The Properties of a Ferrocene–Tetracyanoethylene Charge-Transfer Complex[1]

BY M. ROSENBLUM, R. W. FISH, AND C. BENNETT[2]

The complex of ferrocene with tetracyanoferrocene (TCNE), recently reported by Webster, Mahler, and Benson (ref. 8), and formulated by them as a ferricenium TCNE⁻ salt on the basis of its properties in solution, is shown instead to be a charge-transfer complex. The green 1:1 complex exhibits charge-transfer absorption at 975 and 1150 mμ in the solid state and at 900 and 1075 mμ in cyclohexane solution. Preliminary studies suggest that similar complexes are formed by substituted ferrocenes. The physical properties of the ferrocene–TCNE complex including its infrared, visible, and ultraviolet spectra and its magnetic susceptibility have been determined. Association constants and molar extinction coefficients for TCNE complexes of ferrocene, benzene, and pentamethylbenzene in cyclohexane have been measured. Possible structures of the complex are discussed.

Introduction

Although the iron group metallocenes are commonly regarded as aromatic substances of exceptional reactivity, no stable charge-transfer complexes[3] of these compounds have been described.[4] In large measure this apparent anomaly must be attributed to the relatively low ionization potential of these substances.[5] As a consequence, the neutral charge-transfer state is generally unstable with respect to the radical ions resulting from complete electron transfer, even with acceptor components of only moderate electron affinity. Such is the experience with the commonly employed inorganic acceptor components such as the halogens, and with oxidizing reagents in general. More recently the preparation of several metallocenium complexes, formed by the interacton of ferrocene, nickelocene, or cobaltocene with various quinonoid π-acceptors has been reported.[6]

In the course of our studies of the aromatic properties of the iron group metallocenes, we were led to a careful examination of their reactions with various acceptor components, and report herein the preparation of an isolable charge-transfer complex between ferrocene and tetracyanoethylene (TCNE) whose physical properties are of some theoretical interest.

Preparation and General Properties.—This substance was first observed to form when equimolar quantities of ferrocene and TCNE were ground in a mortar for several minutes. Subsequently, it was found that the same substances separated from hot, concentrated ethyl acetate solutions of the components and were also formed when their cyclohexane solutions were irradiated in a Vycor vessel.

The complex is a green crystalline material whose color is highly reminiscent of ferricenium salts. However, in contrast to these substances, it sublimes readily at room temperature and at a pressure of 0.1 mm. yielding lustrous needles. After several such treatments, a relatively pure sample melting at 115–119° (with decomposition) was obtained, with a composition corresponding to a 1:1 ratio of acceptor and donor components. The thermodynamic and chemical stability of the complex is apparently low since on standing for several days at room temperature the crystalline material decomposes in part to its elements and to ferricenium pentacyanopropenide.[7]

Similar complexes with TCNE are formed by methyl-, 1,1'-dimethyl-, and phenylferrocene but, aside from a determination of the position of their charge-transfer bands, included in Table I, their properties have not as yet been thoroughly examined.

Preliminary examination of ruthenocene and osmocene suggests that neither of these metallocenes form stable complexes with TCNE, since thorough grinding of the components does not result in any perceptible color change indicative of complex formation. However, the presence of such complexes in solution is by no means excluded.

During the course of these investigations, Webster, Mahler, and Benson[8] described a green substance, formed by heating ferrocene and TCNE in a solid phase at 60°, which they formulated as a ferricenium TCNE⁻ salt largely on the basis of its properties in solution (vide infra). However, the physical properties of this substance which we find to be identical with our own are not in accord with this structure but require instead that it be formulated as a charge-transfer complex.

Spectral Properties.—Spectra of the solid complex, determined in KBr suspension, do not possess absorption at 619 mμ typical of the ferricenium cation,[9] but exhibit instead a broad absorption band with two weakly defined maxima at 975 and 1150 mμ which is present in neither the neutral components nor their respective ions. The general appearance of this absorption, shown in Fig. 1, is quite typical of charge-transfer absorption, but its long wave length is exceptional and reflects the relatively low ionization potential of the metallocene.[10]

The position of the charge-transfer band allows a

(1) This work was supported by a generous grant from the National Institutes of Health, U. S. Public Health Service.

