

Short Communication

# Electrochemical Reduction of Benzaldehyde Benzoylhydrazone in Aprotic Media

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The electrochemical reduction of azomethine compounds has been the subject of many investigations.<sup>1</sup> Most of these have been concerned with reactions in protic media, but a few have discussed the mechanism of the reduction in aprotic media.<sup>2–5</sup> Kitaev *et al.* have investigated the polarographic<sup>2</sup> and electrochemical<sup>3</sup> reduction of some aryl- and acyl-hydrazones in *N,N*-dimethylformamide (DMF). They found that the polarographic reduction of phenylhydrazones of salicylaldehyde and benzaldehyde in DMF showed a one-electron wave followed by a second wave with a height approximately corresponding to  $n=3$ . On the basis of the non-reducibility of 1-phenyl-2-benzylhydrazine, they concluded that the reduction involved the cleavage of the nitrogen–nitrogen bond prior to the saturation of the carbon–nitrogen double bond; the products were benzylamine and aniline, and the compounds thus followed the scheme valid in protic media. Benzaldehyde benzoylhydrazone (BBH), on the other hand, was found<sup>3</sup> to give three polarographic waves and to be reduced at the carbon–nitrogen bond prior to the reduction of the nitrogen–nitrogen bond; the final products were benzylamine and benzamide with *N*-benzyl-*N'*-benzoylhydrazine as an intermediate product. Kargin *et al.*<sup>4</sup> have investigated the amino–nitrile cleavage found in disubstituted hydrazones of substituted benzaldehydes induced by the base generated during the reduction. The rate of the cleavage of the nitrogen–nitrogen bond of *N,N*-disubstituted hydrazones as the result of an addition of an electron to the conjugated system has been investigated<sup>5</sup> and it was found that the rate in a series of hydrazones increased approximately linearly with the decrease of the reversible reduction potential of the compounds.

The cleavage of the nitrogen–nitrogen bond in the *N,N*-disubstituted hydrazones in aprotic solvents takes place in the radical anion and, in such a cleavage reaction, one would expect that the cleavage would be the faster,

the less basic the leaving group. The anion of benzamide is less basic than the anion of aniline and one would thus have expected that cleavage of the N–N bond in benzaldehyde benzoylhydrazone would occur more readily than the cleavage in benzaldehyde phenylhydrazone (BPH). However, the hydrogen bonded to nitrogen in the benzoylhydrazone is more acidic than the hydrogen in the phenylhydrazone and the base generated during a reduction could more easily deprotonate the benzoylhydrazone than the phenylhydrazone. It was the aim of this investigation to evaluate the influence of the electrogenerated base on the reduction of benzaldehyde phenylhydrazone and benzaldehyde benzoylhydrazone as model compounds.

## Results and discussion

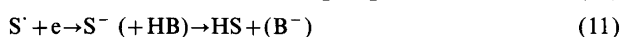
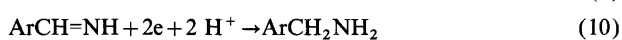
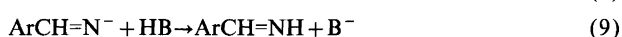
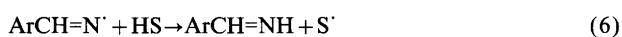
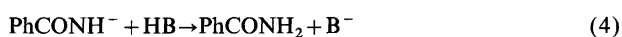
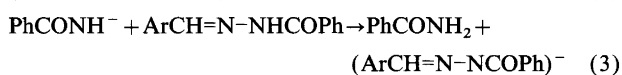
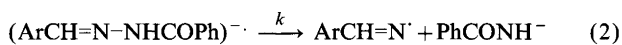
Cyclic voltammograms of the two aforementioned compounds were recorded in DMF containing tetrabutylammonium tetrafluoroborate as supporting electrolyte. Two irreversible reduction waves, at a scan rate of  $1 \text{ V s}^{-1}$ , could be seen. This is in agreement with our previous observations.<sup>5</sup> Bulk electrolyses of each compound were performed at a potential slightly more negative than their first reduction peak potential [ $-2.10 \text{ V vs. SCE}$  (BPH) and  $-1.90 \text{ V vs. SCE}$  (BBH)]. The electrolyses consumed one electron for benzaldehyde phenylhydrazone and about 0.9 electron for benzaldehyde benzoylhydrazone. After work-up, a red oil and a white solid were recovered from the electroreduction of BPH and BBH, respectively.

