

4358 Å. line from high intensity mercury lamps. PSSA was obtained from Dr. W. N. Vanderkoi of the Dow Chemical Co., Midland, Michigan. The molecular weight was approximately 10^6 . The original sample was purified by solution in water, precipitation with isopropyl alcohol in a Waring Blendor and thereafter passage through a column containing cation exchange resin (Dowex 50). EBSA was synthesized from ethylbenzene and sulfuric acid and purified by standard methods.

PSSA was studied in aqueous solutions at a concentration of 0.15 *N* and EBSA was studied at a concentration of 1.0 *N*. It would have been advantageous to study PSSA in more concentrated solution, but this proved impossible because of excessive light scattering. Because of the low concentration of the solutions of PSSA the number of Raman lines detected in these solutions is fewer than that observed in solutions of EBSA and the intensities are also lower. Because of intense light scattering, no lines closer to the exciting line than 965 cm.^{-1} could be observed in solutions of PSSA. The results are recorded in Table I.

TABLE I

RAMAN SPECTRA OF PSSA AND EBSA (cm.^{-1})		
EBSA	PSSA	
620 (w)	...	
780 (s)	...	
965 (w)	965 (vw)	
1035 (w)	1030 (vw)	
1060 (w)	1060 (vw)	
1125 (vs)	1125 (s)	w, weak
1205 (w)	...	s, strong
1450 (w)	1450 (vw)	vw, very weak
1590 (vs)	1590 (s)	vs, very strong

It is clear that the lines appearing in both spectra are identical. The 1125 cm.^{-1} line has been identified by Nisi³ as characteristic of the ionized sulfonic acid residue, whereas the other strong lines arise from the vibrational modes of the *p*-substituted benzene nucleus and are commonly observed in these compounds.⁴

Mock and Marshall have shown that solutions of PSSA have very low apparent degrees of ionization.^{5,6} They have found a degree of ionization of 0.38 which is independent of concentration. The absence of any new lines in the spectrum of PSSA and the observation that the relative intensities of the lines observed are the same as in EBSA strongly suggests that PSSA is completely ionized. This conclusion is in complete accord with nuclear magnetic resonance measurements of the proton shift in solutions of PSSA made in this laboratory.⁷ It is clear, then, that the low apparent degree of ionization of PSSA is due to electrostatic interaction between the hydrogen ions and the polyion. Although the counterions are localized in a small region near the charged polymer skeleton, they do not associate at the skeletal sites as if they were weak electrolytes. The counterions must be as-

(3) H. Nisi, *Jap. J. Phys.*, **6**, 1 (1930).(4) N. S. Ham and A. H. Hamblly, *Aust. J. Chem.*, **6**, 135 (1953).(5) R. A. Mock and C. A. Marshall, *J. Polymer Sci.*, **13**, 263 (1955).(6) R. A. Mock, C. A. Marshall and T. E. Slykhouse, *J. Phys. Chem.*, **58**, 498 (1954).(7) L. Kotin and M. Nagasawa, *J. Am. Chem. Soc.*, in press.

sumed to form a "mobile monolayer" about the polyion skeleton with the very strong electrostatic interactions possible localizing individual counterions in what may be thought of as a quasi-cell in the vicinity of a fixed skeletal charge, but not "on the charge."⁸

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(8) S. Lapanje, J. Haebig, H. T. Davis and S. A. Rice, *ibid.*, in press.

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IRON TRICARBONYL COMPLEXES OF CYCLOHEPTADIENE, CYCLOHEPTADIENE AND CYCLOHEPTADIENIUM ION¹

Sir:

Hydride ion abstraction from π -cycloheptatriene-metal-tricarbonyls (I) by triphenylcarbonium ion has been shown to provide a common route to the π -tropenium ion complexes (II), $(\pi\text{-C}_7\text{H}_7^+)\text{M}(\text{CO})_3\text{BF}_4^-$ where $\text{M} = \text{Mo},^{2a} \text{Cr}^{2b,3}$ and $\text{W}.$ ^{2b} Recently, preliminary undetailed reports of extension of this method by Fischer and Palm⁴ and by Pauson⁵ to the π -cycloheptatriene-iron carbonyl complex, presumed to be $(\pi\text{-C}_7\text{H}_5)\text{Fe}(\text{CO})_2$ by Wilkinson and co-workers⁶ and by Manuel and Stone,⁷ have contended that the product is a π -tropenium ion complex, either $(\pi\text{-C}_7\text{H}_7^+)\text{Fe}(\text{CO})_2^4$ or $(\pi\text{-C}_7\text{H}_7^+)\text{Fe}(\text{CO})_3.$ ⁵ We wish to report our substantially different results which clearly demonstrate that cycloheptatriene reacts with iron pentacarbonyl to give iron tricarbonyl complexes of cycloheptatriene (I, $\text{M} = \text{Fe}$)⁵ and, more slowly, of cycloheptadiene (III), that triphenylcarbonium fluoroborate shows addition rather than hydride ion abstraction with the cycloheptatriene complex (I, $\text{M} = \text{Fe}$) to yield the trityl adduct (IV, $\text{R} = (\text{C}_6\text{H}_5)_3\text{C}-$), and that the stable cycloheptadienium ion complex (IV, $\text{R} = \text{H}$)⁸ is formed readily either by proton addition to the cycloheptatriene complex

