

Photochemistry of an Ozone Complex with Iodomethane in Solid Argon at 17 K. Infrared Spectra of Iodosomethane (CH₃IO) and the Hydrogen-Bonded CH₂O--HI Complex

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Codeposition of iodomethane and ozone in excess argon at 17 K leads to the formation of a molecular complex between iodomethane and ozone, which photodissociates to iodosomethane, CH₃IO, when exposed to 360–470-nm radiation in a 395-nm charge-transfer absorption band. Further photolytic rearrangement of CH₃IO gives iodomethanol (ICH₂OH), methyl hypoiodite (CH₃OI), and formaldehyde by elimination of hydrogen iodide. Because of the close proximity of the formaldehyde–hydrogen iodide molecular pair on formation, two complexes are formed; the more stable one is the hydrogen-bonded complex, CH₂O--HI, and the less stable structure yields the more stable one on sample annealing. The spectra of these CH₂O--HI complexes are free from interference by absorptions of the acid and base submolecules.

Introduction

The formation of molecular complexes between hydrogen fluoride and a variety of bases in cryogenic matrices has recently been well studied and documented.¹ Correlation of infrared spectra of HF hydrogen-bonded complexes and those of complexes involving different HX (X = F, Cl, Br or I) molecules² with similar bases clarifies the relationship between the strength of the hydrogen bond and not only the acidity of the HX molecule but also the basicity of the base. This information is important in understanding the nature of the hydrogen bond. The infrared spectrum of such a complex, formed by codeposition of gaseous mixtures of argon/hydrogen halide and argon/base, is often obscured by absorptions of the parent species together with those of their polymers. In this paper we report the infrared spectrum of a hydrogen-bonded complex between hydrogen iodide and formaldehyde recorded in the absence of the parent species. This was made possible by formation of the complexes during photolysis of argon matrices containing iodomethane and ozone.

Ultraviolet photolysis of ozone in cryogenic matrices is a useful method for effecting oxygen atom transfer to a substrate molecule in a matrix.^{3,4} However it has recently been reported⁵ that visible irradiation can induce photodecomposition of ozone in the charge-transfer band of a molecular complex between ozone and the substrate molecule. Furthermore transfer of an oxygen atom to the substrate led to the characterization of the first simple monomolecular species X–I–O containing a univalent substituent X covalently bound to iodine. This paper gives an account of a matrix study where visible photolysis of a molecular ozone–iodomethane complex results in the formation of iodosomethane and formaldehyde–hydrogen iodide complexes.

Experimental Section

Apparatus. The vacuum and cryogenic techniques used in the present experiments have been described previously.⁶ Infrared spectra were recorded on a Nicolet 7199 Fourier-transform infrared spectrometer in the 400–4000-cm⁻¹ range at 0.25-cm⁻¹ resolution, by using a germanium-coated KBr beam splitter, a liquid-nitrogen-cooled Hg–Cd–Te detector, and CsI optics for the vacuum shroud and cold window. The sample was scanned approximately 750 times; the added interferograms were converted to a single-beam spectrum by a fast Fourier-transform algorithm utilizing times 4 zero filling. This spectrum was then ratioed with a similar spectrum of the cold window without sample to produce a double-beam spectrum. The observed bands are accurate to ±0.1 cm⁻¹. Samples were irradiated for periods of 15–35 min by a BH-6 high-pressure mercury arc lamp (1000 W, Illumination Industries, Inc.) using a 10-cm water filter and a variety of Corning glass filters. The most diagnostic irradiations involved two band-pass filters, which gave access to the regions 240–420 nm (Corning no. 9863, transmits 85% at 320 nm) and 360–470 nm (Corning no. 5113, transmits 40% at 410 nm), and a Pyrex filter, which removed radiation of wavelength shorter than 290 nm.

Chemicals. Argon (Air Products) was used as supplied. Ozone was generated by a static electric discharge (Tesla coil) of oxygen in a Pyrex

Table I. Absorptions (cm⁻¹) Observed for the Molecular Complex CH₃I–O₃ (Species 1) Formed by Codeposition of Argon Samples Containing Ozone and Iodomethane

	precursor		complexes		precursor CD ₃ I
	O ₃	CH ₃ I	CH ₃ I + O ₃	CD ₃ I + O ₃	
		527.8	527.0	495.9	496.4
705.4			704.7	704.6	
		880.4	885.9	658.3	654.6
1104.6			1102.8	1102.8	
		1245.5	1244.4	942.9	944.1

tube immersed in liquid nitrogen;⁷ residual O₂ was removed by pumping at 77 K. Normal isotopic oxygen (Burdett, USP) and 50.3% and 98.0% ¹⁸O-enriched oxygen gas (Yeda, Israel) were used directly. Iodomethane and deuterium-substituted iodomethane (Aldrich) were degassed before use by three freeze–thaw cycles and pumping at 77 K.

Procedure. Ozone and iodomethane were each diluted with argon to a matrix ratio (*M/R*) of 200/1 and deposited at 17 K at an average rate of 2–4 mmol/h. Spectra were recorded at 17 K after deposition, photolysis with 360–470-nm radiation, photolysis with 290–420-nm radiation and warming to 33–35 K.

Results

The sequence of photolysis and warming cycles described above gave rise to a wealth of absorptions, most of which can be assigned to one of six distinct groups. Absorptions in a particular group exhibited a constant relative intensity throughout a single experiment and between different experiments and may, therefore, be associated with the same species. The groups of absorptions, denoted 1–6 and assigned to species 1–6, will be considered separately for clarity and convenience.

