Gas-Phase Ion Chemistry of Oxalyl Chloride: An Electron Bombardment Matrix Isolation FTIR Spectroscopic Study

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The gas-phase ion chemistry of oxalyl chloride has been studied by bombardment of dilute mixtures of oxalyl chloride in rare gases with fast electrons followed by isolation of the decomposition products in the diluent rare gases at 12 K. The major products observed in the matrix by FTIR absorption spectroscopy are phosgene, carbonyl chloride radical, and carbon monoxide. Some CCl was observed when the diluent gas was argon. No ions were identified in the matrix, and it is proposed that the initially isolated ions are neutralized by secondary electrons impinging on the positively biased matrix. A change in the relative intensities of products was observed when the diluent rare gas was changed from argon to krypton and when the mixture was doped with varying concentrations of CO or N_2. These doping experiments give direct evidence for at least two mechanisms for formation of the carbonyl chloride cation, one of which involves secondary decomposition of phosgene radical cation. The products obtained here are compared with those obtained by EI mass spectrometry. It is suggested that the different product intensities observed in EI and CE mass spectra are due to the fact that product decomposition is efficiently quenched in the source following CE ionization.

Introduction

The spectroscopic characterization of molecular ions has been a major research objective in recent years. In the area of matrix isolation, there has been limited success in the mass-selection and FTIR identification of simple molecular anions and cations by Maier,[1] and more recently Leroi and Allison.[2] Non-mass-selective matrix isolation approaches have had more success in the characterization of molecular ions. Notable examples are the electron bombardment work of Szczepanski *et al.*,[3a] neon discharge work of Jacox *et al.*,[4] and X-ray bombardment work of Truttmann *et al.*,[5] all of which have resulted in isolation and spectroscopic characterization of complex molecular ions.

The technique of electron bombardment matrix isolation was originally introduced by Suzer and Andrews[3b] in a matrix isolation study of electron impact on H_2O. More recently, however, Szczepanski *et al.*[3a] have applied this technique to the generation and characterization of large molecular ions which do not undergo significant decomposition prior to their isolation. We have recently shown that application of this technique to smaller molecules with fewer internal degrees of freedom results in the isolation and characterization of a group of products generated from one complex gas-phase precursor ion. A notable example is the generation and isolation of the relatively unstable 1-propen-2-ol[6] by electron bombardment of a dilute gaseous mixture of acetone in argon along with other neutral fragments such as ketene, methyl radical, methane, and CO. Mechanisms for the formation of these products have been elucidated from these studies, and the enol is proposed to be formed via the corresponding enol cation that is the lowest energy isomer of the cation.[7] The isomer H_2CClCl[8] has also been observed by FTIR spectroscopy in the matrix following electron bombardment of CH_2Cl_2/Ar mixtures, and a similar mechanism for its formation has been proposed.

The chemistry of the oxalyl chloride cation has, to our

knowledge, received very little attention. In their attempts to generate neutral ethylenedione, Chen and Holmes[9] report that of all precursors studied, oxalyl chloride yields the largest amounts of $OCCO^{\bullet+}$ on electron impact. The electron impact mass spectrum of oxalyl chloride includes features due to $ClCO^+$, $CO^{\bullet+}$, Cl^+, $CO_2^{\bullet+}$, and small amounts of $Cl_2CO^{\bullet+}$, $C_2O_2Cl^+$, and the molecular ion.[10] The glyoxal radical cation, which is the hydrogen analogue of the oxalyl chloride radical cation, has been the focus of theoretical studies[11] since it is representative of a class of ions containing equivalent sites over which the charge may be delocalized. Conversely, the symmetry may be lowered by localization of the charge on one of the equivalent sites. The oxalyl chloride radical cation is also representative of this class of molecules.

In the present study, dilute gaseous mixtures of oxalyl chloride in argon and krypton were submitted to electron bombardment and subsequent matrix isolation (EBMI). Oxalyl chloride is proposed to be ionized and internally energized by charge exchange collisions with inert gas ions. The oxalyl chloride radical cation then undergoes unimolecular dissociation, and the products are trapped in a rare gas matrix. Neutralization products of matrix-isolated cationic fragments as well as the neutral products of gas-phase decomposition are observed in the matrix by means of FTIR spectroscopy. The effect of adding various amounts of N_2 as quencher of product internal energy and rare-gas Penning states is discussed along with the likely mechanisms for formation of products. Reasons for the difference between gas-phase CE and EI mass spectra are presented and discussed in the context of the results of the present work.

Experimental Section

The apparatus employed in electron bombardment matrix isolation studies is depicted in Figure 1 and is similar to that used by Szczepanski *et al.*[3] in the production, isolation, and characterization of the naphthalene radical cation. The electron beam is accelerated between the filament and the anode (D), which doubles as a Faraday plate to monitor the electron current.

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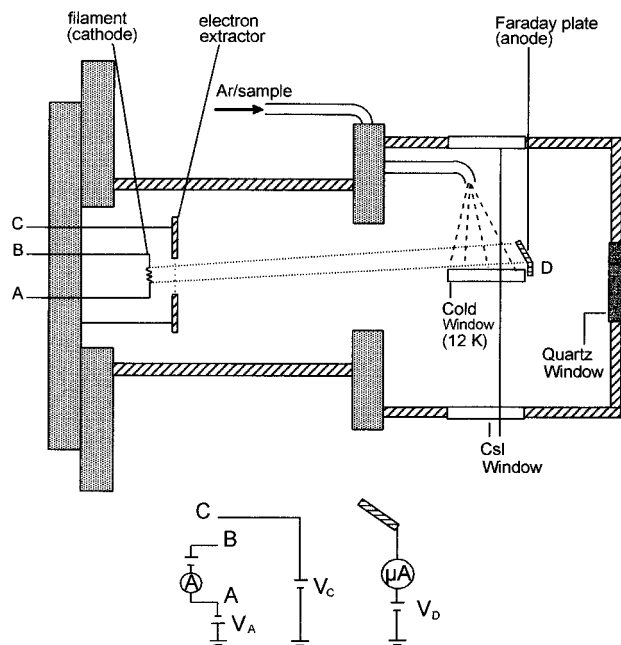⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1997.

