$Co_3(CO)_9CCH_3$,[26] $Rh_2(CO)_4Cl_2$,[32] and $Fe_2(CO)_6(SC_2H_5)_2$.[33]

A more detailed description of the bonding will be deferred until completion of our current investigation of the isomorphous $Ru_3(CO)_{12}$ structure. This study with a less heavy metal (atomic number 44) will provide more accurate carbon and oxygen positional parameters and will make possible a comparison of molecular features of the two compounds.

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CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY,
FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA

Photochemical Formation of Some Metal Hexacarbonyl–Acetonitrile Derivatives

BY GERARD R. DOBSON, MOSTAFA F. AMR EL SAYED, INGO W. STOLZ, AND RAYMOND K. SHELINE

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The photoproduction of several new metal hexacarbonyl derivatives (M = Cr, Mo, W) in the solvent acetonitrile was followed spectrophotometrically by observation of the growth and decay of the carbonyl stretching bands in the 2200–1700 cm.$^{-1}$ region of the infrared. Isolation and analysis of the tungsten derivatives indicate that the reactions involve an equilibrium among the species $M(CO)_6$, $M(CO)_5(CH_3CN)$, $M(CO)_4(CH_3CN)_2$ and, in the cases of Mo and W, $M(CO)_3(CH_3CN)_3$. Arguments are given in support of the hypothesis that the radical $M(CO)_5$ is the initiating species in these reactions.

When the metal hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are dissolved in various organic solvents, and the resulting colorless solutions are exposed to ultraviolet radiation, they turn bright yellow almost immediately, and the color change is accompanied by the formation of new carbonyl stretching bands in the 2200–1700 cm.$^{-1}$ region of the infrared. If acetonitrile is the solvent used, the spectral changes are extensive and complex, suggesting extensive reaction between the solvent and the hexacarbonyl.

Spectra

The spectral changes of the metal hexacarbonyl–acetonitrile solutions were conveniently followed by exposing such solutions to ultraviolet radiation supplied by a General Electric AH-6 mercury arc lamp. Exposures were made directly in sealed sodium chloride infrared cells, and after irradiation the spectra were recorded immediately on a Perkin-Elmer Model 221 prism grating spectrophotometer. Some initial studies were made using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Table I lists the frequencies of the bands observed after such irradiations.

The complex nature of the reactions responsible for the spectral changes is borne out by the observation that the new bands are formed and decay back in a random manner, though, in general, as the irradiation proceeds, bands of lower frequency increase in intensity at the expense of

TABLE I

APPROXIMATE FREQUENCIES, OBSERVED BANDS, 2200–1700 CM.$^{-1}$ REGION, OF IRRADIATED $M(CO)_6$–ACETONITRILE SOLUTIONS

$Cr(CO)_6$ (in cm.$^{-1}$)	$Mo(CO)_6$ (in cm.$^{-1}$)	$W(CO)_6$ (in cm.$^{-1}$)
~2140	~2140	~2140
2075	2075	2075
2020	2030	2025
1980	1985	1980
1940	1945	1940
....	1910	1910
1895	1890	1897
1850	1840	1835
....	1790	1790