Upon codeposition of argon/ozone and argon/iodomethane samples at 17 K, several absorptions (group 1) were observed in the infrared spectrum of the sample that were not observed in spectra of the reagent molecules deposited separately. These bands were completely destroyed by irradiation of the sample for 30 min at 360–470 nm (Figure 1), and their positions are given in Table I. This irradiation had no measurable effect on the isolated O₃ and CH₃I absorptions. Similar visible–ultraviolet experiments gave a broad 395-nm product absorption (*A* = 0.04, fwhm = 30 nm), which was destroyed with Pyrex-filtered mercury arc radiation.

In addition, the infrared spectrum after sample deposition often exhibited weak bands associated with products formed during subsequent photolyses. In particular a very strong sharp band at 723.7 cm⁻¹ and sharp absorptions at 848.0, 858.9, 1223.4, and

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Table II. Absorptions (cm^{-1}) Assigned to Iodosomethane, CH_3IO (Species 2), Formed after Mercury-Arc Irradiation of Argon Matrices Containing Ozone and Iodomethane

precursor CH_3I	photoproduct absorptions ^a				precursor CD_3I	assgnt
	$\text{CH}_3\text{I} + ^{16}\text{O}_3$	$\text{CH}_3\text{I} + ^{16,18}\text{O}_3$	$\text{CH}_3\text{I} + ^{18}\text{O}_3$	$\text{CD}_3\text{I} + ^{16}\text{O}_3$		
527.8	496.6 (0.07)	492.5	492.6	460.4	496.4	$\nu_{\text{C-I}}$ $\nu_{\text{C-I}}$ site
		686.6	686.3			$\nu_{\text{I-}^{18}\text{O}}$ site
	722.2 (0.40)	722.2		722.0		$\nu_{\text{I-}^{16}\text{O}}$ site
	723.7 (1.3)	723.7		723.3		ρ_{CH_3}
	848.0 (0.21)	847.9	847.2	639.6		ρ_{CH_3}
	858.9 (0.16)	858.8	858.7	646.0		δ_{CH_3}
880.4		1222.9	1222.9		654.6	ρ_{CH_3} δ_{CH_3}
1245.5	1223.4 (0.29)	1223.3		938.6	944.1	δ_{CH_3} δ_{CH_3}
	1400.3 (0.44)	1400.3	1400.3			γ_{CH_3} site
	1417.2 (0.06)	1416.6			1044.5	γ_{CH_3} $\rho_{\text{CH}_3} + \delta_{\text{CH}_3}$ site
1431		<i>b</i>	2069.7			$2\delta_{\text{CH}_3}$
	2070.7 (0.02)	<i>b</i>	2080.6			$2\delta_{\text{CH}_3}$
	2081.1 (0.02)		2429.0			$\nu_{\text{CH}_3(\text{s})}$
	2428.6 (0.05)	2428.6		2132.1		$\nu_{\text{CH}_3(\text{s})}$
	2945.3	2944.9				$\nu_{\text{CH}_3(\text{s})}$
2965.7					2150.5	$\nu_{\text{CH}_3(\text{s})}$

^a Figures in parentheses are peak height absorbances. ^b Obscured by $^{16,18}\text{O}_3$ absorptions.

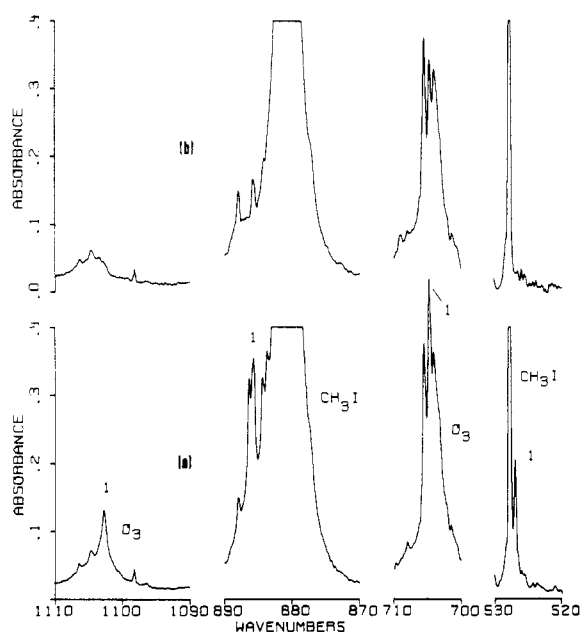


Figure 1. Infrared spectra of a matrix prepared with $\text{Ar}/\text{O}_3 = 200/1$ and $\text{Ar}/\text{CH}_3\text{I} = 200/1$ samples: (a) after codeposition at 17 K; (b) after warming to 26 K, recooling to 17 K, and 360–470-nm photolysis for 30 min. Group 1 absorptions are denoted 1.

