Carbon Dioxide-promoted Electrochemical Reduction of Aromatic Nitro Compounds to Azoxy Compounds in Acetonitrile

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CO_2 was found to promote electrochemical reduction of aromatic nitro compounds in acetonitrile even in the absence of a proton source to produce multi-electron reduction products, azoxy compounds as well as smaller amounts of azo and hydroxylamino compounds.

Of the numerous studies reported, electroreduction of aromatic nitro compounds[1] were almost all performed in protic solvents. The reduction products are known to be nitroso, hydroxylamino, amino, azo, azoxy and hydrazo compounds. These products are generally dependent on the electrolysis conditions, *e.g.* pH, electrode material. The effect of pH may be an important factor. In aprotic solvents such as acetonitrile, aromatic nitro compounds can be reduced electrochemically with one electron to generate the radical anion, which is stable in the solvent and hardly generates any reduction products, although hydroxylamino compounds have been reported in the presence of a weak acid such as phenol in acetonitrile.[2] We report here that CO_2 promotes electroreduction of aromatic nitro compounds in acetonitrile even in the absence of a proton source to produce the corresponding azoxy compounds as well as smaller amounts of azo and hydroxylamino compounds.

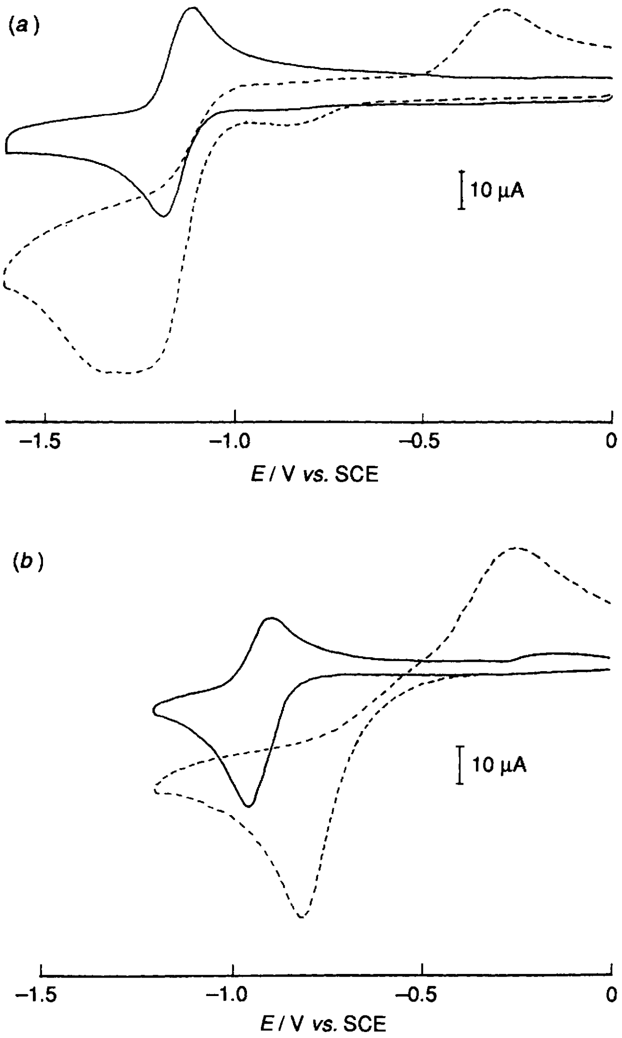

Fig. 1 CVs (scan rate, 0.10 V s^{-1}) of (*a*) nitrobenzene and (*b*) nitrosobenzene (1.0×10^{-3} mol dm^{-3}) under N_2 (————) and CO_2 (- - - - - - -) in acetonitrile containing $(Bu^n_4N)ClO_4$ (0.10 mol dm^{-3}) as the electrolyte with a glassy carbon disk electrode (0.30 cm diameter)

Cyclic voltammograms (CVs) of nitrobenzene were measured in N_2- and CO_2-saturated acetonitrile with a glassy carbon electrode [Fig. 1(*a*)]. Under an N_2 atmosphere the CV exhibited a reversible one-electron reduction–oxidation wave at potential $E_{p/2} = -1.17$ V *vs.* SCE and an irreversible wave at potential $E_p = -2.18$ V *vs.* SCE. On the contrary, in CO_2-saturated acetonitrile the first reduction wave became a large irreversible wave with a peak potential −1.40 V *vs.* SCE, and an oxidation wave at $E_p = -0.28$ V *vs.* SCE appeared. The CVs measured with an Hg electrode were very similar. The CVs of the other aromatic nitro compounds were also essentially the same.

