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Photoreactions of Chromium Hexacarbonyl and Chromium Tetranitrosyl in Frozen Gas Matrices. Infrared Spectral Evidence for Tricarbonyldinitrosylchromium

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The photolysis of Cr(CO)₆ and NO has been studied in frozen gas matrices. The reaction leads to the formation of Cr(NO)₄ in argon and methane matrices. The intermediate complex Cr(CO)₃(NO)₂, which is not seen in noticeable amounts in hydrocarbon solutions, is shown to be stable in the low-temperature matrices. Isotopically substituted ¹³C¹⁶O, ¹⁵N¹⁶O, and ¹⁵N¹⁸O have been used and a D_{3h} geometry has been established for Cr(CO)₃(NO)₂ on the basis of infrared spectra. The photolysis of Cr(NO)₄ in carbon monoxide matrices gives Cr(CO)₃(NO)₂ in addition to Cr(CO)₆. The photolysis of Cr(NO)₄ in argon and methane matrices gives a species Cr(NO)₃(NO*), where the asterisk denotes a unique nitrosyl group with an unusually low value of ν_{NO}. A reaction scheme for Cr(CO)₆ + NO (+hν) → Cr(NO)₄ is proposed in which the first step is the formation of Cr(CO)_x(NO) (x = 4 or 5) via a dissociative mechanism.

Introduction

Although considerable information is available concerning structural aspects of nitrosyls, much of this literature centers on the question of bent vs. linear M-NO coordination.² Certainly, little is known of the chemistry of pure nitrosyls of which only two, Co(NO)₃³ and Cr(NO)₄,^{4,5} have been reported to date.

Most synthetic routes for the preparation of nitrosyl carbonyls employ respective binary metal carbonyls as the starting materials.⁶ In 1973, we⁴ and Herberhold and Razavi⁵ simultaneously reported a photosynthetic route for the preparation of Mn(CO)(NO)₃ and Cr(NO)₄. The procedure involves the photolysis of a solution of the respective binary metal carbonyl while NO is being passed through the solution. In pentane solution Mn₂(CO)₁₀ is converted stepwise into Mn(CO)₄(NO) and finally the green complex Mn(CO)(NO)₃. In the chromium system the compound Cr(CO)₃(NO)₂, which could conceivably occur as an intermediate of the photoinduced nitrosylation, is not formed in noticeable amounts. Instead, photonitrosylation of hydrocarbon solutions of Cr(CO)₆ leads directly to the formation of the dark red complex Cr(NO)₄. The absence of Cr(CO)₃(NO)₂ suggests that the complex might be thermally unstable. However, in light of the fact that similar pentacoordinate and isoelectronic complexes Fe(CO)₅ and Mn(CO)₄(NO) are quite stable, one cannot rule out the possibility that Cr(CO)₃(NO)₂ is simply not an intermediate in the photonitrosylation scheme.

Photonitrosylation reactions, when tried with Mo(CO)₆ and W(CO)₆ as starting materials, yield polymeric compounds the infrared spectra of which suggest the presence of bridging carbonyl and nitrosyl groups.⁷ Binary carbonyls of the nickel group are similar in that Ni(CO)₄ is a stable complex, whereas Pd(CO)₄ and Pt(CO)₄ can be stabilized only in rare gas matrices.⁸

In order to synthesize Cr(CO)₃(NO)₂ and nitrosyls of Mo and W extreme conditions may be necessary. To avoid possible thermal decomposition of Cr(CO)₃(NO)₂, it would be useful to carry out the photonitrosylation at extremely low temperatures. Also to avoid the formation of polynuclear species, and any possible bimolecular reactions of the unstable intermediates, one needs to isolate the reactants as well as intermediates. Both these conditions may be effected in low-temperature inert gas matrices. Matrix isolation techniques have been used in the preparation of isolated molecules or reactive species and in the study of their further reactions. A variety of different techniques can be used to trap these otherwise unstable species in the inert gas solids. The material can be subjected to radiation by high-energy sources such as microwave or electric discharge prior to deposition. In situ photolysis of stable molecules isolated in frozen matrices also has been widely used as a method of generating unstable

fragments for spectroscopic investigations. These fragments can be further used to synthesize new compounds by reaction either with a substrate added to the matrix^{9a} or with the matrix itself.^{9b} Recently, Turner et al.¹⁰ reported the formation of a new complex Os(CO)₂(NO)₂, by photolysis of a matrix containing a mixture of Os(CO)₅, NO, and argon. These workers have also reported the generation of species M(CO)_n (n = 2-5 and M = Cr, Mo, W), by photolysis of the parent hexacarbonyl complexes in argon matrices.¹¹ In this paper we are concerned with the photochemical reaction of Cr(CO)₆ and NO in frozen gas matrices and with the photoreactions of Cr(NO)₄ in inert (argon) and reactive (carbon monoxide) matrices. Isotopically substituted ¹³C¹⁶O, ¹⁵N¹⁶O, and ¹⁵N¹⁸O have been used to establish the geometry of Cr(NO)₂(CO)₃ and other intermediate complexes.