Figure 1. View from above of the electron impact matrix isolation apparatus. Shown here is the path of the electron beam and the path of the gaseous sample. The schematic below shows the electric potentials applied on each of the electrodes, as discussed in the text.

Electrons are produced by passing a 3.5 A current through an 0.008 in. diameter tungsten filament biased at -175 V (V_A). Electrons are accelerated through 325 V by biasing the anode at 150 V (V_D). This high potential drop may not be best suited to give the optimum ionization cross section[12] but does increase ionization by virtue of the number of electrons drawn in front of the cold window, as measured at the Faraday plate. At this high potential the maximum destruction of the precursor is observed. The electron extractor plate is biased at 20 V (V_C).

The Ar/oxalyl chloride (OxCl) mixture, typically a 400/1 mixture by partial pressure, crosses perpendicular to the electron beam directly above the cold CsI window. The gas flow is kept at 0.80 sccm and is monitored by an MKS mass flow controller. The entire apparatus is kept at 10^{-7} Torr using a diffusion pump charged with a Si-based oil. The window is kept a 12 K with a closed-cycle helium refrigeration unit (APD Cryogenics Displex Model 202). Three hours of deposition time was found to be sufficient to yield spectra of all products mentioned unless otherwise noted. After 3 h of ionization and deposition, infrared spectra were recorded at 1 cm^{-1} resolution with a Bomem MB 102 FTIR spectrometer. Irradiation of samples was done with a Kratos LH150 mercury arc lamp powered by a 250 W Kratos Universal Arc Lamp Supply. For annealing of the matrices, the temperature was raised and could be held at an elevated temperature for any period of time using a Scientific Instruments Inc. 9600-1 Silicon Diode Temperature Controller.

Oxalyl chloride (99+%) was purchased from Aldrich and purified by a series of freeze−pump−thaw cycles. Prepurified argon, research-grade krypton, prepurified nitrogen and CP-grade carbon monoxide were all purchased from Matheson of Canada and were used without further purification.

Results and Discussion

Ionization and Neutralization Processes. We are confident that the chemistry occurring in these experiments results from gas-phase ion processes. A large increase in current ($10-10^2$) when gas flow begins, as measured at the Faraday plate, is undoubtedly due to an increase in electron flux as a byproduct of cation formation. However, there is an absence of bands assignable to ions or displaying the behavior of ions (such as a reduction of intensity on annealing or irradiation with low-energy visible light) which can be explained as follows. In the process of ionization, a great number of lower-energy secondary electrons are produced along with charged species. It is expected that a portion of these newly formed electrons would be attracted to the positively charged matrix or to cations in the gas phase. In the gas phase, ion−electron vertical recombination would impart enough internal energy into the newly formed neutral to ensure rapid decomposition. It would be improbable, then, to observe the neutralized counterpart of a cation if neutralization were to occur in the gas phase. However, if the energetic electrons produced in these experiments were to impact the growing matrix, they should have enough mobility to find and neutralize any cations embedded there.[13] Since neutralized primary decomposition products are observed in abundance (Table 1), we conclude that neutralization occurs in the matrix or during cation condensation in the growing matrix, where the energy of neutralization is efficiently quenched.

The process of ionization has been discussed briefly by Szczepanski *et al.*[3] The rare-gas atom, being the most dominant species in the gas mixtures used, is believed to be ionized directly by electron impact (eq 1). Since collisions with other noble gas atoms can only result in charge exchange, the cation produced exists until it captures an electron or collides with a molecular species, M, of lower ionization potential (IP). When the latter takes place, an electron can be transferred from M to the rare gas in a process known as charge exchange, CE (eq 2).

$$Ar + e^- \rightarrow Ar^{\bullet+} + 2e^- \qquad (1)$$

$$Ar^{\bullet+} + M \rightarrow Ar + M^{\bullet+}* \qquad (2)$$
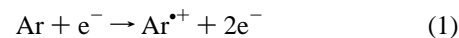
Since the electron transfer is known to be rapid, ionization of M is a vertical process from the point of view of the nuclear coordinates. If the product of the CE reaction is a noble gas atom in its ground electronic state, the molecular cation $M^{\bullet+}$ will have excess internal energy (*) equal to the difference between the electron affinity (EA) of the noble gas and the adiabatic IP of M.[16] This excess internal energy can result in varying degrees of intramolecular rearrangement and unimolecular decompositions, depending on the agent used for ionization and the difference between its EA and the IP of the molecular species of interest.

Szczepanski *et al.*[3] also note the possibility of Penning ionization processes taking place. We can argue on thermodynamic grounds[17] that Penning ionization is not likely to be responsible for the observed reactions. The metastable levels of Ar that are responsible for Penning ionization lie 11.5, 11.6, 11.7, and 11.8 eV above the ground state.[18] Even if the higher level is effecting ionization, CC cleavage of OxCl$^{\bullet+}$ would be endothermic. Extrusion of CO is slightly exothermic, but there is insufficient energy to overcome any significant barrier. Penning ionization of OxCl with Kr metastables is quite endothermic (1.43 eV with lower lying metastable), yet a similar increase in current at the anode and similar decomposition products are observed in EBMI experiments with Kr/OxCl as with Ar/OxCl solutions. In light of these points, we conclude that Penning ionization does not contribute significant to the chemistry observed on EBMI of OxCl. The ionization process is therefore most likely to be via charge exchange.

