# Phenazine Di-*N*-oxide Radical Cation Reactions with Secondary Amines. Evidence for Oxygen Cation Transfer

**Elena M. Koldasheva, Yurii V. Geletii, Alexander F. Shestakov, Alexander V. Kulikov and Alexander E. Shilov***

*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 095 265 5714*

A novel reaction involving $O^+$ transfer from phenazine di-*N*-oxide radical cation ($OPO^{+\cdot}$) to secondary amines to form phenazine mono-*N*-oxide (OP) and nitroxyl radical has been observed and investigated by cyclic voltammetry and EPR methods.

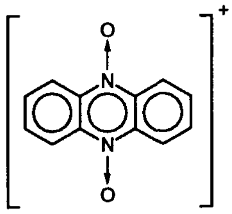
Oxidation of organic substrates by various oxygen donors is attracting much current interest as a possible method of selective oxygen transfer.[1]

One of the possible mechanisms involves $O^+$ transfer, reaction (1),

$$LO^{+\cdot} + B \rightleftharpoons BO^{+\cdot} + L \qquad (1)$$

where L and B are bases. This mechanism was proposed in 1986[2] to explain the unusual selectivity observed in some oxidation reactions[3,4] and was then discussed in several papers.[5–7] No direct evidence, however, has been obtained so far, although some features of oxidation in polar media are well explained by this mechanism.[5] Recently we found that the rather stable phenazine di-*N*-oxide radical cation ($OPO^{+\cdot}$) is a convenient source of $O^+$ and that reaction of $OPO^{+\cdot}$ with hydrocarbon was shown to involve oxidation with $O^{+\cdot}$ transfer from $OPO^{+\cdot}$ as the final stage in a rather complicated reaction mechanism.[7]

$OPO^+$ =



In this paper we examine the reaction between $OPO^{+\cdot}$ and secondary amines [2,2,6,6-tetramethylpiperidine (TMP) and 2,2,6,6-tetramethyl-4-piperidone (TMPO)] chosen in the hope of observing stable nitroxyl radicals (>N–O) as possible reaction products of reaction (1) (formed after deprotonation of the primary radical cation).

The cyclic voltammogram for phenazine di-*N*-oxide (OPO) in the presence of each of the two secondary amines chosen is shown in Fig. 1. In the both cases anodic oxidation of OPO becomes irreversible and is followed by the appearance of a new, irreversible peak with oxidation potential $E = 1.76$ V. This potential coincides with that observed in the oxidation of phenazine mono-*N*-oxide (OP)[7,8],† and thus corresponds to the loss of $O^+$ from $OPO^{+\cdot}$ in its reactions with both amines. The heights of the peak at $E = 1.76$ V and that of OPO are close to each other indicating almost quantitative deoxygenation of OPO. At the same time new reversible peaks appear in the region of lower potentials: $E_0 = 0.65$ and 0.84 V in the presence of TMP and TMPO, respectively [Figs. 1(*a*) and 1(*b*)] which correspond to redox potentials of respective >N–O· and >N$^+$=O (oxoaminium cation).[9] These are the expected peaks if reaction (2) occurs under the experimental conditions. Deprotonation is apparently performed by amines which are the strongest bases in the solution and are present in excess. Nitroxyl radicals formed are partially further oxidised to >N$^+$ =O by the anode or $OPO^{+\cdot}$ present.

