is stable in the presence of azide and that the spin adduct has a half-life of about 20 s.[17] We found that PBN was not oxidized by $IrCl_6^{2-}$. Clearly PBN was a good candidate as a scavenger of N_3 in the reaction of N_3^- with $IrCl_6^{2-}$.[18]

Stopped-flow kinetics studies were performed as previously described.[19] Reactions were performed at $\mu = 1.0$ M ($NaClO_4$), maintained at 25.0 °C, and monitored at 487 nm. Initial concentrations of $IrCl_6^{2-}$ were held at 1×10^{-4} M, while the concentrations of NaN_3 and PBN (Aldrich) were varied from 0.01 to 0.5 M and from 2.0×10^{-4} to 1.8×10^{-2} M, respectively. Under these conditions Ir(IV) decayed with excellent pseudo-first-order kinetics and at rates about 10-fold faster than in the absence of PBN. A first-order dependence on $[N_3^-]$ was found, but the kinetics was independent of the concentration of PBN, except for [PBN] $< 9 \times 10^{-4}$ M where the rates became one-half as fast. In mildly acidic media some retardation occurred as expected for protonation of N_3^-. Essentially identical results were obtained with DMPO as the spin trap. Thus by spin trapping, simple bimolecular kinetics was obtained with a rate constant of $(1.59 \pm 0.18) \times 10^2$ M^{-1} s^{-1}.

PBN's ability to clean up the kinetics indicates that it competes efficiently with $IrCl_6^{3-}$ for N_3; therefore, the rate-limiting step is k_f of Scheme I. The fate of the spin adduct, a nitroxyl radical, in unknown; however, di-*tert*-butylnitroxyl and TEMPO are instantly oxidized by $IrCl_6^{2-}$. This effect should lead to a doubling in the apparent rate constant.

Pulse radiolysis has been established as a useful method for generating transient populations of N_3; indeed, this method was used to measure the rate of oxidation of Fe^{2+} by N_3.[20] Experiments were performed as described previously[21] by monitoring the formation of $IrCl_6^{2-}$ at 487 or 434 nm. Dosimetry was per-

formed by using the SCN^- method. Solutions of $Na_3IrCl_6 \cdot xH_2O$ and NaN_3 (0.01–0.1 M) were prepared at pH 6.5 and saturated with N_2O. Irradiation was accompanied by a prompt rise in absorbance, the magnitude of which was consistent with competition of $IrCl_6^{3-}$ and N_3^- for OH (which was generated both directly and by the reaction of N_2O with e_{aq}^-). On the microsecond time scale this was followed by a pseudo-first-order increase in absorbance, which accounted for complete reaction of N_3 with $IrCl_6^{3-}$ to form $IrCl_6^{2-}$. A first-order dependence on $[IrCl_6^{3-}]$ was found over the concentration range from 1.28×10^{-3} to 4.02×10^{-3} M, but the rate constants were independent of dose, wavelength, and $[N_3^-]$. These experiments lead to a value of $(5.5 \pm 0.6) \times 10^8$ M^{-1} s^{-1} for k_r in Scheme I. It is noteworthy that this rate constant is distinctly less than the diffusion-controlled value as this is in contrast with prior assumptions.[7]

Our measured values for $2k_f$ and k_r yield E_f for the azidyl radical. The ratio of k_f to k_r, K_{eq}, is $(1.45 \pm 0.23) \times 10^{-7}$; since E_f for $IrCl_6^{2-}$ at $\mu = 1.0$ M is 0.93 V,[22] the formal reduction potential for the N_3/N_3^- couple is 1.33 V. This potential is very close to that estimated previously on the basis of the proton affinity of N_3^-.[7]

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Articles

Photochemistry of an Ozone Complex with Trifluoroiodomethane in Solid Argon. Infrared Spectra of CF_3IO, CF_3OI, and Two CF_2O--IF Complexes

LESTER ANDREWS,* MICHAEL HAWKINS,[†] and ROBERT WITHNALL

Codeposition of CF_3I and O_3 in excess argon on a CsI window at 17 K gave a CF_3I--O_3 molecular complex, which photodissociated upon irradiation at 470–1000 nm to yield CF_3IO. Further photolysis at 240–420 nm produced CF_3OI and two CF_2O--IF molecular complexes with a more stable structure for the CF_2O--IF complex preferred on sample annealing.

Introduction

Inorganic iodosyl compounds are considered to be polymeric in the solid state, as shown by the crystal structure of the sulfate $(IO)_2SO_4$,[1] but the vibrational spectrum of $IOSO_3CF_3$ provides

evidence for a discrete IO unit.[2] Recently, monomolecular species of the type X–I–O (X = Cl, CH_3) have been prepared by photolysis of the XI--O_3 complex isolated in solid argon.[3,4] In the

