J. Am. Chem. Soc. **1991**, *113*, 4474–4480

Pronounced Stereochemical Nonrigidity of Several Five- and Eight-Coordinate Complexes and Microwave Dielectric Relaxation

E. N. DiCarlo,[*,†] E. Peter Zurbach,[†] and Ronald J. Clark[‡]

Contribution from the Department of Chemistry, Saint Joseph's University, Philadelphia, Pennsylvania 19131, and Department of Chemistry, Florida State University, Tallahassee, Florida 32306. Received January 14, 1991

Abstract: The possibility of utilizing microwave dielectric relaxation for the dynamic study of ultrafast chemical rate processes of the intramolecular rearrangement type has been explored. In this regard, the dielectric dispersion behavior of several molecules of pronounced stereochemical nonrigidity has been investigated as a function of temperature at several frequencies within the range 0.6–139 GHz; the systems examined were the complex liquid mixture $Fe(CO)_{5-x}(PF_3)_x$ (with $x = 1, 2, 3$, or 4) and benzene solutions of $Zr(acac)_4$, $Th(acac)_4$, and $Ce(acac)_4$ (acac = $CH_3COCHCOCH_3^-$). These five- and eight-coordinate compounds display considerable dielectric absorption at frequencies that are much higher than those consonant with molecular rotational diffusion, the activation energies of the associated processes controlling the dispersions being very small. Arguments are given showing that the present observations, when contemplated along with the results from previous NMR and IR investigations, are best explained in terms of dielectric relaxation induced by chemical effects intrinsically related to the dynamic stereochemistry of these complexes. The energetic and chemical kinetic implications of the dispersion mechanisms advanced in this study are discussed in light of the extensive nonempirical information on the intramolecular mobility of these systems.

Introduction

This investigation is concerned with the inherent significance of chemically induced dielectric relaxation for the dynamic study of several extremely fast intramolecular exchange reactions. It deals with the following stereochemically nonrigid molecules: $Zr(acac)_4$, $Th(acac)_4$, $Ce(acac)_4$, (acac = $CH_3COCHCOCH_3^-$) and $Fe(CO)_{5-x}(PF_3)_x$ (with $x = 1, 2, 3$, or 4). For these complexes, facile vibrational excitation provides a mechanism for rapid permutation of nuclear positions and hence stereoisomerization. Following Muetterties, such intramolecular transformations are referred to as polytopal rearrangements since they may be characterized as traverses of two or more idealized and limiting geometric forms[1–3] (polytopal isomers). Examples of polytopal isomers are the trigonal bipyramid and square pyramid in five-coordination and the square antiprism, dodecahedron, and bicapped trigonal prism in eight-coordinate families.

The greatest proportion of data relevant to stereochemical nonrigidity has come from the application of NMR spectroscopy to the measurement of intramolecular rearrangement processes[4–6] (employing the coalescence phenomenon and total line shape analysis approaches). However, the transitional regions associated with rearrangements involving molecules whose ground-state lifetimes are short compared to the characteristic time scale for the NMR observation cannot be identified by employing this technique.[7,8] For such systems, lowering the temperature does not slow the rearrangement enough for NMR to detect the nuclei in their instantaneously nonequivalent environments, the rearrangements of many tetrakis chelates[9] and of the iron carbonyl–phosphorus trifluoride complexes[10] being classic examples. In addition, a sizable number of rearrangements that fall in this rate category are either too slow to monitor by vibrational and electronic spectral techniques[8] or involve fairly large molecules for which the rotation–vibration spectra are too complex to analyze. In view of the above and the profound effects of dynamics on stereochemistry, the question arises whether chemical kinetic information can be obtained by exploiting the microwave dielectric response of such model systems. Our initial findings in the range of 9–139 GHz on the stereochemically nonrigid $Fe(CO)_5$ molecule point to such a possibility.[11] To further explore this matter, the dielectric relaxation behavior of $Zr(acac)_4$, $Th(acac)_4$, and $Ce(acac)_4$ in benzene solution and the complex liquid mixture $Fe(CO)_{5-x}(PF_3)_x$ (with $x = 1, 2, 3$, or 4) was examined at several frequencies in the range of 0.6–138 GHz. For reasons to be advanced, these particular polytopal systems appeared to be excellent candidates for such a study.

It should be noted at the outset that dielectric investigations have been successfully applied by others to obtain chemical rate data.[12–17] However, these former studies were restricted, for the most part, to macromolecular reacting species, conformational changes of long-chain molecules and biopolymers,[14,15] and a few select rotational isomerizations.[16,17] Other than for the millimeter wave investigations conducted in this laboratory, little experimental effort has been expended in this regard on normal-sized molecules in which vibrational modes provide a mechanism for extremely rapid intramolecular rearrangement. We believe the present study to be worthwhile because of the significant number of interconversions of this character (involving molecules of four-, five-, seven-, and eight-coordination), which have not been susceptible to rate quantification using DNMR and other conventional methods.[7,8]

---

[*] To whom correspondence should be addressed.

[†] Saint Joseph's University.

[‡] Florida State University.

(1) Muetterties, E. L. *Rec. Chem. Prog.* **1970**, *31*, 51.

(2) Muetterties, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 1636.

(3) Muetterties, E. L.; Knoth, W. H. *Polyhedral Boranes*; Marcel Dekker: New York, 1968.

(4) Emsley, T. W.; Feeney, T.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: New York, 1965; Vol. 1, Chapter 9.

(5) Binsch, G. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Interscience: New York, 1968; Vol. 3, p 97.

(6) Johnson, C. S., Jr. In *Advances in Magnetic Resonance*; Waugh, J. S., Academic Press: New York, 1965; Vol. 1, p 33.

(7) Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 769.

(8) Muetterties, E. L. *Acc. Chem. Res.* **1970**, *3*, 266.

(9) Fay, R. C.; Howie, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 1115.

(10) (a) Clark, R. J.; Busch, M. A. *Acc. Chem. Res.* **1973**, *6*, 246. (b) Mahnke, H.; Clark, R. J.; Rosanske, R.; Sheline, R. K. *J. Chem. Phys.* **1974**, *60*, 2997. (c) Mahnke, H.; Clark, R. J.; Sheline, R. K. *J. Chem. Phys.* **1977**, *66*, 4822.

(11) DiCarlo, E. N. *J. Am. Chem. Soc.* **1980**, *102*, 2205.

(12) Schwarz, G.; Bauer, P. J. *Biophys. Chem.* **1974**, *1*, 257.

(13) Sillescu, H. *Adv. Mol. Relax. Processes* **1972**, *3*, 91.

(14) Gaither, R. L.; Vaughan, W. E. *Adv. Mol. Relax. Interact. Processes* **1979**, *15*, 229.

(15) Schwarz, G. *Molecular Relaxation Processes*; Chemical Society Special Publication No. 20; Academic Press Inc.: New York, 1966; p 191.

(16) Williams, G. *Trans. Faraday Soc.* **1968**, *64*, 1934.

(17) Goulon, J.; Rivail, J. L.; Chamberlain, J.; Chantry, G. W. In *Molecular Motions in Liquids*; Lascombe, J., Ed.; D. Reidel Publishing Co.: Holland, 1974; p 163.

