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VIBRATIONAL SPECTRA OF π-OLEFIN TRANSITION METAL COMPLEXES

II. *N*-METHYLMALEIMIDE AND (π-METHYLMALEIMIDE)IRON TETRACARBONYL

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Summary

Infrared and Raman spectra of *N*-methylmaleimide (solid, solution, gas) and of (π-*N*-methylmaleimide)iron tetracarbonyl (solid, solution) have been obtained. An assignment of the normal modes of both molecules is offered and compared with the data for (π-maleic anhydride)iron tetracarbonyl. The change of the ligand modes after coordination to the metal atom is discussed. The C=C stretching vibration in the complex is assigned to the band at 1370 cm^{-1} (1585 cm^{-1} in the free ligand). The decrease in the IR intensity of the out-of-plane CH modes of the ligand after coordination is explained by the lowering of the effective positive charge on olefinic protons due to the electron back-donation from metal to ligand. The upfield shift of the signal of =CH protons in PMR spectrum of the complex supports this conclusion.

Introduction

In the previous paper [1] the vibrational spectra of (π-maleic anhydride)iron tetracarbonyl (MA)$Fe(CO)_4$ have been discussed. It was demonstrated that in contrast to ethylene complexes the C=C stretching vibration is characteristic and its frequency shifts under coordination from 1595 cm^{-1} to 1353 cm^{-1}. The changes of other ligand vibrations were small. It was of interest to study the spectra of a similar complex of another cyclic olefin, *N*-methylmaleimide (MI). Although the spectra of MA have been studied previously, this is not so for MI. In this work an assignment of the MI vibrational frequencies is offerred and then the change on forming (MI)$Fe(CO)_4$ is discussed.

TABLE 1.

VIBRATIONAL SPECTRA (cm^{-1}) OF *N*-METHYLMALEIMIDE

IR			Raman		Assignment
Solid	Solution^a	Gas	Solid	Solution^c	
3098 s	3110 w^c		3100 s	3106 m (p)	$\nu(\mathrm{CH})(\mathrm{A}_1)$
3090 s			3091 s		
3079 (sh)	3070 m^c				$\nu(\mathrm{CH})(\mathrm{B}_1)$
2992 w	3001 vw				
2956 w	2954 m		2956 w	2950 w (br)	
2927 w	2934 (sh)				
2899 w	2904 (sh)				$\nu(\mathrm{CH}_3)$
2880 vw	2860 vw				
1844 vw	1843 vw				
	1833 w				
	1815 vw		1809 w	1806 w	
1773 w	1778 m			1771 vs (p)	$\nu(\mathrm{C{=}O})(\mathrm{A}_1)$
1758 w	1765 w (sh)		1762 vs		
	1743 m		1755 vs		
	1724 vs				$\nu(\mathrm{C{=}O})(\mathrm{B}_1)$
1705 1700 vs (br)			1693 m		
1673 (sh)	1674 s				
	1646 w				
1607 w	1600 w				
1594 m	1591 w		1586 s	1585 s (p)	$\nu(\mathrm{C{=}C})(\mathrm{A}_1)$
1564 vw					
1480 (sh)			1472 w		
1459 vs	1453 vs		1455 m		$\}\ \delta(\mathrm{CH}_3)$
1443 vs	1446 vs		1438 m	1445 w	
1424 (sh)					
1403 s	1403 s				$\}\ \delta(\mathrm{CH}_3)$
1391 vs	1390 vs				
1350 vw	1352 m			*e*	
1342 w	1343 m				
1326 w	1332 m		1322 w (br)		$\nu(\mathrm{ring})(\mathrm{A}_1)$
1304 m	1294 w				
1255 vs	1258 s	1265-1259-1253 (A)			$\delta(\mathrm{CH})(\mathrm{B}_1)$
1218 vw	1217 vw				$\}\ \rho(\mathrm{CH}_3)$
			1148 m	1141 w	
1134 w	1126 m		1136 s	1128 m (p)	$\nu(\mathrm{NCH}_3)(\mathrm{A}_1)$
1113 1109 vs	1103 s	1108-1101-1096 (A)	1108 w		$\nu(\mathrm{ring})(\mathrm{B}_1)$
1054 m	1038 s	1040-1030 (B)	1054 m	1033 m (p)	$\delta(\mathrm{CH})(\mathrm{A}_1)$
940 vs	939 vs	946-942-934 (A)	965 w	948 vw	$\nu(\mathrm{ring})(\mathrm{B}_1)$
866 w					
833 vs	826 vs^{b,c}	837-826-815 (C)	828 w	*e*	$\rho(\mathrm{CH})(\mathrm{B}_2)$
			768 m		
736 vw			736 vs	728 s (p)^d	$\nu(\mathrm{ring})(\mathrm{A}_1)$
695 vs	696 vs	708-701-693 (A)		*e*	$\delta(\mathrm{C{=}O})(\mathrm{B}_1)$
669 w				668 w (p)	
633 w	620 (sh)		636 m		
613 m					$\rho(\mathrm{C{=}O})(\mathrm{B}_2)$
604 (sh)	609 m		606 (sh)	611 s (p)	$\delta(\mathrm{C{=}O})(\mathrm{A}_1)$
			600 m	595 (sh)	$\rho(\mathrm{C{=}O})(\mathrm{A}_2)$
576 vw	568 vw		571 w		
388 s	385 s		382 w	392 w	$\delta(\mathrm{ring})(\mathrm{B}_2)$
			374 vw	370 w (p)	$\delta(\mathrm{ring})(\mathrm{A}_1)$
			356 vw		$\chi(\mathrm{ring})(\mathrm{A}_2)$
281 m	283 m		279 m		$\chi(\mathrm{ring})(\mathrm{B}_2)$
207 w					
167 m					
79 vw					