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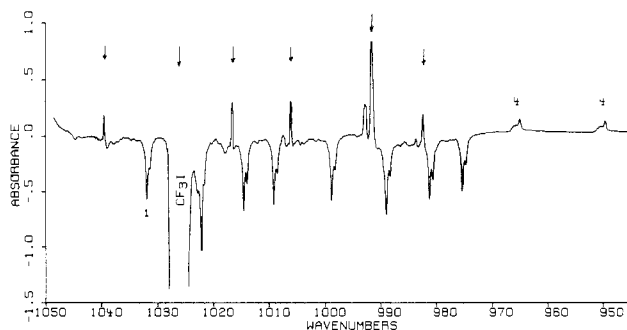
Figure 1. Infrared spectrum in the 1050–940-cm^{-1} region for a matrix prepared by codepositing 36 mmol of Ar/CF$_3$I = 200/1 and 34 mmol Ar/^{16,18}O$_3$ = 200/1 (50% ^{18}O-enriched) samples at 17 K and photolyzing at 240–420 nm for 30 min. Illustrated spectrum is absorbance after photolysis *minus* absorbance after codeposition. The isotopic doublet 4 was produced, and the sharp isotopic octet was almost destroyed by photolysis. The ozone isotopic sextet denoted by arrows appears because of incomplete subtraction of these strong bands.

case of CH$_3$IO, further irradiation gave two different CH$_2$O–HI complexes with the more stable species involving the hydrogen-bonded arrangment.[4] The solid compound CF$_3$IO has been prepared by ozonolysis of CF$_3$I, but the infrared spectrum does not characterize the bonding in the –I–O group.[5]

There have been a number of matrix-isolation studies of simple halocarbon–oxygen species, and one of the aims of these studies was to produce and trap the CF$_3$OO and CF$_3$O radical species.[6–10] Two studies have reported infrared spectra for CF$_3$OO,[7,9] but the CF$_3$O radical has not been detected directly, although its formation is implied through the appearance of the peroxide.[7] The peroxide has served as a photolytic source of CF$_3$O radicals for addition to olefins[11] and for multiphoton dissociation.[12] Here follows a matrix-isolation study of the photoylsis of a complex between CF$_3$I and O$_3$.

Experimental Section

The vacuum and cryogenic apparatus have been described previously.[13,14] Experiments were done with Beckman IR-12 grating and Nicolet 7199 Fourier-transform infrared spectrometers;[3,4] wavenumber accuracy is ±1 and ±0.1 cm^{-1}, respectively. Trifluoromethyl iodide (Peninsular Chemresearch) was condensed and degassed, and the middle fraction was used to prepare Ar/CF$_3$I = 200/1 samples. Ozone was prepared by Tesla coil discharge of oxygen[15] and diluted with argon to Ar/O$_3$ = 200/1. Reagent samples were codeposited at rates of 2 mmol/h for periods of 1–12 h, and spectra were recorded. The matrices were then photolyzed by a high-pressure mercury arc for 30-min periods by using water and Corning glass filters, with the temperature cycled to 33 ± 1 K over a 15-min period, and additional spectra were recorded. For convenience, photolysis with the following filter combinations will be designated A (590–1000 nm, Corning no. 2424 plus water), B (470–1000 nm, Corning no. 3385 plus water), C (360–470 nm, Corning no. 5113 plus water), and D (240–420 nm, Corning no. 9863 plus water).

Results

Experiments were performed to examine the matrix photolysis of CF$_3$I and O$_3$ mixtures with different irradiation wavelengths, ozone isotopes, and sample quantities. The infrared product bands can be divided into at least eight groups on the basis of photolysis and sample warming behavior.
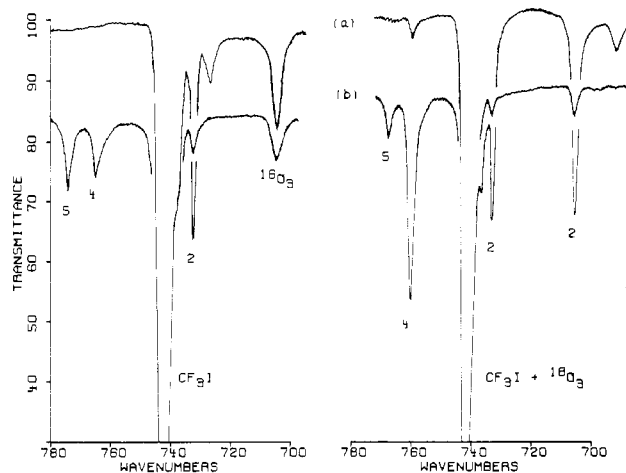
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Figure 2. Infrared spectra in the 780–700-cm^{-1} range for a matrix prepared by codepositing 16–20 mmol each of Ar/CF$_3$I = 200/1 and Ar/O$_3$ = 200/1 samples at 17 K: (left) ^{16}O$_3$; (right) ^{18}O$_3$; (a) after 470–1000-nm photolysis; (b) after 240–420-nm photolysis.

Two sharp bands in the reagent mixture were not common to either reagent sample. These group 1 bands include a strong absorption at 1032 cm^{-1} and a weak 1106-cm^{-1} band. Photolysis with filter A reduced these bands slightly, and irradiation with filters B and D reduced the bands to 70% and 20%, respectively, of their initial absorbances. In the ^{18}O$_3$ study, a strong, sharp 975-cm^{-1} band exhibited similar photolysis behavior.

On codeposition of CF$_3$I with scrambled ^{16,18}O$_3$, the 1032-cm^{-1} band gave way to an octet of absorptions in the ν_3 region of O$_3$ measured by FTIR at 1031.9, 1022.2, 1014.5, 1009.2, 998.8, 988.9, 981.1, and 975.3 cm^{-1} with seven of the components having equal intensity and the component at 1022.2 cm^{-1} slightly stronger. Figure 1 shows the spectrum resulting from subtraction of the absorbance spectrum recorded for the deposited sample from the absorbance spectrum of the sample after irradiation D. The octet of new bands was essentially destroyed by photolysis D.

