Matrix-isolation and Mass Spectrometric Studies on the Vaporisation of Chromium(III) Bromide: Characterisation of Molecular $CrBr_4$, $CrBr_3$ and $CrBr_2$†

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Mass spectrometric and matrix-isolation IR studies on the vaporisation of solid chromium(III) bromide indicated the presence in the vapour of three different chromium halide species, together with molecular bromine. In the initial stages of heating the most volatile chromium species is $CrBr_4$, but at progressively higher temperatures molecular $CrBr_3$ and subsequently $CrBr_2$ are produced. The chromium and bromine isotope structure has been resolved for these latter species, and their IR spectra have been shown to be consistent with planar (D_{3h}) and linear geometries respectively.

The initial experiments on the vaporisation of solid chromium(III) bromide were carried out by Wagner and Stein[1] who studied this system by transpiration. This work was extended by Sime and Gregory,[2] and most recently by Nocker and Gruehn.[3] On the basis of these studies, it was concluded that heating $CrBr_3$ in an inert atmosphere causes decomposition to $CrBr_2$ and the evolution of Br_2 [equation (1)], and that when

$$CrBr_3(s) \longrightarrow CrBr_2(s) + \tfrac{1}{2}Br_2(g) \qquad (1)$$

chromium(III) bromide is heated in a bromine atmosphere at a sufficiently high pressure to suppress decomposition, gaseous $CrBr_3$ and $CrBr_4$ are formed [equations (2) and (3)]. However,

$$CrBr_3(s) \longrightarrow CrBr_3(g) \qquad (2)$$

$$CrBr_3(s) + \tfrac{1}{2}Br_2(g) \longrightarrow CrBr_4(g) \qquad (3)$$

no direct observations were made on the chromium vapour species.

A contemporary study of the vaporisation of solid chromium(II) bromide by mass spectrometry[4] showed several peaks, including Cr^+, $CrBr^+$, $CrBr_2^+$ and $Cr_2Br_3^+$, thus indicating the presence of molecular $CrBr_2$ and its dimer. However, it was not until the work of Cuoni *et al.*[5] and Kovba[6] that any spectroscopic or structural information was available for these species.

Cuoni *et al.*[5] obtained high-temperature Raman spectra of the vapours in the chromium(III) bromide–bromine system, and assigned their spectral features to the tetrahedral molecule $CrBr_4$ by comparison with the known spectrum of molecular $TiBr_4$. Kovba[6] carried out variable-temperature IR studies on the vapours above heated chromium(III) bromide. During the course of his experiments he noted the evolution of bromine, and on the basis of changes in relative band intensities with temperature concluded that molecular $CrBr_4$, $CrBr_3$, $CrBr_2$ and $(CrBr_2)_2$ were present in the high-temperature vapour.

As part of our research programme on the characterisation of high-temperature chemical species, we are interested in the shapes adopted by transition-metal halide molecules,[7] and in the role that they may play in high-temperature corrosion. In our previous studies[8] on the vaporisation of solid chromium(III) chloride we were able to establish unequivocally the identities, shapes and characteristic vibration frequencies of the molecular species $CrCl_4$, $CrCl_3$ and $CrCl_2$ *via* mass spectrometry and matrix-isolation IR spectroscopy. The present paper describes our studies on the corresponding chromium(III) bromide system, and employs a similar strategy based on IR selection rules and the analysis of isotopic frequency and intensity patterns.

Experimental

Samples of solid chromium(III) bromide were prepared by heating chromium metal in bromine vapour at *ca.* 800 °C. The glistening dark crystalline product was purified by sublimation in bromine vapour, and its purity established by elemental analysis and X-ray powder diffraction. In subsequent mass spectrometric and matrix-isolation studies, samples of this material were vaporised *in vacuo* from silica holders heated to *ca.* 500–650 °C by an external furnace. Towards the end of each experiment the less-volatile solid residue was white, and was shown by standard tests to contain chromium(II).

