Electroreduction of Phenylhydrazones in Methanol-Water Mixtures

Vepa KAMESWARA RAO, Chitoor Sivaramakrishnan VENKATACHALAM, and Chatty KALIDAS*
Department of Chemistry, Indian Institute of Technology, Madras 600036, India
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Synopsis. The electroreduction of a few substituted phenylhydrazones on mercury cathode has been studied in methanol-water mixtures using polarography, cyclic voltammetry, micro- and macrocontrolled-potential electrolysis. These compounds are reduced in a single four-electron step to yield the corresponding amino products. A linear relationship between the half-wave potentials ($E_{1/2}$) and Hammett substituent constants (σ) has been observed.

The electrochemical reduction of various phenylhydrazones received the attention of several authors in recent years[1-5] in view of thier biological activity. In our earlier communications,[6,7] the electroreduction of some substituted phenylhydrazones in amphiprotic media has been reported. In continuation of this work, we present here the results of the electrochemical behavior of 2,2-dimethyl-1,3-dioxane-4,5,6-trione 5-(phenylhydrazone) (**1**) and 2,2-dimethyl-1,3-dioxane-4,5,6-trione 5-(4-acetylphenylhydrazone) (**2**) in methanol-water mixtures of varying composition and pH. The effect of substituents on the mechanism of the electrode reaction (Hammett correlation) is also discussed.

Experimental

The phenylhydrazones used in the present work, (**1** and **2**) were prepared by coupling the appropriate diazotized aromatic amine with Meldrum's acid (cyclic isopropylidene malonate). The yellow amber colored compounds were recrystallized from aqueous methanol or benzene-hexane mixture and their purity checked by TLC. The mp of **1** is 171—172 °C (reported[8] value 171—172 °C) and that of **2** is 182 °C. Analysis for compound **2**. Found: C, 57.59; H, 4.87; N, 9.61%. Calcd for $C_{14}H_{14}N_2O_5$: C, 57.69; H, 4.83; N, 9.61%.

Methanol (Reechem) was purified by standard procedure. Potassium chloride (AR) was used as the supporting electrolyte without further purification. Britton-Robinson[9] (BR) and Clark-Cubs (CL) buffers were used to control the pH of the experimental solutions. The dme had the following capillary characteristics: m=0.7933 mg s^{-1} and t=6 s at 53 cm height (uncorrected for back pressure) of the mercury column under open-circuit conditions. A Metrohm EA 290 hanging mercury drop electrode (hmde) having an area of 0.01296±0.006 cm^2 was used for cyclic voltammetric experiments. The polarographic measurements were carried out with a Metrohm E 506 polarecord, saturated calomel as the reference electrode and a platinum foil as the counter electrode. Cyclic voltammograms were recorded employing PAR 175 Universal programmer and PAR 173 potentiostat in conjunction with an x-y recorder (Digital Electronics, Bombay). Electrolysis products were analyzed by HPLC. The details of microcoulometric measurements for determining the number of electrons (n_{app}) transferred in the electrode process have been described previously.[10] Polarograms and cyclic voltammograms were recorded for solutions containing the depolarizer (1.0×10^{-3} M, (1M=1 mol dm^{-3})), the maximum suppressor (0.002% Triton-X-100), supporting electrolyte (KCl) and required amount of buffers (BR and CL) in methanol-water mixtures of various compositions.

All measurements were caried out at 30 °C.

Results and Discussion

The electrochemical reduction of **1** and **2** was carried out in 60—80% (v/v) methanol-water mixtures in the pH range 1.00—7.00. These compounds are found to be unstable in alkaline solutions as indicated by the decrease in polarographic currents with time. This might probably due to the hydrolysis of Meldrum's acid moiety in buffered alkaline media.[11] Both the compounds give a single well-defined dc polarogram and a single ac peak corresponding to the dc step at all pH values in different compositions of methanol-water mixtures. The polarographic data are presented in Tables 1 and 2. Analysis of the polarographic data revealed the diffusion-controlled nature of the electrode process. The half-wave potentials of the depolarizers are shifted cathodically with increase in pH values and with increase in composition of methanol. At a given pH and composition, the summit potentials (E_s) are more negative than the corresponding dc $E_{1/2}$ values thereby indicating the irreversible nature of the