EBMI of Oxalyl Chloride in Argon and Krypton. Electron bombardment of Ar and Kr gas mixtures containing 1 part in

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TABLE 1: New Absorptions Observed after 20 h of Ionization and Subsequent Deposition of a 1 in 400 Mixture of Oxalyl Chloride in Argon

observed band (cm^{-1})	intensity[a]	lit.[b] value (cm^{-1})	assignment
2869.6	m	2870.	hydrogen chloride
2814.6	m		
2802.3	sh		
2662.8	vw		
2482.0	vw	2483.	ν_1 HCO
2259.0	sh		
2248.5	m		
2221.5	vw		
2178.3	sh		
2153.3	sh		
2148.8	sh	2148.8	carbon monoxide, ^{12}C
2138.4	vvs	2138.0	carbon monoxide, ^{12}C
2105.7	vw	2101.4	carbon monoxide, ^{13}C
2090.7	m	2091.7	carbon monoxide, ^{13}C
2049.4	vw		
2039.2	vvw		
1876.4	vs	1876.7	ν_3 ClCO
1863.0	sh	1863.	ν_3 HCO
1839.2	sh	1840.61	$\nu_2 + \nu_5 + \nu_6$ ^{35}Cl$_2$CO
1833.7	sh	1834.71	$\nu_2 + \nu_5 + \nu_6$ ^{35}Cl^{37}ClCO
1829.1	sh	1829.51	$\nu_2 + \nu_5 + \nu_6$ ^{37}Cl$_2$CO
1814.4	vs	1814.	ν_1 Cl$_2$CO
1787.4	m	1784.	ν_2 HCOCl
1650.9	m	1650.98	$2\nu_5$ Cl$_2$CO
1398.0		1399.12	$\nu_2 + \nu_5$ ^{35}Cl$_2$CO
1393.6	sh	1394.63	$\nu_2 + \nu_5$ ^{37}Cl^{35}ClCO
1388.7	sh	1390.12	$\nu_2 + \nu_5$ ^{37}Cl$_2$CO
1305.0	vw	1307.	ν_3 HCOCl
1240.0	vvw		
1160.2	vw	1160.65	$2\nu_4$ Cl$_2$CO
1185.7	w	1087.	ν_2 HCO
1059.8	vvw		
1041.8	vvw		
1023.0	sh		
1018.0	vvw		
1009.7	w	1010.08	$\nu_2 + \nu_6$ ^{35}Cl$_2$CO
1003.5	vw	1004.02	$\nu_2 + \nu_6$ ^{37}Cl^{35}ClCO
997.7	vvw	997.97	$\nu_2 + \nu_6$ ^{37}Cl$_2$CO
955.4	vw		
898.0	vw		
878.7	vvw		
869.7	vvw		
837.3	vvs	837.36	ν_5 Cl$_2$CO
810.2	w	809.81	$\nu_3 + \nu_6$ Cl$_2$CO
736.6	vw	739.	ν_4 HCOCl
721.1	vw		
696.0	m		
658.6	sh		
588.4	w		
580.6	m	580.	ν_4 Cl$_2$CO
569.9	vs	570.1	ν_1 ClCO
		568.29	ν_2 ^{35}Cl$_2$CO
564.8	sh	564.75	ν_2 ^{37}Cl^{35}ClCO
561.4	sh	561.12	ν_2 ^{37}Cl$_2$CO
527.1	vw		
468.2	vw		
460.5	vw	458.	ν_5 HCOCl
334.5	m	334.6	ν_2 ^{35}ClCO
331.4	sh	330.9	ν_2 ^{37}ClCO

[a] Intensity refers to peak height as follows: vvs = above 1.75, vs = 1–1.74, s = 0.5–0.99, m = 0.1–0.49, w = 0.05–0.09, vw = 0.01–0.049, and vvw = less than 0.01 absorbance units. [b] See text for references.

200, 400, or 800 oxalyl chloride (OxCl) all resulted in efficient decomposition of OxCl as is evident by comparison of the infrared spectrum of OxCl in Ar[19] to spectra taken after EBMI. The first part of the spectrum in Figure 2 shows the carbonyl stretching region, and it is obvious that very little OxCl is left after EBMI of 1 part in 400 OxCl in Ar. As well, after EBMI

many new bands appeared compared with the spectrum of the same gas mixture without electron bombardment. Table 1 summarizes the new features appearing after 20 h of EBMI of the 400/1 Ar/OxCl gas mixture.

The bands corresponding to the three isotopomers of phosgene[19a] (Cl$_2$CO) were stable to irradiation with visible and ultraviolet light as well as annealing. Features assigned to the carbonyl chloride radical[20] (ClCO•) were stable to irradiation but slowly decreased in intensity on annealing at 35 K. The Cl$_2$CO and CO band intensity increased slightly during this annealing. The same effects were observed in solid krypton. It was observed that 6 min of annealing at 45 K was more than sufficient to eliminate all absorptions corresponding to ClCO• in Kr and Cl$_2$CO bands did increase significantly. This effect of annealing on ClCO• absorptions has been observed before.[21]

A very weak feature assignable[22] to CCl was observed only in the Ar system. Nothing assignable[22] to CCl$_2$ was observed, possibly due to spectral interference by the OxCl features in that area of the spectrum. An enormous increase in CO was observed, so much so that after EBMI of OxCl the spectral features due to the ^{13}C isotopomer of CO[23] were observed with significant intensity.

