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Photolysis of Matrix-Isolated Hydridotetracarbonylcobalt(I). Evidence for Metal–Hydrogen Bond Homolysis[1]

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The infrared spectrum of matrices containing hydridotetracarbonylcobalt(I) photolyzed by a low-pressure mercury lamp shows evidence of tetracarbonylcobalt in both argon and carbon monoxide matrices. This evidence is corroborated by observations in the electron spin resonance experiment. Signals due to both tetracarbonylcobalt and hydrogen atoms are generated by photolysis of $HCo(CO)_4$ in argon, while photolyses in CO matrices yield the formyl radical and $Co(CO)_4$.

The photolysis of matrix-isolated $HCo(CO)_4$ has produced unexpected evidence for metal–hydrogen bond cleavage. The results reported herein were obtained during attempts to produce the coordinatively unsaturated $HCo(CO)_3$. This long sought after molecule was first hypothesized to play a role in hydroformylation reactions using $HCo(CO)_4$ as a catalyst.[2] However, attempts at observing $HCo(CO)_3$ under hydroformylation conditions have failed.[3] The matrix isolation technique is well suited for studies of energetic species, especially those, like $HCo(CO)_3$, which can be produced by the photolysis of metal carbonyls. Many examples of this sort of process have appeared in the literature.[4] In particular, for the only other metal carbonyl hydride which has been studied by matrix techniques, it was claimed that the photolysis of $HMn(CO)_5$ yielded $HMn(CO)_4$.[5] The photolysis of $HCo(CO)_4$ was recently reported, and the most intense new bands in the infrared spectrum which grow in on photolysis were assigned to $HCo(CO)_3$.[6] In this paper evidence will be shown which compels reassignment of most of these bands to $Co(CO)_4$; thus the photolytic process is best described by eq 1.

$$HCo(CO)_4 \xrightarrow{h\nu} H\cdot + Co(CO)_4 \qquad (1)$$

Metal–hydrogen bond homolysis has not been thought to be an important photolytic process. Several instances have been reported previously. Grebenik et al.[7] have reported the photolysis of $Re(\eta^5\text{-}C_5H_5)_2H$ in CO matrices yields HCO radicals, presumably formed by the homolysis of hydrogen–rhenium bonds. Endicott et al.[8] rationalized the behavior of $Rh(NH_3)_5(H_2O)H^{2+}$ upon photolysis by a chain mechanism which was thought to be initiated by rhodium–hydrogen bond homolysis. Kinetic evidence was also used by Hoffman and Brown[9] to postulate the homolysis of tungsten–hydrogen bonds in substitution reactions of $W(CO)_3(\eta^5\text{-}C_5H_5)H$. The spectroscopic evidence presented in this report puts the possibility of this kind of reactivity on a very firm basis.

Experimental Section

$HCo(CO)_4$ was prepared by reacting $Co_2(CO)_8$ (Pressure Chemical Corp.) with sodium amalgam in diethyl ether. The solvent was stripped off, and either D_3PO_4 or H_3PO_4 (65%) was added. A stream of N_2 gas was used to sweep the evolving $HCo(CO)_4$ into a thimble cooled by liquid nitrogen. The thimble was then removed from the synthesis apparatus and attached to the glass transit tube of the matrix isolation equipment which has already been described for the infrared experiment.[10] $HCo(CO)_4$ was exposed to the atmosphere during the attachment of the sublimation source to the matrix apparatus, but at close to liquid-nitrogen temperatures. Immediately after this exposure and before warming, the $HCo(CO)_4$ container was pumped to high vacuum. No visible evidence of decomposition was ever noted. However, in one instance, bands assignable to $Co_2(CO)_8$ were present in the infrared spectrum. All gases were obtained from Matheson and purified of oxygen with catalyst R3-11.[11] Matrix gases were admitted to the matrix apparatus through a calibrated needle valve from a closed container of purified 10 atom % methane in argon, carbon monoxide, or argon. As the pressure of the reservoir dropped, the needle valve was opened to maintain a constant flow. Flow rates of 1–5 mmol/h were maintained. The sublimation source was kept at −127 °C during the deposit with a 1-propanol slush bath. The extreme viscosity of 1-propanol meant that the bath had to be constantly tended in order to maintain a uniform evaporation rate. Infrared spectra were recorded on a Beckman 4260 spectrophotometer, operated with a spectral slit width of 1–2 cm^{-1}. The wavelength drive was calibrated by using CO and DCl gases, and all frequencies have been corrected to vacuum conditions.