0002-7863/91/1513-4474$02.50/0

Table I. Critical Frequencies, ν_m, Relaxation Times, τ, Critical Losses, ϵ_m'', Critical Loss Slopes, a_m'', Activation Energies, E_a, and Effective Dipole Moments, μ (20 °C)

	$Fe(CO)_{5-x}(PF_3)_x$[a,b]			$Ce(acac)_4$[c]			$Zr(acac)_4$[d]			$Th(acac)_4$[e]		
T, °C	ν_m, GHz	τ, ps	ϵ_m''	ν_m, GHz	τ, ps	a_m''	ν_m, GHz	τ, ps	a_m''	ν_m, GHz	τ, ps	a_m''
10	47	3.4	0.0352	29	5.5	3.75				43	3.7	0.70
20	57	2.8	0.0306	31	5.1	3.74	159	1.0	0.77	47	3.4	0.96
30	67	2.4	0.0273	33	4.9	3.78				50	3.2	0.94
40	73	2.2	0.0241	37	4.3	3.97	227	0.7	0.68			
50	94	1.7	0.0201							61	2.6	1.08
60							318	0.5	0.84			

[a] The mixture was of the following composition (mol %): 18.7, 47.0, 32.9, and 1.3 in x = 1, 2, 3, and 4, respectively. $Fe(CO)_5$ was not detected. [b] $E_a = 2.9 \pm 0.6$ kcal mol^{-1}, $\mu = 0.32$ D. [c] $E_a = 1.4 \pm 0.6$ kcal mol^{-1}, $\mu = 2.28$ D. [d] $E_a \approx 3$ kcal mol^{-1}, $\mu = 1.1$ D. [e] $E_a = 1.6 \pm 0.4$ kcal mol^{-1}, $\mu = 1.16$ D.

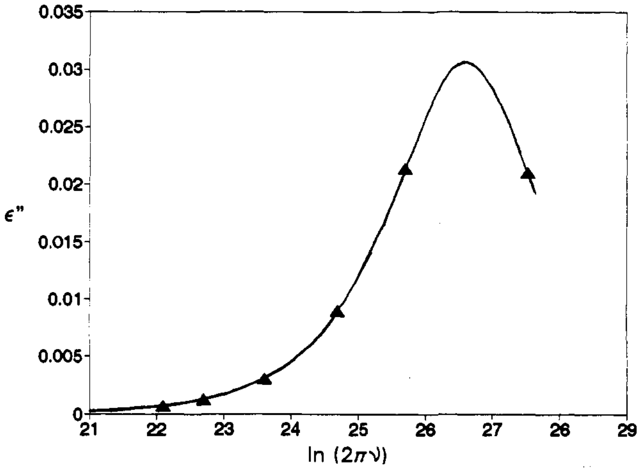

Figure 1. ϵ'' vs ln ($2\pi\nu$) for $Fe(CO)_{5-x}(PF_3)_x$ in benzene solution at 20 °C.

Experimental Section

Apparatus. Static dielectric constants, ϵ_0, were measured at a radio frequency of 0.002 GHz, and dielectric constants, ϵ', and losses, ϵ'', were determined at microwave frequencies of 139, 23.6, 9.1, 3.0, 1.2, and 0.6 GHz. The static dielectric constant apparatus, which is capable of detecting changes in capacitance of ~0.002 pF, has been previously described along with an associated error analysis.[18] The 139-GHz apparatus is a microwave analogue of the Michelson optical interferometer.[19] The error in the measured ϵ'' is ±0.0001 or ±2% (whichever is larger), and that in ϵ' is less than 0.2%. The 23.6- and 9.1-GHz measurements were made by employing the standing-wave method.[20] The error in ϵ'' has been found to be ±0.00005 or ±2% (whichever is larger) and ±0.0001 or ±2% (whichever is larger) at 9.1 and 23.6 GHz, respectively. The error in ϵ' has been estimated to be ~0.2% at both 9.1 and 23.6 GHz. The coaxial line resonant cavity method was used for measurements at 3.0, 1.2, and 0.6 GHz, the errors in ϵ' and ϵ'' having been found to be ±0.5 and ±2%, respectively.[19] For all measurements, temperature was maintained to within 0.01 °C of the desired temperature.

Materials. Reagent grade, thiophene-free benzene obtained from the Fisher Scientific Co. was fractionally distilled over sodium and stored over Drierite, n_D^{20} 1.50111. The acetylacetonates, obtained from the J.T. Baker Chemical Co., were purified by repeated crystallization from benzene–petroleum ether and by drying under vacuum over phosphorus pentoxide; mp 172.0–172.5, 193.8–194.8, and 152.5–153.8 °C for $Th(acac)_4$, $Zr(acac)_4$, and $Ce(acac)_4$, respectively. The complex mixture $Fe(CO)_{5-x}(PF_3)_x$, prepared by the reaction of $Fe(CO)_5$ with PF_3 at elevated temperatures and pressures,[21] had a mean composition of about x = 2.2 as determined by gas–liquid chromatography.

Results and Discussion

For each of the acetylacetonates investigated, 8–10 benzene solutions were employed, the mole fractions of the most concentrated solutions being ~0.04. Due to the prohibitive cost of chromatographically isolating sufficient quantities of the individual compounds of the $Fe(CO)_{5-x}(PF_3)_x$ series, studies were made on a mixture of composition (mol %) 18.7, 47.0, 32.9, and 1.3 in x = 1, 2, 3, and 4, respectively—$Fe(CO)_5$ was not detected. (Hereafter, this mixture will simply be referred to as $Fe(CO)_{5-x}(PF_3)_x$.) The solution results were treated in the following manner. The values of the static dielectric constant, ϵ_0, the microwave dielectric constants, ϵ', and loss, ϵ'', were plotted against the mole fraction of solute in solution and slopes in the limit of zero concentration, a_0, a', and a'', respectively, were obtained by the method of least squares. The latter were fitted to the Cole–Cole dispersion and absorption equations[22] to obtain the critical frequencies, i.e., the frequencies of maximum absorption, ν_m, the corresponding mean relaxation times, τ, the critical (maximum) loss slopes, a_m'', and the distribution coefficients, α. For $Fe(CO)_{5-x}(PF_3)_x$, the values of ϵ_0, ϵ', and ϵ'' were used in the re-

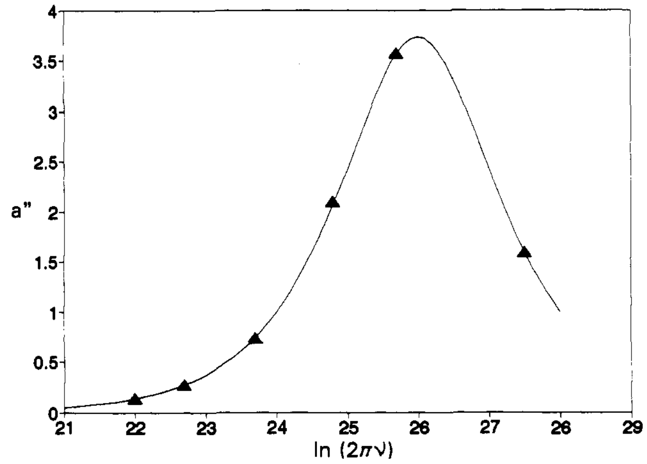

Figure 2. a'' vs ln ($2\pi\nu$) for $Ce(acac)_4$ in benzene solution at 20 °C.

