CYCLIC VOLTAMMETRIC STUDIES ON THE ELECTROREDUCTION OF PEROXIDES IN APROTIC MEDIA

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Cyclic voltammetric studies on the reduction of di-t- butylperoxide (t-BuOOBu-t) and t-butylhydroperoxide (t-BuOOH) have been carried out in three dipolar aprotic solvents, namely, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO) and acetonitrile (AN), at a glassy carbon (gc) electrode. A single irreversible peak corresponding to a two-electron reduction of these peroxides to the corresponding alkoxides, is observed in each of the three solvents. The values of voltammetric peak potentials are compared in the three solvents. The reduction is observed to be diffusion limited for lower concentrations and adsorption limited at higher concentrations of the peroxide. Cyclic voltammetry is found useful for quantitative estimation of these peroxides with ± 1% accuracy, upto 10^{-4} M concentration.

Keywords: Di-t-butylperoxide, t-Butylhydroperoxide, cyclic voltammetry and aprotic media.

INTRODUCTION

The important classes of peroxides include dialkyl, diaryl and diacyl peroxides, alkyl or aryl hydroperoxides and ozonides. Several of these peroxides are used as polymerisation initiators, as intermediates in the combustion of gasoline and in the air oxidation of many organic compounds [1,2]. Newer methods of synthesising peroxides including by electrochemical means, are gaining importance [3]. However, most electrochemical studies on the peroxides are restricted to their polarographic behaviour. In aqueous media, the electrochemical reduction of peroxides occurs in a single, irreversible, two electron step, to the alcohol.

$$ROOR' + 2e^- + 2H^+ \longrightarrow 2ROH \ (R = alkyl, \ R' = alkyl \ or \ H)$$
$$(1)$$
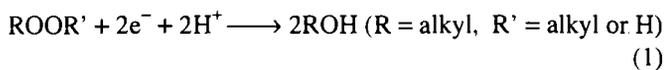
Strength of O-O bond is affected by the mode of substitution. Electron donating substituents increase whereas electron withdrawing substituents diminish the electron density in the O-O bond and accordingly a higher or lower $E_{1/2}$ is observed. Polarographic studies in aprotic media have shown that a single electron transfer occurs, to yield the peroxide radical which is further reduced to the alcohol in presence of proton

donors like phenol. Di-t-butylperoxide is reported to be reduced at -2.5 V versus SCE at 0.2 Vs^{-1} by cyclic voltammetry at a gc electrode, in DMF medium, with the position and shape of the voltammogram being unaffected by the addition of acids stronger than t-BuOH. Controlled potential electrolysis of di-tertiary butyl peroxide in DMF and AN lead to the consumption of two Faraday per mole [4]. Polarographic estimation upto 10^{-4} M concentration (with 1-2% accuracy) and 10^{-6} M concentration (with 10% accuracy) has been reported for organic peroxides [2].

In view of the importance of peroxides in general and due to very few available reports on their electrochemical behaviour, the present work was taken up, which reports the results of cyclic voltammetric studies carried out on the relatively stable peroxides, di-t-butyl peroxide and t-butyl hydroperoxide, in DMF, DMSO and AN at a gc electrode.

EXPERIMENTAL

Di-t-butylperoxide and tetrabutyl ammonium perchlorate employed in the present investigation were from Aldrich and 80% t-butylhydroperoxide in di-t-butylperoxide was from Fluka. They were used without further purification. Stock solutions of the peroxides in the corresponding solvents were

prepared from which suitable amounts were taken for preparing required concentrations of the peroxides. Studies on di-t-butylperoxide were carried out in the concentration range of 0.5 to 30 mM and that on t-butylhydroperoxide in di-t-butyl peroxide, in the range of 0.5 to 115 mM.

Cyclic voltammograms were recorded in DMF, DMSO or AN containing 0.1 M n–Bu$_4$NClO$_4$, in a conventional three electrode cell with gc as working electrode, aqueous SCE as reference and Pt as counter electrode. Other details are given in a previous communication [5].

