Table VI. Crystal Field and Racah Parameters for $V(CO)_6$ (cm^{-1})

$10Dq$	Ds	Dt	B	C^a
29 300	1215	365	450	1800

^{a} Estimated value.

Table VII. States Expected for the Charge-Transfer Bands from the e_g and b_{2g} π^* Orbitals to the a_{2u} and e_u σ^* Orbitals

Electron Config'n	Designation
$e_g{}^4 a_{2u}$	$^2A_{2u}$
$e_g{}^3 b_{2g} a_{2u}$	$^2E_u(1)$
$e_g{}^4 e_u$	$^2E_u(2)$
$e_g{}^3 b_{2g} e_u$	$^2A_{1u}, {}^2A_{2u}, {}^2B_{1u}, {}^2B_{2u}$

Table VIII. Tentative Assignments for the Electronic Spectrum of $V(CO)_6$

Transition	λ, nm	$\bar{\nu}$, cm^{-1}	Transition	λ, nm	$\bar{\nu}$, cm^{-1}
$^2E_g(2) \leftarrow {}^2B_{2g}$	388.2	25 758	$^2A_{2u} \leftarrow {}^2B_{2g}$	283.0	35 336
$^2E_g(3) \leftarrow {}^2B_{2g}$	363.0	27 546	$^2E_u(2) \leftarrow {}^2B_{2g}$	269.2	37 147
$^2B_{1g} \leftarrow {}^2B_{2g}$	341.6	29 274	$^2B_{2u} \leftarrow {}^2B_{2g}$	260.0	38 462
$^2E_g(4) \leftarrow {}^2B_{2g}$	341.0^a	29 317^a	$^2B_{1u} \leftarrow {}^2B_{2g}$	242.5	41 237
$^2A_{1g} \leftarrow {}^2B_{2g}$	317.2	31 526	$^2A_{2u} \leftarrow {}^2B_{2g}$	226.0	44 248
$^2E_g(5) \leftarrow {}^2B_{2g}$	312.5	32 000	$^2A_{1u} \leftarrow {}^2B_{2g}$	220.0	45 455
$^2E_u(1) \leftarrow {}^2B_{2g}$	295.4	33 852			

^{a} Calculated value.

From a first-order analysis of the ESR spectrum, Pratt and Meyers[3] have calculated that $10Dq \leq 36\ 200$ cm^{-1} and $3Ds - 5Dt \leq 1880$ cm^{-1}. The proposed assignments were permuted until the calculated crystal field parameters satisfied these limits. These parameters were then tested by calculating the expected d–d spectrum and comparing it to the observed d–d spectrum. The parameters listed in Table VI reproduced the observed spectrum quite well as shown in Figure 4c and satisfied both upper limits for the crystal field parameters. Consequently, these parameters were used to assign the observed d–d spectrum.

Since the photoelectron spectrum of $V(CO)_6$ indicates the ligand bonding molecular orbitals are at least 5 eV lower in energy than are the metallike d orbitals,[2b] the charge-transfer bands are most likely transitions from the b_{2g} and e_g π^* orbitals to the a_{2u} and e_u σ^* orbitals. The states expected for these one-electron transitions are listed in Table VII. Since only the two ^2E_u states and the $^2B_{1u}$ states are electronic dipole allowed, these transitions are expected to give rise to the three strongest bands observed in the spectrum. Using this and the calculated d-orbital energies, tentative assignments for the charge-transfer spectrum have been made. The assignments for all of the observed electronic transitions of $V(CO)_6$ are given in Table VIII.

Conclusions

As expected from previous studies, $V(CO)_6$ was found to have D_{4h} symmetry in matrices at low temperatures. The electronic spectrum of $V(CO)_6$ in a CO matrix was examined and tentative assignments have been made for the bands contained in the spectrum. Approximate crystal field and Racah parameters have been determined.

$V_2(CO)_{12}$ has been identified from the ir spectrum, and a tentative structure has been proposed for this molecule.

Registry No. $V(CO)_6$, 14024-00-1; $V_2(CO)_{12}$, 58815-50-2.

