state spectrum, corresponding to ~35% *trans*-$[Cr(en)_2Cl_2]^+$, ~65% *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$, was observed during the period ~2.2–3 hr.

At 35.0° pseudo first-order rate constants for the reversible reactions

$$\textit{trans-}[Cr(en)_2(OH_2)Cl]^{+2} + Cl^- \underset{k_{13}}{\overset{k_{31}}{\rightleftharpoons}} \textit{trans-}[Cr(en)_2Cl_2]^+ + H_2O \quad (8)$$

in 10.2 *F* HCl are: $k_{13} + k_{31} = (6.0 \pm 3.0) \times 10^{-4}$ sec.$^{-1}$, $k_{31} = (1.7 \pm 0.5) \times 10^{-4}$ sec.$^{-1}$, and by (difference) $k_{13} = (4.3 \pm 3.0) \times 10^{-4}$ sec.$^{-1}$. The uncertainty in the latter is so great that one can say only that aquation of *trans*-$[Cr(en)_2Cl_2]^+$ is not more than one order of magnitude, if at all, faster in 10.2 *F* HCl than in 0.10 *F* HCl at 35.0°.

The *trans* isomer of the above complexes reacts more slowly at 35° than the *cis* isomer in chloride anation. This relation also holds for aquation in 0.1 *F* HCl, but in 10–11 *F* HCl the experimental errors were large enough to obscure the comparison.

Spectra.—The visible absorption spectra of nearly all the complexes involved in this investigation have been described previously.[2,7] Determination of the spectra of *cis*- and *trans*-$[Cr(en)_2Cl_2]^+$ and of *cis*- and *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ in ~6 and ~11 *F* HCl showed that the wave lengths of the absorption maxima and minima for a given complex are the same within a 6-mμ range as in 0.1–0.2 *F* HNO_3 (1.3 *F* HNO_3 and 2 *F* HCl for *cis*-chloroaquo) at ~25°. However, the molar absorbancy indices at the absorption maxima and minima of a given complex were found to change up to 35% and their ratio for the two main peaks up to 17% in going from the above dilute acid to the concentrated acid solutions. Thus, use of spectra for quantitative determinations of concentrations of these complexes may require determination of the molar absorbancy indices in the particular medium of interest.

Comparison of Reaction Rates for Cr and Co Complexes.—Fig. 1 summarizes the rate constants at 35.0° for the system of aquation and isomerization reactions which appear to occur when *cis*- and *trans*-$[Cr(en)_2Cl_2]^+$ are dissolved in 0.1 *F* HNO_3 in the dark. Chloride anation rates are not included since they have been determined under greatly different concentration conditions. From a summary[14] of the limited comparative data available for the cobalt(III) analogs, there appear to be no striking rate differences between these Cr complexes and their Co analogs despite the prediction of crystal-field theory (ignoring the influence of solvent water) that lower activation energies would be expected for aquation and similar reactions of the d^3 chromium(III) complexes than for the d^6 cobalt(III) complexes. A more detailed comparison, as well as an understanding of the mechanisms of these reactions, must await further research, including resolution of the over-all rate constants into rate constants of individual characterized reactions for the cobalt complexes and determinations of E_a and ΔS^{0*} for both the chromium and cobalt systems.

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[14] C. S. Garner and D. J. MacDonald, in S. Kirschner (ed.), "Advances in the Chemistry of the Coördination Compounds," Macmillan Co., New York, N.Y. 1961, p. 266–275. More recent values of k_{56} for isomerization of *trans*-$[Co(en)_2(OH_2)_2]^{+3}$ to the *cis* isomer have been obtained by W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961), namely 4.0×10^{-5} sec.$^{-1}$ in 1 *F* $HClO_4$ at 37.5°, and by J. Y. Tong, private communication, namely 3.4×10^{-5} sec.$^{-1}$ in 0.004–1.0 *F* $HClO_4$ at 35° ($k_{56} \dotplus k_{65}$) from which $k_{65} < 0.1 \times 10^{-5}$ sec.$^{-1}$, redetermined by Kruse and Taube, has been subtracted).

CONTRIBUTION FROM UNIVERSITY CHEMICAL LABORATORIES,
LENSFIELD ROAD, CAMBRIDGE, ENGLAND

The Infrared Spectra of Substituted Metal Carbonyls

BY L. E. ORGEL

Received July 31, 1961

The assignment of the CO stretching frequencies in substituted carbonyls of the type $[L_nM(CO)_{6-n}]$ is attempted.

