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Determination of the Barrier to Rotation of the Cyclobutadienyl Ring in Solid Tricarbonyl(η-cyclobutadienyl)iron(0), $(\eta\text{-C}_4\text{H}_4)\text{Fe(CO)}_3$, from Proton Spin–Lattice Relaxation Time Measurements and Vibrational Spectra

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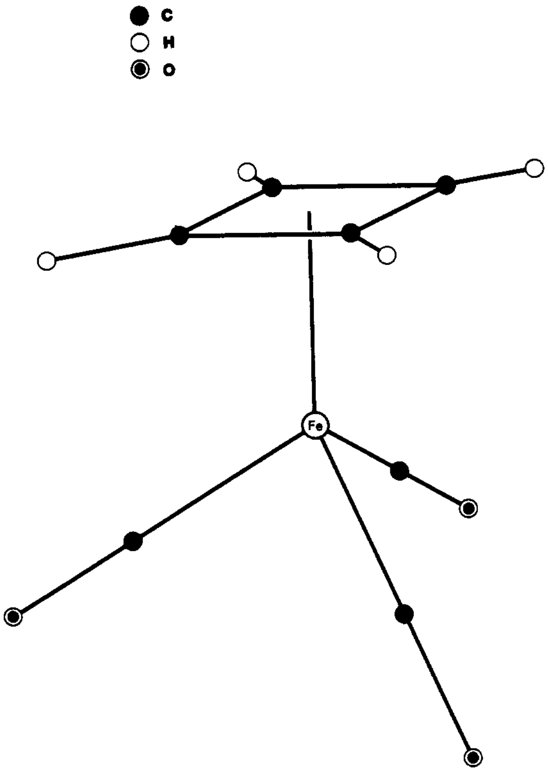
Proton spin–lattice relaxation time measurements on solid tricarbonyl(η-cyclobutadienyl)iron(0), $(\eta\text{-C}_4\text{H}_4)\text{Fe(CO)}_3$, can be interpreted in terms of two relaxation processes arising from two inequivalent lattice sites, while low-temperature FT-IR and Raman spectroscopic studies suggest that there are at least four molecules present in the unit cell. The activation energies for ring rotation from the T_1 measurements are 15.2 and 22.1 kJ mol^{-1}. The corresponding values from the Raman data, assuming a simple torsional oscillator model, are temperature dependent and range from 13.9 to 16.4 and 15.1 to 19.1 kJ mol^{-1} on going from 50 to 10 K.

Introduction

The detailed structures and conformation of the aromatic rings in π-arene organometallic complexes have been the subject of several recent theoretical studies.[1-3] Chinn and Hall[1,2] have proposed that the bond lengths in the arene ring depend upon the conformation such that bonds eclipsed by a carbonyl group are longer than those that are trans. Thus the ring structures do not possess the ideal symmetries of a square, pentagon, or hexagon, etc. Since the internal barriers to rotation in complexes of the general form $C_nH_nM(CO)_m$ are very low[3] (except for (benzene)chromium tricarbonyl), the testing of such theories requires extremely careful X-ray crystallographic studies[4,5] to determine small distortions of molecules that exhibit large torsional motions. It is useful, therefore, to know the barriers to rotation in the solid state, i.e., to gain information on the molecular dynamics as well as the structure.

We have reported previously on studies of the barriers to ring rotation of the cyclopentadienyl ring in various different environments, measured from the temperature dependence of the proton spin–lattice relaxation times,[6-8] and in related studies, Chhor and Lucazeau[9-11] have used Raman and infrared spectroscopic methods to derive torsional barrier heights. In the present work, we describe the proton spin–lattice relaxation and vibrational spectroscopic results for the cyclobutadienyliron tricarbonyl complex, $(\eta\text{-C}_4\text{H}_4)\text{Fe(CO)}_3$. This complex is expected, on theoretical grounds,[2] to be distorted, but the available information on the structure of the unsubstituted complex, although it is the parent compound of the series, is limited. There are early electron diffraction[12,13] and microwave[14] spectroscopic studies of the vapor phase, but the crystal structure has not been reported. Several investigations of the partially oriented NMR spectrum in nematic liquid crystal solvents have been described, of which two are specifically concerned with the ring distortion.[15,16]



