<u>b.</u> EC of ET₂NH in the Presence of NaHCO₃. The anode compartment of the cell contained 100 cm³ 4 M NaCl solution, 5 cm³ (0.048 mole) Et₂NH and 6.05 g (0.072 mole) NaHCO₃; electrolysis was carried out as described above. The gases evolved from the anode compartment were passed through a trap at -78°C. After passing 2F of electricity (Q = 9264 C) per mole of amine electrolysis was terminated and a mixture of Et₂NCl with a little water was distilled off in vacuo. The chloramine was separated from the water, mixed with the contents of the trap (Et₂NCl), dried over fused CaCl₂, and redistilled. This gave 3.22 g (62%) Et₂NCl, bp 30°C (60 mm), np²¹ 1.423 (bp 94°C at 760 mm). The IR and ¹H NMR spectra were identical with those given in [10].

<u>c. EC of Et₂NH₂Cl in the Presence of NaHCO₃</u>. The anode compartment of the cell contained 100 cm³ 4 M aqueous NaCl, 5.48 g (0.05 mole) Et₂NH₂Cl and 12.6 g (0.15 mole) NaHCO₃. The electrolysis and isolation of the product were carried out as in the last example. This gave 3.63 g (70%) Et₂NCl with bp 30°C (60 mm), n_D^{21} 1.432.

<u>Electrochemical Preparation of MeNCl₂, EtNCl₂, PrNCl₂, BuNCl₂ and Me₂NCl. These compounds were obtained by procedures similar to those described above. Since MeNCl₂, EtNCl₂ and PrNCl₂ are explosive in the pure state we worked only with solutions in CCl₄. Pure BuNCl₂ and Me₂NCl were obtained as colorless oils with bp 40°C (30 mm) and n_D^{21} 1.4547 for BuNCl₂ and bp 42°C (760 mm) for Me₂NCl. The yield of Me₂NCl as a separated product was low on account of its considerable volatility. The IR and ¹H NMR spectra of the substances obtained were identical with those given in [10].</u>

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ANODIC ELECTROLYSIS OF KETOXIMES AND ALDOXIMES: MECHANISM

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The key step in the electrochemical oxidation of ketoximes which determines the composition of the electrolysis products is the reaction of the intermediate oxoimmonium cation with the original oxime, whereas in the case of aldoximes, the key step is dimerization of the iminoxyl radicals.

It has been reported [1, 2] that the differences in the voltammetric behavior of ketoximes and aldoximes on oxidation at a platinum anode are due to differences in the reactivities of the intermediate iminoxyl radicals. This in turn will affect the composition of the products of the electrolysis of ketoximes and aldoximes. The aim of the present investigation was to use electrolytic data and voltammetric measurements in considering anodic oxi-

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TABLE 1. Yields and Properties of Electrolysis Products of Benzophenone Oxime (E = 1.7 V, 0.2 N NaClO₄, abs. MeCN, Pt anode)

Compound	Yield, %	тр, °С"	PMR (δ, ppm (C ₆ H ₅); (CD ₃) ₂ CO)	m/z [M]+	Found/Calculated, %		
					C	н	N
₽h₂CO	65	48	7,49m 11,03s (1H, 	182	-	-	
$\begin{array}{c} PhCOOH\\ Ph_2C=N-O-N=CPh_2\\ \downarrow\\ O\end{array}$	13 12	120 207–210	- 7,54m 7,90 m	122 392, 376 [M~O]+	79,55 79,59	<u>5,11</u> 5,10	7,11 7,14
$\frac{Ph_2C=N-N=CPh_2}{\bigcup_{O}}$	5	159-161	7,61 m 7,84 m	376, 360 [M-O]+	83,13	5,19 5.32	7,47
Ph ₁ C=N-N=CPh ₂ +	Trace	154-156	7,86m	360, 180 [M-NCPh ₂]+	86,96 86,67	5,52 5,56	7,86
Ph ₂ C=N-O-N=CPh ₂ ‡ *	1	169-171	7,57 m	376, 196 [M-NCPh ₂]+	-		-

*The mp's were in agreement with the reported values. +The PMR spectrum and elemental analysis are given for a sample obtained as in [6].

#This compound has been reported in the literature, but no physicochemical constants were given.



dation of ketoximes and aldoximes from a single point of view. Of considerable interest in this connection are data on the chemical oxidation of oximes (definite similarities have been noted [1] between the chemical and electrochemical oxidation of ketoximes). For this reason, we selected benzophenone oxime Ph_2C -NOH (BPO) and benzaldoxime PhCH-NOH (BAO) as starting materials, the chemical oxidation of which has been most thoroughly investigated.

