Tetrahedron Letters No. 6, pp 393 - 396, 1975. Pergamon Press. Printed in Great Britain.

# CATALYTIC ELECTROCHEMICAL REDUCTION OF THE CARBON-CHLORINE BOND

John W. Sease* and Richard C. Reed[1,2]
Department of Chemistry, Wesleyan University
Middletown, Connecticut 06457

(Received in USA 18 June 1974; received in UK for publication 23 December 1974)

The ready reduction of alkyl halides by electrochemically generated naphthalene radical anions[3-7] and the known electrochemical behavior of aromatic hydrocarbons suggests that alkyl halides, although not directly reducible in an electrochemical cell, should be reducible when suitable aromatic hydrocarbons are added to act as catalytic electron-transfer agents.[8-11] We have found this to be so, but have been completely unsuccessful in attempts to carry out similar transfer reactions with bromine compounds. The synthetic importance of an electrochemical carbon-chlorine bond-reduction procedure prompts this preliminary report, even though experimental work is still in progress and we can as yet only speculate as to the reasons for the non-occurence of catalytic electron transfer with bromine compounds.

The behavior of systems which we have investigated polarographically (Table I) in dimethylformamide was typical of that reported for such catalytic systems.[12-15] The relatively large diffusion currents observed for halide-hydrocarbon systems satisfied all three criteria for catalytic current deduced by Delahay and Stiehl.[13] Current was 1) proportional to the aromatic hydrocarbon concentration, 2) independent of the height of the mercury column, and 3) proportional to the square root of the organic chloride concentration.

Cyclic voltammograms of these systems were found to be consistent with the catalytic electron-transfer mechanism. Normally naphthalene undergoes a reversible one-electron reduction at all sweep rates. However, when 0.001 M naphthalene solution was made 0.01 M in 6-chloro-1-hexene, the naphthalene reduction became irreversible at sweep rates up to 5 v/sec. Between 5 v/sec and 30 v/sec the voltammograms corresponded to a quasi-reversible process, whereas above 30 v/sec the voltammograms once again showed the two peaks characteristic of a reversible reduction and reoxidation. In summary, at slow sweep rates the electron from the naphthalene radical anion reacted with 6-chloro-1-hexene faster than it was reoxidized to naphthalene. At increasingly faster sweep rates reoxidation began to compete with electron transfer to the alkyl chloride and finally became faster than the transfer reaction.

From controlled-potential electrolysis at a mercury pool cathode in dimethylformamide containing 0.1 M tetraethylammonium bromide, 0.0005 M naphthalene and 0.01 M chlorohexane or 6-chloro-1-hexene we obtained about 80% hexane or 25% methylcyclopentane and 60% hexene respectively. By contrast, when aromatic hydrocarbon was absent,

TABLE I

| Aromatic Hydrocarbon | $E_{1/2}$* | Halogen Compound** | Catalytic Transfer*** |
|---|---|---|---|
| Biphenyl | -1.81 | $C_6H_{13}Cl$, $C_6H_{11}Cl$ | Yes |
| | | $C_6H_{13}F$ | No |
| o-Terphenyl | -1.78 | $C_6H_{13}Cl$ | Yes |
| o-Quaterphenyl | -1.75 | $C_6H_{13}Cl$, $C_6H_{11}Cl$ | Yes |
| Naphthalene | -1.71 | $C_4H_9Cl$, $C_6H_{13}Cl$, $C_6H_{11}Cl$, $C_6H_5Cl$ | Yes |
| | | $C_6H_{13}F$ | No |
| Phenanthrene | -1.68 | $C_4H_9Cl$, $C_6H_{13}Cl$, $C_8H_{17}Cl$, $C_6H_5Cl$ | Yes |
| | | $C_6H_5F$, $C_7H_7F$ | No |
| Triphenylene | -1.64 | $C_4H_9Cl$, $C_6H_{13}Cl$ | Yes |
| 1,1-Binaphthyl | -1.63 | $C_6H_{13}Cl$ | Yes |
| p-Terphenyl | -1.55 | $C_6H_{13}Cl$ | Yes |
| p-Quaterphenyl | -1.41 | $C_4H_9Cl$, $C_6H_{13}Cl$, $C_6H_{11}Cl$ | No |
| 2,2-Binaphthyl | -1.41 | $C_6H_{13}Cl$, $C_4H_9Br$, $C_6H_4BrCl$ | No |
| Pyrene | -1.30 | $C_4H_9Cl$, $C_6H_{13}Cl$, $C_4H_9Br$, $C_6H_{13}Br$ | No |
| Anthracene | -1.11 | $C_4H_9Cl$, $C_6H_{13}Cl$, $C_6H_{13}Br$ | No |
| 9,10-Diphenylanthracene | -1.04 | $C_4H_9Br$, $C_6H_4BrCl$ | No |

