for anchimeric acceleration in the acetolysis of 7-norbornyl *p*-toluenesulfonate.

Predominant retention of configuration in the solvolysis of deuterated *p*-bromobenzenesulfonate Ia is readily explained by the postulate that nonclassical ion II is an intermediate. The corresponding undeuterated nonclassical ion was proposed in 1958 by Winstein, *et al.*, in their work on the acetolysis of 7-norbornyl *p*-bromobenzenesulfonate in order to explain the fact that the rearranged acetate formed in this solvolysis, 2-bicyclo[3.2.0]heptyl acetate, is exclusively the *trans* isomer.[12] The presence of some *syn*-7-norbornyl product in the present work may be explained by concurrent SN2 reaction (unlikely since added sodium acetate does not change the proportion of *syn* to *anti* acetate in the acetolysis product) or by "leakage" to classical ion III. "Leakage" to a classical ion seems reasonable since there appears to be little if any rate enhancement in acetolysis.[8-10] There may be some rate enhancement, though. (Acceleration by a factor of up to ten or so would not be distinguishable from the scatter in the Foote and Schleyer correlations.)

It was hoped that the results of the formolysis might provide a means of choosing between the classical and nonclassical ion interpretations. If nonclassical ions are involved, formolysis at a lower temperature (here, 100°) would be expected to give relatively more retention than does acetolysis at a higher temperature (here, 205°) on the basis of the fact that in solvolysis of *erythro*- and *threo*-3-phenyl-2-butyl *p*-toluenesulfonates the amount of retention of configuration increases from 95% to over 99% in going from acetic acid at 75° to formic acid at 25°.[13] On the other hand, if retention is to be explained on the basis of front-side collapse of ion pairs, formolysis at 100° would be expected to give much more inversion than does acetolysis at 205°, on the basis of the fact that Jenny and Winstein found that acetolysis of *p*-methoxyphenylethyl *p*-toluenesulfonate at 75° needed to be described in terms of ion pairs and dissociated ions while formolysis at 25° was explained in terms of dissociated ions only.[14] Also, Winstein, *et al.*, report this same finding for 2,4-dimethoxyphenylethyl arenesulfonates.[15] The experimental observations of 10 ± 5% inversion in acetic acid at 205° and 15 ± 5% inversion in formic acid at 100° if anything fit the ion-pairing explanation slightly better than they do the nonclassical ion explanation, but are clearly about midway between the extremes cited above. It is therefore not possible to make a clear-cut choice between the classical and nonclassical ion interpretations at this point.

Further work on the solvolysis of 7-norbornyl *p*-bromobenzenesulfonate is in progress.

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(10) Two of the twenty compounds used by Foote in his correlation have been shown to have structures different from those accepted at the time the correlation was published.[11] Also, 7-norbornyl *p*-toluenesulfonate is itself used in establishing the correlation. Consequently, the least-squares line of the Foote correlation was recalculated omitting the two compounds whose structures were incorrect (case A) and omitting these two compounds and also omitting 7-norbornyl *p*-toluenesulfonate (case B). The results are: case A: $\log k_{\mathrm{rel}} = -0.132 (\nu_{\mathrm{CO}} - 1720)$, correlation coefficient -0.98; case B: $\log k_{\mathrm{rel}} = -0.133 (\nu_{\mathrm{CO}} - 1720)$, correlation coefficient -0.95. The observed rate for 7-norbornyl *p*-toluenesulfonate is $\log k_{\mathrm{rel}} = -7.00$. The calculated rate is $\log k_{\mathrm{rel}} = -7.00$ (case A) and -7.04 (Case B).

(11) P. von R. Schleyer, W. E. Watts, and C. Cupas, *J. Am. Chem. Soc.*, **86**, 2722 (1964).

(12) S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).

(13) D. J. Cram, *ibid.*, **74**, 2129, 2137 (1952).

(14) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958).

(15) S. Winstein, B. Appel, R. Baker, and A. Diaz, Special Publication No. 19, The Chemical Society, London, 1965, p 120.

