Formation of Molecular Chromium(IV) Oxide (CrO_2) by Photolysis of $Cr(CO)_6$ in O_2-doped Argon Matrices

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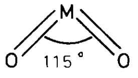
The binary chromium oxide, CrO_2, is produced upon prolonged broad-band u.v.–visible irradiation of $Cr(CO)_6$ isolated in O_2-doped argon matrices at *ca.* 12 K. Infrared spectroscopic studies involving isotopic substitution with ^{18}O show that CrO_2 is a non-linear dioxo molecule with an upper limit for the O–Cr–O bond angle of 117 ± 3°. Measurements of the intensities of the infrared absorptions arising from the symmetric and antisymmetric CrO_2 stretches of this molecule give a value for O–Cr–O of 112 ± 2°, confirming the non-linear structure.

Chromium dioxide, CrO_2, is an intermediate in the decomposition of CrO_3 to Cr_2O_3. It has metallic conductivity and its ferromagnetic properties lead to its commercial use in the manufacture of magnetic recording tapes. Although the solid material has been the subject of some study,[1] the structure of molecular CrO_2 has remained uncertain. Matrix isolation studies have revealed that the corresponding molecules MoO_2[2] and WO_2[3] are both non-linear dioxo species (**I**) with the O–M–O bond angles close to 115°.



(**I**)

There have been a number of reports of matrix-isolated CrO_2, though the findings have not been consistent. These experiments are summarised in Table 1, where it can be seen that two main routes to matrix-isolated CrO_2 exist; one being sputtering of Cr atoms and co-condensation with O_2–Ar mixtures,[4,5] and the other involving photo-oxidation of $Cr(CO)_6$ in matrices containing O_2[6-8] or CO_2.[9] However, none of these methods generates CrO_2 free of other molecules. The photo-oxidation reactions involve CO and CO_2,[6-8] while the sputtering method uses excess of O_2 and involves the possibility of perturbation by Cr atoms. With these results in mind, we have carried out experiments to produce and characterise the molecule CrO_2 by photolysing $Cr(CO)_6$ in O_2-doped argon matrices. In this way we hoped to carry out a more thorough study of CrO_2 than had been made previously, to determine the bond angle of the molecule, and also to assess the perturbing effect of other molecules on CrO_2. For example, does O_2 co-ordinate to CrO_2 in a manner similar to its co-ordination to WO_2 forming the molecule $WO_2(O_2)$?[8]

Experimental

The cryogenic equipment used at Reading for these experiments was as follows. An Air Products 202 OSP 'Displex' closed-cycle helium refrigerator was used to cool a caesium iodide window, on which matrices were deposited, to about 12 K. This window was mounted on the cold tip of the refrigerator inside a shroud maintained at a pressure below 5×10^{-7} Torr by an Edwards model EO2 air-cooled oil-vapour diffusion pump, backed by an Edwards ED 100 oil-sealed rotary pump. Indium gaskets were used to provide good thermal contact between the caesium iodide window and the cold tip of the refrigerator. Mixtures were prepared on a vacuum line using standard manometric techniques and were deposited onto the cold window by pulsed deposition.

The photolysis source was an Applied Photophysics 150-W high-pressure xenon lamp. Spectra were recorded on a Perkin-Elmer model 983 infrared spectrometer, and were calibrated using the rotational lines of ammonia vapour. The position of an i.r. absorption was measured with a typical resolution and accuracy of ± 0.2 cm^{-1}. $Cr(CO)_6$ (98% pure) was supplied by Ventron Alfa products, and was used without further purification. Argon (99.999% pure) and oxygen (99.999% pure) were used as supplied by Argo International Ltd. $^{18}O_2$ (99.4 atom % ^{18}O) was used as received from Amersham International, while a scrambled mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$, containing the isotopomers in roughly a 1:2:1 ratio, was used as supplied by Merk, Sharp, and Dohm.

Force-constant calculations were carried out using the Asym 20 program of Professor I. M. Mills on the Amdahl computer of the University of Reading.

Results and Discussion

Formation of CrO_2.—Our experiments have shown that broad-band u.v.–visible irradiation of an argon matrix, initially

Table 1. Summary of the results of experiments involving infrared spectroscopic detection of matrix-isolated CrO_2

Method of production	$\nu_{asym}(Cr^{16}O_2)$/cm^{-1}	ρ^a	θ^b/°	Ref.
Sputtering Cr atoms; condensation with O_2–Ar mixtures	978	1.15	105	4
Sputtering Cr atoms; condensation with O_2–Ar mixtures	971^c			5
Photo-oxidation of $Cr(CO)_6$ by O_2 in Ar matrices	971^c			7
Photo-oxidation of $Cr(CO)_6$ by O_2 in Ar matrices	971			8
Photo-oxidation of $Cr(CO)_6$ by CO_2 in Ar matrices	964	0.75	108	9
Photo-oxidation of $Cr(CO)_6$ by O_2 in Ar matrices	969.8	0.25	112	This work

^{a} ρ = Asymmetry parameter (see text). ^{b} θ = O–Cr–O bond angle. ^{c} The bands listed for these experiments were not assigned, but are likely to belong to CrO_2.

