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The use of electrogenerated hypobromite for the phase transfer catalysed oxidation of benzyl alcohols

D. PLETCHER, N. TOMOV

Department of Chemistry, The University, Southampton, UK

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A simple procedure for the oxidation of benzyl alcohols to aldehydes is described. The oxidizing agent is hypobromite generated by the anodic oxidation of aqueous bromide and the reactions are carried out *in situ* in an undivided cell in an amyl acetate/water emulsion containing 2% tetrabutylammonium bisulphate.

1. Introduction

Recently a simple and high yield procedure for the oxidation of benzyl alcohols was described [1]; an aqueous sodium hypochlorite solution was stirred with a solution of the alcohol in ethyl acetate in the presence of a phase transfer catalyst, tetrabutylammonium bisulphate. The reactions were limited to activated alcohols, however, and the reaction time was 30–60 min. In this work the kinetics of such hypohalite oxidations have been studied with a view to increasing the scope of these two-phase oxidations and to finding conditions where the reactions may be coupled to the electrogeneration of the oxidizing agent (i.e. the reaction half-life is a few seconds).

A procedure for the electrogeneration and *in situ* use of hypobromite for the two-phase oxidation of alcohols to aldehydes is described. This is the first report of such an application of phase transfer catalysis in electrosynthesis although Eberson and Helgee [2, 3] have used phase transfer agents to supply the nucleophile for the anodic substitution of aromatic hydrocarbons in methylene chloride/water mixtures.

2. Experimental

The chemicals used in this work were A. R. sodium bromide and sodium bicarbonate, G. P. R. grade amyl acetate, hyamine 2389, cetyltrimethylammonium bromide, 10% aqueous sodium hypochlorite, amyl acetate (all B. D. H. Ltd), tetrabutylammonium bisulphate (Labkemi AB) and distilled water. The alcohols and aldehydes were all obtained from B. D. H. Ltd, Aldrich Chemicals or Koch Light Ltd. All were used without purification.

The cell is shown in Fig. 1. The platinum gauze anode, real area 100 cm^2, was separated from the nickel gauze cathode by 1 cm. The stirrer, 2 cm above the cathode was a four segment propeller made from a 6 cm PTFE disc by cutting four narrow strips at an angle of 45° to the horizontal. The electrolyses at constant current were carried out with a Chemical Electronics 20/20 A potentiostat.

All quantitative analyses were carried out by g. l. c. using a Perkin Elmer F17 instrument and a 2 m column of 4% XE 60 silicon oil on chromosorb W (80–100 mesh); typically the column temperature was programmed between 75 and 160° C to obtain good separation. Products were identified both by comparison of retention times with available standards and by g. l. c./mass spectroscopy run on a Pye 104/AEI MS 12 instrument.

3. Results and discussion

Using g. l. c. to monitor the consumption of the substrate and the formation of benzaldehyde, the kinetics of the two-phase reaction between benzyl alcohol in amyl acetate and aqueous sodium hypochlorite was investigated as a function of the reaction conditions; the results of these experiments are summarized in Table 1. In all cases the reactions were carried out in an enclosed beaker

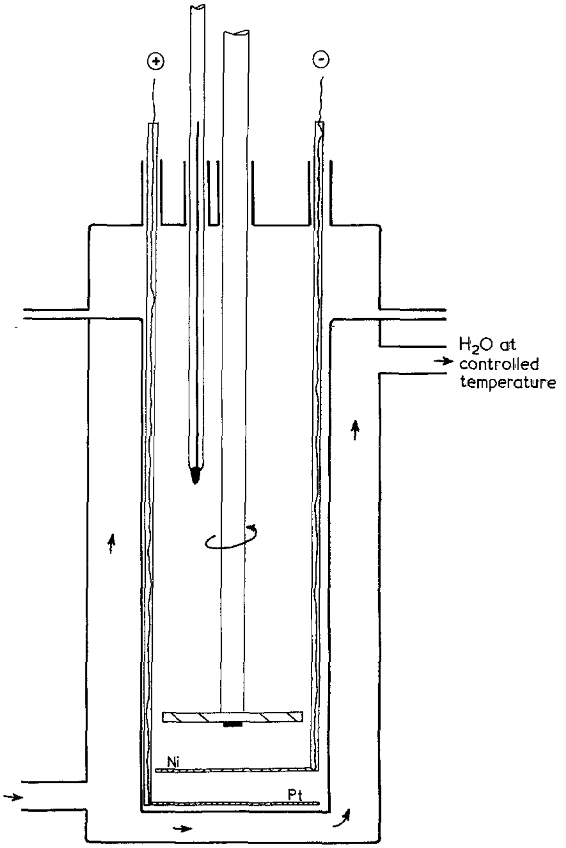

Fig. 1.

