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Electrochemical Behaviors of 4-(2-thiazolylazo)-resorcinol in Acetonitrile

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The electrochemical behaviors of 4-(2-thiazolylazo)-resorcinol (TAR) in acetonitrile solution was studied by DC polarography, cyclic voltammetry, controlled-potential coulometry and UV-V is spectroscopy. The electrochemical reduction of TAR occurs in four-one electron reduction steps in acetonitrile solution. The products of the first and the third electron transfer are speculated to be a relatively stable anion radical. The second electron transfer to the dianion is followed by a chemical reaction producing a protonated species. The product of the fourth electron transfer also produces the corresponding amine compounds with a following reaction. Also every reduction wave was diffusion controlled. The first reduction wave is considerably reversible and the other waves are less reversible.

Introduction

Although the electrochemical reduction of azobenzene and related compounds has been studied extensively¹⁻⁶, relatively few studies of the reaction in aprotic media have been reported. Florence³ reported that azobenzene is reduced via a two-electron electrode reaction to hydrazobenzene in the wide range of pH.

However, if strongly electron-releasing substituent groups such as -OH or -NH₂ are present, the hyrazo derivative is unstable so reduced via a single four electron electrode reaction to amine compound.

Aylward *et al.*⁷ reported the polarographic reduction of azobenzene in dimethylformamide (DMF) solution. They proposed that azobenzene is reduced in a rapid one-electron transfer reaction to the anion radical and in a second slow electron transfer to produce a stable dianion.

The aim of this investigation was to study the electroche-

mical reduction of 4-(2-thiazolylazo)-resorcinol(TAR) in acetonitrile(AN) solution using a variety of electrochemical techniques. Then, the polarographic and cyclic voltammetric behavior of TAR in AN solution will be described. The constant potential coulometric reduction of TAR, the analysis of the reduction products, the reversibility of reaction and the type of reduction currents will be given. A mechanism consistent with the experimental results will be proposed.

Experimental

Reagent. 4-(2-thiazolylazo)-resorcinol (TAR) was obtained from Aldrich Co. and was used without further purification. The purification of acetonitrile that was used to solvent based on Coetzee method⁸ and tetraethylammonium perchlorate (TEAP) was used as supporting electrolyte was synthesized by Kolthoff method⁹.

Polarographic Measurement. Conventional DC polaro-

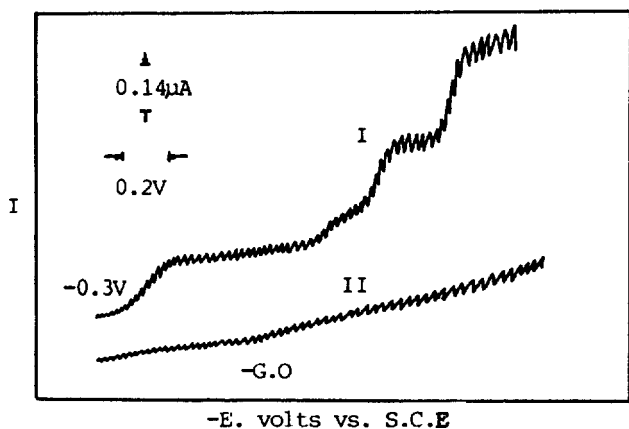


Figure 1. DC polarograms of 5.0×10^{-5} M TAR(I) and residual current (II) in 5.0×10^{-3} M TEAP-AN solution at 25°C .

Table 1. DC Polarographic Half wave Potentials(E_{dmc}) and Diffusion Currents(i_d) of 5.0×10^{-5} M TAR in 5.0×10^{-3} M TEAP-AN Solution at 25°C

reduction step	E_{dmc} (volts vs. S.C.E)	i_d (μA)
1st wave	-0.53	0.182
2nd	-1.21	0.112
3rd	-1.53	0.224
4th	-1.70	0.294

grams of TAR in AN solution were recorded with a Yanaco p-8 type polarograph using 5.0×10^{-3} M TEAP as supporting electrolyte. A three electrode system¹⁰ using a Yanaco PT-8 type was employed for all conventional DC polarograms measurements. The reference electrode was saturated calomel electrode (S.C.E) with salt bridge¹¹. The glass capillary dropping mercury electrode (DME) had the following characteristics; mercury column height was 72.7cm in open circuit, flow rate of mercury was 1.6mg/sec, drop time was 4.37 sec.