1400.3 cm^{-1} all increased in absorbance at a similar rate during 360–470-nm irradiation of the matrix (group 2). In one experiment, the sample was warmed to 26 K for 127 min and re-cooled to 17 K before photolysis and the above absorptions grew by a factor of 4 at the expense of the group 1 bands listed in Table I, and additional weak absorptions appeared at 2428.6 and 2945.3 cm^{-1} . After 360–470-nm irradiation of the sample, four weaker absorptions associated with group 2 appeared in the infrared spectrum at 492.6, 2020.7, 2081.2, and 2428.6 cm^{-1} . The major group 2 absorptions are shown in Figure 2; all group 2 bands are listed in Table II with the corresponding absorptions observed when $^{18}\text{O}_3$ rather than $^{16}\text{O}_3$, and CD_3I rather than CH_3I , were used. The strongest product band observed in these studies, 723.7 cm^{-1} ($A = 1.3$, $\text{fwhm} = 0.6 \text{ cm}^{-1}$), exhibited an ^{18}O shift of 35.6 cm^{-1} and a D shift of only 0.4 cm^{-1} , and it appeared as a doublet in 50.3% ^{18}O -enriched-ozone experiments. In contrast, bands at 492.6, 848.0, 858.9, 1223.4, and 2945.3, cm^{-1} exhibited large D shifts and ^{18}O -shifts of less than 1.0 cm^{-1} . Subsequent exposure of the matrix to 290–420-nm radiation for 30 min caused a 50%

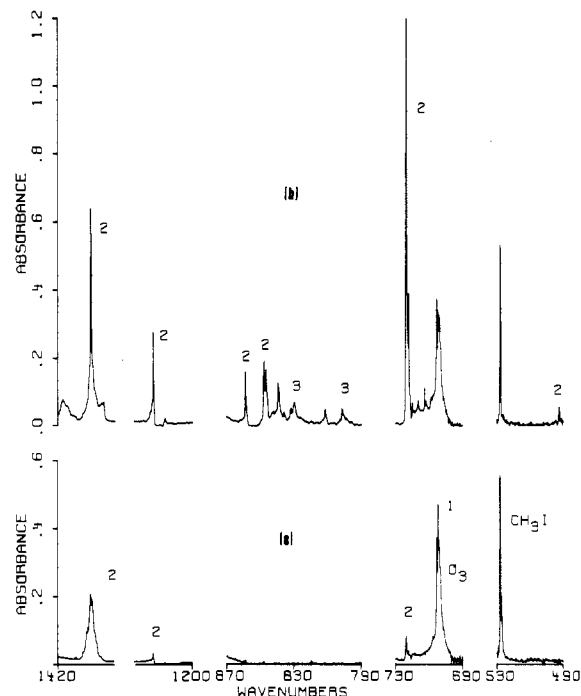


Figure 2. Infrared spectra of a matrix prepared with $\text{Ar}/\text{O}_3 = 200/1$ and $\text{Ar}/\text{CH}_3\text{I} = 200/1$ samples: (a) after codeposition at 17 K; (b) after warming to 26 K, recooling to 17 K, and 360–470 nm photolysis for 30 min. Group 2 and 3 absorptions are so marked.

reduction in the intensity of group 2 absorptions, and a further decrease was observed after the sample was warmed to 34 K for 15 min.

A third set of absorptions (group 3) maintained a low intensity (less than 0.035 absorbance units) throughout a particular experiment yet increased during both stages of photolysis and during the warming cycle also. These absorptions at 795.9 and 829.8 cm^{-1} (Figure 2) are given in Table III and were observed at 760.4 and 794.5 cm^{-1} , respectively, in experiments utilizing $^{18}\text{O}_3$ and at 799.6 and 830.4 cm^{-1} with CD_3I and $^{16}\text{O}_3$. More significantly, experiments employing ozone enriched to 50.3% ^{18}O gave rise to absorptions at 823.7 and 771.4 cm^{-1} , which were absent from spectra of either isotopically pure samples. Unfortunately the low intensity of group 3 bands prevented observation of absorptions at 760.4 and 829.8 cm^{-1} in the isotopically scrambled samples, but one was detected at 794.4 cm^{-1} .

Table III. Absorptions (cm⁻¹) Tentatively Assigned to CH₃I/O₃ (Species 3)

photoproduct absorptions				assgnt
CH ₃ I + ¹⁶ O ₃	CH ₃ I + ^{16,18} O ₃	CH ₃ I + ¹⁸ O ₃	CD ₃ I + ¹⁶ O ₃	
		760.4		
795.9	711.4		799.6	$\nu_{\text{IO}_2(\text{s})}$
	794.5	794.5		
829.8	823.7		830.4	$\nu_{\text{IO}_2(\text{as})}$

Figure 3. Infrared spectra of a matrix prepared with Ar/O₃ = 200/1 and Ar/CH₃I = 200/1 samples: (a) after codeposition at 17 K; (b) after warming to 33 K for 15 min and recooling to 17 K. Group 4 and 5 bands are indicated.

The positions of absorptions comprising groups 4 and 5 lie within 15 cm⁻¹ of absorptions of formaldehyde in solid argon, although none were coincident. Both sets of absorptions grew during both stages of photolysis, but while those of group 4 disappeared completely after warming to 34 K, those of group 5 increased in intensity (Figure 3). The most intense absorptions associated with species 4 and 5 were observed at 1736.2 and 1729.9 cm⁻¹, respectively. The former exhibited shifts of 33.8 and 45.0 cm⁻¹ in experiments where ¹⁶O₃ was replaced by ¹⁸O₃ and CH₃I by CD₃I, respectively, and the corresponding isotopic shifts observed for species 5 were 33.0 and 43.7 cm⁻¹. The absorptions of groups 4 and 5 are summarized and compared to those of isolated formaldehyde in Table IV. No counterpart to the species 5 absorption at 2120 cm⁻¹ could be detected for species 4. This band was broad (fwhm = 10 cm⁻¹) and exhibited a strong deuterium counterpart at 1515 cm⁻¹. Within experimental error, its position was not affected by ¹⁸O isotopic enrichment. All absorptions assigned to species 4 and 5 showing ¹⁸O isotopic shifts appeared as doublets in the spectra of samples containing 50.3% ¹⁸O-enriched ozone.

