Electrochemical Reduction of Aza-heteroaromatic Compounds.

Part II. Effect of Cationic Charge on the Formation of
Aza-phenanthrenyl Radicals

By

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Synopsis

p-Phenanthroline di-methiodide (I_a) and its related compounds, such as p-phenanthroline mono-methiodide (II_a), 5,6-benzoquinoline methiodide (III_a), and 3,4-benzoquinoline methiodide (IV_a), were electrolyzed at the potentials corresponding to the first d.c. polarographic reduction waves and the reduction products were characterized by polarography, cyclic voltammetry, ultra-violet and visible spectroscopy, and NMR spectroscopy. Only the one-electron electrochemical reduction product of I_a was a stable radical because of the electrostatic (cationic) repulsion between charged molecules, and was highly sensitive to oxidants. The same cation radical was also obtained by reduction with sodium dithionite. The same one-electron reduction products of II_a , III_a and IV_a were immediately coupled to produce dimers. The two-electron electrochemical reduction product of I_a was not so sensitive to oxidants as the one-electron reduction product of I_a .

Introduction

In a previous paper¹⁾, we reported that the first polarographic reduction step of quaternary ammonium salts of aza-heteroaromatic compounds (R^+) corresponds to the one-electron transfer which does not involve protonation process even in aqueous solutions. And moreover, it may be easily suggested that the disproportionation reaction, in the case of R^+ at least, could be avoided without regard to the corresponding free bases (R).

Thus, the controlled potential electrolysis of R^+ may be suited to observe the behavior of the one-electron transfer product, radical. The radical is considered to 1) be suffi-

ciently stable to survive, 2) dimerize immediately, 3) disproportionate into a quaternary ammonium salt and a two-electron reduction product, 4) react with a substrate which coexists in the system.

As for N-alkylpyridinyl radicals, ones derived from non-substituted or 3-substituted pyridinium salts are usually unstable. On the other hand, others which have such substituents as methylcarbonyl³⁾, methoxycarbonyl³⁾⁴⁾, and benzothiazolyl⁴⁾ in the 4-position, and methyl viologen radical⁵⁾⁶⁾, are known to be stable enough at room temperature under anaerobic conditions. All these substituents are mainly characterized by their resonating and electron-withdrawing effects. In particular, a substituent having an electronic charge seems to contribute to an inhibition of a radical association. In order to compare effectiveness of a resonating character, an electron-withdrawing character and a charge repulsion for stabilization of a radical, it may be suitable to choose the following compounds: 3, 4-benzoquinoline methiodide (IV_a) and 5, 6-benzoquinoline methiodide (III_a) which have larger conjugated systems than pyridine methiodide (V); p-phenanthroline mono-methiodide (II_a) which has a heteroatom (nitrogen) at the 8-position of III_a; and p-phenanthroline di-methiodide (I_a) which has one more positive charge than II_a. In the present paper, we produce the one-electron transfer of the above four compounds (I_a-IV_a) by means of controlled-potential electrolysis and speculate the structures of the one-electron reduction products polarographically and spectrometrically.

Experimental

Materials and general procedures

Materials, I_a (mp 259–261°C); II_a (mp 169–170°C); III_a (mp 202–204°C); IV_a (mp 194–196°C), were prepared by the methods described in the literatures and were purified by recrystallization from ethanol. Solvents were purified by the procedures referred in the preceding paper¹⁾.

Polarograms were recorded by the same procedure as described in the preceding paper, using a Yanagimoto Polarograph Model P8-AP equipped with a three-electrode circuit. Two different capillaries were used for the dropping mercury electrodes. They had the following characteristics: DME-A; at $h=60$ cm, $m=1.986$ mg sec⁻¹ and $t=4.35$ sec; DME-B; at $h=60$ cm, $m=0.949$ mg sec⁻¹ and $t=4.28$ sec on open circuit in 1M potassium chloride solution.

For controlled potential electrolysis, a Yanagimoto Controlled Potential Electrolyzer Model VE-3 or a Nichiaki Potentiostat Type NP-1A was used with mercury pool as a working electrode (cathode). An apparatus assembly was shown in Fig. 1. A platinum plate or a carbon rod was used as an anode. A reference electrode was a saturated calomel electrode (SCE) connected to a sample solution by a saturated potassium chloride agar bridge. In the case of the electrolysis in aprotic solvents, tetra-n-butylammonium perchlorate methylcellulose bridge was inserted between the agar bridge and the sample solution. This sample solution had the same components with those of polarographic measurements. The catholytes and the anolytes were compartmented by use of glass frits to each other.

