

Short Communications

Kinetics and Mechanisms of the Voltammetric Reduction of Heteroaromatic *N*-Oxides in Aprotic Media. The Protonation of 1,4-Diphenylphthalazine *N*-Oxide Anion Radical by Diethyl Malonate in *N,N*-Dimethylformamide

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Although the polarographic reduction of heteroaromatic *N*-oxides in aqueous solution is well characterized,^{1–5} only little work has been reported on the voltammetric reduction of these compounds in aprotic media.^{4–7} In solvents like acetonitrile and *N,N*-dimethylformamide, DMF, the general trend seems to be that reversible one-electron couples are observed, even at low sweep rates, for the formation of the anion radicals in the absence of deliberately added proton donors. However, the dianions, formed by further reduction of the anion radicals, are protonated too fast by the solvent system to allow for the detection of their back oxidation.⁸ Thus, the voltammetric behavior of heteroaromatic *N*-oxides resembles that observed for a large number of other aromatic compounds.

The reversibility of the substrate/anion radical couple disappears as expected upon addition of acid, and a new reduction peak is observed at potentials 200–300 mV more negative than that for the substrate reduction peak. The new peak could be demonstrated to be due to reduction of the parent heteroaromatic compound, which is formed as a result of the reaction between the *N*-oxide anion radical and the proton donor.⁸

In this paper we wish to report the results of a kinetic/mechanistic study of the protonation of the 1,4-diphenylphthalazine *N*-oxide anion radical, DPP^{•-}, by diethyl malonate, H₂DEM,^{9–11} in DMF, which we believe provides the first set of quantitative data for protonation of anion radicals of this type.

The kinetics were studied by derivative cyclic voltammetry, DCV.¹² The value of the switch potential, E_{sw} , relative to E_0 was adjusted to -0.150 V to minimize the interference of the product, 1,4-diphenylphthalazine, DPP. The rate was monitored through measurements of $v_{0.8}$, the sweep rate necessary to keep the ratio of the derivative peak currents, R'_1 , equal to -0.8. This numerically high value was chosen primarily to secure low conversion in order to further reduce the possible influence of the DPP formed and in order to allow the reaction to be treated kinetically as a true pseudo first order process in the concentration ranges of the study.

Data to provide the reaction order in H₂DEM are shown in the first column in Table 1. The slope of the plot, $\log v_{0.8}$ vs. $C_{H_2DEM}^0$ was found to be equal to 0.95, and this value together with the linearity of the plot ($r=0.999995$) leaves little doubt that the reaction is first order in H₂DEM. The data in the second column demonstrate that the rate appears to be insensitive to the substrate concentration, at least as long as C_{DPP}^0 is kept below 2 mM at $C_{H_2DEM}^0=20$ mM. The reaction order in substrate/anion radical, $R_{A/B}=1+z$,¹² where z is given as $d\log v_{0.8}/d\log C_{DPP}^0$, was found to be equal to 0.94. Considering that the

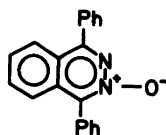
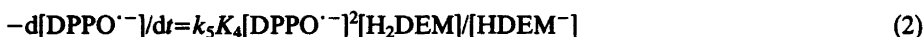
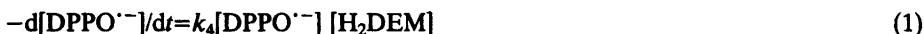
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Table 1. Derivative cyclic voltammetry data for the protonation of 1,4-diphenylphthalazine *N*-oxide anion radical by diethyl malonate in *N,N*-dimethylformamide.