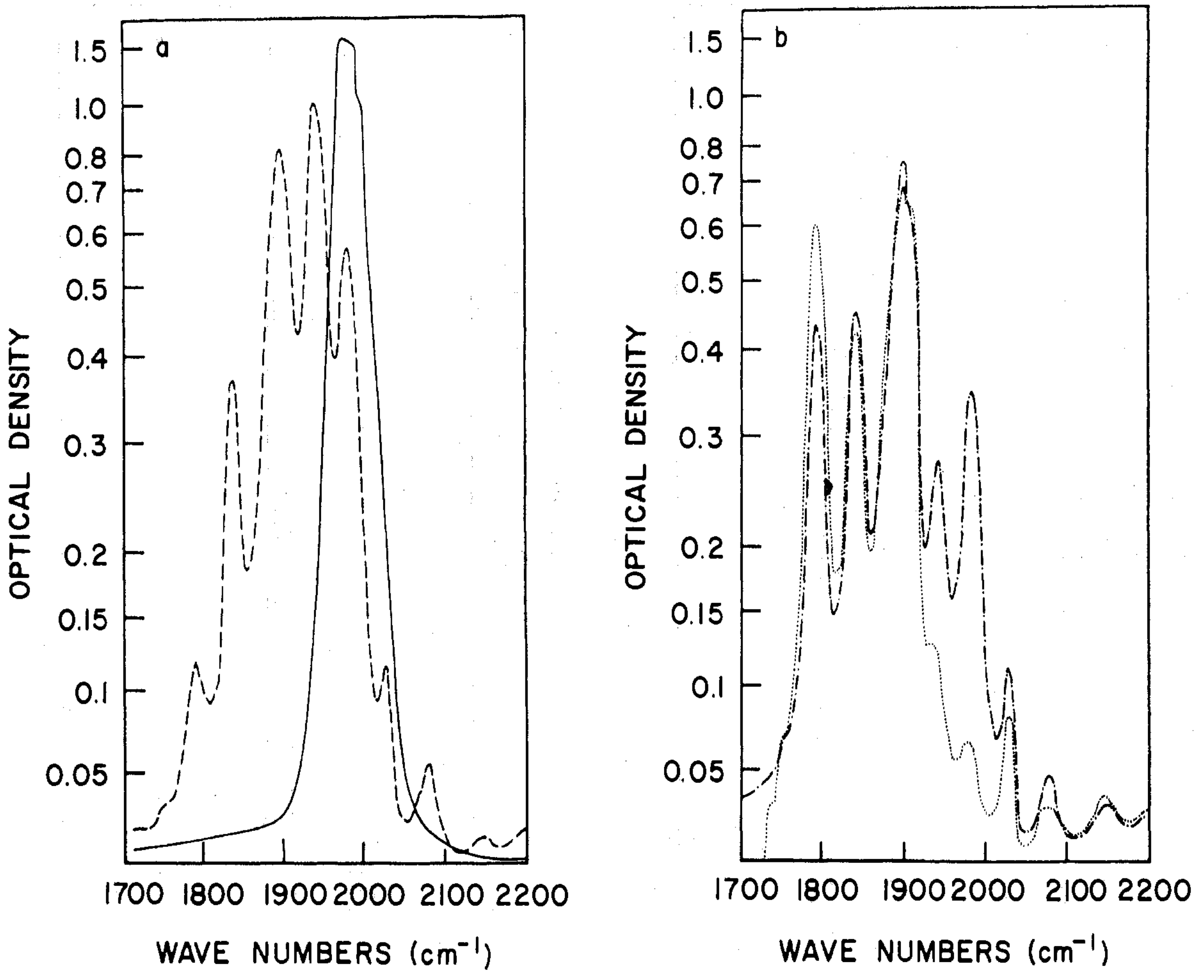

Fig. 1.—The infrared spectra of $W(CO)_6$ in CH_3CN: (a) ——— before irradiation, – – – – immediately after a 20 sec. exposure; (b) . . . . after allowing solution to stand after exposure for 16 min. and reëxposing for 2.5 min., — · — after standing for 3 min. after completion of this last exposure.

those of higher frequency. For tungsten hexacarbonyl, the spectra of whose solutions are most clearly defined, the changes can be seen in Fig. 1. The spectra of molybdenum hexacarbonyl–acetonitrile solutions are similar; those of chromium hexacarbonyl solutions are shown in Fig. 2.

For the reaction of $W(CO)_6$ with CH_3CN, one can see from Fig. 1 that after a long period of irradiation, $W(CO)_6$ is almost completely destroyed with the formation of new bands of lower frequency.

After the irradiation has ceased, however, the concentration of $W(CO)_6$ progressively increases. This observation, coupled with the observed randomness of band formation and decay, suggests that the reactions involve the formation of an equilibrium mixture of perhaps several complexes. Three such complexes have in fact been isolated, and analytical data show them to have the formulas $W(CO)_5(CH_3CN)$, $W(CO)_4(CH_3CN)_2$, and $W(CO)_3(CH_3CN)_3$. The infrared spectra of these compounds are shown in Fig. 3–5. While our work was in progress, Strohmeier and Schönauer[1] reported the synthesis of $W(CO)_5(CH_3CN)$ and $W(CO)_4(CH_3CN)_2$ by methods similar to ours.