Polarograms were recorded without pipetting out electrolyzed solutions using the long dropping mercury electrode, DME-A. The quantity of electricity required for

Fig. 1. Electrolytic cells.

a, anode (Pt plate) b, terminal of Hg cathode c, DME d, SCE
 e, TBAP-methylcellulose-bridge f, KCl-agar-bridge g, magnetic
 stirrer h, sintered glass i, cathode (Hg) j, saturated KCl solution
 k, N₂ gas inlet l, N₂ gas outlet m, thermometer n, UV spectro-
 scopic cell o, anode (C rod)

electrolysis was recorded with a Toa Electronic Polyrecorder Model EPR-2TB.

For the measurements of UV spectra, a Hitachi Double Beam Spectrophotometer Model 124 was used. The electrolytic cell of Type B in Fig. 1 was employed in order to keep away the intervention of oxygen in electrolyzed solutions. By the free rotation of the UV cell joint, perfect reduction of catholytes was practicable.

Cyclic voltammetry was measured using Nichiakiki NS₂-Functionwave Generator, potentiostat NP-1A and Yokogawa X-Y Recorder Type 3077. The components of

the measured solution and the apparatus assembly were the same as those of polarography (platinum rod was used as a cathode).

Nuclear magnetic resonance spectra were recorded with a Hitachi Perkin-Elmer R-20 High Resolution NMR Spectrometer at 60 Mcps using tetramethylsilane as a reference. Spectra of I_a were measured at concentration of about 5 w/v % in acetonitrile, hydrogen oxide, deuterium oxide, and d_6 -dimethyl sulfoxide (d_6 -DMSO). After the first spectroscopic measurements, a sufficient amount of zinc powder or sodium dithionite was added to the solution, which was warmed for a few minutes. The NMR spectra of the resulting deep red solution were recorded.

An example of a procedure of electrolysis: One-electron reduction of I_a .

In the electrolytic cell, type C, shown in Fig. 1, 100 ml of 1.0 mM solution of I_a in Britton-Robinson buffered solution (pH 10) containing 1/15 M sodium sulfate was degassed with nitrogen for at least 30 minutes prior to the electrochemical reduction. Nitrogen gas was bubbled throughout the electrolysis. Immediately after the electrolysis set in at the potential corresponding to the first reduction wave (-0.75 v), the solution turned orange red and then deep red in color. The electrolysis was stopped when no decrease of current was recognized. No appreciable difference between the polarograms before and after the spectrophotometric measurement was observed. When the deep red solution was exposed to air, it immediately turned orange yellow. The polarogram was recorded after the solution was degassed again with nitrogen. The reduction wave at -0.63 v recovered by 91% in comparison with that of the polarogram before the electrolysis.

Results and Discussion

Coulometric measurements of one-electron reduction.

As shown in Table 1, the results of coulometric measurement indicate that each

Table 1. The electron numbers (n) required for the reduction and the restoration yield to the starting materials measured from the reduction products staying in solutions.

Material	Conc. (mM)	Solution	Controlled potential ($-v$ vsSCE)	n	Restoration yield (%) (leaving time in the air)
I_a	1.0	pH 10	0.75	0.9	91 (2-3 min.)
I_a	0.5	pH 10	0.75	1.0	90 (2-3 min.)
I_a	1.0	pH 7	0.80	1.0	6 (2 hrs.)
I_a	0.5	DMF	0.60	0.9	—
I_a	0.5	DMF	1.20	1.9	—
I_a	1.0	pH 10	1.20	1.7	38 (2 hrs.)
II_a	0.5	pH 10	1.10	0.8	61 (2 hrs.)
II_a	0.5	DMF	1.00	1.0	—
III_a	0.5	pH 10	1.10	1.2	47 (2 hrs.)
III_a	0.5	DMF	1.10	1.2	—
IV_a	0.5	DMF	1.00	1.0	—
(ref.)					
I_a	1.0	pH 10	$Na_2S_2O_4$ (equivalent)		80 (2-3 min.)
I_a	1.0	pH 10	$NaBH_4$		16 (2 hrs.)

compound absorbs one-electron per molecule by the electrochemical reduction at the potential corresponding to the first wave regardless of whether the solvent is aprotic or not. This fact means that one-electron reduction products of these compounds do not disproportionate or reduce the coexisting substrate at any appreciable rate. If such reactions should occur, the number of electron required to reduce a molecule (n)

Fig. 2. D.c. and a.c. polarograms^{*)} of 5,6-benzoquinoline methiodide (III_a) in the DMF containing proton donor.
 conc. of phenol ; ——— 0mM, — · — · — 1mM, - - - - - 5mM
^{*)} concn. of (III_a) ; 0.5mM, capillary ; DME-B

Fig. 3. Polarographic change^{*)} of p-phenanthroline di-methiodide (I_a) in the DMF, before and after the electrolysis.

