Reactions of Chlorine Dioxide with Organic Compounds

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Abstract

Data on the reactivity of chlorine dioxide with organic compounds from various classes are summarized. Early investigations of the reactions of chlorine dioxide were occurred in aqueous or predominantly aqueous solutions in general, because it used in drinking water treatment and in industry as bleaching agent. However, chlorine dioxide was not used widely as reagent in organic synthesis.

In last decades the number of publications on the studying interaction of the chlorine dioxide in organic medium increased. In table presented the rate constants reactions of chlorine dioxide with organic compounds published through 2004. Most of the rate constants were determined spectrophotometrically by decay kinetics of chlorine dioxide at 360 nm. Chlorine dioxide may be used for oxidation of organic compounds, because chlorine dioxide is enough reactive and selective as an oxidant with a wide range of organic compounds based on these reaction rate constants. But the application of chlorine dioxide as reagent in organic synthesis is restrained by the lack of data on the kinetics and mechanism of reactions involving chlorine dioxide, as well as data on the product yields and composition, temperature and solvent effects, and catalysts. The pathways of products formation and probable mechanisms of reactions are discussed in the review.

Introduction

Chlorine dioxide OClO has found wide application in industry as a moderately strong oxidant. For more than half a century it has been used for odor control and disinfection in water preparation. It has a number of advantages over molecular chlorine; thus ClO_2 is less liable to give chlorine derivatives with organic compounds compared to Cl_2. Another important application is cellulose bleaching. ClO_2 is currently regarded as a reagent for sewage processing and purification of oil products from sulfides.

Chlorine dioxide is a large-tonnage industrial reagent, generally produced on-site in view of the high explosion hazard. Today world's production of ClO_2 amounts to several dozen thousand tons per year.

Recently, ClO_2 has attracted close attention of atmospheric chemists in view of its potential role in ozone depletion. Various aspects of chlorine dioxide photochemistry were investigated in detail [1].

Surprising as it is, the organic aspects of chlorine dioxide chemistry have not received adequate attention in the literature. In view of major applications of ClO_2, reactions of interest to researchers are primarily reactions with chief contaminants of drinking water (phenols, hydrocarbons, *etc.*) in aqueous solutions with pH = 3-9 and with very low concentrations of oxidized substances (10^{-6}-10^{-4} M). Insufficient data are available on reactions of ClO_2 with organic compounds in organic solvents and in the gas phase, restricting its potential applications in organic synthesis.

Of reviews available in the present-day literature it is worthwhile to mention book [2] and articles [3-5]. Several aspects of chlorine dioxide chemistry associated with cellulose bleaching are highlighted in monograph [6]. Regrettably, no review papers with full account of currently available data have appeared in the literature on reactions of ClO_2 with organic compounds. The aim of this review is to fill this gap and draw the attention of both organic and physical chemists to this promising oxidant.

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Chlorine Dioxide: Properties and Molecular Structure

Under normal conditions, chlorine dioxide OClO is a readily liquefiable yellow-green gas that smells like molecular chlorine. The boiling point of ClO_2 is 9.7±0.3°C. In the liquid state it is brownish red and extremely explosive. At -59°C the substance is consolidated. Evaporation heat is 6.3±0.1 kcal/mole, the critical temperature is -192°C, and the critical pressure is 85 atm. The density of ClO_2 decreases from 1.973 g/cm³ at -60°C to 1.653 g/cm³ at 5°C. Chlorine dioxide is soluble in water, acetic and sulfuric acids, carbon tetrachloride, and some other organic solvents.

The formation enthalpy of ClO_2 was determined experimentally in a number of works [7]; in [8] the recommended value is 23.0±2.0 kcal/mole. An isomer of chlorine dioxide, chlorine peroxide ClOO, has almost the same formation enthalpy, 23.0±1.0 kcal/mole [8]; however, it is extremely kinetically unstable and was observed in low-temperature matrices only [9]. Quantum-chemical calculations of relative stability for these two isomers of ClO_2 give contradictory data [10] because of the similarity of their potential energies. Below the formula ClO_2 is understood to be chlorine dioxide OClO.

The ionization potential of chlorine dioxide is 10.33±0.02 eV [11]; electron affinity is 2.378±0.006 eV [12]. The redox potential in an aqueous solution is $E(ClO_2/ClO_2^-) = 0.94$ V [13].

Chlorine dioxide has odd number of electrons (33). This is a stable radical that does not tend to dimerize under normal conditions. In the gas phase, the EPR spectrum of ClO_2 was not observed because of the large number of rotational levels in the chlorine dioxide molecule [7]. In solution, ClO_2 generally gives a broad singlet in the EPR spectrum. Under certain circumstances, the spectral line becomes more complicated, transforming into a quartet due to hyperfine splitting on the [35]Cl and [37]Cl nuclei, for which hyperfine structure constants are 1.70±0.03 and 1.37±0.03 mT, respectively [14]. The EPR spectrum of ClO_2 adsorbed on various surfaces is still more complex [15,16]; chlorine dioxide, therefore, may be used as a spin probe [17].

Previous works reported that chlorine dioxide does not dimerize in the solid state [7]. However, recently it was shown [18,19] that below -108°C ClO_2 forms loosely bonded diamagnetic dimers of head-to-tail type relative to the Cl–O bonds.

The molecular structure of chlorine dioxide is nonlinear with symmetry group C_{2v}.
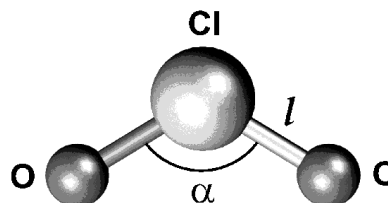
The Cl–O bond length l and the O–Cl–O angle α were determined in a number of works by electron diffraction and spectroscopy [7]. Microwave studies provided most exact data: $l = 1.470$ Å and $\alpha = (1.792$ D) [21]. In the IR spectrum of gaseous chlorine dioxide, the frequencies corresponding to the symmetric deformation vibrations and to the symmetric and asymmetric stretching vibrations are 447.7, 945.6, and 1110.1 cm⁻¹ [22-25]. One can also observe overtones and composite frequencies: 1870.0, 2031.0, 2954.0, and 3333.0 cm⁻¹.

