Ion-pairing Effects on the Reduction of Nitroarenes in Propan-2-ol Solutions: an Electrochemical Investigation

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The electrochemical reduction of 1-chloro-4-nitrobenzene in propan-2-ol was studied by means of cyclic voltammetry at a glassy-carbon electrode with LiSCN, NaSCN, KSCN, and Bu^n_4NSCN as support electrolytes. With Bu^n_4NSCN a two-wave process obtains, corresponding to an overall four-electron reduction (a reversible one-electron process followed by an irreversible three-electron process). With KSCN, NaSCN, and LiSCN the second wave is progressively shifted to more anodic potentials, to the point where it merges into the first peak, which is unaffected by the nature of the cation. Additions of 18-crown-6 to the solutions containing Na^+ and, particularly, K^+ result in shifts of the second wave to more negative potentials. The resulting voltammetric curves closely resemble that observed with Bu^n_4NSCN. Additions of 18-crown-6 to solutions of Li^+ have no effect at all on the cyclic voltammetry curves. The observed phenomena are explained in terms of ion-pairing effects, and suggest that the electrochemical reduction of 1-chloro-4-nitrobenzene in propan-2-ol proceeds *via* formation of the radical anion, followed by a second electron transfer to give the dianion. The relevance of these observations to the mechanism of reduction promoted by alkoxide ions is briefly discussed.

Treatment of nitroaromatic compounds with alkoxide ions in alcoholic solutions leads to products derived from reduction of the nitro group *via* the intermediacy of $ArNO_2^{-\cdot}$ and ArNO species.[1,2] We have pointed out that even substrates bearing nucleofugic substituents may undergo reduction of the nitro group more readily than aromatic nucleophilic substitution.[2]

1-Chloro-4-nitrobenzene is an interesting case. In deoxy-genated solutions of Pr^iOK in Pr^iOH it gives exclusively products of reduction, mainly 4,4'-dichloroazoxybenzene and 4-chloroaniline.[2a] It is sufficient, however, to add 18-crown-6, other alkali metal ion complexing agents, or tetra-alkyl-ammonium salts to bring about a drastic change in reactivity and to obtain the substitution product, 1-isopropoxy-4-nitrobenzene, in quantitative yield.[2c,d]

This behaviour can be understood in terms of ion-pairing effects, with 'free' alkoxide ions exhibiting, as expected, enhanced nucleophilic reactivity. Ion-pairing effects also operate in the reduction process, but, interestingly, in quite the opposite direction: the rate of reduction is markedly depressed in the presence of crown-complexed alkali cations or tetra-alkylammonium ions.[2c,d] In studying these phenomena, it turned out to be helpful to generate the reduction reactive intermediates electrochemically, and to investigate their behaviour by means of electroanalytical techniques.

The electrochemical reduction of nitroarenes has been studied extensively in many solvent systems,[3] but no data are reported for pure propan-2-ol solutions.

In protic solvents (pH < 12), reduction of nitroarenes leads to hydroxylamines [equation (1)] *via* the nitroso derivatives, ArNO. A single polarographic wave is observed, which corresponds to an overall transfer of four electrons.[3] The nature of the rate-determining step is pH-dependent: in aqueous solution (pH 6—11)[4] and in alcohol–water mixtures[5] protonation of the first intermediate, $ArNO_2^{-\cdot}$, is rate-determining.

$$ArNO_2 + 4e + 4H^+ \longrightarrow ArNHOH + H_2O \quad (1)$$
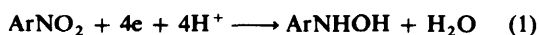
In aprotic solvents two polarographic waves are observed. The first, monoelectronic, leads to the species $ArNO_2^{-\cdot}$,[6] the second, a three-electron step, involves reduction of $ArNO_2^{-\cdot}$ accompanied by protonation–elimination steps leading eventually to the hydroxyamino derivative.[7]

While reduction of halogenonitrobenzenes in aprotic solvents can lead to dehalogenation *via* loss of halide ion from the intermediate radical anion,[3a] such a process has never been observed in protic solvents.[2,8]

In this paper the results are reported of an investigation of the electrochemical reduction of 1-chloro-4-nitrobenzene in propan-2-ol in the presence of various cations. The principal technique employed was cyclic voltammetry, which is particularly suitable for studying transient intermediates.