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Pulsed Nuclear Magnetic Resonance Study of the Molecular Dynamics of Fluxional Organometallic Molecules in the Solid State.
1. Complexes Containing Cyclooctatetraene Ligands

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Motion of the cyclooctatetraene moiety in the series of fluxional organometallic molecules $C_8H_8Fe(CO)_3$, $C_8H_8Fe_2(CO)_5$, and $(C_8H_8)_2Ru_3(CO)_4$ in the solid state is confirmed by measurements of T_1, the spin–lattice relaxation time, and $T_{1\rho}$, the spin–lattice relaxation time in the rotating frame, and accurate values obtained for the activation energies. The results are discussed in relation to the structure and bonding in the compounds and to the results from high-resolution NMR measurements in solution as well as the results from continuous-wave NMR and x-ray crystallographic investigations in the solid state.

Introduction

The structure and bonding of fluxional organometallic compounds has been extensively investigated in recent years.[2]

In these compounds, the bonding between the metal atom and the ligand is localized at some point in the latter, as shown by x-ray diffraction studies in the solid, but the bonding in solution is of a dynamic nature, the point of attachment continually changing and the static structure being observed only at low temperatures. In this light, the properties of I,

$C_8H_8Fe(CO)_3$, II, $C_8H_8Fe_2(CO)_6$, III, $C_8H_8Fe_2(CO)_5$, and IV, $(C_8H_8)_2Ru_3(CO)_4$, have been extensively investigated.[3-16] The structure of each compound has been determined by x-ray diffraction. The compounds I, III, and IV are fluxional; a single proton resonance peak is observed in solution at room temperature, indicating that the point of attachment of metal to ring is continually changing. After some dispute, it has been concluded[2] that the rearrangement mechanism in I (cyclooctatetraneneiron tricarbonyl) is by a series of 1,2 shifts
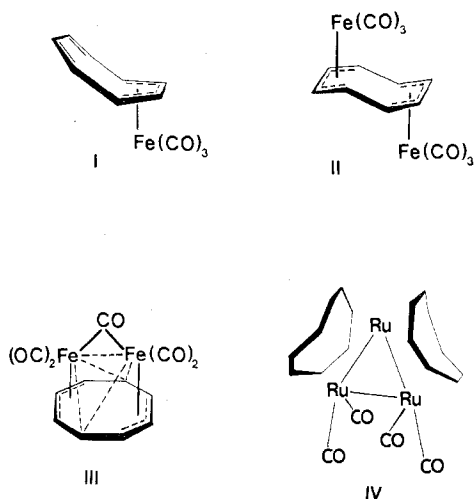
of the metal atom. Similar rearrangement mechanisms have been proposed for II (cyclooctatetraenediiron pentacarbonyl) and IV (bis(cyclooctatetraene)triruthenium tetracarbonyl). Compound II was found to be nonfluxional, the cyclooctatetraene ring being quite rigidly bound to the metal atoms.

The behavior of each of the compounds I–IV in the solid state has recently been investigated by wide-line NMR.[17,18]

It was shown in these studies that the cyclooctatetraene rings in I, III, and IV possess considerable motional freedom in the solid state at room temperature. The reorientation process was stopped (on an NMR time scale) and a rigid structure was obtained for the compounds I and IV by lowering the temperature. In the case of III the proton resonance remained unchanged over the temperature range 306–77 K, and it was concluded that the C_8H_8 ring was still rotating at 77 K. Compound II was rigid over the temperature range 430–77 K. Because no disorder was observed in the crystal structures of I, III, and IV, the reorientation must be the "jumping" of the cyclooctatraene ring between positions of minimum potential (which are the positions detected by x-ray diffraction), but also, this motion must involve the distortion of the ring and rearrangement of the localized bonds and the bonding to the metal atom, simultaneous with the rotation. A definite model for the motion may thus be deduced, and solid-state NMR is a useful complementary technique to x-ray crystallography and solution NMR for the study of this type of molecule.