The first photolysis product absorptions, group 2, detected as weak shoulders in the original sample deposit, were increased 10-fold with photolysis A and 5-fold more with B and were almost destroyed by C and D. After photolysis D, sample warming to 32 K doubled the 732 cm^{-1} group 2 band (1202 cm^{-1} absorption was shared with species 3). Figure 2a (left) shows the sharp 732.3-cm^{-1} band (absorbance A = 0.20) (group 2) and weaker 726.5-cm^{-1} satellite absorption produced by irradiation B, which reduced the 704-cm^{-1} band of ^{16}O$_3$ by 30%, and Figure 2a (right) shows the corresponding 706.0- and 692.0-cm^{-1} ^{18}O$_3$ counterparts and a new 733.4-cm^{-1} absorption, whose ^{16}O$_3$ counterpart was probably obscured by the very strong 742-cm^{-1} CF$_3$I absorption. Two experiments with mixed isotopic ozone (^{16,18}O$_3$) revealed only the same features as the ^{16}O$_3$ and ^{18}O$_3$ experiments. Additional strong 1202-cm^{-1} and weak 1214-cm^{-1} bands exhibited the group 2 photolysis behavior; these bands did not show shifts with ^{18}O$_3$. Figure 2b shows the marked decrease of group 2 bands and the appearance of new features (group 4 and 5) upon photolysis D.

The next major group of product bands (group 3) was not detected after A, but a small yield was produced by B, a marked increase by C, and still more with photolysis D. Figure 3 shows the 1241- and 1203-cm^{-1} group 3 bands and the weaker 1202-cm^{-1} group 2 band produced by B and the substantial growth in group 3 bands with D, which markedly increased the new 1242-cm^{-1} (group 4) band and produced weaker 1235- (group 3) and 1222-cm^{-1} (group 6) bands. Two substantially weaker (50-fold) bands, at 915 and 320 cm^{-1}, are also associated with group 3. These bands and their oxygen-18 isotopic counterparts are listed in Table I. Mixed isotopic experiments gave the same bands as the pure isotopic experiments.

The third set of photolysis product bands (group 4) was not detected after B, a trace was seen after C and a large yield was produced by D, which is illustrated in Figure 4a for the mixed isotopic ozone reaction product in the 1900-cm^{-1} region. Addi-
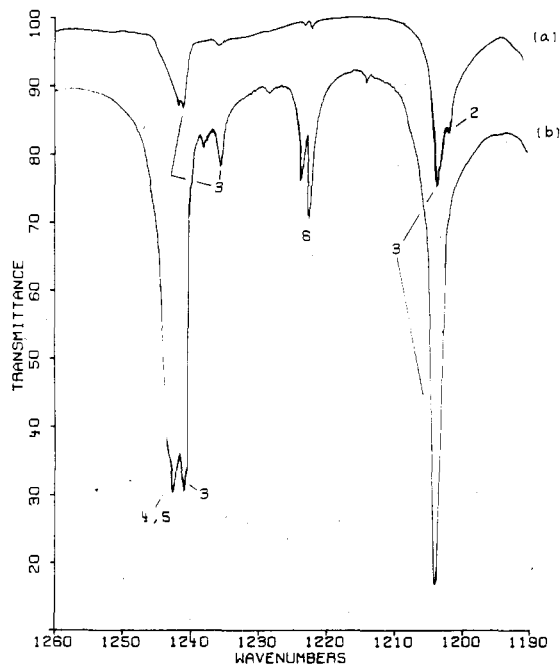
Figure 3. Infrared spectra in the 1260–1190-cm^{-1} spectral range for a matrix prepared by codepositing 2 mmol each of Ar/CF$_3$I = 200/1 and Ar/O$_3$ = 200/1 samples at 17 K: (a) after 470–1000-nm photolysis; (b) after 240–420-nm photolysis.

Table I. Groups of Product Absorptions (cm^{-1}) Observed in CF$_3$I and O$_3$ Codeposition and Photolysis Studies in Solid Argon

group 1		group 2		group 3		group 4[b]	
1106		1202	(1202)	1235.0	(1216.0)	1938.9	(1906.4)
1032	(976)[a]	1214	(1214)	1240.8	(1236.4)	1911.2	(1877.4)
				1203.2	(1193.0)	1242	(1241)
		732.3	(706.0)	914.9	(896.7)	965.1	(949.7)
			(733.4)	320	(318)	764.6	(760.5)
						621	(611)
						591	(591)

group 5[b]		group 6		group 7		group 8	
1968.2	(1936.1)	1223.2		799.4	(759.7)	1287	
1883.4	(1849.0)	1222.0	(1220.8)			1198	(1196)
1242	(1241)						
985	(969)						
773.7	(769.7)						
617	(607)						
595	(595)						

[a] Oxygen-18 counterparts are given in parentheses. [b] Unperturbed FTIR measurements for OCF$_2$ in solid argon are 1941.5, 1913.6, 1237.8, 965.3, and 769.0 cm^{-1}.

tional group 4 bands and their ^{18}O counterparts are given in Table I. Sample warming virtually destroyed the group 4 bands and produced another similar set identified as group 5 in Figure 4b. Again other group 5 bands are given in the table. The only ambiguity concerns the 1242-cm^{-1} band, which changes shape on warming and appears to contain absorption for both groups.

