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The Polarographic Reduction of 5*H*-Benzo[a]phenothiazin-5-ones in Non-aqueous Media

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The polarographic behavior of 5*H*-benzo[a]phenothiazin-5-one and its ring-substituted derivatives at a dropping mercury electrode was studied in N,N-dimethylformamide (*DMF*). Each compound gave well-defined two reduction waves, the half-wave potentials of which linearly correlated with the *Hammett* substituent constant σ_p. For the parent compound, 5*H*-benzo[a]phenothiazin-5-one, the polarographic behavior was also investigated in selected other solvents. From the similarity with the behavior of anthraquinone, the results obtained in a mixed solvent, *DMF*—methylcellosolve, were explained by assuming a disproportionation reaction between the parent compound and its dianion.

(Keywords: 5H-Benzo[a]phenothiazin-5-one; Polarographic reduction)

Die polarographische Reduktion von 5H-Benzo[a]phenothiazin-5-onen in nichtwäßrigen Medien

Es wurde das polarographische Verhalten von 5*H*-Benzo[a]phenothiazin-5-on und dessen ringsubstituierten Derivaten an der tropfenden Quecksilberelektrode in N,N-Dimethylformamid (*DMF*) untersucht. Alle Verbindungen gaben zwei wohldefinierte Reduktionswellen, deren Halbwellenpotentiale mit den *Hammett*'schen Substituentenkonstanten σ_p eine gute lineare Korrelation ergaben. Bezüglich der Stammsubstanz, 5*H*-Benzo[a]phenothiazin-5-on, wurde das polarographische Verhalten auch in einigen anderen Lösungsmitteln untersucht. Aus Parallelen mit dem Verhalten von Anthrachinon wurden die Ergebnisse, die in *DMF*—Methylcellosolv als gemischtem Lösungsmittel erhalten wurden, unter der Annahme einer Disproportionierungs-Reaktion zwischen der Stammverbindung und dessen Dianion erklärt.

Introduction

There have been few studies of polarographic reduction of quinone imines, although that of quinones have extensively been investigated by

Table 1. *The half-wave potentials of 5H-benzo[a]phenothiazin-5-ones*

Compound	$-E_{1/2}$(V vs. S.C.E.)	
	1st wave	2nd wave
1. 5*H*-benzo[a]phenothiazin-5-one	0.79	1.40
2. 6-acetyl-	0.62	1.23
3. 6-propionyl-	0.63	1.25
4. 6-butyryl-	0.64	1.22
5. 6-benzoyl-	0.64	1.19
6. 6-bromo-	0.67	1.28
7. 6-chloro-	0.68	1.31
8. 6-methyl-	0.86	1.33
9. 6-propyl-	0.87	1.38
10. 6-butyl-	0.87	1.34
11. 6-tert-butyl-	0.93	1.28
12. 6-phenyl-	0.77	1.20
13. 6-ethylthio-	0.74	1.29
14. 6-propylthio-	0.75	1.27
15. 6-isopropylthio-	0.75	1.26
16. 6-butylthio-	0.74	1.20
17. 6-phenylthio-	0.68	1.25
18. 6-methoxy-	0.83	1.31
19. 6-amino-	0.98	1.42
20. 6-methylamino-	0.92	1.41
21. 6-ethylamino-	0.92	1.46
22. 6-isopropylamino-	0.94	1.55
23. 6-*tert*-butylamino-	0.89	1.48
24. 6-phenylamino-	0.79	1.33
25. 6-acetylamino-	0.78	1.21
26. 6-N-(acetylanilino)-	0.66	1.27

many workers[1—10]. As a part of our continuing studies on the synthesis, configuration and chemical reactivity of quinone imines[11—20], we investigated the polarographic behavior of 5*H*-benzo[a]phenothiazin-5-one and its ring-substituted derivatives in various non-aqueous solvents. In the present paper, we mainly discuss the effect of ring substitution on the polarographic reduction of these compounds in N,N-dimethylformamide (*DMF*) as well as the disproportionation reaction between the parent compound and its dianion in particular solvents.

Results and Discussion

The d.c. polarograms were measured in *DMF* in the presence of tetraethylammonium perchlorate as a supporting electrolyte. The results are tabulated in Table 1. Each compound gave a polarogram consisting of well-defined two waves of similar height, the difference in the half-wave potential between the two waves being about 50 mV.

