Complex formation between chlorine dioxide and 2,2,6,6-tetramethylpiperidin-1-oxyl

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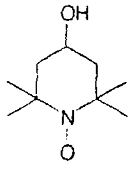
The complex formation of ClO_2 with 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO) in acetone, acetonitrile, *n*-heptane, diethyl ether, carbon tetrachloride, and toluene was studied spectrophotometrically at −20 to +20 °C. The thermodynamic parameters of complex formation were determined at 20 °C. The transformation of the complex into the oxoammonium salt $TMPO^+ClO_2^-$ was found.

Key words: chlorine dioxide, 2,2,6,6-tetramethylpiperidin-1-oxyl, oxoammonium salt, charge transfer complex.

Oxoammonium salts prepared from nitroxyl radicals[1,2] are of great interest as oxidants. It is known[3,4] that nitroxyl radicals are efficient catalysts for oxidation reactions. It was assumed that the corresponding oxoammonium salts are intermediates in these catalytic processes. In this connection, the study of the reactions of nitroxyl radicals that afford oxoammonium salts is urgent.

The formation of the ClO_2 complexes with the nitroxyl radical 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl (**1**) has previously[5] been reported. In this work, we studied the complex formation of ClO_2 with 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO) (**2**) in different solvents and the transformation of the complex into the oxoammonium salt (**2a**).



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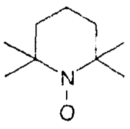

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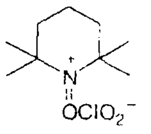

2a

Experimental

Chlorine dioxide was prepared by the reaction of $KClO_3$ with oxalic acid in the presence of H_2SO_4.[6] The ClO_2 formed was passed through a trap with P_4O_{10} for dehydration and then adsorbed on a column filled with silica gel and pre-cooled to 0 °C. To obtain solutions of ClO_2, the column was heated in a thermostat to 30—35 °C, and ClO_2 was blown out with argon into a trap with a solvent. The concentration of ClO_2 in a solution was determined iodometrically using the Brei method[6] and spectrophotometrically.[7] Potassium perchlorate and oxalic acid (reagent grade) were purified by recrystallization from water. Sulfuric acid (special-purity grade) was used as received. TMPO was recrystallized from *n*-heptane. All solvents were purified by known procedures.[8]

The complex formation of ClO_2 with TMPO was studied spectrophotometrically on a Specord M40 (Carl Zeiss Jena) instrument in a special cell cooled with a flow of cold gaseous nitrogen (Fig. 1). The temperature in the cell was monitored by a thermocouple. The 2-mL cell was loaded with the solvent (1—2 mL), a solution of TMPO ($2.4 \cdot 10^{-3}$—$19.2 \cdot 10^{-3}$ mmol), and a solution of ClO_2 ($4 \cdot 10^{-4}$ mmol). A solution of TMPO ($2.4 \cdot 10^{-3}$—$19.2 \cdot 10^{-3}$ mmol) was placed in a reference cell. The cells were thermostatted at −20 to +20 °C, and the spectrum of the solution was recorded.

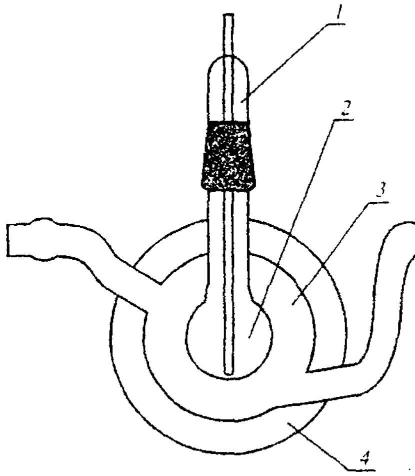

Fig. 1. Thermostatted quartz cell for spectrophotometric measurements: *1*, cap with thermocouple; *2*, quartz spectrophotometric cell; *3*, quartz jacket of the thermostat; and *4*, quartz vacuum jacket.

