Characterisation of CrO_2Br_2 and CrO_2BrCl by Matrix-isolation Infrared Spectroscopy

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Chromyl bromide, CrO_2Br_2, has been prepared by the reaction between HBr and CrO_2Cl_2, and its i.r. spectrum recorded in low-temperature matrices. In particular, characteristic $^{52}Cr{=}O$ stretching modes are observed at 995.4 and 982.6 cm^{-1} (Ar matrix) and analysis of the chromium isotope structure on these bands leads to an estimate of *ca.* 107° for the OCrO bond angle in the C_{2v} monomer. The most intense Cr–Br stretching mode lies at 403.5 cm^{-1}. Similar matrix studies on *mixtures* of CrO_2Br_2 and CrO_2Cl_2 reveal the existence of molecular CrO_2BrCl, with characteristic absorptions at *ca.* 996, 985.5 [v(Cr=O)], 483 [v(Cr–Cl)], and 412.5 [v(Cr–Br)] cm^{-1}.

Chromyl fluoride and chromyl chloride are well established stable compounds for which there exists considerable structural[1,2] and spectroscopic[3–6] data. However, the third member of this series, chromyl bromide, is difficult to prepare,[7,8] and apart from a solution u.v.–visible spectrum,[8] has only been characterised by elemental analysis.

This paper describes i.r. matrix-isolation studies on CrO_2Br_2 in which the most intense fundamentals are assigned, and chromium isotope shifts used to estimate the OCrO bond angle. Spectroscopic evidence is also obtained for the molecular species CrO_2BrCl. This compound may be synthesised by mixing together CrO_2Cl_2 and CrO_2Br_2, in a reaction similar to that used for the preparation of the mixed-halide species CrO_2ClF.[9]

Experimental

Synthesis of CrO_2Br_2.—Chromyl bromide has previously been obtained by halogen exchange between CrO_2Cl_2 and liquid HBr,[7] and by the reaction of CF_3COBr with CrO_3.[8] We have investigated both these routes, and have also examined halogen exchange between BBr_3 and CrO_2Cl_2 in $CFCl_3$. All these reactions were found to yield intensely purple products which decomposed at $>$ *ca.* 215 K. However, in our experience only the first method[7] yielded 'pure' CrO_2Br_2 (see below). The products from the CF_3COBr–CrO_3 reactions always gave i.r. spectra containing absorptions characteristic of CF_3CO groups, probably $(CF_3CO)_2O$, whilst in the third route, excess BBr_3 (m.p. 227 K) proved impossible to separate without extensive thermal decomposition of the CrO_2Br_2.

CrO_2Cl_2 (Aldrich) was distilled before use, and HBr (BDH) was used as received. The preparation was conducted on an all-glass vacuum line fitted with Teflon taps; joints were greased with Kel-F. Since CrO_2Br_2 decomposes in contact with glass at $>$ *ca.* 215 K, the traps were kept as small and as near together as was practical. In a typical synthesis CrO_2Cl_2 (*ca.* 1 mmol) and HBr (*ca.* 8 mmol) were condensed successively in a 77-K trap, and the mixture warmed cautiously to *ca.* 190 K (ethyl acetate slush). An intense purple colour developed immediately the mixture liquified, and after 20 min at this temperature, the excess HBr and HCl together with some Br_2 were removed under high vacuum. Further warming to *ca.* 215 K resulted in the sublimation of a purple material, along with further generation of Br_2. Elemental analysis of this purple material gave a Cr:Br ratio of 1:1.9. Although CrO_2Br_2 appeared stable at <200 K for long periods, it decomposed rapidly at $>$ *ca.* 220 K, and had only a finite lifetime in the vapour phase. Indeed, every sublimation of CrO_2Br_2 appeared to involve some decomposition to Br_2 and an involatile brown residue. However the mass spectrum (70 eV, *ca.* 1.1×10^{-17} J) of the vapour showed a molecular ion $CrO_2Br_2^+$.