^{a} Solution in CCl_4. ^{b} In $CHCl_3$. ^{c} In CH_2Cl_2. ^{d} In CS_2. ^{e} The region of the solvent bands.

Results and discussion

N-Methylmaleimide

The symmetry of MI molecule is C_s, but taking into consideration the fact that CH_3-group vibrations are characteristic and scarcely interact with skeletal vibrations it is possible to use the C_{2v} symmetry of the molecule in the analysis and consider the CH_3-group as a point mass. This is convenient for comparing vibrations of the same symmetry for MA and MI.

(a). Skeletal modes

Considering the CH_3-group as a point mass for the MI molecule 24 normal modes are expected: 17 in-plane ($9A_1 + 8B_1$) and 7 out-of-plane ($3A_2 + 3B_2$). The A_2 modes are only Raman active, A_1, B_1 and B_2 are IR and Raman active. For the CH_3-group 9 additional vibrations are expected (vide infra). The following criteria were used in the assignment of vibrational modes: polarization of the Raman lines, band envelopes in the IR spectrum of the gas, spectra of MA and another relative molecules.

For analysis of the gas-phase IR spectrum the main moments of inertia of MI molecule were calculated. The parameters used are the following: r(C=O) 1.189 Å, r(CN) 1.47 Å, r(CC) 1.47 Å, r(C=C) 1.303 Å, r(CH) 1.09 Å, $\angle$ CNC 108°, $\angle$ CCC 109°, $\angle$ CCN 108°. These data are for MA, because there are no data available for MI. The results obtained are the following: I_{xx} 265 × 10^{-40} g cm^2, I_{yy} 768 × 10^{-40} g cm^2, I_{zz} 518 × 10^{-40} g cm^2 (z-axis coincides with the axis of symmetry, x axis is in the ring plane, y axis is perpendicular to it). From these values for A_1 modes the B-type bands are expected without Q branch with PR distance about 9 cm^{-1} at 367 K. For B_1 modes the A-type bands are expected with $\Delta\nu$ PR = 12 cm^{-1} and Q branch of middle intensity and for B_2 modes C-type bands with $\Delta\nu$ PR about 18 cm^{-1} and strong Q branch [2].