Of the available quantum-chemical calculations for chlorine dioxide we primarily mention publications [26-28], reporting MRCI (multi-reference configuration interaction) calculations using quadruple-zeta basis sets for potential energy surface investigations of the ClO_2 molecule in the ground and excited states. The geometrical structural data obtained agree very well with experiment. However, the calculation procedures are too labor-consuming to be used in practical calculations on complex systems with chlorine dioxide. Attempts to employ the G2 and G2(MP2) methods did not lead to quite satisfactory results at the MP2/6-31G(d) level, but justified using these methods for calculating the energy characteristics of chlorine oxides [10]. The G2(MP2) method gave slightly worse results compared to G2, but demanded less computational effort. Density functional theory methods, actively developed over the past decade, proved very efficient for both geometry and energy calculations for ClO_2 [29-31]. The best results were obtained with Becke's B3LYP three-parameter hybrid functional. Using this functional with large basis sets yields a satisfactory degree of accuracy in calculating the geometry of ClO_x oxides, as well as their bond dissociation energies and formation enthalpies [30]. Topological analysis of electron density in chlorine oxides [31] indicated that electron spin density for an odd electro in ClO_2 is concentrated on the chlorine atom.

The ground state of the chlorine dioxide molecule is $^2B_1$ [32]. A transition to the first excited state, $^2A_2$,

corresponds to an absorption band with a clear-cut rotational structure in the range 510-270 nm with a maximum at ~360 nm (Fig. 1).

The UV spectrum recorded in vacuum has three band systems associated with the first (183, 163 nm) and the second (157 nm) ionization potentials. The first system consists of three, the second of seven, and the third of eight bands. Photochemistry of ClO_2 is discussed in detail in a recent review [32].

Reactions of Chlorine Dioxide with Organic Compounds

Reactions of chlorine dioxide with organic compounds were generally investigated in aqueous solutions with low concentrations of reagents. Emphasis was laid on the reaction products, while the physicochemical characteristics of the processes are ill-defined. The kinetic data on the reactivity of chlorine dioxide with organic compounds are summarized in Table 1.

Analysis of Table 1 indicates that chlorine dioxide is enough reactive as an oxidant with a wide range
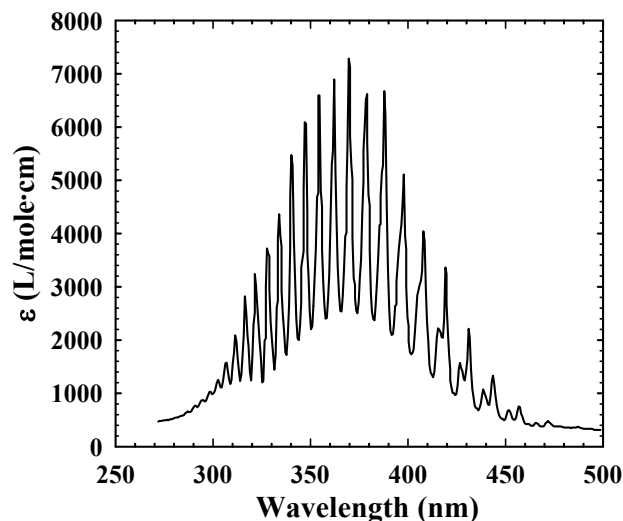
Fig. 1. Electronic absorption spectrum of the transition $^2B_1 \rightarrow {}^2A_2$ for chlorine dioxide in a gas phase.

of organic compounds.

Major products and physicochemical principles underlying reactions of chlorine dioxide with various organic compounds are considered below.

Table 1
Second-order rate constants for reactions of chlorine dioxide with organic compounds

	Compound	Solvent	pH	T, °C	I, eV	k, (M^{-1}·s^{-1})	Refs.
	Hydrocarbons						
1	Allylbenzene	H_2O	2-7	23		~10^{-3}	[33]
		H_2O	7	25		$2.5 \cdot 10^{-3}$	[34]
2	Anthracene	H_2O	7	20		$3.3 \cdot 10^3$	[35]
3	Indene	H_2O	7	25		2	[36]
4	o-Xylene	H_2O	2	23		<10^{-5}	[33]
5	Mesitylene	H_2O	8	23		<10^{-5}	[33]
6	α-Methylstyrene	H_2O	7	25		$4.6 \cdot 10^{-1}$	[34]
7	p-Methylstyrene	H_2O	7	25		$1.6 \cdot 10^{-1}$	[34]
8	trans-α-Methylstyrene	H_2O	7	25		1.2	[34]
9	Naphthalene	H_2O	5	23		<0.3	[33]
10	Styrene	H_2O	7	25		$6.2 \cdot 10^{-2}$	[34]
11	p-Phenylstyrene	H_2O	7	25		$1.0 \cdot 10^{-1}$	[34]
12	p-Chlorostyrene	H_2O	7	25		$4.1 \cdot 10^{-1}$	[34]
13	Cyclohexene	H_2O	5-7	23		~$3 \cdot 10^{-2}$	[33]
		H_2O	7	25		$2.2 \cdot 10^{-2}$	[33]

