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Photooxidation of Matrix-Isolated Nickel Tetracarbonyl in the Presence of Dioxygen

Anthony J. Downs,* Tim M. Greene, and Charles M. Gordon[†]

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, England

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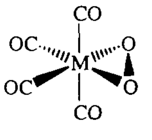
UV Photolysis (λ = *ca.* 254 nm) of $Ni(CO)_4$ molecules isolated in O_2-doped argon matrices at *ca.* 20 K has been monitored by reference to the IR spectra of the matrices. These spectra indicate that $Ni(CO)_4$ undergoes photooxidation to give four distinct nickel carbonyl intermediates **A**−**D** with the release of CO and CO_2, ultimately to arrive at the final product $(\eta^2\text{-}O_2)_2Ni$. The stoichiometry and likely structure of each intermediate **A**−**D** have been deduced by analysis of the number, energies, and relative intensities of its IR absorptions, with particular reference to the response to ^{13}CO- and ^{18}O-enrichment. Hence, the following identities have been inferred: **A**, $Ni(CO)_3$; **B**, $(\eta^2\text{-}O_2)Ni(CO)_2$; **C**, $(O_2)Ni(CO)_3$; and **D**, $O{=}Ni(CO)_2$. The system exhibits some photoselectivity, and reversal of the reactions leading to **A**−**D** can be effected under the action of UV radiation with wavelengths near 313 nm or by annealing the deposit to *ca.* 30−35 K. A partial mechanism is proposed to account for the course of the matrix reactions.

1. Introduction

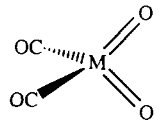
The activation of dioxygen through coordination to a transition metal remains a matter of intense interest,[1−3] because of the vital rôle the controlled transfer of oxygen plays in biology and in the commercial production of numerous chemicals. However, the details of the actual oxygen transfer in processes of this sort are still poorly characterized. A primary objective of a fuller understanding must be an accurate description of the binding to the metal of dioxygen (and species derived from it) throughout the reaction sequence, and the vibrational properties associated with the ν(O−O) or ν(M−O) fundamentals (M = metal) offer one of the most widely exploited means of probing this binding.[1,3−10]

Matrix-isolation methods provide a relatively direct way of exploring the interaction of dioxygen with an unsaturated metal center.[11] Hence, for example, the cocondensation of nickel, palladium, or platinum atoms with pure dioxygen or argon doped with O_2 gives rise to the peroxo derivatives $(\eta^2\text{-}O_2)M$ and $(\eta^2\text{-}O_2)_2M$ (M = Ni, Pd, or Pt).[12,13] Similar experiments with mixtures of O_2 and N_2 show IR absorptions implying the formation of mixed dioxygen-dinitrogen species of the type $(\eta^2\text{-}O_2)M(N_2)_n$ (M = Ni, Pd, or Pt; n = 1 or 2).[14] Hence, too, sputtering has been used to engineer the formation and trapping of the diatomic NiO molecule.[15] However, the intervention of metal clusters is a potential complication in such cocondensation experiments. A strategy that reduces the problem of products containing more than one metal atom is employed here, namely, UV photolysis of a metal carbonyl isolated at high dilution in an O_2-doped matrix. Unsaturated metal carbonyls like $M(CO)_4$, where M = Cr,[5,7,8] Mo,[6−8] W,[6−8] or Fe,[9,10] bind and activate O_2 molecules with respect to photodissociation, giving oxometal carbonyl intermediates like **I**, **II**, and **III** and, ultimately, binary metal oxides MO_n (n = 2, 3, or 4). Carbon dioxide is also a photoproduct derived, it appears, by concerted photoelimination from one or more oxometal carbonyl intermediates.



M = Mo or W

I



M = Cr, Mo, or W

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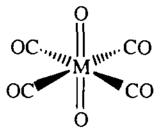

M = Cr, Mo, or W

III

Here we describe the results of some matrix experiments designed to investigate the photooxidation of nickel tetracarbonyl. UV photolysis of this precursor is known to give rise initially to the 16-electron molecule $Ni(CO)_3$[16] which may be

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* Author to whom correspondence should be addressed.

[†] Present address: School of Chemistry, Queen's University, Belfast BT9 5AG, U.K.

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expected to interact with O_2. The evolution of the matrix reactions has been charted by IR spectroscopy, the response to ^{13}CO- and ^{18}O-enrichment providing vital clues to the stoichiometries and likely structures of the products.

2. Experimental Details

The experiments were carried out broadly in accordance with the procedures described elsewhere.[6−10] An Air Products "Displex" 202 closed-cycle refrigerator gave window temperatures down to *ca.* 18 K inside a shroud maintained at a pressure below 10^{-7} Torr (*ca.* 1.33×10^{-5} Pa). Temperatures were measured with a chromel vs iron-doped gold thermocouple or with a hydrogen vapor bulb. Matrices were invariably formed by pulsed deposition.[17] IR spectra were recorded with a Mattson "Galaxy" FTIR spectrometer, affording a resolution of 0.5 cm^{-1}.

Nickel tetracarbonyl (*ex* ICI) was purified by fractional condensation in vacuo, the glass vacuum line being shrouded in aluminium foil to minimize the risk of photodecomposition; the purity of the sample was checked by reference to the IR spectrum of the vapor.[18] Samples of $Ni(CO)_4$ enriched in ^{13}CO were prepared simply by leaving a mixture of the vapor of the isotopically natural carbonyl with an excess of ^{13}CO (^{13}C, 99 at.%; ^{18}O, <1%; Cambridge Isotope Laboratories) to equilibrate for about 60 min at room temperature[19] and then bleeding the gaseous mixture slowly through a spiral trap held at 77 K. The degree of ^{13}C-enrichment was estimated by measuring the IR spectrum of the vapor. Argon, CO, and O_2 were used as supplied by BOC (research grade). $^{18}O_2$ (98 at.%; MSD Isotopes) and a statistical mixture of the isotopomers $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ (^{18}O, 53.56 at.%; Enritech Enrichment Technologies) were similarly used as supplied.

Photolysis was achieved with radiation from a 500-W medium-pressure mercury arc (Oriel), a 40-mm column of water contained in a quartz cell being used to minimize the intensity of IR radiation incident upon the deposit. In addition, interference filters (Oriel) were also used to transmit UV radiation at wavelengths near 254 or 313 nm.

The wavenumbers and relative intensities of the ν(C—O) features in the IR spectra of individual products incorporating $Ni(CO)_n$ fragments at varying levels of ^{13}CO-enrichment were calculated on the basis of an energy-factored force field using simple iterative refinement programs; IR spectra were then simulated with a program that constructed Lorentzian band shapes based on the calculated intensities.[20] The calculations were performed on a VAX computer operated by the Oxford University Computing Service.