———— before electrolysis
 - · - · - after one-electron reduction
 - - - - after two-electron reduction
^{*)} concn. of (I_a) ; 0.5mM, capillary ; DME-B

would be more than a unit. By the electrochemical reduction at the second wave plateau, I_a absorbs two electrons per molecule under the same conditions.

Table 1 also shows the recovery yield to the starting materials, the value of which are measured after the electrolysis under the aerobic condition and the stirring of the reacted solutions polarographically. The recovery yield at pH 10 becomes larger in the order of $III_a < II_a < I_a$.

Speculation of reduction products by polarography and cyclic voltammetry.

Polarograms of III_a are shown in Fig. 2. In an aprotic solvent a new d.c. wave appears at less negative potential than that of the second wave on addition of a proton donor (phenol). The a.c. peak (a) corresponding to the first wave is higher than the peak (b) corresponding to the second wave. The latter disappears altogether on the addition of phenol, while the former is not influenced at all. These facts suggest the following three interpretations; 1) one-electron reduction product has higher reversibility, namely, is more oxidizable than two-electron reduction product, 2) oxidation reaction of one-electron reduction product involves no deprotonation reaction, 3) two-electron reduction involves a protonation step and with the increase of the concentration of phenol the oxidation process is exceedingly interrupted.

A cyclic voltamogram of I_a also suggests that the first reduction step of I_a is a reversible one electron transfer (in DMF solution: a cathodic peak, -0.496 v; an anodic peak, -0.430 v; the difference in potential of the two, 66 mv), while the second is not (a cathodic peak, -1.036 v; a small anodic peak in comparison with the corresponding cathodic peak, -0.68 v). This result is consistent with Hünig's observation⁷.

Oxidation waves after the electrolysis.

The polarographic change during the controlled potential electrolysis of the DMF solution of I_a is shown in Fig. 3. The oxidation potential and the height of the anodic wave of I_a after the electrolysis are nearly equal to those of the first wave; the reduction potential and the height of the cathodic wave after the electrolysis, are nearly equal

Fig. 4. Polarographic change*) of p-phenanthroline dimethiodide (I_a) in pH 10, before and after the electrolysis.

- before electrolysis
- · - · - just after one-electron reduction
- after staying in the air of — · — · —
- after two-electron reduction

*) concn, of (I_a) ; 1.0 mM, capillary ; DME-B

to those of the second wave before the electrolysis. The same behavior is observed on the controlled potential electrolysis in buffered solution of pH 8, 9 and 10 (Fig. 4). When the electrolyzed solution is exposed to air, reduction wave is restored almost quantitatively at the original position owing to the oxidation with dissolved oxygen. The recovery yields are already shown in Table 1.

When the controlled potential electrolysis of II_a , III_a and IV_a are carried out in DMF solutions at the potentials corresponding to the first waves, an oxidation wave is observed in every case at less negative potential than that of the original reduction wave (Fig. 5 and Table 2). In each case of the electrolysis in buffered solution of pH 10 at the potential corresponding to the first wave, yellow precipitates are obtained.

Fig. 5. Polarographic change*) of p-phenanthroline monomethiodide (II_a) and 5,6-benzoquinoline methiodide (III_a) in the DMF, before and after the one-electron reduction.

— before electrolysis of II_a
 — — — after electrolysis of II_a
 - · - · - before electrolysis of III_a
 · · · · · after electrolysis of III_a

*) concn. of (II_a) or (III_a) ; 0.5mM, capillary ; DME-B

Table 2. Polarographic data before and after of the one-electron reduction.
 $E_{1/2}$, v vs SCE ; I_d (diffusion current constant),
 $\mu\text{A} \cdot \text{mM}^{-1} \cdot \text{l} \cdot \text{mg}^{-2/3} \cdot \text{sec}^{1/2}$

Material	Conc. (mM)	Solution	Before electrolysis		After electrolysis	
			First reduction wave $-E_{1/2}$ (I_d)	Second reduction wave $-E_{1/2}$ (I_d)	Oxidation wave $-E_{1/2}$ (I_d)	Reduction wave $-E_{1/2}$ (I_d)
I_a	1.0	pH 10	0.63 (1.67)	1.01 (0.98)	0.62 (1.16)	1.07 (0.88)
I_a	1.0	DMF	0.46 (1.22)	0.91 (1.25)	0.45 (1.05)	0.88 (1.27)
II_a	0.5	DMF	0.82 (1.70)	1.92 (0.89)	0.49 (1.41)	2.20 (2.96)
III_a	0.5	DMF	0.90 (1.66)	2.16 (0.72)	0.56 (1.27)	2.52 (2.73)
IV_a	0.5	DMF	0.83 (1.61)	2.45 (0.63)	0.27 (1.49)	2.65 (0.77)