Table 1
Continued

	Compound	Solvent	pH	T, °C	I, eV	k, (M^{-1}·s^{-1})	Refs.
Alcohol								
14	2,4-Hexadien-l-ol	H_2O	2-10	23		~9	[33]
15	2,5-Dimethylfuran	H_2O	2-10	23		~$1.2 \cdot 10^2$	[33]
		H_2O	2-6			$1 \cdot 10^2$	[35]
16	Glucose	H_2O				<10^{-2}	[37]
17	Methanol	H_2O	2.3	35	0.2	$4.7 \cdot 10^{-5}$	[38]
18	Propan-2-ol	H_2O	7.0	35	0.2	$2.6 \cdot 10^{-5}$	[39]
		C_7H_{16}		30		$5.9 \cdot 10^{-5}$	[40]
		CCl_4		30		$7.4 \cdot 10^{-5}$	[40]
		C_6H_6		30		$8.6 \cdot 10^{-5}$	[40]
		$C_4H_8O_2$		30		$3.8 \cdot 10^{-5}$	[40]
		C_6H_5Cl		30		$4.1 \cdot 10^{-5}$	[40]
		$CH_3C-OOC_2H_5$		30		$2.0 \cdot 10^{-5}$	[40]
		$C_2H_4Cl_2$		30		$4.1 \cdot 10^{-5}$	[40]
		CH_3CN		30		$2.7 \cdot 10^{-5}$	[40]
19	2-Methylpropan-1-ol	C_7H_{16}		30		$5.2 \cdot 10^{-5}$	[40]
20	Butan-1-ol	C_7H_{16}		30		$6.4 \cdot 10^{-5}$	[40]
21	Butan-2-ol	C_7H_{16}		30		$13.7 \cdot 10^{-5}$	[40]
22	3-Methylpentan-1-ol	C_7H_{16}		30		$6.3 \cdot 10^{-5}$	[40]
23	Heptan-4-ol	C_7H_{16}		30		$5.3 \cdot 10^{-5}$	[40]
24	Decan-2-ol	C_7H_{16}		30		$13.6 \cdot 10^{-5}$	[40]
25	Cyclohexanol	C_7H_{16}		30		$23.3 \cdot 10^{-5}$	[40]
26	Borneol	C_7H_{16}		30		$63.6 \cdot 10^{-5}$	[40]
27	Furfuryl alcohol	H_2O	3-9	23		0.37	[33]
		H_2O	3-9			~0.5	[37]
Ketones and aldehydes								
28.	Acetone	H_2O	6	23		<10^{-5}	[33]
29.	Benzaldehyde	H_2O	8	23		<$3 \cdot 10^{-4}$	[32]
30.	Benzo-2,3-dihydrophthalazine-1,4-dione	H_2O	7			$3 \cdot 10^5$	[41]
31.	Butyryl aldehyde	H_2O				<10^{-2}	[37]
32.	2,3-Dihydro-1,4-phthalazinedione	H_2O	7			$1.5 \cdot 10^5$	[41]
33.	5,5-Dimethyl-1,3-cyclohexanedione	H_2O	2-5	23		~$2 \cdot 10^4$	[33]
34.	2-Pentanone	H_2O	6	23		<$3 \cdot 10^{-5}$	[33]

Table 1
Continued

	Compound	Solvent	pH	T, °C	I, eV	k, (M^{-1}·s^{-1})	Refs.
	Carboxylic acids and their anions						
35	Ascorbate ion	H_2O		22	0.1	$1 \cdot 10^7$	[42]
36	Acetate ion	H_2O	8			$<10^{-2}$	[37]
37	4-Hydroxybenzoate ion	H_2O	2-6	23		$6 \cdot 10^6$	[33]
38	Glyoxylate ion	H_2O		23	0.1	$<10^{-2}$	[37]
		H_2O		22		$5 \cdot 10^8$	[42]
39	Indigotrisulfonate ion	H_2O	7	23		$>2.5 \cdot 10^5$	[33]
		H_2O				$>2 \cdot 10^5$	[37]
40.	Linolic acid	H_2O				$<10^{-2}$	[37]
41.	2-Methyl-1-propanethiol anion	H_2O		23		$7.5 \cdot 10^8$	[33]
42.	Salicylate dianion	H_2O	7.0-10.5	23		$6 \cdot 10^7$	[33]
43.	Salicylate ion	H_2O	1.5-6	23		<46	[33]
		H_2O	3-8			$\sim 1 \cdot 10^2$	[37]
44.	Formate ion	H_2O				$6 \cdot 10^{-4}$	[43]
		H_2O				$<10^{-2}$	[37]
45.	Phthalic acid	H_2O	6	23		$<10^{-3}$	[33]
46.	Fumarate ion	H_2O	3.6	23		$<10^{-5}$	[33]
	Phenols and related compounds						
47.	6-(Dimethylamino)-2,3-dihydrophthalazine-1,4-dione	H_2O	7			$1.5 \cdot 10^6$	[41]
48.	4-(tert-Butyl)phenoxide ion	H_2O	2-7	23		$1.5 \cdot 10^8$	[33]
49.	Anisole	H_2O	5	23		$<2 \cdot 10^{-3}$	[33]
		H_2O				$<10^{-2}$	[37]
50.	4-Acetylphenoxide ion	H_2O	2.0-6.5	23		$8 \cdot 10^5$	[33]
51.	1,4-Benzoquinone	H_2O	7	23		$<5 \cdot 10^{-3}$	[33]
		H_2O	8			$<10^{-2}$	[37]
52.	4-Bromophenoxide ion	H_2O	~ 12	21		$2.7 \cdot 10^7$	[44]
53.	3-Hydroxyphenoxide ion	H_2O	2.5-6	23		$4.8 \cdot 10^7$	[33]
54.	1,3-Dihydroxybenzene	H_2O	2.5-6.0	23		40	[33]
55.	1,4-Dihydroxybenzene	H_2O	2-6	22	0.1	$3 \cdot 10^4$	[42]
56.	1,4-Dihydroxybenzene dianion	H_2O				$1.7 \cdot 10^9$	[46]
57.	1,3-Dihydroxybenzene dianion	H_2O	~ 12	22		$1.4 \cdot 10^9$	[44]
58.	1,2- Dihydroxybenzene monoanion	H_2O	2-4.5	23		$2 \cdot 10^9$	[33]
59.	1,4-Dihydroxybenzene monoanion	H_2O				$9.0 \cdot 10^8$	[46]