The Structure of Cyclooctatetraeneiron Tricarbonyl in Solution[1]

Sir:

We recently reported that cyclooctatetraeneiron tricarbonyl ($COTFe(CO)_3$) *in solution* has a 1,3-diene-bonded structure (I) and that the nmr spectrum of the compound at −145° is that of the "frozen" structure I.[2] Two other groups of workers, Cotton, Davison, and Faller (CDF)[3] and Keller, Shoulders, and Pettit (KSP),[4] subsequently reached conclusions different from ours. We now show that our original interpretation is correct, and that the deductions of CDF and KSP are invalid.

That $COTFe(CO)_3$ has structure I in the crystalline state is well established[5] and is not in dispute. CDF[3] present two arguments against $COTFe(CO)_3$ having structure I *in solution*, and they suggest a 1,5-diene-bonded (tub) structure under these conditions.

CDF's first argument is that the infrared C–H stretching bands of $COTFe(CO)_3$ in solution are different from those found in the solid, but are similar to those of 1,5-diene-bonded (tub) COT complexes. However, the great similarity of the fingerprint region of $COTFe(CO)_3$ in the solid and in solution[5,6] was ignored by CDF. These spectra are presented in Figure 1, together with the spectra of $COTMo(CO)_4$[7] and $COTW(CO)_4$,[8] two compounds which have 1,5-diene-bonded (tub) structures and which display the expected[9] two sharp lines in their nmr spectra (τ 4.46, 5.80 and 3.66, 5.25, respectively).

In the structurally significant fingerprint region (1600–750 cm^{-1}), only very small differences (0.1–0.3%) in the frequencies of $COTFe(CO)_3$ are observed between the solid and solution spectra. The general

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(1) (a) Research supported in part by the National Science Foundation; (b) research sponsored in part by the U. S. Army Research Office (Durham).

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

(3) F. A. Cotton, A. Davison, and J. W. Faller, *ibid.*, **88**, 4570 (1966).

(4) C. E. Keller, B. A. Shoulders, and R. Pettit, *ibid.*, **88**, 4760 (1966).

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

(6) R. T. Bailey, E. R. Lippincott, and D. Steele, *J. Am. Chem. Soc.*, **87**, 5346 (1965).

(7) H. D. Kaesz, S. Winstein, and C. G. Kreiter, *ibid.*, **88**, 1319 (1966).

(8) This complex has recently been prepared in these laboratories by procedures similar to those used in the preparation of the molybdenum analog (A. Maasbol, unpublished work).

(9) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 1 (1965).