A sharp, weak band appeared at 799 cm^{-1} (group 7) with photolysis C, increased with D, and showed little change on sample warming. The oxygen-18 counterpart appeared at 759 cm^{-1}, and a stronger intermediate mixed isotopic component was observed at 789 cm^{-1}. Additional bands that appear on sample warming are listed as group 8 in Table I; these bands are not necessarily due to the same species.

A complementary method of preparing these new infrared absorptions was developed over the course of several studies. Oxygen atoms were prepared in a blind (off-axis) microwave discharge of Ar/O$_2$ = 100/1 and codeposited with an Ar/CF$_3$I = 200/1 sample for 20 h. Strong group 2 bands (1202 cm^{-1}, A = 0.70; 732 cm^{-1}, A = 0.20) were observed in the initial sample deposit along with a sharp 1251-cm^{-1} band (A = 0.20), a weak group 3 band (1241 cm^{-1}, A = 0.04) and no group 4 and 5 bands.
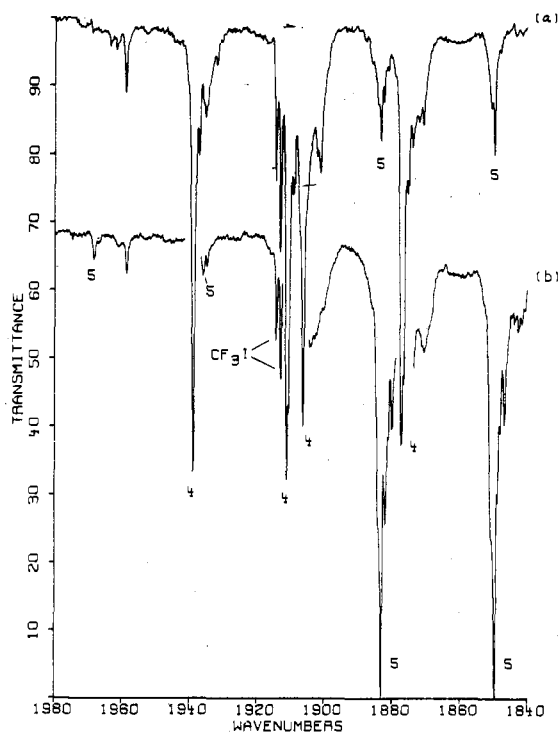

Figure 4. Infrared spectra in the 1980–1840-cm^{-1} region for a matrix prepared by codepositing 36 mmol of Ar/CF$_3$I = 200/1 and 34 mmol of Ar/^{16,18}O$_3$ = 200/1 (50% ^{18}O enriched) samples at 17 K: (a) after 240–420-nm photolysis; (b) after warming to 33 K for 15 min and recooling to 17 K. The upper pair of labeled bands are due to the ^{16}O species and the lower pair are due to the ^{18}O species.

Irradiation (290–1000 nm) for 20 min destroyed the group 2 bands and produced very strong group 3 bands (1241 cm^{-1}, 1203 cm^{-1}, A = 1.4) and weak group 4 bands (1939 cm^{-1}, A = 0.03; 1911 cm^{-1}, A = 0.05).

Two experiments were performed in an attempt to observe the visible/ultraviolet spectrum of matrix samples containing CF$_3$I and O$_3$. Even with 4 times more sample than required to observe a broad 395-nm absorption (A = 0.04) in analogous CH$_3$I + O$_3$ studies,[4] no absorption could be observed in the visible or near-ultraviolet regions below 320 nm for the CF$_3$I + O$_3$ matrix system. Complementary oxygen atom discharge experiments with CF$_3$I produced only the structured vibronic progression for IO beginning at 468 nm and peaking at 422 nm.

Discussion

The major groups of photolysis products will be identified, and the structure of the complex and the photochemical processes will be discussed.

Group 1. The group 1 bands are noteworthy in their relationship to ozone bands.[15] The stronger band appears 7 cm^{-1} lower than the strongest ozone absorption (ν_3) at 1039 cm^{-1}, and the weaker band occurs 2 cm^{-1} above the weakest ozone absorption (ν_1) at 1104 cm^{-1}. In addition the photolysis presented in Figure 2 shows a decrease in the 704-cm^{-1} ozone band (ν_2), which implies group 1 and ozone have coincident absorption at 704 cm^{-1}. All of the evidence indicates that the group 1 bands are due to O$_3$ in the CF$_3$I–O$_3$ complex, species **1**. An increase in the ν_1–ν_3 separation
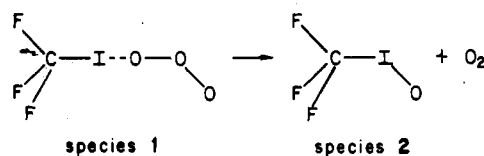
for the O$_3$ submolecule in species **1** implies a more obtuse O–O–O angle and the open CF$_3$I--O–O–O arrangement. The group 1 bands photolyze in concert with A and B radiation and serve as the photochemical precursor to the group 2 bands.