Pulse NMR experiments can also yield useful information about motional processes occurring in the solid state[19] and are the best method available for the determination of the energies involved in these processes.[20,21] Assuming that T_1 is determined by dipolar interactions and that the motion present can be described by a correlation time τ_c, then T_1 is defined by eq 1,[22] where C is a constant and ω_0 is the resonance frequency.

$$\frac{1}{T_1} = C\left[\frac{\tau_c}{1 + \omega_0^2\tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2\tau_c^2}\right] \tag{1}$$

The correlation time τ_c is assumed to obey an Arrhenius-type dependence on temperature (eq 2), and a

$$\tau_c = \tau_\infty \exp(E_a/RT) \tag{2}$$

combination of eq 1 and 2 will describe the temperature dependence of the relaxation time and allow the determination of E_a, the activation energy for the process. Thus a plot of log T_1 against $1/T$ (K^{-1}), results in a V-shaped curve with a minimum where $\omega_0\tau_c = 0.62$, which yields the constant C in eq 1. At high temperatures, where $\omega_0\tau_c \gg 1$, the limiting slope of the curve is proportional to E_a, and at low temperatures, where $\omega_0\tau_c \gg 1$, the limiting slope of the curve is proportional to $-E_a$. In practice, a least-squares fit to all of the data is

performed to evaluate E_a using the minimum of the curve and the limiting slopes to give approximate initial values of C and E_a. Since the minimum in the curve occurs when $\omega_0\tau_c = 0.62$, the choice of resonance frequency ω_0 may be used to place the curve in a convenient temperature range. The two curves should still coincide at the high-temperature limit.

The mechanism for spin–lattice relaxation in the rotating frame differs from that in the laboratory frame in that it samples spectral density of the local field fluctuations at low frequencies ($\sim\gamma H_1$ where H_1 is the resonant radiofrequency field) in addition to those in the region of the Larmor frequency ($\sim\gamma H_{app}$).

In order to determine $T_{1\rho}$, one needs to satisfy the condition $\gamma H_{app} > \gamma H_1 > H^l$, where H^l is the local dipolar field, so that at resonance the effective field in the rotating frame is H^l.

If it is assumed that the relaxations occur via time-dependent dipole–dipole interactions and that the fluctuations can be described by an exponential correlation function with a characteristic correlation time τ_c, the spin–lattice relaxation time in the rotating frame $T_{1\rho}$ is described by eq 3.[23–25] In

$$\frac{1}{T_{1\rho}} = C\left[\frac{5\tau_c}{2(1 + \omega_0^2\tau_c^2)} + \frac{\tau_c}{1 + \omega_0^2\tau_c^2} + \frac{3\tau_c}{2(1 + 4\omega_1^2\tau_c^2)}\right] \tag{3}$$

this equation, C is the same constant as in eq 1, and τ_c and ω_0 are the correlation time and resonance frequency, respectively, again as in eq 1. ω_1 is the magnitude of the radiofrequency magnetic field and must be determined experimentally.

The temperature dependence of $T_{1\rho}$ should have a similar form to that of T_1 but with its minimum at a lower temperature than T_1 and coalescing with the T_1 curve in the high-temperature limit ($\omega_0\tau_c \gg 1$). The temperature dependence of $T_{1\rho}$ can also be used to obtain values of E_a and τ_c for a reorientation process. Further, measurement of $T_{1\rho}$ has, in some circumstances, certain advantages over measurement of T_1, particularly for molecular motions in lower frequency ranges, since, as temperature decreases, $\omega_0\tau_c$ becomes larger than unity for a particular type of motion; hence T_1 will become longer and more difficult to measure experimentally. Also, in certain instances, the T_1 minimum is not obtained before the compound under study melts or decomposes. In such circumstances, measurement of $T_{1\rho}$ may well reveal a minimum and allow the determination of τ_∞ and C.

From a minimum value of either curve, the constant C can be evaluated and is common to both eq 1 and 3, and by suitable data treatment the activation energy can be found. Since E_a can be found from *both* the T_1 and $T_{1\rho}$ data, reliable values are usually obtained.

The purpose of the present work was twofold: first, to substantiate the occurrence of motion in these compounds as detected by the slow-passage NMR results and, second, to obtain better values for the activation energies for the reorientation processes involved. The present paper presents the results of these studies on a representative series of fluxional organometallics containing cyclooctatetraene ligands.

Experimental Section

The T_1 and $T_{1\rho}$ measurements were made for all compounds using a coherent rf pulse spectrometer operating at 14 MHz. In the case of compound I ($C_8H_8Fe(CO)_3$), T_1 measurements were also made at 5.3 MHz.