Table 1

Continued

	Compound	Solvent	pH	T, °C	I, eV	k, $(M^{-1} \cdot s^{-1})$	Refs.
	Phenols and related compounds						
60	2,5-Dimethylphenoxide ion	H_2O	2-6	23		$6.8 \cdot 10^8$	[33]
61	2,4-Dimethylphenol	H_2O	2-6	23		$9 \cdot 10^2$	[33]
62	2,5-Dimethylphenol	H_2O	2-6	23		$1 \cdot 10^2$	[33]
63	2,4-Dichlorophenoxide ion	H_2O	2-5	23		$2.2 \cdot 10^7$	[33]
64	2,4-Dichlorophenol	H_2O	2-3			$\sim 1 \cdot 10^2$	[37]
65	2-Methylphenoxide ion	H_2O	2-6	23		$4.4 \cdot 10^8$	[33]
		CH_3CN				$5.0 \cdot 10^{-3}$	[47]
66	3-Methylphenoxide ion	H_2O		23		$1.0 \cdot 10^8$	[33]
		H_2O	~ 12	21		$4.7 \cdot 10^7$	[43]
67	4- Methylphenoxide ion	H_2O	2.5-6.0	23		$5.2 \cdot 10^8$	[33]
		H_2O	~ 12	21		$2.6 \cdot 10^8$	[43]
68	2-Methylphenol	H_2O	2.5-6.0	23		16	[33]
69	3-Methylphenol	CH_3CN		25		$2.4 \cdot 10^{-2}$	[47]
70	4-Methylphenol	H_2O	2.5-6.0	23		50	[33]
		H_2O	<3.5			$1 \cdot 10^2$	[37]
			6			$1 \cdot 10^4$	
		CH_3CN		25		0.35	[47]
71	2-Methoxy-4-formylphenoxide ion	H_2O	2-2.6	23		$1.8 \cdot 10^8$	[33]
72	2-Methoxyphenoxide ion	H_2O	3.0-5.5	23		$1.2 \cdot 10^9$	[33]
73	3-Methoxyphenoxide ion	H_2O	~ 12	21		$4.9 \cdot 10^7$	[44]
74	4-Methoxyphenoxide ion	H_2O	3.0-5.5	23		$1.7 \cdot 10^9$	[33]
		H_2O	11.7	25	0.02	$1.0 \cdot 10^9$	[47]
		H_2O	12			$7.4 \cdot 10^8$	[46]
75	2-Methoxyphenol	H_2O	3-6	23		$1.0 \cdot 10^3$	[33]
76	4-Methoxyphenol	H_2O		23		$2.5 \cdot 10^4$	[33]
77	4-Nitrophenoxide ion	H_2O	0.2-1.5	23		$4 \cdot 10^3$	[33]
		H_2O	~ 12	21		$<4 \cdot 10^5$	[43]
78	4-Nitrophenol	H_2O	0.2-2	23		0.14	[33]
79	Pentachlorophenoxide ion	H_2O	2-2.5	23		$1.4 \cdot 10^3$	[33]
80	4-Sulfonatophenoxide ion	H_2O	3-7	23		$1.0 \cdot 10^6$	[33]
81	2,4,6-Trimethylphenoxide ion	H_2O	2-6	23		$4 \cdot 10^9$	[33]
82	2,4,6-Trichlorophenoxide ion	H_2O	2.2-4.0	23		$5.3 \cdot 10^6$	[33]

Table 1
Continued

		Solvent	pH	T, °C	I, eV	k, (M^{-1}·s^{-1})	Refs.
	Compound						
Phenols and related compounds							
83	2,4,6-Trichlorophenol	H$_2$O		23		<800	[33]
84	Phenoxide ion	H$_2$O		23		4.9·10^7	[33]
		H$_2$O				2.7·10^7	[49]
85	Phenol	H$_2$O				0.24	[49]
		i-C$_4$H$_9$OH		25		6.1·10^{-3}	[50]
		C$_2$H$_5$OH		25		6.0·10^{-3}	[50]
		C$_4$H$_8$O$_2$		25		1.1·10^{-2}	[50]
		(CH$_3$)$_2$CO		25		1.1·10^{-2}	[50]
		CH$_3$CN		25		1.5·10^{-2}	[50]
		CH$_3$COOC$_2$H$_5$		25		1.7·10^{-2}	[50]
		C$_2$H$_4$Cl$_2$		25		28.0·10^{-2}	[50]
		C$_7$H$_{16}$		25		37.0·10^{-2}	[50]
		CCl$_4$		25		49.0·10^{-2}	[50]
86	2-Chlorophenoxide ion	H$_2$O	2-5	23		3.5·10^7	[33]
87	4- Chlorophenoxide ion	H$_2$O	2-5	23		3.5·10^7	[33]
88	2-Chlorophenol	H$_2$O	2-5	23		1.5	[33]
89	4-Cyanophenoxide ion	H$_2$O	~ 12	21		≤ 4·10^3	[44]
90	4-Ethylphenoxide ion	H$_2$O	2.0-5.5	23		8.0·10^8	[33]
91	4-Ethylphenol	H$_2$O	2-6	23		50	[33]
92	4-*tert*-Butylphenol	CH$_3$CN		25		3.3·10^{-2}	[47]
93	2-Cyclohexylphenol	CH$_3$CN		25		2.8·10^{-2}	[47]
94	2,6-Di-*tert*-butyl-4-methylphenol	CH$_3$CN		25		40	[47]
Amines and related compounds							
95	Alanine	H$_2$O	8-10	23		< 10^{-2}	[33]
		H$_2$O	8			< 10^{-2}	[37]
96	3-Aminophthalate ion	H$_2$O				1.5·10^5	[51]
97	2-Aminoethanol	H$_2$O		27	0.2	1.4·10^{-2}	[52]
98	Aniline	H$_2$O	6.9			4.5·10^5	[46]
99	Benzylamine	H$_2$O		27		3.9·10^{-2}	[51]
		H$_2$O	8.96	25	0.2	4.1·10^{-2}	[53]
100	Benzyl-*tert*-butylamine	H$_2$O		27	0.2	2.8·10^2	[52]
		H$_2$O	8.4	25	0.2	2.9·10^2	[53]