(2) National Science Foundation Undergraduate Research Participant, Summer, 1962.

(3) For a general treatment of the theory of charge-transfer complexes, see: (a) R. S. Mulliken, J. Am. Chem. Soc., **74**, 811 (1952); (b) G. Briegleb, "Elektronen Donator Acceptor Komplexe," Springer Verlag, Berlin, 1961.

(4) Brand and Snedden, Trans. Faraday Soc., **53**, 894 (1957), observed a weak absorption band for solutions of ferrocene in various alkyl halides, which they attributed to charge-transfer excitation but, with the exception of this observation, no evidence for the existence of neutral charge-transfer complexes of the iron group metallocenes has been provided.

(5) L. Friedman, A. P. Irsa, and G. Wilkinson, J. Am. Chem. Soc., **77**, 3689 (1955).

(6) (a) J. C. Goan, E. Berg, and H. E. Podall, J. Org. Chem., **29**, 975 (1964); (b) L. R. Melby, et al., J. Am. Chem. Soc., **84**, 3374 (1962).

(7) Similar decomposition of the TCNE complex of durene has been noted by A. Bekoe and K. N. Trueblood; cf. D. J. Cram and R. H. Bauer, ibid., **81**, 5971 (1959), ref. 6.

(8) O. W. Webster, W. Mahler, and R. E. Benson, ibid., **84**, 3678 (1962).

(9) G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, ibid., **74**, 2125 (1952).

(10) The wave length of this absorption is close to that reported by H. Kuroda, et al., J. Chem. Phys., **36**, 457 (1962), for the TCNE complex of anthanthrene (900 and 1150 mμ), which of a series of catacondensed aromatic hydrocarbon complexes exhibited the longest wave length charge-transfer band.
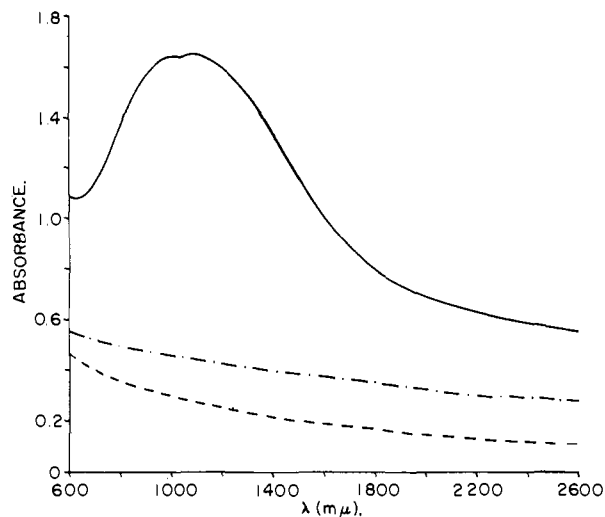
Fig. 1.—Charge-transfer band of ferrocene tetracyanoethylene complex, taken in KBr: ———, 2.0 mg. of complex in 100 mg. of KBr; – – – –, 1.0 mg. of ferrocene in 100 mg. of KBr; – · – · –, 1.8 mg. of tetracyanoethylene in 100 mg. of KBr.

Fig. 2.—Ultraviolet and visible absorption spectrum of ferrocene–tetracyanoethylene complex in KBr; ca. 0.5 mg. of complex in 100 mg. of KBr.

uniquely unencumbered view of the absorption of the complex throughout the ultraviolet and visible regions of the spectrum (Fig. 2). With the exception of the peak at 252 mμ, which may reasonably be identified with the single intense absorption band of TCNE (λ_{max} 260 mμ, ϵ 16,000),[11] the remaining peaks find little correspondence with those present in the spectrum of ferrocene. In particular, the ferrocene absorption at 440 mμ (ϵ 91) appears to have undergone a very considerable hypsochromic shift and possibly an increase in intensity as well. The second peak in this region of the spectrum may be related to electronic transitions in either the donor or acceptor components, since both exhibit low intensity absorption near 320 mμ.[12]

By contrast with the electronic spectrum of the complex, its vibrational spectrum is essentially a composite of its component spectra.[13] The single notable exception is a shift of the 12.2 μ ferrocene band, associated with a C–H out-of-plane bending mode, to 12.0 μ in the complex. This assignment is confirmed by the absence of absorption in this spectral region in the TCNE complex of decadeuterioferrocene, and by a similar shift of the C–D absorption peak from its position at 15.74 μ in deuterioferrocene to 15.50 μ in this complex.[14]

The high donor capacity of ferrocene is further manifested by dissociation of the complex to an equilibrium mixture of the neutral components and their respective ion radicals, even in solvents of relatively low dielectric constant such as chloroform and methylene chloride.[15]

(11) J. Czekalla, Z. Elektrochem., **63**, 1157 (1961). A weaker band at 320 mμ (ϵ 400) is also reported.