with an efficient propeller shaped stirrer. It can be seen that the phase transfer catalyst is essential in order to carry out the reaction at a reasonable rate, that tetrabutylammonium ion is the best of the phase transfer catalysts employed and that the rate of reaction increases markedly with its concentration. In addition the rate of reaction may be increased by the use of a higher temperature and the addition of bromide ion. This latter factor is due to the intermediate formation of hypobromite which is known to react more rapidly than hypochlorite with many species [4].

On the basis of these data the oxidation of four alcohols were studied under the following conditions where the reactions should be rapid; 40 mmol of alcohol in 30 ml of amyl acetate was stirred with 30 ml of 10% aqueous sodium hypochlorite containing sodium bromide (7 g) and tetrabutyl ammonium bisulphate (2 g) at 70° C. With benzyl alcohol and *p*-methylbenzyl alcohol the conversion to the aldehydes was quantitative and complete after 2 min but with 2-phenylethanol and 2-*p*-chlorophenylethanol the reactions were continued for 30 min and the major products were the corresponding phenylacetic acids. The conversions remained low, however; from the phenylethanol reaction 19 mmol of acid + 13 mmol of alcohol were isolated while from the *p*-chloro derivative 13 mmol of acid + 14 mmol of alcohol was recovered.

Hence it was concluded that, certainly in the case of benzyl alcohols, their reactions with hypobromite would be fast enough to allow the electrogeneration of the oxidizing agent to be coupled to the phase transfer catalysed oxidation of the alcohols. The success of this electrosynthetic procedure is, however, dependent on two additional factors not present in the chemical hypochlorite reactions. Firstly the basic electrode reaction is the formation of bromine which must be hydrolysed rapidly before the bromine can accumulate in the organic phase. Secondly the hypobromite is not entirely stable in aqueous media and it can disproportionate to bromide and bromate; this reaction would of course lead to loss of current efficiency. The rates of both the hydrolysis of bromine and the disproportionation of hypobromite are strongly pH dependent and hence careful control of the pH of the electrolysis medium (7–10) is essential. This can be assisted by the use of an undivided cell where the cathode reaction is hydrogen evolution and generation of

Table 1. Rate of formation of C_6H_5CHO (mmol) from oxidation of $C_6H_5CH_2OH$ by hypochlorite as a function of phase transfer agent and other experimental conditions; 9·2 mmol of $C_6H_5CH_2OH$ in 25 cm^3 of amyl acetate was stirred with 25 cm^3 of 10% aqueous NaClO. Analysis by g.l.c.

Phase transfer agent	*None*	*0·5 g Bu_4NHSO_4*	*0·5 g hyamine 2389*	*0·5 g $C_{16}H_{33}(CH_3)_3NBr$*	*0·5 g Bu_4NHSO_4*	*5·0 g Bu_4NHSO_4*	*0·5 g Bu_4NHSO_4 + 5·0 g NaBr*
T(° C) t(min)	20	20	20	20	70	20	20
1	–	0·4	0·1	0·3	1·6	4·2	2·2
3	–	1·1	0·3	0·8	3·4	7·1	5·5
5	–	1·7	0·5	1·3	5·3	8·1	7·8
15	0·2	4·2	1·3	3·3	7·2	9·1	8·3
60	0·7	9·2	3·9	8·7	8·4	9·2	8·5

Table 2. Oxidation of $C_6H_5CH_2OH$ as a function of electrolysis conditions. In all cases 350 cm^3 aqueous NaBr (1·0 M) + $NaHCO_3$ (0·5 M) + alcohol (0·1 mol) in 65 cm^3 amyl acetate was stirred efficiently. The electrolyses were terminated after the passage of 2 F mol^{-1} of starting material

