Contribution from the Department of Inorganic Chemistry,
University of Oxford, Oxford OX1 3QR, England

Matrix Photooxidation of the Metal Carbonyls $M(CO)_6$ (M = Cr, W) by the Isoelectronic Molecules Carbon Dioxide and Nitrous Oxide

MATTHEW J. ALMOND, ANTHONY J. DOWNS,* and ROBIN N. PERUTZ[1]

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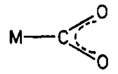
Photolysis of the hexacarbonyl molecules $M(CO)_6$ (M = Cr or W) in the presence of either CO_2 or N_2O has been explored by examining the IR, Raman, and UV–visible spectra of solid argon or methane matrices at ca. 20 K. Hence it has been established that the hexacarbonyl undergoes photooxidation at the hands of CO_2 or N_2O, the reaction proceeding in three stages. First, photolysis gives rise to a complex of the type $XO\cdots M(CO)_5$ (X = OC or N_2), which is photochromic, being readily converted to $Y\cdots M(CO)_5$ (Y = Ar, CH_4) and $M(CO)_6$ with the release of CO_2 or N_2O. Second, complexing activates the CO_2 or N_2O molecule to photodissociation at wavelengths far in excess of the normal thresholds, so that continued UV photolysis leads to oxidation of the metal carbonyl to oxo–metal carbonyl intermediates $O_xM(CO)_y$ containing M=O groups, e.g. *trans*-$O_2W(CO)_4$; there is simultaneous reduction of CO_2 to CO and of N_2O to N_2. In addition, $Cr(CO)_6$ but not $W(CO)_6$ gives what is believed to be a binuclear intermediate incorporating CO_2. Finally, after prolonged UV photolysis, oxidation of the metal carbonyls affords the binary metal oxide molecules CrO_2 and WO_3.

1. Introduction

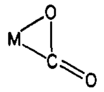
Because of the unusual thermodynamic stability of carbon dioxide,[2,3] activation of the molecule by transition-metal centers evokes particular interest. It is also of commercial significance in the search for hydrocarbon fuel sources other than petroleum, with attention centering especially on systems having the capacity to reduce carbon dioxide to carbon monoxide. Recent results have illustrated the ability of carbon dioxide to coordinate to transition-metal centers and also to react to form other coordinated ligands.[2,3]

Two distinct modes of coordination of CO_2 to transition metals have been identified by diffraction methods,[2,3] viz.

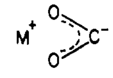
η^1 C-coordination



η^2 side-on coordination



In the former, exemplified by $[Co(n\text{-Pr-salen})K(\eta^1\text{-}CO_2)(thf)]_n$[4a] and $Rh(\eta^1\text{-}CO_2)(Cl)(diars)_2$,[4b] the CO_2 is coordinated to the transition metal through carbon while the oxygen atoms *may* interact with a second metal center (e.g. the potassium ion in the cobalt complex). Side-on coordination is found in $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$[5] and $Nb(\eta^5\text{-}C_5H_4Me)_2(CH_2SiMe_3)(\eta^2\text{-}CO_2)$.[6] A third mode of coordination involving a CO_2^- molecular anion has been recognized when M is an alkali-metal atom:[7]



Yet a fourth has been proposed on the basis of spectroscopic studies linked with ab initio calculations:[8a]

η^1 end-on coordination M–O=C=O

Extended Hückel calculations imply that this is likely to be the starting point for the coordination of CO_2 to a metal fragment with two electrons less than the closed-shell configuration, although interconversion to a side-on geometry can follow with relative ease.[8b] According to a recent study by Tranquille and Mascetti,[9] the deposits formed by cocondensing Ti, V, Ni, or Cu atoms with carbon dioxide display IR spectra suggestive of side-on-coordinated CO_2 complexes of these metals. Annealing the condensate formed from Ni atoms and CO_2 to temperatures above 80 K is said to result in reduction of the CO_2 to CO.

The ability of lithiated and anionic transition-metal complexes to react with CO_2 to form metal carbonyls was demonstrated initially by the reaction of CO_2 with $[Mo(\eta\text{-}C_5H_5)_2(H)Li]_4$ to form $Mo(\eta\text{-}C_5H_5)_2CO$.[10] Since then Maher and Cooper have shown the generality of reactions of the type illustrated by[11]

$$M'_2[W(CO)_5] + 2CO_2 \rightarrow W(CO)_6 + M'_2CO_3$$

$$M' = \text{Li or Na}$$

and have presented evidence for the intermediacy of an η^1-CO_2 complex in these reactions.[12] However, when CO_2 reacts with the anion $[RM(CO)_5]^-$ (R = H, CH_3; M = Cr, Mo, W), the product is found to be the carboxylato complex $[RC(O)OM(CO)_5]^-$.[13] Catalytic conversion of CO_2, H_2, and CH_3OH to methyl formate has been achieved with use of $[HRu_3(CO)_{11}]^-$.[14] Reduction of CO_2 to CO can also be effected by neutral metal carbonyls such as $Cp_2M(CO)_2$ (Cp = η^5-C_5H_5):[15]

$$4Cp_2Ti(CO)_2 + 4{}^{13}CO_2 \rightarrow [(Cp_2Ti)_2(\mu_3\text{-}CO_3)]_2 + 8CO + 2{}^{13}CO$$

$$3Cp_2Zr(CO)_2 + 3CO_2 \rightarrow [Cp_2ZrO]_3 + 9CO$$

While being isoelectronic with CO_2, the molecule N_2O is known to undergo even fewer reactions with transition-metal complexes. In the only established complex, $[Ru(NH_3)_5N_2O]^{2+}$, the N_2O is thought to be η^1 coordinated through the terminal N atom.[16] Solutions of $(\eta^5\text{-}C_5H_5)_2V$ at −78 °C absorb N_2O to give a wine red solution;[17] when this solution is warmed, it liberates N_2 gas

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(1) Present address: Department of Chemistry, University of York, Heslington, York YO1 5DD, England.