(12) It is perhaps worth noting that the approximate energy difference between these peaks (1900 cm.$^{-1}$) is close to the difference in energy of the two charge-transfer absorption maxima.

(13) The intensity of the absorption peaks at 8.95, 9.10, 10.89, and 12.40 μ in the spectrum of TCNE is apparently diminished significantly in the complex and the weak band at 8.06 μ does not appear in the complex. Cram and Bauer (ref. 7) observed a similar disappearance of the latter peak in the infrared spectrum of the [3.4]paracyclophane–TCNE complex.

(14) For a detailed analysis of the infared and Raman spectra of ferrocene and decadeuterioferrocene, cf. E. R. Lippincott and R. D. Nelson, Spectrochim. Acta, **10**, 307 (1958), and L. S. Mayants, B. V. Lokshin, and G. B. Shaltuper, Opt. i Spektroskopiya, **8**, 317 (1962).

(15) Such behavior is exceptional for charge-transfer complexes involving organic donor and acceptor components and finds a parallel only with donors of very low ionization potentials such as the aromatic amines. For examples, see H. Kainer and A. Übele, Ber., **88**, 1147 (1955); D. N. Stamires and J. Turkevich, J. Am. Chem. Soc., **85**, 2557 (1963); R. Foster and T. J. Thompson, Trans. Faraday Soc., **59**, 296 (1962), and ref. 6b.
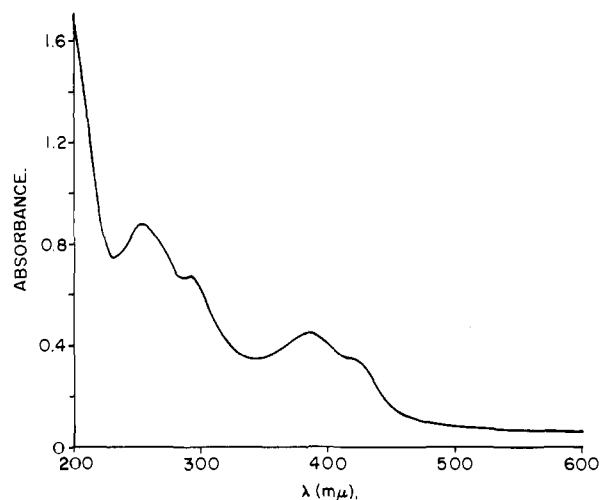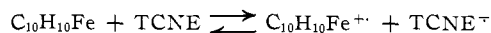
In these solutions no absorption indicative of the presence of the charge-transfer complex is evident. The equilibrium constant for the reaction

$$C_{10}H_{10}Fe + TCNE \rightleftharpoons C_{10}H_{10}Fe^{+\cdot} + TCNE^{-}$$

in acetonitrile, first observed by Webster, Mahler, and Benson,[8] is readily determined from the intensity of the complex absorption pattern near 400 mμ, which is characteristic of the tetracyanoethylene radical ion.[8] The calculated value of 2.5×10^{-3} for the equilibrium constant was found to be in good agreement with the approximate one calculated from the paramagnetic shift observed for the ferrocene proton resonance signal in acetonitrile solutions containing varying proportions of TCNE. The ferricenium ion itself does not exhibit resonance absorption, owing apparently to rapid spin-lattice relaxation, but its position may be estimated to be near 20 p.p.m. from tetramethylsilane by extrapolating the chemical shifts observed for a series of ferrocene–ferricenium soutions to zero ferrocene concentration.[16]

Both osmocene and ruthenocene react like ferrocene with TCNE in acetonitrile solutions, as indicated spectrophotometrically by the immediate formation of the TCNE anion radical.

