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Electrochemical Reduction of p-Methylphenacyl Bromide

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The electrochemical reduction of carbon-bromine bond in p-methylphenacyl bromide has been studied employing d.c. polarographic and cyclic voltammetric techniques in 50% (v/v) DMF-water and ethanol-water mixtures. The effect of solvent and the nuclear substitution on the reduction of C-Br bond is discussed. Diffusion coefficient and forward rate constant values are evaluated and reported. The possible electrochemical reduction mechanism is proposed.

INTRODUCTION

In continuation of our earlier work on substituted phenacyl bromides[1-6], p-methylphenacyl bromide has been chosen for the present study. The ease of reduction of C-Br bond in α-haloketones is facile when compared to the analogous normal halides. The reduction of phenacyl bromides is found to be complicated by the appearance of maxima, hydrolysis, etc.[7] The presence of keto group adjacent to the C-Br bond facilitates C-Br cleavage in α-haloketones. In the present investigation d.c. polarographic and cyclic voltammetric techniques are employed for the study of the title compound.

EXPERIMENTAL

The title compound was prepared by the bromination[8] of p-methylacetophenone supplied by Ega Chemie, West Germany. The bromination was carried out in equimolar quantities in 2 : 1 ether-dioxan mixture at 15–20°C. The reaction mixture was stirred for two hours and then the ethereal layer was separated and evaporated under vacuum. The product was recrystallised from alcohol and the melting point was found to be 50.5°C (lit., 51°C)[8]. The solution was prepared by dissolving the required quantity of the substance in the solvent and made up with the supporting electrolyte to get the desired concentration. AnalaR grade chemicals were used for the preparation of the supporting electrolytes in double distilled water. The test solution was deoxygenated and then voltammograms were obtained. All experiments were carried out at 28 ± 1°C. The voltammograms were taken on the day of the preparation of the solution.

D.C. polarograms were taken by Polarographic Analyzer Model 364 (PARC) using BD8 Kipp & Zonen Recorder. Cyclic voltammograms were recorded by 'Metrohm' unit Model E 506 Polarecord coupled with E612VA Scanner using model 2000 X-Y/t Digigraphic Recorder. The dropping mercury electrode of flow rate 2.444 mg/s was used as working

electrode while saturated calomel electrode was used as reference electrode in d.c. polarography. The hanging mercury drop electrode of area 0.02704 cm^2 was used as working electrode and Ag/AgCl(S), Cl^- electrode as reference electrode in cyclic voltammetry. Elico Digital pH meter was used for pH measurements.

RESULTS AND DISCUSSION

1. D.C. Polarographic Results

Two waves were observed for the reduction of p-methylphenacyl bromide over a pH range from 1.5 to 10.0 in d.c. polarography. But well-defined waves are not obtained in acidic and basic media. A typical d.c. polarogram obtained in acetate buffer of pH 5.5 is shown in Fig. 1, where

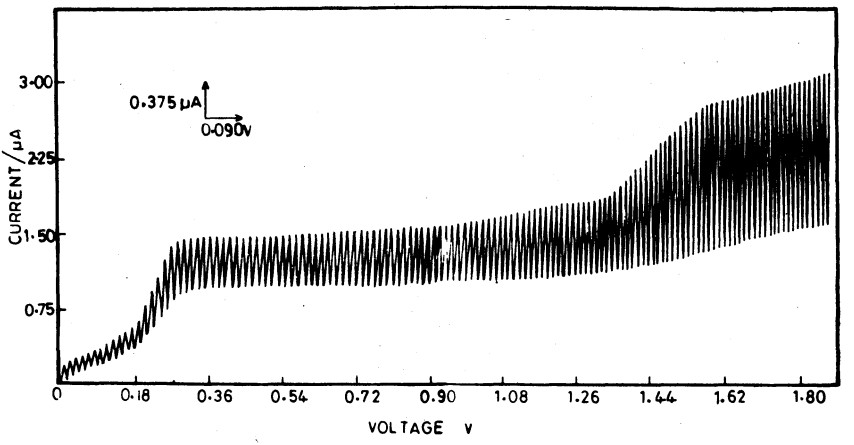


Fig. 1. Typical d.c. polarogram for the reduction of p-methylphenacyl bromide—Supporting electrolyte: Acetate buffer of pH 6.7; Concentration: 0.5 mM; Solvent: 5% DMF; Drop time: 3 sec.

the two waves appeared at −0.225V and −1.53V vs. SCE respectively. The first wave is attributed to the reduction of C-Br bond since the $E_{1/2}$ of second wave is found to coincide with that of the reduction wave of the keto group in p-methylacetophenone. The large maxima obtained for the reduction of C-Br bond in ethanolic medium was suppressed by the addition of 0.001% solution of Triton X-100. The reduction of C-Br is observed only in neutral media whereas the keto group is reduced in all the media studied. The reduction process of C-Br bond is found to be diffusion controlled and adsorption free as evidenced by the linear plots of i_d vs. C and i_d vs. $h^{1/2}$ passing through the origin. The electron transfer in the reduction process of C-Br bond is noticed to be irreversible as can be seen from the log-plot analyses, disobedience of Tome's criterion and dependence of half-wave potential on the concentration of the depolariser. Typical kinetic data are calculated and reported in Table 1.