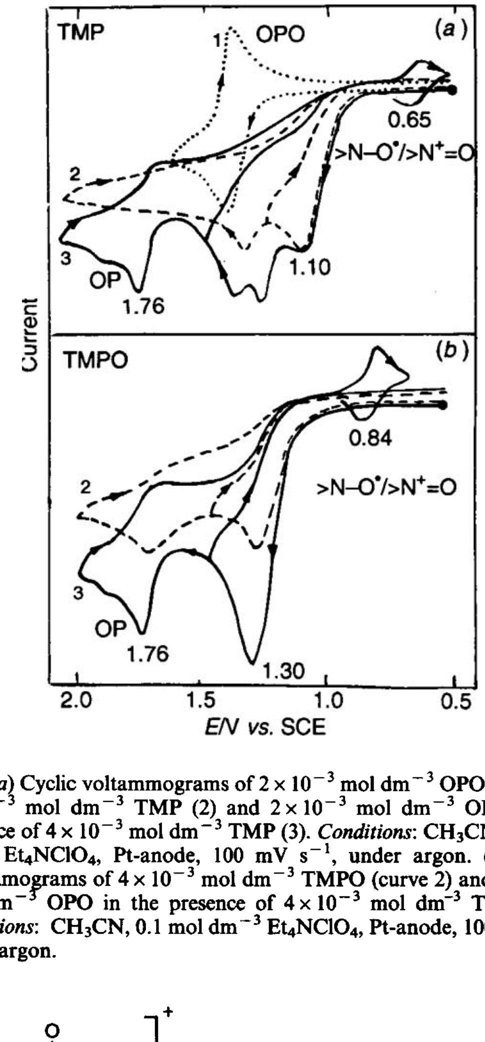
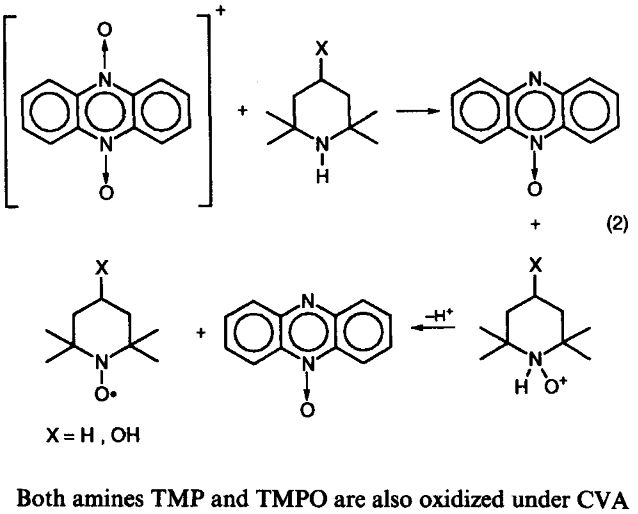


**Fig. 1**(*a*) Cyclic voltammograms of $2 \times 10^{-3}$ mol dm$^{-3}$ OPO (curve 1), $4 \times 10^{-3}$ mol dm$^{-3}$ TMP (2) and $2 \times 10^{-3}$ mol dm$^{-3}$ OPO in the presence of $4 \times 10^{-3}$ mol dm$^{-3}$ TMP (3). *Conditions*: $CH_3CN$, 0.1 mol dm$^{-3}$ $Et_4NClO_4$, Pt-anode, 100 mV s$^{-1}$, under argon. (*b*) Cyclic voltammograms of $4 \times 10^{-3}$ mol dm$^{-3}$ TMPO (curve 2) and $2 \times 10^{-3}$ mol dm$^{-3}$ OPO in the presence of $4 \times 10^{-3}$ mol dm$^{-3}$ TMPO (3). *Conditions*: $CH_3CN$, 0.1 mol dm$^{-3}$ $Et_4NClO_4$, Pt-anode, 100 mV s$^{-1}$, under argon.



(2)

Both amines TMP and TMPO are also oxidized under CVA conditions (see Fig. 1) at $E_a = 1.10$ and $E_a = 1.30$ V, respectively, the oxidation peak being irreversible with $n < 1$, where $n$

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† The small wave with $E_a \sim 1.9$ V on the peak shoulder of OP oxidation is observed on the CVA curve of OP itself and may be caused by the oxidation of products of $OP^+$ destruction.

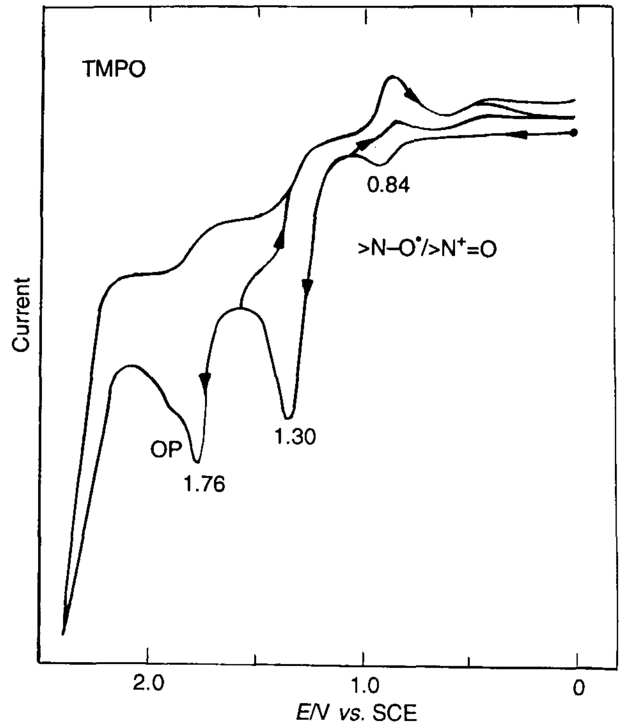

**Fig. 2** Cyclic voltammogram of the reaction mixture after controlled potential electrolysis of $2 \times 10^{-3}$ mol dm$^{-3}$ OPO followed by the reaction of $OPO^{+\cdot}$ with $4 \times 10^{-3}$ mol dm$^{-3}$ TMPO. *Conditions*: $CH_3CN$, 0.1 mol dm$^{-3}$ $Et_4NClO_4$, Pt-anode, 100 mV s$^{-1}$, under argon.

