2081 cm^{-1} which are indicative of two kinds of coordinated NCSe$^-$ ions.

A less obvious formulation which *is* consistent with all experimental evidence may be written $[Fe^{sp}(bipy)_2(NCSe)_2]_2[Fe^{sf}(bipy)_2(NCSe)_2]\cdot(bipy)$, where Fe^{sp} and Fe^{sf} denote spin-paired and spin-free iron(II), respectively.[18] The space group Pmnb is centrosymmetric having one eightfold set of general equivalent positions and three sets of fourfold special equivalent positions. Of the latter, one set is characterized by m, the others by $\bar{1}$. It may be assumed that all the atoms of the $[Fe^{sp}(bipy)_2(NCSe)_2]_2$ unit occupy general positions. Furthermore, it is conceivable that Fe^{sf} atoms occupy $\bar{1}$ sites, thus requiring a *trans* arrangement of the $[Fe^{sf}(bipy)_2(NCSe)_2]$ complex. This inference would account for both the small value of ΔE_Q as well as its large temperature dependence; *cf. trans*-$[Fe(py)_4(NCS)_2]$.[19] Finally, bipy in *trans* arrangement may or may not occupy the remaining $\bar{1}$ sites of the other set.

Numerous other formulations were checked and found inadequate. Iron(III) impurities as possible cause of anomalous magnetic effects[20] were ruled out on the basis of analytic and spectroscopic results. Therefore, we suggest that the compound studied might represent the first example of a crystal containing two out of three iron(II) ions in a spin-paired configuration, while the remaining iron(II) is spin free. Presumably, all three iron(II) ions are in approximately octahedral coordination. This arrangement may be considered as analogous to that encountered in the yellow Lifschitz nickel(II) complexes.[21,22]

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[18] Coordination numbers higher than six are considered very unlikely.

[19] For *trans*-$[Fe(py)_4(NCS)_2]$, we found $\Delta E_Q = 1.59 \pm 0.04$ mm/sec at 293°K and $\Delta E_Q = 2.02 \pm 0.04$ mm/sec at 77°K.

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Anodic Substitution Reactions of Aromatic Hydrocarbon Cation Radicals. Unequivocal Evidence for ECE Mechanism

Sir:

The mechanism of anodic substitution and addition reactions of aromatic hydrocarbons (pyridination, cyanation, hydroxylation, etc.) has been of continuing interest to organic electrochemists.[1-12] It was shown that the primary pathway for such processes must normally involve electrooxidation of the hydrocarbon species.[4-6] Aromatic hydrocarbon radicals formed from one-electron anodic oxidations were shown to have long lifetimes in anhydrous solvents[13-14] and to be susceptible to nucleophilic attack.[15]

The stoichiometry of such reactions is clear. In the pyridination of anthracene, two electrons are removed per molecule of hydrocarbon and two molecules of nucleophile (pyridine) are consumed. Lund isolated the anthracene 9,10-dipyridinium diperchlorate long ago.[1] There has been much discussion regarding the correct sequence of electron transfer and chemical attack steps. Suggestions have included (a) initial two-electron loss from hydrocarbon followed by nucleophilic attack,[1-3] (b) two-electron loss from hydrocarbon *concerted with* ("assisted by") nucleophilic attack,[4,5,7] (c) a radical-chain mechanism terminated by pairing of hydrocarbon and nucleophile radicals.[11,12]

We have obtained from rotated disk electrode (RDE) measurements positive evidence that the reaction sequence is an ECE process consisting of: electron transfer oxidation of hydrocarbon to cation radical; chemical attack of cation radical by unoxidized nucleophile; and further electron transfer oxidation of cation radical–nucleophile adduct (easier to oxidize than the parent hydrocarbon by virtue of incorporation of the electron-rich nucleophile).

For the pyridination reactions considered herein such a scheme would be written as

$$\mathrm{Ar} \rightleftharpoons \mathrm{Ar}\cdot^{+} + e^{-} \qquad \text{(E)}$$

$$\mathrm{Ar}\cdot^{+} + \mathrm{Py} \longrightarrow \mathrm{ArPy}\cdot^{+} \qquad \text{(C)}$$

$$\mathrm{ArPy}\cdot^{+} \rightleftharpoons \mathrm{ArPy}^{2+} + e^{-} \rightsquigarrow \text{proton loss or second nucleophile attack} \qquad \text{(E)}$$

where Ar is the aromatic hydrocarbon and Py is pyridine or a 4-substituted pyridine.

The two-electron-transfer steps were separated by measuring limiting currents at a RDE where the rate of stirring is competitive with the rate of the intervening chemical reaction. This is, we believe, the first unequivocal evidence for an ECE mechanism describing the electrochemical incorporation of a nucleophilic moiety into an aromatic hydrocarbon.

The various electrochemical and RDE techniques were conventional and have been described amply in the literature[13-18] Platinum RDE's constructed after Marcoux[13] with geometric areas of 0.045 and 0.202

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cm^2 were used. All studies were in acetonitrile with 0.2 M tetraethylammonium perchlorate as supporting electrolyte. All potentials are referred to the aqueous sce.

9,10-Diphenylanthracene (DPA) was selected as a hydrocarbon whose cation radical is quite stable yet interacts with a variety of nucleophiles at rates which are in a favorable range to demonstrate the ECE process.