Results and Discussion

The electrochemical reduction of 1-chloro-4-nitrobenzene in anhydrous propan-2-ol has been investigated at room temperature in the presence of various electrolytes by means of cyclic voltammetry.

The electrolytes used were M^+SCN^- salts, in which M^+ is Li^+, Na^+, K^+, or $Bu^n_4N^+$. The choice of thiocyanate as common anion was determined by the superior solubility, in propan-2-ol, of KSCN relative to other potassium salts. Since the oxidation wave of thiocyanate in propan-2-ol on a glassy-carbon electrode occurs at a potential *ca.* 500 mV more anodic than on a mercury electrode, the former was used in our experiments in order to have as large a 'window' as possible.

The voltammetric profiles for the reduction of 1-chloro-4-nitrobenzene in propan-2-ol in the presence of the four different cations (MSCN 0.08m) are shown in Figure 1(a—d). In the case of LiSCN [Figure 1(a)] a single reduction wave is observed with peak potential E_p^{red} −1.05 V. As the cation is changed to Na^+, K^+, and $Bu^n_4N^+$, the picture also changes in two respects: (i) a wave at a less cathodic potential becomes increasingly evident, barely as a shoulder in the case of Na^+, but clearly separated in
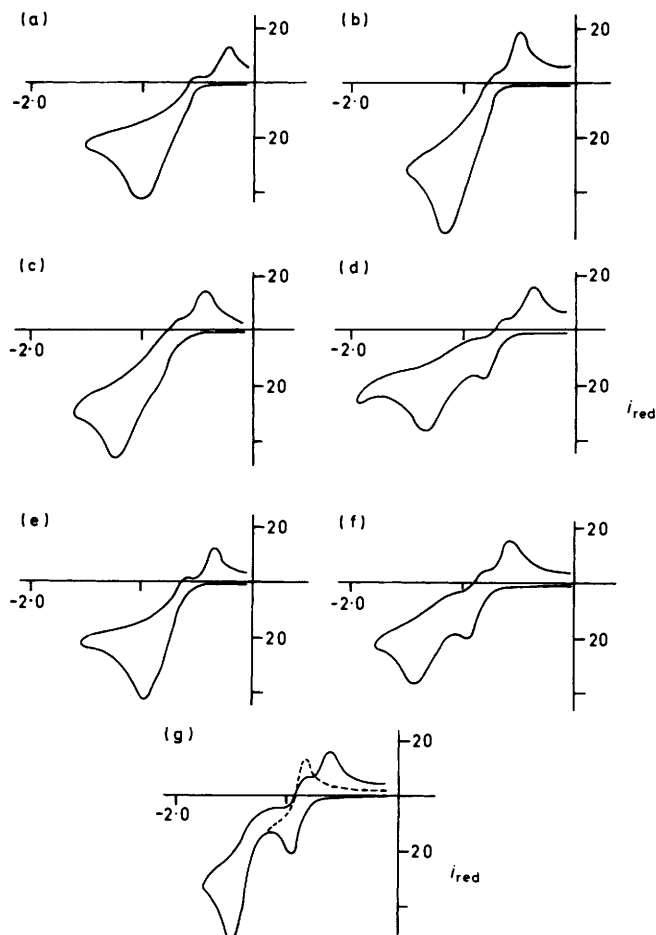
Figure. Cyclic voltammetry curves for the reduction of 1-chloro-4-nitrobenzene (1.3 × 10⁻³M) in propan-2-ol at a glassy-carbon electrode in the presence of 0.08M-M⁺SCN⁻, and [for (e)—(g)] of 0.08M-18-crown-6: M⁺ = Li⁺ (a), (e); Na⁺ (b), (f); K⁺ (c), (g); Buⁿ₄N⁺ (d). Units are volts (V) for the abscissa and μA for the ordinate. The broken line in (g) refers to an experiment in which the potential sweep was reversed at a value of −1.3 V
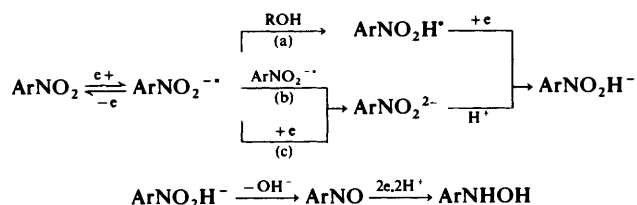
solutions containing the Li⁺, Na⁺, and K⁺ salts. These effects [Figure 1(e—g)] cannot be explained in terms of adsorption of the added ether on the electrode surface,¹² but can be understood in terms of complexation equilibria involving the metal cations and the 18-crown-6. Indeed, the cyclic voltammetric curves of solutions containing Li⁺ ions, which are known not to bind to this crown ether to any significant extent,¹³ are virtually identical with and without 18-crown-6 [Figure 1(a and e), respectively]. Na⁺ and K⁺ ions, on the other hand, are known to be strongly complexed by the 18-crown-6, the complexation constants being,¹⁴ in methanol at 25 °C, 1.2 × 10⁶ and 2 × 10⁴ l mol⁻¹ for K⁺ and Na⁺, respectively. The cyclic voltammetric curves obtained with solutions containing Na⁺ and K⁺ and equimolar amounts of the 18-crown-6 [Figure 1(f and g)] show a split of the original wave into two components, the first with E_p^{red} −0.96 V and the second with E_p^{red} −1.45 V (Na⁺) and E_p^{red} −1.52 V (K⁺). The resulting voltammetric curves closely resemble that observed with Buⁿ₄NSCN [Figure 1(d)]. Parallel reduction experiments carried out at controlled potentials have established that the first peak is due to a one-electron and the second to a three-electron reduction process. Intermediate behaviour between those shown in Figure 1(c and g) was observed for solutions containing 18-crown-6 in less than equimolar amounts relative to K⁺ (curves not shown). Complexation of K⁺ and Na⁺ ions by crown ethers modifies the ion pairs between these cations and negatively charged reduction intermediates, and consequently alters their reactivity.

