Activation of CO_2 by laser-ablated group 6 metal atoms

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The primary reaction products of laser-ablated group 6 atoms with CO_2 prove to be the insertion products OMCO and $O_2M(CO)_2$ (M = Cr, Mo, W) which are isolated in argon matrices and identified by the effects of isotopic substitution on their IR spectra.

Carbon dioxide is a naturally abundant carbon source that has been implicated as a contributor to the predicted global warming often referred to as the 'greenhouse effect'. The interaction between CO_2 and transition-metal centres is receiving increased attention[1–4] as the possibilities of recycling CO_2 generated in industrial emissions[5] and also of replacing petroleum with CO_2 as the starting material for the synthesis of fine chemicals[6] both represent exciting and important goals. Previous studies of the interaction of metal atoms with CO_2 in low-temperature matrices focussed on the interaction of Li,[7] Cs[8] and Al[9] with CO_2. Additionally the interaction of several of the first-row transition metals, including Cr, with CO_2 has been investigated both experimentally in solid CO_2[10] and theoretically.[11] In this laboratory, the reactions of B, U, Ti and Be with CO_2 have been investigated and all four were found to insert into CO_2 to give OMCO (M = B, U, Ti, Be) as the primary reaction product.[12–15] Much attention has been devoted to the organometallic chemistry of CO_2 and a comprehensive review has recently been published.[4] The main problem with the chemistry of CO_2 lies in its inherent thermodynamic stability and methods of 'activating' CO_2 are consequently actively being sought. We have studied the reactions between laser-ablated group 6 metal atoms and CO_2–Ar mixtures and have trapped the reaction products, including OMCO and $O_2M(CO)_2$, in argon matrices and identified them by the effects of isotopic substitution.

The technique used for matrix investigation of the reactions of pulsed laser-ablated metal atoms has been detailed previously.[12–16] FTIR spectra were recorded on a Nicolet 550 at 0.5 cm^{-1} resolution. Typically mixtures of between 0.5 and 2%

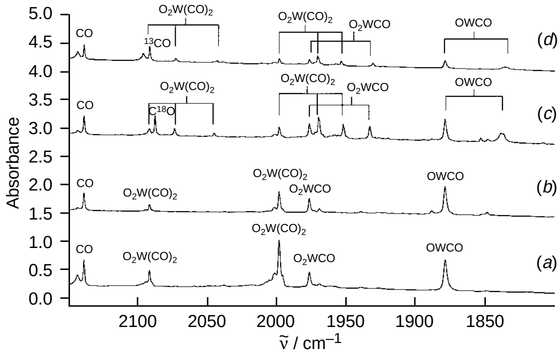

Fig. 1 IR spectra in the region 2150–1800 cm^{-1} for samples from the reactions of W atoms with CO_2 mixtures in argon during condensation at 6–7 K; (*a*) 2% CO_2, (*b*) 0.5% CO_2, (*c*) 0.5% $C^{16}O_2$–$C^{16}O^{18}O$–$C^{18}O_2$ and (*d*) 0.5% $^{12}CO_2$–$^{13}CO_2$ after annealing to 20 K followed by broad-band UV photolysis and further annealing to 30 K

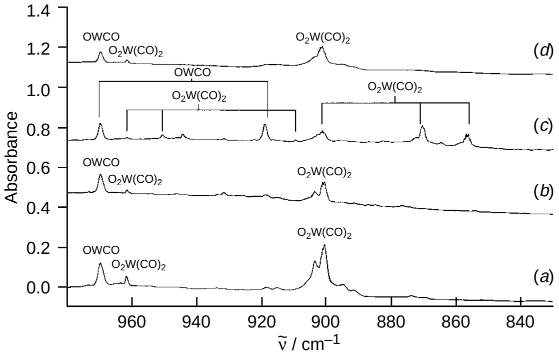

Fig. 2 IR spectra in the region 980–830 cm^{-1} for samples from the reactions of W atoms with CO_2 mixtures in argon during condensation at 6–7 K; (*a*) 2% CO_2, (*b*) 0.5% CO_2, (*c*) 0.5% $C^{16}O_2$–$C^{16}O^{18}O$–$C^{18}O_2$ and (*d*) 0.5% $^{12}CO_2$–$^{13}CO_2$ after annealing to 20 K followed by broad-band UV photolysis and further annealing to 30 K