Experimental Section

Cryogenic temperatures were obtained using an Air Products AC-3L-110 "Cryotip" in two-stage mode (20 K) or an Air Products "Displex" closed cycle helium refrigerator CSW202 (10 K). Details of the apparatus are described elsewhere.^{7,12} Infrared spectra were recorded on a Unicam SP-100¹² or a Beckman IR-97 spectrophotometer, calibrated regularly with water vapor and standard gases.¹³ In all the experiments, a germanium filter was used to allow only infrared radiation from the Nernst glower through the sample. All matrix gases were research grade (99.999%) and were obtained from the British Oxygen Co. (argon, carbon monoxide)¹² or the Matheson Gas Co. (argon and methane).⁷ Pure nitric oxide was prepared from CP grade NO (98%, Matheson Gas Co.) according to the method described elsewhere.⁷ Chromium hexacarbonyl, supplied by Ventron, Inc., was further purified by sublimation. Chromium tetranitrosyl was prepared in small quantities by direct gas-phase photonitrosylation of Cr(CO)₆ or in larger quantities by solution photonitrosylation. Samples of ¹³C-enriched chromium hexacarbonyl (90%) and ¹⁵N¹⁸O (95%) were kindly provided by L. H. Jones of Los Alamos Scientific Laboratories, Los Alamos, N.M. ¹⁵N¹⁶O (90%) was supplied by Stohler Isotopic Chemicals Inc. Standard gas handling techniques were employed for sample preparations prior to deposition. The matrices were deposited on the CsI plate using a pulse method.¹⁴ The pulses were each 15 mL and pressure was varied between 40 and 60 mm. Typical matrix gas to carbonyl ratio employed was 2-3 × 10³:1. In experiments with NO, the matrix to NO to carbonyl ratio was 2-3 × 10³:20:1. Matrices were photolyzed with a medium-pressure mercury lamp (Philips HPK 125 W or Hanovia Type 200 W). To produce shortwave radiation (220 < λ < 280 nm) a combination of absorbing materials (NiSO₄ + CoSO₄ + Cl₂ gas) or a 7-54 Corning glass filter was used.

Results and Discussion

Photoreactions of Cr(CO)₆. Figure 1a shows the infrared spectrum of Cr(CO)₆ in an argon matrix at 10 K in the carbonyl stretching region. Only one band (F_{1u}) is expected for an octahedral carbonyl in this region. The origin of the extra band at 1995.8 cm⁻¹ has been discussed by Graham et al.¹¹ Photolysis of the matrix with unfiltered mercury lamp

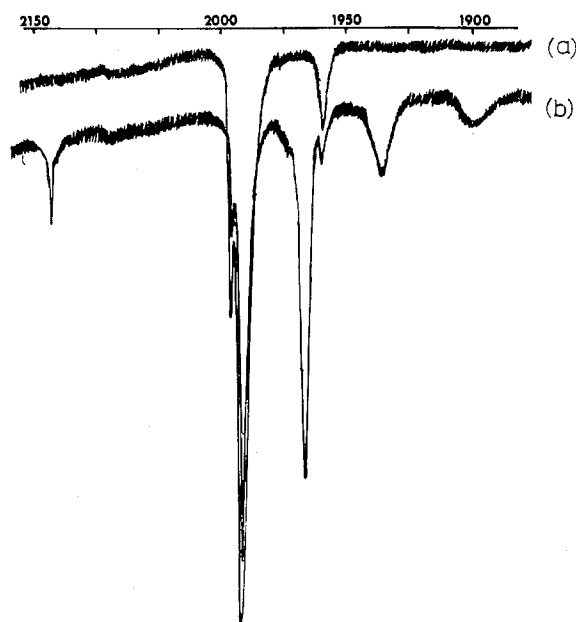


Figure 1. Infrared spectra (cm^{-1}) of $\text{Cr}(\text{CO})_6$ isolated in an argon matrix: (a) spectrum after deposition of the sample at 10 K, (b) spectrum after photolysis for 15 min with mercury lamp radiation.