Spectroscopic Studies.—Matrix-isolation studies were carried out by co-condensing samples of CrO_2Br_2 (from a 210-K trap) with a large excess of argon or nitrogen (BOC 99.999%) onto a cooled (12 K) caesium iodide window.[10] Separate spray-on tubes were used for the matrix gas and the sample, and the path traversed by the CrO_2Br_2 was kept as short and straight as possible to minimise sample decomposition. Owing to the transitory nature of vapour phase CrO_2Br_2, no estimate could be made of the matrix ratios, but they are believed to be well in excess of 1 000:1. Infrared spectra were subsequently obtained using a Perkin-Elmer 983G spectrophotometer. Attempts were also made to obtain u.v.-visible spectra of matrix-isolated CrO_2Br_2, but these were frustrated by the presence of Br_2.

The search for the mixed-halogen species CrO_2BrCl was carried out by slowly warming mixtures of CrO_2Cl_2 and CrO_2Br_2 over the temperature range 150—210 K and taking successive i.r. spectra of the matrix-isolated species.

Results and Discussion

Figure 1(*a*) shows a typical survey spectrum obtained when a sample of CrO_2Br_2 is sublimed out of a *ca.* 210-K trap, and the vapour species co-condensed with a large excess of argon at *ca.* 12 K. Three prominent bands are observed at 995.4, 982.6, and 403.5 cm^{-1}, and these are assigned to a single species on the basis of their constant intensity ratio over a large number of experiments. A very weak feature at *ca.* 305 cm^{-1} also appears to be correlated with this species. Under higher resolution, it is found that the higher frequency bands show multiplet structure, whilst the intense absorption at 403.5 cm^{-1} includes a partially resolved shoulder at 399 cm^{-1}. This absorption, together with its second derivative, which displays the shoulder more clearly, is shown in Figure 1(*c*). Nitrogen matrices gave similar spectra under low resolution but closer examination revealed extensive band splitting. This phenomenon was also noted in the matrix i.r. study on CrO_2Cl_2,[6] and for this reason, all the detailed results described here refer to argon matrices. Earlier matrix-isolation studies on (C_{2v}) CrO_2F_2[5] and CrO_2Cl_2[6] have shown that the two stretching modes v(Cr=O) lie in the region 950—1 050 cm^{-1}, and that the antisymmetric (B_1) stretch lies above the A_1 symmetric stretch. These studies have also shown that the chromium isotope frequency span (^{50}Cr–^{54}Cr) is greater for the B_1 mode, being *ca.* 10.8 cm^{-1} in CrO_2F_2[5] and *ca.* 11.3 cm^{-1} in CrO_2Cl_2.[6] We therefore assign the bands at 995.4 and 982.6

Table 1. Vibrational fundamentals (cm^{-1}) for chromyl halides CrO_2X_2 (X = F, Cl, or Br)

CrO_2F_2		CrO_2Cl_2			CrO_2Br_2	
Gas[3,4]	N_2 matrix[5]	Gas[6]	Liquid[4]	Ar matrix[6]	Ar matrix (this work)	Mode
1 016	1 013.9	1 002.0	994	997.8	995.4	B_1 ν(Cr=O)
1 006	1 006.7	991.0	984	983.6	982.6	A_1 ν(Cr=O)
789	784.8	502.7	497	501.3	403.5	B_2 ν(Cr–X)
727	721.7	470.0	465	467.9	399.0	A_1 ν (Cr–X)
364	—	355.8	357	355.9	(305?)	A_1 δ(CrO_2)
304	—	—	263	257.0	—	B_2
274	—	—	216	212.0	—	B_1
259	—	—	230	—	—	A_2 τ
208	—	—	144	139.2	—	A_1 δ(CrX_2)