The configuration for the ESR experiment of the apparatus is diagrammed in Figure 1. ESR spectra were obtained on a Varian E-3 spectrometer at 9 GHz. The data were treated to a crude analysis without detailed curve fitting.[12] The spectrometer operates with a modulation frequency of 100 kHz, and modulation amplitudes were typically 10 G. Such a large setting causes some distortion of such narrow lines but yields maximum signal to noise. The microwave power was set at 1.5 mW for the recording of most spectra. The instrument was calibrated by using a very sharp impurity in the quartz vacuum shroud which was in turn calibrated by using DPPH. The field sweep was assumed to be linear. Deposits were made on an oxygen-free hard copper rod cooled by the Air Products Heli-trans LT-3-110 system.

Photolyses were accomplished by using low-pressure mercury lamps.[13] A total of 90% of the radiant energy occurs at 254 nm for these types of sources. No attempt was made to filter their output.

Results and Discussion

Figure 2a shows a typical spectrum of $HCo(CO)_4$ matrix isolated in argon. Although the argon deposition rate was kept quite constant, the deposition rate of $HCo(CO)_4$ varied, and hence, the degree of isolation of $HCo(CO)_4$ varied from one experiment to another. The variation in evaporation rates of $HCo(CO)_4$ seems to depend on the exposed surface area and on the condition of the 1-propanol slush bath. 1-Propanol becomes extremely viscous at its melting point, and the bath most certainly becomes thermally stratified. The deposit which gave the spectrum of Figure 2a took 1 h to produce, and the

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.
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[10] Sweany, R. L.; Brown, T. L. *Inorg. Chem.* **1977**, *16*, 415–421.
[11] Finely dispersed copper on an inert carrier, Chemical Dynamics Co., South Plainfield, New Jersey 07080.
[12] The analysis of the hyperfine structure of paramagnetic species in the glassy state is difficult; see for example: Neiman, R.; Kivelson, D. *J. Chem. Phys.* **1961**, *35*, 156–161.
[13] General Electric, G8T5, and Hamamatsu Corp., Model 937-001.

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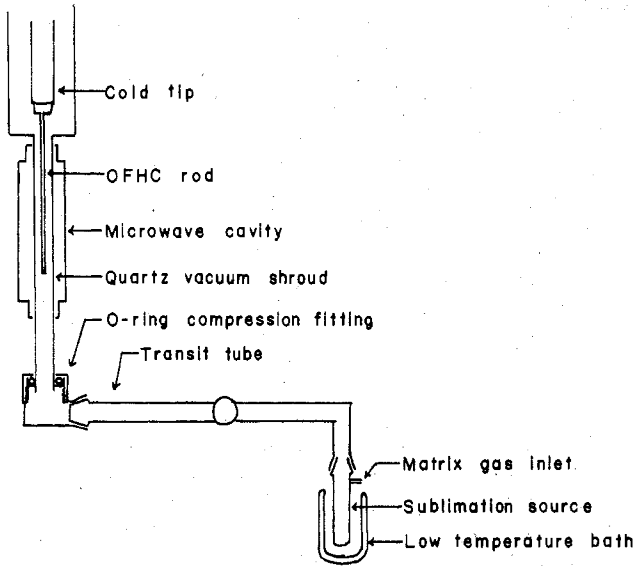

Figure 1. Configuration of apparatus for the observation of ESR spectra.