$(\eta\text{-C}_4\text{H}_4)\text{Fe(CO)}_3$

Experimental Section

$(\eta\text{-C}_4\text{H}_4)\text{Fe(CO)}_3$ was obtained from Strem Chemical Co., and was purified by slow sublimation in the dark at room temperature (10^{-3} torr). Samples were stored in sealed vials under either vacuum or inert atmosphere (N$_2$ or argon) and kept in the dark and refrigerated when not in use.

Proton spin–lattice relaxation times were measured at 33 MHz by using the inversion recovery method on a Spin-Lock CP2 pulse spectrometer. The sample temperature was controlled by a flow of cooled N$_2$ gas, and the temperature was measured with a digital thermocouple. Raman spectra were recorded on an Instruments S.A. spectrometer equipped with a Jobin-Yvon U-1000 1.0-m double monochromator and a Columbia Data Products minicomputer. A Spectra Physics Model 164 argon ion laser (514.5-nm line, about 15–70 mW at the samples) was used for excitation, and the observed frequencies were calibrated against a standard neon lamp (accuracy ±0.2 cm^{-1}).

Variable-temperature measurements were made with either a Cryodyne Cryocooler (Cryogenics Technology Inc., Model 21) or a Displex cryostat. Irradiation with more than 50 mW of laser power at room temperature led to sample decomposition. Infrared spectra were mea-

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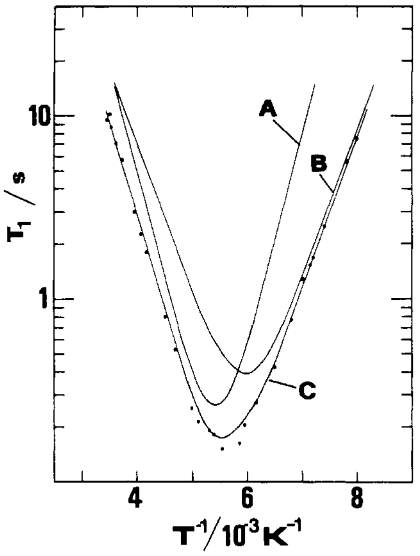

Figure 1. Variation of proton spin-lattice relaxation time T_1 with reciprocal temperature (K^{-1}) for solid $(\eta\text{-}C_4H_4)Fe(CO)_3$. A and B are the calculated curves of processes 1 and 2; C is the best fit for the summation of curves A and B.

Table I. Comparison of Barriers for Ring Rotation in (η-Arene)metal Tricarbonyl Complexes

complex	E_a, kJ mol^{-1}	ref	V_0, kJ mol^{-1}	ref
$(\eta\text{-}C_4H_4)Fe(CO)_3$				
process 1	15.2	*a*	13.9	*a*
process 2	22.1	*a*	15.1	*a*
$(\eta\text{-}C_5H_5)Mn(CO)_3$	7.2	8	9.5	9
$(\eta\text{-}C_5H_5)Re(CO)_3$	7.2	8		
$(\eta\text{-}C_6H_6)Cr(CO)_3$	17.6	18	19.6	18
$[(\eta\text{-}C_7H_7)Cr(CO)_3]^+$	12.8	19		
$[(\eta\text{-}C_7H_7)Mo(CO)_3]^+$	13.6	19		

[a] This work.

sured on a Nicolet 6000 FT-IR spectrometer using a mercury-cadmium-telluride detector (accuracy ±0.2 cm^{-1}). The samples were cooled by a cold N_2 gas flow to 225 K. The temperature control in all measurements was ±1 K.