Mass spectra were obtained using the VG quadrupole instruments SXP 400 and 12-12S operating in cross-beam mode, typically at 70 or 20 eV as described previously.[8] The general features of our matrix-isolation equipment have also been described elsewhere.[8] In the present studies high-purity argon (BOC 99.999%) was found to be the most suitable matrix gas, and IR spectra were obtained at temperatures of *ca.* 12 K using Perkin-Elmer 983G and Bio-Rad FTS 60A instruments. Controlled diffusion was carried out at temperatures up to *ca.* 40 K, but no significant changes in band intensity were observed prior to boil-off.

Results

When chromium(III) bromide is sublimed *in vacuo* a variety of coloured products may be obtained. Initially, at the lowest temperatures (*ca.* 500 °C), a yellow-brown sublimate is observed, and with continued heating this gives way to a green sublimate. The residual material gradually becomes paler, and ultimately white. Further prolonged heating yields a white sublimate which on analysis proves to be chromium(II) bromide.

In our mass spectrometric experiments the most intense peaks in the spectrum of the vapours above heated chromium(III) bromide corresponded to Br_2^+, HBr^+ and Br^+, but in addition signals arising from Cr^+, $CrBr^+$, $CrBr_2^+$, $CrBr_3^+$ and $CrBr_4^+$ were also observed. However, the relative intensities of these latter signals showed a significant temperature depend-

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† *Non-SI units employed:* eV ≈ 1.60×10^{-19} J, dyn = 10^{-5} N.

ence, with CrBr$_4^+$ only being observed in the initial stages of vaporisation (*ca.* 500–550 °C) and CrBr$_2^+$ becoming more predominant at *ca.* 650 °C.

Numerous matrix infrared experiments were performed under a variety of conditions, but of these only a few spectra need be discussed in detail. Fig. 1(*a*) shows part of the argon-matrix infrared spectrum obtained from a sample of chromium(III) bromide heated to *ca.* 500 °C for *ca.* 20 min. At this stage in the vaporisation the off-axis sublimate is yellow-brown, and two prominent bands are present at *ca.* 375.5 and 312 cm^{-1}. These two features, however, did not maintain a constant intensity ratio, and must therefore correspond to different species.

On continued deposition at *ca.* 550 °C, a feature at *ca.* 393 cm^{-1} begins to grow in, as shown in Fig. 1(*b*), and on still further deposition at *ca.* 650 °C a prominent peak at *ca.* 362 cm^{-1} appears, accompanied by a weaker feature at *ca.* 347 cm^{-1}. Fig. 1(*c*) shows a typical spectrum obtained at *ca.* 650 °C *after extensive prior heating at ca. 600 °C.* Under these conditions the band at 312 cm^{-1} is effectively absent. On the basis on these experiments it is therefore concluded that at least four quite distinct species may be isolated in argon matrices when chromium(III) bromide is vaporised over the temperature range 500–650 °C.

Spectral Interpretation and Discussion

The mass spectrometric studies reported here at *ca.* 500 °C clearly show that molecular CrBr$_4$ is present in the high-temperature vapour even at *low pressures*, and also establish that at *ca.* 650 °C molecular CrBr$_2$ is present in the vapour. The CrBr$_3^+$ signal in the mass spectrum could conceivably arise entirely as a result of fragmentation, but in view of the presence of a *third* IR feature at 393 cm^{-1} we believe that a significant proportion of this signal comes from molecular CrBr$_3$. Support for this comes from the fact that at higher temperatures the CrBr$_3^+$ signal was observed in the absence of CrBr$_4^+$.

