'Chromyl Carbonyl'. Synthesis of $[CrO_2(CO)_2]$ † in Low-temperature Matrices

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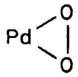
Photolysis of $[Cr(CO)_6]$ in O_2-doped Ar matrices at low temperatures produces, *inter alia*, a species which contains both CO and O_2. Experiments with ^{13}CO-enriched $[Cr(CO)_6]$ and with matrices doped with $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ show that this species contains two CO groups and two oxygen atoms double-bonded to the metal. This structure is thus 'chromyl carbonyl' and further evidence for this comes from the photochemical generation of the species from chromyl chloride in solid CO. The generation of CO and CO_2 during the carbonyl photolysis suggests a possible mechanism involving oxidation of CO to CO_2 on the metal centre.

THE technique of matrix isolation has been much exploited for the generation and characterization of molecular metal oxides and these experiments have provided examples of four different modes of M–O_2 bonding. When alkali metals are co-condensed with O_2 or O_2/Ar mixtures the principal product[1] is $M^+O_2^-$ but when O_2 is passed over heated molybdenum,[2] O=Mo=O (angle OMoO *ca.* 118°) is produced, together with several higher oxides. Co-condensation of palladium atoms and O_2 generates PdO_2 and $Pd(O_2)_2$ with sideways-bonded dioxygen,[3] the frequency pattern of the i.r. bands supporting a triangular structure (below), while it has been suggested that similar experiments[4] with chromium produce $Cr(O_2)_2$, with end-bonded dioxygen, Cr–O=O.



Some time ago, we showed[5] that photolysis of $[Fe(CO)_5]$ in low-temperature matrices produced $[Fe(CO)_x]$ ($x = 4$, 3, and 2) and eventually Fe atoms. More recently we have used this method[6] to generate Fe atoms in the presence of O_2, forming FeO_2. This route to metal oxides overcomes some of the disadvantages of the co-condensation method. These experiments, and related ones with $[Cr(CO)_6]$, to produce a range of oxides, will be fully reported elsewhere.

Here we describe the results of experiments with $[Cr(CO)_6]$ in Ar matrices doped with O_2. These provide definitive evidence for a mixed carbonyl/oxygen species, $[CrO_2(CO)_2]$, which almost certainly contains the bent O=Cr=O group (as in CrO_2Cl_2) and is the first 'chromyl carbonyl'.

RESULTS AND DISCUSSION

Photolysis of $[Cr(CO)_6]$ *in Solid* O_2.—When $[Cr(CO)_6]$, matrix-isolated in solid O_2 at 20 K (*ca.* 1 : 3 000), is irradiated with a medium pressure Hg arc, striking changes are observed in the i.r. spectrum (not illustrated). The 'parent' $[Cr(CO)_6]$ is rapidly photolysed away and i.r. bands due to CO, CO_2, and O_3 appear. In addition, there are two new bands at 971 and 964 cm^{-1}. A similar band at 971 cm^{-1} was observed by Ogden[4] on co-condensing Cr atoms with O_2 but unfortunately this band was not assigned, since Ogden was more concerned with characterizing $[Cr(O_2)_2]$. However, the two bands are clearly due to a Cr/O_2 species of some sort and it is probable that the doublet represents the 'matrix splitting' of a single vibrational mode, a ubiquitous problem in O_2 matrices.

There was no evidence in our photolysis experiment for any Cr species containing CO groups. Presumably in the presence of such an excess of O_2 the photolysis of $[Cr(CO)_6]$ to form Cr/O_2 species is extremely efficient. In order to increase the chance of observing possible photochemical intermediates we repeated the experiment with $[Cr(CO)_6]$ in Ar/O_2 (95 : 5) matrices.

Photolysis of $[Cr(CO)_6]$ *in* Ar/O_2 (95 : 5).—Prolonged photolysis of $[Cr(CO)_6]$ in an Ar matrix, doped with 5% O_2, produces more i.r. bands than the experiments in O_2 matrices. In the region 1 000—950 cm^{-1}, there are two sharp bands at 988 and 981 cm^{-1}, as well as bands (somewhat matrix-shifted), due to the same Cr/O_2 species, as observed in pure O_2, see Figure 1. In the C–O stretching region there are several bands, apart from $[Cr(CO)_6]$ itself, see Figure 1(*a*) and Table 1. The *two* highest frequency bands in Figure 1(*a*) are due to molecular CO. These two bands arise because the absorption of CO is perturbed if the CO is trapped in the same matrix cage as a molecule of CO_2. This is confirmed by the observation[7] of the *same* doublet in the spectrum of CO isolated in an Ar matrix, doped with CO_2 [see the inset spectrum in Figure 1(*a*)]. There are two

TABLE 1

Photolysis products of $[Cr(CO)_6]$ in Ar/O_2 (95 : 5) matrix

I.r. band $\tilde{\nu}$/cm^{-1}	Assignment
2 144	CO/CO_2 pair
2 141	CO
2 125	ν(C–O) of photolysis product
2 063	ν(C–O) of photolysis product
1 965	$[Cr(CO)_5]$
988	Product *containing* CO
981	Product *containing* CO
971	Product *without* CO
964	Product *without* CO

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† Dicarbonyldioxochromium.