Group 2. The group 2 bands include an important diagnostic, namely the sharp 732.3-cm^{-1} band, which shifted to 706.0 cm^{-1} with oxygen-18 and showed no intermediate component with mixed isotopic ozone. This 26.3-cm^{-1} isotopic shift is slightly less than the 37.4-cm^{-1} value predicted for a harmonic I–O vibration. The proximity of the intense symmetric C–F$_3$ bending mode[16] of CF$_3$I at 742 cm^{-1} suggests mode mixing and partial symmetric C–F$_3$ bending character for the 732.3-cm^{-1} vibration, which on the basis of the large ^{18}O shift, is primarily an I–O stretching vibration. The new 733.4-cm^{-1} band for the ^{18}O species **2** is appropriate for the symmetric C–F$_3$ bending mode, which has a small amount of I–O stretching character, and is obscured by the CF$_3$I band for the ^{16}O species. The strong 1202-cm^{-1} band exhibited no ^{18}O shift, and it is in the region expected for an antisymmetric C–F stretching vibration for a CF$_3$ group. The weaker 1214-cm^{-1} band is probably due to one of the other C–F stretching modes.

Thus, the vibrational data show that species **2** contains coupled I–O stretching and symmetric C–F$_3$ bending modes and a strong C–F$_3$ antisymmetric stretching mode not coupled with oxygen motions. These observations indicate the CF$_3$–I–O identity and bonding arrangement for species **2**. The identity of species **2** as CF$_3$IO is substantiated by the complementary O atom discharge experiments where species **2** was the major product of the CF$_3$I and O atom cocondensation reaction. The formation of CF$_3$IO in O atom addition experiments and on sample warming after ultraviolet photolysis in CF$_3$I/O$_3$ experiments suggests that ground-state oxygen atoms add to CF$_3$I with little or no activation energy.

It is noteworthy that solid CF$_3$IO exhibits absorptions[5] at 1210 and 750 cm^{-1}, near the strongest bands of the matrix-isolated molecule. The I–O stretching fundamental for CF$_3$–I–O may be compared to those for CH$_3$–I–O (723.7 cm^{-1})[4] and Cl–I–O (779.1 cm^{-1}).[3] In these cases, a larger ^{18}O shift characteristic of an almost pure I–O mode was observed owing to the lack of a nearby vibrational mode for coupling.

The 726.5-cm^{-1} satellite band was stronger relative to the 732.3-cm^{-1} species **2** band on photolysis A, but the bands tracked together on irradiations B and C. The 34.0-cm^{-1} ^{18}O shift indicates a more purely I–O stretching fundamental. It is suggested that the weaker satellite bands are due to a CF$_3$–I–O--O$_2$ species where interaction with the remaining oxygen molecule affects the structure of the CF$_3$–I–O part.

A comparison with similar CH$_3$I studies[4] is of interest. On the basis of I–O vibration absorbances in CH$_3$IO and CF$_3$IO, the species **1** and species **2** yields in the present experiment are a factor of 6 lower than the experiment with corresponding CH$_3$I species. This may account for failure to observe the weak near-ultraviolet absorption through which photolysis of species 1 proceeds.

Group 3. Absorptions in this group include two strong C–F stretching vibrations, one with a 4-cm^{-1} and the other with 10-cm^{-1} ^{18}O shift, one medium-intensity band at 1235 cm^{-1}, and two weaker bands, one at 914.9 cm^{-1} in the C–O stretching region and the other at 320 cm^{-1} in the low-frequency deformation region. The 914.9-cm^{-1} band exhibited an 18.2-cm^{-1} shift with ^{18}O, almost the 21.5-cm^{-1} shift calculated for a pure harmonic C–O stretching vibration. This agreement is sufficient for characterization of the 914.9-cm^{-1} band as a C–O stretching fundamental. These characteristic group frequencies, the photochemical production of group 3 absorptions from group 2, particularly in the O atom discharge experiments where species **2** is the predominant major product, and comparison with spectra[8] for CF$_3$OF and CF$_3$OCl (Table II) support assignment of the group 3 bands as CF$_3$OI, species **3**. The 1241- and 1203-cm^{-1} bands are clearly due to
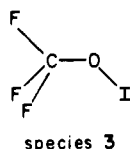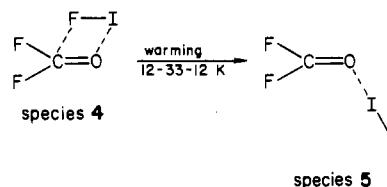
species **3**

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Table II. Argon-Matrix Fundamentals (cm^{-1}) for CF$_3$OF, CF$_3$OCl, and CF$_3$OI

CF$_3$OF[a]	CF$_3$OCl[a]	CF$_3$OI	assgnt[b]
1290	1268	1241	C–F antisym
1252	1219	1203	C–F antisym
1214	1200		C–F sym
945	918	915	C–O str
883	781		O–X str
435	397	320	C–O–X bend

^{a} Data from ref 8. ^{b} Assignments from ref 18.

C–F stretching fundamentals, probably the two antisymmetric fundamentals resulting from the loss of CF$_3$ degeneracy in species **3**. The C–O stretching fundamental for species **3** is almost the same as for CF$_3$OCl and is below the value for CF$_3$OF, which interacts with the O–F stretching mode.[17,18] The 320-cm^{-1} band fits in the trend for the low-frequency C–O–X deformation mode and is below the 435-cm^{-1} value for CF$_3$OF.[17,18] Finally, the 1235-cm^{-1} band is in excellent agreement with the sum 915 + 320 = 1235 cm^{-1} and is appropriate for a combination band; the ^{18}O counterparts are in accord, and the 1235-cm^{-1} band intensity is probably enhanced by Fermi resonance interaction with the strong 1203-cm^{-1} antisymmetric C–F stretching fundamental.

