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VIBRATIONAL SPECTRA OF AND BONDING IN (CYCLOBUTADIENE)IRON TRICARBONYL

D. C. ANDREWS AND G. DAVIDSON
Department of Chemistry, University of Nottingham, Nottingham NG7 2RD (Great Britain)

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SUMMARY

The vibrational spectrum of (cyclobutadiene)iron tricarbonyl is reported and assigned. This is the first reported detailed description of the vibrations of an unsubstituted, π-complexed cyclobutadiene ring.

INTRODUCTION

The free cyclobutadiene molecule exists only as a transient species, and calculations suggest[1] that it is a rectangular molecule, with alternate single and double bonds. X-ray studies on (tetraphenylcyclobutadiene)iron tricarbonyl[2], and electron-diffraction investigations of $(C_4H_4)Fe(CO)_3$[3,4] show, however, that the C_4-ring π-bonded to a transition metal is square, with, therefore, extensive electron delocalisation around the ring. Furthermore, the cyclobutadiene system in such complexes possesses many aromatic properties[5].

We report here the first detailed investigation of the vibrational spectrum of a complex containing an unsubstituted C_4H_4 ring π-bonded to a metal. The only previous assignments for a four-membered ring in a π-complex were made, using IR data only, by Fritz[6], for the molecule $[C_4(CH_3)_4NiCl_2]_2$.

EXPERIMENTAL

$(C_4H_4)Fe(CO)_3$ was prepared by the method of Pettit and Henery[7] [from dichlorocyclobutene[8] and $Fe_2(CO)_9$]. Purification was achieved by sublimation *in vacuo*.

IR spectra were run on a Perkin–Elmer 521 (from 4000–300 cm^{-1}), as liquid films or solutions in CCl_4. The instrument was calibrated using known peaks of CH_4, HBr, CO, H_2O and NH_3; the frequencies are all expected to be accurate to ±2 cm^{-1}.

Raman spectra were obtained using a Cary Model 81 spectrometer, with a Spectra-Physics 125 He–Ne laser as excitation source (output approximately 60 mW at 632.8 nm). Spectra were observed for solid samples, for the pure liquid and for CCl_4 solutions. Samples did not seem to suffer any decomposition over a period of several hours, and the spectra given were reproducible. Liquid samples were held in a capillary tube (i.d. approximately 1 mm). Depolarisation ratios were obtained by rotating the plane of the incident light and passing the scattered light through a polaroid analyser (the capillary cell was calibrated against a one-pass liquid cell which gave accurate ρ values).

RESULTS AND DISCUSSION

The IR and Raman frequencies observed for $(C_4H_4)Fe(CO)_3$ are listed in Table 1, together with the assignments of these frequencies, which will be discussed below.

TABLE 1

VIBRATIONAL SPECTRA AND ASSIGNMENT FOR $(C_4H_4)Fe(CO)_3$
All figures in cm^{-1}.

