Journal of Organometallic Chemistry, 214 (1981) 381—390
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ELECTROCHEMICAL BEHAVIOR OF 1,2,3-TRIFERROCENYLCYCLOPROPENES

ALBERT J. FRY *, PRATAP S. JAIN and RICHARD L. KRIEGER

Hall-Atwater Laboratories of Chemistry, Wesleyan University, Middletown, Connecticut 06457 (U.S.A.)

(Received December 17th, 1980)

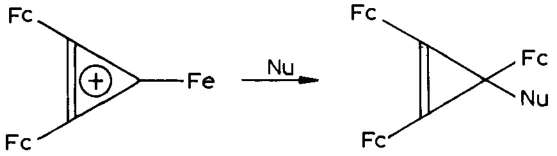
Summary

A series of 3-substituted 1,2,3-triferrocenylcyclopropenes was synthesized and investigated by ^{13}C NMR spectroscopy and cyclic voltammetry. The latter shows three reversible waves associated with stepwise oxidation of the three iron sites; the spacings indicate weak interaction between the ferrocene groups in the corresponding mixed-valence species. 3-*p*-Tolyl-1,2,3-triferrocenylcyclopropene rearranges thermally at a much greater rate than does its phenyl analog, tetraphenylcyclopropene.

Introduction

There has been much interest in recent years in the physical and spectroscopic properties of "mixed-valence" ferrocenes, that is, substances containing two ferrocene subunits, in which one iron nucleus is the ferricenium and the other in the ferrocene oxidation state [1]. Strong interaction between the two sites is associated with the appearance of a variety of phenomena not exhibited by isolated ferrocene or ferricenium units. Such phenomena include new electronic transitions, enhanced electrical conductivity in the crystal state, etc. It has been observed [2] that $\Delta E°$, the difference between the first and second electrochemical anodic oxidation potentials of a biferrocene, provides a good qualitative measure of the degree of interaction between the two ferrocene units in the corresponding mixed-valence ferrocene, hence voltammetry is a good way of surveying polyferrocenes for possible interesting mixed-valence behavior.

In the course of previous study [3,4] of the electrochemical reduction of the triferrocenylcyclopropenium ion (I), we had occasion to prepare a series of triferrocenylcyclopropenes (II) by nucleophilic attack upon I. In the present manuscript we discuss the anodic electrochemical behavior of such substances, including a few not previously reported, and the results of initial attempts to prepare mixed-valence salts of these substances.

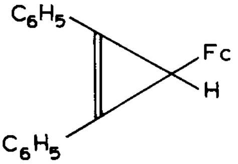


(I)

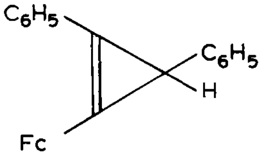
(IIa , Nu = H)
(IIb , Nu = CN)
(IIc , Nu = OCH_3)
(IId , Nu = CH_3)
(IIe , Nu = p-$CH_3C_6H_4$)

Results and discussion

Compounds IIa—IIc were prepared as previously described [3], by the action of sodium borohydride, cyanide, and methoxide, respectively, upon I. Compounds IId and IIe were prepared in straight-forward fashion by reaction of methyllithium and *p*-tolylmagnesium bromide, respectively, with I. 1,2-Diphenyl-3-ferrocenylcyclopropene (III) and 1,3-diphenyl-2-ferrocenylcyclopropene (IV) (as an inseparable mixture) were prepared by sodium borohydride reduction of the diphenylferrocenyl cyclopropenium ion [14].



(III)

