

# Voltammetric Reductions of some Substituted-phenacyl Bromides

K. M. RAO and S. JAYARAMA REDDY\*

Department of Chemistry, S. V. University, Tirupati-517 502

Manuscript received 11 February 1988, accepted 6 April 1988

Substituted-phenacyl bromides, such as *m*-nitro, *p*-phenyl, *p*-methyl, *p*-methoxy and *m*-methoxyphenacyl bromides have been reduced electrochemically at dropping mercury electrode and hanging mercury drop electrode using d.c. polarography and cyclic voltammetry in 50% (v/v) ethanol-water and DMF-water mixtures. Comparative account of their reduction behaviour in different buffer systems is discussed. The effect of solvent on the reduction process and the possible general reduction mechanism are discussed. The kinetic parameters, such as diffusion coefficients and forward rate constant values have been evaluated and reported.

SYSTEMATIC studies on electrochemical reduction of compounds involving carbon-halogen linkage have been carried out by Elving<sup>1</sup> and Wawzonek<sup>2,3</sup> and reviewed critically by others<sup>4-7</sup>. The ease of reductive dehalogenation of simple monohaloalkyl halides is in the order, R-I > R-Br > R-Cl and tertiary R-X > secondary R-X > primary R-X. In polyhalomethyl groups, such as X<sub>3</sub>C or X<sub>2</sub>CR, the fission of carbon-halogen bond takes place in a stepwise manner. The fission of the first C-X bond will be easier than the remaining C-X bonds, with C-F<sub>3</sub> being an exception. 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>8,9</sup>. As a part of our earlier work<sup>10</sup> on substituted-phenacyl bromides, *m*-nitro-, *p*-phenyl-, *p*-methyl-, *p*-methoxy- and *m*-methoxyphenacyl bromides have been selected for the present study employing d.c. polarographic and cyclic voltammetric techniques. Ethanol-water (1:1) and DMF-water (1:1) mixtures were used as solvents in the pH range 1.5-10.0.

## Experimental

All the compounds were prepared by the direct bromination of the corresponding acetophenones<sup>11</sup> in 1:2 dioxane-ether mixture. The compounds were recrystallised several times from ethanol. The purity of the sample was tested by the sharp melting points. The test solutions were prepared by dissolving the required quantity of the substance in ethanol and DMF as the case may be and made up with the supporting electrolyte to get the desired concentration. AnalaR grade samples were used for the preparation of the supporting electrolytes in double-distilled water. The test solution was deoxygenated by passing purified nitrogen gas and then voltammograms were taken. All the experiments were carried out at 28 ± 1°. The voltammo-

grams were taken on the day of the preparation of the solutions.

D.c. polarograms were taken by polarographic Analyzer 364 (PARC) coupled with BD8 Kipp & Zonen recorder. Cyclic voltammograms were obtained by Metrohm E 506 polarecord coupled with E 612 VA scanner using model 2000 X-Y/t digigraphic recorder. The dropping mercury electrode (flow rate, 2.444 mg s<sup>-1</sup>) was used as working electrode and saturated calomel electrode as reference electrode in d.c. polarography. The hanging mercury drop electrode of area 0.02704 cm<sup>2</sup> was used as working electrode and Ag/AgCl(s), Cl<sup>-</sup> electrode as reference electrode in cyclic voltammetry. A Elico digital pH meter was used for pH measurements.

## Results and Discussion

**Polarographic study:** Two waves are observed for the reduction of *p*-phenyl-, *p*-methyl-, *p*-methoxy- and *m*-methoxyphenacyl bromides where the first wave is attributed to the cleavage of C-Br bond and the second one due to the reduction of keto group. This is confirmed by the comparison of  $E_{1/2}$  value of the second wave with that of the keto group in the corresponding acetophenone which was found to coincide. In the case of *m*-methoxyphenacyl bromide, two waves are obtained which are due to the reduction of C-Br bond and keto groups, respectively (Fig 1). A large maximum is observed for the reduction wave of C-Br bond in alcoholic medium in all the compounds which is suppressed by the addition of 0.002% Triton X-100. However, in DMF medium, no such maximum is observed. In all the compounds, with increasing concentration, the half-wave potential of the C-Br wave is found to increase towards negative side which indicates the irreversible nature of the electron transfer in the reduction process. The reduction process of C-Br

