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Polarographic Studies in Acetonitrile and Dimethylformamide. IV. Stability of Anion-free Radicals[1,2]

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The polarographic reduction of stilbene, naphthalene, phenanthrene, biphenyl, *o*-terphenyl, *m*-terphenyl, diphenylacetylene and phenylacetylene in dimethylformamide containing tetra-*n*-butylammonium iodide as a supporting electrolyte, has been carried out. The results point to the formation of monovalent anion-free radicals as intermediates in the reduction of the first seven hydrocarbons. Substantiation for the mechanism of reduction was obtained by the isolation of products in the large scale electrolytic reduction of naphthalene, phenanthrene and diphenylacetylene in the absence and presence of carbon dioxide. Agreement of the results obtained with the data reported by magnetic susceptibility and spectra measurements on sodium addition products of aromatic hydrocarbons indicates that the polarographic method offers a satisfactory and rapid method of determining which aromatic hydrocarbons are capable of forming stable monovalent anion-free radicals with alkali metals.

The mechanism of the addition of alkali metals to arylated olefins and aromatic hydrocarbons has been the subject of many investigations. Anion-free radicals and divalent anions have been suggested as intermediates in such reactions in aprotic solvents.

The formation of anion-free radicals has been suggested chemically in the addition of sodium to naphthalene, biphenyl[4] and stilbene.[5]

Such structures have been confirmed by spectroscopy,[6,7] and by magnetic susceptibility measurements[8] for addition products of sodium with various aromatic hydrocarbons.

Previous polarographic studies in acetonitrile and dimethylformamide[9] have shown that this method is capable of furnishing evidence for the existence of stable anion-free radicals in the reduction of stilbene and anthracene. Polarographic studies by others[10,11] in 96% dioxane–water mixtures have pointed to such intermediates in the reduction of anthracene and numerous other hydrocarbons but not for naphthalene or stilbene. The report of only one wave for stilbene indicates that 96% dioxane–water is more acidic than dimethylformamide and is not as useful for such studies.

In the present work the polarographic reduction of naphthalene, biphenyl, phenanthrene, *o*-terphenyl, *m*-terphenyl, phenylacetylene and diphenylacetylene in dimethylformamide has been studied in order to determine whether anion-free radicals are produced in this solvent from these compounds electrolytically.

Experimental[12]

The solutions were studied in a cylindrically shaped cell with a mercury pool anode and fitted with side arms for the anode connection and for admission of nitrogen. The cell was thermostated by a water-bath controlled at 25 ± 0.1°.

The current–voltage curves were obtained with a Sargent model XII polarograph having a current scale calibration of 0.00497 μ a./mm. at a sensitivity of one.

The dropping mercury electrode was operated at 60 cm. pressure and had a droptime of 3.40 seconds in dimethylformamide (open circuit). The $m^{2/3}t^{1/6}$ value was 1.356 mg.$^{2/3}$sec.$^{-1/2}$.

The dimethylformamide was purified in a manner similar to that reported previously.[9] The hydrocarbons used were obtained from stock and purified by crystallization or distillation.

Electrolytic Reductions.—The electrolytic reductions of the various hydrocarbons in the absence and presence of carbon dioxide were carried out in a similar manner to that described earlier.[9]

Electrolysis of Naphthalene.—Naphthalene (6.4 g.) was dissolved in 150 ml. of dimethylformamide containing 0.155 *M* tetra-*n*-butylammonium iodide and placed in the cathode compartment. An equal volume of the solvent with supporting electrolyte was placed in the anode compartment and the dissolved air in the cell was removed by bubbling nitrogen through the solution for an hour. Direct current was passed through the cell for 23.5 hours and decreased from 0.30 to 0.05 amp. in this period. The catholyte became faintly green in color during this period.

Removal of the solvent under reduced pressure and then steam distillation gave 5.8 g. of naphthalene.

Electrolysis of Naphthalene and Carbon Dioxide.—A solution similar to the above was electrolyzed while a stream of carbon dioxide was passed through the catholyte. The catholyte remained colorless and the current dropped from 0.30 to 0.10 amp. in a 23-hour period.

