A STUDY OF THE VIBRATIONAL SPECTRUM OF ETHYLENEIRON TETRACARBONYL

D. C. ANDREWS AND G. DAVIDSON

Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD (Great Britain)

SUMMARY

An almost complete assignment of the vibrational modes of the complex $(C_2H_4)Fe(CO)_4$ has been made. The (strongly coupled) CH_2 in-plane symmetric deformation and $C=C$ stretching frequencies are 1510 and 1193 cm^{-1}, with the $Fe-(C_2H_4)$ stretch and tilts at 361, 305 and 401 cm^{-1}.

INTRODUCTION

The only complexes which contain ethylene π-bonded to a transition metal which have been studied by vibrational spectroscopy are $K[PtCl_3(C_2H_4)] \cdot H_2O$ (Zeise's salt), the Pd analogue, and the two dimeric species $[MCl_2(C_2H_4)]_2$ (M = Pd, Pt). Numerous workers[1-9] have attempted to assign the vibrations of the coordinated ethylene molecule, but it has not proved possible to obtain agreement on this. Indeed, two recent papers on Zeise's salt disagree on the assignment of almost all of the normal modes[6,9]. In an attempt to throw some light upon this confused system, and as part of a series of investigations on the vibrational spectra of (hydrocarbon)M-(CO)$_n$ complexes[10-13], we have investigated the IR and, as far as possible, the Raman spectrum of $(C_2H_4)Fe(CO)_4$.

EXPERIMENTAL

Ethyleneiron tetracarbonyl was prepared by the method of Murdoch and Weiss[14], *i.e.* a suspension of $Fe_2(CO)_9$ in 40°–60° petroleum ether was treated with ethylene at a pressure of 50 atm for 48 h at room temperature. The product was purified by fractional distillation.

IR spectra of the complex were run in the vapour phase, as a pure liquid, in CS_2 solution and in the solid phase (in a low-temperature cell cooled with liquid N_2), using a Perkin–Elmer 521 spectrometer 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}.

It proved to be impossible to obtain Raman spectra of the pure liquid or of solutions, in *e.g.* CS_2, because of rapid and extensive photochemical decomposition.

TABLE 1

INFRARED SPECTRUM OF $(C_2H_4)Fe(CO)_4$

Solid	Pure liquid	CS$_2$ solution			Gas phase	Assignment
		Concd.	Med.	Dilute		
	3965 m					
3220 m						
	3078 m	3071 m	3070 w		3080 m	$v(CH_2)$, B_2
	3015 m	3004 m	3004 w		3014 m	2×1510
2955 m	2980 w	2950 vw	2950 vw		2970 m	$v(CH_2)$, B_1
2920 m	2920 m	2920 m	2920 m		2930 m	$v(CH_2)$, A_1
2875 m $\}$	2850 w	2850 vw	2850 vw		2880 w	
2850 m $\}$						
2805 m						
	2755 vvw					
	2720 vw					
	2698 vvw					
	2680 vw					
	2640 vw					
	2580 w					
	2530 vvw					
	2455 m, br				$\{$ 2480 w	
					$\{$ 2440 w	
	2320 vw					
	2195 vw					
	2080 vs	2080 vs	2080 vs	2081 s	2095 s	$v(CO)$, A_1
~1990 vvs, br	~2000 vvs, br	~2000 vs, br	~2000 vs, br	2002 vs	2020 vs	$v(CO)$, A_1
				1996 vs	2003 vs	$v(CO)$, B_1
				1970 vs	1988 vs	$v(CO)$, B_2
	1555 w					
	1508 m				1510 w	$\delta(CH_2)_{sym}$, A_1
1476 m $\}$						
1467 m $\}$	1447 ms				1445 w	$\delta(CH_2)_{asym}$, B_1
1361 m	1382 w				1382 w	
1317 w						
1263 w	1265 vw					
	1250 vw					
1195 m	1193 s	1195 s	1196 m	1192 w	1193 s	$v(C=C)$, A_1
1153 vw	1120 w	1125 w	1120 vw		1130 w	
1080 w $\}$	1082 ms	1080 w			1085 vw	$\rho_t(CH_2)$, A_2
1076 w $\}$						
1030 w	1023 m	1030 m	1030 m		1033 w	$\rho_w(CH_2)$, B_1
977 w	985 w	985 w			988 w	
938 w	940 m	940 m	938 w		940 w	$\rho_w(CH_2)$, A_1
884 w	880 vw					
859 w	872 vw					
804 w	781 m				798 vw	$\rho_t(CH_2)$, A_2
720 m $\}$	710 s	705 m	706 m		708 m	$\rho_r(CH_2)$, B_2
682 m $\}$						$\}$
670 m $\}$						$\delta(Fe-C-O)$
640 vs, br	641 vvs, br $\}$	640 vs	632 vs	630 s	638 vs	$(2A_1 + 2A_2 + 2B_1 +$
	635 (sh) $\}$					$2B_2)$
620 vs, br	615 vs	615 s	612 m		621 vs	
590 s	585 s	580 s	588 s		590 s	

