dispersed metal clusters can generally be improved by addition of the NaOH.[15] However, this is not true in the present case. Probably the OH group produced by adsorption of OH on the cluster surface will not be stable enough to improve the catalytic activity by a ligand effect.

These considerations can support the idea that the ligand effect of the OH groups, which may be produced by hydrogenation of the surface-adsorbed oxygen, is not the main reason for the higher activity of the clusters prepared under air than those prepared under nitrogen.

Thus, as for the oxidized Pd/Pt bimetallic clusters, not the ligand effect but the surface defect is expected to be an important factor for the appearance of higher activity. The structural defects in the clusters formed during the oxidation process are more sensitive to the increase of the catalytic activity than the surface-adsorbed oxygen. From this point of view, assumption (2) can be a considerable factor for the appearance of higher activity.

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Characterization of Molecular Alkali Metal Iodates by Mass Spectrometry and Matrix Isolation IR Spectroscopy

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Samples of the solids MIO_3 (M = Li, Na, K, Rb, Cs) have been vaporized in vacuo and the ternary products characterized by mass spectrometry, and by infrared spectroscopy in low-temperature nitrogen, oxygen, and argon matrices. The *molecular* species KIO_3, $RbIO_3$, and $CsIO_3$ have been identified for the first time and their IR spectra shown to be consistent with overall C_{3v} symmetry involving tridentate coordination. This conclusion is further confirmed, in the case of $CsIO_3$ isolated in argon, by a detailed analysis of ^{18}O isotope patterns. In contrast, samples of $LiIO_3$ and $NaIO_3$ appeared to undergo decomposition to the iodide and oxygen.

Introduction

Alkali metal iodates have been known for many years,[1] and although a number of studies have been carried out[2-4] on the mechanism of their thermal decomposition, there appear to have been no serious attempts to investigate the composition of the high-temperature vapor. For the analogous chlorates, matrix isolation studies[5-7] have convincingly demonstrated that *molecular* chlorates $MClO_3$ are formed on vaporization and have established the symmetry of these species to be C_{3v}.

It is therefore of some interest to explore whether corresponding ternary salt molecules might similarly be present in iodate systems, and this paper describes our matrix isolation and mass spectrometric studies on these systems.

In the particular case of $CsIO_3$, there is an added significance to this work in that radioactive Cs and I are both well-known nuclear decay products, and it is important to establish as wide a data base as possible in order to predict the thermodynamic behavior of high-temperature systems involving these elements.

Sample Preparation

The samples of potassium and sodium iodate used in these studies were obtained commercially (B.D.H., 99.9%), and used

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without purification. Rubidium and cesium iodates were prepared by the quantitative reaction of a saturated solution of iodic acid (B.D.H.) with the appropriate carbonate or chloride (Aldrich, 99.9%). In each case, the resulting white precipitate was washed with ice-cold water, filtered, and dried. Lithium iodate samples were prepared by mixing equimolar solutions of iodic acid and lithium hydroxide (B.D.H., 99.9%), followed by evaporation to dryness. The purity of each salt was established by standard quantitative methods and by a comparison of the Nujol-mull IR spectrum with previous studies.[8-10]

Samples of oxygen-18 enriched cesium iodate were prepared by isotopic exchange. In a typical synthesis, ca. 1 g of iodic acid was dissolved in 500 mg of $H_2{}^{18}O$ (90 atom % ^{18}O, Aldrich) and the solution allowed to stand for several days at room temperature to facilitate equilibration. Cesium iodate was then precipitated by slowly adding solid cesium carbonate to the solution until effervescence (CO_2) ceased. The ^{18}O-enriched $CsIO_3$ was then vacuum-dried. The extent of isotopic enrichment was initially estimated by Nujol-mull IR spectroscopy, and subsequent matrix isolation experiments indicated that this experimental procedure yielded a completely scrambled product with a typical enrichment of ca. 50%.