Irradiation at 360–470 nm also produced six new absorptions that increased with further 290–420-nm photolysis and are classified as group 6. The ¹⁶O₃ and CH₃I product absorptions, which appeared at 998.6, 1159.2, and 3350 cm⁻¹, were observed at 969.8, 1154.7, and 3339 cm⁻¹, respectively, after ¹⁸O isotopic enrichment of the sample, and in each case, a doublet was observed after 50.3% ¹⁸O isotopic enrichment. While the band at 998.6 cm⁻¹ suffered a 26.7-cm⁻¹ shift to 971.9 cm⁻¹ in samples containing CD₃I, those at 1159.2 and 3350 cm⁻¹ were affected to a much greater extent, with deuterium shifts to 886.7 and 2478 cm⁻¹, respectively. The three remaining absorptions associated with group 6 were observed at 1466.0, 2814.6, and 2936.8 cm⁻¹. These features were affected very little by ¹⁸O isotopic enrichment, but those between 2800 and 2950 cm⁻¹ were shifted to 2063.2 and 2233.5 cm⁻¹ in the spectra of samples containing CD₃I, as given in Table V.

Several weak absorptions in each experiment were difficult to characterize. Of these, two absorptions near 1060 and 500 cm⁻¹

Table IV. Absorptions (cm⁻¹) of Formaldehyde and Formaldehyde–Hydrogen Iodide Molecular Complexes (Species 4 and 5) Isolated in Solid Argon at 17 K

CH ₂ O ^a	CH ₃ I + ¹⁶ O ₃	shift ^b	CH ₃ I + ¹⁸ O ₃	CD ₃ I + ¹⁶ O ₃	assgnt
1168.4	1168.5	+0.1	1167.2	987.0	CH ₂ O
	1170.9	+2.5	1169.6	988.0	species 4
1499.9	1494.6	-5.3	1484.2	1100.9	species 4
	1495.3	-4.6	1485.2	1101.1	species 5
1742.3	1729.9	-12.4	1696.9	1686.2	CH ₂ O
	1736.2	-6.1	1702.4	1691.2	species 5
	2120.0		2120.0	1515.0	species 4
2797.9	2798.4	+0.5	2798.0	2072.8	CH ₂ O
	2806.1	+8.2	2805.2	2079.7	species 4
2864.3	2867.3	+3.0	2852.9	2183.1	species 5
	2877.1	+12.8	2861.2	2194.8	CH ₂ O
					species 4
					species 5

^a Reference 11. ^b Displacement of complex modes relative to CH₂O values.

Table V. Absorptions (cm⁻¹) in the Infrared Spectrum of the Photolysis Products of Ozone and Iodomethane in Solid Argon Assigned to Iodomethanol, ICH₂OH (Species 6)

¹⁶ O ₃	^{16,18} O ₃	¹⁸ O ₃	CD ₃ I	assgnt
			845	ν_{DCX}
998.6	969.8	969.8 (0.46) ^a	971.9	ν_{CO}
	998.6			
	1154.7	1154.7 (0.11)		$\delta_{\text{COH}}(\text{ICH}_2\text{OH})$
1466.0	1466.1	1466.2 (0.07)		
			2063.2	$\delta_{\text{CH}_2}(\text{ICH}_2\text{OH})$
2814.6		2813.9 (0.06)		
			2233.5	$\nu_{\text{CH}_2}(\text{ICH}_2\text{OH})$
2936.8		2936.9 (0.08)		
	3339	3339 (0.09)		$\nu_{\text{OH}}(\text{ICH}_2\text{OH})$
3350	3350		2478	

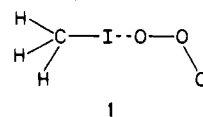
^a Figures in parentheses are peak height absorbances.

appeared to be related. The former grew in at 1074.1 cm⁻¹ on irradiation of a sample containing ¹⁶O₃ and CH₃I, increased in intensity after 290–420-nm irradiation, and decreased by 12% on warming to 34 K. On ¹⁸O isotopic enrichment to 50.3%, a doublet was observed with a second low-frequency component at 1051.2 cm⁻¹, shifted by 22.9 cm⁻¹ with respect to the first absorption. No corresponding absorption was detected in spectra of samples containing CD₃I. Bands at 504.4 and 508.7 cm⁻¹ were observed after irradiation of matrices containing ¹⁸O₃ and CH₃I and ¹⁶O₃ and CD₃I, respectively. No corresponding absorption was observed in experiments utilizing natural isotopic iodomethane and ozone, although the intense iodomethane absorption at 528 cm⁻¹ was not decreased in intensity after sample irradiation as in the two experiments involving isotopic enrichment. Finally the sharp, weak 839.4-cm⁻¹ band in Figure 2b increased by 40% on sample warming and exhibited an ¹⁸O counterpart at 802.8 cm⁻¹.

Discussion

Band assignment and the identification of species 1–6 will be considered separately for each species. The photochemical interconversion of the products will then be discussed.