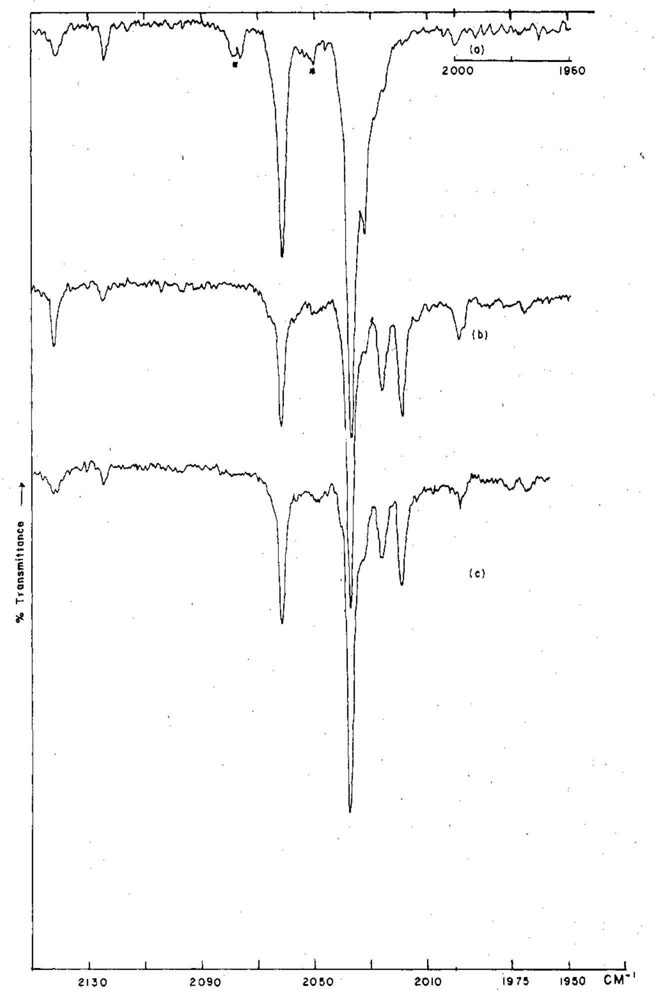

Figure 2. (a) Infrared spectrum of $HCo(CO)_4$ matrix isolated in argon at 10 K prior to photolysis. The asterisks mark absorptions due to $Co_2(CO)_8$. Segment from 2000 to 1960 cm^{-1} reduced from 10 to 20 cm^{-1}/in. with 1-cm^{-1} intervals. (b) Same matrix after 70-min photolysis with a low-pressure mercury lamp. (c) Same matrix as in Figure 2b after about 25 min at 25 K.

Table I. Comparison of Infrared Spectral Data in Argon between This Work and That of Ref 6

data[a,b]	assignt[a]	data[c]	assignt[c]
2140 (0.4, 0.7, 0.2)[d]	CO	2140	CO
2120.8 (0.4, 0.1, 0.2)	$HCo(CO)_4$ (A_1 mode)	2123	$HCo(CO)_4$
2075.4	$Co_2(CO)_8$		
2073.0	$Co_2(CO)_8$		
2058.9 (3.5, 1.8, 2.1)	$HCo(CO)_4$ (A_1 mode)	2059	$HCo(CO)_4$
2048.7	$Co_2(CO)_8$	2048	impurity
2034.1 (10, 5.8, 6.8)	$HCo(CO)_4$ (E mode)	2037	$HCo(CO)_4$
2022.9 (. . ., 1.4, 1.2)[e]	$Co(CO)_4$ (A_1 mode)	2025	$HCo(CO)_3$
2016.2 (. . ., 1.7, 1.6)[e]	$Co(CO)_4$ (E mode)	2018	$HCo(CO)_3$
1997 (0.2, 0.4, 0.3)	$HCo(CO)_3$ and $HCo(CO)_3{}^{13}CO$	1999	$HCo(CO)_3{}^{13}CO$ or impurity

[a] This work. [b] Estimated error on feature is ±1.0 cm^{-1}. Data are taken from spectra shown in Figure 2. [c] Reference 6. [d] Absorbance at ν_{max} in Figure 2a–c, respectively, relative to the feature at 2034 cm^{-1} in Figure 2a (=10). [e] Relative intensity of 2022.9- and 2016.2-cm^{-1} bands varied with respect to each other.

bands are as sharp as ever observed. Deposits which were made at substantially faster rates were not as well resolved. This deposit is taken as well-isolated $HCo(CO)_4$ although deposits made in this fashion will always be subject to doubt as to the true state of isolation. The instability of $HCo(CO)_4$ makes it very difficult to premix matrix samples prior to deposit.

The spectrum in Figure 2a closely resembles that reported by Wermer et al.[6] and obtained by Rest.[14] When the matrix is photolyzed with the radiation of a low-pressure mercury lamp, changes in the infrared spectrum occur which also resemble those reported in the earlier work. Table I indicates the observed frequencies, those reported by Wermer et al.,[6] and our respective assignments.