* All potentials are referred to a Cd(Hg)/$CdCl_2$, $CdCl_2 \cdot H_2O$, NaCl electrode in DMF.[16] This electrode is approximately 0.75 v. positive with respect to the S.C.E.

** $C_6H_5F$ = Fluorobenzene ($E_{1/2} \ll -2.1$ v., *i.e.*, more negative than); $C_6H_{13}F$ = 1-Fluorohexane ($\ll -2.1$); $C_7H_7F$ = *p*-Fluorotoluene ($\ll -2.1$); $C_4H_9Cl$ = 1-Chlorobutane ($< -2.1$); $C_6H_5Cl$ = Chlorobenzene (-1.88); $C_6H_{11}Cl$ = 6-Chloro-1-hexene ($< -2.1$); $C_6H_{13}Cl$ = 1-Chlorohexane ($< -2.1$); $C_8H_{17}Cl$ = 1-Chlorooctane ($< -2.1$); $C_4H_9Br$ = 1-Bromobutane (-1.51); $C_6H_5Br$ = Bromobenzene (-1.50); $C_6H_{13}Br$ = 1-Bromohexane (-1.52); $C_6H_4ClBr$ = *m*-Chlorobromobenzene(-1.53).

*** Catalytic transfer was said to occur if the height of the aromatic hydrocarbon wave increased greatly when alkyl halide was present.

electrolysis of alkyl chloride at the same potential for the same length of time produced only negligible quantities of reduction products. The observed products are consistent with the reaction scheme already proposed for radical anion-alkyl halide reactions in other aprotic solvents,[3,7] the methylcyclopentane resulting from rearrangement at the free-radical stage.[17]

$$\text{Naph} + e^- \longrightarrow \text{Naph}\cdot^-$$

$$\text{Naph}\cdot^- + \text{R-Cl} \xrightarrow{k} \text{Naph} + \text{R}\cdot + \text{Cl}^- \quad \text{(Rate-determining)}$$

$$\text{Naph}\cdot^- + \text{R}\cdot \longrightarrow \text{Naph} + \text{R:}^-$$

$$\text{R:}^- + \text{H}^+ \text{ (from } Et_4N^+, \text{ R-Cl, or } H_2O) \longrightarrow \text{R-H (80-100\%)}$$

$$\text{Naph}\cdot^- + \text{R}\cdot \longrightarrow \quad \longrightarrow \text{Mono- + dialkyl-dihydronaphthalenes}$$

Similar results were obtained when phenanthrene and triphenylene were used as transfer agents and would be expected for other aromatic compounds listed in Table I which also showed catalytic currents. Some alkylation of naphthalene probably occurred, although no direct analysis for such products was carried out. The difference in magnitude of the residual naphthalene currents before and after alkyl chloride electrolysis suggested a loss of 15-20% of the naphthalene.

The abnormally large residual currents observed for solutions of naphthalene or phenanthrene suggest that the radical anion can also transfer electrons to the solvent or electrolyte, but at a much slower rate than to chloroalkane. These currents did not decrease with time even after more than one electron had passed through the solution for each molecule of naphthalene or phenanthrene originally present. When a solution containing naphthalene or phenanthrene but no organic halide was electrolyzed, the green color of naphthalene radical anion or the orange-brown color of phenanthrene radical anion appeared within 30-60 seconds; the color faded within a few minutes after the current was stopped but reappeared again when electrolysis was resumed. Electrolysis of halide-aromatic hydrocarbon mixtures yielded no color until the chloroalkane reduction had been essentially completed.