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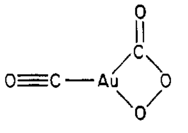
and deposits black crystals of $(\eta^5\text{-}C_5H_5)_5V_5O_6$. The presumption is that the wine red solution contains an N_2O complex, but this could not be isolated. Similarly, $(\eta^5\text{-}C_5H_5)_2Cr$ reacts with N_2O to form $(\eta^5\text{-}C_5H_5)_4Cr_4O_4$, presumably with concurrent reduction of N_2O to N_2.[18]

The direct impetus to the present research came from studies in this laboratory and by Turner, Poliakoff, et al. at Nottingham concerning the photooxidation reactions of matrix-isolated metal carbonyls. These have shown that photolysis of $M(CO)_6$ molecules (M = Cr, Mo, W) in matrices doped with dioxygen yields a number of intermediates containing both coordinated oxygen and carbonyl ligands.[19,20] Some of the intermediates have been characterized in the process of elucidating the mechanisms of the reactions. In a similar vein, Ozin et al. have cocondensed gold atoms with mixtures of CO and O_2 to gain spectroscopic evidence for intermediates such as carbonylgold(II) peroxyformate (I).[21]



I

It is a striking feature of all these systems that CO_2 is a principal product. Studies involving $W(CO)_6$ and the isotopomer $^{18}O_2$ have shown that one oxygen atom of the CO_2 originates in free or coordinated CO and the other in an O_2 molecule. Thus rupture of the O–O bond of O_2 has taken place but at wavelengths >300 nm, far in excess of the threshold required for photodissociation of the free O_2 molecule.[22] Corresponding reactions of $W(CO)_6$ in O_2-doped nitrogen matrices have been shown to yield N_2O.[23] It was with these results in mind that we considered the role of CO_2 and N_2O in the reactions. Do these molecules behave like N_2[24] or CH_4[25,26] in complexing with unsaturated metal carbonyl fragments and, if so, does the interaction affect the photochemistry of CO_2 and N_2O as it plainly affects the photochemistry of O_2?

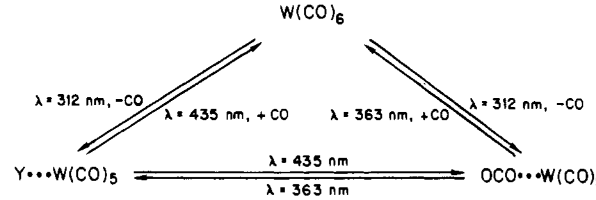
In this paper we present IR, Raman, and UV–visible spectroscopic evidence to show that $M(CO)_6$ molecules undergo photooxidation at the hands of CO_2 or N_2O in changes that proceed via a complex series of intermediates in three distinct stages. In the first place, photolysis gives rise to a complex of the type $XO\cdots M(CO)_5$ (M = Cr, W; X = OC, N_2), which is photochromic, being readily converted to $Y\cdots M(CO)_5$ (Y = matrix gas) and $M(CO)_6$ with the release of CO_2 or N_2O. The second stage entails oxidation of the metal carbonyl yielding oxo–metal carbonyl intermediates $O_xM(CO)_y$ containing M=O groups. At the same time CO_2 is reduced to CO and N_2O to N_2. Finally, after prolonged photolysis, binary metal oxides are produced, all the CO groups initially coordinated to the metal having been released as either free CO or CO_2.

2. Experimental Section

The cryogenic equipment used at Oxford has been described elsewhere.[24,27] An Air Products CSW 202B "Displex" closed-cycle helium refrigerator gave window temperatures of ca. 20 K inside a shroud maintained at a pressure below 10^{-7} torr.

Mixtures were prepared in a vacuum line with use of standard manometric techniques and deposited thence on the cold support. A CsI window was used for nearly all the IR experiments except those involving $OWCl_4$, when a LiF window was used, through which the mixture was photolyzed. A LiF window was used for all the UV–visible experiments and a polished aluminum block for all experiments involving Raman spectroscopy. Pulsed deposition[28] was favored for all experiments except those with $OWCl_4$, which required slow spray-on, with the sample of $OWCl_4$ held at 70 °C.

Scheme I



The photolysis source was either a Philips HPK 125-W medium-pressure or a Hanovia "Uvitron" 100-W high-pressure mercury arc. The radiation was filtered with either a Balzers interference filter (band-pass ca. 15 nm) or, for broad-band UV irradiation, with two 50-mm quartz cells filled with saturated aqueous solutions of $CoSO_4$ and $NiSO_4$, respectively.

IR spectra were recorded on a Perkin-Elmer Model 225 or 580A spectrophotometer and UV–visible spectra on a Perkin-Elmer Model 330 spectrophotometer. Raman spectra of matrix samples were excited at 514.5 nm with a Spectra-Physics Model 165 Ar^+ laser and recorded on a Spex Ramalog 5 spectrophotometer.[29]

$W(CO)_6$ (99% pure) was supplied by Koch-Light and $Cr(CO)_6$ (98% pure) by Ventron Alfa Products. All matrix gases (grade "X") were used as received from BOC, while ^{13}CO and $^{18}O_2$ (both 99% enriched) were similarly used as received from BOC Prochem. Enrichment of the metal hexacarbonyls in ^{13}CO was carried out by the method described by Perutz and Turner.[30] $^{13}CO_2$ was prepared by combusting ^{13}CO in $^{16}O_2$ at a total pressure of 5 torr in a 5-L bulb, the reaction being initiated by a microwave discharge produced by a Microtron Model 200 (Electro-Medical Supplies Ltd.). The $^{13}CO_2$ was separated from unchanged starting materials by passage through a spiral trap held at 77 K. $C^{16}O^{18}O$ was similarly prepared by the combustion of $C^{16}O$ in $^{18}O_2$.

3. Results and Discussion

3.1. Formation of the Complexes $OCO\cdots M(CO)_5$ and $N_2O\cdots M(CO)_5$.

Irradiation of an argon or methane matrix containing CO_2 and $W(CO)_6$ in the proportions 2000:100:1 at wavelengths near 312 nm yields $Y\cdots W(CO)_5$ (Y = Ar, CH_4) and free CO, as reported previously.[25,30] This is shown by the appearance in the IR spectrum of bands at 1935, 1970, and 2140 cm^{-1} and, with methane as the host material, by the appearance in the UV–visible spectrum of an absorption at 405 nm. In addition, there is formed a second species A. In an argon matrix, this is characterized by IR bands at 1926 and 1956 cm^{-1} close to those of $Y\cdots W(CO)_5$; in a methane matrix, it gives rise to IR bands at 1923 and 1946 cm^{-1} as well as a distinct absorption in the near-ultraviolet at 346 nm.

Photolysis at wavelengths near 435 nm, corresponding to the tail of the visible absorption band of $Y\cdots W(CO)_5$, increases the concentration of A. A is shown to be photochromic since irradiation of the matrix at wavelengths near 363 nm causes a decrease in the intensity of all the bands associated with it and a concomitant growth of those associated with $Y\cdots W(CO)_5$ and $W(CO)_6$.

Scheme I illustrates the proposed reaction sequence in which $W(CO)_5$ complexed with a matrix molecule can be reversibly converted to a similar complex implicating CO_2. Figure 1 illustrates the changes in the IR spectrum that accompany photolysis.

