of the dianion and an effort is currently being made to characterize these products by x-ray crystallographic methods.

Oxidation of Tricobalt Carbon Derivatives. In acetone, at both platinum and mercury electrodes, no oxidation waves were detected and it is therefore understandable that all attempts to chemically oxidize the clusters with retention of the metal–metal framework failed (e.g., with AgPF$_6$, halogens). We conclude that the redox behavior of the tricobalt carbon clusters is limited because of the particular delocalized bonding structure of these clusters.

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# Infrared Spectra of Matrix-Isolated Dicobalt Octacarbonyl. Evidence for the Third Isomer[1]

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The infrared spectra of dicobalt octacarbonyl matrix-isolated in Ar, hexane, and several other matrices have been examined. From the IR spectra of photolyzed matrices and of matrices subjected to visible radiation following photolysis, it is possible to assign absorptions to three isomeric forms of Co$_2$(CO)$_8$. Two of these are the accepted isomeric forms. The third has no bridging CO groups. The IR spectrum is in best accord with a structure of D_{2d} symmetry, in which the Co–Co bond axis lies in the plane of the trigonal-bipyramidal arrangement at each metal. The isomers are observed to interconvert rapidly. Conversion of the nonbridged D_{3d} isomeric form to the bridged form occurs in hexane matrices with $\Delta G^\ddagger = 6.4 \pm 0.4$ kcal/mol at 84 K.

Dicobalt octacarbonyl, Co$_2$(CO)$_8$, exhibits interesting and unusually complex structural characteristics. In the solid state the structure is of C_{2v} point group symmetry, **1**, involving a

1   2
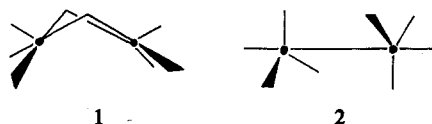
pair of bridging CO groups.[3] In solutions, the presence of a second form involving no bridging CO groups is evident in the IR spectra. The nonbridged form has been assigned a D_{3d} symmetry structure, **2**.[4,5] More recently, Bor and Noack have suggested the presence of still a third isomer,[6] on the basis of two bands in the CO stretching region in solution IR spectra, not assignable to either **1** or **2**.

Dicobalt octacarbonyl is of considerable interest because it is a precursor to substances of importance as catalysts, notably HCo(CO)$_4$, and because under reaction conditions Co$_2$(CO)$_8$ may be involved in equilibria with active catalytic species.[7] However, there is very little information in the literature regarding the kinetics of Co$_2$(CO)$_8$ reactions.

Typically, reaction with a substituting ligand such as phosphine leads to disproportionation

$$Co_2(CO)_8 + 2L \rightarrow Co(CO)_{5-n}L_n^+,Co(CO)_4^- + (n-1)CO$$
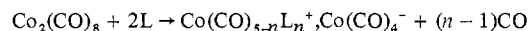
where the value of n is dependent on the base.[8] Most usually, $n = 2$. Reactions with phosphites lead under appropriate conditions to products of the form $RCOCo(CO)_n[P(OR)_3]_{4-n}$, as a result of a Michaelis–Arbuzov type rearrangement.[8,9] Heating of the salts of the form $Co(CO)_{5-n}L_n^+,Co(CO)_4^-$ leads to additional reaction to form compounds of the type $Co_2(CO)_{8-n}L_n$, where most usually $n = 2$. These contain a Co–Co bond and no bridging carbonyls in the solid state, although there is some evidence for equilibrium in solution with bridging forms, depending on the nature of L.[10]

$Co_2(CO)_8$ reacts readily with H_2 to form $HCo(CO)_4$; the rates of both forward and reverse steps and the equilibrium constant for the reaction

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4$$
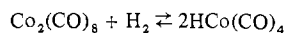
have been evaluated.[11,12] In the absence of a nucleophile, $Co_2(CO)_8$ decomposes on heating in solution to form $Co_4(CO)_{12}$.

In solution $Co_2(CO)_8$ reacts very rapidly with nucleophiles such as phosphines to give the ionic products described above. Heck in 1963 measured the rate of reaction of $Co_2(CO)_8$ with PPh_3 at -72 °C.[13] A few years earlier, Keeley and Johnson[14] and then Basolo and Wojcicki[15] had examined the kinetics of exchange of ^{14}CO with $Co_2(CO)_8$ and found the reaction to be first order in $Co_2(CO)_8$ and zero order in CO. The rate of the exchange reaction, however, was observed to be much slower than substitution by PPh_3. This would seem to rule out CO dissociation as the rate-determining step in the reaction with PPh_3, as pointed out by Heck.[13]

A knowledge of the structural species present under reaction conditions is clearly prerequisite to an interpretation of kinetics data. Accordingly, we have studied the IR spectra of $Co_2(CO)_8$, isolated in matrices at low temperatures. Photolysis of the matrices has been employed as a means of distinguishing absorptions due to distinct isomers.

Experimental Section

Matrix Isolation Technique. Matrices were formed in an Air Products Heli-Trans system. Temperatures of about 8 K were attained using liquid helium. Temperatures in the range of 65–87 K were attained using liquid nitrogen; temperatures in the range 77–65 K were achieved by pumping on liquid nitrogen. All temperatures were monitored within the sodium chloride or potassium bromide substratum using a gold (0.07 atom % iron) vs. chromel thermocouple inserted into a hole drilled through the crystal and packed tightly with indium.