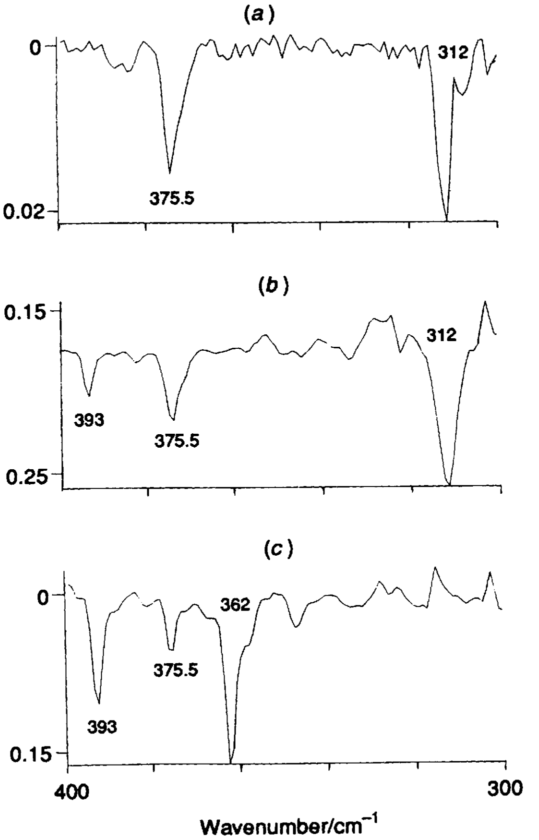

Fig. 1 Argon matrix IR spectra (resolution 2 cm^{-1}) obtained from the vaporisation of chromium(III) bromide: (*a*) after *ca.* 20 min deposition at 500 °C; (*b*) after further deposition at 550 °C; (*c*) after deposition at 650 °C, after prior heating at 600 °C

Isotopic Studies.—In addition to the resolution of isotopic features in the mass spectra of all the ions reported the majority of the IR bands observed in these studies showed chromium and/or bromine fine structure. Chromium has four isotopes in natural abundance 4.3 (^{50}Cr); 83.8 (^{52}Cr); 9.5 (^{53}Cr) and 2.4% (^{54}Cr), whilst bromine has two 50.7 (^{79}Br) and 49.3% (^{81}Br). The resolution of isotopic effects in the matrix IR studies is an important aspect of species identification.

Bromine. The band at *ca.* 312 cm^{-1} is close to the gas-phase fundamental[9] of molecular Br$_2$ (*ca.* 318 cm^{-1}), and to the Raman feature centred at 316 cm^{-1} observed in Ar–CS$_2$–Br$_2$ mixtures at low temperatures.[10] Under high resolution (0.3 cm^{-1}) this band appears as *two* closely spaced 1:2:1 triplets [see Fig. 2(*a*)], with components at 314.2, 312.3, 310.4 and 312.9, 311.0, 309.2 cm^{-1}. As Table 1 shows, the splittings within the upper (more intense) triplet are in excellent agreement with those calculated for the species ^{79}Br$_2$, ^{79}Br^{81}Br and ^{81}Br$_2$.

This assignment is supported by the analysis of the electronic *emission* spectrum of Br$_2$ in argon reported by Thirumalai *et al.*[11] In their study of the progression in the X–B system they report values of 315 and 1.55 cm^{-1} respectively for ω_e and $\omega_e x_e$ in isolated Br$_2$ which are in excellent agreement with our