Table 2. List of frequencies of i.r. absorptions seen during the photo-oxidation of $Cr(CO)_6$ in an O_2-doped Ar matrix, and their behaviour on prolonged photolysis

ν/cm^{-1} [a]	Intensity after 30 min photolysis [b]	Change in intensity after 275 min photolysis [c]	Assignment
2 340	sm	inc.	CO_2 [d]
2 140	sm	inc.	CO [e]
2 125	m	dec.	$CrO_2(CO)_2$ [f]
2 063	m	dec.	$CrO_2(CO)_2$ [f]
2 054	w	dis.	$CrO_2(CO)_3$ [g]
2 025	wm	dis.	$Cr(CO)_4(O_2)$ [g]
1 986	s	dis.	$Cr(CO)_6$ [h]
1 969/1 962 [d]	wm	dis.	$Ar \cdots Cr(CO)_5$ [h]
1 934	wm	dis.	$Ar \cdots Cr(CO)_5$ [h]
996	w	dis.	$Cr(CO)_4(O_2)$ [g]
984	wm	dec.	$CrO_2(CO)_2$ [f]
969	m	inc.	CrO_2 [i]
960	wm	inc.	CrO_2 [i]
944	wm	dec.	unassigned
929	w	dec.	unassigned
660	m	dis.	$Cr(CO)_6$ [h]
654	m	inc.	CO_2 [j]
450	m	dis.	$Cr(CO)_6$ [h]

[a] ±1 cm^{-1}. [b] s = Strong, m = medium, w = weak. [c] inc. = Increases, dec. = decreases, dis. = disappears. [d] Matrix-split mode. [e] Ref. 11. [f] Ref. 7. [g] Ref. 6. [h] Ref. 10. [i] This work. [j] Ref. 12.

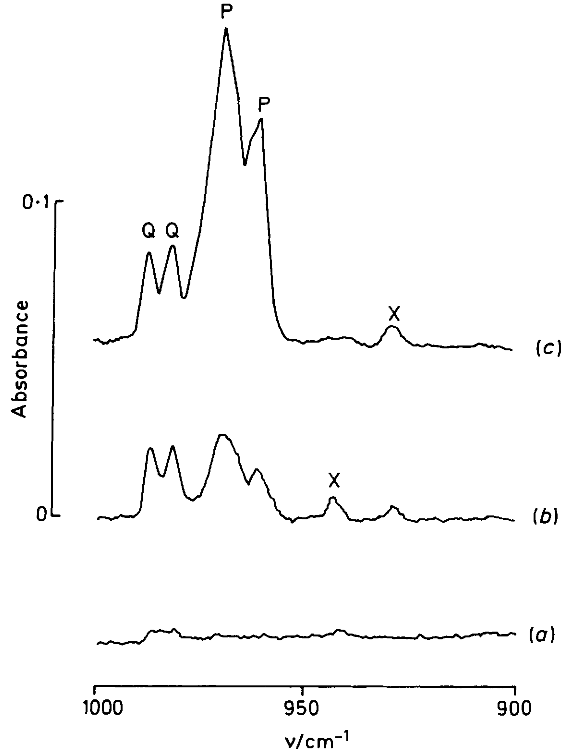


Figure 1. Infrared absorption spectra of a matrix initially containing $Cr(CO)_6$, O_2, and Ar in the approximate proportions 1:100:2000. (*a*) After deposition at 12 K. (*b*) After broad-band u.v.–visible photolysis for 30 min. (*c*) After broad-band u.v.–visible photolysis for 120 min. Bands marked P are assigned to CrO_2, those marked Q to $CrO_2(CO)_2$, and those marked X are unassigned

containing O_2 and $Cr(CO)_6$ in the approximate proportions $Ar:O_2:Cr(CO)_6 = 2000:100:1$, yields $Ar \cdots Cr(CO)_5$ and free CO, as reported previously.[10] Continued photolysis generates a number of intermediates having both CO and oxygen co-ordinated to the chromium metal centre. These intermediates have already been the subject of some study.[6–8] The first oxo–carbonyl intermediate to be detected is the peroxo complex $Cr(CO)_4(\eta^2\text{-}O_2)$.[6] This is highly photolabile, and disappears after *ca.* 30 min photolysis to yield, amongst other things, the well characterised molecule 'chromyl carbonyl,' $CrO_2(CO)_2$,[7] which is reasonably stable under the conditions of our experiments, and persists in low concentrations even after 275 min of broad-band photolysis. Ultimately, however, all co-ordinated carbonyl groups are lost from the chromium metal centre yielding binary chromium oxides alongside free CO[11] and CO_2.[12] This is shown by the disappearance of i.r. absorptions in the region of the spectrum associated with ν(C–O) stretching fundamentals of co-ordinated carbonyl groups[13] and the growth of new bands in the region of the spectrum associated with M=O or O–O stretching fundamentals [see, for example, the values quoted for the wavenumbers of ν(O–O) and ν(M=O) stretching vibrations in Table 3 of ref. 7].