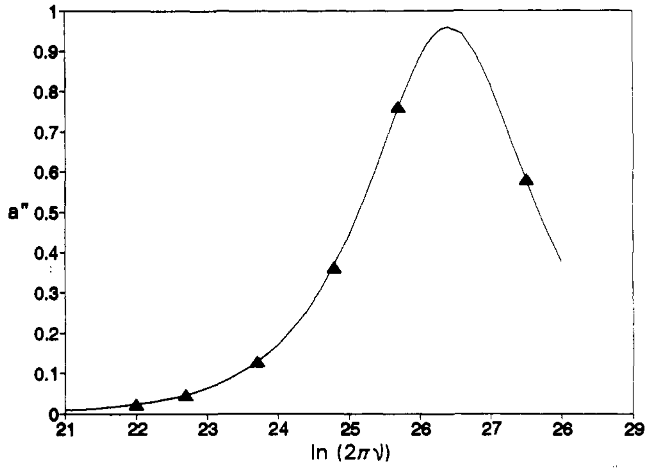

Figure 3. a'' vs ln ($2\pi\nu$) for $Th(acac)_4$ in benzene solution at 20 °C.

---

(18) DiCarlo, E. N.; Logan, T. P.; Stronski, R. E. *J. Phys. Chem.* **1968**, *72*, 1517.

(19) DiCarlo, E. N.; Zurbach, E. P. *Chem. Phys. Lett.* **1972**, *15*, 563.

(20) DiCarlo, E. N.; Stronski, R. E.; Varga, C. E. *J. Phys. Chem.* **1969**, *73*, 3433.

(21) Clark, R. J. *Inorg. Chem.* **1964**, *3*, 1395.

(22) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, *9*, 341.

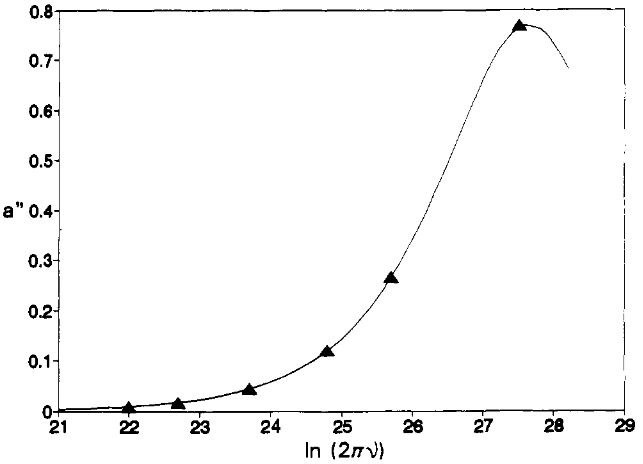

Figure 4. a″ vs ln (2πν) for Zr(acac)$_4$ in benzene solution at 20 °C.

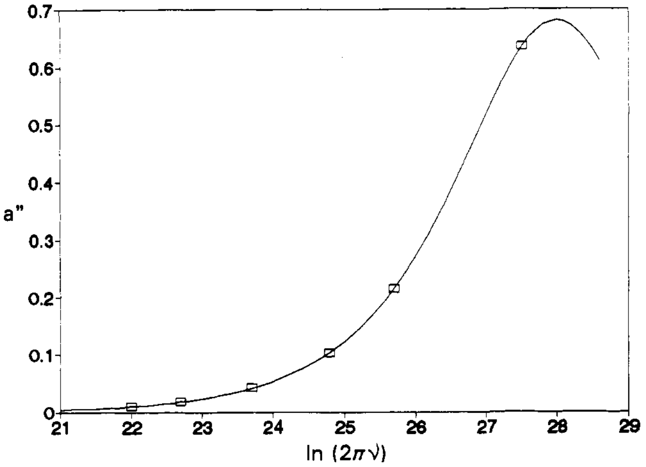

Figure 5. a″ vs ln (2πν) for Zr(acac)$_4$ in benzene solution at 40 °C.

duction of the data. Table I contains the best fit values of ν_m, τ, and a_m'' (ϵ_m'' for Fe(CO)$_{5-x}$(PF$_3$)$_x$) along with apparent energies of activation for dielectric relaxation, E_a, and effective dipole moments, μ. The following comments are in order concerning the experimental observations upon which the tabulated data are based.

As reflected in the ν_m values, the losses displayed in the range of 9–139 GHz were found to be in the proximity of the absorption maxima of these systems (except for those shown by Zr(acac$_4$)) and those exhibited in the range of 0.6–3 GHz were all found to be on the low-frequency side of the respective peak absorption. (See Figures 1–6.) Obviously, the above observations are insufficient to delineate the absorption line shape at frequencies far greater than ν_m. However, for the frequencies of chief concern, i.e., those near $2\pi\nu\tau \approx 1$, the relaxation behavior of Fe(CO)$_{5-x}$(PF$_3$)$_x$, Th(acac)$_4$, and Ce(acac)$_4$ conforms, well within the uncertainty of the data, to a dispersion for which $\alpha \approx 0$ at all temperatures investigated, while that of Zr(acac)$_4$ appears to follow a dispersion with a small distribution coefficient ($\alpha \approx 0.07$, 0.14, and 0.03 at 20, 40, and 60 °C, respectively). Due to the high critical frequencies of these systems, the dielectric results obtained from measurements in the range of 0.6–3 GHz were of only limited value in deducing the relaxation times of the associated processes controlling the dispersions. However, the data obtained at the higher measuring frequencies were within the main region of absorption for Ce(acac)$_4$, Th(acac)$_4$, and Fe(CO)$_{5-x}$(PF$_3$)$_x$ and did permit the quantitative evaluation of their τ values. In an effort to reduce the uncertainty in the determination of τ and its temperature coefficient, three critical frequency determinations were made at the given temperatures for each system. For Fe(CO)$_{5-x}$(PF$_3$)$_x$, repeated determinations were made by using the same sample, while for the acetylacetonates different sets of freshly prepared solutions were employed. The ν_m and resultant τ data

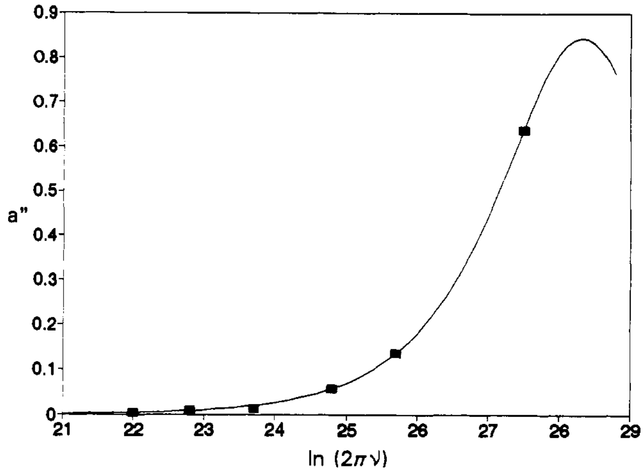

Figure 6. a″ vs ln (2πν) for Zr(acac)$_4$ in benzene solution at 60 °C.

are the averages of the three values obtained, each of the three determinations being in agreement to within 3% for Ce(acac)$_4$, Th(acac)$_4$, and Fe(CO)$_{5-x}$(PF$_3$)$_x$. The relaxation times obtained for Zr(acac)$_4$ are necessarily less reliable (particularly the 40 and 60 °C values) since they were extrapolated from data far removed from the maxima of the absorption curves. (See Figures 5 and 6.) Relative to each other, they are estimated to be good to 10%, but the absolute error may be as large as 25%. The τ values found for Th(acac)$_4$ and Zr(acac)$_4$ are decidedly shorter than those reported in another study[23] wherein the dispersion was examined solely in terms of dielectric losses obtained at only two microwave frequencies. Owing to insufficient frequency coverage of the dispersion region, the former values (4–6 ps) are, at best, extreme upper limit estimates, the two measuring frequencies employed in the earlier work (9 and 25 GHz) being on the low-frequency side of the absorption maximum. This is clearly reflected in the ν_m data of Table I.

