

Kinetics & Mechanism of Polarographic Reduction of Acetophenone & *p*-Bromoacetophenone in Aqueous Ethanol

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The polarographic behaviour of acetophenone and *p*-bromoacetophenone in aqueous ethanol (20%, v/v) has been studied at $25 \pm 0.1^\circ\text{C}$ as a function of pH, using Britton-Robinson (BR) buffer. The reduction of the depolarizers in different steps has been found to be diffusion-controlled and irreversible. The kinetic parameters (αn_a and $k_{f,h}^\circ$) have been calculated by Koutecky's method. A tentative mechanism has been put forward for the reduction process of each depolarizer. Besides, the effect of substituent (Br) on the kinetics of the electrode reaction of acetophenone has also been investigated.

Only a few studies^{1,2} dealing with kinetics and mechanism of irreversible electrode processes of the aromatic ketones have been undertaken so far. Keeping this in view, we report here the results of our studies on the polarographic behaviour of acetophenone and *p*-bromoacetophenone as a function of pH.

Acetophenone (BDH) was redistilled and *p*-bromoacetophenone (BDH) was recrystallised before use. The other chemicals used were of AR (BDH) grade. The concentrations of acetophenone and *p*-bromoacetophenone in aqueous ethanol (20%, v/v) were maintained at 1.0×10^{-3} moldm⁻³. Desired pH values were maintained by the addition of Britton-Robinson (BR) buffers. KCl (0.1 moldm⁻³) was used as a supporting electrolyte. A manual polarograph (Toshniwal CL02A) in conjunction with polyflex galvanometer (Toshniwal PL50) was used. All the measurements were made at $25 \pm 0.1^\circ\text{C}$. Purified nitrogen was bubbled for removing the dissolved oxygen. The potentials were measured against a saturated calomel electrode (SCE).

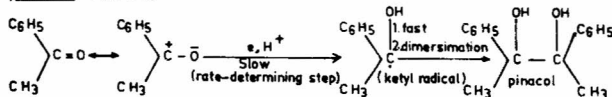
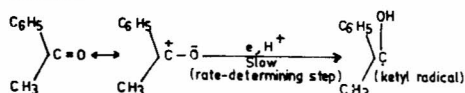
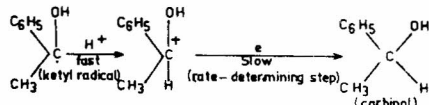
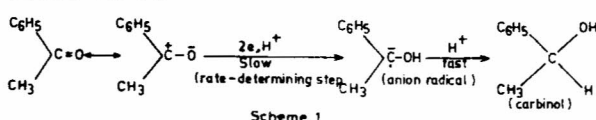
The number of electrons (n) involved in the reduction of acetophenone and *p*-bromoacetophenone at different pH values was determined by millicoulometric method³ as 1 and 2 for the pH ranges 1.81-3.29 and 4.10-11.98 respectively for acetophenone and for the pH ranges 1.81-4.10 and 5.02-11.98 respectively for *p*-bromoacetophenone. Ilkovic equation was used to calculate the value of the diffusion-coefficient, D at different pH values. The potential-dependent rate

constant, $k_{f,h}$ was calculated by Koutecky's method^{4,5}. The kinetic parameters (αn_a and $k_{f,h}^\circ$) were calculated⁶ from the plots of $\log k_{f,h}$ versus $E_{d,e}$. Throughout the measurements the current at the end of the drop (i.e. the maximum current) was recorded. The dme had the following characteristics; for acetophenone: $m = 1.75$ mg/s; $t = 2.93$ s; $m^{2/3}t^{1/6} = 1.74$ mg^{2/3}s^{-1/2} (in 0.1 moldm⁻³ KCl, open circuit) $h_{\text{corr}} = 59.5$ cm; for *p*-bromoacetophenone: $m = 1.83$ mg/s; $t = 3.15$ s; $m^{2/3}t^{1/6} = 1.814$ mg^{2/3}s^{-1/2} (in 0.1 moldm⁻³ KCl, open circuit); $h_{\text{corr}} = 50$ cm.