Table 1 Observed IR absorptions (cm^{-1}) of the dominant products in the reaction of laser-ablated group 6 atoms with CO_2 trapped in an Ar matrix at *ca.* 6–7 K

Molecule	CO_2	$^{13}CO_2$	$^{12}CO_2$–$^{13}CO_2$	$C^{18}O_2$	$C^{16}O_2$–$C^{16}OC^{18}O$–$C^{18}O_2$	Assignment
OCrCO[a]	2014.4	1969.7	2014.4, 1969.7	1967.3	2014.4, 1967.3	ν(C–O)
	866.3	866.3	866.3	829.5	866.3, 829.5	ν(Cr–O)
OMoCO[b]	1847.0	1804.3	1847.0, 1804.3	1806.1	1847.0, 1806.1	ν(C–O)
	951.8	952.4	951.8, 952.4	905.3	951.8, 905.3	ν(Mo–O)
OWCO	1879.0	1837.0	1879.0, 1837.0	1838.8	1879.0, 1838.8	ν(C–O)
	969.6	969.6	969.6	918.9	969.6, 918.9	ν(C–O)
$O_2Cr(CO)_2$[a]	2123.2	2074.8	2123.2, 2074.8	2075.3	2123.2, 2107.2, 2075.3	ν(C–O)
	2059.7	2013.8	2059.7, 2013.8	2011.6	2058.7, 2027.6, 2011.6	ν(C–O)
	981.4	981.4	981.4	945.1	981.4, 975.4, 945.1	ν(Cr–O)[c]
	941.6	941.6	941.6	892.2	941.6, 903.0, 842.2	ν(Cr–O)[d]
$O_2Mo(CO)_2$[b]	2101.9	2053.9	2101.9, 2084.0, 2053.8	2054.7	2101.9, 2084.6, 2054.7	ν(C–O)
	2020.1	1975.4	2020.1, 1991.4, 1975.4	1972.7	2020.1, 1990.0, 1972.7	ν(C–O)
	885.6	885.6	885.6	846.1	885.6, 856.7, 846.1	ν(Mo–O)[c]
$O_2W(CO)_2$	2091.1	2042.9	2091.1, 2072.7, 2042.9	2045.1	2091.1, 2073.4, 2045.1	ν(C–O)
	1998.2	1953.6	1998.2, 1970.4, 1953.6	1952.1	1998.2, 1969.7, 1952.1	ν(C–O)
	961.6	961.6	961.6	909.4	961.6, 944.3, 909.4	ν(W–O)[d]
	901.1	901.1	901.1	856.1	901.1, 870.4, 856.1	ν(W–O)[c]

[a] Refers to ^{52}Cr. [b] Refers to ^{98}Mo. [c] Antisymmetric M–O stretch. [d] Symmetric stretch.

CO_2 in Ar were deposited at a rate of *ca.* 3 mmol h^{-1} for 1–2 h onto a CsI window held at 6–7 K while the metals were ablated using 35–50 mJ $pulse^{-1}$ of the YAG 1064 nm fundamental.

Figs. 1 and 2 show the effects of isotopic substitution upon the IR spectra of matrix-isolated deposits containing the products from the reaction of W with CO_2 in Ar. The frequencies of the observed bands from the reactions of CO_2 with Cr, Mo and W and their proposed assignments are presented in Table 1.

