expected for a C(sp^2)–Mn bond (calculated from covalent radii).

The ring bonded to the two metal atoms is only slightly distorted from planarity; the mean plane formed by atoms C_{11}, C_{12}, C_{13}, and C_{14} is bent at an angle of 4° to that formed by atoms C_{11}, C_{14}, and C_{15}. The ring appears nevertheless to have retained essentially aromatic character, as evidenced by the fact that the C–C bond lengths around the ring range between 1.40 and 1.44 Å, which compares well with the values of 1.40–1.43 Å in the other C_5H_5 ring and with the values expected for these rings.[11–13]

We believe that the products VI and VII have structures analogous to that of V, with the variation that there will be a H atom instead of a CO group bonded to the Re atom in VII, as indicated by nmr and ir (which is required by the 18-electron rule).

The products incorporate in a novel way interesting features of the chemistry of transition metal complexes that are of current interest. In the first place, the structure of V suggests a new possibility for the dimer recently reported for titanocene,[15] namely, one containing intramolecular bridged C_5H_4 rings. In the second place, it is likely that the first step in the reactions leading to complex V or VI is probably loss of H_2 from a coordinated dicyclopentadienylmetal dihydride as shown in eq 1. This has a parallel in a reaction recently reported for dicyclopentadienyltantalum trihydride (2) by Barefield, Parshall, and Tebbe.[7] We have tested the

$$\underset{\text{II}}{(C_5H_5)_2MoH_2} + \underset{\text{I}}{CH_3Mn(CO)_5} \rightleftharpoons$$

$$[(C_5H_5)_2MoH_2\cdot Mn(CO)_4(COCH_3)] \qquad (1a)$$

$$\Big\downarrow {-H_2, \text{ CO shift}}$$

$$[(C_5H_5)_2(CO)Mo\cdot Mn(CO)_4(CH_3)] \qquad (1b)$$

$$\swarrow \text{aromatic substitution}$$

$$\underset{\text{V}}{(C_5H_5)(CO)\overline{Mo\text{-}\mu\text{-}C_5H_4\text{-}Mn}(CO)_4} + CH_4$$

$$(C_5H_5)_2TaH_3 \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} (C_5H_5)_2TaH \underset{-L}{\overset{+L}{\rightleftharpoons}} (C_5H_5)_2TaH\cdot L \qquad (2)$$

hydrides II and III under the conditions of our reaction, but without acceptor I, and find that they do not lose hydrogen. Thus, although not favored by equilibrium, adduct formation (1a) most likely initiates the reaction sequence. Following closely behind the loss of H_2, or perhaps concerted with it, would be a shift of CO into the empty coordination site on the Mo (or W). This would be analogous to the addition of ligand as a second step reported in reaction 2. Finally, reaction 1 is completed by a novel intramolecular aromatic substitution of Mn on the adjacent cyclopentadienyl ring accompanied by elimination of CH_4, analogous to the similar irreversible elimination reported by Keim (reaction 3).[16] To demonstrate this reaction for a derivative of Mn, we have heated VIII (reaction 4) for 3 hr in refluxing toluene to give the intramolecular aromatic substitution product IX, as shown.[17]

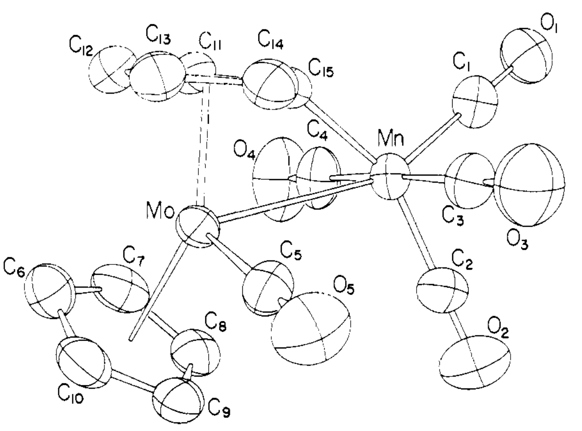


Figure 1. The structure of $(C_5H_5)(CO)\overline{Mo\text{-}\mu\text{-}C_5H_4\text{-}Mn}(CO)_4$; the molecule is rotated by 20° (clockwise) around the *z* axis and projected onto the *y–z* plane. The ellipsoids enclose 50% of the probability distribution and the hydrogens have been excluded for clarity.