radiation results in the formation of $\text{C}_{4v}\text{Cr}(\text{CO})_5$ and lower carbonyl fragments. The yield of $\text{Cr}(\text{CO})_5$ increases if short-wavelength radiation ($\lambda < 380 \text{ nm}$) is used for photolysis. However, owing to recombination reactions with CO, the steady-state concentration of lower carbonyls $\text{Cr}(\text{CO})_x$ ($x = 1-4$) does not build up to an appreciable extent. A mixture of $\text{Cr}(\text{CO})_6$ and Ar, when passed through a microwave discharge and deposited at 10 K, gives a spectrum which is essentially identical with those reported earlier for species $\text{Cr}(\text{CO})_x$ ($x = 2-4$).^{15,16} Unfortunately, the overall efficiency of the breakdown of hexacarbonyl using a microwave discharge is low.

The infrared spectrum of a mixture of $\text{Cr}(\text{CO})_6$ and NO in an argon mixture at 10 K is shown in Figure 2a. Two lower bands in the NO stretch region (1863 and 1776.9 cm^{-1}) have been assigned to nitric oxide dimer, and the band at 1871.5 cm^{-1} is due to monomeric nitric oxide.¹⁷ Several new bands are seen (Figure 2b) after irradiation of this sample at 10 K with radiation from a mercury lamp which was passed through a 7-54 Corning glass filter. In addition to the usual bands which are assigned to the species $\text{Cr}(\text{CO})_5$, three new bands appear at 2002 , 1758 , and 1728 cm^{-1} . Annealing of the matrix sample to 35 K does not alter the spectrum very much except that one sees the formation of polymeric nitric oxide at the expense of reduction in concentration of monomeric and dimeric NO.

Figure 2c shows the spectrum of the same matrix at 10 K after it was irradiated with unfiltered mercury lamp radiation at 18 K for 30 min. There is a tremendous change in the spectrum indicating that simultaneous annealing and higher wavelength light is needed for the reaction to proceed. In this spectrum we see two new bands at 2052 and 1705 cm^{-1} . The band which was originally at 1728 cm^{-1} appears to have grown into two overlapping bands at 1728 and 1725 cm^{-1} . Once again, annealing of the matrix has very little effect on the spectrum. The spectrum in Figure 2d shows the state of affairs after additional photolysis at 20 K. The bands at 2052 and 1705 cm^{-1} have grown simultaneously and the bands at 2002 and 1758 cm^{-1} have decreased in intensity.

The result after several photolysis and annealing experiments is a sharp band at 1725.5 cm^{-1} , although it can only be accomplished by prolonged photolysis of the matrix at 25 K. The bands in the Cr-C-O and Cr-N-O deformation region are

