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Interaction of chlorine dioxide with nitroxyl radicals

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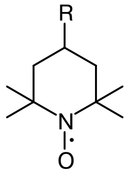
The formation of charge transfer complexes between chlorine dioxide and nitroxyl radicals (2,2,6,6-tetramethylpiperidin-1-oxyl, 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, 4-oxo-2,2,6,6-tetramethylpiperidin-1-oxyl, 4-methoxy-2,2,6,6-tetramethylpiperidin-1-oxyl, 4-acetylamido-2,2,6,6-tetramethylpiperidin-1-oxyl, 2,2,5,5-tetramethyl-4-phenyl-3-imidazolin-1-oxyl, and bis(4-methoxyphenyl) nitroxide) in acetone, acetonitrile, *n*-heptane, diethyl ether, carbon tetrachloride, toluene, and dichloromethane was found by spectrophotometry at −60—+20 °C. The thermodynamic parameters of complex formation were determined. The radical structure affects its complex formation ability. The charge transfer complex is transformed into the corresponding oxoammonium salt.

Key words: chlorine dioxide, nitroxyl radicals, charge transfer complexes, oxoammonium salts.

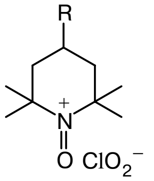
It has previously[1—4] been shown that nitroxyl radicals form complexes with both organic and inorganic compounds. Donor-acceptor complexes of di-*tert*-butyl-*N*-oxyl with such electron acceptors as tetracyanoethylene, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, chloranyl, and phenol were found by ESR and optical spectroscopy.[3] For the tetracyanoethylene and phenol complexes, λ_{max} (790 and 423 nm, respectively) were measured and equilibrium constants (4.0 and 6.4 L mol^{-1}, respectively) were determined. The formation of a charge transfer complex (CTC) between the nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-oxyl and iodine has been found[2] from the appearance of a broad absorption band in the visible spectral region with λ_{max} = 470 nm. In the cycle of works (see, *e.g.*, Refs. 1 and 5) studying the complex-forming ability of nitroxyl radicals with organic compounds by NMR spectroscopy, the authors showed that nitroxyl radicals are strong complex-forming agents, acting as both electron acceptors and donors. Theoretical and experimental methods proved reliably that nitroxyls form complexes of different types involving orbitals of both the radical and ligand. Five-membered nitroxyls give weaker complexes than six-membered radicals. For example, the complex formation constants with methanol are 0.2 and 3.5 L mol^{-1} for 2,2,5,5-tetramethyl-4-phenyl-3-imidazolin-1-oxyl and 2,2,6,6-tetramethylpiperidin-1-oxyl (**1**), respectively.[5]

In the previous works,[6,7] we found the complex formation of compound **1** and 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (**2**) with an inorganic one-electron oxidant, chlorine dioxide, and measured the equilibrium constants.

The purpose of this work is to reveal the influence of the structure of nitroxyl radicals on the spectral and thermodynamic parameters of their complexes with ClO_2 for 4-oxo-2,2,6,6-tetramethylpiperidin-1-oxyl (**3**), 4-methoxy-2,2,6,6-tetramethylpiperidin-1-oxyl (**4**), 4-acetamido-2,2,6,6-tetramethylpiperidin-1-oxyl (**5**), 2,2,5,5-tetramethyl-4-phenyl-3-imidazolin-1-oxyl (**6**), and bis(4-methoxyphenyl)-*N*-oxyl (**7**).

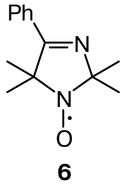


1—5



1a—4a

R = H (**1**, **1a**), OH (**2**, **2a**), =O (**3**, **3a**), OMe (**4**, **4a**), NHC(O)Me (**5**)



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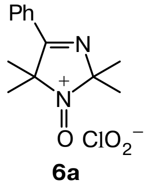
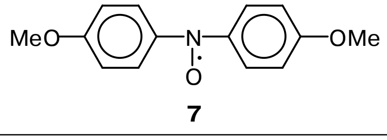


6a



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† Deceased.