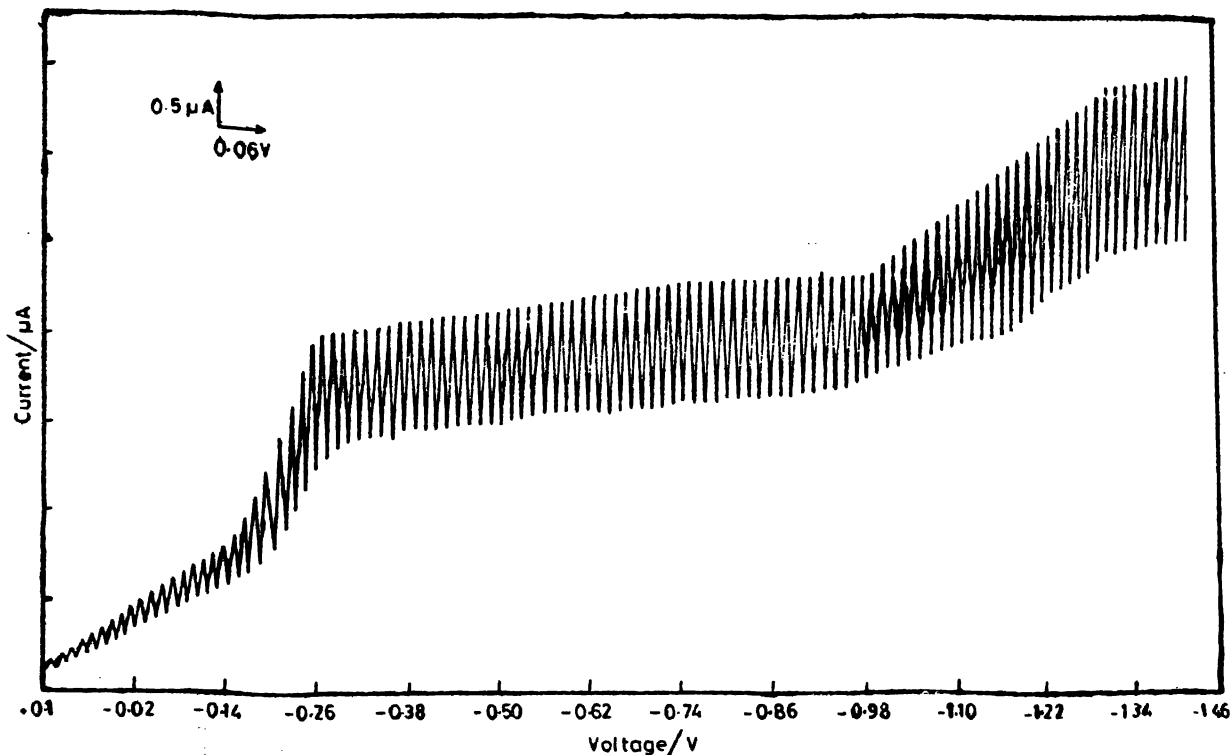


Fig. 1. Typical d.c. polarogram for reduction of *m*-nitrophenacyl bromide; supporting electrolyte = acetate buffer of pH 5.5, concn. = 1.0 mM, solvent = 20% ethanol, drop time = 3 s.

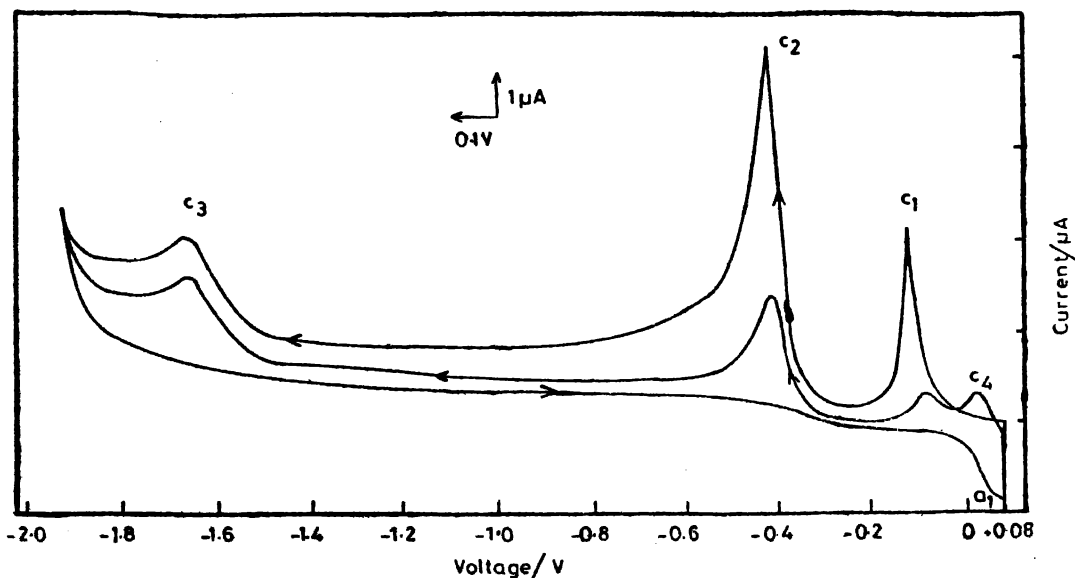


Fig. 2. Typical cyclic voltammogram run for the reduction of *m*-nitrophenacyl bromide; supporting electrolyte = acetate buffer of pH 5.5, concn. = 0.1 mM, solvent = 20% ethanol, scan rate = 40 mV s<sup>-1</sup>.

