In the case of (η-C_4H_4)Fe$(CO)_3$, the reverse situation appears to obtain.

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Matrix Isolation Study of the Fluoride Adduct of Oxalyl Fluoride: Evidence for a Fluorine-Bridged Anion

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The salt/molecule reaction technique, coupled with matrix isolation, was employed to investigate the possible structural isomers of the $C_2F_3O_2^-$ anion, ion paired with a Cs^+ cation. This species was synthesized through the reaction of CsF with oxalyl fluoride; since a gas-phase sample of oxalyl fluoride consists of an equilibrium mixture of cis and trans isomers, two reaction products were observed. Each was characterized by one intense carbon–oxygen stretching mode in the 1450–1500-cm^{-1} region, as well as a single, intense C–F stretch near 900 cm^{-1}. These spectral features are suggestive of a fluorine-bridged structure, a result that is supported by the observation of low-frequency modes near 400 cm^{-1}, which are assigned to the stretching mode of the bridging fluorine for each product ion. CNDO/S calculations suggest a stable local minimum for the bridged anionic form as well. Warming the matrix to room temperature left a solid residue on the window, which was identified as cesium trifluoroacetate. This indicates that the bridged form has limited stability and rearranges at room temperature or below to the more stable $CF_3CO_2^-$ form.

Introduction

The salt/molecule technique has been coupled with matrix isolation on numerous occasions for the synthesis of unusual anionic intermediates.[1-8] The majority of these have been formed through a fluoride ion (F^-) transfer from CsF to a suitable acceptor, forming a fluoride-containing anion. Recently, a thorough gas-phase study[9] of such fluoride-transfer reactions was reported, to extend previous studies in this area.[10-12] One system reported there was the addition of F^- to oxalyl fluoride, $C_2O_2F_2$, which was of particular interest because of three possible structures for the product ion. These included a symmetric bridged form and an unsymmetrical form in which the fluoride interacts with one of the carbons. In addition, rearrangement to the trifluoroacetate anion, $CF_3CO_2^-$, is feasible, although the barrier may well be high. Since these structural isomers can readily be distinguished by infrared spectroscopy and since the salt/molecule technique in conjunction with matrix isolation provides an excellent route to the synthesis of the product anion in a condensed-phase medium, an investigation was undertaken into the reaction products arising from the codeposition of CsF with oxalyl fluoride in argon matrices.

Experimental Section

All of the experiments here were conducted on a typical matrix isolation system, which has been described previously.[13] Oxalyl fluoride (PCR) was introduced into the vacuum system from a lecture bottle and subjected to one or more freeze–thaw cycles prior to dilution in argon to the desired ratio. CsF was loaded into a stainless steel Knudsen cell and outgassed under vacuum for several hours at temperatures slightly below its vaporization temperature of 500 °C. Matrices were then formed through the codeposition of samples of Ar/CO_2F_2 with CsF onto a 14 K cold window. Survey scans were run intermittently during deposition and at the end of the 20–22 h of deposition. High-resolution spectra were recorded over regions of interest, at a resolution of 1 cm^{-1} and an accuracy of about 1 cm^{-1}.

Table I. Comparison of the Stretching Modes of the $C_2F_3O_2^-$ Anions and Related Species

species	$\nu_{\text{C-O}}$, cm^{-1}	$\nu_{\text{C-F}}$, cm^{-1}	$\nu_{\text{C-F}}$(br),[b] cm^{-1}	ref
$C_2F_3O_2^-$ (cis)	1498	980	395	*a*
$C_2F_3O_2^-$ (trans)	1457	881	376	*a*
COF_3^-	1514	808, 930		1
CO_2F^-	1316, 1749	883		2

[a] This work. [b] Stretching mode of the bridging fluorine.

Results and Discussion

An initial blank experiment of oxalyl fluoride in argon with M/R = 500 showed a moderately complex spectrum which could not be interpreted in terms of a single absorber. Rather, the spectra were very similar to that of solid oxalyl fluoride, for which it was concluded that both the cis and trans forms were present upon gas-phase deposition, with relatively more trans than cis.[14] This is particularly apparent in the carbonyl stretching region, where an extremely intense absorption was noted at 1860 cm^{-1} for the trans isomer (the second carbonyl stretch is infrared inactive), and a moderately intense band was noted near 1890 cm^{-1}, for the more intense carbonyl stretch of the cis isomer. In all, the spectra were in good agreement with the literature spectra of a mixture of cis and trans isomers. The codeposition of CsF with a similar sample of Ar/$C_2O_2F_2$ = 500 gave rise to a number of new infrared absorptions, which could not be attributed to either parent species. Two distinct bands of medium intensity were noted at 1457 and 1498 cm^{-1}, while a quite intense, sharp band was noted