3. Results and Discussion

3.1. Overview. An argon matrix containing $Ni(CO)_4$ and O_2 [typically in the proportions $Ar:O_2:Ni(CO)_4$ = *ca.* 1500:150:1] gave an IR spectrum very similar to the one described previously for $Ni(CO)_4$ isolated in a pure argon matrix.[21] The matrix was irradiated with UV light at λ = *ca.* 254 nm and the progress of any reactions surveyed at regular intervals by reference to the IR spectrum. In addition to absorptions arising from unchanged $Ni(CO)_4$,[21] free CO,[22] and CO_2,[23] numerous new features developed with photolysis, these occurring in the regions of the IR spectrum associated with ν(C—O) (1900−2200 cm^{-1}) and either ν(Ni═O) or ν(O—O) fundamentals (800−1100 cm^{-1}). Absorptions in the region 400−600 cm^{-1} associated with ν(Ni—C) and δ(Ni—C—O) fundamentals of $Ni(CO)_4$ decayed but were not replaced by any new feature of significant intensity. Prolonged photolysis at λ = *ca.* 254 nm extending over periods of up to 8 h depleted the matrix in $Ni(CO)_4$, but never to less than 30% of its initial concentration, and the IR spectrum displayed only very small changes in the intensity of the various bands over periods of more than 6 h. This contrasts with the behaviors of $M(CO)_6$ (M = Cr, Mo, or W)[6−8] and $Fe(CO)_5$[9,10] molecules, photolysis of which in the presence of O_2 leads under comparable conditions to the destruction of all the species containing coordinated CO. The explanation probably lies in part in the deterioration in the optical properties of the matrix brought about by photolysis, in part in the proximity of the UV absorption bands characterizing $Ni(CO)_4$,[24] $Ni(CO)_3$,[25] and the photooxidation products.

Attempts to record the UV−vis absorption spectra of any of the photoproducts proved fruitless, presumably because of the small concentrations that it was possible to generate. However, the response of the matrices to photolysis gave some useful clues to the likely locations of UV absorption bands associated with some of the products.

Changes in the conditions of photolysis revealed that the relative proportions of photoproducts formed by radiation having λ = *ca.* 254 nm could be altered. Thus, some of the product bands decayed when the matrix was exposed to UV radiation with λ = *ca.* 313 nm, while others increased in intensity. Similar changes in the IR spectrum were also evoked by annealing the matrix at temperatures up to *ca.* 30−35 K. These relative changes in the sets of product bands proved most instructive. Thus, by scrutinizing the growth and decay patterns of the new bands, it was possible to assign each of the more prominent features to one of five distinct photoproducts, **A**−**E**.

Experiments have been carried out to investigate the effects of varying the matrix concentration of $Ni(CO)_4$ (from 0.1 to 0.02%) and of O_2 (from 2−20 up to 100%). Reducing the concentration of $Ni(CO)_4$ caused merely a uniform reduction in the intensities of all the IR bands associated with the different photoproducts; these results suggest that each of the main absorbers contains only a single Ni atom. Increasing the concentration of O_2 in the matrix between 2 and 20% brought about no detectable enhancement in the buildup of product bands. Some experiments were carried out with $Ni(CO)_4$ isolated in a pure dioxygen matrix, but the resulting IR spectra displayed bands that were both shifted and matrix-split when compared with those of $Ni(CO)_4$-doped argon matrices containing O_2 in lower concentrations. The splitting is presumably exacerbated by the existence of two phases, α- and β-oxygen, at the temperatures employed.[12]

The strategy for identifying the intermediates **A**−**E** was as follows. Firstly, the number, energies, and relative intensities of the ν(C—O) absorptions attributable to each intermediate were compared with the features expected for an $Ni(CO)_n$ fragment, subject to variations of stoichiometry and geometry, and with due account of the vibrational properties reported previously for such fragments.[16,26−28] Secondly, experiments leading to partial enrichment of the intermediate in ^{13}CO were carried out. These entailed the matrix isolation of $Ni(^{12}CO)_{4-n}(^{13}CO)_n$ isotopomers (where n = 0−4) with overall levels of ^{13}CO-enrichment amounting to 27 or 82%. With the additional information thus derived, it was possible once again to compare

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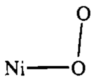
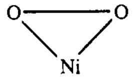
the number, energies, and relative intensities of the observed ν(C—O) bands with the properties calculated for different $Ni(CO)_n$ fragments[20,29] and, hence, to determine n and the likely geometry of the nickel carbonyl moiety in a given product. In this way, it was also possible to estimate the OC—Ni—CO bond angles. Since there was not enough information to calculate independently bond angles and dipole derivative ratios, however, all such ratios have been set equal to unity, as in the study of the photooxidation products of iron pentacarbonyl.[9,10]

The mode of coordination and the number of oxygen atoms bound to the nickel center in the major photoproduct **B** were determined by reference to the effects of ^{18}O-enrichment. Separate experiments were performed with $^{16}O_2$, $^{18}O_2$, with a mixture of the two "symmetrical" isotopomers $^{16}O_2$ and $^{18}O_2$, and finally with a scrambled mixture of all the isotopomers $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$. The first three experiments allow for measurement of the $^{16}O-^{18}O$ isotopic shifts and assessment of the number of O_2 molecules added to the metal center, as well as indicating whether the addition is concerted or nonconcerted. In principle, the fourth experiment allowed a distinction to be drawn between an NiO fragment and each of the possible structures **IV**—**VI** likely to be assumed by an NiO_2 fragment. How the method works has been exemplified previously.[5-13]


IV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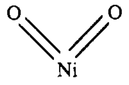
VI

Each of the photoproducts **A**—**E** will be discussed separately.

3.2. Photoproduct A. Intermediate **A** is characterized by only one detectable IR band, and this occurs in the ν(C—O) region at 2018.7 cm^{-1}. Together with free CO, it is formed from nickel tetracarbonyl by irradiation with light having wavelengths near 254 or at 313 nm, while annealing of the matrix caused a decrease in the intensity of the infrared band due to **A** with an accompanying growth of the absorptions due to $Ni(CO)_4$.

The primary product of UV photolysis of $Ni(CO)_4$ has been shown to be $Ni(CO)_3$; as formed in a pure argon matrix, this has been characterized previously by a strong IR absorption at 2016 cm^{-1}, as well as a weaker one at 2066 cm^{-1}.[16] It is further reported[16] that annealing the matrix to 30 K for 5 min resulted in approximately 50% regeneration of the parent tetracarbonyl through recombination of $Ni(CO)_3$ and photoejected CO. The spectroscopic and photolytic properties of **A**, together with its response to annealing, suggest that it is the tricarbonyl, $Ni(CO)_3$. Figure 1 shows the effects of UV photolysis on a matrix-isolated sample of $Ni(CO)_4$ in pure argon with no oxygen dopant. As may be seen, a band appeared in the IR spectrum at 2016.8 cm^{-1}, although there was no evidence of a weaker feature in the vicinity of 2066 cm^{-1}.