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Table 1. Parameters of the ClO_2 complex with TMPO in different solvents at 20 °C

Solvent	λ_{max} /nm	ε*	K /L mol^{-1}	$\Delta H°$ /kcal mol^{-1}	$\Delta S°$ /cal (mol K))$^{-1}$	$\Delta G°$ /kcal mol^{-1}
Acetone	485.2	20.74	7.3	−9.5	−28.6	−1.1
Acetonitrile	488.9	37.40	3.6	−8.3	−25.7	−0.8
Heptane	470.6	1.92	23.4	−10.0	−28.1	−1.8
Diethyl ether	478.7	4.22	9.3	−7.4	−20.9	−1.3
Carbon tetrachloride	480.5	2.24	26.6	−11.4	−32.5	−1.9
Toluene	479.6	2.38	20.0	−12.8	−38.3	−1.6

* ε is the dielectric constant.[10]

The kinetics of TMPO consumption was monitored by ESR spectroscopy on an SE/X 2544 instrument with additional modulation (100 kHz) at 20 °C. A solution (1 mL) of TMPO in CCl_4 ($2 \cdot 10^{-2}$ mol L^{-1}, 0.02 mol) was placed in the cell, and a solution (1 mL) of ClO_2 ($2 \cdot 10^{-2}$ mol L^{-1}, 0.02 mmol) in CCl_4 was added. The reaction mixture (0.1 mL) was sampled from the cell, and the sample was 10-fold diluted with CCl_4. The sample of the resulting solution was loaded into an ESR tube, and the ESR spectrum was recorded. The concentration of TMPO was determined from a calibration plot.

To obtain the oxoammonium salt, equal volumes of equimolar toluene solutions of ClO_2 and TMPO were mixed. The precipitate formed was filtered off, washed with the solvent, and dried *in vacuo*. The IR spectrum of the salt was recorded on a Specord M80 instrument (Carl Zeiss Jena) in Nujol in a KBr cell. Found (%): C, 48.8; H, 8.4; Cl, 14.4; N, 6.0, O, 22.4. $C_9H_{18}ClNO_3$. Calculated (%): C, 50.5; H, 8.5; Cl, 14.9; N, 5.9; O, 20.2.

Results and Discussion

When solutions of ClO_2 and TMPO in diethyl ether, *n*-heptane, CCl_4, acetone, acetonitrile, and toluene are mixed, the resulting mixture becomes intensely dark-red. An unstructured broad absorption band with λ_{max} at 470—490 nm appears in the electronic spectra (Table 1). In polar solvents, λ_{max} shifts to the long-wave region (bathochromic shift), which is characteristic of charge transfer complexes.[9] The UV spectrum of ClO_2 exhibits no noticeable change (Fig. 2).

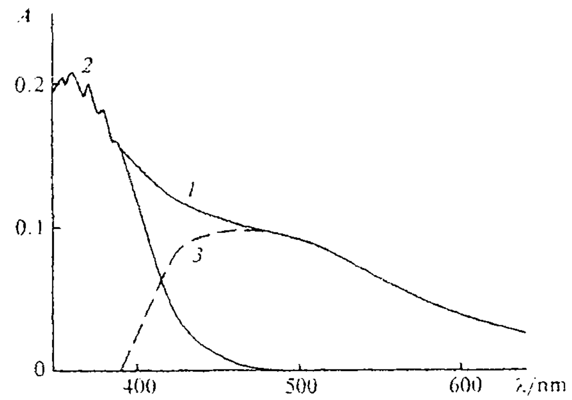


Fig. 2. Electronic spectra of diethyl ether solutions at 20 °C: *1*, mixture containing [TMPO] = $2 \cdot 10^{-4}$ mol L^{-1} and [ClO_2] = $2 \cdot 10^{-4}$ mol L^{-1} with [TMPO] = $2 \cdot 10^{-2}$ mol L^{-1} as the reference solution; *2*, solution with [ClO_2] = $2 \cdot 10^{-4}$ mol L^{-1}; and *3*, spectrum of the complex obtained by the subtraction of spectrum *2* from spectrum *1*.

Changes in the ESR spectra of TMPO and ClO_2 were not observed. When the solution was cooled from −20 to −80 °C, the intensity of its color was enhanced. This suggests the formation of a complex between ClO_2 and TMPO.

The results of measuring the absorbance A of the complex in the −20 to +20 °C interval show that $[ClO_2]_0 \cdot l/A$ increases linearly as the inverse TMPO concentration in all solvents increases (this plot for acetone is presented in Fig. 3), where $[ClO_2]_0$ is the initial concentration of ClO_2, and l is the optical path length in the cell.