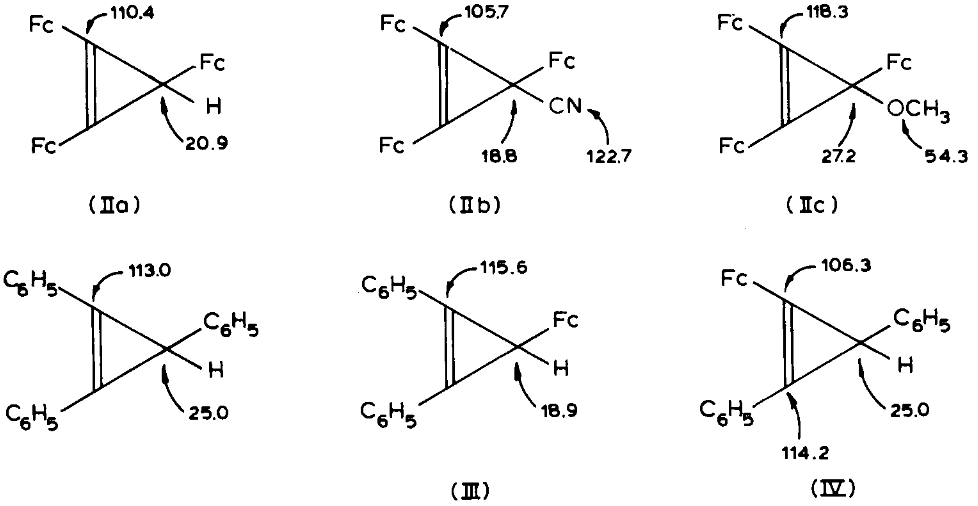


(IV)

Because the ^{13}C NMR spectra of compounds II display certain characteristic features which are useful for structural elucidation, and which indeed have previously been so used [4], we feel it worthwhile to summarize their spectra briefly. The resonances of the ring carbons of IIa—IIc and some related substances are shown in Scheme 1. It may be seen that the ring carbons of a ferro-

SCHEME 1

^{13}C NMR ASSIGNMENTS FOR SUBSTITUTED CYCLOPROPENES



cenylcyclopropene always appear at higher field than the corresponding phenyl substance, presumably because of the greater electron-supplying power of the ferrocenyl substituent. Compounds IIa—IIc exhibit similar features for the ferrocene carbons: (a) an eight-line multiplet with two of the lines of distinctly lower intensity and higher field than the other six, and (b) of the two most intense lines, the larger is at lower field by 0.4—0.9 ppm. We assign the two upfield lines to the substituted ferrocene carbons (bound to the three-membered ring) [3] and the two most intense lines as the two kinds of unsubstituted cyclopentadienyl ring. ^{13}C NMR spectra were not obtained for IId and IIe.

Electrochemistry

Anodic voltammetry was carried out on compounds IIa—IIe (except IIc, which was too unstable) at a platinum disc electrode in acetonitrile containing 0.1 *M* tetrabutylammonium hexafluorophosphate (TBAHFP). In general, three reversible one-electron waves, corresponding to stepwise oxidation of the three iron nucleii, are observed (Fig. 1). Although adsorption and precipitation phenomena complicate some of the voltammograms, especially those measured at the slower sweep rates, voltammograms such as those shown in Fig. 1 can be obtained if a freshly cleaned electrode is used and the voltammogram is measured on the first cycle; the electrode must be cleaned between voltammograms measured at different scan rates.

It was of interest to us to know accurately the three oxidation potentials of each compound, inasmuch as the difference in redox potentials of the individual ferrocene subunits in diferrocenes has been shown to be correlated to the degree of interaction between the subunits in the mixed-valence species [2]. It was clear however that direct measurement from the voltammograms of ΔE°, the spacing between individual voltammetric peaks, could not afford data of high

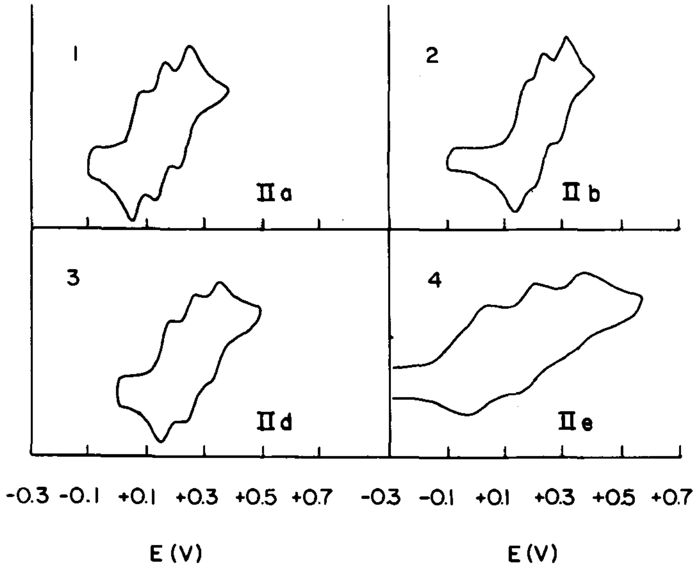


Fig. 1. Cyclic voltammograms of triferrocenylcyclopropenes at 1 V s^{-1}.