bond is found to be diffusion-controlled and adsorption-free as can be seen from the linear plots of  $i_a$  vs  $C$  and  $i_a$  vs  $\sqrt{t}$  passing through the origin.

**Cyclic voltammetric study:** As in d.c. polarography, two peaks are obtained for all the com-

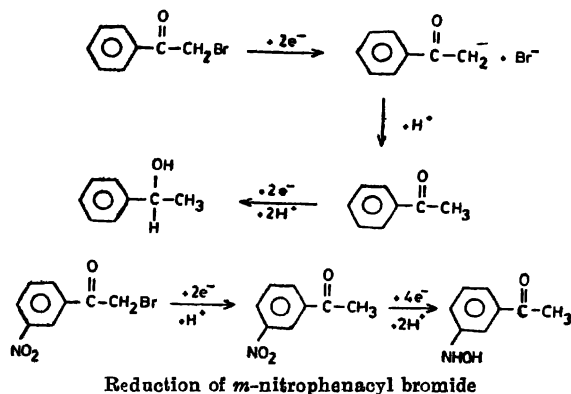
pounds, viz. *p*-phenyl-, *p*-methoxy- and *m*-methoxyphenacyl bromides except in *p*-methylphenacyl bromide where the second peak is found to merge with hydrogen evolution. In all the compounds, the first peak is attributed to the reduction of C-Br bond and the second peak to the reduction of keto

group. In the case of *m*-nitrophenacyl bromide, three peaks ( $C_1$ ,  $C_2$  and  $C_3$ ) are obtained (Fig. 2) which may be due to the reduction of C-Br bond, nitro and keto groups, respectively. When the scan is reversed after crossing the potential at  $C_2$ , an anodic peak ( $a_1$ ) is obtained at more positive potential than  $C_1$ . Hence, this  $a_1$  is probably due to the oxidation of the reduction product obtained at  $C_2$ . This redox couple  $C_2$  and  $a_1$  is found to exhibit the quasi-reversible nature as seen from the separation of their peak potentials.

In general, the reductive cleavage of C-Br bond in all the compounds is found to be irreversible due to the fact that with the increase of scan rate the  $E_p$  values are found to increase towards negative side. The reduction process of C-Br bond is also found to be adsorption-free in all the compounds except in the case of *m*-nitrophenacyl bromide where slight adsorption complications are noticed from  $i_p$  vs  $v^{1/2}$  plots.

**Evaluation of number of electrons :** The number of electrons involved in the reduction process of C-Br bond in all the compounds is worked out as two from the results of millicoulometric experiments. Similarly, for *m*-nitrophenacyl bromide, four electrons are involved in the reduction of nitro group to give the hydroxylamine. Controlled potential electrolysis results indicate that the product obtained at the potential of C-Br wave or peak to be the corresponding acetophenone. From the comparison of peak currents of C-Br peak with those of keto group, it is found that the reduction process of keto group also involves two electrons in all the media studied in general.

**Mechanism of electrode process :** The general electrochemical reduction mechanism for all the substituted phenacyl bromides studied may be proposed as follows.



The nuclear substitution (*p*-phenyl, *p*-methoxy, *p*-methyl, *m*-nitro, and *m*-methoxy) is seen to have no noticeable effect on the ease of reduction of the C-Br bond in phenacyl bromides. This may be due to the fact that the C-Br bond is two carbon atoms away from the benzene nucleus which considerably weakens the expected mesomeric and/or inductive effect of the nuclear substituent. The cleavage of C-Br bond, in general, is found to be facile in all the compounds, apparently due to the presence of carbonyl group adjacent to the C-Br bond. On the other hand, the substituent effect is noticeable on the keto group reduction. The ease of reduction of keto group follow the order, *p*-phenyl- > *p*-

 TABLE 1—COMPARISON OF  $E_p$  VALUES OF SUBSTITUTED-PHENACYL BROMIDES

Solvent=50% ethanol, scan rate=40 mV s<sup>-1</sup>  
(Data from C-Br reduction)