Table 1. Polarographic Data of Compound (**1**) (1.0×10^{-3} M) in 60% (v/v) Methanol-Water Mixture at Various pH Values Containing 0.002% Triton-X-100 as Maximum Suppressor and 0.2 M KCl as Supporting Electrolyte

No.	pH	Wave height / μA	Half-wave potential, $-E_{1/2}$/V vs. SCE	$-(E_{3/4}-E_{1/4})$ / V	$-dE/d\log(\frac{i_d-i}{i})$	Summit potential, $-E_s$/V vs. SCE
1	1.24[a]	9.05	0.380	0.100	0.111	0.44
2	3.37	9.30	0.650	0.120	0.127	0.75
3	4.51	9.70	0.700	0.110	0.111	0.80
4	5.25	9.20	0.745	0.075	0.100	0.83
5	6.40	9.70	0.795	0.115	0.100	0.91
6	6.91	9.90	0.885	0.150	0.123	0.94

a) 0.1 M HCl (unbuffered).

Table 2. Polarographic Data of Compound **2** (1.0×10^{-3} M) in 60% (v/v) Methanol-Water Mixture at Various pH Values Containing 0.002% Triton-X-100 as Maximum Suppressor and 0.2 M KCl as Supporting Electrolyte

No.	pH	Wave height / μA	Half-wave potential, $-E_{1/2}$/V vs. SCE	$-(E_{3/4}-E_{1/4})$ / V	$-dE/d\log(\frac{i_d-i}{i})$	Summit potential, $-E_s$/V vs. SCE
1	1.31[a)]	8.5	0.255	0.060	0.063	0.35
2	3.54	8.4	0.465	0.120	0.115	0.58
3	4.25	8.4	0.540	0.110	0.119	0.62
4	5.35	8.7	0.595	0.070	0.098	0.66
5	6.79	8.3	0.710	0.115	0.106	0.80

a) 0.1 M HCl (unbuffered).

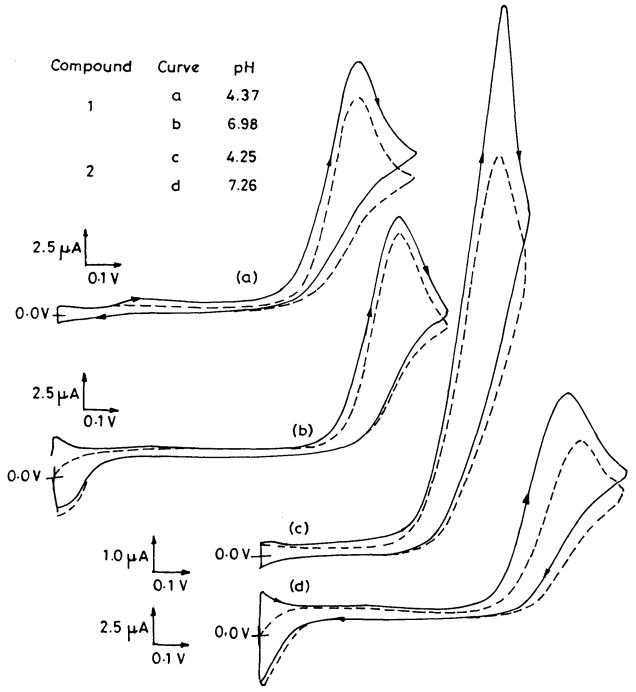


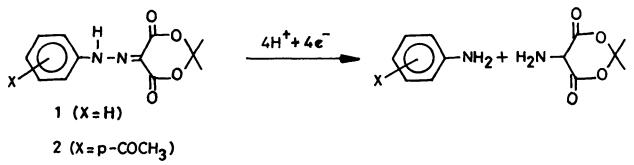
Fig. 1. Cyclic voltammograms of **1** and **2** in buffered 60% (v/v) methanol-water mixture containing 0.002/Triton-X-100 as maximum suppressor and 0.2 M KCl as supporting electrolyte; sweep rate, 0.100 V s^{-1}. Solid lines represent firstsweep and broken lines represent repeated cycle.

electrode process. The $(E_{3/4}-E_{1/4})$ and the slope values of $-E$ vs. $\log(i_d-i)/i$ plots also confirm the irreversible behavior.

