Journal of Organometallic Chemistry, 70 (1974) 437—443

VIBRATIONAL SPECTRA OF π-OLEFIN—TRANSITION METAL COMPLEXES

I. (π-MALEIC ANHYDRIDE)IRON TETRACARBONYL

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(Received October 10th, 1973)

Summary

The infrared and Raman spectra of solutions and solid samples of (π-maleic anhydride)iron tetracarbonyl have been studied. An assignment of the normal modes is suggested and the ligand vibrations in the complex are compared with the data for maleic and succinic anhydrides. The C=C stretching frequency of maleic anhydride shifts from 1595 to 1352 cm^{-1} after coordination with the metal. The essential decrease of the IR intensities of out-of-plane CH modes is noted for the complex and explained by the lowering of the effective charge on the olefinic protons due to back-donation from metal to ligand.

Introduction

Several papers dealing with the vibrational spectra of π-olefin transition metal complexes have been published in recent years. However, the results of IR investigations do not permit a quantitative assessment of the nature of the change in ligand vibrations upon its coordination with metal. With the development of laser Raman spectroscopy it became possible to study this problem in more detail. For an example we mention here discussion on the spectra of the Zeise's salt $K^+[C_2H_4PtCl_3]^-$. Originally the IR band at 1515 cm^{-1} of this compound (shifted by ca. 150 cm^{-1} in comparison with free ethylene) was assigned to the C=C stretching vibration. Using the results of a laser Raman study Hiraishi [1] concluded that the band at 1243 cm^{-1} should be assigned to the C=C vibration; this assignment was also in agreement with the result of a normal coordinate analysis made by Babushkin et al. [2]. Thus the ν(C=C) shift owing to the coordination was ca. 400 cm^{-1}. It was then shown that the above assignment is incorrect [3, 4]. The ν(C=C) vibration in ethylene is non-characteristic and is mixed essentially with the bending vibrations of CH groups attached to the double bond. Both bonds to which the C=C stretch makes a large contribution (1623 and 1353 cm^{-1} for the free ethylene molecule) are shifted to 1515 and 1243 cm^{-1} respectively in the coordinated ethylene. If in the free ethylene molecule the principle contribution of the C=C stretch is to the higher frequency band, the situation is reversed in the coordinated ethylene and the 1243 cm^{-1} band has stronger intensity in the Raman spectra. Powell et al. [4, 5] described the effect of coordination by taking the sum of the shifts of both bands which are sensitive to coordination. In the case of the Zeise's salt this is ca. 210 cm^{-1}. In the case of a Zeise's salt containing deuterated ethylene the C=C vibration is more characteristic and coupling with CD_2 bending vibrations is small. Hence the ν(C=C) band of C_2D_4 (1515 cm^{-1}) shifts to 1350 cm^{-1} in the complex and the shift of the $\beta(CD_2)$ band is small (from 980 to 960 cm^{-1}). The 1350 cm^{-1} mode contains the principle contribution of the C=C stretching vibration and is more intense in the Raman spectrum. The total shift is nearly the same as in C_2H_4 (~ 180 cm^{-1}).

It is interesting to compare the spectra of a cyclic olefin, maleic anhydride (MA), and their coordinated counterparts. Analysis of the spectra of the complex is facilitated by detailed studies of the spectra of MA [6, 7] and some of its derivatives [8, 9]. In the present paper we report a study of vibrational spectra of the complex (MA)Fe(CO)$_4$ and its assignments, and discuss the changes in the ligand spectra upon coordination.

Results and discussion

For the 18-atom molecule (MA)Fe(CO)$_4$ 48 normal modes are expected. The molecule has C_s symmetry, but it is assumed that in the π-complexes there is a little interaction between the vibrations of the organic ligand and the skeleton since they are located in different spectral regions and mix only negligibly. The method of "local symmetry" is therefore applicable. This being the case vibrations of the complex may be divided into the following groups: 21 ligand modes, 21 modes of the Fe(CO)$_4$ moiety, 3 metal—ligand stretching vibrations, 2 ligand bending modes with respect to the Fe(CO)$_4$ group and 1 torsion mode (rotation about the metal—ligand bond). IR and Raman spectra and assignments are given in Table 1. The assignment is discussed below.