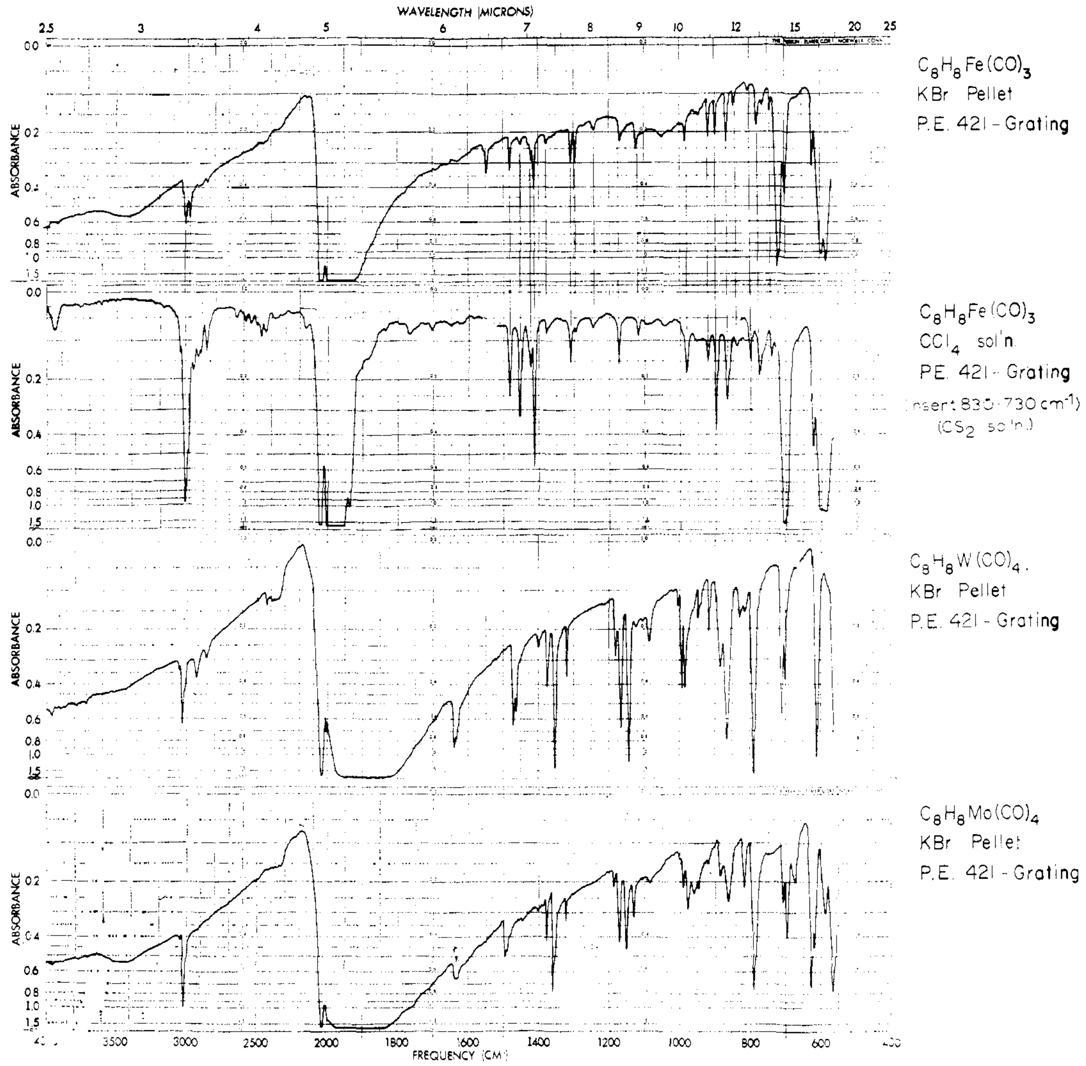
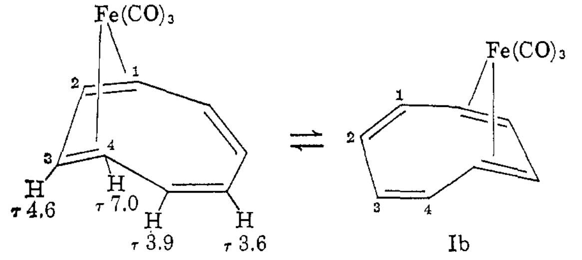


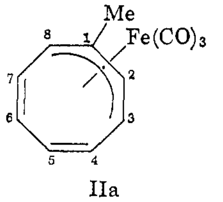
Figure 1.

similarity of the fingerprint region of the spectra of the molybdenum and tungsten (tub) complexes is to be contrasted with the great differences between these spectra on the one hand and the spectra of the iron complex on the other. Therefore, despite the slight variation in the precise shape of the C–H stretching band[10] of COTFe(CO)$_3$ in the solid and liquid phases, the infrared evidence is overwhelmingly in favor of a single structure (1,3-diene bonded) in the two phases.

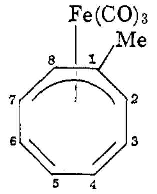


Ia

Ib



IIa



IIb

CDF's second argument is that the chemical shifts found for COTFe(CO)$_3$ at $-145°$ are not those expected for structure Ia, especially for the protons on C$_1$ and C$_4$.[11] However, their suggested alternative tub structure certainly does not have the expected chemical shifts,[12] nor does it explain the widths[2] of the bands of the nmr spectrum of COTFe(CO)$_3$ at $-145°$.