This paper describes the characterisation of the major binary oxide product by infrared spectroscopy and isotopic substitution with ^{18}O. The changes observed in the i.r. spectrum during progressive broad-band photolysis are illustrated in Figure 1, while Table 2 lists the frequencies of all i.r. bands observed during the reaction.

Spectrum of CrO_2.—Figure 2 illustrates the ν(Cr=O) region of the i.r. spectrum of the products generated by prolonged broad-band photolysis of $Cr(CO)_6$ in Ar matrices doped with different isotopomers of O_2. Spectrum (*a*) shows that when $^{16}O_2$ is the matrix dopant, the principal features in this region of the spectrum are absorptions at 969.8 and 960.2 cm^{-1}. These lie close in energy to the absorptions at 971 and 964 cm^{-1} observed by Poliakoff *et al.*[7] on photolysis of $Cr(CO)_6$ in O_2-doped argon matrices and assigned by them to a product containing no co-ordinated CO groups. Moreover, the more intense high-frequency absorption lies close in energy to the i.r. absorption at 971.5 cm^{-1} observed by Ogden and co-workers[5] on co-condensation of Cr vapour with O_2–Ar mixtures. In our experiments there is also a weak i.r. absorption at 944.0 cm^{-1} [see Figure 2 (*a*)]. This is likely to correspond to the weak i.r. absorption at 939.5 cm^{-1} reported by Ogden and co-workers, which also appeared on co-condensation of Cr vapour with O_2–

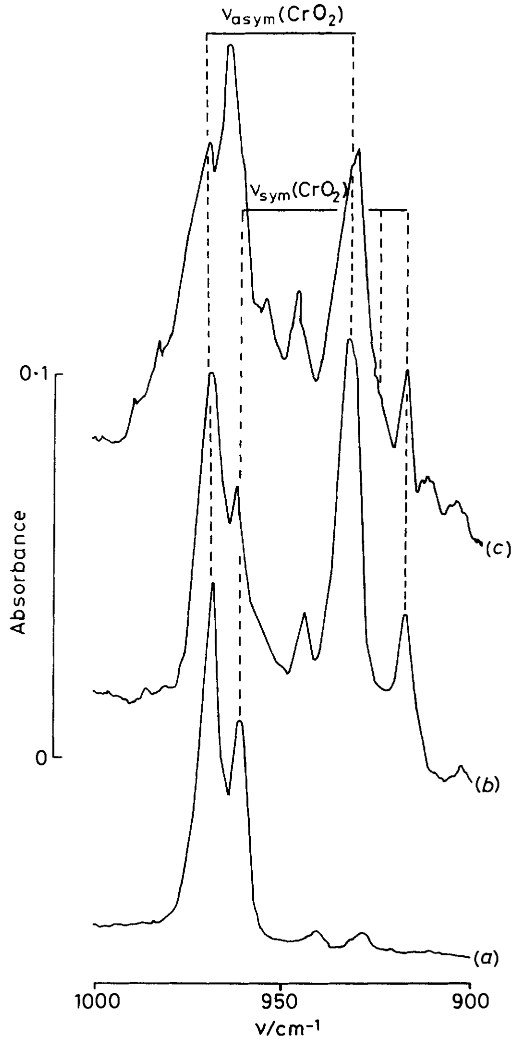


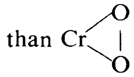
Figure 2. Infrared absorption spectra of argon matrices, at 12 K, initially containing $Cr(CO)_6$ and various isotopomers of O_2. (*a*) Matrix initially contained $Cr(CO)_6$, $^{16}O_2$, and Ar in the approximate proportions 1:100:2000. (*b*) Matrix initially contained $Cr(CO)_6$, $^{16}O_2$, $^{18}O_2$, and Ar in the approximate proportions 1:50:50:2000. (*c*) Matrix initially contained $Cr(CO)_6$, $^{16}O_2$, $^{16}O^{18}O$, $^{18}O_2$, and Ar in the approximate proportions 1:25:50:25:2000. Each matrix has been subjected to 275 min broad-band u.v.–visible photolysis