Similar behavior is observed if $W(CO)_6$ is photolyzed in a matrix doped with N_2O or if a matrix containing $Cr(CO)_6$ and either CO_2 or N_2O is irradiated. In the $Cr(CO)_6$ experiments,

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Table I. Wavenumbers of C-O Stretching Bands Observed in the IR Spectra and Wavelengths of Absorptions Observed in the UV-Visible Spectra of Argon or Methane Matrices Containing $M(CO)_6$ (M = Cr, W) together with CO_2 or N_2O after 30-min Photolysis at $\lambda = 312$ nm

parameters	$W(CO)_6/CO_2$	$W(CO)_6/N_2O$	$Cr(CO)_6/CO_2$	$Cr(CO)_6/N_2O$	assignt[a]
IR wavenumbers, cm^{-1} [b]	1986 (1968)	1986	1988	1987	$M(CO)_6$
	2140 (2140)	2140	2140	2140	CO
	1970 (1968)	1968	1972	1973	$Ar\cdots M(CO)_5$
	1935 (1932)	1935	1936	1935	
	1956 (1946)	1950	1952	1950	$XO\cdots M(CO)_5$
	1926 (1923)	1925	1925	1925	
wavelengths of UV-vis abs max, nm[c]	225	224	227	226	$M(CO)_6$
	285	286	280	280	
	405	405	493	490	$CH_4\cdots M(CO)_5$
	346	360	370	383	$XO\cdots M(CO)_5$

[a] X = OC, N_2; M = Cr, W. [b] Argon matrices, except for results in parentheses, which refer to methane matrices; error limits ±1 cm^{-1}. [c] Methane matrices; error limits ±1 nm.

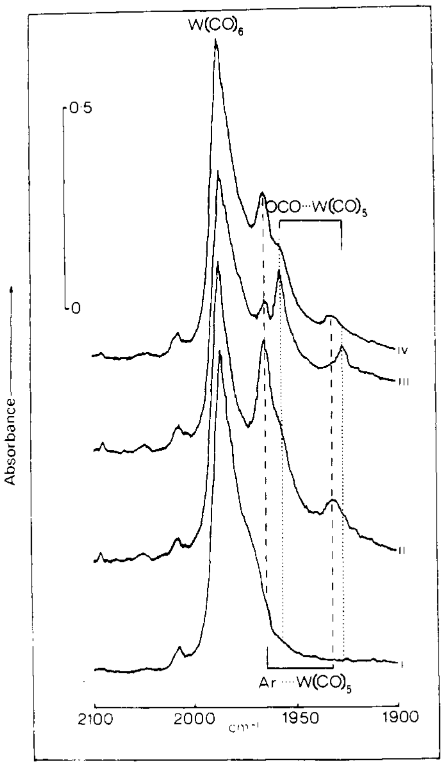


Figure 1. C–O stretching region of the infrared spectrum displayed by a CO_2-doped Ar matrix containing $W(CO)_6$ (Ar:CO_2:$W(CO)_6$ = ca. 2000:100:1) at 20 K: (i) after deposition; (ii) after 30-min photolysis at λ = ca. 312 nm, showing the appearance of bands due to $Ar\cdots W(CO)_5$ and $OCO\cdots W(CO)_5$; (iii) after 30-min photolysis at λ = ca. 435 nm, showing the conversion of $Ar\cdots W(CO)_5$ to $OCO\cdots W(CO)_5$; (iv) after 30-min photolysis at λ = ca. 363 nm, showing the conversion of $OCO\cdots W(CO)_5$ to $Ar\cdots W(CO)_5$.

the wavelengths of photolyzing radiation giving the maximum yield of $OCO\cdots Cr(CO)_5$ or $N_2O\cdots Cr(CO)_5$ are near 543 nm, a finding consistent with the UV–visible spectrum of $Y\cdots Cr(CO)_5$ reported previously.[25] Figure 2 illustrates the changes in the UV–visible spectrum of a methane matrix containing $Cr(CO)_6$ and N_2O brought about by photolysis. The relative yields of the competing changes

$$Y\cdots M(CO)_5 \xrightarrow{XO} XO\cdots M(CO)_5$$

$$Y\cdots M(CO)_5 \xrightarrow{CO} M(CO)_6$$

induced by visible photolysis do not vary significantly with the natures of the metal M (=Cr, W), the matrix Y, or the reagent XO (X = OC, N_2). Table I lists the bands seen in all the above experiments.

We have sought to determine the stoichiometry of the complex formed between $W(CO)_5$ and N_2O by carrying out a series of experiments in which methane matrices were doped with a constant amount of $W(CO)_6$ but with different amounts of N_2O (CH_4:N_2O = 50:1 to 5:1), and the absorbance of the UV band at 360 nm was measured in each case. Plotting log (absorbance) for this band as a function of log (concentration) for the N_2O yields a straight line with a gradient *n*, where *n* is the number of N_2O

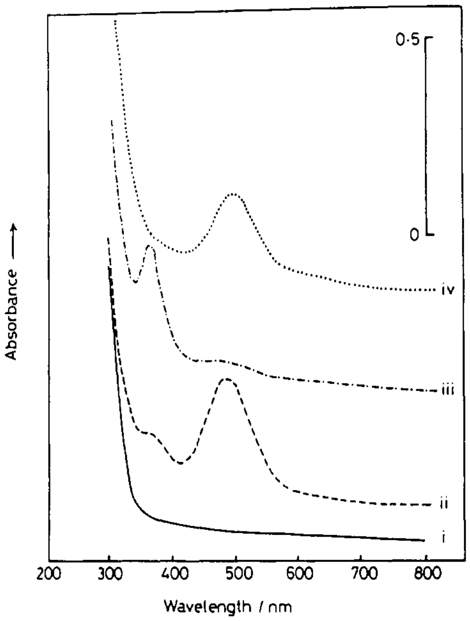


Figure 2. Ultraviolet–visible spectrum of an N_2O-doped CH_4 matrix containing $Cr(CO)_6$ (CH_4:N_2O:$Cr(CO)_6$ = ca. 1000:100:1) at 20 K: (i) after deposition; (ii) after 30-min photolysis at λ = ca. 312 nm, showing the appearance of bands due to $CH_4\cdots Cr(CO)_5$ and $N_2O\cdots Cr(CO)_5$; (iii) after 30-min photolysis at λ = ca. 435 nm, showing the conversion of $CH_4\cdots Cr(CO)_5$ to $N_2O\cdots Cr(CO)_5$; (iv) after 30-min photolysis at λ = ca. 363 nm, showing the conversion of $N_2O\cdots Cr(CO)_5$ to $CH_4\cdots Cr(CO)_5$.