The matrix observed in Figure 2a showed bands which appear to be due to $Co_2(CO)_8$. This was a unique occurrence, and the sublimation source was probably contaminated. Gas phase decomposition of $HCo(CO)_4$ yielding $Co_2(CO)_8$ probably does not occur to a significant extent during deposit because the bands assigned to $Co_2(CO)_8$ were not observed in any other matrix deposit. The impurity probably originated from the decomposition of $HCo(CO)_4$ in the sublimation source during its attachment to the apparatus. If $Co_2(CO)_8$ was located near the top of the coolant level, it could have volatilized when the top of the bath warmed due to thermal stratification.

As a result of photolysis the band at 2140 cm^{-1} which was weakly present before photolysis becomes more intense. The increase in free CO, as evidenced by the band at 2140 cm^{-1}, suggests the photolysis process involves the loss of CO by some carbonyl species. It should be noted that $Co_2(CO)_8$ is also photolyzed and accounts for some of the CO which is observed.[15] Following the photolysis, the matrix was annealed at 25 K for a period of about 25 min during which time the matrix was exposed to the visible radiation of the Nernst glower (Figure 2c). The band due to free CO declined in intensity to approximately 40% of its highest intensity. The band at 1997 cm^{-1} also declined significantly to 60% of its highest intensity. The behavior of the band at 1997 cm^{-1} suggests that it is due to a CO-deficient species, presumably $HCo(CO)_3$. The bands, however, at 2022.9 and 2016.2 cm^{-1} retained 90% of their highest intensity. $Co(CO)_4$ in argon matrices containing 10% carbon monoxide exhibits infrared bands at 2024.0 and 2014.4 cm^{-1}.[12] This suggests that the

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(14) Rest, A. J., unpublished data generously shared.

(15) Sweany, R. L.; Brown, T. L. *Inorg. Chem.* **1977**, *16*, 421–424.

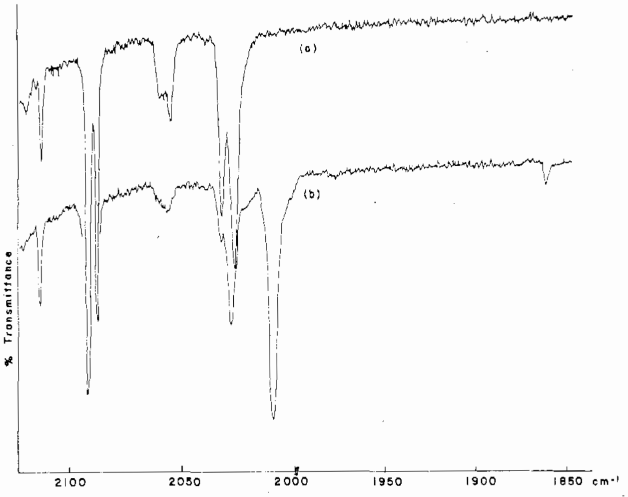

Figure 3. (a) Infrared spectrum of $HCo(CO)_4$ isolated in carbon monoxide at 10 K prior to photolysis. (b) Same matrix after 40 min of photolysis with a low-pressure mercury lamp.

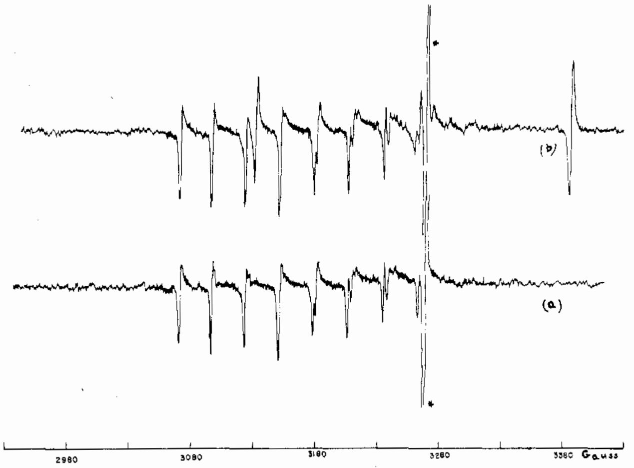

Figure 4. (a) ESR spectrum of $HCo(CO)_4$ isolated in argon at 10 K showing $Co(CO)_4$. The asterisks mark an impurity in the quartz vacuum shroud at $g = 2.005$. (b) Same matrix as in Figure 4a after about 60-min photolysis with a low-pressure mercury lamp.

species causing the bands at 2022.9 and 2016.2 cm^{-1} is $Co(CO)_4$ and that it forms due to metal–hydrogen bond homolysis.