Introduction

The C–O stretching frequencies of metal carbonyls decrease as the extent of π-electron donation from the metal to the carbonyl group increases. The steady fall of the carbonyl frequency along the series $Ni(CO)_4$, $[Co(CO)_4]^-$,

$[Fe(CO)_4]^{2-}$ is a typical example of this effect. However, for all but the most symmetrical carbonyls the spectrum in the C–O stretching region is complex and a detailed assignment of the different bands is essential if the maximum amount of useful information is to be obtained.

In the past the number of observed carbonyl frequencies often has been used to help in inferring the geometrical structure of carbonyls. Systematic attempts to identify the different vibrations, however, are almost restricted to studies of the parent carbonyls of high symmetry, for example the hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$.[1] The object of the present paper is to extend those assignments to compounds of the type $[L_nM(CO)_{6-n}]$ where M is a d^6 atom or ion such as V^-, Cr^0, or Mn^+. The procedure adopted depends on the application of very elementary theoretical arguments to the spectra of a considerable range of related compounds. The interpretation of our assignments in terms of the theory of the electronic structure of carbonyls will be the subject of a subsequent publication.

Theory

The regular octahedral hexacarbonyls of chromium, molybdenum, and tungsten each have three carbonyl stretching vibrations of symmetries A_{1g}, E_g (doubly degenerate), and T_{1u} (triply degenerate) as illustrated in Figure 1. Only the last is active in the infrared, although the frequencies of the others can be determined from the Raman spectrum. The observed frequencies[1] are given in Table I.

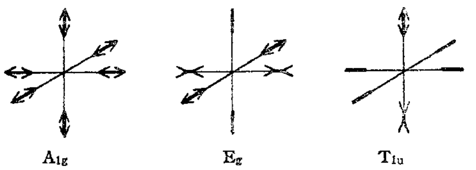

Fig. 1.—The carbonyl stretching vibrations of $M(CO)_6$ molecules. Only one component of each degenerate mode is shown.

TABLE I

VIBRATION FREQUENCIES OF METAL HEXACARBONYLS

	Cr	Mo	W
$A_{1g}{}^{1b}$	2062.8	2119.1	2121.3
$E_g{}^{1b}$	2020.5	2021.7	2015.2
$T_{1u}{}^{1a}$	2000	2000	...

It should be noted that the frequency of the transition which is observed in the infrared is the lowest of the three frequencies. A theoretical study[2] shows that the observed order of frequencies is given correctly by a Urey–Bradley force field, but that the separation between the A_{1g} frequency and the others is much greater than that predicted by the theory. We believe that this is due to a strong interaction between the C–O stretching vibrations of the individual carbon monoxide molecules which makes it more difficult to stretch them simultaneously than to stretch some and shorten others by a similar amount. We shall return to this subject in a later paper; for the moment it is sufficient to remember the presence of such a positive interaction.

For only two types of compound are the spectra of substituted carbonyls directly comparable with those of the parent hexacarbonyl, namely, for *trans*-$[L_2M(CO)_4]$ and *trans*-$[L_4M(CO)_2]$ where L is an axially symmetric ligand. In each case there is just one allowed C–O vibration in the infrared and in each case this corresponds exactly to the T_{1u} vibration of the hexacarbonyl. Apart from very small effects due to the change in the "effective mass" of the central metal ion, etc., changes in the allowed frequency along the series $M(CO)_6$, *trans*-$[L_2M(CO)_4]$, and *trans*-$[L_4M(CO)_2]$ are directly attributable to the "electronic" influence of *cis* substitution. Raman spectra for these substituted compounds would be very valuable, but unfortunately they have not been recorded.

A monosubstituted carbonyl $[LM(CO_5]$ has symmetry C_{4v}. Formal symmetry rules show that the vibrations may be classified as

E	allowed, x,y polarized
$2A_1$	allowed, z polarized
B_1	forbidden

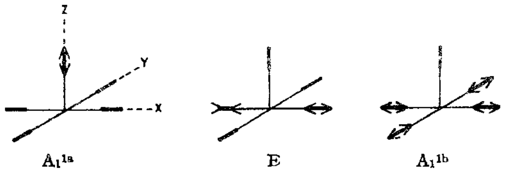

Fig. 2.—The allowed carbonyl stretching frequencies of $[LM(CO)_5]$ molecules. Only one component of the E mode is shown.