Apparent activation energies for the observed relaxation processes of Fe(CO)$_{5-x}$(PF$_3$)$_x$, Th(acac)$_4$, and Ce(acac)$_4$ were obtained from least-squares straight line fits of ln τ vs T^{-1}, the errors in E_a being assessed at the 90% confidence level. It is difficult to assess the uncertainty in the activation energy found for Zr(acac)$_4$. Although the ln τ vs T^{-1} plot of this system is quite linear, the tabulated E_a value is regarded as a rough estimate since the relaxation times upon which it is based (particularly the 40 and 60 °C values) were generated from data obtained at frequencies far removed from the main region of absorption.

The effective dipole moments were evaluated for the common temperature 20 °C. Those of the acetylacetonates were found by employing the Debye equation modified for dilute solutions. In terms of a_m'' and the distribution parameter, α, it takes the form[24]

$$\mu^2 = \frac{27kTM_1v_1}{4\pi L(\epsilon_1 + 2)^2}\left[\frac{2a_m''(1 + \sin(\alpha\pi/2))}{\cos(\alpha\pi/2)}\right]$$

where k, L, and M_1 are the Boltzmann constant, Avogadro's number, and the molecular weight of the solvent, respectively, and v_1 and ϵ_1 are the values of the specific volume and dielectric constant obtained by extrapolation to zero mole fraction, respectively. In all cases, v_1 and ϵ_1 agreed with the standard values of 1.1376 and 2.2827 for pure dry benzene at 20 °C to within 0.01%. The integrated intensity of the absorption (the term in brackets) reduces to $2a_m''$ for $\alpha = 0$, the latter being the case for all of the systems investigated except Zr(acac)$_4$ for which a small distribution coefficient ($\alpha \approx 0.07$ at 20 °C) was noted. The values found for Zr(acac)$_4$ and Th(acac)$_4$ are properly designated as

---

[23] DiCarlo, E. N.; Watson, E., Jr.; Varga, C. E.; Chamberlain, W. J. *J. Phys. Chem.* **1973**, *77*, 1073.

[24] DiCarlo, E. N.; Zurbach, E. P.; Gallacher, C. V. *J. Am. Chem. Soc.* **1985**, *107*, 5081.

"apparent" moments, considering the preponderance of evidence that points to symmetrical (ground-state) structures for these chelates in solution.[9,23,25] Sufficient structural data from nondielectric studies are not available to enable such a classification of the moment evaluated for Ce(acac)$_4$. The following contributions to the solution static polarization, P_s, correspond to the observed effective moments: 25, 28, and 108 cm^3 for Zr(acac)$_4$, Th(acac)$_4$, and Ce(acac)$_4$, respectively. The moment of the complex liquid mixture was obtained in an analogous fashion by using the ϵ_m'' value and the average molecular weight of the mixture in the calculation. This was possible since the measured losses were fairly low, the ϵ_m'' value being only 3 times greater than that of the nonpolar liquid Fe(CO)$_5$.[26] A contribution of $\sim$2 cm^3 to the static polarization corresponds to the moment obtained for the liquid mixture.

(I) Mechanistic Considerations. Molecular rotational motions are by far the main causes of dielectric relaxation in liquids. However, other mechanisms of an internal character may also compete with classical diffusion processes, the pertinent example for the problem at hand being a process involving high-amplitude intramolecular motions, the latter being formally considered as the kinetic aspect of a chemical equilibrium between various species. If these motions bring about changes in the system's dielectric properties, they may give rise to specific behavior in dielectric relaxation. Concerning the use of dielectric dispersion measurements for the study of stereochemically nonrigid molecules, the possibility exists that the respective exchange process (if dielectrically active) may influence the dielectric response by providing a means of orienting dipoles without actually rotating them—chemical relaxation via interconversion of polytopal isomers.[11] Quite generally, a potential chemical mechanism of orientation can always be noted for any rearrangement that involves a traverse of geometric forms whose dipole moments differ. However, to be of practical significance, the chemical effect must be clearly reflected in the dynamic dielectric behavior.

The theoretical formalism for relating chemical and rotational relaxation has been the subject of several papers, and the rate condition that must be realized to clearly distinguish between molecular rotational and chemical contributions to the dielectric behavior of dipolar reaction systems has been delineated.[27] In order to facilitate the discussion of the possible mechanistic implications of the present results (vide infra), a brief summary will be given of the essentials of the chemical relaxation phenomenon as they relate to the particular reaction systems being considered. For this purpose, we focus specifically on a model polytopal rearrangement that brings about changes of dipole moments and that involves limiting polytopal forms that lack the type of polar groupings capable of contributing to dielectric relaxation by internal rotation in the usual sense.[28] In addition, the absence of nonrotational relaxation phenomena (other than chemically induced relaxation) will be assumed, justification for the latter assumption being given in a subsequent section of this article.

Upon the application of an electric field, E, the polytopal system will adapt to a new equilibrium distribution of effective dipole axes, viz., a preferential orientation with respect to the direction of the field. At very low field densities ($E \rightarrow$ O), the system establishes this distribution as fast as possible. Consequently, when the possibility exists for the dipole correlation to be completely lost in time either by molecular rotation or by the occurring intramolecular transformation, the chemical process can be expected to affect the dielectric response only if its rate is comparable to that of molecular rotational diffusion, viz., only if $\tau_{ch} \approx \tau_r$, where τ_r is the rotational relaxation time and τ_{ch} is the chemical relaxation time associated with the stereoisomerization process.[11,27] Competition between the two relaxation modes leads to an observed relaxation time, τ, of the usual form, viz., $\tau = \tau_{ch}\tau_r(\tau_r + \tau_{ch})^{-1}$.

Although chemically induced orientation would compete with the rotational diffusion mechanism if $\tau_r \approx \tau_{ch}$, under this condition the difference between τ_r and τ (observed) is not sufficiently large for a direct determination of τ_{ch}, the latter requiring a $\tau_r \gtrsim 10\tau_{ch}$. Therefore, we will concern ourselves with the experimental consequences of the two limiting dynamic situations for which, in principle, it would be possible to distinguish between molecular rotational and chemical relaxation through absorption data covering a suitably wide frequency range.[11,27]

If $\tau_r \ll \tau_{ch}$, i.e., if molecular rotational diffusion occurs much faster than the intramolecular rearrangement, the chemical process would have no effect on the dielectric behavior. The resulting dispersion would be completely controlled by the rotational diffusion of the molecular dipoles as evidenced by its appearance in the range of rotational relaxation frequencies. This condition, which precludes the investigation of chemical rate processes by the dielectric technique, ordinarily holds true for solution processes.

