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On Berry Pseudorotation in ML_5 Molecules and Microwave Dielectric Absorption

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Abstract: The possibility of applying microwave dielectric relaxation to the study of an extremely rapid chemical rate process of the intramolecular rearrangement type has been explored. A dispersion investigation at temperatures between −10 and 30 °C and several frequencies within the range, 0.002–135 GHz, has been conducted on iron pentacarbonyl, $Fe(CO)_5$, which is known to undergo axial/equatorial internal ligand exchange at a rate that is much too fast to monitor by NMR methods and too slow for electronic or vibrational spectral techniques. The study shows that $Fe(CO)_5$, whose instantaneous structure is of D_{3h} symmetry and therefore nonpolar, exhibits significant microwave absorption in the range of 0.3–5 cm^{-1}. The present dielectric results, when considered in the light of previous nondielectric investigations, appear to be best explained in terms of a fluxional relaxation model involving very rapid interconversion of nonpolar and transiently polar configurations. In the context of the mechanism proposed, the temperature dependence of the observed relaxation is indicative of a very low activation energy, 1.9 ± 0.3 kcal mol^{-1}, for the ligand exchange process occurring in $Fe(CO)_5$. Tetraphenylantimony bromide, $(C_6H_5)_4SbBr$, which would not be anticipated to undergo facile intramolecular rearrangement, was also examined. Its relaxation behavior, in benzene solution at 25 °C, was found to be consistent with dielectric dispersion completely controlled by rotational diffusion of permanent molecular dipoles.

Recently,[1] it was shown that iron pentacarbonyl, $Fe(CO)_5$, exhibits significant microwave dielectric absorption in the range of 0.3–5 cm^{-1}. This observation was considered to be quite meaningful, particularly in reference to the dynamic nature of this molecule's structure since rotational absorption involving its "ground" vibrational state is forbidden by symmetry. The equilibrium configuration of $Fe(CO)_5$ is the trigonal bipyramid[2] (TBP, D_{3h} point group) and consequently is nonpolar. After a consideration of various mechanistic possibilities, the unusually high-frequency dispersion and the temperature coefficient of its associated relaxation time were qualitatively explained on the basis of this molecule's well-established fluxional nature.[1] Earlier ^{13}C NMR studies on $Fe(CO)_5$ found only one resonance line down to the lowest possible solution temperature even though two signals (3:2 ratio) would be expected for the TBP ground-state geometry, pointing to an extremely rapid exchange of carbonyl ligands between nonequivalent sites.[3] All known aspects of dynamical stereochemistry for $Fe(CO)_5$ and numerous other ML_5 complexes[4] (PF_5, $Sb(CH_3)_5$, AsF_5) which also show apparent magnetic equivalence of ligand nuclei are in accordance with the Berry pseudorotation (BPR) mechanism[5] or a permutational equivalent.[6] In the Berry rearrangement, TBP and square-pyramidal (SP) geometries are traversed via small angle deformation motions, thereby enabling two axial and two equatorial positions of the TBP to be simultaneously interchanged in a single step.[5,6] The inability to observe temperature coalescence of NMR spectral lines for $Fe(CO)_5$ (which is indicative of a very low barrier to internal ligand exchange) reflects, in terms of the classic Berry permutation process, a correspondingly small energy difference between the TBP and SP structures.[7]

The purpose of the present work is to demonstrate, via a simple relaxation model, that extremely rapid BPR in ML_5 molecules can, in principle, lead to a distinct microwave dielectric relaxation effect which directly reflects the dynamics of the chemical rate process. In addition, dielectric dispersion results obtained on a dipolar five-coordinate molecule, i.e., $(C_6H_5)_4SbBr$, which is expected to have a long ground-state lifetime, are reported and compared with those observed for fluxional $Fe(CO)_5$.

