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Complexes of Chlorine Dioxide with Nitroxyl Radicals

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Abstract: Chlorine dioxide forms red-colored (λ_{max}=480 nm) CT complexes with persistent piperidine and imidazoline nitroxyl radicals in diethyl ether, *n*-pentane, carbon tetrachloride, methylene chloride and on silica gel surface. Equilibrium constants, enthalpy and entropy of formation and extinction coefficient of the complex between ClO_2 and 2,2,6,6-tetramethyl-4-oxypiperidin-1-oxyl 1 in diethyl ether were determined. In Et_2O the complex is stable under normal conditions, in other media it transforms into the oxoammonium salt. © 1999 Elsevier Science Ltd. All rights reserved.

Chlorine dioxide is a promising oxidant which is intensively utilized in industry for bleaching and water treatment.[1] However its application in organic synthesis is surprisingly limited. Moreover, there is a lack of data on reactions of ClO_2 with organic compounds, particularly in non-aqueous media.[1, 2] Interactions of chlorine dioxide with phenols[3] and primary and tertiary amines[4] are the most studied today. Oxidation of alcohols[5] and some sulfur-containing amino-acids[6] by ClO_2 in water has also been reported. It is well-established that the most characteristic reaction of chlorine dioxide is reduction via electron transfer,[1] so ClO_2 reacts as a one-electron oxidant:

$$ClO_2 + e^- \longrightarrow ClO_2^-$$

Recently,[7] it has been shown that sterically hindered secondary and tertiary amines are easily oxidized by electron transfer into persistent nitroxyl radicals (>N-O·). It seems very likely, that in reactions with chlorine dioxide such amines also give nitroxyls. Indeed, we have observed[8] formation of nitroxyl radicals under oxidation of 2,2,6,6-tetramethyl-subsituted piperidines and 2,2,5,5-tetramethyl-subsituted imidazolines by ClO_2 in organic solvents and on silica gel surface. The non-quantitative yield of nitroxyls suggested that >N-O· is consumed in secondary reactions with chlorine dioxide. Golubev et al.[9] report that in aqueous media ClO_2 oxidizes nitroxyls to oxoammonium salts with a rate constant 5×10^6 M^{-1} s^{-1}. Herein we show that in non-aqueous media chlorine dioxide forms charge-transfer (CT) complexes with piperidine (**1, 2**) and imidazoline (**3**) nitroxyl radicals which slowly transform further into oxoammonium salts.

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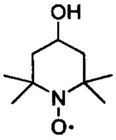
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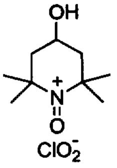
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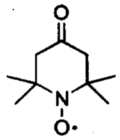
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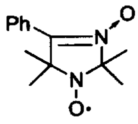
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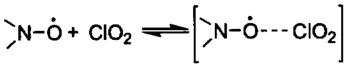
When solutions of chlorine dioxide in diethyl ether, *n*-pentane, carbon tetrachloride or methylene chloride are added to 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl **1** in the same solvent, the mixture turns dark red.[10] The same effect is observed in the interaction of gaseous ClO_2 with **1** adsorbed on silica gel. Cooling to *ca.* -78 °C results in reversible color intensification. In the UV-VIS spectrum, additional absorption in the range of 450–500 nm appears (Fig. 1), while ClO_2 absorption does not change. No changes are observed in EPR spectra of nitroxyl **1** and ClO_2 (both substances are paramagnetic). On the basis of these data one may suggest formation of complexes between nitroxyl and chlorine dioxide in these media.



$$>N-\dot{O} + ClO_2 \rightleftharpoons \left[>N-\dot{O}\cdots ClO_2\right] \quad (1)$$

On the other hand, no complex formation is observed in acetone, acetonitrile and benzene. In ethanol, the complex is not formed but reaction takes place and the reagents are consumed. 2,2,6,6-Tetramethyl-4-oxopiperidin-1-oxyl **2** reacts with ClO_2 similarly to **1**. In the case of imidazoline nitroxyl **3** in diethyl ether, a visible change in color appears only at low temperature (*ca.* -78 °C). Further, we performed a detailed study of the reaction between nitroxyls and chlorine dioxide using **1** as a model compound.

Assuming the stoichiometry of the complex to be 1:1 using the Benesi-Hildebrand method,[11] we determined the equilibrium constants K for the complex formation in diethyl ether at various temperatures (-10 – +20 °C) and the extinction coefficient of the complex $\varepsilon = (4.6 \pm 0.9) \times 10^3\ (M\ cm)^{-1}$ at $\lambda = 500$ nm.[12]

T, C	20	10	0	-10
K, M^{-1}	13.5	19.6	29.0	39.5

From the dependence of K on temperature the enthalpy and entropy of complex formation were determined: $\Delta H^0 = -5.6 \pm 1.3$ kcal / mole, $\Delta S^0 = -13.8 \pm 4.6$ cal / (mole K).