If $\tau_r \gg \tau_{ch}$, i.e., if rotational diffusion of all of the reacting molecules proceeds much slower than the internal exchange process, the dielectric response at very low field densities would directly reflect the chemical mechanism of dipole orientation. Under this circumstance, the chemical process only affects the dielectric relaxation, the static dielectric constant remaining unchanged. (For $E \rightarrow$ O, the chemical equilibrium is not perturbed and therefore no chemically induced dielectric polarization due to additionally produced dipoles can occur.)[27a] For such a limiting case, a dispersion region having a τ essentially given by τ_{ch} would appear at measuring field frequencies considerably higher than those consistent with rotational orientation of the reaction partners, its amplitude being determined by the mean square dipole moment of the occurring (dielectrically active) isomer interconversion process. It should be noted that coupling with uniform electric fields can also occur for a mutual exchange or fluxional process (one resulting in no "net" change in molecular configuration) involving a molecule with a nonpolar ground-state geometry.[11] The previously studied Fe(CO)$_5$ rearrangement and the present ones involving Zr(acac)$_4$, Th(acac)$_4$, and probably Ce(acac)$_4$ fall in this category. This is possible for a mutual exchange that occurs via a rearrangement pathway in which a transiently dipolar state is traversed as the molecule passes from the instantaneous structure with a given permutation of the nuclei to an equivalent instantaneous structure with a different permutation of nuclei. For such cases, contributions to the static polarization arising from preferential alignment of the short-lived dipole via the fluxional motion and dispersion due to its relaxation can arise along the lines as described earlier,[11] the observed relaxation time reflecting the average lifetime of the fluxional molecule in a polar configuration.

Considering the severely restrictive rate condition that must be realized for the occurrence of a chemically controlled dispersion at low field densities, one can rarely hope to observe such a phenomenon. (Due to the large rotational diffusion coefficients of normal-sized molecules in solution and the magnitude of typical intramolecular rearrangement barriers, $\tau_r \ll \tau_{ch}$ would certainly be true for the vast majority of stereoisomerizations.) Obviously, chemical relaxation can only be expected to affect the dielectric behavior of rather select stereochemically nonrigid systems, i.e., those wherein virtually all the molecules undergo "ultrafast" conformational change.[11] Such rearrangements would necessarily involve energetically comparable geometric isomers for which the degree of deformation required for interconversion is extremely small. In this respect, we believed the present internal exchange

---

[25] (a) Finn, A. E.; Hampson, G. C.; Sutton, L. E. *J. Chem. Soc.* **1938**, 1254. (b) Coop, I. E.; Sutton, L. E. *J. Chem. Soc.* **1938**, 1269.

[26] DiCarlo, E. N.; Zurbach, E. P. *J. Am. Chem. Soc.* **1978**, *100*, 3959.

[27] (a) Schwarz, G. *J. Phys. Chem.* **1967**, *71*, 4021. (b) Provder, T.; Vaughan, W. E. *J. Chem. Phys.* **1967**, *46*, 848. (c) Williams, G. *Trans. Faraday Soc.* **1968**, *64*, 1219. (d) Williams, G. *Adv. Mol. Relax. Processes* **1970**, *1*, 409. (e) Anderson, J. E. *Ber. Bunsen-Ges. Phys. Chem.* **1971**, *75*, 294. (f) Anderson, J. E.; Fryer, P. A. *J. Chem. Phys.* **1969**, *50*, 3784. (g) Gerne, B. J.; Giniger, R. *Biopolymers* **1973**, *12*, 1161. (h) Goulon, J.; Rivail, J. L. *Protons and Ions Involved in Fast Dynamic Phenomena*; Elsevier Scientific Publishing Co.: Amsterdam, 1978; p 105. (i) Williams, G. *Chem. Rev.* **1972**, *72*, 55. (j) Cole, R. H. *J. Chem. Phys.* **1965**, *42*, 637. (k) Lauritzen, J.; Zwanzig, R. *Adv. Mol. Relax. Processes* **1973**, *5*, 339. (l) Brondeau, J.; Goulon, J. *C. R. Acad. Sci., Paris, C. R.* **1975**, *A281*, 715.

[28] An example of dipolar relaxation via *normal* internal rotation is methoxy group reorientation in liquid anisole, a process that results in dielectric absorption at frequencies far higher than those for which the overall molecular rotation is apparent.

processes to possibly qualify as dielectrically pertinent systems, a wealth of empirical and nonempirical information suggesting intrinsically very low rearrangement barriers.[7,8,29–32] Furthermore, with regard to the visibility and possible detection of any concomitant chemical relaxation effect, they possess the following favorable characteristics.

The exchange of the relevant conformers is not accompanied by large variations in anisotropy, and therefore effects due to the modification of the diffusional properties of the species during reaction can be expected to be small.[14,27e–g] (Effects of this type, which can give rise to typical contributions to chemical relaxation, may become significant for systems exhibiting a very large number of internal degrees of freedom, e.g., chain molecules, or for reaction systems consisting of strongly anisotropic reactants.)

The idealized and limiting polytopal forms of each of the reaction systems are fairly bulky, a characteristic that reduces the detrimental influence of molecular rotational diffusion.

The rearrangements involve molecules that lack internal rotational relaxation modes. Since relaxation via internal group rotation results in microwave absorption at frequencies far higher than those for which overall molecular rotation is apparent,[28] the absence of such processes is an important simplifying feature; their occurrence would exacerbate the interpretational problem by giving rise to a high-frequency dispersion that would probably overlap that conceivably due to relaxation via the operative exchange process.

Permutations of nuclear positions in the $Fe(CO)_{5-x}(PF_3)_x$ complexes necessarily result in variations in dielectric properties. Considerable changes in dipole moments can also attend polytopal rearrangements of the $M(acac)_4$ complexes. For such eight-coordinate chelates, two of the three most energetically favorable geometric forms are nonpolar, viz., the square antiprismatic and the dodecahedral forms, while the third, the bicapped trigonal prismatic (BTP) form, is significantly polar. Consequently, if one of the configurations traversed during the course of the rearrangment has the BTP geometry, the occurring exchange process (if sufficiently rapid) could manifest itself in pronounced chemical relaxation losses.

(II) Origin of the Microwave Absorption. The purpose of the following discussion is to demonstrate that the present observations may well reflect a dielectric relaxation mechanism inherently associated with the pronounced stereochemical nonrigidity of these systems. We initially pursue this matter by showing the implausibility of a variety of other processes known to contribute to dielectric relaxation.

Dielectric losses in condensed media are usually explained as the relaxation losses of rotating permanent dipoles. Although the ground-state geometry of $Ce(acac)_4$ is open to question, a great deal of information obtained from both structural and static polarization studies favors nonpolar equilibrium configurations for $Zr(acac)_4$ and $Th(acac)_4$.[9,23,25] Consequently, rotational absorption involving the "ground" vibrational states of these chelates is forbidden by symmetry. Also, the τ data (Table I) conclusively show the relaxation to be associated with a process of much higher frequency than one involving overall molecular rotation. The ν_m value for rotational relaxation would certainly not be above ~0.9 GHz ($\tau_r \approx 180$ ps) for dipolar compounds of this size and shape—tris(trifluoroacetylacetonato)aluminum(III), $Al(acacF_3)_3$, which behaves as an essentially rigid dipole,[24] has a τ_r value of 159 ps ($\nu_m = 1$ GHz) in benzene solution at 25 °C. In any event, a molecular rotational diffusion mechanism cannot possibly account for the microwave absorption of the tetrakis chelates being considered. The same conclusion holds for the mixture of iron carbonyl–phosphorus trifluoride complexes. The detection of only a single distinct absorption region for a system consisting of dipolar species differing significantly in size, in itself, argues against such a process. In addition to this anomaly, none of the compounds constituting this system would be expected to have rotational relaxation times sufficiently short to account for the observed dispersion, an estimate of the τ_r value of even the smallest dipolar complex in the mixture $Fe(CO)_4PF_3$, based on its TBP structure, being ~35 ps ($\nu_m \approx 5$ GHz) as compared to the measured value, 3.4 ps ($\nu_m = 47$ GHz).

