Inorg. Chem. **1980**, *19*, 463–465

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Resonance Raman and Ultraviolet Absorption Spectra of the Triiodide Ion Produced by Alkali Iodide–Iodine Argon Matrix Reactions

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Received May 2, 1979

Matrix reactions of alkali iodide and iodine molecules were performed to produce the $M^+I_3^-$ species for spectroscopic comparison to triiodide ion solution data. Strong ultraviolet absorptions at 287 and 355 nm and a strong resonance Raman fundamental at 113 ± 1 cm^{-1} with five overtones are in excellent agreement with previous solution spectra. The salt–molecule reaction technique produces new $M^+X_3^-$ species, which are clearly representative of the polyhalide ion itself.

Introduction

The salt–molecule matrix reaction was developed in this laboratory to produce new ionic species for spectroscopic study. The technique was applied first to the less stable trihalide species[1-4] $M^+F_3^-$, $M^+Cl_3^-$, and $M^+Br_3^-$, bihalide ions[5,6] $M^+HCl_2^-$ and $M^+HBr_2^-$, and mixed fluoride ions[7] $M^+BrF_2^-$ and $M^+IF_2^-$. For completion of these studies, a comparison of the $M^+I_3^-$ species produced by the alkali iodide–iodine matrix reaction and the stable triiodide ion in solid and solution phases was deemed important.

The triiodide ion has been studied extensively by ultraviolet, infrared, and resonance Raman spectroscopic methods, and its structure and bonding have received much attention.[8-11] The purpose of this study is not to review the large body of literature on the triiodide ion but to compare the spectroscopic properties of the $M^+I_3^-$ ion pair in solid argon and the I_3^- ion in solution and thus to evaluate the salt–molecule matrix reaction technique as a method for synthesizing other less stable polyhalides.

Experimental Section

The cryogenic apparatus for performing Raman scattering and ultraviolet absorption studies on matrix-isolated species has been described.[12,13] Samples for Raman study were deposited on a tilted copper wedge, and ultraviolet experiments used a sapphire window, cooled to 12–16 K with closed-cycle "Cryodyne" coolers (Cryogenic Technology, Inc.). Alkali iodide salts were heated behind a sliding door under vacuum before codeposition of salt vapor at 450–500 °C with Ar/I_2 mixtures at a rate of 2 mmol/h for several hours. The Ar/I_2 samples were prepared by adding argon to a 3-L bulb containing iodine crystals.

Ultraviolet spectra were recorded on a Cary 17 spectrophotometer and Raman spectra on a Spex Ramalog using dc amplification and argon and krypton ion laser excitation.

Results

Absorption Spectra. The absorption spectra of 10 different experiments are represented by the spectrum shown in Figure 1 for the CsI cocondensation reaction with iodine for 3 h using $Ar/I_2 = 3000/1$. The strong absorption at 520 nm is due to iodine,[3] the 248-nm absorption is assigned to CsI, and the 287- and 355-nm features are due to a reaction product. When CsI vapor from a 475 °C Knudsen cell was condensed with only argon for 2 h, a strong, sharp 248-nm absorption (*A* (absorbance units) = 0.6) was observed; later in this same experiment, an argon/iodine sample ($Ar/I_2 = 2000/1$) was codeposited with the CsI vapor stream, and the 287- and 355-nm absorptions appeared in the spectrum.

A similar experiment was performed with NaI from a 500 °C Knudsen cell. After 2-h codeposition of NaI and argon, a broad, weak shoulder was observed at 250 nm (*A* = 0.05). An $Ar/I_2 = 2000/1$ sample was codeposited with the NaI vapor stream for 2 h, and strong new product bands appeared at 286 and 353 nm; the 250-nm band was resolved with a peak at 255 nm, and I_2 appeared at 520 nm. The sample was thermal cycled to 38 K and recooled to 15 K. The 288- and 352-nm absorptions increased threefold while the 255-nm absorption appeared to decrease as it was resolved from the scattering sample background.