Group 4. The group 4 absorptions were produced in small yield by 360–470 nm irradiation and in large yield by 240–420 nm irradiation. These bands are sharp, and they agree to ±5 cm^{-1} with the strongest absorptions for OCF$_2$ measured in this laboratory (Table I, footnote *a*). In addition, a new group 4 band at 591 cm^{-1} can reasonably be assigned to perturbed IF on the basis of the 603-cm^{-1} gas phase and argon-matrix fundamentals.[19,20] Accordingly, the group 4 bands characterize species **4** as an IF

species **4**   species **5**

perturbed OCF$_2$ complex. Since the frequency displacements are small, the intermolecular interaction is relatively weak, and a weak dipole–dipole attractive molecular pair is suggested for species **4**. Sample annealing to 33 K over a 15-min period virtually destroyed species **4** and produced more than an order of magnitude growth in group **5** absorptions. In contrast to the photolysis of matrix-isolated CF$_3$OF and CF$_3$OCl,[6,8] no absorptions were detected in the present experiments for isolated OCF$_2$. It is not surprising that the larger IF photoproduct does not escape the matrix site of photodecomposition. At least one band in the CF$_3$OCl study (971.9 cm^{-1}),[8] however, provides evidence for a CF$_2$O--ClF complex, although isolated OCF$_2$ appears to be the major photoproduct.

Group 5. Absorptions in group 5 were produced in small quantity by 240–420-nm photolysis and in large yield on sample warming. The spectrum of species **5** is similar to that of OCF$_2$, but the displacements are larger than those for species **4**, so it is concluded that species **5** is a more strongly perturbed OCF$_2$ complex with IF. The ν_2 symmetric C—F$_2$ stretch is blue shifted 20 cm^{-1} and the ν_1 symmetric C==O stretch is red shifted 30 cm^{-1} from OCF$_2$ values; these changes substantially reduce the Fermi resonance interaction between $2\nu_2$ and ν_1 for species **5** as is seen in the very weak $2\nu_2$ observed for species 5 at 1968.4 cm^{-1} as compared to species 4 at 1938.9 cm^{-1} and isolated OCF$_2$ at 1941.5 cm^{-1}. The IF fundamental in species **5**, 595 cm^{-1}, is displaced less than the IF fundamental for species **4**, 591 cm^{-1}. It is suggested that the stronger intermolecular interaction between OCF$_2$

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and IF involves the O and I atoms in a head-to-tail dipole–dipole arrangement for species **5**. Perhaps the stability of species **5** over species **4** arises from decrease of repulsions between fluorine lone pairs. The smaller perturbation on the I–F stretching vibration for species **5** is consistent with the lighter fluorine atom not being involved in the weak intermolecular bonding.

It is of interest to compare the hydrogen-bonded complex[4,21] CH_2O--HI with the more stable CF_2O--IF species. If the red shift in C=O stretching modes on complex formation is an accurate indication of the intermolecular interaction, species **5** exhibited a 30-cm^{-1} red shift and CH_2O--HI sustained a 12-cm^{-1} red shift. This suggests that complex **5** is at least as strong as the hydrogen-bonded complexes.

Group 6. The sharp 1223.0-cm^{-1} doublet was produced in trace quantity by photolysis B and in moderate yield by D and was reduced by one-third on sample warming. The doublet exhibited a 1.2-cm^{-1} ^{18}O shift, which suggests an antisymmetric C–F stretching vibration with a very small amount of coupling to a C–O stretching motion. The 1223.2-, 1222.0-cm^{-1} doublet is tentatively assigned to the intense antisymmetric C–F stretching mode of the CF_3O free radical for the following reasons: (1) its reduction on sample warming is accompanied by growth of the strongest $(CF_3O)_2$ band[8] as a shoulder at 1161 cm^{-1}, (2) a weak unassigned 1223-cm^{-1} band appeared in the recent F + CO experiments of Jacox,[10] which gave very strong OCF and OCF_2 product bands, and (3) its formation by dissociation of I from CF_3OI requires only that I be trapped on the CF_3 side to prevent recombination of I and CF_3O. In this regard, a similar 240–420-nm irradiation of an Ar/CF_3I = 200/1 sample produced a new 1247 cm^{-1} band, which is appropriate[22] for CF_3 (perhaps perturbed by I), and sample warming destroyed the 1247-cm^{-1} band and produced two C_2F_6 bands at 1242 and 1110 cm^{-1}.

This possible observation of CF_3O at 1223 cm^{-1} in solid argon derives some support from calculations of the vibrational spectrum of CF_3O, which predict two strong C–F stretching modes at 1265 and 1272 cm^{-1} for the Jahn–Teller distorted $^2A'$ ground state.[23] Taking similar calculations of the antisymmetric C–F stretching mode in OCF_2 as a predictor of matrix fundamentals, this scaled calculation can result in fundamentals too large by at least 20 cm^{-1}, and for a distorted free radical, even more error could reasonably be expected. Finally, the CF_3O radical is apparently short-lived in the gas phase, rapidly decomposing to give OCF_2 and F owing to the low C–F bond dissociation energy in CF_3O.[24] The cold matrix environment may deactivate CF_3O and reduce its decomposition rate.