This suggests that ClO_2 and the TMPO radical form a 1 : 1 complex:

$$ClO_2 + {>}NO^{\cdot} \rightleftharpoons ClO_2...TMPO.$$

Indeed, at $[TMPO]_0 \gg [ClO_2]_0$, which was also observed in our experiments, the stability constant

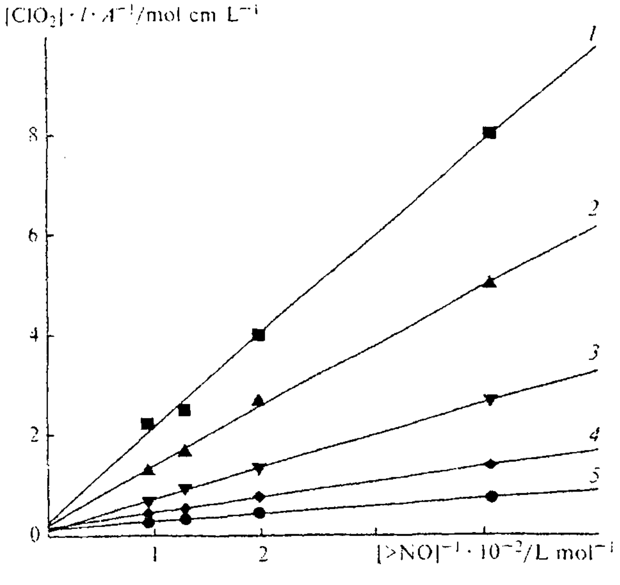


Fig. 3. Parameter $[ClO_2] \cdot l/A$ as a function of the inverse concentration of TMPO at different temperatures (acetone as the solvent): T/°C = 20 (*1*), 10 (*2*), 0 (*3*), −10 (*4*), and −20 (*5*).

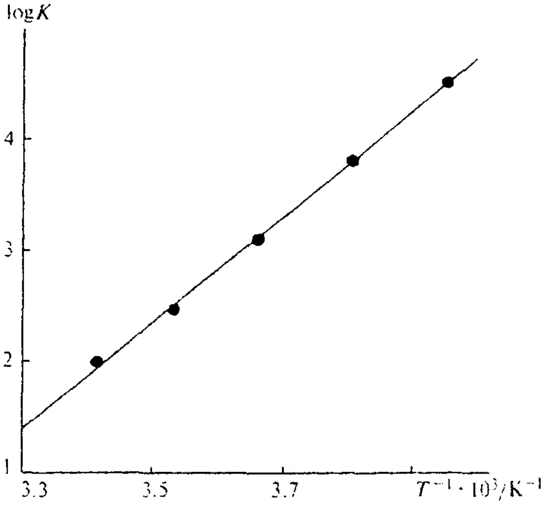


Fig. 4. Dependence of log$K$ on the inverse temperature (acetone as the solvent).

$$K = \frac{[ClO_2...TMPO]_0}{[TMPO]_0([ClO_2]_0 - [ClO_2...TMPO]_0)}.$$

From where $[ClO_2...TMPO]_0 = A/\varepsilon\cdot l$,

$$\frac{[ClO_2]_0 l}{A} = \frac{1}{\varepsilon} + \frac{1}{K\cdot\varepsilon}\frac{1}{[TMPO]_0},$$

where $[TMPO]_0$ is the concentration of the complex, and ε is the molar absorption coefficient.

The last equation makes it possible to determine ε^{-1} and $(K\cdot\varepsilon)^{-1}$ (see Fig. 3) and, hence, the stability constants K (see Table 1).

The thermodynamic parameters of complex formation (ΔH°, ΔS°, ΔG°) presented in Table 1 were obtained from the temperature dependence of K (Fig. 4).

$$\log K = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}.$$

In the solvent studied, a linear relationship between ΔH° and ΔS° (compensation effect) was found (Fig. 5).

