

# Electrochemical Reduction of Benzyl Nitrate and Benzyl Nitrite

Henrik Balslev and Henning Lund\*

Department of Organic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

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Esters of nitric acid have been reported<sup>1,2</sup> to be polarographically reducible in a pH-independent wave to the alcohol and nitrite; it has, however, been mentioned in a review<sup>3</sup> that in aprotic media, benzyl nitrate is reduced electrochemically to a mixture of benzyl alcohol and benzaldehyde. Benzyl nitrite forms mainly benzaldehyde during electrochemical reduction in DMF. These results could be explained by different reaction routes, and this note reports an investigation of the reaction mechanism of these reductions.

## Results and discussion

Cyclic voltammetry (CV) of benzyl nitrate in *N,N*-dimethylformamide (DMF) containing tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) showed at moderate sweep rates ( $v < 1 \text{ V s}^{-1}$ ) an irreversible peak at about  $-1.2 \text{ V}$  (vs. Ag/AgI,  $0.1 \text{ M I}^-$ ) followed by a peak at the potential of benzaldehyde ( $-1.5 \text{ V}$ ). The first peak was rather broad indicating a small heterogeneous electron-transfer rate constant similar to that found for the reduction of aliphatic alkyl halides, for which a dissociative electron transfer to an antibonding  $\sigma$ -orbital has generally been assumed.

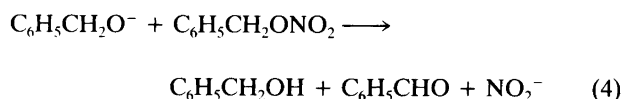
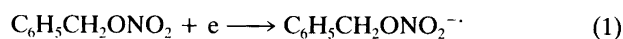
On increasing  $v$  the first peak shifts to more negative values and eventually begins to merge with the reduction of benzaldehyde. At sufficiently high values of  $v$ , where the first wave merged almost completely with the second reduction peak, the benzaldehyde anion radical, formed at the foot of the combined wave, acts as an electron-transfer reagent, and a sharp peak results. The rate of the homogeneous electron transfer from the benzaldehyde anion radical to benzyl nitrate is much higher than the rate of the heterogeneous electron transfer from the electrode.

On addition of phenol to the medium the height of the first peak increases at the expense of the second one; however, even addition of  $0.3 \text{ M}$  phenol did not completely eliminate the second peak. Addition of the hydrogen atom donor, cumene, had no effect on the voltammogram.

Preparative electrochemical reduction of benzyl nitrate (ca.  $0.1 \text{ M}$ ) at the potential of the foot of the first peak yielded benzyl alcohol and benzaldehyde in the ratio 1.4:1. On addition of phenol ( $0.5 \text{ M}$ ) the ratio increased to about 100:1, whereas addition of cumene ( $0.8 \text{ M}$ ) changed the ratio only slightly (2.5:1).

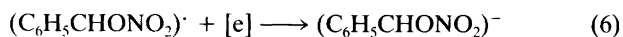
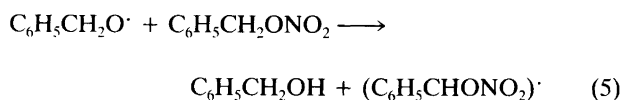
*A priori* three reaction paths (A, B1, B2, Scheme 1) might explain the formation of an (approximate) 1:1 ratio of benzyl alcohol and benzaldehyde on reduction of benzyl nitrate. The scheme requires an electron consumption of  $1 \text{ F mol}^{-1}$  ( $n = 1$ ); the experimentally found value was consistently somewhat lower. The explanation is probably that  $\text{NO}_2^-$  formed in reaction (2) attacks benzyl nitrate in a nucleophilic substitution reaction ( $\text{S}_{\text{N}}2$ ) with formation of nitrate and benzyl nitrite<sup>4</sup> which, as described below, reacts

### Path A



### Path B1

Reaction (1) and (2) followed by



### Path B2

Reactions (1), (2) and (5) followed by



Scheme 1.

in a base-catalyzed reaction to benzaldehyde and a small amount of benzyl alcohol. On addition of an excess of  $\text{NaNO}_2$  in DMF to a solution of benzyl nitrate in DMF, complete transformation into benzyl nitrite was found to take place within 15 to 20 min.

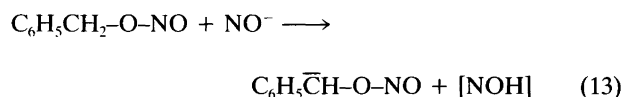
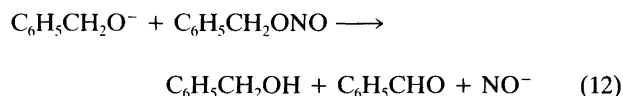
The electron transfer to the benzyloxy radical and other species [eqns. (3), (6) and (9)] may occur from the electrode or from the benzyl nitrate anion radical. Attack of base on benzyl nitrate [eqn. (4)] resulting in the formation of benzaldehyde and nitrite has previously been described as has the competing nucleophilic attack of nitrite on benzyl nitrate.<sup>4</sup>

As addition of phenol changes the ratio of benzyl alcohol to benzaldehyde from 1.4 to  $> 100$ , whereas addition of the hydrogen donor cumene has only a slight influence on the ratio, the preparative results suggest that the main reaction sequence is (1) to (4) and the rate at which the radical formed in reaction (2) abstracts a hydrogen atom is too low to make reaction (5) an important pathway. It cannot be excluded that  $\text{C}_6\text{H}_5\text{CH}_2\text{O}^-$  abstracts a proton from the solvent and that the anion of the solvent as a base attacks benzyl nitrate. The occurrence of a reduction peak of benzaldehyde in CV points to a very fast overall deprotonation of benzyl nitrate, so an extra acid-base reaction seems unlikely.

