It may well be that the above procedure will be restricted to aromatic acids only. Octanoic acid was not reduced to *n*-octane by the procedure described, although it is of interest that the anhydrides of certain aliphatic acids could be isolated by distillation[9] from the mixture after the first step of the reaction sequence.

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Electronic Structure of Ferricenium Ion

Sir:

The ground-state electronic configurations for ferrocene and the ferricenium ion have been formulated through a combination of theoretical and experimental effort.[1-5] Noteworthy among the recent work is an electron spin resonance study[5] of $Fe(cp)_2^+$ in various compounds at 20°K, establishing a $^2E_{2g}(a_{1g})^2(e_{2g})^3$ ground state.[6] The lowest excited state, $^2A_{1g}(a_{1g})^1(e_{2g})^4$, previously has been assumed to lie 16,200 cm^{-1} above the $^2E_{2g}$ state.[3,4] In this communication we report the results of detailed magnetic susceptibility studies which provide further characterization of the ground electronic state of the ferricenium ion and evidence from low-temperature spectra that the electronic transition at 16,200 cm^{-1} is of the charge-transfer type.

The anisotropic *g* values ($g_{\parallel} = 4.36$ and $g_{\perp} = 1.30$) extracted from the esr spectrum[5] of the ferricenium ion at 20°K can be quantitatively interpreted by taking into account spin-orbit coupling and the effect of low-symmetry crystal fields on a $^2E_{2g}$ ground state. Employing as a basis set the wave functions for the resulting pair of Kramers doublets,[7] we have diagonalized the $\hat{L} + 2\hat{S}$ matrix, yielding the energy levels in a magnetic field and thus the theoretical expression for the temperature dependence of the susceptibility. In this treatment the extent of the temperature dependence of the effective magnetic moment of the ferricenium ion is primarily determined by a parameter (δ) which gauges the magnitude of the distortion from D_5 symmetry. The theoretical curves of μ_{eff} *vs.* *T* for two different values of δ show clearly (Figure 1) that the magnetic moment associated with the $^2E_{2g}$ state is expected to be strongly dependent on temperature.

We have measured the magnetic susceptibilities of four crystalline ferricenium salts from 300 to 42°K using a vibrating sample magnetometer. The experimental μ_{eff} *vs.* *T* curves are displayed in Figure 1. The most striking result is that the magnetic moment of the ferricenium ion in these compounds is relatively independent of temperature and definitely does not exhibit the behavior predicted for it on the basis of a $^2E_{2g}$ state with a temperature-independent δ. Thus the $^2E_{2g}$ theoretical susceptibility expression can be modified to account for two possibilities: (a) temperature dependence of the low-symmetry crystal field, $\delta(T)$, or (b) thermal population of the $^2A_{1g}$ state ($\mu_{eff} \simeq 1.73$ BM). We have found that either of these modifications separately is capable of explaining the experimental data, the former requiring δ to vary typically from $\sim$150 cm^{-1} at 42°K to $\sim$350 cm^{-1} at 300°K and the latter requiring[8] $\Delta E[^2A_{1g} - E''(^2E_{2g})] \simeq 350$ cm^{-1}. We are undertaking a single-crystal magnetic susceptibility study over a temperature range in an attempt to decide the relative importance of the two factors.

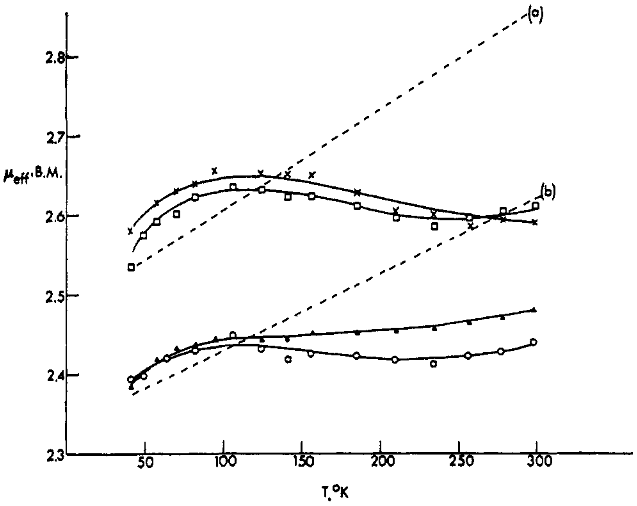

Figure 1. Curves of the effective magnetic moment (μ_{eff}) *vs.* temperature for four ferricenium salts: ×, $[Fe(cp)_2](PF_6)$; □, $[Fe(cp)_2]$(picrate); △, $[Fe(cp)_2](I_3)$; ○, $[Fe(cp)_2](BF_4)$. The dashed lines (a) and (b) are theoretical curves for a $^2E_{2g}$ ground state experiencing low-symmetry crystal fields (δ) of 200 and 350 cm^{-1}, respectively.