KSP[4] accept the 1,3-diene-bonded structure I for COTFe(CO)$_3$ in solution, but they present the same objections as did CDF[3] to our assignments of chemical

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(10) The change in the C–H band of COTFe(CO)$_3$ on going from solid to solution appears to be due to a broadening of the low-frequency band of the C–H doublet and is not necessarily indicative of a structural change.

(11) On the basis of our published spectrum,[2] we estimate that the highest chemical shift occurring in COTFe(CO)$_3$ at $-145°$ is *ca.* τ 5.7. Because of the peculiar structure of I, known 1,3-diene–iron tricarbonyl complexes may not be good model compounds. Furthermore, an examination of the literature[3,4,9] indicates that H$_1$ and H$_4$ in 1,3-diene complexes have rather variable chemical shifts.

(12) Bonding of metals to olefins results in a high-field shift of the olefinic protons. These shifts[9] are very similar (1.7 and 1.5 ppm, respectively) for norbornadiene and COT upon bonding to Mo(CO)$_4$. This should also be true for the corresponding Fe(CO)$_3$ complexes. For norbornadiene this shift[9] is 3.5 ppm. Therefore the high-field protons in a tub COTFe(CO)$_3$ complex should be at τ 4.3 + 3.5 = 7.8, whereas the observed shift is $\tau \lesssim 5.7$ ppm.

shifts at −145°. They agree that the spectrum at −145° is that of I, but propose that the valency tautomerism Ia $\rightleftarrows$ Ib is still very rapid at −145°. By using plausible chemical shifts (see Ia), they predict that the low-temperature spectrum should consist of two bands at τ 4.1 and 5.5, roughly as observed.[13]

KSP[4] claim support for their theory from the fact that the nmr spectrum of methylcyclooctatetraeneiron tricarbonyl ($MeCOTFe(CO)_3$) consists of three bands (τ 4.33, 4.92, and 5.50; intensity ratios of 3:2.3:1.8) at room temperature and of two bands (τ 4.05 and 5.62, reported as of "approximately equal areas") at −120°. They argue that the room-temperature band at τ 5.50 must be the average between two bands, one of which is of the normal olefinic type and at low field; therefore, the other band must be at much higher field than τ 5.5 for the average to be at τ 5.5. It is quite clear that this argument is fallacious as is shown below. Thus the nmr spectrum of $MeCOTFe(CO)_3$ does not support the ideas of KSP.[14]

We now show that the data of KSP on $MeCOTFe(CO)_3$ are actually in excellent agreement with our interpretation.[2] The evidence indicates that the $Fe(CO)_3$ group prefers to be attached to certain carbon atoms of the ring of MeCOT, a possibility ignored by KSP. These carbons are 8123 and 7812 in IIa and IIb, respectively. In our view, the spectrum at low temperatures is that of frozen IIa and IIb, whereas at room temperature the chemical shifts are the average of those in IIa and IIb. On this basis, and using[15] the value τ 4.1 for any of the protons of noncomplexed olefinic groups and τ 5.4 for any of the iron-bonded olefinic protons, the chemical shifts shown in Table I are predicted for $MeCOTFe(CO)_3$ at −145° and at room temperature. The predicted low-temperature spectrum (τ 4.1 and 5.4, relative intensities 4:3) and the high-temperature spectrum (τ 4.1, 4.75, and 5.4, relative intensities 3:2:2) are in substantial agreement with those reported by KSP.[4] Valency tautomers with the $Fe(CO)_3$ at positions different from those in IIa or IIb give calculated spectra in gross disagreement with the experimental data and thus cannot be present in significant amounts.

Table I. Predicted Chemical Shifts for IIa and IIb

Positions	Chemical shifts at −145°, τ IIa	IIb	Av of IIa and IIb (intensity) at room temp
2 and 8	5.4, 5.4	5.4, 5.4	5.4 (2)
3 and 7	5.4, 4.1	4.1, 5.4	4.75 (2)
4 and 6	4.1, 4.1	4.1, 4.1	4.1 (3)
5	4.1	4.1	4.1

The spectra of a deuterated derivative of $MeCOTFe(CO)_3$, described in the accompanying communication,[16] confirm our conclusions.