The correlation between the equilibrium constant and the solvent nature by the Brownstein and Dimroth equations is unsatisfactory, the correlation coefficients being 0.63 and 0.36, respectively. It is most likely that the complicated character of the dependence of the equilibrium constant on the solvent nature is related to the solvation of all reactants: ClO_2, nitroxyl radical, and the complex. It is well known that nitroxyl radicals in solutions form complexes with solvents.[11] This explains the absence of complex formation of radical **1** with ClO_2 in acetone and acetonitrile.[5]

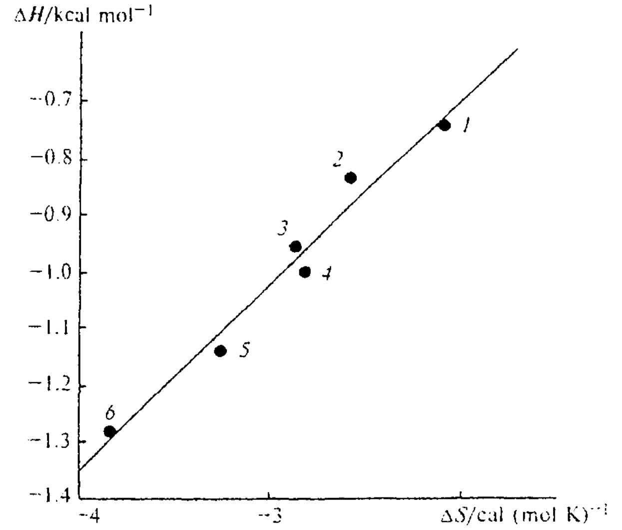


Fig. 5. Compensation effect in the ClO_2—TMPO system in different solvents: *1*, diethyl ether; *2*, acetonitrile; *3*, acetone; *4*, heptane; *5*, CCl_4; and *6*, toluene.

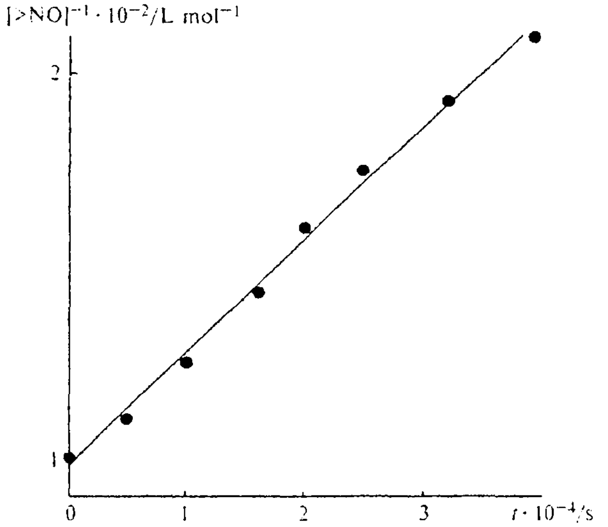
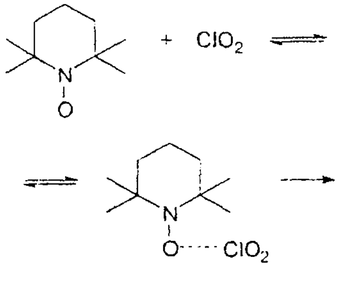


Fig. 6. Time profile of $1/[TMPO]$ (20 °C, CCl_4 as the solvent, $[TMPO]_0 = [ClO_2]_0 = 10^{-2}$ mol L^{-1}).

The color of all solvents gradually disappears with time, and a finely crystalline yellowish precipitate is formed. The intensity of the ESR signals of TMPO and ClO_2 decreases simultaneously. The kinetics of TMPO consumption obeys a second-order equation (first-order with respect to the nitroxyl radical and to ClO_2) (Fig. 6). At 20 °C the reaction rate constant $k_{eff} = (2.8\pm0.9)\cdot 10^{-3}$ L (mol^{-1} s^{-1}).

Scheme 1



The crystalline product that formed is diamagnetic; however, the ESR signal characteristic of TMPO appears with time. Photoirradiation and the presence of water accelerate this process. The IR spectrum of the crystalline product contains an intense band at 1624 cm^{-1}, which is absent from the spectra of the reactants and characteristic of the $>^{+}N=O$ group. Absorption with a maximum at 454 nm appears in the UV spectrum (acetonitrile as the solvent), which additionally confirms the formation of the ammonium salt[12] (Scheme 1).

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