A study of the ^{13}CO-enriched isotopomers of $Ni(CO)_3$ isolated in pure argon matrices was undertaken. IR spectra were measured following broad-band photolysis of argon matrices containing $Ni(CO)_4$ enriched by 27 and 82% in ^{13}CO. The spectra are shown in Figure 2. Included also in Figure 2 are the ν(C—O) spectra simulated on the basis of a planar D_{3h} tricarbonyl moiety. The observed and calculated frequencies are given in Table 1. Since none of the totally symmetric modes of the $Ni(CO)_3$ molecule was observed, the results of such calculations need to be considered critically. In particular, it is noteworthy that the high-frequency $\nu(a_1)$ mode for $Ni(^{12}CO)_3$ is predicted by our calculations to come at 2106.7 cm^{-1}. This is considerably higher than the value of 2066 cm^{-1} reported by Rest and Turner.[16] However, any attempts to include this value resulted in a significantly worse fit to the observed frequencies, so we have left the calculation as it stands. The values of the force constants (k_{CO} = 1692.8 N m^{-1}, $k_{CO,CO}$ = 50.0 N m^{-1}) are in good agreement with those calculated by DeKock (k_{CO} = 1700 N m^{-1}, $k_{CO,CO}$ = 57 N m^{-1}),[27] even allowing for the fact that he was forced to estimate the interaction force constant by comparison with those of $Ni(CO)_2$ and $Ni(CO)_4$. It is to be noted that DeKock, who generated matrix-isolated $Ni(CO)_3$ by the reaction of metal atoms with CO, failed also to observe any IR band near 2066 cm^{-1}. It appears therefore that $Ni(CO)_3$ is

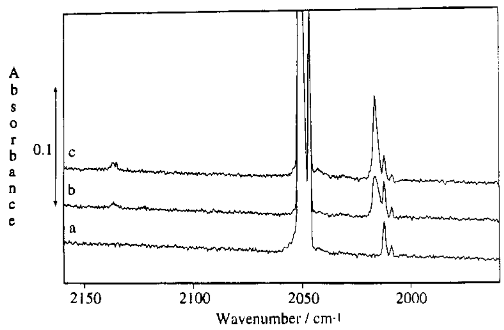

Figure 1. IR spectrum of $Ni(CO)_4$ isolated in an Ar matrix ($Ar:Ni(CO)_4$ = *ca.* 1:2000) in the region 1960—2160 cm^{-1}: (a) after deposition; (b) after 60 min of photolysis at *ca.* 254 nm; (c) after 120 min of broad-band photolysis.

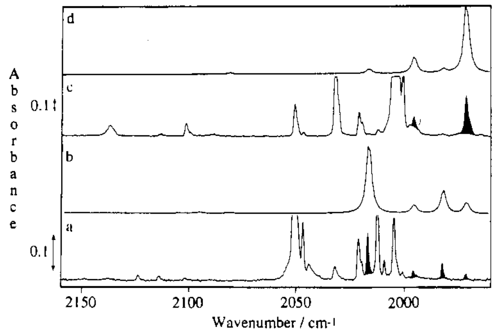

Figure 2. Stacked plot comparing the IR spectrum observed for $Ni(CO)_3$ in the region 1960—2160 cm^{-1} (bands marked by black infilling) with that predicted on the basis of a planar tricarbonyl of D_{3h} symmetry with the force constants given in Table 1: (a) observed and (b) predicted for 27% ^{13}CO-enrichment; (c) observed and (d) predicted for 82% ^{13}CO-enrichment.

Table 1. ν(C—O) Modes of Different $^{12}CO/^{13}CO$ Isotopomers of $Ni(CO)_3$ Isolated in an Ar Matrix: Wavenumbers (cm^{-1}) Observed and Calculated for a Planar Tricarbonyl Molecule

obsd	calcd[a]	mode	molecule
b	2106.7	a_1'	$Ni(^{12}CO)_3$
2016.8	2016.6	e'	
c	2095.3	a_1	$Ni(^{12}CO)_2(^{13}CO)$
2016.8	2016.6	b_2	
1982.3	1982.3	a_1	
c	2081.3	a_1	$Ni(^{12}CO)(^{13}CO)_2$
1995.8	1995.7	a_1	
1971.4	1971.6	b_2	
b	2059.7	a_1'	$Ni(^{13}CO)_3$
1971.4	1971.6	e'	

[a] Calculated on the assumption of an energy-factored force field for an $Ni(CO)_3$ unit with D_{3h} symmetry; k_{CO} = 1692.8 N m^{-1} and $k_{CO,CO}$ = 50.0 N m^{-1}. [b] IR-inactive. [c] Too weak to be observed.

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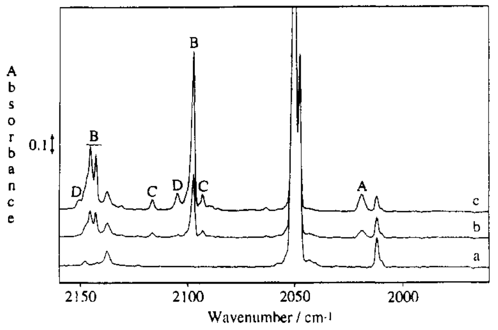
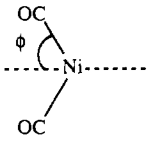


Figure 3. IR spectrum of $Ni(CO)_4$ isolated in an O_2-doped Ar matrix ($Ar:O_2:Ni(CO)_4$ = 1500:150:1) in the region 1960–2160 cm^{-1}, showing the effects of photolysis at wavelengths near 254 nm: (a) after deposition; (b) after 60 min of photolysis; (c) after 180 min of photolysis.

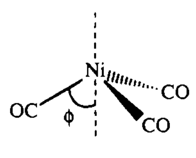
either planar or distorted only slightly from planarity, such that the high-frequency ν(C—O) mode (a_1) remains too weak to be detected in IR absorption.

3.3. Photoproduct B. **B** is the dominant intermediate formed by irradiation of $Ni(CO)_4$ in the presence of O_2 at wavelengths near 254 nm. The concentration of **B** reaches a maximum after approximately 2 h of photolysis at *ca.* 254 nm and then shows a slight decrease as further photooxidation products are formed. Irradiation at 313 nm decreases the concentration of **B**, as does annealing the matrix to temperatures up to 35 K. In one experiment, it was found that irradiation at *ca.* 313 nm following photolysis at *ca.* 254 nm resulted in the decay of **B**, with a growth in the bands due to **A** and the parent tetracarbonyl. The implication of this finding is that the formation of photoproduct **B** from **A** is reversible under appropriate conditions. The growth of photoproduct **B** is shown in Figure 3. **B** is characterized by no less than three IR absorptions, *viz.*, two in the ν(C—O) region (a doublet at 2145.2/2142.8 cm^{-1} and a singlet at 2097.3 cm^{-1}) and one in the region associated with ν(O—O) or ν(Ni=O) modes (at 978.0 cm^{-1}).