A number of mixed alkali halide salt–halogen reactions were also done. A NaBr cocondensation with an $Ar/Br_2 = 500/1$ sample produced only a strong absorption at 263 nm with a very weak shoulder at 315 nm. The reaction of NaBr with iodine gave a very strong 274-nm absorption while the reaction of NaI with Br_2 produced a very strong 288-nm absorption with a 340-nm shoulder.

Similar mixed reactions were performed with the cesium–chlorine–bromine system. The CsCl reaction with an $Ar/Cl_2 = 200/1$ sample produced a strong 250-nm absorption,[14] and with an $Ar/Br_2 = 600/1$ mixture, a strong 248-nm band appeared. The reactions of CsBr with Cl_2 gave a strong 273-nm absorption and Br_2 produced a strong 268-nm band with a weak 320-nm shoulder.

Raman Spectra. A thorough Raman study of the $MI-I_2$ matrix reaction was performed in 30 experiments using Ar/I_2 concentrations of 400/1 to 4000/1 and Knudsen cell temperatures from 450 to 500 °C. Considerable effort was required to find the optimum conditions for maximum product yield and good optical quality of the sample. Most of these studies yielded a fundamental at 113 ± 1 cm^{-1} and one or more overtones along with aggregated I_2 at 180 ± 1 cm^{-1} and isolated[15] I_2 at 212 ± 1 cm^{-1}. The most extensive spectrum observed in this work is illustrated in Figure 2 by using 476.5-nm excitation on a sample prepared by depositing an $Ar/I_2 = 3000/1$ mixture with CsI from a 475 °C Knudsen cell for 3 h. The Raman spectrum contains an intense fundamental labeled ν at 113 ± 1 cm^{-1} and a series of overtones out to $6\nu_1$ which are listed in Table II. The aggregated iodine fundamental was observed at 180 ± 1 cm^{-1} along with overtones at 360 and 540 cm^{-1} which are labeled $(I_2)_n$ in the figure. The isolated I_2 fundamental was observed at 212 cm^{-1}. An

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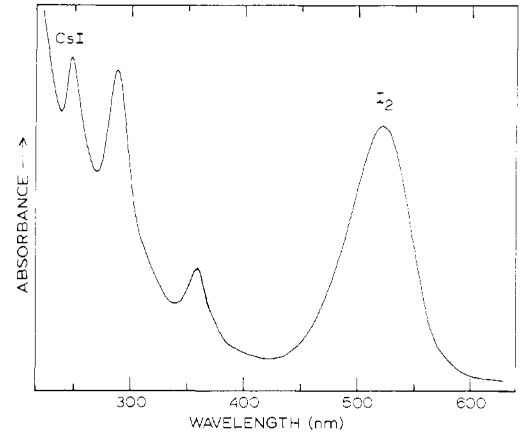

Figure 1. Absorption spectrum recorded after codepositing CsI vapor from 475 °C Knudsen cell with $Ar/I_2 \approx 3000/1$ sample for 3 h on a 16 K sapphire plate.

additional broad feature appeared at 170 ± 2 cm^{-1} with a broad shoulder at 145 ± 5 cm^{-1}. In general the overtone series was more extensive with blue excitation as compared to green and red; however, different laser power for 457.9, 476.5, and 488.0 nm prevented any quantitative comparison of intensities among the blue exciting lines. With green exciting lines, which are within the strong iodine absorption band at 520 nm, the strong resonance Raman I_2 and $(I_2)_n$ series dominate the spectrum.