Although the main path seems to be path A it cannot be excluded that a minor reaction route involves path B1 and/or B2. Of these, B2, in which  $\text{NO}_2$  is formed as described in Ref. 5 for an analogous reaction between an alkoxy radical and ethyl nitrate, might explain a yellow colour produced during the reduction; apart from that there is no evidence to choose between B1 and B2.

Cleavage of  $\text{C}_6\text{H}_5\text{CH}_2\text{ONO}_2^-$  between carbon and oxygen to a benzyl radical and nitrate ion would be expected to give toluene, bibenzyl, dibenzyl ether, or benzylmercury compounds. None of these compounds have been isolated or identified by gas chromatography (GLC), so if such a cleavage occurs, it happens only to a minor degree.

Benzyl nitrite on CV in DMF gives an irreversible peak at ca.  $-1.0$  V (vs.  $\text{Ag}/\text{AgI}$ ,  $0.1$  M  $\text{I}^-$ ). A preparative reduction at  $-0.9$  V yielded benzaldehyde alone or together with a small percentage of benzyl alcohol with  $n = 0.1$ – $0.2$  in different experiments. The very low electron consumption points to a chain reaction and the following reaction scheme is suggested. The yield of benzaldehyde was  $80 \pm 5\%$  determined by GLC with naphthalene as an internal standard; no other compounds were detected by GLC; peaks due to toluene, bibenzyl, dibenzyl ether, or benzylmercury compounds were not observed. The yield of benzyl alcohol depended on the water content of the DMF; when very dry DMF was used the yield of benzyl alcohol was less than 1%.

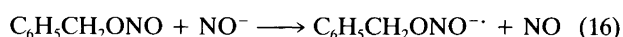


#### Scheme 2.

Eqns. (10)–(12) initiate the chain reaction, and the chain consists of eqns. (13) and (14). The chain is terminated if the benzyl alcohol anion or  $\text{NO}^-$  abstract a proton from a proton donor more acidic than benzyl nitrite. Small differences in the concentration of such proton donors in the solvent are probably responsible for the small differences in electron consumption and yield of benzyl alcohol. The reaction is, in fact, a base-catalyzed decomposition of benzyl nitrite.

No attempts have been made to detect  $\text{N}_2\text{O}$  [eqn. (15)] and its presence is thus only speculative; in this connection, however, it might be of interest that in the reduction of dialkyl nitrosamines in aqueous alkaline solution, in which  $\text{NO}^-$  is also probably formed as an intermediate,  $\text{N}_2\text{O}$  was formed.<sup>6</sup>

A chain reaction could also be established if  $\text{NO}^-$  could transfer an electron to benzyl nitrite according to eqn. (16).



The polarographic reduction of  $\text{NO}$  in dimethyl sulfoxide to the anion (or the dimeric dianion) has been described.<sup>7</sup> The reduction of  $\text{NO}$  in DMF was found to occur at approximately the same potential as benzyl nitrite. A homogeneous electron transfer from  $\text{NO}^-$  [or from  $(\text{NO})_2^{2-}$ ]<sup>7</sup> to benzyl nitrite might thus be possible; the cleavage and further reaction of benzyl nitrite would provide the driving force for the catalytic cycle to proceed.

Of these two mechanisms the former involving a base-catalyzed reaction seems the most likely for the following reasons. Addition of a small amount of tetrabutylammonium hydroxide to a solution of benzyl nitrite in DMF produced benzaldehyde and no benzyl alcohol; the reduction of  $\text{NO}$  is irreversible, which means, that the life-time of  $\text{NO}^-$  is probably too short for an effective chain reaction to occur; furthermore, the chain reaction involving electron transfer would produce a 1:1 mixture of benzaldehyde and benzyl alcohol which does not accord with the experiments.

**Experimental**

*GLC analysis.* The GLC analyses were performed with a Hewlett-Packard 5890 gas chromatograph with a non-polar capillary column OV 101 (25 m,  $\phi$  0.25 mm); injection temperature 200 °C, start temperature of 80 °C for 5 min going to 250 °C with a rate of 8 °C min<sup>-1</sup>.

*Reduction of benzyl nitrate.* Benzyl nitrate (0.250 ml) in dry *N,N*-dimethylformamide (DMF, 20 ml) containing tetrabutylammonium tetrafluoroborate (0.1 M) deaerated with nitrogen was reduced at a mercury cathode at -1.0 V (vs. AgI/Ag, 0.1 M I<sup>-</sup>). To the solution was added a known amount (approximately 0.12 g) of naphthalene as an internal standard for the GLC analysis. In some experiments a proton donor (phenol) or a hydrogen atom donor (cumene) was also added. The reduction consumed between 0.55 and 0.9 F mol<sup>-1</sup> depending on the cell and the initial concentration. The catholyte was analyzed by GLC; a typical experiment gave 50–55 % benzyl alcohol and 35–40 % benzaldehyde.

*Reduction of benzyl nitrite.* Benzyl nitrite was electrolyzed at -0.9 V (vs. Ag/AgI, 0.1 M I<sup>-</sup>) in a manner similar to that described above with a charge consumption of 0.1–0.2 F mol<sup>-1</sup>, depending on the proton content of the medium.

Analysis by GLC using naphthalene as an internal standard gave, typically, 0–10 % benzyl alcohol and 80 ± 5 % benzaldehyde. The highest yields of benzaldehyde and lowest yields of benzyl alcohol were obtained when the catholyte was passed through a column of active alumina prior to the electrolysis.

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