

Activation of CO₂ by laser-ablated group 6 metal atoms

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The primary reaction products of laser-ablated group 6 atoms with CO₂ prove to be the insertion products OMCO and O₂M(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 CO₂ and transition-metal centres is receiving increased attention^{1–4} as the possibilities of recycling CO₂ generated in industrial emissions⁵ and also of replacing petroleum with CO₂ as the starting material for the synthesis of fine chemicals⁶ both represent exciting and important goals. Previous studies of the interaction of metal atoms with CO₂ in low-temperature matrices focussed on the interaction of Li,⁷ Cs⁸ and Al⁹ with CO₂. Additionally the interaction of several of the first-row transition metals, including Cr, with CO₂ has been

investigated both experimentally in solid CO₂¹⁰ and theoretically.¹¹ In this laboratory, the reactions of B, U, Ti and Be with CO₂ have been investigated and all four were found to insert into CO₂ 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 CO₂ and a comprehensive review has recently been published.⁴ The main problem with the chemistry of CO₂ lies in its inherent thermodynamic stability and methods of 'activating' CO₂ are consequently actively being sought. We have studied the reactions between laser-ablated group 6 metal atoms and CO₂-Ar mixtures and have trapped the reaction products, including OMCO and O₂M(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%

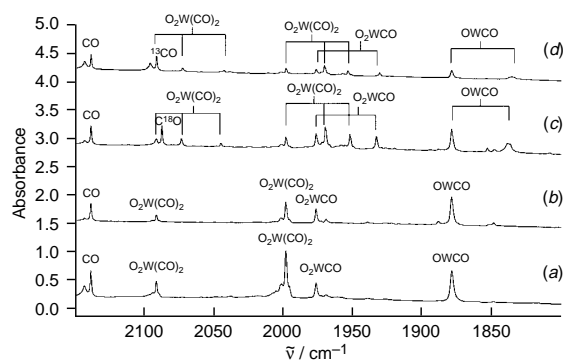


Fig. 1 IR spectra in the region 2150–1800 cm⁻¹ for samples from the reactions of W atoms with CO₂ mixtures in argon during condensation at 6–7 K; (a) 2% CO₂, (b) 0.5% CO₂, (c) 0.5% C¹⁶O₂-C¹⁶O¹⁸O-C¹⁸O₂ and (d) 0.5% ¹²CO₂-¹³CO₂ after annealing to 20 K followed by broad-band UV photolysis and further annealing to 30 K

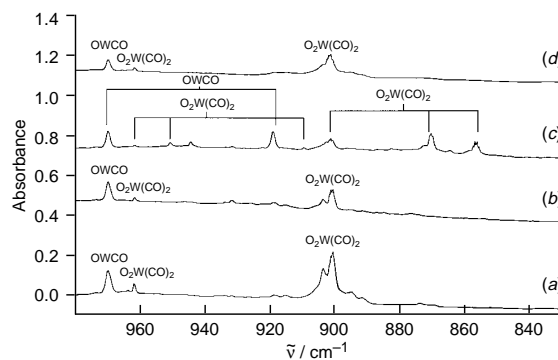


Fig. 2 IR spectra in the region 980–830 cm⁻¹ for samples from the reactions of W atoms with CO₂ mixtures in argon during condensation at 6–7 K; (a) 2% CO₂, (b) 0.5% CO₂, (c) 0.5% C¹⁶O₂-C¹⁶O¹⁸O-C¹⁸O₂ and (d) 0.5% ¹²CO₂-¹³CO₂ after annealing to 20 K followed by broad-band UV photolysis and further annealing to 30 K

Table 1 Observed IR absorptions (cm⁻¹) of the dominant products in the reaction of laser-ablated group 6 atoms with CO₂ 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 O 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 ₂ Cr(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 ₂ Mo(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
	2091.1	2042.9	2091.1, 2072.7, 2042.9	2045.1	2091.1, 2073.4, 2045.1	ν(C–O)
O ₂ W(CO) ₂	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 ⁵²Cr. ^b Refers to ⁹⁸Mo. ^c Antisymmetric M–O stretch. ^d Symmetric stretch.

CO₂ 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 CO₂ in Ar. The frequencies of the observed bands from the reactions of CO₂ 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% CO₂-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 ¹³CO₂ and C¹⁸O₂, 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 ¹²CO₂-¹³CO₂, C¹⁶O₂-C¹⁸O₂ and C¹⁶O₂-C¹⁶O¹⁸O-C¹⁸O₂ 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 CO₂ in which there was no evidence for the insertion reaction.^{10†}

O₂M(CO)₂: the other main product from these reactions proved to arise from the insertion of the metal atoms into two CO₂ molecules. As might be anticipated, by raising the concentration of CO₂ from 0.5 to 2% the relative yield of O₂M(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 CO₂, the bands at 2091.1 and 1998.2 cm⁻¹ can be assigned to the symmetric and antisymmetric CO stretching modes of O₂W(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 O₂W(CO)₂ molecule. Reaction with ¹³CO₂ gave bands at 2042.9, 1953.6, 961.6 and 901.1 cm⁻¹, whereas reaction with C¹⁸O₂ gave bands at 2045.1, 1952.1, 909.4 and 856.1 cm⁻¹. Reaction with either C¹⁶O₂-C¹⁸O₂ or C¹⁶O₂-C¹⁶O¹⁸O-C¹⁸O₂ 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 CO₂ molecules. Reaction with a ¹²CO₂-¹³CO₂ 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 O₂¹⁸⁻²¹ and bands in these spectra were assigned to the O₂M(CO)₂ molecules. The CO stretching region in these experiments was extremely congested but the bands that are observed here for O₂Mo(CO)₂ and O₂W(CO)₂ are essentially the same as those observed by Almond *et al.* for their species 'C' which was assigned to O₂M(CO)₂, not those observed for their species 'D' which was assigned to O₂M(CO)₂.²⁰ Our results for O₂Cr(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(μ-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 CO₂ shifts to 1674.5 cm⁻¹ on reaction of W with ¹³CO₂ and 1675.9 cm⁻¹ on reaction of W with C¹⁸O₂. It shows a 1:2:1 triplet at 1713.4, 1692.8 and 1675.9 cm⁻¹ upon reaction with either C¹⁶O₂-C¹⁸O₂ or C¹⁶O₂-C¹⁶O¹⁸O-C¹⁸O₂, and a 1:2:1 triplet at 1713.4, 1691.9 and 1674.5 cm⁻¹ upon reaction with a ¹²CO₂-¹³CO₂ 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 CO₂, presumably due to further reaction of OWCO with CO₂. The lack of an analogous 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 O₂MCO, OCr(CO)₂ and the CO₂ complex Cr(η¹-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 CO₂ reaction product, occurs at almost the same energy as the antisymmetric stretch of CrO₂, 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 CrO₂ in a CO₂ matrix.

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