All test solution were thoroughly degassed with nitrogen gas saturated with acetonitrile and a continuous stream of nitrogen gas was passed over the solution while measurement were being taken.

Cyclic Voltammetric and Coulometric Measurements. Cyclic voltammetric measurements were made with PAR Model 174A polarographic analyzer and PAR Model 175 universal programmer. The voltammograms were recorded with X-Y recorder (Houston series X-Y recorder). The working electrode used for cyclic voltammetry was

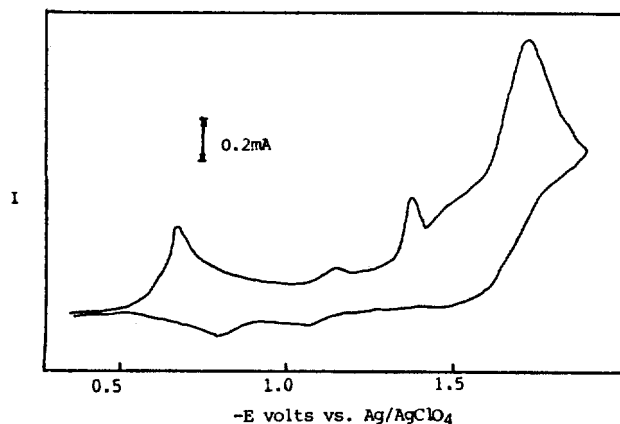


Figure 2. Cyclic voltammogram of 1.0×10^{-3} M TAR in 0.1M TEAP-AN solution at 25°C , scan rate 500 mV/sec.

hanging mercury dropping electrode (PAR Model 303A static mercury drop electrode system). The auxiliary electrode was platinum gauze electrode. The reference electrode with glass frit tip was Ag/AgClO₄ electrode (0.1M AgClO₄ in acetonitrile). All test solution were also degassed using nitrogen gas saturated with acetonitrile. Coulometric determination of the number of electrons involved in reduction process was undertaken by the use of PAR Model 179 digital coulometer containing potentiostat/galvanostat PAR Model 173.

Results and Discussion

DC polarographic and Cyclic Voltammetric Behavior of TAR. The Figure 1 shows typical polarogram of TAR. The polarographic reduction of TAR in a AN solution containing 5.0×10^{-3} M tetraethylammonium perchlorate(TEAP) is shown four well-defined waves. The half wave potentials(E_{dmc}) and diffusion currents(i_d) of each reduction step are given in Table 1.

The plot of i_d versus the square root of the mercury column height($h^{1/2}$) linear for each reduction step. The temperature coefficient($1/i \times di/dT \times 100$) (%) values have nearly 1.6% for each reduction step.

These results indicate that the waves are diffusion controlled¹².

The plot of E_{dmc} versus $\log(i/i_d)$ is also linear. The slopes of the plot from first wave to fourth wave are 69mV, 100mV, 120mV and 87mV respectively. If each reduction step is one electron process, these results indicate that the first reduction step is considerable reversible and the other reduction steps are less reversible.

The typical cyclic voltammogram of TAR in AN solution at HMDE is shown in Figure 2.

Table 2. Cyclic voltammetric data of 1.0×10^{-3} M TAR in 0.1M TEAP-AN solution at 25°C

scan rate (mV/sec)	1st wave		2nd wave		3rd wave		4th wave	
	$-E_p$ (mV)	i_p (μA)	$-E_p$ (mV)	i_p (μA)	$-E_p$ (mV)	i_p (μA)	$-E_p$ (mV)	i_p (μA)
50	596.1	130	1175.2	30	1335.7	140	1746.5	220
100	601.1	200	1192.5	40	1364.0	190	1761.5	310
200	610.6	290	1219.9	60	1391.3	290	1771.4	460
500	618.0	410	1234.4	95	1445.4	440	1793.9	710
1000	632.9	560	1254.7	130	1466.1	590	1812.6	1012