$$[(C_6H_5)_3P]_3RhCH_3 \longrightarrow (C_6H_5)_2\overline{P\text{-}\mu\text{-}C_6H_4\text{-}Rh}[P(C_6H_5)_3]_2 + CH_4 \qquad (3)$$

$$\underset{\text{VIII}}{(C_6H_5)_3PMn(CO)_4CH_3} \longrightarrow \underset{\text{IX}}{(C_6H_5)_2\overline{P\text{-}\mu\text{-}C_6H_4\text{-}Mn}(CO)_4} + CH_4 \qquad (4)$$

In the formation of VII starting from IV, no H_2 can be lost after initial coordination, but a decarbonylation of the intermediate acyl derivative, followed by aromatic substitution with loss of CH_4, can account for the product. The decarbonylation will compete with the reverse of adduct formation, and this could account for the greater reaction time required for the formation of

$$\underset{\text{VII}}{(C_5H_5)(H)\overline{Re\text{-}\mu\text{-}C_5H_4\text{-}Mn}(CO)_4}$$

The unusual ring system in these derivatives is susceptible to chemical attack. In the treatment of V with acid, the Mn–C_{15} bond is cleaved and the C_5H_5 ring is restored (nmr) in an ionic derivative presently under study. We are attempting to cleave the Mn–C_{15} bond with H_2 or simply to observe if with D_2 there is appreciable deuteration of the ring (which would proceed through a deuterated intermediate $(C_5H_5)(C_5H_4D)(CO)Mo\cdot Mn(CO)_4D$). Also, we are attempting to obtain ring expansion by the reaction of CO and other carbenoid species with the new derivatives.

Acknowledgment. We wish to thank the members of the crystallographic group at UCLA, in particular Dr. J. Bell, M. Murphy, and E. Maverick, for helpful discussions in the structure determination reported here, and the UCLA Computing Center for an intramural grant to defray in part the computing expenses in this work.

R. Hoxmeier, B. Deubzer, H. D. Kaesz*
Department of Chemistry,[18] University of California
Los Angeles, California 90024

Received November 21, 1970

---

(15) H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, **92**, 6182 (1970).

(16) W. Keim, *J. Organometal. Chem.*, **14**, 179 (1968).

(17) *Anal.* (H. King, UCLA) Calcd for $C_{22}H_{14}MnO_4P$: C, 61.70; H, 3.27. Found: C, 61.65; H, 3.46. Mass spectrum, parent ion at *m/e* 428, shows successive loss of four CO's; ir (hexane) (cm^{-1}) 2067 (m), 1987 (s), 1983 (s), 1952 (s); nmr (acetone-d_6, external TMS), complicated phenyl resonance centered at τ 2.62, no Mn–CH_3 resonance.

(18) Publication No. 2752.

Anodic Substitution. An Alternative to the ECE Mechanism

Sir:

The anodic reaction between pyridine and anthracene originally described by Lund[1] has received a great deal

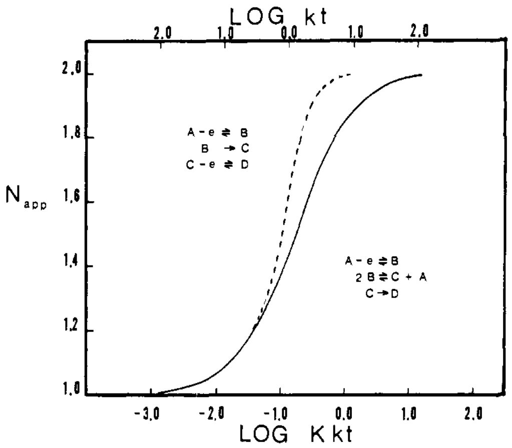


Figure 1. Digital simulation of chronoamperometric working curves for the disproportionation mechanism (solid line) and for the ECE mechanism (broken line).