Thin-layer chromatography (silica gel; 4:1  $\text{CHCl}_3$ – $\text{CH}_2\text{Cl}_2$ ) of the reduction mixture of BPH allowed positive identification of benzaldehyde. HPLC separation of the products from the reduction of benzaldehyde phenylhydrazone showed three major peaks. They were identified as benzonitrile, benzaldehyde and aniline by their individual retention times and by injection

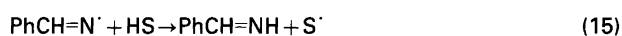
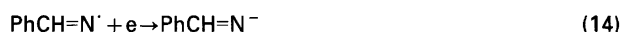
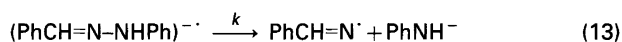
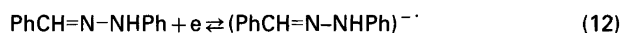
of a mixture of these three compounds and comparison with the original chromatogram. The product distribution shows that the cleavage of the nitrogen–nitrogen bond of the radical anion as well as the base-catalysed elimination of aniline with formation of benzonitrile are operative during the bulk reduction of benzaldehyde phenylhydrazone.

Benzaldehyde benzoylhydrazone, *N*-benzyl-*N'*-benzoylhydrazine and benzamide could not be distinguished from each other by the above-mentioned thin-layer chromatography. An NMR spectrum (CDCl<sub>3</sub>) of the reaction mixture showed clearly the signal of benzaldehyde benzoylhydrazone and no trace of the *N*-benzyl-*N'*-benzoylhydrazine. The HPLC chromatogram of the product mixture from the reduction of benzaldehyde benzoylhydrazone showed four peaks, one being unidentified. The major peak was attributed to the starting material (68%), the two others to benzamide (19%) and benzaldehyde (6%), respectively. *N*-Benzyl-*N'*-benzoylhydrazine was also injected into the column. Its retention time differed from that of BBH and the other products in the reaction mixture, and none of the peaks detected in the reaction mixture presented a UV spectrum similar to that of the hydrazine. Scheme 1 summarises the proposed reduction mechanism of benzaldehyde benzoylhydrazone.

In the work-up of the bulk electrolysis catholyte, the anion, (ArCH=N–NHCOPh)<sup>•-</sup>, is protonated to BBH and PhCH=NH hydrolysed to benzaldehyde. The electron transfer [eqn. (1)] is followed by cleavage of the radical anion [eqn. (2)]. Eqns. (3)–(11) show the succession of reactions after the cleavage. Eqns. (3) and (5) show why the reduction of benzaldehyde benzoylhydrazone is different from the reduction of BPH, that is, the attack of an electrogenerated base at the most acidic proton, which is on the nitrogen atom. For comparison purposes, the proposed electroreduction mechanism for BPH is depicted in Scheme 2.



Scheme 1.



Scheme 2.