Matrices were formed using the arrangement shown in Figure 1. With bath temperatures from -25 to -35 °C, $Co_2(CO)_8$ evaporates slowly. Matrix gas was admitted just above the subliming solid. The flow rate was maintained in the range of 2–3 mmol/h with a Hoke Micro-Mite needle value. The mixing ratio of $Co_2(CO)_8$ to matrix molecules cannot be determined for deposits made in this fashion. However, there is evidence for essentially complete isolation. By varying the rate of sublimation of $Co_2(CO)_8$ while maintaining the flow rate of matrix gas constant, a fourfold range of concentration was achieved. The relative intensities of the bands did not change significantly, nor were any new features observed. This concentration independence suggests that aggregation or dimerization is not occurring. Further evidence of good isolation is the narrow bandwidths observed in argon, typically between 2 and 4 cm^{-1} at half-height.

Materials. Dicobalt octacarbonyl was purchased from Pressure Chemical Corp. It was recrystallized from olefin-free pentane in an inert-atmosphere box and stored under refrigeration when not mounted on the apparatus. During the experiment when matrices were not being deposited, it was kept at 77 K. $Co_4(CO)_{12}$ was occasionally encountered in samples which had been stored under vacuum for a prolonged period. Bands due to $Co_4(CO)_{12}$ were observed in matrices formed from contaminated $Co_2(CO)_8$; it is difficult to separate $Co_2(CO)_8$ from $Co_4(CO)_{12}$ by sublimation. Hydridotetracarbo-
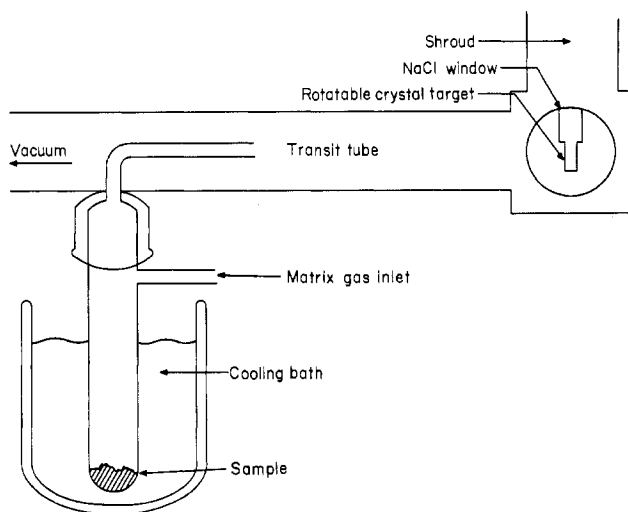

Figure 1. Apparatus for matrix deposition of volatile metal carbonyl compounds.

nylcobalt(I), $HCo(CO)_4$, was prepared by a published procedure.[16] It was collected directly into the thimble used for the matrix isolation experiments following a series of distillations through traps containing Aquasorb.

The matrix gases, Ne, Ar, N_2, O_2, Xe, and CH_4, of 99.9% purity, were purchased from Air Products Corp. They were passed through 3A molecular sieves before use.

Spectra. Infrared spectra were observed with a Beckman IR-9 spectrophotometer, operated with a spectral slit width of 1–3 cm^{-1} at 2000 cm^{-1}. Frequency calibration was carried out using gaseous CO and water vapor standards. Occasionally the visible light of the Nernst glower was filtered from the sample beam with an infrared-pass filter, with a cutoff at 4000 cm^{-1}. For precise analyses of band intensities the infrared spectra were digitized on an Autotrol Model 3400 card punch using 0.4-cm^{-1} intervals and resolved using a computer program written by Pitha and Jones.[17] The program calculates the best fit with the observed spectrum, using a product function of Lorentzian and Gaussian band shapes. The observed bands were fit with predominantly Lorentzian functions.

Attempts were made to obtain the Raman spectra of $Co_2(CO)_8$ in matrices, using the 647.1-nm line of a krypton ion laser in a 90° scattering configuration. Both spot and line focusing techniques were attempted. Invariably there was evidence of darkening and sample decomposition, and no useful spectra were obtained.

Photolyses. The important photolysis experiments were performed using a low-pressure mercury pen lamp source and a 200-W high-pressure mercury vapor source. More than 90% of the output of the low-pressure lamp is in the line at 254 nm. The high-pressure lamp was usually filtered, using narrow band-pass filters centered at 350, 311, or 254 nm.

