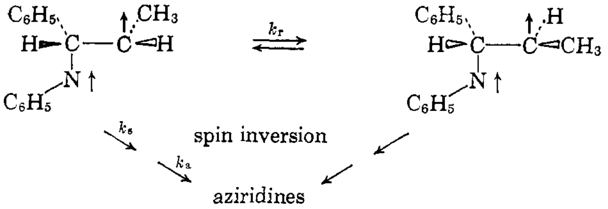

Because ring closure should be rapid, as in direct photolysis, the loss of stereospecificity suggests that spin inversion is slower than bond rotation ($k_s < k_r$). The similarity of product composition from I and II indicates equilibration of triplet diradicals is approached, if not actually obtained. Predominance of the thermodynamically less stable *cis*-aziridine may reflect rate differences in the ring-closure process.

In summary, predominant retention of geometry is observed in the direct photolysis. Thus, ring closure is more rapid than bond rotation in the singlet 1,3-diradical. On the other hand, rotational equilibrium is approached under conditions leading to a triplet 1,3-diradical. It is therefore concluded that spin inversion is slow relative to σ-bond rotation. The results provide confirmatory evidence for Skell's proposal.[1]

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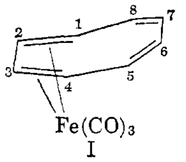
Valence Tautomerism in Cyclooctatetraene–IronTricarbonyl

Sir:

Cyclooctatetraene–iron tricarbonyl is an interesting complex in that it is one of the first systems isolated which indicated that certain olefin–metal π complexes might be capable of undergoing extremely rapid valence tautomerism. Dickens and Lipscomb[1] have shown that in the solid state the arrangement of the atoms are as indicated in I; in this system the iron atom is bonded to one conjugated diene unit with the remaining two double bonds not being involved in coordination to the metal atom. In order to explain the observed single proton nmr absorption at τ 4.76 for the complex these authors suggested that some dynamic effect was occurring in solution.



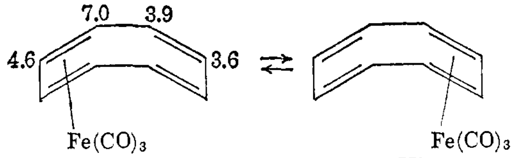
I

Recently Winstein and co-workers[2] have reported that at −150° the spectrum of this complex consists of two peaks of equal areas separated by 80 cps and have taken this as evidence that at this temperature the dynamic effect has been stopped and the system is "frozen" into structure I. We have also been studying this and related systems, and while we agree with the experimental data reported by these workers, we wish to report an alternate interpretation of these results.

The spectrum of I at −120° consists of two absorptions of equal areas at τ 4.06 and 5.44.[3] Winstein and co-workers attribute the low-field absorption to the four olefinic protons and the high-field absorption to the four protons of the diene–iron tricarbonyl moiety in I. However, it is characteristic of derivatives of butadiene–iron tricarbonyl complexes that there is a large difference in chemical shift between the internal hydrogens (2 and 3 in I) and the terminal hydrogens (1 and 4) of the diene ligand. In a series of 39 butadiene–iron tricarbonyl complexes studied either in our laboratories or reported by other workers, these two types of protons are invariably found to be separated by 80 cps or more; the internal protons and the terminal protons for cyclic diene complexes typically fall in the range τ 4.5–5.0 and 6.5–7.3, respectively.[4] Particularly on the basis of the absence of absorption in the neighborhood of τ 7.0 we therefore consider that the observed spectrum at −150° does not correspond to the rigid system I.

Evidence that absorptions at higher fields than τ 5.5 are involved in system I is indicated from a study of substituted cyclooctatetraene–iron tricarbonyl complexes. In addition to the parent system we have also found a temperature-dependent nmr spectrum of the $Fe(CO)_3$ complexes of methyl-, ethyl-, phenyl-, triphenylmethyl-, and carbomethoxycyclooctatetraene.[5] At +30°, the spectrum of the methyl derivative consists of a doublet centered at τ 4.33, a triplet at 4.92, and a doublet at 5.50, having areas of 3, 2.3 and 1.8, respectively; the methyl group appears as a sharp singlet at τ 8.13 (area 3). At −120° the spectrum is drastically changed and consists of approximately equal areas centered at τ 4.05 and 5.62 with widths at half-height of 16 and 21 cps, respectively; the CH_3 absorptions remain at τ 8.1. It is clear that at room temperature the absorption at τ 5.50 results from averaging of protons in different chemical environments; since olefinic character must be involved in this averaging process, then in some contributing structures these protons must absorb at considerably higher values in order that the average value be τ 5.5. That the introduction of the methyl group has not given rise to any sigficant change in chemical shift of the ring protons in the methyl derivative as compared to the parent system is indicated by the fact that the weighted average of the three regions of absorption in the room-temperature spectrum of the methyl complex is τ 4.8, which is identical with that of the single peak found for the parent system at room temperature.

It seems to us that a more reasonable way of accommodating the appearance of the spectrum of cyclooctatetraene–iron tricarbonyl at −150° is to assume that it is undergoing isomerization indicated by IIa ⇄ IIb at this temperature.



IIa IIb

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[1] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 37, 2084 (1962).

[2] C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3444 (1966).

[3] Reported at the Robert A. Welch Symposium on Organometallic Compounds, Nov 1965. The proceedings of this meeting are currently in press.

[4] R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, 1, 12 (1964).

[5] Details of the variation in the nmr spectrum of these complexes will be published later.

