JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2001; **14:** 38–42

Complex of chlorine dioxide with TEMPO and its conversion into oxoammonium salt

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Received 3 March 2000; revised 5 September 2000; accepted 20 September 2000

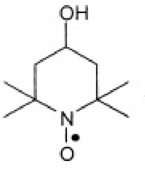
ABSTRACT: Complex formation between chlorine dioxide and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and its thermodynamic characteristics were studied in a number of organic solvents. The complex was shown to transform into the oxoammonium salt. The kinetics of this reaction were studied, and the equilibrium constants of the TEMPO·ClO_2 complex, determined by direct measurements and from kinetic data, were found to be in good agreement. The electronic structure of the complex is discussed in the light of recent theoretical results. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: nitroxyl radicals; chlorine dioxide; oxoammonium salts; complexes

INTRODUCTION

Oxoammonium salts are of great interest nowadays owing to their oxidative potential for synthetic organic chemistry.[1] Oxidation reactions catalyzed by nitroxyl radicals have been proposed to proceed via the formation of intermediate oxoammonium salts, which further oxidize the substrate and re-transform into nitroxyl.[2] [3] Consequently, the study of the reactions of nitroxyl radicals leading to oxoammonium salts is of great importance.

Recently, we have found that chlorine dioxide, which is known to be an oxidant of moderate strength,[4] forms a complex with 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (TEMPOL, **1**). The formation of the oxoammonium salt has also been observed in this system.[4] This present work deals with the complexation of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, **2**) in various organic solvents and with the subsequent transformation of the complex formed into the oxoammonium salt (**2a**).



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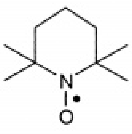

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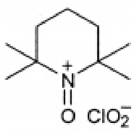

(2a)

EXPERIMENTAL

Chlorine dioxide was prepared from potassium chlorate and oxalic acid with the addition of 9 M aqueous sulfuric acid.[5] Chlorine dioxide was purified from traces of chlorine by adsorption of gaseous ClO_2 on silica gel and purging with argon.[6] Pure chlorine dioxide was desorbed from silica at 30 °C with an argon flow and dissolved in the solvents of interest. The ClO_2 concentration was measured by iodimetric titration[6] and spectrophotometrically.[7] TEMPO was recrystallized from heptane. All the solvents used were purified by conventional methods.

The complexation of chlorine dioxide with TEMPO was studied spectrophotometrically on a Specord M40 spectrophotometer (Carl Zeiss Jena) using a special quartz cell (2 ml) cooled by a cold gaseous nitrogen flow. The temperature in the spectrophotometric cell was monitored by a thermocouple. In a typical experiment, 1–2 ml of solvent was placed in the cell and TEMPO (2.4×10^{-3}–19.2×10^{-3} mmol) and ClO_2 (4×10^{-3} mmol) solutions were added. The reference cell contained a 2.4×10^{-3}–19.2×10^{-3} mmol solution of TEMPO. Spectra were taken when the target temperature in the cell (+20 to −20 °C) had been obtained.

To obtain the oxoammonium salt, equal volumes of ClO_2 and TEMPO solutions of the same concentrations were mixed and the precipitate formed was filtered, washed with solvent and dried in vacuum. IR spectra of the precipitate were taken on a Specord M80 spectrometer (Carl Zeiss Jena) in liquid paraffin or in KBr.

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Contract/grant sponsor: Russian Foundation for Basic Research; *Contract/grant number:* 99-03-33195.

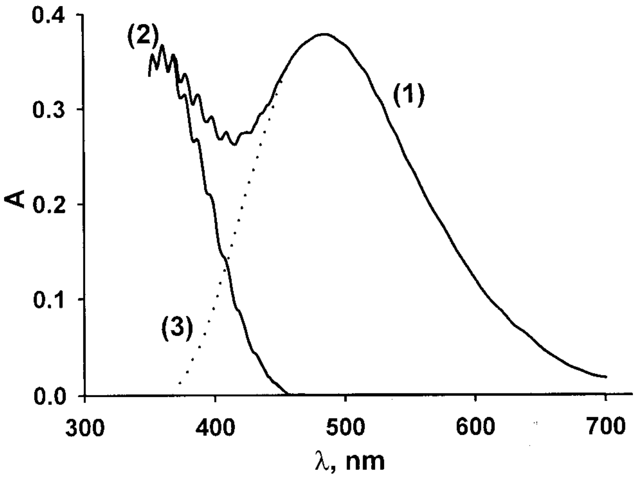


Figure 1. UV–VIS spectra (diethyl ether, 20 °C): (1) mixture of 3×10^{-2} M [TEMPO] and 1.4×10^{-3} M $[ClO_2]$; reference solution, 3×10^{-2} M [TEMPO]; (2) solution of 1.4×10^{-3} M $[ClO_O]$ (3) subtraction of spectrum (2) from spectrum (1)

