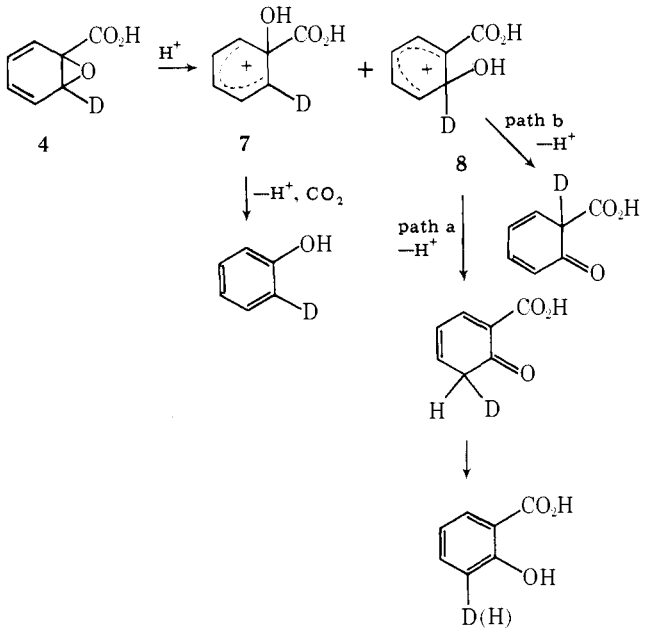
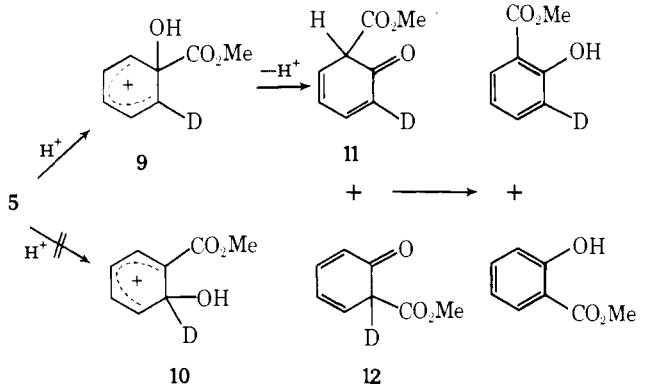
pH 1 in 9:1 MeOH-H_2O (40:60), pH 2.5 in 9:1 HOAc-H_2O (32:68), neat, crystalline state (20:80).

Deuterium-labeled acid **4**, prepared by hydrolysis of **5**,[10] decomposed neat to afford phenol with complete retention of deuterium and salicylic acid with 72% retention of deuterium.[11] Deuterium retention in the salicylic acid from reaction of **4** in CF_3CO_2H and in aqueous solution at pH 7.4 (phosphate buffer) was 64 and 81%, respectively. The data are consistent with oxirane ring opening to **7** and **8**, the former of which



undergoes decarboxylation to phenol, and the latter undergoes migration of deuterium via path a and subsequent enolization to salicylic acid with observed deuterium retention consistent with that expected because of the isotope effect.[12] The NIH shift via path b would result in complete loss of deuterium and appears not to be significant. The possiblity of pathways involving carboxyl participation to form α- or β-lactone intermediates in the reactions described above can not be ruled out.

Ester **2** in CF_3CO_2H rearranges to methyl salicylate in quantitative yield. Under similar conditions deuterium-labeled ester **5** affords methyl salicylate with 55% retention of deuterium,[11] consistent with the established mechanism for the NIH pathway in which protonated **5** undergoes cleavage of the oxirane ring with exclusive formation of the more stable cation **9** rather than **10**. Proton loss from **9** with migration of the



carbomethoxy group affords **11** and **12** (about equivalent amounts) that isomerize to the observed product.[11,13,14]

The results described above support the suggestion that 1,2-oxide of benzoic acids may be intermediates in biological oxidative decarboxylation reactions and that **1** may be an intermediate in the ortho hydroxylation of benzoic acid. The aromatization of **2** provides the first case of carboalkoxy migration in the aromatization of arene oxides.

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(14) Preliminary product studies with methyl-substituted 2-carbomethoxyoxepins are also in concurrence with the conclusion that the reaction pathway involves exclusive carbomethoxy migration.

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Interpretation of the Microwave Dielectric Relaxation of Iron Pentacarbonyl in Terms of the Molecule's Fluxional Nature

Sir:

We have recently obtained results which show that iron pentacarbonyl, $Fe(CO)_5$, exhibits significant microwave dielectric absorption in the range of 0.3–5 cm^{-1}. This observation appears to be quite meaningful particularly in terms of the dynamic aspect 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

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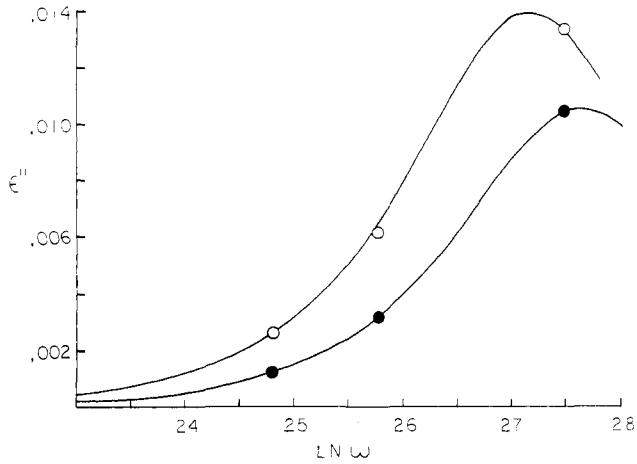

Figure 1. Dielectric loss, ϵ'', vs. ln ω for $Fe(CO)_5$: ○, −10 °C; ●, 30 °C.