Results and Discussion

Evidence for a Third Isomer. The IR spectrum of $Co_2(CO)_8$ matrix-isolated in argon at about 8 K is shown in Figures 2A and 3A. The spectrum of matrix-isolated $Co_2(CO)_8$ in Ar has been reported previously by Hanlan and co-workers.[18] Except for the fact that our spectra exhibit less evidence of decomposition because of a lower sample temperature, the spectra are generally in good agreement. We first present evidence that the observed spectrum is due to three distinct species. Photolysis of matrix-isolated $Co_2(CO)_8$ with a low-pressure mercury lamp results in decreased intensity of all bands in the spectrum (Figures 2B and 3B) and the appearance of several new absorptions, marked with asterisks. These new bands, resulting from the photodecomposition of $Co_2(CO)_8$, are the subject of detailed analysis in the paper that follows this; our concern at the present will be only with the behavior under photolysis of those absorptions present in the original deposit. The absorptions originally present do not all lose intensity at equal rates on photolysis. One group, which
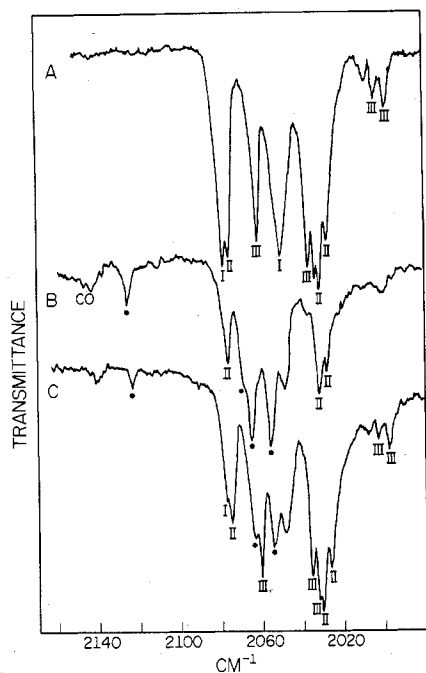
Figure 2. Infrared spectra in the 2160–1980-cm^{-1} region of Co$_2$(CO)$_8$ matrix-isolated in Ar. A represents the spectrum before photolysis; B represents the spectrum after 30 min of photolysis with 254-nm radiation. Both spectra were recorded with the high-energy cutoff filter in place. Spectrum C shows the effect of exposing the photolyzed matrix for about 1 h to the Nernst glower output.
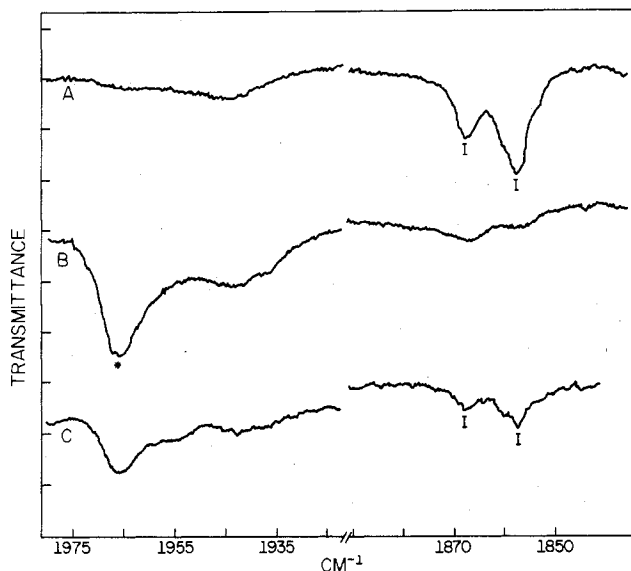

Figure 3. Infrared spectra in the 1975–1825-cm^{-1} region of Co$_2$(CO)$_8$ matrix-isolated in Ar, before and after photolysis. See caption to Figure 2 for meaning of A, B, and C.

Table I. Comparison of Matrix Isolation and Solution Spectra of Co$_2$(CO)$_8$

Freq in Ar matrix, cm^{-1} [a],[b]	Assignment	Freq in hexane soln, cm^{-1} [6]	Assignment
2117 (0.1)	I[c]	2111.8	I
		2107.2	I
2076.4 (10.0)	I	2071.0	I
2073.5 (4.3)	II	2068.8	II
2059.2 (5.2)	III	2058.6	III
2051.5 (1.9)	II[d]		
2050.1 (1.9)	I[d]	2044.0	I
2047.6 (7.8)	I[d]	2042.4	I
2042.8 (1.8)	III[d]		
2035.3 (7.0) ⎫	III	2030.7	I + II
2032.3 (4.9) ⎭			
2029.8 (7.3) ⎫	II	2022.7	II
2025.7 (4.8) ⎭			
2021.7 (0.7)	?		
2007.1 (0.4)	I(^{13}CO)	2001.7	I(^{13}CO)
2006.4 (0.6)	III(^{13}CO)		
2002.1 (1.4) ⎫	III	1991.0	III
1996.4 (2.0) ⎭			
1867.9 (2.7) .	I	1866.0	I
1857.4 (4.2)	I	1857.2	I

[a] Numbers in parentheses are relative integrated intensities taken from spectra resolved by curve fitting. [b] Bands thought to be split by matrix effects are indicated by braces. [c] Assignment to a particular isomer is in doubt because of low intensity of the band. [d] Assignment in doubt because of severe overlapping of bands.

recovery (set III), while the others (set I) are much slower to recover. The bands belonging to these different sets, Figures 2C and 3C, were identified by extensive observations of relative absorbances at various times under various conditions and times of sample irradiation. By careful measurements of absorbances of all bands at various stages in the cycle, before, during, and after photolysis and Nernst glower irradiation, most of the bands in the original spectrum can be assigned to three mutually exclusive sets. These results are consistent only with the presence of three distinct species in the original matrix isolation spectrum.

The frequencies assigned to each of the three species are listed in Table I. The disappearance and reappearance of those absorptions in the 2150–1950-cm^{-1} region that are assigned to set I correlate very well with the behavior of the pair of bands at 1868 and 1857 cm^{-1} (Figure 3), assigned to the bridging CO groups. Assignments of bands in the 2055–2040-cm^{-1} interval were rendered difficult because of extensive splittings due to the matrix. A band at 2051.5 cm^{-1} appears to belong to set II. The band at 2058.9 cm^{-1} is quite unambiguously assignable to set III. With less certainty we assign the band at 2042.9 cm^{-1}, which appears as a shoulder, also to set III. The three sets cannot be reduced in number by assuming one of the sets is simply due to site splittings. Each set is represented by at least one absorption which can be unambiguously assigned. The bands of set I are uniquely characterized by the absorptions at 1857 and 1868 cm^{-1}. Set III is distinguished by the band at 2059 cm^{-1}, too far removed from other bands to be due to site splitting.[22] Finally, set II must be distinct because its components retain significant intensity after photolysis.

