

# Electrochemical Reduction and Evaluation of Kinetic Parameters of some Substituted Phenacyl Bromides in Non-aqueous Media

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Substituted phenacyl bromides, like *m*-nitro, *m*-methoxy, *p*-phenyl, *p*-methoxy, *p*-methylphenacyl bromides have been reduced electrochemically under dropping mercury electrode and hanging mercury drop electrode employing d.c. polarography and cyclic voltammetry in 50% (v/v) DMF-water mixture. The cleavage of C-Br bond involves two-electron irreversible reduction process to give their corresponding acetophenones. Comparative account of their reduction behaviour in various supporting electrolytes is discussed. The kinetic parameters such as transfer coefficient, diffusion coefficient and heterogeneous forward rate constant values have been evaluated.

Electrochemical reduction of compounds having carbon-halogen bond has been studied<sup>1</sup>. In  $\alpha$ -haloketones, the reduction of carbon-halogen bond takes place at more positive potentials than in analogous normal halides. A few investigations have been carried out on  $\alpha$ -haloketones<sup>2</sup>. As a part of our earlier work<sup>3</sup> on substituted phenacyl bromides, electrochemical techniques, such as d.c. polarography and cyclic voltammetry have been chosen to understand their reduction mechanism in non-aqueous media. Experimental details of this report are given in our earlier report<sup>4</sup>.

## Results and Discussion

Two waves/peaks are obtained for the reduction of substituted phenacyl bromides in 50% DMF-water mixtures in all the supporting electrolytes studied. Typical cyclic voltammogram for the reduction of *p*-methoxyphenacyl bromide in acetate buffer of pH 5.5 is given in Fig. 1. The first wave is attributed to the cleavage of C-Br bond and the second one to the reduction of keto group. This is confirmed by the comparison of  $E_p$  or  $E_{1/2}$

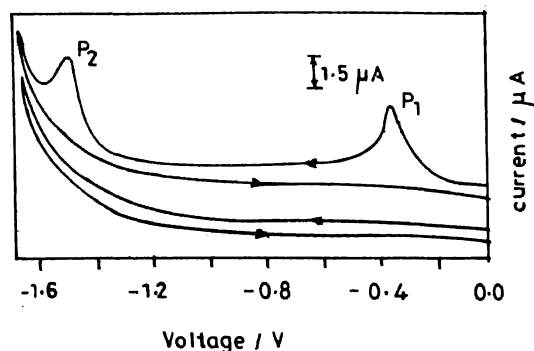


Fig. 1. Typical cyclic voltammogram for the reduction of *p*-methoxyphenacyl bromide in acetate buffer of pH 5.5; concn : = 0.5 mM, solvent : 50% DMF, scan rate = 40 mV s<sup>-1</sup>.

of the second wave with that of the keto group in the corresponding acetophenone which is found to coincide. In all the compounds studied, the shift of  $E_{1/2}$  of the first wave corresponding to the reduction process of C-Br bond towards negative side with increase of substrate concentration and similarly  $E_p$  values of the first peak corresponding to the reduction of C-Br bond with increase of pH (Table 1) indicate that the electron transfer is irreversible. This is also supported by the absence

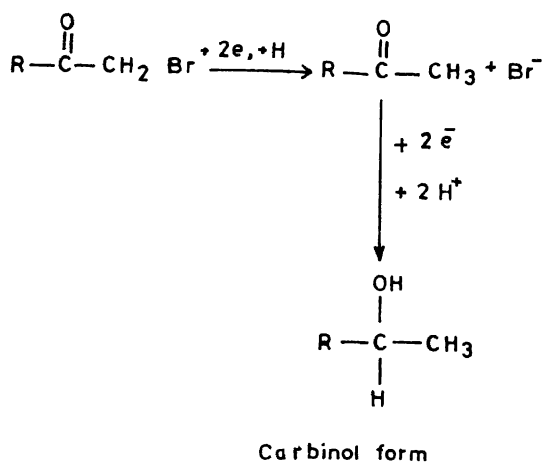
TABLE 1— COMPARISON OF  $E_p$  VALUES OF SUBSTITUTED PHENACYL BROMIDES\*