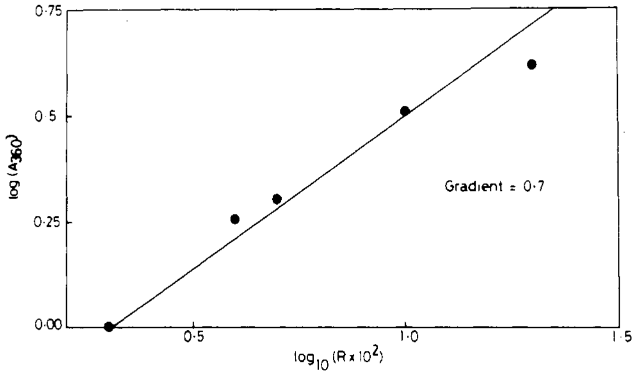


Figure 3. Log–log plot showing the dependence of the absorbance at 360 nm, A_{360} in arbitrary units, on the mole ratio $R = N_2O$:CH_4 for N_2O-doped CH_4 matrices containing $W(CO)_6$ (CH_4:N_2O:$W(CO)_6$ = ca. 1000:20–200:1). Each measurement was made after 30-min photolysis at λ = ca. 312 nm.

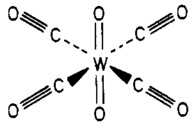
molecules associated with the complex.[31] As shown in Figure 3, such a plot gives a value of $n = 0.7$; within the limits of experimental error, this is consistent with a complex having the composition $N_2O\cdots W(CO)_5$.

The spectroscopic properties of the species $XO\cdots M(CO)_5$ (X = OC, N_2) listed in Table I give some clues to the nature of the binding of the XO moiety. The position of the lowest energy ligand field transition of $LCr(CO)_5$ is sensitive to the nature of L, the wavelength varying from 533 nm (L = Ar)[25] through 489 (L = CH_4),[25] 460 (L = CH_3OH),[32] 420 (L = NH_3),[25] and ~390 (L = CH_3CN)[3] to 364 nm (L = N_2).[24] We note too that Lewis bases such as thf induce a low-frequency shift of the ν(CO) bands of $M(CO)_5$ by 30–40 cm^{-1},[34] whereas weak π acceptors such as N_2 cause an increase of 10–20 cm^{-1}.[24] For comparison $CH_3CNW(CO)_5$ (in hexane) is found to absorb at 1948 and 1931 cm^{-1}.[35] Thus both the UV and IR results suggest that CO_2 and N_2O perturb the π-bonding network of $M(CO)_5$ in a manner and degree comparable with the perturbation induced by CH_3CN in the complex $CH_3CNM(CO)_5$.

The IR spectra of the photolyzed matrices show no vestige of any new bands in the regions 1100–1300 and 1600–1800 cm^{-1} characteristic of η^1 C-coordination[4] or η^2 side-on coordination[5,6] of CO_2. In the absence of any direct IR evidence of coordinated CO_2, the response of the $M(CO)_5$ unit is consistent with η^1 end-on coordination of the CO_2 molecule to the 16-electron $M(CO)_5$ fragment, corresponding to the mode judged energetically by EH methods to offer the easiest access.[8b]

3.2. Formation of Intermediate Species $O_xM(CO)_y$. Irradiation of an argon or methane matrix doped with $W(CO)_6$ and CO_2 at wavelengths near 312 nm for longer than 60 min gives rise to small quantities of at least two new species, B and C, characterized by the growth of relatively weak absorptions in the IR spectrum; these occur at 2042 and 2096 cm^{-1}, respectively. Such high frequencies suggest that the bands arise from the stretching vibrations of one or more CO groups attached to an oxidized tungsten atom.[34,36] Unfortunately it was not possible to discern any IR absorption attributable to an M=O stretching mode, presumably for want of intensity occasioned by the very low concentration of these species in the matrix.

That the bands belong to two distinct species is shown by irradiation of the matrix at wavelengths near 363 nm, which causes the band at 2096 cm^{-1} to grow while that at 2042 cm^{-1} decays. The band at 2096 cm^{-1} coincides with the most intense absorption of the species *trans*-dioxotungsten tetracarbonyl (II), a major and relatively stable product in the photooxidation of $W(CO)_6$ isolated in O_2-doped matrices.[20] When a similar experiment is performed with $W(CO)_6$ 97% enriched in ^{13}CO, the band at 2096 cm^{-1} gives way to one at 2051 cm^{-1} corresponding to the position of the most intense absorption of *trans*-$O_2W(^{13}CO)_4$ as formed from $W(^{13}CO)_6$ and O_2.[20]



II

In an attempt to identify the species B absorbing at 2042 cm^{-1}, we examined the effect of photolyzing $OWCl_4$ isolated in a pure CO matrix. Broad-band UV irradiation of the solid deposit met with very little response, but when the matrix mixture was similarly irradiated *during* deposition, the IR spectrum of the condensate revealed a number of new bands. These testified to the formation of the radical ClCO[37] and included, together with a number of weak features close to 1950 cm^{-1}, a band at 2041 cm^{-1}, which may belong to B. An experiment with CO_2 and $W(CO)_6$ 97% enriched in ^{13}CO showed that the band associated with B shifts to 1999 cm^{-1}. Similarly, broad-band UV photolysis of $OWCl_4$ with an excess of ^{13}CO yields a deposit with an IR band at 1997 cm^{-1}. On this evidence B is plausibly identified as a monooxo–tungsten carbonyl species, $OW(CO)_x$, where x is possibly 4.

Scheme II

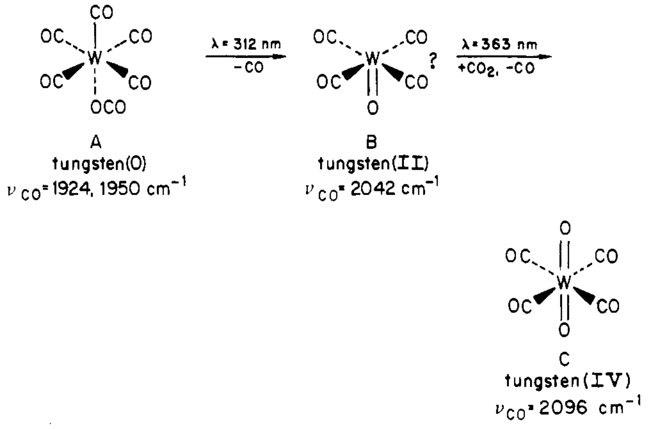


Table II. Wavenumbers of IR Bands Associated with the Species B and C and Their Chromium Analogues, As Produced by Photolysis of Argon Matrices Containing $M(CO)_6$ (M = Cr, W) together with CO_2 or N_2O^a

species B		species C			
OW-(^{12}CO)$_4$	OW-(^{13}CO)$_4$	*trans*-O_2W-(^{12}CO)$_4$	*trans*-O_2W-(^{13}CO)$_4$	Cr analogue of B	Cr analogue of C
2042^b	1999^b	2096^b	2051^b	2041^b	2084^b
2041^c		2095^c		2040^c	2086^c
2041^d	1997^d	2096^e	2051^e		