It should be pointed out that, in the presence of 18-crown-6-complexed K⁺, the species ArNO₂⁻· is formed in a reversible process (discussed later), much as is the case in aprotic solvents. As for the decay of this key intermediate, conceivable pathways involve protonation, dismutation, and heterogeneous one-electron reduction (Scheme). Protonation of ArNO₂⁻· has been

Scheme.

the case of Buⁿ₄N⁺ with E_p^{red} −0.82 V, and (ii) the second wave is shifted towards more cathodic potentials, E_p^{red} being −1.16 V for Na⁺, −1.24 V for K⁺, and −1.35 V for Buⁿ₄N⁺.

Examples are known of shifts of the first or second wave in the electroreduction of aromatic compounds induced by changes in the positive counterion.⁹ These phenomena are usually attributed to ion pairing and depend on the solvent–cation system and on the extent of charge delocalization in the negatively charged products of reduction.⁹·¹⁰ In particular, shifts towards less cathodic potentials have been reported for the first reduction wave of nitroarenes in dimethylformamide (DMF) as the size of the cation decreases.¹¹ Thus, in DMF 1-chloro-4-nitrobenzene is easier to reduce in the presence of Na⁺ (E_p^{red} −0.945 V) than of Et₄N⁺ (E_p^{red} −1.020 V).¹¹ In propan-2-ol, analysis of the first reduction wave, when it is detectable at all, is made difficult by overlap with the second wave [Figure 1(a,b)]. It appears, however, that transfer of the first electron is not affected by the nature of the cation, whereas significant effects are observed on the position of the second reduction wave.

These phenomena have been further investigated by studying the effect on the cyclic voltammetric curves of additions of equimolar amounts of the cyclic ether 18-crown-6 to the

identified as the rate-limiting step in the electroreduction of nitroarenes in water⁴ and alcohol–water mixtures.⁵ On the other hand, [4-O₂NC₆H₄Cl]⁻·, generated by means of pulse radiolysis in water in the presence of 1M-PrⁱOH, decays by a second-order process typical of a dismutation reaction.⁸

Protonation of ArNO₂⁻· [Scheme, path (a)] appears unlikely both in the presence and in the absence of crown ether for two reasons. First, protonation of the radical anion (pK_a < 4)¹⁵ by propan-2-ol, which has been shown to be an unfavourable process in liquid ammonia,⁷ should also be unfavourable in pure alcohol. Second, the addition of crown ethers in modifying the ArNO₂⁻·K⁺ ion pair should also alter the rate of protonation¹¹ and hence shift the first reduction wave. As no such shift is observed, protonation must occur on the dianion rather than on the radical anion.