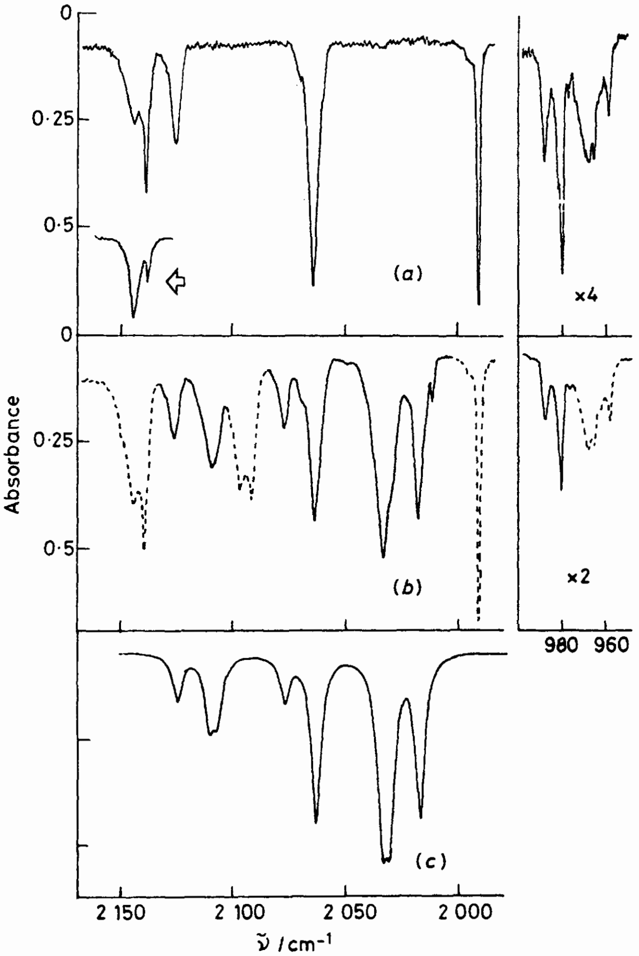

FIGURE 1 (*a*) Infrared spectra in the C–O stretching region and the region 1 000—950 cm^{-1}, following prolonged u.v. photolysis of [Cr(CO)$_6$] in an Ar matrix, doped with 5% O_2 {[Cr(CO)$_6$] : Ar *ca.* 1 : 2 000} at 20 K. Arrowed: i.r. spectrum of CO in an Ar matrix doped with 5% CO_2. (*b*) As for (*a*), except that the [Cr(CO)$_6$] is approximately 50% enriched with ^{13}CO; (——) bands of Cr/CO/O_2 photolytic product, (– – – –) bands due to CO, ^{13}CO, [Cr(CO)$_6$], and Cr/O_2 species. (*c*) Theoretical spectrum of the Cr(CO)$_2$ group with 50% ^{13}CO enrichment; calculated using an energy-factored force field, assuming slight C_s perturbation from C_{2v} and with force constants $k_{CO}(1)$ = 1 766, $k_{CO}(2)$ = 1 776, and k_{CO_1,CO_2} = 51.25 N m^{-1}; computer-drawn with Lorentzian band-shapes of width at half-height of 4 cm^{-1}

bands at 2 125 and 2 063 cm^{-1}, which can be shown, by measuring relative intensities, to be due to a single species which is the same as that responsible for the bands at 988 and 981 cm^{-1}. This species must therefore contain both CO and oxygen groups, but its characterization requires the use of isotopes.*

To establish the number of CO groups, ^{13}CO-enriched [Cr(CO)$_6$] was photolysed in an O_2/Ar matrix. Figure 1(*b*) shows the i.r. spectrum in the C–O stretching region.† The interpretation of this spectrum is straightforward and follows the usual methods.[8] Table 2 lists the positions of the bands, their assignment and force constants, and Figure 1(*c*) shows the predicted spectrum. It is clear from these results that the species contains two CO groups. However, the bands assigned to (O^{12}C)(O^{13}C)Cr/O_2 are broader than those assigned to the (^{12}CO)$_2$ and (^{13}CO)$_2$ analogues. This may be because of a slight vibrational inequivalence in the two CO groups and a rather better fit is obtained by allowing for this (Table 2). The two bands of the (^{12}CO)$_2$ species, 2 125 and 2 063 cm^{-1}, have intensities in the ratio 1 : 2.8. Bond angles between CO groups are readily estimated from such intensity ratios,[9] although the reliability of this method is conjectural. Assuming its validity and an approximate C_{2v} structure for the Cr(CO)$_2$ group, a bond angle (θ) of 118° is estimated from the equation $I(b_2)/I(a_1) = 2.8 = \tan^2(\theta/2)$.