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[13] The high-field band[2] of $COTFe(CO)_3$ is actually much too broad and complex to be due to four protons all having the same chemical shift, as is required by KSP's theory.

[14] These authors do not attempt to explain the spectra of $MeCOTFe(CO)_3$. We find that it is impossible to explain both the room- and low-temperature spectra of $MeCOTFe(CO)_3$ with KSP's theory.

[15] For this calculation we have used rounded values of the chemical shifts given by KSP.[4]

[16] F. A. L. Anet, *J. Am. Chem. Soc.*, **89**, 2491 (1967).

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Valency Tautomerism in Methylcyclooctatetraeneiron Tricarbonyl[1]

Sir:

We have shown[2] that the nmr data of Keller, Shoulders, and Pettit on methylcyclooctatetraeneiron tricarbonyl (I) can best be explained on the basis that the $Fe(CO)_3$ group exhibits a preference for bonding with carbon atoms 1, 2, 7, and 8 (Ia) or 1, 2, 3, and 8 (Ib) of the ligand, and that valency tautomerism, Ia $\rightleftarrows$ Ib, is fast (on the nmr time scale) at room temperature, but slow at −145°. An examination of the nmr spectrum of methyl-*d*-cyclooctatetraene-2,3,4,5,6,7-d_6-iron tricarbonyl (II), presented in this communication, confirms our deductions and clearly shows that the terminal and internal protons in the iron-bonded diene moiety of II have only slightly different chemical shifts.

Lithium aluminum hydride reduction of cyclooctatetraenyl-2,3,4,5,6,7-d_6-methyl-*d* bromide[3] in diethyl ether gave methyl-*d*-cyclooctatetraene-2,3,4,5,6,7-d_6 (III)[4] as a yellow oil, isolated by glpc. Reaction of III with an equimolecular amount of $Fe_2(CO)_9$ in boiling hexane for a few minutes gave, after removal of the solvent, the dark red complex[5] II, which was purified by evaporative distillation *in vacuo*.

The nmr spectrum of II in deuterated chloroform showed only two bands: the CH_2D protons at τ 8.15 and the ring proton at τ 5.44. The high-field chemical shift of the ring proton is only consistent with IIa and IIb being the dominant species at room temperature.[6]

In $CHCl_2F$ solution, the ring proton in II changed from a sharp line at room temperature to two sharp lines at −145° (Figure 1). No change was observed in the CH_2D band, apart from some broadening at very low temperatures.[7] At the coalescence temper-

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[1] Work supported by National Science Foundation Grant No. G.P. 3780.

[2] F. A. L. Anet, H. D. Kaesz, A. Maasbol, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 2489 (1967).

[3] F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, unpublished results; *cf.* F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Am. Chem. Soc.*, **86**, 3576 (1964). The undeuterated compounds have been prepared previously: A. C. Cope and H. C. Campbell, *ibid.*, 74, 179 (1952); A. C. Cope, R. M. Pike and D. F. Rugen, *ibid.*, 76, 4945 (1954).

[4] The rate of bond shift in III has been determined from the temperature dependence of the nmr spectrum, which also confirms the structure and isotopic labeling of the compound (to be published).

[5] The same procedure applied to cyclooctatetraene was found to give a good yield of pure iron tricarbonyl complex. Mass spectra of II showed a ratio of I-d_7:I-d_6:I-d_5 of 30:5:1 and a cracking pattern consistent with its structure.

[6] Other tautomers would have the ring proton at least half of the time in the unbonded diene portion of the molecule and would therefore exhibit a low chemical shift (τ <5). The presence of appreciable amounts of these tautomers would lower the average chemical shift of the ring proton of II, as compared with the high-field band (*ca.* τ 5.5) in the spectrum of $COTFe(CO)_3$ at −145°.

[7] The greater broadening of the CH_2D protons relative to the ring proton is consistent with the closeness of the two protons in the CH_2D