which the two ends of the molecule are nearly in contact decreases greatly with increasing number of methylene groups. In addition, the rate ratio for $n = 3$ in t-butyl alcohol is 0.75 as compared to the value of 0.55 in benzene. Since the solvent properties of t-butyl alcohol are quite different from those for benzene (for example, the viscosities at 23° are a factor of 10 different[16]), this shows that k_{et} depends to the same extent on these properties, as does k_{q}. The logical conclusion to be drawn from both of these considerations is that in the $n = 2$–4 compounds intramolecular energy transfer occurs by the same mechanism as bimolecular quenching—namely the exchange mechanism which requires a collision between the donor and acceptor.

The quenching curve for the $n = 1$ compound is composed of two linear portions with differing slopes. These results imply that energy transfer occurs from two different excited states in this compound. Further work is in progress on this compound.

Acknowledgment. We are pleased to acknowledge the support (in part) of this work by National Institutes of Health Grant GM-12988.

[16] For experimental estimates cf diffusion rate constants in tertiary alcohols see P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968). Wagner concludes that the diffusion rate constant in t-butyl alcohol is somewhat larger than would be calculated from the viscosity.

[17] Alfred P. Sloan Fellow.

[18] National Institutes of Health Predoctoral Fellow, 1965–1968.

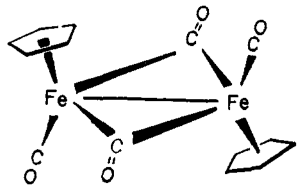
Dwaine O. Cowan,[17] Anthony A. Baum[18]
Department of Chemistry, The John Hopkins University
Baltimore, Maryland 21218

Received November 15, 1969

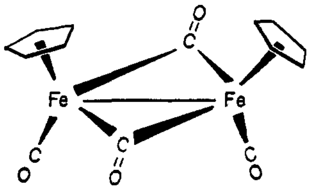
A Definitive Identification of the Structures of Dicyclopentadienyldiiron Tetracarbonyl in Solution

Sir:

It was shown in 1958 that $(C_5H_5)_2Fe_2(CO)_4$ has the molecular structure I in the only crystalline form then recognized.[1] Investigations of the vibrational spectra of solutions of this substance[2,3] showed that some kind and degree of rearrangement of I must occur in solution. Benzene and cyclohexane solutions were shown to contain polar molecules (apparent dipole moment, number averages, 3.1 and 2.4 D).[4] More recently, two new, detailed studies were published. Cotton and Yagupsky[5] studied the CO stretching fundamentals as well as overtones and combinations, by employing CS_2 and heptane solutions, and considered that all their data could be accounted for by assuming that the iron compound in CS_2 solution is almost entirely made up of molecules with structure II plus a trace of some noncentrosymmetric, nonbridged isomer (probably of C_{2v} or C_2 symmetry). The Ru analog was postulated to consist of a roughly equimolar mixture of the same two structures. Fischer, Vogler, and Noack[6] studied the CO stretching fundamentals as a function of temperature. They drew essentially the same conclusions as to the presence of two isomers in solution, and Noack[7] estimated that the cis-bridged isomer is more stable than the nonbridged isomer by ~4 and ~1.5 kcal/mol for the iron compound and its ruthenium analog, respectively. Bryan, *et al.*,[8] have recently confirmed the existence of structure II in a second crystal form obtainable at low temperatures from polar solvents.



I(C_{2h})



II(C_{2v})

The "two-structure" hypothesis for the solutions was soon challenged by Manning,[9] who studied solutions in more polar solvents. On the basis of various small effects (broadenings, occasional splittings, and variations in relative intensities), he was led to propose a "three-structure" model in which those spectral features attributed in the two-structure model to II (or its Ru analog) are now attributed to a mixture of I and II. In our view, Manning's observations fall short of proving the three-structure hypothesis; nevertheless, Manning makes a good case that such a hypothesis is plausible. It thus appeared that some independent and definitive experiment was required. We have carried out such an experiment and give here a preliminary account of the results.