TABLE 2

Infrared spectrum of ^{13}CO-enriched [CrO$_2$(CO)$_2$] in the C–O stretching region (cm^{-1})

Expt.	Calc.[a]	Assignment	
2 125	2 124.01	[CrO$_2$(^{12}CO)$_2$]	$\nu(a_1)$ [b]
ca. 2 110	2 110.1	[CrO$_2$(^{13}CO)(^{12}CO)]	
ca. 2 106	2 106.45	[CrO$_2$(^{12}CO)(^{13}CO)]	
2 076	2 076.66	[CrO$_2$(^{13}CO)$_2$]	
2 063	2 063.12	[CrO$_2$(^{12}CO)$_2$]	$\nu(b_2)$ [b]
ca. 2 034	2 033.95	[CrO$_2$(^{12}CO)(^{13}CO)]	
ca. 2 030	2 030.43	[CrO$_2$(^{13}CO)(^{12}CO)]	
2.016.5	2 017.14	[CrO$_2$(^{13}CO)$_2$]	

[a] Calculated on the assumption of a structure with two carbonyl groups slightly distorted from C_{2v} symmetry, see Figure 1; $k_{CO}(1)$ = 1 766; $k_{CO}(2)$ = 1 776; k_{CO_1,CO_2} = 51.25 N m^{-1}. [b] The a_1 and b_2 notation, of course, only strictly applies to a C_{2v} structure.

The bands in the region 1 000—900 cm^{-1} are weak and the use of $^{16}O_2$/$^{18}O_2$ isotopic mixtures is likely to be made more complicated by the two products absorbing in this region [Figure 1(*a*), Table 1]. Thus it is essential to devise a method of producing the [CrO$_x$(CO)$_2$] species in the virtual absence of the Cr/O_2 product before the oxygen isotope can be used. This was eventually achieved by a series of pulse depositions each followed by u.v. photolysis for *ca.* 5 s. Although the overall photolysis of [Cr(CO)$_6$] was relatively small, very little Cr/O_2 was obtained and, by using multiple scan/computer averaging, it was possible to record excellent spectra in this region [see Figure 2(*a*)]. It is important to know whether the two bands at 988 and 981 cm^{-1} are due to different vibrational modes of [CrO$_x$(CO)$_2$], or are merely a matrix-splitting of a single mode. The bands are almost certainly due to a matrix-splitting, because there is a substantial change in their relative intensities when the matrix is annealed to 38 K, Figure 2(*b*). In fact, the intensity pattern of the pair of bands at 988 and 981 cm^{-1} matches that obtained on prolonged photolysis (Figure 1).

Two experiments are possible with oxygen isotopes. Either an $^{16}O_2$/$^{18}O_2$ mixture or a fully 'scrambled' $^{16}O_2$/$^{16}O^{18}O$/$^{18}O_2$ mixture can be used, and the two experiments provide different information. The results

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* It is striking that the C–O stretching bands of this carbonyl species are much broader than that of [Cr(CO)$_6$]. The reason for this broadness is not known, but it may be caused by the photo-ejected CO or CO_2.

† The region 1 000—900 cm^{-1} is unaffected by ^{13}CO substitution, as can also be seen in Figure 1(*b*).

of the $^{16}O_2/^{18}O_2$ experiment are shown in Figure 3(*c*). It can be seen that $^{18}O_2$ produces only two new bands, at 951 and 944 cm^{-1}, both shifted 37 cm^{-1} from the 988/981 cm^{-1} $^{16}O_2$ doublet, and showing the same change in intensity on annealing.* This shows that [$CrO_x(CO)_2$] cannot contain more than two oxygen atoms (*i.e.*, $x = 1$ or 2). In molecules of the kind O_2PdO_2, O_2CuO_2, and O_2CrO_2 there is sufficient coupling for the $^{16}O_2/^{18}O_2$ unscrambled substitution to produce a complex pattern in this region of the spectrum.

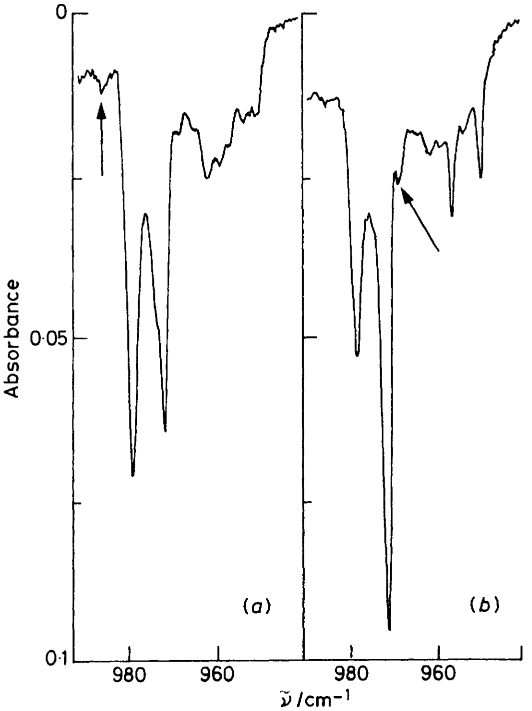


FIGURE 2 (*a*) Infrared spectrum following successive pulse-deposition at 20 K and brief (*ca.* 5 s) u.v. photolysis cycles of [$Cr(CO)_6$] in Ar doped with 5% O_2. (*b*) Spectrum after annealing to 38 K and recooling to 20 K. The arrows indicate weak absorptions possibly due to chromium isotopic pattern (see Table 4)