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Experimental

Chlorine dioxide was prepared by the reaction of potassium chlorate with oxalic acid in the presence of sulfuric acid.[8] Gaseous ClO_2 was passed through a trap with P_4O_{10} for dehydration and then through a pre-cooled to 0 °C column packed with silica gel L 40/100 (Chemapol), where ClO_2 was adsorbed at a reduced (~0 °C) temperature.[9] The column was heated in a thermostat at 30—35 °C, and ClO_2 was removed by an argon flow into a trap filled with a solvent. The concentration of ClO_2 in a solution was determined iodometrically by the Bray method[8] and spectrophotometrically.[10] Potassium chlorate and oxalic acid (reagent grade) were twice recrystallized from water. Sulfuric acid (special purity grade) was used without purification. The synthesis of the nitroxyl radicals has been described previously.[11,12] Solvents were purified by known procedures.[13]

The complex formation of ClO_2 with the nitroxyl radicals was studied by a published procedure.[7] The concentration of nitroxyls **3—6** was varied within $(1.2—9.6) \cdot 10^{-3}$ mol L^{-1}, the chloride dioxide concentration was $2 \cdot 10^{-4}$ mol L^{-1}, and the temperature of experiments was 20——60 °C. The complex formation of ClO_2 with nitroxyl **7** was studied in a standard cell at ~20 °C: a solvent (2—3 mL) and a solution of the radical $(7.2 \cdot 10^{-4}—3.36 \cdot 10^{-3}$ mmol) were introduced into a 3-mL cell, and then a solution of ClO_2 $(1.5 \cdot 10^{-4}$ mmol) was added. A solvent (2—3 mL) and a solution of the radical $(7.2 \cdot 10^{-4}—3.36 \cdot 10^{-3}$ mmol) were placed into a reference cell, and then the spectrum of the solution was recorded.

To obtain oxoammonium salts **3a**, **4a**, and **6a**, we mixed equimolar amounts of ClO_2 and the nitroxyl in toluene. The precipitate that formed was filtered off, washed with a solvent, and dried *in vacuo*. The IR spectrum of the salt was recorded on a Specord M-80 instrument (Carl Zeiss Jena) in Nujol.

Results and Discussion

Chlorine dioxide forms CTC with nitroxyl radicals **1—7**. This is indicated by the following facts: an intense dark-red (red-violet for radical **7**) color appears upon mixing of solutions of ClO_2 and radicals **3—5** and **7** in acetone, acetonitrile, heptane, diethyl ether, tetrachloromethane, toluene, and dichloromethane. An additional structureless absorption band in the region of 450—500 nm (at 570—600 nm for radical **7**) appears in the electronic spectra in the case of radicals **3—5** (Fig. 1). Maxima of the absorption bands appear at 460—490 nm (Table 1) for radicals **3—5** and at 590 nm for radical **7**. When a solution of ClO_2 is mixed with radical **6** in heptane, the color characteristic of the complex appears

Table 1. Parameters of charge transfer complexes of ClO_2 with nitroxyl radicals in several solvents at 20 °C (measurement errors do not exceed 15%)