OMCO: the dominant product from the reactions of group 6 metal atoms with 0.5% CO_2–Ar mixtures is the direct insertion product OMCO. Full details are given in Table 1 for all three metals which behave in an analogous fashion. In the case of tungsten, absorptions at 1879.0 and 969.6 cm^{-1} correspond to the CO and WO stretching fundamentals of the OWCO molecule. In experiments run with $^{13}CO_2$ and $C^{18}O_2$, these bands shift to 1837.0 and 969.6 cm^{-1} and 1838.8 and 918.9 cm^{-1}, respectively, confirming that this molecule contains a CO and a WO group, based upon comparison of observed isotopic frequency ratios with calculated harmonic diatomic ratios. Experiments run with $^{12}CO_2$–$^{13}CO_2$, $C^{16}O_2$–$C^{18}O_2$ and $C^{16}O_2$–$C^{16}O^{18}O$–$C^{18}O_2$ all revealed isotopic doublets in the CO stretching region and the latter two revealed doublets in the WO stretching region. This isotopic pattern confirms the presence of exactly one CO group and exactly one WO group allowing definitive spectral assignment of these bands to the OWCO molecule. For both Cr and Mo isotopic splittings due to the natural abundances of the metal isotopes were observed for the MO stretching fundamental and the observed statistical distribution confirmed the presence of exactly one metal atom. These findings are in contrast to a previous study of the reaction of thermally generated chromium atoms with neat CO_2 in which there was no evidence for the insertion reaction.[10]†

$O_2M(CO)_2$: the other main product from these reactions proved to arise from the insertion of the metal atoms into two CO_2 molecules. As might be anticipated, by raising the concentration of CO_2 from 0.5 to 2% the relative yield of $O_2M(CO)_2$ to OMCO increases. In the CO stretching region for all three metals, the symmetric and antisymmetric CO stretching fundamentals were both observed. In the case of the reaction of W with CO_2, the bands at 2091.1 and 1998.2 cm^{-1} can be assigned to the symmetric and antisymmetric CO stretching modes of $O_2W(CO)_2$ while the bands at 961.6 and 901.1 cm^{-1} can be assigned to the symmetric and antisymmetric WO stretching modes of the $O_2W(CO)_2$ molecule. Reaction with $^{13}CO_2$ gave bands at 2042.9, 1953.6, 961.6 and 901.1 cm^{-1}, whereas reaction with $C^{18}O_2$ gave bands at 2045.1, 1952.1, 909.4 and 856.1 cm^{-1}. Reaction with either $C^{16}O_2$–$C^{18}O_2$ or $C^{16}O_2$–$C^{16}O^{18}O$–$C^{18}O_2$ gave rise to 1 : 2 : 1 triplets for all four bands. This is indicative of the presence of precisely two equivalent CO groups and two equivalent oxygen atoms and confirms that the two oxygens and CO groups bound to the tungsten must come from two different CO_2 molecules. Reaction with a $^{12}CO_2$–$^{13}CO_2$ mixture revealed a 1 : 2 : 1 isotopic triplet for both CO stretching fundamentals further confirming the presence of two equivalent CO groups. In the cases of both Cr and Mo, the presence of exactly one metal atom is clearly demonstrated by the statistical distribution of the metal isotopic pattern for the M–O antisymmetric stretching fundamental. There have been numerous previous studies involving the photolysis of $M(CO)_6$ with O_2[18–21] and bands in these spectra were assigned to the $O_2M(CO)_2$ molecules. The CO stretching region in these experiments was extremely congested but the bands that are observed here for $O_2Mo(CO)_2$ and $O_2W(CO)_2$ are essentially the same as those observed by Almond *et al.* for their species 'C' which was assigned to $O_2M(CO)_x$, not those observed for their species 'D' which was assigned to $O_2M(CO)_2$.[20] Our results for $O_2Cr(CO)_2$ do however confirm the previous correct identification of this molecule.[18,20]

Other bands: the previously characterised metal monoxides, MO,[21–23] were observed although this represents the first reported isolation of CrO (846.5 cm^{-1}) in a matrix. In the case of the reaction with tungsten, a bridged species $OW(\mu\text{-}CO)_2WO$, the dimer of OWCO, is formed. Only the antisymmetric CO stretching mode is observed in a region typical for bridging CO groups. The observed band at 1713.4 cm^{-1} from the reaction of W with CO_2 shifts to 1674.5 cm^{-1} on reaction of W with $^{13}CO_2$ and 1675.9 cm^{-1} on reaction of W with $C^{18}O_2$. It shows a 1 : 2 : 1 triplet at 1713.4, 1692.8 and 1675.9 cm^{-1} upon reaction with either $C^{16}O_2$–$C^{18}O_2$ or $C^{16}O_2$– $C^{16}O^{18}O$–$C^{18}O_2$, and a 1 : 2 : 1 triplet at 1713.4, 1691.9 and 1674.5 cm^{-1} upon reaction with a $^{12}CO_2$–$^{13}CO_2$ mixture, indicating two equivalent CO groups. The product is not observed in reactions involving CO and its yield is suppressed by using higher concentrations (2%) of CO_2, presumably due to further reaction of OWCO with CO_2. The lack of an analagous product for Cr or Mo probably reflects the greater strength of the metal–metal bonding, present in such a complex, of tungsten. DFT calculations confirm the presence of metal–metal bonding in this molecule. Other products observed include the molecules O_2MCO, $OCr(CO)_2$ and the CO_2 complex $Cr(\eta^1\text{-}OCO)$ and these results will be discussed in a full paper.