If the [$CrO_x(CO)_2$] species contained *three* oxygen atoms, then in the reaction with the $^{16}O_2/^{18}O_2$ mixture, the product would contain not only $^{16}O_3$ and $^{18}O_3$ but also ($^{16}O_2{}^{18}O$) and ($^{18}O_2{}^{16}O$) and a peculiar force field would be required if these four species were to give rise to only one pair of bands.

To distinguish between [$CrO(CO)_2$] and [$CrO_2(CO)_2$] requires the use of the mixed isotope $^{16}O^{18}O$ and an experiment with scrambled $^{16}O_2/^{16}O^{18}O/^{18}O_2$ is shown in Figure 3(*b*). It is clear that this experiment produces a *different* pattern from the unscrambled $^{16}O_2/^{18}O_2$ mixture [Figure 3(*c*)]. If the species were [$CrO(CO)_2$], the scrambled and unscrambled mixtures should have produced *identical* spectra. Unfortunately, the bands arising from the $^{16}O^{18}O$ species overlap those due to the $^{16}O_2$ substituted molecule because of the matrix-splitting. Nevertheless, it is clear that the band pattern consists of three pairs of bands [988/981 ($^{16}O_2$), 981/974 ($^{16}O^{18}O$), and 951/944 cm^{-1} ($^{18}O_2$)], and this triplet pattern proves that the molecule contains two *equivalent* oxygen atoms, as in [$CrO_2(CO)_2$]. The positions of the $^{16}O^{18}O$ bands are extremely asymmetric with respect to the $^{16}O_2$ and $^{18}O_2$ bands, and this asymmetry is extremely important in deciding how the O_2 group is bonded to the Cr atom.

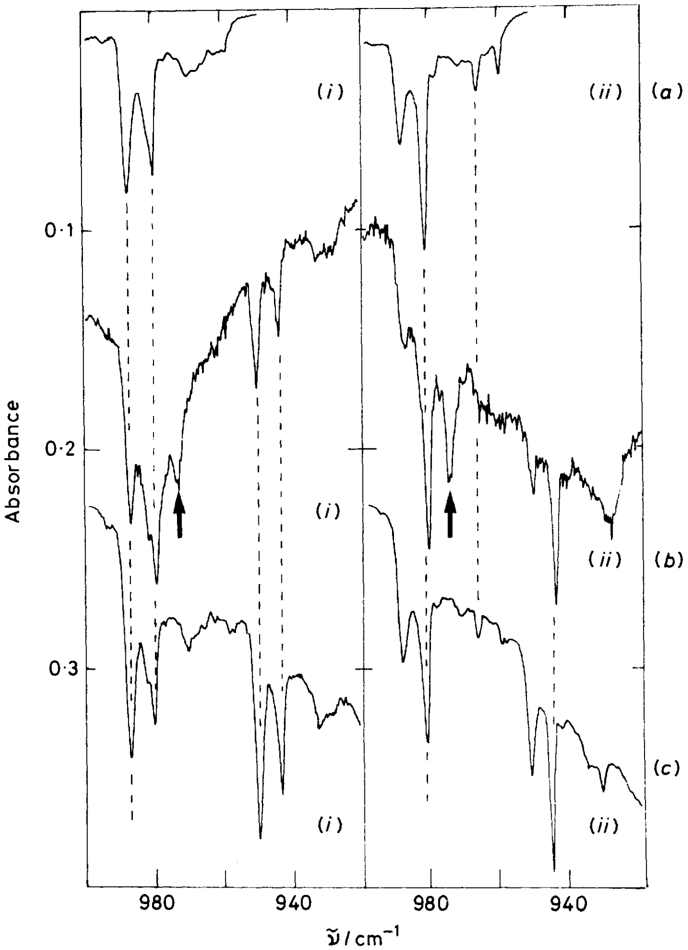
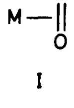


FIGURE 3 (*a*) Infrared spectra, before (*i*) and after (*ii*) annealing, following successive pulse-deposition and brief photolysis cycles of [$Cr(CO)_6$] in Ar doped with 5% $^{16}O_2$ [*i.e.*, same as Figure 2(*a*)]. (*b*) As for (*a*), except Ar doped with $^{16}O_2/^{16}O^{18}O/^{18}O_2$ (*ca.* 1 : 2 : 1). The arrows indicate the position of a new feature due to the use of $^{16}O^{18}O$; the intensity pattern shows that the other, high-frequency component of the expected doublet lies under the band at 981 cm^{-1}. (*c*) As for (*a*), except Ar doped with $^{16}O_2/^{18}O_2$ (*ca.* 1 : 1)