Radical	$E_{p/2}$[12] /V	σ'' [12]	Solvent	E_T^N [15]	λ_{max} /nm	K /L mol^{-1}	$\Delta H°$ /kJ mol^{-1}	$\Delta S°$ /J mol^{-1} K^{-1}	$\Delta G°$ /kJ mol^{-1}
1	0.25	0	Acetone	0.355	485.2	7.3	−39.7	−119.5	−4.7
			Acetonitrile	0.460	488.9	3.6	−34.7	−107.4	−3.2
			Heptane	0.012	470.6	23.4	−41.8	−117.5	−7.4
			Diethyl ether	0.117	478.7	9.3	−30.9	−87.4	−5.3
			Dichloromethane	0.309	490.9	12.8	−35.2	−99.1	−6.2
			Tetrachloromethane	0.052	480.5	26.6	−47.7	−135.9	−7.9
			Toluene	0.099	479.6	20.0	−53.5	−160.1	−6.6
2	0.34	0.23	Acetone	0.355	485.2	4.2	−35.5	−102.6	−5.4
			Acetonitrile	0.460	485.2	2.7	−41.8	−134.0	−2.5
			Tetrachloromethane	0.052	474.1	23.9	−44.8	−126.1	−7.8
			Dichloromethane	0.309	485.4	5.6	−42.8	−130.3	−4.6
			Toluene	0.099	473.2	12.7	−24.6	−61.0	−6.7
			Diethyl ether	0.117	476.6	13.5	−33.1	−57.1	−16.4
3	0.44	0.51	Acetone	0.355	467.3	6.8	−30.4	−88.0	−4.6
			Acetonitrile	0.460	481.5	—	—	—	—
			Diethyl ether	0.117	462.9	3.8	−40.4	−112.4	−7.5
			Dichloromethane	0.309	474.1	2.7	−34.0	−107.0	−2.4
			Toluene	0.099	460.2	8.5	−24.5	−65.7	−5.3
4	0.35	0.25	Acetone	0.355	480.5	9.4	−33.7	−96.1	−5.5
			Acetonitrile	0.460	483.3	2.5	−41.1	−132.5	−2.3
			Tetrachloromethane	0.052	475.0	12.1	−54.8	−164.8	−6.5
			Dichloromethane	0.309	480.8	4.6	−45.0	−141.2	−3.6
			Toluene	0.099	474.1	3.2	−34.5	−107.7	−2.9
			Diethyl ether	0.117	470.6	7.7	−36.4	−107.6	−4.9
			Heptane	0.012	465.3	6.2	−42.8	−131.2	−4.4
5	0.40	—*	Acetone	0.355	481.4	9.3	−40.3	−119.5	−5.3
			Acetonitrile	0.460	482.4	4.8	−36.1	−110.0	−3.8
			Dichloromethane	0.309	485.2	5.2	−38.2	−116.0	−4.0
6	0.60	—*	Heptane	0.012	438.4	0.8**	−29.7	−103.3	0.6
7	0.20	—*	Dichloromethane	0.309	568.2	693.0	—	—	—

* The σ'' value is absent.

** Obtained from the temperature plot of the logarithm of equilibrium constant.

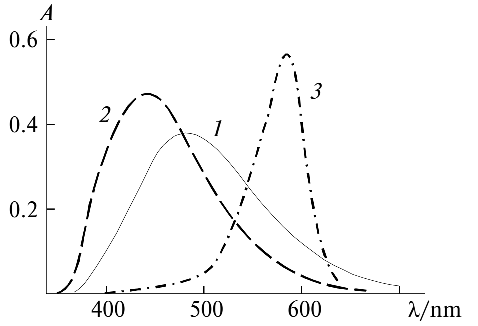


Fig. 1. Electronic absorption spectra of chlorine dioxide complexes with nitroxyl radicals: *1*, $[ClO_2]_0 = 2 \cdot 10^{-4}$ mol L^{-1}, $[\mathbf{4}]_0 = 7.2 \cdot 10^{-3}$ mol L^{-1}, solvent dichloromethane, 20 °C; *2*, $[ClO_2]_0 = 2 \cdot 10^{-4}$ mol L^{-1}, $[\mathbf{6}]_0 = 7.5 \cdot 10^{-3}$ mol L^{-1}, solvent heptane, −50 °C; and *3*, $[ClO_2]_0 = 5 \cdot 10^{-5}$ mol L^{-1}, $[\mathbf{7}]_0 = 2.5 \cdot 10^{-4}$ mol L^{-1}, solvent dichloromethane, 20 °C.

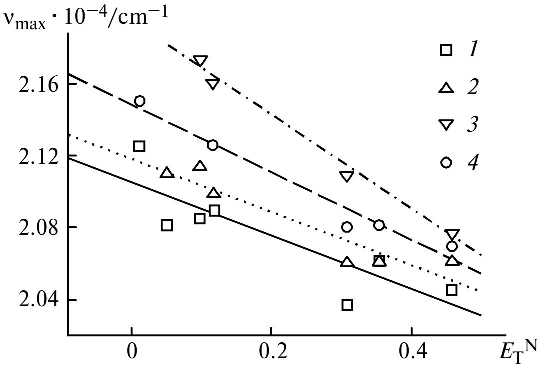


Fig. 2. Plot of the frequency of the maximum of the absorption band (ν_{max}) of charge transfer complexes **1**—**4** (curves *1*—*4*, respectively) *vs.* E_T^N parameter in the series of solvents at 20 °C.

only on cooling of the solution to −20—−50 °C, and the absorption band maximum is detected at 438 nm.

