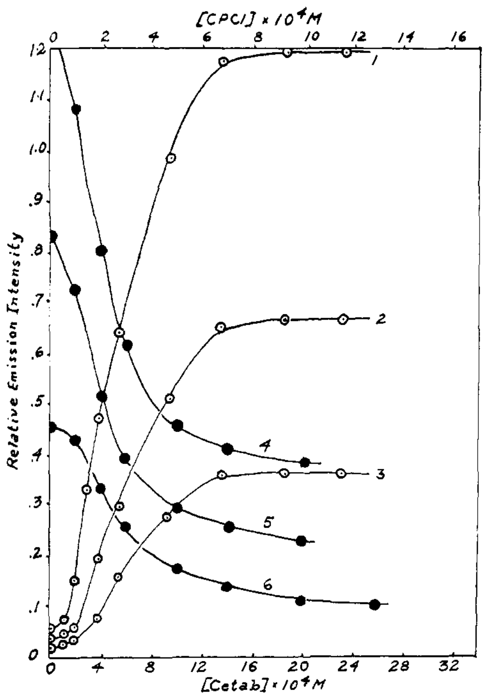

Figure 2. Emission intensity of DG in the presence of Cetab or CPCl for several concentrations of DG: open circle curves, Cetab; curves 1, 2, and 3, DG concentrations 13×10^{-5} *M*, 3.25×10^{-5} *M*, and 1.72×10^{-5} *M*, respectively; closed circle curves, CPCl; curves 4, 5, and 6, DG concentrations 13×10^{-5} *M*, 6.5×10^{-5} *M*, and 3.72×10^{-5} *M*, respectively. In the experiments using Cetab, DG was irradiated at 380 nm; for the CPCl experiments DG was irradiated at 375 nm. The relative intensity scale is arbitrary.

respectively,[15] in fair agreement with the break points given above. It thus appears that DG interacts with detergent monomers, while no interaction with micelles is apparent.[16]

We further note that interaction of DG with the aliphatic compound Cetab gives rise to a marked intensity increase while the aromatic compounds CPBr or CPCl cause considerable quenching of DG emission. In all cases interaction results in a blue shift in DG emission of 30–35 nm, indicating a low dielectric constant for the environment of the fluorescing species.

In the presence of low concentrations of Cetab or CPBr the absorption spectrum of DG also changes. As in the emission experiments, absorbance changes occurred only in the range below or near the cmc of the added detergent with little or no further change once the cmc was exceeded. In water DG displays prominent absorption maxima at 244 and 285 nm with a system of shoulders in the 315–340-nm region. In dilute acid only the 285-nm peak is seen, while in the presence of dilute cationic detergents the DG spectrum shows maxima at 250 and 335 nm; similar spectra are recorded for DG in dilute base or in 95:5 ethylene glycol–water. These data would indicate that interaction of DG with the surfactants results in depressing the zwitterionic (protonated amine) form of DG while favoring formation of the free base.

We have found that tetramethylammonium bromide was quite ineffective at concentrations up to $1\text{–}2 \times 10^{-2}$ *M* to cause marked changes in either the emission or absorption spectra of DG. Furthermore, the anionic detergents sodium dodecyl sulfate or sodium taurocholate were found to cause essentially no changes in the absorption spectrum of DG and only relatively subtle changes in DG emission at concentrations below or near the cmc's of these surfactants, 8×10^{-3} and 3×10^{-3} *M*, respectively.[15,17]

It appears that a positive charge and a hydrophobic chain of some unknown length are required for effective DG–detergent interaction. Mixed salt formation between the detergent and the carboxylate function of DG is the most reasonable explanation for our data. The presence of the carbon chain in the vicinity of the DG naphthyl system would lower the dielectric constant in the neighborhood of the fluorescent moiety, thus accounting for both the observed emission and absorption changes.