Group 7. The weak, sharp 799-cm^{-1} band appeared only in the thick sample deposits and showed a large ^{18}O shift to 759 cm^{-1} and a mixed ^{16}O–^{18}O isotope component at 789 cm^{-1}. This evidence supports a tentative assignment of the 799-cm^{-1} band to CF_3IO_2 with two equivalent oxygen atoms. In support of this assignment, the solid compound has an I–O stretching fundamental[5] at 790 cm^{-1}, and a similar band[4] was observed for matrix-isolated CH_3IO_2 at 830 cm^{-1}.

Group 8. The 1287- and 1198-cm^{-1} bands appeared with moderate intensity only after sample warming, which characterized some type of aggregate species. Their proximity to the strongest matrix absorptions[8] of CF_3OF suggests an I atom perturbed CF_3OF as a tentative identification of species **8**.

Structure of the Complex. The octet of absorptions observed in the ν_3 region of O_3 when CF_3I was codeposited with scrambled $^{16,18}O_3$ (Figure 1) clearly indicates that the O_3 moiety of the CF_3I--O_3 complex is asymmetric with respect to interchange of terminal O atoms; the two bands due to the 16–16–18 isotope are split by 7.7 cm^{-1} for CF_3I attachment at each end of this asymmetric ozone isotope and the two bands for the 16–18–18 isotope are similarly split by 7.8 cm^{-1}. This contrasts markedly with the

Scheme I

species 1

470–1000 nm

species 2

species 3

+ O_2 240–420 nm

species 4

warming

species 5
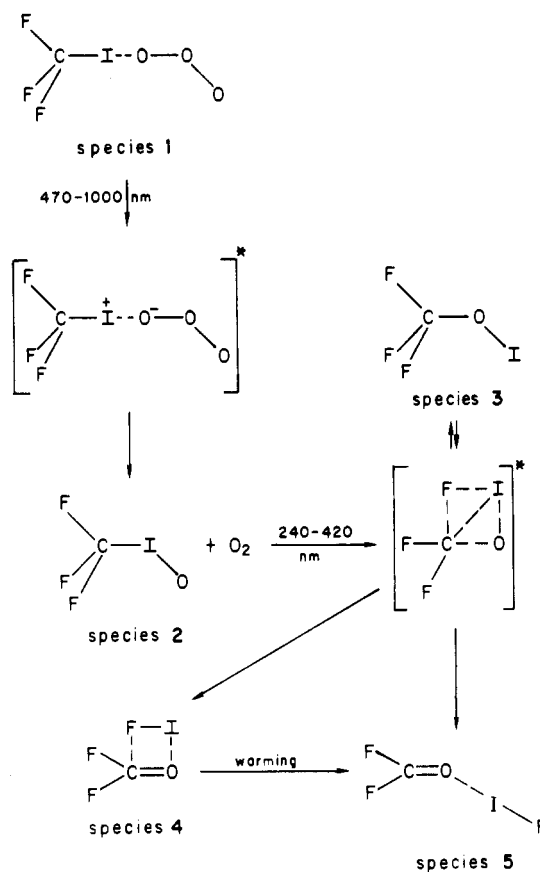
geometry of the PH_3--O_3 complex, where scrambled $^{16,18}O_3$ gave a sextet in the ν_3 region of O_3, which indicates that the O_3 moiety is symmetric with respect to interchange of terminal O atoms in the phosphine complex.[25]

Photochemistry. The most interesting feature of the CF_3I--O_3 complex is that it photodissociates efficiently with 470–1000-nm radiation, which can photodissociate matrix-isolated ozone but with considerably reduced efficiency.[26] Similar behavior has been found for molecular O_3 complexes with ICl and CH_3I.[3,4] It is suggested that the 470–1000-nm radiation excites a charge-transfer transition and the excited ionic state relaxes by O^- transfer to CF_3I^+ to give the photoproduct species **2** as illustrated in Scheme I. The increased ionization energy of CF_3I, as compared to that of CH_3I, is due to the perfluoro effect,[27,28] which may account for the lower photochemical yield of CF_3IO in these studies, as compared to that of CH_3IO.[4] Further, irradiation with near-ultraviolet light destroys species **2** and leads to a transition state, Scheme I, that serves as a precursor to the major photolysis product species **3** and **4** and the minor photolysis product species **5**. Sample warming allows rearrangement of the molecular pairs in species **4** and produces the more stable species **5** structure.

Conclusions

Codeposition of CF_3I and O_3 at high dilution in argon formed a CF_3I--O_3 molecular complex, which was dissociated by visible photolysis to give CF_3IO, probably involving a charge-transfer mechanism. The same CF_3IO species was prepared by codeposition of CF_3I and O atoms from a blind microwave discharge tube. On near-ultraviolet irradiation, the iodoso compound rearranged to CF_3OI and eliminated IF to give two different CF_2O--IF complexes. The less stable arrangment gave ±5-cm^{-1}

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displacements from CF_2O frequencies, but the more stable structure gave shifts up to 30 cm^{-1}, which suggests that the latter complex is at least as strong as similar hydrogen-bonded complexes.

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Note Added in Proof. Complementary mercury arc photolysis experiments have been done with $Ar/O_2/CF_3I$ matrix samples at 4 K.

These studies gave similar product spectra including perturbed OCF_2 species, group 3 and group 6 absorptions.[29]

Registry No. 2, 56407-83-1; 3, 97551-33-2; CF$_3$I, 2314-97-8; O$_3$, 10028-15-6; ^{18}O$_3$, 21424-26-0; ^{16,18}O$_3$, 97551-32-1; CF$_2$O, 353-50-4; IF, 13873-84-2; Ar, 7440-37-1.