Discussion

The dielectric dispersion of $Fe(CO)_5$, as the pure liquid, was previously investigated at frequencies of 2 MHz, 9.2, 24.4, and 135 GHz,[1] and at several temperatures[8] between −10 and 30 °C. For the sake of clarity, the prominent features of the latter study will be briefly summarized. In general, the relaxation behavior at all of the temperatures investigated displays the same basic characteristics and appears to follow, well within the uncertainty of the data, a common form of the absorption curve. The −10 and 30 °C absorption results are depicted in Figure 1 on the basis of a Debye exponential decay function. Taking the 30 °C observations as an example, a contribution to the static polarization of ~0.4 cm^3 (corresponding to an effective moment of 0.14 D) dispersing according to the Debye form of the loss curve with a relaxation time, τ, of 1.0 ps accounts for the relaxation behavior. Although the present data are too limited to necessitate interpretation in terms of a single Debye-type relaxation, knowledge of the exact line shape of the absorption (requiring measurements at still higher frequencies) would not change the magnitude of the τ values to any appreciable extent and consequently would not alter the main point to be made.[9] Table I contains the pertinent end results derived from the frequency dependence of the dielectric losses, assuming a single Debye-type absorption.[10] From a

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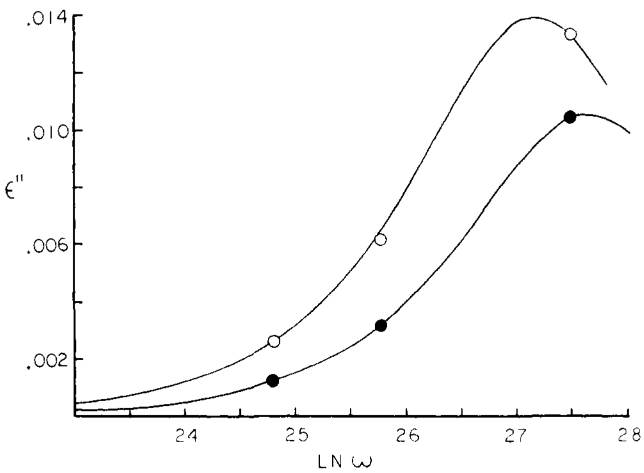

Figure 1. Dielectric loss, ϵ'', vs. ln ω for $Fe(CO)_5$: ○, −10 °C; ●, 30 °C.

Table I. Critical Wavelengths,[a] λ_m, Relaxation Times, τ, and Activation Energy, E_a, for $Fe(CO)_5$

T, °C	−10	0	10	20	30
λ_m, cm	0.30	0.26	0.23	0.21	0.19
τ, ps	1.6	1.4	1.2	1.1	1.0
E_a = 1.9 ± 0.3 kcal mol^{-1}					

[a] Resultant average of four determinations at each temperature.

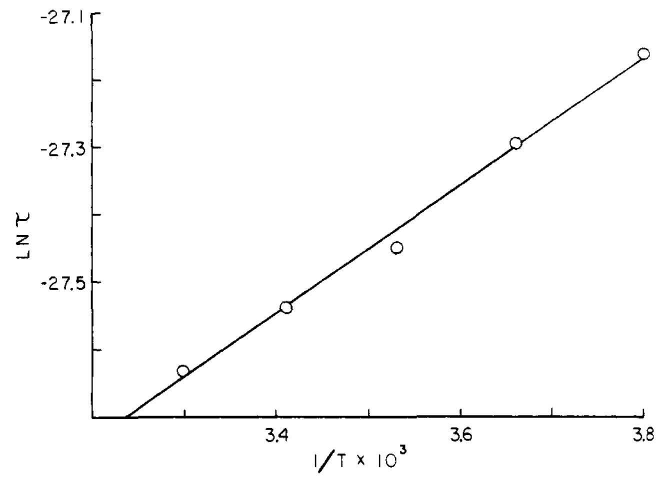

Figure 2. Ln τ vs. $1/T$ for $Fe(CO)_5$.

least-squares linear fit of the τ data as a function of temperature (Figure 2), the apparent energy of activation for the observed relaxation is calculated to be 1.9 ± 0.3 kcal mol^{-1} (95% confidence interval).

Dielectric losses in the microwave region are normally explained as the relaxation losses of rotating permanent dipoles. $Fe(CO)_5$, whose instantaneous structure is of D_{3h} symmetry, has no permanent dipole moment. In addition to this anomaly, the wavelength corresponding to maximum loss for a mechanism involving rotation is very unlikely to be below 1.5 cm (τ_r of ~8 ps) for $Fe(CO)_5$ or polar impurities in $Fe(CO)_5$.[9,11] (The λ_m observed for toluene[12] is 1.7 cm, τ_r of ~9 ps.) In any event, the τ data (Table I) show the relaxation to be associated with a process of much higher frequency than one involving molecular rotational diffusion.