Experimental Methods

The vaporization of alkali metal iodate samples took place from resistively heated silica sample holders under typical high-vacuum conditions (ca. 10^{-6} mbar). The general features of our mass spectrometric and matrix isolation equipment have been described elsewhere.[11,12]

However, for these iodate systems, vaporization was often accompanied by partial sample decomposition involving the intermittent release of oxygen. This proved to be a major problem in obtaining good mass spectral data but only affected the IR studies to the extent that the matrix cage environment of a trapped species could be anticipated to contain molecular oxygen in addition to argon or nitrogen. In view of this, a few experiments were also carried out using *oxygen* as the *matrix* in order to ensure a reasonably homogeneous environment. All three matrix gases had a stated purity of 99.999% (B.O.C.) and were typically used in >1000-fold excess.

Caution. Care should be exercised in heating alkali metal iodates in vacuo due to the possibility of explosions.

Mass Spectrometric Studies

As indicated above, the evolution of oxygen during sample vaporization presented severe problems in obtaining satisfactory mass spectra, and it was only possible to obtain reliable results for the cesium system. When samples of $CsIO_3$ were heated to ca. 800 K, intense ion peaks were observed corresponding to Cs^+ and I^+, together with weaker features attributable to $CsIO_3{}^+$, $CsIO_2{}^+$, and $CsIO^+$. At the same time, a white sublimate was observed to condense on the cooler, off-axis walls of the inlet system. Subsequent analysis by powder XRD showed that this sublimate was primarily solid $CsIO_3$, with a small amount of CsI.

The appearance potentials for the ions Cs^+, $CsIO_2{}^+$, and $CsIO_3{}^+$ were estimated as ca. 9.1, 10.3, and 9.2 eV, respectively, and there was no evidence for the existence of higher mass species. The first ionization potential of atomic cesium is known to be 3.9 eV,[13] indicating that the Cs^+ signal is clearly a fragment, and we similarly believe that $CsIO^+$ and $CsIO_2{}^+$ are fragments arising from a single neutral precursor, $CsIO_3$.

Matrix Isolation Studies

Cesium Iodate. Figure 1a shows a typical argon matrix survey spectrum obtained from the vaporization of cesium iodate at ca. 750 K. Four bands are observed, at 803.0, 786.4, 355.8, and 302.2 cm^{-1}, and numerous experiments, some involving controlled diffusion, established that these absorptions all arise from the same trapped species. Figure 1b shows these absorptions under higher resolution. In nitrogen matrices, four similar bands were observed, but two of the absorptions now appeared as closely spaced doublets (Figure 1c). The frequencies of the observed bands are summarized in Table I.

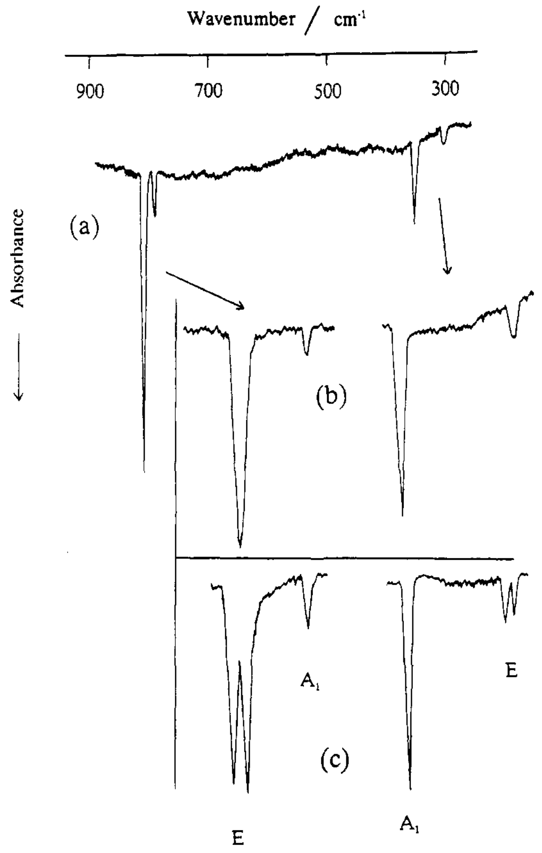

Figure 1. Matrix IR spectra obtained from the vaporization of cesium iodate: (a) low-resolution argon matrix spectrum; (b) (inset) bands observed in (a), under higher resolution; (c) the same spectral features as in (b), but with nitrogen as the matrix environment.