The critical question is the assignment of the 988 and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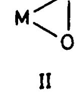
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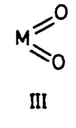
III

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* The fact that the two bands, at 988 and 981 cm^{-1}, show exactly the *same* isotopic shift and the 951/944 bands have the same intensity distribution as the 988/981 pair is strong support for their assignment to a matrix-split band. If the 988/981 bands were due to two different molecules then it is unlikely that such exact matching would occur.

981 cm^{-1} bands. Of the three possible structures, 'sideways' (I), 'triangular' (II), 'dissociated' or 'double-bonded' (III), for the O_2 part of $[CrO_2(CO)_2]$, structure I can be eliminated because the O–O stretching vibration for species of this type occurs near 1 100 cm^{-1}, and moreover the $^{16}O_2/^{16}O^{18}O/^{18}O_2$ pattern is very symmetrical.[*] Unfortunately, both the O–O stretching vibrations of 'triangular' species such as NiO_2, PtO_2, and CoO_2 and the M=O asymmetric stretching vibrations of a double-bonded species such as (III, M = Mo) and CrO_2Cl_2 absorb in the region 900—1 000 cm^{-1}. To shed further light on the problem, we attempted to generate $[CrO_2(CO)_2]$ by an entirely different route, from CrO_2Cl_2 and CO.

Photolysis of CrO_2Cl_2 *in Solid* CO.—Chromyl chloride isolated in a large excess of solid CO shows the two Cr=O stretching modes at 999s and 985m cm^{-1} (not illustrated).[†] Prolonged u.v. photolysis destroyed the CrO_2Cl_2 and produced new absorptions at 1 003/1 000, 1 880, 1 987, and 2 067 cm^{-1}. The bands at 1 003/1 000 cm^{-1} are presumably due to some CrO_2Cl species, COCl has its strongest absorption [11] at 1 880 cm^{-1}, and $[Cr(CO)_6]$ absorbs [12] at 1 987 cm^{-1} in a pure CO matrix. The band at 2 067 cm^{-1} is at almost the same frequency as one of the CO stretches of $[CrO_2(CO)_2]$ (in an Ar/O_2 matrix). The low intensity of this band means that the 988/981 bands would have been too weak to observe, particularly since they would have been overlapped by the CrO_2Cl_2 bands. The other CO stretch at 2 123 cm^{-1} would be obscured by absorptions of the CO matrix itself. Thus in solid CO, CrO_2Cl_2 can be photolysed to give $[Cr(CO)_6]$ and perhaps $[CrO_2(CO)_2]$ among other products. Since CrO_2Cl_2 unquestionably contains a double-bonded group (III), $[CrO_2(CO)_2]$ may also do so.

The Structure of $[CrO_2(CO)_2]$.—In $[CrO_2(CO)_2]$, distinction between triangular (II) and double-bonded (III) structures would be greatly helped by observation of all the vibrational modes. For a number of MO_2 species supposed to have a triangular structure, weak bands assigned to the asymmetric M–O stretches have been observed in the region 500—400 cm^{-1}. For the best characterized double-bonded species, MoO_2, the symmetric Mo=O stretch has been observed [2] as a weak band near to the asymmetric stretch, which is itself split into a number of components corresponding to the different isotopes of Mo. In the present experiments, we have been unable to observe any low-frequency absorptions assignable to $[CrO_2(CO)_2]$. Presumably they are too weak, and although there are weak features in the region 1 000—950 cm^{-1} (Figure 2), they cannot positively be assigned to a CrO_2 symmetric stretch or Cr isotope satellites. Thus we are forced to distinguish between the two structures on the basis of a detailed analysis of the $^{16}O/^{18}O$ spectra.

TABLE 3

Frequency (cm^{-1}) of O–O and M=O stretching vibrations of some MO_2 species

		$^{16}O^{16}O$	$^{16}O^{18}O$	$^{18}O^{18}O$	$^{16}O_2/^{18}O_2$ shift	$^{16}O_2/^{16}O^{18}O$ shift	Asymmetry [a]	Ref.
ν(O–O)	NiO_2	966.2	940.1	913.6	52.6	26.1	0.99	3
	PdO_2	1 024.0	995.5	967.0	57.0	28.5	1.00	3
	PtO_2	926.6	901.4	875.2	51.4	25.1	0.98	3
	AuO_2	1 091.7	1 060.6	1 029.8	61.9	31.1	1.00	*b*
ν_3(M=O) [c]	MoO_2	905.6	875.5	864.6	41.0	30.1	1.47	2
	WO_2	937.2	901.2	889.8	47.4	36.0	1.52	*d*
	PuO_2	794.2	781.7	754.5	39.7	12.5	0.63	*e*
	$CrO_2(CO)_2$	981	974	944	37	7	0.38	This work