Ar mixtures. In addition to these bands we also observe a very weak absorption at 929.0 cm⁻¹. In order to determine which, if any, of these absorptions arise from the same molecule we carried out studies involving doping the matrix with varying amounts of $Cr(CO)_6$ or O_2, and photolysing the matrix for different periods of time. These studies showed that the bands at 969.8 and 960.2 cm⁻¹ could be assigned to the same molecule, since the ratio of their intensities always remained constant at $I_{969.8}:I_{960.2} = 2.6:1$ in all experiments. Furthermore, if the matrix was annealed to 38 K for 10 min the relative intensities of the bands at 969.8 and 960.2 cm⁻¹ remained the same. This suggests that they arise from two distinct vibrational modes of the same molecule, rather than a matrix splitting of one mode. However, the two weak bands at 944.0 and 929.0 cm⁻¹ showed intensities which did not parallel those of the more intense features at 969.8 and 960.2 cm⁻¹ (see Figure 1). Indeed in some experiments, either one or both of these weak features could not be detected. Thus they can be assigned to other minor products of the reaction.

One possible assignment of the bands at 969.8 and 960.2 cm⁻¹ is that the more intense high-frequency absorption arises from the antisymmetric stretch of a bent O=Cr=O molecule, while the less intense low-frequency absorption arises from the symmetric stretch of the same molecule. In order to confirm this we have studied the spectra of the product containing ^{18}O [Figure 2, spectra (*b*) and (*c*)]. Spectrum 2(*b*) shows that when a mixture of $^{16}O_2$ and $^{18}O_2$ replaces pure $^{16}O_2$ as the matrix dopant, the bands at 969.8 and 960.2 cm⁻¹ are replaced by a pair of doublets at 969.8 and 960.2 and 931.8 and 915.5 cm⁻¹ each with an intensity ratio of *ca.* 2.6:1. This is the pattern expected for O=Cr=O if *both* the oxygen atoms have been derived from the same oxygen molecule, so that the only isotopomers present are $Cr^{16}O_2$ and $Cr^{18}O_2$. In all of the intermediate dioxo species produced by photolysis of $Cr(CO)_6$ in O_2-doped matrices it has been shown that both of the oxygen atoms are always derived from the same oxygen molecule.[6–8] So this result is entirely consistent with earlier findings.

The absorptions at 969.8 and 960.2 cm⁻¹ occur in the region of the i.r. spectrum associated not only with ν(Cr=O) modes but also with ν(O–O) modes of η^2-co-ordinated O_2 groups (peroxo ligands) attached to a metal centre (see Table 3 of ref. 7). However, in the latter case the O_2 unit would be expected to behave largely as an O_2 molecule uncoupled to the Cr atom and thus the shift in frequency on $^{18}O_2$ substitution would be expected to follow approximately equation (1),[14] where *m* is

$$\nu(^{16}O_2/^{18}O_2) = [m(^{18}O)/m(^{16}O)]^{\frac{1}{2}} \qquad (1)$$

the relative atomic mass of the oxygen isotope. On this model the absorptions at 969.8 and 960.2 cm⁻¹ would be expected to shift to 914.3 and 905.3 cm⁻¹ respectively. These shifts are much larger than the shifts we observe. This is persuasive evidence that the product contains Cr=O rather than  moieties.

Spectrum 2(*c*) shows that when a scrambled mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in the approximate proportions 1:2:1 is the matrix dopant a highly complicated pattern of bands is seen in place of the pair of bands when pure $^{16}O_2$ is the matrix dopant. This spectrum is not entirely easy to interpret. However, some features can be identified. It is clear that the absorption corresponding to $\nu_{asym}(Cr^{16}O^{18}O)$ is asymmetrically disposed between the $\nu_{asym}(Cr^{16}O_2)$ and $\nu_{asym}(Cr^{18}O_2)$ bands. A useful measure of the asymmetry of the $^{16}O_2$–$^{16}O^{18}O$–$^{18}O_2$ band pattern is the asymmetry parameter ρ, defined by equation (2).

$$\rho = \frac{2[\nu(^{16}O_2) - \nu(^{16}O^{18}O)]}{[\nu(^{16}O_2) - \nu(^{18}O_2)]} \qquad (2)$$

A symmetrical band pattern has ρ = 1.0. For CrO_2, it can be calculated that for ν_{asym}, ρ = 0.25. It is expected that $\nu_{sym}(Cr^{16}O^{18}O)$ would occur near to 922 cm⁻¹. Although a weak shoulder, close in energy to this value can be seen in Figure 2(*c*), the assignment of this band remains tentative. It is possible that it is wholly or partially obscured by the broad feature centred at 931.8 cm⁻¹ corresponding to $\nu_{asym}(Cr^{18}O_2)$. The highly unsymmetrical pattern reflects the fact that ν_{sym} and ν_{asym} lie close in energy for the molecule CrO_2. It should be noted that for CrO_2, $\rho(\nu_{asym})$ is less than 1, whereas $\rho(\nu_{sym})$ is greater than 1. This is expected when $\nu_{asym} > \nu_{sym}$ (as in the case of CrO_2) since the two stretching vibrations of $Cr^{16}O^{18}O$ move apart in energy when coupling occurs. Table 3 lists observed and calculated frequencies for the three isotopomers, $Cr^{16}O_2$, $Cr^{16}O^{18}O$, and $Cr^{18}O_2$.

