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THE VIBRATIONAL SPECTRUM OF (MALEIC ANHYDRIDE)IRON TETRACARBONYL

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Summary

On the basis of solid-phase IR and Raman spectra, with some solution data for the IR, a reasonably complete vibrational assignment has been made for the modes of maleic anhydride in (maleic anhydride)iron tetracarbonyl. Shifts in ν(C=C) and δ(CH) are consistent with a strong interaction with the metal, but relatively little coupling between the modes. More restricted assignments were made for modes associated with the (maleic anhydride)—iron and $Fe(CO)_4$ fragments.

Introduction

Since it proved to be impossible to obtain a complete vibrational assignment for (ethylene)iron tetracarbonyl [1], it was decided to study the more stable, if more complicated, species (maleic anhydride)iron tetracarbonyl.

Experimental

(Maleic anhydride)iron tetracarbonyl was prepared by the method originally described by Weiss et al. [2]; the reaction of freshly-prepared $Fe_2(CO)_9$ and resublimed maleic anhydride. Purification was achieved by sublimation in vacuo.

The pale-yellow solid is only sparingly soluble in polar solvents such as CH_2Cl_2, and so IR solution spectra were only informative in the regions associated with C≡O and C=O stretching. Solid phase spectra were obtained from KBr discs. A Perkin—Elmer 521 spectrometer was used to obtain spectra from 4000—300 cm^{-1}, spectra were calibrated using known peaks of H_2O, NH_3, CH_4 and CO, and the positions of all peaks are accurate to ±2 cm^{-1}.

Raman spectra were obtained using a Cary Model 81 Raman spectrophotometer, with 180° scattering, using a Spectra-Physics Model 125 He—Ne laser as excitation source (approx. 60 mW at 632.8nm). Spectra were calibrated using known peaks of indene; peak positions are accurate to ±2 cm^{-1}; except for some very weak and/or broad features for which an uncertainty of ±5 cm^{-1} must be assumed. Unfortunately, solutions of the complex decomposed rapidly when irradiated by the laser, and so only solid-phase Raman data are available. No noticeable decomposition of the solid was observed during the running of Raman spectra, but as a precaution the sample was renewed periodically.

Results and discussion

The observed solid-phase vibrational frequencies and the proposed assignment for (maleic anhydride)iron tetracarbonyl are listed in Table 1, with IR

TABLE 1

OBSERVED VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR (MALEIC ANHYDRIDE)IRON TETRACARBONYL

(C_s symmetry, all figures in cm^{-1})

Infrared (KBr disc)	Raman (solid)	Assignment[a]
3560 m(br)		
3100 m		C—H stretch, A''
2934 ms		C—H stretch, A'
2860 m		
2700 vw		
2475 w		
2128 vs	2138 vs	C≡O stretch, A'
	2084 s	
2010 vvs(br)	2061 vs	C≡O stretch, A'
	2050 s	C≡O stretch, A'
	2019 s	C≡O stretch, A''
1820 vs(br)	1820 s	C=O stretch, A'
1760 vvs(br)	1750 ms	C=O stretch, A''
1585 w		
1510 wm		
1470 w		
1420 vw		
1388 w		
1353 ms	1355 vm	C=C stretch, A'
1322 m		C—O stretch, A''
1300 w		
1290 w		
1252 s		
1234 s	1240 vw(br)	C—H i.p. deform, A'
1225 s		
1091 s	1088 w	C—H i.p. deform., A''
1063 ms	1065 m	C—O stretch, A'
891 s	888 ms	C—C stretch, A'
860 vs	860 vw	C—C stretch, A''
835 s	835 vs.	C—H o.o.p. deform, A'
	763 m	
750 ms	752 w	C—H o.o.p deform, A''
708 vs	707 m	Ring bend, A''
630 vs	628 s	Ring bend, A'
608 vs		and Fe—C—O bends
590 vs	589 wm	
480 s	481 w	Fe—C stretch + ?
461 ms	458 w	C=O i.p. deform, A', and
411 s	414 ms	(maleic anhydride) tilt.
370 wm	372 vs	(M.a.)—Fe stretch, A'

[a] i.p. in-plane; o.o.p out-of-plane; M.a. maleic anhydride.