The precipitates momentarily reduce silver ion to silver metal. When the electrolyzed solutions are stirred at room temperature for two hours, the original reduction waves are restored in 61% and 47% yield for II_a and III_a , respectively (Table 1). From these results, it is obvious that one-electron reduction product of I_a is different from those of II_a , III_a , and IV_a .

Structure of one-electron reduction product of I_a .

The light yellow solution of I_a ($\lambda_{\text{max}}^{\text{pH}10} = 306$ and $317 \text{ m}\mu$) turns deep red after electrolysis. The deep red solution shows a broad absorption in a visible region [$\lambda_{\text{max}}^{\text{pH}10} = 510 \text{ m}\mu$ ($\epsilon 880$), $\lambda_{\text{max}}^{\text{DMF}} = 510 \text{ m}\mu$ ($\epsilon 1200$)]. When the solution is exposed to air, it immediately turns orange [$\lambda_{\text{max}}^{\text{pH}10} = 455 \text{ m}\mu$ ($\epsilon 310$)]. Karrer and *et al.*⁸⁾ reduced I_a with sodium dithionite and obtained a deep red solution. They concluded from the pressure determination that a semiquinoid species would have been formed⁹⁾. Kato and Ohta¹⁰⁾ reduced I_a with zinc powder and obtained the same deep red species as Karrer did. After the deaeration of the solution of I_a under the same conditions as the polarographic measurement, sodium dithionite is added to this solution in slight excess. The solution immediately turns deep red and an oxidation wave appears at the same potential as that of the one-electron electrochemical reduction product. A deep red solution obtained by the reduction of I_a with zinc dust or sodium dithionite shows no NMR signal at all, indicating the quantitative formation of a stable paramagnetic species¹¹⁻¹⁴⁾ (Fig. 6).

The solutions after the one-electron electrochemical reduction of II_a - IV_a are yellow [II_a , $\lambda_{\text{max}}^{\text{DMF}} = 400 \text{ m}\mu$ ($\epsilon 2100$); III_a , $\lambda_{\text{max}}^{\text{DMF}} = 373 \text{ m}\mu$ ($\epsilon 2600$)]. In the case of II_a , the spectrum is similar to the dihydro compounds, namely, the reduction products with sodium borohydride or sodium dithionite⁸⁾. The discrepancy in potential between the oxidation and the reduction wave indicates the reduction accompanied by the formation of a covalent bond. These findings suggest that the one-electron reduction pro-

Fig. 6. NMR change of p-phenanthroline di-methiodide (I_a) in d_6 -DMSO, before and after of the solution obtained by the reduction with zinc dust,
a) before reduction b) after reduction

Wurster's salt. In the case of II_a-IV_a, they lack charge repulsion and so spontaneous dimerizations may occur. Aza- or diazaphenanthrene does not sufficiently stabilize a neutral free radical. The effect of anionic charge on the reduction of aza-heteroaromatic compounds will be detailed in the next paper.

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含窒素複素環式化合物の電気化学的還元(第2報)

アザ-フェナントレニルラジカルの生成におよぼす陽電荷の効果

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p-フェナントロリンジメチオジド(I_a)およびその関連化合物である *p*-フェルナントロリンモノメジド(II_a), 5,6-ベンゾキノリンメチオジド(III_a)および3,4-ベンゾキノリンメチオジド(IV_a)を, それらの直流ポーラログラム第1波相当の電位でもって電解し, 還元生成物をポーラログラフィー, サイクリックボルトンメトリー, 紫外可視吸収スペクトルおよび核磁気共鳴吸収スペクトルによって検討した. その結果I_aの

1電子相当の還元体のみがラジカルとして安定であった. それは荷電分子間の静電的(カチオン)反発のためであって, ラジカルは酸化剤に対しては反応性に富んでいる. このカチオンラジカルはまた亜二チオン酸ナトリウムによる還元によっても得られる. 一方同じ1電子還元体でもII_a, III_a, IV_aの場合には直ちに2量化してしまう. I_aの2電子相当の還元体は, 1電子相当の還元体程酸化剤に対して反応性に富んでいない.