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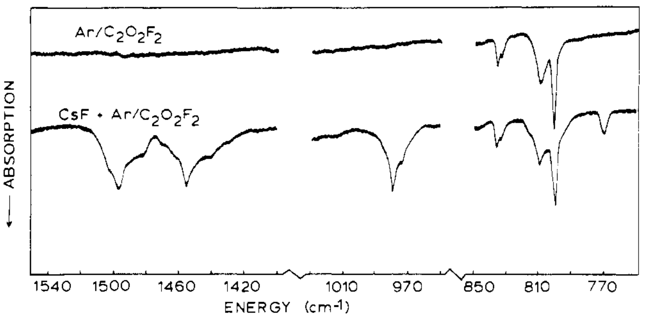

Figure 1. Infrared spectra, over selected spectral regions, of the reaction product arising from the codeposition of a sample of $Ar/C_2O_2F_2 = 500$ with CsF. The top trace shows a blank spectrum of $C_2O_2F_2$ in argon, contrasted to the spectrum of a reaction run in the lower trace.

at 980 cm^{-1}. At slightly lower energies, absorptions of medium intensity were noted at 881, 770, and 550 cm^{-1}, while a somewhat more intense product band was noted at 376 cm^{-1}. The spectral region 1500–1800 cm^{-1} was quite clear and free of absorptions, other than weak bands due to impurity H_2O near 1600 cm^{-1}. This sample was then annealed to 35 K and recooled to 14 K; other than a slight broadening of the product bands, no changes were noted. At the conclusion of this experiment, the cold window was warmed to room temperature, and the volatile materials were pumped off. The cold window was then rescanned, and broad absorptions were noted near 1230, 1460, and 1720 cm^{-1}. Further experiments on this system consisted of codeposition experiments employing varying amounts of CsF and different M/R ratios for $C_2O_2F_2$. In these experiments, the above product bands were noted, and their intensities were observed to change in a manner consistent with the change in amount of reactant. Further, they appeared to show a constant intensity ratio with respect to one another in these experiments, to the degree to which this could be determined for the weaker bands.

The spectra described above contained a number of medium-intensity, distinct spectral features, which cannot be attributed to either parent species and consequently must be attributed to one or more reaction products. Since the spectra clearly indicated the presence of both cis and trans isomers of the parent oxalyl fluoride and each should be comparably reactive, it is likely that two similar reaction products were formed. These products might be envisioned as either distinct new anionic species, as has been observed in previous salt/molecule studies, or loosely bound complexes. In the former case, large shifts from the band positions of the parent molecules are anticipated, while in the latter case, relatively small perturbation is expected. Regardless of the specific assignments (which are made below), the spectra clearly show dramatic shifts of several hunderd wavenumbers or more for these bands. These shifts are of the same magnitude as those found in previous salt/molecule studies, for example the reaction of CsF with COF_2 to form the $Cs^+COF_3^-$ ion pair.[1] Consequently, the spectra strongly indicate that fluoride ion transfer has occurred and that the resulting products can be described as $Cs^+C_2F_3O_2^-$. This result is consistent with the measurement[9] of a substantial fluoride ion affinity, 45.7 kcal/mol, for $C_2F_2O_2$.

Assignments can be made for the observed absorption by comparison to spectra of a variety of similar anionic species, as well as to the parent oxalyl fluoride spectrum. Each of the two reaction products, arising from the reaction of CsF with the parent cis and trans isomers, should have two carbon–oxygen stretching modes, in the spectral region below 1800 cm^{-1}. For example, the carbon–oxygen stretch of COF_2 shifted[1] from about 1870 to 1510 cm^{-1} upon fluoride ion addition to form COF_3^-. The position and intensities of these bands will, however, depend strongly on the structure of the products. The two bands at 1457 and 1498 cm^{-1} are clear candidates for two of these modes. Their separation and relative intensities are quite similar to the intense carbon–oxygen stretching modes of the parent trans and cis isomers near 1860 and 1890 cm^{-1}, respectively. This suggests that the 1457-cm^{-1} product band can be assigned to a C–O stretch of the reaction product of F^- with the trans isomer and the 1498-cm^{-1} band to a C–O stretch of the reaction product with the cis isomer. The only alternative assignment would be to the two C–O stretching modes of one of the reaction products. This is a less desirable alternative in that it requires a structure (see below) in which both C–O modes are of equal infrared intensities (in the trans isomer of the parent $C_2O_2F_2$ one is very intense and the other forbidden) *and* a structure in which both are perturbed to approximately the same degree. Further, no bands were observed in the region 1500–1800 cm^{-1} which could be assigned to the reaction product of CsF with the second isomer of oxalyl fluoride. Since the structures of the two isomers are similar, the two should have comparable reactivity, and such bands should be present. Consequently, these two product bands are best assigned as one of the two C–O stretching modes for the reaction products of CsF with the trans and the cis isomers of the parent. The lack of observation of the second mode for each must be due to either lack of intensity or coincidence.