^{a} Wavenumbers in cm^{-1}; error limits ±1 cm^{-1}. ^{b} This work; CO_2-doped matrices. ^{c} This work; N_2O-doped matrices. ^{d} Produced by photolysis of $OWCl_4$ during deposition with an excess of CO. ^{e} Produced by photolysis of $W(CO)_6$ in an O_2-doped matrix.[20]

We appear then to have a novel route to *trans*-dioxotungsten tetracarbonyl (C) as illustrated in Scheme II. The products B and C are also generated on UV photolysis of $W(CO)_6$ in matrices containing N_2O.

Photolysis of $Cr(CO)_6$ isolated in a matrix doped with CO_2 or N_2O likewise yields two products whose photochemical and spectroscopic properties are analogous to those of B and C. Attempts at more rigorous characterization of these two species have been unsuccessful, principally because the low concentrations in which they are formed preclude investigations of the intensity patterns associated with the isotopomers $O_xCr(^{12}CO)_z(^{13}CO)_{y-z}$. However, they may well be the chromium analogues of B and C. Neither of the products has an IR spectrum consistent with that of "chromyl carbonyl", $O_2Cr(CO)_2$, a major product of the UV photolysis of $Cr(CO)_6$ when isolated in O_2-doped matrices.[19]

Table II lists the IR bands exhibited by B and C and by the products of the reactions involving $Cr(CO)_6$; it also compares the frequencies with those of (i) C as formed in O_2-doped matrices[20] and (ii) the species believed to be a monooxo–tungsten carbonyl generated by photolysis of $OWCl_4$ in the presence of an excess of CO. Figure 4 shows the changes observed in the C–O stretching region of the IR spectrum at this stage in the reaction.

3.3. Production of an Unknown Chromium Carbonyl Derivative. UV photolysis of $Cr(CO)_6$ when isolated in a CO_2-doped argon or methane matrix results in the growth of a broad IR band near 1820 cm^{-1} (see Figure 5a). This band remains when all the other

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(31) Compare, for example: Moskovits, M.; Hulse, J. E. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 471. Hawkins, M.; Andrews, L.; Downs, A. J.; Drury, D. J. *J. Am. Chem. Soc.* **1984**, *106*, 3076.

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(35) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *Inorg. Chem.* **1963**, *2*, 323.

(36) See for example: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980.

(37) Jacox, M. E.; Milligan, D. E. *J. Chem. Phys.* **1965**, *43*, 866.

Table III. Wavenumbers of the IR Bands Associated with the Binary Oxides Formed as the Ultimate Products of Prolonged Photooxidation of $M(CO)_6$ (M = Cr, W) Isolated in Argon Matrices Doped with $C^{16}O^{18}O$

$Cr(CO)_6/C^{16}O^{18}O$		$O_2Cr(CO)_2$ [a]	$W(CO)_6/C^{16}O^{18}O$		WO_3 [b]
ν/cm^{-1} [c]	assignt	ν/cm^{-1}	ν/cm^{-1} [c]	assignt	ν/cm^{-1}
964 (1)	ν_3 $Cr^{16}O_2$	981	915 (1)	$\nu_3(e')$ $W^{16}O_3$	914
950 (2)	ν_3 $Cr^{16}O^{18}O$	974	890 (1)	$W^{16}O_2{}^{18}O$	892
925 (1)	ν_3 $Cr^{18}O_2$	944	880 (1)	$W^{16}O^{18}O_2$	883
			870 (1)	$\nu_3(e')$ $W^{18}O_3$	872

[a] Produced by photolysis of $Cr(CO)_6$ in an O_2-doped matrix.[19] [b] Produced by cocondensation of W atoms with O_2.[41] [c] Error limits ±3 cm^{-1}. Figures in parentheses denote approximate relative intensities.

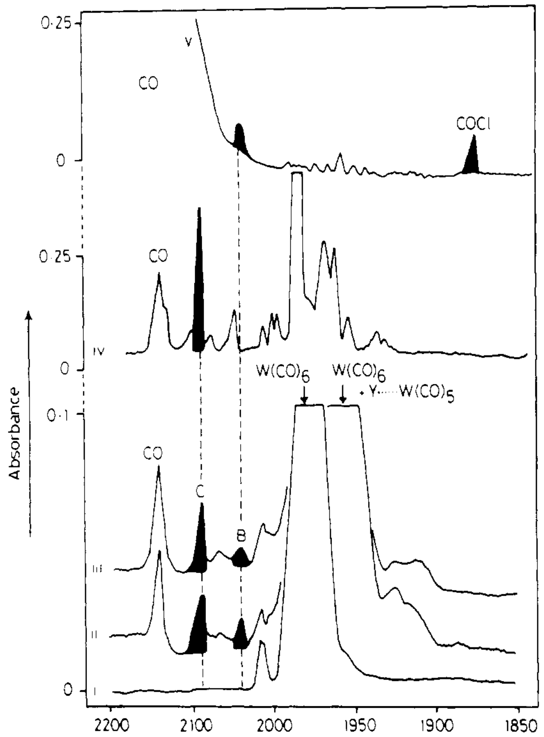


Figure 4. C–O stretching region of the infrared spectra of various matrices showing the growth or decay of bands associated with the oxotungsten carbonyl species B and C. (i) Spectrum of a CO_2-doped Ar matrix containing $W(CO)_6$ ($Ar:CO_2:W(CO)_6$ = ca. 2000:100:1) after deposition. (ii) Spectrum of the same matrix after 60-min photolysis at λ = ca. 312 nm. (iii) Spectrum of the same matrix after 30-min photolysis at λ = ca. 363 nm, showing the growth of the band due to C and the simultaneous decay of that due to B. (iv) Spectrum of an O_2-doped Ar matrix containing $W(CO)_6$ ($Ar:O_2:W(CO)_6$ = ca. 2000:100:1) after 30-min photolysis at each of the following wavelengths: (a) λ = ca. 312 nm; (b) λ = ca. 435 nm, and (c) λ = ca. 363 nm. This gives a high yield of *trans*-$O_2W(CO)_4$ as evidenced by the growth of the absorption at 2096 cm^{-1}.[20] (v) Spectrum of a CO matrix containing $OWCl_4$ photolyzed during deposition at 20 K with broad-band ultraviolet radiation. One of the products gives a band at 2042 cm^{-1} coincident with the band attributed to B in spectra ii and iii.