The reversibility of the electrode processes was investigated by the *Tomes'* method of obtaining values of $E_{1/4}$ and $E_{3/4}$ for a reversible cathodic wave which should be about 55/n mV, where n denotes the number of electrons involved in the electrode process. The results

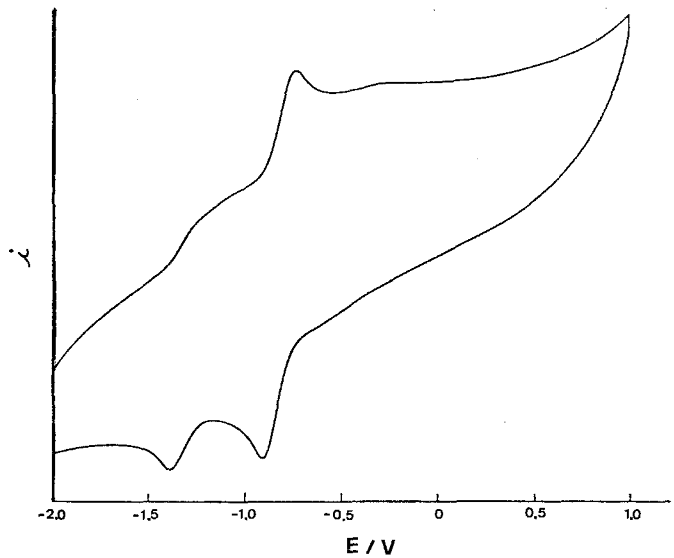


Fig. 1. Cyclic voltammogram of 5*H*-benzo[a]phenothiazin-5-one in *DMF*: scan rate 0.05 vs^{-1}

obtained were 50 to 60 mV for the first waves and about 80 mV for the second waves, suggesting that the first reduction step is reversible and a one electron transfer, whereas the second one is irreversible. As can be seen from representative examples shown in Fig. 1, the cyclic voltammograms also suggest that the first reduction step is reversible but the second step irreversible for all the compounds tested.

Although the formation of dianions as the final products could not be identified, the reduction reactions involved may reasonably be described by Scheme 1 (where *R* is the substituent group).

The half-wave potentials of the first and the second waves for 6-substituted 5*H*-benzo[a]phenothiazin-5-ones are plotted against the *Hammett* substituent constants σ_p. As is shown in Fig. 2 linear relation-

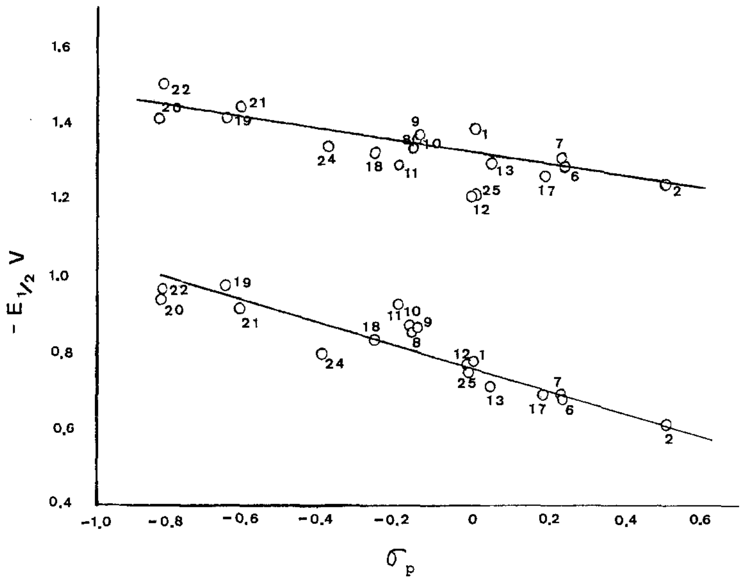
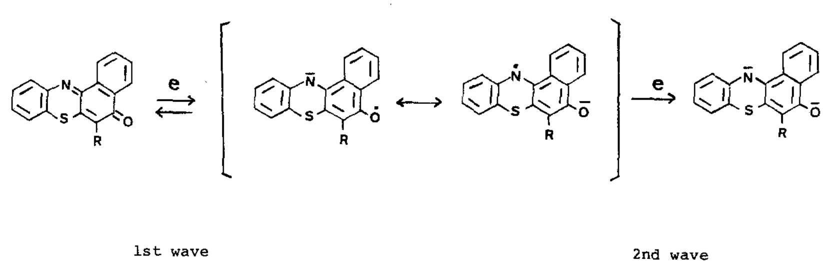


Fig. 2. Plot of $E_{1/2}$ vs. *Hammett* substituent constant σ_p for 6-substituted 5*H*-benzo[a]phenothiazin-5-ones

Scheme 1



ships with a negative slope are observed between them, except phenylamino and *t*-butyl groups for the first wave and phenyl and acetylamino groups for the second wave. The polarographic reduction would therefore occur at the 12-position of the compounds, i.e. through the electron migration to the ring nitrogen atom.