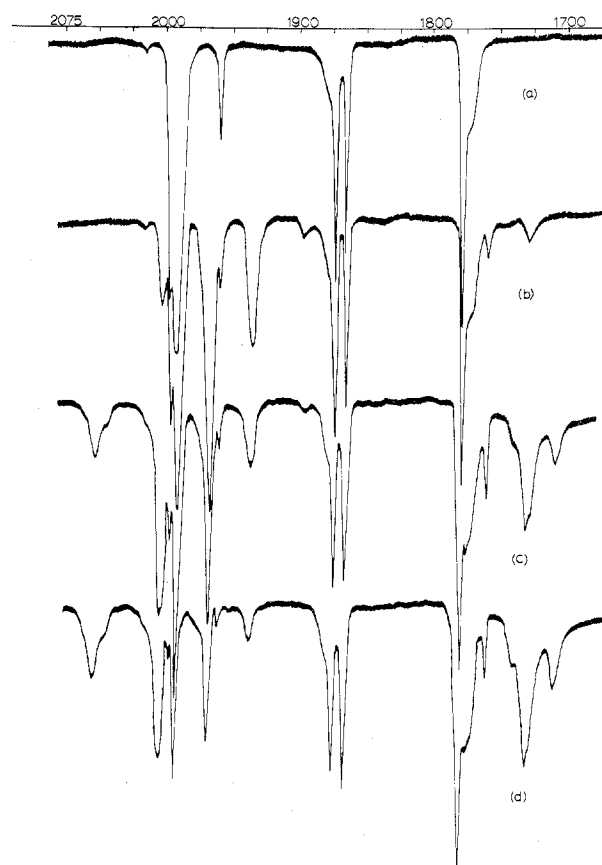


Figure 2. Infrared spectra of the photolysis reaction of $\text{Cr}(\text{CO})_6$ and NO in an argon matrix (all spectra taken at 10 K): (a) upon initial deposition of the mixture of $\text{Cr}(\text{CO})_6$, NO, and Ar; (b) after irradiation of the sample at 10 K for 15 min with radiation from a mercury lamp filtered with a 7-54 Corning glass filter; (c) after further irradiation of the sample with unfiltered mercury lamp radiation for 30 min at 18 K; (d) after additional photolysis of the matrix at 20 K for 20 min.

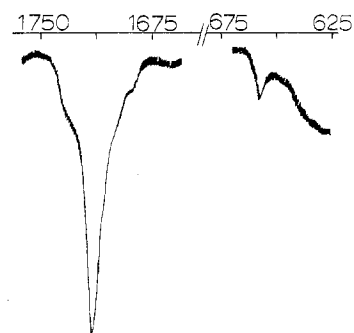


Figure 3. Infrared band (cm^{-1}) of Cr-N-O deformation for $\text{Cr}(\text{NO})_4$ in an argon matrix. The nitrosyl stretching band is also shown for comparison.

weak and can be seen only when appreciable concentration of the species is built up in the matrix. Figure 3 shows one such spectrum. The band at 662.1 cm^{-1} is very weak and appears only when the intensity of 1725.5 cm^{-1} band is quite high.

We assign the 1725.5 and 1728 cm^{-1} bands in the normal isotopic species to $\text{Cr}(\text{NO})_4$ (see below). These two bands merge into a single feature at 1725.5 cm^{-1} after repeated annealing. The same band in the methane matrix appears at 1720.4 cm^{-1} and in a pentane solution of $\text{Cr}(\text{NO})_4$ at 1719.6 cm^{-1} . The Cr-N-O deformation for $\text{Cr}(\text{NO})_4$ in pentane solution occurs at 653.2 cm^{-1} whereas in an argon matrix the frequency of this band is 662.1 cm^{-1} . Furthermore, $\text{Cr}(\text{NO})_4$, when isolated in an argon matrix, gives a sharp band at 1725

Table I. Observed Bands (cm⁻¹) and Proposed Assignments in the Reaction of Cr(CO)₆ and NO in Argon Matrices

Matrix reactants	ν _{CO}				ν _{NO} ^a				δ(CrNO) Cr(NO) ₄
	Cr(CO) ₆	Cr(CO) ₅	Cr(CO) ₃ - (NO) ₂	Cr(CO) _x - (NO) (x = 4, 5)	Cr(CO) _x - (NO) (x = 4, 5)	Cr(NO) ₄	Cr(CO) ₃ - (NO) ₂	Cr(CO) ₅ - (NO) ₂	
Cr(CO) ₆ and NO	1990	1965	1932	2052	2002	1757.5	1725.5	1705	661.2
Cr(CO) ₆ and ¹⁵ N ¹⁸ O	1990	1965	1932	2052	2002	1726	1693.8	1673	
Cr(CO) ₆ and ¹⁵ N ¹⁸ O	1990	1965	1932	2052	2001	1685	1652.6	1632.5	
Cr(¹³ CO) ₆ and NO	1946.5	1922		2008	1985.5	1758	1725.5	1705	

^a Bands are also observed for monomeric NO (1871.5 cm⁻¹) and dimeric NO (1863 and 1776.9 cm⁻¹) in the argon matrices. For ¹⁵N¹⁸O these bands are observed at 1789.5, 1701.3, and 1698.0 cm⁻¹.

cm⁻¹ which under high resolution consists of three components (1728.0, 1725.3, and 1722.4 cm⁻¹), caused by matrix effects, of which the component at 1725.3 cm⁻¹ is the strongest. The corresponding NO stretching absorptions for Cr(¹⁵N¹⁸O)₄ and Cr(¹⁵N¹⁶O)₄ in the argon matrix appear at 1652.5 and 1693 cm⁻¹, respectively. These isotopic shifts are of the same magnitude as those for Cr(NO)₄ in pentane solution.⁷ The fact that the Cr(NO)₄ band appears in the beginning of the photolysis reaction at 10 K indicates the presence of diffusion in argon matrices at these temperatures.