A comparison of the carbonyl stretching frequencies for these three compounds with those observed for the irradiated $W(CO)_6$–CH_3CN solutions is given in Table II.

The spectra in Fig. 1 can be completely explained by the formation of the three compounds if one assigns the weak band at about 2140 cm.$^{-1}$ to carbon monoxide evolved during the irradiation, but still present in the infrared cell. This is not unreasonable in light of the fact that the uncharged CO molecule is experimentally found to have its missing Q branch at 2155 cm.$^{-1}$ in the gas phase.

[1] W. Strohmeier and G. Schönauer, *Ber.*, **94**, 1346 (1961).

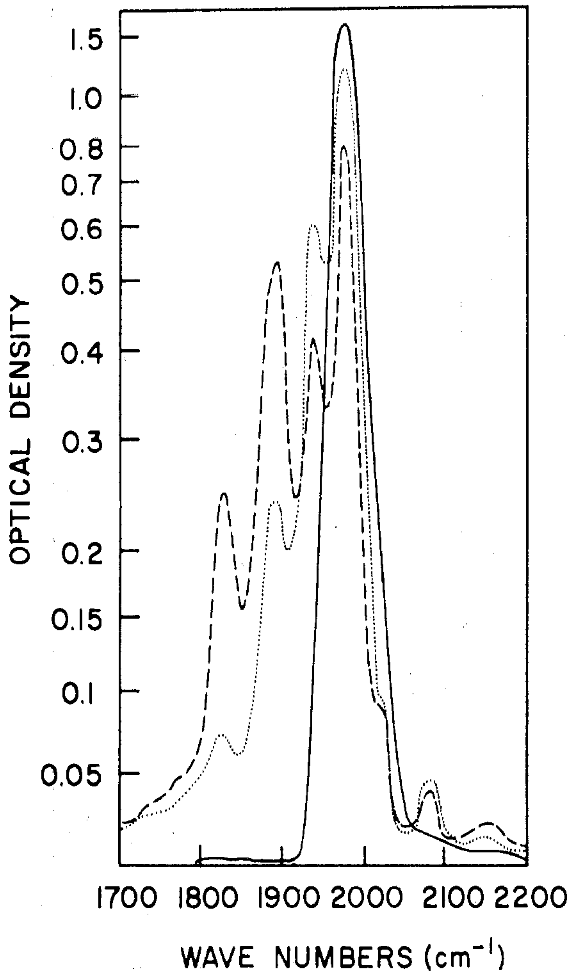

Fig. 2.—The infrared spectra of $Cr(CO)_6$ in CH_3CN: ——— before irradiation; – – – – immediately after a 20 sec. exposure; . . . . 15 min. after completion of the exposure.