bands originating in new carbonyl-containing species have disappeared. Its frequency does not change when $^{13}C^{16}O_2$ or $^{12}C^{16}O^{18}O$ replaces $^{12}C^{16}O_2$ but decreases to ca. 1780 cm^{-1} when $Cr(CO)_6$ 97% enriched in ^{13}CO is used. We conclude therefore that it arises from a chromium carbonyl species derived from $Cr(CO)_6$. Its diffuseness and relative weakness have prevented bands of the different $^{12}CO/^{13}CO$ isotopomers from being observed and have thereby frustrated definitive characterization. On the other hand, the low frequency of the band favors either a species with a small number of CO groups coordinated to a chromium atom in an oxidation state ≤ 0[34] or a bridging CO group of a binuclear species. Photolysis of a CO_2-doped argon matrix containing $Cr(CO)_6$ at high dilution ($Ar:Cr(CO)_6$ = 10 000:1) gives rise to the bands near 2040 and 2085 cm^{-1} associated with the chromium analogues of B and C, but there is no hint of the band near 1820 cm^{-1}. On the other hand, with a matrix ratio $Ar:Cr(CO)_6$ = 500:1, the band near 1820 cm^{-1} is relatively much more intense than those near 2040 and 2085 cm^{-1}. This dependence on the concentration of $Cr(CO)_6$ argues in favor of a bimolecular reaction giving rise to a binuclear product. By analogy with the behavior of CS_2,[2,36] we can postulate species such as III and IV.

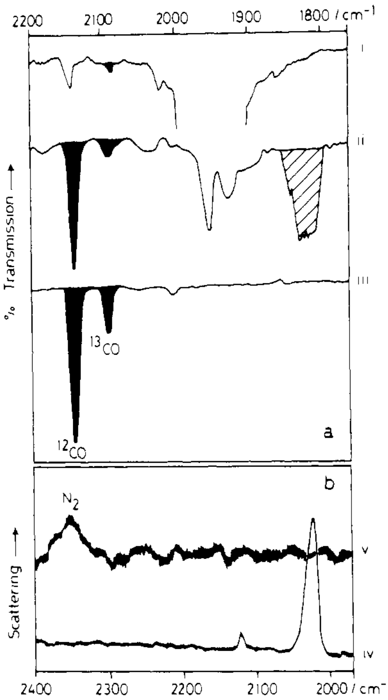
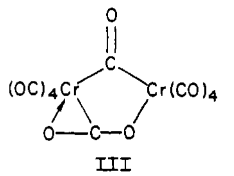
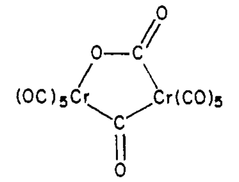


Figure 5. (a) Infrared spectra showing the reduction of $^{13}CO_2$ to ^{13}CO in $^{13}CO_2$-doped Ar matrices containing $Cr(^{12}CO)_6$ ($Ar:^{13}CO_2:Cr(^{12}CO)_6$ = ca. 2000:100:1): (i) spectrum of the matrix after deposition; (ii) spectrum of the same matrix after 90-min photolysis with broad-band ultraviolet radiation, showing the growth of the broad absorption centered at 1820 cm^{-1} (see text); (iii) spectrum of the same matrix after 960-min photolysis with broad-band ultraviolet radiation, showing the buildup of free ^{12}CO and ^{13}CO. (b) Raman spectra showing the reduction of N_2O to N_2 in N_2O-doped Ar matrices containing $W(CO)_6$ ($Ar:N_2O:W(CO)_6$ = ca. 1000:100:1): (iv) spectrum of the matrix after deposition; (v) spectrum of the same matrix after 120-min photolysis with broad-band ultraviolet radiation.



III



IV

It is interesting that no similar band is seen when $Cr(CO)_6$ is photolyzed in N_2O-doped matrices nor when $W(CO)_6$ is photolyzed in matrices doped with either CO_2 or N_2O. The findings point to the formation of a binuclear species implicating only Cr, CO, and CO_2; chromium is more susceptible than tungsten to aggregation processes of this sort, and CO_2 may induce the formation of a species such as III or IV.

We cannot explain why this species should be so slow to decompose, but its survival may stem simply from the circumstance that its UV-visible absorption bands do not overlap well with the wavelengths at which the photolyzing radiation is most efficient.

3.4. Reduction of CO_2 to CO and of N_2O to N_2. The oxidation of the tungsten carbonyl species, as already described, is accompanied by reduction of CO_2 to free CO. This was established by an experiment involving photolysis of a matrix containing $^{13}CO_2$ and $M(^{12}CO)_6$ (M = Cr or W), whence it emerged that ^{13}CO is a photoproduct. Such a product must result, not from fission of M-C bonds, but from photoreduction of $^{13}CO_2$. The IR spectrum illustrated in Figure 5a demonstrates this buildup of ^{13}CO.

To determine whether N_2O is similarly reduced to free N_2, we have recorded the Raman spectrum of a matrix containing $W(CO)_6$ and N_2O before and after 120-min photolysis at $\lambda = 312$ nm. The long photolysis time inevitably produced a highly scattering matrix, giving a Raman spectrum of relatively poor quality. Nevertheless, the results illustrated in Figure 5b confirm by the development of scattering near 2330 cm^{-1} [38] that N_2 is indeed a photoproduct.

3.5. Oxidation of Coordinated CO to CO_2. It was observed that the oxidation of the metal hexacarbonyl and the reduction of N_2O to N_2 in N_2O-doped matrices is accompanied by the formation of free CO_2, as shown by the appearance and growth of an IR band at 2340 cm^{-1}.[39] That the CO_2 originates from the oxidation of coordinated CO and not from the adventitious presence of CO_2 impurity was established beyond doubt by repeating the experiments with $M(CO)_6$ (M = Cr, W) 97% enriched in ^{13}CO; photolysis then gave a band at 2295 cm^{-1} characteristic of $^{13}CO_2$.[39] Since N_2O normally requires radiation at wavelengths <200 nm for photodissociation,[40] these reactions can be described as photosensitization of N_2O.

We presume that photooxidation of coordinated CO to CO_2 also occurs on photolysis of matrices containing $M(CO)_6$ and CO_2. Unfortunately an experiment designed to verify this presumption involving the photolysis of $M(^{13}CO)_6$ in a $^{12}CO_2$-doped matrix was frustrated by the intense, broad band due to the $^{12}CO_2$ dopant that obscured any sign of the $^{13}CO_2$ photoproduct.