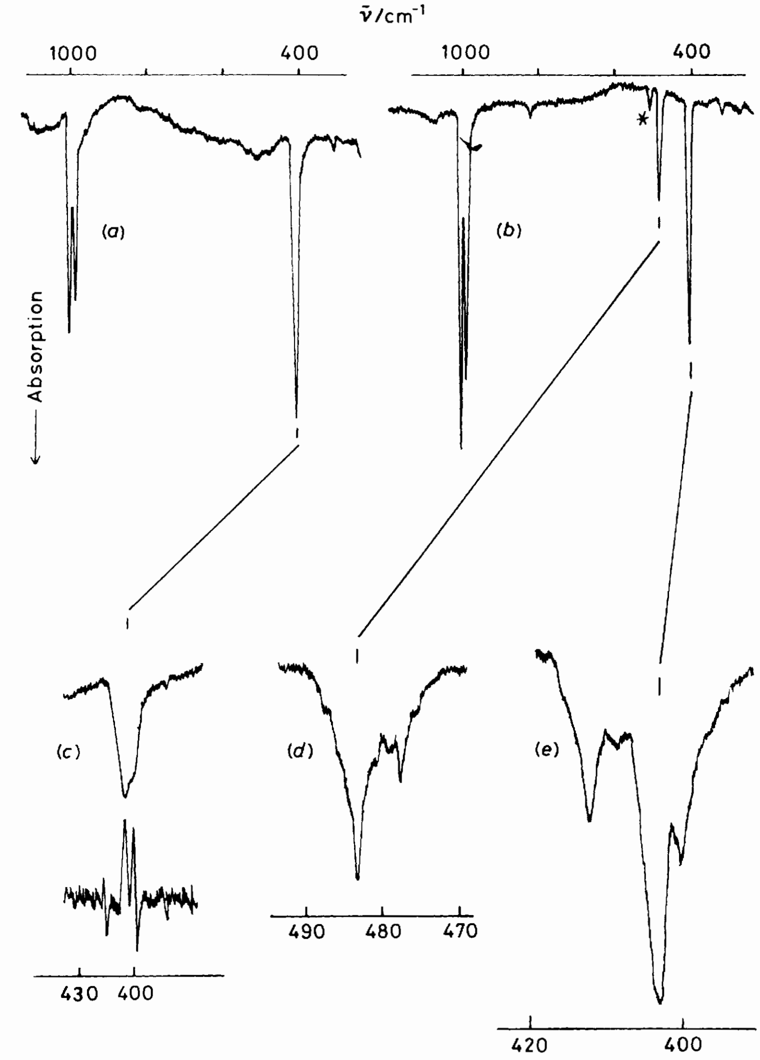

Figure 1. Argon matrix i.r. spectra showing (*a*) prominent bands of CrO_2Br_2 under low resolution; (*b*) bands obtained from a sample of CrO_2Br_2 containing a small amount of CrO_2Cl_2; (*c*) the band at 403.5 cm^{-1} in (*a*) under higher resolution, together with its second derivative; (*d*) the band at 483 cm^{-1} in (*b*) under higher resolution (0.9 cm^{-1}); (*e*) the band at *ca.* 400 cm^{-1} in (*b*) under higher resolution. (0.9 cm^{-1})

cm^{-1} as the B_1 and A_1 Cr=O stretching modes respectively in the isostructural molecule CrO_2Br_2.

In addition to these fundamentals, molecular CrO_2Br_2 (C_{2v}) is expected to show two i.r. active (A_1 + B_2) Cr–Br stretching modes, and four i.r. active bending modes ($2A_1$ + B_1 + B_2). By comparison with literature data on CrO_2Cl_2, the four bending modes are expected to be weak and to lie below *ca.* 360 cm^{-1}, but we would expect to see *two* relatively intense Cr–Br stretching modes. In CrO_2F_2,[4] the two Cr–halogen stretching modes lie at 789 and 727 cm^{-1}, whilst in CrO_2Cl_2[4] they are at lower frequency, and closer together (497 and 465 cm^{-1}). The reasons for this lie mainly in the relative masses of the chromium and halogen atoms, and it may be shown that in CrO_2Br_2, the two Cr–Br stretches would be expected to be even closer together, and to lie in the range 350—450 cm^{-1}.