Concerning other possibilities, it was previously shown[1] that (i) dielectric loss originating from $Fe(CO)_5$ molecules excited in degenerate vibrational states[13] is not a tenable alternative,[14,15] and (ii) the observed absorption is probably not connected with the "collisionally" controlled relaxation mechanism postulated to account for the microwave dispersion previously found in other nonpolar liquids[16-19] (e.g., cyclohexane, carbon tetrachloride, benzene, and carbon disulfide). Finally, a supposition not considered previously, i.e., that long-wavelength tails of vibrational, IR absorption bands are being observed, conflicts with two features of the dynamic behavior. First, in the frequency range investigated, the losses systematically decrease with increasing temperature (Figure 1), whereas an increase of the loss in the low-frequency tail would be expected for absorption from such a cause.[16] (The line breadths of infrared bands, particularly low-frequency difference bands, increase with temperature.) Second, measurements up to 135 GHz show the maximum loss to be in the microwave region.[1,9]

In view of the foregoing reasons, it appears justifiable to examine the possible relation between the pronounced stereochemical nonrigidity of $Fe(CO)_5$[3] and its microwave dielectric absorption and associated static polarization, P_s. The relevant P_s is equivalent to an effective dipole moment of ~0.1–0.2 D, and it was suggested[1] that the moment most probably originates directly as a result of an internal transformation of the molecule. Specifically, it was pointed out that a chemically controlled polarization process pictured in terms of BPR could realistically accommodate the low-frequency observations.[1] If such a process is, in fact, responsible for the establishment of equilibrium in the electric field, the observed frequency dependence of the dielectric loss would be uniquely connected with it. In this vein, we will consider the specific rate condition for which the dielectric relaxation behavior is consistent with such an intramolecular rearrangement.

Berry Pseudorotation in ML_5 Systems Coupled to Molecular Rotational Relaxation

While other internal exchange mechanisms differing in intermediate configurations are possible, the Berry process[5] is most strongly supported by discriminating experimental evidence.[6] Therefore, in the ensuing analysis, Berry pseudorotation (BPR) will be employed as a description for the stepwise connectivity of trigonal-bipyramidal conformers. The Berry exchange pathway, i.e., TBP ⇄ SP ⇄ TBP′, leaves the molecule in a rotated and permuted form of its initial state. For an ML_5 reaction system, the pseudorotated conformer (TBP′) and the original configuration (TBP) are of equal free energy content and nonpolar while the intermediate square-pyramidal exchange state has a small transient dipole moment. Since dielectric properties change during the course of BPR, the potential exists for a chemical mechanism of dielectric relaxation.[20]

A simple model will be treated that takes into account the possible occurrence of dielectric relaxation via both molecular rotation and fluxional reorientation. We consider a coupled process which is as uncomplicated as possible but nonetheless discloses the basic aspects of the phenomenon. The fluxional behavior of the ML_5 system will be characterized by BPR[5] and its molecular rotational diffusion is depicted as a jump process between two alternate dipole positions aligned parallel and antiparallel to the external field direction.[21] It is to be emphasized that the use of BPR in the above visualization is merely for the purpose of the model discussion and does not carry the implication that the physical motions involved or the configuration of the intermediate polar state need correspond precisely to the idealized Berry mechanism. Also, with regard to employing Fröhlich's simple bistable model[21] as a description for the rotational aspect of the problem, an analysis of a more general model wherein the transient dipoles point in all directions in space would not alter the essential features of the system's dynamic behavior.[22]

Let [PS] represent the concentration of transiently polar square-pyramidal ML_5 species whose moment vectors are aligned parallel and [SP] the concentration whose moment vectors are antiparallel to the external field, E. Because of the Boltzmann equilibrium factor, each moment, μ, in the presence of a static measuring field, has a relative probability, $\exp(\mu E \cos\theta/kT)$, of being aligned at an angle θ to the field, $\theta = 0$ representing parallel alignment. In addition, since the field affects the energies of the square-pyramidal ML_5 forms but not those of the "equivalent" trigonal-bipyramidal structures, the coupling model involves the simultaneous equilibria given below. It is important to note that this dynamic scheme carries the implication that the pseudorotating time, i.e., the average time spent by a pseudorotating molecule in a polar configuration, is long enough to enable the molecule to distinguish between the two alternate ways of pseudorotating. (If this condition is not met, the system cannot differentiate the two accessible polar forms due to the field and there would be no possibility of chemically controlled relaxation via the fluxional motion.)

