

Electro-chemical Investigations of Some Acetoacetarylides

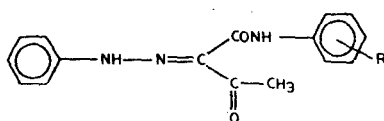
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Electrochemical behaviour of acetoacetarylides has been studied at d.m.e. and at pyrolytic graphite electrode by various techniques. The reduction of these compounds takes place in a single, pH-dependent step involving four electrons. The products of electrolysis have been identified by TLC and gas chromatography. The effect of substituents has been represented in the terms of Hammett equation and the effect of cations has been explained on the basis of double layer structure.

Acetoacetarylides have been used as intermediates for the preparation of a large number of biologically important compounds¹. A literature survey revealed that the electro-chemical behaviour of α -diazophenyl acetoacetarylides(I) has not been elucidated. In this paper we report the results of our studies on the electro-chemical behaviour of (I) with particular reference to the reduction mechanism at dropping mercury electrode and pyrolytic graphite electrode using polarography, cyclic voltammetry and coulometric techniques. The products of electro-reduction have been identified by gas chromatography. The effect of substituents has been represented in the terms of Hammett equation.



Materials and Methods

α -Diazophenyl acetoacetarylides were synthesised in the laboratory by the method reported in the literature^{2,3}. All the compounds were recrystallised from ethanol and their purities were confirmed by elemental analyses and spectral data.

Stock solutions of all these compounds (2mM) were prepared in N,N-dimethylformamide (A.R.; 99.9%) without further purification. Britton-Robinson buffers in the pH range 3.0-11.2 were prepared in doubly distilled water. Polarograms were recorded on a Cambridge pen recording polarograph. The capillary had the following characteristics, $m = 1.27 \text{ mg s}^{-1}$, $t = 3.94 \text{ s}$ at $h = 70 \text{ cm}$ in 1.0 M KCl at 0.0 V. All the

potentials are with respect to the SCE. Linear and cyclic sweep voltammetry measurements, using rough pyrolytic graphite electrode, were carried out using a Micronics cyclic voltameter. The graphite electrode was gently rubbed with a sand paper and washed with distilled water after each run as has been reported by Dryhurst^{4,5}. The number of electrons involved in the reduction was determined by coulometry using a mercury pool or rough pyrolytic graphite (RPGE) as a working electrode and platinum gauze as a counter electrode. The change in current with time was monitored and the n value was determined by the method suggested by Lingane⁶. The spectral changes during the electro-reduction were monitored by using a UV-VIS (C. Zeiss, Zena) specord spectrophotometer. The effect of cations on the electrode process was studied by taking chlorides of lithium, sodium, potassium, rubidium and cesium.

Electrolysis was carried out by taking 4-6 mg of the starting material at the mercury pool or RPGE as working electrode. Nitrogen gas was bubbled throughout the electrolysis; the progress of electrolysis was monitored by recording a cyclic voltammogram and it was stopped when 95% of the reduction was achieved. Electrolysed solution was extracted with ether (3 $\times$ 25 ml) to remove buffer constituents, and it was concentrated *in vacuo* and analysed by an Aimil Nucon gas chromatograph using 3% SE-30 silica gel on chromosorb W as the adsorbent. The temperature of injector and detector was maintained at 210°C. The temperature of the column was raised from 70°C at a rate of 6°C/min until a final temperature of 210°C was reached.

The solutions for recording polarograms and voltammograms were prepared by mixing 1.0 ml of the stock solution, 2.0 ml of dimethylformamide, 0.4 ml gelatin (0.01%) and 6.6 ml of appropriate buffer in a stream of purified nitrogen gas. For investigating the effect of cations, 1.0 ml of buffer was replaced by 1.0 ml of appropriate supporting electrolyte (1.0M).