The solvent was removed under reduced pressure and the residue after being made alkaline with 100 ml. of 5% sodium hydroxide was steam distilled; 1.5 g. of naphthalene was obtained. The alkaline solution remaining from the distillation after filtration gave upon acidification 3.62 g. of an acid melting at 178–200°. Purification by reprecipitation from sodium hydroxide with subsequent recrystallization from isopropyl alcohol gave 1,4-dicarboxy-1,4-dihydronaphthalene. This structure was indicated by its melting point of 224–227° and neutralization equivalent of 111.5. No 1,2-dicarboxy-1,2-dihydronaphthalene could be isolated using the method of Walker and Scott.[13]

Electrolysis of Phenanthrene.—Phenanthrene (8.9 g.) was reduced under conditions similar to those given for naphthalene for 27 hours. During the electrolysis 9,10,9',10'-tetrahydro-9,9'-biphenanthrene (3.9 g.) collected in the side arm and on the sintered glass disk of the electrolytic cell. The white solid after recrystallization from benzene melted at 284°.

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[2] Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1958.

[3] Abstracted in part from the Ph.D. Thesis, February, 1958, of D. Wearring.

[4] N. D. Scott, J. F. Walker and V. L. Hansley, THIS JOURNAL, **58**, 2442 (1936).

[5] J. W. B. Reesor, J. G. Smith and G. F. Wright, *J. Org. Chem.*, **19**, 940 (1954).

[6] D. E. Paul, D. Lipkin and S. I. Weissmann, THIS JOURNAL, **78**, 116 (1956).

[7] R. L. Ward and S. I. Weissmann, *ibid.*, **76**, 3612 (1954).

[8] T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1954).

[9] S. Wawzonek, E. W. Blaha, R. Berkey and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).

[10] G. I. Hoijtink, J. Van Schooten, E. de Boer and W. Ij. Aalhersberg, *Rec. trav. chim.*, **73**, 355 (1954).

[11] G. I. Hoijtink, *ibid.*, **73**, 895 (1954).

[12] Melting points are not corrected.

[13] J. F. Walker and N. D. Scott, THIS JOURNAL, **60**, 951 (1938).

Anal. Calcd. for $C_{28}H_{22}$: C, 93.85; H, 6.15. Found: C, 93.35; H, 6.05.

Phenanthrene (3.7 g.) was recovered from the filtrate. The presence of 9,10-dihydrophenanthrene was not demonstrated because of the small amount present.

9,9′-Biphenanthrene.—A mixture of 9,10,9′,10′-tetrahydro-9,9′-biphenanthrene (1.15 g.) and sulfur (0.43 g.) was heated at 250° for 10 hours. The cooled residue when extracted with chloroform gave a viscous mass. Further extraction of this product with benzene, and then clarification with decolorizing carbon and cooling, gave 0.22 g. of 9,9′-biphenanthrene melting at 186°. The literature reports 184–185°.[14]

Electrolysis of Phenanthrene and Carbon Dioxide.—Phenanthrene (8.9 g.) was reduced in the presence of carbon dioxide for 25 hours. Removal of the solvent and then extraction with ether gave 2.34 g. of phenanthrene. The insoluble residue now was extracted with 100 ml. of 10% sodium hydroxide. The extract upon acidification gave a gummy mass which crystallized from chloroform and gave 2.8 g. of *trans*-9,10-dicarboxy-9,10-dihydrophenanthrene. After two crystallizations from chloroform the acid melted at 230–232° (the literature value[15] is 235–242°) and gave a neutralization equivalent of 133.5. The dimethyl ester prepared from methanol and sulfuric acid melted at 128° in agreement with the literature.[15]

Electrolysis of Diphenylacetylene.—Diphenylacetylene (8.9 g.) was reduced for 30 hours starting with a current of 0.45 amp. and decreasing to 0.20 amp. at the end of the electrolysis. Removal of the solvent under reduced pressure followed by steam distillation gave 5.4 g. of bibenzyl melting at 52°; no depression in melting point was observed when mixed with an authentic sample. The residue from the steam distillation when extracted with ether gave 1,2,3,4-tetraphenylbutane (0.3 g.) melting at 85–86° and identical with an authentic sample. No 1,2,3,4-tetraphenyl-1,3-butadiene was found.