Elementary arguments enable us to make much more useful predictions. First, the E vibration corresponds closely to the T_{1u} vibration of the

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(1) (a) N. J. Hawkins, H. C. Mattraw, W. W. Sabol, and D. R. Carpenter, *J. Chem. Phys.*, **23**, 2422 (1955). (b) A. Danti and F. A. Cotton, *ibid.*, **28**, 736 (1958).

(2) H. Murata and K. Kawai, *ibid.*, **27**, 605 (1957).

parent hexacarbonyl and should account for very roughly $^4/_5$ of the total intensity of absorption.[3] The two A_1 vibrations are made up from the stretching mode of the unique carbonyl group and the symmetrical breathing mode of the other four. If these A_1 motions did not couple together the former would be allowed, accounting for the remaining $^1/_5$ of the total intensity, while the latter would be almost forbidden (it still could have a small intensity due to non-coplanarity of the radial carbonyl groups and to electronic migration along the four-fold axis accompanying the symmetrical stretching of the radial carbonyl groups). In fact the two A_1 modes interact and some of the intensity of the strongly allowed one must be transferred to the other.

This elementary discussion leads us to expect a very strong band, a band which is less strong by a factor of roughly four, and a third much weaker band. The sign of the interaction constant between carbonyl groups places the weak A_1 band at a higher frequency than the E band, and analogy with the hexacarbonyls suggests that for example in molybdenum compounds there should be an interval of 100–120 cm.$^{-1}$ between them. The position of the stronger A_1 band cannot be predicted.

The most complicated case is that of *cis*-$[L_2M(CO)_4]$ compounds which have symmetry C_{2v}. It is convenient to consider the *trans* pair of carbonyl groups first since they give rise to an antisymmetric B_1 stretching mode corresponding to one component of the T_{1u} mode of the hexacarbonyl and an almost forbidden A_1 mode. The other two carbonyls give two allowed vibrations of symmetry A_1 and B_2 which should have comparable intensities (Fig. 3). Finally the two A_1 modes must interact. We expect, as in the pentacarbonyls, a pair of bands, one very strong and the other weak, separated by 100–120 cm.$^{-1}$, and in addition two bands of intermediate strength. Again the relative position of the two pairs of bands cannot be deduced from elementary theory.

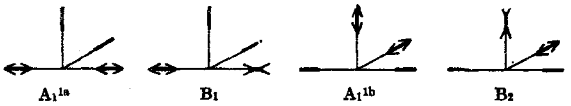

Fig. 3.—The carbonyl stretching frequencies of *cis*-$[L_2M(CO)_4]$ molecules.

Analogous arguments show that in *cis*-dicarbonyls there should be two bands of comparable strength, while in symmetrical C_3 tricarbonyls we expect two bands, a degenerate one at lower frequency having very roughly twice the intensity of the band due to the non-degenerate A_1 vibration. Finally, in unsymmetrical tricarbonyls we again should have a pair of bands separated by about 100 cm.$^{-1}$ and one further moderately strong band due to the unique carbonyl group.

We shall see later that in most carbonyl compounds *trans* pairs of carbonyl groups have stronger C–O force constants than carbonyl groups *trans* to substituents. This leads to a very characteristic spectrum consisting of a number of intense carbonyl bands separated by about 100 cm.$^{-1}$ from a weak high frequency band. This feature occurs also in certain 5-coördinated carbonyls, but in an octahedral complex it is diagnostic of a pair of *trans* carbonyls in a molecule of relatively low symmetry.

Phosphine Substituted Carbonyls of Chromium, Molybdenum, and Tungsten

These compounds have been studied by many workers and a variety of infrared spectra have been reported. This discussion rejects all spectra obtained from solids, since crystal splitting of bands often makes the assignment of vibrations impossible. It concerns mainly the compounds of molybdenum, although the assignments are very readily extended to chromium and tungsten in the rather few cases where the experimental data are available.

It should be noted that solution effects on carbonyl frequencies can amount to about 10 cm.$^{-1}$, and that the effect of changing the ligand from an alkyl to an aryl phosphine is of about the same magnitude. Hence there is some uncertainty in comparisons between the work of different laboratories.

trans-$[(P(C_2H_5)_3)_2Mo(CO)_4]$ has a single intense carbonyl frequency at 1887 ± 2 cm.$^{-1}$.[4] It is clearly the E_u frequency. Unfortunately, the other vibration frequencies are unknown since no Raman data are available.