Another interesting observation from Figure 1 is that the magnetic moment of the ferricenium ion is a function of the anion. This is interpreted as another indication of the great sensitivity of $\mu_{eff}(^2E_{2g})$ to changes in the magnitude of the distortion from D_5 symmetry. Changes in the range shown can be accounted for simply by the small differences in intermolecular interactions in the four compounds investigated.

Electronic absorption spectra for ferricenium ion at 300 and 77°K are shown in Figure 2. The band at 16,200 cm^{-1} is of moderate intensity and exhibits vibrational structure at 77°K. The vibrational progression is assigned to the symmetric ring–metal stretching frequency, which is found[9,10] at 303 cm^{-1} in ferrocene.

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(1) R. Prins and J. D. W. van Voorst, *J. Chem. Phys.*, **49**, 4665 (1968), and references therein.

(2) J. Smith and B. Meyer, *ibid.*, **48**, 5436 (1968).

(3) D. A. Levy and L. E. Orgel, *Mol. Phys.*, **4**, 93 (1961).

(4) D. R. Scott and R. S. Becker, *J. Phys. Chem.*, **69**, 3207 (1965).

(5) R. Prins and F. J. Reinders, *J. Amer. Chem. Soc.*, **91**, 4929 (1969).

(6) E. Saito [*J. Chem. Phys.*, 50, 3539 (1969)] has reported a ferricenium esr spectrum at 77°K, generated by γ irradiation of ferrocene, which is in disagreement with the results of ref 5. We believe the ferricenium esr spectrum of ref 5 is probably the valid one because of the similarity with results obtained in an esr study of the analogous Fe(III) dicarbollide complexes.[7]

(7) A. H. Maki and T. E. Berry, *J. Amer. Chem. Soc.*, **87**, 4437 (1965).

(8) A near degeneracy of the $^2E_{2g}$ and $^2A_{1g}$ ferricenium states is entirely consistent with one interpretation of the electronic spectrum of ferrocene. The energy difference $\Delta E(^2A_{1g} - {}^2E_{2g})$ is equal to[3] $\Delta\epsilon^{core}(e_{2g} - a_{1g}) + 20B$, where *B* is the Racah parameter. Our best low-temperature spectrum of ferrocene places the d–d transitions as follows: $^1A_{1g} \rightarrow a^1E_{1g}$, 21,800; $^1A_{1g} \rightarrow {}^1E_{2g}$, 24,000; $^1A_{1g} \rightarrow b^1E_{1g}$, 30,800 cm^{-1}. For ferrocene this gives $\Delta\epsilon^{core}(e_{2g} - a_{1g}) = -7100$ cm^{-1} and $20B = 7800$ cm^{-1}. Assuming no drastic changes occur in $\Delta\epsilon^{core}$ and *B* in going from $Fe(cp)_2$ to $Fe(cp)_2^+$, $\Delta E(^2A_{1g} - {}^2E_{2g})$ is estimated to be relatively small.

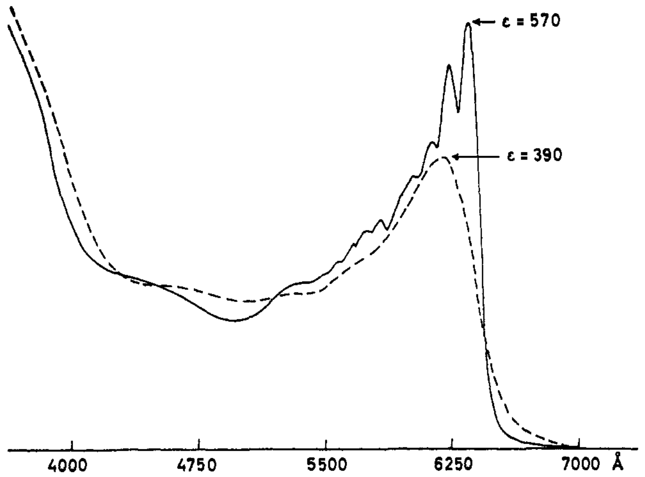

Figure 2. Electronic absorption spectra of $[Fe(cp)_2](BF_4)$ in 10 *M* LiCl aqueous solution: - - - -, 300°K; ——, 77°K.

The origin (0,0) of the system is placed at 15,733 cm^{-1} and the average spacing between peaks in the progression is 280 cm^{-1}. The 16,200-cm^{-1} band is assigned as primarily $^2E_{2g} \rightarrow {}^2E_{1u}$, which is the allowed charge-transfer transition from the e_{1u} bonding ligand level to the hole in the e_{2g} metal level. By analogy to ferricyanide,[11] low-energy ligand → metal charge-transfer transitions are expected in the ferricenium spectrum. As a final point of interest, the integrated intensity of the 16,200-cm^{-1} system increases by approximately 20% in going from 300 to to 77°K (1.9×10^{-3} to 2.3×10^{-3}); this unusual intensity enhancement is compatible with the increase at 77°K in the population of the E′′ component of the $^2E_{2g}$ state.

