

Electrochemical Reduction of Oximes in Aprotic Media

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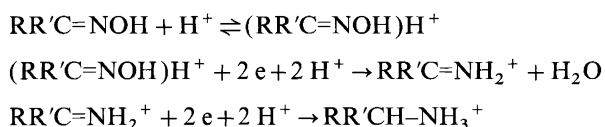
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Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

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The electrochemical reduction in *N,N*-dimethylformamide of (*Z*)- and (*E*)-benzaloximes, derivatives thereof and some ketoximes has been investigated. The bases electrogenerated during the reduction of the benzaloximes and their derivatives induce a catalytic elimination reaction producing benzonitrile. Two mechanisms are discussed, one in which the electrogenerated base eliminates water from the incoming substrate and one in which the base abstracts a proton from the intermediate benzaldimine radical with formation of benzonitrile radical anion; this radical anion then reduces the incoming substrate. The electrogenerated base formed during the reduction of the ketoximes deprotonates the oxime to the less reducible oxime anion. During the reduction of an acylated oxime, the parent oxime is formed, probably by cleavage induced by the electrogenerated base, but direct cleavage of the radical anion to the oxime might be possible.

The electrochemical reduction of oximes has been the subject of many investigations over the past four decades.^{1,2} Most of the investigations have involved aqueous or aqueous-alcoholic media. Oximes of aromatic aldehydes and ketones are usually reduced in acid solution in a four-electron reduction to the amine, whereas the oximes are not generally reducible in alkaline solution. In 1959 it was suggested³ that the first two-electron reduction resulted in the cleavage of the oxygen–nitrogen bond with formation of the imine which was reducible at the potential necessary for the reduction of the oxime, Scheme 1. In a few cases the reduction of an oxime took place in two two-electron steps and in these cases, reduction at the potential of the first step led to the isolation of the imine.⁴ Benzaloxime gave, on reduction at pH about 12, some benzylhydroxylamine in addition to benzylamine,⁵ but the mechanism of the hydroxylamine formation was not established.



Scheme 1.

In unbuffered aqueous-alcoholic media, the *E*-isomer

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(*syn*, α) shows two polarographic waves, the first one being kinetic in nature, whereas the *Z*-isomer (*anti*, β) gives a single wave at about the same potential as the first wave of the *E*-isomer.^{6,7} It was also found that the diffusion current constant of the *E*-isomer was about 3/5 of that of the *Z*-isomer. Based on these observations, a method was proposed to distinguish between the two isomers.⁷ Under similar conditions both the *Z*- and *E*-isomers of 4-chloro- and 4-methoxy-benzophenone oximes showed two polarographic waves, the first one being kinetic in nature. It was suggested that a reaction involving a proton transfer from oxygen to nitrogen ($>\text{C}=\text{N}-\text{OH} \rightleftharpoons >\text{C}=\text{NH}^+-\text{O}^-$) was responsible for the kinetic wave.⁷

Shono and coworkers⁸ have studied the coupling of radical anions of ketones with *O*-methyloximes in 2-propanol. They pointed out a possible difference between the *Z*- and *E*-isomers of the *O*-methyloximes in the intramolecular coupling reaction; based on the percentage of the recovered starting *O*-methyloxime it seemed that the *Z*-isomer (*anti*) reacted faster than the *E*-isomer (*syn*).

Electrochemical reduction of oximes of some aromatic carbonyl compounds in *N,N*-dimethylformamide (DMF) containing tetraethylammonium perchlorate in the presence of phenol as a proton donor resulted in the formation of amines in a reaction analogous to that in aqueous solution.⁹ In anhydrous DMF no benzylamine was found

in the reduction of benzaldoxime; some *N,N'*-dibenzylhydrazine was detected by TLC in the catholyte. This compound was assumed to have been formed through a radical dimerization followed by reduction.

Polarography in DMF of oxime ethers of the type, $>C=N-O-CH_2-CO-NH-Ar$, showed two two-electron waves;¹⁰ the first wave was suggested to result in a cleavage of the nitrogen-oxygen bond, but the nature of the electrode reactions was not established by product studies.

These two publications seem to be the only publications on the reduction of oximes in non-aqueous media. It is therefore the purpose of this paper to investigate the reduction mechanism of some oximes in DMF, with special regard to the role of electrogenerated bases in the product formation, in a manner similar to that for the reduction of different hydrazone derivatives in DMF.^{11,12}

Results and discussion

(E)-Benzaldoxime. The cyclic voltammogram (CV) of *(E)*-benzaldoxime (**1**) in DMF containing tetrabutylammonium tetrafluoroborate, TBABF₄, shows a small irreversible reduction peak ($E_p = -2.15$ V vs. SCE, 0.1 V s⁻¹) followed by peaks from a reversible reduction ($E^0 = -2.24$ V vs. SCE). As the scan rate is increased, the first peak shifts towards lower potentials to become part of the reversible wave as a shoulder. At still higher sweep-rates (> 10 V s⁻¹) only the reversible redox system is observed. Attempts to outrun the cleavage of the radical anion of **1** using an ultramicroelectrode was unsuccessful at least up to 40 kV s⁻¹.