(continued)

TABLE 1 (contd.)

Solid	Pure liquid	CS₂ solution			Gas phase	Assignment
		Concd.	Med.	Dilute		
567 m					540 w	
496 m	488 s	492 s	492 s	490 m	480 m	v(Fe–CO), B_1 or B_2
478 m	470 m					v(Fe–CO), B_2 or B_1
440 s	448 ms	458 m	458 m			v(Fe–CO), A_1
430 s	425 m	422 m			430 m	v(Fe–CO), A_1
398 w	401 ms	400 s				v(Fe–C₂H₄), B_1 or B_2
350 m	356 m	355 m				v(Fe–C₂H₄), A_1
	305 w					v(Fe–C₂H₄), B_2 or B_1

It was found, however, that the complex was stable in the solid phase at low temperatures, and a spectrum could be obtained using a cell of the type described by Carlson[15]. The coolant employed was liquid N_2, and the temperature of the sample was approx. $-150°$. The spectrometer used was 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 632.8 nm). Spectra were calibrated using known peaks of indene, and all peaks are accurate to ± 2 cm^{-1} (± 5 cm^{-1} for some very weak and/or broad bands).

RESULTS AND DISCUSSION

The observed IR spectra (gas phase, liquid, CS₂ solution and solid phase) are summarised in Table 1, and the low-temperature solid-phase Raman shifts are listed in Table 2.

TABLE 2

RAMAN SPECTRUM OF (C₂H₄)Fe(CO)₄ (SOLID)

2021 w	v(CO), A_1	957 w, br	ρ_w(CH₂), A_1
1991 s	v(CO), B_1	817 w, br	ρ_t(CH₂), A_2
1975 m	v(CO), B_2	485 w	v(Fe–CO), B_1 or B_2
1463 w	? δ(CH₂)$_{sym}$, A_1	443 m	v(Fe–CO), A_1
1439 w	δ(CH₂)$_{asym}$, B_1	427 s	v(Fe–CO), A_1
1399 w	?	393 m	v(Fe–C₂H₄), B_1 or B_2
1201 w	v(C=C), A_1	361 s	v(Fe–C₂H₄), A_1
1057 w	ρ_t(CH₂), A_2		

(1). Selection rules and vibrational analysis

Electron-diffraction studies[16] show that coordination at the Fe atom in (C₂H₄)Fe(CO)₄ is trigonal-bipyramidal, with the ethylene occupying one equatorial position (Fig. 1). The molecular symmetry is, therefore, C_{2v}. The vibrational analysis

can be divided conveniently into two sections, involving (*a*) internal vibrations of the coordinated ethylene molecule and (*b*) vibrations of $Fe(CO)_4$ and also those involving the whole $(C_2H_4)-Fe-(CO)_4$ molecule.
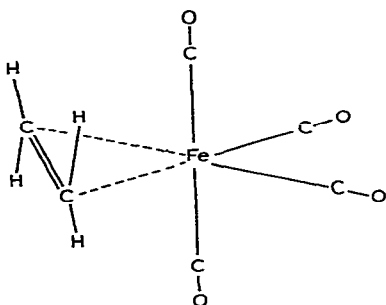

Fig. 1. Molecular structure of $(C_2H_4)Fe(CO)_4$.