(1) Partial support of this work by the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

(2) (a) H. J. Dauben, Jr. and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958); (b) H. J. Dauben, Jr., L. R. Honnen and D. J. Bertelli, Abstracts, 15th Southwest Regional Meeting, American Chemical Society, Baton Rouge, La., Dec. 3, 1959, p. 89.

(3) J. D. Munro and P. L. Pauson, *Proc. Chem. Soc.*, 267 (1959).

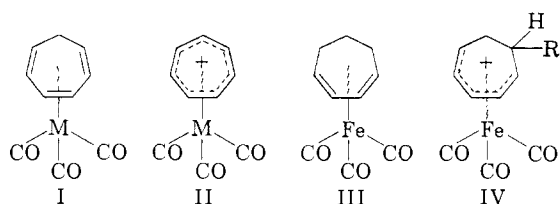
(4) Unpublished results of E. O. Fischer and C. Palm, quoted by R. D. Fischer, *Chem. Ber.*, **93**, 165 (1960).

(5) P. L. Pauson, *Proc. Chem. Soc.*, 297 (1960), originally proposed that cycloheptatriene and tropenium ion formed iron dicarbonyl complexes but later suggested that iron tricarbonyl complexes were produced.

(6) R. Burton, M. L. H. Green, E. W. Abel and G. Wilkinson, *Chemistry and Industry*, 1592 (1958).

(7) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960).

(8) G. Winkhaus and G. Wilkinson, *Proc. Chem. Soc.*, 312 (1960), have mentioned that Burton, Pratt and Wilkinson have derived salts of $\text{C}_7\text{H}_5\text{Fe}(\text{CO})_3^+$ from cycloheptadiene by an unspecified method.



(I, M = Fe) or by hydride ion abstraction from the cycloheptadiene complex (III).^{8a}

Heating of equimolar amounts of cycloheptatriene and iron pentacarbonyl under nitrogen at 135° yielded product mixtures in which the ratio, cycloheptatriene complex (I, M = Fe):cycloheptadiene complex (III), determined mass spectrometrically,⁹ decreased with time from 19:1 in 1 day to 2:1 in 5 days. Pure cycloheptatriene complex was obtained by repeated fractional recrystallization of the 1–2 day product mixture from hexane at –78° as an orange liquid, sensitive to light and air (b.p. 60° (0.5 mm), f.p. ca. –2°; infrared (neat, CO region), 4.89 μ s, 5.08 μ s; n.m.r. (CS₂, approx. band centers and relative intensities), 4.2 and 4.8 τ (2), 4.7 τ (2), 6.8 τ (2), 7.6 τ (2); calcd. for (C₇H₈)Fe(CO)₃: C, 51.77; H, 3.48; O, 20.69; Fe, 24.07; found: C, 52.00; H, 3.52; O, 20.76; Fe, 24.01). The cycloheptadiene complex (III), shown to be present in the product mixture by chemical and physical means, was obtained pure most readily by direct preparation from cycloheptadiene and iron pentacarbonyl in methylcyclohexane under nitrogen at 160° for 36 hr. as a yellowless air-sensitive liquid (b.p. 60° (0.5 mm.), f.p. ca. +5°; infrared (neat), 4.90 μ s, 5.09 μ s; n.m.r. (CCl₄), 4.8 τ (2), 7.0 τ (2), 8.1 τ (4), 8.6 τ (2); calcd. for (C₇H₁₀)Fe(CO)₃: C, 51.32; H, 4.31; O, 20.51; Fe, 23.86; found: C, 51.53; H, 4.48; O, 20.68; Fe, 23.80).

Triphenylcarbonium fluoroborate reacts with the cycloheptatriene complex (I, M = Fe) in dichloromethane to give a 96% yield of the adduct fluoroborate (IV, R = (C₆H₅)₃C[–]) as pale yellow crystals (m.p. gradual darkening above 100°; infrared (KBr), 4.7 μ s, 4.87 μ s, 5.08 μ m; calcd. for [(C₆H₅)₃C[–]–C₇H₈⁺]Fe(CO)₃BF₄[–]: C, 61.95; H, 4.12; F, 13.11; B, 1.92; found: C, 61.65; H, 4.45; F, 12.78; B, 1.75) and *no* triphenylmethane. Hydride ion abstraction from the cycloheptadiene complex (III) (or from mixtures with the cycloheptatriene complex) by triphenylcarbonium fluoroborate in dichloromethane produced 93% triphenylmethane and 92% of the cycloheptadienium ion complex fluoroborate (IV, R = H)⁸ as stable bright yellow crystals (m.p. gradual darkening above 150°; infrared (KBr), 4.76 μ s, 4.87 μ s, 5.08 μ m; n.m.r. (D₂SO₄), 3.1 τ (1), 4.2 τ (2), 5.2 τ (2), 7.5 τ (2), 8.2 τ (2); calcd. for (C₇H₉⁺)Fe(CO)₃BF₄[–]: C, 37.55; H, 2.84; F, 23.76; Fe, 17.46; found: C, 37.83;