Magnetic Properties.—Although ionic dissociation in moderately polar solvents suggests an appreciable degree of electron transfer in the ground state of the ferrocene complex, neither the crystalline material, as noted by Webster, Mahler, and Benson,[8] nor its solutions in cyclohexane exhibit e.p.r. absorption. However, the possibility of considerable spin correlation in the complex, similar to that discussed recently by Chestnut and Phillips[17] for a series of tetracyanoquinodimethane salts, may not be excluded.

Bulk susceptibility measurements of the solid complex (Gouy method) indicated that the substance was paramagnetic with a calculated magnetic moment of 0.63 B.M.[18] This is considerably below the value of

(16) This calculated chemical shift represents a considerably smaller displacement of proton resonance than has been observed for the neutral paramagnetic metallocenes, nickelocene, titanocene, and vanadocene, and corresponds to a negative spin density on the rings; H. M. McConnell and C. H. Holm, J. Chem. Phys., **27**, 314 (1957); **28**, 749 (1958).

(17) D. B. Chestnut and W. D. Phillips, ibid., **35**, 1002 (1961).

(18) At a 27° temperature and a field strength of 5200 gauss.

4.1 B.M. expected for a ferricenium TCNE⁻ salt based upon the observed magnetic moment of the cation.[19] Moreover, the susceptibility of the complex, which varied somewhat depending on its method of preparation, purification, and on conditions of storage, exhibited field dependence typical of a ferromagnetic substance. It seems likely that minor impurities resulting possibly from decomposition of the complex are responsible for this behavior since the magnitude of the observed susceptibility is such that a concentration of ferromagnetic impurity of about 1 part in 10^5 would suffice to account for the results.[20]

Complex Association Constant and Molar Extinction Coefficient.—Although the complex is not detectable in moderately polar solvents, its presence in cyclohexane is evidenced by the characteristic broad absorption, with maxima at 900 and 1075 mμ, exhibited by these solutions. Neither the ferricenium ion nor the tetracyanoethylene anion radical is detectable in these solutions. The association constant for complex formation and the molar extinction coefficient of the complex have been determined in these solutions by application of the Benasi–Hilderbrand equation.[21] For a 1:1 complex, a dimensionless association constant K_x may be defined by the expression

$$K_x = (C)/(\{(TCNE) - (C)\}\{[B] - [C]\})$$

where (C) is the equilibrium molar concentration of complex, (TCNE) is the stoichiometric molar concentration of tetracyanoethylene, and [B] − [C] is the mole fraction of uncomplexed donor. Since the determinations are generally carried out under conditions in which the molar concentration of donor is much greater than that of TCNE, the expression [B] − [C] may be replaced by [B]. By substitution of $(\log I_0/I)/l\epsilon$ for (C) and rearrangement of terms, we have

$$\frac{(TCNE)l}{\log (I_0/I)} = \frac{1}{K\epsilon[B]} + \frac{1}{\epsilon}$$

where $\log I_0/I$ is the optical density, l is the path length, and ϵ is the molar extinction coefficient of the complex. By plotting the quantity on the left against $1/[B]$ a straight line is obtained with an intercept equal to $1/\epsilon$ and a slope of $1/K\epsilon$.

The values of K_x and ϵ for the TCNE complex of ferrocene, together with those of benzene and pentamethylbenzene, are summarized in Table I. Included

TABLE I
ASSOCIATION CONSTANTS (K_x) AND MOLAR EXTINCTION
COEFFICIENTS (ϵ_{max}) FOR TETRACYANOETHYLENE COMPLEXES

	Methylene chloride			Cyclohexane		
Donor	K_x	λ_{max}, mμ	ϵ_{max}	K_x	λ_{max}, mμ	ϵ_{max}
Benzene	2.00	384	3570	14.5	382	2130
Pentamethylbenzene	123	520	3270	200	500	3580
Ferrocene	...	...	...	39[a]	900, 1075	465[a]
Methylferrocene					975, 1125	
1,1'-Dimethylferrocene					1050, 1225	
Phenylferrocene					950	

[a] Average of the two maxima.

(19) F. Englemann, *Z. Naturforsch.*, **8b**, 775 (1953); G. Stolzle, Dissertation, University of Munich, 1961; ref. 9.