TABLE 1

CYCLIC VOLTAMMETRIC BEHAVIOR OF TRIFERROCENYLCYCLOPROPENES [a]

Compound	Scan Rate [b]	E_1 [c]	S_1 [d]	E_2 [c]	S_2 [d]	E_3 [c]	S_3 [d]
IIa	10	0.03	62	0.18	84	0.35	57
	5	0.03	64	0.20	83	0.37	59
	2	0.02	72	0.18	77	0.36	65
	1	0.03	66	0.19	71	0.37	62
	0.2	0.04	60	0.20	70	0.38	59
IIb	10	0.20	93	0.34	69	0.49	67
	5	0.19	74	0.32	65	0.48	71
	2	0.19	83	0.33	63	0.48	62
	1	0.19	71	0.32	63	0.47	66
	0.2	0.18	79	0.32	63	0.47	69
IId	10	0.03	74	0.21	91	0.40	77
	5	0.02	78	0.20	84	0.38	82
	2	0.03	65	0.20	82	0.39	76
	1	0.02	65	0.20	89	0.38	62
	0.2	0.02	71	0.21	84	0.38	69
IIe	10	0.05	72	0.24	113	0.44	67
	5	0.03	86	0.24	94	0.43	75
	1	0.02	105	0.24	78	0.42	58
	0.2	0.03	59	0.23	93	0.39	62

[a] Potentials are measured relative to silver/0.01 *M* silver nitrate; add + 0.3 V to correct to S.C.E. [b] Volts s^{-1}. [c] Computed oxidation potentials (see text). [d] Slope of plot of $\log[I/(I_{\mathrm{Lim}} - I)]$ vs. *E*.

accuracy, because of both the closeness of the peaks in some cases and the well-known inaccuracies associated with measurement of peak potentials in general as a consequence of their relative broadness. For this reason we developed a computer-based method for accurate determination of the three individual oxidation potentials from voltammograms such as those shown in Fig. 1. Inasmuch as we feel that the method is of considerable interest in its own right, we intend to describe it in detail elsewhere. Briefly, it consists of convolution [5,6] of the linear sweep voltammogram (forward sweep only) to produce a voltammogram with the same shape as a polarogram with three overlapping waves, followed by a multi-parameter least-squares fit [7] of the convoluted data to the theoretical equation for such a polarogram. In Table 1 are presented the results of such analysis for each of the cyclopropenes as measured over a range of scan rates. In addition to the various oxidation potentials, the slopes of the plot of $\log[I/(I_d - I)]$ vs E for each wave, where I and I_d are the instantaneous and total convoluted currents, are also tabulated as a guide to the reversibility of the wave; a slope of 59.2 mV is expected for a reversible process at 25°C.

A number of conclusions may be reached by inspection of the data in Table 1. First, the compounds generally undergo three reversible one-electron oxidations; this is evident from (a) the scan-rate independence of the oxidation potentials, (b) the values of the $\log[I/(I_d - I)]$ slopes, and (c) the general appearance of the voltammograms. The *p*-tolyl derivative IIe deviates somewhat from this generalization; its voltammetry is complicated by anodic filming, which is a problem with all of the compounds but especially this one, and is especially noticeable at low scan rates.

Secondly, we note the relative insensitivity of both the first oxidation poten-

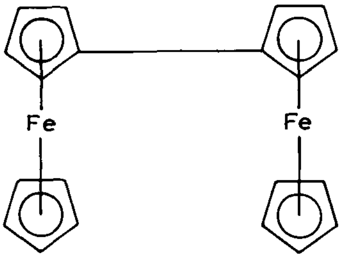
TABLE 2

OXIDATION POTENTIALS OF 3-X-1,2,3-TRIFERROCENYLCYCLOPROPENES

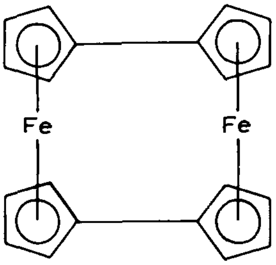
Compound	X	E_1 (V) [a]	$E_1 - E_2$ (V) [a]	$E_2 - E_3$ (V) [a]
IIa	H	0.03	0.15	0.17
IIb	CN	0.19	0.14	0.15
IId	CH	0.02	0.18	0.18
IIe	p-$CH_3C_6H_4$	0.03	0.20	0.18