TABLE I: Vibration Frequencies (cm^{-1}) and Spectroscopic Assignments of IR Bands Observed in Matrix Isolation Studies on the Vaporization of Alkali Metal Iodates

	observed frequencies[a]			assignment
compd	argon	nitrogen	oxygen	(IO_3 modes)
$CsIO_3$	803.0	811.2/807.4	806.8/803.6	E str
	786.4	793.4	787.4	A_1 str
	355.8	355.3	354.4	A_1 bend
	302.2	309.0/304.2		E bend
$RbIO_3$	805.7	809.4/807.6	806.3	E str
	788.8	793.0	789.9	A_1 str
	358.4	357.2		A_1 bend
KIO_3	808.2	807.6		E str
		786.2		A_1 str
$NaIO_3$	1000	1003		*b*

[a] Frequency accuracy ±0.5 cm^{-1}, but see text regarding reproducibility. [b] Assigned to NaO_4.[16,17]

However, it soon became evident that these frequencies were subject to small and apparently random shifts, sometimes up to ca. 2 cm^{-1}. This variation in band position is not a general feature of matrix IR studies, but the phenomenon *has* previously been observed in related studies on the vaporization of alkali metal selenates and selenites.[14] In this latter case, it was suggested that the variation in frequency might be due to the presence of molecular oxygen in the matrix, and as indicated above, we believe that a similar explanation is appropriate here. Table I therefore also includes the frequencies we obtained using a pure oxygen matrix. Here, spectral transmission was generally poorer, but band positions were somewhat more reproducible.

Matrix IR Studies on Isotopically Enriched $CsIO_3$. Four independent experiments were carried out on isotopically enriched cesium iodate, and Figure 2a shows a typical argon matrix spectrum in the I–O stretching region obtained from a sample

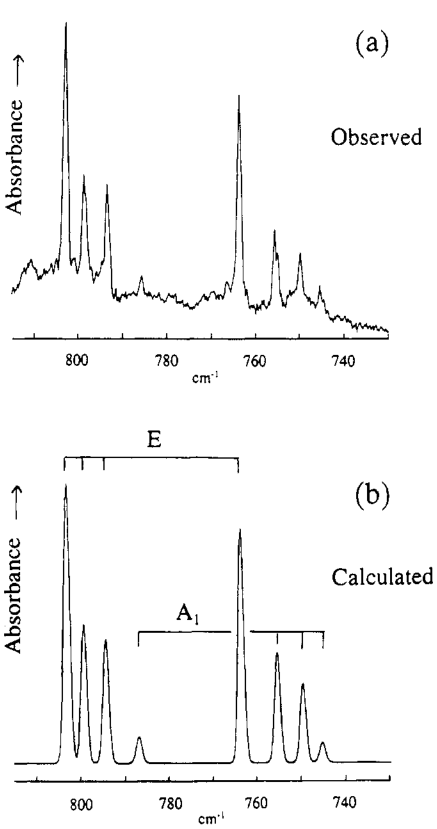

Figure 2. Argon matrix IR spectra obtained in the I–O stretching region from ^{18}O-enriched cesium iodate: (a) observed high-resolution spectrum; (b) calculated spectrum, assuming 48% enrichment, showing correlation with parent E and A$_1$ modes.

of CsIO$_3$ enriched with ca. 50 atom % ^{18}O. This spectrum is complex and does not exhibit any obvious binomial intensity pattern. In the bending region, only those components associated with the more intense feature at ca. 356 cm^{-1} were observed, and these were found at 355.8, 350.6, 345.2, and 339.7 cm^{-1}. The frequencies of the various isotopic components found in these experiments are listed in Table II.

Rubidium Iodate. Samples of rubidium iodate yielded very similar matrix IR spectra to those from the cesium system, and the frequencies obtained are summarized in Table I. In particular, nitrogen matrices again showed an intense doublet, 809.4/807.6 cm^{-1}, whereas this feature appeared as a singlet in argon. These absorptions occurred at slightly different frequencies from those in the cesium system and thus provide evidence for direct cation involvement in the isolated species.