Band Assignments and Identification of Products. Species 1. The absorptions listed in Table I are assigned to a molecular complex (CH₃I)_x(O₃)_y, formed on codeposition of ozone and iodomethane. This behavior has been observed previously for ozone and an iodine-containing molecule in argon matrices.⁵ The assignment is made on the basis that the spectrum of species 1



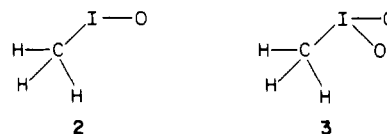
is similar to those of ozone and iodomethane, except for small perturbations, and that species 1 readily photodissociates (Figure

1). Unlike the previous study, these perturbations are not sufficient to yield absorptions associated with the complex that do not overlap those of the parent species. Consequently it was not possible to conduct intensity/concentration studies to determine the value of x and y in the formula $(\text{CH}_3\text{I})_x(\text{O}_3)_y$. The absorptions associated with ozone in the complex at 1102.8 and 704.7 cm^{-1} show a maximum perturbation of 2 cm^{-1} . This contrasts with a shift of 21 cm^{-1} observed for the antisymmetric stretching vibration in ozone on complexation with iodine monochloride⁵ and suggests a much weaker complex between iodomethane and ozone than between iodine monochloride and ozone, which may be the result of a difference in polarity of the $\text{CH}_3\text{-I}$ and I-Cl bonds. That a specific interaction between molecular ozone and iodomethane does occur is evidenced by the sharpness of the absorptions associated with the complex (fwhm = 1.0 cm^{-1} on average). The carbon-iodine stretching vibration of iodomethane is perturbed by 0.15% while the CH_3 rocking vibration⁸ is perturbed by 0.67% from its position in uncomplexed iodomethane. Evidently, there is some interference between the ozone moiety and the methyl group in the complex, possibly as a result of steric hindrance to the rocking motion.

The weak interaction between ozone and iodomethane, as measured by perturbation in the vibrational spectra of the parent molecules, is sufficient to cause a substantial change in the photochemical behavior of ozone as a submolecule in the complex. Cleavage of an oxygen-oxygen bond is possible in ozone complexed with iodomethane by irradiation into the 395-nm absorption of the complex with 360-470-nm light, while uncomplexed ozone can photodissociate with similar facility in argon matrices only on irradiation with ultraviolet light (310-220 nm). Ozone photodissociates in the visible region with much lower probability, and this process has been observed for ozone isolated in solid argon by using 488-nm argon ion laser excitation.⁷ It is, however, not clear if a $\text{SO}_3\text{-O}_3$ complex was involved in the 578-nm photochemical formation of SO_4 , but a higher yield was reported with 313-nm irradiation.⁴ That the photodecomposition of the ozone-iodomethane molecular complex 1 proceeds in such a way is evidenced by the nature of species 2.

Species 2 and 3. The infrared spectrum of species 2 parallels that of iodomethane quite closely (Table II). Absorptions at 492.6, 1223.4, and 2945.3 cm^{-1} lie in close proximity to iodomethane bands at 527.8, 1245.5, and 2965.7 cm^{-1} . The 527.8- cm^{-1} band is due to the $\text{CH}_3\text{-I}$ stretching vibration of iodomethane; the 32.2- cm^{-1} D isotopic shift and zero ^{18}O isotopic shift characteristic of the 492.6- cm^{-1} species 2 band suggest assignment to a similar $\text{CH}_3\text{-I}$ stretching vibration. The large D isotopic shifts observed for the 1223.4- and 2945.3- cm^{-1} absorptions of species 2 ($\nu_{\text{H}}/\nu_{\text{D}}$ ratios of 1.303 and 1.381, respectively) support assignment of these bands to C-H bending and C-H stretching modes of vibration, respectively. New species 2 absorptions were observed at slightly lower wavenumbers than the doubly degenerate C-H deformation and CH_3 rocking vibrational modes of iodomethane. Although the D isotopic counterpart of the 1400.3- cm^{-1} band was not observed (possibly obscured by the intense absorption of ozone at 1040 cm^{-1}), the bands at 858.9 and 848.0 cm^{-1} exhibited large D isotopic shifts with $\nu_{\text{H}}/\nu_{\text{D}}$ ratios of 1.330 and 1.324, respectively. The similarities between the spectra of iodomethane and species 2 suggest the formation of a molecule containing a $-\text{CH}_3$ group and a C-I bond. Furthermore, the molecule belongs to a point group with less symmetry than C_{3v} , of which iodomethane is a member, as evidenced by the lifting of the degeneracy of the CH_3 rocking mode. The intense absorption at 723.7 cm^{-1} , exhibiting an ^{18}O isotopic shift of 35.6 cm^{-1} , provides evidence that species 2 is iodomethane, CH_3IO . The calculated ^{18}O isotopic shift for a diatomic, I-O vibration with a ^{16}O value of 723.7 cm^{-1} is 36.6 cm^{-1} , which agrees well with that observed.

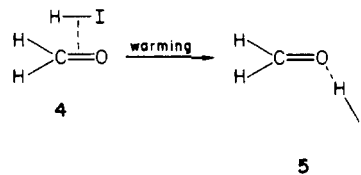
Iodomethane should have a nonlinear C-I-O unit, with C_s symmetry, as shown in structure 2. The CH_3 rocking vibrational mode therefore has two components, one perpendicular to and



one in the C-I-O plane. The reduction in vibrational frequency of the I-O oscillator of iodomethane (723.7 cm^{-1}) in comparison with that of iodosyl chloride⁵ (779.1 cm^{-1}) reflects the relative electron-withdrawing powers of the methyl group and chlorine atom. Thus electron density is more effectively withdrawn from the IO (p-p) π^* orbitals through interaction with the more electronegative substituent, chlorine.