The features at 1705 and 2052 cm⁻¹ in the normal isotope experiments grow simultaneously and can be attributed to one species. The corresponding absorption positions in the ¹⁵N¹⁶O, ¹⁵N¹⁸O, and Cr(¹³CO)₆ experiments are given in Table I. Both these bands are rather broad and after reaching a certain intensity seem to maintain a steady-state concentration in the matrix through photolysis and annealing experiments. For the reasons discussed below, we assign these bands to trigonal-bipyramidal Cr(CO)₃(NO)₂ with axial NO groups.

The number of bands seen for Cr(CO)₃(NO)₂ support a D_{3h} structure, since any other type of structure is expected to give more than two bands. A trigonal-bipyramidal structure is expected since the other two members of this isoelectronic series, Mn(CO)₄(NO)¹⁸ and Fe(CO)₅,¹⁹ also have trigonal-bipyramidal structures. The single band in the NO stretching region suggests that both nitrosyls in Cr(CO)₃(NO)₂ are axial.²⁰

Further evidence that bands at 1705 and 2052 cm⁻¹ are due to Cr(CO)₃(NO)₂ comes from frequency shifts in the isotopically substituted NO and CO experiments. Since in D_{3h} Cr(CO)₃(NO)₂, NO, and CO stretches in the infrared belong to different symmetry species (A₂' for ν_{NO} and E' for ν_{CO}), we do not expect the CO stretching frequency to shift in going from ¹⁴N¹⁶O to ¹⁵N¹⁸O. Conversely, in experiments with Cr(¹³CO)₆ and normal NO, we do not expect any change in the NO stretching frequency as compared to the normal isotopic species. Thus, the absence of a measurable frequency shift for CO modes upon substitution of labeled NO and vice versa (Table I) point to a D_{3h} species. It is possible, however, that the NO and CO stretching modes simply do not mix appreciably. For example, the A₁ CO stretch mode for Co(CO)₃(NO) is not shifted by substitution of ¹⁵N¹⁸O even though the NO stretch also transforms as A₁.²¹ Assignment of these bands to Cr(CO)₃(NO)₂ is further substantiated by the fact that the same bands appear during the photolysis of Cr(NO)₄ isolated in a carbon monoxide matrix (see below). Finally it is of interest to mention that the carbonyl stretching mode of Cr(CO)₃(NO)₂ always has a shoulder on the low-frequency side. This occurs in both argon and methane matrices. Unfortunately, it is not possible to confirm whether it is due to matrix splitting or a small C_{2v} distortion of the D_{3h} structure. Similar splittings observed in the matrix-isolated Fe(CO)₅ were attributed to matrix effects.²²

The 2002-cm⁻¹ band in Figure 2b appears to be related in intensity to the 1757.5-cm⁻¹ band. However, from our observations in a large number of experiments, we note that the

intensity of the 1757.5-cm⁻¹ band is rather erratic in behavior. One of the reasons for this is the proximity of this weak band to the intense multimetric nitric oxide bands. Upon annealing the matrix to higher temperatures, the 1757.5-cm⁻¹ feature merges into the broad nitric oxide bands. Since these bands do not appear when Cr(CO)₆ or NO²³ alone is photolyzed in an argon matrix and are seen only when both Cr(CO)₆ and NO are present, it is reasonable to conclude that these bands belong to some intermediate nitrosylcarbonyl complex. An exceedingly weak band is also observed at 2097–2098 cm⁻¹ when the intensity of the 2002-cm⁻¹ band is very high. However, the former is much weaker than the latter band and a definitive relation between the two cannot be claimed.

Since the bands discussed above appear in the beginning of the reaction, they must belong to a species with a large number of carbonyl groups and perhaps not more than one nitrosyl group. We tentatively assign these bands to a species of the type Cr(CO)_xNO, where x = 4 or 5.

The total number of infrared CO and NO stretching bands expected for Cr(CO)₅NO is 4: 2 A₁ + E for CO stretch and 1 A₁ for NO stretch. The number of infrared bands expected for Cr(CO)₄NO in C_{3v} geometry is also 4. The species Cr(CO)₄NO is C_{4v} configuration and should, however, give only three bands (A₁ + E for CO stretch and 1 A₁ for NO stretch) in the infrared spectrum. The number of bands that we observed in the spectrum, as mentioned above, is also 3. However, in the absence of a definitive relationship between the two CO stretch bands (at 2002 and 2098 cm⁻¹) and the lack of another CO stretch band, it is not possible to say whether the species we observe is Cr(CO)₅NO or Cr(CO)₄NO. Unfortunately, isotopic frequency shifts provide no additional information about the structure of this intermediate complex.