Discussion

Absorption Spectra. The absorption spectra of CsI and NaI reaction products with I_2 in solid argon are nearly identical within the error of measurement, and the matrix spectra are in very good agreement with solution and solid spectra of the triiodide ion.[8] The two absorptions at 287 and 355 nm are assigned to the $\sigma_g \rightarrow \sigma_u^*$ and $\pi_g \rightarrow \sigma_u^*$ transitions[8] of I_3^- in the $Cs^+I_3^-$ ion pair, respectively. The relative intensities of these two absorptions are independent of environment although the latter absorption is sharper for the ion pair. The argon matrix isolated $M^+I_3^-$ ion-pair species formed by reaction 1

$$M^+I^- + I_2 \rightarrow M^+I_3^- \qquad (1)$$

is, therefore, a representative triiodide ion. The triiodide optical absorptions increased markedly on sample warming to 38 K, which indicates that reaction 1 has very little activation energy.

It is interesting to contrast the $\sigma_g \rightarrow \sigma_u^*$ and $\pi_g \rightarrow \sigma_u^*$ transition energies of I_3^- with the analogous $\sigma_g \rightarrow \sigma_u^*$ and $\pi_g \rightarrow \sigma_u^*$ transitions of I_2^-. The former are 287 and 355 nm, and the latter are 382 and 686 nm, both paired with the Cs^+ counterion.[3] Apparently, the trihalide system leads to a stronger interaction producing an electronically more stable system when the anion electron is delocalized over three centers as compared to two centers. The increase in energy for the $\sigma_g \rightarrow \sigma_u^*$ transition from 26 200 to 34 800 cm^{-1} from I_2^- to I_3^- and the stability of triiodide ion at room temperature demonstrate this point.

Table I. Absorption Band Positions (nm) Produced by Alkali Halide-Halogen Molecule Matrix Reactions

	halogen		
alkali halide	I_2	Br_2	Cl_2
CsI	287, 355		
NaI	286, 353	288, 340 sh[c]	
NaBr	274, ...	263, 315 sh	
CsBr		268, 320 sh	273[a]
CsCl		248, ...	250[b]

[a] Reference 3. [b] Reference 14. [c] sh = shoulder.

Table II. Comparison of Resonance Raman Fundamental and Overtone Progressions (cm^{-1}) for the Triiodide Ion in Several Environments with the Diiodide Ion in Solid Argon

	$Cs^+I_3^-$ (Ar)[a]	I_3^- (H_2O)[b]	I_3^- (CH_3OH)[b]	$Cs^+I_2^-$ (Ar)[a]
ν_1	113 ± 1	116	111	115
$2\nu_1$	225 ± 1	234	223	230
$3\nu_1$	336 ± 1	351	342	343
$4\nu_1$	447 ± 2	460	455	457
$5\nu_1$	558 ± 2	580	572	570
$6\nu_1$	668 ± 2	690	684	682

[a] Matrix isolated in solid argon at 16 K; from this work and ref 17. [b] Solution spectra using rotating sample; from ref 10.

A similar conclusion may be drawn for the tribromide ion species. The $Cs^+Br_3^-$ and $Na^+Br_3^-$ observations are almost the same, 268 and 263 nm, respectively, with a weak 315-nm shoulder. In the $Cs^+Br_3^-$ solid, the strong band appears at 259 nm with a weak 323-nm shoulder, and in CH_2Cl_2 solution, the band peak shifts to 272 nm. Again the relative intensity of the two transitions is the same for the argon matrix isolated ion pair and Br_3^- in solution and solid phases.[8,10]

The mixed species $Na^+IBr_2^-$ and $Na^+I_2Br^-$ at 288 and 274 nm, respectively, are near the stronger bands for $Na^+Br_3^-$ at 263 nm and $Na^+I_3^-$ at 286 nm. The mixed spectrum probably contains contributions from symmetric and asymmetric species[1] which complicates any rationalization of the band positions.