$$\begin{tikzcd}
& {[PS]} \arrow[dr, shift left, "k_1"] \arrow[dl, shift left, "k_1"] \arrow[dd, shift right, "k_3"'] & \\
{[TBP]} \arrow[ur, shift left, "k_0"] \arrow[dr, shift left, "k_0"] & & {[TBP']} \arrow[ul, shift left, "k_0"] \arrow[dl, shift left, "k_0"] \\
& {[SP]} \arrow[uu, shift right, "k_4"'] \arrow[ul, shift left, "k_2"] \arrow[ur, shift left, "k_2"] &
\end{tikzcd}$$

At experimental field densities such that $\mu E/kT \ll 1$, the field has no effect on the overall chemical equilibrium and thus the static dielectric constant is unchanged.[20] The only effect of the field is to cause very slight deviations from the state corresponding to $E = 0$, i.e., random distribution of axes. Assuming a thermally activated rate process for the polytopal interconversion, the chemical rate constants, k_1 and k_2, may be expressed as

$$k_1 = k_{\text{intra}} \exp(-\mu E/kT) \quad (1)$$

$$k_2 = k_{\text{intra}} \exp(+\mu E/kT) \quad (2)$$

where k is the Boltzmann constant, T is the absolute temperature, and k_{intra} is the rate constant representative of the intramolecular transformation. The rotational constants, k_3 and k_4, can be designated as

$$k_3 = D_r \exp(-\mu E/kT) \quad (3)$$

$$k_4 = D_r \exp(+\mu E/kT) \quad (4)$$

where D_r is the molecular rotational diffusion coefficient associated with passage over a rotational energy barrier,[21] H, i.e.,

$$D_r = C \exp(-H/kT) \quad (5)$$

where C is a constant factor of the system. For the condition, $E = 0$,

$$k_1 = k_2 = k_{\text{intra}} \quad (6)$$

$$k_3 = k_4 = D_r = 1/2\tau_r \quad (7)$$

where τ_r is the reciprocal of the frequency of jumps across the rotational barrier, i.e., the rotational relaxation time.[21]

The following rate equations apply to the above dynamic scheme:

$$d[PS]/dt = -(2k_1 + k_3)[PS] + k_4[SP] + k_0[TBP] + k_0[TBP'] \quad (8)$$

$$d[SP]/dt = -(2k_2 + k_4)[SP] + k_3[PS] + k_0[TBP] + k_0[TBP'] \quad (9)$$

For equilibrium in the electric field, $d\{[PS] - [SP]\}/dt = 0$, and consequently

$$\left\{\frac{[PS] - [SP]}{[PS] + [SP]}\right\}_e = \frac{(k_2 - k_1) + (k_4 - k_3)}{(k_2 + k_1) + (k_4 + k_3)} \quad (10)$$

Equation 10 effectively determines the static polarization in terms of the model process. Under the condition, $\mu E/kT \ll 1$,

$$k_1 = k_{\text{intra}}(1 - \mu E/kT) \quad (11)$$

$$k_2 = k_{\text{intra}}(1 + \mu E/kT) \quad (12)$$

$$k_3 = D_r(1 - \mu E/kT) \quad (13)$$

$$k_4 = D_r(1 + \mu E/kT) \quad (14)$$

Therefore, for the equilibrium state,

$$\left\{\frac{[PS] - [SP]}{[PS] + [SP]}\right\}_e = \frac{\mu E}{kT} \quad (15)$$

from which the pertinent static polarization, $P_s = \{[PS] - [SP]\}_e\mu$, follows as

$$P_s = \{[PS] + [SP]\}(\mu^2 E/kT) \quad (16)$$

(This result is analogous to that obtained by Fröhlich[21] for a system of dipoles, each of which is assumed to possess only two equilibrium positions separated solely by the usual overall molecular rotation barrier.) It is seen that $P_s \propto \mu^2E/kT$ since the total number (N) of bistable dipoles,

$$N = \{[PS] + [SP]\} \quad (17)$$

is constant; the chemical process is not perturbed at very low field densities.[20]