is the number of electrons. The value $n < 1$ might be explained by the protonation of starting amines in the course of a scan by aminium radical cations $>NH^{+\cdot}$ formed. Therefore, it could be suggested that nitroxyl radicals are formed not *via* $O^+$ transfer, reaction (2), but by oxygen atom transfer, reaction (3).

$$>N^{\cdot} + OPO \rightarrow >N\text{–}O^{\cdot} + PO \qquad (3)$$

However, peaks at 0.65 and 0.84 V are absent when scanning does not reach the beginning of the OPO peak (1.2 V) indicating that no oxygen atom transfer takes place from an uncharged OPO molecule. At the same time, disproportionation of two free radicals, reaction (4),

$$OPO^{+\cdot} + >N^{\cdot} \rightarrow OP + >N^+{=}O \qquad (4)$$

cannot be excluded from consideration, although it seems less likely because of the low concentration of both radicals. Taking into account the irreversible character of the CVA peaks for the amines one would assume that radicals produced *via* oxidation would disappear in some fast side reactions.

The higher intensity of the peak $>N\text{–}O^{\cdot}/>N^+{=}O$ in the case of TMPO as compared with that of TMP is also evidence in support of reaction (2). Indeed, the rate of TMPO oxidation at the anode is lower (because of its higher redox potential) and the concentration of the amine near the anode is therefore presumably higher.

To confirm the formation of nitroxyl radicals the reactions of $OPO^{+\cdot}$ with TMP and with TMPO were performed in bulk. The electrolysis of OPO alone in $CH_3CN$ was carried out under a controlled potential $E = 1.4$ V. The relative stability of $OPO^{+\cdot}$ allows it to accumulate in the solution. After *ca.* 2–3 min of electrolysis ($Q \sim 100$ C dm$^{-3}$) of OPO solution ($2 \times 10^{-3}$ mol dm$^{-3}$) the current was switched off and the amine was added at once to the anolyte, resulting in an immediate change of the solution colour from deep red (caused by $OPO^{+\cdot}$) to the bright yellow of the starting OPO solution. The EPR spectra of the anolyte in both cases were shown to contain three lines of equal intensity and correspond to the spectra of nitroxyl radicals [$g = 2.005(8)$, $a_N = 15.8$ G and $g = 2.0055$, $a_N = 14.7$ G for TMP and TMPO nitroxyl radicals respectively]. From EPR signal intensities the concentrations of the radicals were estimated to be $0.5 \times 10^{-4}$ and $1 \times 10^{-4}$ mol dm$^{-3}$, respectively.

The cyclic voltammogram of the anolyte (Fig.2) contains a reversible peak for $>N\text{–}O^{\cdot}$ oxidation to $>N^+{=}O$ on scanning in an anodic direction. Its height corresponds to the total yield of ($[>N\text{–}O^{\cdot}] + [>N^+{=}O]$), which exceeds 10% ($2 \times 10^{-4}$ mol dm$^{-3}$) with respect to the starting [OPO].

The yield of $>N\text{–}O^{\cdot}$ determined by EPR is lower than the total yield of $>N\text{–}O^{\cdot}$ and $>N^+{=}O$ together determined by CVA, the latter being close to the [OP] formed (determined by UV spectroscopy, $\lambda = 267$ nm, $\varepsilon = 1.3 \times 10^5$ mol dm$^{-3}$ cm$^{-1}$[10]). This may be explained by $>N^+{=}O$ formation from $>N\text{–}O^{\cdot}$ in reaction (5) or in reaction (4).

$$OPO^{+\cdot} + >N\text{–}O^{\cdot} \rightarrow OPO + >N^+{=}O \qquad (5)$$

Taking into account the stability of the oxoaminium cation $>N^+{=}O$ under the reaction conditions (there is no reducing agent to convert it to $>N\text{–}O^{\cdot}$), EPR observation of the nitroxyl radical provides futher evidence for $O^+$ transfer from OPO to amine, its contribution to the total yield in reactions (2) and (4) being not less than 25%.

The results presented in this paper therefore demonstrate directly the possibility of $O^+$ transfer from $OPO^{+\cdot}$ to bases such as secondary amines TMP or TMPO.

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