Raman Spectra. The strong 113 ± 1 cm^{-1} fundamental and five overtones with regularly decreasing intensities are due to the resonance Raman spectrum of a major reaction product. The regularly decreasing intensity pattern of the overtone series is reminiscent of the first resonance Raman observation in matrices, that of the dichloride ion in the $M^+Cl_2^-$ species[16] and

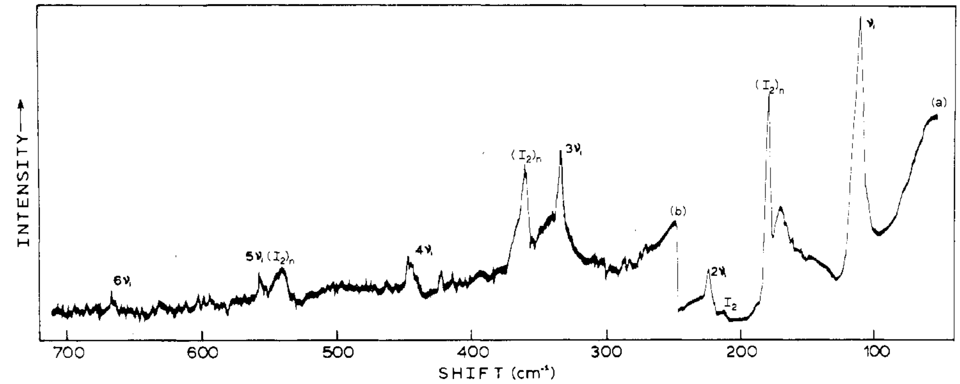

Figure 2. Raman spectrum of sample prepared by codepositing CsI vapor from 475 °C Knudsen cell with $Ar/I_2 \approx 3000/1$ sample for 3 h on a 12 K tilted copper wedge: excitation 300 mW of 476.5-nm radiation at sample; slit widths 130 μm; scan speed 25 cm^{-1}/min; (a) 0.3 × 10^{-9} A range, (b) 0.1 × 10^{-9} A range.

the analogous diiodide ion.[17] Agreement with the I_3^- fundamental and overtone progressions from solution spectra listed in Table II confirms the assignment to I_3^- and the matrix identification of the $M^+I_3^-$ species.

Several points are worthy of contrast between the matrix and solution spectra. The $M^+I_3^-$ vibrational potential function is slightly more anharmonic in the cubic sense as the vibrational spacing decreases with increasing quantum number slightly more for the $M^+I_3^-$ ion pair. Resonance enhancement was attained with 476.5-nm excitation in the $M^+I_3^-$ species, which is rather far out the red wing of the absorption, whereas the solution species required ultraviolet excitation in the $\pi_g \rightarrow \sigma_u^*$ absorption band.[10,11]

The shoulder at 145 ± 5 cm^{-1} in the Raman spectrum is appropriate for the ν_3 mode of I_3^-, and similar features have been assigned accordingly in the earlier resonance Raman investigations.[10,11] However, a very recent Raman study of triiodide ion in solution as a function of iodide concentration has demonstrated a concentration dependence for the 155-cm^{-1} signal which indicates the presence of a higher polyhalide.[18] The matrix data provide no additional information on this feature. The broad band at 170 cm^{-1} is probably due to a higher aggregate species. Since the Raman intensity at 170 cm^{-1} varied relative to the $(I_2)_n$ fundamental at 180 cm^{-1} and the I_3^- mode at 113 cm^{-1} in the experiments performed here, the 170-cm^{-1} signal is due to a different molecular species, most likely a higher polyiodide. The $Cs^+I_5^-$ ion pair could be formed in a CsI matrix reaction with $(I_2)_2$ or by the reaction of another I_2 molecule with $Cs^+I_3^-$.

A final comparison between the resonance Raman spectra of the $Cs^+I_2^-$ and $Cs^+I_3^-$ iodide species is appropriate; vibrational data for the former are given in the last column in Table II.[17] Two pieces of evidence show that different spectra are obtained for diiodide ion and triiodide ion: the fundamental and overtones differ by more than the error of measurement even though the values are close, and red excitation produces a resonance Raman spectrum of I_2^- owing to a strong 686-nm absorption for this anion whereas blue excitation gives a resonance Raman spectrum for I_3^-. Both I_2^- and I_3^- involve "one-electron" or "half-order" bonds, and their symmetric stretching vibrational fundamentals are nearly the same, and both are about half of the I_2 fundamental value (212 cm^{-1})[15] which, of course, involves an electron-pair bond.