There are also some weak features present in Figures 2(*b*) and 2(*c*) between 945 and 950 cm⁻¹. These appear not to belong to CrO_2, since their growth and decay characteristics are different from those of the bands of CrO_2. There is, however, no sign of

Table 3. Observed and calculated frequencies for the symmetric and antisymmetric stretching vibrations of the molecules $Cr^{16}O_2$, $Cr^{16}O^{18}O$, and $Cr^{18}O_2$

Mode	Isotopomer	$\nu_{obs.}$/ cm^{-1} [a]	$\nu_{calc.}$/ cm^{-1} [b]	$\nu_{obs.} - \nu_{calc.}$/ cm^{-1}
$\nu_{asym.}$	$Cr^{16}O_2$	969.8	970.0	−0.2
	$Cr^{16}O^{18}O$	965.0	965.9	+0.9
	$Cr^{18}O_2$	931.8	931.3	+0.5
$\nu_{sym.}$	$Cr^{16}O_2$	960.2	959.9	+0.3
	$Cr^{16}O^{18}O$	*ca.* 923 [c]	922.0	*ca.* +1.0
	$Cr^{18}O_2$	915.5	914.7	+0.8

[a] $\nu_{obs.}$ ±0.2 cm^{-1}. [b] $\nu_{calc.}$ Using an O–Cr–O bond angle of 112°, *f*(Cr=O) = 673.0, and *f*′(Cr=O, Cr=O) = 50.0 N m^{-1}. Five observed frequencies were entered into the refinement calculation, and five cycles of the refinement were used. [c] The assignment of the shoulder near 923 cm^{-1} to ν_{sym} of $Cr^{16}O^{18}O$ is tentative, and this value was not used in the refinement calculation. However, the observed frequency of 923 cm^{-1} is close to the calculated value of 922 cm^{-1} for the frequency of this mode.

any band corresponding to a molecule $CrO_2(O_2)$, analogous to the molecule $WO_2(O_2)$ which has been produced by photolysis of $W(CO)_6$ in O_2-doped matrices.[8]

From the frequencies of the absorptions of the different isotopomers of CrO_2 it is possible to calculate a value of the O–Cr–O bond angle (θ) of CrO_2. The $\nu_{asym}(Cr^{16}O_2):\nu_{asym}(Cr^{18}O_2)$ ratio gives an upper limit[15,16] of $\theta < 117 \pm 3°$. The intensity ratio of ν_{sym} and ν_{asym} provides an alternative route to θ,[17] and from this ratio of 1:2:6 a value of $\theta = 112 \pm 2°$ may be calculated. Thus CrO_2 is shown to have a bond angle close to 112°, since a consideration of anharmonicity suggests that the upper limit of 117 ± 3°, calculated from the $^{16}O/^{18}O$ shift of ν_{asym} should be lowered by about 4—5 cm^{-1}.[18]

Formation of CrO_2 *in Different Matrices.*—In order to assess the degree of perturbation of CrO_2 by O_2, CO, and the matrix host material, argon, experiments were carried out in which CrO_2 was generated by 240 min broad-band u.v.–visible photolysis of $Cr(CO)_6$ in the following matrices: (*i*) 5% O_2-doped Ar; (*ii*) 10% O_2-doped Ar; (*iii*) 16% O_2-doped Ar; (*iv*) 10% O_2-doped CO, and (*v*) 10% O_2-doped CH_4. In each case the ratio of $Cr(CO)_6$ to overall matrix material was 1:2000. In O_2-doped argon matrices two bands were observed at 969.8 and 960.2 cm^{-1} in approximately a 2.6:1 intensity ratio, and this pattern of bands was not changed when the concentration of O_2 in the matrix was increased from 5%, through 10%, to 16%. Nor were any new bands observed in matrices containing 10 or 16% O_2. In 10% O_2-doped CO matrices two bands were observed at 968.2 and 960.4 cm^{-1} in approximately a 2.4:1 intensity ratio. Similarly, in a 10% O_2-doped methane matrix two bands at 967.0 and 959.7 cm^{-1}, with an intensity ratio close to 2.6:1 were seen. No new absorptions were seen in the ν(Cr=O) region of the spectrum at this stage of photolysis in O_2-doped CO or CH_4 matrices. These spectra are illustrated in Figure 3. Thus it is concluded that the CrO_2 molecule is little perturbed by O_2 or CO and its spectrum is only slightly altered by moving from argon to methane matrices. Certainly, there is no sign of a molecule $CrO_2(O_2)$, analogous to the molecule $WO_2(O_2)$ formed when $W(CO)_6$ is photolysed in an O_2-doped argon matrix.[8] Neither is there any sign, after 240 min broad-band u.v.–visible photolysis of the formation of CrO_3 in any of the matrices studied, nor of oxidation of the methane matrix to methanol or formaldehyde. By contrast, when $W(CO)_6$ is subjected to 150 min broad-band u.v.–visible photolysis in O_2-doped methane matrices, WO_3 is seen as a photoproduct and the formation of WO_3 is accompanied by oxidation of the methane matrix to methanol and formaldehyde.[8]