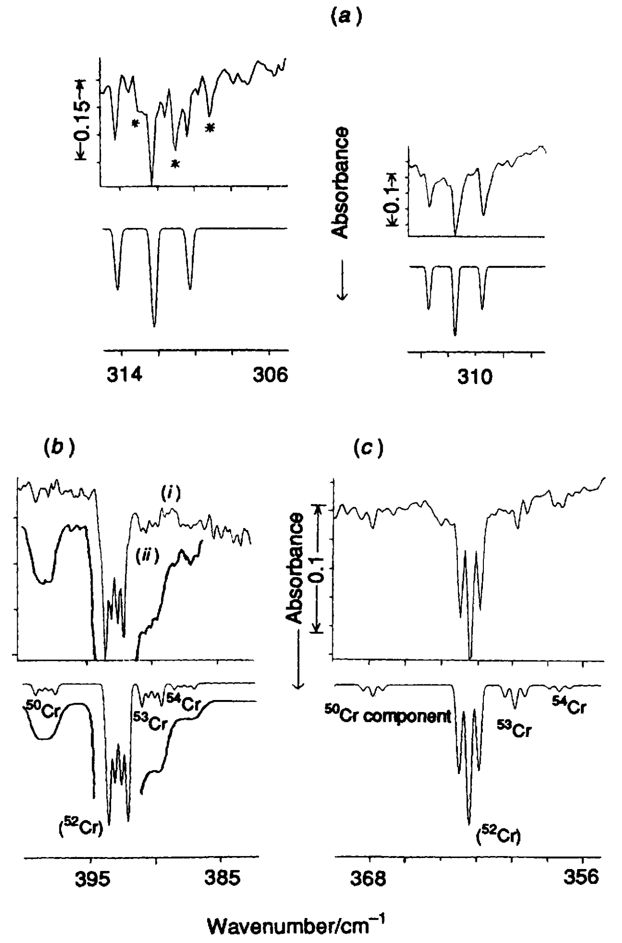

Fig. 2 Principal IR spectral features at higher resolution: observed (above) and calculated (*a*) bromine isotopic structure on the argon matrix band at *ca.* 312 cm^{-1}; the features denoted (*) are attributed to Br$_2$ molecules on a second trapping site (Inset: the same spectral region in a nitrogen matrix); (*b*) bromine and chromium isotopic structure on the argon matrix band at *ca.* 393 cm^{-1} [resolution 0.3 (*i*), 1.0 cm^{-1} (*ii*)]; (*c*) bromine and chromium isotopic structure on the argon matrix band at *ca.* 362 cm^{-1}

Table 1 Observed and calculated vibrational wavenumbers (cm^{-1}) of the vapours over heated chromium(III) bromide isolated in argon matrices

Observed	Calculated*	Assignments
	399.0	${}^{50}Cr^{79}Br_3$
398.5	398.6	${}^{50}Cr^{79}Br_2{}^{81}Br$
	398.1	${}^{50}Cr^{79}Br^{81}Br_2$
	397.6	${}^{50}Cr^{81}Br_3$
393.6	393.6	${}^{52}Cr^{79}Br_3$
393.1	393.1	${}^{52}Cr^{79}Br_2{}^{81}Br$
392.7	392.6	${}^{52}Cr^{79}Br^{81}Br_2$
392.2	392.1	${}^{52}Cr^{81}Br_3$
390.8	391.0	${}^{53}Cr^{79}Br_3$
390.5	390.5	${}^{53}Cr^{79}Br_2{}^{81}Br$
390.0	390.0	${}^{53}Cr^{79}Br^{81}Br_2$
389.6	389.6	${}^{53}Cr^{81}Br_3$
	388.5	${}^{54}Cr^{79}Br_3$
388.0	388.0	${}^{54}Cr^{79}Br_2{}^{81}Br$
	387.5	${}^{54}Cr^{79}Br^{81}Br_2$
	387.0	${}^{54}Cr^{81}Br_3$
380.0	380.5	${}^{50}CrBr_4$
375.5	375.5	${}^{52}CrBr_4$
373	373.1	${}^{53}CrBr_4$
371	370.8	${}^{54}CrBr_4$
	368.4	${}^{50}Cr^{79}Br_2$
367.8	367.9	${}^{50}Cr^{79}Br^{81}Br$
	367.3	${}^{50}Cr^{81}Br_2$
363.0	363.0	${}^{52}Cr^{79}Br_2$
362.4	362.5	${}^{52}Cr^{79}Br^{81}Br$
361.9	361.9	${}^{52}Cr^{81}Br_2$
360.4	360.4	${}^{53}Cr^{79}Br_2$
359.9	359.9	${}^{53}Cr^{79}Br^{81}Br$
359.3	359.3	${}^{53}Cr^{81}Br_2$
	357.9	${}^{54}Cr^{79}Br_2$
357.4	357.4	${}^{54}Cr^{79}Br^{81}Br$
	356.8	${}^{54}Cr^{81}Br_2$
314.2	314.2	${}^{79}Br_2$
312.3	312.3	${}^{79}Br^{81}Br$
310.4	310.3	${}^{81}Br_2$

* Based on the parameters: $CrBr_3$ $f_r = 2.29$, $f_{rr} = 0.09$ mdyn $Å^{-1}$, symmetric stretch 230 cm^{-1}; $CrBr_2$ $f_r = 1.88$, $f_{rr} = 0.36$ mdyn $Å^{-1}$, symmetric stretch 220 cm^{-1}.

measured fundamental. Also, additional and independent IR experiments in *nitrogen* matrices revealed a *single* well resolved triplet, with components at 313.5, 311.5, 309.6 cm^{-1}, as shown (inset) in Fig. 2(*a*).