Results and Discussion

Spin-Lattice Relaxation Measurements. For a single relaxation process, the spin-lattice relaxation time, T_1, is given by eq 1, where

$$1/T_1 = \tfrac{2}{3}C\tau[1/(1 + \omega^2\tau^2) + 4/(1 + 4\omega^2\tau^2)] \qquad (1)$$

$\tau = \tau_0 \exp(E_a/RT)$, E_a is the activation energy, ω is the resonance frequency (in rad s^{-1}), and C is a constant.

This equation gives a V-shaped curve when ln T_1 is plotted vs. reciprocal temperature. However, the low- and high-temperature sides of the experimental curve have different slopes (Figure 1), and it was not possible to fit the results by using a single relaxation process. We therefore assume that there are two crystallographically inequivalent lattice sites such that there is a different activation energy for ring rotation associated with each site. The observed T_1 behavior is thus due to two overlapping curves with minima quite close together. A fit obtained by using a SIMPLEX procedure gave consistent results for two barrier heights, but the τ_0 and C values are highly correlated and only approximate values for these parameters could be obtained. The values, however, are reasonable ($\tau_0 = 4.1 \times 10^{-14}$ and 1.7×10^{-15} s; $C = 5.5 \times 10^8$ and 8.3×10^8 rad^2 s^{-2}) and are closely similar to those for other η-arene metal complexes.[8]

In Table I, the measured barriers are compared for the metal tricarbonyl derivatives of different arene ring sizes. Since there is no internal barrier to rotation for the C_4, C_5, and C_7 complexes, these measured barriers reflect the local packing around the arene ring. In the case of the (benzene)chromium derivative, where an internal barrier does occur,[8,17,18] the different contributions to the total barrier have been estimated from atom–atom potential calculations,[8] and the intermolecular barrier is about 14 kJ mol^{-1}. Clearly, the crystal packing in $(\eta\text{-}C_4H_4)Fe(CO)_3$ is such that the barrier to rotation is much higher in this case than for the larger rings. This observation is encouraging in that the torsional amplitudes of the ring should be reduced compared with, for instance, those of the cyclopentadienylmetal tricarbonyls. A study of the crystal structure, particularly at low temperature, should reveal the expected distortion of the cyclobutadienyl ring.

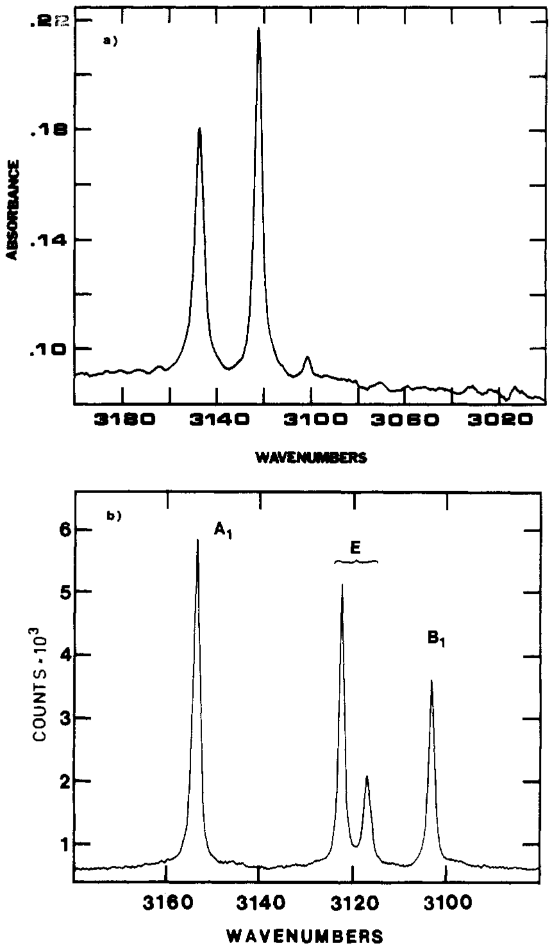

Figure 2. Vibrational spectra of solid $(\eta\text{-}C_4H_4)Fe(CO)_3$ in the ν(C-H) region: (a) FT-IR spectrum at 225 K, 300 scans, 1-cm^{-1} resolution; (b) Raman spectrum at 50 K, 514.5-nm excitation (70 mW), 110-μm slits, 1 scan, 10 s point^{-1}, 0.4 cm^{-1} steps.