A_1 modes. The 9 A_1 modes can be classified tentatively as C—H, C=O, C=C, C=N, C—C and N—Me stretching vibrations, C—H, C=O and ring-bending vibrations. In the Raman spectra polarized lines are found at 3106, 1771, 1586, 1128, 1033, 728, 611 and 370 cm^{-1}. The 1033 cm^{-1} band has the B-type envelope ($\Delta\nu$ PR = 10 cm^{-1}). Most of these bands have frequencies rather similar to the corresponding MA bands, which facilitates the assignment (see Fig. 1). The most pronounced difference was observed for the 728 cm^{-1} ring mode (871 cm^{-1} for MA) with the predominant participation of CC bonds. The other ring mode [predominantly ν(CN)] is located at 1322 cm^{-1} in the IR and Raman spectra (1243 cm^{-1} for MA). The polarization of this band was not measured due to its small intensity. But this is the only band in the Raman spectrum in the 1150—1400 cm^{-1} region. For the maleimide molecule the band at 1350 cm^{-1} has been assigned to this vibration [3]. The 1128 cm^{-1} band is connected apparently with the N—Me stretching mode.

B_1 modes. The four bands with A-type shape in the IR spectrum of gaseous MI at 1259 cm^{-1} ($\Delta\nu$ PR 12 cm^{-1}), 1101 cm^{-1} ($\Delta\nu$ PR 12 cm^{-1}), 942 cm^{-1} ($\Delta\nu$ PR 12 cm^{-1}) and 701 cm^{-1} ($\Delta\nu$ PR 15 cm^{-1}), which correspond to bands at 1309, 1057, 896 and 699 cm^{-1} in MA, can be assigned to C—H bending, ring stretching [ν(CC) and ν(CN)] and in-plane C=O bending modes respectively.

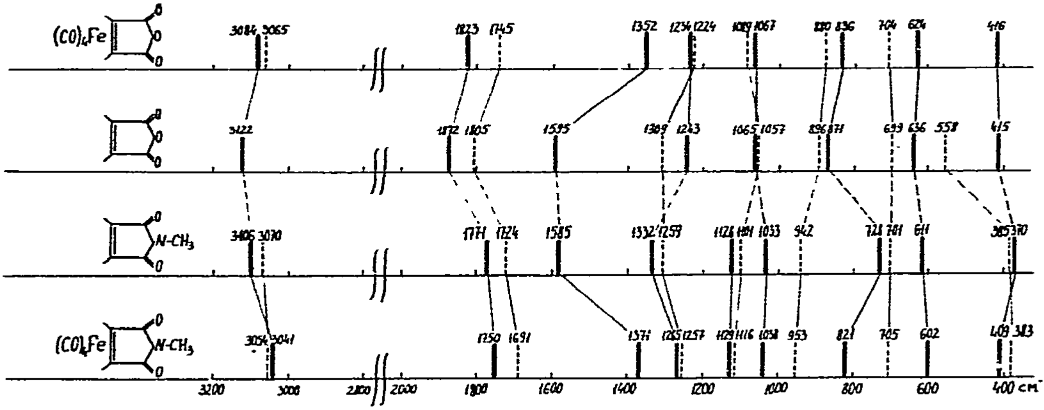

Fig. 1. In-plane vibrations (cm^{-1}) of maleic anhydride, maleic anhydride in $(MA)Fe(CO)_4$, N-methylmaleimide and N-methylmaleimide in $(MI)Fe(CO)_4$. ——— A_1 modes, ------ B_1 modes.

Additionally the C—H and C=O stretching, ring bending and CH_3 rocking modes are expected. To $\nu(CH)$ the IR band 3070 cm^{-1} is assigned. In spite of its formal activity the strong $\nu(CO)$ IR band 1724 cm^{-1} was not observed in the Raman spectra. In practice for $\nu(CO)$ modes the rule of mutual exclusion takes place: The A_1 mode is very weak in the IR spectrum and the B_1 mode in the Raman. Many weak IR bands in the $\nu(CO)$ region were observed, probably due to the overtones. The strong IR band at 385 cm^{-1} can be assigned to the ring deformation (415 cm^{-1} for MA). The assignment of the N—CH_3 rocking vibration is not clear.