Similar observations can be made about the C–F stretching modes; these are anticipated to shift to lower energy upon anion formation, and product bands at 980 and 881 cm^{-1} are readily assigned in this fashion. Again, since each parent isomer has one intense C–F stretching mode (1265 cm^{-1} for the cis isomer, and 1110 cm^{-1} for the trans isomer), one anticipates two intense C–F stretching absorptions, one for each product. The shifts of 980 and 881 cm^{-1} from the parent modes are comparable, and the relative intensities are also similar to those of the parent modes. On the basis of the arguments outlined above for the carbon–oxygen stretching modes, these are assigned to the more intense C–F stretching modes, one each, of the reaction products of CsF with the cis and trans isomers of the parent. The somewhat weaker product absorption at 770 cm^{-1} is some 35 cm^{-1} to lower energy of the C–C stretching mode of the parent cis isomer (a mode that is forbidden for the trans isomer). Since this mode should be markedly perturbed by anion formation, the 770-cm^{-1} absorption is readily assigned to the C–C stretching mode of the reaction product of CsF with the cis isomer. The comparable mode for the reaction product with the trans isomer is necessarily activated as a center of symmetry cannot be maintained in the product, but is likely to be very weak and not observed. Assignment of the three final product absorptions, at 376, 395, and 550 cm^{-1}, are dependent on the structure of the product species and can be assigned only after this has been considered.

The three most likely structures for the two product anions are (1) a symmetrical, fluorine-bridged structure, (2) an unsymmetrical structure with the fluoride ion interacting with (binding to) one of the two carbons of the parent, and (3) the rearrangement product $CF_3CO_2^-$. This third possibility can be ruled out by comparison to the known, room-temperature spectrum of the anion;[15] there are considerable differences in the spectrum, particularly in the carbon–oxygen stretching region. As anticipated, the two equivalent C–O stretching modes of $CF_3CO_2^-$ interact strongly and split into symmetric and antisymmetric modes, occurring at 1450 and 1680 cm^{-1}, respectively. The observed spectrum, particularly in the region 1500–1800 cm^{-1}, is not consistent with this structure. In structure 2, two very different carbon–oxygen stretches would be anticipated, one with substantial single-bond character and one with substantial double-bond character. Moreover, since the symmetry of the product anion is dramatically reduced, both should be moderately intense. The observation of one C–O stretch for each product anion with a very large shift to lower energy does not match well with this proposed structure. Rather, the spectra are well accounted for by structure 1, with a fluorine bridge above the carbons (*without* C–C bond rupture). Here, both carbon–oxygen bonds should be perturbed to the same degree and should shift to lower energy. However, the "oxalyl fluoride" portion of the product anion should still be relatively close to planar (see calculations below). Consequently, the symmetric combination of the C–O stretches (which is for-

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bidden for the trans isomer of the parent and very weak for the cis isomer) should remain quite weak in the product anion. Similarly, the observation of only one C–F stretch for each product anion argues for the bridged structure. If this structure is correct, then one would anticipate a stretching mode of the bridging fluorine for each anion. Previous studies[16–18] of fluorine-bridged species have located this mode in the range 400–500 cm^{-1}. This model, of course, is *not* perfect in that, for the present system, C–C bond rupture did not occur. The pair of absorptions at 376 and 395 cm^{-1} are likely candidates for this mode in each of the product anions. Their intensity ratio is comparable to the cis/trans ratio of the parent, and the separation (cis at 395 cm^{-1} and trans at 376 cm^{-1}) is similar to the cis/trans separation for other vibrational modes (e.g., the 1456- and 1497-cm^{-1} C–O stretches). The observation of these bands that may be assigned to the bridging fluorine (and have no other ready assignment) supports the possibility of a bridging structure for the two product anions.

Calculations

The interaction of a fluoride ion with oxalyl fluoride was also investigated in a series of calculations at the CNDO/S level, with complete geometry optimization for the ground state. Initial calculations focused on the trans isomer, and the geometry of F$^-$ attack was varied over a wide range. Two local minima were found in the process, the first of which was a fluorine-bridged structure. The optimized geometry for this structure showed a lengthening of the C–O, C–F, and C–C bonds relative to the parent and only a few degrees deviation from planarity. The fluoride ion was found to sit directly above this nearly planar oxalyl fluoride subunit, with equivalent C–F distances of 1.45 Å, which is quite reasonable for a bridging structure. The second local minimum corresponded to the unsymmetrical structure (2) above. While no reliable energy difference between the two isomeric forms of the anion could be determined, the calculations do demonstrate the stability of the bridged form and support the possibility of its formation. A similar set of calculations was then carried out with the cis isomer, and comparable results were obtained.