Our low-resolution spectrum [Figure 1(*a*)] shows an intense band at 403.5 cm^{-1} which on closer examination [Figure 1(*c*)] consists of two components at 403.5 and 399 cm^{-1}, and we assign these bands as the B_2 and A_1 Cr–Br stretching modes respectively. Table 1 compares our band assignments for CrO_2Br_2 with those of CrO_2F_2 and CrO_2Cl_2.

It is evident from Figure 1(*a*) that the bending modes in CrO_2Br_2 are either very weak, or that they lie below the limit of our spectrometer. This latter case will certainly apply to the A_1 $CrBr_2$ bend and possibly also the rocking modes (B_1 + B_2), but we would expect to observe the A_1 CrO_2 bend. In CrO_2F_2 and CrO_2Cl_2 this mode lies at *ca.* 360 cm^{-1} (Table 1), but our spectra showed no sign of an absorption in this region. Instead, we observed a weak band at *ca.* 305 cm^{-1} which appeared to correlate with the other CrO_2Br_2 absorptions. This is clearly significantly shifted from the expected position and its assignment therefore remains tentative. However, it is possible that this mode in CrO_2Br_2 is significantly mixed with the A_1 Cr–Br stretch, and as a result one might anticipate a shift to lower frequency.

Table 2. Observed and calculated frequencies (cm^{-1}) for isotopic Cr=O stretching modes in matrix-isolated CrO_2Br_2

	Calculated[b]				
Observed[a]	I	II	III	Assignment[c]	
1 001.2	1 001.2	1 000.8	1 001.0	^{50}Cr	B_1 Cr=O
995.4	995.4	995.4	995.4	^{52}Cr	
992.7	992.6	992.8	992.7	^{53}Cr	
989.9	989.9	990.4	990.1	^{54}Cr	
986.6	985.8	986.4	986.1	^{50}Cr	A_1 Cr=O
982.6	982.6	982.6	982.6	^{52}Cr	
980.8	981.1	980.8	980.9	^{53}Cr	
979.0	979.6	979.0	979.3	^{54}Cr	

[a] Frequency accuracy ±0.5 cm^{-1}. [b] Assuming OCrO angles of 111, 102, and 107° respectively for calculations I, II, and III; values of F_R and F_{RR} in calc. III are 7.076 and 0.396 mdyn $Å^{-1}$ respectively (dyn = 10^{-5} N). [c] Isotope abundances (%): ^{50}Cr, 4.3; ^{52}Cr, 83.8; ^{53}Cr, 9.6; and ^{54}Cr, 2.4.

Bond Angle Estimate in CrO_2Br_2.—Figure 2(*a*) shows the two Cr–O stretching modes at 995.4 and 982.6 cm^{-1} under high resolution; both show clear evidence of chromium isotope fine structure. If one assumes that these modes are effectively uncoupled from the other fundamentals, this additional frequency data may be used to estimate the angle OCrO. In particular, OCrO may be estimated[11] from equations (1) and (2), where $\lambda = 4\pi^2\nu^2$, F_R and F_{RR} are the principal and

$$\lambda A_1(\text{Cr=O}) = (F_R + F_{RR})\left(\frac{1}{M_O} + \frac{2\cos^2\theta}{M_{Cr}}\right) \qquad (1)$$

$$\lambda B_1(\text{Cr=O}) = (F_R - F_{RR})\left(\frac{1}{M_O} + \frac{2\sin^2\theta}{M_{Cr}}\right) \qquad (2)$$

interaction Cr=O stretching constants, M_{Cr} and M_O are the atomic mass of chromium and oxygen, and 2θ is the angle OCrO. Knowledge of the A_1 and B_1 frequencies of different isotopic species thus leads directly to two estimates for this bond angle.