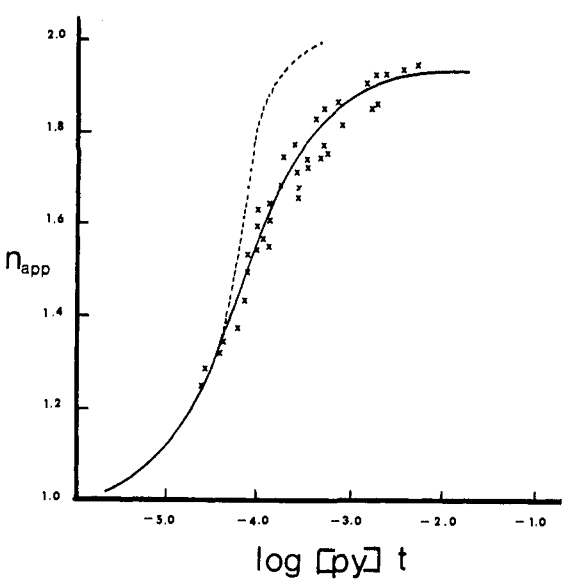


Figure 2. Experimental chronoamperometric data for the anodic reaction of pyridine and DPA.

of recent attention.[2-4] Much of the interest in this reaction has been due to the fact that it serves as an easily studied model for all anodic substitution reactions. When it became apparent that the anodic oxidation of aromatic hydrocarbons proceeded through an initial one-electron transfer,[5-7] an ECE reaction in which the cation radical underwent nucleophilic attack appeared to be the most likely mechanism for anodic substitution. For the pyridination case this ECE mechanism could be written

$$\mathrm{Ar} \rightleftarrows \mathrm{Ar}\cdot^{+} + \mathrm{e}^{-} \qquad (1)$$

$$\mathrm{Ar}\cdot^{+} + \mathrm{Py} \longrightarrow \mathrm{ArPy}\cdot^{+} \qquad (2)$$

$$\mathrm{ArPy}\cdot^{+} \rightleftarrows \mathrm{ArPy}^{2+} + \mathrm{e}^{-} \qquad (3)$$

$$\mathrm{ArPy}^{2+} \longrightarrow \text{further reaction}$$

Rotated disk electrode (RDE) studies of the 9,10-diphenylanthracene (DPA)-pyridine reaction have indicated that this is a highly plausible mechanism, and furthermore these studies have unequivocally demonstrated that the initial step in this reaction is a one-electron transfer.[2]

The existence of an alternative mechanism has, however, been clearly demonstrated.[8,9] Schematically this disproportionation mechanism could be represented as follows for the DPA-pyridine reaction

$$\mathrm{Ar} \rightleftarrows \mathrm{Ar}\cdot^{+} + \mathrm{e}^{-} \qquad (4)$$

$$2\mathrm{Ar}\cdot^{+} \rightleftarrows \mathrm{Ar} + \mathrm{Ar}^{2+} \qquad (5)$$

$$\mathrm{Ar}^{2+} + \mathrm{Py} \longrightarrow \mathrm{ArPy}^{2+} \qquad (6)$$

$$\mathrm{ArPy}^{2+} \longrightarrow \text{further reaction}$$

This disproportionation was shown to be the mechanistic pathway for the reaction between thianthrenium perchlorate and water.[8,9] The fact that two outwardly similar reactions could proceed through such obviously different mechanisms seemed curious and worthy of further study.

Mechanisms involving disproportionation are not unknown to electrochemistry and have been treated in depth by two recent papers.[10,11] Both of these studies made it quite clear that the ECE and disproportionation mechanisms were quite similar and care was necessary in order to distinguish between them. Feldberg, using his method of digital simulation,[12] generated the chronamperometric working curves for an irreversible disproportionation and several alternative mechanisms. In this work it was suggested that the alternative mechanisms be given serious consideration because they avoided the thermodynamic paradox presented by disproportionation. This work further illustrated the difficulty inherent in distinguishing between various similar mechanisms.