Figure 4 shows the metal–carbon and carbonyl deformation region of the IR spectrum of Co$_2$(CO)$_8$ in Ar. The assignments shown for this region are quite tentative; we have relied heavily on Noack's earlier work.[5]

Further evidence for the existence of three isomers is provided by experiments in which Co$_2$(CO)$_8$ is matrix-isolated in hexane at 77 K, Figure 5. All of the absorptions in this spectrum are broader and thus relatively poorly resolved. In addition, they are shifted 3–4 cm^{-1} to lower frequency. Nevertheless, it is clear that the bands due to set III are of

we refer to collectively as II, is much less diminished by photolysis than the others.

Exposure of the photolyzed matrix to the source of the IR instrument, a Nernst glower at 1650 K, causes a substantial but incomplete recovery in the intensities of bands originally present, with concurrent loss in intensity of the newly formed lines. Exposure times of about 40 min served to complete all of the recovery observed in a particular sample. Apparently, the visible radiation present in the source causes a partial reversal of the process resulting from 254-nm radiation. There is considerable precedent for this behavior.[19-21] For the present, the most significant point is that, of the set of absorptions substantially reduced on photolysis, only part make a rapid
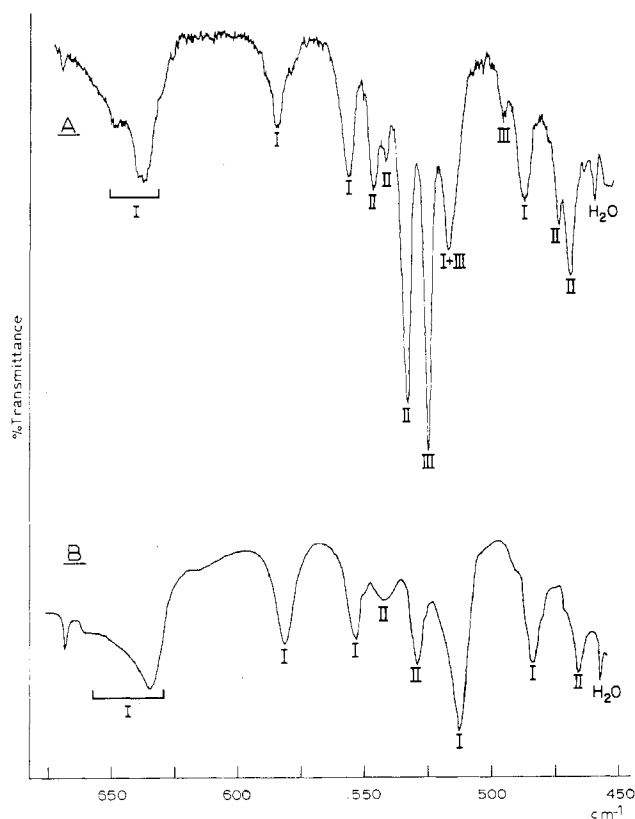
Figure 4. IR spectra in the region 450–670 cm^{-1} of $Co_2(CO)_8$ matrix-isolated in argon at 10 K (A) and in hexane at 77 K (B). Absorptions due to III are essentially absent from spectrum B.

Figure 5. IR spectrum of $Co_2(CO)_8$ matrix-isolated in hexane at 77 K. Note the absence of absorption at 2055 cm^{-1} due to isomer III and the reduced intensity of the band at 2021 cm^{-1} due to isomer II, as compared with the spectrum of a deposit at 65 K, Figure 6A.

very low intensity. Figure 6 shows the effect of maintaining the matrix deposit at 78 K for periods of 1 and 7 h, with no exposure to the Nernst glower. The band at 2067 cm^{-1}, which appears as a shoulder on the more intense band at 2073 cm^{-1}, and the band at 2021 cm^{-1} are assigned to set II. These bands decline in intensity as the matrix is maintained at 78 K while at the same time the bands of set I increase slightly in intensity.

These results support the assignment of the absorptions seen in argon to three sets. They also strongly suggest that set III does not correspond to an impurity in $Co_2(CO)_8$; if this were the case, the bands would appear in the hexane matrices as well. The results are consistent with a facile conversion of isomeric form 3 into one of the other two forms. The higher heat of condensation of hexane and the resulting higher temperature of deposit in hexane afford the energy required for isomer conversion (vide infra).

Table I shows the absorption frequencies in the 2130–1800-cm^{-1} region reported by Bor and Noack for hydrocarbon solutions.[6] Although there is a shift to higher frequencies in the matrix isolation spectra, the solution and matrix isolation spectra correlate very well. A major difference arises from the fact that the latter are better resolved because the lines are much narrower.