Table 1—Polarographic Characteristics and Kinetic Parameters for Electrode Reaction of Acetophenone and *p*-Bromoacetophenone at Different pH Values

pH	$-E_{1/2}$ (v) (SCE)	$D \times 10^6$ (cm ² /s)	αn_a	$k_{f,h}^\circ$ (cm/s)
Acetophenone				
1.81	1.06	5.54	0.68	3.91×10^{-13}
1.98	1.09	8.64	0.67	2.89×10^{-13}
3.29	1.23	7.54	0.62	4.82×10^{-14}
4.10				
First step	1.25	7.36	0.72	5.22×10^{-16}
Second step	1.44		0.64	3.42×10^{-16}
5.02				
First step	1.35	7.01	0.72	3.89×10^{-17}
Second step	1.51		0.65	1.15×10^{-17}
6.09				
First step	1.36	6.84	0.72	3.28×10^{-17}
Second step	1.51		0.64	1.78×10^{-17}
7.00	1.48	6.09	0.89	2.57×10^{-22}
7.95	1.50	6.76	0.91	4.30×10^{-23}
8.95	1.55	6.17	0.93	2.43×10^{-24}
10.32	1.59	4.12	0.90	1.96×10^{-24}
11.98	1.65	3.35	0.92	1.00×10^{-25}
<i>p</i> -Bromoacetophenone				
1.81	0.92	6.48	0.74	9.97×10^{-12}
1.98	1.04	7.13	0.71	6.33×10^{-13}
3.29	1.08	7.18	0.74	5.34×10^{-14}
4.10	1.16	9.32	0.75	3.52×10^{-15}
5.02				
First step	1.18	6.45	0.74	2.76×10^{-15}
Second step	1.38		0.61	2.25×10^{-15}
6.09				
First step	1.25	7.85	0.74	1.03×10^{-16}
Second step	1.46		0.59	9.46×10^{-16}
7.00	1.36	6.14	0.95	1.38×10^{-21}
7.95	1.38	7.13	0.94	5.89×10^{-22}
8.95	1.40	5.84	0.94	4.29×10^{-22}
10.32	1.46	5.28	0.93	4.98×10^{-23}
11.98	1.54	4.68	0.95	1.29×10^{-24}

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ACETOPHENONE**pH RANGE** 1.81–3.29**pH RANGE** 4.10–6.09**FIRST STEP:****SECOND STEP:****pH RANGE** 7.00–11.98

Scheme 1

The current-voltage curves of acetophenone and *p*-bromoacetophenone were obtained in the pH range 1.81–11.98. Acetophenone gives a single one-electron reduction wave in the pH range 1.81–3.29, while two waves are obtained in the pH range 4.10–6.09, each involving one electron. In neutral and alkaline media a composite wave of two electrons results. *p*-Bromoacetophenone gives one-electron reduction wave in the pH range 1.81–4.10 while two waves, each involving one electron, result in the pH range 5.02–6.09. In neutral and alkaline media (pH range 7.00–11.98), the reduction occurs in a single two-electron reduction step. Various tests⁷ of irreversibility indicate that the polarographic reduction of acetophenone and *p*-bromoacetophenone in different steps is irreversible. Plots of i_d versus $\sqrt{h_{\text{corr}}}$ for various steps are linear and pass through the origin thereby showing the diffusion-controlled nature of the waves.

The values of kinetic parameters (αn_a and $k_{f,h}^\circ$) of the irreversible electrode reaction of acetophenone and *p*-

bromoacetophenone have been calculated and the values for various steps have been presented in Table I. The number of protons (p) involved in the rate-determining step of the reduction of acetophenone and *p*-bromoacetophenone at dme has been calculated^{8,9} to be one from the ratio of the slopes of $E_{1/2}$ versus pH $\left(\frac{2.303}{nF} pRT\right)$ plot to the wave slope $\left(\frac{2.303}{nF} RT\right)$

The number of electrons involved in the rate-determining step (n_a) is generally equal to 1. On the basis of the above mentioned stoichiometry of the rate-determining step for different ranges of pH, the mechanism in Scheme 1 can be proposed for the polarographic reduction of acetophenone and *p*-bromoacetophenone.

A perusal of the Table I shows that the value of $k_{f,h}^\circ$ for the electrode reaction of *p*-bromoacetophenone is much larger for different steps as compared to that for the acetophenone in the entire pH range. Since the polarographic reduction of these two ketones has been studied under identical conditions, a larger value of $k_{f,h}^\circ$ for the electrode reaction of *p*-bromoacetophenone clearly shows that the electrode reaction of acetophenone is rendered less irreversible as a result of the substitution of Br atom in the nucleus. This is borne out by the less negative $E_{1/2}$ values of *p*-bromoacetophenone as compared to those of acetophenone. This conclusion is based on the consideration¹ that Br, being an electron-withdrawing group, would decrease the electron density around the ketonic group thereby rendering its reduction at dme easier.

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