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Results and Discussion

All the compounds (Table 1) under investigation get reduced in a single four-electron step giving well-defined reduction waves in the pH range 3.0–11.2. The limiting current of the wave is diffusion controlled as evidenced by the linear plots of i_d vs $\sqrt{h}$ and i_d vs C (concentration of the depolariser). The low value of temperature coefficient ($1.1.2\%$ deg^{-1}) further confirms the diffusion controlled nature of the electrode process. The reversibility of the electrode process was tested by using log plots and it was found to be irreversible in the entire pH range studied. The shift in half wave potential towards more negative values with increase in concentration of the depolariser, further confirms the irreversible nature of the wave and the possible role of adsorption. The $E_{1/2}$ is pH -dependent and is shifted towards more negative potentials in the pH range 3.0–9.2; it becomes constant thereafter. The plots of $E_{1/2}$ vs pH are linear in the range 3.0–9.2 and follow the relations given in Table 1. It has been reported^{7,8} that the plots of $E_{1/2}$ vs pH can be represented by sets of linear segments of different slopes and that intersections give the value of pK of oxidised or reduced species. It was interesting to observe that pK values of all these compounds lie in the same range (Table 1). The polarographic characteristics of these compounds are also summarised in Table 1.

Linear and cyclic sweep voltammetric studies at scan rate of 5mVs^{-1} and 200mVs^{-1} for compound 1 indicate a well-defined cathodic peak at the rough pyrolytic graphite electrode. In the reverse sweep no peak was observed. A few typical linear sweep voltammograms are represented in Fig. 1. The peak potential (E_p) is linearly dependent on pH upto pH 9.2 and is constant thereafter. The identical values of dE_p/dpH and $\Delta E_p/dpH$ indicate that reduction of these

compounds occurs by the same mechanism at both the electrodes.

Controlled potential electrolysis of the parent compound (1) at mercury pool cathode or at pyrolytic graphite electrode (area 6 cm^2) consumed 4.0 ± 0.2 (average $\pm$ maximum deviation) electrons in the pH range 3.0–11.2.

Intermediate and product characterisation

The spectral changes during electroreduction in the region 325–625 nm were monitored to characterise any intermediate formed during the electroreduction. In the course of electrolysis, the absorption band at 380 nm decreased in intensity systematically and no intermediate or product was formed that absorbed at a lower or a higher wavelength. After about 25 min, the electrolysis was stopped. The ether extracts of the

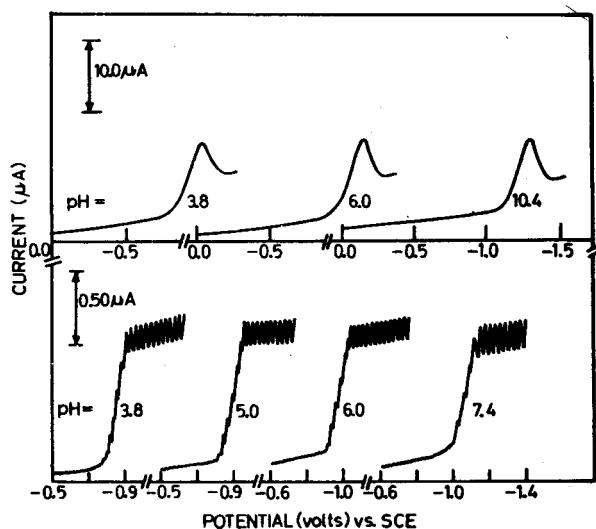
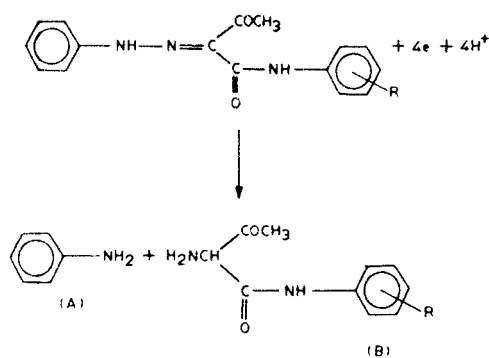


Fig. 1—Some typical voltammograms and polarograms of 0.2 mM compound 1 at different pH

Table 1—Polarographic Characteristics of α -Diazophenyl Acetoacetarylides at pH 6.0