The first peak is assumed to be the reduction of the oxime whereas the reversible peak was identified as that of benzonitrile (**2**) (PhCN), both by its reversible potential and from the increase in both the cathodic and anodic peaks on the addition of a sample of **2** to the solution. There is a striking difference between the height of the irreversible peak and the height of the reversible peak (Fig. 1a). This might indicate that the formation of PhCN involves a fast catalytic reaction occurring close to the electrode. Another indication of this is that the first wave disappears upon multiscanning whereas the height of the benzonitrile wave remains unchanged. It should be kept in mind that the transformation of benzaldoxime into benzonitrile does not involve a reduction.

During CV of the benzaldoxime in DMF, to which an excess of tetrabutylammonium hydroxide had been added, the two waves disappeared and an irreversible wave at a more negative potential (-2.7 vs. SCE, 1 V s⁻¹) was observed; this wave was assumed to be caused by the reduction of the benzaldoxime anion, as the benzaldoxime is regenerated on neutralizing the base. It was also found that the tetrabutylammonium salt of benzaldoxime during CV gave a similar reduction peak. An oxidation peak ($E_{p,ox} = -0.1$ V vs. SCE, 1 V s⁻¹) was

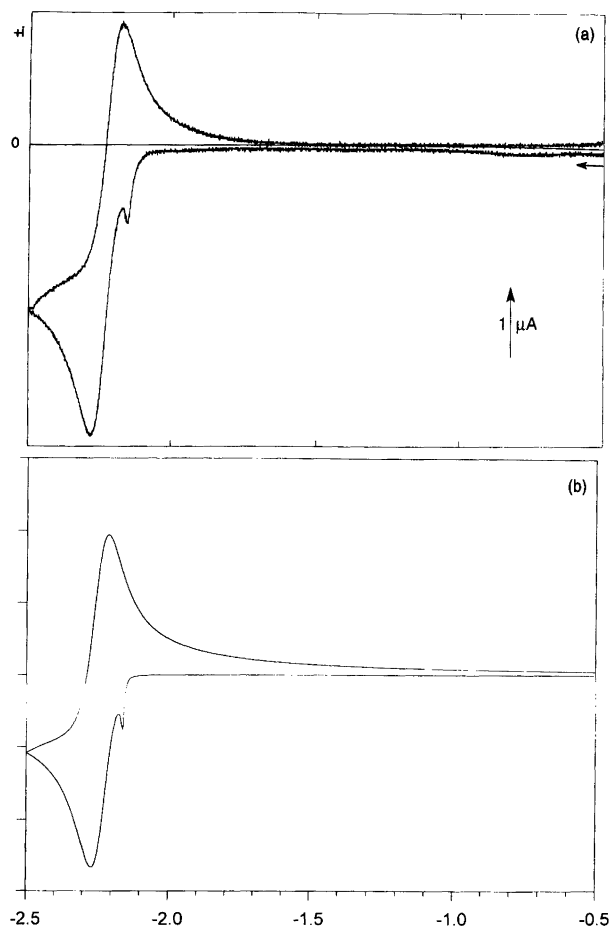


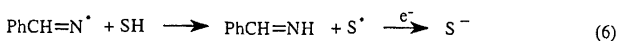
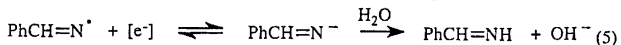
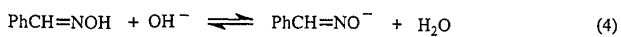
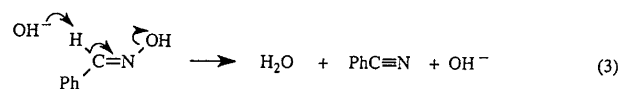
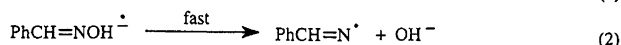
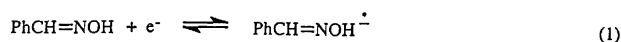
Fig. 1. (a) Cyclic voltammogram at a gold working electrode of a 2 mM *(E)*-benzaldoxime solution in DMF-0.1 M TBABF₄. The scan rate is 0.1 V s⁻¹. (b) Simulated cyclic voltammogram using the following input: $E^0(1) = -2.42$ V vs. SCE, $E^0(2) = -2.24$ V, $k_8 = 1$ cm s⁻¹, $k_2 = 5 \times 10^5$ s⁻¹; $k_7 = 10^6$ M s⁻¹, $k_8 = 10^7$ M s⁻¹, $[1] = 2$ mM.

recorded and attributed to the oxidation of the benzaldoxime anion.

The formation of benzonitrile may occur by base-induced elimination of water from the oxime analogous to the aminonitrile elimination of *N,N*-disubstituted hydrazones.^{11,12} However, such an elimination would have to compete with deprotonation of the oxygen, and one would expect a base to deprotonate the oxime oxygen rather than the central carbon thus forming an oxime anion. This anion would have a much lower tendency to eliminate water than the oxime.