Figure 1 shows the 100-MHz pmr spectrum of $(C_5H_5)_2Fe_2(CO)_4$ as a function of temperature and solvent dielectric constant. The upper four spectra, taken on a solution in $C_6D_5CD_3$–CS_2, show that the single peak observed at 25° collapses and finally separates into two peaks of similar but not equal intensities, which are sharp at ~−75°. These results prove that the solutions contain two species in *comparable* quantities which interconvert rapidly at temperatures above ~−40°. We can see no acceptable alternative to the view that the two interconverting species are I and II and presume that the nonbridged structure is an intermediate through which the interconversion is effected. The bottom spectrum is obtained in a solvent whose dielectric constant is raised by addition of CD_2Cl_2. This should displace the *cis–trans* equilibrium in favor of the *cis* species, and,

[1] O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

[2] H. Stammreich, G. Wilkinson, and F. A. Cotton, *J. Inorg. Nucl. Chem.*, **9**, 3 (1959).

[3] K. Noack, *ibid.*, **25**, 1383 (1963).

[4] E. Weiss, H. Hubel, and R. Merenyi, *Chem. Ber.*, **95**, 1155 (1962).

[5] F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967).

[6] R. D. Fischer, A. Vogler, and K. Noack, *J. Organometal. Chem.*, **7**, 135 (1967).

[7] K. Noack, *ibid.*, **7**, 151 (1967).

[8] R. F. Bryan, P. T. Greene, D. S. Field, and M. J. Newlands, *Chem. Commun.*, 1477 (1969).

[9] A. R. Manning, *J. Chem. Soc., A*, 1319 (1968); 1498 (1969).

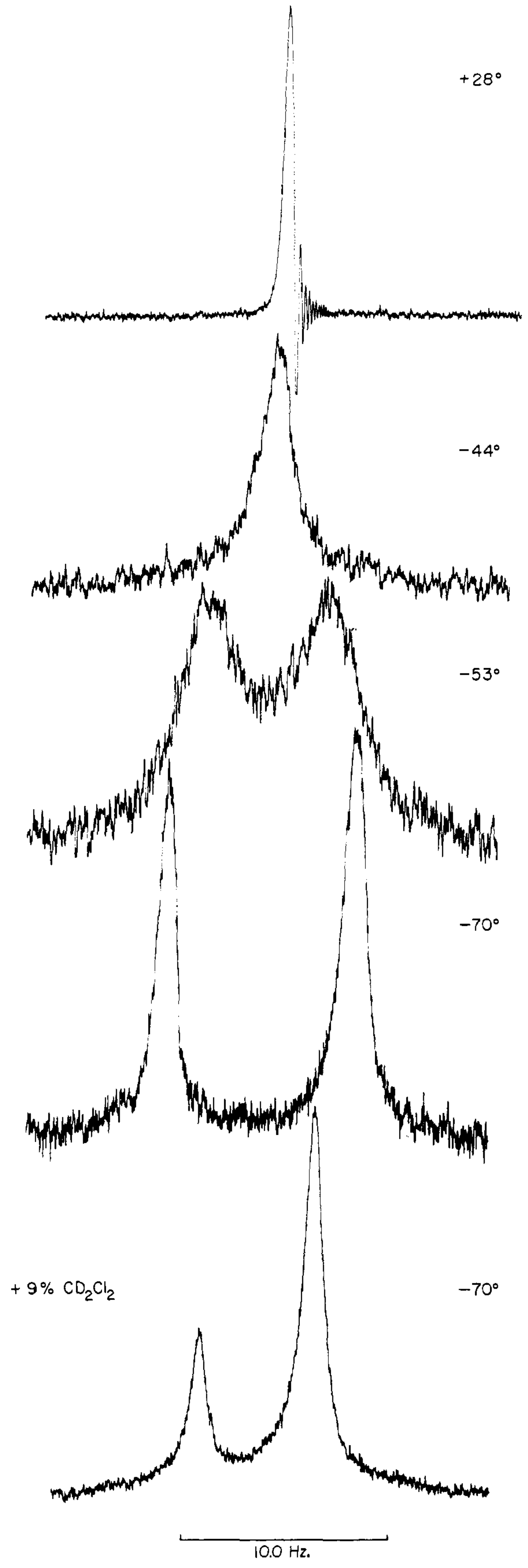


Figure 1. Pmr spectra (100 MHz) for $(C_5H_5)_2Fe_2(CO)_4$ at various temperatures. Upper four traces made using $C_6D_5CD_3$–CS_2 (1/3, v/v). Lower trace made using same solvent to which ~9% volume of CD_2Cl_2 was added.

in accord with this, the intensity ratio of the two peaks is substantially affected.