Vibrational Spectra. On the basis of the spin-lattice relaxation studies, we assumed that there must be inequivalent lattice sites in the crystal leading to different local potential energy surfaces for ring rotation. Splittings of the vibrational peaks can occur since the spectra in the solid state reflect not only the molecular symmetry but also the site and crystal symmetries. Furthermore, if it is possible to assign the torsional modes, then a barrier height for a torsional oscillator can be obtained and compared with the values obtained by NMR methods.

The vibrational spectra for $(\eta\text{-}C_4H_4)Fe(CO)_3$ for the liquid, solution, and solid states have been reported by several groups.[20-22] In the present study, no significant changes in the Raman spectra were observed between room temperature and 10 K, confirming the absence of any phase change. However, the Raman spectra do show considerable sharpening of the peaks, especially in the

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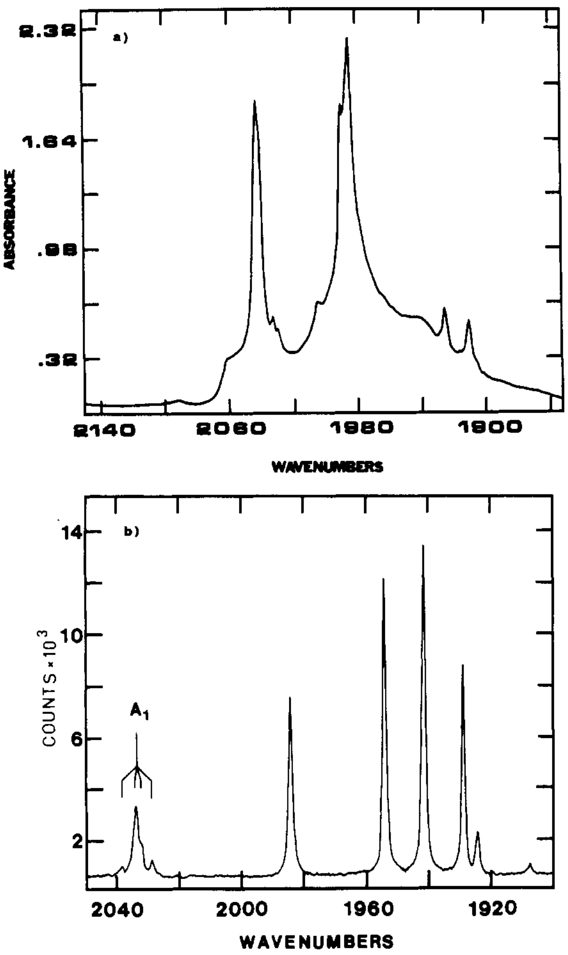

Figure 3. (a) FT-IR and (b) Raman spectra of solid (η-C$_4$H$_4$)Fe(CO)$_3$ in the ν(CO) region. Same experimental conditions as in Figure 2.