Up to the present, there was no data on complexes of chlorine dioxide with organic compounds. However, nitroxyls are known to form complexes with various organic compounds.[13] The structure of these complexes (n-σ, π-σ, π-π, π–n) depends on the type of ligand. To determine the structure of the complex we observed, further investigations are required. But from the available data on solvent effects on complex formation one can infer that chlorine dioxide is coordinated to the π-system of the nitroxyl. Actually, the complex is not observed in solvents which are able to form strong π–π interactions with nitroxyls.[13] Since the π orbital of nitroxyl is occupied by solvent, formation of its complex with ClO_2 is unlikely. In solvents that are only capable of weak π-n (diethyl ether, methylene chloride, carbon tetrachloride) and π-σ (pentane) interactions, nitroxyls readily form complexes with chlorine dioxide at ambient temperatures. The enthalpy of formation of nitroxyl-chlorine dioxide complex (-5.5 ± 1.3 kcal / mole) is close to values obtained by Buchachenko *et al.* for π-π complexes between $>N-O\cdot$ and different ligands (-3.0 – -6.3 kcal / mole).[13]

In methylene chloride, carbon tetrachloride and *n*-pentane the red coloration characteristic of the complex gradually disappears and a yellowish microcrystalline solid precipitates from solution. The EPR signals of nitroxyl **1** and ClO_2 disappear upon the precipitation. The rate of complex conversion depends on the nature of the solvent, *e.g.* in CCl_4 a precipitate is formed in a period of 10-50 minutes after the mixing of reagents (the period depends on initial concentrations). In CH_2Cl_2 and n-C_5H_{12} precipitation is remarkably slower, while in diethyl ether the complex is stable for a long time (at least for two weeks at +5 °C). On a silica surface, the disappearance of the red coloration and EPR signal occurs in one hour at 20 °C.

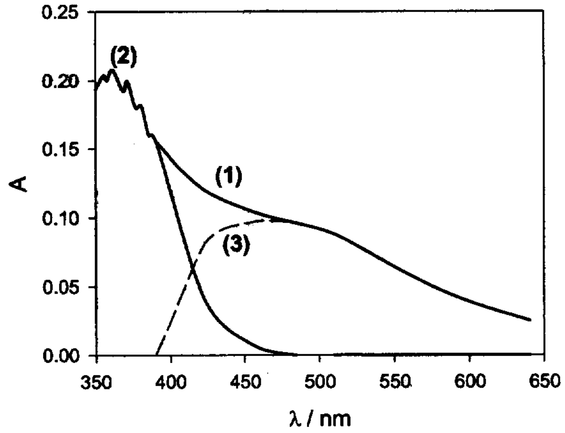
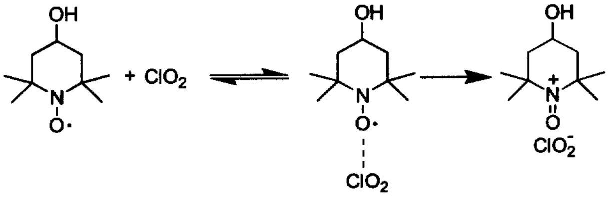


Fig. 1. UV-VIS spectra (Et_2O, 21°C): (1) mixture of [**1**]=$2 \cdot 10^{-2}$ M and [ClO_2]=$2 \cdot 10^{-4}$ M, in reference cell [**1**]=$2 \cdot 10^{-2}$ M, (2) solution of [ClO_2]=$2 \cdot 10^{-4}$ M relatively to Et_2O, (3) spectrum of the complex estimated by subtraction of spectrum (2) from spectrum (1)

The freshly prepared product of complex conversion is diamagnetic, but in time it gives the EPR signal of nitroxyl **1**. Irradiation by visible light and the presence of moisture accelerates nitroxyl formation. The IR spectrum of the product shows an intensive band at $\bar{\nu}$=1612 cm^{-1} characteristic of the $>N^+=O$ group.[14b] Reaction of nitroxyls with various oxidants (Cl_2, Br_2) is known to lead to oxoammonium salts,[14] also, they were proposed to be the key intermediates in nitroxyl-catalysed oxidation of formic acid[9,15] by chlorine dioxide in water. Therefore, the product we obtained can be unambiguously assigned to 2,2,5,5-tetramethyl-4-hydroxypiperidin-1-oxo chlorite **1*a***. In contrast to oxoammonium chlorides and bromides,[14c] chlorite **1*a*** is insoluble in inert polar solvents such as acetone and acetonitrile, so we could not obtain its UV-VIS spectrum. Like other oxoammonium salts[16] it reacts with water and ethanol to give mixture of products with the nitroxyl radical among them. This explains fast consumption of the reagents during interaction of the nitroxyl with chlorine dioxide in ethanol. Since 2,2,5,5-tetramethyl-4-hydroxypiperidin-1-oxo chlorite has an OH group, it would be expected to react (perhaps slowly) with itself, so, the precipitate we obtained may be contaminated by self-oxidation products.

Thus, reaction of chlorine dioxide with nitroxyl radicals proceeds through CT-complex formation. The complex converts to an oxoammonium salt, these compounds are known to be effective oxidants that will find application in organic synthesis.[16] The reaction of ClO_2 with nitroxyls strongly depends on the nature of the solvent.



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10. Golubev *et al.* (V.A. Golubev, G.N. Voronina, E.G. Rozantsev, *Isv. AN SSSR, Ser. Khim*, **1970**, 2605-2608) had observed similar coloration during interaction of prolidinoxyl with molecular bromine.

11. Golubev *et al.* (V.A. Golubev, G.N. Voronina, E.G. Rozantsev, *Isv. AN SSSR, Ser. Khim*, **1970**, 2605-2608) had observed similar coloration during interaction of prolidinoxyl with molecular bromine.

12. Dependence of adsorption A ($\lambda = 462$ nm) on nitroxyl concentration C_I was studied under constant concentration of chlorine dioxide C_{ClO2} ($C_I >> C_{ClO2}$). Equilibrium constant K and extinction coefficient ε were determined from linear dependence in coordinates of the Benesi-Hildebrand equation ($C_{ClO2} \times l \times A^{-1}$ vs. C_I^{-1})

$$C_{ClO2} \times l \times A^{-1} = \varepsilon^{-1} + (K \times \varepsilon)^{-1} \times C_I^{-1}$$

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