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First-wave oxidation of vicinal dioximes corresponds to the transfer of two electrons and two protons to give furoxans, which are further oxidized at the potentials of the second wave. It is shown that the key step in the electrochemical cyclization of vicinal dioximes is oxidation of the intermediate iminoxyl radicals to oxoimmonium cations, which react with the adjacent oxime group.

It has been shown [1-3] that vicinal dioximes (DO) undergo electrochemical oxidation (EO) in MeCN with the transfer of two electrons and two protons to give furoxans (FO). However, the mechanism put forward by Jugelt, et al. [3], on the basis of galvanostatic electrolysis data requires further confirmation, since the possibility of further oxidation [4] of the final FO was not taken into account. This led us to reexamine the anodic oxidation of DO, on the assumption that general features are present which relate the oxidation of DO to the mechanism of EO of monoximes, investigated by the authors previously [5-7]. It was established in these reports that the oxidation of aldoximes involves removal of one electron and one proton with the formation of iminoxyl radicals, which then dimerize to unstable nitrosodimers. The oxidation of ketoximes, on the other hand, involves the more rapid oxidation of the iminoxyl radicals at the electrode to give the oxoimmonium cations (OI), which react with the starting ketoxime [6, 7].

The compounds selected for study were the following DO:

 $\begin{array}{c} R-C--C-R' \\ \parallel \\ NOH NOH \\ R=R'=Ph \text{ (amphi-form) (a); } R=R'=Me \text{ (anti-form) (b); } \\ R=R'=\text{ mesityl (amphi-form) (c); } R=Ph, R'=H \text{ (amphi-form) (d); } \\ R=Cl, R'=H \text{ (e).} \end{array}$

RESULTS AND DISCUSSION

The polarization curves for the oxidation of DO (a-e) each show two waves, the $E_{1/2}$ and i_{lim} values for which vary slightly according to the substituents (Table 1). Judging from the linearity of the dependence of the limiting current (i_{lim}) on concentration of DO, which passes through the origin, and on the square root of the number of rotations of the electrode, these are diffusion-type waves. Coulometric determination of the number of electrons n at the first wave gives a value close to two, although unlike ketoximes and aldoximes [5-7], n is independent of the duration of electrolysis.

Potentiostatic electrolysis at the plateau of the first oxidation wave of DO results in it decreasing, and disappearing completely by the end of the electrolysis, whereas the second wave remains largely unaffected. Examination of the reaction mixtures by UV spectroscopy and TLC showed that the principal products of the electrolysis of DO (a-e) were the corresponding FO (Table 1), the yields of which reached 89%. It can therefore be concluded that the first EO wave corresponds to two-electron oxidation of the DO, whereas the second wave clearly corresponds to EO of the FO formed at the first wave. It was found that addition to the solution after electrolysis of the appropriate FO resulted only in an increase in the height of the wave, $E_{1/2}$ remaining unchanged.

Further information on the mechanism of oxidation of DO was obtained using a rotating disk electrode with a ring. It was found that when the first wave potential is maintained

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TABLE 1. Characteristics of the Electrooxidation Waves for Dioximes at a Rotating Disk Platinum Electrode in 0.1 N LiClO₄ in MeCN, and Yields of Furoxans with Their λ_{max} and ϵ Values (C = 1 \cdot 10^{-3} mole/liter, S = 7.61 \cdot 10^{-3} cm², m = 2400 rpm)

DO.	First wave		Second wave	Viold		
	E _{1/2} , V (i _{1im} , μΑ)	n	E _{1/2} , V (i _{lim} , μΑ)	of FO, %	$\lambda_{\max}, mm(\epsilon)$	
(a) (b) (c) (d) (e)	1,51 (15,5) 1,63 (16,5) 1,82 (17,4) 1,56 (15,1) 1,27 (13,6)	1,87 2,03 2,10 2,00 1,70	1,94 (14,9) 2,09 (24,3) 2,55 * (21,0) 2,06 (18,7) 1,69 (37,6)	74 84 89 86 † 52 ‡	283 (5700) 263 (7775) 273 (11000) 3-Ph-FO -285 (7800) 4-Ph-FO -270 (7100) 3-Cl-FO -263 (5300)	

*Polarization curves obtained in 0.1 N Bu₄NBF₄ in MeCN. +3-Ph-F0:4-Ph-F0 = 1:9. #3-C1-F0:4-C1-F0 = 1:4.