Potassium Iodate. The vaporization of potassium iodate samples often resulted in extensive sample decomposition, with the evolution of significant amounts of oxygen, but on careful heating to ca. 750 K, characteristic IR bands could be observed in the I–O stretching and bending regions (Table I), which were again shifted in frequency in comparison with the Cs and Rb systems. These experiments also yielded occasional weak features at 834, 791, and 785.5 cm^{-1} (N$_2$ matrices), and these are the subject of a continuing investigation.[15]

Sodium Iodate and Lithium Iodate. When samples of sodium iodate were heated under similar deposition conditions, there was a violent evolution of oxygen, and continued heating resulted in the growth of a weak spectral feature at ca. 1000 cm^{-1}. No absorptions were observed at ca. 800 cm^{-1}. At the same time, a thin metallic film could be observed on the off-axis walls of the deposition system. Ultimately, a white sublimate was produced, which proved to be sodium iodide. We assign the IR absorption at ca. 1000 cm^{-1} to molecular NaO$_4$, formed by a cocondensation reaction between atomic Na and oxygen. This reaction has previously been reported by Andrews et al.[16,17] and was also observed in our earlier study on the vaporization of alkali metal selenates and selenites.[14]

TABLE II: Observed and Calculated Frequencies (cm^{-1}) for ^{18}O-Enriched CsIO$_3$ Molecules Isolated in Argon Matrices

obsd[a]	calcd[b]	species	symmetry	
803.0	803.0	I-16-16-16	E	C_{3v}
	803.0	I-18-16-16	A″	C_s
799.0	798.9	I-18-18-16	A′	C_s
793.6	793.8	I-18-16-16	A′	C_s
786.4	786.4	I-16-16-16	A$_1$	C_{3v}
763.6	763.6	I-18-18-18	E	C_{3v}
	763.6	I-18-18-16	A″	C_s
755.4	755.4	I-18-16-16	A′	C_s
749.7	749.5	I-18-18-16	A′	C_s
745.4	745.4	I-18-18-18	A$_1$	C_{3v}
355.8	355.8	I-16-16-16	A$_1$	C_{3v}
350.6	350.6	I-18-16-16	A′	C_s
345.2	345.3	I-18-18-16	A′	C_s
339.7	339.7	I-18-18-18	A$_1$	C_{3v}
302.2	302.2	I-16-16-16	E	C_{3v}
	302.2	I-18-16-16	A″	C_s
	295.2	I-18-18-16	A′	C_s
	293.4	I-18-16-16	A′	C_s
	286.2	I-18-18-16	A″	C_s
	286.2	I-18-18-18	E	C_{3v}

[a] Frequency accuracy ±0.5 cm^{-1}. [b] Assuming force constants F_R = 5.313 mdyn/Å, F_{RR} = 0.092 mdyn/Å, F_α = 1.771 (mdyn Å)/rad^2, $F_{\alpha\alpha}$ = 0.523 (mdyn Å)/rad^2, and a value of 106° for the IO$_3$ interbond angle.

Samples of lithium iodate yielded a steady evolution of oxygen on heating, and at ca. 750 K a white sublimate was observed on the cooler parts of the apparatus. No bands were observed in the I–O stretching region, and the white sublimate was shown by analysis to be solid lithium iodide.

Spectral Interpretation and Discussion

The mass spectrometric results on cesium iodate strongly indicate the presence of molecular CsIO$_3$ in the vapor phase, and the four IR bands observed in the argon matrix spectra from this system are therefore provisionally assigned to this species. The vibrational fundamentals of the iodate ion are well-documented[8–10] with stretching modes A$_1$ + E lying at ca. 750 and 770 cm^{-1} and bending modes A$_1$ + E at ca. 370 and 340 cm^{-1}. Our matrix features at 780–810 and 300–350 cm^{-1} thus clearly lie in the IO$_3$ stretching and bending regions, respectively. Furthermore, it is known that, for IO$_3^-$, the intensity of the E stretch is significantly greater than the A$_1$ stretch, and this indicates that in these matrix studies the higher frequency stretching mode has E symmetry.