Interaction of structurally complex colored indicator dyes with oppositely charged detergents has been noted by several workers to occur at concentrations well below the cmc's of the latter.[18] Interpretations have been varied in these more complex systems, however.[18,19] Our data suggest to us that such interaction may be a quite general occurrence, with many charged or ionizable organic compounds capable of participating in ionic complex formation with detergent monomers. Such interactions may have important consequences for the chemical and physical properties of the latter, especially in light of recent interest focused on the reactivity of organic compounds in detergent solutions.[20]

As mentioned above the binding of ANS compounds to proteins has typically been ascribed simply to the presence of a "hydrophobic site" in the latter. Our results may suggest, however, that for effective binding a positively charged center (*e.g.*, a protonated amine or guanidinium-containing residue) in the vicinity of the hydrophobic site may be of importance.

Acknowledgment. Much appreciation is expressed to Dr. Martin C. Carey for many helpful discussions and the gift of several of the chemicals used in this study.

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(15) P. Mukerjee and K. J. Mysels, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **36** (1970).

(16) For a review of detergent solution properties and the meaning of cmc relevant to this discussion, see P. H. Elworthy, A. T. Florence, and C. B. MacFarlane, "Solubilization by Surface Active Agents," Chapman and Hall, Ltd., London, 1968, Chapter 1.

(17) M. C. Carey and D. M. Small, *J. Colloid Interface Sci.*, **31**, 382 (1969).

(18) (a) W. U. Malik and S. Pal Verma, *J. Phys. Chem.*, **70**, 26 (1966); (b) R. Heque and W. U. Malik, *ibid.*, **67**, 2082 (1963); (c) K. Tori and T. Nakagawa, *Kolloid-Z. Polym.*, **191**, 42 (1963), and earlier references.

(19) See, for example: (a) O. P. Mukerjee and K. Mysels, *J. Amer. Chem. Soc.*, **77**, 2937 (1955); (b) E. L. Colichman, *ibid.*, **72**, 1834 (1950); (c) E. L. Colichman, *ibid.*, **73**, 1795 (1951).

(20) See R. R. Hautula and R. L. Letsinger, *J. Org. Chem.*, **36**, 3762 (1971), and references cited therein.

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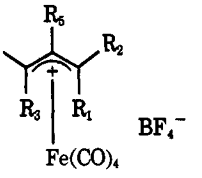
Protonation Reactions of Tricarbonyldieneiron Complexes. The Formation of Tetracarbonylallyliron Cations

Sir:

Several investigations of the behavior of tricarbonyldieneiron compounds in the presence of strong acids

Table I. Proton Nmr Data of Tetracarbonylallyliron Cations in Trifluoroacetic Acid Solution[a,b]

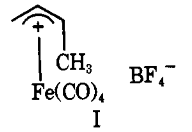


Compd	R_1	R_2	R_3	R_4	R_5
I	CH_3	H	H	H	H
	8.28 (d)	4.33 (m)	6.28 (d of d)	5.43 (d of d)	4.33 (m)
II	CH_3	CH_3	H	H	H
	8.10 (s)	7.65 (s)	6.65 (d of d)	5.70 (d of d)	4.30 (d of d)
III[c]	CH_3	CH_3	CH_3	CH_3	H
	7.75	7.63	7.75	7.63	4.72
IV	$(CH_3)_2CH$	H	H	H	CH_3
	8.58 (s, 7 H)	5.05 (m)	6.32 (d)	5.55 (d of d)	7.50 (s)
V[c]	CH_3	CH_3	H	H	CH_3
	8.06	7.72	6.56	5.80	7.54

[a] Peak positions are in τ units relative to internal tetramethylsilane. [b] The cation complexes can be recovered from this medium by precipitation in cold ether. [c] All the resonance signals for this cation appear as singlets.