As previously mentioned, internal group rotations can be eliminated as a possible loss mechanism since the molecules of the systems under consideration, regardless of their overall polarity, lack the type of polar groupings for which such internal motion would be dielectrically active. Concerning other alternatives, the following points are pertinent.

The speculation that the microwave losses (previously reported for $Zr(acac)_4$ and $Th(acac)_4$ at 25.7 and 9.1 GHz) might be due to very highly damped oscillations of the chelate rings[23] has not been supported by subsequent far infrared studies, the following points being relevant to this earlier surmise. It has been demonstrated that a heavily damped Lorentzian oscillator of low resonant frequency would exhibit a maximum in its dielectric loss profile at a frequency below its resonant frequency, viz., that at which the profile of its optical absorption coefficient, $\alpha(\bar{\nu})$, maximizes.[33,34] The quantitative assessment of such an effect is expressed in terms of a damping factor, $r = \Delta\bar{\nu}_{1/2}/\bar{\nu}_0$, where $\Delta\bar{\nu}_{1/2}$ and $\bar{\nu}_0$ are the half-width and resonant frequency in wave numbers, respectively. For values of $r > 3$, corresponding to extremely high damping, it has been shown[33] that the dielectric loss maximum occurs at a frequency, $\bar{\nu}_m$, lower than $\bar{\nu}_0$ by a factor of $\sim 1/r$, i.e., $\bar{\nu}_m \approx \bar{\nu}_0/r$. Consequently, for the present loss peaks (Table I) to be compatible with such a damped resonance, very broad $\alpha(\bar{\nu})$ bands centered at unusually low resonant frequencies would necessarily be required—e.g., $\bar{\nu}_m \approx 5$ cm^{-1} ($\tau \approx 1$ ps) would be consistent with a $\Delta\bar{\nu}_{1/2} \approx 100$ cm^{-1} and a $\bar{\nu}_0 \approx 20$ cm^{-1}. No such absorption peaks have been detected in the submillimeter solution spectra (20–130 cm^{-1}) of $Th(acac)_4$ and $Ce(acac)_4$[35] and would be unrealistic to expect for the $Fe(CO)_{5-x}(PF_3)_x$ complexes. (To our knowledge, no far infrared observations on $Zr(acac)_4$ exist.)

The losses are certainly not a reflection of long-wavelength tails of vibrational, infrared absorption bands. The measurements up to 139 GHz definitely show the dielectric loss peak, in all cases, to definitely in the microwave region (see ν_m data of Table I).

With regard to $Zr(acac)_4$ and $Th(acac)_4$, which in all likelihood have nonpolar instantaneous structures, the losses cannot be explained as arising from molecules excited in degenerate vibrational states. While such excited molecules have been shown to possess effective dipole moments that can interact with uniform electric fields,[36] the present absorption (associated with effective moments of 1.1–1.2 D) is much too great to be reconciled with such an effect. For example, the effective dipole moment connected with the vibrationally induced rotational absorption of PF_5 has been found to be 1.3×10^{-3} D.[37]

The molecular distortion or collisional interaction hypothesis that has been suggested to account for the microwave absorption and excess polarization shown by benzene and several other nonpolar liquids[38] is also untenable for these systems. In terms

---

(29) Cotton, F. A. *Acc. Chem. Res.* **1968**, *1*, 257.

(30) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(31) Muetterties, E. L. In *MTP International Review of Science*; Tobe, M. L., Ed.; Inorganic Chemistry Series One; University Park Press: Baltimore, MD., 1972, Vol. 9, 37.

(32) (a) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047. (b) Strich, A.; Veillard, A. *J. Am. Chem. Soc.* **1973**, *95*, 5574. (c) Altmann, J. A.; Yates, K.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1976**, *98*, 1450. (d) Rauk, A.; Allen, L. C.; Mislow, K. *J. Am. Chem. Soc.* **1972**, *94*, 3035. (e) Shapley, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305. (f) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257. (g) Demuynck, J.; Strich, A.; Veillard, A. *Nouv. J. Chim.* **1977**, *1*, 217 and references cited therein.

(33) Hill, N. E. *Chem. Phys. Lett.* **1968**, *2*, 5.

(34) Chamberlain, J. *J. Chem. Phys. Lett.* **1968**, *2*, 464.

(35) Haigh, J.; Jinks, K. M.; Sutton, L. E.; Wadding, D. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1561.

(36) Dalton, B. J. *J. Chem. Phys.* **1971**, *54*, 4745.

(37) Mills, I. M.; Watson, J. K. G.; Smith, W. L. *Mol. Phys.* **1969**, *16*, 329.

of this theory, the microwave absorption is caused by translational relaxation of temporary dipoles induced in polarizable molecules by molecular electric fields evoked by surrounding neighbors. If local molecular configurations unique to the dissolved state contribute to the static polarization, large differences between the vapor and solution radio frequency polarizations of these compounds would be expected, e.g., 28 cm^3 (corresponding to $\mu = 1.16$ D) in the case of $Th(acac)_4$. Actually, the static polarizations in the gas phase[25b] and in solution[25a] agree to within 1 cm^3 for this compound. This same argument applies to the $Zr(acac)_4$ system, the observed effective moment being simply too large to be interpreted in terms of multipole-induced dipoles between collision partners. In fact, attempts to explain the microwave absorption of nondipolar liquids as having its origins in a quadrupole-induced dipole appearing in the molecules have been modestly successful only for cases where the effective dipole moments are very small, ~0.1 D.[39,40] In addition, it has been shown that any microwave losses resulting from such intermolecular processes would be causally associated with accompanying submillimeter absorption peaks.[38] Of the systems being considered, only $Th(acac)_4$ in benzene solution displays a submillimeter optical absorption maximum (at 222 cm^{-1}). However, this peak has been attributed by Fay and Pinnavaia[41] to Th–O asymmetric stretching, a contention that has been supported by the observation that it has an absorption intensity comparable to the intensities associated with the metal–oxygen stretching peaks observed for other metal acetylacetonates in the 300–500 cm^{-1} region.[35]

Because of the foregoing points, the possibility that the microwave dispersion of the systems under study is indicative of relaxation via isomer interconversion must be considered. The present observations, taken in isolation, tentatively suggest such a process. More significantly, a considerable amount of other information inferentially indicates the possibility of a chemically controlled dielectric response. At this juncture, we focus on ancillary evidence dealing with the energetics and the stereochemistry of the intramolecular rearrangements proposed for these molecules in order to provide a more substantive reason for accepting this explanation.

(A) $Fe(CO)_{5-x}(PF_3)_x$. These trigonal-bipyramidal complexes show apparent magnetic equivalence of ligand nuclei.[10] All known aspects of dynamical stereochemistry in five-coordinate molecules that exhibit this behavior are in accordance with the Berry rearrangement mechanism[30] or a permutational equivalent. In the Berry rearrangement, trigonal-bipyramidal (TBP) and square-pyramidal polytopal forms are traversed via a small bending mode, thereby enabling two axial and two equatorial positions of the TBP to be simultaneously interchanged in a single step. A brief summary of the extensive information relating to the stereochemical nonrigidity of these complexes follows.

