0 and 1. It is also interesting to note that $\bar{n}$ apparently is independent of both the concentration of vanadium(V) and the temperature in the investigated ranges (Figure 9A-F). This supports strongly the spectrophotometric evidence that only monomeric vanadium(V) species are present in the melts under investigation. Furthermore, the spectrophotometric conclusion that the ratio $VO_2SO_4^-$:$VO(SO_4)_3^{3-}$ is temperature dependent is indirectly confirmed, as $\bar{n}$ for both $VO_2SO_4^-$ and $VO(SO_4)_3^{3-}$ (or $VO_2SO_4S_2O_7^{3-}$) is zero. Hence, no shift in $\bar{n}$ would be observed as a function of temperature.

It is, however, clear that a fairly large number of vanadium species with $\bar{n}$ in the range 0-1 can be imagined. Of these, vanadates can be ruled out since they are only found in strongly basic media. Polymeric species can generally be ruled out on the basis of the invariance of $\bar{n}$ with concentration and from the spectral behavior. Further, the found $\bar{n}$ values are in the range 0-1 and the found ν values in the range 0-2. Since $\bar{n}$ and ν are interrelated, only the following single-species dissolution reactions (giving rise to formation of oxo sulfato complexes) are possible within these ranges:

$$V_2O_5 + nS_2O_7^{2-} \rightarrow 2VO_{(5-n)/2}(SO_4)_n^{n-} \qquad (21)$$

$$\bar{n} = 0 \text{ and } \nu = 2$$

$$V_2O_5 + nS_2O_7^{2-} + 2SO_4^{2-} \rightarrow 2VO_{(5-n)/2}(SO_4)_{n+1}^{(n+2)-} \qquad (22)$$

$$\bar{n} = 1 \text{ and } \nu = 0$$

In these reactions n is furthermore restricted to be an uneven integer with the values 1 and 3 only, since a value of 5 implies the coordination of the small V^{5+} ion to 5 or 6 sulfate ions. This gives altogether the species $VO_2SO_4^-$, $VO(SO_4)_3^{3-}$, $VO_2(SO_4)_2^{3-}$, and $VO(SO_4)_4^{5-}$. Because of the large negative charge, $VO(SO_4)_4^{5-}$ is not probable. It can now be seen that the species left are the same as given in eq 16 and 20.

This result does in fact not contradict the already mentioned investigation[16] of V_2O_5 in molten NH_4HSO_4 at 200 °C. It was concluded here that the species VO_2^+ is formed in an acidic medium and $VO_2SO_4^-$ in basic. It is not clear, however, that these really are the species formed, but the investigation confirms that an exchange of sulfate ions is taking place, and this exchange is acid/base controlled. It is further interesting to note that recently Glazyrin et al.[41] from an examination of the phase diagram for V_2O_5-$K_2S_2O_7$ and on the basis of IR spectroscopy proposed the existence of the compounds KVO_2SO_4, $K_4(VO_2)_2(SO_4)_2S_2O_7$, and $K_3VO_2SO_4S_2O_7$. It can be seen that the anions for two of these compounds are identical with the ones proposed in the present paper (i.e., with $VO(SO_4)_3^{3-}$ given in the isomeric form $VO_2SO_4S_2O_7^{3-}$).

The curved lines in Figure 9 are drawn with the assumption that eq 20 represents the system. Due to the small change in $[S_2O_7^{2-}]$, this model could not be distinguished from eq 16. The result of the calculations is already shown in Table V, and a close agreement with the spectrophotometric results is observed.

Acknowledgment. The authors wish to thank Dr. M. Gaune-Escard, Université de Provence, for providing us with the calorimetric data for $K_2S_2O_7$. Further thanks are due to Statens tekniskvidenskabelige Forskningsråd for financial support.

Registry No. K_2SO_4, 7778-80-5; $K_2S_2O_7$, 7790-62-7; V_2O_5, 1314-62-1.