(*a*). *Internal vibrations of* C_2H_4. The standard methods of vibrational analysis give the following numbers and symmetries for these vibrations:
(*i*)   C–H stretches: $A_1+A_2+B_1+B_2$
(*ii*) C–C stretch: A_1
(*iii*) CH_2 deformation (in-plane, scissors): A_1+B_1
(*iv*) CH_2 deformation (in-plane, rock): A_2+B_2
(*v*) CH_2 deformation (out-of-plane, twist): A_2
(*vi*) CH_2 deformation (out-of-plane, wag): A_1+B_1
All of these vibrations will be active in both IR and Raman spectra except for those of A_2 symmetry, which are forbidden in the IR. A_1 vibrations would give polarised Raman bands in gas- or liquid-phase spectra.

(*b*). *Vibrations of* $-Fe(CO)_4$ *and* $(C_2H_4)-Fe-(CO)_4$. A similar analysis gives the following numbers and symmetry types for these vibrations:
(*i*)   C–O stretches: $2A_1+B_1+B_2$
(*ii*)   Fe–CO stretches: $2A_1+B_1+B_2$
(*iii*) Fe–(C_2H_4) stretch: A_1
(*iv*)   OC–Fe–CO deformations: $A_1+A_2+B_1+B_2$
(*v*) $(C_2H_4)-Fe-(CO)_4$ deformations: $A_1+B_1+B_2$
(*vi*) $(C_2H_4)-Fe$ torsion: A_2
(*vii*) $(C_2H_4)-Fe$ tilt: B_1+B_2
(*viii*) Fe–C–O deformations: $2A_1+2A_2+2B_1+2B_2$
The vibrations under (*iii*) and (*vii*) are classified assuming the existence of one bond from the Fe to the centre of the C=C bond of the C_2H_4. If the alternative idealisation of two Fe–C bonds is adopted then the vibration listed under (*iii*) would then be described as a symmetric FeC_2 stretch, with the two under (*vii*) as an antisymmetric FeC_2 stretch and a C_2H_4 tilt, respectively.

(2). Assignment of ethylene vibrations

A coordinated ethylene molecule in an environment of C_{2v} symmetry should give four C–H vibrations (see above), of which three would be IR active, and which will be found in the region 2900–3100 cm^{-1}. In $(C_2H_4)Fe(CO)_4$ four bands are found there, all of comparable intensity in the gas phase. This suggests that none of them could be assigned to the (forbidden) A_2 mode, since that would be unlikely to give a band as intense as those which are allowed, especially in the gas-phase spectrum, where intermolecular forces will be quite weak.

In the absence of Raman polarisation studies, an unequivocal assignment is difficult to achieve. It seems that the band at 3014 cm^{-1} (gas phase), however, can be assigned as an overtone (2×1510; for a discussion on the assignment of this fundamental, see below). We are then left with bands at 3080, 2970 and 2930 cm^{-1}. Earlier workers[6,7,9] have given widely varying assignments for C–H stretches in Zeise's salt. We prefer the assignment of Grogan and Nakamoto[6] for the A_1 and B_2 modes: 2930 cm^{-1}, A_1; 3080 cm^{-1}, B_2, with the A_2 not observed, and the B_1 mode (following Hiraishi[9]) assigned to the band at 2970 cm^{-1}.

The lower frequencies are very difficult to assign to specific modes because of extensive coupling between modes of the same symmetry and similar frequency. This occurs particularly for the C=C stretch and the symmetric in-plane CH_2 deformation (scissors), both of A_1 symmetry. Hiraishi[9] assigned the C=C stretch in Zeise's salt to a band at 1243 cm^{-1}, with the CH_2 scissors at 1515 cm^{-1}, but Sheppard[17] has shown that it is not possible to consider these modes separately in Zeise's salt, and therefore it is not valid to draw conclusions about the strengths of bonding interactions from the observed frequencies. The same situation will apply in the present example, and it will be necessary to consider the two modes together. Two bands, at 1510 cm^{-1} and 1193 cm^{-1}, can be assigned to the two coupled vibrations, $\delta(CH_2)_{sym}$ and $\nu(C=C)$, with the out-of-phase CH_2 scissors, $\delta(CH_2)_{asym}$, B_1, at 1445 cm^{-1}. All three give rise to bands in the solid phase Raman spectrum (1463, 1201, 1439 cm^{-1}).