TABLE 2

IR VIBRATIONAL FREQUENCIES FOR THE CARBONYL GROUPS IN (MALEIC ANHYDRIDE)IRON TETRACARBONYL (C_s SYMMETRY), IRON PENTACARBONYL, (ETHYLENE)IRON TETRACARBONYL AND FREE MALEIC ANHYDRIDE

$Fe(CO)_4$ group (CH_2Cl_2 solution)	$Fe(CO)_5$[a]	$Fe(CO)_4$ in $(C_2H_4)Fe(CO)_4$[b] (vapour)
2120 (A')	2112 (A')	2095 (A_1)
2065 (A')	2034 (A'_1)	2020 (A_1)
2049 (A')	2027 (A''_2)	2003 (B_2)
2030 (A'')	2013 (E')	1988 (B_1)
Complexed maleic anhydride (CH_2Cl_2 solution)	**Free maleic anhydride (CCl_4 solution)**	
1836 (A')	1858 (A_1)	
1771 (A'')	1784 (B_1)	

[a] Ref. 3. [b] Ref. 1.

solution data on the carbonyl stretching frequencies [$\nu(C{\equiv}O)$ and $\nu(C{=}O)$] in Table 2, together with equivalent data from $(C_2H_4)Fe(CO)_4$ [1], $Fe(CO)_5$ [3] and free maleic anhydride [4].

Vibrational analysis

No crystal structure has been determined for the complex under consideration, but it may be reasonably assumed to be analogous to that found for (fumaric acid)iron tetracarbonyl [5], with the olefinic double bond in the equatorial plane of the molecule (Fig. 1).

The molecule possesses overall C_s symmetry. The numbers and symmetries of the vibrational modes of maleic anhydride are given in Table 3 for C_{2v} (appropriate for the free molecule) and C_s (for the complexed molecule) symme-

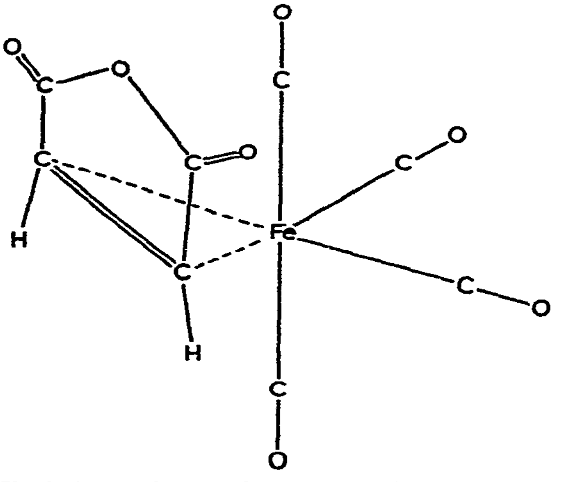

Fig. 1. Assumed molecular structure of (maleic anhydride)iron tetracarbonyl.

TABLE 3

NORMAL VIBRATIONAL MODES OF MALEIC ANHYDRIDE UNDER C_{2v} AND C_s SYMMETRY

Type of mode	C_{2v}	C_s
C—H stretch	$A_1 + B_1$	$A' + A''$
C=O stretch	$A_1 + B_1$	$A' + A''$
C=C stretch	A_1	A'
C—O stretch	$A_1 + B_1$	$A' + A''$
C—C stretch	$A_1 + B_1$	$A' + A''$
CH in-plane def.	$A_1 + B_1$	$A' + A''$
C=O in-plane def.	$A_1 + B_1$	$A' + A''$
In-plane ring def.	$A_1 + B_1$	$A' + A''$
CH out-of-plane def.	$A_2 + B_2$	$A'' + A'$
C=O out-of-plane def.	$A_2 + B_2$	$A'' + A'$
Out-of-plane ring def.	$A_2 + B_2$	$A'' + A'$

tries, while those for $Fe(CO)_4$, and the whole-molecule modes, are listed in Table 4 (All vibrations are IR- and Raman-active except for A_2 modes under C_{2v} symmetry which are IR-forbidden; A_1 and A' modes would give rise to polarised Raman bands in solution).

Assignment for the maleic anhydride fragment

The lack of Raman polarisation data will render such an assignment rather difficult, but some assistance is given by comparisons with published data on free maleic anhydride [4, 6]. In the absence of Raman polarisation data we may also make some use of the fact that the A' modes (C_S symmetry) will in general give more intense Raman bands than related A'' modes.