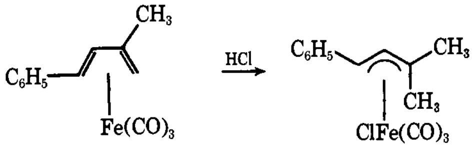
have been undertaken recently in order to determine the exact nature of these complicated reactions.[1,2] Whatever subsequent changes may take place, there has been general agreement that the initial step involves protonation of the diene and formation of a π-allyl ligand. In the case of noncoördinating acids at normal temperatures, the end result was thought to be electron-deficient tricarbonylallyliron cations such as those first characterized by Pettit and Emerson.[3,4] Our own investigations of allyliron carbonyl complexes had progressed to the point that a comparison of the properties of the electron-deficient cations with their tetracarbonyl analogs[5] seemed appropriate.

Initially we sought to study the tricarbonyl systems *in situ* and therefore examined the spectral properties of tricarbonylbutadieneiron in trifluoroacetic acid solution. The initial pattern observed from an nmr sample was virtually identical with that reported for the tricarbonyl-*anti*-1-methyl cation in liquid SO_2.[1,6] The infrared spectrum of this freshly prepared solution exhibited three bands in the $\nu_{C=O}$ region at 2110 (m), 2055 (s), and 2030 (s) cm^{-1}; upon standing for 0.5 hr new bands appeared which were centered at 2150 and 2080 cm^{-1}.[7] After 3 hr at room temperature the $\nu_{C=O}$ region was again examined and the bands at 2150 and 2080 cm^{-1} had become predominant. Parallel changes had taken place in the nmr sample as well and strong new signals were observed in addition to weaker ones corresponding to those in the original spectrum. We sought to isolate the new material and therefore treated tricarbonylbutadieneiron with a sixfold excess of HBF_4 in acetic anhydride during 2.5 hr. This treatment, followed by precipitation in cold ether, afforded an 86% yield[8] of crude tetracarbonyl-1-methylallyliron fluoroborate. The infrared spectrum of the salt[9] in nitromethane exhibits $\nu_{C=O}$ at 2080, 2088, 2100, and 2145 cm^{-1} and is thus clearly similar to other tetracarbonyl derivatives.[5] A comparison of the nmr spectral properties of this cation with others bearing methyl groups at terminal positions (see Table I) together with the well-documented ability of iron carbonyl groups to shield anti substituents[10] seems to justify the assignment of the anti configuration to this compound.



I

Pettit and Emerson observed that proton addition occurred exclusively at C_1 in tricarbonyl-2-methyl-1,3-butadieneiron.[3] Under our conditions this diene complex is converted to compound II which has the same allyl ligand reported earlier. Whitesides and Arhart[2] have reported that protonation occurs at C_4 in a related system



By analogy with these two systems, tricarbonyl-2,4-dimethylpenta-1,3-dieneiron might be expected to protonate at C_1 preferentially to give the known[5] cation III. However, only the unsymmetrical cation IV is initially produced.[11]

On the basis of X-ray and proton nmr spectral data, Nesmayanov and his coworkers have suggested that severe eclipsing interactions would destabilize compounds containing an allyl ligand with a bulky sub-

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(1) D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **91**, 6968 (1969).

(2) T. H. Whitesides and R. W. Arhart, *ibid.*, **93**, 5297 (1971).

(3) G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962).

(4) G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind.* (*London*), 836 (1964).

(5) D. H. Gibson, R. L. Vonnahme, and J. E. McKiernan, *Chem. Commun.*, 720 (1971).