The two CH_2 wagging vibrations, $\rho_w(CH_2)$, $A_1 + B_1$, are expected to occur in the region of 1000 cm^{-1}. Two bands, at 940 and 1033 cm^{-1}, can be so assigned, but it is difficult to differentiate between them. Following Hiraishi[9], the lower frequency band is assigned to the totally symmetric vibration.

The last IR active ethylene vibration is the CH_2 rock (B_2), which has been assigned in Zeise's salt to a band in the region 700–850 cm^{-1}. In $(C_2H_4)Fe(CO)_4$ the only band which is obviously a fundamental is found at 708 cm^{-1} (IR only), which is close to the value suggested by Hiraishi[9] for Zeise's salt.

There are three A_2, IR forbidden, vibrations, a C–H stretch, a CH_2 rock and a CH_2 twist. No evidence for a band corresponding to the first was found, but two bands were observed which were quite strong in the condensed phases, but very weak indeed in dilute solutions or in the gas phase. This behaviour suggests that they might be A_2 fundamentals, becoming allowed in the condensed phases through intermolecular interactions. The bands are found at 1085 and 798 cm^{-1}, and they can be assigned, under this assumption, to the CH_2 rock (1085) and CH_2 twist vibrations (798) of A_2 symmetry. There are Raman bands at 1057 and 817 cm^{-1} (broad) which may correspond to these IR bands. Shifts of this order of magnitude between IR- and Raman-allowed components of bands in solid-phase spectra are by no means unusual,

and are consistent with the postulation of significant intermolecular coupling in the condensed phases.

(3). *Assignment of vibrations of $Fe(CO)_4$ and of $(C_2H_4)-Fe-(CO)_4$*

The vibrational spectrum of $Fe(CO)_5$ has never been completely and unambiguously assigned (except in the C–O stretching region), although it has been studied very frequently[18-25]. The assignment of most of the vibrations is quite definite, however, and will be of some use in the present analysis, as will Butler and Spendjian's study[26] of the $v(CO)$ region in *cis*-$Fe(CO)_4X_2$ (X = I, Br), which possesses an $Fe(CO)_4$ fragment of C_{2v} symmetry. The four predicted C–O stretching vibrations $(2A_1 + B_1 + B_2)$ are all IR active, and four bands are observed in the gas-phase IR spectrum, and in dilute solutions, at 2095, 2020, 2003 and 1988 cm^{-1} (all strong to very strong). The solid phase Raman spectrum contains 3 $v(CO)$ bands, at 2021 (weak), 1991 (strong), 1975 (medium) cm^{-1}. The highest-frequency band (2095 cm^{-1}) is assigned to the A_1 (all in-phase) C–O stretch, with the band of next highest frequency (2020 cm^{-1}) as the other A_1 mode (equatorial and axial C–O stretches out-of-phase). The common observation that for totally symmetric $v(C-O)$ vibrations the Raman bands are rather weak (contrary to the position for most other vibrations) supports these assignments which are also consistent with those for $Fe(CO)_5$[23-25]. The two remaining bands are clearly the B_1 and B_2 modes, but there is almost no evidence upon which to base an assignment. In *cis*-$Fe(CO)_4Br_2$, the B_1 and B_2 modes are at 2083 and 2060 cm^{-1} respectively[26], and we can therefore assign tentatively the 2003 cm^{-1} band as B_1, the 1988 cm^{-1} as B_2.

The $v[Fe-(CO)]$ vibrations are also four in number, and they will be found in the region 400–500 cm^{-1}, with the $Fe-(C_2H_4)$ stretching and tilting vibrations at a slightly lower frequency. Strong Raman bands at 443 and 427 cm^{-1} can be assigned to the 2 $v[Fe-(CO)]$ of A_1 symmetry (there are medium to strong IR bands clearly analogous to these). A weaker Raman band at 485 cm^{-1} may be assigned to one of the remaining $Fe-(CO)$ stretches (IR band at 488 cm^{-1}), with the last one corresponding to an IR band at 470 cm^{-1} (with no Raman counterpart). There is at present no evidence which could be used to assign these to the individual B_1 and B_2 modes. Symmetric M–(π-hydrocarbon) stretching modes generally give very strong Raman bands[9-13,27-29] in the region 300–400 cm^{-1}. Thus, a strong Raman band at 361 cm^{-1} can be assigned to $v[Fe-(C_2H_4)]$ of A_1 symmetry. The two remaining vibrations expected in this region are the B_1 and B_2 symmetry $Fe-(C_2H_4)$ tilts, which can be assigned to the IR bands at 401 cm^{-1} (medium strong with a Raman band at 393 cm^{-1}) and 305 cm^{-1} (weak, no Raman counterpart).

