm^{-1}. These spectral features and in particular the vibrational band at 1815 cm^{-1} (labeled m in Figure 3, curve f) appeared to be very well resolved at 185 K. They belong to a new reaction product that we identified as malonyl dichloride ($ClC(O)-CH_2-C(O)-Cl$) by comparison with its infrared spectra in matrix isolation spectroscopy.[34] Indeed, the vibrational bands measured in an argon matrix[34] for the most stable conformer of malonyl dichloride at 1805 and 1799 cm^{-1} ($C{=}O$ stretching modes), at 974 cm^{-1} ($C-C$ stretching modes), and at 624 cm^{-1} ($C-Cl$ stretching modes) are in good agreement with the frequencies of the new bands previously described. Above 190 K, the sample began to sublimate and disappeared above 200 K.

We also studied, in the same conditions, the reactivity of C_3O_2 over more and more diluted amorphous hydrate substrates. Thus, for the 1:3 (at 120 K) and 1:6 (at 135 K) HCl:H_2O ratios we detected only the ketene, while for a 1:12 ratio no product was observed. The dilution effect involved a decrease in the probability of founding the $H_3O^+Cl^-$ species in the first layers of the surface substrate. This probability became very weak for 1:6 and quasizero for 1:12 ratios. From this, we conclude that the presence of $H_3O^+Cl^-$ monohydrate over or near from the surface can take a prominent part in the reaction with C_3O_2 by promoting its protonation. Similar results have been obtained by Viggiano et al.[35,36] for the reactivity of chlorine nitrate ($ClONO_2$) with $H_3O^+(H_2O)_n$ clusters. They also shown that the reactivity is negligible with $H_3O^+(H_2O)_{n\geq1}$. The more solvated protons relative to the higher hydrate of HCl (di- and trihydrates) seem to be less reactive than that of monohydrate.

SCHEME 1: Postulated Mechanisms Describing the Thermal Reactions



C. Spectral Identification of the Chlorine Species. Our assignment of the reaction products to chloroformylketene and malonyl dichloride is undoubtedly confirmed by comparison made in Figure 4 of their infrared spectra (Figure 4b) with those registered at 145 K (Figure 4, curve a) and 190 K (Figure 4, curve c) on the hydrate films and previously reported in Figure 3B. The spectra of pure chloroformylketene and malonyl dichloride were obtained from the condensation of their mixture in gaseous phase as a glass onto the cold cryostat window followed by its low warming (0.5 K/min) from 80 to 200 K. Due to their different saturation pressures for a given temperature, the chloroformylketene began to sublimate from 120 K and disappeared at 145 K while the malonyl dichloride was still stable until 200 K. The difference between the spectra of the glass at 190 and 120 K gave the infrared vibrational spectrum of malonyl dichloride as positive absorption bands and that of chloroformylketene as negative bands (Figure 4, curve b). Negative bands at 1038 and 651 cm^{-1}, relative to chloroformylketene, do not correspond exactly to positive bands in Figure 4, curve a. We believe that these bands are hidden in part by the evolution with the temperature of the HCl mono- and dihydrate vibrational bands in this spectral and temperature ranges (see Figure 3A).

D. Chemical Process Description. Although C_3O_2 does not react with HCl in gaseous or condensed phases,[17,18] we showed in section B that this reaction has become possible at very low temperature on ionized surface. This surface, mainly constituted by $H_3O^+Cl^-$ monohydrate species at 85 K (reaction 1 in Scheme 1), promotes the chloroformylketene formation. We propose to explain this reaction by a two-step ionic chemical process. The first step could be a surface reaction between C_3O_2 and H^+ coming from $H_3O^+Cl^-$ (reaction 2 in Scheme 1). As previously said in the Introduction, protonation of C_3O_2 occurs on the central carbon, and the produced bisacylium ion is stabilized by resonance. In a second step, the bisacylium ion reacts with Cl^- to produce chloroformylketene (reaction 3 in Scheme 1; we have chosen the most stable s-trans conformer but s-cis can also be considered). This process exhibits the catalytic role of ice water. H_2O produced in reaction 3 participates in the dilution of ionic HCl hydrates. Chloroformylketene in interaction with the substrate is still present until 145 K whereas, onto the CsBr substrate, it begins to sublimate in vacuum from 120 K and disappears at 145 K. Above 145 K, chloroformylketene begins to react with $H_3O^+Cl^-$ to form malonyl dichloride through an ionic mechanism (reactions 4 and 5 in Scheme 1). This latter product was not observed in more diluted hydrate films, poor in $H_3O^+Cl^-$. This point supports the assumption that the less solvated proton in monohydrate $H_3O^+Cl^-$ is more reactive than that in the higher hydrate species.

Little is known about the environment of the reactants during these processes, but remembering that C_3O_2 is deposited on hydrate amorphous films at 80 K, a part of these molecules could be incorporated in micropores near the surface. The annealing processes in the 135−145 K range could reorganize the film and probably lead to carbon suboxide and chloroformylketene in interaction with the ionic monohydrate species embedded into the first layers of the bulk. Chlorine nitrate ($ClONO_2$) and HCl incorporation into a pure ice lattice, in the 180−210 K stratospheric temperature range, has been already reported[37,38] as the result of dynamic processes.

Conclusion

We showed in this paper that carbon suboxide (C_3O_2) reacts with hydrogen chloride (HCl) at low temperature through the formation of ionic monohydrate ($H_3O^+Cl^-$) species created from a HCl:H_2O solid mixture. The reaction products have been identified by their infrared spectra as chloroformylketene (ClC(O)−HC=C=O) and malonyl dichloride (ClC(O)−CH_2−C(O)Cl). To describe this reactional process, we assume an ionic mechanism in which H_2O plays the role of catalyst. When the hydrate films are poor in $H_3O^+Cl^-$, the reaction goes on until its completion and produces essentially the chloroformylketene. C_3O_2, H_3O^+, or H^+ being identified in the ice mantle of the Halley comet, the results presented here could give information on the cryochemical reactivity of interstellar icy middles.

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