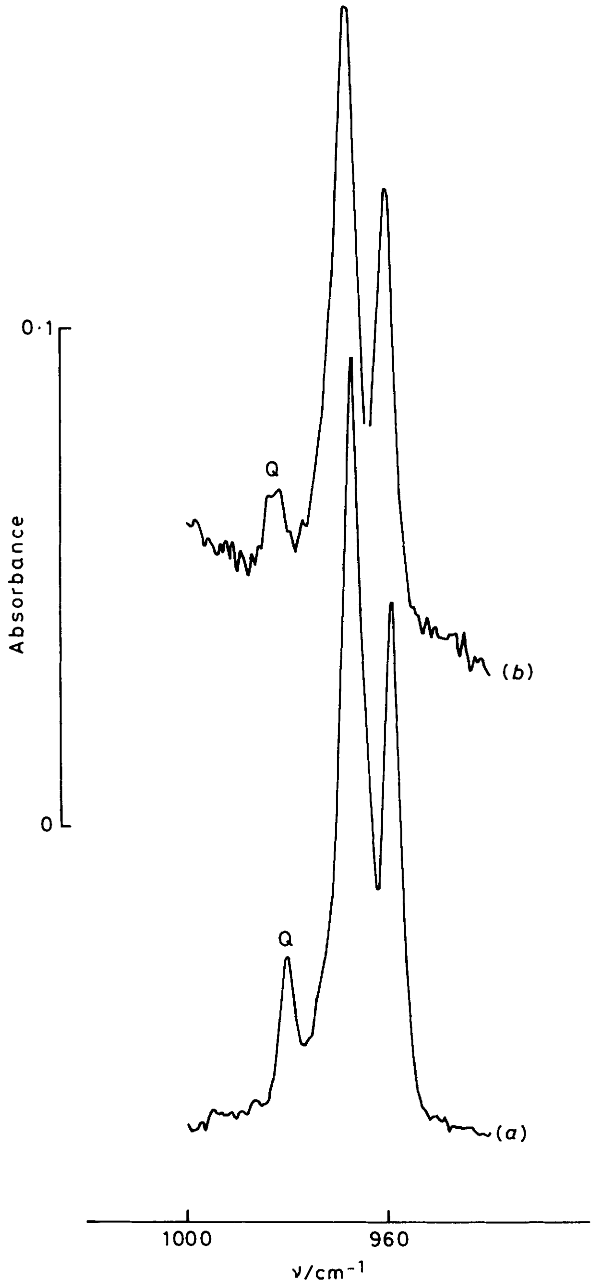


Figure 3. Infrared absorption spectra of matrices, at 12 K, after 240 min broad-band u.v.–visible photolysis. (*a*) Matrix initially contained $Cr(CO)_6$, $^{16}O_2$, and CH_4 in the approximate proportions 1:200:2000. (*b*) Matrix initially contained $Cr(CO)_6$, $^{16}O_2$, and CO in the approximate proportions 1:200:2000. The band marked Q in each case is assigned to the molecule $CrO_2(CO)_2$

Comparison of CrO_2 *with* MoO_2 *and* WO_2.—The molecules MoO_2[2] and WO_2[3] have been previously studied in inert-gas matrices by i.r. spectroscopy. MoO_2 was produced by passing O_2 over molybdenum heated to between 1 700 and 2 200 °C, and was trapped in argon or neon matrices.[2] The i.r. spectrum of MoO_2 isolated in solid neon shows an unresolved band at 948 cm^{-1}, which is assigned to the symmetric stretch (ν_1). In addition there is a second band which shows molybdenum

Table 4. A comparison of the frequencies of the symmetric and antisymmetric stretching vibrations, the O–M–O bond angles, and the stretching force constants of MO_2 molecules (M=Cr, Mo, or W) isolated in low-temperature matrices

	$^{52}Cr^{16}O_2$ [a]	$^{98}Mo^{16}O_2$ [b]	$^{184}W^{16}O_2$ [c]
ν_1/cm^{-1}	960.2	948.0	975.53
ν_3/cm^{-1}	969.8	899.3	937.23
θ/°	112 ± 2	116 ± 3	114 ± 3
f(M=O)/N m^{-1}	673	701	796
f'(M=O, M=O)/N m^{-1}	50.0	86.5	58.1

[a] This work; ±0.2 cm^{-1}. [b] Ref. 2. [c] Ref. 3.

isotope structure, centred around 900 cm^{-1}, which is assigned to the antisymmetric stretch (ν_3). The ^{16}O–^{18}O isotopic shift of the band corresponding to ν_3 allows a value of $\theta_u = 118.9°$ to be calculated, and a consideration of anharmonicity[18] of similar ABA molecules suggests that this value should be lowered to give a true value of θ of about 116°.