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Photolysis of Matrix-Isolated Hydridotetracarbonylcobalt(I). Comparison of the Probabilities of Carbonyl Loss with Hydrogen Atom Loss

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The photolysis of $HCo(CO)_4$ in CO matrices can be accounted for by two processes. A process of CO loss is observed as CO exchange in ^{13}CO matrices, and a process of metal-hydrogen bond homolysis is observed especially when the CO loss process is suppressed. The relative quantum yields have been estimated to be eight losses of CO for every loss of hydrogen with use of 254-nm radiation. The first electronic transition that is observed for $HCo(CO)_4$ is at 227 nm, which is assigned to be the LMCT from the hydrogen. This assignment is consistent with the intensity of the transition, the observed photochemistry, and several calculations of the ground-state electronic structure that have appeared in the literature.

The photolysis of $HCo(CO)_4$ in matrices shows evidence of metal-hydrogen bond homolysis.[1] Also, it is apparent that $HCo(CO)_3$ is formed in argon matrices, although the infrared band assigned to $HCo(CO)_3$ is less intense than those observed for $Co(CO)_4$. Taken at face value, it would seem that the quantum yield for hydrogen atom loss is larger than that for CO loss. However, such an analysis ignores the possibility of fragment recombination during photolysis. Previously, I attempted to elucidate the cage effect for the hydrogen atom loss process as described by eq 1. It was concluded that the

$$HCo(CO)_4 \rightarrow H\cdot + \cdot Co(CO)_4 \qquad (1)$$

photolysis event that is not reversed is that which results from the hydrogen atom being ejected from the immediate vicinity of $Co(CO)_4$. It was not then possible to discuss the cage effect for CO loss, as described by eq 2. This paper reports the

$$HCo(CO)_4 \rightarrow HCo(CO)_3 + CO \qquad (2)$$

results of isotope exchange studies, which indicate a large cage effect for reaction 2. The major result of photolysis of $HCo(CO)_4$ may well be CO loss, which is efficiently reversed in both argon and CO matrices. In this respect $HCo(CO)_4$ resembles $HMn(CO)_5$[2,3] and $R_3Si(CO)_4$.[4]

Experimental Section

Equipment and procedures for studying matrices of $HCo(CO)_4$ have been described previously.[1] Positions of infrared bands are

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[1] Sweany, R. L. *Inorg. Chem.* **1980**, *19*, 3512-3516.

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[3] Church, S. P.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7515.

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Table I

source	dist from matrix, cm	wavelength	intens, 10^{10} einstein s^{-1}
low-pressure Hg	5	principally 254 nm	3
medium-pressure Hg	30	270-301 nm	2
		270 nm	2

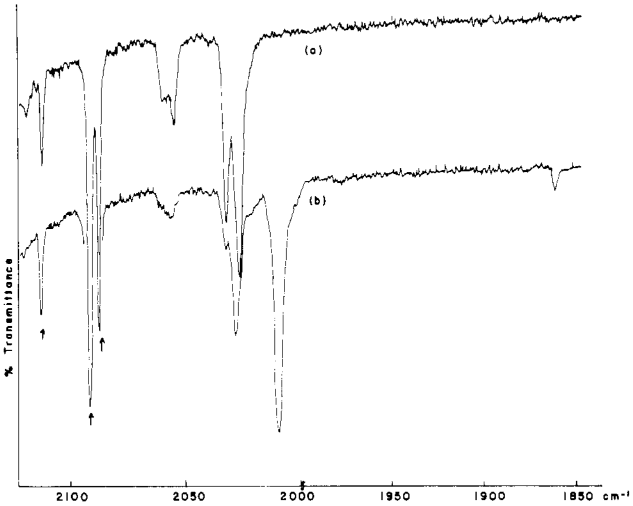

Figure 1. $HCo(CO)_4$ matrix isolated in ^{12}CO: (a) spectrum before photolysis; (b) spectrum after 40-min photolysis with a low-pressure mercury lamp. Arrows mark the positions of observed isotopic isomers of CO. Spectrometer order break occurred at 2000 cm^{-1}. The scan rate was 20 cm^{-1} in.$^{-1}$ above order break and 25 cm^{-1} in.$^{-1}$ below the order break.