Fig. 1

Fig. 2

Fig. 1. 1) Polarization curves obtained using a rotating disk electrode with a ring for the electrooxidation of dimethylglyoxime (b) (C = 1.10^{-3} mole/liter, m = 3600 rpm) in 0.1 N LiClO₄ in dry MeCN: a) at the disk electrode (S_d = 0.239 cm²); b) at the ring electrode (S_r = 0.261 cm²) at E_d = 1.8 V. The curves 2 are those for the base electrolyte.

Fig. 2. Polarization curve for the electrooxidation of the dimethylglyoxime anion (b), obtained using a rotating disk electrode ($S_d = 7.61 \cdot 10^{-3} \text{ cm}^2$) in 0.5 N NaOH in abs. methanol ($C = 1 \cdot 10^{-3} \text{ mole/liter}$, m = 1600 rpm).

at the disk electrode, the cathode wave (I) is seen at the ring electrode, with $E_{1/2} = -0.5 V$ (Fig. 1), which by analogy with our earlier work [6] is attributed to the H⁺ wave. The current yield N of the wave for all the DO was 0.81-0.87, the electrode efficiency coefficient being 0.442, indicating the removal of 2H⁺ [8] from one DO molecule. An anode-cathode wave (II) was also seen at the ring electrode, with $E_{1/2}$ around 0.42-0.54 V (Table 2), the N value for which was low (<0.1). To judge from the $E_{1/2}$ values, wave (II), as in [6], may be attributed to the iminoxyl radical-oxoimmonium cation (OC) system. It is clear that the DO cationradicals formed on removal of an electron are rapidly deprotonated to iminoxyl radicals, a large proportion of which are further oxidized to the OC. This is shown by the marked preponderance of the cathode branch of wave (II) over the anode branch (Fig. 1 and Table 2). However, the height of wave (II) is considerably less than that of the analogous wave in ketoximes [6], obviously owing to the more rapid disappearance of the DO oxoimmonium cation by chemical reaction in the bulk of the solution. It has previously been shown that the chemical reaction involved in the case of ketoxime OC is with the starting oxime to give the nitrosodimers [6, 7]. It may be assumed that dioxime OC react similarly, the preferred reaction being intramolecular, with the second oxime group, to give the FO. The rate of

TABLE 2. Values of $E_{1/2}$, i_r (μA),* and Current Yield (N) for Wave (II) at a Ring Electrode in the Oxidation (current i_d) of Dioximes at a Disk Electrode in 0.1 N LiClO₄ in MeCN ($S_r = 0.261 \text{ cm}^2$; $S_d = 239 \text{ cm}^2$; $E_d = E_{1/2}$, m = 3600 rpm)

DO	E1/2	i <u>d</u>	ⁱ r	i ^a r	i ^c ir	$N = \frac{i_r n_d}{i_d n_r} [8] ,$
(a)	0,48	221,5	8,85	0,65	$\begin{array}{r} 8,20 \\ 24,30 \\ 2,25 \\ 12,15 \\ 6,20 \end{array}$	0,04
(b)	0,47	333,8	26,70	2,40		0,08
(c)	0,43	250,0	2,50	0,25		0,01
(d)	0,42	220,8	13,25	1,10		0,06
(e)	0,54	221,7	6,65	0,45		0,03

 i_r^c is the current of the cathode and i_r^a the current of the anode branch.

this reaction is quite high, as shown by the direct presence of the FO oxidation wave on the polarization curves for DO (see above), together with the low values of the current yields at the ring electrode for the OC. Taking the value of N to be 0.01-0.08, the rate of cyclization of the OC to FO has been calculated to be $\sim 10^3 \sec^{-1}$ [8].