The vibrational fundamental of molecular Br_2 would not normally be expected to be IR active, and we believe that its appearance here arises from the formation of a weak adduct with the matrix, or as a result of trapping in a non-centrosymmetric matrix site. The formation of an adduct with adventitious impurities[12] is discounted, since this would be expected to produce an IR feature at a frequency *different* from that obtained from the emission studies. The observation of a *well resolved* bromine isotope pattern provides a strong indication that this feature does *not* arise from Br_2 clusters.

Chromium tetrabromide. As indicated previously, chromium tetrabromide has been identified by both Raman[5] and IR spectroscopy[6] as a product of the high-temperature vaporisation of solid chromium(III) bromide. In particular, five bands were observed in the Raman at 224, 60, 368, 71 and 123 cm^{-1}, and these were assigned as the fundamental modes ν_1–ν_4 and the overtone $2\nu_2$, respectively, by comparison with (tetrahedral) $TiBr_4$. On this basis, the two T_2 fundamentals (ν_3 and ν_4) should also be present in the IR spectrum. This prediction is in good agreement with the *in situ* IR studies of the vapour species by Kovba,[6] where a band centred at 370 cm^{-1} was assigned to $CrBr_4$ on the basis of variable-temperature studies.

Our argon-matrix spectra obtained from chromium(III) bromide vaporised at *ca.* 500 °C show a prominent feature at *ca.* 375.5 cm^{-1} which correlates with the appearance of a signal corresponding to $CrBr_4{}^+$ in the mass spectrum, and is assigned to the ν_3 T_2 fundamental of $CrBr_4$ by comparison with these earlier studies. Despite numerous attempts to observe isotopic structure, this band remained relatively broad (*ca.* 2 cm^{-1}), even at a spectral resolution of 0.3 cm^{-1}, and no bromine isotope structure could be resolved. Attempts to observe chromium isotope structure were hindered by the fact that this band appeared to reach a limiting intensity after which point it was effectively superseded by the 393 and 362 cm^{-1} features. However, weak broad shoulders were noted at *ca.* 380, 373 and 371 cm^{-1} which are assigned as chromium isotope features.

Chromium tribromide. The band at *ca.* 393 cm^{-1} may be provisionally assigned to molecular $CrBr_3$ on the basis of the persistence of the $CrBr_3{}^+$ signal in the higher-temperature mass spectrometric studies. Under medium resolution (1 cm^{-1}) weak satellites were observed at 398.5, 390(sh) and 388(sh) cm^{-1} and together with the intense component at 393 cm^{-1} this pattern is identified as arising from the four naturally occurring isotopes of chromium.

Under higher resolution (0.3 cm^{-1}) all four chromium isotopomers show evidence of further structure which may be assigned to bromine isotopic effects with varying degrees of confidence. The most convincing bromine isotope structure appears on the most intense feature at *ca.* 393 cm^{-1}, where four partially resolved components may be identified at 393.6, 393.1, 392.7 and 392.2 cm^{-1}. Fig. 2(*b*) shows typical spectra recorded at 1 and 0.3 cm^{-1} resolution, and it is particularly significant that for the latter the *outer* components of this quartet are more intense than are the central ones.

By analogy with our previous characterisation[8] of molecular $CrCl_3$, the most likely structure for molecular $CrBr_3$ is trigonal planar (D_{3h}), and our initial interpretation of this spectrum is based on this geometry.

As has been discussed elsewhere,[8,13] the halogen (X) isotope structure associated with the degenerate vibrations in species MX_3 is expected to show a clear departure from a binomial intensity distribution as a result of the loss of vibrational degeneracy in *partially* substituted species such as MX_2X'. In the case of D_{3h} $CrBr_3$, the effect of the two bromine isotopes will be to produce a bromine isotope pattern with an intensity distribution close to 5:3:3:5 for the E′ stretch of *each* of the *chromium* isotopic features. It has also been shown that the positions and intensities of these isotopic components can be very satisfactorily modelled using a simple 'stretch-only' force field.[8,13]