The absorptions of sets I and II correspond closely with Bor and Noack's assignments of absorptions to isomers 1 and 2, respectively. Absorptions reported by Bor and Noack at 2030.7 and 2022.7 cm^{-1} are seen as pairs of lines in the matrix isolation spectra in Ar. The pairs of lines at 2035.3 and 2032.3 cm^{-1} in Ar are seen also as a doublet in CH_4, N_2, and Xe matrices but as a single line in Ne, O_2, and CO. We conclude that the splittings observed in Ar are due to site effects. (This matter is discussed in more detail below.) A ^{13}CO band observed in solution at 2001.7 cm^{-1} and assigned to 1 is identified in the matrix isolation spectrum as a band at 2007.1 cm^{-1}.
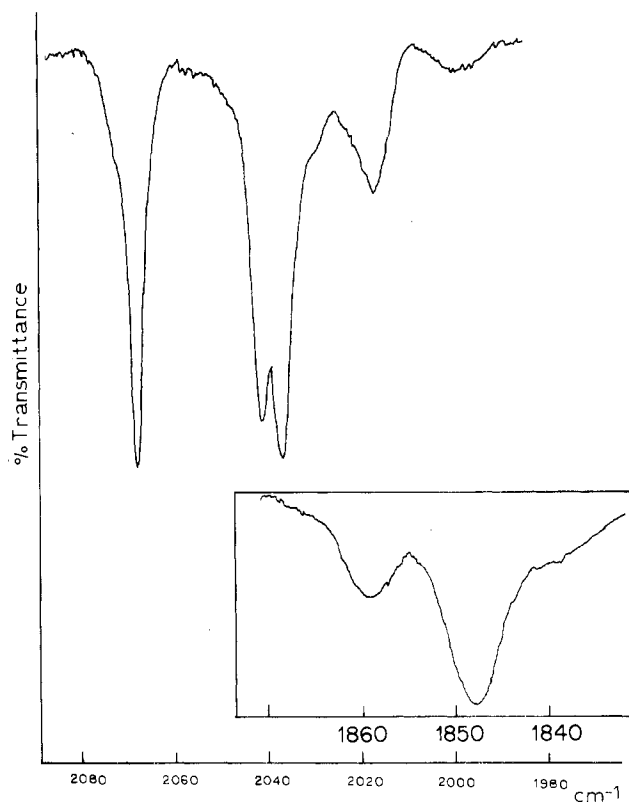
Bor and Noack assigned absorptions at 2058.6 and 1991.0 cm^{-1} to a third isomer of $Co_2(CO)_8$. These correspond well to two of the absorptions in our set III. These absorptions are more intense by a factor of about 4 in the matrix isolation spectra as compared with the solution spectrum. Our results suggest that all of the absorptions of our set III may be assigned to a third isomeric form of $Co_2(CO)_8$.

Assignment of the set III absorptions to various decomposition products of $Co_2(CO)_8$ can be ruled out. There is first of all the fact that the spectra are highly reproducible, using different samples of $Co_2(CO)_8$ and different matrix gases. (Figures of the spectra in various matrices and a table of observed frequencies are available as supplementary material. See notice at end of paper.) The IR spectrum of $Co_4(CO)_{12}$, a product of thermal decomposition of $Co_2(CO)_8$, is well-known. We have examined the IR spectrum of the substance matrix-isolated in Ar. One intense absorption is coincident with the 2059-cm^{-1} absorption of set III. However, an equally intense absorption of $Co_4(CO)_{12}$ at 2068 cm^{-1} is not observed in any matrix isolation spectra of $Co_2(CO)_8$.

Using ESR, $Co(CO)_4$ radicals have been observed in evaporated $Co_2(CO)_8$, deposited at 77 K.[23] In addition, $Co(CO)_4$ has been observed in the mass spectrum of pyrolyzed $Co_2(CO)_8$.[24] Turner and co-workers have observed the IR spectrum of $Co(CO)_4$ in CO matrices.[25] More recently, Ozin and co-workers have very thoroughly studied all of the Co-(CO)$_n$ species in matrices.[18] While the 2029-cm^{-1} absorption assigned to $Co(CO)_4$ is coincident with a band assigned to set II, a second absorption at 2011 cm^{-1} is not seen in any of our spectra.

Still a third possible contributor to set III is a cobalt carbonyl species resulting from loss of CO, e.g., $Co_2(CO)_7$ or $Co_2(CO)_6$. These species have been postulated as intermediates in formation of $Co_4(CO)_{12}$ from $Co_2(CO)_8$ in solution.[26]
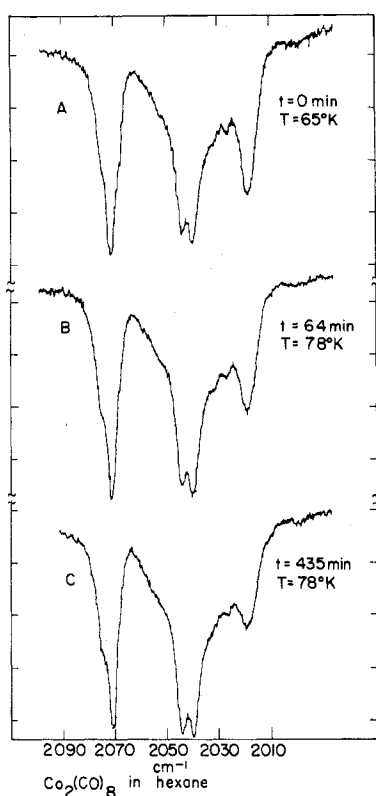
Figure 6. IR spectra of Co$_2$(CO)$_8$ matrix-isolated in hexane at 65 K (A) and then maintained at 78 K for a period of time, B and C. Note the decrease in intensities of bands at 2070 cm^{-1} (shoulder) and 2021 cm^{-1}, due to isomer II.