(a) Ligand vibrations

The double bond multiplicity should decrease upon coordination of MA, thus one may expect the structure and spectrum of the coordinated MA molecule to be intermediate between the free MA and succinic anhydride (SA). Complete assignments on the basis of IR and Raman spectra of normal and deuterated molecules in different states (gaseous, dissolved, crystalline), and the normal mode analysis are made for both molecules [6, 7]. The spectra of MA and SA are quite similar, the most pronounced differences being observed in the region of CH modes due to a replacement of =CH by CH_2 groups; the 1280 cm^{-1} band in SA replaces the 1595 cm^{-1} mode in MA. A comparison of the spectra of MA and SA with coordinated MA is given in Fig. 1 for in-plane modes. It may be seen that most of the vibrations of MA in which the contribution from the C=C stretching vibration is negligible do not change significantly in the complex molecule and could therefore be assigned by comparison with the MA spectrum.

TABLE 1

INFRARED AND RAMAN SPECTRA OF (π-MA)Fe(CO)$_4$.

IR		Raman		Assignment
Solid	Solution [a]	Solid	Solution [b]	
3089 w	3085 w	3084 m	*c*	ν(CH)($A_1 + B_1$)
		3076 (sh)	*c*	
3065 (sh)		3068 w	*c*	
2964 w	2980 vw		*c*	
2928 w	2932 vw		*c*	
2858 w	2858 w		*c*	
2120 s	2116 s	2133 m	2116 s, p	ν(CO)(A_1)
2080 s		2080 m		
2052 vs	2058 vs	2057 m	2061 m, dp	ν(CO)(B_1 or B_2)
2043 s	2046 vs	2042 m		ν(CO)(A_1)
2029 s	2028 s	2032 m	2030 m, dp	ν(CO)(B_1 or B_2)
2010 s		2013 m		
1824 s	1823 s	1821 w	1823 s, p	ν(C=O)(A_1)
1816 w		1809 s		
1795 vs		1795 vw		
1767 (sh)	1768 s	1765 (sh)	1764 w	
1747 s		1744 s		ν(C=O)(B_1)
1712 w	1708 vw			
1580 w				
	1360 vw			
1353 m	1352 m	1354 m	*c*	ν(C=C)(A_1)
1325 w	1317 w			
1300 w				
1288 w				
1253 m				
1234 s		1235 vw		ν(ring)(A_1)
1223 s	*c*	1224 vw		
1089 m	1080 s	1087 w		δ(ring)(B_1)
1063 m	1048 w	1067 m		δ(CCH)(A_1)
891 m		883 m	*c*	
878 w	880 s	877 (sh)		ν(ring)(B_1)
857 s		856 w		
836 w	837 w	833 vs	836 s, p	ν(ring)(A_1)
		761 m	*c*	
748 w	*c*			
703 s	704 m	704 m	*c*	δ(C=O)(B_1)
643 w				
628 s	625 s	625 vs	624 s, p	ρ(C=O)(A_1)
621 s	615 w	615 w		ρ(C=O)(B_2)
601 s	603 s			$\}$ δ(Fe—CO)
588 m	592 m			
479 m	488 m	487 m		ν(Fe—CO) (A_1, B_1, B_2)
461 m	458 m	450 w	444 w	
	432 w	441 w	428 w	
410 m	413 w			δ(ring)(A_1)
		413 s	404 s, p	ν(Fe—CO)(A_1)
		399 w		
370 w		371 s	376 s, p [d]	ν(FeL)(A_1)
			342 w	
200 vw				
169 w				
160 (sh)		160 m		
120 w		120 m		
		100 vs		

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[a] Solution in CCl$_4$ and CHCl$_3$. [b] Solution in CH$_2$Cl$_2$. [c] Not observed because of overlapping with the solvent bands. [d] Solution in CS$_2$.

The free MA molecule has C_{2v} symmetry and 21 normal modes (15 in-plane, $8A_1 + 7B_1$, and 6 out-of-plane, $3A_2 + 3B_2$). The A_2 vibrations are forbidden in the IR spectrum but allowed in the Raman spectrum. Ligand symmetry is reduced to C_s upon coordination, however, for the sake of convenience in the comparison with MA we shall describe its vibrations in terms of C_{2v} symmetry.