accurate to ±1.0 cm^{-1} when peaks are well resolved. Carbon-13 monoxide was obtained from Merck at 90% enrichment and was used as received. Photolyses were accomplished with a low-pressure mercury lamp and a medium-pressure mercury lamp (GTE Sylvania H39KB-175 W), the glass shroud of which had been removed. This lamp was used either with no filters or with glass filters. A Pyrex glass plate cut off rapidly in the region of 270 nm (OD = 2.0 at 270 nm). An ordinary glass plate exhibited a sharp cutoff at 301 nm, at which point its optical density was 2.0. Although the medium-pressure mercury lamp is inherently more intense than the low-pressure lamp, its bulk prevented it from being as close to the cryostat. The amount of energy reaching a typical matrix was measured by ferrioxalate actinometry. The conditions of a typical experiment were reproduced by placing the solution actinometer inside the heat shields of the cryostat and irradiating it through the quartz vacuum window used for the bulk of these experiments. Table I presents the results of duplicate calibrations. The quantum yield for the conversion of $Fe(C_2O_4)_3^{3-}$ to $Fe^{2+}(aq)$ is fairly constant in the interval from 254 to 366 nm so that the several lines of the source could be simultaneously measured within a frequency region bounded by the filter cutoffs.[5]

Near-infrared, visible, and ultraviolet spectra were measured with a Cary 17 from 10000 to 184 nm. The spectrometer was ordinarily not operated with a nitrogen purge. The presence of oxygen in the spectrometer did not affect the measuring of the spectrum of $HCo(CO)_4$ at its first recorded absorption at 227 nm. At shorter wavelengths the photometric errors become quite large and the slits were operated nearly to their limits. Better resolution was obtained by operating with a nitrogen purge. However, even with 5-Å resolution, no fine structure could be detected and spectra appeared similar to those taken under low-resolution conditions.

Results and Discussion

Figure 1 shows the spectrum of $HCo(CO)_4$ in a CO matrix before and after photolysis with a low-pressure mercury lamp. After 40 min of photolysis substantial conversion of $HCo(CO)_4$ to $Co(CO)_4$ is effected. In addition, a band due to HCO is observed at 1861 cm^{-1}.[1] The spectrum of $Co(CO)_4$ has been observed previously;[6,7] two reasonably intense bands are observed at 2010.7 and 2028.8 cm^{-1}. A third band is very weak and is observed at 2107 cm^{-1}. In the spectrum shown in Figure 1b, the band that is observed to grow in upon photolysis is at 2010.5 cm^{-1}, within experimental error of what is observed for $Co(CO)_4$. The position of the other strong absorption of $Co(CO)_4$ is covered by residual intensity due to $HCo(CO)_4$. Here the residual absorption is due to the E symmetry mode of $HCo(CO)_4$, which has been split by solid-state effects. The contour of these two absorptions at 2028.0 and 2033.2 cm^{-1} is modified by photolysis, and the band maximum shifts to 2029.4 cm^{-1}. The two intense modes due to $HCo(CO)_4$ do not lose intensity upon photolysis at the same rate. The broad band at 2056 cm^{-1} is attenuated to a larger extent than the pair at 2030 cm^{-1}. This can be rationalized by assuming that $Co(CO)_4$ is indeed produced and that its absorption at 2028.8 cm^{-1} accounts for the frequency shift and extra intensity of the pair of bands at 2030 cm^{-1}.

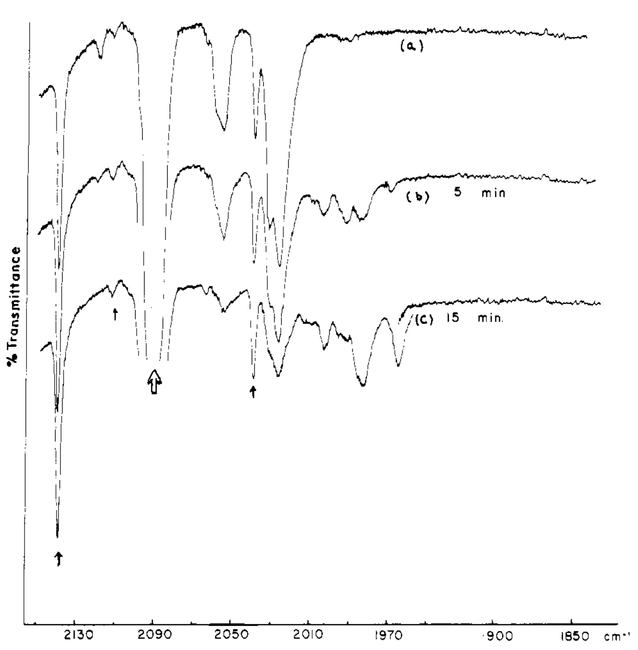

Figure 2. HCo(CO) matrix isolated in ^{13}CO: (a) before photolysis; (b) after 5-min photolysis; (c) after 15-min photolysis. Order break occurs at 1970 cm^{-1} in (b) and at 1960 cm^{-1} in (c). Arrows mark the positions of observed isotopic isomers of CO.