Table I. Critical Wavelengths,[a] λ_m, Relaxation Times, τ, and Activation Energy, E_a

$T \pm 0.03$ °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
$E_a = 1.9 \pm 0.3$ kcal mol^{-1}					

[a] Resultant average of four independent determinations at the given temperature, each of which were in agreement to within 3%.

trigonal bipyramid[1] (D_{3h} point group). The frequency at which the dispersion appears and the temperature coefficient of its associated relaxation time indicate that the observed absorption is most probably connected with some form of facile intramolecular motion(s). ^{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 anticipated for the trigonal-bipyramidal (TBP) ground-state geometry, pointing to an unusually rapid exchange of carbonyl ligands between nonequivalent sites.[2]

The purpose of the present communication is to demonstrate that a plausible physical explanation of the microwave losses exhibited by $Fe(CO)_5$ can be given on the basis of the molecule's well-established fluxional nature. In the context of the proposed interpretation, the temperature dependence of the relaxation time is indicative of a very low activation energy, ~2 kcal mol^{-1}, for the ligand exchange process occurring in $Fe(CO)_5$.

Static dielectric constants were measured at 2 MHz and dielectric constants and losses were determined at frequencies of 135, 24.4, and 9.2 GHz at several temperatures between −10 and 30 °C as previously described.[3,4] Table I contains the pertinent end results derived in terms of a single Debye-type absorption.[3] To ensure preservation of the chemical integrity of the system, it was necessary to restrict the present study to a rather narrow temperature interval.[5] For illustrative purposes, 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, $\bar{\mu}$ of 0.14 D) dispersing according to the Debye form of the loss curve with a τ of 1.0 ps accounts for the relaxation behavior.[6] From a least-squares linear fit of the τ data as a function of temperature, the experimental activation energy, E_a, 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 1.1 cm (τ_r of ~6 ps) for $Fe(CO)_5$ or polar impurities in $Fe(CO)_5$.[6,7] (The λ_m observed for toluene[8] is 1.25 cm—τ_r of ~7 ps.) Concerning other alternatives, the following points are pertinent.

The observed absorption does not appear to be connected with the "collisionally" controlled relaxation mechanism postulated to account for the microwave dispersion previously found in other nonpolar liquids[9,10] (e.g., cyclohexane and carbon tetrachloride). Not only are the dielectric losses of these systems smaller than those of $Fe(CO)_5$ but also are believed to be causally associated with accompanying far infrared (Poley) absorption[10,11] (in the 30-80-cm^{-1} range) which is almost certainly not due to intramolecular modes.[12]

Finally, dielectric loss originating from $Fe(CO)_5$ molecules excited in degenerate vibrational states[13] is not a tenable alternative. While such molecules do have effective dipole moments[14,15] and can couple with uniform electric fields, the magnitude of the present absorption (associated with a $\bar{\mu}$ of 0.1-0.2 D) is too great to be consistent with such an explanation.[16]

In view of the foregoing reasons, it would appear justifiable to consider the possible relation between the pronounced stereochemical nonrigidity of $Fe(CO)_5$[2] and its microwave dielectric dispersion. For $Fe(CO)_5$ and numerous other pentacoordinate complexes, the stereoisomerization process alluded to earlier is in accordance with the Berry pseudorotation (BPR) mechanism.[17] The dielectric losses exhibited by $Fe(CO)_5$ may very well be reflective of such an intramolecular rearrangement. Although $Fe(CO)_5$ has no permanent dipole moment, the Berry exchange pathway is inherently associated with changes in polarity—the exchanging nonpolar TBP ground-state form passes through a slightly polar SP configuration (C_{4v}) on the way to the pseudorotated conformer ($D_{3h} \rightleftarrows C_{4v} \rightleftarrows D_{3h}$). The observed relaxation times are much too short to be consistent with a rigid rotational diffusion mechanism involving $Fe(CO)_5$ in a polar configuration.[6,7] To account for this observation it is postulated that (i) the effective moment (~0.1-0.2 D) originates directly as a result of the interconversion, TBP ⇄ SP, and (ii) the polytopal transformation is so rapid that the moment induced changes or vanishes in a time much shorter than that required for molecular rotation of the SP form.[18] In the context of this rapidly fluctuating model, the germane polarization (~0.4-0.5 cm^3) is explained as arising from the fact that, in the presence of a low frequency measuring field, pseudorotations for which this dipole is aligned with the field are favored by a Boltzmann factor[19] with some effective temperature[20]—"fluxional" orientation. If the relevant low frequency polarization originates as pictured, the microwave dielectric dispersion reflects directly the dynamics of the polytopal rearrangement.[18] For dielectric dispersion controlled by BPR, relaxation would become apparent when the period of the measuring field approaches the "pseudorotational" or fluxional relaxation time, τ_f, i.e., the time required to establish the associated moment specifically via the TBP-SP interconversion. (It is important to note that, if fluxional reorientation is in fact operative, dielectric absorption would 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 transiently 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.