RESULTS AND DISCUSSION

Typical cyclic voltammograms recorded for the reduction of di-t- butylperoxide and t-butylhydroperoxide in DMF,DMSO and AN at a representative concentration are shown in Figs. 1(Ia, b and c and IIa, b and c). It can be seen that in

general, the peaks are well defined and both the peroxides are reduced at a highly negative potential in an irreversible, single, two-electron step to the alkoxide, resulting from the O-O bond cleavage, as follows:

$$t-BuOOBu-t + 2e^- \longrightarrow 2t-BuO^- \quad (2)$$

$$t-BuOOH + 2e^- \longrightarrow t-BuO^- + OH^- \quad (3)$$
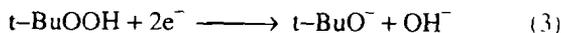
Slow protonation from the solvent supporting electrolyte can take place to yield the alcohol.

For the cyclic voltammograms of t-butylhydroperoxide in each of the three solvents, the peaks were not as sharp as was observed for the reduction of di-t-butyl peroxide because of the immediate rise in currents due to the reduction of di-t-butyl peroxide at a slightly more negative potential (The hydroperoxide is an 80% solution stored in di-t-butyl peroxide). However, the peak current and peak potential values could be accurately calculated.

The plots of the cathodic peak currents ($i_{p,c}$) versus concentration(C) of the two peroxides in DMF, DMSO and AN, are shown in Fig. 2. It can be seen that upto a particular
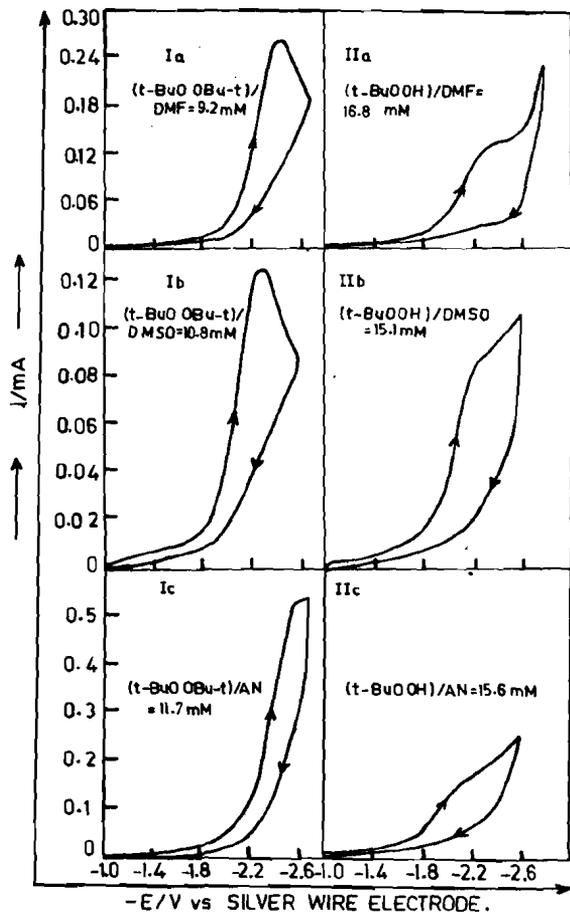

Fig. 1: Typical cyclic voltammograms for the reduction of di-t- butyl peroxide(I) and t-butyl hydroperoxide(II) in DMF,DMSO and AN at a gc electrode at a sweep rate of 0.1 Vs^{-1} (Concentrations are given in the figure)
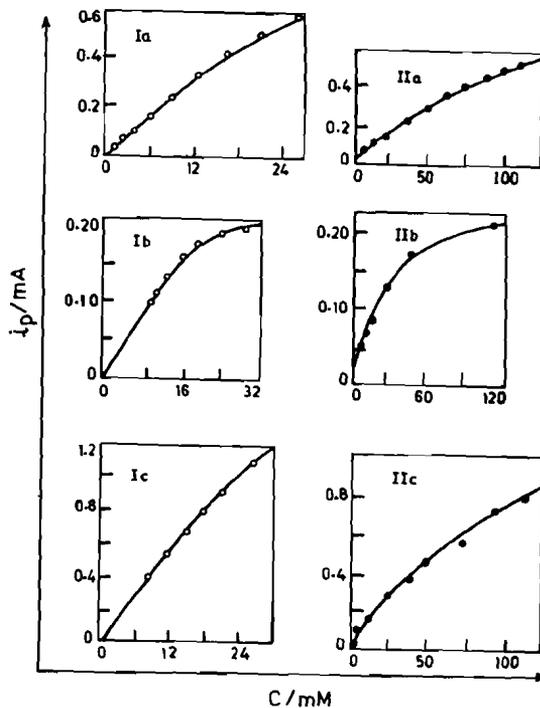