When $HCo(CO)_4$ is irradiated with 254-nm radiation in ^{13}CO matrices, changes are apparent in a fraction of the time it takes to form large amounts of $Co(CO)_4$. Figure 2 shows the results of 5 and 15 min of irradiation with 254-nm radiation. For the most part, the bands that grow in are assignable to molecules of $HCo(CO)_4$ with varying degrees of incorporation of ^{13}CO. The analysis of the spectra is complicated by the presence of $Co(CO)_4$, which is itself evidencing ^{13}CO incorporation. The band, for example, at 1964.5 cm^{-1}, which becomes quite prominent after 15 min of irradiation, is certainly due to $Co(^{13}CO)_n(^{12}CO)_{4-n}$. The irradiation of $HCo(CO)_4$ in ^{13}CO with a Pyrex-filtered, medium-pressure mercury lamp gave only a very small amount of ^{13}CO incorporation after 40 min. No amount of homolysis was observed over the same time span; however, longer photolysis times would have to be used to determine whether the same relative quantum yields result from the longer wavelength irradiation. It will be shown later that these longer wavelengths are simply not

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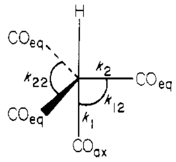
Table II. Factored Force-Field Fit of $HCo(CO)_4$[a]



obsd (used in regression)	calcd	assigt	molecule	sym
2119.0[b]	2118.1	A_1	$HCo(^{12}CO)_4$	C_{3v}
2054.9	2055.1	A_1		
2028.0	2028.0	E		
2111.8	2111.9	A′	$HCo(^{12}CO)_3(^{13}CO)$	C_s
1991.2	1991.7	A′		
2104.7	2105.6	A′	$HCo(^{12}CO)_2(^{13}CO)_2$ (both ^{13}CO's are equatorial)	C_s
2003.7	2002.8	A′		
1982.8	1983.0	A″		

[a] k values for the structure shown are as follows: $k_1 = 17.509$ mdyn Å^{-1}; $k_2 = 16.962$; $k_{12} = 0.303$; $k_{22} = 0.352$. [b] Frequencies are accurate to ±1.0 cm^{-1} when well resolved from neighboring features.

absorbed to a significant extent.

The spectra of all the related isotopic isomers due to $Co(CO)_4$ have been calculated and published.[6,7] A factored force field for $HCo(CO)_4$ was determined that calculates the observed bands that can be unambiguously assigned to $HCo(CO)_4$ (see Table II). The structure of $HCo(CO)_4$ is C_{3v} symmetry as determined by gas-phase electron diffraction.[8] The spectrum of $HCo(CO)_4$ shows considerable disruption due to matrix effects. The best fit of the spectrum was obtained with use of the frequencies of maximum absorbance. The isomers for which assignments could be made contained the label in the equatorial plane. This is not to be taken as evidence that substitution occurs preferentially at the cis positions. There is no such expectation based on studies of Atwood and Brown.[9] The absorptions of isomers with axial substitution fall too close to other absorptions so that it is difficult to unambiguously assign a band to an isomer with axial substitution or measure its frequency. Although the Co–H stretch should mix with the CO stretching modes, this coordinate was omitted from the force-field calculation. A very weak absorption is observed at 1938 cm^{-1} in thick deposits of $HCo(CO)_4$, which corresponds to a band at 1935 cm^{-1} that was observed by Edgell and assigned to the metal–hydrogen stretch.[10] The carbonyl bands that appear at low frequencies might be expected to mix with the metal–hydrogen stretch to a greater degree than those of the all carbon-12 isomer. The shift in the low-frequency A_1 carbonyl stretching mode, which was observed for $DCo(CO)_4$ in argon, was not resolved in CO matrices, nor were there significant shifts in bands when a sample that contained $DCo(CO)_4$ was photolyzed in a ^{13}CO matrix. Omission of the metal–hydrogen stretching coordinate, therefore, should not lead to serious error.