In considering the time-dependent properties of the model, the gradual increase of polarization with time to its equilibrium value will be examined. For this purpose, we start with the equilibrium state corresponding to $E = 0$, i.e., $[PS] = [SP]$, and assume that at the time $t = 0$ the field is applied. From eq 8 and 9 we obtain

$$d\{[PS] - [SP]\}\,dt = -(2k_1 + 2k_3)[PS] + (2k_2 + 2k_4)[SP] \quad (18)$$

Using eq 11 through 14, together with eq 17, eq 18 becomes

$$\frac{1}{(2k_{\text{intra}} + 2D_r)}\,\frac{d\{[PS] - [SP]\}}{dt} = -\{[PS] - [SP]\} + \frac{\mu EN}{kT} \quad (19)$$

Since at time $t = 0$, $[PS] = [SP]$, eq 19 has as its solution

$$\{[PS] - [SP]\} = (\mu EN/kT)\{1 - \exp[-(2k_{\text{intra}} + 2D_r)t]\} \quad (20)$$

The time-dependent polarization, $P(t)$, follows as

$$P(t) = P_s\{1 - \exp[-(2k_{\text{intra}} + 2D_r)t]\} \quad (21)$$

and thus approaches its equilibrium value exponentially. From (20) and (21), it is seen that Berry pseudorotation coupled to rotational relaxation leads to an observed relaxation time,

$$\tau = 1/(2k_{\text{intra}} + 2D_r) \quad (22)$$

Note that eq 19-22 contain both D_r and k_{intra}, the appearance of k_{intra} indicating that the fluxional rate process, "as incorporated in the model" may, in principle, affect the dielectric relaxation of the system.[23] Using (7), eq 22 can be expressed in the form,

$$\tau = \tau_r\tau_f/(\tau_r + \tau_f) \quad (23)$$

where

$$\tau_f = 1/2k_{\text{intra}} \quad (24)$$

i.e., the relaxation time associated with the possible fluxional

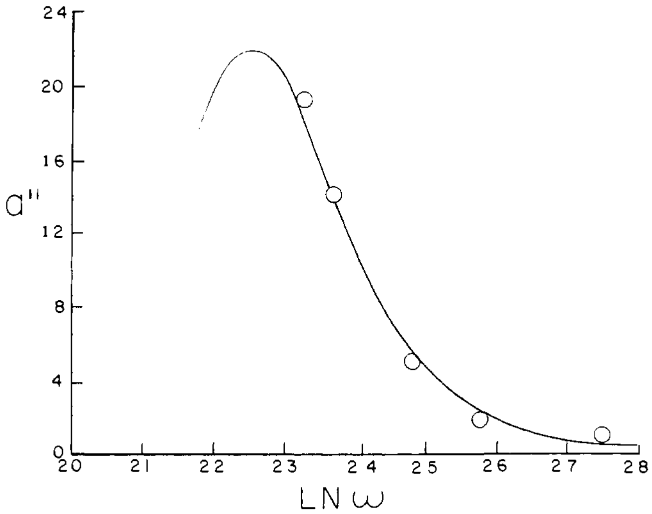

Figure 3. a'' vs. ln ω for $(C_6H_5)_4SbBr$ in benzene solution at 25 °C. The solution data were treated in the manner described earlier (see ref 32). The values of a'', i.e., $d\epsilon''/dc_2$, where c_2 is mole fraction of $(C_6H_5)_4SbBr$, were obtained from loss measurements on six solutions in the c_2 range of 0.0001-0.0027.

reorientation of the system. For the case, $\tau_r \gg \tau_f$, τ is essentially given by τ_f, and the observed dielectric relaxation would reflect the operative chemical rate process.[24] Therefore, only for ML_5 systems wherein virtually all the molecules undergo "extremely rapid" polytopal rearrangement can one hope to observe such an effect. Considering what is presently known about potential barriers to fluxional motion, $Fe(CO)_5$ may be such a pertinent reaction system. In light of the preceding discussion, we now examine the microwave dielectric absorption exhibited by $Fe(CO)_5$.