The *(E)*-benzaldoxime was reduced with a low, constant current and the reaction followed by analysing samples by GC. At $n = 0.4-0.6$ the benzonitrile formed began to be reduced and the reduction was stopped. Compound **2** was formed in 60-83% yield and, besides unchanged **1**, small amounts of other products were observed. A catalytic sequence based on an E2-elimination from the substrate is presented in Scheme 2.

According to Scheme 2, the oxime is reduced to the radical anion [eqn. (1)] which then reacts in a fast



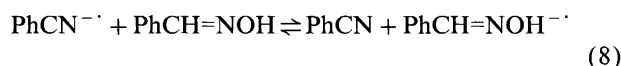
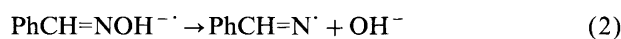
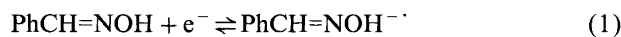
Scheme 2.

follow-up reaction [eqn. (2)]; this is supposed to be the rapid cleavage of the oxygen–nitrogen bond. The hydroxide ion may attack the oxime in an irreversible E2 elimination [eqn. (3)] or deprotonate the oxime oxygen in a reversible reaction [eqn. (4)]. The elimination produces benzonitrile, water and a hydroxide ion, which again can bring about deprotonation or an elimination. A hydroxide ion is thus consumed in the attack on the hydrogen at the azomethine group, but another hydroxide ion is generated in the elimination, thus making the reaction catalytic. Both the reversible deprotonation of the oxime oxygen and the irreversible base-catalysed elimination have to be very fast, in fact so fast that a substantial part of the oxime diffusing towards the electrode undergoes elimination to benzonitrile before it reaches the electrode surface thus explaining the low peak height of the first peak of benzaldoxime. A significant feature of the reactions would be that the elimination can be considered to be an irreversible reaction whereas the deprotonation of oxygen is a rapid reversible reaction. The azomethine radical may further accept an electron from the electrode or from a radical anion and the anion thus formed may be protonated [eqn. (5)]. Alternatively, the azomethine radical can abstract a hydrogen atom from the solvent to form the imine and a solvent radical; the latter being further reduced to the anion [eqn. (6)]. These reactions may explain part of the electron consumption, but cannot be important, as only small amounts of reduction products were detected.

The proposed reaction scheme was simulated, but the simulations based on Scheme 2 seem not to be completely satisfactory. A broad anodic peak at a slightly higher potential than the anodic peak of **2** was seen, when reasonable values of rate constants were used. Furthermore, there is little difference between the voltammograms of benzaldoxime and its *O*-methyl ether and this would indicate that reaction (4) has only a small influence on the voltammograms. In view of the general observation that deprotonation from oxygen is faster than deprotonation from carbon, one would have expected reaction [eqn. (4)] to influence the voltammogram more than is observed. Although conditions in DMF are different from those in water the fact that benzaldoxime is synthesized in a reaction between benzaldehyde

and hydroxylamine in 20% aqueous sodium hydroxide also gives less credibility to the scheme.

Another reaction sequence is shown in Scheme 3; here the hydroxide group formed in reaction (2) attacks the central C–H bond with formation of water and the radical anion of benzonitrile [eqn. (7)]. The radical anion of **2** would reduce the incoming oxime with generation of benzonitrile and the radical anion of **1** [eqn. (8)] so the chain would be reactions (2), (7) and (8). This reaction sequence has some analogy to the reduction of azobenzene in the presence of benzophenone pinacol in which the electrogenerated base deprotonates the pinacol; the pinacol anion is cleaved to the radical anion of benzophenone. It is this radical anion that reduces the incoming azobenzene. In CV the peak of azobenzene nearly disappears.¹³ Compound **2** formed in reaction (8) is then reduced at the electrode in a reversible reaction (9).



Scheme 3.

The scheme avoids the question of deprotonation of the oxime oxygen if it is assumed that the hydroxide ion attacks the imine radical before they diffuse apart. Benzonitrile radical anion is not very basic and a concentration of 50 mM of water in DMF was found to be of little consequence for the reversibility of the CV of benzonitrile at a sweep rate of 0.4 V s⁻¹, so the backward reaction (7) would not prohibit the catalytic circle. The driving force for the reactions would be reaction (2), as reaction (8) is slightly endergonic. Some imine radical is further reduced to the imine anion which is hydrolysed to benzaldehyde or, after protonation, reduced further. The isolated benzaldehyde is probably formed in this way.