The above interpretation of the dielectric data is credible on several counts. The unusually high frequency dispersion and low activation energy can, in principle, be qualitatively ra-

tionalized with a fluxional process wherein rotational diffusion proceeds more slowly than the intramolecular rearrangement occurring.[18] This rate condition may very well be satisfied by stereoisomerizations involving limiting polytopal forms for which the degree of deformation required for interconversion is extremely small. On intuitive grounds, Berry pseudorotation is the most attractive mechanism to invoke in this regard since, for TBP molecules having equivalent ligands, it would be anticipated to occur at a very fast rate and does involve a very slightly polar intermediate configuration.[21] 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[2,22] (no temperature coalescence of NMR spectral lines can be observed), it is thought to occur down to at least 100 K[23], and is believed to be associated with a barrier certainly <5 kcal mol^{-1}.

In summary, it is realized that the dielectric evidence, considered in isolation, is in no way conclusive. However, the results of this investigation, when contemplated in the light of previous nondielectric studies, appear to be best explained at present by the fluxional mechanism proposed.

Studies dealing with the possible application of microwave dielectric relaxation to the elucidation of extremely rapid polytopal rearrangements are continuing in this laboratory.

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(16) As shown by Mills et al.,[14] the effective dipole moment associated with the vibrationally induced rotational absorption can be obtained from the intensity of the IR transition $0-2\nu_6(E')$. The value obtained for PF_5 is ~1.3 × 10^{-3} D.[15]
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(19) Formally, the relevant contribution to the static polarization is obtained by averaging over all pseudorotating molecules.
(20) If such a polarization process is operative, the system establishes the distribution of effective dipole axes via the chemical process itself; i.e., the molecule distinguishes between the two alternate ways of pseudorotating.[18] Therefore, 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. (H. Fröhlich, "Theory of Dielectrics", Clarendon Press, Oxford, 1958, p 81 ff.) E.N.D.C. is indebted to Professor R. S. Berry for informative discussions regarding this point.
(21) During the course of BPR in $Fe(CO)_5$, (i) the iron atom need not move since 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 intermediate C_{4v} state are all relatively small compared with alternate mechanisms suggested for the fundamental step in the rearrangement.[15]
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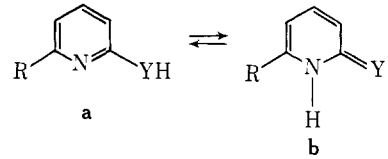
Solvent Effects on Protomeric Equilibria: Quantitative Correlation with an Electrostatic Hydrogen-Bonding Model

Sir:

The possibility of developing a quantitative model for the effect of molecular environment on protomeric equilibria is offered by our recent work which provides the energy difference between isolated heterocyclic protomers in the gas phase and in solution.[1,2] The energy of transfer of such an equilibrium from the gas phase to solution may be discussed in terms of the energies of (1) the interaction of the electrostatic reaction field of the solvent with the different dipoles of the protomeric isomers (ΔE_{ele}), (2) hydrogen-bond acceptance by and donation to the solute from the solvent ($\Delta E_{H_{do}}$ and $\Delta E_{H_{ac}}$), (3) solvent cavitation (ΔE_{cav}), and (4) van der Waals interactions (ΔE_{vdW}).[3,4] Previous analyses of protomeric equilibrium constants have focused on ΔE_{ele},[1,5] a combination of $\Delta E_{H_{ac}}$ and $\Delta E_{H_{do}}$,[6] ΔE_{cav},[7] or on correlation with empirical Z values.[8] We wish to report that solvent effects on the protomeric equilibrium of 6-chloro-2-hydroxypyridine (**1a**)-6-chloro-2-pyridone (**1b**), 2-hydroxypyridine (**2a**)-2-pyridone (**2b**), 4-hydroxypyridine (**3a**)-4-pyridone (**3b**), 2,6-di-*tert*-butyl-4-hydroxypyridine (**4a**)-2,6-di-*tert*-butyl-4-pyridone (**4b**), 6-chloro-2-thiolpyridine (**5a**)-6-chloro-2-thiopyridone (**5b**), 2-thiopyridine (**6a**)-2-thiopyridone (**6b**), and 4-thiolpyridine (**7a**)-4-thiopyridone (**7b**) can be quantitatively analyzed in



1a–1b, R = Cl; Y = O
2a–2b, R = H; Y = O
5a–5b, R = H; Y = S
6a–6b, R = Cl; Y = S

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