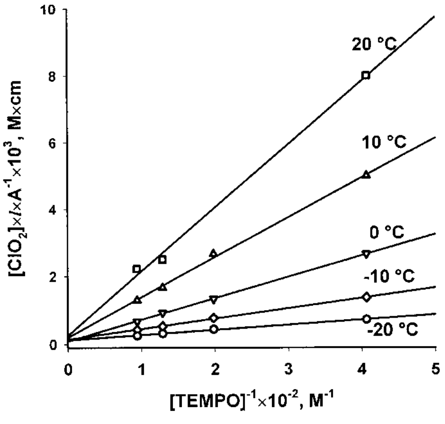


Figure 2. Complex absorption at maximum wavelength vs TEMPO concentration in the coordinates of the Benesi–Hildebrand equation at different temperatures (solvent, acetone; λ = 485 nm, $[ClO_2]_0 = 2 \times 10^{-4}$ M)

RESULTS AND DISCUSSION

On mixing of chlorine dioxide and TEMPO solutions in organic solvents, namely acetone, acetonitrile, *n*-heptane, diethyl ether, carbon tetrachloride and toluene, the mixture acquired a dark red color. Electronic absorption spectra showed an additional wide band without hyperfine structure in the range of 450–500 nm (Fig. 1). The absorption maximum was found to be red shifted with increase in the dielectric constant of the solvent, a feature characteristic of charge-transfer complexes.[8] It should be noted that the spectrum of chlorine dioxide itself does not show any changes, nor do the EPR spectra of both ClO_2 and TEMPO. Cooling of the ClO_2–TEMPO mixture to −80 °C causes pronounced intensification of the color. All these observations indicate the formation of a charge-transfer complex between chlorine dioxide and TEMPO.

The dependence of the complex absorption on the TEMPO concentration at constant chlorine dioxide concentration ($[TEMPO] \ll [ClO_2]$) is fitted with the Benesi–Hildebrand[9] equation:

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

where $[ClO_2]_0 l/A$ ($[ClO_2]_0$ = initial chlorine dioxide concentration, l = length of optical path and A = absorption) shows a linear dependence on the reciprocal of TEMPO concentration in all solvents and at all temperatures studied (+20 to −20 °C) (the correlation for acetone solutions is shown in Fig. 2). Therefore, it can be concluded that chlorine dioxide and TEMPO form a 1:1 complex:

$$ClO_2 + TEMPO \rightleftharpoons ClO_2 \cdot TEMPO$$

From the Benesi–Hildebrand equation, the molar absorptivity and the equilibrium constant *K* of the complex were determined (Table 1). From the temperature dependence of *K* the thermodynamic characteristics of complex formation were calculated (Table 1, Fig. 3). There is no apparent correlation between the equilibrium constant and the nature of the solvent, which is probably explained

Table 1. Wavelengths of maximum absorption (nm), equilibrium constants (M^{-1}), complexation enthalpy (kcal mol^{-1}), entropy (cal mol^{-1} K^{-1}) and Gibbs free energy for the complex of chlorine dioxide with TEMPO in different solvents (20 °C) (errors do not exceed 15%)

Solvent	λ	*K*	Δ*H*°	Δ*S*°	Δ*G*°	Solvent dielectric constant
$n\text{-}C_7H_{16}$	470.6	23.4	−10.0	−28.1	−1.8	1.92
CCl_4	480.5	26.6	−11.4	−32.5	−1.9	2.24
$C_6H_5CH_3$	479.6	20.2	−12.8	−38.3	−1.6	2.38
$(CH_3CH_2)_2O$	478.7	9.3	−7.4	−20.9	−1.3	4.22
$(CH_3)_2CO$	485.2	7.3	−9.5	−28.6	−1.1	20.74
CH_3CN	488.9	3.6	−8.3	−25.7	−0.8	37.40

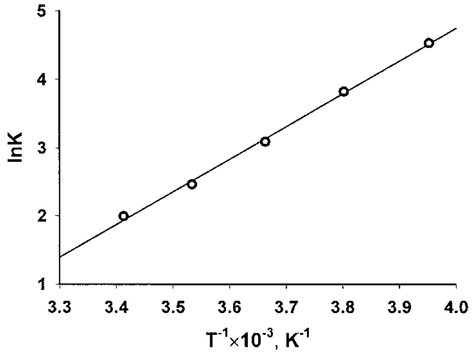


Figure 3. Dependence of logarithm of $ClO_2{}^{\bullet}$TEMPO complex equilibrium constant on the reciprocal temperature (solvent = acetone)