The spectrum of $[P(C_2H_5)_3Mo(CO)_5]$ is reported to consist of two peaks, at 1942 cm.$^{-1}$ and 2064 cm.$^{-1}$, the stronger of which is composed of two close-lying but resolvable bands.[4] In the

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[3] The assumption involved here is that transition moments in the carbonyl groups are constant and that "interaction" between carbonyls may be neglected. It is a very poor approximation, but suffices here.

[4] R. Poilblanc and M. Bigorgne, *Compt. rend.*, **250**, 1064 (1960).

light of our later analysis and of analogy with $RMn(CO)_5$ compounds it seems safe to assume that it is the 1942 cm.$^{-1}$ band which is more intense.[5a] To guide in our assignment we assume that the effect of *cis*-substituents on carbonyl stretching force constants is roughly linear in the number of *cis*-substituents. Then, from the results on the *trans*-diphosphine, we expect the stronger band at about 1944 cm.$^{-1}$ $\left(\frac{2000 + 1887}{2}\right)$. The corresponding weak member of the doublet should occur at roughly 2063 cm.$^{-1}$ (1944 + 119). The excellence of the agreement with experiment must be fortuitous, but nonetheless we may feel some confidence in the assignments

E	~1942
A_1^{1a}	~1942
A_1^{1b}	2065

cis-$[(P(C_2H_5)_3)_2Mo(CO)_4]$ is reported to have four bands at 2014 ± 2, 1915 ± 1, 1900.5 ± 1, and 1890 ± cm.$^{-1}$, but no relative intensities are quoted.[4] Fortunately such data are available for the closely related *cis*-$[(P(C_6H_5)(C_2H_5)_2)_2Mo(CO)_4]$,[5b] namely: 2012, strong; 1907, shoulder; 1895, very strong; 1866, strong. The actual spectra show that the 2012 cm.$^{-1}$ band is much weaker than the other resolved CO bands and leaves little doubt of the correctness of the assignments

2012	A_1 (*trans*)
1907	B_1 (*cis*)
1895	B_1 (*trans*)
1866	B_2 (*cis*)

The 1895 peak is just where it should be if the effects of *cis*-substituents are additive (for it corresponds to the 1887 peak of the *trans*-compound). The separation between the frequencies of the *trans*-carbonyl pair is 117 cm.$^{-1}$. It is worth remarking that the difference between the frequencies reported for the $(P(C_2H_5)_3)$ and $(P(C_6H_5)(C_2H_5)_2)$ compounds is rather larger than we should have anticipated. However, the three bands in the 1900 cm.$^{-1}$ region overlap and this makes it difficult to obtain accurate frequencies.

The tricarbonyls studied are all of the symmetrical type.[5b] They have just two strong bands at about 1845 cm.$^{-1}$ and 1935 cm.$^{-1}$, as expected. Finally *cis*-dicarbonyls are reported to have pairs of transitions at about 1780 cm.$^{-1}$ and 1850 cm.$^{-1}$.

Thus we were able to give a consistent account of the data if we suppose that each *cis* phosphine substitution lowers the stretching frequency of carbonyls by about 50 cm.$^{-1}$, the latter substitutions producing somewhat smaller effects than the first. Further, we must suppose that the frequency of a carbonyl group *trans* to a phosphine is lowered rather more.

Miscellaneous Group VI Carbonyls

The spectra of a great variety of substituted carbonyls of the general type $[L_3M(CO)_3]$ have been reported. There is no need to comment on these at present, since the two bands correspond in the expected way with the two allowed transitions. Rather more interesting are the group of compounds which can be considered as trisubstituted carbonyls, namely, the $[ACr(CO)_3]$ compounds in which A is an aromatic or pseudoaromatic molecule such as benzene, naphthalene, or thiophene.[6] Here we expect a splitting of the degenerate E mode if the electron donor property of the aromatic system is markedly different in two mutually perpendicular directions. While there are a number of unexplained features of the spectra there is no doubt that a small splitting is observed in the dimethylaniline, aniline, naphthalene, and thiophene compounds and this confirms that the degenerate mode does have the *lower* frequency.

Two particularly interesting compounds with almost identical spectra are $[XMo(CO)_4]$ where X is *o*-phenanthroline or α,α'-dipyridyl.[7] The recorded bands are at 2020 (m), 1901 (v-s), 1877 (s), and 1826 (s) for the dipyridyl complex. The higher pair are due to the *trans* pair of carbonyls and have an appropriate separation of 104 cm.$^{-1}$. The *cis*-carbonyl frequencies have been depressed far more than in phosphines and have come out clear of the *trans* pair at 1877 cm.$^{-1}$ and 1826 cm.$^{-1}$. This is in very sharp contrast with the situation in *cis*-diphosphines.