ν(C-O) Region of B. The average wavenumber of the ν(C—O) modes of **B** (2128.4 cm^{-1}) is appreciably higher than the wavenumber of the corresponding mode of **A**, and it seems reasonable therefore to suppose that the metal center in **B** has a formal oxidation state higher than zero. Moreover, the observation of two ν(C—O) fundamentals in the IR spectrum argues in favor of either a nonlinear $Ni(CO)_2$ constituent with C_{2v} symmetry (**VII**) or a pyramidal $Ni(CO)_3$ constituent with C_{3v} symmetry (**VIII**). The relative intensities of the two bands imply a semivertical angle ϕ subtended by the CO oscillators with respect to the principal axis of either model in the order of 52°.[29,30] It is a relatively straightforward matter to distinguish between the models **VII** and **VIII** by partially enriching **B** in ^{13}CO and comparing the number, energies, and intensities of the resulting absorptions with those calculated for each of the two models.



VII



VIII

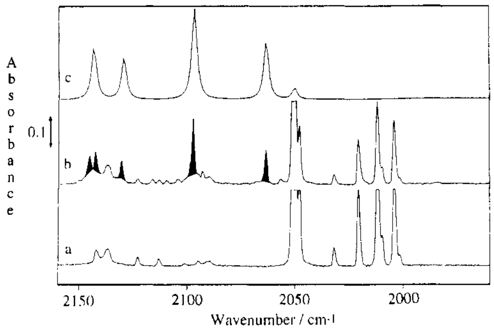


Figure 4. Stacked plot comparing the IR spectrum in the region 1960–2160 cm^{-1} observed for **B** with 27% ^{13}CO-enrichment (bands marked by black in-filling) with that predicted on the basis of a bent dicarbonyl fragment with the geometry and force constants given in Table 2: (a) on deposition; (b) after 60 min of photolysis at *ca.* 254 nm; (c) simulated spectrum.

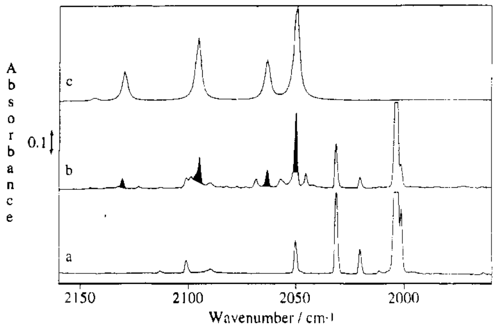


Figure 5. Stacked plot comparing the IR spectrum in the region 1960–2160 cm^{-1} for **B** with 82% ^{13}CO-enrichment (bands marked by black in-filling) with that predicted on the basis of a bent dicarbonyl fragment with the geometry and force constants given in Table 2: (a) on deposition; (b) after 60 min of photolysis at *ca.* 254 nm; (c) simulated spectrum.

Table 2. ν(C—O) Modes of Different $^{12}CO/^{13}CO$ Isotopomers of B Isolated in an O_2-Doped Ar Matrix: Wavenumbers (cm^{-1}) Observed and Calculated for a Bent $Ni(CO)_2$ Fragment

obsd	calcd[a]	mode	molecule
2144.0[b]	2143.7	a_1	$Ni(^{12}CO)_2$
2097.3	2097.1	b_2	
2130.5	2129.8	a′	$Ni(^{12}CO)(^{13}CO)$
2063.3	2063.8	a′	
2095.1	2095.9	a_1	$Ni(^{13}CO)_2$
2050.5	2050.4	b_2	

[a] Calculated on the assumption of an energy-factored force field for an $Ni(CO)_2$ unit with C_{2v} symmetry and a semivertical angle ϕ = 52° (**VII**); k_{CO} = 1816.6 N m^{-1} and $k_{CO,CO}$ = 39.9 N m^{-1}. [b] The average value of the matrix-split components was used.

Experiments showed that ^{13}CO-enrichment of **B** gave distinct new bands at 2130.5, 2063.3, and 2050.5 cm^{-1}. As revealed in Figures 4 and 5 and Table 2, the features of the spectra match closely those predicted for an angular $Ni(CO)_2$ moiety (**VII**); no such fit could be obtained for a pyramidal $Ni(CO)_3$ moiety (**VIII**) (see Figure 6 and Table 3). Problems of overlap tended to confuse the picture. Thus, the ν(C—O) modes of the all-^{13}CO isotopomer were found to occur at *ca.* 2095.1 and 2050.5 cm^{-1}; the first virtually coincides with the lower-energy ν(C—O) mode of the all-^{12}CO isotopomer and the second with the IR-active ν(C—O) mode of $Ni(^{12}CO)_4$. Nevertheless, close scrutiny of the intensities of the relevant bands leaves little room for doubt regarding the essential features of the spectrum or the identification of the absorber.

ν(Ni=O) or ν(O—O) Region of B. The band at 978.0 cm^{-1} in the infrared spectrum of the matrix deposit following photolysis at *ca.* 254 nm is assigned to **B** by virtue of its behavior following photolysis at varying wavelengths and its response to annealing. Furthermore, the band is observed to

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(30) See, for example: Smit, W. M. A. *J. Mol. Struct.* **1973**, *19*, 789.

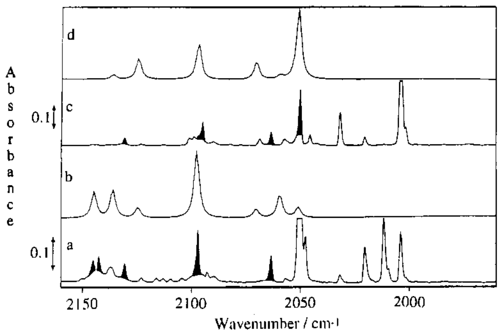

Figure 6. Stacked plot comparing the IR spectrum in the region 1960–2160 cm^{-1} for **B** (bands marked by black in-filling) with that predicted for a pyramidal tricarbonyl fragment with the geometry and force constants given in Table 3: (a) observed and (b) predicted for 27% ^{13}CO-enrichment; (c) observed and (d) predicted for 82% ^{13}CO-enrichment.

Table 3. ν(C—O) Modes of Different $^{12}CO/^{13}CO$ Isotopomers of B Isolated in an O_2-Doped Ar Matrix: Wavenumbers (cm^{-1}) Observed and Calculated for a Pyramidal $Ni(CO)_3$ Fragment

obsd	calcd[a]	mode	molecule
2144.0[b]	2145.7	a_1	$Ni(^{12}CO)_3$
2097.3	2098.0	e	
c	2136.8	a_1	$Ni(^{12}CO)_2(^{13}CO)$
2097.3	2098.0	b_2	
2063.3	2059.7	a_1	
2130.5	2125.3	a_1	$Ni(^{12}CO)(^{13}CO)_2$
c	2070.8	a_1	
2050.5	2051.2	b_2	
2095.1	2097.8	a_1	$Ni(^{13}CO)_3$
2050.5	2051.2	e	

[a] Calculated on the assumption of an energy-factored force field for an $Ni(CO)_3$ unit with C_{3v} symmetry and a semivertical angle $\phi = 52°$ (**VIII**); $k_{CO} = 1805.4$ N m^{-1} and $k_{CO,CO} = 27.2$ N m^{-1}. [b] The average value of the matrix-split components was used. [c] Not observed.