Loss of CO from Co$_2$(CO)$_8$ has been proposed also in the reaction of H$_2$ with Co$_2$(CO)$_8$[12] and in substitution reactions of Co$_2$(CO)$_8$. As a test of the hypothesis that set III may correspond to a coordinatively unsaturated species, Co$_2$(CO)$_8$ was deposited in Ar/CO matrices containing 1–5% CO. The spectra were identical with those obtained in pure Ar. At still higher CO concentrations the absorptions are broader and less well resolved. However, there is no evident change in relative intensities of bands assigned to the three sets. It thus appears that Co$_2$(CO)$_7$ or Co$_2$(CO)$_6$ is not present in substantial concentration in the matrices. (These experiments also would seem to rule out the unlikely possibility that set III corresponds to Co$_2$(CO)$_9$, which is thought to form in the presence of CO at high pressure.[27]) It is worth noting here that we do believe Co$_2$(CO)$_7$ to be formed under photolysis, as discussed in the following paper.

It might be hypothesized that some of the bands in the spectrum of Co$_2$(CO)$_8$ arise from interaction with traces of atmospheric constituents. However, the spectra of Co$_2$(CO)$_8$ in O$_2$ and N$_2$ are very similar to those seen in Ar. Absorption frequencies were shifted somewhat, and the lines in N$_2$ spectra are considerably broader, but the overall features are qualitatively unchanged.

Although is is difficult to imagine a means by which HCo(CO)$_4$ could be formed in Co$_2$(CO)$_8$ matrices, the matrix isolation IR spectrum of HCo(CO)$_4$ in Ar was obtained for comparison purposes. The solution spectrum of this compound exhibits absorptions at 2052 and 2030 cm^{-1}.[28] The matrix isolation spectrum exhibits three absorptions ascribable to HCo(CO)$_4$, at 2120.5, 2057.6, and 2033.9 cm^{-1}. The positions of these bands and their relative intensities are different from those observed for set III. In addition, the bands at 2022 and 1996 cm^{-1}, assigned to set III, are absent in the spectrum of HCo(CO)$_4$. In a recent report of the IR spectrum of Co$_2$(CO)$_8$ in hydrocarbon solution[29] bands observed at 2053

Table II

Isomer	Symmetry	Modes	
		IR active	IR inactive
a	D_{3d}	2 A$_{2u}$ + E$_u$	2 A$_{1g}$ + E$_g$
b	C_{2h}	A$_u$ + 3 B$_u$	3 A$_g$ + B$_g$
c	D_{2d}	2 B$_2$ + 2 E	2 A$_1$
d	D_{4d}	B$_2$ + E$_1$	A$_1$ + E$_2$ + E$_3$

and 2032 cm^{-1} were assigned tentatively to HCo(CO)$_4$. Our results clearly rule out that unlikely possibility; the observed bands were doubtless due to isomer III.

To summarize, the matrix isolation IR spectra of Co$_2$(CO)$_8$ are consistent with the existence of a third isomeric form of Co$_2$(CO)$_8$, which we shall refer to as **3**. On the basis of the relative intensities of the IR absorptions, **3** represents a substantial fraction, perhaps as much as 30%, of the vapor-phase molecules at room temperature. The IR spectrum of **3** in the CO stretching regions consists of four bands and a ^{13}CO band. There is no evidence of absorptions ascribable to bridging CO groups.

Structure of the Third Isomer. It is useful to consider briefly the structures assigned to other M$_2$(CO)$_8{}^n$ species. Hanlan and Ozin have formed Co$_2$(CO)$_8$, Rh$_2$(CO)$_8$, and Ir$_2$(CO)$_8$ by a metal atom CO codeposition technique.[30] All of these substances exhibited IR absorptions assignable to a bridged isomer. For Co$_2$(CO)$_8$ a second isomer, assigned structure **2**, was also seen.

Poliakoff and Turner have reported the spectrum of a species assigned composition Fe$_2$(CO)$_8$, presumed to be formed by photolysis of Fe$_2$(CO)$_9$.[31] On the basis of comparisons with Noack's data, they assigned structures **1** and **2** to this species. Prolonged photolysis following initial formation of the Fe$_2$(CO)$_8$ led to preferential loss of the bridged species, a result similar to that obtained in the present work. However, it is not clear that neutral Fe$_2$(CO)$_8$ should in fact behave similarly to Co$_2$(CO)$_8$, since it is two electrons short of being isoelectronic with it. The species Fe$_2$(CO)$_8{}^{2-}$, which *is* isoelectronic with Co$_2$(CO)$_8$, exists in the solid state as the nonbridged form, analogous to **2**.[32] In solution, however, there may be appreciable amounts of a bridged form.[33]

Compounds of the form Co$_2$(CO)$_6$L$_2$, in which L is a phosphine or phosphite, possess a nonbridged structure in the solid state[34] with the ligands L situated in axial positions in a structure analogous to **2**. In solution some quantity of bridged isomer may be formed, depending on L.

In none of the systems just discussed is there precedent for a nonbridged structure that is an alternative to **2**. As possible structures for **3** we consider only those that have only terminal CO groups. Assuming that the possible idealized geometries at each cobalt are square pyramidal or trigonal bipyramidal, the Co–Co bond might occupy either^f of the two types of stereochemical positions in either geometry. We restrict our consideration to structures having the same geometry at each metal and involving the same stereochemical location of the Co–Co bond at each metal. This is justified on the grounds that the totally symmetric CO stretching mode would be IR active and moderately intense if the local symmetries of the two cobalt centers were different. An absorption should thus be seen for isomer **3** in the 2080–2140-cm^{-1} region. No absorption ascribable to set III was noted in this region, even in exceptionally thick deposits in both Ar and Ne. While the possibility exists that the intensity of the totally symmetric CO stretching mode is accidentally zero, it seems more reasonable to suppose that the molecular symmetry renders this mode IR inactive.