(6) It seems possible to reconcile the syn–anti controversy which has attended HCl additions to these diene complexes as follows: if HCl addition is performed in polar media,[1] anti product is obtained; in nonpolar media the structure of the diene controls the stereochemistry of the product and syn product will be obtained from those systems capable of free rotation after proton addition.[2,4]

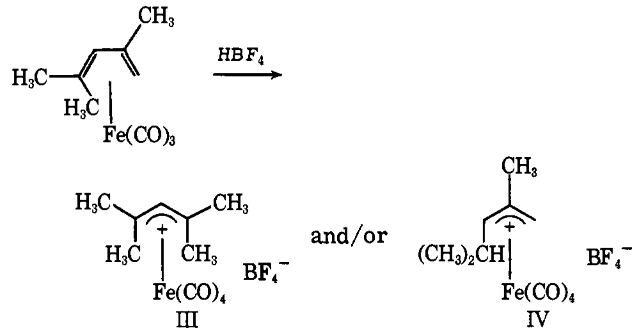
(7) The first spectrum compares favorably with that of tricarbonyl-2-methylallyliron fluoroborate[4] which exhibits $\nu_{C=O}$ at 2108, 2058, and 2043 cm^{-1} in nitromethane solution.

(8) The yield is calculated on the basis that 4 mol of tricarbonyldiene complex will yield 3 mol of tetracarbonylallyliron cation.

(9) *Anal.* Calcd for $C_8H_7FeO_4BF_4$: C, 31.02; H, 2.28; Fe, 18.03. Found: C, 30.73; H, 2.34; Fe, 17.73.

(10) See ref 2 and references cited therein.

(11) The interconversion of cations IV and III will be discussed in a separate publication.



stituent at C_2 if four additional ligands were bound to the iron atom.[12] Kaesz has further pointed out that some destabilization is expected in allyl complexes having anti substituents since these also would seriously interfere with an axial ligand in a pentacoordinate system.[1] As all of the cations listed in Table I possess one or both of these features, it seems that the steric limitations are not as stringent as earlier studies suggested.

From earlier work as well as our own observations of the changes which occur in the $\nu_{C\equiv O}$ region of the infrared spectrum during these reactions, it seems clear that protonation of the diene precedes carbon monoxide transfer. If it can be assumed that the geometry of a tricarbonyl cation is closely related to that of the corresponding diene complex, then the easiest way to convert the system to a trigonal bipyramid would seem to involve a path in which the entering carbon monoxide ligand assumes an axial position which is syn to C_2 of the allyl ligand. Systems which possess a substituent at this position should be slower to react than those which merely have an anti 1 substituent. In line with this the reaction which yields cation IV is somewhat slower than the ones which yield I and II but the slowest reaction yet examined is that of tricarbonyl-2,3-dimethyl-1,3-butadieneiron[13] in which cation V is obtained. A yield of only 5% is obtained after 3.5 hr.

We are now studying other dienes in hopes of establishing the steric limitations as well as the mechanism of the disproportionation reactions.

Acknowledgment. We thank the Research Corporation and the University of Louisville Arts and Sciences Research Committee for financial support of this work and American Standard for a Beckman IR-12 infrared spectrometer.

[12] A. N. Nesmayanov, Yu. A. Ustynyuk, I. I. Kritskaya, and G. A. Schembelov, *J. Organometal. Chem.*, **14**, 395 (1968).

[13] We thank J. D. Smith for the preparation of this compound.

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Lattice Control of Free Radicals from the Photolysis of Crystalline Acetyl Benzoyl Peroxide[1]

Sir:

It is well known that homolysis of diacyl peroxides can open a Pandora's box of products especially under conditions where induced decomposition is important.[2] Thermolysis or photolysis of acetyl benzoyl peroxide (ABP) as a neat liquid at 60–80° gives a number of products resulting from induced decomposition which are absent after comparable homolysis in chlorobenzene solvent.[3] The first 11% of thermolysis of undiluted ABP is unusually rapid and gives 25% of the induced decomposition product, toluene, which is formed in only 2% yield in chlorobenzene solvent. Conversely, the geminate radical coupling product, methyl benzoate,[4] which accounts for 21% of the solution products, is formed in only 3% yield.