For $Fe(CO)_5$, the τ data conclusively demonstrate that the relaxation is predominantly connected with a process of much higher frequency than one involving rotation of the molecule in a polar configuration.[9,11] (Molecular volume considerations indicate a τ_r of ~8-10 ps for a molecule the size and shape of $Fe(CO)_5$.) In terms of the coupled model, this observation reflects a polytopal transformation which is so rapid that the effective moment (~0.1-0.2 D), originating via the interconversion, TBP $\rightleftarrows$ SP, changes or vanishes in a time much shorter than that required for rotational diffusion of the SP form. In this context, the germane polarization is explained as arising from the fact that, in the presence of a low-frequency or static-measuring field, pseudorotations for which the transient dipole is aligned with the field are favored over those which lead to an antiparallel dipole.[25] For such a case, the system achieves the equilibrium distribution of effective dipole axes via the chemical process itself; i.e., the molecule distinguishes between the two alternate ways of pseudorotating—"fluxional" orientation. Consequently, thermal considerations will enter even if complete thermal equilibration according to Eyring's absolute rate theory is not attained, and the lower barrier to pseudorotation will be favored by a Boltzmann factor with some effective temperature.[26] Averaged over all pseudorotating molecules, a fluxional contribution to the static polarization will be produced. This will not occur for fields of such a high frequency that they have reversed before the $Fe(CO)_5$ molecules have time to pseudorotate. At intermediate frequencies there will be an out-of-phase component of the polarization, and therefore dispersion and absorption, arising from the relaxation of the short-lived dipole moment, will be present at these frequencies. For dispersion controlled by BPR, relaxation would become apparent when the period of the measuring field approaches the time required to set up the associated moment specifically via the TBP-SP interconversion. Of course, if the microwave dispersion is due to a fluxional reorientation process, dielectric absorption would necessarily occur at angular frequencies close to that for which $\omega\tau_f = 1$, immaterial of the detailed physical motions really involved in the relaxation or the actual configuration of the intermediate polar state. Since the rate of fluxional reorientation clearly depends upon the respective potential barriers, an activation energy of ~2 kcal mol^{-1} follows for the $Fe(CO)_5$ internal exchange from this explanation of the observed dynamic behavior.

This interpretation of the dielectric data is credible on several counts. Given the existence of a polarization process as depicted above, the unusually high-frequency dispersion and very low activation energy observed for $Fe(CO)_5$ can, in principle, be rationalized. Of course, the occurrence of the restrictive rate condition, $\tau_r \gg \tau_f$, would only be possible in rather select stereochemically nonrigid systems, i.e., those involving limiting polytopal forms for which the degree of deformation required for interconversion is extremely small. In this regard, the Berry process ($D_{3h} \rightleftarrows C_{4v} \rightleftarrows D_{3h}$) is the most attractive mechanism to invoke since, during the course of BPR in $Fe(CO)_5$, (i) the iron atom need not move because it lies at the molecular center of gravity and (ii) the movement required of the carbonyl ligands, the steric hindrance, and the energy change in reaching the slightly polar intermediate C_{4v} state are all relatively small compared with alternate mechanisms suggested for the fundamental step in the rearrangement.[7] Consequently for pseudorotating $Fe(CO)_5$, the condition, $\tau_r \gg \tau_f$, may well be satisfied. Finally, the foregoing explanation given for the origin of the relaxation absorption is also quantitatively consistent with ancillary physical evidence and theoretical expectations relating to this problem; i.e., the $Fe(CO)_5$ axial/equatorial exchange is extremely fast[3,27] (temperature coalescence of NMR spectral lines has not been observed), it is thought to occur down to at least 100 K,[28] and it is believed to be associated with a barrier certainly less than 5 kcal mol^{-1}.