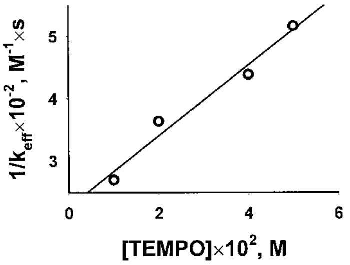


Figure 4. Dependence of reciprocal second-order effective rate constant of the reaction between ClO_2 and TEMPO on TEMPO concentration (solvent, heptane; 20 °C)

by specific solvation of all the species involved (ClO_2, TEMPO and complex): it is well known that nitroxyls form complexes of different strength with almost all solvents.[10]

With time the color intrinsic to $ClO_2{}^{\bullet}$TEMPO complex fades and a yellowish microcrystalline solid precipitates from solution. This process is accompanied by a decrease in the EPR signals of TEMPO and ClO_2. The crystalline product formed is diamagnetic, but after some time an EPR signal characteristic of TEMPO gradually appears, irradiation and humid air accelerate the process of TEMPO recovery. Such a behavior is typical of oxoammonium salts, which transform back to nitroxyl radicals on reaction with water.[11] The IR spectrum of the fresh precipitate showed an intense band at 1624 cm^{-1}, which is not observed in the IR spectra of the reagents and is characteristic of the $>N^+{=}O$ group.[12] The UV–VIS spectrum of the precipitate dissolved in acetonitrile shows an absorption at 454 nm which is also typical of oxoammonium salts.[12] Identification of the precipitate as **2a** is supported by elemental analysis: C 50.7, H 8.4, N 6.0, O 20.4, Cl 14.5% (calculated for **2a**: C 50.5, H 8.5, N 5.9, O 20.2, Cl 14.9%).

The kinetic studies of this reaction showed that at $[\mathrm{TEMPO}]_0 \ll [ClO_2]_0$ chlorine dioxide depletion obeys pseudo-first-kinetics order; the corresponding rate constants k' are listed in Table 2. The analysis of these data reveals that k' has a non-linear dependence on TEMPO concentration, and the effective second-order rate constant $k_{\mathrm{eff}} = k'/[\mathrm{TEMPO}]_0$ decreases with increase in TEMPO concentration. The following empirical equation was found to describe the dependence of k_{eff} on $[\mathrm{TEMPO}]_0$ (Fig. 4):

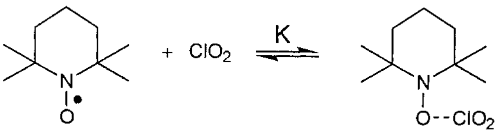
$$K_{\mathrm{eff}} = \frac{a}{1 + b[\mathrm{TEMPO}]_0}$$

where a and b are constant at a given temperature.

Table 2. Pseudo-first-order k' and effective second-order k_{eff} rate constants for the reaction between ClO_2 and TEMPO at different concentrations of TEMPO (0.01–0.05 M) (heptane, 20 °C, $[ClO_2]_0 = 10^{-3}$ M) (errors do not exceed 15%)

Rate constant	0.01 M	0.02 M	0.04 M	0.05 M
$k' \times 10^5$ (s^{-1})	3.70	5.50	9.12	9.68
$k_{\mathrm{eff}} \times 10^3$ (M^{-1} s^{-1})	3.7	2.75	2.28	1.94

This dependence can be explained by the reaction scheme shown in Eqns (1) and (2).



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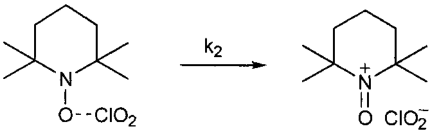


(2)

Using this scheme, the rate of the reaction is described by the following expression:

$$W = \frac{k_2K[ClO_2][\mathrm{TEMPO}]}{1 + K[\mathrm{TEMPO}]}$$

Comparison of the above two expressions shows that $k_2\,K = a$ and $K = b$. Therefore, we can calculate K and k_2 from kinetic data presented in Table 2 (for the reaction in heptane): $1/a = (2.27 \pm 0.24) \times 10^2$, m^2 s and $b/a = (5.69 \pm 0.70) \times 10^3$, m s, and consequently $K = 25.0$ m^{-1} and $k_2 = 1.76 \times 10^{-4}$ s^{-1}. It can be seen that the values of K obtained by the Benesi–Hildebrand method and from kinetic date are in excellent agreement (for heptane, $K = 23.4$ M^{-1} by the Benesi–Hildebrand method and 25.0 M^{-1} from kinetic data). It should be noted that the kinetics of complex conversion are too slow to affect the values of equilibrium constant K measured by the Benesi–Hildebrand method.