Conclusions

Matrix reactions of alkali iodide and iodine molecules were performed to synthesize the $M^+I_3^-$ ion pair for spectroscopic study. Strong ultraviolet absorptions at 287 and 355 nm and a strong resonance Raman fundamental at 113 ± 1 cm^{-1} and five overtones with regularly decreasing intensities were observed for the $Cs^+I_3^-$ species. These data are in excellent agreement with ultraviolet and resonance Raman spectra of triiodide ion solutions.[10,11] The $M^+X_3^-$ salt–molecule matrix reaction product is representative of the triiodide ion, which substantiates the use of this synthetic technique to produce new unstable polyhalide ions like the trifluoride ion.[1]

Acknowledgment. The authors gratefully acknowledge financial support for this research from the National Science Foundation under Grant CHE 76-11640 and the assistance of Dr. B. S. Ault with several of the early Raman experiments. Dr. A. Loewenschuss acknowledges sabbatical support from The Hebrew University, Jerusalem, Israel.

Registry No. $Cs^+I_3^-$, 12297-72-2; $Na^+I_3^-$, 12593-83-8; $Na^+BrI_2^-$, 72138-51-3; $Na^+IBr_2^-$, 72138-52-4; $Na^+Br_3^-$, 21109-91-1; $Cs^+Br_3^-$, 17060-10-5; $Cs^+ClBr_2^-$, 22325-19-5; CsI, 7789-17-5; NaI, 7681-82-5; NaBr, 7647-15-6; CsBr, 7787-69-1; CsCl, 7647-17-8; I_2, 7553-56-2; Br_2, 7726-95-6.

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Paramagnetic Organometallic Molecules. 8.[1] An ESR Study of the Redox Chemistry of Iron Carbonyl Species

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Received January 5, 1979

An ESR study of THF or CH_2Cl_2 solutions of $Fe_3(CO)_{12-n}L_n$ (L = CO, $P(OR)_3$, PR_3), $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$, which have been reduced by electrolytic methods or by alkali metals or have been photolyzed, is presented. The radical anions of the above compounds have been characterized at low temperature. However, the iron-containing radical anions readily undergo what are believed to be disproportionation reactions to Fe(II), Fe(−I), and Fe(−II) via the intermediacy of the dianions $[Fe_3(CO)_{12-n}L_n]^{2-}$. The hydrido anion $[HFe_3(CO)_{11}]^-$ is an ultimate product in reductions in THF or when $Fe_3(CO)_{12}$ is photolyzed. No evidence was found for an oxidation or reduction mode for $Fe_3(CO)_{11}^{2-}$. Solutions of $Fe_2(CO)_9$ in THF on reduction give essentially the same ESR spectra as $Fe_3(CO)_{12}$. It is found that small concentrations of $Fe_3(CO)_{12}^{-}\cdot$ are produced in THF solutions of $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$, even in the absence of an external reducing agent.

Introduction

Previous papers[2-4] on the tricobalt carbon clusters demonstrated that the redox behavior of this type of metal carbonyl can be elucidated if both electrochemical and spectral techniques are utilized. Since the unpaired electrons occupy a σ^* Co_3 orbital in the tricobalt carbon clusters, it was of interest to compare other trinuclear clusters which do not have a nonmetal capping group. The iron group carbonyls $M_3(CO)_{12}$, with which this paper is concerned, make an interesting comparison because there is formally one extra carbonyl group per metal atom[5] and, at least in the solid phase, some carbonyls may bridge the metal–metal bond.[6] Further, a large number

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