A 90°–τ–90° pulse sequence was used to measure T_1, and the amplitude (A_∞) of the free induction decay (FID) signal following the first 90° pulse and A_τ of the FID following the second pulse were monitored using a digital boxcar integrator. For each value of τ, at least 10 amplitude measurements were averaged. The FID signal was found to decay exponentially according to

$$\ln(A_\infty - A_\tau) = \ln A_\infty - \tau/T_1 \tag{4}$$

$T_{1\rho}$ was determined by the forced transitory precession or "spin-locking" technique. A 90° pulse with H_1 along the x' axis (x' is the x axis in the rotating frame) was used. As soon as this pulse was completed, the phase of the rf was changed by 90° so that H_1 lay along the y' axis (y' is the y axis in the rotating frame). The amplitude A_τ of the FID signal following both pulses and a baseline value (A_0) following the second pulse only were monitored as before using signal-averaging techniques. The FID signal was again found to decay as in eq 4; however τ in this case is the time that the second pulse is switched on.

Since, for a pulse of constant H_1 (where H_1 is the magnitude of the radiofrequency magnetic field, $\omega_1 = \gamma H_1$), the length of the pulse t_p (s) determines the angle θ (radius) by which M precesses (eq 5),

$$\theta = \gamma H_1 t_p \qquad (5)$$

H_1 may be determined experimentally. In the present work, H_1 was evaluated by finding the average pulse length required to change θ by 180° as judged by the complete inversion of the FID after the pulse.

A least-squares computer program was used to fit the experimental data to eq 4 to obtain values for both T_1, $T_{1\rho}$, and the standard deviations. In general the error assigned to the T_1 measurement was about ±5%. For the $T_{1\rho}$ values the error is greater due to pulse instability, heating effects of the pulses, and poorer signal to noise ratios and is estimated to be ~±10%.

Samples were sealed in 10-mm o.d. thin-walled NMR tubes and the temperature of the sample was varied using a gas flow cryostat. The temperature of the gas was monitored by a copper/constantan thermocouple placed just below the sample and was regulated electronically. The temperature of the sample was measured directly using a second copper/constantan thermocouple inserted into the bulk of the sample.

Several freshly prepared samples of each compound were used in each case. The samples were prepared as described previously[17,18] and had melting points and physical properties consistent with those previously described.

Results

Both T_1 and $T_{1\rho}$ measurements were made for each of the compounds I–IV over the accessible range of temperature where the signal to noise ratio permitted data collection between 77 K and the melting or decomposition point of the compound. The results for each of the compounds will be discussed individually.

$C_8H_8Fe(CO)_3$ **(I).** The temperature dependence of T_1 over the temperature range 250–350 K was first measured at 14 MHz and was found to be very temperature dependent indicative of the presence of motion (Figure 1). Unfortunately the minimum of T_1 was not obtained before the compound began to decompose. T_1 was then measured over the same temperature range at a lower frequency of 5.3 MHz, in an attempt to define the T_1 minimum and hence obtain values for the activation energy E_a, the constant τ_∞, and the constant C. The T_1 curve is shifted to lower values (Figure 1) but unfortunately, even at this lower frequency, the T_1 minimum was not found before the sample melted. $T_{1\rho}$ was then measured at 14 MHz over the same temperature range and was observed to go through a minimum at about 285 K (Figure 1). Values of τ_∞ and C were obtained from a computer fit to the experimental $T_{1\rho}$ data and are given in Table I. These values were then used as a starting point to fit the T_1 data at both 14 and 5.33 MHz. The theoretical plots are shown in Figure 1 along with the experimental points. Good fits were obtained in each case yielding the values of E_a, τ_∞, and C given in Table I.