Footnotes

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† The band observed in ref. 10 at 960 cm^{-1}, tentatively assigned to a CO_2 reaction product, occurs at almost the same energy as the antisymmetric stretch of CrO_2, an almost inevitable impurity in a reaction involving thermally generated Cr atoms. With no isotopic data and no associated carbonyl stretches this band is most likely due to CrO_2 in a CO_2 matrix.

References

1 J. A. Ibers, *Chem. Soc. Rev.*, 1982, **11**, 57.
2 C. Creutz, in *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*, ed. B. P. Sullivan, K. Krist and H. E. Guard, Elsevier, Amsterdam, 1993, ch. 2.
3 M. Arreseta, E. Quarntana and I. Tommasi, *New J. Chem.*, 1994, **18**, 133.
4 D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063.
5 M. M. Halmann, *Chemical Fixation of Carbon Dioxide. Methods for Recycling CO_2 into Useful Products*, CRC Press, Boca Raton, FL, 1993.
6 See for example, A. R. Cutler, P. K. Hanna and J. C. Vites, *Chem. Rev.*, 1988, **88**, 1363.
7 Z. H. Kafafi, R. H. Hauge, W. E. Billups and J. L. Margrave, *J. Am. Chem. Soc.*, 1983, **105**, 3886.
8 Z. H. Kafafi, R. H. Hauge, W. E. Billups and J. L. Margrave, *Inorg. Chem.*, 1984, **23**, 177.
9 A. M. LeQuere, C. Xu and L. Manceron, *J. Phys. Chem.*, 1991, **95**, 3031.
10 J. Mascetti and M. Tranquille, *J. Phys. Chem.*, 1988, **92**, 2177.
11 G. H. Yeung, *Mol. Phys.*, 1988, **65**, 669.
12 T. R. Burkholder and L. Andrews, *J. Phys. Chem.*, 1993, **97**, 3500.
13 T. J. Tague, Jr., L. Andrews and R. D. Hunt, *J. Phys. Chem.*, 1993, **97**, 10 920.
14 G. V. Chertihin and L. Andrews, *J. Am. Chem. Soc.*, 1995, **117**, 1595.
15 L. Andrews and T. J. Tague, Jr., *J. Am. Chem. Soc.*, 1994, **116**, 6856.
16 T. R. Burkholder and L. Andrews, *J. Chem. Phys.*, 1991, **95**, 8697.
17 G. V. Chertihin, W. D. Bare and L. Andrews, unpublished work.
18 M. Poliakoff, K. P. Smith, J. J. Turner and A. J. Wilkinson, *J. Chem. Soc. Dalton Trans.*, 1982, 651.
19 J. A. Crayston, M. J. Almond, A. J. Downs, M. Poliakoff and J. J. Turner, *Inorg. Chem.*, 1984, **23**, 3051.
20 M. J. Almond, J. A. Crayston, A. J. Downs, M. Poliakoff and J. J. Turner, *Inorg. Chem.*, 1986, **25**, 19.
21 M. J. Almond and A. J. Downs, *J. Chem. Soc., Dalton Trans.*, 1988, 809.
22 T. C. Devor and J. L. Gole, *Chem. Phys.*, 1989, **133**, 95.
23 J. K. Bates and D. M. Gruen, *J. Mol. Spectrosc.*, 1979, **78**, 284.
24 D. W. Green and K. M. Ervin, *J. Mol. Spectrosc.*, 1981, **89**, 145.

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