3.6. Production of Binary Metal Oxides. Prolonged broad-band UV photolysis of matrices containing $Cr(CO)_6$ or $W(CO)_6$ in the presence of CO_2 or N_2O results ultimately in the formation of binary metal oxides. Figure 6 shows the region 850-1000 cm^{-1} associated with the M=O stretching fundamentals in the IR spectra of the following samples after 960-min UV photolysis: (a) an argon matrix containing $W(CO)_6$ and CO_2 and (b) an argon matrix containing $Cr(CO)_6$ and CO_2.

With the ambition of identifying these products, we performed experiments using $C^{16}O^{18}O$. Table III lists the frequencies of the bands seen for the various isotopomers of the metal oxides. Hence we conclude that the final products of the photooxidation of $Cr(CO)_6$ and $W(CO)_6$ are CrO_2 and WO_3, respectively.

The IR spectrum of matrix-isolated WO_3 has been reported more than once.[41] The frequencies observed and the effects on the bands of ^{18}O enrichment are wholly consistent with the results of experiments using $W(CO)_6$ and $C^{16}O_2$ or $C^{16}O^{18}O$. Regarding the matrix-isolated CrO_2 molecule, the precedents are relatively sparse.[42] However, the use of $C^{16}O^{18}O$ for the photooxidation of $Cr(CO)_6$ isolated in an argon matrix produces an unsymmetrical triplet of bands at ca. 965, 950, and 925 cm^{-1} with relative intensities approximately in the ratio 1:2:1. Despite the weakness of the bands, the frequencies and isotopic pattern suggest that they originate in the antisymmetric stretching fundamental of a bent CrO_2 molecule. There are obvious similarities with the IR spectra of the matrix-isolated molecules $O_2Cr(CO)_2$[19] and MoO_2.[43] In the case of MoO_2, the symmetric Mo=O stretching mode gives rise to a relatively weak absorption on the high-frequency side of the stronger absorption associated with the antisymmetric stretching mode. In the circumstances of the present experiments, it is likely that the symmetric stretching mode of CrO_2 is too weak to be detected. This would mean that it was less intense than the absorption due to the antisymmetric stretching mode by a factor of at least 3, a conclusion implying an O=Cr=O bond angle considerably greater than 90° (which would give rise to absorptions of equal intensity for the two modes).

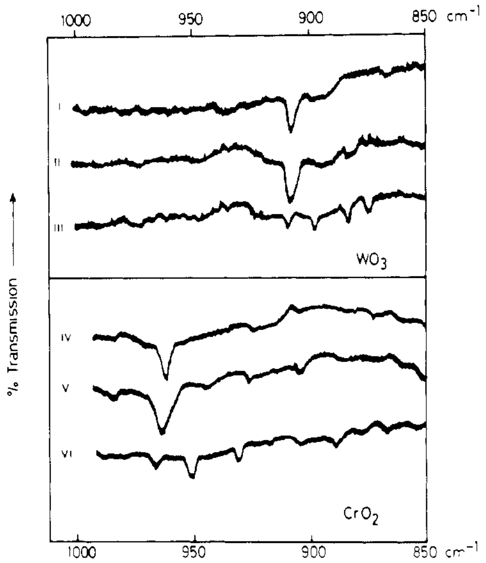


Figure 6. Infrared spectra showing the growth of new bands in the M=O stretching region of XO-doped Ar matrices containing $M(CO)_6$ (X = OC, N_2; M = Cr, W; Ar:XO:$M(CO)_6$ = ca. 2000:100:1) after 960-min photolysis with broad-band ultraviolet radiation: (i) X = OC, M = W; (ii) X = N_2, M = W; (iii) XO = $C^{16}O^{18}O$, M = W; (iv) X = OC, M = Cr; (v) X = N_2, M = Cr; (vi) XO = $C^{16}O^{18}O$, M = Cr. The bands in spectra i-iii are assigned to ν_3 for the different isotopomers of the D_{3h} molecule WO_3 and the bands in spectra iv-vi to ν_3 for the different isotopomers of the C_{2v} molecule CrO_2.

4. Conclusions

We set out in search of novel CO_2 and N_2O complexes derived from the hexacarbonyls $Cr(CO)_6$ and $W(CO)_6$ and to investigate the effect of CO_2 and N_2O on the matrix photochemistry of these metal carbonyls. We have shown that complexes are indeed formed between the metal pentacarbonyl fragment and CO_2 or N_2O, viz. XO$\cdots$M(CO)$_5$ (X = OC or N_2; M = Cr or W) and that such association activates the CO_2 or N_2O molecule, allowing photoreduction to CO or N_2. At the same time the metal carbonyl is oxidized; one of the products derived from $W(CO)_6$ is the species *trans*-dioxotungsten tetracarbonyl, $O_2W(CO)_4$. This molecule has been characterized previously, being a primary product of the photooxidation of $W(CO)_6$ by O_2; reasons for the comparative stability of this molecule have been given elsewhere.[20] The final products of oxidation of $Cr(CO)_6$ and $W(CO)_6$ are shown to be CrO_2 and WO_3, respectively. In none of the experiments did we detect signs of free[44] or coordinated[3] CO_3, although this might

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(38) Tinti, D. S.; Robinson, G. W. *J. Chem. Phys.* **1968**, *49*, 3229. Jodl, H. J.; Bolduan, F. *Ibid.* **1982**, *76*, 3352.

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(41) Weltner, W., Jr.; McLeod, D., Jr. *J. Mol. Spectrosc.* **1965**, *17*, 276. Green, D. W.; Ervin, K. M. *Ibid.* **1981**, *89*, 145.

(42) One study of the cocondensation of Cr atoms with O_2 in an Ar matrix cites values of $\nu_{antisym}$(Cr=O) = 978, 955, and 938 cm^{-1} for the molecules $Cr^{16}O_2$, $Cr^{16}O^{18}O$, and $Cr^{18}O_2$, respectively (Serebrennikov, L. V.; Mal'tsev, A. A. *Vestn. Mosk. Univ., Ser. 2: Khim.* **1975**, *16*, 251). Although the values are 5-15 cm^{-1} higher than those we associate with the same isotopomers, the $^{16}O/^{18}O$ shift of 40 cm^{-1} exhibited by the C_{2v} molecules $Cr^{16}O_2$ and $Cr^{18}O_2$ is close to what we find (39 cm^{-1}).

(43) Hewett, W. D., Jr.; Newton, J. H.; Weltner, W., Jr. *J. Phys. Chem.* **1975**, *79*, 2640.