The products observed for the decomposition of the oxalyl chloride radical cation are not totally unexpected; nevertheless, the mechanisms for their generation require some discussion. The simplest and most likely mechanism for ClCO• formation is the CC cleavage of OxCl•+ to form ClCO• and the carbonyl chloride cation (ClCO+). Thermodynamically, this is not the most favored process;[17] however, the barrier for cleavage of an extremely weak C–C bond[24] may be low enough to make this process the one with the lowest activation energy requirement. CC cleavage of OxCl•+* still leaves the products with much energy, and since the barrier for ClCO• decomposition is very low,[25] 29 kJ mol^{-1} (0.30 eV), the neutral is not as likely to survive long enough to reach the growing matrix as the cation, which is known to have a high barrier to decomposition.[10] The large amount of ClCO• observed after EBMI of OxCl/Ar and OxCl/Kr mixtures therefore provides further indirect evidence that ion chemistry is being observed. Furthermore, this is confirmation that neutralization occurs near or in the matrix since gas-phase neutralization of ClCO+ would likely result in its rapid decomposition.

In the electron impact mass spectrum of OxCl,[10] the most prominent feature is at m/z 63 corresponding to ClCO+. There is only a very small signal due to the phosgene radical cation (Cl$_2$CO•+) at m/z 98. In our experiments employing charge exchange ionization with Ar•+, one of the major products observed in the matrix is Cl$_2$CO. Cl$_2$CO can be formed directly as a neutral by extrusion of CO•+ from OxCl•+ (eq 3), but extrusion of neutral CO is much more thermodynamically favored (eq 4). The product that retains the positive charge in unimolecular decompositions of cations is the product with the lower IP,[26] and since IP(Cl$_2$CO) < IP(CO),[27,28] the more favorable process will be the one producing Cl$_2$CO•+ and neutral CO.

$$OxCl^{\bullet+} \rightarrow CO^{\bullet+} + Cl_2CO \qquad \Delta_r H = 298 \text{ kJ mol}^{-1} \quad (3)$$

$$OxCl^{\bullet+} \rightarrow CO + Cl_2CO^{\bullet+} \qquad \Delta_r H = 47 \text{ kJ mol}^{-1} \quad (4)$$

Reactions 3 and 4 are both endothermic; however, the 4.85 eV (468 kJ mol^{-1}) transferred to OxCl•+ by ionizing with Ar•+ makes both processes quite exothermic. Intuitively, one would expect a significant barrier for the concerted extrusion of CO from OxCl•+, forming Cl$_2$CO•+. Using Ar•+ as the charge
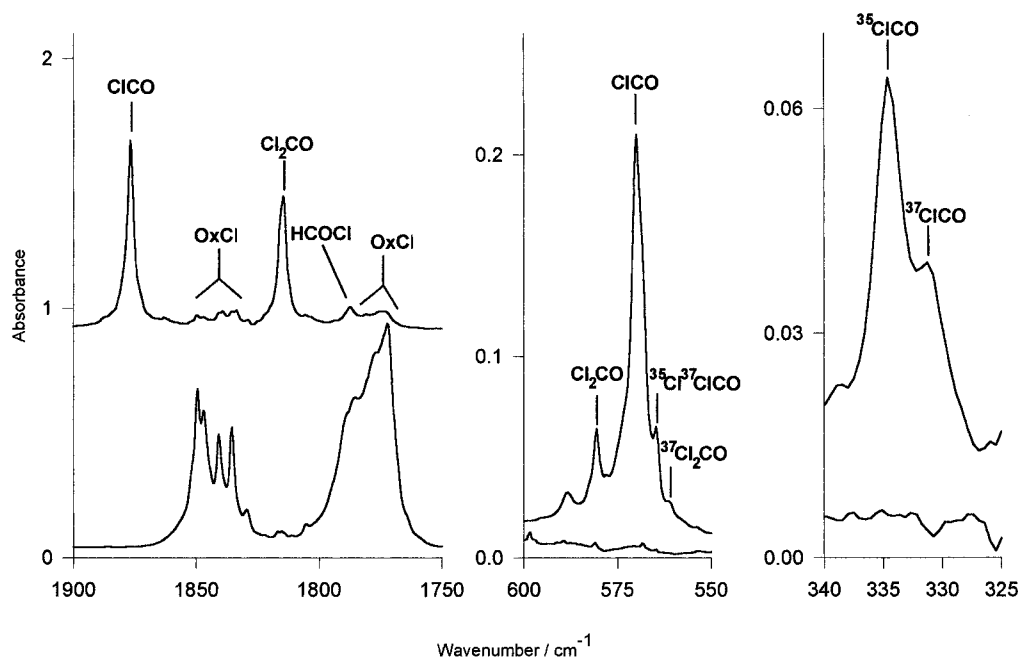
Figure 2. FTIR spectra of product region after 3 h of electron bombardment and subsequent matrix isolation of a 1 in 400 mixture of oxalyl chloride in Ar (top spectrum) and simple deposition of the same mixture for 3 h (bottom spectrum).

exchange agent seems to facilitate overcoming this barrier. We conclude that by using charge exchange with $Ar^{\bullet+}$, $Cl_2CO^{\bullet+}$ is formed by concerted extrusion of CO. This cation can then be isolated in the matrix where it is neutralized.

Both Cl_2CO and $ClCO^{\bullet}$ can also be produced as neutrals in the matrix or in the gas phase by recombination of chlorine atom with $ClCO^{\bullet}$ and CO respectively. The latter process is known to be exothermic and barrierless.[21,25] These mechanisms are unlikely in our experiments due to the very low concentration of non-rare-gas species that would be present in the gas phase. Recombination in the matrix is unlikely on the basis of concentration of reactants and extremely limited diffusion of Cl atoms in an Ar matrix[15] at 12 K. Further evidence of this comes from the fact that in the experiments where the OxCl concentration was varied there was no difference in relative intensities of the various products, as might be expected with an increase in the concentrations of Cl, ClCO, and CO. This suggests that recombination is not a mechanism by which the observed products are formed in this system.

