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NOTES

Chronoamperometry of Some Substituted Phenacyl Bromides

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Chronoamperometry of substituted phenyl bromide like *p*-phenyl, *p*-methyl, *p*-methoxy and *m*-methoxy phenacyl bromide has been studied under hanging mercury drop electrode (HMDE) in 50% (v/v) ethanol-water mixtures. Adsorption phenomena are characterised from $it^{1/2}$ *vs.* t plots and diffusion coefficient and forward rate constant values have been evaluated at specific step potentials.

Chronoamperometric technique has been widely used to understand the charge transfer, coupled chemical reaction rates and adsorption in the vicinity of the electrode. Laitenin and Kolthoff[1,2] carried out precise studies of linear diffusion at solid electrodes. In recent work, Jayarama Reddy and coworkers[3,4] have extensively exploited this technique in evaluating kinetic parameters such as diffusion coefficients and rate constants which were found to be more reliable and precise when compared to those obtained from other techniques.

Experimental details were given in our earlier report[5]. In the present study, phenacyl bromides with different substituents in the benzene nucleus have been reduced under HMDE in 50% (v/v) ethanol-water media.

Cyclic voltammograms (CV) were recorded for all the compounds in various supporting electrolytes. A specific potential has been chosen from the diffusion controlled region of the CV of each compound to record the chronoamperograms. At this potential, the maximum rate of mass transport by diffusion will be obtained. Well defined chronoamperograms have been obtained for the reduction of all the compounds studied. From the linearity $it^{1/2}$ vs. t (i = current in μA, t = time in sec) plots for the reduction of the C–Br bond, the constancy of the product $it^{1/2}$ is taken as a criterion for linear diffusion. The reduction process is found, in general, to be diffusion controlled and adsorption free for all compounds. The kinetic data obtained from this technique are more reliable since the reduction processes are adsorption free. Typical kinetic data are summarised in Table 1.

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TABLE 1
TYPICAL CHRONOAMPEROMETRIC DATA OF SUBSTITUTED PHENACYL BROMIDES IN ACETATE BUFFER OF pH 5.5.
Solvent = 50% ethanol; Concn = 0.5 mM

	Compound	Diffusion coefficient $D \times 10^6/cm^2 s^{-1}$	Forward rate constant	
			At step potential	$k_{f,h} \times 10^{-3}/cms^{-1}$
1.	*p*-phenyl phenacyl bromide	2.87	–0.32 V	0.549
2.	*p*-methoxy phenacyl bromide	0.90	–0.20 V	7.980
3.	*p*-methyl phenacyl bromide	12.97	–0.26 V	1.197
4.	*m*-methoxy phenacyl bromide	2.12	–0.32 V	5.012

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