Substitution of PF_3 into $Fe(CO)_5$ yields species similar to the parent with PF_3 distributed over all possible coordination sites, all members of the series $Fe(CO)_{5-x}(PF_3)_x$ being readily isolated by gas–liquid chromatography.[42] Although the IR spectra of these compounds demonstrate that, based on a TBP structure, each composition x contains significant amounts of every possible geometric isomer, efforts to isolate the respective individual isomers have failed. (The symmetry classifications of the stereoisomers for $x = 1$–4 are as follows: $x = 1$, C_{3v} and C_{2v}; $x = 2$, D_{3h}, C_{2v}, and C_s; $x = 3$, D_{3h}, C_{2v}, and C_s; $x = 4$, C_{3v} and C_{2v}.) Complete assignments of the CO stretching frequencies have been made.[43] However, the NMR spectra of each of the different compositions show all PF_3 groups to be equivalent at temperatures down to at least −120 °C with no broadening of the resonance lines,[10] spectra reminiscent of those displayed by the $Fe(CO)_5$ molecule[44] for which the rate of axial–equatorial ligand exchange in solution has been estimated to be as high as 10^{12} s^{-1}.[45] Because intermolecular CO and PF_3 substitution is quite slow, except at much higher temperatures, it has been concluded that the isomers of each composition x undergo intramolecular rearrangement at speeds much faster than the NMR time scale but slower than the vibrational time scale.[10] This behavior clearly indicates that substitution of the much heavier PF_3 groups does not substantially decrease the rate of rearrangement of any of the members of the series ($x = 1$–4). In addition, it has been reported that PF_3 group nonequivalence required for the D_{3h} ground-state symmetry of several $M(PF_3)_5$ species (M = Fe, Ru, or Os) is not evident in the NMR spectra even at −160 °C,[46] an observation that is also strikingly similar to the low-temperature ^{13}C NMR result obtained for $Fe(CO)_5$.[44] Hence, PF_3 exchange in such species would appear to occur with a facility comparable to that of CO exchange in $Fe(CO)_5$, a process for which activation barriers of 0.5–2 kcal mol^{-1} have been estimated by a number of methods.[11,45,47] In this comparative vein, the microwave dispersion detected for $Fe(CO)_5$[26] is also notable; however, the stereochemical significance that has been attributed to this earlier finding[11] is more appropriately addressed in the subsequent consideration of the dielectric absorption shown by $Zr(acac)_4$, another nonpolar molecule that is also believed to be fluxional.[9]

In view of the above complementary information and the arguments given earlier, we conclude that chemically induced relaxation is the only satisfactory explanation of the dynamic dielectric response of the liquid mixture studied. A concise summary of the rationale for this deduction follows.

No dispersion in the range of rotational relaxation frequencies was observed although of the ten stereoisomers known to be present in the mixture (see above) eight are permanently dipolar, the two of D_{3h} symmetry being nonpolar. In contrast, the frequency dependence of the relaxation losses of the stereochemically rigid $(C_6H_5)_4SbBr$ molecule is clearly in accord with dipole orientation via rotation of a molecule of its size and shape[11]—$\tau_r = 158$ ps ($\nu_m = 1$ GHz) in benzene solution at 25 °C.

The process of axial–equatorial ligand exchange in $Fe(CO)_{5-x}(PF_3)_x$, which interconverts the TBP isomers for each value of x (viz., $C_{3v} \rightleftarrows C_{2v}$ for $x = 1$ and 4; $D_{3h} \rightleftarrows C_{2v} \rightleftarrows C_s$ for $x = 2$ and 3), is necessarily attended by dipole moment changes. If, as inferred from NMR spectra, the rate of exchange in these isomers approaches that of the $Fe(CO)_5$ exchange, the condition $\tau_r \gg \tau_{ch}$ may very well be satisfied even by the smallest complex in the mixture. Given such a rate, the appearance of relaxation losses at measuring field frequencies much higher than those consistent with rotational orientation of the system's permanent molecular dipoles is explained.

Finally, the result obtained for the Arrhenius activation energy is a realistic one for the dispersion mechanism that has been advanced. Although lack of sufficient sample quantities prevented dielectric studies on individual members of the series, the (mixture) value of ~3 kcal mol^{-1} (Table I) is a reasonable measure of the barrier associated with isomer interconversion in such complexes in light of the aforementioned NMR indications and the E_a values

---

(38) (a) Poley, J. Ph. *J. Appl. Sci. B* **1955**, *4*, 337. (b) Gebbie, H. A.; Stone, N. W. B.; Findlay, F. D.; Pyatt, E. C. *Nature* **1965**, *205*, 377. (c) Chantry, G. W.; Gebbie, H. A. *Nature* **1965**, *208*, 378. (d) Leroy, Y.; Constant, E. *C. R. Acad. Sci. Ser. 2* **1966**, *262*, 1391. (e) Chantry, G. W.; Gebbie, H. A.; Lassier, B.; Wyllie, G. *Nature* **1967**, *214*, 163. (f) Chamberlain, J. E.; Werner, E. B. C.; Gebbie, H. A.; Slough, W. *Trans. Faraday Soc.* **1967**, *63*, 2605. (g) Davies, M.; Pardoe, G. W. F.; Chamberlain, J. E.; Gebbie, H. A. *Trans. Faraday Soc.* **1968**, *64*, 847. (h) Garg, S. K.; Bertie, J. E.; Kilp, H.; Smyth, C. P. *J. Chem. Phys.* **1968**, *49*, 2551. (i) Stumper, U. *Adv. Mol. Relax. Processes* **1975**, *7*, 189.

(39) Pardoe, G. W. F. *Trans. Faraday Soc.* **1970**, *66*, 2699.

(40) Davies, G. J.; Chamberlain, J.; Davies, M. *J. Chem. Soc., Faraday Trans. 2*, **1973**, *69*, 1223.

(41) Fay, R. C.; Pinnavaia, T. J. *Inorg. Chem.* **1968**, *7*, 508.

(42) (a) Clark, R. J. *Inorg. Chem.* **1964**, *3*, 1395. (b) Udovich, C. A.; Clark, R. J.; Haas, H. *Inorg. Chem.* **1969**, *8*, 1066.

(43) Haas, H.; Sheline, R. K. *J. Chem. Phys.* **1967**, *47*, 2996.

(44) (a) Cotton, F. A.; Danti, A.; Waugh, J. S.; Fessenden, R. W. *J. Chem. Phys.* **1958**, *29*, 1427. (b) Bramley, R.; Figgis, B. N.; Nyholm, R. S. *Trans. Faraday Soc.* **1962**, *58*, 1893.

(45) (a) Spiess, H. W.; Mahnke, H. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 990. (b) Sheline, R. K.; Mahnke, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 314.

(46) Jesson, J. P.; Meakin, P. *J. Am. Chem. Soc.* **1973**, *95*, 1344.

(47) (a) Cotton, F. A.; Hanson, B. E. In *Molecular Rearrangements*; Demayo, P., Ed.; Academic Press: New York, 1980; Chapter 12. (b) Burdett, J. K.; Gryzbowski, J. M.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 5728.

estimated for CO exchange in $Fe(CO)_5$.[11,45,47]

(B) $M(acac)_4$. Tetrakis(β-diketonates) undergo very rapid stereochemical rearrangements.[9,48] Reaction paths involving geometric isomer interconversions are energetically favorable ones for such rearrangements. Concerning the possibility of a concomitant chemical dielectric relaxation effect, the following stereochemical aspects are pertinent.