In order to assess the effectiveness of photons on CO exchange, it is important to be able to determine how many of the original molecules of the all carbon-12 isomer remain at any time. The only band of this isomer that can be unambiguously followed is the high-frequency A_1 mode, which is unfortunately very weak. The rate at which this band declines upon photolysis is substantially faster in ^{13}CO than in ^{12}CO. In ^{12}CO, the only chemical reason for its decline is as a result of homolysis. The process is presumably unaffected by the mass of carbon and accounts for some of the loss of intensity of the band in ^{13}CO matrices as well. The excess rate in ^{13}CO is accounted for by CO exchange. The time dependence of the intensity of this was treated as pseudo-first-order behavior, and the results of that treatment are contained in Table III.

Table III. Pseudo-First-Order Rate Constants Calculated from Optical Density Changes of the 2119.0-cm^{-1} Band

matrix	time interval, min	change in OD	k_{pseudo},[a] min^{-1}
^{12}CO	20	0.028	0.019
	40	0.083	0.031
	16	0.038	0.010
	45	0.061	0.013
			av = 0.018
^{13}CO	5	0.026	0.147
	5	0.013	0.162
	10	0.024	0.115
			av = 0.141

[a] $k_1I_a/k_6I_a = 8$.

Although the qualitative results of these experiments are plainly evident, a more quantitative treatment of the data depends on several assumptions. For example, constant illumination is assumed although the products of the exchange reaction and $Co(CO)_4$[7] all absorb at 254 nm. Two problems arise. First, the intensity of the lamp is attenuated by the products of reaction and a pseudo-first-order treatment of the data is not rigorously justified. Second, it is possible to regenerate $HCo(^{12}CO)_4$ by photolysis. A plausible mechanism for photosubstitution is given by eq 3–7. The photodissociation

$$HCo(^{12}CO)_4 \xrightarrow{k_1I_a} HCo(^{12}CO)_3 + {}^{12}CO \tag{3}$$

$$HCo(^{12}CO)_3 + {}^{12}CO \xrightarrow{k_2} HCo(^{12}CO)_4 \tag{4}$$

$$HCo(^{12}CO)_3 + {}^{13}CO \xrightarrow{k_3} HCo(^{12}CO)_3(^{13}CO) \tag{5}$$

$$HCo(^{12}CO)_3(^{13}CO) \xrightarrow{k_4I_a} HCo(^{12}CO)_2(^{13}CO) + {}^{12}CO \tag{6}$$

$$HCo(^{12}CO)_3(^{13}CO) \xrightarrow{k_5I_a} HCo(^{12}CO)_3 + {}^{13}CO \tag{7}$$

of ^{12}CO described by eq 3 leads to a local abundance of ^{12}CO approaching 80% in the cage. The rate law for the loss of $HCo(^{12}CO)_4$ can be simplified by assuming that $[HCo(CO)_3]$ conforms to the steady-state approximation, $k_2 = k_3$, $[^{13}CO] = 4[^{12}CO]$, and $k_1 = 4k_5$ and that it is unlikely that any isomer with more than one carbon-13 monoxide will photoexchange back to the all carbon-12 isomer:

$$-d[HCo(^{12}CO)_4]/dt = \\ {}^4\!/\!{}_5k_1I_a\{[HCo(^{12}CO)_4] - {}^1\!/\!{}_{16}[HCo(^{12}CO)_3(^{13}CO)]\} \tag{8}$$

$$= {}^4\!/\!{}_5k_1I_a[HCo(^{12}CO)_4] \tag{9}$$

where I_a = light intensity. For homolysis

$$\begin{gathered} HCo(^{12,13}CO)_4 \xrightarrow{k_6I_a} H + Co(^{12,13}CO)_4 \\ -d[HCo(^{12}CO)_4]/dt = k_6I_a[HCo(^{12}CO)_4] \end{gathered} \tag{10}$$