B_2 modes. The strong IR band of C-type at 826 cm^{-1} ($\Delta\nu$ PR 22 cm^{-1}) in the spectrum of the gaseous MI is assigned to the out-of-plane CH bending mode (c.f. 840 cm^{-1} for MA). The bands at 613 and 283 cm^{-1} are assigned to the out-of-plane modes of C=O and of the ring by analogy with MA. The rocking out-of-plane N—Me mode is not assigned.

A_2 modes. The three A_2 modes of MI are assigned to the lines at 768, 595 and 356 cm^{-1}, observed only in the Raman spectrum. These are analogous to the lines observed at 762, 537 and 270 cm^{-1} for MA.

(b). Methyl group modes

9 vibrations are expected for the CH_3-group: 3 stretching, 3 bending, 2 rocking and torsional modes. The 2902, 2954, 3001 cm^{-1} bands are assigned to $\nu(CH)$. The local symmetry C_{3v} in all probability is not applicable in this case. The 1340, 1400 and 1450 cm^{-1} bands correspond to internal bending vibrations of the CH_3-group as for other CH_3-containing compounds. All these bands have a doublet structure in the solution IR spectra. We assign tentatively the weak IR and Raman bands 1141 and 1217 cm^{-1} to the external bending modes. The torsional mode has a low frequency and was not assigned.

(π-N-Methylmaleimide)iron tetracarbonyl

60 normal vibrations are expected for the $(MI)Fe(CO)_4$ molecule with C_s symmetry, i.e. 33 ligand vibrations, 21 vibrations of the $Fe(CO)_4$ moiety and 6

metal-to-ligand vibrations. The ligand modes do not interact significantly with the $Fe(CO)_4$ modes, which, except for CO stretching vibrations, are located in the region below 700 cm^{-1} and can be analysed separately.

(a). Ligand modes

The local symmetry of the ligand in the complex is C_s, but to simplify the comparison with the free ligand spectra we will use the C_{2v} symmetry in the discussion. This is possible, because the in-plane and out-of-plane modes are not mixed significantly and can be separated. The Raman polarization data and the free ligand spectra were used for the assignment. Most of the ligand modes are not changed significantly in the spectrum of the complex. The spectral data are presented in Table 2 and Fig. 1. Here we discuss only the ligand frequencies sensitive to the coordination.

The polarized Raman line at 1370 cm^{-1} is assigned to the C=C stretching vibration (1353 cm^{-1} for $(MA)Fe(CO)_4$). The shift with respect to the free ligand is 214 cm^{-1}. In contrast to the MA complex some ring frequencies are changed: 1265 and 821 cm^{-1} in the complex and 1322 and 728 cm^{-1} in the MI spectra. The stretching C=O and =CH frequencies decrease in the spectra of the complex. The same phenomenon was observed earlier for MA. Such shift in ν(CH) frequency is connected with some decrease in the C=C bond order and with the corresponding increase of the p-character of the C—H bond. Other A_1 modes are at 1038, 602, 409 cm^{-1} (polarized in the Raman spectrum) and 1129 cm^{-1} observed in the IR spectrum only and assigned to N—Me stretch (1128 cm^{-1} for the free ligand).

The B_1 modes are at 3034, 1691, 1257, 1116, 953 and 701 cm^{-1} using the analogy with free MI. The low frequency ring mode coincides with the vibrations of the $Fe(CO)_4$ moiety (385 cm^{-1} for the free ligand). In the spectra of the complex in this region two bands at 391 and 383 cm^{-1} were observed. The 391 cm^{-1} band is strong in the Raman spectrum and weak in the IR spectrum. The 383 cm^{-1} band is strong in the IR and was not observed in the Raman spectrum. This fact permits us to assign the 383 cm^{-1} band to the ring deformation and the band at 391 cm^{-1} to the Fe—CO stretching mode (404 cm^{-1} in $(MA)Fe(CO)_4$).

