of the enzyme. It is also reasonable to postulate that the —Ⓜ—NH_2 in Scheme III is an amine or imidazole group on the enzyme.[27] Further obvious extensions of this work, e.g., trapping of the "C_1 unit" in the form of imine or Schiff base, trapping of the enzymatically formed DPM (**8**),[25] and investigation of "headless" tripyrrylmethane and tetrapyrrylmethane as possible "intermediates", are in progress.

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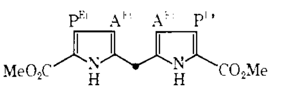
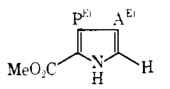


i



ii

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Matrix Reactions of Alkali Metal Fluoride Molecules with Fluorine. Infrared and Raman Spectra of the Trifluoride Ion in the $M^+F_3^-$ Species

Sir:

The trihalide anions, X_3^-, have generated considerable synthetic and theoretical interest; spectroscopic studies of these anions have been carried out in solids and solutions[1,2] and in inert matrices.[3,4] While Cl_3^-, Br_3^-, and I_3^- have been investigated thoroughly, the most reactive member of this group, F_3^-, has never been observed. It is known that CsF catalyzes oxidative fluorination reactions,[5,6] and it is possible that this reaction proceeds through an F_3^- intermediate species. Several recent studies have shown that matrix reactions of alkali halide salt molecules with halogen molecules in argon matrices form the $M^+X_3^-$ ion pair, for X = Cl, Br, I.[3,4,7] Analogous studies of the reaction of MF salt molecules with F_2 should provide a method of stabilizing the elusive F_3^- species and obtaining spectroscopic information and an indication of the nature of the bonding in the F_3^- anion.

Salt-molecule reactions were carried out in a manner similar to those reported in earlier papers.[3,8] The argon and fluorine mixture was deposited on a CsI window held at 15 K, while the alkali fluoride salt vapor was evaporated from a Knudsen cell and deposited simultaneously with the gas sample. Approximately 585 °C was required to produce the necessary vapor pressure of KF, while 640 and 495 °C were required for RbF and CsF, respectively. Infrared spectra were recorded after 20–30 h of deposition on a Beckman IR-12 infrared spectrophotometer. In Raman experiments, the salt and gas mixture was deposited on a polished copper block for 3–5 h. Raman spectra were obtained using argon ion laser excitation and a Spex Ramalog spectrometer.

KF, RbF, and CsF were each deposited in argon matrices without added reagent, and three infrared bands were observed in each experiment, at 396, 306, and 275 cm^{-1} with KF, at 345, 266, and 230 cm^{-1} with RbF, and at 313, 248, and 207 cm^{-1} with CsF. In each case, the highest energy band was most intense, and it appeared slightly below the gas phase wavenumber value for the MF monomer;[9] this band can be assigned confidently to the MF monomer vibration in an argon matrix. KF has been observed at 395 cm^{-1} in an argon matrix,[10] in agreement with the value obtained here. The two lower energy bands were of comparable intensity, and they can be assigned to two modes of the cyclic $(MF)_2$ dimer species. The $(KF)_2$ values of 306 and 275 cm^{-1} are in agreement with reported values,[10] and the band positions for $(RbF)_2$ are reasonable for the heavier alkali metal species. Also, in these experiments a weak band was observed near 350 cm^{-1}, which is labeled A in Figure 1 and is likely due to a complex between the MF salt and im-