Table 1
Continued

	Compound	Solvent	pH	T, °C	I, eV	k, (M$^{-1} \cdot$s^{-1})	Refs.
				Amines and related compounds			
101	N-*tert*-Butylpyrrolidine	H$_2$O		27	0.2	1.3$\cdot$10^6	[52]
102	1-Hydroxypiperidine	H$_2$O				4$\cdot$10^4	[54]
103	Glycine	H$_2$O	8	23		<10^{-3}	[33]
104	Diazobicyclol,4-[2.2.2]octane	H$_2$O	7	25	0.2	4.1$\cdot$10^4	[55]
105	Diazobicyclol,4- [2.2.2]octane radical cation	H$_2$O	9	25		1.3$\cdot$10^4	[55]
106	Diisopropylamine	H$_2$O	8.93	27	0.2	3.5$\cdot$10^2	[52]
		H$_2$O		25	0.2	3.6$\cdot$10^2	[53]
107	N,N-Dimethyl-3-methoxybenzylamine	H$_2$O		27	0.2	2.9$\cdot$10^4	[52]
108	N,N-Dimethyl-3-nitrobenzylamine	H$_2$O		27	0.2	6.2$\cdot$10^3	[52]
109	N,N-Dimethyl-3-chlorobenzylamine	H$_2$O		27	0.2	1.6$\cdot$10^4	[52]
110	N,N-Dimethyl-4-fluorobenzylamine	H$_2$O		27	0.2	2.0$\cdot$10^4	[52]
111	N,N-Dimethyl-4-methylbenzylamine	H$_2$O		27	0.2	3.5$\cdot$10^4	[52]
112	N,N-Dimethyl-4-methoxybenzylamine	H$_2$O		27	0.2	4.9$\cdot$10^4	[52]
113	N,N-Dimethyl-4-nitrobenzylamine	H$_2$O		27	0.2	4.5$\cdot$10^3	[52]
114	N,N-Dimethyl-4-chlorobenzylamine	H$_2$O		27	0.2	2.0$\cdot$10^4	[52]
115	N,N--N'-Dimethylphenylurea	H$_2$O	7	20		0.3	[56]
116	Dimethylamine	H$_2$O	6.8-9.3	24		5$\cdot$10^2	[33]
117	N,N-Dimethylaniline	H$_2$O	9.6			6.5$\cdot$10^7	[46]
118	N,N-Dimethylbenzylamine	H$_2$O		27	0.2	2.7$\cdot$10^4	[52]
119	2,3-Dimethylindole	H$_2$O				1.1$\cdot$10^8	[57]
120	N,N-Dimethyl-*tert*-butylamine	H$_2$O	7-9	27	0.2	2.3$\cdot$10^5	[52]
121	Diethylamine	H$_2$O	7.14	26		~1$\cdot$10^3	[58]
122	N-Isopropylbenzylamine	H$_2$O		27	0.2	9.1	[52]
123	Imidazole	H$_2$O	5.6	23		<10^{-4}	[33]
124	Luminol, monoanion	H$_2$O	8.1			2.9$\cdot$10^6	[59]
		H$_2$O	7			1$\cdot$10^6	[41]
		H$_2$O	8			2$\cdot$10^6	[60]
125	N-Methyl-4-methoxybenzylamine	H$_2$O		27	0.2	2.7$\cdot$10^2	[52]
126	Methylamine	H$_2$O		23		≤ 10	[33]
		H$_2$O	7-10			< 1	[37]
127	1-Methylindole	H$_2$O				1.6$\cdot$10^4	[57]
128	2-Methylindole	H$_2$O				8.1$\cdot$10^5	[57]

Table 1
Continued

	Compound	Solvent	pH	T, °C	I, eV	k, $(M^{-1} \cdot s^{-1})$	Refs.
	Amines and related compounds						
129	3-Methylindole	H_2O				$1.9 \cdot 10^6$	[57]
130	N-Methylpiperidine	H_2O		27	0.2	$8.7 \cdot 10^4$	[52]
131	Urea	H_2O	9	23		$<10-6$	[33]
132	Piperidine	H_2O		27	0.2	$2.4 \cdot 10^3$	[52]
133	Piperidine-1-oxyl	H_2O				$>5 \cdot 10^6$	[54]
134	2,2,6,6-Tetramethylpiperidin-1-ol	H_2O	~ 7	22	0.1	$4 \cdot 10^4$	[42]
135	Tyrosine dianion	H_2O	~ 12			$8.2 \cdot 10^7$	[61]
136	Trimethylamine	H_2O		23		$6 \cdot 10^4$	[33]
137	Tryptophan	H_2O	~ 12			$7.6 \cdot 10^5$	[61]
138.	Triethylamine	H_2O	6.60	27	0.2	$2.0 \cdot 10^5$	[53]
		H_2O	6.56	26		$2 \cdot 10^5$	[58]
139	p-Phenylenediamine	H_2O	9.2			$3.5 \cdot 10^8$	[46]
140	Cysteine	H_2O	8.5	23		7	[33]
		H_2O	2.5			$\sim 1 \cdot 10^2$	[37]
			0.5			$\sim 1 \cdot 10^3$	
141	Cystine	H_2O	2			~10	[37]
	1,3-Dioxacycloalkanes						
142	2-Isopropyl-1,3-dioxolane	CCl_4		25		$1.9 \cdot 10^{-4}$	[62]
143	2-Phenyl-1,3-dioxolane	CCl_4		25		$8.28 \cdot 10^{-4}$	[62]
144	2,2-Pentamethylene-1,3-dioxolane	CCl_4		25		$4.3 \cdot 10^{-5}$	[62]
145	4-Chloromethyl-1,3-dioxolane	CCl_4		25		$1.2 \cdot 10^{-5}$	[62]
146	2-Phenyl-4-chloromethyl-1,3-dioxolane	CCl_4		25		$2.5 \cdot 10^{-4}$	[62]
147	4-Methyl-1,3-dioxane	CH_3CN		25		$1.0 \cdot 10^{-6}$	[62]
148	2-Isopropyl-4-methyl-1,3-dioxane	CH_3CN		25		$5.0 \cdot 10^{-6}$	[62]
149	2-Phenyl-4-methyl-1,3-dioxane	CH_3CN		25		$4.9 \cdot 10^{-6}$	[62]
150	2-Phenyl-5,5-dimethyl-1,3-dioxane	CH_3CN		25		$3.0 \cdot 10^{-6}$	[62]
	Thiols						
151.	Ethanediol	CCl_4		40		0.10	[63]
152	Propanethiol	CCl_4		25		$5.9 \cdot 10^{-2}$	[63]
		$n-C_7H_{16}$		25		$1.7 \cdot 10^{-3}$	[63]
		$C_4H_8O_2$		25		$7.2 \cdot 10^{-2}$	[63]
		C_6H_6		25		$2.6 \cdot 10^{-3}$	[63]