A surprising feature of the electron-transfer process is its apparent limitation to chlorine compounds. Attempts to reduce alkyl and aryl bromides with aromatic radical anions having half-wave potentials slightly more positive than those of the organic halogen compound have been completely unsuccessful (Table I.) We agree with Garst and Barton[7]that catalytic reduction of the carbon-chlorine bond is possible only because of the relatively high activation energy and correspondingly slow rate of the electrochemical reaction. The potential for the reduction is far negative of the electrocapillary maximum, so that there is a high potential gradient and a highly structured double layer at the electrode surface; this in conjunction with the relatively polar nature of the carbon-chlorine bond can lead to rather considerable enthalpy and entropy effects in the transition state. Such effects should be far smaller in the interaction of the carbon-chlorine bond with an aromatic radical anion, which has a delocalized charge and a relatively loose solvation shell. In terms of this picture failure to obtain electron transfer with alkyl bromides can be attributed to a more positive electrode potential, which is closer to the electrocapillary maximum, and to a lower polarity of the carbon-halogen bond.

Failure to obtain electron-transfer reduction of fluorine compounds can be attributed to the presence of $Et_4N^+$. The rate of reaction in DME between alkyl fluorides and naphthalene radical ions is critically dependent upon the nature of the cation;[7] the rate in DMF containing $Et_4N^+$ should be very slow.[7a] The most rapid reduction should occur when $Li^+$ is present but unfortunately this ion is reduced more readily than naphthalene and its presence would prevent the formation of naphthalene radical anion. However, with a suitable non-amalgam-forming electrode reduction of fluorine compounds should be possible by electrolytic generation of lithium metal and in situ formation of lithium naphthalene.

The graphical procedure of Delahay and Stiehl,[13] when applied to the polarographic data, gave a value of $k = 320\ M^{-1}sec^{-1}$ for the naphthalene-chlorohexane transfer. This value is only an approximation since its computation does not take into account competitive side reactions such as alkylation or transfer to solvent. Nevertheless it is in quite good agreement with the value of $490 \pm M^{-1}sec^{-1}$ obtained by Fry and Britton[18] by potential-step measurements on the phenanthrene-chlorooctane system.

Presently we are investigating the dependence of product identity and yield on the specific aromatic hydrocarbon acting as a transfer reagent and the ratio of transfer reagent to alkyl chloride.

We are indebted to Professors S. Bank and A. J. Fry for several valuable discussions.

## REFERENCES

1. Taken in part from the M.A. and Ph.D. theses of Richard C. Reed, Wesleyan University, 1968 and 1970.
2. Presently at Hartwick College, Oneonta, New York, 13820.
3. G.D. Sargent, J.N. Cron, and S. Bank, J. Amer. Chem. Soc., 88, 5363 (1966).
4. J.F. Garst, P.W. Ayers, and R.C. Lamb, J. Amer. Chem. Soc., 88, 4260 (1968).
5. S.J. Cristol and R.V. Barbour, J. Amer. Chem. Soc., 88, 4262 (1966); 90, 2832 (1968).
6. J.F. Garst, Accounts Chem. Res., 4, 400 (1971).
7. J.F. Garst and F.E. Barton II, J. Amer. Chem. Soc., 96, 523 (1974); a) J.F. Garst, Private communication.
8. S. Wawzonek and D. Wearring, J. Amer. Chem. Soc., 81, 2067 (1959).
9. M. E. Peover in Bard, "Electroanalytical Chemistry, A Series of Advances," Vol. 2, Dekker, New York, 1967.
10. R. Brown and J.A. Harrison, J. Electroanal. Chem., 21, 387 (1969).
11. A.J. Fry, "Synthetic Organic Electrochemistry," New York, Harper and Row, 1972, pp. 111-112, 134, 199.
12. I.M. Kolthoff and J.J. Lingane, "Polarography," Interscience, New York, 2nd Ed., 1952, p. 235.
13. P. Delahay and G.L. Stiehl, J. Amer. Chem. Soc., 74, 3500 (1952).
14. L. Meites and S.A. Moros, Anal. Chem., 31, 23 (1959).
15. D.H. Geske and A.J. Bard, J. Phys. Chem., 63, 1057 (1959).
16. L.W. Marple, Anal. Chem., 39, 844 (1967).
17. M. Julia, Accounts Chem. Res., 4, 386 (1971).
18. A.J. Fry and W.E. Britton, Anal. Chem., in press.