(8a) NOTE ADDED IN PROOF.—Hydride ion abstraction from the 1,3-cyclohexadiene complex, (π -C₆H₆)Fe(CO)₃, originally prepared by Halam and Pauson (*J. Chem. Soc.*, 642 (1958)), has furnished the analogous cyclohexadienium ion complex, [(π -C₆H₇)Fe(CO)₃]⁺, BF₄[–], which is being investigated as a source of the unknown benzene complex, (π -C₆H₆)Fe(CO)₃. Also, E. O. Fischer and R. D. Fischer (*Angew. Chem.*, **72**, 919 (1960)) have prepared the same cyclohexadienium ion complex.

(9) Intensities of the mass number 204 and 206 peaks, corresponding to the mono-decarbonylated fragments, were used for analysis since the mass 232 parent ion peak of cycloheptatriene-iron-tricarbonyl could not be detected, and the mass 234 parent ion peak of cycloheptadiene-iron-tricarbonyl had only weak intensity.

H, 3.11; F, 23.90; Fe, 17.76), identical with the product obtained immediately in 90% yield by treatment of the cycloheptatriene complex (I, M = Fe) with 48% fluoroboric acid in propionic anhydride. The cycloheptadienium complex salt (IV, R = H) is stable to boiling ethanol but reacts with potassium iodide in acetone at 25° in 3 hr. to give a 45% yield of the substitution product, (π -C₇H₇)Fe(CO)₃I, as stable maroon crystals (m.p. 86–89° (dec.); infrared (KBr), 4.96 μ s, 5.08 μ s, 5.16 μ m; n.m.r. (Cl₃CCOCCl₃), 3.1 τ (2), 6.1 τ (2), 7.7 τ (2), 8.5 τ (2); calcd.: C, 32.56; H, 2.73; Fe, 16.83; found: C, 32.67; H, 2.85; Fe, 16.93).

Structures assigned to the products are supported by the carbonyl absorptions that shift as expected^{2b} to shorter wave lengths with cationic ligands and to longer wave lengths on anionic substitution, and by proton resonance spectra containing 4 or 5 groups of absorptions with appropriate chemical shifts^{2b,10} in the range 3.0–8.5 τ and with correct intensities.

The theoretical conclusion of Brown¹¹ that excess electrons in iron carbonyl complexes are stabilized only when the organic ligand contains low-lying empty orbitals for back-donation provides explanation of the greater instability and the pronounced electrophile-accepting property of the electron-surfeit cycloheptatriene complex.¹² The more general deduction, by Brown¹¹ as well as others, that greater stabilization results when excess charge on the metal atom can be dispersed onto electron-accepting ligands, very likely provides rationalization not only of the hydride-donating property of the cycloheptadiene complex and of the enhanced stability of the cycloheptadienium ion complex, but also of the apparent need of an iron tricarbonyl moiety in the cycloheptatriene complex as well as all other known, stable, half-sandwich complexes of iron carbonyl with acyclic and monocyclic unsaturated ligands.¹³ The mechanism of the formation of the cycloheptadiene complex from cycloheptatriene and iron pentacarbonyl, which may prove to involve an iron carbonyl hydride intermediate as found in other cases,^{5,8,14} is under investigation.

(10) M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 989 (1960).

(11) D. A. Brown, *J. Inorg. Nuclear Chem.*, **10**, 39, 49 (1959), and **13**, 212 (1960).

(12) The greater stability of the related tropone-iron-tricarbonyl complex (W. Hübel and E. Weiss, *Chemistry and Industry*, 703 (1959)) is attributable to the presence of an additional empty bonding orbital.¹¹

(13) Cf., H. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4749 (1960).

(14) H. W. Sternberg and I. Wender, *Chem. Soc. (London) Spec. Publ.* No. 13, p. 39, 1959.

(15) Standard Oil Company (California) Predoctoral Research Fellow, 1960–1961.

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REACTION OF DIBORON TETRACHLORIDE WITH AROMATIC SUBSTANCES

Sir:

Diboron tetrachloride has been shown to react with certain unsaturated aliphatic substances,^{1,2}

(1) G. Urry, J. Kerrigan, T. Parsons and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 5299 (1954).

(2) P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry and H. I. Schlesinger, *ibid.*, **81**, 6328 (1959).