In ^{13}CO the rate of disappearance of $HCo(^{12}CO)_4$ is equal to the sum of the rate equations, (9) and (10). k_6 is determined independently from the photolysis in ^{12}CO. The pseudo-first-order treatment of the data is justified if the light intensity is constant. The fact that the optical density due to $HCo(CO)_4$ rarely exceeds 1.0 at the band maximum (227 nm, vide infra) suggests that there is not a great deal of attenuation of radiation at 254 nm due to isomers of $HCo(CO)_4$. On the other hand, $Co(CO)_4$ strongly absorbs photons at 254 nm;[7] as a

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(10) Edgell, W. F.; Summit, R. *J. Am. Chem. Soc.* **1961**, *83*, 1772–1773.

result the reported values of k_6 may be smaller than is actually the case. Observations of short duration are not as affected because large quantities of $Co(CO)_4$ will not have accumulated. The errors in using only the optical density at $\bar{\nu}_{max}$ of a weak absorption band will account for the greatest portion of the random error. Variations in lamp placement and nonuniform warm-up procedures will also contribute to a lesser degree. The results show that CO loss is 8 times more probable than hydrogen atom loss, if there is no cage effect for hydrogen atom loss.

The behavior of $HCo(CO)_4$ is not unlike that of $HMn(CO)_5$ and $R_3SiCo(CO)_4$.[2-4] In either system, the dominant photoprocess is that of CO loss but homolysis is still observed. The latter process is particularly important in situations in which the CO loss process is effectively reversed as was the case for $HMn(CO)_5$ and $HCo(CO)_4$ in CO matrices or in situations in which the homolysis results in the mobilization of $Co(CO)_4$ as was the case for polymer-bound $R_3SiCo(CO)_4$. It is also important to link the observed chemistry of $HCo(CO)_4$ with that of $H_2Fe(CO)_4$. Although hydrogen molecules are ejected from $H_2Fe(CO)_4$, the nature of the transition, which results in metal–hydrogen bond cleavage, may not be grossly different.[11,12]

The electronic spectrum of $HCo(CO)_4$ has been measured in argon, ^{12}CO, and ^{13}CO. A typical spectrum is shown in Figure 3. Although this example is of an argon matrix, the gross features are not changed in CO. Most apparent is an intense band at 227 nm, which occurs as a shoulder on a much more intense band at about 187 nm. The latter is somewhat in doubt because it comes so close to the lower wavelength limit of the spectrometer. The cryostat is equipped with NaCl windows, which account for a gradual rise in the base line upon which the spectrum of $HCo(CO)_4$ is superimposed. On occasion, weak features are observed to longer wavelengths than 227 nm. Their intensities do not correlate with the intensity of the band at 227 nm, and in some matrices they are not apparent at all. The infrared spectra of the same matrices that are used for ultraviolet–visible spectra were routinely measured. No impurities such as $Co_2(CO)_8$ were present. The optical density at λ_{max} of the band at 227 nm is of the same order of magnitude as that of the E vibrational mode.

This comparison of ultraviolet and infrared intensities leads one to believe that the electronic transition is intense; a fact that is consistent with its being assigned charge-transfer character. It is possible to estimate its intensity from the comparison with the infrared band by using typical integrated intensities of infrared bands in metal carbonyls. Intensities of the infrared bands rarely exceed 10^6 M^{-1} cm^{-2} but frequently exceed 10^5 for the more intense modes of a molecule.[13] From the observed band width at half-height of 5 cm^{-1}, the molar decadic extinction coefficient, ϵ, for the E mode should range between 5500 and 55 000.[14] The value of ϵ for the transition at 227 nm should be of the same magnitude. This is larger than ligand field transitions of $Cr(CO)_6$ and its monosubstituted derivatives.