No features assignable to ethylenedione[29] (OCCO) were observed, and its absence is expected considering the energetics of its formation. On charge exchange with $Ar^{\bullet+}$, the energy available for ionization and reaction of OxCl is 15.76 eV. This energy lies on the threshold of the appearance energy of $OCCO^{\bullet+}$ from OxCl, found by Chen and Holmes to be 15.7 ± 0.1 eV.[9] It should, however, be possible under other conditions to generate OCCO since its lowest spin-allowed dissociation limit is 310 kJ above the minimum corresponding to OCCO in its triplet state.[30] Changing the matrix gas, and therefore the charge-exchange agent, to neon (IP = 21.56 eV) would more than satisfy the energetics of formation of $OCCO^{\bullet+}$. This ion could then be trapped in the matrix and neutralized for spectroscopic characterization. A complication may be that $OCCO^{\bullet+}$ would be formed from OxCl and $Ne^{\bullet+}$ having too much internal energy to survive the time between formation and isolation in the matrix. This problem may be solved by doping the gas mixture with a quenching gas (effects of which are discussed in detail below) to remove the excess energy from $OCCO^{\bullet+}$ in the gas-phase.

Bands were assigned to three hydrogen-containing species: HCO,[31a] HCl,[22] and HCOCl.[31b] The relative intensities of these

bands increased only slightly on going to higher concentrations of oxalyl chloride in the starting gas mixture. It is assumed that these products are formed by some recombination mechanism with $H^{\bullet}$ or H^+ and the corresponding non-hydrogenated species. $H^{\bullet}$ and H^+ are likely products of EBMI of water impurities and are known to have mobility in the Ar matrix.[21]

In the Kr system, $Kr^{\bullet+}$ is the charge exchange agent and only transfers 14.00 eV into OxCl, of which 10.91 eV are used in ionizing oxalyl chloride,[32] leaving 3.09 eV (298 kJ mol^{-1}) for unimolecular reaction. There is less energy available, therefore, for decomposition compared to the Ar system. The products of decomposition are similar to that observed in the Ar system, but their relative yields differ and there is no CCl observed. It should also be mentioned that extrusion of $CO^{\bullet+}$ to form neutral Cl_2CO is thermoneutral for the Kr system. Therefore, Cl_2CO could only be produced as a radical cation from $OxCl^{\bullet+}$ using $Kr^{\bullet+}$ as charge exchange agent as in eq 4 above if there was an energy barrier. That Cl_2CO is observed in the Kr experiments again supports the conclusion that it is initially formed as a cation, as proposed for the Ar system.

The intensity of the ν_1 band of $ClCO^{\bullet}$ dropped by a factor of 2 while the ν_1 band of Cl_2CO saw a 6-fold decrease in intensity on going from the Ar to the Kr system (compare Figures 2 and 3). This may be explained by considering that the barrier for concerted extrusion of CO by $OxCl^{\bullet+}$, forming $Cl_2CO^{\bullet+}$, is the process with the higher activation energy requirement. Since $OxCl^{\bullet+}$ is formed with less internal energy in the charge exchange reaction of OxCl with $Kr^{\bullet+}$ than with $Ar^{\bullet+}$, it is expected that much less $Cl_2CO^{\bullet+}$ would be produced.

N_2 and CO Doping Experiments.[33] When N_2 and CO were used in place of the noble gas it was found that little product was observed and features corresponding to the precursor, OxCl, were most abundant. In fact, the straight deposition spectrum and the spectrum taken after EBMI were virtually identical using pure N_2 or CO as the matrix support gas. This observation suggested that the diatomic molecules were acting as quenchers, removing the excess internal energy deposited into $OxCl^{\bullet+}$ during the ionization process and stabilizing it with respect to unimolecular dissociation. It was therefore decided to explore the effect of adding varying amounts of N_2 or CO to the gas mixture, keeping the concentration of OxCl fixed.

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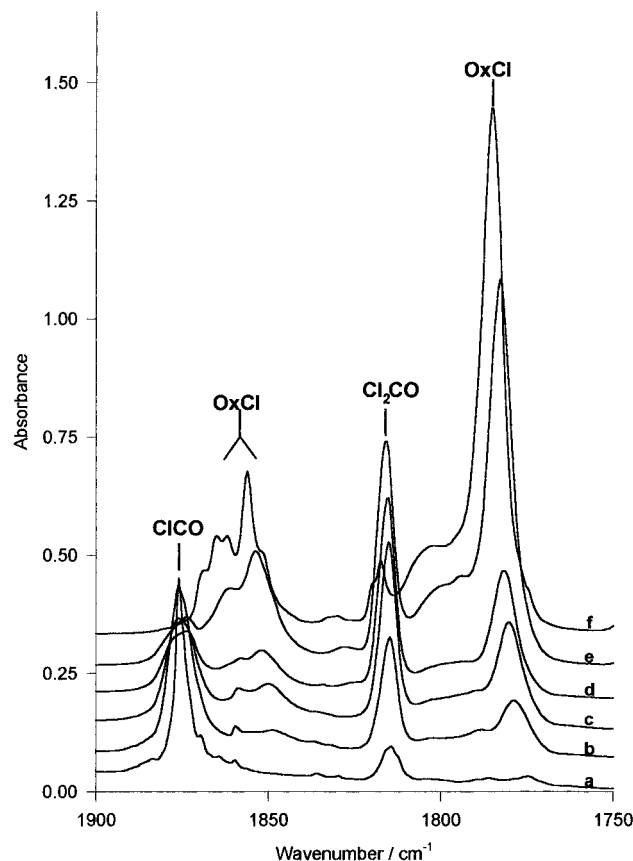
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Figure 3. FTIR spectra in the region of C=O stretching modes taken after 3 h of electron bombardment and subsequent matrix isolation of 1 in 400 oxalyl chloride to N$_2$ + Kr at different concentrations (mol %) of N$_2$: (a) 0%, (b) 17.3%, (c) 30.5%, (d) 50.4%, (e) 71.7% and (f) 100% N$_2$.