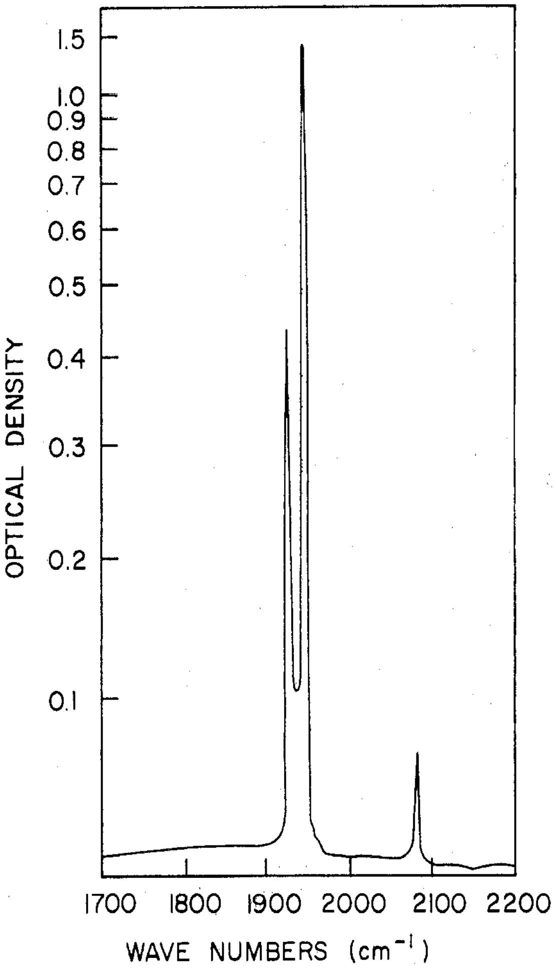

Fig. 3.—The infrared spectrum of $W(CO)_5(CH_3CN)$ in *n*-hexane.

Figure 1 and the data in Table II show that as a $W(CO)_6$ in CH_3CN solution is irradiated, $W(CO)_5(CH_3CN)$ is first formed. As the irradiation is continued, the concentrations of $W(CO)_4(CH_3CN)_2$ and finally $W(CO)_3(CH_3CN)_3$ increase. The reverse process is noted if the cell is allowed to stand after irradiation, $W(CO)_6$ eventually being re-formed in appreciable amounts. These observations are consistent with the equilibrium

$$\begin{aligned} W(CO)_6 + 3CH_3CN &\rightleftharpoons W(CO)_5(CH_3CN) + \\ 2CH_3CN + CO &\rightleftharpoons W(CO)_4(CH_3CN)_2 + \\ CH_3CN + 2CO &\rightleftharpoons W(CO)_3(CH_3CN)_3 + 3CO. \end{aligned}$$

Assuming this equation to be valid, the preparation of $W(CO)_5(CH_3CN)$ would be favored if a small amount of acetonitrile and an excess of CO were used in the preparation. One would further expect the equilibrium to be shifted toward $W(CO)_4(CH_3CN)_2$ by the removal of CO as it is evolved, and by the presence of an excess of acetonitrile in the reaction mixture. These predictions are confirmed by the conditions under which the two compounds actually are most efficiently prepared.

Experimental

Acetonitriletungstenpentacarbonyl and Di-(acetonitrile)-tungstentetracarbonyl.—These two compounds were prepared by methods essentially similar to those reported by Strohmeier and Schönauer.[1] Acetonitriletungstenpentacarbonyl was obtained in 40% yield as a light yellow crystalline solid, m.p. 83°. It is very soluble in polar organic solvents, moderately soluble in non-polar solvents, and insoluble in water. In solution it slowly decomposes to $W(CO)_6$ and $W(CO)_4(CH_3CN)_2$ and for this reason cannot be purified by crystallization from solution.

Anal. Calcd. for $C_7H_3O_5NW$: C, 23.03; N, 3.84; H, 0.83; W, 50.40. Found: C, 23.42; N, 3.83; H, 1.21; W, 49.97.

Di-(acetonitrile)-tungstentetracarbonyl was obtained in 65% yield, and is soluble in polar solvents and chloroform,

TABLE II

A COMPARISON OF THE CARBONYL STRETCHING FREQUENCIES OBSERVED IN THE IRRADIATED $W(CO)_6$–CH_3CN SOLUTION WITH THOSE OF $W(CO)_5(CH_3CN)$, $W(CO)_4(CH_3CN)_2$, and $W(CO)_3(CH_3CN)_3$

Bands obsd. in irradiated $W(CO)_6$–CH_3CN soln.	Bands obsd. for $W(CO)_5$-(CH_3CN) in n-C_6H_{14}	Bands obsd. for $W(CO)_4$-$(CH_3CN)_2$ in CH_3CN	Bands obsd. for $W(CO)_3$-$(CH_3CN)_3$ in CH_3CN
~2140	Assigned as CO..................		
2075	2085		
2025		2024	
1980	Assigned as $W(CO)_6$...............		
1940	1948		
	1931		
1910			1913
1897		1900	
1835		1842	
1790			1790

slightly soluble in toluene and benzene, and insoluble in water. It melts with decomposition in a sealed tube at 181°.