Photoreactions of Cr(NO)₄. (a) In Argon. The infrared spectrum of Cr(NO)₄ in an argon matrix at 20 K consists of a band in the terminal N–O stretching region which corresponds to the single F₂ fundamental expected for T_d symmetry. Under optimum resolution the band possesses three components at 1728.0, 1725.3, and 1722.4 cm⁻¹. Photolysis at various wavelengths throughout the visible and near-ultraviolet produces some conversion to a product with infrared absorptions at 1714, 1711, 1703, 1699, and 1450 cm⁻¹. The relative intensities of these bands appear fairly constant irrespective of the photolysis source used and can therefore be assigned to a single species. Brief photolysis with shorter wavelength ultraviolet light (220 < λ < 280 nm) causes the amount of product present to decrease.

The product bands around 1700 cm⁻¹ are in the normal region for terminal nitrosyl vibrations and from the 3 to 4 cm⁻¹ separation between pairs it seems reasonable that two fundamentals are involved, with the splittings arising from matrix effects (cf. the 3 cm⁻¹ splitting of the components of the F₂ band of Cr(NO)₄). The product band at 1450 cm⁻¹ can be explained either as due to a bridging nitrosyl ligand (1600–1400 cm⁻¹) or as due to an unusual type of terminal nitrosyl ligand with an exceptionally low wavenumber stretching frequency. The bridging nitrosyl possibility, which

Table II. Observed Frequencies (cm^{-1}) for Species with Unusually Low Nitrosyl Stretching Bands in Argon Matrices

	ν_{CO}	ν_{NO}		
$\text{Cr}(\text{NO})_3(\text{NO}^*)$		1714	1703	1450
		1711	1699	
$\text{Mn}(\text{CO})(\text{NO})_2(\text{NO}^*)^a$	2105	1728	1505	(1479) ^b
	2100	1772	1725	(1473)
$\text{Mn}(\text{CO})_4(\text{NO}^*)$	2017		1465	
	1972			
$(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{NO}^*)^c$			1392	(1368)
			1390	(1366)

^a Data from ref 26. ^b $^{15}\text{N}^{16}\text{O}$ isotopic data in parentheses.

^c Data from ref 27.

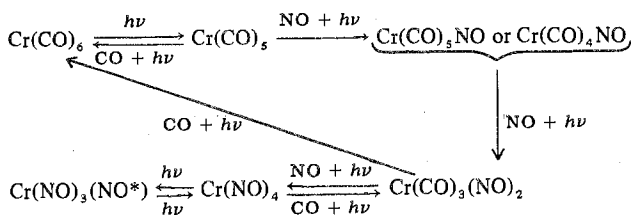
would have of necessity arisen from aggregation in the matrix, is extremely unlikely because of the dilution used in the experiment ($10^4:1$).

Other examples of mononuclear species with low wave-number nitrosyl vibrations have been found for species generated from $(\pi\text{-C}_5\text{H}_5)\text{NiNO}$, $\text{Mn}(\text{CO})(\text{NO})_3$, and $\text{Mn}(\text{CO})_4\text{NO}$ in low-temperature matrices and these results are given in Table II. In the cases of $\text{Mn}(\text{CO})(\text{NO})_3$ ²⁶ and $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{NO})$,²⁷ the molecules which gave species with the highest (1500 cm^{-1}) and lowest (1390 cm^{-1}) bands, respectively, it was demonstrated (using $^{15}\text{N}^{16}\text{O}$ parent molecules) that appropriate band shifts were observed.