The frequencies of the various chromium isotopic species are listed in Table 2, together with three sets of calculated band positions, each associated with a different choice of OCrO angle. If one takes the chromium isotope frequencies for the B_1 mode to estimate this angle, an almost exact fit is obtained by choosing a value of 111°. However, the fine structure on the A_1 mode is then only poorly reproduced (calc. I). Alternatively, the

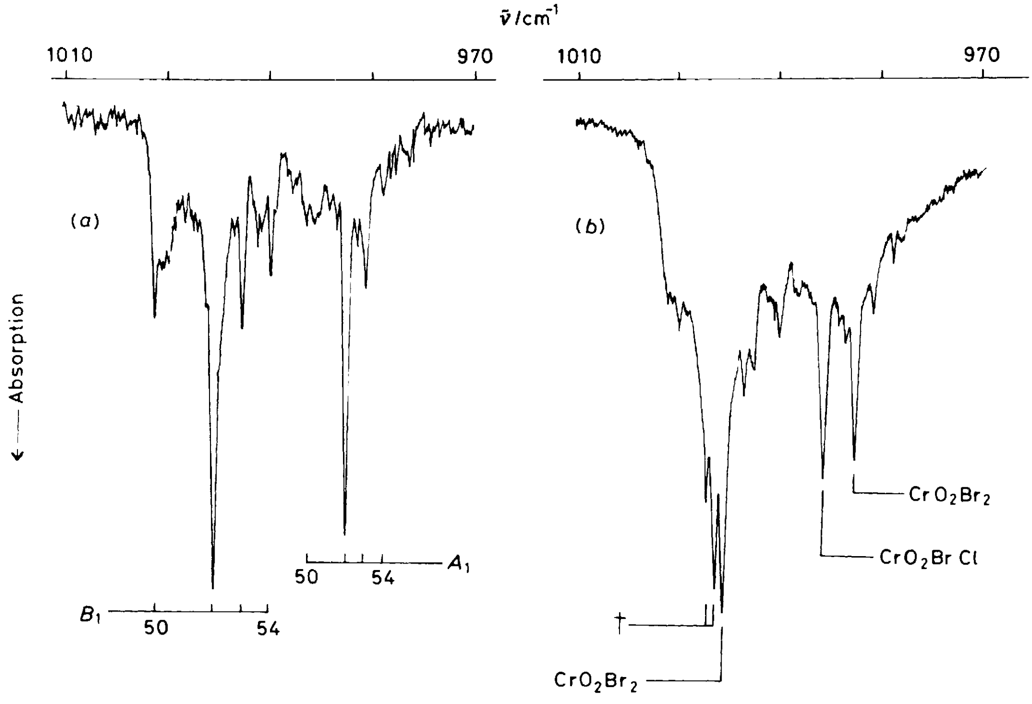

Figure 2. High-resolution i.r. spectra (0.5 cm^{-1}) in the Cr=O stretching region obtained from (*a*) CrO_2Br_2 isolated in argon and (*b*) CrO_2Br_2 and CrO_2BrCl isolated in argon

A_1 mode isotopic structure is accurately predicted with a bond angle of 102° (calc. II). The choice of an intermediate angle (107°) minimises the errors in both fundamentals (calc. III), and it is interesting to note that this angle is very close to the most recently accepted values in CrO_2F_2 (107.8°)[1] and CrO_2Cl_2 (108.5°).[2]

It should be noted that the use of equations (1) and (2) above to estimate the OCrO bond angle represents an approximation even within the assumption of a harmonic force field, since interaction with lower frequency modes has been ignored. Thus although the equations are identical to those which would apply to a C_{2v} triatomic *molecule*, it is not possible to carry over the usual predictions[12] regarding the effect of anharmonicity on the accuracy of the bond angle. Indeed, it would appear that in both CrO_2Cl_2[6] and CrO_2Br_2, central atom isotope shifts in the B_1 Cr=O stretch result in an *upper* limit for the OCrO angle, rather than the 'expected' lower limit.[12] For these molecules, the effect of neglecting coupling with the lower frequency modes appears to more than compensate for the neglect of anharmonicity.