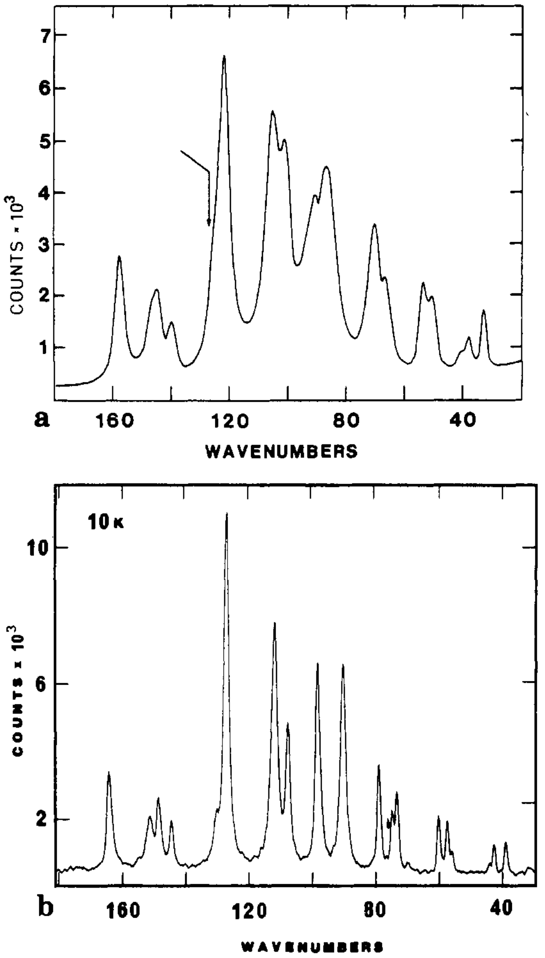

Figure 4. Low-frequency Raman spectra of solid (η-C$_4$H$_4$)Fe(CO)$_3$. Conditions: (a) see Figure 2; (b) 10K, 514.5-nm excitation (65 mW), 60-μm slits, 1 scan, 25 s point^{-1}, 0.2-cm^{-1} steps.

lattice region at 10 K, indicating perhaps a decrease in torsional motion with decreasing temperature. Since there are some differences between the results obtained in the present work and the previous assignments given by Aleksanyan and Nefedova,[22] our complete assignments are presented in Table II. FT-IR and Raman spectra for solid (η-C$_4$H$_4$)Fe(CO)$_3$ in the ν(C–H) and ν(CO) regions are shown in Figures 2 and 3.

The normal modes for isolated (η-C$_4$H$_4$)Fe and Fe(CO)$_3$ moieties can be assigned on the basis of C_{4v} and C_{3v} local symmetries, respectively. The C–H vibrations transform as a$_1$(IR/R) + e(IR/R) + b$_1$(R) and the two CO stretches as a$_1$(IR/R) + e(IR/R). In the solid state, the degeneracies of the e modes may be lifted and any previously inactive modes may now become active due to site and factor group symmetry effects.

In the Raman spectra of solid (η-C$_4$H$_4$)Fe(CO)$_3$, the e ν(C–H) mode (ν_{14}) is clearly split into a doublet, while in the infrared an unresolved shoulder appears and a peak attributable to the b$_1$ ν(C–H) mode (ν_{11}) is evident. Despite the difference in temperature for the two measurements (IR 77 K; Raman 50 K), the band positions of the e and b$_1$ modes in the Raman and infrared spectra correspond well, but there is a 7-cm^{-1} difference for the a$_1$ mode (ν_1).

The ν(CO) region shows more peaks in both the infrared and Raman than the two (a$_1$ + e) predicted for the isolated Fe(CO)$_3$ moiety. The a$_1$ mode (ν_{18}) is split into four and the e mode (ν_{23}) into at least six components, suggesting a minimum of four molecules per unit if these splittings are due to factor group effects alone. There are no significant differences in the Raman spectra recorded at 50 and 10 K, and the correspondence between the infrared data obtained at 77 K and the Raman spectra is quite good. It is clear that there is no phase change over the temperature range investigated. The overall splitting of the e ν(CO) mode (ca. 70 cm^{-1}) is much larger than the values reported for both (η-C$_5$H$_5$)Mn(CO)$_3$[23] and (η-C$_5$H$_5$)Re(CO)$_3$[24] (ca. 40 cm^{-1}) and for (η-C$_6$H$_6$)Cr(CO)$_3$[25] (ca. 20 cm^{-1}), which have four and two molecules per unit cell, respectively. This distinct difference in splitting behavior for (η-C$_4$H$_4$)Fe(CO)$_3$ may possibly be due to inequivalent lattice sites as suggested by the NMR measurements.