In order to examine the reduction products we performed controlled-potential electrolyses of aromatic nitro compounds in CO_2-saturated acetonitrile solutions containing $Bu^n_4NClO_4$ as the electrolyte. An Hg pool was used as the electrode. The reduction potential was generally set around the peak potential of the reduction wave observed in the CO_2-saturated solution of the aromatic nitro compounds. 3–3.5 F flowed during the electrolysis of nitrobenzene and then the current drastically decreased. The electrolysis was stopped after 100 C (corresponding to 4 F) had flowed. The reduction products were isolated from the reaction mixtures by thin-layer chromatography on silica gel with chloroform–light petroleum (1 : 1 v/v) and subsequently identified as azoxy compounds by ^1H NMR spectroscopy. Quantitative analysis of the reduction products was performed by gas chromatography using an OV-17 column. The results are listed in Table 1 with the reduction potential measured by cyclic voltammetry under both N_2 and CO_2 atmospheres. In each case the main products were azoxy compounds, but azo and hydroxylamino compounds were also produced. Formation of bis(tetrabutylammonium) carbonate also occurred. The stoichiometry of formation of azoxy and azo compounds was considered to follow reactions (1) and (2).

Formation of hydroxylamino compounds requires protons. During electroreduction (−1.10 V *vs.* SCE) of nitrobenzene (3.0×10^{-2} mol dm^{-3}, 17 cm^3), 145 μmol of phenylhydroxylamine and a small amount of but-1-ene was produced after 100 C had flowed. But-1-ene is known to be a decomposition product of the tetrabutylammonium cation.[3] Therefore, the nitrobenzene radical anion was suggested to abstract a proton from the tetrabutylammonium cation to produce phenylhydroxylamine.

At low concentrations of CO_2 the CVs exhibited a second reduction wave around −1.65 V *vs.* SCE with the first one-electron reversible redox couple. This indicates that the first stage of electrochemical reduction followed an ECE mechanism and that during the first stage of the reaction the adduct of nitrobenzene radical anion and CO_2 was generated.


(1)

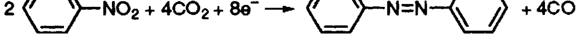
(2)

Table 1 Electrochemical reduction of nitrobenzene derivatives and nitrosobenzene in CO_2-saturated acetonitrile[a]

	Reduction potential[b]			Products[c]/μmol		
Substrate	N_2 $E_{p/2}$	CO_2 E_p	E	Azoxy	Azo	Hydroxylamino
$C_6H_5NO_2$	−1.17	−1.40	−1.30	81.6 (64.0)	38.4 (30.1)	trace
p-$ClC_6H_4NO_2$	−1.05	1.20	−1.20	51.3 (40.2)	16.2 (12.6)	42.0 (16.7)
p-$MeOC_6H_4NO_2$	−1.12	−1.33	−1.30	47.3 (38.0)	42.3 (33.9)	19.3 (8.0)
p-$MeC_6H_4NO_2$	−1.20	−1.39	−1.40	52.6 (41.3)	12.9 (10.1)	28.2 (11.1)
C_6H_5NO	−0.92	−0.82	−1.10	63.8 (50.5)	22.1 (17.4)	20.3 (8.9)

[a] Controlled potential electrolyses of acetonitrile solutions (17 cm^3) containing substrates (1.5×10^{-2} mol dm^{-3}) and an electrolyte $Bu^n{}_4NClO_4$ (0.15 mol dm^{-3}) were performed at the potential listed as E. (Electrolysis potential, V *vs.* SCE) with an Hg pool electrode (3.0 cm diameter). [b] Determined by cyclic voltammetry: the conditions were as in Fig. 1. [c] Amounts of products were analysed by gas chromatography after 100 C had been consumed. Current efficiencies (%) in parentheses.

We proposed that this was a carbonate-type adduct in which CO_2 became attached to an oxygen atom of a nitro group, and that the adduct was furthermore reduced to give nitrosobenzene and carbonate dianion. The CV of nitrosobenzene exhibited a reversible one-electron redox couple at $E_{p/2} = 0.92$ V *vs.* SCE under an N_2 atmosphere in acetonitrile [Fig. 1(*b*)]. Under atmospheric CO_2 the CV exhibited a large irreversible reduction wave at $E_p = -0.82$ V *vs.* SCE with a large oxidation wave at $E_p = -0.25$ V *vs.* SCE. Accordingly, nitrosobenzene could be reduced at the same potential as nitrobenzene, and it was suggested that azoxybenzene was generated from a coupling reaction of nitrosobenzene under the same electrolysis conditions. The electroreduction of nitrosobenzene gave the same products, azoxy and azobenzene, as the reduction of aromatic nitro compounds. Furthermore, the CV of azoxybenzene, which was reversible under N_2, became irreversible under CO_2, and the electrolysis of azoxybenzene in CO_2-saturated acetonitrile gave azobenzene with a current efficiency of 52.5%. Therefore, it is strongly suggested that azobenzene is produced *via* azoxybenzene, although there was hardly any electroreduction of azoxybenzene due to the negative reduction potential.

In summary, electrochemical reduction of aromatic nitro compounds occurred readily in the presence of CO_2 even in acetonitrile in the absence of proton sources to generate bimolecular products, azoxy and azo compounds. CO_2 was found to react with a one-electron reduced species, the nitro compound radical anion, and to play the role of both an electron and oxygen acceptor for the radical anion.

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