In order to determine whether or not the two mechanisms in question were electrochemically distinguishable, digital simulation of the chronoamperometric working curve was carried out for the reversible disproportionation mechanism (eq 4–6). The rate law used for the simulation assumed rapid equilibrium for reaction 5 and was of the form

$$\frac{-\mathrm{d}[\mathrm{Ar}^{+}]}{\mathrm{d}t} = \frac{kK[\mathrm{Ar}^{+}]^2}{[\mathrm{Ar}]}$$

where k is the pseudo-first-order rate constant for eq 6 and K is the equilibrium constant for eq 5. It should be noted that this particular scheme is not paradoxical since a large value of k readily compensates for a small value of K. The resulting working curve is shown in Figure 1. Also shown in this figure is the working curve for the ECE mechanism which was calculated according to Alberts and Shain.[13]

Although the two curves are to an extent similar it is clear that experimental points obtained over three

---

(1) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

(2) G. Manning, V. D. Parker, and R. N. Adams, *J. Amer. Chem. Soc.*, **91**, 4584 (1969).

(3) V. D. Parker and L. Eberson, *Tetrahedron Lett.*, 2839 (1969).

(4) V. D. Parker and L. Eberson, *ibid.*, 2843 (1969).

(5) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967).

(6) J. Phelps, K. S. V. Santhanam, and A. J. Bard, *J. Amer. Chem. Soc.*, **89**, 1752 (1967).

(7) L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *ibid.*, **89**, 5766 (1967).

(8) H. J. Shine and Y. Murata, *ibid.*, **91**, 1872 (1969).

(9) Y. Murata and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969).

(10) M. Mastragostino, L. Nadjo, and J. M. Saveant, *Electrochim. Acta*, **13**, 721 (1968).

(11) S. W. Feldberg, *J. Phys. Chem.*, **73**, 1238 (1969).

(12) S. W. Feldberg *Electroanal. Chem.*, **3**, 199 (1969).

(13) G. S. Alberts and I. Shain, *Anal. Chem.*, **35**, 1859 (1965).

orders of magnitude in time should allow the distinction to be made. This also points out one of the disadvantages of RDE studies, namely, that laminar flow is not obtained over an adequately large range of rotation rates. In Figure 2 chronoamperometric data are shown for several experiments in which pyridine was added to DPA. The measurements were made at a planar platinum electrode in acetonitrile which was 0.1 *M* in tetraethylammonium perchlorate and 8.0×10^{-4} *M* in DPA. The pyridine concentrations used were 5.8×10^{-3} *M*, 1.1×10^{-2} *M*, 2.2×10^{-2} *M*, and 4.1×10^{-2} *M*. The solid line represents the simulation for the disproportionation mechanism with $K = 4.0 \times 10^{-6}$ (calculated from the 320-mV separation between the first and second oxidation waves of DPA) and a rate constant of (4.5×10^6) [pyridine]. In actuality, for this particular case, the assumption of slow equilibrium was found to provide a better fit, and the simulation shown is for the case

$$K = \frac{k_f}{k_r} = \frac{4 \times 10^3}{1 \times 10^9}$$

The broken curve is the working curve for the ECE mechanism included for the purposes of comparison. The experimental data clearly favor the disproportionation mechanism. It should be borne in mind, however, that in reality these data only indicate that the first-order ECE interpretation is doubtful, and disproportionation provides a satisfactory alternative for which there exists a chemical precedent. It is also obvious that data obtained over shorter time intervals could easily fit either curve. One can only begin to distinguish between the two mechanisms when data are available over the entire range of variation for the particular working curve. This work demonstrates that at present one cannot unequivocally assign the mechanism of the DPA–pyridine reaction to the ECE pathway, and it further suggests that the disproportionation mechanism is a more likely route.

Acknowledgment. The author is indebted to the Research Corporation for a Frederick Gardner Cottrell grant-in-aid and to Drs. R. N. Adams, A. J. Bard, and H. J. Shine for helpful discussions.