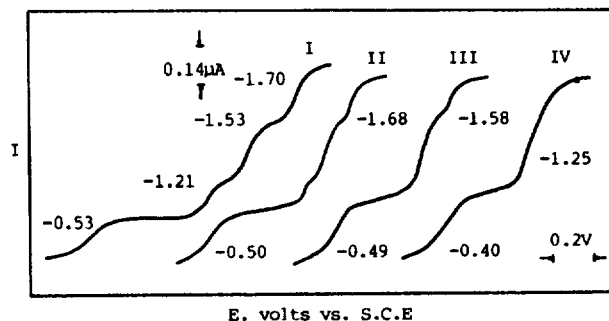


Figure 3. Change of DC polarograms of 5.0×10^{-5} M TAR in 5.0×10^{-3} M TEAP-AN solution by adding water at 25°C . Water contents; I = 0, II = 0.02, III = 0.04, IV = 0.22 (ml). Initial volume; 5 ml. Arabic figures are half wave potential of each reduction wave.

The reduction of TAR in AN solution containing 0.1M TEAP at a HMDE occurs with four steps also.

The cyclic voltammetric data at different scan rate (v) for each reduction step are given in Table 2.

The plot of peak current (i_p) versus the square root of scan rate ($v^{1/2}$) is linear. The plot of i_p versus concentration is also linear in the concentration range of 0.25×10^{-3} M \sim 2.0×10^{-3} M. These results also indicate that all waves are diffusion controlled¹³.

The peak potential (E_p) is a function of scan rate (v), shifting in a negative direction by an amount $30/\alpha n_a$ mV at 25°C for each tenfold increase in scan rate. If peak potentials shift to more negative potential with increasing scan rate, the reduction wave is less reversible. Thus, if each reduction step is one electron process, the results of Table 2 indicate that first reduction step is considerable reversible and the other reduction steps are less reversible.

Effect of Protonating Agent. To gain further insight into the over-all reduction mechanism of TAR in AN solution, the effect of varying amounts of a source of proton donor such as water upon their electrochemical behavior was examined.

The effect of water on the polarographic reduction wave of TAR is shown in Figure 3. The addition of water causes the first wave and the third wave to increase in height with the expense of the second wave and the fourth wave. Also all waves shift to positive potential. This behavior is entirely analogous to that found with many aromatic hydrocarbons in the presence of a proton donor¹⁴⁻¹⁶.

The explanation of this effect is probable the same; *i.e.* if intermediate is anion radical, protonation of anion radical occurs with adding proton donor (reaction 2). The protonation of the anion radical causes that concentration of anion radical decrease.

Thus height of the first wave and the third wave increase with the expense of the second wave and the fourth wave. Also the product resulting from protonation of the anion radical lead to a species more easily reduced than the parent azo compound, then reduction potential shifts to positive potential (reaction 3).

These results indicate that one-electron process producing anion radical which is stable at the first reduction step and the third reduction step. And at the second reduction step and the fourth reduction step, this anion radical is reduced via a one-electron process to dianion.

Table 3. Results of the Controlled Potential Coulometry

reduction step	number of coulomb (coulomb)	n
1st step	0.07	1.4
2nd step	0.10	2.1
3rd step	0.17	3.5
4th step	0.20	4.2

*Concentration of sample solution (C); 5.0×10^{-5} M in 5.0×10^{-3} M TEAP-AN solution, initial sample volume; 10ml.

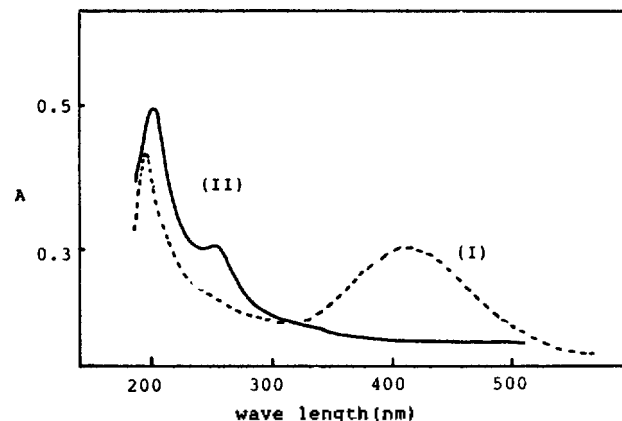
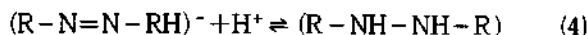
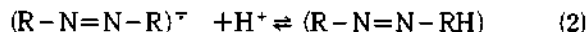
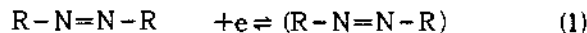


Figure 4. UV-Vis. spectra of 5.0×10^{-5} M TAR in TEAP-AN solution before (I) and after (II) controlled potential electrolysis at -1.9 volt vs. S.C.E.