Fig. 2: A plot of i$_{p,c}$/mA versus C(mM) for the reduction of di-t-butyl peroxide and t-butyl hydroperoxide in DMF, DMSO and AN

TABLE I: Cyclic voltammetric cathodic peak potentials ($-E_{p,c}/V$) for the reduction of di-t-butylperoxide and t-butylhydroperoxide at a gc electrode in DMF, DMSO and AN (Sweep rate = 0.1 Vs^{-1})

Solvent	$-E_{p,c}/V$ for t-BuOOBu-t		$-E_{p,c}/V$ for t-BuOOH	
	1 mM	25 mM	1 mM	25 mM
DMF	2.40	2.45	2.32	2.40
DMSO	2.29	2.32	2.22	2.31
AN	2.57	2.58	2.10	2.20

concentration of the peroxides, the i_p–C plot is linear (passing through the origin), showing diffusion-limited behaviour and thereafter, the plot is non-linear, indicating the role of adsorption. This holds good in all the media studied, for both the peroxides, though the concentration upto which linearity persists, varies, depending on the peroxide and the solvent. Cyclic voltammetry is found useful for the quantitative estimation with ± 1% accuracy for 10^{-4} M concentration of these peroxides.

The cathodic peak potentials for the cyclic voltammetric reduction of di-t-butyl peroxide and t-butyl hydroperoxide at two representative concentrations of 1 mM and 25 mM of the peroxide, in the three solvents at a sweep rate of 0.1 Vs^{-1}, are listed in Table I.

CONCLUSION

The following inferences can be drawn from Table I and from the above studies:

* The cathodic peak potentials for both di-t-butylperoxide and t- butylhydroperoxide in each of the three solvents,

namely, DMF, DMSO and AN, are shifted to more negative values, with increase in the concentration of the corresponding peroxide.

* t-BuOOH is reduced more easily (at less negative potentials) as compared to t-BuOOBu-t, at a gc cathode, in each of the three solvents.

* For t-BuOOBu-t, the reduction potential for O-O bond cleavage increases in the order (reduction becomes more difficult): DMSO < DMF < AN.

* For t-BuOOH, the reduction potential for O-O bond cleavage increases in the order (reduction becomes more difficult): AN < DMSO < DMF.

* The O-O bond reduction at a gc electrode, is diffusion limited for lower concentrations and adsorption limited for higher concentrations, of the peroxide.

* Cyclic voltammetry is useful for quantitative estimation of these peroxides with ± 1% accuracy, upto 10^{-4} M concentration.

REFERENCES

1. R D Mair and R T Hall, *Organic Peroxides*, Vol II (D Swern) Wiley Int, New York (1971) 535
2. A J Bard and H Lund, *Encyclopedia of Electrochemistry of the Elements*, Vol XI, Marcel Dekker, Inc New York (1978) 316-328
3. J Yoshida, S Nakatani and S Isoe, *Electroorganic Synthesis*, (Ed) R D lLittle and N L Weinberg, Marcel Dekker, Inc. New York (1991) 166
4. M S Workentin, F Maran and D M Wayner. *J Amer Chem Soc*, **117** (1995) 2120
5. D Vasudevan and H Wendt, *J Electroanal Chem*, **192** (1995) 69