IR			Raman		Assignment
Liq. film	CCl_4 soln.	Solid	Liq. film	CCl_4 soln.	
3130 w			3134 w, dp.		C–H str. (A_1+B_1+E)
			2908 w, pol.		
2640 w					
2560 w					
2518 w					
2470 w					
2358 m					
2265 w					
2045 vs	2052 s	2041 m 2033 m	2051 m, pol.	2051 m, pol.	C–O str. (A_1)
1965 vs	1971 s	1990 m 1979 m 1953 s 1936 m	1979 s, dp.	1976 s, dp.	C–O str. (E)
1325 s		1329 w 1319 w	1330 m, dp.		C–C str. $(E+?B_2)$
1232 s		1235 m	1235 s, pol.	1231 m, pol.	C–C str. (A_1)
1172 w (br)					
1015 w					
975 m					i.p.[a] C–H def. (E)
			964 m, dp.		i.p. C–H def. (B_2)
			957 (sh).	958 w, dp.	i.p. ring def. (B_1)
937 s			940 m, dp.		o.o.p.[b] C–H def. (E)
822 s			825 m, pol.		o.o.p. C–H def. (A_1)
775 w			774 w		o.o.p. C–H def. (B_1)
610 vs	610 m		612 w, pol.		Fe–C–O def. (A_1)
			606 w, ?dp.		
585 vs	588 m				Fe–C–O def. (E)
511 s	510 w	513 m	514 m, dp.		Fe–(CO) str. (E)+ Fe–C–O def. (E)
			506 m, dp.		o.o.p. ring def. (B_1)
470 s	470 w	469 m	472 m, dp.		Ring tilt (E)
			431 s, pol.		Fe–(CO) str. (A_1)
396 m		403 s	399 s, pol.	394 s, pol.	(Ring)–Fe str. (A_1)
			135 w, ?pol.	131 w, ?pol.	C–Fe–C def. (A_1)
			104 s, dp.	112 s, dp.	C–Fe–C def. (E)
			94 s, dp.		(Ring)–Fe $(CO)_3$ def. (E)

[a] In-plane. [b] Out-of-plane.

Vibrational analysis

The electron-diffraction results of Davis and Speed[4] indicate that there is only a very low barrier to the rotation of the C_4H_4 ring with respect to the $Fe(CO)_3$ moiety. Consequently it seems reasonable to attempt an assignment of the observed spectra in terms of the "local symmetry" of the (C_4H_4)–Fe (C_{4v}) and $Fe(CO)_3$ (C_{3v}) fragments.

For the (C_4H_4)–Fe unit, we expect the following numbers and types of vibration (C_{4v}):

(a) C–H stretching: A_1+B_1+E
(b) C–C (ring) stretching: A_1+B_2+E
(c) In-plane ring deformation: B_1
(d) Out-of-plane ring deformation: B_1
(e) In-plane C–H deformation: A_2+B_2+E
(f) Out-of-plane C–H deformation: A_1+B_1+E
(g) Ring–Fe stretching: A_1
(h) Ring tilt: E
(i) Ring torsion: A_2

(N.B. In systems of C_{4v} symmetry, only A_1 and E modes are IR-active, while A_2 modes are totally inactive. Thus A_1, B_1, B_2 and E are Raman-active, with A_1 giving polarised bands.)

For the $Fe(CO)_3$ unit (C_{3v}) we expect:

(a) C–O stretching: A_1+E
(b) Fe–(CO) stretching: A_1+E
(c) Fe–C–O deformation: A_1+A_2+2E
(d) C–Fe–C deformation: A_1+E
and, in addition:
(e) (Ring)–Fe–$(CO)_3$ deformation: E

(All of these vibrations will be IR- and Raman-active, except those of A_2 symmetry.)

Assignment of frequencies to the (C_4H_4)–Fe unit

Only one band was observed in the region associated with ν(C–H) vibrations of an aromatic C_nH_n ring, at 3130 cm^{-1} (IR) and 3134 cm^{-1} (R, dp.). This must, therefore, be assigned to the A_1, B_1 and E C–H stretching vibrations. It compares very closely with, *e.g.* the two ν(C–H) bands found for $(C_5H_5)V(CO)_4$[9], at 3128 cm^{-1} and 3110 cm^{-1}.

In π-bonded cyclopentadienyl and arene ligands the totally symmetric "ring-breathing" C–C stretch is found at ~1100 cm^{-1} (for $C_5H_5^-$, *e.g.* ref. 10) and at ~1000 cm^{-1} (for C_6H_6, *e.g.* refs. 11, 12). The difference may perhaps be ascribed to the greater number of π-electrons involved per C–C bond in the 5-membered ring system, and so we might expect to find the C_4H_4 ring (with 4 π-electrons) giving a ring-breathing vibration ~1000 cm^{-1}. Such vibrations generally give rise to intense, strongly polarised Raman bands, however, and no such bands were observed in the 1000 cm^{-1} region. There was a band of this type at 1233 cm^{-1}, and we assign this to the A_1 C–C stretch. It remains to consider the reason for the high value for this frequency; a likely explanation appears to be connected with the strain present in such a small ring, which makes a simultaneous increase or decrease of all 4 C–C bonds a matter of some difficulty.