2. Cyclic Voltammetric Results

As in d.c. polarography, two cathodic peaks were obtained for the reduction of p-methylphenacyl bromide out of which the first peak may be due to the reduction of C-Br bond and the second one may be due to the reduction of keto group. The second peak was found to merge with hydrogen evolution in all the supporting electrolytes. A typical cyclic voltammogram in acetate buffer of pH 5.5 in DMF-Water mixture is shown in Fig. 2. Well defined peaks were observed in DMF medium. The reduction of C-Br bond is found to be diffusion controlled and adsorption free

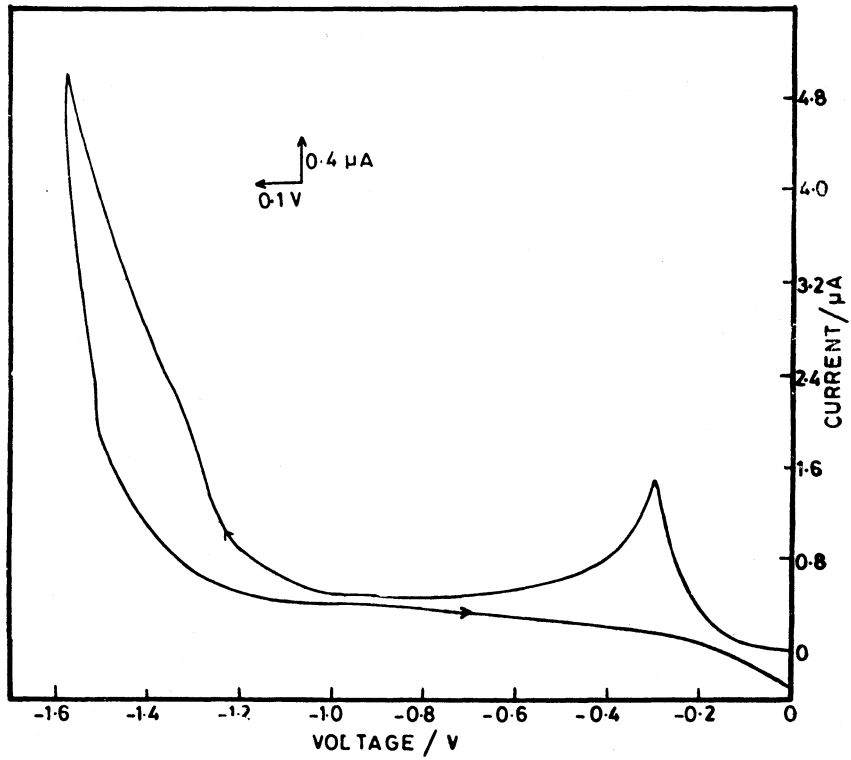


Fig. 2. Typical cyclic voltammogram for the reduction of p-methylphenacyl bromide—Supporting electrolyte: Acetate buffer of pH 5.5; Concentration: 0.5 mM; Solvent: 50% DMF; Scan rate: 40 mV S^{-1}.

in all the media except in Clarks and Lubs buffer of pH 1.5 where slight adsorption complication due to reactant was observed as evidenced by the i_p vs. $v^{1/2}$ plots. The electron transfer in the process of C-Br cleavage is found to be irreversible as seen from the shift of peak potential towards negative side and absence of anodic peak in the reverse scan. Typical kinetic data are evaluated and reported in Table 2.

TABLE 1

TYPICAL D.C. POLAROGRAPHIC DATA OF P-METHYLPHENACYL BROMIDE (C-Br bond reduction)

Concentration: 0.5 mM; Drop time: 3 sec

Sl. No.	Supporting electrolyte	$-E_{1/2}/V$	$i_d/\mu A$	dn_a	$D\times10^6/cm^2\ s^{-1}$	$k^0_{f,h}/cms^{-1}$
1.	Clarks and Lubs bufier pH 1.5	Ill-defined waves				
2.	Acetate buffer pH 5.5	(a) 0.128	2.9	0.96	20.71	1.33×10^{-1}
		(b) 0.140	2.0	1.11	9.85	1.06×10^{-1}
3.	Acetate buffer pH 6.7	(a) 0.212	2.3	1.12	13.02	5.51×10^{-3}
		(b) 0.216	1.6	0.98	6.30	2.81×10^{-3}
4.	Ammonia buffer pH 8.2	(a) 0.210	2.2	1.25	11.92	6.74×10^{-3}
		(b) 0.186	1.8	1.35	7.97	2.19×10^{-2}
5.	Carbonate buffer pH 10.0	Ill-defined waves				
6.	0.1 M $LiClO_4$ solution	(a) 0.30	2.5	1.02	15.39	1.62×10^{-4}
		(b) 0.33	1.7	0.98	7.11	3.84×10^{-5}