A mixture of tungsten oxides containing, amongst others, WO_2 has been trapped in matrices by sputtering a tungsten cathode in a gas mixture of O_2 and a large excess of argon or krypton, and condensing the products at 14 K. The isotopomer $^{184}W^{16}O_2$ isolated in krypton shows ν_1 at 975.53 and ν_3 at 937.23 cm^{-1}. For this molecule a value of $\theta_u = 119.4 \pm 0.5°$ is calculated, while anharmonicity corrections suggest a true value for θ of 114 ± 3°.

Table 4 lists the observed wavenumbers of ν_1 and ν_3 for the $M^{16}O_2$ molecules (M = Cr, Mo, or W). It also lists the calculated O–M–O bond angles (θ) and the stretching force constants f(M=O) and f'(M=O, M=O). From this table several interesting comparisons can be made. First, it can be seen that for CrO_2, $\nu_3 > \nu_1$, whereas for MoO_2 and WO_2, $\nu_1 > \nu_3$. This follows, since for the three molecules the antisymmetric, ν_3, vibration involves more motion of the metal than the symmetric, ν_1, vibration and chromium is the least heavy of the three metals. This observation is in line with previous measurements of ν_{sym} and ν_{asym} for the MO_2 units of related molecules, *e.g.* CrO_2Cl_2, where $\nu_{asym} > \nu_{sym}$[19] and MoO_2Cl_2[20] and WO_2Cl_2,[20] where $\nu_{sym} > \nu_{asym}$. Secondly, the stretching force constant f(M=O) shows an increase from 673 N m^{-1} for CrO_2, through 701 N m^{-1} for MoO_2[2] to 796 N m^{-1} for WO_2.[3] This reflects the increasing strength of M=O bonds on descending a group of transition metals and is a trend reflected by other similar molecules. For example, the oxofluoride molecules MOF_4 (M = Cr, Mo, or W) show i.r. absorptions corresponding to the ν(M=O) stretch at 1 027.7 cm^{-1} (M=Cr),[21] at 1 045 cm^{-1} (M=Mo),[22] and at 1 053 cm^{-1} (M=W)[22] (all spectra being recorded for the molecules isolated in an argon matrix). Allowing for the mass difference between Cr, Mo, and W these values indicate an increase in the f(M=O) stretching force constant as the group is descended. The interaction force constant f'(M=O, M=O) shows a less clear trend. The values for CrO_2 and WO_2 are similar, while that for MoO_2 is somewhat higher.

Finally, the bond angles for CrO_2, MoO_2, and WO_2 are very similar, all around 114°. This similarity is reflected by other dioxo molecules of Cr, Mo, and W, *e.g.* CrO_2Cl_2 (O–Cr–O = 108°),[23] MoO_2Cl_2 (O–Mo–O = 109°),[20] and WO_2Cl_2 (O–W–O = 107°).[20]

Comparison of CrO_2 *with* $CrO_2(CO)_2$ *and* CrO_2F_2.—It is interesting to compare the spectroscopic properties of CrO_2 with the dioxochromium molecules $CrO_2(CO)_2$[8] and CrO_2F_2,[24] both of which have been studied in argon matrices by infrared spectroscopy. CrO_2F_2 molecules isolated in an argon matrix show ν_1 (the symmetric CrO_2 stretch) at 1 006.7 cm^{-1} and ν_6 (the antisymmetric CrO_2 stretch) at 1 013.9 cm^{-1}.[24] This situation, where ν_{asym} is greater than ν_{sym} by *ca.* 7 cm^{-1}, closely parallels that observed for CrO_2 where $\nu_{asym} > \nu_{sym}$ by *ca.* 9 cm^{-1}. The frequencies of ν_{sym} and ν_{asym} in CrO_2F_2 are greater than those of CrO_2 by some 45 cm^{-1}. This is presumably because Cr is in a formal oxidation state of +6 in CrO_2F_2, as opposed to +4 in CrO_2, so the Cr=O bonds are expected to be rather stronger in CrO_2F_2. This follows the trend seen for the molecules MoO_2[2] and MoO_2Cl_2[23] and WO_2[3] and WO_2Cl_2[23] where the M=O stretching vibrations occur at higher frequency when the metal is in the higher oxidation state.