For the Kr system, values of A_{ClCO}, A_{Cl_2CO}, and A_{OxCl} are plotted against % N$_2$ in Figure 4 and spectra in the carbonyl stretch region are shown for various values of % N$_2$ in Figure 3. As is evident from Figures 3 and 4, bands corresponding to OxCl, Cl$_2$CO, and ClCO• *all* initially increase with % N$_2$ at N$_2$ levels below about 18%. Features due to ClCO• then begin decreasing in intensity, while amounts of Cl$_2$CO continue to increase until the level of N$_2$ reaches between 60 and 70%. OxCl features continuously increase in intensity with increased N$_2$. It should also be noted that the area under the CO feature drops continuously with increased N$_2$ composition, such that its area in pure N$_2$ is only about 12% of the area found in pure Kr.

It is proposed that N$_2$ efficiently quenches *all* the internally excited primary decomposition products in the gas phase: Cl$_2$CO•+, ClCO+, and ClCO•. It is obvious as well that N$_2$ also quenches the newly formed OxCl•+*. The quenched species are then isolated in the matrix where the ions are subsequently neutralized.

From these results it is evident that more Cl$_2$CO•+ is produced with N$_2$ present than is observed as neutral Cl$_2$CO in the matrix when no N$_2$ is present. Energetic Cl$_2$CO•+ formed as in eq 4a must decompose further before being trapped in the matrix. The products for this secondary decomposition are ClCO+ and chlorine atom (eq 5).

$$OxCl^{•+}* \rightarrow CO + Cl_2CO^{•+}* \tag{4a}$$

$$Cl_2CO^{•+}* \rightarrow Cl^• + ClCO^+ \tag{5}$$

These results suggest that a second mechanism for formation of ClCO+ in the gas phase exists besides simple CC cleavage

of OxCl•+*; secondary decomposition of internally hot Cl$_2$CO•+ (eq 5). The fact that the amount of ClCO• levels off and starts to decrease at about 18% N$_2$ is a result of the two separate processes for its production being suppressed by N$_2$ quenching (eqs 6 and 7)

$$Cl_2CO^{•+}* + N_2 \rightarrow Cl_2CO^{•+} + N_2^* \tag{6}$$

$$OxCl^{•+}* + N_2 \rightarrow OxCl^{•+} + N_2^* \tag{7}$$

The amount of Cl$_2$CO observed increases due to eq 6, until higher levels of N$_2$ are attained, and then eq 7 becomes more important, also cutting off the source of Cl$_2$CO•+.

Doping in the Ar system was not performed since N$_2$ or CO would be ionized in a collision with Ar•+ due to their lower IP (see ref 33). It is expected that if a quenching agent could be found with a higher IP than Ar similar results would be attained as just described for Kr.

It should be noted that adding a small amount of N$_2$ (0.25%) to the gas mixtures (OxCl/Ar and OxCl/Kr) and subjecting the mixture to EBMI resulted in no observable difference in the EBMI infrared spectrum compared to when N$_2$ was absent. Kenty,[34a] and much earlier Worthing and Rudy,[34b] observed that when small amounts of N$_2$ were present (<0.2%) in a gaseous mixture of Ar or Kr that was passed through a discharge, the emissions due to Ar or Kr were quenched. They concluded that the lower metastable levels of Ar and Kr were efficiently quenched in the presence of these small amounts of N$_2$. If these metastable states of the rare gas were causing Penning ionization of OxCl, a difference in the ratios of *some* products would be expected due to a lower amount of internal energy being deposited into OxCl•+ compared to charge exchange. This is further evidence that Penning ionization is not an important process in these experiments.

Comments on the Mass Spectra of OxCl. These quenching studies, using various diluent as well as dopant gases, answer some questions pertaining to the mass spectrum of OxCl. Why,
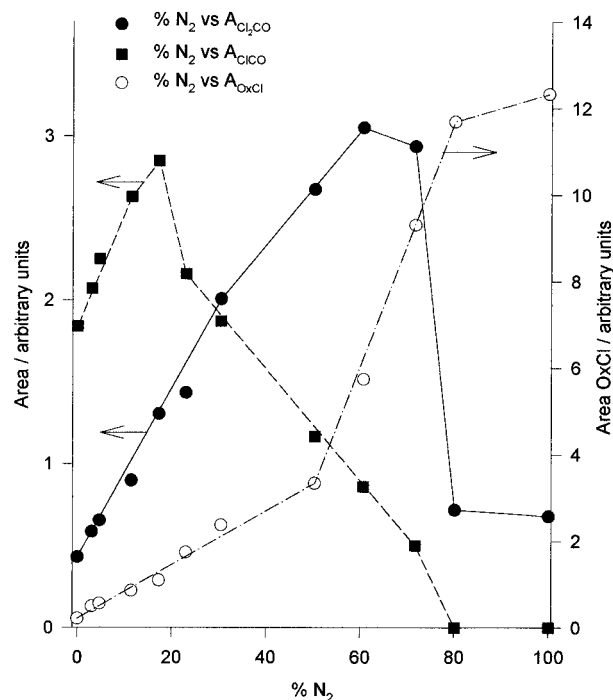

Figure 4. Plots of the areas under the C=O stretching mode of phosgene(●, left axis), carbonyl chloride radical (■, left axis), and oxalyl chloride(○, right axis) versus mol % N$_2$ in Kr; the lines are included to guide the eye.