Two Raman bands, one having a coincident IR band, due to the antisymmetric ring stretches should be observed, but only one is seen in each spectrum, at 1327 cm^{-1} (depolarised in the Raman spectrum). This can be assigned certainly to the E mode, leaving the B_2 mode (Raman-active only) unobserved, unless it is coincident with the former.

C–H deformation vibrations in the plane of the C_4 ring (B_2+E) would be expected to occur at higher frequencies than those perpendicular to it (A_1+B_1+E). There should be only one polarised Raman line and in the region 700–1000 cm^{-1} only one is found, at 825 cm^{-1}, with a strong IR band at 822 cm^{-1}. This is therefore assigned to the A_1 out-of-plane C–H deformation. Two definite IR bands, at 975 cm^{-1} (no Raman counterpart) and at 937 cm^{-1} (depolarised Raman band at 940 cm^{-1}) must be E modes. On the basis that in-plane C–H deformations usually occur at higher frequencies, the former is assigned thus, leaving the 938 cm^{-1} band as the out-of-plane mode. The two remaining C–H deformations are Raman active only, and three bands are possible candidates for these (with the third as an in-plane ring deformation, see below). The assignments for these bands are a little arbitrary, but the following appears to be the most reasonable: 964 cm^{-1} (B_2, in-plane C–H deformation); 774 cm^{-1} (B_1, out-of-plane C–H deformation, there is a weak IR counterpart to this band, due either to a slight breakdown in C_{4v} selection rules or, more likely, to an overtone, 2 x 396 — see below).

The final Raman band in this region (which has no IR counterpart) is at 957 cm^{-1}, and it is assigned as the B_1 in-plane ring deformation. The out-of-plane ring deformation (B_1) is usually found at a much lower frequency[10], and in this case it is assigned to a depolarised Raman band at 506 cm^{-1}.

We must now consider the vibrations associated with the (C_4H_4)–Fe unit as a whole. There are three such modes, and one (the A_2 ring torsion) is totally inactive. Of the remaining two, the symmetric (Ring)–Fe stretch (A_1) can be assigned quite confidently to the strong, polarised Raman line at 399 cm^{-1} (medium intensity IR analogue). This is in agreement with observed (Ring)–M stretches for (C_5H_5)–M[10,13] and (C_6H_6)–M[11,14,15] systems. The frequency is appreciably greater than in (hydrocarbon) iron tricarbonyl complexes which contain less symmetrical organic fragments *e.g.* (butadiene)iron tricarbonyl, (351 cm^{-1})[16] and (cyclo-octatetraene)iron tricarbonyl (330 cm^{-1})[17], indicating that perhaps the cyclobutadiene ring can form quite a strong bond to the Fe atom. The ring tilting vibration generally occurs at a higher frequency than the (Ring)–M stretch, and the most reasonable assignment is to a depolarised Raman line of medium intensity at 472 cm^{-1} (strong IR band at 470 cm^{-1}).

Assignment of frequencies to the Fe(CO)$_3$ unit

In this section published data on other (hydrocarbon)iron tricarbonyl complexes[16,17] will be of some assistance in the assignment. As we are assuming that the local symmetry of C_{3v} will be sufficient, there should be just two C–O stretching modes (A_1+E). The symmetric stretch must correspond to the strong polarised Raman E_1 1975 (IR; R, depol.). These are very similar to the frequencies found for the butadiene[16] and cyclo-octatetraene[17] complexes.