(i). In-plane modes. An assignment of the bands at 1823 and 836 cm^{-1} to A_1 type is confirmed by their polarization in the Raman spectrum. The bands at 624 and 404 cm^{-1} are also polarized but in the same region the $Fe(CO)_4$ skeletal modes are expected. The 624 cm^{-1} band is close to 636 and 629 cm^{-1} bands in MA and SA respectively (the planar bending CO modes in the cycle). The bending FeCO modes may be in the same region but the corresponding lines are weak in the Raman spectrum while the line at 624 cm^{-1} is strong. Similar lines in the Raman spectra of MA and its chloro- and bromo-derivatives are also strong [8, 9], thus we may assign the 624 cm^{-1} line to the ligand mode.

The 416 cm^{-1} IR band is very close to 415 and 412 cm^{-1} bands in MA and SA, but these are weak in the Raman spectra, while the complex shows a strong polarized line at 404 cm^{-1}. We expect to find the Fe—CO stretching vibration in the same region and it should be strong in the Raman and weak in its IR spectrum by analogy with other carbonyl complexes. We thus assign the 416 cm^{-1} band to the ligand mode and the 404 cm^{-1} Raman line to the Fe—CO vibration.

Assignment of the bands at 1235, 1224, 1087 and 1067 cm^{-1} to A_1 and B_1 classes is tentative because polarization data in the Raman spectrum could not be obtained owing to their weak intensity. In the CH stretching region for MA only the 3122 cm^{-1} band was observed. Due to weak kinematic coupling the splitting of symmetrical and antisymmetrical CH modes is negligible and they practically coincide; one may thus expect that in the complex the splitting would be rather small. A weak band at 3085 cm^{-1} is observed in the solution IR spectrum. In the IR and Raman spectra of solids this band is present along with a shoulder near 3065 cm^{-1}. The bands are weak and we failed to measure their degree of depolarization. The IR spectrum also shows weak bands at 2860, 2930 and 2980 cm^{-1} which are absent in the Raman spectrum. It thus seems that these bands do not belong to the fundamental modes since the large splitting of two fundamental bands (one of them being near 3080 cm^{-1}) is rather unlikely. A frequency shift from 3122 to 3080 cm^{-1} demonstrates some decrease in the C=C band order with the increase of *p*-character of the CH bond.

It is most interesting to elucidate the effect of complex formation on C=C stretching modes. Normal coordinate analysis [6, 7] shows that in MA, in contrast with ethylene, this vibration is rather characteristic: contribution from other ring coordinates and from CH is negligible in this vibration. On the other hand the band at 1243 cm^{-1} in MA is mainly connected with the ring vibration (according to calculations), changes negligibly on going to SA (1225 cm^{-1}) and is observed at 1234 cm^{-1} in the complex. In the 1250—1600 cm^{-1} region of the spectra of the complex only one comparatively strong band is observed at 1352 cm^{-1} which we assign to the stretching C=C modes in the complex. Frequency shift with respect to the ligand is considerable (243 cm^{-1}), but it is close to the total shift of the two bands in ethylene and other olefins associated with the C=C modes viz.: 264 cm^{-1} for $(\pi\text{-}C_2H_4)Fe(CO)_4$ [10], 209 cm^{-1} for Zeise's salt [1], 194 cm^{-1} for $K^+[(\pi\text{-}trans\text{-butene})PtCl_3]^-$ [4]. If, according to Powell et al. [4, 5], one were to use the total frequency shift (in percent) as a measure of bond strength then for $(MA)Fe(CO)_4$ it is 15.2%, and for the other three above-mentioned compounds 19.6, 14.0 and 12.8% respectively. Moreover it is known that in the case of ethylene derivatives where the C=C modes are more characteristic (C_2D_4, C_2Me_4) the shift after coordination with the metal is 160—170 cm^{-1} which approaches the total shift of the two bands containing the C=C modes in the above-mentioned compounds. Model calculations carried out have shown that the change of force constant for a C=C bond on coordination is the factor most responsible for the change of spectrum of coordinated olefins. Thus when the force constant of ethylene is taken as a reference [11] and only the C=C bond force constant is varied, all other parameters being kept constant, then its decrease from 9.1 to 7.1 mdyn/Å shifts the 1623 and 1342 cm^{-1} modes of ethylene to 1518 and 1263 cm^{-1} (1515 and 1243 cm^{-1} in Zeise's salt) while in C_2D_4 the 1515 and 981 cm^{-1} bands are shifted to 1349 and 980 cm^{-1} [1353 and 962 cm^{-1} in the spectrum of $K^+[(C_2D_4)PtCl_3]^-$]. The value 7.1 mdyn/Å corresponds to the bond order of C=C which is intermediate between a single and a double bond. Similar model calculations of MA using the force field from ref. [6] have shown that on decrease of the C=C bond force constant one may obtain frequencies similar to those of MA in the complex.