Two medium-intensity IR bands at 3100 and 2934 cm^{-1} are assigned as the two C—H stretches. Mirone and Chiorboli [4] and Di Lauro et al. [6] disagree in their assignments of these modes, but the lower frequency mode in the complex has been assigned tentatively to the A' mode. The frequencies are significantly lower than those for the free ligand (3180, 3123 cm^{-1}) which indicates a reduction in the unsaturation of the olefinic carbons [as was also observed for $(C_2H_4)Fe(CO)_4$ [1]].

TABLE 4

NORMAL VIBRATIONAL MODES FOR THE $Fe(CO)_4$ FRAGMENT, TOGETHER WITH THOSE INVOLVING THE WHOLE (MALEIC ANHYDRIDE)IRON TETRACARBONYL MOLECULE

Type of mode[a]	C_{2v}	C_s
C≡O stretching (equatorial)	$A_1 + B_1$	$A' + A''$
C≡O stretching (axial)	$A_1 + B_2$	$2A'$
Fe—C stretching (equatorial)	$A_1 + B_1$	$A' + A''$
Fe—C stretching (axial)	$A_1 + B_2$	$2A'$
Fe—C—O def. (equatorial	$A_1 + A_2 + B_1 + B_2$	$2A' + 2A''$
Fe—C—O def. (axial)	$A_1 + A_2 + B_1 + B_2$	$2A' + 2A''$
C—Fe—C def.	$2A_1 + A_2 + B_1 + B_2$	$3A' + 2A''$
(M.a.)—Fe stretch	A_1	A'
(M.a.)—Fe tilt	$B_1 + B_2$	$A'' + A'$
(M.a.)—Fe torsion	A_2	A''
(M.a.)—Fe—(CO)$_4$ def.	$B_1 + B_2$	$A'' + A'$

[a] (M.a.) = maleic anhydride.

The next bands assignable to maleic anhydride are at 1836 and 1771 cm^{-1} (IR, CH_2Cl_2 solution), which are clearly associated with the anhydride carbonyl stretches. That at higher frequency is assigned as the symmetric (A') mode, the lower frequency feature being due to the A'' vibration (by analogy with the free ligand). Two Raman bands (solid-phase) are seen at 1820, 1750 cm^{-1}. The lowering of ν(C=O) frequencies on complexing (1858, 1784 cm^{-1} in the free maleic anhydride) may be related to the electron donation from the iron to the ligand. Some of this charge must be delocalised onto the carbonyl group, favouring the form $>C^{+}—O^{-}$, and leading to a decrease in the C—O bond order. There is also a decrease in the separation of the symmetric and antisymmetric ν(C=O) modes, hence the extent of coupling between the vibrating carbonyl groups is decreased due to the altered electron distribution in the ligand.

A normal coordinate analysis of free maleic anhydride [6] suggests that there is little coupling between the C=C stretch and the symmetric CH deformation. The situation in the complex appears to be similar, with ν(C=C) being assigned to the only Raman band between 1250 and 1600 cm^{-1} i.e. 1355 cm^{-1} (IR 1353 cm^{-1}), with δ(CH) being associated with the feature at 1240 cm^{-1} (IR 1234 cm^{-1}). Powell et al. [7] have suggested that the percentage shifts on complexing of ν(C=C) and δ(CH) give an indication of the strength of the bonding interaction with the metal. The shifts here are 15.0% and 0.5% respectively, giving a total of 15.5%, corresponding to a strong bonding interaction. Individually, the percentage shifts are typical of those observed [7] when there is little or no coupling between the modes.

The antisymmetric (A'') δ(CH) mode is assigned to a strong IR band at 1091 cm^{-1} (Raman, 1088 cm^{-1}), with a somewhat weaker absorption at 1063 cm^{-1} (Raman, 1065 cm^{-1}) being assigned to the symmetric C—O stretch (A'). The antisymmetric C—O stretch (A''), expected at higher frequency, is assigned to a medium intensity band (IR only) at 1322 cm^{-1}.

The two C—C stretches are expected to occur around 900 cm^{-1}, and are assigned as follows: 891 (Raman 888), A', and 860 cm^{-1} (Raman 860 cm^{-1}) A'' C—C stretch.