This assignment is supported by the observation that, for CsIO$_3$ in nitrogen matrices, the band at ca. 809 cm^{-1} and also that at 306 cm^{-1} appear as *doublets* (Figure 1c) whereas the corresponding features in argon are singlets. It is now reasonably well-established[18] that nitrogen matrices can induce small splittings in degenerate modes, and, for CsIO$_3$ in nitrogen, we may identify the two doublets as the "E" stretch and bend and assign the singlets as the corresponding A$_1$ modes. These conclusions may be unequivocally confirmed by an analysis of the spectra of ^{18}O-enriched samples.

Vibrational Analysis of ^{18}O Isotope Patterns. Initial support for the presence of a C_{3v} iodate unit comes from the three additional components associated with the A$_1$ bend, since isotopic enrichment will produce just three additional iodate species which would contribute to this pattern: I^{16}O$_2$^{18}O, I^{16}O^{18}O$_2$, and I^{18}O$_3$. However, these bands were relatively weak, and the most convincing evidence comes from a detailed analysis of the more intense features in the stretching region.

As indicated above, the isotope pattern in the I–O stretching region is complex and is not immediately characteristic of a vibrating unit with C_{3v} symmetry. There are basically two reasons for this. Firstly, the most prominent features will arise from the *degenerate* E stretching vibration, and, since this degeneracy will be lifted for the partially-substituted isotopomers, the intensity pattern will not follow binomial statistics. Secondly, in addition to the E stretch, this spectral region includes components arising from the weaker A_1 stretch, which is only ca. 20 cm^{-1} lower in frequency than the E. This A_1–E frequency separation is *less than* the ^{16}O–^{18}O isotope shifts, and, under these circumstances, a significant perturbation of simple frequency and intensity patterns is to be anticipated.[19] Because of this, the spectra obtained here for ^{18}O-enriched $CsIO_3$ show little resemblance to the isotope patterns previously obtained[5] for chlorates, where the E and A_1 stretching Cl–O modes were well-separated.

Three models of increasing complexity were used to interpret the ^{18}O isotope patterns observed for $CsIO_3$ in argon and thereby confirm the C_{3v} structure of matrix isolated $CsIO_3$. The first of these was a "stretch only" model, which employed one principal and one interaction I–O stretching constant, together with one I–O–I bond angle as variable parameters. This model is thus similar to that previously employed in other systems,[19,20] and although it could satisfactorily reproduce the *frequencies* of all eight isotopic components observed in the stretching region (Figure 2a), the basic intensity ratio I_E/I_{A1} for the parent molecule was found to differ significantly from that observed.

Inclusion of the I–O–I bending modes, however, resulted not only in a very satisfactory simulation of *all* the observed frequencies but also generated a much more convincing intensity pattern. Table II compares the observed and calculated frequencies obtained using this model, while Figure 2b shows a complete spectral simulation in the stretching region. With the inclusion of the bending modes, this model incorporates a total of four force constants, and the values of these parameters are included in Table II.

As a final refinement, an attempt was made to investigate whether the (as yet unobserved) cation vibrations might significantly affect the vibrational modeling of the IO_3 modes and hence the validity of our C_{3v} model. This was done by choosing various values for the (A_1 + E) Cs–O modes within the frequency range 50–150 cm^{-1}, evaluating two additional force constants, and then incorporating these into a third spectral simulation of the isotope patterns. Our conclusions were that this procedure did not result in any significant *improvement* in the simulation of either band positions or relative intensities.

The presence of cations in these molecules can only therefore be inferred here by the observation of small frequency shifts in the IO_3 modes. However, although having only a minimal effect on the apparent properties of the IO_3 unit, the position of the cation modes can be shown to have a significant effect on the thermodynamic functions of these molecules, and the results of this analysis will be presented elsewhere.[21]

Conclusions

The aim of this study was to investigate the vaporization of alkali metal iodates and, in particular, to characterize any new molecular species. In the cases of lithium and sodium iodates, heating in vacuo resulted in extensive decomposition, but for the remaining iodates in the group new ternary species were identified. These proved to be *molecular* MIO_3 species (M = K, Cs, Rb), and, using isotopic substitution, it has been shown that these molecular iodates have C_{3v} structures and involve tridentate coordination similar to that found in the analogous chlorate systems.

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