(ii). Out-of-plane modes. There are six out-of-plane modes ($3A_2 + 3B_2$) in MA, the A_2 mode being IR inactive. The ligand symmetry in the complex is reduced to C_s, but one may expect that if formally allowed, the A_2 modes should be weak in the IR spectra. The B_2 class contains ρ(CH) and ρ(CC) modes and one ring bending mode, the latter being in the low frequency region. The weak 614 cm^{-1} IR band has been assigned to ρ(CO) of MA similar to that observed in the complex at 615 cm^{-1}. The out-of-plane CH vibrations are the most interesting. The corresponding bands in the IR spectra of olefins and diolefins are known to be the most prominent. In the IR spectrum of MA this band is near 840 cm^{-1} and is very strong, its integrated intensity (solution in acetonitrile) is 1.06×10^4 $l \cdot mol^{-1} \cdot cm^{-2}$. We failed to identify the corresponding band in the spectra of the complex in the 700—1050 cm^{-1} region because of its low intensity. This phenomena has already been discussed in connection with norbornadiene complexes of transition metals [12] and was explained as a demonstration of lowering of an effective charge on olefinic protons due to coordination. Assuming a positive charge (as is accepted) at the hydrogen atoms, such a change could be explained by electron donation from the occupied metal *d*-orbitals to the antibonding double bond π-orbital. The existence of the positive charge at the hydrogen atoms is also demonstrated by the fact that the MA proton signals in the PMR spectra shift upfield [δ 7.29 ppm for MA and 4.37 ppm for (MA)Fe-$(CO)_4$ in acetone solution], i.e. the MA proton shielding is enhanced on complex formation. For a positive charge at hydrogen this results in a decrease in agreement with the lower intensity in the IR spectrum.

(b). Skeletal vibrations of LFe(CO)₄

Skeletal vibrations were assigned in terms of C_{2v} symmetry. On formation of the complex from MA and $Fe(CO)_5$ the MA molecule may enter both the axial (C_{3v} symmetry) and equatorial (C_{2v} symmetry) positions. The C_{2v} symmetry of the complex is demonstrated by the presence of 4 strong bands due to CO stretching vibrations in the IR spectrum: 2116, 2058, 2046 and 2028 cm^{-1} ($2A_1 + B_1 + B_2$). For C_{3v} symmetry only 3 bands are expected ($2A_1 + E$). The 2116 cm^{-1} band is polarized in the Raman spectrum and assigned to the A_1

mode. This assignment is in agreement with the common rule for all carbonyl complexes, that the totally symmetric in-phase mode has the highest frequency. The lines at 2061 and 2030 cm^{-1} are depolarized in the Raman spectrum and they belong to B_1 and B_2 species. It is interesting to note that the band at 2046 cm^{-1} is not observed in the solution Raman spectrum. This may be explained by the fact that if the mode at 2116 cm^{-1} is due to vibrations of all 4 CO groups in-phase then the second A_1 mode is a result of the vibration of 2 CO groups out of phase to 2 other CO groups. It is natural to assume that the polarizability derivatives for all CO groups in bond direction are of the same sign. In this case the polarizability change on stretching the two CO bonds in the antiphase vibration may be compensated by an opposing change of sign upon contraction of two other CO bonds. This results in a sharp decrease of the Raman line intensity, although this line is formally allowed by symmetry.