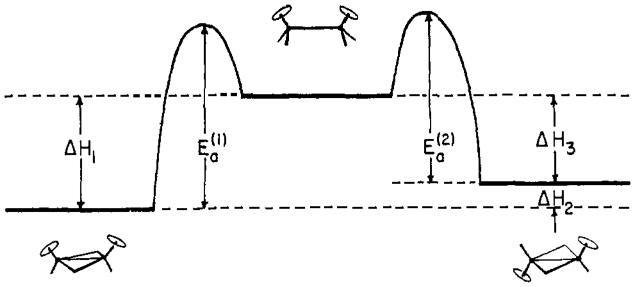


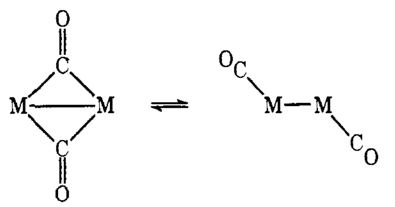
Figure 2. Schematic diagram of reaction coordinate for interconversion of *cis*-bridged, *trans*-bridged, and nonbridged structures of $(C_5H_5)_2Fe_2(CO)_4$.

With constant solvent ($C_6D_5CD_3$–CS_2) composition, the intensity ratio varies with temperature from -70 to $-92°$. The logarithm of the intensity ratio plotted against T^{-1} gives a straight line. This line can be extrapolated to ~25° and the isomer ratio (*trans*/*cis* $\approx$ 0.75 at 25°) estimated therefrom. This estimate agrees well with an estimate made in the manner suggested by Manning from the infrared spectrum (*trans*/*cis* $\approx$ 0.77 at 25°). This agreement is extremely important since it shows that in the infrared and nmr measurements we are dealing with the same phenomenon.

Figure 2 shows a schematic diagram for the interconversion reaction in $C_6D_5CD_3$–CS_2 (1/3, v/v). We estimate that $\Delta H_2 \approx 1.0 \pm 0.2$ kcal/mol. Noack's estimate that ΔH_1 and ΔH_3 are ~4 kcal leads to the expectation that $\Delta E_a{}^1 \approx \Delta E_a{}^2 \gtrsim 4$ kcal; from nmr line-shape measurements we tentatively estimate an activation energy of 13 ± 2 kcal.

Since $\Delta H_1 \approx \Delta H_3 \approx 1.5$ kcal/mol for the Ru compound, we expect E_a to be only ~10 kcal and rapid interconversion of *cis*-bridged, *trans*-bridged, and nonbridged species should occur down to temperatures well below $-100°$. In accord with this $(C_5H_5)_2Ru_2(CO)_4$ has a single sharp nmr line down to $-100°$.

The pmr experiments reported here, as well as other results we shall publish elsewhere, resolve the question of the structure(s) of $(C_5H_5)_2Fe_2(CO)_4$ in solution definitively in favor of Manning's three-structure model. However, the results have, in our opinion, an importance which transcends their role in resolving this specific problem. They provide the first strong proof that bridged–nonbridged structure interconversions, of the type



can occur very rapidly and can therefore form the basis for an extensive and important class of stereochemically nonrigid or fluxional molecules.[10]

(10) This investigation was supported, in part, by the National Science Foundation under Grant No. GP-7034X.

(11) National Science Foundation Predoctoral Fellow, 1965–1960.

(12) National Science Foundation Predoctoral Fellow, 1966–1970.

J. G. Bullitt,[11] F. A. Cotton, T. J. Marks[12]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received January 10, 1970