The data in Table 1 show that an increase in the solvent polarity results in a long-wave shift of the absorption band maxima (bathochromic shift), which is typical[14] of CTC. For radicals **1**—**4** (Fig. 2), we found a correlation (R = 0.75, 0.88, 0.99, and 0.96, respectively) of the ν_{max} frequency with the solvent parameter E_T^N characterizing the solvent polarity.[15]

In the piperidine series of radicals **1**—**4**, ν_{max} increases uniformly in the solvent studied with an increase in σ″ of the substituent in position 4 of the piperidine cycle (σ″ is the constant of substituents in the 1,4-cyclohexane series[16]). Figure 3 presents, as an example, this dependence for solutions of **1**—**4** in dichloromethane (for radical **5** the σ″ value is unknown).

We also found a correlation between ν_{max} and the potential of the peak half-height of the oxidation of the nitroxyl group ($E_{p/2}$). A similar dependence is characteristic of CTC and indicates that all nitroxyls under study are electron donors of the same class and complexes are formed due to the same electron interactions between ClO_2 and the radical[4] (Fig. 4).

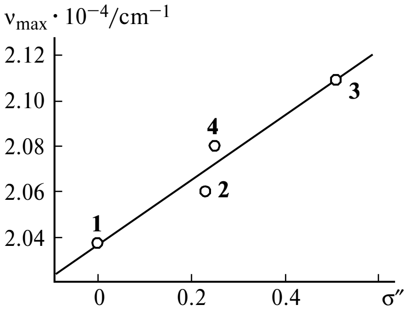


Fig. 3. Plot of ν_{max} *vs.* σ″ of the substituent in position 4 of the piperidine cycle of nitroxyl radicals **1**—**4**; solvent dichloromethane.

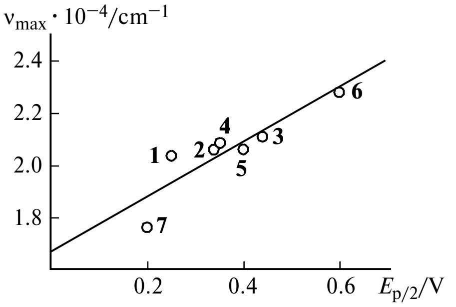


Fig. 4. Plot of ν_{max} *vs.* potential of the oxidation half-peak of the nitroxyl group of radicals **1**—**7**; solvent dichloromethane.

On storage (1—2 days) of solutions of the samples in all solvents, the color characteristic of CTC disappears and a yellow fine-crystalline precipitate is formed. The process is accompanied by a decrease in the intensity of the ESR signals from the radicals and ClO_2.

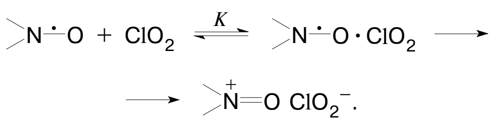
The crystalline product is diamagnetic; however, the ESR signal characteristic of the initial nitroxyl radical is detected after some time. Photoirradiation and the presence of water accelerate this process, which is stipulated by the fact that the product formed from the complex is very reactive, it oxidizes the solvent and transforms into the nitroxyl radical.[17] The IR spectrum of the crystalline products exhibits intense bands, which are absent from the spectra of the reactants and characteristic of the $>^+N=O$ group in the oxoammonium salts,[17] at 1624 (**1a**), 1612 (**2a**), 1632 (**3a**), 1640 (**4a**), and 1684 cm^{-1} (**6a**). The absorption with maxima at 454 (**1a**), 450 (**3a**), 449 (**4a**), and 469 nm (**6a**) (solvent acetonitrile) appears in the UV spectra, which is also characteristic of the oxoammonium salts[18] (the UV spectrum of compound **2a** is not presented due to a low solubility of this compound in acetonitrile). The results of elemental microanalysis of compounds **1a**, **3a**, **4a**, and **6a** are presented in Table 2.