Similarly to Scheme 2, Scheme 3 was digitally simulated. The simulation scheme is composed of the steps (1), (2), (7), (8) and (9). The simulation (Fig. 1b) reproduces the experimental curve reasonably well; the purpose of the simulation was to show that Scheme 3 gave a better qualitative picture of the CV than Scheme 2. The simulation uses $k_2 = 5 \times 10^5 \text{ s}^{-1}$ as a reasonable value as a sweep rate of 40 kV s⁻¹ could not outrun the cleavage. The catalytic sequence might be dependent on the presence of the low (and variable) concentration of water in DMF; this feature is difficult to reproduce in the simulation; attempts¹⁴ to simulate the azobenzene/benzophenone pinacol catalytic sequence¹³ met with similar difficulties. The conclusion is that the reduction of **1** is probably a mixed reaction with Scheme 3 playing an

important part, but with minor influence from some base-induced E2-elimination.

(*E*)-Benzaldoxime-*O*-methyl ether (**3**). The voltammogram presents two reduction waves. The first irreversible reduction wave ($E_p = -2.14$ V, 1 V s^{-1}) is small as compared with the second reversible wave. The latter was identified by its E° value as benzonitrile. Addition of **2** produces an increase of the current of the reversible wave. Reduction schemes are similar to those proposed for the reduction of benzaldoxime, with the difference that the base is now the methoxide ion; as the compound has no protons bound at oxygen no competing deprotonation takes place. In this case both schemes could work, but the similarities of the cyclic voltammograms of the benzaldoxime and its methyl ether suggest that reactions similar to Scheme 3 dominate.

(*E*)-*O*-Benzoylbenzaldoxime (**4**). The CV of the *O*-benzoylbenzaldoxime presents three reduction peaks (Fig. 2). An irreversible reduction wave ($E_p = -1.74$ V vs. SCE, 1 V s^{-1}) is observed, which is then followed by the reversible wave of benzonitrile, preceded by a shoulder. As the scan rate is decreased, the shoulder shifts towards positive potentials to become a peak. The behaviour of these two last waves is therefore analogous to that observed for the reduction of benzaldoxime. Both CV and a preparative reduction show the formation of **1** during the reduction of **4**, so the formation of **2** is not just an E2-elimination catalysed by benzoate, although it was shown that even benzoate [pK_a (PhCOOH, DMSO) = ca. 11]¹⁵ is basic enough to catalyse such an elimination from **4** with formation of **2**.

Two reactions might explain the formation of **1** during the reduction of **4**. One is that a base (OH^- , PhCH=N^-) generated in the reduction could attack the benzoate group with formation of **1** and benzoate or

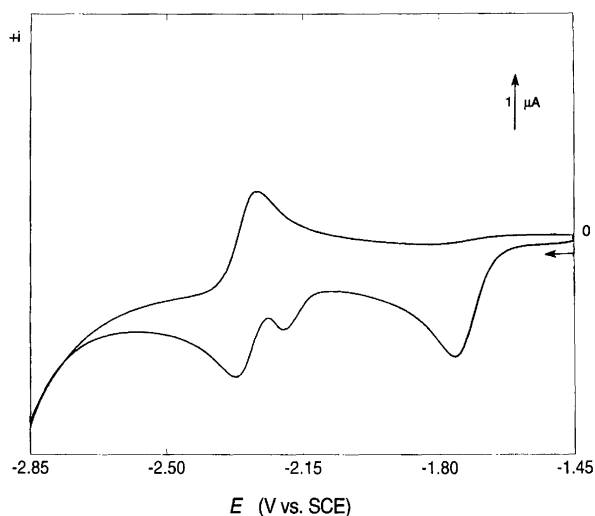
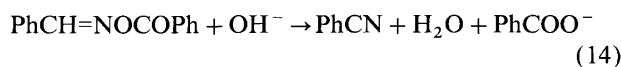
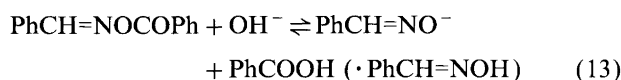
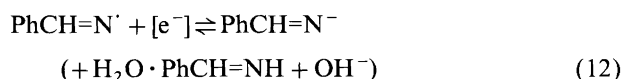
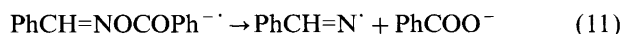
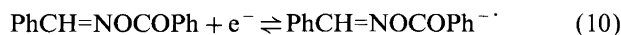


Fig. 2. Cyclic voltammogram at a gold working electrode of a 2 mM (*E*)-*O*-benzoylbenzaldoxime solution in DMF-0.1 M (TBA)BF₄. The scan rate is 0.1 V s^{-1} .

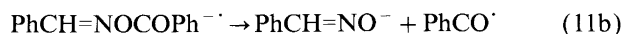
PhCH=NCOPh (which could react further) as shown in Scheme 4a. Another possibility is that cleavage of **4**⁻ occurred between the carbonyl group and oxygen with a direct formation of **1**.