RESULTS AND DISCUSSION

The chemical oxidation of ketoximes, particularly BPO, by $Pb(OAc)_4$ [3] or $K_3[Fe(CN)_6]$ [4, 5] results in the formation of the nitrosodimers (A) and (B), which are capable of undergoing further reactions [3-6]. (See scheme on following page.)

The less stable dimer (B) is readily converted into (C), which under more severe conditions is converted into (D) [6]. The dimer (A) is more stable, although this too is partially converted into (E) in the course of the reaction [3]. It is not by change, therefore, that the nature and ratios of the products of the chemical reaction are markedly dependent on the conditions under which it is carried out. In addition to compounds (A)-(E), oxidation of BPO gave high yields of the ketone, and small amounts of benzoic acid. It would be expected that these compounds would also be present in the electrochemical oxidation products of ketoximes. In fact, the product of the anodic electrolysis (E = 1.7 V) of BPO is benzophenone. In addition, the reaction mixture contained the dimers, (A), (C), (E), and (D), together with benzoic acid (Table 1).

We have reported previously [1] that the reaction of the intermediate oxoimmonium cation with the starting oxime is the principal process. However, the yields of nitrosodimers as obvious products of this reaction on electrolysis of BPO are low. We have found that the dimer (A) is itself capable of undergoing oxidation under the electrolysis conditions. Its polarization curve shows an anodic wave with $E_{1/2} = 1.6$ V. Electrolysis at the potentials of this wave affords benzophenone in near-quantitative yields. This explains both the high yield (65%) of benzophenone and also the low yield of the dimer (A) (12%) on electrolysis of BPO. The formation of small amounts of the dimer (E) is obviously due either to oxidation of (A) at the electrode, or to slow chemical reaction of the latter in solution [3]. The presence of compounds (C) and (D) in the reaction mixture is probably due to further reactions of the unstable dimer (B) [7] which, from its structure, should undergo oxidation at the electrode even more readily than the dimer (A). On the other hand, according to Brokenshire, et al. [7], the dimer (B) may decompose as follows: $(B) \rightarrow 2Ph_2CO + N_2$, and it may also react with BPO to give (C), iminoxyl, and hydroxyl radicals.

In general, from the voltammetric [1] and electrolysis data at a controlled potential, the following mechanism for the electrochemical oxidation may be given, with the broken lines indicating possible minor stages.



The formation of nitrosodimers of various types as intermediates is due to the existence of several resonance structures for the oxoimmonium cation.

$$RR'C = NO^+ \leftrightarrow RR'C = N = O \leftrightarrow RR'C - N = O$$
(I)
(II)
(III)
(III)

The greatest spin density in iminoxyl radicals is localized at the oxygen atom [8]. It may therefore be assumed that on oxidation of the iminoxyl radical (scheme 1), the electron is removed from the oxygen to give the oxoimmonium cation (I). In this form, the cation probably reacts preferentially with the starting oxime to give the dimer (A). Obviously, the contribution of the most preferred resonance structure (III) to this reaction is small, since in both the chemical [7] and electrochemical oxidation of BPO no products were detected, the formation of which could be attributed to form (III).

In contrast to ketoximes, the principal processes governing the composition of the anodic electrolysis products of aldoximes, according to [2], are reactions involving the intermediate iminoxyl radical. The high rates of these reactions impose kinetic restrictions on the oxidation of the iminoxyl radical to the oxoimmonium cation, thus rendering this step less important.

The principal reaction of the iminoxyl radicals generated in the chemical oxidation of benzaldoxime (BAO) is dimerization to give phenylaldazine bis-N-oxide PhCH-N-N-CHPh(F), which is unstable, readily undergoing further reactions in solution at room temperature to give 3,5-diphenyl-1,2,4-oxadiazole (DPO), benzaldehyde, benzoic acid, benzonitrile, and nitrogen [7, 9].

It was found that electrolysis of BAO at the first wave (E = 1.5 V) gives a complex mixture of products (Table 2), the main product being benzaldehyde (64%). In addition, small amounts of benzoic acid, DPO, diphenylfuroxan, and trace amounts of benzonitrile and phenylnitromethane were present in the reaction mixture. Clearly [7, 9], the formation of large amounts of benzaldehyde is due to decomposition of the dimer (F), which gives benzaldehyde as the main product.