The results of elemental analysis for the oxoammonium salt prepared from radical **2** are poorly reproducible. This can be explained, most likely, by the oxidation of the hydroxyl group in salt **2a** because oxoammonium salts are efficient oxidants for hydroxyl-containing organic compounds.[19,20] We failed to isolate oxoammonium salts for radicals **5** and **7**.

Table 2. Elemental analysis data of compounds **1a**, **3a**, **4a**, and **6a** (the content of elements was calculated for chlorites of the corresponding oxyls)

Compound	$\frac{\text{Found}}{\text{Calculated}}$ (%)				
	C	H	Cl	N	O
1a	49.8	8.4	14.4	6.0	21.4
	50.5	8.5	14.9	5.9	20.2
3a	45.0	6.5	14.5	5.6	28.4
	45.5	6.8	14.9	5.9	26.9
4a	46.9	7.7	13.8	5.4	26.2
	47.3	8.0	14.0	5.5	25.2
6a	53.9	5.8	11.7	10.0	18.6
	54.8	6.0	12.5	9.8	16.9

Analysis of these results indicates that the complex formed by the reaction of ClO_2 with nitroxyls is further transformed into the oxoammonium salt



Since the rate of irreversible transformation of the complex into the oxoammonium salt is lower by many orders of magnitude than the rate of equilibrium establishment of complex formation,[7] we determined the equilibrium rate constants of CTC in the studied solvents at different temperatures based on measurements of the absorbance A (at λ_{max}) of the complex (the contribution of absorbance of the studied reactants and final products to A can be neglected under these conditions) using the Benesi—Hildebrand equation[21]

$$\frac{[ClO_2]_0 l}{A} = \frac{1}{\varepsilon} + \frac{1}{K\varepsilon}\cdot\frac{1}{[>NO^{\bullet}]_0},$$

where $[ClO_2]_0$ and $[>NO^{\bullet}]_0$ are the starting concentrations of chlorine dioxide and the nitroxyl radical, respectively; l is the optical path length in the cell; ε is the molar absorption coefficient of CTC; and K is the equilibrium constant. The obtained values are presented in Table 1.

The high equilibrium constant for the ClO_2 complex with radical **7** is due, most likely, to a relatively low potential of the oxidation half-peak of the nitroxyl group ($E_{p/2}$) and stabilization by aromatic substituents of the charge appeared on the N atom.

A comparison of the obtained results (except those for radical **7**) with published data (Table 3) shows that the K equilibrium constants of the complexes with ClO_2 are close to the complex formation constants of the nitroxyls with such acceptors as tetracyanoethylene, phenol, iodine, and 2,5-dimethylphenol.

The previously reported data[6] on the absence of the complex formation of radical **2** with ClO_2 in acetone and acetonitrile are explained, most likely, by a comparatively low ε value (~1000 L mol^{-1} cm^{-1} in both cases), which impedes spectrophotometric measurements. However, decreasing the temperature and increasing concentrations of the reactants, which increase the equilibrium concentration of the complexes, we were able to detect their formation and measure the spectral and thermodynamic parameters (see Table 1).

Depending on the solvent nature, the equilibrium constant may differ, decreasing with an increase in the medium polarity (Fig. 5).

The influence of the structure of radicals **1—4** on the K value is most pronounced when dichloromethane is used as the solvent. In this case, $\ln K$ correlates well with the σ'' value of the substituent in position 4 of the piperidine cycle of radicals **1—4** (as mentioned previously, for radical **5** the σ'' value is unknown) (Fig. 6). The negative sign of the ρ'' constant (ρ'' is the constant of the reaction series reflecting the intensity of the substituent influence, in our case, it is equal to -3.02) determined from the tangent slope of the straight line indicates that the introduction of electron-withdrawing substituents into the nitroxyl molecule hinders complex formation and decreases the equilibrium constant K.