[a] E_n = the nth oxidation potential, in acetonitrile relative to silver/silver nitrate reference.

tials and the spacings (in volts) between the first and second, and second and third, oxidation potentials to the nature of the substituent at C(3) (Table 2). The magnitudes of the latter spacings are significant: statistical theory for a substance with three identical, non-interacting electroactive sites predicts [8] that such a substance will exhibit three waves with $\Delta E_{1,2} = \Delta E_{2,3} = (RT/F) \ln 3 = 0.028$ V. The actual spacings are greater than this value for all of the compounds studied, demonstrating that the ferrocene groups do interact with each other. However, the extent of interaction is weak. For example, in biferrocenyl (V)



(V)

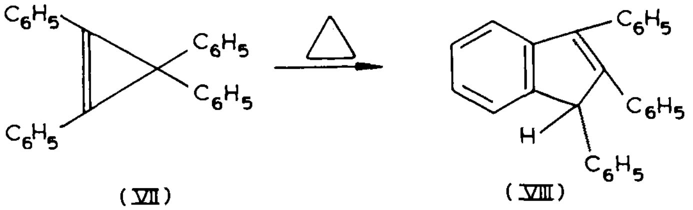


(VI)

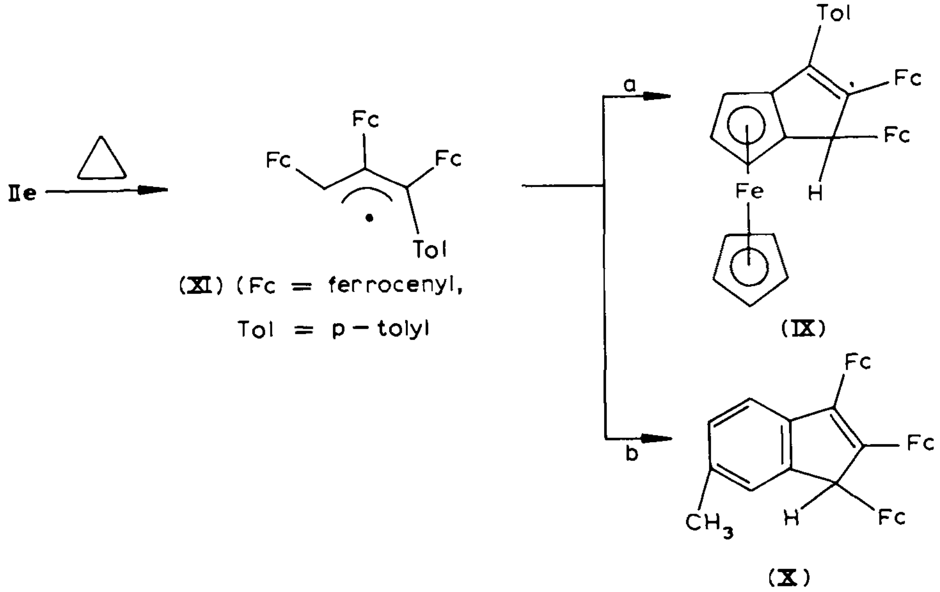
and bisfulvalenediiron (VI) the two redox waves are separated by 0.33 and 0.59 V, respectively [2]. Since strong intervalence interaction appears to be associated with a large separation between redox potentials, we may expect to see only weak intervalence character in the mixed-valence species derived from the compounds in Table 1. This appears to be the case, judging from the low electrical conductivities of the mixed-valence salts we prepared (vide infra).