Derivatives of Manganese and Rhenium Carbonyls

A second group of compounds which has been studied extensively consists of derivatives of manganese and rhenium of the type $[LM(CO)_5]$,

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(5)(a) This has now been confirmed; (b) J. Chatt and Watson, private communication.

(6) Fischer, *Chem. Ber.*, **83**, 165 (1960).

(7) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

TABLE II

INFRARED SPECTRA IN THE CARBONYL REGION OF SOME MANGANESE AND RHENIUM PENTACARBONYLS

	A_1^{1a}	E	A_1^{1b}	Extra bands
$CF_3Mn(CO_5)$[11]	2144 (w-m)[a,b]	2050 (ss)	2025 (s)	
$CH_3Re(CO)_5$[11]	2125 (w-m)	2010 (ss)	1979 (s)	2068 (w) 2040 (w-m)
$CF_3COMn(CO)_5$[11]	2138 (w-m)	2047 (ss)	2034 (w-sh)	2076 (m)
$C_6H_5CORe(CO)_5$[11]	2134 (m)	2018 (ss)	2001 (s)	2068 (m) 1978 (m)
$Mn(CO)_5I$[9]	2136 (w)	2056 (s)	2017 (s)	1987
$Re(CO)_5I$[9]	2156 (w)	2055 (s)	1995 (s)	

[a] w = weak, m = medium, s = strong, sh = shoulder. [b] Only relative intensities within a group of compounds studied by a single author are potentially significant.

where L may be a halogen,[8-10] alkyl, aryl, or acyl[11] radical. Some typical frequencies are given in Table II. In each case we have made the obvious assignment of bands which is suggested by our previous analysis.

A few points deserve special attention. First we note that for *trans* pairs of carbonyl groups in manganese compounds the characteristic separation between strong and weak bands lies in the range 80–95 cm.$^{-1}$. In rhenium derivatives the separation is a good deal larger, varying from 100 to 115 cm.$^{-1}$. For both metals the smallest separation is reported for the iodide.

A comparison of the spectra of $[Mn(CO)_5Cl]$, $[Mn(CO)_5Br]$, and $[Mn(CO)_5I]$ shows that the two frequencies of the four radial carbonyl groups move as a pair relative to the frequency of the axial carbonyl group.[8-10] This is another less extreme example of the differential effect of substituents on the *cis* and *trans*-carbonyl groups which we have encountered previously for amine and phosphine-substituted molybdenum carbonyls. It will prove of considerable interest in the analysis of the bonding in terms of σ and π effects.

In many acyl manganese carbonyls and in both the alkyl and the acyl rhenium compounds there are a number of extra bands.[11] Usually it is quite easy to pick out the three "normal" frequencies, but the source of the others is quite obscure. In certain cases there are as many as six carbonyl frequencies reported, so that one is obliged to postulate either the occurrence of Fermi resonances or the presence of impurities or isomers. For the acyl compounds there is a further interesting possibility.

The acyl group, unlike others which we have considered, lacks even approximate axial symmetry, although in acyl metal carbonyls there is probably a symmetry plane including the R–CO–M group. This should lead to a small and possible resolvable splitting of the intense E transition, and, more important, to the appearance of the B transition with low intensity. The occurrence of a single weak extra band between the E and higher frequency A_1 bands therefore is understable. However, since many of the extra bands in these compounds cannot be explained in this way we do not wish to suggest this explanation as more than a possibility.

Appeal.—The carbonyl frequencies are almost the only set of numerical data at present available which give fairly direct information about bonding in metal carbonyls. The precision required of the spectra in detailed theoretical studies exceeds that needed for identification of new compounds, etc. The following would be of enormous help to the theoretician: (1) Infrared spectra of solutions rather than or in addition to those of mulls. (2) Reproduction of at least one typical spectrum from those of each group of related molecules. (3) Frequencies determined as accurately as possible, since an error of much greater than 2 cm.$^{-1}$ often makes comparisons between different compounds unrewarding. (4) Raman spectra whenever possible.

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(8) E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *J. Chem. Soc.*, 3149 (1958).

(9) E. W. Abel, M. H. Bennett, and G. Wilkinson, *Chem. & Ind.* (London), 441 (1960).

(10) E. D. Brimm, M. A. Lynch, and W. J. Sesny, *J. Am. Chem. Soc.*, **76**, 3831 (1954).

(11) W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, **94**, 862 (1961).