Compound	Yield, %	mp, °C*	PMR (δ, ppm (CD ₃) ₂ CO)	m/z [M]+	Other charac- teristics*				
PhCHO	64	-	7.2m. (5H, C ₆ H ₅) 9,8s (1H, CHO)	-	n _D =1,5446 ·				
$\mathbf{Ph-C-N}$	7	101-102	7,78 m (5H, C ₆ H ₅) 8,22 m (5H, C ₆ H ₅)	222	_				
Ph-C-C-Ph	3	116-117	-	238	$\lambda_{max} = 283$ nm ($\epsilon = 5700$)				
PhCOOH ·	8	122	-	122	ļ				

TABLE 2. Yields and Properties of Electrolysis Products of Benzaldoxine (E = 1.5 V, 0.2 N NaClO₄, dry MeCH, Pt anode)

*According to literature data.

$$\begin{array}{c} 0 \\ \uparrow \\ PhCH=N-N=CHPh \rightarrow 2PhCHO + N_2 \\ \downarrow \\ 0 \end{array}$$
(2)

Benzoic acid is formed by the further oxidation of benzaldehyde [7, 10], the amounts present in the reaction mixture increasing at higher potentials (E = 1.9 V). The presence of DPO and diphenylfuroxan in the products may be rationalized, by analogy with [9], by formation of the dimer (F) under the electrolysis conditions, this then decomposing partially to give benzonitrile oxide, which reacts with BAO to give DPO, and dimerizing to give diphenylfuroxan. Another source of benzonitrile oxide could be the oxoimmonium cation, formed [2] by oxidation at the electrode of a small proportion of the iminoxyl radicals.

$$PhCH = NO' \xrightarrow{-e} PhCH = NO' \xrightarrow{-H+} PhC \equiv N \rightarrow 0$$
(3)

Partial hydrolysis of the oxoimmonium cation gives the trace amounts of phenylnitromethane [11].

To summarize, the findings discussed above, in conjunction with the results of voltammetric studies [2] of the electrochemical oxidation of aldoximes, suggest the following scheme as a likely one for the electrochemical oxidation of aldoximes (the broken lines represent possible minor stages).



Polarization curves for the oxidation of aldoximes are known [2] to show two waves, although the nature of the second wave remains rather unclear. We have found that during electrolysis of BAO at the first wave $(E_{1/2} = 1.51 \text{ V})$, the height of the second wave $(E_{1/2} =$ 1.92 V) increases (by a factor of ~1.5). It may be assumed that this wave corresponds to the oxidation of the products formed by electrolysis of BAO at the first wave. Actually, under the experimental conditions $E_{1/2}$ for the oxidation of benzaldehyde is 2.25 V, for DPO 2.13 V, and for diphenylfuroxan, 1.82 V. In addition, at the potentials of the second wave, by analogy with benzophenone oxime (see above), oxidation of the dimer (F) may occur. It may therefore be assumed that the second wave on the polarization curves of aldoximes is complex, and clearly corresponds to the oxidation of products formed by the rapid reactions of intermediates generated at the potentials of the first wave.

EXPERIMENTAL

Electrolyses were carried out in a thermostated $(20 \pm 0.1^{\circ}C)$ diaphragm cell in an inert atmosphere. The operating electrode was a platinum plate (S = 20 cm²), and the auxiliary electrode was a graphite rod of diameter 1 cm. In the anode compartment of the cell was placed 70 ml of a 0.2 N solution of NaClO₄ in dry MeCN containing 0.01 mole of BPO or BAO. In the cathode compartment was placed 50 ml of base electrolyte. The anolyte was stirred with a magnetic stirrer. Electrolyses were carried out in potentiostatic mode until 2F/mole for BPO or 1F/mole for BAO had been passed through. The reference electrode used was an Ag/Ag⁺ electrode in MeCN. The required potential at the operating electrode was applied using a P-5827m potentiostat.

In order to isolate the products of the electrolysis of BPO, the analyte was concentrated to 10-15 ml, treated with ether (3 × 50 ml), and the base salt filtered off. The ether solution was dried, and the solvent removed under reduced pressure. The dry residue was treated with hot alcohol (2 × 20 ml). The residual, insoluble solid was compound (A). From the alcoholic solution, following removal of the solvent by column chromatography on silica gel (40/100) there were obtained (C), (D), and (E) (eluent chloroform/carbon tetrachloride (0.8-2)/1), together with benzophenone and benzoic acid (chloroform/carbon tetrachloride, 5/1).

To isolate the electrolysis products of BAO, the anolyte was evaporated under reduced pressure, then treated as above. After removal of the ether, the residue on column chromatography (silica gel, chloroform/carbon tetrachloride (6-1)/1) gave 3,5-diphenyl-1,2,4-oxadiazole, diphenylfuroxan, benzaldehyde, and benzoic acid.

Identification of the electrolysis products (Tables 1 and 2) was carried out by TLC, UV, IR, mass, and PMR spectroscopy, comparison with authentic samples, and elemental analysis. IR spectra were obtained on a UR-20 apparatus, PMR spectra on a Bruker AW-250, and UV spectra on a Specord M40.

BPO and BAO were obtained by standard procedures from benzophenone or benzaldehyde and hydroxylamine. The methods of purification of the solvents and obtaining voltammetric curves have been given [1, 2].

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