Rearrangement of 3-aryl-1,2,3-triferrocenylcyclopropenes

When IIe is heated for two hours under nitrogen at 50°C in $CHCl_3$, it is transformed to the extent of about 95% into two substances (90 : 10), which may be separated by column chromatography over alumina. Microanalytical and mass spectral data establish these substances as isomers of the starting material. The 200 MHz NMR spectrum of the slower-moving major product shows three strong resonances of equal intensity at δ 3.7, 4.0, and 4.2 ppm, arising from unsubstituted cyclopentadienyl rings; each of these three resonances consists of two peaks in the ratio of 57 : 43. This contrasts sharply with the spectrum of IIa—IIe, in all of which the two types of unsubstituted cyclopentadienyl rings appear as two singlets in 2 : 1 ratio. By analogy with the known thermal rearrangement [9] of 1,2,3,3-tetraphenylcyclopropene (VII) to 1,2,3-triphenylindene



(VIII), and because the NMR spectrum indicates retention of the *p*-tolyl moiety (two overlapping AB quartets in the aromatic region), we assign this material structure IX as a 57 : 43 mixture of stereoisomers about the asymmetric carbon. By the same token, and because (a) integration indicates retention of only three aromatic protons, and (b) it also exhibits three types of unsubstituted ring (three sharp resonances of equal intensity at 3.7, 3.9, and 4.2 ppm), we assign structure X to the faster-moving isomer. Rearrangements of this sort are fairly common in the cyclopropene series [10]. Substances IX and X may reasonably be understood as arising by thermal ring-opening of IIe to a diradical XI (well-precedented in cyclopropene chemistry). Closure of XI by intramolecular homolytic attack on either the ferrocene (path a) or tolyl (path b) substituents,

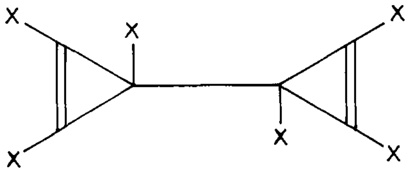


with subsequent aromatization, would generate IX or X, respectively [9]. Thermal opening of cyclopropenes is well-known; the driving forces are presumably relief of the ca. 56 kcal of cyclopropene ring strain [11] and formation of an allylic π-system, as in XI.

Compound IIe rearranges enormously faster than its phenyl analog VII. The half-life of IIe at 50°C is ca. 30 minutes, while from literature data [9] VII may be estimated to have a half-life of ca. 10^{11} minutes at 50°C meaning that IIe rearranges faster than VII by a factor of roughly 10^8—10^9. We are unable to account in detail for this large difference (although much of it is undoubtedly steric in origin) but are not surprised by it, in view of our previous discovery that hexaferrocenyl-bis-cyclopropenyl (XII, X = ferrocenyl) has a half-life under one hour at room temperature [4], while its phenyl counterpart (X = C_6H_5) requires temperatures on the order of 150° C in order to rearrange at comparable rate [12].

Attempted synthesis of mixed-valence species

Because the first and second oxidation potentials of the various triferrocenylcyclopropenes are very similar, one would expect it to be difficult to prepare a single-oxidized mixedvalence compound. This turned out to be the case. Thus, reaction of IIe with tetracyanoquinomethane (TCNQ) afforded a substance (XII) with formula corresponding to $\text{IIe}^{2+}\ 2(\text{TCNQ})_2^-$, rather than the expected [13] $\text{IIe}^+\ (\text{TCNQ})_2^-$. Similarly, oxidation of IIa by TCNQ afforded a substance whose analysis corresponded to $\text{IIa}^{2+}\ 2(\text{TCNQ})_2^-$. On the other hand, oxidation of IIe by molecular iodine did afford a singly-oxidized substance, $\text{IIe}^+\ \text{I}^-$. The electrical conductivities of these materials are unexceptional (see Experimental). Although this was predictable from the voltammetric results, it was disappointing, inasmuch as we had hoped that the presence of the third iron nucleus would permit increased dispersal of charge in the mixed-valence species and consequently strong mixed-valence interaction.



(XII)

Experimental

Materials

Triferrocenylcyclopropenium and 1,2-diphenyl-3-ferrocenylcyclopropenium tetrafluoroborates and cyclopropenes IIa—IIc were prepared by literature procedures [3,14].

NMR spectra

Proton spectra were measured at 200 MHz using the Varian XL-200 spectrometer at Wesleyan University. ^{13}C NMR spectra were measured on the Bruker WH-270 spectrometer at Yale University.

Preparation of 3-methyl- and 3-p-tolyl-1,2,3-triferrocenylcyclopropene (IId—IIe)

These materials were made by reaction of excess *p*-tolylmagnesium bromide or methyllithium with triferrocenylcyclopropenium tetrafluoroborate (I) in tetrahydrofuran at —78° C. These reactions were characterized by a change in color from the intense red of I to the orange of the products. Reactions were worked up by pouring into water, extraction with ether, and final drying and evaporation of the ether. The crude material was then purified by dry column chromatography on alumina.