Several calculations have appeared in which the HOMO of $HCo(CO)_4$ has been claimed to be the orbital having most to do with cobalt–hydrogen bonding.[12,15-17] Any excitation of an electron from this orbital would move an electron either onto the metal or into the carbonyl-centered orbitals and thus be charge transfer in nature. This simple picture is at odds with PES spectra of $HCo(CO)_4$ in which the binding energy of the orbital assigned to the metal–hydrogen bond is at 11.5 eV.[18] Metal-centered orbitals have been assigned to two transitions in the PES spectrum between 8 and 10 eV. That the PES spectrum should lead directly to the ordering of the eigenvalues has been contested.[12,19] The observed ionization energies must be modeled with some allowance for relaxation. Calculations by Guest et al.[12] very nearly model the ordering found in the PES spectrum using a calculation in which the HOMO is M–H bonding in nature for $HMn(CO)_5$ and $H_2Fe(CO)_4$. A more detailed analysis of the electronic structure of $HCo(CO)_4$ and its properties is in preparation.[17]

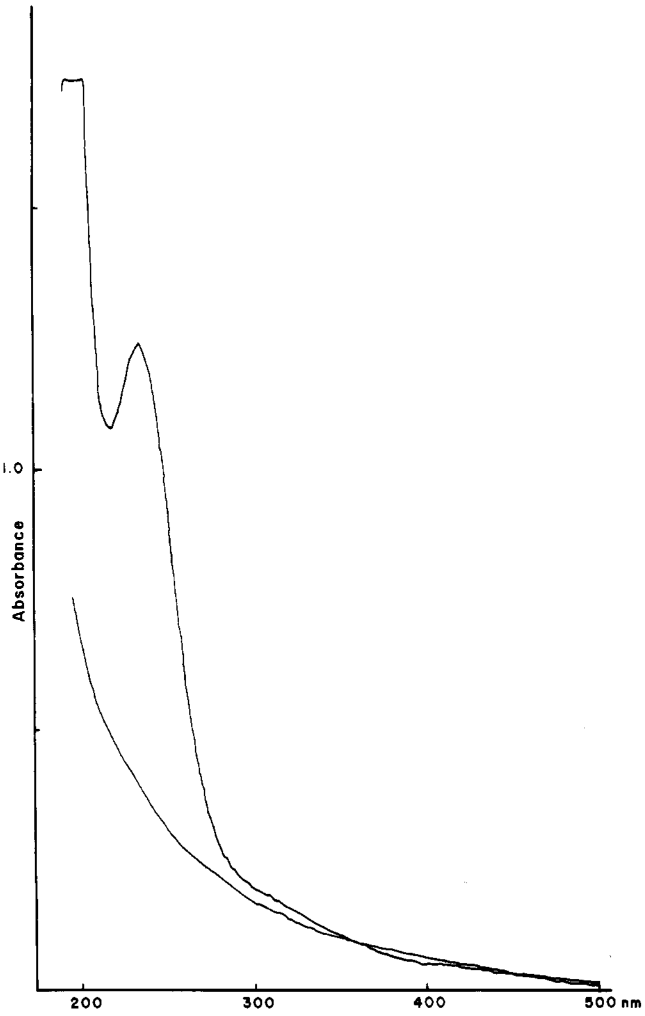

Figure 3. Visible–ultraviolet spectrum of $HCo(CO)_4$ in argon. Lower trace shows background absorptions of the cryostat windows. The spectrometer was not being purged during the recording of these spectra.

There is, however, no evidence of weak ligand field transitions to shorter wavelengths of 227 nm. Samples have been examined for which transitions of intensity of 1% of that of 227 nm should be detectable. This would require ϵ to be less than 550. Although the possibility exists that ligand field transitions this weak are present in the singlet manifold, it is unlikely. Such low intensities are observed for very symmetric molecules in which there is little covalency between the metal and ligands. These qualities do not describe $HCo(CO)_4$. The values of ϵ for the lowest energy spin-allowed ligand field

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(19) Calabro, D. C.; Lichtenberger, D. L. *Inorg. Chem.* **1980**, *19*, 1732–1734.

transition of $Cr(CO)_6$ is 700, and for less symmetric derivatives of the form $LCr(CO)_5$ it is 1400.[20]

In conclusion, the description of the electronic structure of $HCo(CO)_4$ which best accounts for the photochemistry is one in which the HOMO is metal–hydrogen σ bonding in character with electron density residing mostly on the hydrogen. Excitation of an outer electron into the virtual orbitals is charge transfer in nature and results in metal–hydrogen bond weakening. This interpretation is consistent with several calculations that are published and with the calculation of Boudreaux. Of the plausible virtual orbitals that might become populated, there are those that are σ^* with respect to metal–carbon bonding, σ^* with respect to metal–hydrogen bonding, or π^* with respect to carbon–oxygen bonding. The latter orbitals are related to the 2π level of CO and are probably too high in energy to be involved in transitions in the neighborhood of 230 nm. Therefore, the band at 227 nm must be $\sigma \rightarrow \sigma^*$ in character and must be LMCT although electron density may be delocalized into the carbonyl ligands as well. This description of a LUMO may imply metal–carbon weakening as well in the excited state.