If we assume that the protons have the values indicated in IIa, which are within the normal range expected for each type, then the isomerization IIa $\rightleftarrows$ IIb would give rise to a spectrum consisting of two areas of absorption at τ 4.1 and 5.5 in agreement with what is observed.

Such a process alone, of course, would not account for the single peak observed at room temperature, suggesting that at least one other process must also be occurring at the higher temperature. Several such processes can be considered: (a) a mechanism in which one double bond in I displaces another olefinic ligand, three such rapid reactions could then render all eight protons equivalent; (b) the $Fe(CO)_3$ group moves from the center of one C–C bond to the next, in which case seven such reactions would render the protons equivalent; this mechanism would also require a double bond shift of the olefinic bonds; (c) the $Fe(CO)_3$ group moves to the center of the ring to form a relatively unstable symmetrical complex and then returns to the diene formulation; depending on the nature of the ring in the symmetrical species this particular mechanism may or may not result in a shift of the double bonds.

The symmetry and multiplicity of the peaks observed in the spin-decoupling experiments with carbomethoxycyclooctatetraene–iron tricarbonyl at −55° indicate that the rearranging process is such that, on the average, the ligand possesses a plane of symmetry. Therefore, at least one mechanism involving a double bond shift (possibly b) must be operating at this temperature. With such a process, the chemical shifts employed in IIa would then lead to a single peak at τ 4.8, which again is what is observed.

We consider then that at least two types of degenerate valence tautomerism reactions are involved in the rearrangement of I at room temperature. The facility of the process is quite remarkable and is probably related to the size of the metal orbitals involved in the bonding; the orbitals being larger, the bond-making process can be much further advanced before the bond-breaking process begins to be felt in the metal reactions as compared to reactions involving purely carbon–carbon bonds. This would have the effect of lowering the activation energy for the rearrangement of the organometallic species.

(6) We thank the National Science Foundation and the U. S. Army Research Office (Durham) for financial assitance. We also thank Professor M. J. S. Dewar for helpful discussion.

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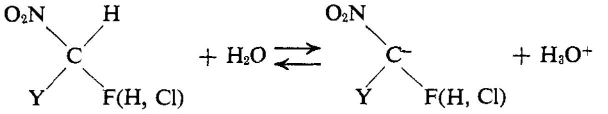
Fluoronitroaliphatics. I. The Effect of α Fluorine on the Acidities of Substituted Nitromethanes[1]

Sir:

Although a number of workers have concluded from deuterium exchange studies that the α-fluorine substituent increases the acidity of polyhaloaliphatic hydrocarbons, but to a lesser extent than α chlorine or α bromine,[2] direct measurements of C–H acidities in compounds of the type R_1R_2CFH are confined to a single recent communication on fluorodinitromethane.[3]

We wish now to report ionization constant measurements for a series of substituted fluoronitromethanes as well as their hydrogen and chlorine analogs.

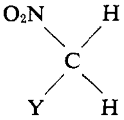


Y = Cl, COOEt, CONH$_2$

These systems differ from the polyhaloaliphatic hydrocarbons in two important regards: (a) the presence of a nitro group permits ready determination of the ionization constants by spectrophotometric means; (b) the central carbon in the nitrocarbanion is sp^2 hybridized with the negative charge delocalized over the π system formed by the central carbon, the nitro group, and the negative substituent Y.

Listed in Table I are the apparent pK values for the three series of mononitromethanes,[4] determined spectrophotometrically in aqueous solutions of ionic strength 0.06, as well as ionization enthalpies and entropies for two of the series as obtained from pK measurements at 25 and 40°. Also included are literature data for dinitromethane and the halodinitromethanes.[5]

Table I. Apparent Ionization Constants of Substituted Nitromethanes

	pK_a in water, μ = 0.06 ± 0.01 25 ± 0.1°	 40 ± 0.1°	ΔH, kcal/mole	ΔS, eu
Y = COOEt				
X = Cl	4.16			
H	5.75			
F	6.28			
Y = CONH$_2$				
X = Cl	3.50	3.56	−1.7	−22
H	5.18	5.15	0.9	−21
F	5.89	5.82	1.9	−20
Y = Cl				
X = Cl	5.99	5.98	0.3	−26
H	7.20	7.16	1.1	−29
F	10.14	9.92	6.3	−25
Y = NO$_2$				
X = Cl	3.80			
H	3.57			
F	7.70 (20°)[3] 7.70 (25°)[5]			

It may be seen that, while α chlorine in most cases leads to the expected increase in C–H acidity relative to X = H, *the effect of α fluorine is in the opposite direction,*

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(1) Presented in part at the Third International Symposium on Fluorine Chemistry, Munich, Sept 1965.

(2) J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 1406 (1957); J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956); S. Andreades, *ibid.*, **86**, 2003 (1964).

(3) V. I. Slovetskii, L. V. Okhobystina, A. A. Feinzil'berg, A. I. Ivanov, L. J. Birynkova, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2063 (1965); The pK_a reported by these workers in water at 20° corresponds exactly with that observed by Dr. T. N. Hall of these laboratories at 25°.

(4) The synthesis of the fluoronitromethanes will be described elsewhere.

(5) Dinitromethane: R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953); redetermined by Slovetskii *et al.*;[3] chlorodinitromethane: T. N. Hall, *J. Org. Chem.*, **29**, 3587 (1964); fluorodinitromethane: T. N. Hall, these laboratories, private communication; Slovetskii, *et al.*[3]