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Circular Dichroism of (Ethylenediaminetetrapropionato)rhodate(III) Ion

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The ethylenediaminetetrapropionate ion (edtp) is sexidentate in the complex [Rh(edtp)]$^-$. The infrared, electronic absorption, and circular dichroism spectra are reported. The Λ configuration is assigned to the (+)$_D$ enantiomer by comparison of the CD spectrum with those of Rh(III) edta-type complexes for which absolute configurations are known from X-ray crystallography. Although the electronic absorption intensities are not large for [Rh(edtp)]$^-$, the CD intensities are unexpectedly great in comparison to those of other edta-type complexes of Rh(III).

Introduction

The structure of the [Co(edta)]$^-$ complex[1] shows notable departures from regular octahedral coordination, indicating that the chelate rings are strained. The two glycinate rings (designated as G rings) lying in the plane of the diamine ring are considerably more strained than the out-of-plane glycinate rings (designated as R rings). The larger Cr(III)$^{2-4}$ and Rh(III)^{3,5} metal ions tend not to form sexidentate edta complexes because of greater ring strain.

The 1,3-pdta,[6] SS-edds,[7-10] and eddda[11,12] ligands (1,3-pdta = 1,3-propanediaminetetraacetate ion; SS-edds = (SS)-ethylenediamine-N,N'-disuccinate ion; eddda = ethylenediamine-N,N'-diacetate-N,N'-di-3-propionate ion) form six-membered chains when coordinated, and the formation of their sexidentate Rh(III) complexes can be attributed to the relief of strain of chelate rings. Such complexes containing the ligand with mixed (five- and six-membered) rings are of interest in the study of the influence of chelate ring size and their arrangement about a central metal ion and other factors on optical activity.

The sexidentate Rh(III) complexes with eddda,[13,14] SS-edds,[7,14] and 1,3-pdta[15] have been prepared, and their CD spectra were studied. In this paper the edtp ligand (edtp = ethylenediaminetetrapropionate ion), in which four carboxylate groups are lengthened with respect to the edta ligand, has been used in the preparation and resolution of the corresponding sexidentate Rh(III) complex. The IR, electronic absorption, and CD spectra of the complex are reported.

Experimental Section

All reagent-grade chemicals and solvents were obtained commercially and used without further purification.

Optical isomers are identified by the sign of the optical rotation at a specified wavelength, λ [(+)$_\lambda$ or (−)$_\lambda$]. The chirality is designated as Δ or Λ assigned according to ref 16.

Preparation of Ethylenediaminetetrapropionic Acid, H$_4$edtp. This ligand was prepared by a modification of the method given by Van Saun and Douglas.[17] From 142 g (1.3 mol) of 3-chloropropionic acid, 87 g (2.2 mol) of NaOH, and 14 cm^3 (0.23 mol) of ethylenediamine was obtained 12 g of a mixture that contained H$_4$edtp.

The pure H$_4$edtp was obtained by a gel filtration technique using G-10 Sephadex. The mixture (1.5 g) was passed through a column (40 cm ×

5 cm) with use of distilled water for elution. The eluate was monitored by pH (pH ~3–4 for pure H$_4$edtp) or by testing for Cl$^-$. The eluate containing H$_4$edtp was evaporated to dryness; yield 0.7 g. Anal. Calcd for H$_4$edtp, C$_{14}$H$_{24}$O$_8$N$_2$ (M_r 348.36): C, 48.27; H, 6.94; N, 8.04. Found: C, 48.11; H, 6.99; N, 7.80.

Preparation of Sodium (Ethylenediaminetetrapropionato)rhodate(III) Dihydrate, Na[Rh(edtp)]·2H$_2$O. Rhodium trichloride trihydrate (1.32 g, 5 mmol) was dissolved in 3 cm^3 of water in a Pyrex tube. To this mixture was added a solution obtained by dissolving 1.74 g (5 mmol) of H$_4$edtp in 5 cm^3 of 4 M NaOH (20 mmol). The tube was sealed and the mixture heated at 145 °C in a oil bath for 7 h. After that the mixture was cooled to room temperature and the tube was chilled in ice and opened carefully. The yellow solution obtained was filtered off, and the filtrate was then introduced into a 55 cm × 4.5 cm column containing QAE A-25 Sephadex anion-exchange resin in the Cl$^-$ form. NaCl solution (0.1 M) was used for elution (ca. 0.5 cm^3/min). The eluate with −1 charge was obtained and evaporated under vacuum at 40 °C to a volume of 10 cm^3 and then cooled overnight in a refrigerator. The deposited NaCl was removed and the filtrate was desalted by passage through a G-10 Sephadex column, eluting with distilled water. Then the eluate was concentrated to a volume of 5 cm^3. After the addition of 15 cm^3 of ethanol, the solution was left in a refrigerator for 4 days. The crystals were collected, washed with ethanol and then ether, and air-dried; yield 1.2 g (47%). Anal. Calcd for Na[Rh(edtp)]·2H$_2$O, NaRhC$_{14}$H$_{24}$O$_{10}$N$_2$ (M_r 506.25): C, 33.22; H, 4.77; N, 5.53. Found: C, 32.34; H, 5.04; N, 5.80.

Resolution of Sodium (Ethylenediaminetetrapropionato)rhodate(III)

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