Table 2 presents the half-wave potentials of 5*H*-benzo[a]phenothiazin-5-one in various solvents. It is found that 5*H*-

Table 2. *The half-wave potentials of 5H-benzo[a]phenothiazin-5-one in various solvents*

<table>
<tr><th rowspan="2">Solvents</th><th colspan="2">—$E_{1/2}$ (V vs. S.C.E.)</th></tr>
<tr><th>1st wave</th><th>2nd wave</th></tr>
<tr><td>Dimethyl Sulfoxide</td><td>0.74</td><td>1.22</td></tr>
<tr><td>N,N-Dimethylformamide</td><td>0.79</td><td>1.40</td></tr>
<tr><td>Acetone</td><td>0.87</td><td>1.12</td></tr>
<tr><td>Acetonitrile</td><td>0.85</td><td>1.16</td></tr>
<tr><td>Methylcellosolve</td><td colspan="2">0.54</td></tr>
<tr><td>Ethanol</td><td colspan="2">0.56</td></tr>
<tr><td>Methanol</td><td colspan="2">0.52</td></tr>
</table>

Table 3. *Effect of composition of mixed solvent on the half-wave potentials of 5H-benzo[a]phenothiazin-5-one*

<table>
<tr><th colspan="2">Composition of mixed solvent</th><th colspan="2">—$E_{1/2}$ (V vs. S.C.E.)</th></tr>
<tr><th>DMF (%)</th><th>MCS (%)</th><th>1st wave</th><th>2nd wave</th></tr>
<tr><td>100</td><td>0</td><td>0.79</td><td>1.40</td></tr>
<tr><td>90</td><td>10</td><td>0.68</td><td>1.00</td></tr>
<tr><td>80</td><td>20</td><td>0.66</td><td>0.88</td></tr>
<tr><td>70</td><td>30</td><td>0.60</td><td>0.86</td></tr>
<tr><td>60</td><td>40</td><td>0.59</td><td>0.86</td></tr>
<tr><td>50</td><td>50</td><td colspan="2">0.59</td></tr>
<tr><td>40</td><td>60</td><td colspan="2">0.58</td></tr>
<tr><td>30</td><td>70</td><td colspan="2">0.57</td></tr>
<tr><td>20</td><td>80</td><td colspan="2">0.56</td></tr>
<tr><td>10</td><td>90</td><td colspan="2">0.55</td></tr>
<tr><td>0</td><td>100</td><td colspan="2">0.54</td></tr>
</table>

benzo[a]phenothiazin-5-one exhibits only one reduction wave in such solvents as methanol, ethanol and methylcellosolve (MCS), and well-defined two waves in *DMF*, *DMSO*, acetone and acetonitrile.

The half-wave potentials of 5*H*-benzo[a]phebothiazin-5-one in solvent mixtures of *DMF* and *MCS* were also investigated as a function of the volume ratio of the solvents. The results are summarized in Table 3. In pure *DMF*, 5*H*-benzo[a]phenothiazin-5-one exhibits well-defined two reduction waves: With an increase in the volume ratio of *MCS*, both waves move toward more positive potentials. With further increase in the volume ratio, the second wave diminishes and only a single wave appears at more positive potentials. In the presence of large amount of *MCS*, moreover, 5*H*-benzo[a]phenothiazin-5-one gives a single wave which is approximately equal in height to the sum of the two waves obtained in pure *DMF*. In the present study, however, no efforts have been made to substantiate the nature of the electrode process by additional measurements, the disproportionation reactions to form mono-anions as final products are well-known for quinones such as 1,4-benzoquinone[21], 1,2-naphthoquinone[21], 1,4-naphthoquinone[21], anthraquinone[22] and dihidronaphthacenequinone[23], which are closely related to the compounds under investigation. The disappearance of the second reduction waves and the observed shifts in the half-wave potential with increasing volume ratio of *MCS* could therefore be explained by the following disproportionation reaction:

5*H*-Benzo[a]phenothiazin-5-one
+ 5*H*-Benzo[a]phenothiazin-5-one dianion
→ 2(5*H*-Benzo[a]phenothiazin-5-one radical monoanion).

Conclusion

The half-wave potentials of the first and the second cathodic waves for 5*H*-benzo[a]phenothiazin-5-ones in *DMF* are reasonably correlated with the *Hammett* substituent constant, σ_p. On the other hand, the polarographic behaviour of 5*H*-benzo[a]phenothiazin-5-one in solvent mixtures of *DMF* and *MCS* suggests the disproportionation reaction of 5*H*-benzo[a]phenothiazin-5-one and its dianion to form the monoanion in *MCS*-rich media.