It was considered worthwhile to examine a five-coordinate molecule which would be anticipated to have a much more stereochemically rigid structure than $Fe(CO)_5$. For this purpose we chose tetraphenylantimony bromide, $(C_6H_5)_4SbBr$.[29] A distribution coefficient[30] of 0.06, an average μ = 5.67 D, and a τ of 158 ps[31] (λ_m 29.8 cm) give the best fit to the observed solution absorption[32] (Figure 3). As expected, the relaxation behavior displayed by this system is representative of dielectric dispersion completely controlled by rotational diffusion of its permanent molecular dipoles.[31] The only conclusion to be drawn, in the context of this paper, is simply that $(C_6H_5)_4SbBr$ possesses a rigid structure on the microwave time scale; the observed microwave dispersion indicates neither the absence nor the existence of BPR in $(C_6H_5)_4SbBr$.[24] Obviously, the physical details of the relaxation model invoked for $Fe(CO)_5$ do not pertain to $(C_6H_5)_4SbBr$ whose possible stereoisomers are dipolar. However, a correlation function treatment for permanently dipolar structures which may have pseudorotation modes in addition to overall molecular rotation[33] should result in essentially the same conclusion; i.e., if molecular rotation proceeds more slowly than internal molecular rearrangement, the chemical process will be reflected in the dielectric relaxation behavior.[20]

In summary, it is realized that dielectric evidence, considered in isolation, is never conclusive. However, the dielectric data obtained for $Fe(CO)_5$, when contemplated in the light of results from previous nondielectric studies, appear to be best explained at present by the fluxional mechanism proposed. Further dielectric dispersion investigations on other highly fluxional systems of both a polar and nonpolar nature are clearly necessary to substantiate or reject this explanation. With this aim, studies on complexes which are excellent models for $Fe(CO)_5$, i.e., $Fe(PF_3)_x(CO)_{5-x}$,[34] are being conducted in this laboratory.

Experimental Section

The experimental apparatus and techniques used herein have been extensively described elsewhere.[10,35] $Fe(CO)_5$, obtained from Alfa Products (assay: 99.5%), was triply distilled immediately prior to measurement and all operations were carried out in subdued light. $(C_6H_5)_4SbBr$, purchased from PCR Research Chemicals Inc., was repeatedly recrystallized from methanol, mp 210-213 °C.

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(24) For $\tau_r \ll \tau_f$, if dielectric absorption is exhibited in a particular frequency range, it would necessarily be completely controlled by molecular rotational diffusion, irrespective of whether or not an intramolecular transformation is occurring.

(25) On the average, the pseudorotating molecule spends more time in the PS than in the SP alignment.

(26) See ref 21, p 81. E.N.D.C. is indebted to Professor R. S. Berry for informative discussions regarding this point.

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(29) On the basis of the electronegativity rule, the Br atom occupies the axial site of TBP and the basal position of SP. A Berry rearrangement in $(C_6H_5)_4SbBr$ would require traverse of an energetically unfavorable isometric state with Br occupying an equatorial position: E. L. Muetterties, *Acc. Chem. Res.*, **3**, 266 (1970).

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(31) The magnitude of τ (158 ps) is what would be expected for overall molecular rotation of a molecule of this size.[10]

(32) The solution data were treated in the manner described earlier: A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly, and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 3447 (1950).

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(34) The NMR spectra of $Fe(PF_3)_x(CO)_{5-x}$ show all PF_3 groups to be equivalent down to −120 °C with no broadening of the spectral lines. The isomers of each composition are probably undergoing extremely rapid intramolecular rearrangement since intermolecular CO and PF_3 substitution is quite slow: R. J. Clark and M. A. Busch, *Acc. Chem. Res.*, **6**, 246 (1973).

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Alkali Hydroxide Ion Pairs. A Raman Study

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Abstract: Difference Raman spectroscopy of aqueous LiOH, NaOH, NaOD, and KOH vs. water reveals low-frequency spectra consisting of two bands. The one at lower frequencies is depolarized or weakly polarized, the other highly polarized. The spectral features are assigned to hydrated ion pairs with stoichiometry $MOH \cdot H_2O$ in which an almost symmetric O-M-O linkage exists. The proton fluxionality of this species is discussed and its implication to the OH stretching portion of the spectrum is considered.

The structure and properties of aqueous solutions of strong acids and bases have been topics of abiding interest. Solutions of strong bases in particular show several unique and sometimes puzzling physical properties which occasionally manifest themselves in their spectroscopy. So, for example, the mean activity coefficient of alkali hydroxide solutions of equal concentration decreases in the order CsOH > KOH > NaOH > LiOH, opposite to that found for the analogous alkali halides. To account for this, Harned and Owen[1] proposed that a form of "localized hydrolysis" takes place in which the hy-

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