Table 3. Complex formation constants (K) of nitroxyl radicals at 20 °C

Radical	Compound	Method of determination	Solvent	K/L mol^{-1}	Ref.
Di-*tert*-butyl-*N*-oxyl	Tetracyanoethylene	Optical spectroscopy	Diethyl ether	4.0	3
	Tetracyanoethylene	ESR spectroscopy	Toluene	5.0	3
	Phenol	Optical spectroscopy	Toluene	6.4	3
	Phenol	ESR spectroscopy	Toluene	6.7	3
	Pyrromellitic dianhydride	ESR spectroscopy	THF	1.1	3
	Phtalic anhydride	ESR spectroscopy	THF	0.6	3
1	Tetracyanoethylene	Optical spectroscopy	Chloroform	5.6	4
	Iodine	Optical spectroscopy	Cyclohexane	2.5	2
	Methanol	NMR spectroscopy	CCl_4	3.5	1
	tert-Butylamine	NMR spectroscopy	CCl_4	1.5	1
	2,5-Dimethylphenol	NMR spectroscopy	CCl_4	4.0	1
	Mesitylene	NMR spectroscopy	CCl_4	0.4	1
2	*tert*-Butyl hydroperoxide	NMR spectroscopy	CCl_4	5.7	1
6	Methanol	NMR spectroscopy	CCl_4	0.2	1

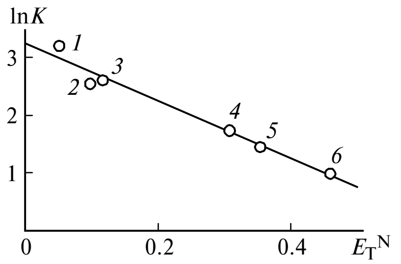


Fig. 5. Plot of lnK *vs.* E_T^N parameter of the solvent for radical **2** at 20 °C: *1*, tetrachloromethane; *2*, toluene; *3*, diethyl ether; *4*, dichloromethane; *5*, acetone; and *6*, acetonitrile.

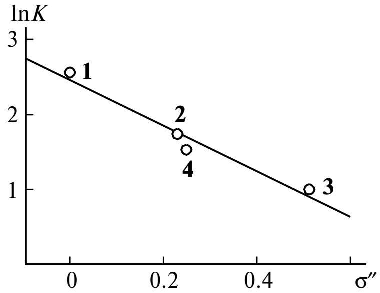


Fig. 6. Plot of lnK *vs.* σ″ of the substituent in position 4 of the piperidine cycle of radicals **1—4** at 20 °C; solvent dichloromethane.

This agrees with the correlation of lnK of radicals **1—6** with the potential of the oxidation half-peak of the nitroxyl group (Fig. 7), and the data for radical **7** do not correspond to the presented dependence. The same tendency is fulfilled in other solvents.

Using the temperature dependence of the equilibrium constant

$$\log K = -\Delta G^\circ/(RT) = -\Delta H^\circ/(RT) + \Delta S^\circ/R$$

we calculated the thermodynamic parameters of complex formation (see Table 1).

For radicals **1—5** of the piperidine series, a linear dependence (correlation effect) between the ΔH° and ΔS° values is fulfilled in the series of solvents studied

$\Delta H^\circ = -2.38 + 322.68\Delta S^\circ$, $r = 0.97$ (**1**);

$\Delta H^\circ = -17.27 + 194.69\Delta S^\circ$, $r = 0.81$ (**2**);

$\Delta H^\circ = -4.30 + 300.54\Delta S^\circ$, $r = 0.91$ (**3**);

$\Delta H^\circ = -2.81 + 304.87\Delta S^\circ$, $r = 0.96$ (**4**);

$\Delta H^\circ = 11.57 + 432.13\Delta S^\circ$, $r = 0.98$ (**5**).

Here r is the correlation coefficient.

The compensation effect was also found for solutions of **1—4** in the same solvent

$\Delta H^\circ = -5.09 + 293.22\Delta S^\circ$, $r = 0.99$ (acetone);

$\Delta H^\circ = -8.37 + 248.47\Delta S^\circ$, $r = 0.99$ (acetonitrile);

$\Delta H^\circ = -7.13 + 268.76\Delta S^\circ$, $r = 0.93$ (dichloromethane).

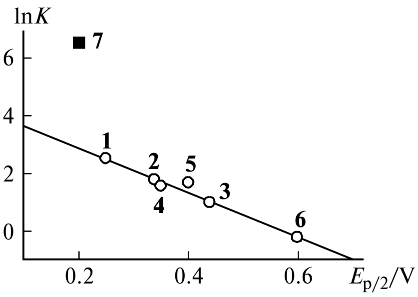


Fig. 7. Plot of lnK *vs.* potential of the oxidation half-peak of the nitroxyl group for radicals **1—7** at 20 °C; solvent dichloromethane.