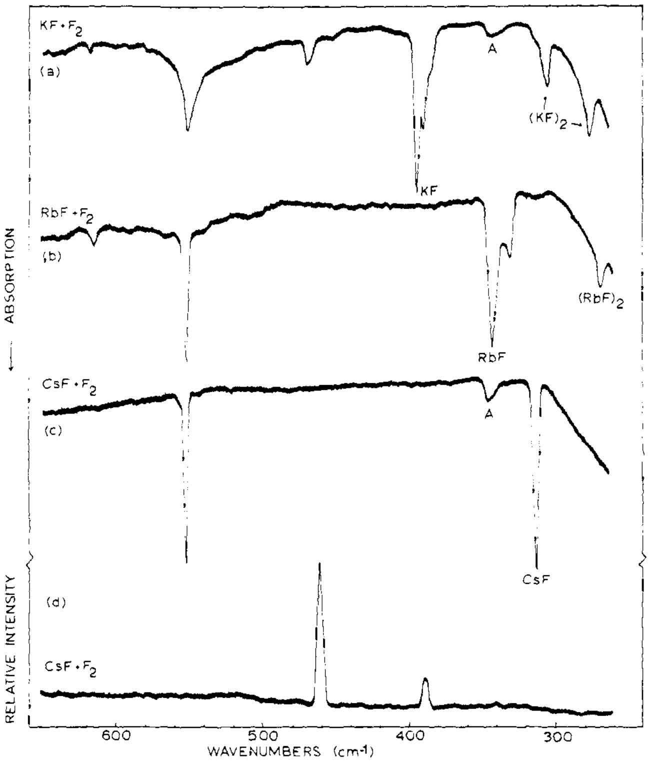

Figure 1. Infrared and Raman spectra of the reaction products of alkali fluoride salt molecules with F_2 in argon matrices at 15 K. Trace (a) shows the infrared spectrum of the reaction products of KF with a sample of Ar/F_2 = 100, while traces (b) and (c) illustrate infrared spectra of the reaction products of RbF and CsF with samples of Ar/F_2 = 400. Trace (d) shows the Raman spectrum of the reaction products of CsF with a sample of Ar/F_2 = 100, scanned at 50 cm^{-1}/min, using 4765 Å excitation and a power of 20 mW at the sample.

purity water molecules. Such a complex has been observed for the MCl and MBr salts, at 470 and 440 cm^{-1}, respectively.[3,4] Finally, a sample of Ar/F_2 = 100 was deposited in one experiment, and three infrared bands were observed, at 262, 708, and 899 cm^{-1}, which persisted in all F_2 experiments, and accordingly they are attributed to impurities in the sample.

When CsF was deposited with a sample of Ar/F_2 = 400, a single new infrared absorption was observed at 550.5 cm^{-1}. This band was quite intense, and extremely sharp, as is shown in trace (c) of Figure 1. When a similar sample of Ar/F_2 = 400 was deposited with CsF at a higher oven temperature, the same band at 550.5 cm^{-1} was observed, and a second, weaker band was seen near 595 cm^{-1}. However, when this sample was warmed to about 40 K to allow diffusion, and then recooled to 15 K, the band at 550.5 cm^{-1} remained unchanged, while the band at 595 cm^{-1} disappeared.

In a similar manner, RbF was deposited with a sample of Ar/F_2 = 400, and a single band was observed, also quite sharp and intense, at 550.5 cm^{-1}, which is depicted in trace (b) of Figure 1. When the concentration of RbF was increased with another sample of Ar/F_2 = 400, the 550-cm^{-1} band remained intense, and a second band appeared at 611 cm^{-1}. However, as in the CsF experiment, this band disappeared upon diffusion, while the 550-cm^{-1} band remained.

KF was also deposited with a sample of Ar/F_2 = 400, and the infrared spectrum of this reaction mixture showed a single band near 549.6 cm^{-1}, somewhat broader and weaker than the Cs and Rb counterpart bands. KF was then deposited with a sample of Ar/F_2 = 100, and this experiment produced the 549.6-cm^{-1} band with increased intensity, and a weak band near 462 cm^{-1}, as shown in trace (a) of Figure 1. Upon diffusion of the sample, the 549.6-cm^{-1} band decreased slightly, and the 462-cm^{-1} band increased considerably.

CsF was deposited with Ar/F_2 in several Raman experiments. When CsF was treated with a sample of Ar/F_2 = 100, two bands were observed in the Raman spectrum at 461 and 389 cm^{-1} using 4579, 4765, and 4880 Å laser excitation. These two bands showed an intensity ratio of about 5/1, as is shown in trace (d) of Figure 1. Both bands decreased slowly in intensity with prolonged exposure to the laser light, although the 389-cm^{-1} band was found to decrease much more rapidly than the 461-cm^{-1} band. Also, when the matrix was warmed to 40 K to allow diffusion, and recooled to 14 K, the 389-cm^{-1} band disappeared entirely, and the 461-cm^{-1} band remained intense. A range of concentrations of the gas mixture and the salt was used, and these two bands showed considerable variation in relative intensity. Similar RbF experiments produced an almost identical Raman spectrum. Finally, in these experiments a weak Raman band was observed near 892 cm^{-1}, which is attributed to F_2.[9]