(a) 50% ethanol (b) 50% DMF

TABLE 2

TYPICAL CYCLIC VOLTAMMETRIC DATA OF P-METHYLPHENACYL BROMIDE (C-Br reduction)

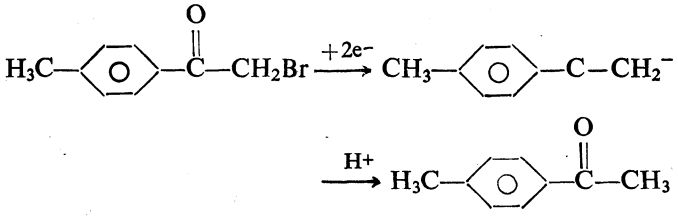
Concentration: 0.5 mM; Scan rate: 40 mVS^{-1}

Sl. No.	Supporting electrolyte	$-E_p/V$	$i_p/\mu A$	αn_a	$D\times10^6/cm^2\ s^{-1}$	$k^0_{f,h}/cms^{-1}$
1.	Clarks and Lubs buffer pH 1.5	(a) 0.19	1.98	0.60	2.42	2.41×10^{-4}
		(b)	ill-defined peaks			
2.	Acetate buffer pH 5.5	(a) 0.28	3.36	0.96	4.37	3.65×10^{-8}
		(b) 0.30	1.32	1.20	0.53	4.12×10^{-10}
3.	Acetate buffer pH 6.7	(a) 0.29	1.12	0.80	0.58	5.10×10^{-8}
		(b) 0.32	1.0	0.68	0.80	9.68×10^{-8}
4.	Ammonia buffer pH 8.2	(a) 0.39	2.4	0.80	3.34	5.43×10^{-9}
		(b) 0.37	0.68	0.96	0.18	2.61×10^{-10}
5.	Carbonate buffer pH 10.0	(a) 0.30	0.72	0.96	0.20	3.78×10^{-9}
		(b)	No reduction is observed			
6.	0.1 M $LiClO_4$ solution	(a) 0.40	1.32	0.68	1.40	1.53×10^{-8}
		(b) 0.44	1.20	0.68	1.15	4.84×10^{-9}

(a) 50% Ethanol (b) 50% DMF

From the results thus obtained, it is seen that the reduction process of C–Br bond involves an irreversible two-electron addition. Methyl substituent is found to have no noticeable effect on the cleavage of C–Br bond. This may be because the substituent is two carbon atoms away from the C–Br bond. D.C. polarographic diffusion coefficient values are considered as more reliable since no adsorption complications are observed on the dropping mercury electrode. The forward rate constant values are found to decrease slightly with increase of pH as expected. With the increase in solvent composition in the solution, the $E_{1/2}$ values are found to increase towards negative side indicating the reduction process to be difficult which may be due to the possible adsorption of solvent molecules on the electrode surface[9].

From controlled potential electrolysis results, the product at the potential of the first wave was found to be p-methylacetophenone. Millicoulometric results also indicate that the number of electrons involved in the reduction process of C–Br bond is two. From polarographic results, on comparing the diffusion current values of C–Br bond and keto group, the number of electrons involved in the reduction of keto group is found out to be two. Hence, the reduction mechanism for p-methylphenacyl bromide may be proposed as follows :



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REFERENCES

1. A. Sivarami Reddy, S. Jayarama Reddy and V. R. Krishnan, *Trans. SAEST*, **17**, 241 (1982).
2. A. Sivarami Reddy and S. Jayarama Reddy, *J. Indian Chem. Soc.*, **63**, 752 (1986).
3. ———, *J. Electrochem. Soc. India*, **33**, 125 (1984).
4. ———, *Indian J. Chem.*, **22A**, 777 (1983).
5. ———, *Trans. SAEST*, **19**, 269 (1984).
6. ———, *J. Electrochem. Soc. India*, **33**, 129 (1984).
7. M. I. Shevchuk and A. V. Dombrovskii, *Zh. Obshch. Khim.*, **33**, 1135 (1963).
8. P. J. Elving and J. T. Leone, *J. Amer. Chem. Soc.*, **82**, 5076 (1960).
9. K. Ganapathi and M. Ramanujam, *Indian J. Chem.*, **21(A)**, 1031 (1984).

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