Table 1
Continued

	Compound	Solvent	pH	T, °C	I, eV	k, (M^{-1}·s^{-1})	Refs.
		Thiols					
152	Propanethiol	$(C_2H_5)_2O$		25		0.8	[63]
		$CH_3OOC_2H_5$		25		0.1	[63]
		$(CH_3)_2CO$		25		3.8	[63]
		CH_3CN		25		52.7	[63]
153	2-Methylpropanethiol	CCl_4		40		0.2	[63]
154	Hexanethiol	CCl_4		40		0.1	[63]
155	Decanethiol	CCl_4		40		$4.1 \cdot 10^{-2}$	[63]
156	Hexadecanethiol	CCl_4		40		$7.4 \cdot 10^{-2}$	[63]
157	Cyclohexanethiol	CCl_4		40		$7.3 \cdot 10^{-2}$	[63]
158	Benzenethiol	CCl_4		40		4.18	[63]
159	2-Methylbenzenethiol	CCl_4		40		3.07	[63]
160	Benzenemethanthiol	CCl_4		40		$1.5 \cdot 10^{-2}$	[63]
161	2-Mercaptoethanol	CCl_4		40		0.32	[63]
				25		0.14	[63]
		$C_4H_8O_2$		25		0.11	[63]
		C_6H_6		25		0.83	[63]
		$(C_2H_5)_2O$		25		2.8	[63]
		$CH_3COOC_2H_5$		25		0.11	[63]
		$(CH_3)_2CO$		25		5.5	[63]
		CH_3CN		25		11.4	[63]

Hydrocarbons

Saturated hydrocarbons

Data about reactions of chlorine dioxide with saturated hydrocarbons are rather contradictory. According to [5], chlorine dioxide is unreactive with alkanes and cycloalkanes. However, in the patent literature it was reported that acid products formed after prolonged (for 2 days, 50-100°C) treatment of oil hydrocarbons (> C$_7$) with ClO$_2$ [64]. Cyclohexane was reported to react with chlorine dioxide bubbled through it at 50-55°C in a quantity of 3 moles of ClO$_2$ per 0.15 mole of reactant C$_6$H$_{12}$; adipic acid and chlorocyclohexane were identified among reaction products [65][#]:
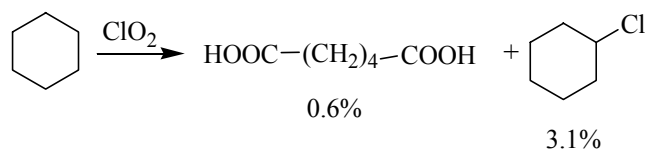
#(Here and below molar ratios are given; yields are given in mole percent relative to the initial quantity of the organic compound, unless stated otherwise.)

Chlorocyclohexane is also oxidized into adipic acid [66]. The reactivity of chlorine dioxide with saturated hydrocarbons seems to be low, and occasional observation of oxidative transformations is probably explained by reactions of radicals formed by thermolysis or photolysis of chlorine dioxide or by reactions with impurities. Indeed, according to [36], the presence of a molecular chlorine impurity leads to a fast reaction between chlorine dioxide and compounds unreactive with pure ClO_2.

Olefins

Early investigations carried out in the 1960-70s aimed at establishing the products of oxidation of various compounds containing a C=C double bond with chlorine dioxide. Reactions of ClO_2 with cyclohexene [67,68], methyloleate [69], and stilbenes [70] were investigated. Oxidation of pure cyclohexene with chlorine dioxide taken in insufficient amount forms a rather complex mixture of products:

| $C_6H_{10}/ClO_2=35/1$ | 16% | 11% | 11% | 13% | 5% | 3% | 3% |
| $C_6H_{10}/ClO_2=7/1$ | 13% | 15% | 7% | 14% | 7% | 4% | 0% |
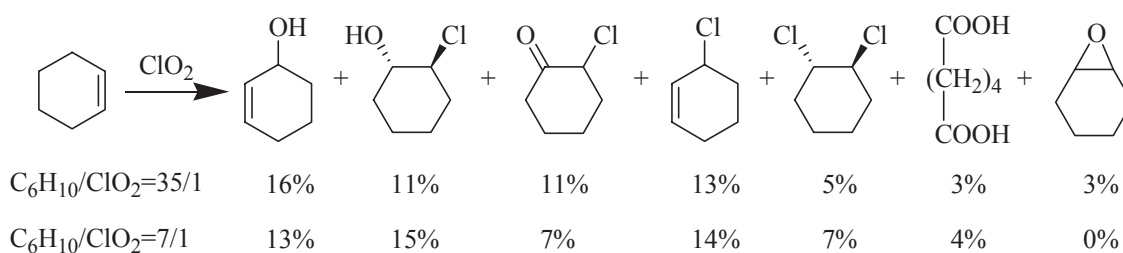
Oxidation with large quantities of chlorine dioxide ($C_6H_{10}/ClO_2 = 1.5/1$) in aqueous suspension led to glutaric and succinic acids in addition to the above-stated products. In acid media (pH < 2), glutaric acid is the major product.

Oxidation of unsaturated fatty acids and their ethers with aqueous chlorine dioxide occurs similarly, except that ketones form as major products instead of alcohols [2,69], as demonstrated for methyloleate used as an example [69]:
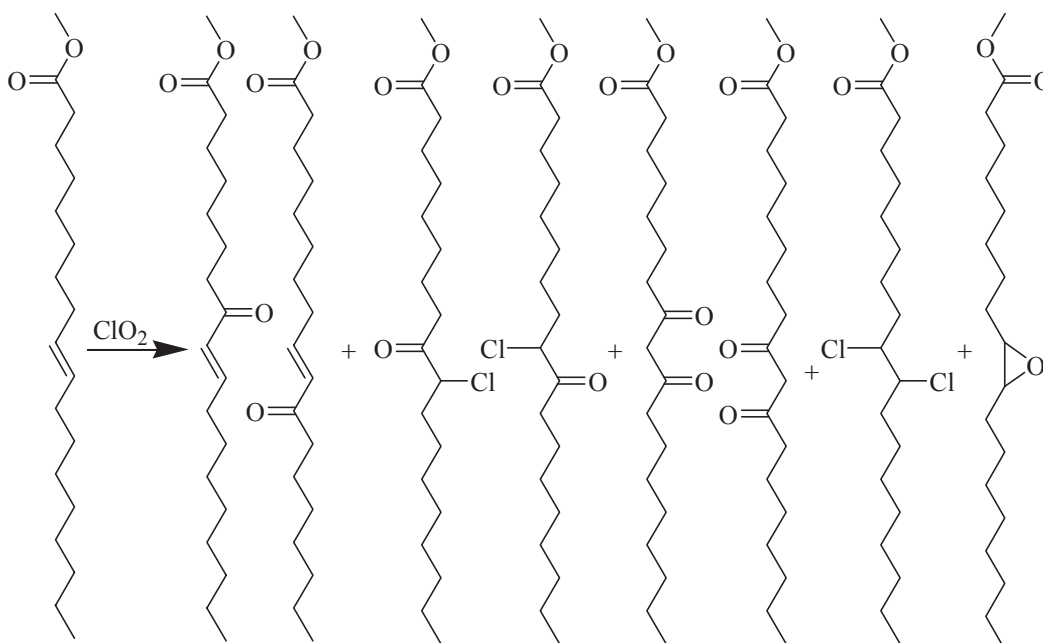
The compositions and yields of the oxidation products of stilbene and their derivatives are strongly dependent on the structure of the starting compound

and on the reaction medium [70]. Oxidation of *trans*-stilbene was investigated using carbon tetrachloride and water as reaction media (stilbene/ClO_2 = 1/2):