$C_8H_8Fe_2(CO)_6$ **(II).** In the case of this compound, no signal was observed at room temperature or lower temperatures. This is thought to be caused by a combination of a very short T_2 and a finite dead time for the spectrometer (approximately 10–20 μs) and is consistent with the molecule being rigid in the lattice as found previously by wide-line NMR studies.[17]

$C_8H_8Fe_2(CO)_5$ **(III).** T_1 and $T_{1\rho}$ were measured for this compound over the temperature range 130–77 K and both

Table I. Values for the Activation Energy, E_a, Together with the Values for the Constant τ_∞ Used in Eq 2 and the Constant C used in Eq 1 and 3

| | | $10^{-9}C$, | Activation energy, kcal/mol | | |
Compd	τ_∞, s	s^{-2}	$T_1{}^a$	$T_{1\rho}{}^b$	Waugh^c
$C_8H_8Fe(CO)_3$	7.63×10^{-14} ^{b}	3.59^b	9.07^a 9.28^d	9.29	8.9
$C_8H_8Fe_2(CO)_5$	3.98×10^{-13} ^{a}	2.56^a	1.90^a	2.13	
$(C_8H_8)_2Ru_3(CO)_4$	1.12×10^{-12} ^{a}	2.07^a	5.15^a	6.03	6.15

^{a} Values obtained from T_1 measurements at 14 MHz. ^{b} Values obtained from $T_{1\rho}$ measurements at 14 MHz. ^{c} Values obtained using the procedure of ref 26. ^{d} T_1 measurements made at 5.3 MHz.
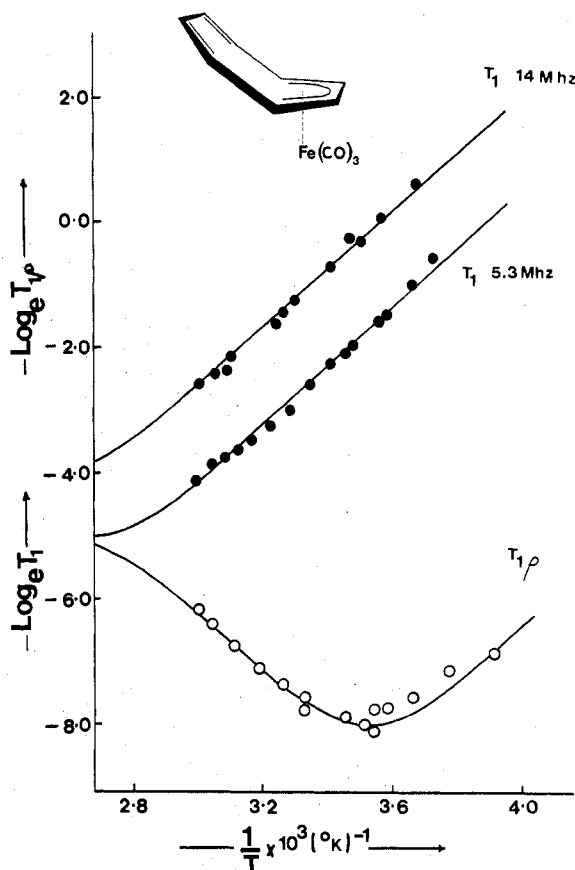

Figure 1. Variation of ln T_1 (T_1 in seconds) and ln $T_{1\rho}$ ($T_{1\rho}$ in seconds) against the reciprocal of absolute temperature for C_8H_8-Fe(CO)$_3$ in the solid state. The filled circles represent experimental T_1 data at 14 and 5.3 MHz as indicated, and the open circles, experimental $T_{1\rho}$ data at 14·MHz. The continuous curves are the theoretical relationships obtained using the constants given in Table I. In this case a least-squares fit to the experimental $T_{1\rho}$ data yielded values of τ_∞, C, and E_a. These values were then used to fit the two sets of experimental T_1 data, the values of τ_∞ and C being kept constant and only E_a being allowed to vary.

were found to be very temperature dependent, consistent with the wide-line results which indicated motion of the ring. The values for T_1 were observed to pass through a minimum about 100 K. However, the value for $T_{1\rho}$ was not observed to pass through a minimum above 77 K.