Electrolysis of Diphenylacetylene and Carbon Dioxide.—Diphenylacetylene (8.9 g.) was electrolyzed in the presence of carbon dioxide for 24.5 hours. Removal of the solvent with subsequent addition of 100 ml. of 5% sodium hydroxide gave a dark precipitate of tetrabutylammonium iodide and tetrabutylammonium tetraiodomercurate which was removed by filtration. The alkaline filtrate after extraction with benzene gave upon acidification 12.5 g. of a pale yellow solid. Fractional crystallization from 50 ml. of hot ethyl acetate gave 1.21 g. of diphenylfumaric acid which after one crystallization from glacial acetic acid had a melting point of 263–265° (lit. 260°, 271° depending on the rate of heating[16]) and a neutralization equivalent of 134. Evaporation of the ethyl acetate and crystallization from ethanol (25 ml.) gave diphenylmaleic anhydride (0.5 g.). This compound crystallized from glacial acetic acid and melted at 157–158° (lit.[16] 158°). The alcoholic filtrate after heating with 50 ml. of water and one drop of sulfuric acid for several hours gave on cooling 3.68 g. of *meso*-diphenylsuccinic acid. This acid melted at 222° after one crystallization from methanol and proved identical with an authentic sample.

Results

Polarographic data obtained for the various hydrocarbons in dimethylformamide containing tetrabutylammonium iodide are given in Table I and compared with the results for stilbene. The waves in all cases were well defined.

To study the effect of protons upon the reduction, water was added to a solution of naphthalene in increasing amounts and the results are summarized in Table II.

To help formulate electrode reactions, large scale electrolytic reductions were carried out with naphthalene, phenanthrene and diphenylacetylene in the absence and presence of carbon dioxide. The results are summarized in the Experimental section.

TABLE I

POLAROGRAPHIC BEHAVIOR OF VARIOUS AROMATIC HYDROCARBONS IN DIMETHYLFORMAMIDE CONTAINING 0.155 *M* TETRA-*n*-BUTYLAMMONIUM IODIDE

Compound	Concn.[a]	Wave	$E_{1/2}$ v. *vs.* Hg pool	I_d[b]
trans-Stilbene	1.00	1	−1.64	2.09
		2	−1.94	2.24
Naphthalene	1.00	1	−1.91	2.02
Phenanthrene	1.00	1	−1.86	1.59
Diphenylacetylene	1.00	1	−1.69	1.92
		2	−1.96	2.31
Biphenyl	1.81	1	−1.95	1.44
o-Terphenyl	0.71	1	−1.90	2.24
		2	−2.06	2.74
m-Terphenyl	1.00	1	−1.86	1.37
Phenylacetylene[c]	1.50	1	−1.97	8.32

[a] Millimoles per liter. [b] $I_d = i_d/Cm^{2/3}t^{1/6}$. [c] The capillary had a droptime of 3.8 sec. and $m^{2/3}t^{1/6}$ of 1.858.

TABLE II

EFFECT OF WATER ON THE POLAROGRAPHIC BEHAVIOR OF NAPHTHALENE IN DIMETHYLFORMAMIDE CONTAINING 0.155 *M* TETRA-*n*-BUTYLAMMONIUM IODIDE

Water added to 10 ml. solution,[a] ml.	$E_{1/2}$	i_d	I_d[b]
0	−1.91	2.74	2.02
1	−1.91	3.43	2.78
2	−1.93	3.53	3.12
5	−1.91	4.61	5.10

[a] 0.001 *M* solution. [b] Corrected for the change in concentration of naphthalene.