43%   36%   7%

44%   15%   12%
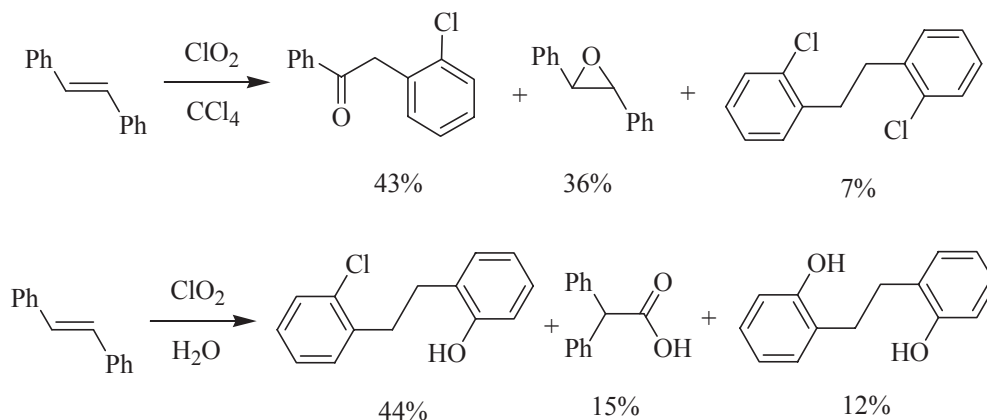
It is believed [70] that the first stage is addition of chlorine dioxide at a double bond. When the reaction is performed in water, an epoxy derivative is probably formed, but it quickly decomposes. The introduction of oxygen-containing substituents in the phenyl ring changes the products drastically: only acids and aldehydes were identified with low yields (stilbene/ClO$_2$ = 1/1.3):

10%   <1%

<1%   <1%
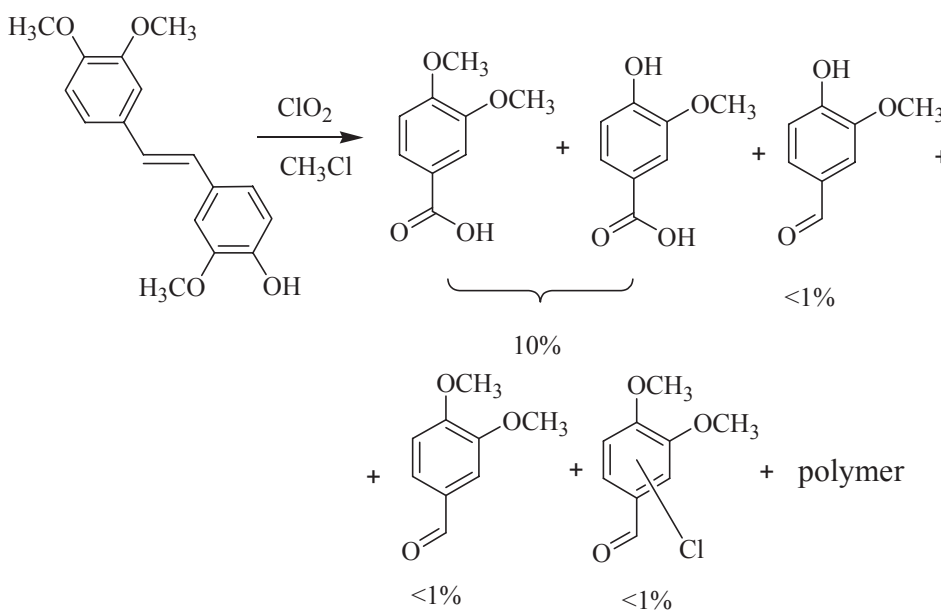
A dark polymer formed in addition to the products of oxidative cleavage of the C=C bond. As the changed reagents are present in nearly equal proportion, it is unlikely that ClO$_2$ initiates vinyl radical polymerization. It is more likely that polymerization is associated with the oxidation of the phenol –OH group. Oxidation of stilbenols in organic and aqueous media also leads to a complex mixture of products formed by attack at the alcohol group or by attack at the C=C double bond (stilbenol/ClO$_2$ = 1/1.3):

25%   19%   11%   5%
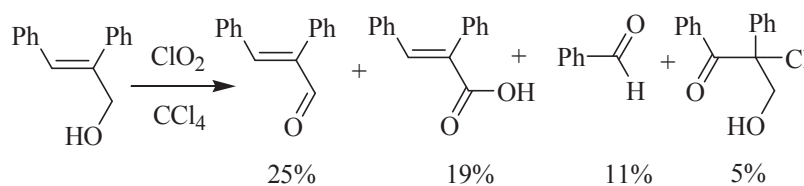
Introduction of methoxy groups in the phenyl rings accelerates the reaction and changes the products: oxidation preferably occurs with cleavage of the C=C double bond (stilbenol/ClO$_2$ = 1/1):