The computed spectra accompanying Fig. 2(*b*) show the simulated chromium and bromine isotope structure for molecular $CrBr_3$, assuming the basic D_{3h} structure. Only two Cr–Br stretching potential constants, f_r(principal) and f_{rr}(interaction), were retained in the force field, and the numerical results of this modelling are reproduced in Table 1. The agreement is very satisfactory for the principal ^{52}Cr components, and there is also a degree of correspondence with some of components in the weaker ^{n}Cr quartets. In these calculations, it is necessary to include an estimate of the position of the *symmetric* Cr–Br stretch, and this was arbitrarily chosen as 230 cm^{-1} a value suitably close to that previously observed for $CrBr_4$. However, the computed patterns are essentially unaffected by the exact value chosen.

With the presence of one atom of Cr indicated by the four *chromium* isotopic components, and existence of a C_3 symmetry axis confirmed by the non-binomial Br_3 intensity pattern, the only other conceivable assignment for this band is to a *pyramidal* (C_{3v}) $CrBr_3$ molecule. This structure would be expected to show a second IR feature in the Cr–Br stretching region, and would also yield isotopic shifts for Cr and Br which are different from those for D_{3h} symmetry. On the basis of model calculations, we estimate that such spectral differences would be detectable for Br–Cr–Br bond angles < *ca.* 110°, and a C_{3v} structure with a bond angle in the range 110–120° cannot be entirely discounted. However, there are no positive reasons for preferring the C_{3v} structure over D_{3h}.

Chromium dibromide. By analogy with molecular $CrCl_2$,[8] and other transition-metal dibromides,[14] molecular $CrBr_2$ is expected to have a linear structure with point group $D_{\infty h}$, and the position of its IR active stretch has been estimated[6] as *ca.* 365 cm^{-1}. Our assignment of the band at *ca.* 362 cm^{-1} to this species is confirmed by both chromium and bromine isotope structure.

Under medium resolution, weak chromium isotope satellites were identified at 367.8, 359.9 and 357.4 cm^{-1}, and under high resolution (0.3 cm^{-1}) the principal (^{52}Cr) feature shows the characteristic 1:2:1 triplet pattern expected for a non-degenerate mode involving the movement of two equivalent bromine atoms. Fig. 2(*c*) shows the entire 362 cm^{-1} band at 0.3 cm^{-1} resolution, and the accompanying computed spectrum shows the isotope pattern expected for linear $CrBr_2$. The numerical data are summarised in Table 1 and it is clear that there is very satisfactory agreement with the observed spectrum. As in the case of $CrBr_3$, only two parameters were retained in the force field, and the arbitrary value assigned to the totally symmetric stretch had minimal effect on the calculated isotope patterns.

The possibility that $CrBr_2$ may be *non-linear* rests on similar criteria to those discussed for $CrBr_3$ above, but our results provide no positive reasons for proposing this structure.

The weaker feature at *ca.* 347 cm^{-1} which appears at the same time as the main $CrBr_2$ band is tentatively assigned to the dimer Cr_2Br_4. This assignment is supported by reference to Kovba's work,[6] where a feature at 340 cm^{-1} found to grow in prominence at higher temperatures and pressures was assigned to a dimer. In our experiments it always remained weak and showed no resolvable structure.

Conclusion

These experiments provide the first direct evidence of the existence of molecular $CrBr_3$, and confirm the presence of $CrBr_4$, $CrBr_3$ and $CrBr_2$ as high-temperature molecular species present in the vaporisation of chromium(III) bromide. The most volatile of these species is $CrBr_4$ and its matrix IR spectrum is consistent with the previously assumed tetrahedral structure. The predominant chromium species, however, based on IR intensities, is molecular $CrBr_3$ and this appears to adopt the same planar structure as that of the previously identified $CrCl_3$. At higher temperatures monomeric $CrBr_2$ predominates, and a linear geometry is indicated based on isotope shifts.

In addition, an IR spectrum of Br_2 has been obtained which shows a well resolved isotope pattern, and it is suggested that this is evidence for a specific interaction involving an isolated Br_2 molecule as opposed to an absorption arising from a cluster of type $(Br_2)_n$.

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