Anal. Calcd. for $C_8H_6O_4N_2W$: C, 25.42; N, 7.41; H, 1.60; W, 48.60. Found: C, 25.22; N, 7.47; H, 1.84; W, 48.56.

Tri-(acetonitrile)-tungstentricarbonyl.—Two hundred mg. of $W(CO)_4(CH_3CN)_2$ was dissolved in 40 ml. of acetonitrile, and the solution was irradiated under a stream of purified nitrogen for 8 hr. The reaction mixture then was filtered under nitrogen and the acetonitrile was removed by vacuum distillation at 35° to leave the light brown product. An alternate method of preparation involved irradiation of a solution of $W(CO)_6$ in acetonitrile in a cooled tube through which nitrogen was bubbled for 40 hr. After filtration and vacuum distillation at 35° to remove the acetonitrile, the product remained. $W(CO)_3(CH_3CN)_3$ had no melting point in a sealed tube at temperatures up to 250°, was soluble in acetonitrile and nitromethane, and dissolved with decomposition in acetone. It was insoluble in other common organic solvents and in water. $W(CO)_3$-$(CH_3CN)_3$ is quite unstable, even under nitrogen in the pure state, and therefore no accurate chemical analysis could be made. However, in an incomplete irradiation of 1 mmole of $W(CO)_6$ in acetonitrile which produced $W(CO)_3(CH_3CN)_3$ contaminated with a small amount of $W(CO)_4(CH_3CN)_2$ (determined spectrophotometrically), 2.81 mmoles of carbon monoxide gas was evolved. In a similar determination using $Mo(CO)_6$, the molybdenum derivative was produced with the evolution of 3.03 mmoles of CO for each mmole of $Mo(CO)_6$ used.

Other Systems

Spectra similar to those in Fig. 3–5 were obtained by irradiating $Mo(CO)_6$ in acetonitrile, indicating the formation of the three compounds $Mo(CO)_5(CH_3CN)$, $Mo(CO)_4(CH_3CN)_2$, and Mo-$(CO)_3(CH_3CN)_3$. Evidence of this nature also has been obtained for the formation of $Cr(CO)_5$-(CH_3CN) and $Cr(CO)_4(CH_3CN)_2$, but not for the formation of $Cr(CO)_3(CH_3CN)_3$. During the

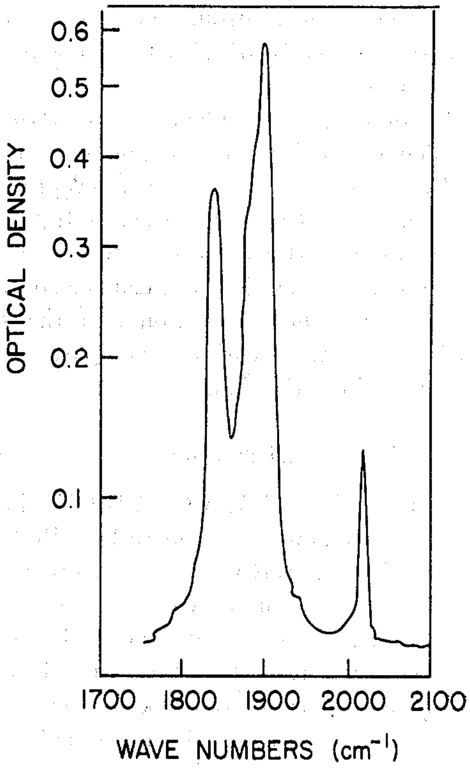

Fig. 4.—The infrared spectrum of $W(CO)_4(CH_3CN)_2$ in acetonitrile.