in electron impact ionization mass-spectrometric experiments, is $Cl_2CO^{\bullet+}$ only observed in minute quantities? The explanation comes from the fact that $Cl_2CO^{\bullet+}$ is likely to have excess vibrational energy on formation and decomposes such that it is not detected in significant abundance. The fact that we observe Cl_2CO in such good abundance in our experiments, even without N_2 present, is that some of the initially internally hot $Cl_2CO^{\bullet+}$ formed is quenched by Ar and Kr. It is proposed that by adding a quenching gas, such as N_2, or even Ar or Kr, in the source for EI experiments, a greater intensity of $Cl_2CO^{\bullet+}$ and the molecular ion will be observed along with a lower abundance in the $ClCO^+$ signal. As well, it is proposed that a metastable ion peak would probably be observed corresponding to Cl_2-$CO^{\bullet+}$ in a metastable ion spectrum of $OxCl^{\bullet+}$.

It has been suggested that the only reason for observed differences in the relative intensities of peaks in mass spectra obtained when the ionization process is changed from EI to CE is simply the difference in internal energies of the ions formed by the two processes.[35,36] The internal energy incurred upon a newly formed ion in a CE reaction is specific (for example 15.76 eV − IP(of reactant) for CE with $Ar^{\bullet+}$), but ionization by EI gives ions with a large range of internal energies. This may in fact give differing intensities in mass spectra, but the fact that the charge-exchange agent is also a quenching agent to our knowledge has not been discussed as having an effect on product ratios. The differing degrees of fragmentation are not only a result of the ionization process but also a result of more of the primary (and to lesser degrees secondary, tertiary, etc) decomposition products being quenched by what is essentially a bath of quenching gas in the source. Adding a quenching gas is not a new concept, however, since mass spectrometrists often use N_2 in the ion source to stabilize metastables. It is now suggested that CE ionization has the same effect of stabilizing metastables in the source since the CE agent is also likely to have quenching capabilities.

Conclusions

The results of the N_2-doped experiments show that $Cl_2CO^{\bullet+}$ formed from the unimolecular decomposition of $OxCl^{\bullet+}$ is a metastable species and, in the absence of an efficient quenching species, decomposes rapidly to $ClCO^+$ and chlorine atom. These results also show conclusively that $ClCO^{\bullet}$ detected in the matrix originates from at least two distinct mechanisms, CC cleavage of $OxCl^{\bullet+}$ and the secondary decomposition of Cl_2-$CO^{\bullet+}$, the former mechanism initially producing both the radical and cation of carbonyl chloride. These mechanisms were not elucidated by simple EI mass spectrometry. We have shown that by adding a more efficient quenching agent such as N_2 to the initial gas mixture, it is possible to increase the amount of a metastable product observed. The N_2 serves to internally cool the products, halting further decomposition.

We believe that this technique may find use in the isolation and spectroscopic characterization of some important molecules that have eluded direct spectroscopic observation to date. These include molecules such as $OCCO$,[9,30] oxirene,[37] oxywater,[38] and the tautomers of formamide[39a,b] and *N*-methylformamide.[39a,c] All except oxywater have been observed in NRMS experiments, and all are proposed to be obtainable through the corresponding radical cations. The correct choice of precursors, charge exchange agent, and quenching agent may result in the matrix isolation and direct observation of these very important and interesting molecules.

References and Notes

(1) Maier, J. P. *Int. J. Mass Spectrom. Ion Processes* **1991**, *104*, 1.

(2) (a) Godbout, J. T.; Halasinski, T. M.; Leroi, G. E.; Allison, J. *J. Phys. Chem.* **1996**, *100*, 2892. (b) Halasinski, T. M.; Godbout, J. T.; Allison, J.; Leroi, G. E. *J. Phys. Chem.* **1994**, *98*, 3930.

(3) (a) Szczepanski, J.; Roser, D.; Personette, W.; Eyring, M.; Pellow, R.; Vala, M. *J. Phys. Chem.* **1992**, *96*, 7876. (b) Suzer, S.; Andrews, L. *J. Chem. Phys.* **1988**, *88*, 916.

(4) Jacox, M. E.; Irikura, K. K.; Thompson, W. E. *J. Chem. Phys.* **1996**, *104*, 8871.

(5) Truttmann, L.; Asmis, K. R.; Bally, T. *J. Phys. Chem.* **1995**, *99*, 17844.

(6) Zhang, X. K.; Parnis, J. M.; Lewars, E. G.; March, R. E. *Can. J. Chem.* **1997**, *75*, 276.

(7) Osterheld, T. H.; Brauman, J. I. *J. Am. Chem. Soc.* **1993**, *115*, 10311.

(8) Zhang, X. K. Ph.D. Thesis, Queen's University, Kingston, ON, Canada, 1993.

(9) Chen, H.; Holmes, J. L. *Int. J. Mass Spectrom. Ion Processes* **1994**, *133*, 111.

(10) Chen, H. M.Sc. Thesis, University of Ottawa, Ottawa, ON, Canada 1992

(11) Langenberg, J. H.; Ruttink, P. J. A. *Theor. Chim. Acta* **1993**, *85*, 285.

(12) Vallance, C.; Harland, P. W.; Maclagan, R. G. A. R. *J. Phys. Chem.* **1996**, *100*, 15021.

(13) Energetic electrons are known to have mobility in cryogenic rare-gas matrices. Proof of this comes from experiments where cations are photobleached[14] by low- energy photons and where cations are produced by photoionizing in the presence of a dilute electron acceptor[15] such as CCl_4.