Identification of species 3 on the basis of absorptions listed in Table III, which are denoted as group 3, is tentative. Bands at 829.8 and 795.9 cm^{-1} lie at too low a frequency to be assigned to C-O vibrational stretching modes, and their large ^{18}O isotopic shifts of 35.3 and 35.5 cm^{-1} support this conclusion. These isotopic shifts are, however, consistent with those expected for the anti-symmetric and symmetric stretching vibrational modes of an $-\text{IO}_2$ unit. Two features of the infrared spectrum of species 3 from experiments utilizing scrambled 50.3% ^{18}O -enriched ozone lend support for this tentative assignment. First, two absorptions appear at 823.7 and 771.4 cm^{-1} , which are associated with the spectra of neither the natural isotopic ozone nor the 98.0% ^{18}O -enriched sample and may therefore be the center components of two triplets of absorptions. Second, if this is the case, the triplets at 760.4, 771.4, and 795.9 cm^{-1} and 794.5, 823.7, and 829.8 cm^{-1} exhibit a marked asymmetry, as observed in the infrared spectra of the isotopically scrambled species $\text{ClI}^{16}\text{O}_x^{18}\text{O}_{2-x}$ ($x = 0-2$).⁵ Finally the absorptions at 829.8 and 795.9 cm^{-1} exhibit little D isotopic shift and were observed at 830.4 and 799.6 cm^{-1} with the CD_3I reagent. Group 3 absorptions are tentatively assigned to the molecule CH_3IO_2 (3) with a pyramidal structure about the central iodine. It is perhaps reassuring that the wavenumber separations between $\nu_{\text{IO}}(\text{OICl})$, $\nu_{\text{IO}_2(\text{s})}(\text{O}_2\text{ICl})$, and $\nu_{\text{IO}_2(\text{as})}(\text{O}_2\text{ICl})$ of 65.6 and 34.8 cm^{-1} , respectively are very similar to those assigned here between $\nu_{\text{IO}}(\text{OICH}_3)$, $\nu_{\text{IO}_2(\text{s})}(\text{O}_2\text{ICH}_3)$, and $\nu_{\text{IO}_2(\text{as})}(\text{O}_2\text{ICH}_3)$ of 72.2 and 33.9 cm^{-1} , respectively.

Species 4 and 5. The identification of species 4 and 5 is straightforward; the new absorptions listed in Table IV are similar in energy and relative intensity to those observed previously for formaldehyde,^{9,11} also listed for comparison. It follows, then, that species 4 and 5 are due to formaldehyde perturbed by hydrogen iodide trapped in the same matrix cage after photodissociation of CH_3IO . The species 5 bands at 2120 and 1729.9 cm^{-1} are in good agreement with absorptions at 2123 and 1728 cm^{-1} produced by codeposition of CH_2O and HI and assigned to the hydrogen-bonded complex.¹² Growth of species 5 at the expense of species 4 on sample warming demonstrates that the hydrogen-bonded arrangement, depicted by structure 5 following the known structure of the corresponding HF complex,¹³ is more stable than the other submolecule arrangement suggested to be unstable structure 4 trapped by the matrix cage.



The displacement of CH_2O fundamentals in species 5 is greater than in species 4, which also points to a stronger submolecule interaction for species 5. The large red perturbations of the $\text{C}=\text{O}$

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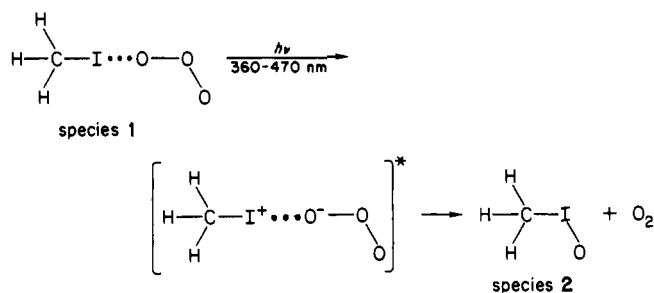
(9) Khoshkoo, H.; Nixon, E. R. *Spectrochim. Acta, Part A* 1973, 29A, 603; *Chem. Phys. Lett.* 1977, 50, 187.
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stretching fundamental are consistent with involvement of the carbonyl group in bonding to the HI submolecule. The blue shifts in the C–H stretching fundamentals in the complexes are due to reduction in the “lone-pair effect”,^{12,15} which is responsible for lower C–H fundamentals in the CH₂O molecule; the hydrogen-bonded arrangement polarizes the lone pair more effectively and leads to the large blue shift. Furthermore, the 2120-cm⁻¹ band for species 5 exhibits a shift on complete deuterium substitution to 1515 cm⁻¹ and no ¹⁸O shift; this $\nu_H/\nu_D = 2120/1515 = 1.399$ ratio and the band position¹⁴ indicate assignment to the H–I stretching fundamental for 5, in agreement with Bach and Ault.¹² The 7-cm⁻¹ difference in DI fundamentals for CD₂O–DI (1515 cm⁻¹, present work) and CH₂O–DI (1522 cm⁻¹, codeposition)¹² provides further evidence for interaction between the C=O and D–I stretching fundamentals through the hydrogen bond, as discussed in earlier studies.^{11,12} The outstanding difference between species 4 and 5 is the failure to observe the H–I stretching fundamental for species 4; this is due to the lack of intensity enhancement for the H–X species not involved in hydrogen bonding.¹⁶ Species 4 is a formaldehyde–hydrogen iodide molecule pair *not* involving the acid hydrogen in bonding, which readily rearranges to the hydrogen-bonded structure on sample warming. Similar complexes involving CH₂O and Cl₂ or ICl have been reported.¹⁰ Finally, the ability to form the CH₂O–HI complex without excess acid and base submolecule present allows the definitive observation of five fundamentals of the CH₂O submolecule in these two complexes, which confirms that the hydrogen-bonded structure 5 is the more stable arrangement of the submolecules in this complex. A similar advantage has been employed for study of the C₂H₄–HI complex produced by photolysis of ethyl iodide¹⁷ and the C₂H₂–HX complexes produced from photolysis of the vinyl halides.¹⁸