[a] Asymmetry = $2[\tilde{\nu}(^{16}O^{16}O) - \tilde{\nu}(^{16}O^{18}O)]/[\tilde{\nu}(^{16}O^{16}O) - \tilde{\nu}(^{18}O^{18}O)]$. [b] D. McIntosh and G. A. Ozin, *Inorg. Chem.*, 1976, **15**, 2869. [c] No data are available for ^{18}O-substituted CrO_2Cl_2, and we have omitted several other species, *e.g.* FeO_2 which has bands at 945.9, 930.8, and 911.4 (S. Abramowitz, N. Acquista, and I. R. Levin, *Chem. Phys. Lett.*, 1977, **50**, 423) since there is some controversy (see G. Blyholder, S. Chang, and J. Fernandez, *Inorg. Chem.*, 1981, **20**, 2813) over the structure of these species. [d] D. W. Green and K. M. Ervin, *J. Mol. Spectrosc.*, 1981, **89**, 145. [e] D. W. Green and G. J. Reedy, *J. Chem. Phys.*, 1978, **69**, 544.

The number of well characterized species of triangular (II) and double-bonded (III) structures is small. Nevertheless, the two most striking differences between the O–O stretches of the triangular structures and the asymmetric M=O stretches of the double-bonded structures are (*i*) the absolute value of the wavenumber shift ($M^{16}O_2$ minus $M^{18}O_2$), which is significantly larger for the triangular structure, and (*ii*) the position of the $M^{16}O^{18}O$ band relative to those of $M^{16}O_2$ and $M^{18}O_2$. For both II and III, substitution by $^{16}O^{18}O$ lowers the symmetry from C_{2v} to C_s and allows mixing between modes previously of different symmetry. In the case of the triangular structure, this coupling is likely not to be very large since the other modes are well removed in frequency, and the frequency of the $M^{16}O^{18}O$ absorption will be almost exactly half way between the frequencies of the $M^{16}O_2$ and $M^{18}O_2$ species. On the other hand, there is likely to be substantial coupling between the 'asymmetric' and 'symmetric' stretches of structure III, and the bands of $M^{16}O^{18}O$ will have frequencies which are significantly shifted from the mean of the $M^{16}O_2$ and $M^{18}O_2$ species. Table 3 shows some data.[‡]

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[*] Cr–O=O can be eliminated since it contains *non-equivalent* O atoms and species of this type appear to absorb at higher frequencies.

[†] The other absorptions [10] of CrO_2Cl_2 are much weaker and several lie at frequencies lower than 400 cm^{-1}, the cut-off of the KBr windows used in our experiments.

[‡] For RhO_2, Hanlan and Ozin [13] assume a triangular structure and that the band at 900 cm^{-1} is the O–O stretch. However, the asymmetry is striking ($^{16}O^{16}O$, 900; $^{16}O^{18}O$, 888; $^{18}O^{18}O$, 862; $^{16}O_2/^{18}O_2$ shift 38; asymmetry parameter 0.63), a point noted by the authors. Perhaps, however, the band at 900 cm^{-1} is actually the ν_3(Rh=O) stretch of double-bonded (III, M = Rh)?

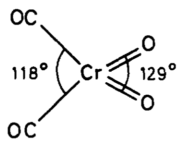
It is clear from Table 3 that $[CrO_2(CO)_2]$ has a $^{16}O_2/^{18}O_2$ shift closer to that of the double-bonded species III than the triangular species II. Moreover, the $^{16}O^{18}O$ band is very asymmetric with respect to the $^{16}O_2$ and $^{18}O_2$ peaks, although the asymmetry is in the opposite direction from that in MoO_2 (structure III), and it seems probable that $[CrO_2(CO)_2]$ has the double-bonded structure (III). This is supported by approximate force-field calculations.

Weltner and co-workers[2] have shown that if it is assumed that the Mo=O vibrations in MoO_2 are totally uncoupled * from the other vibrations of the molecule, then one can calculate values for the two force constants, $k_{(Mo=O)}$ and $k'_{(Mo=O,Mo=O)}$, and the OMoO bond angle,† using the frequencies of the ν_3 asymmetric modes of $Mo^{16}O_2$, $M^{16}O^{18}O$, and $M^{18}O_2$. These force constants and angles can then be used to predict correctly the frequency of the ν_1 symmetric mode of $Mo^{16}O_2$ (calculated, 949 cm^{-1}; observed, 948 cm^{-1}).