Preparative reduction of **4** (0.03 M) yields **2** (60%), **1** (25%), benzaldehyde (10%) and benzoic acid as well as traces of other compounds. This is in accordance with Scheme 4a; the scheme requires that the base-catalysed cleavage of **4** is fast. When a 2×10^{-3} M solution of **4** was reduced and followed by CV only **1** was detectable on the voltammograms. Also in CV it seems that practically all **4** is transformed into **1**, but the relative high yield of **2** in the preparative reduction suggests that under these circumstances, i.e., longer duration and higher ratio of substrate/residual water, a base-induced elimination occurring in the bulk of the catholyte is of importance.

An alternative route (Scheme 4b) could be the cleavage of the carbon-oxygen bond to afford the benzaldoxime anion and the PhCO[•] radical [eqn. (11b)]. The benzaldoxime anion can be protonated by residual water [eqn. (13)] and the reduction scheme of the benzaldoxime thus formed is then identical with that proposed above (Schemes 2 and 3). Similar cleavage of a carbon-oxygen bond is observed during the electroreduction of phenyl benzoate yielding phenol and benzil.¹⁶ The fact that no benzil has been observed during CV of **4** does not necessarily exclude Scheme 4b, as benzil under these basic conditions is rapidly transformed through a benzilic acid type rearrangement; however, no benzilic acid derivatives were isolated, so altogether Scheme 4a seems best to describe the reactions.



Scheme 4a.



Scheme 4b.

Both schemes are followed by the reduction of PhCH=NOH [eqns. (1)–(9)].

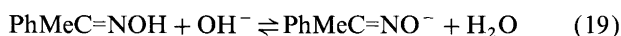
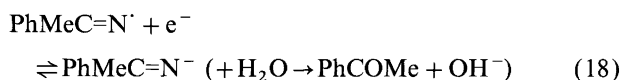
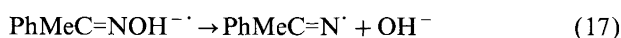
(*Z*)-Benzaldoxime (**5**). The CV is similar to that described above for the *E*-isomer; the cleavage of the nitrogen-oxygen bond leads to the same benzaldimine radical as formed from **1**. The sole difference is in the potential of the first irreversible reduction wave, which

is at a potential 30 mV lower than that of **1** ($E_p = -2.18$ V vs. SCE, 0.1 V s $^{-1}$). This is in accordance with the observations made by Kitaev and co-workers⁹ for the polarographic reduction in DMF of the *E*- and *Z*-isomers of benzaldoxime. It should be noted that *E*-oximes, contrary to observations made in DMF, are more easily reduced in aqueous solution than the *Z*-oximes.^{3,7} This might be due to differences in solvation of the species in protic and aprotic solvents. In the former hydrogen bonding to the solvent might be the predominant effect, whereas in the latter intramolecular hydrogen bonding might be more important and might influence the rate of cleavage.

(*E*)-Acetophenone oxime (**6**). The cyclic voltammogram presents one irreversible wave, which has a peak potential $E_p = -2.52$ V vs. SCE, at a scan rate of 1 V s $^{-1}$. This wave decreases upon multiple scans, the extent of which depends on the waiting time between the two scans. No other wave could be detected before the background current. When the potential range is extended towards positive potential, a reoxidation peak can be seen ($E_p = -0.24$ V vs. SCE), Fig. 3. A small reduction wave corresponding to this anodic peak can be seen on the second sweep. This wave is not present if the scan is initiated at a higher potential than its reversible potential, nor if the switching potential is set before the cathodic peak of (*E*)-acetophenone oxime. When tetramethylammonium hydroxide is added to the solution, the reduction peak decreases, while the intensity of the reversible wave is increased. A possible explanation of the anodic peak could be the oxidation of the oxime anion to a short-lived nitroxyl-type radical, reaction (20), Scheme 5.

Bulk electrolysis at a potential slightly more negative than the first reduction wave ($E_{app} = -2.6$ V vs. SCE) consumed one electron per molecule. The starting oxime

(52% recovered) and acetophenone (47%) were identified by GLC as the reaction components.



Scheme 5.

Fluorenone oxime (**7**). The reduction of fluorenone oxime (Fl=NOH) and its derivatives is of interest as fluorenone imine (**8**) can be prepared and is a relatively stable compound. A reduction mechanism of **8** has been investigated by Hawley and co-workers; **8** was found to be reduced in a nearly reversible reduction (0.2 V s $^{-1}$) at -1.67 V vs. SCE to its radical anion.¹⁷ We have investigated the reduction of fluorenone oxime and *O*-acetylfluorenone oxime.

In the negative direction of potentials, two reduction peaks of **7** can be seen. They are both irreversible up to 50 V s $^{-1}$. The first peak is located at $E_p = -1.67$ V vs. SCE and the second is at $E_p = -2.58$ V vs. SCE. An oxidation peak ($E_{p,ox} = -1.3$ V vs. SCE) is seen on the return scan (switch potential -2.80 V vs. SCE). When the scan range is extended from $+0.21$ V to -2.80 V, no new reduction peak could be detected on the forward scan; however, a new oxidation peak is recorded on the reverse scan. When scans are repeated, this oxidation peak is associated with a reduction peak. They form a reversible wave, having a half-wave potential of $E^\circ = -0.04$ V vs. SCE.