3-Methyl-1,2,3-triferrocenylcyclopropene (IId) is an orange solid, m.p. 142°dec; ^{1}H NMR ($CDCl_3^{1\delta}$): singlet, 1.7 (3 H); singlet, 4.3 (5 H); singlet, 4.1 (10 H); mult. 4—4.6 ppm (12 H). Anal. Found: C, 66.92; H, 5.17. $C_{34}H_{30}Fe_3$ Calcd.: C, 67.37; H, 4.99%.

3-*p*-Tolyl-1,2,3-triferrocenylcyclopropene (IIe) is an orange solid, m.p. 155°C; ^{1}H NMR ($CDCl_3$, δ): singlets at 2.0 (3 H), 3.62 (5 H), and 3.68 (10 H), multiplet, 3.69—4.3 (12 H), AB quartet at 6.9 and 7.4 ppm (4 H). Anal. Found: C, 71.17; H, 5.06. $C_{40}H_{34}Fe_3$ Calcd: C, 70.41; H, 5.02%.

1,2-Diphenyl-3-ferrocenylcyclopropene (III) and 1,3-diphenyl-2-ferrocenylcyclopropene (IV)

Sodium borohydride reduction of diphenylferrocenylcyclopropenium tetrafluoroborate [3] afforded a mixture of cyclopropenes III and IV chromatographically inseparable but consisting of a 1 : 8 mixture of III : IV, as shown by the relative intensities of the cyclopropene ring protons at δ 2.96 and 3.10 ppm (these appear at 2.73 and 3.21 ppm in II and triphenylcyclopropene, respectively). The ^{13}C NMR peaks for the 3-membered ring carbons (Scheme 1) could be observed only by extended accumulation in the presence of the relaxation reagent chromium acetylacetonate [15].

^{13}C NMR spectroscopy

IIa: Eight lines were observed: 67.3 and 67.8 ppm (both weak), 69.6 (most intense), 68.9 (second most intense), and 69.2, 69.4, 69.8, and 69.9 ppm.

IIb: Eight lines were observed in addition to those in Scheme 1: 66.9 and 67.5 ppm (both weak), 69.6 (most intense), 69.2 (second most intense), and 68.8, 69.0, 69.8, and 70.2 ppm.

IIc: Eight lines were observed in addition to those in Scheme 1: 67.3 and 67.4 ppm (both weak), 69.9 (most intense), 69.0 (second most intense), and 69.2, 69.7, 70.0, and 70.1 ppm.

Voltammetry

Cyclic voltammetry was carried out using a Princeton Applied Research Model 170 electrochemistry system. Voltammograms were recorded on a Hewlett- Packard X-Y recorder or, when sweep rates of 1 V sec^{-1} or faster were employed, a Tektronix model 564B storage oscilloscope. The working electrode was a Beckman platinum disk electrode (A = 0.23 cm^2), polished before each run with Buchler 0.03 μm lapping compound. The reference electrode was a silver/0.01 *M* silver nitrate electrode constructed from a length of glass tubing sealed at one end with a short length of porous Vycor by means of a longer piece of heat-shrink Teflon tubing. The solvent was Fisher HPLC grade acetonitrile containing 0.1 *M* tetrabutylammonium hexafluorophosphate. For convolution (semi-integration), Polaroid slides of the oscilloscope trace were projected onto a large (1 m × 1 m) sheet of graph paper, permitting 50—75 points to be taken with good precision.

Electrical conductivity measurements

For conductivity measurements 100—150 mg of finely powdered material were formed into a disk in a press at 3000—4000 psi. The disks so formed had a black mirror-like appearance. They were mounted on a quartz wafer and electrical contacts were made with copper wire leads attached by conductive epoxy resin. A constant D.C. potential was applied along the axis of the disk, and the resulting current was measured with a Kiethley microammeter. The conductivity was measured of several crystals from different preparations. Diameter and thickness of the crystal were obtained by microscopic measurements. The conductivity (σ) is given by $\sigma = IL/VA$, where I is the current in amperes, V is the applied voltage, L is the length between two loads on the diameter, and A is the area of the disk.