Experimental

Polarography

The polarograms were recorded with a Yanaco p-1000 instrument using an H-type cell. The cell was immersed in a constant-temperature water bath at 20 ± 0.1 °C. The dropping mercury electrode used had a flow rate of 2.35 mg/s and a pulsed drop-time of 2.0 s/drop (86.0 cm mercury column height).

Approximately $2 \cdot 10^{-3}$ *M* solutions of the test compounds were prepared by dissolving the accurately weighed solids in *DMF* or other solvents. For the polarographic measurements, 5 ml each of these solutions containing 0.001 g of tetraethylammonium perchlorate as a supporting electrolyte was deaerated with oxygen-free nitrogen gas. All the potentials reported were those against a saturated colomel electrode (S.C.E.).

The cyclic voltammograms were obtained on a Yanaco VMA-010 polarograph. A platinum wire and a glassy-carbon electrode were employed as a reference electrode and a working electrode, respectively. The latter electrode was polished with an oil stone before each measurement.

Reagents

5*H*-Benzo[a]phenothiazin-5-one and its ring-substituted derivatives were obtained according to the reported method[24—29]. Analytical-reagent grade *DMF*, *DMSO*, acetone, acetonitrile, *MCS*, ethanol, methanol, and tetraethylammonium perchlorate were used as received.

References

1 *Passtowski I. J., Beiles R. G.*, J. Allg. Chem. **20**, 522 (1950).
2 *Wawzonek S., Berkey R., Blaha E. W., Runner M. E.*, J. Electrochem. Soc. **102**, 235 (1955).
3 *Austen D. E. G., Given P. H., Ingram D. J. E., Poever M. E.*, Nature **182**, 1784 (1958).
4 *Kolthoff I. M., Reddy T. B.*, J. Electrochem. Soc. **108**, 980 (1961).
5 *Jones R., Spotswood T. M.*, Aust. J. Chem. **15**, 492 (1962).
6 *Poever M. E.*, J. Chem. Soc. **1962**, 4540.
7 *Fritsch J. M., Tatwawdi S. V., Adams R. N.*, J. Phys. Chem. **71**, 338 (1967).
8 *Edwards T. G., Grinter R.*, Trand. Faraday Soc. **69**, 1070 (1968).
9 *Schlossel R. H., Geske D. H., Gulick W. M., Jr.*, J. Phys. Chem. **73**, 71 (1969).
10 *Eggins B. R., Chambers J. Q.*, J. Chem. Soc. Chem. Comm. **1969**, 232.
11 *Ueno Y., Takeuchi Y., Koshitani J., Yoshida T.*, J. Heterocyclic Chem. **18**, 259 (1981).
12 *Ueno Y., Koshitani J., Yoshida T.*, J. Heterocyclic Chem. **18**, 1245 (1981).
13 *Ueno Y., Koshitani J.*, Monatsh. Chem. **112**, 1459 (1981).
14 *Ueno Y., Maeda K., Koshitani J., Yoshida T.*, J. Heterocyclic Chem. **19**, 189 (1982).
15 *Ueno Y.*, Monatsh. Chem. **113**, 641 (1982).
16 *Ueno Y.*, Liebigs Ann. Chem. **1982**, 1403.
17 *Ueno Y.*, J. Heterocyclic Chem. **19**, 1579 (1982).
18 *Ueno Y.*, Monatsh. Chem. **113**, 1059 (1982).
19 *Ueno Y.*, Liebigs Ann. Chem. **1983**, 161.
20 *Hasegawa K., Ueno Y.*, Bull. Chem. Soc. Jpn. **57**, 510 (1984).
21 *Hori F., Urabe N., Yonekura H.*, Denki Kagaku **42**, 15 (1974).
22 *Sakai W., Hori F.*, Denki Kagaku **37**, 623 (1969).
23 *Chia-yu Li., Caspar L., Dixon D. W., Jr.*, Electrochim. Acta **25**, 1135 (1980).
24 *Ueno Y., Shiraki H., Koshitani J., Yoshida T.*, Synthesis **1980**, 313.
25 *Koshitani J., Ueno Y.*, Monatsh. Chem. **113**, 233 (1982).
26 *Ueno Y., Takeuchi Y., Koshitani J., Yoshida T.*, J. Heterocyclic Chem. **19**, 167 (1982).
27 *Koshitani J., Ueno Y.*, J. Prakt. Chem. **325**, 165 (1983).
28 *Ueno Y.*, Liebigs Ann. Chem. **1983**, 159.
29 *Ueno Y.*, Pharmazie **39**, 123 (1984).