(44) Free CO_3 should give bands at 2053, 1894, 1070, 975, and 564 cm^{-1} (on the basis of the wavenumbers cited for the molecule isolated in solid CO_2); the bands near 2040 and 964 cm^{-1} observed in this study have the wrong isotopic shifts for CO_3. See: Weissberger, E.; Breckenridge, W. H.; Taube, H. *J. Chem. Phys.* **1967**, *47*, 1764.

be anticipated as a product of the reaction between the oxo complexes and CO_2.

However, the mechanism leading to the production of *trans*-$O_2W(CO)_4$ in CO_2- or N_2O-doped matrices is quite different from that in O_2-doped matrices. Photooxidation by O_2 gives rise to *trans*-$O_2W(CO)_4$ in which both the oxygen atoms originate in the *same* O_2 molecule: in the experiments described here, each oxygen atom must originate in a *different* CO_2 or N_2O molecule and production of *trans*-$O_2W(CO)_4$ proceeds, we believe, via oxotungsten tetracarbonyl, B.

The observation that CO_2 is reduced to CO is of importance in relation to the fixation of the former molecule via industrial or atmospheric processes.

Acknowledgment. We thank the SERC for supporting this research and for funding a studentship for M.J.A.

Registry No. $W(CO)_6$, 14040-11-0; $Cr(CO)_6$, 13007-92-6; $OW(^{12}CO)_4$, 94136-88-6; $OW(^{13}CO)_4$, 94136-89-7; *trans*-$O_2W(^{12}CO)_4$, 91444-05-2; *trans*-$O_2W(^{13}CO)_4$, 94136-90-0; $OCr(CO)_4$, 94136-91-1; *trans*-$O_2Cr(CO)_4$, 94136-92-2; WO_3, 1314-35-8; CrO_2, 12018-01-8; N_2O, 10024-97-2; CO_2, 124-38-9; Ar, 7440-37-1; methane, 74-82-8.

Contribution from the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, Department of Chemistry, The University of North Carolina at Charlotte, Charlotte, North Carolina 28223, and Naval Research Laboratory, Washington, D.C.

Photochemistry of (2,3,9,10-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)copper(II): Participation of Copper(II) Hydrides

GUILLERMO FERRAUDI,*[†] P. BARRERA,[†] J. GRANIFO,[†] J. H. HAM, IV,[‡] D. PAUL RILLEMA,*[‡]
and ROBERT NOWAK[§]

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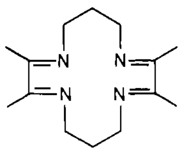
The photochemistry in acidic methanol and the relevant thermochemistry of (2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)copper(II) (ligand abbreviations are 2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4 or L in this work) have been investigated. UV photolysis results in the rapid formation of a transient identified as Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^+$. A minor fraction of the transient is produced in $t < 10$ ns and a major fraction in the microsecond time domain via a second-order process ($k = (5.7 \pm 0.3) \times 10^7$ M^{-1} s^{-1}) that involves the reaction of solvent radicals ($\cdot CH_2OH$) with the copper(II) macrocycle. In perchlorate media, $[ClO_4^-] > 10^{-3}$ M, a first-order isomerization followed in milliseconds ($k = (2.0 \pm 0.3) \times 10^3$ s^{-1}). Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$ then undergoes slow decay by competitive pathways to produce H_2 and Cu_{solv}^+. The product quantum yields ($10^{-3} < \phi_{Cu^+_{solv}} < 10^{-2}$; $10^{-4} < \phi_{H_2} < 10^{-3}$) depend on light intensity, acid concentration, and the concentration of the copper(II) macrocycle. The production of hydrogen is postulated to occur via a copper(II) macrocycle in acid solution. The thermal properties relevant to an interpretation of the photochemistry were as follows: (1) There is a dependence on solvent of $E_{1/2}$ for the $Cu^{II}L/Cu^{I}L$ couple (varies from −0.02 V in CH_2Cl_2 to −0.62 V vs. SCE in H_2O) and the CuL^{2+} electronic absorption spectrum. (2) The $E_{1/2}$ value for the ligand reduction at ∼−1.4 V vs. SCE shifts positively in acidic media until it overlaps the metal(II/I) couple. (3) The spectral properties of Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^+$ generated by coulometric reduction ($n = 1.01$) at −0.60 V vs. SCE in acetonitrile are $\lambda_{max} = 746$ nm with $\epsilon \approx 8 \times 10^3$ M^{-1} s^{-1}.

Introduction

The photochemistry of copper(II) macrocycles is largely determined by electronic and structural features of the macrocyclic ligands that control the accessibility of various charge-transfer states. Complexes in which potentials for the $Cu^{III/II}$ and (macrocycle)/(macrocycle)$^-\cdot$ couples are sufficiently close have reactive charge transfer to ligand states, CTTL, that induce solvolytic and redox reactions.[1,2] For the copper(II) complexes with CTTL states placed at very high energies, the photoreactivity is limited to various ligand to metal charge-transfer states, CTTM, that induce the oxidation of the macrocyclic and ligands in the axial positions.[3] In some copper(II) complexes both the CTTL and CTTM states can be populated by UV light and simultaneous photoreactivity from both states is observed.[4]

The formation of reaction products takes place by mechanisms that involve several steps.[1–6] The copper(II) macrocycles, usually generated in the primary photochemical processes described above or in secondary reactions between radicals and excess copper(II) complex, are unstable in acidic solutions. It has been shown that solvolysis competes with hydride-mediated redox transformations.[5,6] Since the reactivity of the copper(I) species is tied to structural parameters such as the flexibility of the ligand, it is of interest to determine the properties of the copper(I) intermediates with rigid macrocycles. Therefore, the macrocycle effect on the photochemical reactivity of the copper(II) complex and the reactivity of chemical intermediates have been investigated in this work by using 2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4, which has a more rigid framework than previously investigated ligands.[1–3]



2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4

Experimental Section

Materials. All chemicals used in the investigations and preparations were reagent grade, unless otherwise noted. Water was triply distilled over potassium permanganate. Acetonitrile and methylene chloride were stored 48 h over 4-Å molecular sieves before use. Tetrabutylammonium hexafluorophosphate (TBAH) and tetraethylammonium perchlorate (TEAP) were purchased from Southwestern Analytical, Austin, TX. TEAP was dried overnight at 70 °C under vacuum prior to use. Anhydrous $NaClO_4$ was purchased from G. F. Smith. Argon was scrubbed of oxygen impurities either by passage over BTS catalyst or through scrubbing towers containing ∼0.2 M Cr^{2+} in 0.2 M $HClO_4$.

[†] University of Notre Dame.
[‡] The University of North Carolina at Charlotte.
[§] Naval Research Laboratory.

(1) Ferraudi, G.; Endicott, J. F. *Inorg. Chem.* **1977**, *16*, 2672.
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