A good theoretical fit to the experimental T_1 data was first obtained and the values of E_a, τ_∞, and C from this were then used as a starting point to fit the $T_{1\rho}$ data. The theoretical plots are shown together with the experimental results in Figure 2. The values of E_a, τ_∞, and C are given in Table I.
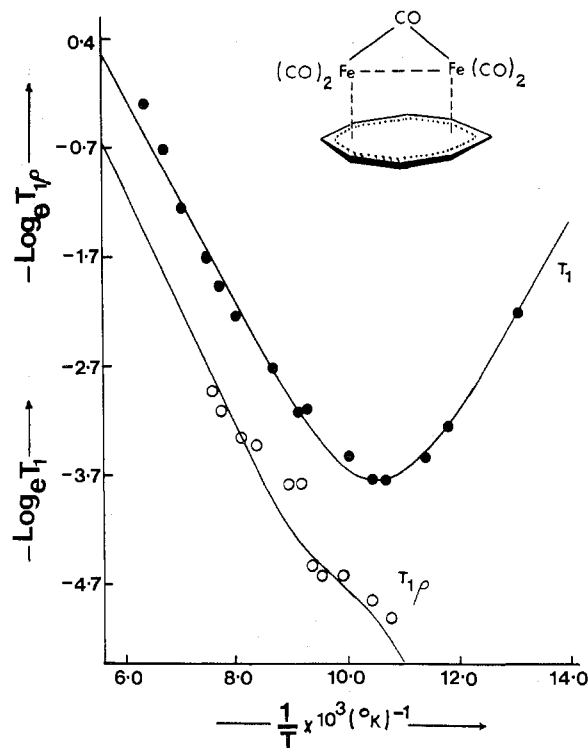
Figure 2. Variation of $\ln T_1$ (T_1 in seconds) and $\ln T_{1\rho}$ ($T_{1\rho}$ in seconds) against the reciprocal of absolute temperature for C_8H_8-$Fe_2(CO)_5$ in the solid state. The filled circles represent the experimental T_1 data and the open circles represent the experimental $T_{1\rho}$ data; both sets of data were collected at 14 MHz. The continuous curves are the theoretical relationships obtained using the constants given in Table I. In this case a least-squares fit to the experimental T_1 data yielded values of τ_∞, C, and E_a. These values were then used to fit the two sets of experimental $T_{1\rho}$ data, the values of τ_∞ and C being kept constant and only E_a being allowed to vary.

Figure 3. Variation of $\ln T_1$ (T_1 in seconds) and $\ln T_{1\rho}$ ($T_{1\rho}$ in seconds) against the reciprocal of absolute temperature for $(C_8-H_8)_2Ru_3(CO)_4$ in the solid state. The filled circles represent the experimental T_1 data and the open circles represent the experimental $T_{1\rho}$ data; both sets of data were collected at 14 MHz. The continuous curves represent the theoretical relationship obtained using the constants given in Table I. In this case a least-squares fit to the experimental T_1 data yielded values of τ_∞, C, and E_a. These values were then used to fit the experimental $T_{1\rho}$ data, the values of τ_∞ and C being kept constant and only E_a being allowed to vary.

$(C_8H_8)_2Ru_3(CO)_4$ **(IV).** Both T_1 and $T_{1\rho}$ were found to be very temperature dependent, consistent with the wide-line NMR results. The T_1 was observed to pass through a minimum about 303 K. However, in the $T_{1\rho}$ experiment, the signal to noise ratio became too small to permit reliable data collection at about 191 K and the expected minimum value of $T_{1\rho}$ could not be determined.

However, a good theoretical fit to the experimental T_1 data was obtained, and the values of E_a, τ_∞, and C from this were used as a starting point to fit the $T_{1\rho}$ data. The theoretical plots are shown together with the experimental results in Figure 3. The values of E_a, τ_∞, and C are again given in Table I.

Discussion

The results from the T_1 and $T_{1\rho}$ experiments on compounds, I, III, and IV fully substantiate the conclusions drawn from the earlier slow-passage NMR experiments that there is motion present in these compounds in the solid state and yield values for the associated activation energies which are considered accurate. These are compared in Table I with the previous more empirical estimates from line width analysis and the Waugh estimate.[26] The agreement between the activation parameters from the T_1 and $T_{1\rho}$ data and the other methods is probably to some extent fortuitous, as the other methods are considerably more empirical. The activation parameters in each case are less than 10 kcal/mol, consistent with the motions occurring below room temperature.