$C_{\text{H}_2\text{DEM}}^0/\text{mM}^a$	$v_{0.8}/\text{V}\cdot\text{s}^{-1}$	$C_{\text{DPPO}}^0/\text{mM}^b$	$v_{0.8}/\text{V}\cdot\text{s}^{-1}$	$C_{\text{DPPO}}^0/\text{mM}^c$	$v_{0.8}/\text{V}\cdot\text{s}^{-1}$
10	0.83	0.4	1.48	0.2	12.9
20	1.61	0.8	1.52	0.4	13.4
40	3.10	1.4	1.47	0.8	13.1
80	5.96	2.0	1.32	1.6	11.9
$\frac{d\log v_{0.8}}{d\log C_{\text{H}_2\text{DEM}}^0}$	0.95	$\frac{d\log v_{0.8}}{d\log C_{\text{DPPO}}^0}$	-0.06	$\frac{d\log v_{0.8}}{d\log C_{\text{DPPO}}^0}$	-0.04

$E_{\text{sw}} - E_0 = -0.150$ V. $^a C_{\text{DPPO}}^0 = 0.5$ mM, $t = 23.5$ °C. $^b C_{\text{H}_2\text{DEM}}^0 = 20$ mM, $t = 21.5$ °C. $^c C_{\text{H}_2\text{DEM}}^0 = 40$ mM, $C_{\text{HDEM}}^- = 20$ mM, $t = 23.0$ °C.

measurements described so far were carried out in unbuffered solutions, the data are in agreement with two rate laws, (1) and (2), in which the rate and equilibrium constants refer to the conventional ECE(h) scheme for ion radical reactions (3)–(6). The two rate laws may be distinguished by



DPPO

testing the dependence of the rate on C_{DPPO}^0 in buffered solution under which conditions (1) and (2) predict different $R_{A/B}$ values, 1 and 2, respectively. The data in the third column were recorded to illuminate this point. It is easily seen that $R_{A/B}$ is close to unity also in this case in agreement with rate law (1) only. However, the magnitude of the rate is larger than expected with the data obtained in unbuffered solutions in mind. This rate difference between buffered and unbuffered conditions is a general phenomenon when H_2DEM is used as a proton donor in DMF,¹³ and is related to the different amounts of the more acidic tautomeric form of H_2DEM present in solution. The question is now whether the equilibrium between these two tautomers will affect the conclusions drawn from the kinetic data. We believe not, since kinetic contributions from the tautomerization reaction are expected to be reflected as inhibition of the reaction, with increasing substrate concentration and an apparent reaction order in H_2DEM higher than one provided that the tautomeric equilibrium is not significantly concentration dependent. None of these effects were observed. However, our data at low values of $C_{\text{H}_2\text{DEM}}^0/C_{\text{DPPO}}^0$ (column 2 and 3) do indicate that contributions of this sort may begin to play a role in determining the rate when the

concentration ratio is smaller than approximately 10. Thus, we conclude that the reaction between $\text{DPPO}^{\cdot-}$ and H_2DEM in the concentration ranges of the study results in kinetic data in agreement with rate law (1) and the ECE(h) mechanism with step (4) being rate determining.

At this point it should be emphasized that the DCV reaction order analysis does not distinguish between the ECE(h) and the ECE mechanism in which step (5) is replaced by the heterogeneous electron transfer reaction (7). The competition between these two routes has



been thoroughly discussed.^{14,15} It appears that the ECE pathway may be ruled out when it is possible to characterize the reaction by a dynamic technique like DCV at the same time as $E'_0 \gg E_0$. The latter requirement is without doubt fulfilled considering the electronic structure of DPPOH^{\cdot} and that E_0 for DPPO is -2.12 V vs. Ag/Ag^+ (DMF).

Under pseudo first order conditions, rate law (1) reduces to (1') and the rate constant k'_4 , and consequently k_4 , may be evaluated from the relationship (8), which was derived from the $k'_4 RT/(v_n F)$ value, 0.0535, obtained by digital simulation^{16,17} of the DCV experiment as the value at which R'_i was equal to -0.8 at $E_{\text{sw}} - E_0 = -0.150$ V.

$$-d[\text{DPPO}^{\cdot-}]/dt = k_4 C_{\text{H}_2\text{DEM}}^0 [\text{DPPO}^{\cdot-}] = k'_4 [\text{DPPO}^{\cdot-}] \quad (1')$$

$$k'_4 = 621 v_{0.8} / T \quad (8)$$

The value of k_4 obtained in this way was equal to $165 \pm 7 \text{ M}^{-1} \text{ s}^{-1}$ taking all the data in the first column into account.

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