The photolysis of $HCo(CO)_4$ leading to $Co(CO)_4$ should not be seriously affected by free CO in the matrix, and, as shown in Figure 3, the photolysis of $HCo(CO)_4$ in CO matrices leads to the development of a single band at 2010.5 cm^{-1} which agrees well with what has already been assigned to $Co(CO)_4$.[16,17] The exposure period of the photolysis which produced the spectrum of Figure 3b was 40 min, nearly half the time required to produce the corresponding spectrum in argon. Roughly, the efficiency of the process producing the 2010.5-cm^{-1} band in CO is 10 times that producing the 2016.2-cm^{-1} band in Ar. No feature corresponding to the band at 1997 cm^{-1} in argon is observed in CO. Also, an absorption is observed at 1861 cm^{-1} which is assignable to the formyl radical formed by capture of the hydrogen atom by CO.[18] Of the three infrared active bands of $Co(CO)_4$, only two have been observed. A band at 2028.8 cm^{-1} is expected, but this position is overshadowed by the principal absorption band of $HCo(CO)_4$; it is evident that a shoulder is present at the expected position as a result of photolysis.

As judged by the bands at 2023 and 2016 cm^{-1}, it appears that the principal products from photolysis are due to metal–hydrogen bond cleavage. Additional experiments further corroborate these results. Deposits of $HCo(CO)_4$ in carbon monoxide and in argon were photolyzed and observed by electron spin resonance spectroscopy. The spectrum of $Co(CO)_4$ is observed even before photolysis. In carbon monoxide matrices the eight-line pattern of $Co(CO)_4$ reported by Hanlan et al.[16] was observed with $g_\perp = 2.138 \pm 0.010$ and $a_\perp = (55 \pm 3) \times 10^{-4}$ cm^{-1} and $g_\parallel = 2.017 \pm 0.010$ and $a_\parallel = (60 \pm 3) \times 10^{-4}$ cm^{-1}. The appearance of $Co(CO)_4$ before photolysis is not unexpected as the infrared spectrum also shows weak shoulders in the positions of $Co(CO)_4$ absorptions prior to photolysis. In CO, the photolysis causes the absorptions due to $Co(CO)_4$ to grow, and, in addition, the doublet pattern of the formyl radical grows in. The components of the g tensor are not resolved: $g_{eff} = 1.997 \pm 0.010$ and $a_{eff} = (126 \pm 3.) \times 10^{-4}$ cm^{-1}. These results are in good agreement with reports of the formyl radical in the literature.[19] The formyl radical presumably is formed by the reaction of H· and matrix CO.

In argon matrices, formyl is not produced. Rather, the ESR spectrum shows only the growth of the signals due to $Co(CO)_4$ and H· upon photolysis. Figure 4 shows the spectrum obtained from an Ar matrix containing $HCo(CO)_4$ before (Figure 4a) and after (Figure 4b) photolysis. The $Co(CO)_4$ spectrum is characterized by $g_\perp = 2.137 \pm 0.010$ and $a_\perp = (55 \pm 3.) \times 10^{-4}$ cm^{-1}. There also appear features which are partially resolved from the main $Co(CO)_4$ spectrum which will be assigned to a second isomer of $Co(CO)_4$ with $g_\perp = 2.135 \pm 0.020$ and $a_\perp = (58 \pm 5) \times 10^{-4}$ cm^{-1}. No feature which could be assigned to the parallel orientation of the molecule was observed in argon. It is presumed that those lines will follow the pattern observed in CO matrices; the spectra observed in argon lacked the intensity for observation of those lines.