The compensation effect is probably explained by the same mechanism of complex formation for all radicals under study.

The following quantum-chemical calculations were used to establish the electronic structure of the complex: B3LYP/cc-pVTZ using correlation-consistent basis sets and analysis of the NBO wavefunction (Natural Bond Orbitals — "natural bond orbitals"). It was found that ClO_2 forms two main types of complexes (Fig. 8): type **A** with the main contribution from the n→σ*(Cl—O) interaction and type **B** with the main contribution from the n→π*(O—Cl—O) and n→d(Cl) interactions. The B3LYP method was also used for the calculation of the structure of the complex for radical **1** (Fig. 9).

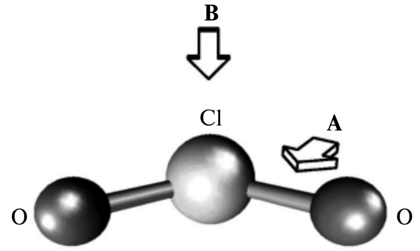


Fig. 8. Assumed directions of coordination for chlorine dioxide complexes of types **A** and **B**.

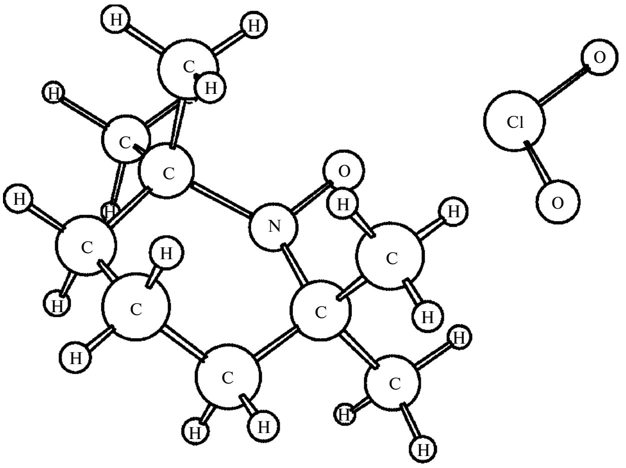
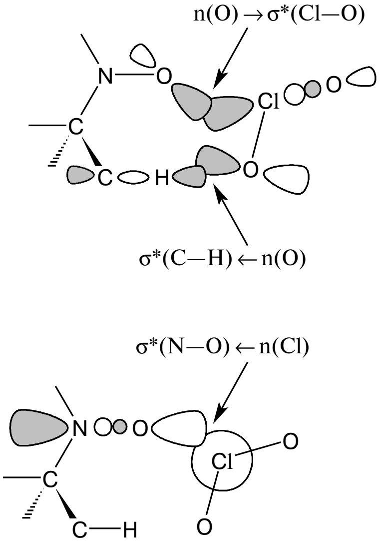


Fig. 9. Structure of the chlorine dioxide complex with radical **1** calculated by the B3LYP/3-21G* method.

According to the NBO calculations, a complex of type **A** is formed by the complex formation of ClO_2 with the nitroxyls. The main donor-acceptor interactions resulting in complex formation are the transfer of the electron density from an unshared pair of the O atom of the >N—O group to the antibonding orbital of the Cl—O bond n(O)→σ*(Cl—O) and the inverse transfer from an unshared electron pair of the O atom in the ClO_2 molecule to the antibonding orbital of the C—H bond of the methyl group of the hydroxyl radical n(O)→σ*(C—H). The complex is additionally stabilized by the transfer of the free electron pair of the Cl atom to the antibonding orbital of the N—O bond n(Cl)→σ*(N—O) (Scheme 1).

Scheme 1



Thus, we studied the formation of complexes of chlorine dioxide with nitroxyl radicals with various structures. It was established that the structure of nitroxyls affects the equilibrium constant: the introduction of electron-withdrawing substituents hinders complex formation, decreases the equilibrium constant, and shifts the absorption maximum of the complex to the blue spectral region. The structure of the complex was calculated by the quantum-chemical methods. The further transformation of the complex into the oxoammonium salt was shown.

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