Fluorenone oxime was reduced in DMF containing 0.1 M Bu $_4$ NBF $_4$. When a sample of the reduced reaction mixture was injected directly into the gas chromatograph a signal from *O*-butylfluorenone oxime, besides other signals, was detected. Apparently the fluorenone oxime anion is butylated by attack on Bu $_4$ N $^+$ during the brief heating to 200°C during the injection, as it was not detected after normal work-up of the catholyte. Isolation of the products gave fluorenone (59%), fluorenone oxime (34%) and fluorenone imine (6%). As no fluorenone was detected on injecting the catholyte directly into the gas chromatograph, the isolated fluorenone is probably formed on hydrolysis of the imine. The fluorenone imine is rather stable in acidic solution and can be extracted from a diethyl ether phase with dilute hydrochloric acid; when this solution is made basic, most of the imine is hydrolysed to fluorenone. This is substantiated by the fact that the ethereal solution of the products was extracted with dilute hydrochloric acid, which was made alkaline and extracted with ether; in this ether phase fluorenone and **8** were found but no 9-aminofluorenone.

The first reduction peak is probably due to the reduction of fluorenone oxime to the radical anion, followed

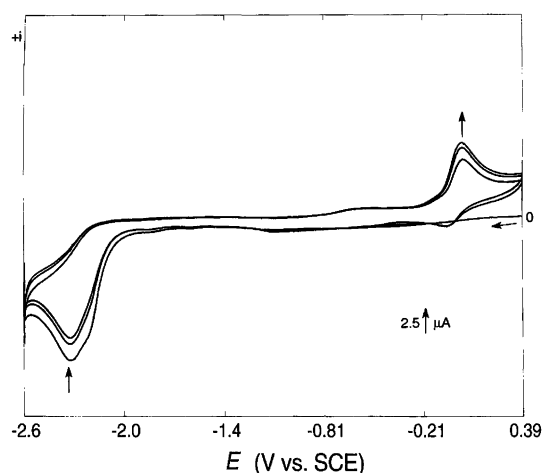
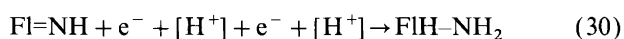
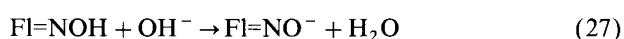
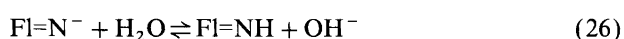
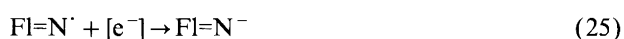
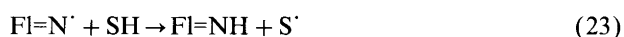
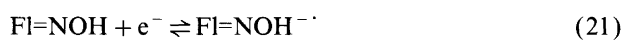


Fig. 3. Cyclic voltammogram at a gold working electrode of a 2 mM (*E*)-acetophenone oxime solution in DMF- 0.1 M (TBA)BF $_4$. The scan rate is 1 V s $^{-1}$. Changes in peak intensities upon multiscanning are indicated by an arrow at the peak.

by its cleavage [eqns. (21) and (22)]. The hydroxide ion may deprotonate fluorenone oxime to the anion [eqn. (27)]. The fluorenone imine radical can abstract a hydrogen from the solvent [eqn. (23)] or be reduced to the anion [eqn. (25)], which can then be protonated by residual water [eqn. (26)]. This results in the formation of fluorenone imine. The imine survives during the reduction despite having a higher reduction potential than the oxime; possibly it is reduced to the radical anion and reoxidized during work-up. The imine radical anion may be responsible for the dark cherry colour observed in the later stages of the reduction. The second peak may be attributed to the reduction of the fluorenone oxime anion. However, both the second peak of **8** and the first peak of 9-aminofluorene come at approximately the same potential, but the latter compound was not detected during a preparative reduction. The first oxidation peak ($E_{p,ox} = -1.3$ V vs. SCE) is the reoxidation of the reduction product from the second peak of **7**, which might be the radical dianion of **7** or the radical anion of **8**. The second oxidation peak ($E_{p,ox} = +0.21$ V vs. SCE) is probably the oxidation of fluorenone oxime anion. The anion can be generated by addition of tetrabutylammonium hydroxide to the solution; the oxidation can then be directly recorded when the potential is swept from -0.5 V vs. SCE towards positive potentials.

The following reduction sequence given in Scheme 6 is proposed.



Scheme 6.