Controlled-Potential Coulometry. Coulometric experiments at a potential corresponding to the plateau of each polarographic reduction wave were carried out determining the number of electrons transferred in each reduction step; *i.e.* the cell for controlled potential electrolysis used large cylindrical type, then the working electrode was used mercury pool. The reference electrode used the Ag/AgClO₄ electrode and the auxiliary electrode was the Platinum gauze. After the solution were thoroughly degassed with purified nitrogen gas saturated with acetonitrile, the quantity of electricity required to entirely electrolysis was measured.

The results for the coulometric experiments of TAR in AN solution are shown in Table 3. In such case, the number of electron transferred, n_{app} is close to one for each reduction step.

These coulometric results suggest that one-electron process occurs during the reduction reaction.

Identification of Reduction Products. The product of controlled potential reduction of TAR in AN solution at a potential corresponding to the plateau of the fourth polarographic wave, -1.9 volt vs. S.C.E was identified by UV-Vis spectrum. The UV-Vis. absorption spectrum of TAR solution resulting from coulometric reduction at a potential corresponding to the plateau of the fourth reduction step is

shown in Figure 4. The absorption band of TAR occurs at about 410nm (curve I) corresponding to the Azo group. The absorption band is disappeared completely when it is electrolyzed. Then new absorption spectrum appear at about 255nm (curve II). The position of the new absorption band in the UV-Vis spectrum of this electrolysis product of TAR coincides with that of amine compound expecting to product¹⁷.

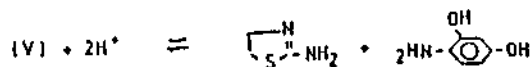
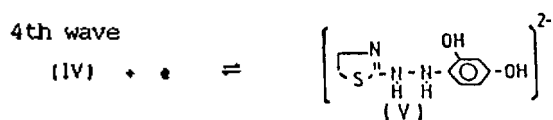
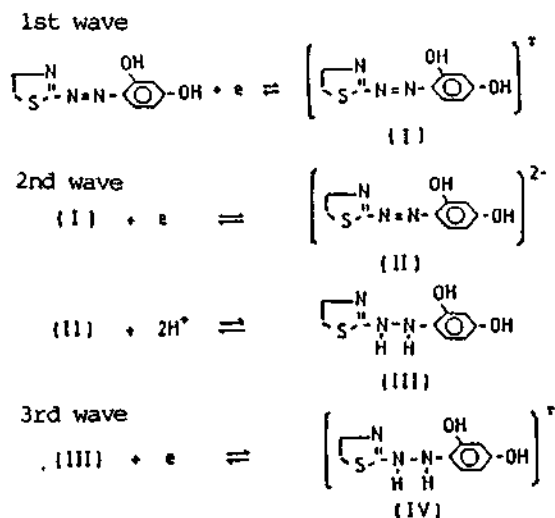
These results suggest that product of controlled-potential electrolysis at a potential corresponding to the plateau of the fourth reduction step of TAR is the amine compound and electrolysis of TAR occurs in Azo group.

Conclusion

Based on the these experimental results for electrochemical reduction behavior of TAR in AN solution, the electrochemical reduction of TAR in AN solution shown four-one electron reduction step. The products of the first and the third electron transfer are speculated to be a relatively stable anion radical. The second and the fourth electron transfer to the dianion is followed by a chemical reaction producing a protonated species. The product of the fourth electron transfer also produces the corresponding amine compound with following reaction.

Each reduction step is diffusion controlled and the first reduction step is considerably reversible and the other reduction steps are less reversible.

The electrochemical reduction mechanism of TAR in the AN solution is proposed as follow:



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