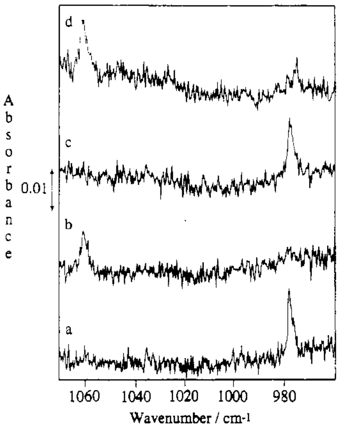

Figure 7. IR spectrum of $Ni(CO)_4$ isolated in an O_2-doped Ar matrix ($Ar:O_2:Ni(CO)_4$ = 1500:150:1): (a) after 60 min of photolysis at *ca.* 254 nm following deposition; (b) after a further 90 min of photolysis at *ca.* 313 nm; (c) after a further 120 min of photolysis at *ca.* 254 nm; (d) after annealing the deposit to approximately 30 K.

shift on ^{13}CO substitution. Thus, at 27% enrichment the band occurs at 976.8 cm^{-1}, while at 82% enrichment it is observed at 976.3 cm^{-1}. This response of the band position clearly indicates the presence of carbonyl ligands bound to the metal. The growth and decay of the band are illustrated in Figure 7.

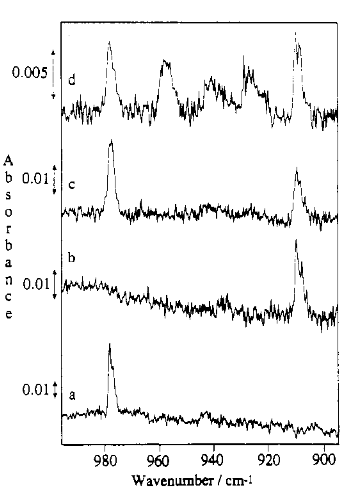

Figure 8. IR spectrum of **B** in the region 890–990 cm^{-1}: observed spectrum (a) for a sample generated from $^{16}O_2$; (b) for a sample generated from $^{18}O_2$; (c) for a sample generated from a mixture of $^{16}O_2$ and $^{18}O_2$ ($^{16}O_2:^{18}O_2$ = *ca.* 1:1); and (d) for a sample generated from a mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ ($^{16}O_2:^{16}O^{18}O:^{18}O_2$ = 1:2.3:1.3).

When **B** was generated in an argon matrix doped with $^{18}O_2$, rather than $^{16}O_2$, the IR band at 978.0 cm^{-1} was replaced by one at 909.8 cm^{-1} (compare Figure 8a,b). At 68.2 cm^{-1}, the $^{16}O—^{18}O$ shift is surprisingly large; the shift to be expected for ν(O—O) of an O_2 unit functioning as an independent harmonic oscillator is 55.7 cm^{-1} and appreciably less than this for ν(Ni=O) of a Ni=O or O=Ni=O unit.[5-10,15] The approximation to a simple diatomic oscillator model by the coordinated O_2 unit has been shown to hold for the peroxonickel complex, $NiO_2(Bu^tNC)_2$.[31]

Preparation of **B** in a matrix including 5% $^{16}O_2$ and 5% $^{18}O_2$ gave just two bands (Figure 8c) at 978.0 and 909.8 cm^{-1} with relative intensities of *ca.* 1:0.88 (the expected ratio for a diatomic oscillator would be 1:0.889).[32] There was no sign of the extra feature or features to be expected (i) if more than one O_2 molecule were coordinated to the metal atom in **B**[12,13] or (ii) if the addition of O_2 were to follow a nonconcerted mechanism.[5-10] By contrast, the use of isotopically scrambled dioxygen (with $^{16}O_2:^{16}O^{18}O:^{18}O_2$ = 1:2.31:1.33) as a source of **B** gave no less than five bands in the region 800–1000 cm^{-1} (Figure 8d). These occurred at 978.0, 957.0, 940.6, 925.9, and 909.8 cm^{-1} with the relative intensities 1:1.07:0.52:0.85:1.11. The experiment with isotopically scrambled O_2 eliminates the possibility that **B** contains a single Ni=O unit. If the intensities of the three central bands in the quintet pattern are added together, the intensity ratios become 1:2.44:1.11, in reasonable agreement with the expected ratio for a simple diatomic oscillator of 1:2.18:1.18. The most plausible explanation consistent with the various effects of ^{18}O-enrichment is that Fermi resonance is occurring between a fundamental and two binary transitions (overtones or combinations), the effects of this resonance being most pronounced for the $^{16}O^{18}O$ derivative of **B**. All the evidence suggests that **B** is a peroxonickel compound, including the (η^2-O_2)Ni fragment, and that the IR absorptions between 900 and 1000 cm^{-1} are associated with ν(O—O) fundamentals in Fermi resonance with two binary transitions. The uncharacteristically large $^{16}O—^{18}O$ shift and the remarkable quintet pattern generated in the experiment with isotopically scrambled O_2 can then be attributed to changes in the degree of interaction between the neighboring vibrational states, reflecting the different responses of the relevant high- and low-energy fundamentals to ^{18}O-enrichment.

Close scrutiny of the spectra shown in Figure 8a,b reveals extremely weak bands centered near 943 and 936 cm^{-1}, respectively. These may be assigned tentatively to the binary

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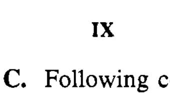
(31) Nakamura, A.; Tatsuno, Y.; Yamamoto, M.; Otsuka, S. *J. Am. Chem. Soc.* **1971**, *93*, 6052.

(32) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; Dover: New York, 1980; p 191 *ff.*

transition component of the Fermi resonance doublet. The bands are too diminished in intensity to be discernible in the mixed $^{16}O_2/^{18}O_2$ experiment, the product now being dissipated as two isotopomers. It should further be noted that the weakness of these bands indicates that they are not responsible for the strong central band of the quintet seen in Figure 8d.