O-Acetylfluorenone oxime. A cyclic voltammogram of this compound shows four reduction peaks. All peaks look irreversible when the scan is reversed at -2.8 V vs. SCE, and only the second peak presents a marked reoxidation peak. The first peak ($E_{p,c} = -1.25$ V, 1 V s^{-1}) can be attributed to the formation of the radical anion of *O*-acetylfluorenone oxime, followed by its cleavage. The imine radical can either abstract a hydrogen atom from the solvent, or be further reduced, homogeneously or heterogeneously, to the anion, which can be protonated. The second peak ($E_{p,c} = -1.67$ V, 1 V s^{-1}) is assigned to the first reduction of fluorenone oxime. The third reduction peak ($E_{p,c} = -2.58$ V, 1 V s^{-1}) was attrib-

uted to the reduction of the fluorenone oxime anion or fluorenone imine anion. The oxidation peak ($E_{p,ox} = -1.3$ V vs. SCE) is located at the same position as the one observed in the cyclic voltammogram of fluorenone oxime. Indeed, when two scans, initiated from a positive potential ($+0.21$ V vs. SCE), are recorded the reversible wave ($E^\circ = -0.04$ V vs. SCE) corresponding to the reversible oxidation of fluorenone oxime anion can be seen. All these assignments were done by comparison of the experimental voltammogram to those of each individual compound. Bulk electrolysis was performed with an applied potential slightly more negative than the first reduction peak. After work-up, fluorenone was recovered. The reduction of fluorenone was therefore investigated. Addition of fluorenone to a solution of *O*-acetylfluorenone oxime does not enhance any of the existing reduction peaks, but produces two new reversible waves. We can conclude that fluorenone is not a direct product of the reduction of *O*-acetylfluorenone oxime. It is assumed that fluorenone imine formed during the electrolysis is hydrolysed to fluorenone during the work-up.

Conclusions

The first step in the electrochemical reduction of the oximes after the uptake of an electron is the cleavage of the radical anion to a hydroxide ion and an imine radical. The imine radical might be reduced further to the imine, which might be hydrolysed to the carbonyl compound. The base generated in these reductions affects the further reactions in ways dependent on the structure of the oxime.

(a) Oximes are slightly acidic and the base may deprotonate the oxime; the oxime anion is reduced at a potential considerably more negative than the oxime; in most cases the anion is not reducible in the available potential region. The base might be the radical anion ('father/son reaction') which is found for acetophenone oxime or a base formed later in the reaction. The result is that a large part of the oxime is 'hidden' as the unreducible oxime anion during the reaction, and on neutralization of the base during work-up the unchanged oxime is isolated together with the reduced products. This is a typical reaction of oximes of ketones. The electron-consuming reaction is the further reduction of the imine radical, sometimes to the imine anion, which may survive as such until work-up, and in some cases the imine is reduced further to the amine. The imine is usually hydrolysed to the ketone during work-up.

(b) Acylated oximes may be attacked by the electro-generated base with formation of the parent oxime which is then reduced. To a certain degree the oxime may be formed by an alternative cleavage of the oxime radical anion with simultaneous formation of the acyl radical. Oximes of acylated oximes of aldehydes may form a nitrile on base-induced E2-elimination.

(c) Aldoximes and their *O*-alkyl ethers form nitriles

during the reduction. The most likely reaction seems to be an attack of the base on the central carbon–hydrogen bond of the radical of the imine, which is formed on cleavage of the radical anion of the oxime. On loss of the aldehydic hydrogen as a proton the radical anion of the nitrile is formed and this species reduces the incoming oxime to its radical anion, thus establishing a catalytic cycle. However, a minor reaction via a base-induced E2 elimination from the oximes might operate simultaneously.

Experimental

Materials. *E*-Benzaldoxime, m.p. 32–34 °C, (33 °C),¹⁸ *Z*-benzaldoxime, m.p. 125–127 °C (126 °C);¹⁸ *O*-benzoylbenzaldoxime, m.p. 104 °C (101–102 °C);¹⁹ acetophenone oxime, m.p. 58–59 °C (59 °C);²⁰ fluorenone oxime, m.p. 194–195 °C (193–194 °C);²¹ *O*-acetylfluorenone oxime, m.p. 76 °C (76 °C).²¹ Fluorenone imine was prepared according to Ref. 22 by treating fluorenone (10 g) with liquid ammonia (40 ml) at room temperature; according to Ref. 22 the reaction takes several weeks, but by adding 1 g ammonium chloride the fluorenone dissolved over one or two days. Evaporation yielded the imine nearly quantitatively.

Equipment. The electrochemical equipment has been described elsewhere.^{11,12,23} The analytical electrochemical cell consisted of a three-electrode arrangement, the working electrode being a gold button (area = 0.0078 cm²), the auxiliary electrode a Pt wire, and the reference electrode Ag/AgI. All potentials are referred to the saturated calomel electrode (SCE). The dimethylformamide (DMF) solution, 0.1 M in TBABF₄, was passed through a column containing freshly activated alumina immediately before use. The analyte concentration was 2 mmol l⁻¹. Oxygen was removed from the solution by bubbling through DMF-saturated nitrogen gas. During the experiments, a gas blanket was left over the solution. Bulk electrolyses were performed in a three-compartment H-cell. After completion of the reductive electrolyses, water was added to the catholyte (same volume), and this solution was extracted with diethyl ether (30 ml portions, three to five times). The collected ether phases were then washed with water and dried over MgSO₄. The solvent was removed *in vacuo*.