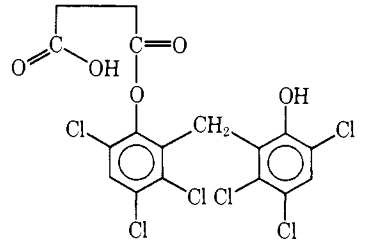
Lynn Marcoux
Department of Chemistry, Texas Tech University
Lubbock, Texas 79409

Received October 19, 1970

Intramolecular Bifunctional Facilitation in Complex Molecules. Combined Nucleophilic and General Acid Participation in Hydrolysis of Hexachlorophene Monosuccinate

Sir:

Intramolecular facilitation of the hydrolysis of carboxylic acid esters and amides has previously been shown to occur by either nucleophilic attack of a neighboring nucleophile such as a carboxylate group[1] at the ester carbon atom or by neighboring groups acting as general acids and bases.[2,3] We have now been able to show that simultaneous bifunctional twofold facilitation can be conferred on hydrolysis of a molecule as complex as hexachlorophene monosuccinate (I), where the participating structures involve formation of an 8-atom and a 5-atom ring. This appears to be the first definitively proven case of a push–pull nucleophilically assisted hydrolytic reaction, although a similar mechanism has been suggested by Morawetz[1] in the hydrolysis of succinylsalicylic acid. Unlike some of the earlier suggested systems of this nature, the present case involves participation of nonadjacent sites and a reaction in largely aqueous ($N_{H_2O} = 0.7$, $N_{CH_3OH} = 0.3$) solution.[3]



I

Intramolecular nucleophilic attack by the succinate carboxylate group at the ester carbonyl carbon atom in I followed by bond rearrangement should lead to the formation of succinic anhydride. Strong evidence that this reaction occurred has been obtained by the chromatographic isolation of succinanilic acid following addition of aniline to a reaction mixture at pH 7.85 (phosphate buffer) at a time when it was calculated that all of I has been hydrolyzed to hexachlorophene. The yield of succinanilic acid obtained in this way was 17% of the succinyl function present. A control experiment using succinic anhydride instead of I yielded 13% of the anhydride in the form of succinanilic acid. The remaining 87% probably was lost in the hydrolysis of the anhydride and in the formation of succinyl phosphate.[4] These results strongly indicated that the reaction proceeded exclusively *via* intramolecular nucleophilic catalysis.

Evidence for additional intramolecular general acid catalysis of this reaction comes from the pH–rate profile for the hydrolysis of I in 50% aqueous methanol at 25° shown in Figure 1. The bell-shaped curve with a maximum around pH 6.8[5] indicated that the monoanion of I is much more unstable with respect to hydrolysis than either the neutral molecule or the dianion. In 50% aqueous methanol, hexachlorophene monosuccinate is estimated to have pK_a values of 5.20 and 8.14 for the carboxylic and phenolic groups, respectively.

This pH–rate profile could be accounted for either on the basis that the phenolic proton in the monoanion of I acts as an intramolecular general acid catalyst by hydrogen bonding with an oxygen atom at the reaction center in a transition state such as II or that the negatively charged oxygen atom in the dianion of I exerts an electrostatic inhibition on the reaction. Although this second possibility cannot be ruled out, we believe

---

(1) (a) H. Morawetz and J. Oreskes, *J. Amer. Chem. Soc.*, **80**, 2591 (1958); (b) H. Morawetz and J. Shafer, *ibid.*, **84**, 3783 (1962).

(2) F. L. Killian and M. L. Bender, *Tetrahedron Lett.*, 1255 (1969).

(3) (a) S. M. Kupchan, S. P. Eriksen, and M. Friedman, *J. Amer. Chem. Soc.*, **88**, 343 (1966); (b) S. M. Kupchan, S. P. Eriksen, and Y. T. S. Liang, *ibid.*, **88**, 347 (1966).

(4) T. Higuchi, G. L. Flynn, and A. C. Shah, *ibid.*, **89**, 616 (1967).

(5) Between pH 5.6 and 8, the reaction is too fast to be accurately measured. The optimal pH for the reaction is therefore obtained from extrapolation.