Two Fe–(CO) stretches should also be found in the 350–500 cm^{-1} region (A_1+E). The symmetric stretch must correspond to the strong polarised Raman line at 431 cm^{-1} (no observed IR analogue), while the degenerate stretch is assigned to a depolarised Raman band at 514 cm^{-1} and a strong IR band at 511 cm^{-1}. These are significantly higher in frequency than the analogous vibrations in (butadiene)iron tricarbonyl: 379 cm^{-1} and 460 cm^{-1}.

It is generally difficult to obtain a complete and unambiguous assignment of individual M–C–O deformations (~500–700 cm^{-1}). For C_{3v} $Fe(CO)_3$ there should be 4 such vibrations, but one (A_2) is inactive. This leaves A_1+2E: the symmetric deformation must give rise to the very strong IR band at 610 cm^{-1}, for the Raman equivalent (612 cm^{-1}), although weak, is definitely polarised. One Fe–C–O deformation of E symmetry is found at 585 cm^{-1} (IR, very strong; no Raman), and the other is apparently coincident with the Fe–(CO) stretch of E symmetry (511 cm^{-1} in the IR). There remains in this region a weak, probably depolarised Raman band at 606 cm^{-1}. This could conceivably be the A_2 deformation (formally forbidden), or alternatively it may be a combination band (*e.g.* $514+94=608$).

The only fundamental vibrations yet to be considered are the two C–Fe–C deformations (A_1+E) and one deformation of the whole (C_4H_4)–Fe–$(CO)_3$ molecule (E). These are to be expected below ~150 cm^{-1}. No IR data were available in this region, but three Raman bands were observed. That at highest frequency (135 cm^{-1}) is weak, but almost certainly polarised. This is assigned to the A_1 C–Fe–C deformation. The other two bands (104, 94 cm^{-1}) are much stronger, and definitely depolarised. These are clearly the required two E modes; that at higher frequency will, by analogy with previous assignments, correspond to the C–Fe–C deformation, leaving the 94 cm^{-1} band as the (C_4H_4)–Fe–$(CO)_3$ deformation.

CONCLUSION

The first detailed observations on the vibrational spectrum of a π-bonded, unsubstituted cyclobutadiene system have been made, and an almost complete assignment of the vibrations of the (C_4H_4)–Fe unit of $(C_4H_4)Fe(CO)_3$ carried out (see

TABLE 2

ASSIGNMENT OF FREQUENCIES FOR $(C_4H_4)Fe$ IN $(C_4H_4)Fe(CO)_3$
C_{4v} symmetry; all figures in cm^{-1}.

C–H stretching:	A_1	3132
	B_1	
	E	
Ring stretching:	A_1	1234
	B_1	?1327
	E	1327
In-plane ring deformation:	B_1	957
Out-of-plane ring deformation:	B_1	506
In-plane C–H deformation:	A_2	not observed
	B_2	964
	E	975
Out-of-plane C–H deformation:	A_1	824
	B_1	774
	E	939
(Ring)–Fe stretching:	A_1	398
Ring tilt:	E	471
Ring torsion:	A_2	not observed

TABLE 3

ASSIGNMENT OF FREQUENCIES FOR $Fe(CO)_3$ AND $(C_4H_4)Fe(CO)_3$ IN $(C_4H_4)Fe(CO)_3$
C_{3v} symmetry; all figures in cm^{-1}.

C–O stretching:	A_1	2051
	E	1979
Fe–(CO) stretching:	A_1	431
	E	513
Fe–C–O deformation:	A_1	611
	A_2	Not observed
	E	585
	E	513
C–Fe–C deformation:	A_1	135
	E	104
(Ring)–Fe–(CO)$_3$ deformation:	E	94

Table 2). The (C_4H_4)–Fe stretching frequencies indicate that there is a strong bonding interaction between the ring and the metal. The vibrational frequencies of the $Fe(CO)_3$ fragment are similar to those of other (hydrocarbon)$Fe(CO)_3$ systems (Table 3).

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