In eight-coordination, the number of reasonable polytopal forms is quite large. However, most coordination compounds generally approximate the D_{4d} square antiprismatic (SAP), D_{2d} dodecahedral (DD), and C_{2v} bicapped trigonal prismatic (BTP) geometries.[49] As demonstrated by theoretical analyses, energy differentiation among these forms should not be large[50] (barring unusual steric constraints). More significantly, in relation to stereochemical nonrigidity, the degree of nuclear displacement required to convert any one of these polytopal isomers into another is quite small.[9,49a]

For the chelates being considered, the definitive empirical findings come from the NMR studies of Fay and Howie.[9] No low-temperature splitting was observed for the methyl proton resonances of $Ce(acac)_4$ and $Th(acac)_4$. However, limiting slow-exchange spectra were found for $Zr(acac)_4$, the single, time-averaged methyl resonance displayed at −59 and −137 °C splitting into two lines of equal intensity below the coalescence temperature of −145 °C, the ring proton resonance remaining a singlet. The spectra in the slow-exchange limit were interpreted in terms of the presence of a single stereoisomer having two equally populated methyl environments and one ring proton environment, the square antiprismatic (SAP) stereoisomer of D_2 symmetry being preferred on the basis of the solid-state structure of $Zr(acac)_4$.[51] From total line-shape analysis of the methyl resonances, the activation energy, E_a, for exchange of acac methyl groups between the two nonequivalent sites of the SAP D_2 stereoisomer was determined to be 4.4 ± 0.3 kcal mol^{-1}. In addition, polytopal rearrangement was shown to be the preferred path for this exchange. Specifically, two alternate mechanisms, i[9] and ii,[52] have been suggested as being the most plausible: (i) SAP $\rightleftarrows$ DD $\rightleftarrows$ SAP′ and (ii) SAP $\rightleftarrows$ BTP $\rightleftarrows$ DD $\rightleftarrows$ SAP′, where SAP and SAP′ are the square antiprismatic stereoisomers of D_2 and D_4 symmetry, respectively. For each of these reaction schemes, the SAP′ complex can return to the initial SAP D_2 complex by the reverse path or convert, via the respective intermediate isomer(s), to a new SAP D_2 stereoisomer, the latter having its acac methyl groups in positions that reflect exchange between the two nonequivalent sites of the original SAP complex. (Possible vibrational modes for the above interconversions have been described.[9,49a]) Both of these exchange pathways should have low activation energies and, therefore, are in qualitative accord with the fluxional nature of this system. However, only path ii is of consequence with regard to the possibility of dielectric relaxation via polytopol isomer interconversion—rearrangement path i would be inactive in the dielectric spectrum of $Zr(acac)_4$ owing to the nonpolarity of all of the stereoisomers traversed.

On the basis of the eliminative arguments outlined earlier, we tentatively suggested that the dielectric behavior of $Zr(acac)_4$ results by virtue of its inherent stereochemical nonrigidity, a suggestion that obviously presupposes a dielectrically active mode. Considering the frequency location and large magnitude of this system's dielectric losses, such an explanation, to be tenable, requires that the dielectrically active process be attended by both extremely rapid and pronounced dielectric property changes. In this respect, mechanism ii is particularly well suited because chemically induced dielectric relaxation, if in fact operative, would involve the BTP C_{2v} state, a transient state of relatively high polarity. We now endeavor to show that our initial inference concerning the origin of the microwave absorption is fully consistent with this molecule's fluxional character as depicted by scheme ii. The dielectric losses of $Zr(acac)_4$ are explained as arising from a chemically induced (or better, a fluxionally induced) moment. The kinetic and energetic implications of this mechanistic interpretation follow.

For operative exchange via mechanism ii, the extremely short observed relaxation time, τ, signifies that the effective dipole moment, 1.1 D, originating via the interconversion SAP $\rightleftarrows$ BTP $\rightleftarrows$ DD changes or vanishes in a time much shorter than that required for rotational diffusion of the BTP form. For this dynamic situation, $\tau_r \gg \tau_{ch} = \tau$, viz., the experimental relaxation time is a measure of the average lifetime of $Zr(acac)_4$ in the polar BTP configuration. In this context, it should be noted that the estimate obtained for E_a (~3 kcal mol^{-1}) does *not* reflect the overall exchange pathway. It represents the average activation energy associated specifically with the passage of the system from polar to nonpolar states, the process that is observed dynamically. (In this regard, the reader is referred to the earlier literature for the detailed analysis of the time-dependent properties of a similar relaxation model that was invoked to explain the microwave losses of $Fe(CO)_5$.[11]) In view of the quite minor degree of bending required to convert the BTP form to either of the nonpolar forms[49a] (SAP and DD), this interpretation of the ultrafast relaxation and its very low activation energy is not unreasonable. Given the existence of a relaxation process as pictured above, the relevant polarization, 25 cm^3, represents the chemical or fluxional contribution to the radio frequency (static) polarization. This contribution will not be produced for fields of such a high frequency that they have reversed in a time much shorter than the average lifetime of $Zr(acac)_4$ in the polar configuration. At measuring-field frequencies comparable to this lifetime, 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.

The low-temperature NMR investigations of $Th(acac)_4$ and $Ce(acac)_4$ failed to supply the kinetic and structural information required for the assignment of possible rearrangement mechanisms. However, as pointed out by Fay and Howie,[9] the narrow methyl resonance line observed for $Th(acac)_4$ certainly suggests that rearrangement of this complex is still fast on the NMR time scale at −160 to −170 °C. (In this respect, the latter researchers draw no conclusion about $Ce(acac)_4$, its methyl resonance becoming very broad at low temperatures.) Although an interpretation of the present results (based on specific rearrangement pathways) is not possible, it nevertheless seems reasonable to postulate that the dielectric behavior of $Th(acac)_4$ and $Ce(acac)_4$ also directly reflects stereoisomerization which involves a sizably polar isomeric state whose dielectric response is controlled by facile vibrational motion. This explanation appears to be the only realistic one in view of the large and anomalously high frequency losses of these systems. (In this context, the exceedingly small E_a values associated with the observed dielectric relaxation again have the same general significance as given previously for $Zr(acac)_4$.)

In summary, it is realized that dielectric evidence, considered in isolation, is rarely conclusive. However, the dielectric data obtained for the five- and eight-coordinate complexes, when contemplated along with the results from previous NMR and IR studies, appear to be best explained in terms of dielectric relaxation induced by chemical effects intrinsically related to the dynamic stereochemistry of these systems.

Acknowledgment. This research was supported by a National Science Foundation grant (CHE-8121068) to E.N.D.C. We are grateful to Professor R. C. Fay for helpful comments regarding mechanism ii. E.N.D.C. sincerely thanks Professor F. A. Cotton for stimulating his interest in fluxional systems and the encouragement he gave during the course of this study.

---

(48) (a) Pinnavaia, T. J.; Fay, R. C. *Inorg. Chem.* **1966**, *5*, 233. (b) Cotton, F. A.; Legzdins, P.; Lippard, S. J. *J. Chem. Phys.* **1966**, *45*, 3461. (c) Serpone, N.; Ishayek, R. *Inorg. Chem.* **1971**, *10*, 2650.

(49) (a) Muetterties, E. L.; Wright, C. M. *Q. Rev. Chem. Soc.* **1967**, *21*, 109. (b) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235. (c) Kepert, D. L. *J. Chem. Soc.* **1965**, 4736.

(50) (a) Britton, D. *Can. J. Chem.* **1963**, *41*, 1632. (b) Claxton, T. A.; Benson, G. C. *Can. J. Chem.* **1966**, *44*, 157. (c) Thompson, H. B.; Bartell, L. S. *Inorg. Chem.* **1968**, *7*, 488.

(51) Silverton, J. V.; Hoard, J. L. *Inorg. Chem.* **1963**, *2*, 243.

(52) Mechanism ii was suggested by Prof. R. C. Fay to E.N.D.C., personal communication.