The product mixtures were analysed by GC or HPLC, and products were identified by GC–MS and NMR spectroscopy. The HPLC system was identical with one previously described.¹⁴ A normal phase column, 250 × 4 mm Spherisorb S5W (Mikrolab A/S, Aarhus, Denmark), through which a 95 : 5 *n*-hexane–dioxane solution was percolated, was used.

The water content in DMF was determined by the Karl Fisher method with a 737 KF Coulometer (Metrohm, Herisau, Switzerland). On average, a water content of 67 μg per ml of solvent was found. This corresponds to a concentration of 3.7 mmol l⁻¹.

Reduction of (*E*)-benzaldoxime. Benzaldoxime (200 mg) was reduced at a carbon electrode with a constant current (10 mA) in dry DMF–0.1 M TBABF₄ containing docosane (50 mg). Samples were withdrawn before the current was applied and at suitable intervals (consumption of 10 coulomb); the samples were analysed by GLC with docosane as an internal standard. GLC showed the formation of benzonitrile and only traces of other products were detected on the chromatograms. In different runs, when $n=0.4$ – 0.6 , the reduction of benzonitrile to the radical anion was seen and the reaction was stopped. According to GLC the yield of benzonitrile varied from 60 to 83% and TLC showed, after work-up, the presence of benzaldehyde and benzaldoxime. No other products were detected by GLC or TLC.

Reduction of *O*-benzoylbenzaldoxime. *O*-Benzoylbenzaldoxime (200 mg) was reduced at the potential of the first wave (–1.8 V vs. SCE) in DMF–0.1 M TBABF₄ at a carbon electrode with docosane as an internal standard. The catholyte was diluted with water, the aqueous phase was extracted three times with diethyl ether, and the ether was washed with water after which GLC indicated **2** (60%), **1** (25%) and benzaldehyde (10%). When a 2×10^{-3} M solution of **4** was reduced at –1.8 V and the reaction followed by CV directly, only **1** was detectable in the catholyte in the voltammograms.

Reduction of fluorenone oxime. Fluorenone oxime (200 mg) was reduced in 35 ml of DMF–0.1 M TBABF₄ at a carbon electrode at –1.8 V vs. SCE. At about $n=1$ the solution was cherry-red and the current became very low. A sample of the catholyte was analysed by GC–MS; besides the compounds isolated (described below) *O*-butylfluorenone oxime was identified by its retention time and by MS by comparison with an authentic sample prepared from butyl iodide and the salt of fluorenone oxime (¹H NMR, CDCl₃): δ 1.01 (t, $J=7.3$ Hz, 3 H), 1.53 (sextet, $J=7.0$, 2 H), 1.81 (quintet, $J=7.0$, 2 H), 4.43 (t, $J=6.5$, 2 H), 7.23–7.47 (m, 4 H), 7.64 (t, $J=6.4$, 2 H), 7.78 (dd, $J=6.6$, 1.1, 1 H), 8.15 (dd, $J=7.2$, 1.1, 1 H). MS IP 70 eV; m/z (% rel. int.): 251 (20), 220 (90), 206 (17), 195 (40), 179 (100), 178 (72), 165 (25), 151 (33). The catholyte was diluted with water and extracted three times with diethyl ether, which was washed twice with water and extracted with 1 M hydrochloric acid. The ethereal solution was dried and evaporated to leave 185 mg of a slightly yellow residue. Analysis of the residue showed it to consist of 108 mg fluorenone, 68 mg fluorenone oxime and 9 mg fluorenone imine. The acidic extract was made alkaline, extracted with diethyl ether, washed with water and dried, and the ether was removed *in vacuo* to leave a residue of 15 mg, consisting of 11 mg fluorenone and 3 mg fluorenone imine, altogether 59% fluorenone, 34% fluorenone oxime and 6% fluorenone imine.

Simulations and fitting of the model (Scheme 3) to the experimental data were performed with the commercial

program Digisim 2.0. The following parameters were used: $E^\circ(1) = -2.42$ V, $E^\circ(2) = -2.24$ V (experimental value), $k_s(1) = 1$ cm s⁻¹, $k_s(9) = 1$ cm s⁻¹, $k_2 = 5 \times 10^5$ s⁻¹, $k_7 = 10^6$ M⁻¹ s⁻¹, $k_8 = 10^7$ M⁻¹ s⁻¹, $[1] = 0.002$ M. The equilibrium constants for eqns. (2) and (7) could be changed within wide limits without affecting the simulated curves. k_2 could not be chosen smaller, as the reaction was not outrun at 40 kV s⁻¹, but higher values [with corresponding change in $E^\circ(1)$] gave less satisfactory results. Therefore, these numbers should not be considered as absolute values: there is a rather large uncertainty associated with the figures. This large uncertainty is not surprising, since (a) there is a large number of parameters to be fitted, (b) these parameters are, to certain extent, all interdependent, and (c) the possibility of an elimination induced by the bases was not included in the simulation scheme.

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