(14) Knight, L. B. Production Methods for ESR studies of Neutral and Charged Radicals. In *Chemistry and Physics of Matrix-Isolated Species*; Andrews, L; Moskovits, M., Ed.; Elsevier: New York, 1987; p 171.

(15) Hudgins, D. M.; Allamandola, L. J. *J. Phys. Chem.* **1995**, *99*, 8978.

(16) Holmes, J. L. *Mass Spectrom. Rev.* **1989**, *8*, 513.

(17) Unless otherwise stated, all thermochemical data is taken from: Lias, S. G.; Bartress, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl 1.

(18) Jacox, M. E. *Rev. Chem. Intermed.* **1978**, *2*, 1. Jacox also mentions that higher energy states are known to rapidly relax radiatively to the lower energy metastables; therefore, they would not contribute to Penning processes.

(19) (a) Mincu, I.; Allouche, A.; Cossu, M.; Aycard, J. P.; Pourcin, J. *Spectrochim. Acta.* **1995**, *51A*, 349. (b) Hisatsune, I. C.; Heicklen, J. *Can. J. Spectrosc.* **1973**, *18*, 77.

(20) Schnöckel, H.; Eberlein, R. A.; Plitt, H. S. *J. Chem. Phys.* **1992**, *97*, 4.

(21) Jacox, M. E.; Milligan, D. E. *J. Chem. Phys.* **1965**, *43*, 866.

(22) Davidovics, G.; Monnier, M.; Schroeder, W.; Verlaque, P.; Pourcin, J.; Bodot, H. *J. Mol. Struct.* **1989**, *197*, 213.

(23) (a) Charles, S. W.; Lee, K. O. *Trans. Faraday Soc.* **1965**, *61*, 614. (b) Leroi, G. E.; Ewing, G. E.; Pimentel, G. C. *J. Chem. Phys.* **1964**, *40*, 2298.

(24) The MP2/6-31G* CC bond length was found to be 2.139 Å, which compares with the CASSCF CC bond length of 2.050 Å for the glyoxal radical cation in ref 11.

(25) Nicovich, J. M.; Kreutter, K. D.; Wine, P. H. *J. Chem. Phys.* **1990**, *92*, 3539.

(26) Stevenson, D. P. *Discuss. Faraday Soc.* **1951**, *10*, 35.

(27) Katrib, A.; Debies, T. P.; Colton, R. J.; Lee, T. H.; Rabalais, J. W. *Chem. Phys. Lett.* **1973**, *22*, 196.

(28) Thomas, R. K.; Thompson, H. *Proc. R. Soc. London* **1972**, *A327*, 13.

(29) No bands in the infrared spectra gave agreement with the HF/DZ+P frequencies in ref 30 or to our own MP2/6-31G* calculations using Guassian 92.

(30) Raine, G. P.; Schaefer, H. F.; Haddon, R. C. *J. Am. Chem. Soc.* **1993**, *105*, 194.

(31) (a) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1969**, *51*, 277. (b) Jacox, M. E.; Milligan, D. E. *J. Chem. Phys.* **1970**, *53*, 2688.

(32) Frost, D. C.; McDowell, C. A.; Pouzard, G.; Westwood, N. P. C. *J. Electron Spectrosc. Relat. Phenom.* **1977**, *10*, 273.

(33) It may be argued that the reason the phosgene features increase faster in intensity is that N_2 is becoming more and more important as the charge exchange agent that has a substantially higher electron affinity (EA < 15.576 eV) than Kr, one that is actually similar to Ar, and has better quenching properties. This argument can be ruled out by considering that a similar trend in A_{ClCO}/A_{Cl_2CO} is observed using CO (IP = 14.01 eV), which has a similar IP to Kr, instead of N_2. As well, on a statistical basis it can be argued that $Kr^{\bullet+}$ is still the major charge transfer agent up to rather high

concentrations of N_2. This argument is based on the fact that $Kr^{\bullet+}$ has a lower EA than the IP of N_2 and so cannot transfer its charge to N_2. Correspondingly, $N_2^{\bullet+}$ has a higher EA than the IP of Kr, and so if N_2 is ionized in the initial electron impact step, it can transfer its charge to Kr. This would not be true for Ar in place of Kr since the IP, and therefore the electron affinity, of Ar is higher than N_2. This last point is the reason that the experiments of varying N_2 concentration were performed in Kr rather than Ar.

(34) (a) Worthing, A. G.; Rudy, R. *Phys. Rev.* **1924**, *23*, 767. (b) Kenty, C. *Phys. Rev.* **1962**, *126*, 1235.

(35) Porter, J. C.; Beynon, J. H.; Ast, T. *Org. Mass Spectrom.* **1981**, *16*, 101.

(36) Melton, C. E. *J. Chem. Phys.* **1960**, *33*, 647.

(37) (a) Vacek G.; Galbraith, J. M.; Yamaguchi, Y.; Schaefer, H. F.; Nobes, R. H.; Scott, A. P.; Radom, L. *J. Phys. Chem.* **1994**, *98*, 8660. (b) Hop, C. E. C. A.; Holmes, J. L.; Terlouw, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 441. (c) Bouma, W. J.; Gill, P. M. W.; Radom, L. *Org. Mass. Spectrom.* **1984**, *19*, 610.

(38) (a) Xie, Y.; Allen, W. D.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *104*, 7615. (b) Huang, H. H.; Xie, Y.; Schaefer, H. F. *J. Phys. Chem.* **1996**, *100*, 6076.

(39) (a) McGibbon, G. A.; Burgers, P. C.; Terlouw, J. K. *Int. J. Mass Spectrom. Ion Processes* **1994**, *136*, 191. (b) Hop, C. E. C. A.; Chen, H.; Ruttink, P. J. A.; Holmes, J. L. *Org. Mass Spectrom.* **1991**, *26*, 679.