Spectroscopic Evidence for CrO_2BrCl.—In some of the preparations designed to yield pure samples of CrO_2Br_2 it was found that small amounts of unreacted CrO_2Cl_2 remained after removing the HBr. This unreacted CrO_2Cl_2 was considerably more volatile than CrO_2Br_2 and could easily be identified by its colour. The reason for its presence is thought to be because the reaction mixture was a little too cold, and insufficient time had elapsed for quantitative halogen exchange. Owing to the difference in volatility, CrO_2Cl_2 could easily be separated from the main product, but subsequent matrix studies on samples of CrO_2Br_2 prepared under these conditions showed additional features in the i.r. spectrum.

Figure 1(*b*) shows a typical spectrum obtained from a sample of CrO_2Br_2 which had been in contact with unreacted CrO_2Cl_2. In addition to the intense Cr–Br stretching mode(s) at *ca.* 403 cm^{-1}, two new bands are observed at *ca.* 502 and 483 cm^{-1}, and the Cr=O absorptions near 1 000 cm^{-1} are anomalously intense. The weak band at *ca.* 502 cm^{-1} (denoted *) may be confidently assigned as the B_2 Cr–Cl stretching mode in CrO_2Cl_2, which is known to be the *most intense* i.r. fundamental in matrix-isolated CrO_2Cl_2.[6] However the presence of this very small amount of CrO_2Cl_2 cannot account for the significant increase in relative intensity of the Cr=O bands, or for the new feature at 483 cm^{-1}.

Figure 1(*d*) shows this 483 cm^{-1} band under higher resolution, where it now appears as a partially resolved doublet (483, 477.5 cm^{-1}) with an intensity ratio close to 3:1. This band lies in the region of the spectrum expected for a Cr–Cl stretching mode, and both the intensity ratio and the magnitude of splitting of these components strongly suggest that it be assigned to the vibration of a single Cr–Cl unit. The simultaneous enhancement of Cr=O intensity suggests that the mixed species CrO_2BrCl has been isolated.

Closer examination of the Cr–Br stretching region [Figure 1(*e*)] reveals not only the 403.5, 399 cm^{-1} doublet, but an additional absorption at 412.5 cm^{-1} which was not present in spectra containing only CrO_2Br_2. We assign this band as the Cr–Br stretch in CrO_2BrCl.

High-resolution studies on the Cr=O stretching region for such deposits showed new absorptions at *ca.* 996 and at 985.5 cm^{-1} [Figure 2(*b*)]. By analogy with the other CrO_2X_2 species, the well resolved feature at 985.5 cm^{-1} is assigned as the symmetric Cr=O stretch in CrO_2BrCl (A' in C_s symmetry) whilst the other intense absorptions (denoted †) are assigned to the antisymmetric stretch.

Finally, spectra were obtained in which there was a significant amount of the mixed-halide species CrO_2BrCl, and these showed an additional weak absorption at 317 cm^{-1}. This band had the same growth characteristics as the band at 483 cm^{-1}, and is assigned to the A' CrO_2 bend. This mode thus lies somewhat higher than the corresponding bend in CrO_2Br_2, but lower than that expected by simple comparison with CrO_2F_2 and CrO_2Cl_2. Interaction with the Cr–Br stretch is again a possible reason for this.

Spectra were also obtained from samples in which CrO_2Cl_2 was deliberately present in excess. In the early stages of deposition, these showed only bands due to the more volatile CrO_2Cl_2, but as the experiment progressed, and the sample temperature increased, the bands assigned to CrO_2BrCl grew in, and finally those due to CrO_2Br_2 appeared.

Conclusions

Molecular CrO_2Br_2 and CrO_2BrCl have been characterised by matrix-isolation i.r. spectroscopy. These species are isostructural with the previously known chromyl halides, and the OCrO angle in CrO_2Br_2 is estimated to be *ca.* 107° from chromium isotope data.

Acknowledgements

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