The value for the activation energy for the reorientation of the cyclooctatetraene ligand in each compound is quite different and can be as low as 2 kcal/mol. It will thus not be
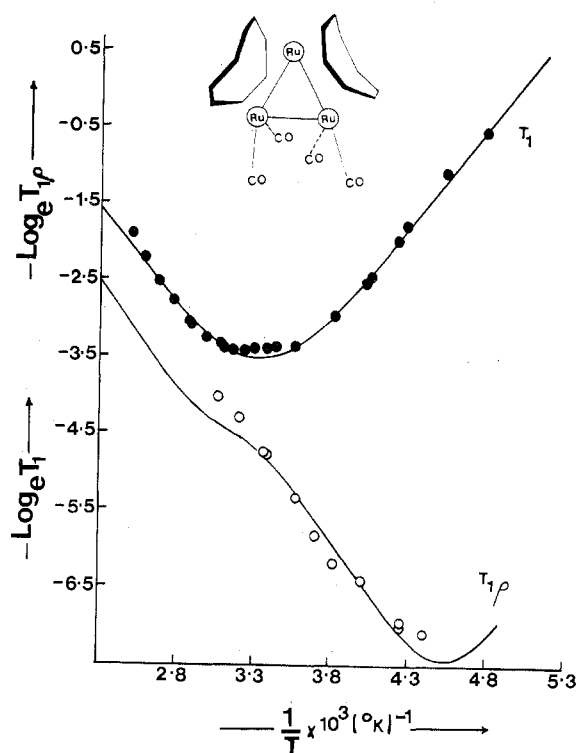
possible to make any generalized comment about the motional behavior to be expected in the solid state from the ligand alone, and predictions of this type will have to be made from the standpoint of the metal–ligand bonding. Conversely, knowledge of the activation parameters may, in suitable cases, allow one to deduce something about the nature of the metal–ligand bonding.

In the case of compounds I and IV, the activation energies are 9.4 and 5.5 kcal/mol, respectively. However, it is not possible to compare these results directly with those from high-resolution NMR studies in solution, as complete line shape analyses have not been done in these latter cases. However, from the temperature ranges over which the changes occur in solution, the activation energies can be estimated to be smaller but of the same order as those obtained in the solid state. Not only do the results clearly indicate that the lattice does not lead to "locked or instaneous structures" as has been suggested[27] but also the comparison with the solution NMR data suggests that lattice interactions are not even the major contributions to the energy barriers. This is of particular interest because in these molecules the grouping which is reorienting is not rigid but has to bend and distort as well as to rotate, and lattice interactions could have been much more important here than in the case of a totally rigid molecule, for example, benzene.

The slow-passage data for $(COT)Fe_2(CO)_5$ indicated that the movement of the ring continued below 77 K and that limiting spectra could not therefore be obtained *at all* in solution. The occurrence of motion at such low temperatures is indicative of a very low barrier to rotation, and its precise determination by the pulse techniques is of particular interest

first because no value at all could be obtained from the slow-passage experiments and second because an accurate value for the activation energy may provide some insight as to the nature of the bonding in this compound not obtainable from other sources.

The activation parameters from both the T_1 and $T_{1\rho}$ data are ~2 kcal/mol (Table I). This value must include at least some contribution from intermolecular interactions within the lattice and may be compared with the values for other compounds where there is little or no restriction to motion from bonding forces. For example, the activation parameters for the motion of the rings in benzene[28] and ferrocene[29-31] in their planes are 3.5 and 2 kcal/mol, respectively. The implication in these results is that there is very little or no barrier to the rotation of the cyclooctatetraene ligand with respect to the metal atoms, which is imposed by the metal–ligand bonding. In the light of these data, a more correct representation of the bonding in this compound may be as in V where there is bonding from the combination of the two iron atoms to the delocalized π-bonding networks of the ring, to indicate that the strength of the bond is relatively evenly distributed around the ring. The more localized bonding scheme based on the x-ray structural data (III) is considered somewhat misleading in this respect.

V
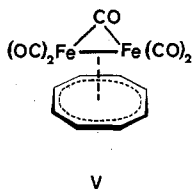
Thus the motion of the unsubstituted cyclooctatetraene ligands in these representative fluxional organometallic molecules in the solid state seems to be a general phenomenon. The effect of the crystal lattice is by no means dominant and activation energies show the same relative trends as they do in solution. The study and characterization of these motions will be a useful complementary study to any x-ray diffraction measurements, and the determination of the energy barriers will give a more complete picture of the nature of the re-orientation processes. In particular cases (such as III above), these measurements may also provide data not obtainable from solution studies and in general will be of importance in understanding the bonding between the two components in the complex.

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