Sl no	Supporting electrolyte	$-E_p/V$ vs Ag/AgCl (s), $Cl^-$ electrode				
		<i>p</i> -Phenylphenacyl bromide (0.5 mM)	<i>p</i> -Methoxyphenacyl bromide (1.0 mM)	<i>m</i> -Nitrophenacyl bromide (0.2 mM)	<i>m</i> -Methoxyphenacyl bromide (1.0 mM)	<i>p</i> -Methylphenacyl bromide (1.0 mM)
1	Acetate buffer of pH 5.5	0.19	0.30	0.08	0.34	0.30
2	Acetate buffer of pH 6.7	0.32	0.31	0.13	0.33	0.32
3	Ammonia buffer of pH 8.2	0.23	0.33	0.19	0.34	0.37
4	0.1 M $LiClO_4$ solution	0.32	0.44	0.23	0.36	0.44

\*Data from C-Br reduction

of anodic peak in the reverse scan of the cyclic voltammogram.

It is also found that the reductive cleavage of carbon-halogen bond is diffusion-controlled and adsorption free in the supporting electrolytes studied as seen from  $i_d$  vs  $C$  and  $i_d$  vs  $h^{1/2}$  plots. The number of electrons involved in the reduction process of C-Br bond and keto group is calculated to be two each from millicoulometric results. A plausible general electrochemical reduction mechanism is proposed based on the results obtained (Scheme 1).



R = Substituted benzene ring of phenacyl bromide  
Scheme 1

Nuclear substitution is seen to have no noticeable effect on the reduction of C-Br bond since it is far away from it. But the ease of reduction of keto group is found to follow the order: *m*-nitro > *p*-methyl > *p*-methoxy > *m*-methoxy > *p*-phenylphenacyl bromide, their half-wave potentials being -1.44, -1.47, -1.48, -1.49 and -1.50 V respectively, in ammonia buffer of pH 8.2 at 0.5 mM concentration. The above conclusion also agrees with the inductive effect offered by the substituents on the reduction of keto group in the substrate molecule.

**Kinetic parameters:** The kinetic parameters such as transfer coefficient ( $\alpha$ ), diffusion coefficient ( $D$ ) and heterogeneous forward rate constant ( $k_{f,h}^0$ ) values have been evaluated (Table 2). The diffusion coefficients are, in general, found to be fairly constant for each compound in all the supporting electrolytes studied. With the increase of pH of the medium, the  $k_{f,h}^0$  values are found to decrease as expected due to the non-availability of  $H^+$  ions in all the supporting electrolytes taken. Diffusion coefficients and forward rate constants are, in general, found to be less in the case of cyclic voltammetry probably due to the adsorption complications observed on the surface of hanging mercury drop electrode

TABLE 2- TYPICAL KINETIC PARAMETERS OF SUBSTITUTED PHENACYL BROMIDES IN ACETATE BUFFER OF pH 6.7\*

Solvent : 50% DMF

Sl. no.	Compd.	$\alpha_{1a}$		$D \times 10^6$ (cm <sup>2</sup> s <sup>-1</sup> )		$k_{f,h}^0$ (cm s <sup>-1</sup> )	
		DCP	CV	DCP	CV	DCP	CV
1.	<i>p</i> -Phenylphenacyl bromide	1.21	1.37	0.91	0.57	$2.44 \times 10^{-4}$	$9.05 \times 10^{-6}$
2.	<i>p</i> -Methoxyphenacyl bromide	0.25	0.60	1.64	0.63	$2.81 \times 10^{-3}$	$2.75 \times 10^{-7}$
3.	<i>m</i> -Nitrophenacyl bromide	1.23	1.20	1.11	0.56	$0.92 \times 10^{-1}$	$2.21 \times 10^{-5}$
4.	<i>m</i> -Methoxyphenacyl bromide	1.52	1.60	0.85	0.52	$1.09 \times 10^{-2}$	$7.87 \times 10^{-8}$
5.	<i>p</i> -Methylphenacyl bromide	0.98	0.68	6.30	0.80	$2.81 \times 10^{-3}$	$9.69 \times 10^{-8}$

\*Data from C-Br reduction; DCP = DC polarography, CV = cyclic voltammetry.

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