In the low-energy region (160–80 cm^{-1}), the internal Raman-active modes are drastically split, the e modes (ν_{27} and ν_{28}) into four components and the a$_1$ mode (ν_{21}) into two (Figure 4). In the region below 80 cm^{-1}, we were unable to reproduce the spectra obtained at 77 K by Howard and Waddington;[26] in particular, the peaks at 7, 17, and 60 cm^{-1} were not observed in our 50 K study. Accordingly, we have reassigned the torsional mode(s) from 60 cm^{-1} to the peaks appearing at 70.4 and 67.5 cm^{-1} in the 50 K spectrum, which are absent in the Raman spectrum of the liquid. These two torsion modes are highly temperature sensitive, shifting to 79.4 and 73.4 cm^{-1}, respectively, at 10 K. The weaker peak appearing at 75.0 cm^{-1} in the 10 K spectrum is most probably attributable to a translationary mode. The complete Raman data for the low-energy region (170–35 cm^{-1}) are compared in Table III.

The torsional barrier is composed of contributions from intra- and intermolecular sources. In molecules of the type C$_n$H$_n$M(CO)$_3$, the internal barrier is zero, or very small, so that motions of the halves of the molecule are uncorrelated. However, the

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Table II. Vibrational Spectral Data (cm^{-1}) of Solid (η-C_4H_4)Fe(CO)$_3$

IR (225 K)	Raman (50 K)[a]	proposed assignts[b]
3147 w	3154 m	a_1 C–H str, ν_1
3123 w	3123 m	e C–H str, ν_{14}
	3117 mw	
3102 vw	3103 m	b_1 C–H str, ν_{11}
2099 vw		ν(CO) + latt modes
2091 vw		
2068 m, sh		
2043 vs	2039 w	a_1 CO str, ν_{18}
2039 s, sh	2036 m (2036.2 mw)	
2033 m[c]	2035 m, sh (2035 m, sh)	
2031 m, sh	2031 w (2031.1 w)	
2021 w		combinations and $\nu(^{13}CO)$
2005 m, sh		
1991 s		
1986 vs	1988 s (1987.3 s)	e CO str, ν_{23}
	1957 vs (1957.3 vs)	
1940 br, m	1944 vs (1943.8 vs)	
	1931 s (1930.9 s)	
1927 m	1927 mw (1927 mw)	
1917 w[c]		
1912 m	1908 w	
1903 w		combinations
1702 vw		
1656 vw		
1628 vw		
1574 w		
1549 wm		
1498 w		
1385 w		
1365 vw		
1324 m	1326 w	e ring str, ν_{15}
1315 vw	1302 w	b_2 ring str, ν_7
1310 vvw		
1235 m	1235 w	a_1 ring str, ν_2
1224 m	1224 vw	
1157 vw		
	1136 vw	a_2 ip C–H def, ν_5[c]
1113 vw		
1074 vw		
1022 w		
984 w		e ip C–H def, ν_{16}
970 vw		
	958 vw, sh	
952 mw	954 w	b_1 ip ring def, ν_{12}
	951 w, sh	
944 w, sh		
937 mw	937 w	b_2 ip C–H def, ν_8
932 mw	931 w	
897 vw		
874 vw		
854 w	859 vw	b_1 oop C–H def, ν_9
847 vw		
	834 w	
823 mw, br		e oop C–H def, ν_3
	794 w	e oop C–H def, ν_{13}
779 w, sh		
777 wm	774 w	
	769 vw, sh	
642 mw	644 w	e Fe–C–O def, ν_{25}
623 m, sh		a_2 Fe–C–O def, ν_{22}[c]
612 m, sh		a_1 Fe–C–O def, ν_{20}
603 m	606 w	
594 s		e Fe–C–O def, ν_{26}
579 m	586 vw	
567 w, sh		
521 mw		a_2 Fe–C–O def, ν_{22}[c]
515 mw	516 w, sh	Fe–CO str
513 mw	514 m	
470 m	471 m	e Fe–ring tilt, ν_{17}
	468 w, sh	
463 w, sh	463 w	
	443 m	b_1 oop ring def, ν_{10}
427 w	428 m	a_1 Fe–CO str, ν_{19}
	425 m	
405 w	408 vs	a_1 Fe–ring str, ν_4