The four isomers shown in Figure 7 remain as viable possibilities. The point group symmetries and IR activity in the CO stretching region are given in Table II.
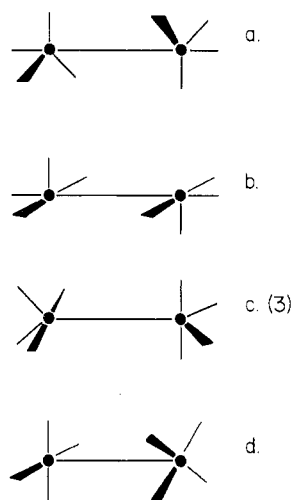
Figure 7. Possible structures for isomer 3 of $Co_2(CO)_8$.

Isomer **2** has been assigned structure a, and we concur in that assignment. The number of observed bands for **3** is too large for d. This leaves b and c, or some rotamer thereof. While an unambiguous choice is impossible, we prefer structure c, in which two $Co(CO)_4$ units with idealized trigonal-pyramidal geometry about the metal are joined by a metal–metal bond in the radial position. This geometrical arrangement is indicated for $Rh_2(PF_3)_8$ by NMR results.[35] The prevalence of splitting in the 2032- and 2000-cm^{-1} bands in several matrices is consistent with a removal of degeneracy due to lattice effects in the two E modes expected for the structure of D_{2d} symmetry. Support for this interpretation comes from observation that the components of the doublets as observed in Ar remain fixed in relative intensity during annealing and photolyses. This suggests that the relative concentrations of species giving rise to each component of the doublet remain fixed. (A similar behavior is observed for the doublet at 2029.8 and 2025.7 cm^{-1}, in Ar, assigned to the E_u mode of isomer **2**.)

In structure c the Co–Co bond is located in the equatorial plane at each cobalt. The two cobalt trigonal bipyramids are visualized as oriented 90° with respect to one another. Structure c is perhaps more attractive than b on the grounds that it preserves trigonal-bipyramidal geometry at cobalt. On the other hand, intramolecular rearrangement in $XCo(CO)_4$ systems is very facile, with activation enthalpies as low at 5 kcal/mol.[36] A square-pyramidal geometry about cobalt is not likely to be greatly higher in energy than the trigonal-bipyramidal.

Isomer Interconversions. The relative quantities of the three isomers observed in the matrices reflect the relative abundances in the gas phase at about room temperature, modified by such interconversions as occur during deposition. It is evident from our results that the interconversion of **3** to **2** is extremely facile. Isomer **3** is reasonably abundant in the rare gas matrices formed at about 10 K. On the other hand, it is absent from hexane matrices formed at 10 K or higher temperature. The higher heat of condensation of hexane apparently causes sufficient local heating during deposition to effect the conversion. A deposit in xenon at 10 K showed the presence of III, although at somewhat reduced level.

As noted in Figure 6, deposition of $Co_2(CO)_8$ in hexane at 65 K results in appearance of only **1** and **2**. Warming of the matrix to temperatures between 78 and 88 K causes slow loss of the bands due to **2**. A concomitant increase in absorptions due to **1** was not always noted; photolysis due to glower irradiation was found to be responsible. When a cutoff filter was used, bands due to **1** were found to grow in. The rate of

interconversion of **2** into **1** was observed in hexane matrices at various temperatures in the range of 77–88 K, by observing the decrease in absorbance of the band at 2020 cm^{-1}. Some difficulties were encountered due to temperature gradients in the matrices, but most of the sample was at a single temperature and disappeared at a single rate. It was possible from the results of several experiments to determine $\Delta G^{\ddagger}$ for the interconversion at 84 K to be 6.4 ± 0.4 kcal/mol. This value represents an upper limit to the free energy barrier for interconversion of **2** into **1**. There is undoubtedly some contribution to $\Delta G^{\ddagger}$ from interaction with matrix molecules. It is noteworthy that the ^{13}C NMR spectra of $Co_2(CO)_8$ in solution exhibit only a single line, to −150 °C.[37,38] In view of the matrix results, it is to be expected that distinct ^{13}C resonances will not be seen above −160 °C.

The low free energy barrier is consistent with the results of a ^1H NMR study of the cis–trans interconversion of [η-$C_5H_5Fe(CO)_2$]$_2$ in solution. Assuming $\Delta S^{\ddagger} \approx 0$, for bridged–nonbridged interconversion, a $\Delta G^{\ddagger}$ value of about 6 kcal/mol for conversion from the less stable nonbridged form to the bridged species is suggested by the equilibrium and kinetics results.[39-41]

In summary, the matrix isolation spectra of $Co_2(CO)_8$ in various matrices show the presence of three distinct isomeric forms, with structures **1, 2,** and **3** (c of Figure 7). The order of free energies at temperatures below 77 K is **1 < 2 < 3**. Conversion of **3** to **2** is extremely facile; conversion of **2** to **1** occurs in hexane matrices with an estimated $\Delta G^{\ddagger}$ of 6.4 kcal/mol at 84 K. These matrix isolation results are in accord with the results of a study of the temperature dependence of the IR spectrum of $Co_2(CO)_8$ in hexane.[42]

In the following contribution we discuss the structures of the product of $Co_2(CO)_8$ photolysis and of species resulting from catalyzed thermal decomposition of $Co_2(CO)_8$.