Discussion of Results

Comparison of the polarographic results for the various compounds with the behavior of stilbene and other compounds studied previously in dimethylformamide[9] indicates that diphenylacetylene and *o*-terphenyl show two one-electron reduction waves at the dropping mercury electrode. Phenylacetylene gives a diffusion current constant which approximates a four-electron change. Naphthalene, phenanthrene, biphenyl and *m*-terphenyl under the same conditions give only a single one-electron wave. To verify this type of reduction the effect of water on the reduction of naphthalene was studied. The results given in Table II indicate that the wave is increased to approximately double its size in the presence of 33.3 volume per cent. of water. This behavior is similar to that observed when stilbene is reduced in the presence of water.[9] The anion-free radical reacts rapidly

$$C_{10}H_8 + e \longrightarrow C_{10}H_8^- \text{ (slow)}$$
$$C_{10}H_8^- + H_2O \longrightarrow C_{10}H_9 + OH^- \text{ (fast)}$$
$$C_{10}H_9 + e \longrightarrow C_{10}H_9^- \text{ (fast)}$$
$$C_{10}H_9^- + H_2O \longrightarrow C_{10}H_{10} + OH^- \text{ (fast)}$$

with water to give a free radical which is reduced immediately. The net result is that in the presence of a sufficient amount of water a two-electron wave is observed for the reduction of naphthalene.

Polarographic reduction of naphthalene, phenanthrene, biphenyl and *m*-terphenyl in dimethylformamide would therefore involve only the addition of one electron and the formation of an anion-free radical. The further addition of a second electron requires potentials which are too negative to attain in dimethylformamide.

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(14) W. E. Bachmann, THIS JOURNAL, **56**, 1365 (1934).

(15) A. Jeanes and R. Adams, *ibid.*, **59**, 2609 (1937).

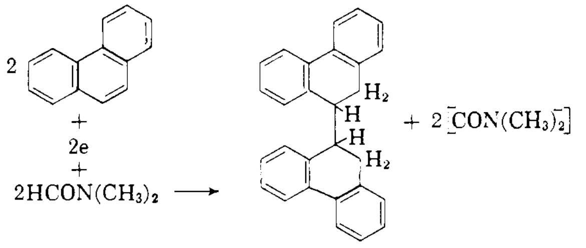
(16) Ramart-Lucas and M. J. Hoch, *Ann. chim.*, **13**, 395 (1930).

More evidence for this mechanism of reduction was obtained from the large scale electrolytic reduction of naphthalene and phenanthrene.

Naphthalene was recovered almost quantitatively from the electrolysis. The solution in the cathode compartment developed a green color during the electrolysis similar to that reported for the sodium addition compound.[6] The isolation of naphthalene indicated that the anion-free radical produced migrated to the anode and was reoxidized to naphthalene by the anode or by the iodine liberated at the anode. These results indicate that the anion-free radical from naphthalene does not dimerize and reacts very slowly with dimethylformamide. Further evidence for the presence of an anion-free radical was obtained by the electrolysis of naphthalene in the presence of carbon dioxide; 1,4 - dicarboxy - 1,4 - dihydronaphthalene was obtained as a product. The wide melting range of 178–200° suggested the presence of a mixture but when the method of Walker and Scott[13] was used in an attempt to separate the crude product into 1,2-dicarboxy-1,2-dihydronaphthalene and 1,4-dicarboxy-1,4-dihydronaphthalene, only the latter was obtained. The formation of 1,4-dicarboxy-1,4-dihydronaphthalene occurs by the step-wise addition of electrons and carbon dioxide as postulated for the production of *meso*-diphenylsuccinic acid from stilbene[9] or by the mechanism suggested by Paul, Lipkin and Weissman.[6]

Since carbon dioxide is reduced at the dropping mercury electrode in the same region,[9] the possibility exists that the reduction product from carbon dioxide may add to the naphthalene and form the acid isolated. To study the feasibility of such a reaction, the reduction of a more reactive unsaturated hydrocarbon, butadiene-1,3, in the presence of carbon dioxide was studied. No acidic products were obtained in this reduction and thus excluded this type of reaction.