The very great asymmetry in the pattern for $[CrO_2(CO)_2]$ suggests, by analogy with MoO_2, the presence of a vibrational mode (ν_1) very close to that observed (ν_3) and which couple on $^{16}O^{18}O$ substitution. Following Weltner's method we calculate a value of *ca.* 129° for the O=Cr=O bond angle [from the $\nu_3(^{16}O_2) - \nu_3(^{18}O_2)$ shift]; from the $^{16}O_2/^{16}O^{18}O/^{18}O_2$ frequencies, we predict that the bands associated with ν_1 will be at 960 ($Cr^{16}O^{16}O$), 924 ($Cr^{16}O^{18}O$), and 911 ($Cr^{18}O^{18}O$) cm^{-1}. Moreover, the force constants calculated on this model [$k_{(Cr=O)} = 692$, $k'_{(Cr=O,Cr=O)} = 88$ N m^{-1}] are encouragingly close to those observed by Weltner for MoO_2 [$k_{(Mo=O)} = 702$, $k'_{(Mo=O,Mo=O)} = 88$ N m^{-1}]. Unfortunately, the region of the spectrum where ν_1 absorptions are expected is obscured by the Cr/O_2 species (Figure 2) and although it is possible to pick out bands which could be assigned to ν_1 and its isotopic partners one cannot do this with any confidence.

Weltner and co-workers observed clearly resolved bands due to the different isotopes of Mo in $Mo^{16}O_2$. For CrO_2Cl_2 and CrO_2F_2 isolated in matrices, Cr isotope patterns have been observed on both the Cr=O and Cr–X modes.[10,15] Unfortunately, the most abundant Cr isotope (^{52}Cr) is present in 83.8% abundance and it is not easy to see bands due to the other isotopes because of their low abundance (^{50}Cr, 4.3%; ^{53}Cr, 9.5%; ^{54}Cr, 2.4%). Certainly in the experiments reported here, the matrix splittings, together with the overall weakness of the absorption of $[CrO_2(CO)_2]$, preclude the confident assignment of bands to Cr isotopic species. However, there are weak features (arrowed in Figure 2) on the high-frequency side of the 988 cm^{-1} peak at *ca.* 995 cm^{-1} and on the low-frequency side of the 981 cm^{-1} peak at *ca.* 978 cm^{-1} which have approximately the correct frequencies and intensities for Cr isotope bands as shown in Table 4.

Despite the difficulties introduced by low intensities and matrix splittings, the spectra and isotopic frequencies are consistent with double-bonded CrO_2 (structure III), and cannot easily be explained on the basis of a triangular structure (II). Thus it seems fairly well established that photolysis of $[Cr(CO)_6]$ in O_2/Ar produces $[CrO_2(CO)_2]$, ' chromyl carbonyl ', with bond angles (OC)Cr(CO) = 118° and OCrO = 129° (below).



The Bonding of O_2 *to Transition Metals.*—In most matrix-isolated metal oxides, O_2 appears to be attached either in a triangular manner (*e.g.*, NiO_2) with formal oxidation state +2, or as two =O groups with formal oxidation state 4. It is perhaps worth noting that the compounds produced by elements at the right-hand side of the periodic table are more inclined to adopt a triangular than a $(=O)_2$ structure, which is consistent with naive concepts of stability of oxidation states.

TABLE 4

Calculated and observed bands (cm^{-1}) for Cr-isotopic ' CrO_2 ' species having angle = 129°

	Calculated	Observed
$^{52}CrO_2$	[988]	988
$^{52}CrO_2$	[981]	981
$^{50}CrO_2$	994	995
$^{53}CrO_2$	978	978

Comparison with other High Oxidation-state Carbonyl Species.—A number of studies have examined the effect of oxidation state on the C–O stretches in some small molecules. Of particular relevance are those of $[CO{\cdot}HgX_2]$ (X = F, Cl, or Br) and $[CO{\cdot}MX_2]$ (M = Ni, Ca, Cr, Mn, Cu, or Zn; X = F or Cl) produced by matrix co-condensation experiments,[16,17] and Ozin's[18] generation of $[CoO_2(CO)_x]$ species also by matrix co-condensation. When CO is bonded to either HgX_2 or MX_2, the CO frequency is shifted *above* that of free CO, because of σ-donation from the weakly antibonding CO 5σ orbital *without* the usual concomitant back donation into the CO π-antibonding orbitals. In $[CrO_2(CO)_2]$, the Cr is in the formal oxidation state 4 and, by analogy with $[CrF_2(CO)]$, should also be unwilling to release electron density into CO antibonding orbitals. On the other hand, there are *two* CO groups in $[CrO_2(CO)_2]$ so that the position of the CO bands quite close to but lower in frequency than free CO is not surprising.

In the series of compounds $[CoO_2(CO)_x]$ (x = 1, 2, and 3) it is argued[18] that the structure of the CoO_2 group is triangular. In these compounds Co is in a formal oxidation state 2 and the CO bands occur at 2 069/2 062 (x = 1), 2 035/2 020 (x = 2), and 2 087, 2 076, 2 050/2 046 cm^{-1} (x = 3). The position of the CO bands of $[CrO_2(CO)_2]$ at 2 128 and 2 065 cm^{-1} is then expected since in this compound the Cr is in a higher oxidation state.