The reaction of an alkali fluoride salt molecule with F_2 is expected to form $M^+F_3^-$ on the basis of a thermodynamic cycle which has been described previously.[8] The reaction of CsF with F_2 in an argon matrix under dilute conditions produced a single, very intense infrared absorption at 550.5 cm^{-1}. Similar reactions employing RbF and KF produced bands at 550.0 and 549.6 cm^{-1}, respectively, while no other product bands were observed in these experiments. The antisymmetric stretch, ν_3, of F_3^- is expected to lie well below the vibrational frequency of F_2 at 892 cm^{-1}, and somewhat above ν_1 of F_2^- at 459 cm^{-1}.[11] With this in mind, the 550-cm^{-1} absorption in each experiment is best assigned to ν_3 of the F_3^- anion in the $M^+F_3^-$ ion pair. The observation that the vibrational frequency varies by less than 1 cm^{-1} with three different cations requires that this vibrational mode be a pure fluorine vibration, not involving the cation to any degree, which supports the assignment to the antisymmetric stretching vibration of a discrete F_3^- anion.

One model for the F_3^- anion is the isoelectronic KrF_2 molecule, which has an antisymmetric stretching frequency of 580 cm^{-1} in solid argon.[12] This is in reasonable agreement with the value obtained here, and provides support for our assignment of the 550-cm^{-1} band to the F_3^- anion. The ratio of ν_3 of Cl_3^- to the frequency of Cl_2 can be used to estimate ν_3 of F_3^- from the vibrational frequency of F_2. This leads to a value of 560 cm^{-1}, while a similar analysis with Br_2 and Br_3^- suggests a value of 590 cm^{-1}. These are sufficiently close to the 550-cm^{-1} band to qualitatively support the assignment of this band to ν_3 of the F_3^- anion.

The Raman spectrum of the reaction products of CsF with F_2 provides information as well. Two Raman bands were observed, at 461 and 389 cm^{-1}, and, in every experiment, the 461-cm^{-1} band was considerably more intense. One of these bands can be assigned to ν_1 of the $Cs^+F_3^-$ ion pair, and the choice of the 461-cm$^-$ band is straightforward. This band lies within 2 cm^{-1} of ν_1 of $Cs^+F_2^-$, and it has been shown that ν_1 of Cl_3^-, Br_3^-, and I_3^- all lie within a few wavenumbers of ν_1 of the appropriate X_2^- anion.[13-15] Also, ν_1 of the model compound KrF_2 is 452 cm^{-1} in a krypton matrix,[16] which supports this assignment. Finally, the 389-cm^{-1} band decreased rapidly upon exposure to the laser light, and upon diffusion of the sample, while the 461-cm^{-1} band was much more stable. Previous salt-molecule reactions have shown that the $M^+Cl_3^-$ and $M^+HCl_2^-$ species are quite stable, and do not decrease upon diffusion.[3,4,8] The 550-cm^{-1} infrared band, ν_3 of F_3^-, did not decrease upon diffusion, which connects it with the 461-cm^{-1}

Raman band, not the 389-cm^{-1} band. The 389-cm^{-1} band can probably be assigned to a less stable, secondary reaction product, possibly involving two salt molecules and one F_2 molecule. Regardless, there is considerable evidence to assign the 461-cm^{-1} Raman band to ν_1 of F_3^- in the $Cs^+F_3^-$ ion pair. This, combined with the ν_3 value of 550 cm^{-1} obtained from the infrared experiments gives two of the three fundamental vibrational bands of the F_3^- anion. The remaining fundamental, the bending mode ν_2, is expected to be considerably less intense, and it was not observed in these studies.

The geometry of the anion may be deduced from this information. As can be seen in traces (c) and (d) of Figure 1, the principle of mutual exclusion holds rigidly within the limits of detectability. ν_3 was not observed in the Raman spectrum, and ν_1 was not observed in the infrared spectrum. This indicates that the F_3^- anion contains a center of symmetry, with a $D_{\infty h}$ structure which is the expected geometry for a symmetrical 22-valence electron species. This result further supports the conclusion that the species formed is a discrete F_3^- anion, and *not* an asymmetric, perturbed $MF \cdot F_2$ species.