Acknowledgment. This research was supported by the National Science Foundation. We thank Professor C. J. Ballhausen for several stimulating discussions.

(9) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, 10, 307 (1958).

(10) J. Bodenheimer, E. Loewenthal, and W. Low, *Chem. Phys. Lett.*, 3, 715 (1969).

(11) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 4260 (1968).

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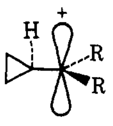
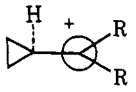
Nuclear Magnetic Double Resonance Studies of the Dimethylcyclopropylcarbinyl Cation. Measurement of the Rotation Barrier

Sir:

The elucidation of the role of the cyclopropyl ring in the chemistry of the cyclopropylcarbinyl and related systems remains a topic of considerable interest.[1] The cyclopropylcarbinyl cation prefers the bisected structure (**1a**) to the perpendicular conformation (**2a**). In the bisected form, the "vacant" p orbital is parallel to the ring and maximum overlap is attained. The magnitude of the energy difference between the two conformations has been estimated by molecular orbital calculations to be: 25 (CNDO),[2a] 9 (EHT),[2b] 19 (AS MO-SCF),[2c] and 22 kcal/mol (NNDO).[2d]



1a, R = H
1b, R = CH_3



2a, R = H
2b, R = CH_3

In 1965, Pittman and Olah reported the direct observation of the dimethylcyclopropylcarbinyl cation.[3] The pmr spectrum showed two nonequivalent methyl groups, and no temperature dependence in the range investigated. They concluded that the ion prefers the bisected form (**1b**). The absence of temperature dependence indicates that rotation around the cyclopropyl–C^+ bond is slow on the nmr time scale. The rotation barrier was estimated to be at least 8–10 kcal/mol.

Although no calculations or direct measurements of the energy difference between the two conformations **1b** and **2b** in tertiary cyclopropylcarbinyl cations have appeared, Schleyer and Buss[1] have estimated that "the difference . . . in tertiary systems, as solvolysis transition states, is 10 kcal/mol. In the free ions themselves this difference might be larger."[4]

Recently Olah and coworkers[5] have reported the complete ^{13}C spectrum of the dimethylcyclopropylcarbinyl cation. The ^{13}C shifts (δ, CS_2) of the carbonium ion carbon and the cyclopropyl methylene carbons were found to be −86.8 and 140.4, respectively. These shifts indicate that part of the charge is delocalized into the cyclopropane ring. Two distinct methyl resonances at 162.7 and 153.9 ppm were observed.

We wish to report the measurement of the rate of rotation in the dimethylcyclopropylcarbinyl cation[6] by the double resonance method of Forsen and Hoffman.[7] This technique enables the determination of much slower rates than can be measured by the conventional line shape method.

In the dimethylcyclopropylcarbinyl cation, the methyl groups, which are exchanged by rotation, occupy magnetically nonequivalent sites. Therefore, a perturbation of the magnetization at one site should be detectable at the other. When the low field methyl resonance was irradiated, we observed decay of the magnetization of the upfield methyl signal. Upon removal of the saturating field, the peak relaxed to its

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(1) For an extensive bibliography see: P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, 88, 2321 (1966); P. von R. Schleyer and V. Buss, *ibid.*, 91, 5882 (1969).

(2) (a) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968). See Table II, footnote *a*. (b) R. Hoffman, *J. Chem. Phys.*, 40, 2480 (1964). (c) T. Yonezawa, H. Nakatsuji, and H. Kato, *Bull. Chem. Soc. Jap.*, 39, 2788 (1966). (d) V. Buss, to be published, cited in P. von R. Schleyer and V. Buss, ref 1. See also C. Trindle and O. Sinanoglu, *J. Amer. Chem. Soc.*, 91, 4054 (1969).

(3) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, 87, 2998, 5123 (1965). See also C. D. Poulter and S. Winstein, *ibid.*, 91, 3650 (1969).

(4) See also J. C. Martin and B. R. Ree, *ibid.*, 91, 5882 (1969).

(5) G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *ibid.*, 92, 2544 (1970). We thank Professor Olah for communicating these results to us prior to publication.

(6) Samples of the ion were prepared from dimethylcyclopropylcarbinol in SO_2–SbF_5–HSO_3F according to the method of Olah.[3] The samples were degassed and vacuum sealed. Nmr spectra were recorded on a Varian HA-100 spectrometer operating in the internal lock mode. A Hewlett-Packard wide range oscillator, Model 200CD, was used for double resonance experiments. Time-dependent spectra were recorded on a Sanborn Recorder, Series 770.

(7) S. Forsen and R. Hoffman, *Acta Chem. Scand.*, 17, 1787 (1963); *J. Chem. Phys.*, 39, 2893 (1963). For an application of this method see: F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 89, 760 (1967).