There are different reasons for the low electricity consumption for BBH and BPH. For BBH the explanation is that B<sup>-</sup> is a strong enough base (p*K*<sub>a</sub> of BH > p*K*<sub>a</sub> of BBH) to deprotonate BBH to BBH<sup>-</sup> [eqn. (5)] which is not reducible at the applied potential. B<sup>-</sup> is, however, not a sufficiently strong base to remove the N–H proton of BPH. For BPH *n* is one because B<sup>-</sup> attacks the C–H proton in BPH in an elimination reaction (E2) with formation of benzonitrile and aniline [eqn. (17)]; the irreversibility of the elimination makes the reaction possible although the acidity of the C–H proton is not high. The amino–nitrile cleavage is also, in principle, a possible route for BBH; however, the deprotonation of BBH by the electrogenerated base, B<sup>-</sup>, is faster than the cleavage and p*K*<sub>a</sub> of BH > p*K*<sub>a</sub> of BBH; the amino–nitrile cleavage is therefore not operative.

Bulk electrolysis of BBH was performed at a potential slightly more negative than the first reduction peak and an excess of methyl iodide was added to the catholyte solution and allowed to react for 2 h. GC analysis of the reaction mixture showed 69% of a product identified as benzaldehyde *N*-methyl-*N*-benzoylhydrazone by its GC retention time. This percentage corresponds well with the percentage of BBH determined by HPLC for an electroreduction without added MeI. Cyclic voltammetry of the bulk mixture was also investigated. The cyclic voltammogram was identical with that of benzaldehyde *N*-methyl-*N*-benzoylhydrazone,<sup>5</sup> with formation of benzonitrile (PhCN), as a result of the amino–nitrile cleavage. Addition of PhCN into the mixture allowed positive identification of the one-electron reversible wave. In addition, in a competition experiment where a proton donor was added to the solution [eqns. (3) and (4) are operative], benzaldehyde, a work-up product of benzaldimine, could be detected in a larger quantity in the reaction mixture compared with the bulk electrolysis run without added proton donor.

In conclusion, the electroreduction of benzaldehyde benzoylhydrazone follows the proposed scheme for the reduction of hydrazones in aprotic media. However, owing to the greater acidity of the proton on the nitrogen atom compared with the acidity of that in benzaldehyde phenylhydrazone, the deprotonation of the starting material [eqns. (3) and (5)] by the electrogenerated base [eqn. (4)] transforms BBH into the anion which is non-reducible at the applied potential. The fast deprotonation

of the nitrogen in BBH also explains why the amino-nitrile cleavage was not observed for BBH.

### Experimental

**Materials.** The solvent, *N,N*-dimethylformamide, and the supporting electrolyte, tetrabutylammonium tetrafluoroborate, were purified according to standard procedures. The electrolyte solution was dried through a column of activated alumina prior use. For HPLC separation, water was triply distilled, and acetonitrile and methanol were of HPLC grade. The solvents were deaerated with argon before use.

**Procedure.** The instrumentation, cells and electrodes have been described previously.<sup>6</sup> Bulk electrolyses were conducted in an H-cell at room temperature. The working electrode was a platinum net, the counter electrode a carbon rod, and potentials were referenced to the Ag/AgI reference electrode. The catholyte [DMF, 0.1 M (TBA)BF<sub>4</sub>] was passed through a column of freshly activated alumina. After reduction, diethyl ether and water were added to the catholyte. The water phase was extracted with diethyl ether (3 × 30 ml), the combined diethyl ether phases were washed with water, dried over MgSO<sub>4</sub>, and the solvent removed *in vacuo*.

The HPLC system was composed of a Waters multisolvent delivery system model 600E equipped with a U6K universal injector, and photodiode array detector model 991. The system was computer driven and spectra were transferred to the computer for further analysis. The

column was a Hyperbond C18 (Shandon), 300 × 3.9 mm, through which a 28:16:56 acetonitrile-methanol-water mixture was percolated. The mobile phase composition was optimised by means of the simplex method.<sup>7</sup> Under these conditions, capacity factors (*k'*) were as follows: benzamide (0.45); unidentified (0.72); benzaldehyde (1.91); *N*-benzyl-*N'*-benzoylhydrazine (2.67); benzaldehyde benzoylhydrazone (2.97).

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