For the LFe(CO)$_4$ moiety an additional 4 Fe—C modes ($2A_1 + B_1 + B_2$), an Fe—L stretching mode (A_1), 2 ring tilts ($B_1 + B_2$), a torsional Fe—L mode (A_2), 8 bending FeCO modes ($2A_1 + 2A_2 + 2B_1 + 2B_2$), 2 bending LFeC modes ($B_1 + B_2$) and 5 bending CFeC modes ($2A_1 + A_2 + B_1 + B_2$) are expected. The A_2 modes are inactive in IR spectra. In analogy with other carbonyl complexes one may expect that the CFeC and LFeC bending modes are below 200 cm^{-1}, the FeL vibrations are usually observed at 300—400 cm^{-1}, Fe—C at 400—550 cm^{-1} and FeCO bending modes at 500—700 cm^{-1}. One may also expect that one of the ring tilts is close to ν(FeL) (an antisymmetric FeL vibration) while the second is the low frequency mode. We assign the bands at 376 and 404 cm^{-1} (strong and polarized in the Raman spectrum) to the FeL and Fe—CO stretching modes respectively (A_1 symmetry class). For comparison it can be noted that in (π-C_2H_4)Fe(CO)$_4$ the bands at 361 and 427 cm^{-1} are assigned to these vibrations. Other stretching Fe—CO modes occur at 488, 444 and 428 cm^{-1} which are also close to the corresponding bands in (π-C_2H_4)Fe(CO)$_4$. [10].

The FeCO bending modes are usually very strong in the IR spectrum and weak in the Raman. It is difficult to assign these bands because the in-plane and out-of-plane CO bending modes of MA are located in the same region. In addition the strong IR bands at 592 and 603 cm^{-1} were observed in the 500—700 cm^{-1} region. Because of the weak intensity in the Raman spectrum we were unable to make polarization measurements for these bands and symmetry assign-

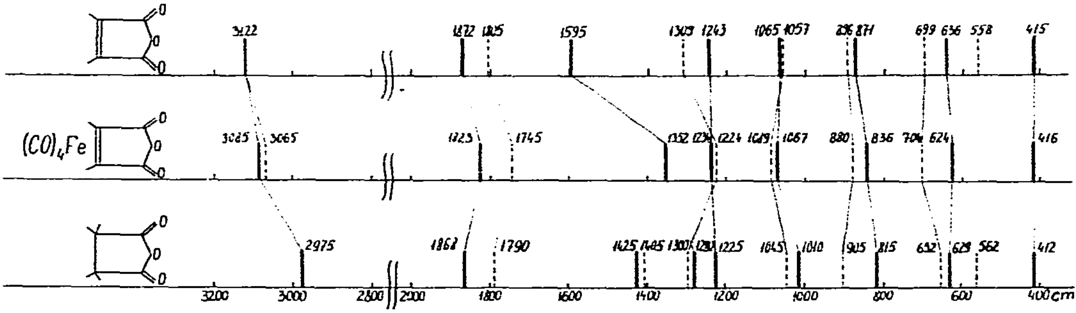

Fig. 1. The in-plane modes (cm^{-1}) of maleic anhydride, succinic anhydride and maleic anhydride in the complex (MA)Fe(CO)$_4$.

ment was impossible. It is also difficult to assign the low frequency bands observed in the IR and Raman spectra of solids (at 100, 120, 160, 169 and 200 cm^{-1}), which we believe are the bending modes of the skeleton.

Experimental

The complex $(MA)Fe(CO)_4$ was prepared by a method previously described [13]. Spectra were run on IR spectrometers UR-20 Zeiss, Perkin—Elmer 457 and FIS-1. Raman spectra were obtained on a laser Coderg-PHO spectrometer with He/Ne laser excitation. The IR spectra were measured on solid samples and CCl_4 and $CHCl_3$ solutions. Raman spectra were measured in CS_2 and CH_2Cl_2 solutions.

The PMR spectra were obtained on acetone solutions on an Hitachi R-20 60 MHz spectrometer.

Acknowledgements

The authors are grateful to Drs. M.I. Rybinskaya and L.V. Rybin for supplying the compounds for investigation, and for valuable discussions.

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