(20) It is of interest to note that commercially available samples of TCNE were also found to be weakly ferromagnetic. Only after repeated crystallization and sublimation was a sample obtained with a field invariant molar susceptibility of -57×10^{-6} c.g.s.

(21) H. A. Benasi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

in the table, for comparison, are K_x and ϵ values determined in methylene chloride solution by Merrifield and Phillips for the TCNE complexes of benzene and pentamethylbenzene.[22]

It must be noted that the accuracy of the values of K_x and ϵ for the ferrocene complex in particular may not be very high, since low values of K_x and ϵ increase the slope of the plot and lead to a relatively greater error in the determination of $1/\epsilon$. Moreover, the low solubility of ferrocene in cyclohexane necessitated a long extrapolation of the plot in the determination of $1/\epsilon$ so that the accuracy of the value of ϵ and thence K_x are as a consequence further reduced. The error in K and ϵ for this complex is estimated to be of the order of 20%.

The hyposchromic shift of the charge-transfer bands for the benzene and pentamethylbenzene complexes in cyclohexane solution is by no means exceptional,[3b,23] as is likewise the increase in the value of K_x in this solution.[3b] However, the comparatively low value of ϵ_{max} for the ferrocene complex is noteworthy, and its possible significance is discussed below.

Structure of the Complex.—Two formulations for the complex must be considered. In structure 1, which is analogous to that found for several complexes involving benzenoid donor and acceptor components,[24] stabiliza-

1   2
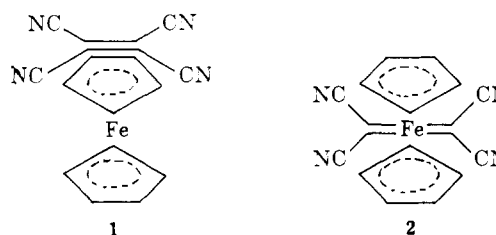
tion of the complex is accomplished through interaction of a filled π-orbital of the cyclopentadienyl ring with a vacant TCNE orbital. The alternative structure 2 attributes the donor role to nonbonding electrons which are largely localized on the metal atom, rather than to ring orbital electrons. Recently Goan, Berg, and Podall[6a] have suggested the possibility of analogous structures for metallocene complexes involving aromatic π-acceptor components. Although a formulation such as 2 is unique, the present evidence cannot exclude it, and indeed the following observations suggest that it may, in fact, best represent the structure of the complex.

The energy of a charge-transfer band may be shown, on theoretical grounds, to be a function of the vertical ionization potential of the donor, and several empirical correlations of these energies for complexes involving a given acceptor have been demonstrated. Such a correlation for TCNE complexes of a number of condensed benzenoid aromatics has recently been provided by Kuroda and co-workers[10] who give the expression

$$h\nu = 0.92I - 5.10 \text{ e.v.}$$

for the regression line which includes the data of Merrifield and Phillips.[22] The ionization potential of ferrocene, derived from this equation, is 6.90 e.v., a value

(22) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

(23) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

(24) H. M. Powell, G. Huse, and P. W. Cooke, *J. Chem. Soc.*, 153 (1943); H. M. Powell and G. Huse, *ibid.*, 435 (1943); T. T. Harding and S. C. Wallwork, *Acta Cryst.*, **6**, 791 (1953); **8**, 787 (1955).

which is in good agreement with the values of 7.05 and 7.57 e.v. determined, respectively, by mass spectrometric[5] and electron impact studies on crystalline ferrocene.[25] These energies are close to the first ionization potential of the free metal atom (7.90 e.v.) and to the values of 6.39[26] and 7.68[27] e.v. calculated by SCF–LCAO methods for the energy of the nonbonding metal $e^{\pm}_{2g}$ ($3d_{\pm 2}$) orbitals of ferrocene. These fully occupied levels lie in the equatorial plane between the rings, and their local symmetry is compatible with the establishment of a donor–acceptor bond with TCNE as depicted in structure 2.

Similar correlations of charge-transfer and ionization potential energies may be demonstrated for substituted ferrocenes as shown in Fig. 3, where the chronopotentiometric $E_{1/4}$ potentials, determined in acetonitrile,[28] have been used as a measure of comparative ionization potentials. Although the data are as yet quite limited, the correlation is good and may constitute a simple method for determining the oxidation potentials of substituted ferrocenes.