Searches of the spectra have failed to reveal any significant absorption in the region 450–500 cm^{-1} corresponding to a ν(Ni—O) fundamental of **B**. On the other hand, the vibrational properties of the peroxo unit of **B** may be expected to have much in common with those of the molecule $(\eta^2\text{-}O_2)NiN_2$ for which the $\nu(^{16}O-^{16}O)$ mode has been located at 977 cm^{-1}.[14] Calculations taking in the enriched isotopomers of $(\eta^2\text{-}O_2)NiN_2$ predicted that ν_{sym}(Ni—O) of $(\eta^2\text{-}^{16}O^{18}O)Ni(N_2)$ occurs at 471.7 cm^{-1}, although experiments failed to detect the band, presumably because of its weakness. If **B** is presumed also to possess a similar mode in the region of 470 cm^{-1}, the first overtone would come into almost exact resonance with ν(O—O) of a $(^{16}O^{18}O)Ni$ isotopomer. It seems highly plausible, therefore, that such an overtone is a candidate for one of the two binary transitions. The nature of the other binary transition remains much more uncertain. Scarcely to be expected is that it has its origin in the other mode of the $(\eta^2\text{-}O_2)Ni$ unit, namely, ν_{asym}(Ni—O), as this is unlikely to be close to 470 cm^{-1}. There is, however, the possibility that it arises from a ν(Ni—C) or δ(Ni—C—O) fundamental which would be expected to occur near 500 cm^{-1}. The possibility that **B** contains an O=Ni=O unit and that there is Fermi resonance between the first overtone of the bending mode and one or both of the ν(Ni=O) modes of the $^{16}O=Ni=^{18}O$ species can be largely discounted on several grounds. However, most telling of the arguments against such a model are (i) the *symmetrical* pattern of bands characterizing the products derived from isotopically scrambled O_2 [*cf.* $O_2Cr(CO)_2$[5] and $O_2Fe(CO)_3$[9]] and (ii) the magnitude of the $^{16}O-^{18}O$ shift which cannot easily be explained by Fermi resonance in this case. With regard to the possibility of Fermi resonance, the more intense, and possibly only detectable, IR absorption due to ν(Ni=O) is the b_2 mode for a bent, or σ_u mode for a linear, O=Ni=O unit, whereas the first overtone of the bending mode contains the representation a_1 or σ_g, respectively. Similar problems of Fermi resonance are believed to arise not only in the molecule SNO[33] but also in the dioxygen–metal complexes $(\eta^2\text{-}O_2)Fe(CO)_4$ (**I**)[9] and oxyhaemoglobin.[34] Hence, this interpretation is not without precedent.

It appears therefore that **B** is peroxonickel dicarbonyl, $(\eta^2\text{-}O_2)Ni(CO)_2$ (**IX**). Its spectroscopic properties resemble those of other peroxonickel derivatives, *e.g.* $(\eta^2\text{-}O_2)Ni$[12,13] and $(\eta^2\text{-}O_2)Ni(N_2)_n$ (n = 1 or 2),[14] and there are also obvious parallels with other oxometal dicarbonyls, *e.g.* $O_2Cr(CO)_2$[5] and $O_2Fe(CO)_3$.[9]



IX

3.4. Photoproduct C. Following continued photolysis of the matrix deposit with light at wavelengths near 254 nm, two infrared bands, both in the ν(C—O) region, were observed to appear and grow in unison. These bands, at 2116.3 and 2092.9 cm^{-1}, are assigned to photoproduct **C**. As shown in Figure 9, the intensity of the bands was increased only slightly by subsequent photolysis at *ca.* 313 nm, while annealing of the matrix deposit caused the higher-frequency band to broaden and the other band to split into a doublet. Experiments starting from $Ni(CO)_4$ enriched in ^{13}CO led to the identification of infrared features assigned to the isotopomers of photoproduct **C**. At the 27% ^{13}CO-enrichment level, a band at 2109.8 cm^{-1} can, by virtue of its response to photolysis and annealing, be assigned to a ^{13}CO-enriched isotopomer of **C**. The absence of this band in the experiments starting from $Ni(CO)_4$ 82% enriched in ^{13}CO points away from a C_{2v} dicarbonyl fragment, for which an infrared absorption due to the mixed isotopomer would be observed at both levels of enrichment, as seen for photoproduct **B**. The ratio of the intensities of the bands at 2116.3 and 2092.9 cm^{-1} gives a semivertical angle ϕ = 48° (see **VII** and **VIII**). Simulations of the infrared spectra of **C** based on a C_{3v} tricarbonyl moiety with a semivertical angle of 48° are shown in Figure 10. Problems of overlap, especially in the 82% enrichment case, make it difficult to compare the simulated and experimental spectra. In particular, it is necessary to take special note of the following points. The band observed for $Ni(^{12}CO)_2(^{13}CO)$ at 2056.8 cm^{-1} overlaps with that observed for **D** (*vide infra*) at 2057.5 cm^{-1}. By comparison with the spectrum of ^{13}CO-enriched **D**, however, an estimate of the intensity that each photoproduct contributes to the band at *ca.* 2057 cm^{-1} may be made, and this has been shown by partial shading of the 2057-cm^{-1} feature in Figure 10. A similar problem is observed for the feature at *ca.* 2069 cm^{-1} and has been treated in the same manner. The observed and calculated frequencies are given in Table 4.

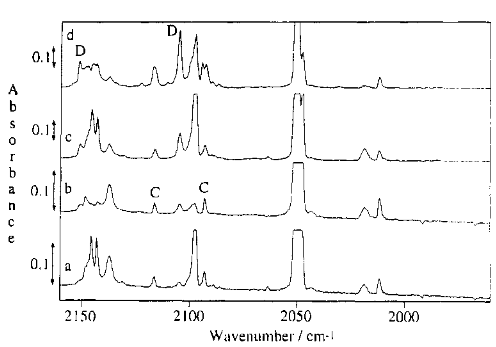


Figure 9. IR spectrum of $Ni(CO)_4$ isolated in an O_2-doped argon matrix ($Ar:O_2:Ni(CO)_4$ = 1500:150:1) in the region 1960–2160 cm^{-1}: spectrum of sample (a) after 60 min of photolysis at *ca.* 254 nm following deposition and (b) after a further 80 min of photolysis at 313 nm; spectrum of separate sample (c) after 360 min of photolysis at *ca.* 254 nm following deposition and (d) after annealing the deposit to approximately 30 K.

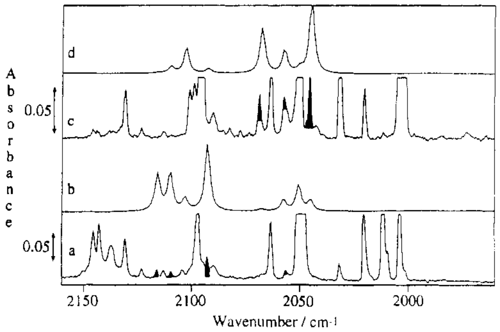


Figure 10. Stacked plot comparing the IR spectrum observed for **C** in the region 1960–2160 cm^{-1} (bands marked by black in-filling) with that predicted for a pyramidal tricarbonyl fragment with the geometry and force constants given in Table 4: (a) observed and (b) predicted for 27% ^{13}CO-enrichment; (c) observed and (d) predicted for 82% ^{13}CO-enrichment.