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* This model, in which all modes except M=O stretches are ignored, has also been used with great success by Ogden and co-workers[14] to predict the isotopic pattern of even quite complex metal oxides.

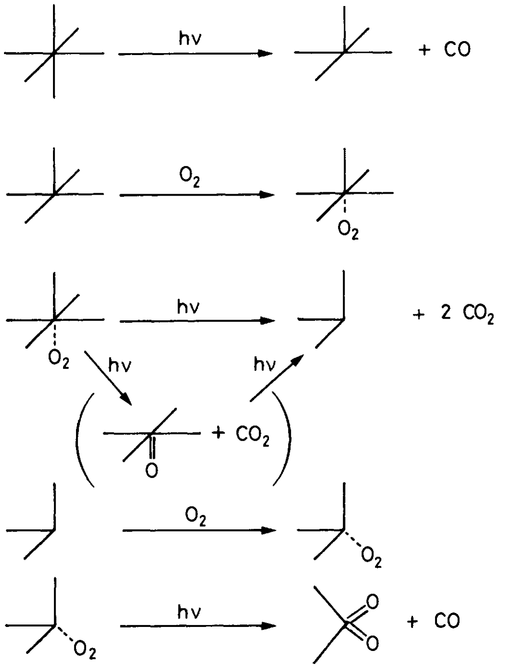
† One can not use such a calculation to estimate the CMC bond angle in a metal carbonyl since the CO groups have no atoms in common and so the *G* matrix contains no angular information.

Mechanism of Formation of [$CrO_2(CO)_2$].—Our experiments provide some clues to the mechanism for the formation of [$CrO_2(CO)_2$] from [$Cr(CO)_6$] and O_2.

(1) In a number of experiments, particularly after very short photolysis times, i.r. bands of low intensity were observed at 2 050 and 2 024 cm^{-1}; these bands disappeared on further photolysis. They are in the CO stretching region to high frequency of the band of [$Cr(CO)_6$] and are probably due to some [$CrO_y/(CO)_x$] species where x is between 6 and 2. This species might well be a photochemical intermediate *en route* to [$CrO_2(CO)_2$].

(2) The generation of [$CrO_2(CO)_2$] from [$Cr(CO)_6$] is accompanied by formation of CO_2 and CO.

(3) The spectrum of photoejected CO shows bands due to isolated CO and to CO · · · CO_2 interacting pairs, Figure 1(*a*). This means that both CO and CO_2 can be generated from the *same* [$Cr(CO)_6$] molecule.



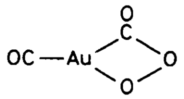
SCHEME

(4) Photolysis of [$Cr(CO)_6$] in the presence of $^{16}O_2/^{18}O_2$ mixtures yields $C^{16}O$, $C^{16}O_2$, and $C^{16}O^{18}O$, but *no* $C^{18}O$ or $C^{18}O_2$. This shows that the oxygen in the photoproduced CO must come from the original carbonyl and that in each CO_2 molecule one oxygen atom originates from a CO group of [$Cr(CO)_6$] and the other atom is provided by the O_2 molecules in the matrix, and also that the O=O bond is broken in the course of the reaction. However, in this experiment (*i.e.*, with $^{16}O_2/^{18}O_2$ but no $^{16}O^{18}O$) there is *no* evidence for [$Cr^{16}O^{18}O(CO)_2$]. This means that both of the O atoms in [$CrO_2(CO)_2$] must originate from the same O_2 molecule.

A mechanism which is *consistent* with these observations can be represented as in the Scheme, where each line represents a CO group.

Further u.v. photolysis produces an oxide species which contains no CO groups at all. Also observed in the final spectrum are bands due to CO_2 and O_3. It is not, however, possible to prove that [$CrO_2(CO)_2$] is a precursor of CO_2 or O_3 but it appears likely.

The above Scheme, which involves the oxidation of CO toC O_2 on the metal centre, is reminiscent of Ozin's [19] elegant matrix experiments, involving co-condensing of Au, CO, and O_2. The intermediate below was



postulated; this decomposed on warming, perhaps *via* OCAuCO, to give Au and CO_2.

Further experiments are planned to probe further the mechanism of these CO/O_2 photochemical reactions.

EXPERIMENTAL

The Air Products CS202 Displex closed cycle refrigerator and associated equipment has been described previously.[5,20] All i.r. spectra were recorded with a Perkin-Elmer model 580A ratio recording spectrophotometer, linked to a Digico Micro-16V computer for multiple scanning and averaging.[6,20] All photolysis was carried out with a Philips HPK 125-W medium pressure mercury lamp.

[$Cr(CO)_6$] and CrO_2Cl_2 (BDH) and Ar and CO (BOC 'Grade X') were all used without further purification. Matrix gas and dopant were premixed at room temperature and the matrices were prepared by pulsed deposition [21] onto a CsBr substrate at 20 K.

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