Sl. No.	R in (I)	$-E_{1/2}$ (V)	i_d (μA)	α_n	I	pK	$-E_{1/2}$ vs pH relation
1	H	0.99	0.85	0.98	1.745	9.3	$-E_{1/2} = 0.055 pH + 0.66$
2	2-Cl	1.00	0.85	0.77	1.745	9.2	$-E_{1/2} = 0.048 pH + 0.71$
3	3-Cl	0.96	0.85	0.96	1.745	9.0	$-E_{1/2} = 0.052 pH + 0.64$
4	4-Cl	0.96	0.95	0.87	1.950	9.4	$-E_{1/2} = 0.045 pH + 0.75$
5	4-Br	1.04	0.85	0.92	1.745	9.2	$-E_{1/2} = 0.052 pH + 0.73$
6	2-CH ₃	1.04	0.95	0.77	1.950	9.2	$-E_{1/2} = 0.048 pH + 0.75$
7	4-CH ₃	1.04	0.86	0.96	1.750	9.1	$-E_{1/2} = 0.048 pH + 0.75$
8	2-OCH ₃	1.08	0.82	0.78	1.694	9.2	$-E_{1/2} = 0.057 pH + 0.77$
9	4-OCH ₃	1.04	0.95	0.87	1.950	9.2	$-R_{1/2} = 0.056 pH + 0.70$
10	2-OC ₂ H ₅	1.08	0.85	0.96	1.745	9.2	$-E_{1/2} = 0.050 pH + 0.78$
11	4-OC ₂ H ₅	1.04	0.82	0.98	1.694	9.2	$-E_{1/2} = 0.048 pH + 0.75$
12	4-COOH	1.12	0.95	0.92	1.950	9.1	$-E_{1/2} = 0.07 pH + 0.68$

electrolysed solution of compound (1) at pH 3.0, 6.0 and 10.4 gave two clear spots in TLC. The gas chromatography of the extract gave two major GC peaks with $R_t \sim 0.53$ and 1.2 min. Thus, it was concluded that in the entire pH range, electroreduction of these compounds gives two products. The product corresponding to $R_t \sim 1.2$ min was identified as aniline (A) on the basis of the retention time of an authentic sample of aniline. The other product in the 4e reduction of α -diazophenyl acetoacetanilide is expected to be 2-aminoacetoanilide (B). This product is known and it was synthesised in the laboratory by the reported method^{9,10}; the retention time of this compound ($R_t \sim 0.53$) was identical with that observed for the first peak. Thus, the reduction of these compounds gives aniline and 2-aminoacetoarylides (B) as the major products of the electroreduction. The following overall mechanism (Scheme 1) can be proposed for the reduction of these compounds:



The above mechanism finds support from the observed spectral behaviour as π -chromophore system does not increase or decrease extensively during reduction. A similar 4e mechanism has also been proposed by a large number of workers¹¹⁻¹⁴ for the reduction of hydrazone group.

Effect of substituents

It is apparent from the data presented in Table I that the values of dE_1/dpH , α , n and I (diffusion current constant) are practically the same for the entire series of compounds and thus it is possible to determine the effect of substituents quantitatively in the terms of the Hammett equation. The values of Hammett substituent constants (σ) were obtained from the literature¹⁵. Fig. 2 presents plot of $-E_1$ vs σ in B.R. buffer of pH 6.0 and it is observed that all the substituents fit in the straight line. The value of specific reaction constant (ρ) was found to be 0.15V. Similar values of specific reaction constants for reduction of hydrazones have also been reported in literature¹⁵.

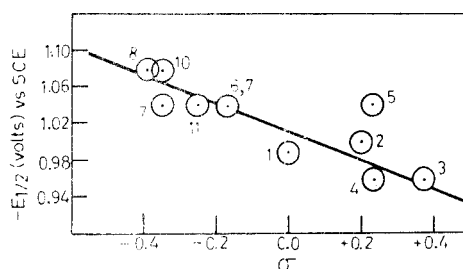


Fig. 2 -Plots of $-E_{1/2}$ versus σ for acetoacetanilides

Effect of supporting electrolytes

The parent compound (1) was also polarographically reduced in the presence of chlorides of lithium, sodium, potassium, rubidium and cesium in order to determine the effect of size of cation on the reduction process. In all the cases, a well-defined reduction wave was obtained. The limiting current of this wave was practically constant for all the cations; however, the E_1 value shifted towards more negative potentials with increase in the size of cation in entire pH range. This can be explained in terms of the change in the structure of the double layer. For a given supporting electrolyte, E_1 is independent of ψ (potential drop in the diffused part of the double layer) or ionic strength but the value of ψ can change from one electrolyte to the other. Such a change will be more effective with cations in case of cathodic reduction at d.m.e. Thus, the decrease in the value of ψ with increase in the size of cation will make the reduction more difficult. The polarograms of compound 1 were also recorded in supporting electrolytes having common cation and different anions, and it was observed that E_1 and i_d remained constant. This behaviour can be explained on the basis of the fact that the effect of cation predominates in the electrical double layer at these potentials.

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