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(33) Hawkins, M.; Downs, A. J. *J. Phys. Chem.* **1984**, *88*, 3042.
(34) Caughey, W. S.; Choc, M. G.; Houtchens, R. A. *Biochemical and Clinical Aspects of Oxygen*; Caughey, W. S., Ed.; Academic Press: New York, 1979; p 4.

Table 4. ν(C—O) Modes of Different $^{12}CO/^{13}CO$ Isotopomers of C Isolated in an O_2-Doped Ar Matrix: Wavenumbers (cm^{-1}) Observed and Calculated for a Pyramidal $Ni(CO)_3$ Fragment

obsd	calcd[a]	mode	molecule
2116.3	2116.1	a_1	$Ni(^{12}CO)_3$
2092.9	2092.8	e	
2109.8	2110.3	a_1	$Ni(^{12}CO)_2(^{13}CO)$
2092.9	2092.8	b_2	
b	2050.8	a_1	
b	2103.3	a_1	$Ni(^{12}CO)(^{13}CO)_2$
2056.8	2057.7	a_1	
2045.4	2045.3	b_2	
2068.6	2068.0	a_1	$Ni(^{13}CO)_3$
2045.4	2045.3	e	

[a] Calculated on the assumption of an energy-factored force field for an $Ni(CO)_3$ unit with C_{3v} symmetry and a semivertical angle $\phi = 48°$ (**VIII**); $k_{CO} = 1782.5$ N m^{-1} and $k_{CO,CO} = 13.2$ N m^{-1}. The reduced mass ratio was allowed to refine. [b] Not observed.

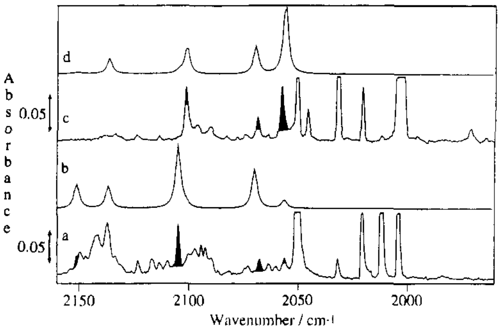


Figure 11. Stacked plot comparing the IR spectrum observed for **D** in the region 1960–2160 cm^{-1} (bands marked by black in-filling) with that predicted for a bent dicarbonyl fragment with the geometry and force constants given in Table 5: (a) observed and (b) predicted for 27% ^{13}CO-enrichment; (c) observed and (d) predicted for 82% ^{13}CO-enrichment.

Unfortunately, it proved impossible to generate photoproduct **C** in sufficient concentration to detect at wavenumbers < 1000 cm^{-1} any IR band which correlated with the ν(C—O) bands, so the nature of the oxygen bound to the tricarbonyl fragment remains a matter of speculation. The most likely explanation is that **C** is formed from $Ni(CO)_3$ by the simple coordination of an O_2 molecule to give $(\eta^2\text{-}O_2)Ni(CO)_3$, but the possibility of an end-on coordinated superoxo or a terminal Ni=O unit cannot be ruled out.

3.5. Photoproduct D. **D** is the final carbonyl-containing photoproduct to be formed following irradiation at *ca.* 254 nm. It was observed to build up only slowly following irradiation at *ca.* 254 nm but to accumulate relatively more rapidly with the decay of **B** as a result of photolysis at *ca.* 313 nm or of annealing (see Figure 9). **D** is characterized by two IR bands, both in the ν(C—O) region and occurring at 2151.3 and 2105.0 cm^{-1}. The ratio of the intensities of the bands gives an angle $\phi = 58°$ (see **VII** and **VIII**). The spectra for photoproduct **D** enriched to 27 and 82% in ^{13}CO are shown in Figure 11 and compared with spectra simulated on the basis of a bent dicarbonyl fragment (**VII**). Again there are problems of overlap. The band shown in Figure 11a at *ca.* 2058 cm^{-1} contains a contribution from **C**, while the feature at 2101.4 cm^{-1} shown in Figure 11c is deceptively intense as a result of overlap with a component of the enriched parent tetracarbonyl (see Figure 5a). Nevertheless, when due account of these problems of overlap is taken, the simulations may be seen to match well the observed spectra. The calculated and observed frequencies are given in Table 5.

Although it must be assumed that **D** contains oxygen strongly bound to nickel, it was not possible to detect at wavenumbers < 1000 cm^{-1} any IR band which correlated with the ν(C—O) bands. The position of the ν(C—O) bands of **D** occurring only 7–8 cm^{-1} higher than the corresponding features of **B** suggest, however, that **D** also contains the nickel atom in the formal oxidation state +2. Furthermore, it is noteworthy that, under conditions which result in an increase in intensity of the ν(C—O) features due to **D**, there was a marked increase in the concentration of CO_2.[23] The most likely explanation, therefore, is that **D** is in fact monooxonickel dicarbonyl, $O{=}Ni(CO)_2$, formed *via* oxygen atom transfer from $(\eta^2\text{-}O_2)Ni(CO)_2$.

Table 5. ν(C—O) Modes of Different $^{12}CO/^{13}CO$ Isotopomers of D Isolated in an O_2-Doped Ar Matrix: Wavenumbers (cm^{-1}) Observed and Calculated for a Bent $Ni(CO)_2$ Fragment

obsd	calcd[a]	mode	molecule
2151.3	2151.1	a_1	$Ni(^{12}CO)_2$
2105.0	2104.9	b_2	
b	2137.0	a′	$Ni(^{12}CO)(^{13}CO)$
2068.6	2070.0	a′	
c	2101.5	a_1	$Ni(^{13}CO)_2$
2057.5	2056.4	b_2	

[a] Calculated on the assumption of an energy-factored force field for an $Ni(CO)_2$ unit with C_{2v} symmetry and a semivertical angle $\phi = 58°$ (**VII**); $k_{CO} = 1829.6$ N m^{-1} and $k_{CO,CO} = 39.7$ N m^{-1}. The reduced mass ratio was allowed to refine. [b] Not observed. [c] Obscured by band of parent nickel tetracarbonyl.

3.6. Photoproduct E. One of the ultimate photooxidation products of $Ni(CO)_4$, **E** is characterized by a single detectable IR band at 1060.7 cm^{-1}. The position of this band was observed to be the same in those experiments employing $Ni(CO)_4$ partially enriched in ^{13}CO, suggesting that photoproduct **E** contains no carbonyl substituents bound to the metal atom. Replacement of $^{16}O_2$ by $^{18}O_2$ caused the band to shift to 1005.2 cm^{-1}. Experiments with a mixture of $^{16}O_2$ and $^{18}O_2$ yielded no less than three bands, the two that had been observed previously and a new broad band centered at *ca.* 1022 cm^{-1}. Unfortunately, no bands due to **E** were discernible in the experiments employing isotopically scrambled O_2, presumably because of the number of separate isotopomers over which the intensity of the ν(O—O) feature was distributed (*vide infra*).