The cation in these ion pairs serves to stabilize the anion, and the larger cations Cs^+ and Rb^+ are much more effective than K^+. The yield of F_3^- from the reaction of KF with F_2 was considerably less than reactions with RbF and CsF. The M^+ ion position in the $M^+F_3^-$ ion pair is probably beside the linear, symmetric F_3^- anion, to maximize cation-anion interaction, rather than at one end of the anion. The absence of a shift in vibrational band position with different cations indicates a pure fluorine vibrational mode not involving the cation.

Finally, a second weak band was observed in the infrared experiments in which a high salt concentration was employed. The species responsible for this absorption was destroyed upon diffusion, which suggests a weakly bound, small aggregate. The second Raman band observed at 389 cm^{-1} may be attributable to this same molecule. A definitive assignment cannot be made, but the sharpness of the bands indicates a well-defined, if weakly bound, species.

The reaction of alkali fluoride salt molecules with F_2 in argon matrices has produced a single sharp, intense infrared band at 550 cm^{-1}, with a strong Raman counterpart band at 461 cm^{-1}. Through analogy to previous salt-molecule reactions, and using KrF_2 as a model compound, these two bands have been assigned to ν_3 and ν_1 of the F_3^- anion in the $M^+F_3^-$ ion pair. Mutual exclusion between the infrared and Raman spectra indicates a center of symmetry for the anion, in a $D_{\infty h}$ geometry, and a lack of shift of band position with the different cations indicates a pure fluorine vibrational mode in a distinct trifluoride anion. The salt-molecule reaction has again proven to be a pseudo-ion-molecule reaction, and the matrix isolation technique has provided a method of trapping a transient species of limited stability.

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Four Degenerate Thermal Isomerizations of 1-Methylspiro[2.4]hepta-4,6-diene. A Test for the Smith Mechanism

Sir:

Recent attempts to define mechanisms for thermal geometrical isomerizations of cyclopropanes have uncovered a dominant or sole contribution from two-center epimerizations: at least 96% of the geometrical isomerization shown by 1-phenyl-2-deuteriocyclopropane at 309.5° occurs through simultaneous epimerizations at C(1) and C(2 or 3),[1] while 100% of the geometrical isomerization of (+)-1,2-*trans*-dideuteriocyclopropane may be ascribed to two-center epimerizations.[2] The *O,O*-trimethylene species,[3,4] generated and collapsing through concerted rotations, thus seems favored over either diradical intermediates affording competition between rotations of end methylene units and C-C bond re-formation,[5,6] leading to both one-center and two-center epimerizations as experimental observables, or the Smith mechanism,[7,8] with one-center epimerizations as the exclusive phenomenologically accessible events.

An asymmetrically substituted cyclopropane is one of a set of eight isomers. One-center and two-center epimerizations with rate constants k_i and $k_{i,j'}$ may describe the processes of geometrical isomerizations; there are 48 rate constants but only 9 independent variables. The situation may be simplified by isotopic substitutions and by selecting systems of high symmetry: the 1-phenyl-2-deuteriocyclopropane isomerization may be kinetically described through four independent variables,[1] while optically active 1,2-*trans*-dideuteriocyclopropane[2] requires only two.

All previous experimental work on the geometrical isomerizations of cyclopropanes has been limited to determinations of one or two phenomenological rate constants,[5,6] and, with one exception,[2] experimental results have been interpretable only through the imposition of extreme simplifying assumptions. As a first step toward complete experimental determination of all rate constants for the geometrical isomerizations of an unsymmetrical cyclopropane, we have measured rates for three distinct degenerate processes shown by the cyclopropyl moiety of 1-methylspiro-[2.4]hepta-4,6-diene, a system selected to test for a Smith mechanism; given the orbital structure of planar methanes, the planar stereochemical version of a spiro[2.4]hepta-4,6-diene should be particularly favored. Planar methane (**1**) has two electrons in a p orbital and six electrons devoted to four equivalent C-H bonds.[10] While planar methane may be some 125 kcal mol^{-1} less stable than T_d methane,[10] one planar tetracoordinate carbon in a cyclopropane gives a system (**2**) estimated through CNDO calculations including