The crystal lattice of an azoalkane can exert a powerful influence over radicals generated by photolysis of the crystalline solid.[1a,5] An analogous influence appears in the photolysis of solid ABP.[6] When exposed to 2537-Å light[7] for 25 hr in an evacuated quartz tube at −69 to −72°, 200 mg of crystalline ABP (mp 36.5–37.5°) softened and coalesced appreciably. Iodometric titration,[8] gas evolution, and pmr analysis showed decomposition to be 15–17% complete. Pmr in CCl_4 showed methyl benzoate and toluene (in the ratio of 1.8:1) as the only detectable products. These products would be expected from cage coupling of methyl with benzoyloxy and phenyl radicals, respectively, since the lifetime of the radical pair in the solid could be sufficient to allow appreciable decarboxylation of the benzoyloxy radical.[4,9]

However, toluene might be formed in the solid by an induced pathway, as it is in the melt, and the possibility that methyl benzoate might also arise by an induced pathway in the solid was especially intriguing in light of the crystal structure of ABP.[10] The acetyl peroxy and benzoyl peroxy groups of ABP are each essentially planar with a synclinal torsional angle of 80° about the peroxide bond. The molecules pack about a screw axis in space group $P2_1/c$ as shown in Figure 1. Dashed lines in Figure 1 indicate intermolecular van der Waals contacts (3.45 Å) between methyl groups and the benzoyl oxygen atoms of molecules related by the screw axis.[11] A methyl radical could attack such a neighbor-

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[1] (a) Solvent Steric Effects. VII. For part VI see K. J. Skinner, R. J. Blaskiewicz, and J. M. McBride, *Israel J. Chem.*, in press. (b) We thank the National Science Foundation for support of this research under Grant No. GP-14607.

[2] See, for example, D. F. DeTar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967), and references therein.

[3] C. Walling and Z. Čekovič, *ibid.*, **89**, 6681 (1967); *cf.* M. M. Schwartz and J. E. Leffler, *ibid.*, **93**, 919 (1971).

[4] The observation of CIDNP in the products of decomposition of ABP in tetrachloroethylene solution demonstrates that *both* methyl benzoate and toluene can be formed by radical recombination in the solvent cage: A. I. Buchachenko, S. V. Rykov, A. V. Kessenikh, and G. S. Bylina, *Dokl. Akad. Nauk SSSR*, **190**, 839 (1970); *Dokl. Chem.*, **190**, 101 (1970).

[5] A. B. Jaffe, K. J. Skinner, and J. M. McBride, *J. Amer. Chem. Soc.*, in press.

[6] The effect of decomposition in the solid state has been studied with acetyl peroxide where photolysis in the solid was accompanied by a dramatic increase of ethane over methane as a product compared to photolysis in solution: O. J. Walker and G. L. E. Wild, *J. Chem. Soc.*, **139**, 1132 (1937).

[7] We thank Professors Harry H. Wasserman and Willis B. Hammond for making their photochemical equipment available to us.

[8] In ethanol, V. R. Kokatnur and M. Jelling, *J. Amer. Chem. Soc.*, **63**, 1432 (1941).

[9] One guess[2] at the rate constant for decarboxylation of this radical is 10^4 sec^{-1}, but the lifetime of the cage could be long enough for this to occur: A. V. Zubkov, A. T. Koritskii, and Ya. S. Lebedev, *Dokl. Akad. Nauk SSSR*, **180**, 1150 (1968); *Dokl. Phys. Chem.*, **180**, 437 (1968).

[10] E. T. Koh and J. M. McBride, to be published. At −30°, the temperature of the diffraction study, the crystals grown from pentane at 5° had monoclinic cell constants a = 8.405, b = 7.522, c = 14.064 Å, β = 82.88°.

[11] Each methyl group is also in van der Waals contact with the acetyl oxygen of the molecule beneath (3.44 Å), with the para carbon of the benzoyl group of a molecule related by a different screw axis (3.74 Å), and with several aromatic hydrogens.