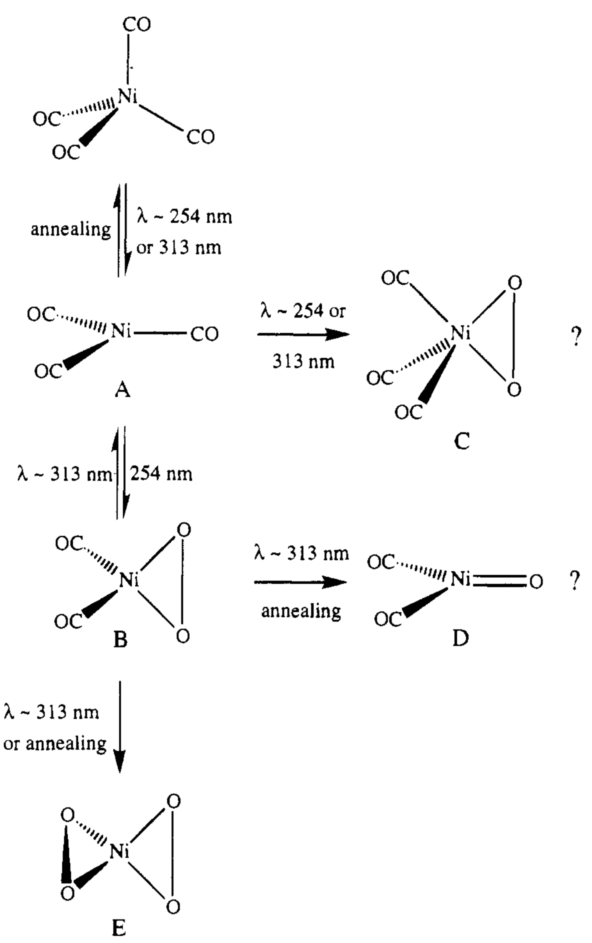
The photoproduct E has been identified previously as a major product of the reactions which take place on cocondensation of nickel atoms with argon doped with O_2,[14] and the spectroscopic properties attributed to it match those displayed by **E** (corresponding infrared bands were observed in the previous study at 1062.0, 1018.2, and 1001.4 cm^{-1}), although small shifts arise from the presence of CO or CO_2 in close proximity to the molecule. Thus, **E** may be identified with the species $(\eta^2\text{-}O_2)_2Ni$. The failure to observe any features in the experiments involving isotopically scrambled O_2 may then be explained by the fact that **E** would give rise to no less than six isotopomers under these conditions.

E is formed by photolysis at *ca.* 313 nm and through annealing of the deposit to temperatures in the region of 30 K. It is itself photolabile, being destroyed by photolysis at *ca.* 254 nm.

4. Conclusions

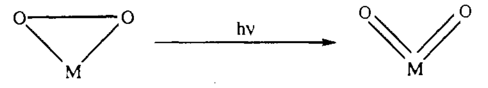
Drawing on the accumulated evidence presented in the previous sections, we infer that the photooxidation of $Ni(CO)_4$ in an O_2-doped argon matrix proceeds along the lines suggested in Scheme 1. Initial photolysis with light at wavelengths near 254 nm causes the release of CO from $Ni(CO)_4$ with the simultaneous formation of the unsaturated species $Ni(CO)_3$ (**A**). In addition to the possibility of recombination with CO, there

Scheme 1



are two further routes disposing of **A**, either (i) reaction with O_2 to give **C**, which is probably $(\eta^2\text{-}O_2)Ni(CO)_3$, or (ii) the photoejection of CO and coordination of O_2 to give the peroxonickel dicarbonyl, $(\eta^2\text{-}O_2)Ni(CO)_2$ (**B**). **B** photodecays relatively slowly after prolonged photolysis at λ = *ca.* 254, but much more rapidly at λ = *ca.* 313 nm, to eliminate CO_2 and give what is probably monooxonickel dicarbonyl, $O{=}Ni(CO)_2$ (**D**). There is competition, however, from two other reaction channels. Of particular note is the finding that **B** is partially converted back to **A** by irradiation at λ = *ca.* 313 nm, indicating the photoreversible uptake of O_2. Yet another option open to photoproduct **B** on irradiation at this wavelength involves conversion to $(\eta^2\text{-}O_2)_2Ni$ (**E**) by the photoejection of two further molecules of CO and the coordination of a second O_2 molecule. The photolability of the $(\eta^2\text{-}O_2)Ni$ unit evident from the behavior of **B** is shared by **E**, which is itself destroyed by irradiation at λ = *ca.* 254 nm. Hence, the experiments imply that dissociation of the $(\eta^2\text{-}O_2)Ni$ unit vies with the cleavage of the O—O or Ni—CO bonds as a potential reaction pathway, so that none of the nickel-containing oxidation products is photostable. Accordingly, it was found that broad-band photolysis of $Ni(CO)_4$ trapped in an O_2-doped argon matrix led to a decrease in the intensity of the bands due to the parent tetracarbonyl, accompanied by the growth of absorptions characteristic of CO_2[23] but of no other infrared features in the ν(C—O) and ν(Ni=O) or ν(O—O) regions.

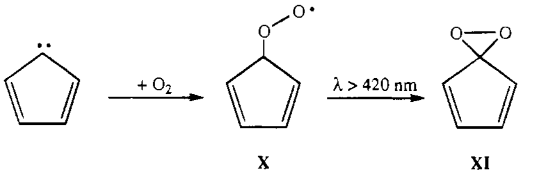
Elimination of O_2 may be a significant aspect of the $Ni(CO)_4/O_2$ system but is not apparently a significant process in the photochemistries of the systems $M(CO)_6/O_2$ (M = Cr, Mo, or W)[5-8] and $Fe(CO)_5/O_2$.[9,10] Such a difference may well be related to the facility of the irreversible reaction 1, which is



(1)

conspicuous in the photooxidation of the group 6 hexacarbonyls and $Fe(CO)_5$, but does not obviously feature in the photooxidation of $Ni(CO)_4$, probably because of the energetic remoteness of the +4 oxidation state of nickel.

The formation of peroxonickel dicarbonyl (**IX**) as the principal photoproduct is reminiscent of how an organic carbene reacts with dioxygen.[35] For example, cyclopentadienylidene combines thermally with O_2 in an argon matrix to form the corresponding carbonyl oxide (**X**), visible photolysis of which results in isomerization to the corresponding dioxirane (**XI**) (eq 2). There is an obvious parallel between the dioxirane and



(2)

peroxonickel dicarbonyl, both of which are noteworthy as sources of singlet oxygen atoms and so share the capacity to function as oxygen transfer agents.[36] No such parallel has yet been established between the carbonyl oxide **X** and any of the products derived from the photooxidation of metal carbonyls. Of superoxometal intermediates of the type **IV** akin to **X** there has been no hint, despite the attentions of various matrix experiments[37] involving, for example, the use of matrices composed of alternate O_2-doped and carbonyl-doped layers of solid argon.

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