Further Considerations

The behavior of the matrix sample upon warming is of interest as well; while annealing to 35 K produced no distinct changes, after warming to room temperature the residue on the window exhibited broad absorptions near 1230, 1460, and 1710 cm^{-1}. These coincide well with the three most intense absorptions of the $\mathrm{CF_3CO_2^-}$ anion, which were observed at 1212, 1450, and 1680 cm^{-1} in the sodium salt.[15] These observations suggest that, upon warming and/or aggregation, rearrangement to the trifluoroacetate anion does occur and that this is the most stable structural form of the $\mathrm{C_2F_3O_2^-}$ anion. However, under matrix isolation conditions, this rearrangement does not have time to occur before condensation and isolation. These observations suggest that detection of the bridged form under normal laboratory conditions is quite unlikely. Consequently, the matrix isolation technique has provided the first, and perhaps only, spectroscopic identification and characterization of the intermediate, fluorine-bridged anion.

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Preparation and X-ray Structures of Compounds Containing the Tetrakis(methylhydroxypyridinato)- and Tetrakis(chlorohydroxypyridinato)dipalladium(II) Molecules

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The synthesis of $[\mathrm{Pd_2L_4}]$ compounds, where L = either the anion 6-methyl-2-hydroxypyridinate (mhp$^-$) or 6-chloro-2-hydroxypyridinate (chp$^-$), has been reinvestigated, with unexpected results. Three crystalline forms of the chp analogue were obtained. All three crystals contained virtually identical molecules, each having a $\mathrm{Pd_2}^{4+}$ unit bridged by four chp$^-$ ligands, possessing D_{2d} symmetry. For compound **1**, $[\mathrm{Pd_2(chp)_4}]\cdot\mathrm{CHCl_3}$, the crystals are triclinic ($P\bar{1}$) with a = 10.407 (3) Å, b = 16.739 (3) Å, c = 8.811 (3) Å, α = 102.30 (2)°, β = 110.43 (2)°, γ = 79.04 (2)°, V = 1394.1 (12) Å^3, and Z = 2 and have a Pd–Pd distance of 2.570 (1) Å. Compound **2**, $[\mathrm{Pd_2(chp)_4}]$, forms orthorhombic crystals ($Pnma$) that are isomorphous with those for $[\mathrm{Pd_2(mhp)_4}]$ previously obtained by Clegg et al. The crystals have a = 15.498 (8) Å, b = 16.012 (13) Å, c = 18.719 (8) Å, V = 4644 (5) Å^3, and Z = 8 and a Pd–Pd separation of 2.563 (1) Å. Compound **3**, $[\mathrm{Pd_2(chp)_4}]\cdot0.5\mathrm{CHCl_3}$, forms triclinic crystals ($P\bar{1}$) with a = 11.167 (3) Å, b = 14.595 (4) Å, c = 16.895 (4) Å, α = 100.77 (2)°, β = 102.36 (2)°, γ = 101.21 (2)°, V = 2562.4 (12) Å^3, and Z = 4 and has a Pd–Pd separation of 2.568 [4] Å. Crystallization of the intermediate compound in the preparation of the mhp analogue yielded triclinic crystals ($P\bar{1}$) with the composition $[\mathrm{Pd_2(mhp)_4}]_5\cdot6\mathrm{CHCl_3}$, compound **4**, which contain a mixture of two isomers of the $[\mathrm{Pd_2(mhp)_4}]$ molecule. Four of the molecules have D_{2d} symmetry, while the fifth has C_{2h} symmetry. The crystals have a = 12.944 (2) Å, b = 26.461 (4) Å, c = 11.390 (2) Å, α = 100.43 (1)°, β = 92.67 (1)°, γ = 78.68 (1)°, V = 3761.8 (9) Å^3, and Z = 5. The cisoid molecule of $[\mathrm{Pd_2(mhp)_4}]$ in compound **4** is the first example of a cisoid (C_{2h}) isomer of an $[\mathrm{M_2(xhp)_4}]$ molecule.

Introduction

In 1982, Clegg, Garner, and Al-Samman[1] reported the preparation and structural characterization of the compound $[\mathrm{Pd_2(mhp)_4}]$ in an unsolvated, orthorhombic crystal form. Compounds of the type $[\mathrm{M_2(xhp)_4}]$, where xhp is a generic abbreviation for 6-X-2-hydroxypyridinate anions, I, have played a very important role in developing the chemistry of metal–metal bonds, ranging from quadruple (for Cr, Mo, W) to single (for Rh, Pt).[2] The structure of Clegg et al's[1] $[\mathrm{Pd_2(mhp)_4}]$ was of the type previously displayed by all unsolvated, neutral $[\mathrm{M_2(xhp)_4}]$ molecules, namely,

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