From the out-of-plane modes the bands of the most interest are the ρ(CH) bands. As was demonstrated earlier [1] their IR intensities change considerably after coordination to the metal atom. In the IR spectrum of MI in acetonitrile solution this band appears at 826 cm^{-1} and has an integrated intensity of 0.7×10^4 $l \cdot mol^{-1} \cdot cm^{-2}$. There are two bands in the IR spectrum of the $(MI)Fe(CO)_4$ in the same region at 832 and 763 cm^{-1}. The 763 cm^{-1} band has an integrated intensity of 0.2×10^4 $l \cdot mol^{-1} \cdot cm^{-2}$. For the 832 cm^{-1} band the measurement was not made because of its low intensity and the limited solubility of the compound. But this band has a much smaller intensity, than the 763 cm^{-1} band. Therefore, in spite of the uncertainty of the assignment, it is possible to conclude that the intensity of the ρ(CH) band is lowered in the complex molecule as compared with the MI molecule. This phenomenon has been discussed in connection with some transition metal complexes [1, 4] and was explained as a manifestation of the lowering of the effective positive charge on olefinic protons after coordination due to the electron donation from occupied metal

TABLE 2. VIBRATIONAL SPECTRA (cm^{-1}) OF (π-*N*-METHYLMALEIMIDE)IRON TETRACARBONYL

IR		Raman		Assignment
Solid	Solution ^{a}	Solid	Solution ^{c}	
3103 vw		3100 m		
	3072 m ^{c}	3072 w	3070 vw	
3059 s		3059 m	3054 w	ν(CH)(B_1)
3048 m			3041 w (p)	ν(CH)(A_1)
3031 w	3033 (sh) ^{b}			
2952 vw	2950 m ^{c}	2946 w (br)		ν(CH_3)
	2897 w ^{c}			
2113 m	2113 m ^{c}	2110 s	2110 s (p)	ν(CO)(A_1)
2053 s	2053 (sh) ^{c}	2050 s	2052 m	ν(CO)(B_1 or B_2)
	2040 vs ^{c}	2045 m		ν(CO)(A_1)
2018 s	2023 s ^{c}	2009 m	2018 m	ν(CO)(B_1 or B_2)
1994 vs	1988 m ^{c}	1982 s	1988 ?	
1973 w		1960 w		
1745 s	1751 s ^{c}	1740 vs	1750 m (p)	ν(CO)(A_1)
	1713 (sh) ^{c}			
1693 vs (br)	1694 vs ^{c}	1682 m	1691 w	ν(CO)(B_1)
	1674 (sh) ^{c}			
1456 w				
1436 s	1435 s	1438 vw		} δ(CH_3)
1383 s	1384 s			
		1375 vw	1371 m (p)	ν(C=C)(A_1)
1362 s	1364 (sh)			} δ(CH_3)
	1352 m	1359 m	*e*	
1327 vw	1324 vw			
			1265 w (p)	ν(ring)(A_1)
1252 s	1257 m	1250 w		δ(CH)(B_1)
1227 (sh)				
1129 m				ν(NMe)(A_1)
1118 s	1116 s	1111 m	1120 w	δ(ring)(B_1)
1104 (sh)				
1054 w	1037 w	1049 s	1038 m (p)	δ(CH)(A_1)
1006 w	1000 (sh)			
947 s	953 s	915 w		ν(ring)(B_1)
924 w				
853 w		849 vs		
	832 w ^{d}			ρ(CH)(B_2) ?
		825 w	821 s (p)	ν(ring)(A_1)
767 m		765 (sh)		
762 m	763 m ^{d}	758 w		ρ(CH)(A_2)
723 (sh)		721 w		ρ(CH)(B_2) ?
707 s	705 s	705 w		ρ(C=O)(B_1)
			669 w	
		636 m		
628 s		627 w	628 m	ρ(C=O)(B_2)
607 s	612 s	599 s	602 s (p)	δ(C=O)(A_1)
589 s	591 s	583 m		} δ(FeCO)
562 vw	558 vw			
485 s	483 m	481 w		} ν(FeC)(A_1, B_1, B_2)
475 m	473 (sh)			
464 w				
454 m	450 m	447 w	450 w	
430 w	429 w	429 w		
411 m	413 m	410 m	409 m (p)	δ(ring)(A_1)
395 w		391 vs	389 (sh)	ν(FeC)(A_1)
380 s	383 m			δ(ring)(B_1)
370 (sh)		373 vs	375 vs (p)	ν(FeL)(A_1)
347 (sh)	350 vw	349 (sh)	347 (sh)	χ(ring)(A_2)
289 s	280 w	284 w		χ(ring)(B_2)
235 (sh)		244 vw		
225 w				
			190 w	
160 m		163 (sh)	160 m	
		158 m		
146 w				
115 vw				
80 vw				