The electrolytic reduction of phenanthrene produced an anion-free radical which dimerized to 9,10,9′,10′-tetrahydro-9,9′-biphenanthrene. The structure of this product was demonstrated by dehydrogenation to 9,9′-biphenanthrene.



The formation of this dimer suggests that the intermediate anion-free radical is not as highly stabilized by resonance as the corresponding intermediate from naphthalene. The insolubility of the product in dimethylformamide may, however, play an important part in its formation.

The reduction of phenanthrene in the presence of carbon dioxide resulted in the formation of *trans* - 9,10 - dicarboxy - 9,10 - dihydrophenanthrene. The isolation of only one isomer suggests that in the manipulations the *cis* isomer, if formed, was converted to the more stable form.

In view of the straightforward results obtained with phenanthrene the large scale reductions of biphenyl and *m*-terphenyl were not carried out.

The appearance of one wave corresponding to four electrons for phenylacetylene suggests a reduction of this compound to ethylbenzene by a mechanism similar to that postulated for the reduction of triphenylethylene to triphenylethane.[9]

The formation of two one-electron waves for diphenylacetylene suggested the mechanism

$$\text{first wave } C_6H_5C{\equiv}CC_6H_5 + e \longrightarrow [C_6H_5\underset{\cdot\cdot}{C}{=}\underset{\cdot}{C}C_6H_5]^- \text{ (slow)}$$

$$\text{second wave } [C_6H_5\underset{\cdot\cdot}{C}{=}\underset{\cdot}{C}C_6H_5]^- + e \longrightarrow [C_6H_5\underset{\cdot\cdot}{C}{=}\underset{\cdot\cdot}{C}C_6H_5]^{=} \text{ (slow)}$$

$$[C_6H_5\underset{\cdot\cdot}{C}{=}\underset{\cdot\cdot}{C}C_6H_5]^{=} + 2HCON(CH_3)_2 \longrightarrow C_6H_5CH{=}CHC_6H_5 + 2[CON(CH_3)_2^-] \text{ (slow)}$$

Stabilization of the anion-free radical from diphenylacetylene is based on the symmetry present in the resonance hybrids, similar to that found with the other hydrocarbons for which anion-free radicals are indicated.

$$[C_6H_5\underset{\cdot}{C}{=}\underset{\cdot\cdot}{C}C_6H_5]^- \longleftrightarrow [C_6H_5\underset{\cdot\cdot}{C}{=}\underset{\cdot}{C}C_6H_5]^- \text{ etc.}$$

The large scale electrolytic reduction of diphenylacetylene alone contributed nothing to the mechanism since only bibenzyl and 1,2,3,4-tetraphenylbutane were obtained; no 1,2,3,4-tetraphenyl-1,3-butadiene was isolated. Stilbene gives similar products. More conclusive evidence for the formation of the dianion from diphenylacetylene was furnished by the results from the large scale electrolysis of diphenylacetylene and carbon dioxide. Diphenylmaleic anhydride and diphenylfumaric acid were isolated together with *meso*-diphenylsuccinic acid. The last acid could be formed by the further reduction of the two unsaturated acids.

Isolation of diphenylmaleic anhydride and diphenylfumaric acid as products in the reduction of diphenylacetylene in the presence of carbon dioxide indicates that the addition of electrons to the triple bond is not stereospecific.

o-Terphenyl was not studied on a large scale since it resembles stilbene in structure and would be expected to behave in a similar fashion.

The results obtained show that stable monovalent anion-free radicals are formed in the electrolytic reduction of naphthalene, *o*-terphenyl, *m*-terphenyl, phenanthrene, stilbene, biphenyl and diphenylacetylene. The results for naphthalene, *m*-terphenyl, phenanthrene and biphenyl are in agreement with the results obtained by magnetic susceptibility measurements[8] and optical absorption spectra[9] on products from these hydrocarbons and sodium. Diphenylacetylene and *o*-terphenyl have not been studied by either one of these methods but on the basis of polarographic results should form monosodium addition products in aprotic solvents.

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