The separation of the two reduction waves of 1-chloro-4-nitrobenzene in the presence of 18-crown-6-complexed K⁺ has allowed us to investigate the first cathodic process in greater detail. Voltammetric measurements carried out at various potential-scan rates (v) in the 0.01—5 V s⁻¹ range reveal a linear dependence of the peak current (i_p) on $v^{1/2}$, thus indicating that the process is not under the kinetic control of any chemical step,

including dismutation. Additional support for this conclusion is provided by a study of the effect of varying the concentration of the electroactive species, 1-chloro-4-nitrobenzene. Since dismutation is a second-order decay process, the cyclic voltammetry curves should be affected by variations in the concentration of $ArNO_2$, were this process competitive under the experimental conditions employed. For 18-crown-6-containing solutions the substrate concentration was increased four-fold in an attempt to bring about conditions of kinetic control and to induce merging of the two waves. In solutions not containing the complexing agent, substrate concentration was reduced ten-fold in order to see whether the two merged waves would separate, thus indicating the operation of a bimolecular process. In neither case was any change detectable in the cyclic voltammetry curves in the voltage scan rate interval 0.1—5 V s^{-1}. Dismutation is therefore not competitive with heterogeneous electron transfer under our experimental conditions.

Electron transfer to give the species $ArNO_2{}^{2-}$ is thermodynamically favoured by association of the radical anion $ArNO_2{}^{-\bullet}$ with cations. As the anion–cation stabilizing interaction is reduced, as is the case when K$^+$ ions are complexed by 18-crown-6, the second step in the electroreduction of 1-chloro-4-nitrobenzene becomes more difficult and the corresponding wave is shifted to more cathodic potentials. This shift, however, could also be caused by a reduced rate of protonation of the dianion, if the reduction of the radical anion to the dianion is a reversible process. Under our conditions, however, there is no evidence for this reversibility.* On the other hand, although protonation of carbanions has been reported to be faster for contact ion pairs than for free ions,[10] proton transfers involving oxygen and nitrogen[16] acid–base pairs should be influenced only to a minor extent by ion pairing and should actually be faster for free anions. The present results, however, do not establish whether protonation of the dianion is affected by the addition of crown ethers.

In conclusion, our results suggest that the mechanism of the electrochemical reduction of nitrobenzenes in propan-2-ol is, as is the case in liquid ammonia in the presence of propan-2-ol,[7] best represented by path (c) of the Scheme. This involves reduction of $ArNO_2{}^{-\bullet}$ to $ArNO_2{}^{2-}$, fast protonation of $ArNO_2{}^{2-}$, and loss of ^-OH to form the nitroso derivative. Nitroso compounds are then reduced, by a similar sequence, to hydroxylamines.[7]

Decay of $ArNO_2{}^{-\bullet}$ to the dianion $ArNO_2{}^{2-}$, possibly via a dismutation reaction,[8] must be considered as a likely rate-limiting step in the chemical reduction of nitroarenes by alkaline alcoholic solutions.[2]

Experimental

Materials.—Reagent grade propan-2-ol was distilled from Mg turnings.[17] 1-Chloro-4-nitrobenzene (Carlo Erba) was recrystallized from ethanol. The thiocyanate salts (Fluka) were dried in an oven at 40 °C under vacuum and used without further purification. 18-crown-6 was prepared according to literature procedures.[18]

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* A shift of the second cathodic peak is observed with varying sweep rate. This could be due to (i) slow charge transfer; (ii) rate-determining protonation of the dianion, generated in a reversible charge-transfer step; or (iii) imperfectly compensated iR drop due to the low solubility of the supporting electrolyte in propan-2-ol. We believe that the second explanation is unlikely because the peak does not have the shape profile typical of the irreversible *EC* mechanism at slow scan rates and because a scan rate of 5 V s^{-1} appears to be too slow to compete with the protonation of the dianion. The counterion effect, as discussed in the text, appears to be in contrast with hypothesis (ii).

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