Thus, the reaction between chlorine dioxide and TEMPO proceeds through the formation of a charge-transfer complex, which further transforms into an

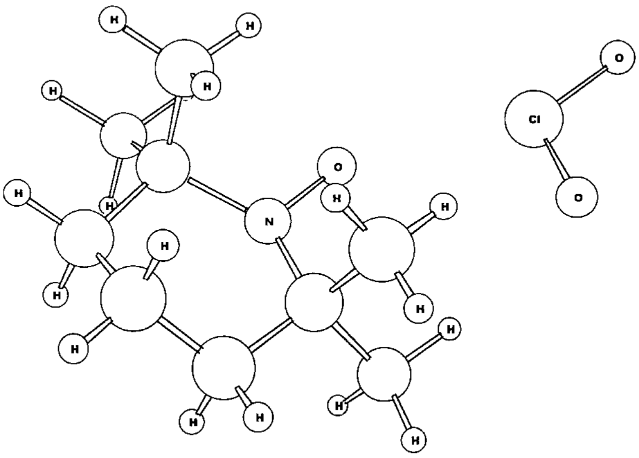
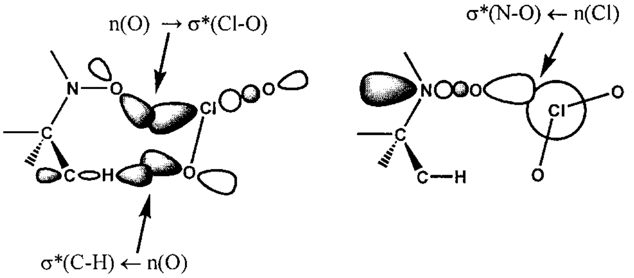


Figure 5. The structure of the chlorine dioxide – TEMPO complex calculated by the B3LYP/3–21G* method

oxoammonium salt via inner-sphere one-electron oxidation of TEMPO by ClO_2. Although the one-electron oxidation is a well-established mechanism for the majority of chlorine dioxide reactions,[7,13,14] charge-transfer complexes of ClO_2 with organic compounds have not been observed before our recent work:[4] nitroxyl radicals are still the only compounds which were found to give charge-transfer complexes with chlorine dioxide. Great efforts have been made in the investigation of nitroxyl radical complexes with different ligands by magnetic resonance methods.[10] These studies have revealed general trends of the structure and stability of the nitroxyl complexes. In terms of electronic structure, these complexes were classified into three major classes: n–σ, π–σ, and π–π (the first orbital concerns the nitroxyl radical and the second the ligand).

The electronic structure of chlorine dioxide complexes has not been considered until our recent theoretical study,[‡] where a series of ClO_2 complexes with several donor molecules have been studied using density functional theory (B3LYP/cc-pVTZ) quantum chemical calculations. The natural bond orbital (NBO) method was applied to determine the dominating charge-transfer interactions in these complexes. It was found that chlorine dioxide can form two types of complexes: (a) with major $n \rightarrow \sigma^*$(Cl—O) charge-transfer interaction and (b) with major $n \rightarrow \pi^*$(O—Cl—O) and $n \rightarrow d$(Cl) interactions. Structures of ClO_2 complexes with some simple nitroxyl radicals (parent nitroxyl, dimethyl nitroxyl and *tert*-butyl nitroxyl) also were considered.[‡] We have also calculated the structure of the $ClO_2{}^{\bullet}$TEMPO complex by the B3LYP method using a simple 3–21G* basis set (Fig. 5).

According to the NBO analysis,[‡] the main charge-transfer interactions in complexes of chlorine dioxide with nitroxyl radicals are the $n(O) \rightarrow \sigma^*$(Cl—O) interaction of the lone pair of the >N—O group and the antibonding orbital of the Cl—O bond, the back hydrogen-bond type interaction of the chlorine dioxide oxygen lone pair with the antibonding orbitals of C—H bonds of the nitroxyl radical methyl groups $n(O) \rightarrow \sigma^*$(C—H) and the donation from the s-character lone pair of the chlorine atom to the antibonding orbital of the N—O bond $n(Cl) \rightarrow \sigma^*$(N—O), as illustrated.



CONCLUSIONS

In inert organic solvents, chlorine dioxide oxidizes 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) to the corresponding oxoammonium salt by an inner-sphere electron-transfer mechanism via the formation of an intermediate complex. The equilibrium constant complex formation depends on the nature of the solvent and is determined by the processes of non-specific and specific solvation of the species involved.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (grant No. 99-03-33195) and the Special Federal Program State Support of Integration of the Higher School and Fundamental Science, 1997–2000.

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