Hanlan et al. studied argon matrices of $Co(CO)_4$ doped with 10 mol % CO and obtained substantially different results.[16] Although they also reported two isomers, $g_\parallel$ was reported to be greater than $g_\perp$ for the isomer which exhibited the strongest absorptions. Although the differences between their results and those reported here cannot be readily explained, the similarities between the spectrum of $Co(CO)_4$ in CO, upon which there is complete agreement, and the spectrum of $Co(CO)_4$ in argon suggest that the features shown in Figure 4 should be assigned to $Co(CO)_4$. Other candidates can be safely ruled out; $Co(CO)_3$ has ESR parameters substantially different from those observed in these spectra,[16] and $Co(CO)_4O_2$ is also radically different in the appearance of its spectrum.[20]

The hydrogen atom spectrum is characterized by $g_{eff} = 2.017 \pm 0.010$ and $a = (480 \pm 3) \times 10^{-4}$ cm^{-1} which is in good agreement with the reported spectrum of H·.[21] A broad, weak resonance at $g = 2.005$ appears as well as a result of photolysis and is tentatively assigned to organic radicals which form by hydrogen abstraction by H· from impurities in the matrix. In matrices containing large amounts of organic molecules, hydrogen abstraction giving organic free radicals is a major result of photolysis. For example, in methylcyclohexane glasses at 77 K, only the spectrum of $Co(CO)_4$ is observed along with an intense feature at $g = 2.00$ which is presumably due to the organic radical formed by abstraction of hydrogen from the host. In matrices containing 10% methane in argon, photolysis

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at 10 K still yields H·, but upon warming to 25 K, the spectrum due to the methyl radical grows in at $g_{eff} = 2.007 \pm 0.01$ and $a = (21.6 \pm 3) \times 10^{-4}$ cm^{-1}. These results are consistent with the reported spectrum of CH_3· and the behavior of H·.[22]

Detailed experiments have not been attempted to demonstrate the assignment of the absorption of 1997 cm^{-1} to $HCo(CO)_3$. The assignment is reasonable because the band correlates with changes in the intensity of free CO in the matrix in the proper manner. Conventional arguments suggest that as a result of the metal bonding to fewer carbonyl ligands, the stretching frequency of the remaining carbonyl ligands should decrease. The energy of the band at 1997 cm^{-1} band is 98.2% of the energy of the band at 2034 cm^{-1} of $HCo(CO)_4$. Perhaps fortuitously, the frequencies for the E modes of $Co(CO)_4$ and $Co(CO)_3$ which are reported by Hanlan et al. show a corresponding decrease of 98.4%. Calculations reported by Grima et al.[23] suggest that the isomer of $HCo(CO)_3$ which is most stable is of C_{3v} symmetry. Infrared evidence for the geometry of $HCo(CO)_3$ is thus far inconclusive. The above agreement is consistent with the assignment of the band to an E mode of a molecule of C_{3v} symmetry.

It is also important to point out that the observation of $Co(CO)_4$ as the major product of photolysis is not to say that the primary photoprocess is homolysis. What is observed is only the photoprocess which is best preserved in the matrix. CO loss may well occur with a greater quantum yield; but, if that is so, recombination must occur more efficiently for CO + $HCo(CO)_3$ recombination than for H· + $Co(CO)_4$ recombination. In an effort to understand what factors contribute to the efficiency of recombination, the photolysis of a matrix containing $DCo(CO)_4$ was attempted. The shift in energy of the band at 2059 to 2051.4 cm^{-1} for the deuteride allows the simultaneous observation of both isotopically labeled species. Both forms were photolyzed with approximately the same efficiency. (See Figure 5.) If the primary photolysis event causes the formation of a caged hydrogen atom with $Co(CO)_4$, the ability of the hydrogen to diffuse away will be strongly dependent on its mass, as the process must involve a large degree of tunneling. That $HCo(CO)_4$ and $DCo(CO)_4$ photolyze with the same efficiency suggests that the hydrogen atom is ejected from a cage with some of the excess energy of the photon used. The bond energy of $HCo(CO)_4$ has been estimated at 58 kcal/mol.[24] The excess energy of the photon of 254 nm amounts to 54 kcal/mol. Thus, it would appear that it is important to provide the hydrogen atom with excess energy to allow its escape from the cage. A detailed wavelength dependence of the photolysis was not attempted. The cage effect for hydrogen atom loss cannot be presumed to be nil as the photolysis process in CO is more efficient than in argon. It was proposed that the formyl radical itself is cleaved by photons of 254 nm.[18] The ability to form formyl which is subsequently photolyzed offers a possible mechanism by which the hydrogen atom can be removed by a series of photolytic steps out of the vicinity of the $Co(CO)_4$ moiety.