In RDE voltammetry, the quantity $(i_L/\omega^{1/2}C)$ is directly related to the number of electrons transferred. As usual, i_L is the limiting current, C is the bulk concentration of electroactive species, and $\omega = 2\pi N$, where N = revolutions per second. The quantity $(i_L/\omega^{1/2}C)$ is independent of ω in the absence of coupled (ECE type) chemical reactions. A plot of $(i_L/\omega^{1/2}C)$ *vs.* $\omega^{1/2}$ is a horizontal straight line corresponding to a n_1 electron process. This is the limiting behavior of DPA in the absence of nucleophiles shown as the lower dotted line of Figure 1 (where DPA acts as a model one-electron oxidation). If an intervening chemical reaction (ECE) is so rapid that it cannot be "outrun" in the range of accessible rotation rates, then $(i_L/\omega^{1/2}C)$ *vs.* $\omega^{1/2}$ will again be a horizontal straight line but limiting proportional to $(n_1 + n_2)$ electrons of the over-all ECE reaction. This is seen in Figure 1 as the upper dotted line corresponding to two-electron behavior.

The quantity n_{obsd} plotted in Figure 1 is given by

$$n_{\text{obsd}} = \frac{(i_L/\omega^{1/2}C)\,(\text{DPA} + \text{nucleophile})}{(i_L/\omega^{1/2}C)\,(\text{DPA alone})}$$

By using the ratio of $(i_L/\omega^{1/2}C)$ for DPA plus nucleophile, compared to DPA alone (which behaves as a one-electron process), n_{obsd} is a direct measure of the average number of electrons transferred and is normalized for solution viscosity, diffusion coefficient, concentration, and electrode area. A more thorough discussion of this and other limiting current comparisons at the RDE is contained in previous literature.[13,17,18]

The experimental points in Figure 1 correspond to the actual behavior of DPA in the presence of the indicated substituted pyridines as nucleophiles. It is clear that the passage of the second electron is competing with the mass transfer since n_{obsd} gradually changes from nearly 2.0 electrons/mole of DPA at low rotation rates to slightly greater than 1 electron/mole at high rotation rates. On the basis of this observation, *the hypothesis that two electrons are transferred as a unit is untenable;* clearly the chemical interaction allowing the second electron to be transferred can be exceeded at high rotation rates.

To provide a semiquantitative framework for the rates of the chemical interactions, the $n_{\text{obsd}} - \omega^{1/2}$ behavior was calculated *via* Feldberg's digital simulation techniques for an ECE reaction and several finite values for chemical rate constants.[18] For interaction of the cation radical of DPA with various pyridines, the rate expression is of the form

$$-(\text{DPA}\cdot^+)/dt = k_2(\text{DPA}\cdot^+)(\text{pyridine}) = k_1(\text{DPA}\cdot^+)$$

where k_1 is a pseudo-first-order rate constant for excess nucleophile. In order to construct the curves from Feldberg's data, the diffusion coefficient for DPA was taken as 1.76×10^{-5} cm^2/sec. The dotted curves of Figure 1 show these calculations for values of k_1 from 3 to 1000 sec^{-1} as indicated on each curve. The experimental points follow the theoretical curves rather closely. More importantly, they are precisely in the order and have roughly the expected magnitudes for interaction of the cation radical with nucleophiles of varying electronegativity. Thus DPA$\cdot^+$ interacts most rapidly with 4-methylpyridine and least rapidly with 4-cyanopyridine, as would be expected from linear-free energy relationships of molecular orbital predictions of these substituents. By interpolation of the data of Figure 1, one can easily estimate the magnitude of the pseudo-first-order rate of the chemical interaction.

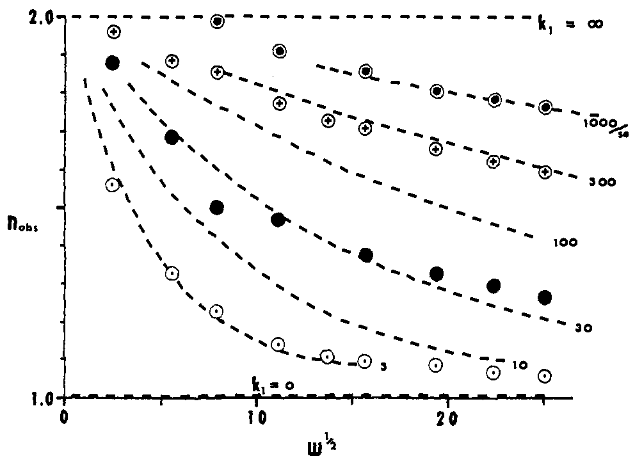

Figure 1. Rate of DPA$\cdot^+$ interactions with pyridine nucleophiles: ◉, 0.50 mM 9,10-DPA + 25 mM 4-methylpyridine; ⊕, 0.50 mM 9,10-DPA + 25 mM pyridine; ●, 0.50 mM 9,10-DPA + 25 mM 4-acetoxypyridine; ⊙, 0.50 mM 9,10-DPA + 25 mM 4-cyanopyridine. All solutions were 0.20 M tetraethylammonium perchlorate in acetonitrile plus the constituents given above.

Many aromatic hydrocarbons and a variety of nucleophiles give similar results at the RDE, and the reaction is a general one for such substitution reactions (cyanation, hydroxylation, etc.). Further studies of this interaction will be reported soon.

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Concurrent General Acid and General Base Catalysis of Esterification

Sir:

In the course of examining the rates of lactonization of a series of phenolic acids (**1**),[1,2] we found the reaction to proceed at a measurable rate in aqueous solution even at pH 7 (30°) and to obey a composite rate

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[1] For the origin of this study, see J. W. Thanassi and L. A. Cohen, *Biochim. Biophys. Acta*, **172**, 389 (1969).

[2] These compounds were prepared by acid-catalyzed alkylation of the corresponding *para*-substituted phenol with methyl 3,3-dimethylacrylate, followed by alkaline saponification of the lactone, according to the general procedure of J. Colonge, E. LeSech, and R. Marey, *Bull. Soc. Chim. Fr.*, 776 (1957). Acceptable elemental analyses were obtained in all cases.