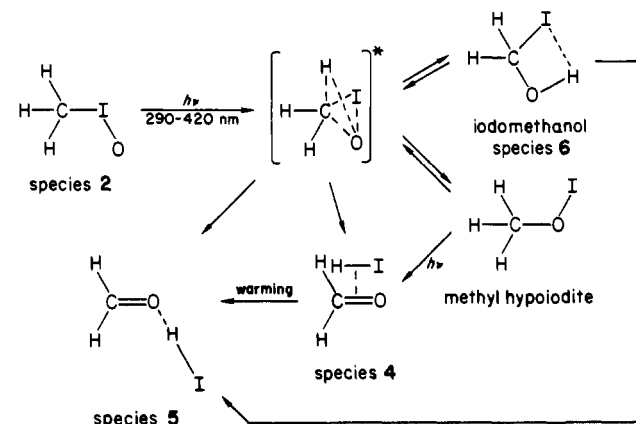
Species 6. The infrared spectrum of species 6 contains three absorptions with positions and ¹⁸O and D isotopic shifts characteristic of the >C–O–H group. The absorption at 998.6 cm⁻¹ is assigned to the C–O stretching vibration on account of its ¹⁸O isotopic shift of 28.8 cm⁻¹ and doublet character when 50.3% ¹⁸O-enriched scrambled ozone was used. A band at 1159.2 cm⁻¹ exhibiting an ¹⁸O isotopic shift of 4.5 cm⁻¹ but a large D isotopic shift ($\nu_H/\nu_D = 1.307$) is assigned to the >C–O–H bending vibration while the O–H stretching vibration is represented by the broad absorption at 3350 cm⁻¹ ($\nu_H/\nu_D = 1.352$). The position of the latter band suggests that there is a degree of hydrogen bonding associated with the C–O–H group since “free” O–H groups usually absorb between 3500 and 3700 cm⁻¹. Since there are no absorptions between 1700 and 1800 cm⁻¹ associated with species 6, the O–H group is alcoholic rather than acidic in nature. Consequently species 6 is considered to be iodomethanol, ICH₂OH, on the basis of these absorptions, the empirical formula of other products identified in these experiments, and its implication in the photochemical processes occurring in the ozone–iodomethane system (see the following section). Furthermore, intramolecular hydrogen bonding would be more a requirement than a possibility, as a result of the proximity and size of the iodine atom. The identification is supported by the presence of absorptions in the C–H stretching region of the spectrum at 2814.6 and 2936.8 cm⁻¹. Unfortunately no assignment to the weaker C–I stretching vibrational mode could be made.

Other Photoproducts. An absorption observed at 1074.1 cm⁻¹ exhibited an ¹⁸O isotopic shift close to that expected for a C–O stretching vibration. A related band near 500 cm⁻¹ was not observed by using isotopes in natural abundance, but the intensity of the 528-cm⁻¹ iodomethane absorption behaved as though a weak absorption was coincident with it. Assuming this, ¹⁸O and D isotopic enrichment reveal that the 528-cm⁻¹ absorption exhibits

Scheme I



Scheme II



¹⁸O and D isotopic shifts of 23.6 and 19.3 cm⁻¹, respectively. While the vibrational frequency is too low for a C–O stretching vibration and the isotopic shifts are incompatible with a C–I stretching vibration, a study of the infrared spectrum of HOI¹⁹ suggests assignment to an O–I stretching vibration. In conjunction with the assignment of the absorption at 1074 cm⁻¹, these bands support the view that methyl hypoiodite, CH₃OI, is present in this system. Calculated values for the missing ν_{C-O} and ν_{O-I} absorptions obtained by treating the molecule as a diatomic harmonic oscillator suggest that ν_{O-I} lies between 527 and 531 cm⁻¹, i.e. coincident with ν_{C-I} of iodomethane, and that ν_{C-O} of CD₃OI lies above 1027 cm⁻¹ and may therefore be obscured by the broad and intense ozone absorption at 1040 cm⁻¹. It is reassuring that, within the limitations of this simple calculation, the observed ¹⁸O and D isotopic shifts for both absorptions are entirely reasonable for CH₃OI. There appeared to be several other sets of absorptions that could not be separated with the confidence imparted by the behavior of groups 1–6; one of these, the weak 839.4-cm⁻¹ band, is clearly due to an I–O vibration, but unfortunately, there is insufficient data to identify these species.

Interconversion of the Photolysis Products. During deposition of the matrix, a molecular complex between ozone and iodomethane was formed and trapped on condensation. A small amount of iodomethane, CH₃IO, was also formed, suggesting that direct reaction or Nernst glower photolysis of the molecular complex may proceed. The reaction is one of oxygen atom transfer and is induced by irradiation of the trapped iodomethane–ozone molecular complex at 360–470 nm (Scheme I); all of the complex photodecomposed during this period of irradiation. This process may, in fact, proceed by a charge-transfer mechanism through the 395-nm absorption band observed for the complex species 1. The ozonide anion in the excited intermediate can readily transfer an O⁻ anion to the methyl iodide cation to give the observed product species 2. The present charge-transfer absorption is somewhat unusual in that the absorption leads directly to atom transfer *in the reverse direction* on relaxation of the excited-state complex. It is likely that iodomethane is formed with excess internal energy; some will be quenched, forming the observed

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iodosomethane, while the remainder may rearrange or dissociate. No evidence was found for further reaction of the O₂ byproduct.