Assuming that the pairs of bands at 1714 and 1711 cm^{-1} and 1703 and 1699 cm^{-1} represent two fundamentals, it appears that the product species has an unusual structure. The separation of the two doublets is much too small for them to be the A_1 and E vibrations of a C_{3v} $\text{Cr}(\text{NO})_3$ moiety (no trace of a band at $\sim 1880\text{ cm}^{-1}$ was observed corresponding to free NO).¹⁴ Such a structure can only be postulated by assuming that both doublets are due to a single split E mode and that there is a further undetected A_1 mode (presumably weak) at higher frequency. However, this type of splitting (11 cm^{-1} between centers of pairs) is outside the range observed for matrix splittings in argon.¹² One possibility is that there are not two but three fundamentals (including a weak high-frequency band which is not observed) corresponding to a C_s symmetry $\text{Cr}(\text{NO})_3(\text{NO}^*)$ species. For the species formed on photolysis of $(\pi\text{-C}_5\text{H}_5)\text{NiNO}$ in a matrix it seemed reasonable, at the time, to formulate it as an ion pair $(\pi\text{-C}_5\text{H}_5)\text{Ni}^+\cdots\text{NO}^-$,²⁷ i.e., an example of photoionization in a matrix. With the discovery of other mononuclear species with a range of unusual nitrosyl vibrations from 1500 to 1400 cm^{-1} , it now seems more likely, although still a matter of semantics, that these species are examples of progressively more electron transfer from metal to nitrosyl.²⁸ The consequences of such electron transfer are (a) that the metal will be relatively electron deficient and thereby be susceptible to ligand attack and (b) that the nitrosyl ligand will become progressively more bent as more electron density is transferred to it. It is presumably the bending of the NO^* nitrosyl ligand which confers C_s symmetry on the $\text{Cr}(\text{NO})_3(\text{NO}^*)$ species.

(b) **In Carbon Monoxide Matrices.** The infrared spectrum of $\text{Cr}(\text{NO})_4$ in a CO matrix at 20 K consists of a single band in the N–O stretch region with components (1729.0 , 1725.4 , and 1720.5 cm^{-1}) which are slightly broader than in argon. Short periods of ultraviolet photolysis produced new bands at 2058 and 1701 cm^{-1} which grew at the same rate and therefore can be ascribed to a single species. Prolonged photolysis with the unfiltered mercury arc caused these new bands to disappear and a band at 1990 cm^{-1} to appear.

The bands at 2058 and 1701 cm^{-1} are consistent with those assigned above to $\text{Cr}(\text{CO})_3(\text{NO})_2$. The small shifts in band positions are consistent with the use of different matrix gases. The band at 1990 cm^{-1} , formed after prolonged photolysis, can

Scheme I

be unambiguously assigned to $\text{Cr}(\text{CO})_6$. The failure to observe $\text{Cr}(\text{CO})_x\text{NO}$ ($x = 4$ or 5 , see above) in experiments with $\text{Cr}(\text{NO})_4$ in CO matrices is analogous to the failure to find intermediate nitrosyl species during the photolysis of $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Fe}(\text{CO})_2(\text{NO})_2$ in CO matrices.¹⁰ It probably arises from difficulties in choosing photolysis sources, which will be selective when irradiating molecules with broad and overlapping absorption bands, to produce a particular product species as detected by infrared spectroscopy, rather than nonexistence of the species concerned.

Conclusions

Matrix experiments of photonitrosylation reactions of $\text{Cr}(\text{CO})_6$ and NO reveal that the reaction proceeds through the intermediate complex $\text{Cr}(\text{CO})_3(\text{NO})_2$. While the $\text{Cr}(\text{CO})_3(\text{NO})_2$ intermediate is stable in a low-temperature matrix, it apparently decomposes in hydrocarbon solution at room temperature. The first step in the reaction is the formation of $\text{Cr}(\text{CO})_x(\text{NO})$ ($x = 4$ or 5) via $\text{Cr}(\text{CO})_5$. A reaction scheme leading to the formation of $\text{Cr}(\text{NO})_4$ and including the photoreactions of $\text{Cr}(\text{NO})_4$ is shown in Scheme I. Due to lack of any other intermediate species in the course of the reaction, it is not possible to predict whether the formation of $\text{Cr}(\text{CO})_3(\text{NO})_2$ from $\text{Cr}(\text{CO})_x(\text{NO})$ ($x = 4$ or 5) proceeds via $\text{Cr}(\text{CO})_4(\text{NO})_2$ or by a dissociative mechanism via $\text{Cr}(\text{CO})_3(\text{NO})$. It is not clear, at present, whether the formation of $\text{Cr}(\text{CO})_x\text{NO}$ is a one- or two-photon process involving the prior formation of $\text{Cr}(\text{CO})_5$ and the same applies to the possibility of intermediates such as $\text{Cr}(\text{NO})_3\text{NO}^*$ in the reaction leading to the formation of $\text{Cr}(\text{CO})_3(\text{NO})_2$ from $\text{Cr}(\text{NO})_4$. Further quantitative photochemistry, e.g., quantum yields, will be required to evaluate such possibilities.