Voltammetric measurements in alkaline media have confirmed the validity of the assumption that the iminoxyl radical and OC are formed as intermediates. In fact, the polarization curves for the oxime (b) (Fig. 2) obtained in 0.5 N NaOH in methanol* show two diffusion waves with $E_{1/2}$ values of 0.07 and 0.52 V. Coulometric measurements showed that EO at the first wave involves the transfer of one electron with the formation of the iminoxyl radical. At higher potentials, this radical is oxidized to the OC, to which the second wave on the voltammograms corresponds. As was to be expected, electrolysis at the first wave did not result in the formation of FO even in trace amounts, whereas on electrolysis at the second wave, i.e., under conditions in which OC are formed, the FO is obtained in yields as high as 90%.

To summarize, the experimental results obtained for the anodic oxidation of DO enable a mechanism to be put forward in which the key step is oxidation of the iminoxyl radical to the OC.

In conclusion, the following considerations are relevant. The mechanism of the chemical oxidation of DO to FO has not yet been established [10]. We have previously shown [6] that the chemical oxidation of ketoximes involves the intermediate formation of iminoxyl radicals, which are then oxidized to the OC. Similarly, chemial oxidation of DO could give rise to OC. The possibility of this reaction



occurring is a real one, since, as has been shown above, iminoxyl radicals are oxidized much more readily ($E_{1/2} = 0.42-0.54$ V) than the oxime group ($E_{1/2} = 1.27-1.85$ V). In the light of these findings, it is readily understandable why, during the chemical oxidation of DO with lead tetraacetate, no iminoxyl biradicals, postulated as possible intermediate species in the formation of FO, were detected [11]. From what has been said, it may be concluded that both chemical and electrochemical oxidation of the iminoxyl radicals formed in the first step result in the formation of OC, reaction of which with the adjacent oxime group gives the FO.

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*Under these conditions, one of the oxime groups in the DO dissociates ($pK_a = 9-13$) to give the corresponding anion [9].

EXPERIMENTAL

The conditions for carrying out the voltammetric measurements and electrolysis at controlled potentials, and the equipment required, were similar to those described previously [5-7]. The reference electrode was $Ag/0.1 \text{ N } Ag^+$ in MeCN. The base electrolyte was 0.1 N LiClO₄ in dry MeCN or 0.5 N NaOH in abs. methanol.

The electrolysis of the DO (C = 0.02 mole/liter) was carried out in 0.25 N NaClO₄ in dry MeCN, or 0.5 N NaOH in abs. methanol in a diaphragm cell at potentials corresponding to the plateau of the first oxidation wave of the DO. The anode was a rotating platinum electrode (S 2 cm²), and the cathode a graphite rod of diameter 1 cm. Identification of the furoxans formed on electrolysis was carried out by TLC, by comparison with authentic samples, by voltammetric measurement of the $E_{1/2}$ values of the waves for their oxidation, and spectrophotometrically (Specord M40) using the known values of λ_{max} and ε (Table 1). Quantitative determinations of the FO were carried out by spectrophotometry, the solutions being analyzed immediately following electrolysis. The ratios of the 3- and 4-isomers of Ph-FO and Cl-FO were determined by spectrophotometry after the isomers had been separated by TLC on Silufol UV-254 plates (eluents: 1) hexane:benzene = 1:4; 2) chloroform:CCl₄ = 3:1), and from the ratios of the integral intensities of the signals for the protons of the furoxan ring in positions 3 and 4 in the PMR spectra (Bruker AM-250, 250 MHz), in (CD₃)₂CO, δ , ppm: 3-Ph-FO, 9.2 (C⁴-H); 4-Ph-FO, 8.1 (C³-H); 3-Cl-FO, 8.9 (C⁴-H); 4-Cl-FO, 7.8 (C³-H).

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