It might be argued that the bands observed in the infrared cannot be assigned to the same species as was observed by the ESR experiment; the ESR signals would have to be much more intense if they are to account for the species which appear in the infrared experiment due to the inherent sensitivity differences of the two experiments. However, it should be pointed out that the exposed surface area of the rod in the ESR experiment is much smaller than the surface area which is exposed to irradiation in the infrared experiment. In addition, the lamp intensity is less at the sample in the ESR experiment than in the infrared experiment. This is because the lamp must be placed farther from the sample in the ESR experiment and its radiation must be admitted into the cavity through a grid which cuts the intensity roughly in half.

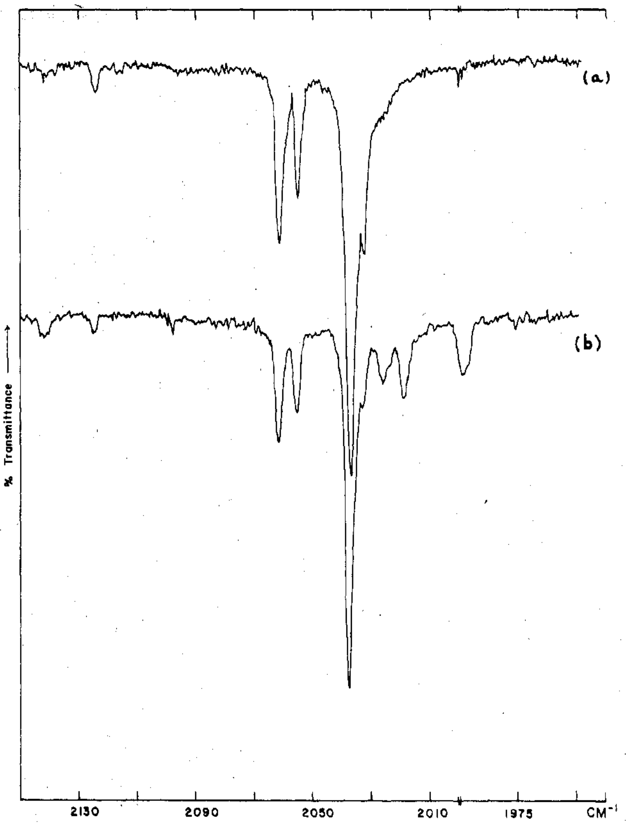

Figure 5. (a) Infrared spectrum of a mixture of $DCo(CO)_4$ and $HCo(CO)_4$ before photolysis. The band at 2051.4 cm^{-1} is assigned to the deuteride. (b) Same matrix after 40-min photolysis.

Wermer et al.[6] noted shoulders on the 2034 cm^{-1} absorption of freshly deposited matrices before photolysis in the positions expected for absorptions which result from photolysis. If these weak absorptions are due to decomposition products, they must now be assigned to $Co(CO)_4$. The deposits in those studies were made by using a metal tube to introduce the matrix materials into the cryostat. The tube had to be cooled to −78 °C in order to obtain a successful deposit. In the studies reported here, the tubing was glass and did not have the same catalytic ability to decompose $HCo(CO)_4$. On occasion, a metal mirror did form on the glass as a result of $HCo(CO)_4$ decomposition, and subsequent deposits of $HCo(CO)_4$ failed. It appears metals are very efficient in causing the decomposition of $HCo(CO)_4$ in the gas phase. Similar behavior was noted for $Co_2(CO)_8$. A new band at 2016.6 cm^{-1} in the spectrum of $Co_2(CO)_8$ appeared as a result of pyrolysis which was tentatively assigned to $Co(CO)_4$.[15] This work substantiates that assignment.

The two bands exhibited by $Co(CO)_4$ at 2016.2 and 2022.9 cm^{-1} vary in intensity with respect to each other. Although detailed curve resolution was not attempted, the band at 2022.9 cm^{-1} has been observed to be nearly as intense as the band at 2016.2 cm^{-1} and, in other instances, only about 75% as intense as the band at 2016.2 cm^{-1}. This behavior may result from the overlap of an unresolved band of $HCo(CO)_3$ or of some other species with that of $Co(CO)_4$. It may also be that both bands are assignable to the E mode of $Co(CO)_4$ which has been split by a lower matrix site symmetry. If this latter explanation is correct, the A_1 mode of $Co(CO)_4$ is unobserved and presumably is buried under the feature at 2034 cm^{-1} due