Finally it may be noted that the comparatively low value for the extinction coefficient of the ferrocene complex is more readily rationalized in terms of structure 2. Murrell[29] has recently shown that the most important contribution to the intensity of the charge-transfer transition is derived from interaction of the charge-transfer state with donor-excited states. For ferrocene the most probable such donor-excited state is that associated with either or both the 440 or 325 mμ absorption peaks. These transitions have recently been shown to be polarized perpendicular to the rings,[30] and would thus be expected to interest strongly with the charge-transfer transition associated with structure 1 but not with 2.

In summary, it must be noted that these arguments can by no means be said to be conclusive, and it is clear that a definitive solution to this structural problem must therefore await more compelling experimental evidence.

Experimental

Preparation of the Complex. Method A.—A mixture of 1.86 g. (10.0 mmoles) of ferrocene and 1.28 g. (10.0 mmoles) of tetracyanoethylene was ground to a fine powder in a mortar. The green complex formed after several minutes of continuous grinding and was purified by sublimation at room temperature and 0.10 mm. pressure. An analytical sample melted with decomposition at 115–119°.

Anal. Calcd. for $C_{16}H_{10}N_4Fe$: C, 61.18; H, 3.22; N, 17.83. Found: C, 61.43; H, 3.43; N, 17.90.

Method B.—Equimolar amounts of ferrocene and TCNE were dissolved in hot ethyl acetate and the hot concentrated solution was allowed to cool slowly. Long flat green needles, m.p. 104–109°, separated, together with platelets of ferrocene. The complex may also be prepared, although less advantageously, by crystallization from chloroform–hexane solutions. On prolonged standing these solutions deposit black needles, m.p. >280°, similar in spectral properties to the substance formed on decomposition of the crystalline complex (see below).

(25) Quoted in ref. 4 as a private communication from Reed, their ref. 16 and appendix IX. The value given by Reed has been corrected for the heat of sublimation of ferrocene (0.76 e.v.) as determined by J. W. Edwards and G. L. Kington, *Trans. Faraday Soc.*, **58**, 1323 (1962).

(26) E. M. Shustorovich and M. E. Dyatkina, *Dokl. Akad. Nauk S.S.S.R.*, **128**, 1234 (1959).

(27) M. Yamazaki, *J. Chem. Phys.*, **24**, 1260 (1960).

(28) G. L. K. Hoh, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, **83**, 3949 (1961).

(29) J. N. Murrell, *ibid.*, **81**, 5037 (1959).

(30) S. Yamada, A. Nakahara, and R. Tsuchida, *J. Chem. Phys.*, **22**, 1620 (1954); *Bull. Chem. Soc. Japan*, **28**, 465 (1955).
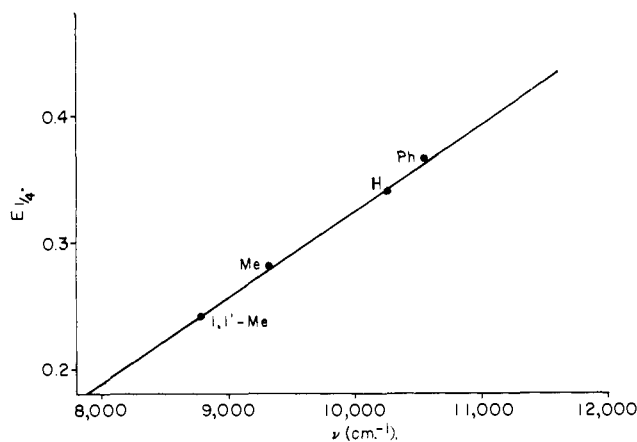
Fig. 3.—Relationship between the oxidation potentials of substituted ferrocenes and the energy of their tetracyanoethylene charge-transfer bands.

Method C.—A mixture of 50.0 ml. of degassed cyclohexane, 2.0 g. of ferrocene, and 5.2 g. of TCNE (solution saturated with TCNE) was placed in a Vycor tube equipped with a nitrogen bubbler and reflux condenser. The system was cooled externally and agitated by bubbling nitrogen through the solution while it was irradiated with a G.E. sunlamp. After 1 hr. of irradiation, green needles of the complex were observed to form on the side of the tube. The complex did not form when a similar solution in a Pyrex flask was irradiated for 48 hr.