[a] Data obtained at 10 K for the ν(CO) region are given in parentheses. [b] Nomenclature from ref 23 with minor modifications. [c] Based on calculated values from ref 21.

barrier to rotation of the M(CO)$_3$ moiety in the solid state is very high (over 50 kJ mol^{-1} in the cyclopentadienyl complexes[8]), and so the torsional frequency must arise from the motion of the ring in an intermolecular potential. Assuming that the tricarbonyl group remains fixed, the simple harmonic oscillator approximation can be used to derive the barrier by using eq 2, where I_z is the

$$V_0 = 8\pi^2 c^2 I_z \bar{\nu}^2 / n^2 \qquad (2)$$

moment of inertia of the cyclobutadienyl ring about the principal axis and n is the multiplicity of the barrier. The moment of inertia of the ring was calculated from the structural data given by Davies and Speed[12] to be 1.14 × 10^{-45} kg m^2. With the present assignments of the torsional frequencies and a multiplicity of 4, the calculated torsional barriers are 13.9 and 15.1 kJ mol^{-1} (at 50 K) and 16.4 and 19.1 kJ mol^{-1} (at 10 K), compared with the spin–lattice relaxation time values of 15.2 and 22.1 kJ mol^{-1}.

At this stage, it should be emphasized that the NMR method depends upon the rate at which the cyclobutadienyl ring surmounts the barrier, whereas the torsional frequencies depend upon the shapes of the potential functions near the minima. Furthermore, the torsional frequencies are temperature dependent and the zero-point energies have been neglected. In view of these differences, the agreement between the two types of measurement is surprisingly good. Comparisons of activation energies with potential barrier heights have been discussed by Ratcliffe and Waddington,[27-32] for a variety of systems, with the general conclusion that, for groups with fairly small moments of inertia, such as ammonium or methyl substituents, the torsional potential barriers are generally higher than the NMR activation energies.

Table III. Comparison of the Raman Spectral Data (cm^{-1}) in the 170–35-cm^{-1} Region at 50 and 10 K

50 K	10 K	proposed assignts
157.6 m	164.4 mw	e ring–Fe(CO)$_3$ def, ν_{28}
147.0 w, sh	151.6 w	
145.2 w	148.8 mw	
140.0 w	144.8 w	
126.5 sh	130 sh	e C–Fe–C def, ν_{27}
122.4 s	127.4 vs	
105.2 ms	112.0 ms	
101.0 ms	107.8 m	
91.0 m	98.6 m	a_1 C–Fe–C def, ν_{21}
87.2 m	90.4 m	
70.4 m	79.2 mw	R_z and $R_{z'}$; librational modes
67.5 m	75.0 w	
	73.4 mw	
	70.2 vvw	
53.6 w	60.2 w	R_x and R_y; librational modes
50.4 w	57.6 w	
	55.9 vw, sh	
	44.4 vw, sh	
42.1 w	42.8 vw	translational lattice modes
39.7 w, sh	39.2 vw	
33.2 w		

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In the case of (η-C_4H_4)Fe(CO)$_3$, the reverse situation appears to obtain.

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Matrix Isolation Study of the Fluoride Adduct of Oxalyl Fluoride: Evidence for a Fluorine-Bridged Anion

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The salt/molecule reaction technique, coupled with matrix isolation, was employed to investigate the possible structural isomers of the $C_2F_3O_2^-$ anion, ion paired with a Cs^+ cation. This species was synthesized through the reaction of CsF with oxalyl fluoride; since a gas-phase sample of oxalyl fluoride consists of an equilibrium mixture of cis and trans isomers, two reaction products were observed. Each was characterized by one intense carbon–oxygen stretching mode in the 1450–1500-cm^{-1} region, as well as a single, intense C–F stretch near 900 cm^{-1}. These spectral features are suggestive of a fluorine-bridged structure, a result that is supported by the observation of low-frequency modes near 400 cm^{-1}, which are assigned to the stretching mode of the bridging fluorine for each product ion. CNDO/S calculations suggest a stable local minimum for the bridged anionic form as well. Warming the matrix to room temperature left a solid residue on the window, which was identified as cesium trifluoroacetate. This indicates that the bridged form has limited stability and rearranges at room temperature or below to the more stable $CF_3CO_2^-$ form.