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Matrix Isolation Spectra of the Thermal and Photochemical Decomposition Products of Dicobalt Octacarbonyl[1]

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The infrared spectrum of the product of photochemical decomposition of Co$_2$(CO)$_8$ in argon matrices is reported. Evidence is presented that the major product is Co$_2$(CO)$_7$, and that this species has no bridging CO groups. Irradiation of matrix-isolated Co$_2$(CO)$_8$ in argon at 350 nm results in no appparance of Co(CO)$_4$ radicals. However, irradiation of Co$_2$(CO)$_8$ in CO matrices at 254 nm causes formation of Co(CO)$_4$ as well as Co$_2$(CO)$_7$. Passage of Co$_2$(CO)$_8$ over an active cobalt metal surface before matrix isolation causes complete decomposition, so that no matrix spectra are seen. On less active cobalt surfaces some decomposition occurs, and Co(CO)$_4$ is seen in the matrices. An absorption due to a second decomposition species, possibly Co$_2$(CO)$_6$, is also seen.

In the previous article we have presented evidence for the existence of three isomeric structural forms for dicobalt octacarbonyl in matrix isolation spectra.[2] In this paper we discuss the infrared spectra of cobalt carbonyl species produced as a result of thermal or photochemical decomposition of Co$_2$(CO)$_8$.

The most likely pathways for decomposition of Co$_2$(CO)$_8$ are homolysis of the Co–Co bond, to produce Co(CO)$_4$, or dissociative loss of CO, to produce Co$_2$(CO)$_7$. Presumably, metal–metal bond cleavage would occur from one of the nonbridged isomeric forms of Co$_2$(CO)$_8$. This mode of decomposition is rendered likely by estimates of a low metal–metal bond energy in Co$_2$(CO)$_8$.[3,4] The mass spectrum of Co$_2$(CO)$_8$[3] and ESR spectra of deposits of Co$_2$(CO)$_8$ in glasses at low temperature provide evidence for the presence of Co(CO)$_4$.

Dissociative loss of CO has been invoked to account for the kinetics of several reactions of Co$_2$(CO)$_8$, e.g., with acetylenes[6] and with H$_2$.[7] In fact, the equilibrium constant for the reaction

$$Co_2(CO)_8 \; \rightleftarrows \; Co_2(CO)_7 + CO \qquad (1)$$

has been estimated by Ungvary and Marko to be on the order of 10^{-5} atm at room temperature.[8]

Experimental Section

Most of the relevant experimental details appear in the previous paper.[2] The pyrolysis experiment reported here was conducted by modifying the apparatus shown in Figure 1 of ref 2. The 100 × 18 mm Pyrex tube leading into the vacuum shroud of the cryostat was wound with resistance wire secured in place with glass fiber tape. The heater was insulated with spun-glass insulation. A thermocouple was inserted beneath the insulation in the middle of the heated region to provide a crude estimate of temperature. The electronic spectrum of Co$_2$(CO)$_8$ was obtained using a Cary Model 14.

Results and Discussion

Photolysis of Co$_2$(CO)$_8$. When a matrix of Co$_2$(CO)$_8$ is photolyzed with ultraviolet light, bands due to Co$_2$(CO)$_8$

decline in intensity as new bands appear. When a photolyzed matrix is subsequently exposed to visible radiation, e.g., the Nernst glower source of the spectrometer, the changes caused by photolysis are reversed. In the previous paper[2] we employed the decline and reappearance of the bands of Co$_2$(CO)$_8$ to demonstrate the existence of three isomers.

Among the new bands produced by photolysis of Co$_2$(CO)$_8$, a band at 2139 cm^{-1} can be assigned to free CO. The infrared spectrum of a deposit of Co$_2$(CO)$_8$ in argon which has been subjected to extensive photolysis is shown in Figure 1. New bands occur at 2123.0, 2066.0, 2062.5, 2053.2, 1967, 1955, and 1947 cm^{-1}. In addition, a band which does not correlate in terms of its intensity variations with the seven bands also appears at 2046.0 cm^{-1}. The bands at 1967, 1955, and 1947 cm^{-1} are quite broad relative to the bands at higher energy. In neon matrices only two bands are observed in this lower frequency region; possibly the bands at 1955 and 1947 cm^{-1} in Ar are due to solid-state splittings of a single normal mode.

Assignment of the new bands to Co$_2$(CO)$_7$ is based on the following considerations.

(1) The new bands do not correspond to any of the mononuclear cobalt carbonyl species reported by Hanlan and co-workers;[9] thus the new bands must be due to dinuclear species. (CoCO is reported to have infrared bands at 1956.0 and 1949.0 cm^{-1}, frequencies close to two of those observed in our matrices. However, the presence of this species is highly unlikely in light of the fact that none of the other mononuclear cobalt carbonyls are observed either upon initial photolysis or subsequent visible light irradiation.)

(2) When the photolyzed matrix is exposed to the radiation of the Nernst glower, the extent of recovery of the Co$_2$(CO)$_8$ spectrum and the rate at which recovery occurs are directly related to the amount of CO in the matrix. In argon matrices the bands assigned to Co$_2$(CO)$_7$ decline by about 60% of their maximum intensity, after which the rate of decline becomes