Supporting electrolyte	- $E_p/V$ vs Ag/AgCl (s), Cl <sup>-</sup> electrode				
	<i>p</i> -Phenylphenacyl bromide 0.5 mM	<i>p</i> -Methylphenacyl bromide 0.5 mM	<i>p</i> -Methoxyphenacyl bromide 1.0 mM	<i>m</i> -Methoxyphenacyl bromide 1.0 mM	<i>m</i> -Nitrophenacyl bromide 2 mM
Acetate buffer, pH 5.5	0.23	0.28	0.15	0.11	0.08
Acetate buffer, pH 6.7	0.32	0.29	0.21	0.17	0.09
Ammonia buffer pH 8.2	0.34	0.39	0.21	0.18	0.16
0.1 M LiClO <sub>4</sub> solution	0.42	0.40	0.30	—	0.31

TABLE 2—TYPICAL KINETIC PARAMETERS FOR SUBSTITUTED-PHENACYL BROMIDES IN ACETATE BUFFER OF pH 5.5

Solvent=50% ethanol,  
(Data from C-Br reduction)

Compd.	$\alpha n_a$		$D \times 10^6$ cm <sup>2</sup> s <sup>-1</sup>		$k_p^h$ cm s <sup>-1</sup>	
	D.O.P.	C.V.	D.O.P.	C.V.	D.O.P.	C.V.
<i>p</i> -Phenylphenacyl bromide	1.61	0.96	4.56	4.06	$1.36 \times 10^{-2}$	$3.56 \times 10^{-6}$
<i>p</i> -Methoxyphenacyl bromide	1.98	1.20	4.21	7.23	$1.11 \times 10^{-1}$	$1.01 \times 10^{-7}$
<i>p</i> -Methylphenacyl bromide	0.96	0.96	2.71	4.97	$1.33 \times 10^{-1}$	$3.65 \times 10^{-9}$
<i>m</i> -Nitrophenacyl bromide	1.62	0.96	2.70	1.80	—	$8.15 \times 10^{-6}$
<i>m</i> -Methoxyphenacyl bromide	1.44	1.2	4.44	3.35	$14 \times 10^{-1}$	$6.11 \times 10^{-8}$

D.O.P.=D c. polarography, C.V.=Cyclic voltammetry.

methoxy- > *m*-nitro- > *p*-methoxy- > *p*-methyl-phenacylbromides. With increase in the solvent composition the  $E_p$  or  $E_{1/2}$  values are noticed to increase towards negative side which may probably be due to the adsorption of solvent molecules on the electrode surface<sup>12</sup>. A comparative account of half-wave potentials for C-Br reduction with increase in pH of the medium is given in Table 1.

**Kinetic parameters:** The kinetic parameters like transfer coefficient, diffusion coefficient and heterogeneous forward rate constant values have been evaluated for all the compounds. Diffusion coefficient values are found to be in satisfactory agreement in both the techniques for all the compounds. With increase of pH of the medium, the forward rate constant values are noticed to decrease as expected. Typical  $\alpha_n$ ,  $D$  and  $k_{f,h}^0$  values obtained in acetate buffer of pH 5.5 are presented in Table 2.

#### Acknowledgement

The authors are grateful to C.S.I.R., New Delhi for financial assistance.

#### References

1. P. J. ELVING, *Record. Chem. Prog.*, 1953, **14**, 99.
2. S. WAWZONEK, *Anal. Chem.*, 1956, **28**, 688.
3. S. WAWZONEK, *Anal. Chem.*, 1958, **30**, 661.
4. M. R. RIFI in "Organic Electrochemistry", ed. M. M. BAIZER, Marcel Dekker, New York, 1973, Chap. VI.
5. M. R. RAFI in "Techniques of Electroorganic Synthesis", ed. N. L. WEINBERG, Wiley, New York, 1975, Part II, pp. 170-191.
6. W. J. SETTINERI and L. D. MCKEEVER in "Techniques of Electroorganic Synthesis", ed. N. L. WEINBERG, Wiley, New York, 1975, Part II, Chap. X.
7. J. CASANOVA and L. EBERSON in "The Chemistry of Carbon-Halogen Bond", ed. S. PATAI, Wiley, New York, 1973, Part II, Chap. 15.
8. P. J. ELVING and R. VAN ATTA, *Anal. Chem.*, 1965, **27**, 1908.
9. P. J. ELVING and J. T. LEONE, *J. Am. Chem. Soc.*, 1960, **82**, 5076.
10. A. S. REDDY and S. J. REDDY, *J. Indian Chem. Soc.*, 1986, **63**, 752.
11. M. I. SHERVCHUK and A. V. DOMBROVSKII, *Zh. Obshch. Khim.*, 1963, **33**, 1135.
12. K. GANAPATHI and M. RAMANUJAM, *Indian J. Chem., Sect. A*, 1982, **21**, 1031.