During the second period of irradiation, this time at 290–420 nm, the iodomethane–ozone molecular complex is already depleted and iodosomethane is photodecomposed. Since neither uncomplexed ozone nor iodomethane is affected by this radiation, iodosomethane must be a common precursor to all the photoproducts. Excited iodosomethane may eliminate HI directly or rearrange to methyl iodate or iodomethanol, which can eliminate HI (Scheme II). While these experiments do not provide incontrovertible evidence for the detection of methyl hypoiodite and iodomethanol compounds in the photodecomposition of iodosomethane, several absorptions have been observed in the relevant "fingerprint" regions of their infrared spectra. Either could also be a suitable precursor to formaldehyde and hydrogen iodide, and with regard to the formation of two complexed formaldehyde species on photolysis, it may be significant that methyl hypoiodite would give a formaldehyde–hydrogen iodide molecular pair in the wrong orientation for hydrogen bonding to occur. When the matrix is warmed, rotation of HI could occur, and as the formaldehyde and hydrogen iodide are formed in such close proximity, it is hardly surprising that all of the less stable formaldehyde complex is depleted. While the occurrence of two different HI and formaldehyde complexes after photolysis is not, of course, proof that methyl hypoiodite and iodomethanol are acting as precursors to differently oriented molecular pairs (either precursor could produce excited hydrogen iodide with enough energy to rotate into or away from the correct orientation for hydrogen bonding to occur), the possibility exists. Work on chemical laser²⁰ systems provides supporting evidence that iodomethanol might be expected to yield formaldehyde; Lin proposed the reaction of ¹D oxygen atoms with chloromethanes Cl_{4-n}CH_n to give chloromethanols, Cl_{4-n}CH_{n-1}OH (*n* = 1–3), which serve as precursors for hydrogen chloride and chlorinated formaldehyde H_xCl_{2-x}CO (*x* = 0–2). Furthermore, elimination of hydrogen iodide from iodomethanol places the acid hydrogen adjacent to the carbonyl oxygen and facilitates formation of the hydrogen-bonded complex 5. Finally, the above photochemical pathway has distinct analogies to that reported for CH₃NO₂ and CH₃ONO, which photolyze to give the H₂CO–HNO complex.^{21,22}

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The small yield of CH₃IO₂ can be accounted for by a similar mechanism to that proposed for formation of ClIO₂,⁵ which involves further reaction between iodosomethane and oxygen atoms released by decomposition of excited iodosomethane.

Conclusions

Codeposition of iodomethane and ozone in argon matrices leads to the formation of a molecular complex between iodomethane and ozone, which exhibited a 395-nm absorption band and photodissociated with 360–470-nm mercury-arc radiation presumably involving a charge-transfer mechanism. The iodosomethane photoproduct, CH₃IO, is probably formed initially with excess internal energy; this excited intermediate species is either quenched by the matrix or it rearranges to iodomethanol (ICH₂OH) or methyl hypoiodite (CH₃OI) or it eliminates HI. The infrared spectrum of iodosomethane is closely related to that of the parent iodomethane, and the I–O bond is weaker than that found in iodosyl chloride.

Photodecomposition of the quenched iodosomethane can be initiated by irradiation at 290–420 nm. The yields of both iodomethanol and methyl hypoiodite are thereby increased as are those of two formaldehyde–hydrogen iodide molecular complexes. Both iodomethanol and methyl hypoiodite can also serve as precursors to the photoproducts involving formaldehyde, the latter formed by elimination of hydrogen iodide from the precursors. Warming the matrix leads to a reduction in several photoproducts; however, the formaldehyde–HI hydrogen-bonded complex increased at the expense of the other formaldehyde–HI complex. Indeed depletion of the latter is complete under these conditions and is a consequence of the proximity of the hydrogen iodide molecule on photodecomposition of the precursors. The infrared spectrum of the complex can be measured without interference from that of either parent and is consistent with a hydrogen-bonded structure.

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Registry No. CH₃I, 74-88-4; O₃, 10028-15-6; ¹⁸O₃, 21424-26-0; CD₃I, 865-50-9; CH₃IO, 97551-34-3; ICH₂OH, 50398-30-6; CH₃OI, 26466-04-6; HI, 10034-85-2; CH₂O, 50-00-0; Ar, 7440-37-1.

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Thermodynamics and Kinetics of Aqueous Ferric Phosphate Complex Formation[†]

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The equilibria and kinetics of complexation of iron(III) with phosphoric acid (at pH < 2) were studied at 25 and 50 °C at ionic strength $\mu = 2.5$ M by using spectrophotometric and stopped-flow techniques. The results are consistent with the formation of two complexes, FeH₂PO₄²⁺ and Fe(H₂PO₄)₂⁺. The second species could only be detected by the analysis of kinetic data. The equilibrium constants, extinction coefficients, rate constants, and activation parameters for the formation of these complexes are given. A mechanism is proposed to account for the observed hydrogen ion dependency of the apparent forward rate constants.

Introduction

Complexation reactions between iron(III) and phosphate ions play an important role in soil chemistry, water treatment, and corrosion. Numerous investigators^{1–22} have postulated the formation of various species (Table I), depending on the experimental conditions, methods of analysis, and interpretation of the results.

Few studies, however, reported thermodynamic data (especially at elevated temperatures), and no kinetic information on these

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