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[a] Solution in CCl_4. [b] In $CHCl_3$. [c] In CH_2Cl_2. [d] In CS_2. [e] The region of the solvent bands.

d-orbitals to the antibonding double bond π-orbital. This conclusion is supported by the PMR spectra: the signal of the =CH protons of MI shifts upfield on complex formation (from δ 6.85 for MI to δ 4.09 ppm for (MI)Fe$(CO)_4$ in acetone solution), i.e. the MI proton shielding is enhanced. The assignment of the other out-of-plane modes is tentative (see Table 2).

Methyl group vibrations do not change significantly as compared with MI. However, the bending modes are not split in the solution IR spectra (only the 1352 cm^{-1} band has a shoulder at 1364 cm^{-1}).

(b). LFe(CO)₄ modes

Four bands in the IR spectrum of (MI)Fe$(CO)_4$ in solution in the CO stretching region support the C_{2v} symmetry of the Fe$(CO)_4$ moiety (equatorial substitution in the trigoanl-bipyramidal Fe$(CO)_5$ molecule). The higher frequency line is polarized in the Raman spectrum and therefore assigned to the A_1 mode. The lines at 2052 and 2018 cm^{-1} are depolarized and assigned to the modes of B_1 and B_2 classes. The band at 2040 cm^{-1} must be the second A_1 line, but it was not observed in the Raman spectra. The same phenomenon was observed for (MA)Fe$(CO)_4$ and the reason has been discussed previously [1]. The weak 1988 cm^{-1} IR band is probably due to the ^{13}CO vibration. Other LFe$(CO)_4$ vibrations are very similar to the corresponding (MA)Fe$(CO)_4$ vibrations. Therefore the assignment is given in Table 2 without comments.

Experimental

The IR spectra were run on IR spectrometers Zeiss UR-20, Perkin—Elmer 457 and FIS-1 using solid samples (KBr discs, nujol mull) and CCl_4 and $CHCl_3$ solutions. The IR spectrum of MI in gas phase were obtained with 10 m multipass cell at 94° on IKS-16 spectrometer. The Raman spectra of both solid samples and solutions in CS_2 and CH_2Cl_2 were recorded on a laser spectrometer Coderg PHO with He/Ne laser (6328 Å). PMR spectra were obtained on a Hitachi R-20 60 MHz instrument in acetone solution.

(N-Methylmaleimide)iron tetracarbonyl

1.11 g (0.01 mol) of MI in 40 ml of absolute acetone was added to 3.64 g (0.01 mol) $Fe_2(CO)_9$ and stirred for 1.5 hour at 40°. After evaporation of the mixture, the residue was recrystallized from acetone and yielded 1.12 g (40%) of (MI)Fe$(CO)_4$, m.p. 120—125° (dec.). (Found: C, 38.76; H, 2.09; Fe, 19.54; $C_9H_5FeNO_6$ calcd.: C, 38.74; H, 1.81; Fe, 20.02%.)

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