The remaining in-plane modes of the maleic anhydride are unfortunately expected to be found in the frequency region 700—400 cm^{-1}, where many $Fe(CO)_4$ modes will be. However, tentative assignments may be proposed, as follows: 708 (Raman 707), A'' ring bend; 630 (strong Raman band at 628), A' ring bend; 411 cm^{-1} (Raman 414 cm^{-1}), A' C=O bend. The A'' C=O bend is left unassigned.

The 6 out-of-plane modes are all expected below 900 cm^{-1}, and similar difficulties exist. The A' C—H bend is almost certainly at 835 cm^{-1} (strong, coincident Raman band), while the analogous antisymmetric A'' bend is at 750 cm^{-1} (Raman, 752 cm^{-1}). The two out-of-plane C=O deformations, and the two out-of-plane ring deformations have been left unassigned.

The proposed assignments of maleic anhydride modes are summarised and compared with those for the free ligand in Table 5.

Assignment for the $Fe(CO)_4$ fragment and for the whole (maleic anhydride)-$Fe(CO)_4$ molecule

The absence of Raman polarisation data will again result in ambiguities

TABLE 5

VIBRATIONAL ASSIGNMENTS FOR FREE AND COMPLEXED MALEIC ANHYDRIDE (cm^{-1})

Type of mode	Free (C_{2v})^a	Complexed (C_s)
C—H stretches	3180 (B_1)	3100 (A'')
	3123 (A_1)	2934 (A')
C=O stretches	1858 (A_1)	1836 (A')
	1784 (B_1)	1771 (A'')
C=C stretch	1595 (A_1)	1354 (A')
C—O stretches	1268 (B_1)	1322 (A'')
	1068 (A_1)	1064 (A')
C—C stretches	871 (A_1)	890 (A')
	897 (B_1)	860 (A'')
CH in-plane defs.	1244 (A_1)	1237 (A')
	1057 (B_1)	1090 (A'')
C=O in-plane defs.	410 (A_1)	411 (A')
	566 (B_1)	
In-plane ring defs.	695 (B_1)	708 (A'')
	644 (A_1)	630 (A')
Out-of-plane CH defs.	835 (B_2)	835 (A')
	766 (A_2)	751 (A'')
Out-of-plane C=O defs.	615 (B_2)	
	537 (A_2)	
Out-of-plane ring defs.	340 (B_2)	
	268 (A_2)	

^{a} Ref. 4.

in the assignment. The four expected carbonyl stretches ($3A' + A''$) are observed in dilute solutions in the IR spectrum; 5 bands are seen in the solid-phase Raman spectra, hence factor group splitting is significant. Specific assignments for these bands are difficult, but by analogy with (ethylene)iron tetracarbonyl it is proposed that the three higher-frequency modes are those of A' symmetry. Despite this tentative assignment; we see that the carbonyl stretches are higher than in $Fe(CO)_5$ [3]. This indicates that maleic anhydride is a better π-electron acceptor than CO, which in turn is better than ethylene [1]. A similar observation has been made with reference to maleic anhydride complexes of Cr and Mn [8].

As noted above, a number of maleic anhydride modes occur in the region associated with Fe—C—O deformations and Fe—C stretches. Fifteen vibrational modes associated with the $Fe(CO)_4$ and (maleic anhydride)Fe fragments are expected within the range 700—300 cm^{-1} (8 Fe—C—O deformations, 4 Fe—C stretches and 3 Fe— (Maleic anhydride) modes). The only features assignable to such modes are, however, 630, 608, 590 cm^{-1} [δ(Fe—C—O)]; 480, 461, 411 cm^{-1} [ν(Fe—C)] and 372 cm^{-1}. [ν(Fe— maleic anhydride)]. The great intensity of the last band in the Raman spectrum makes its assignment as the A' mode virtually certain.

No assignments can be made for the 8 remaining modes expected in this region, nor for the low-frequency skeletal deformation modes or iron—(maleic anhydride) torsion.

Conclusion

A reasonably complete vibrational assignment for the maleic anhydride modes, and some assignments for the $Fe(CO)_4$ and whole-molecule modes, in (maleic anhydride)iron tetracarbonyl are consistent with a strong organic ligand-metal interaction in this molecule.

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Note added in proof

Another study of the vibrational spectrum of (maleic anhydride)iron tetracarbonyl has appeared [B.V. Lokshin, V.T. Aleksanyan and Z.S. Klemenkova, J. Organometal. Chem., 70 (1974) 437]. These results agree in all essential details with those presented here.