Bu_4NHSO_4 added (g)	I (A)	T (° C)	$C_6H_5CH_2OH$ recovered (mol)	C_6H_5CHO formed (mol)
7	10	20	0·049	0·038
7	10	45	0·027	0·065
7	10	65	0·026	0·072
17	10	45	0·020	0·071
35	10	45	0·026	0·064
0	10	45	0·035	0·036
7	5	45	0·032	0·068

Table 3. Conversion of alcohol to aldehyde (or ketone). Electrolysis conditions; 350 cm^3 aqueous NaBr (1·0 M) + $NaHCO_3$ (0·5 M) + 65 cm^3 amyl acetate + 0·1 mol alcohol + 7 g Bu_4NHSO_4, efficient stirring, $I = 10\,A$, $T = 45°$ C. The electrolyses were terminated after 2 F mol^{-1} of alcohol

Alcohol	Alcohol recovered (mol)	Aldehyde formed (mol)
$C_6H_5CH_2OH$	0·027	0·065
p-CH_3–$C_6H_4CH_2OH$	0·037	0·060
p-CH_3O–$C_6H_4CH_2OH$	0·026	0·068
p-NO_2–$C_6H_4CH_2OH$	0·062	0·027
$C_6H_5CH(OH)$–CH_3	0·051	0·044*
$C_6H_5CH(OH)$–C_6H_5	0·024	0·076*

* Corresponding ketone.

hydroxide (c.f. the epoxidation of olefins via hypobromite [5]).

A series of constant current electrolyses were carried out in the cell shown in Fig. 1, using benzyl alcohol as the substrate. 0·1 mol of the alcohol in 65 cm^3 of amyl acetate were added to the cell with 350 cm^3 of water containing sodium bromide (1·0 M) and sodium bicarbonate (0·5 M) to maintain the electrolyte slightly basic. The electrolyses were then carried out at a series of temperatures, current densities and concentrations of the phase transfer agent and the results are presented in Table 2. In most cases the organic yield of aldehyde was very good but the conversion (the electrolyses were terminated after the passage of 2 F mol^{-1} i.e. 30 min) and the current yields depended on the exact electrolysis conditions. The extent of the reaction in the absence of the phase transfer catalyst was surprising but benzyl alcohol has some solubility in water and it should be noted that in this case the total recovery of alcohol and aldehyde was much lower than in the other conditions suggesting competing reactions.

It was clear that the mass transport conditions were critical in determining the extent of electrolysis and indeed the products; in a few cases further oxidation to bromobenzene could be detected. Hence the rate of rotation of the stirrer, its shape and position with respect to the electrodes was of major importance. All the results reported in this paper were carried out under identical mass transport conditions using the propellor shaped stirrer. The reaction is now being studied in more sophisticated cells than this simple stirred tank reactor and where the mass transfer may be more exactly described.

On the basis of these experiments, a current of 10 A, a temperature of 45° C and 2% tetrabutylammonium bisulphate were selected as suitable conditions for the electrolysis of a series of alcohols. The results for electrolyses terminated after 2 F mol^{-1} of alcohol are reported in Table 2. The conversion varies with the structure of the alcohol but in all cases the amount of aldehyde in the system increased linearly with time and the conversion approached 100% on the passage of a sufficient excess of coulombs through the cell. Presumably the deviation of the current yields from 100% is due to oxygen evolution and the formation of the inactive bromate; in the absence of an alcohol to react with the hypobromite, tetrabutylammonium bromate precipitated in the cell. An experiment on the oxidation of benzyl alcohol without the addition of sodium bicarbonate gave similar results since the electrolysis medium rapidly became slightly basic.

Hence it can be seen that this two-phase procedure represents a convenient electrosynthetic method for the conversion of these alcohols to aldehydes. Moreover in the cell employed the energy consumption is relatively low, typically with a current of 10 A the cell voltage was 6–8 V and this could be lowered further by a reduction of the electrode spacing. Some more complex alcohols also undergo oxidation although simple aliphatic alcohols react too slowly for the chemical reaction to be coupled to the electrogeneration of hypobromite; bromate is generally formed.

The exact nature of the mechanism of these electrosynthetic reactions is not entirely clear and it is not certain that the reaction takes place completely in the organic phase. It seems probable, however, that the phase transfer catalysed route is of major importance.

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