General Properties.—The solid complex is stable over a period of several months when kept at 0°, but decomposes at room temperature, especially when exposed to light. Small white crystals of TCNE form on the surface of the complex which darken progressively on standing at room temperature for several days. A portion of the decomposition product consists of black needles, which on dissolution in chloroform gives a deep green solution with broad absorption at 618 mμ characteristic of the ferricenium ion and two peaks at 398 and 417 mμ typical of the pentacyanopropenide anion.[31]

The complex is insoluble in water. It dissolves partially in dilute hydrochloric acid to give a blue-green ferricenium solution. Its solutions in acetonitrile, which exhibit absorption typical of the ferricenium cation and the TCNE anion, are stable in the absence of oxygen. When exposed to air, slow oxidation occurs, as evidenced by a steady increase in absorption at 618 mμ. Concurrently the complex absorption pattern near 400 mμ typical of TCNE⁻ disappears and is replaced by doublet absorption at 398 and 417 mμ indicative of the pentacyanopropenide anion. Methylene chloride and chloroform gave similar results, except that the complex is less soluble in these solvents.

Spectra.—Infrared spectra were determined with a Perkin–Elmer Infracord spectrophotometer, and visible and ultraviolet spectra with a Cary recording spectrophotometer, Model 14; n.m.r. spectra were recorded with a Varian spectrometer (HR-60) and peak positions were determined with respect to internal tetramethylsilane by sidebanding; e.p.r. spectra were recorded with a Strand Lab Model 601 spectrometer[32] at 6.3 Kc. modulation and an operating frequency of 9.3 kMc.

Magnetic Susceptibility.—Measurements were made by the Gouy method employing the apparatus described by Holm and Cotton.[33] A preliminary check of our procedures with freshly sublimed ferrocene led to a susceptibility of -115×10^{-6} c.g.s. (lit. value[9] -125×10^{-6} c.g.s.). A more recent determination by Prof. R. Mason, Sheffield University (private communication), yielded a value of -105×10^{-6} c.g.s. for ferrocene.

The sample of the complex used in these determinations was prepared by grinding together 7.12 g. of ferrocene (χ_m -115×10^{-6} c.g.s.) and 4.91 g. of TCNE, recrystallized several times from methylene chloride and then sublimed (χ_m $- 57 \times 10^{-6}$ c.g.s.).

(31) W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

(32) We are indebted to Prof. T. R. Tuttle of our department for carrying out these determinations.

(33) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959). We are indebted to Prof. Cotton for providing us with the use of this apparatus.

Measurements taken at 300°K. gave the following representative molar susceptibilities with field strengths in gauss given in parentheses: $+194 \times 10^{-6}$ (4.2–4.3 $\times$ 10³), $+165 \times 10^{-6}$ (5.2 $\times$ 10³), $+93 \times 10^6$ (5.9 $\times$ 10³).

Secondary Isotope Effects in Solvolysis of Various Deuterated Benzhydryl Chlorides[1]

By A. Streitwieser, Jr., and H. S. Klein[2]

Solvolysis kinetics were determined for various deuterated benzhydryl chlorides in 80 and 70% aqueous acetone at 25.00°. Ring deuteriums cause rate accelerations of the following magnitude per D: *ortho*, 1.9%; *meta*, 1.5%; *para*, 1.0%. These unusual positional effects are discussed, but no unambiguous interpretation is possible at this time. Benzhydryl-α-d chloride shows a normal α-D rate depression of 12%.

Various observations show that deuterium has a significant electron-donating inductive effect relative to hydrogen.[3] The effect of deuterium on the acidity of carboxylic acids depends on the position of attachment down the chain in much the same way as the normal inductive effect of nonisotope substituents.[4,5] Comparable electron-donating effects have been established for deuterium substituted on a benzene ring in the acidities of benzoic acid[5] and anilinium ions[6] and in the formation of diphenylmethyl[7] and triphenylmethyl cations.[8] In the present study, we report the details of the *o*-, *m*-, and *p*-substitution of deuterium in solvolysis of benzhydryl chloride.