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Registry No. $\text{Cr}(\text{CO})_6$, 13007-92-6; $\text{Cr}(\text{NO})_4$, 37355-72-9; $\text{Cr}(\text{CO})_3(\text{NO})_2$, 66290-50-4; $\text{Cr}(\text{CO})_5$, 42386-76-5; $\text{Cr}(\text{CO})_4$, 66290-49-1; $\text{Cr}(\text{CO})_3$, 53059-21-5; $\text{Cr}(\text{CO})_2$, 66290-47-9; $\text{Cr}(\text{CO})$, 66290-46-8; $\text{Cr}(\text{CO})_4(\text{NO})$, 66290-45-7; $\text{Cr}(\text{CO})_3(\text{NO})_2$, 66290-44-6; $\text{Cr}(\text{CO})_3(\text{NO})$, 66290-43-5.

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Photochemistry of Macrocyclic Copper(II) Complexes. Photoinduced Redox Reactions of Cu[13-AtH]²⁺¹

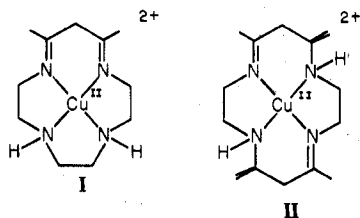
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The photochemical reactivity of the Cu[13-AtH]²⁺ complex is noticeable only for ultraviolet irradiations (254–370 nm). Photolyses, carried out in the presence of various alcohols, produced aldehydes or ketones. Two Cu(II) macrocyclic complexes, one characterized as Cu[Me₂[13]monoeneN₄]²⁺, were products of the reaction. The dependence of the quantum yields on experimental variables (acid concentration, scavenger concentration, light intensity, excitation wavelength) is explained in terms of a proposed reaction mechanism. The primary product, a Cu(III) cation–ligand radical, was postulated by a comparison with the behavior already reported for Cu[[14]dieneN₄]²⁺.

Introduction

Although the study of the macrocyclic complexes of various metal ions has been a very active field of research, the photochemistry of these compounds has not been explored until recently.^{2–9} The chemical properties already reported for these complexes show that they present some potentially interesting features for photochemical studies. Modifications in the structure of the tetraaza macrocyclic ligand, for example, in the degree of unsaturation or in the ring size, have a marked influence on the relative stability of accessible oxidation states for a given metal ion.¹⁰ Further, restrictions for rearrangement of the ligand configuration and the ability of the ligand to produce steric hindrance in reactive positions change with each ligand. Therefore, the chemical reactivity of the metal ion can be modified by these means.^{11–13} In this regard, if the various structural effects which have influence on the properties of the compounds in their ground states are somehow reflected in the behavior of the excited states, a largely tunable photochemical reactivity could be expected.^{14,15} Results obtained on the photochemistry of Cu[13-AtH]²⁺ (I) are reported here and compared with previous results of Cu[[14]dieneN₄]²⁺ (II).



Experimental Section

Photochemical Procedures. Ultraviolet photolyses were carried out in a Rayonet merry-go-round reactor using Rayonet lamps with spectral distributions appropriate to the experiment. A superpressure mercury point source combined with an Oriel 7242 monochromator was used for excitations at various wavelengths (300, 370, and 500 nm). The light intensity was found between 3×10^{-4} and 8×10^{-4} einstein/(L min) for the experimental arrangements indicated above. Ferrioxalate was used as a primary actinometric reference.¹⁶ The light was frequently tested with Co(NH₃)₅Br²⁺.¹⁷

Quantum yields were obtained using already reported procedures.^{2,17} Solutions used for such determinations absorbed more than 99.9% of the incident light (optical density ≥ 3 at the wavelength of excitation). Product concentrations were obtained at various periods of the irradiation. The slopes of the curves of the product concentration vs. time, extrapolated at zero time, were used for quantum yield calculations.

Solutions were deaerated with solvent-saturated nitrogen streams or with vacuum.² Photolyses were also carried out in presence of oxygen using solutions equilibrated under 1 atm of gas.

Flash photolyses were carried out in an instrumental setup built in this laboratory. Two FP-8-100C Xenon Corp. flash lamps were fired in series at voltages between 10 and 3 kV. The capacitor bank was formed with one, two, or three 5-μF capacitors connected in parallel. Pulses with a lifetime of 30 μs were obtained for energies below 300 J/flash. Optical detection was used in this system. The light beam used for such a purpose was obtained from a 300-W Xenon Eimac lamp coupled with collimating lenses and filters. The light was directed through the sample cell and into an optical baffle and a monochromator. A 20 cm optical path sample cell was used for observation of the transients. Cutoff filters were used in order to irradiate in preselected regions.¹⁸