For $CrO_2(CO)_2$ only one ν(Cr=O) mode (the antisymmetric stretch) is observed. This is seen as a matrix-split doublet at 988, 981 cm^{-1}, about 15 cm^{-1} higher than the ν_3 mode of CrO_2. Although the absorption corresponding to $\nu_{sym}(CrO_2)$ of $CrO_2(CO)_2$ was not observed, the asymmetry parameter, ρ [equation (2)] of the three bands corresponding to $\nu_{asym}(CrO_2)$ of the molecules $Cr^{16}O_2(CO)_2$, $Cr^{16}O^{18}O(CO)_2$, and $Cr^{18}O_2(CO)_2$ has been calculated as $\rho = 0.38$,[7] similar to the value of $\rho = 0.25$ we calculate for ν_{asym} of CrO_2. This implies that $\nu_{sym}(CrO_2)$ of $CrO_2(CO)_2$ lies slightly to high energy of $\nu_{asym}(CrO_2)$ for the same molecule, while the highly asymmetric pattern suggests that $\nu_{sym}(CrO_2)$ and $\nu_{asym}(CrO_2)$ are close in energy for $CrO_2(CO)_2$, as they are in CrO_2.

Conclusions

The results described in this paper provide considerable evidence that the ultimate product of photolysis of $Cr(CO)_6$ in O_2-doped argon matrices is the non-linear dioxide molecule CrO_2. A comparison of the positions of the i.r. absorptions of this product in our experiments, with i.r. bands observed for CrO_2 in other experiments (Table 1) shows that there are some slight differences in frequency. For example, the i.r. spectrum observed for CrO_2 produced by photo-oxidation of $Cr(CO)_6$ by O_2 (this work) shows slight differences from the i.r. spectrum of CrO_2 produced by photolysis of $Cr(CO)_6$ in CO_2-doped argon matrices.[9] These changes are most probably caused by differences in matrix environment.

Serebrennikov and Mal'tsev[4] carried out a study of the co-condensation of Cr atoms with O_2 and cite values of ν_{asym} 978,955, and 938 cm^{-1} for the molecules $Cr^{16}O_2$, $Cr^{16}O^{18}O$, and $Cr^{18}O_2$ respectively. The wavenumbers of these vibrations differ from the corresponding values observed for CrO_2 in our experiments by *ca.* ±8 cm^{-1}. Although the ^{16}O–^{18}O shift of 40 cm^{-1} reported by them for ν_{asym} of the C_{2v} molecules $Cr^{16}O_2$ and $Cr^{18}O_2$ is similar to the value of 38.0 cm^{-1} which we find, the asymmetry parameter, ρ [equation (2)] of the three bands assigned to $\nu_{asym}(CrO_2)$ of the molecules $Cr^{16}O_2$, $Cr^{16}O^{18}O$, and $Cr^{18}O_2$ is rather different in the two sets of experiments. We obtain a value of $\rho = 0.25$ which fits our observation that $\nu_{asym} > \nu_{sym}$. However, the wavenumber values cited by Serebrennikov and Mal'tsev give rise to a value of $\rho = 1.15$, which would imply that $\nu_{sym} > \nu_{asym}$. Not only is this contrary to our observations, but it is also in conflict with results for other similar molecules, *e.g.* CrO_2F_2[24] and $CrO_2(CO)_2$.[7]

It appears likely that the molecule CrO_2 is, to some extent, affected by the presence of other species in the matrix, *e.g.* O_2, CO, CO_2, or, in the case of sputtering experiments, Cr atoms. However, our work has shown that the change in frequency of the i.r. bands of $Cr^{16}O_2$, produced under identical photolysis conditions in O_2-doped argon, O_2-doped CO, or O_2-doped methane matrices, is quite small (±2 cm^{-1}).

The formation of CrO_2 as the final product of the photo-oxidation of $Cr(CO)_6$ in O_2-doped argon matrices can be compared with the production of metal oxides on the photo-oxidation of $Mo(CO)_6$ and $W(CO)_6$ in O_2-doped matrices.[6,8]

In the case of $Mo(CO)_6$, MoO_2 is seen as a product alongside MoO_3.[6,8] Prolonged broad-band photolysis causes the conversion of MoO_2 to MoO_3. In contrast WO_2 is not seen as a product when $W(CO)_6$ is photo-oxidised.[8] Rather WO_3 is the final product and this is formed from the molecule $WO_2(O_2)$[8] where the tungsten metal centre is in a formal oxidation state of +6. In our experiments there is no sign of further oxidation of CrO_2 to CrO_3. Although these differences in behaviour may result solely from differences in absorption characteristics of the oxide molecules involved, they appear to reflect the increased ease with which the +6 oxidation state is attained as the group is descended.

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