The photochemistry of other late first-row transition-metal hydridocarbonyls can be similarly explained on the basis of the work of Guest et al., and this expectation is being confirmed by this and other matrix studies. A very similar picture is presented for $CH_3Co(CO)_4$ although the photochemistry has not been studied in detail.[21] Also, these conclusions are very similar to those of many authors in studies of metal–metal bonded systems.[22]

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Registry No. $HCo(CO)_4$, 64519-62-6.

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Matrix Isolation Investigation of the Fluoroformate Anion

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The fluoroformate anion has been isolated for the first time in a condensed-phase synthesis, in argon matrices. The anion was formed through the gas-phase reaction of a CsF molecule with CO_2 and isolated in an ion pair with Cs^+. Two C–O stretching modes were detected at 1316 and 1749 cm^{-1}, along with a C–F stretching mode at 883 cm^{-1}. Complete isotopic labeling allowed determination of a planar C_{2v} structure for this anion, with bands quite comparable to a series of isoelectronic or isostructural species. Normal coordinate calculations determined a value of 10.2 mdyn/Å for the C–O stretching force constant, suggestive of considerable double-bond character for the carbon–oxygen bonds, while a value of 4.2 mdyn/Å was calculated for the C–F stretching force constant. CNDO/2 calculations were also performed, and these predict a geometry similar to that which was observed.

Introduction

The fluoroformate anion, CO_2F^-, has been the object of numerous synthetic attempts.[1,2] By analogy to the isoelectronic carbonate anion and the formate anion HCO_2^-, the fluoroformate anion should be quite stable. However, all synthetic attempts have failed in condensed phases, although the anion has been formed in ion cyclotron resonance studies.[3] The ICR studies determined that the fluoride ion affinity of CO_2 is 32 kcal/mol, which, while not as large as for strong Lewis acids like BF_3 and SiF_4, is still quite large. It has been postulated that the failure to form the CO_2F^- anion in condensed-phase synthesis is due to the high lattice energy of CsF, which must be overcome for products to form.[2,3]

The salt/molecule technique was developed several years ago, in conjunction with matrix isolation, for the study of halide-containing anions in ion pairs.[4-6] In this method, an alkali halide salt is vaporized and is allowed to undergo a gas-phase reaction with a suitable partner, before the product is quenched into an inert matrix. Halide ion transfer has been shown to occur in many cases such as to form HCl_2^-, SiF_5^-, and COF_3^- ions paired with alkali metal cations. The cation, while present, does not perturb the anion to a large degree. Studies have shown that the large diffuse cations, particularly Cs^+, provide the least perturbation.[7]

The salt/molecule technique appeared to be an appropriate weapon for a synthetic attempt at the fluoroformate anion; this method eliminates lattice-energy considerations as the salt is vaporized prior to reaction. The reaction, then, between gas-phase CsF and CO_2 might yield the $Cs^+CO_2F^-$ ion pair, which could be trapped for spectroscopic study. Consequently, a series of reactions of CsF with isotopically enriched samples of CO_2 in argon was conducted, and the products were analyzed.

Experimental Section

The matrix isolation experiments carried out in this study were conducted on a standard matrix isolation system which has been described previously.[8] CsF was the primary salt employed and was vaporized at roughly 500 °C from a resistively heated oven. Since CsF is extremely hygroscopic, the salt was dried and outgassed thoroughly at roughly 400 °C prior to the start of an experiment. CO_2 (Matheson), $^{13}CO_2$ (Merck, 99% ^{13}C), $C^{18}O_2$ (Merck 94% ^{18}O), and $C^{18}O_2$ (Isotope Labeling Corp., 50% ^{18}O) were purified by one or more freeze–thaw cycles prior to sample preparation. Argon was used as the matrix gas in most experiments, and was used without purification.

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