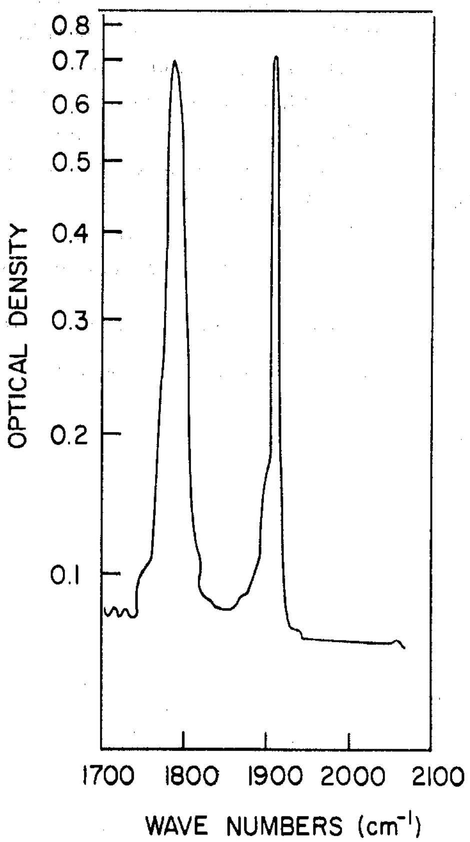

Fig. 5.—The infrared spectrum of $W(CO)_3(CH_3CN)_3$ in acetonitrile.

course of our work, Strohmeier[1,2] also has reported the synthesis of $Cr(CO)_5(CH_3CN)$ and $Mo(CO)_4(CH_3CN)_2$.

In addition, there is evidence for the formation of analogous series of compounds utilizing several other ligands possessing π-acceptor orbitals or whose structures allow them to function as electron donors. It will be of interest to see if there is a close correlation between the spectra of such systems. This correlation and the structure of some of these carbonyl complexes is presently under investigation.

Discussion

The production of $W(CO)_5(CH_3CN)$ in this series of reactions is presumed to be initiated by the formation of $W(CO)_5$. The average bond energies for $Ni(CO)_4$ and $Fe(CO)_5$ are, respectively, 95 and 89 kcal. $mole^{-1}$, and should be slightly less for the hexacarbonyls.[3] Since the ultraviolet light used for the irradiation does not exceed 140 kcal. $mole^{-1}$ in energy, it is probable that only one bond is broken during a single act of excitation. Of the two possible dissociations, to $W(CO)_5$ and CO, or to $W(CO)_5^{-1}$ and CO^{+1}, the former seems more likely. A species CO^{+1} probably would have an exceedingly short lifetime, and therefore the reconversion of CO^{+1} to CO would be rapid. This is inconsistent with the observed reversibility of the production of this possible species, for CO and $W(CO)_5^{-1}$ could not combine to yield $W(CO)_6$.

In view of these arguments, experimental work was carried out to give further evidence for the presumed formation of $W(CO)_5$. When $W(CO)_6$ dissolved in *n*-hexane, in an inert atmosphere, or a KBr pellet containing $W(CO)_6$ was irradiated, the characteristic yellow color mentioned earlier appeared despite the lack of an electron donor to promote complex formation. At room temperature the color soon disappeared in each case, but at −70° the color persisted for longer periods of time. As was true in the case of the irradiation of hexacarbonyls in acetonitrile, the formation of the yellow color was accompanied by spectral changes in the carbonyl stretching region of the infrared; a new band was noted at about 1945 $cm.^{-1}$. Similar results, also attributed to the formation of $M(CO)_5$, have been noted[4] by Orgel when metal hexacarbonyls were irradiated in a methylmethacrylate polymer matrix. That such a postulated species could be a reactive intermediate is further indicated by the rapid formation of a fluffy brown precipitate, presumably an oxidation product of the intermediate, when $W(CO)_6$ is irradiated in *n*-hexane in the presence of air. A colorless solution remains after the reaction. Work along these lines is continuing in an effort to throw further light on the kinetics and mechanism of these reactions.

Acknowledgments.—This research was begun in the summer of 1959, at which time evidence for the formation of several of the reported complexes was obtained. We thank the U. S. Atomic Energy Commission for both its patience and financial support, and Research Corporation for financial assistance during the initial stages of the work. We would further like to thank Mr. U. V. Rao for experimental help in purifying some of the carbonyls used in this work.

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[3] J. Cable and R. K. Sheline, *Chem. Rev.*, **56**, 1 (1956).

[4] L. E. Orgel, *Nature*. **191**, 1387 (1961).