Introduction

The salt/molecule technique has been coupled with matrix isolation on numerous occasions for the synthesis of unusual anionic intermediates.[1-8] The majority of these have been formed through a fluoride ion (F^-) transfer from CsF to a suitable acceptor, forming a fluoride-containing anion. Recently, a thorough gas-phase study[9] of such fluoride-transfer reactions was reported, to extend previous studies in this area.[10-12] One system reported there was the addition of F^- to oxalyl fluoride, $C_2O_2F_2$, which was of particular interest because of three possible structures for the product ion. These included a symmetric bridged form and an unsymmetrical form in which the fluoride interacts with one of the carbons. In addition, rearrangement to the trifluoroacetate anion, $CF_3CO_2^-$, is feasible, although the barrier may well be high. Since these structural isomers can readily be distinguished by infrared spectroscopy and since the salt/molecule technique in conjunction with matrix isolation provides an excellent route to the synthesis of the product anion in a condensed-phase medium, an investigation was undertaken into the reaction products arising from the codeposition of CsF with oxalyl fluoride in argon matrices.

Table I. Comparison of the Stretching Modes of the $C_2F_3O_2^-$ Anions and Related Species

species	ν_{C-O}, cm^{-1}	ν_{C-F}, cm^{-1}	ν_{C-F}(br),[b] cm^{-1}	ref
$C_2F_3O_2^-$ (cis)	1498	980	395	*a*
$C_2F_3O_2^-$ (trans)	1457	881	376	*a*
COF_3^-	1514	808, 930		1
CO_2F^-	1316, 1749	883		2

[a] This work. [b] Stretching mode of the bridging fluorine.

Experimental Section

All of the experiments here were conducted on a typical matrix isolation system, which has been described previously.[13] Oxalyl fluoride (PCR) was introduced into the vacuum system from a lecture bottle and subjected to one or more freeze–thaw cycles prior to dilution in argon to the desired ratio. CsF was loaded into a stainless steel Knudsen cell and outgassed under vacuum for several hours at temperatures slightly below its vaporization temperature of 500 °C. Matrices were then formed through the codeposition of samples of Ar/CO_2F_2 with CsF onto a 14 K cold window. Survey scans were run intermittently during deposition and at the end of the 20–22 h of deposition. High-resolution spectra were recorded over regions of interest, at a resolution of 1 cm^{-1} and an accuracy of about 1 cm^{-1}.

Results and Discussion

An initial blank experiment of oxalyl fluoride in argon with M/R = 500 showed a moderately complex spectrum which could not be interpreted in terms of a single absorber. Rather, the spectra were very similar to that of solid oxalyl fluoride, for which it was concluded that both the cis and trans forms were present upon gas-phase deposition, with relatively more trans than cis.[14] This is particularly apparent in the carbonyl stretching region, where an extremely intense absorption was noted at 1860 cm^{-1} for the trans isomer (the second carbonyl stretch is infrared inactive), and a moderately intense band was noted near 1890 cm^{-1}, for the more intense carbonyl stretch of the cis isomer. In all, the spectra were in good agreement with the literature spectra of a mixture of cis and trans isomers. The codeposition of CsF with a similar sample of Ar/$C_2O_2F_2$ = 500 gave rise to a number of new infrared absorptions, which could not be attributed to either parent species. Two distinct bands of medium intensity were noted at 1457 and 1498 cm^{-1}, while a quite intense, sharp band was noted

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