Mixed-valence salts of IIa or IIe were prepared by refluxing the cyclopropene and tetracyanoquinodimethane (TCNQ) or iodine in hot acetonitrile for 30 min. The black complexes precipitated as microcrystalline powders; they were washed successively with cold acetonitrile, dichloromethane, and diethyl ether, and dried in vacuo. The stoichiometry of the TCNQ product was not affected by variations in the ratio of TCNQ to cyclopropene employed. $\text{IIa}^{2+}\ 2(\text{TCNQ})_2^-$ and the corresponding derivative of IIe exhibited conductivities of ca. 5×10^{-5} Ω^{-1} cm^{-1} at room temperature. IIa^+I^- exhibited a lower conductivity, ca. 10^{-8} Ω^{-1} cm^{-1}.

Acknowledgements

Acknowledgement is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society for partial support of this research. The National Science Foundation also supported the research, through grant no. CHE-7904907 to A.J.F. The 200 MHz spectrometer was purchased in part by grants from the National Science Foundation and the Dreyfus Foundation. ^{13}C NMR spectra were measured at the Southern New England High Field NMR Facility at Yale University in part by N.I.H. grant no. I-P07-PR00798 from the Division of Research Resources.

Appendix

Measurement of E^0's from the cyclic voltammograms was carried out in the following manner:

(a) The voltammetric currents on the forward (anodic) sweep were digitized manually from a large-scale plot produced as described in the Experimental section;

(b) the currents were convoluted [5] with the function $t^{-1/2}$ using a series expansion recommended by Evans [6];

(c) the currents were then fitted to the equation

$$I = I_d \left[\frac{k_1}{1 + \exp[(E_1^0 - E)/S_1]} + \frac{k_2 - k_1}{1 + \exp[(E_2^0 - E)/S_2]} + \frac{1 - k_2}{1 + \exp[(E_3^0 - E)/S_1]} \right]$$

where $k_1 = I_1/I_d$ and $k_2 = (I_1 + I_2)/I_d$ using a standard multi-parameter least-squares technique [7]. The computer program used accepts as input a set of current-potential points, convolutes the voltammetric currents (i) to produce a new set of convoluted currents (I), then finds the values (by a variational procedure) of E_1, E_2, E_3, S_1, S_2, S_3, and I_1, I_2, and I_3 (the three respective E^0's, slopes and currents) which represent the best fit of the experimental data to the theoretical equation. Running times on a DEC-20 computer are 15—30 seconds.

References

1 D.O. Cowan, C. LeVanda, J. Park, and F. Kaufman, Acc. Chem. Res., 6 (1973) 1.
2 W.H. Morrison, Jr., S. Krogsrud, and D.N. Hendrickson, Inorg. Chem., 12 (1973) 1998.
3 I. Agranat, E. Aharon-Shalom, A.J. Fry, R.L. Krieger, and W.O. Krug, Tetrahedron, 35 (1979) 733.
4 A.J. Fry, R.L. Krieger, I. Agranat, and E. Aharon-Shalom, Tetrahedron Lett., (1976) 4803.
5 J.C. Imbeaux and J.M. Saveant, J. Electroanal. Chem., 44 (1973) 169.
6 H.W. Vandenborn and D.H. Evans, Anal. Chem., 46 (1974) 643.
7 L. Meites and L. Lampugnani, Anal. Chem., 45 (1973) 1317.
8 J.B. Flanagan, S. Margel, A.J. Bard, and F.C. Anson, J. Amer. Chem. Soc., 100 (1978) 4248.
9 M.A. Battiste, B. Halton, and R.H. Grubbs, Chem. Commun., (1967) 907.
10 A. Padwa, Acc. Chem. Res., 12 (1979) 310.
11 G. Closs, Adv. Alicyclic Chem., 1 (1966) 53.
12 R. Breslow, P. Gal, H.W. Chang, and J.L. Altman, J. Amer. Chem. Soc., 87 (1965) 5139.
13 C. LeVanda, K. Bechgaard, D.O. Cowan, U.T. Mueller-Westerhoff, P. Eilbracht, G.A, Candela, and R.L. Collins, J. Amer. Chem. Soc., 98 (1976) 3181.
14 M. Cais and A. Eisenstadt, J. Amer. Chem. Soc., 89 (1967) 5468.
15 R.J. Abraham and P.J. Loftus, Proton and Carbon-13 NMR Spectroscopy, Heyden Publishing Co., London, 1978, p. 119.