The Fe–C–O deformations will be situated between 500 and 700 cm^{-1}, and they will be much stronger in the IR than in the Raman spectrum. No Raman bands were seen in this region, although 4 IR bands could be detected. As there are 6 IR active Fe–C–O deformations expected for this model, a complete assignment cannot be made, and individual assignments must be largely arbitrary.

The skeletal deformation modes, below 150 cm^{-1}, were not observed, nor was any band which could be attributed to the $Fe-(C_2H_4)$ torsion, which is of A_2 symmetry.

REFERENCES

1 J. CHATT AND L. A. DUNCANSON, *J. Chem. Soc.*, (1953) 2939.
2 H. B. JONASSEN AND J. E. FIELD, *J. Amer. Chem. Soc.*, 79 (1957) 1275.
3 D. B. POWELL AND N. SHEPPARD, *Spectrochim. Acta*, 13 (1958) 69.
4 D. B. POWELL AND N. SHEPPARD, *J. Chem. Soc.*, (1960) 2519.
5 S. I. SHUPACK AND M. I. ORCHIN, *Inorg. Chem.*, 3 (1964), 374.
6 M. J. GROGAN AND K. NAKAMOTO, *J. Amer. Chem. Soc.*, 88 (1966) 5454.
7 J. PRADILLA-SORZANO AND J. P. FACKLER JR., *J. Mol. Spectrosc.*, 22 (1967) 80.
8 M. J. GROGAN AND K. NAKAMOTO, *J. Amer. Chem. Soc.*, 90 (1968) 918.
9 J. HIRAISHI, *Spectrochim. Acta, Part A*, 25 (1969) 749.
10 G. DAVIDSON AND E. M. RILEY, *J. Organometal. Chem.*, 19 (1969) 101.
11 G. DAVIDSON, *Inorg. Chim. Acta*, 3 (1969) 596.
12 G. DAVIDSON AND E. M. RILEY, *Spectrochim. Acta, Part A*, 27 (1971) 1649.
13 D. C. ANDREWS AND G. DAVIDSON, *J. Chem. Soc. A*, in press.
14 H. D. MURDOCH AND E. WEISS, *Helv. Chim. Acta*, 46 (1963) 1588.
15 G. L. CARLSON, *Spectrochim. Part A*, 24 (1968) 1519.
16 M. I. DAVIS AND C. S. SPEED, *J. Organometal. Chem.*, 21 (1970) 401.
17 N. SHEPPARD, unpublished observations, presented at the 2nd Int. Raman Conf., Oxford, 1970.
18 F. T. KING AND E. R. LIPPINCOTT, *J. Amer. Chem. Soc.*, 78 (1956) 4192.
20 H. STAMMREICH, O. SALA AND Y. TAVARES, *J. Chem. Phys.*, 30 (1959) 856.
21 R. S. MCDOWELL AND L. H. JONES, *J. Chem. Phys.*, 36 (1962) 3321.
22 W. F. EDGELL, W. E. WILSON AND R. SUMMITT, *Spectrochim, Acta*, 19 (1963) 863.
23 L. H. JONES AND R. S. MCDOWELL, *Spectrochim. Acta*, 20 (1964) 248.
24 G. BOR. *Inorg. Chim, Acta*, 3 (1969) 191.
25 M. BIGORGNE, *J. Organometal. Chem.*, 24 (1970) 211.
26 I. S. BUTLER AND H. K. SPENDJIAN, *J. Organometal. Chem.*, 18 (1969) 145.
27 I. J. HYAMS, R. T. BAILEY AND E. R. LIPPINCOTT, *Spectrochim. Acta, Part A*, 23 (1967) 273.
28 J. R. DURIG, A. L. MARSTON, R. B. KING AND L. W. HOUK, *J. Organometal. Chem.*, 16 (1969) 425.
29 D. M. ADAMS AND A. SQUIRE, *J. Chem. Soc. A*, (1970) 814.