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to $HCo(CO)_4$. The effect of a hidden small band on the intensity of the 2034 cm^{-1} could not be discerned. In addition, a splitting of 7 cm^{-1} is larger than what one usually expects for argon matrices. For example, bands split by the matrix of the three isomers of $Co_2(CO)_8$ are only split by approximately 4 cm^{-1} or less. The close proximity of these bands to those reported by Hanlan et al.[16] in Ar/CO matrices suggests that the bands should be assigned to the A_1 and E modes of $Co(CO)_4$. The larger separation between the bands in the matrix doped with CO can be the result of site perturbations or molecular distortion. The analysis of how much $Co(CO)_4$ deviates from tetrahedral symmetry has been based on infrared[17,25] and ESR[16] experiments. The splitting observed in these experiments between the two most intense bands is the smallest splitting yet reported for $Co(CO)_4$ in argon matrices and is the same as was reported for $Ir(CO)_4$ and $Rh(CO)_4$.[25] The hydrogen atom is not probably located in the immediate vicinity of $Co(CO)_4$ nor are there any CO molecules doped in the matrix to cause site perturbations as was the case in earlier studies. Thus, the molecule probably exists in a uniform argon environment. Although the molecule is presumably less distorted than is the case in CO matrices, it is interesting to note that the ESR spectra are nearly identical in the two matrices.

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Registry No. $HCo(CO)_4$, 16842-03-8; $Co(CO)_4$, 58207-38-8; $DCo(CO)_4$, 62342-66-9.

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Tris(2,2′-bipyridine)ruthenium(II)-Photosensitized Oxidation of Antimony(III) and Production of Hydrogen Peroxide in Dilute Hydrochloric Acid Solution

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The formation reaction of hydrogen peroxide and the oxidation reaction of antimony(III) proceed continuously with the irradiation of visible light in the oxygen-dissolved 0.5 M HCl solution containing $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and Sb(III). The kinetic and quenching experiments have suggested a mechanism in which the electron transfer from the lowest excited state of $Ru(bpy)_3^{2+}$ to a dissolved oxygen molecule occurs.

Introduction

The irradiation of tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) with visible light results in the formation of a charge-transfer excited state ($[Ru(bpy)_3^{2+}]^*$) which is commonly considered as a triplet charge-transfer excited state.[1] Reactions of $[Ru(bpy)_3^{2+}]^*$ involve energy-transfer reactions,[2] electron-transfer reactions to the luminescence quenchers,[3] and those from the luminescence quenchers.[4]

However, one serious problem in the use of photochemically generated $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{+}$ as the strong oxidant and reductant, respectively, is associated with the fast back-reactions with the products of the quenchers.[5]

We found that the oxidation of Sb(III) and the formation of H_2O_2 proceeded continuously in $Ru(bpy)_3^{2+}$/Sb(III)/O_2/dilute HCl with the irradiation of the visible light. In this paper we report a study on the mechanism of the photoinduced reactions in this system.

Experimental Section

$[Ru(bpy)_3Cl_2]\cdot 6H_2O$ was prepared by the method described elsewhere[6] and recrystallized 3 times from water. A stock solution of Sb(III) in dilute HCl was usually prepared by dissolving GR grade $SbCl_3$ (Kanto Kagaku) in 2.5 M HCl. A stock solution of Sb(III) in dilute H_2SO_4 was prepared by warming $SbCl_3$ with small amounts of concentrated H_2SO_4 until evolution of white smoke, and then the residue was dissolved in 2.5 M H_2SO_4. Hydrolysis occurs if the acidity is below 2.5 M, but the process is very slow.[7] In all cases, freshly prepared samples for the irradiation were always used to avoid hydrolysis of the Sb(III). The concentration of HCl in the irradiation samples was usually kept at 0.5 M. The concentrations of Sb(III) and Sb(V) were determined by means of a Yanagimoto P-8 polarograph.[8] A typical procedure for the determination of hydrogen peroxide was as follows: 1 aliquot of the irradiation sample was poured into a column (10-mm diameter and 30-mm length) of cation-exchange resins (Dowex 50-X8, 100–200 mesh, the hydrogen form) followed by washing with water. The concentration of hydrogen peroxide in

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