Results and Discussion

Various deuterated bromobenzenes were prepared as follows: Bromination of benzene-d_6 gave bromobenzene-d_5. *p*-Dibromobenzene was converted to the mono-Grignard reagent and decomposed with deuterium oxide to give bromobenzene-d_5. Repeated exchanges of aniline with DCl–D₂O gave aniline-2,4,6-d_3 which, by the Sandmeyer reaction, gave bromobenzene-2,4,6-d_3. Nitration of bromobenzene-2,4,6-d_3 gave the *p*-nitro compound which, on reduction and deamination, gave bromobenzene-2,6-d_2. Bromination of acetanilide-2,4,6-d_3, hydrolysis, and deamination gave bromobenzene-3,5-d_2. Benzhydrols were prepared from each bromobenzene by Grignard reaction with ethyl formate. Benzhydrol-α-d was prepared by reduction of benzophenone with lithium aluminum deuteride. The benzhydrols so obtained analyzed for >90% of the required deuterium. Benzhydryl chlorides were prepared by treatment of the benzhydrols with hydrogen chloride and were stored in Dry Ice–acetone under nitrogen until used. The infrared spectrum of benzhydryl-2,3,4,5,6,2′,3′,4′,5′,6′-d_{10} chloride showed that no hydrogen–deuterium exchange occurred on storage.

Solvolysis kinetics were run on each benzhydryl

chloride in 70 and 80% aqueous acetone by following conductometrically the decrease in resistance of the solution as HCl was generated. Each reaction was followed for several half-lives during which about 80 readings were taken. The usual integrated first-order rate equation was applied to each point using an infinity point taken after about 20 half-lives. For each solvent, a calibration curve of resistance *vs.* concentration was determined. Second-, third-, and fourth-order polynomial equations in conductance were fitted to the data. A third-order polynomial (eq. 1) gave the best results in 80% acetone, whereas in 70% acetone the assumption that the concentration is proportional to conductance gave results equal to the best polynomial fit.

$$(\text{HCl in } 80\% \text{ acetone}) = -659{,}330(1/R)^3 +$$
$$1828.9(1/R)^2 + 5.6040(1/R) - 0.000012697 \quad (1)$$

Because of the large quantity of data to be handled, a program was written for the IBM 7090 which took the input resistance and time data for each run, converted resistance to HCl concentration, and applied the first-order equation. A value for k was printed out to correspond to each point taken. This procedure was not perfect. The integrated first-order rate constants diminished during the course of a run by a few parts per thousand, undoubtedly because of the inadequacy of expressing concentration as a polynomial in reciprocal resistance. Theoretically, it would have been better to express $1/R$ as a polynomial in $\sqrt{c}$, but such a form is less desirable in machine computations where $1/R$ is given and c is to be found. In practice, all of the runs showed the same degree of decrease in k during the run; for greater consistency, an average value was taken at the same reaction time for each run. In general, this procedure gave rate constants reproducible to a few tenths per cent.

The results of the kinetics are summarized in Tables I and II. In addition, the equilibrium constant for the solvolysis in 80% aqueous acetone was determined by adding benzhydrol to a known amount of HCl and determining the resistance at equilibrium. Two determinations gave $K = 1.85 \pm 0.21$ moles/l.; hence, at the kinetic concentrations ($\sim 10^{-3}$ moles/l.), the solvolysis goes $\sim 99.9\%$ to completion in qualitative agreement with an earlier report.[9]

The summary of the isotope effects in Table II shows

(1) This research was supported in part by a grant from the National Science Foundation.

(2) National Science Foundation Predoctoral Fellow, 1959–1961; University of California Fellow, 1961–1962.

(3) E. A. Halevi, "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 109.

(4) E. A. Halevi, M. Nussim, and A. Ron, *J. Chem. Soc.*, 866 (1963).

(5) A. Streitwieser, Jr., and H. S. Klein, *J. Am. Chem. Soc.*, **85**, 2759 (1963).

(6) C. Bernasconi, W. Koch, and H. Zollinger, *Helv. Chim. Acta*, **46**, 1184 (1963).

(7) H. S. Klein and A. Streitwieser, Jr., *Chem. Ind.* (London), 180 (1961).

(8) A. J. Kresge, K. N. Rao, and N. N. Lichtin, *ibid.*, 53 (1961).

(9) G. C. Church, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 966 (1940).