The cyclic voltammetric data of phenylhydrazones indicate the diffusion-controlled and irreversible nature of the electrode processes. Figure 1 shows typical cyclic voltammograms of the compounds **1** and **2** obtained in 60% (v/v) methanol in acidic and neutral media. Both the compounds give a single cathodic peak in the forward scan and no anodic peak in the reverse direction indicating the irreversible behavior of the electrode process. The diffusion-controlled nature of the electrode process was indicated by the linear relationship between the cathodic peak current values ($i_{p,c}$) and the square root of the scan rate ($v^{1/2}$). In all the cases, however, an anodic peak (close to 0.0 V) is observed in the reverse scan in neutral buffered methanol-water mixtures. The peak separation of the redox couple (ΔE_p) around 0.070 V suggests a quasi-reversible single electron-transfer step in the oxidation of the product formed at the electrode surface in neutral media.

The microcoulometric experiments carried out at the limiting region of the polarographic waves of **1** and **2** showed a transfer of four electrons ($n_{app}=4$) in the reduction step. The controlled-potential electrolysis of **1** and **2** yielded aniline (retention time 3.3 min) and *p*-aminoacetophenone (retention time 3.14 min), respectively, as the final products. The retention times of the electrolysis products were found to be in good agreement with those of the authentic samples. The other expected product, namely, amino-substituted Meldrum's acid could not be identified possibly due to its hydrolysis during working up procedure in basic medium.

Based on the results obtained, the following stoichiometry is suggested for the reduction of the phenylhydrazones in buffered methanolic solutions under acidic and neutral conditions:



1 (X=H)

2 (X=p-$COCH_3$)

It may be pointed out that the deliberate addition of pure aniline or *p*-aminoacetophenone in the reduction of **1** and **2** did not increase the peak height of the anodic wave observed very close to 0.0 V in the reverse scan in cyclic voltammetric experiments. This positively suggests that the observation of the anodic peak during the reverse scan may be due to the oxidation of amino-substituted Meldrum's acid formed at the electrode surface during the cathodic reduction of phenylhydrazones.

An attempt has been made in the present investigation to correlate the half-wave potentials of phenylhydrazones with Hammett substituent constants (σ). Such a correlation was possible due to a similar behavior of these compounds at the electrode-electrolyte interface. The Hammett equation when applied to reversible as well as irreversible electrode processes, $dE_{1/2}=\rho\sigma$ belongs to the family of linear free energy relationships (LFER)-equations.[12] Figure 2 shows

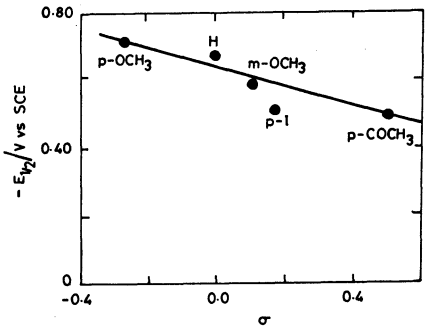


Fig. 2. Hammett correlation for various substituted phenylhydrazones in 60% (v/v) methanol-water mixtures at pH=4.00.

such a Hammett correlation for various substituted phenylhydrazones in 60% (v/v) methanol-water mixture at a constant pH. The linear plot has a ρ-value of 0.308 with a correlation coefficient 0.895. It may be noted from the correlation that the ease of reduction of these phenylhydrazones decreases in the order *p*-$COCH_3$<*p*-I<*m*-OCH_3<*p*-OCH_3 with decreasing order of the electron withdrawing nature of the substituents studied.

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