42%   24%   25%

20%
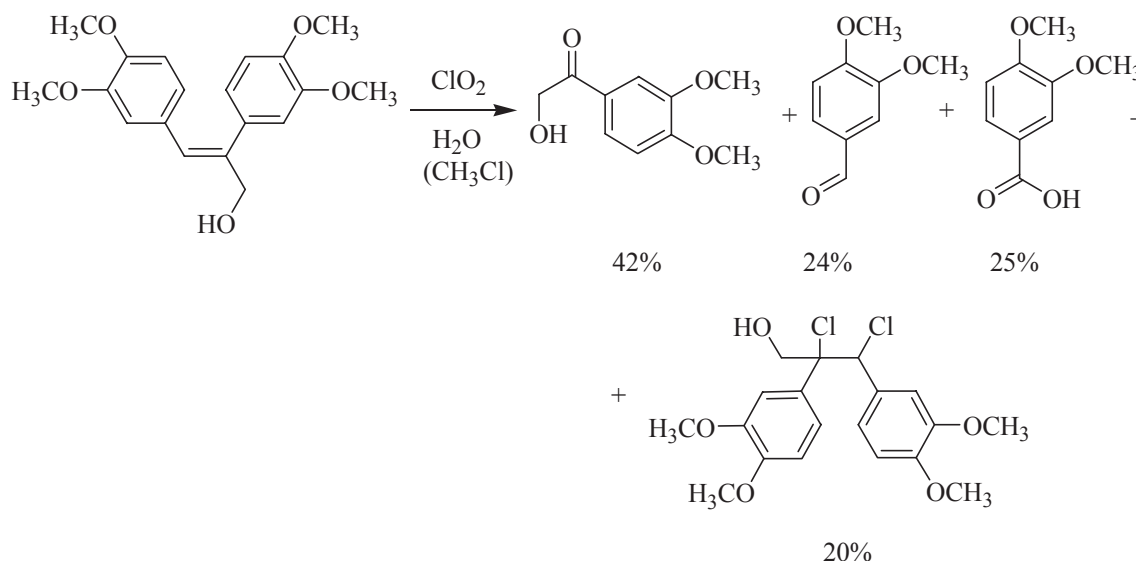
In the stated publications [67-70], emphasis was laid on isolating the products of oxidation of olefins with chlorine dioxide, while the reaction kinetics and intermediates were not investigated. An *a priori* mechanism implies the primary attack of chlorine dioxide at the allyl position with homolytic elimination of the α-hydrogen atom [67]:
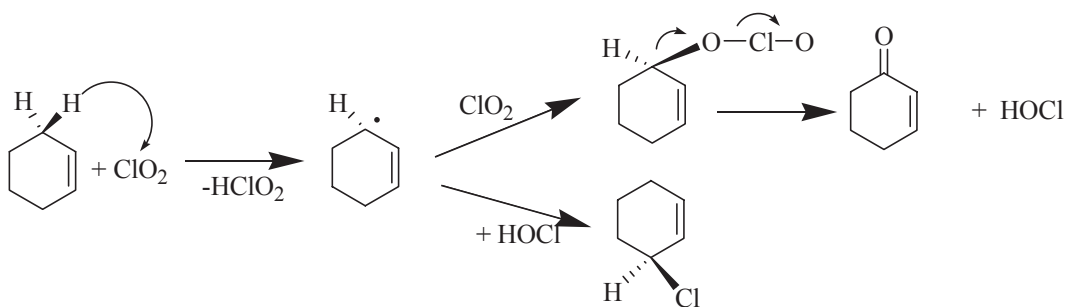
A number of works investigating the reaction kinetics and the products of oxidation of olefins with chlorine dioxide in aqueous media were performed in the 1980s [34,36,71]. Studies were carried out for indene, several *para*-substituted styrenes, and allylbenzene. The reaction with indene is one of the fastest reactions, and it was studied most meticulously. For olefins in general, it was found that the reaction kinetics obeys the first-order kinetic law for both reagents:

$$w = k_2[> C=C <][ClO_2]$$

The reaction stoichiometry depends on pH: at pH ≥ 7, one olefin molecule reacts with two ClO$_2$ molecules, while at pH ≤ 4, the reagents react in equimolar ratio. In the former case, the reaction with ClO$_2$ is also a first-order reaction; *i.e.*, the limiting stage involves only one chlorine dioxide molecule. Major reaction products are the corresponding diols and chlorohydrins. The general scheme for the reactions of chlorine dioxide with olefins at pH ≤ 4 is as follows:
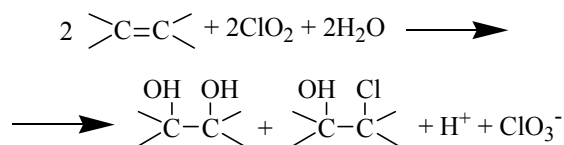
The reaction rate decreases with increasing pH and decreasing dielectric constant of the solvent, which agrees with the formation of charged species at the limiting stage. Substitution of deuterowater for water does not alter the reaction rate.

The mechanism of allyl hydrogen elimination by chlorine dioxide conflicts with the absence of the isotope effect due to the replacement of indene by [1,1,3-D$_3$]indene:
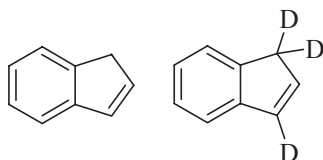
It is also inconsistent with the fact that ClO$_2$ reacts with olefins containing no allyl or benzyl hydrogen atoms (*e.g.*, styrenes). For the reaction of chlorine dioxide with *para*-substituted styrenes, the rate constant increases with the electrophilic constants of the substituent σ$^+$:

$$\log k' = -0.70 - 1.43\ \sigma^+$$

The reaction rate increases oppositely to the ionization potentials of olefins:

8.0 eV   8.2 eV   8.4 eV

8.7 eV   9.2 eV
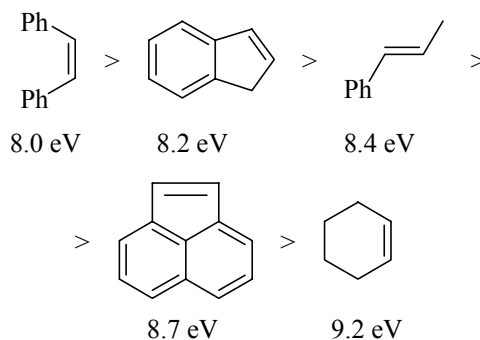
Based on the data obtained, the authors of [34,36, 71] suggested a mechanism that involves an electron transfer from the olefin to chlorine dioxide as a primary act, forming the corresponding radical cation:

$$\mathord{>}C{=}C\mathord{<}\ +\ ClO_2\ \longrightarrow\ \overset{+}{>}\!C\!-\!\dot{C}\!\mathord{<}\ +\ ClO_2^-$$
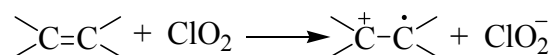
The products of indene oxidation are explained within the framework of the following scheme [36]:
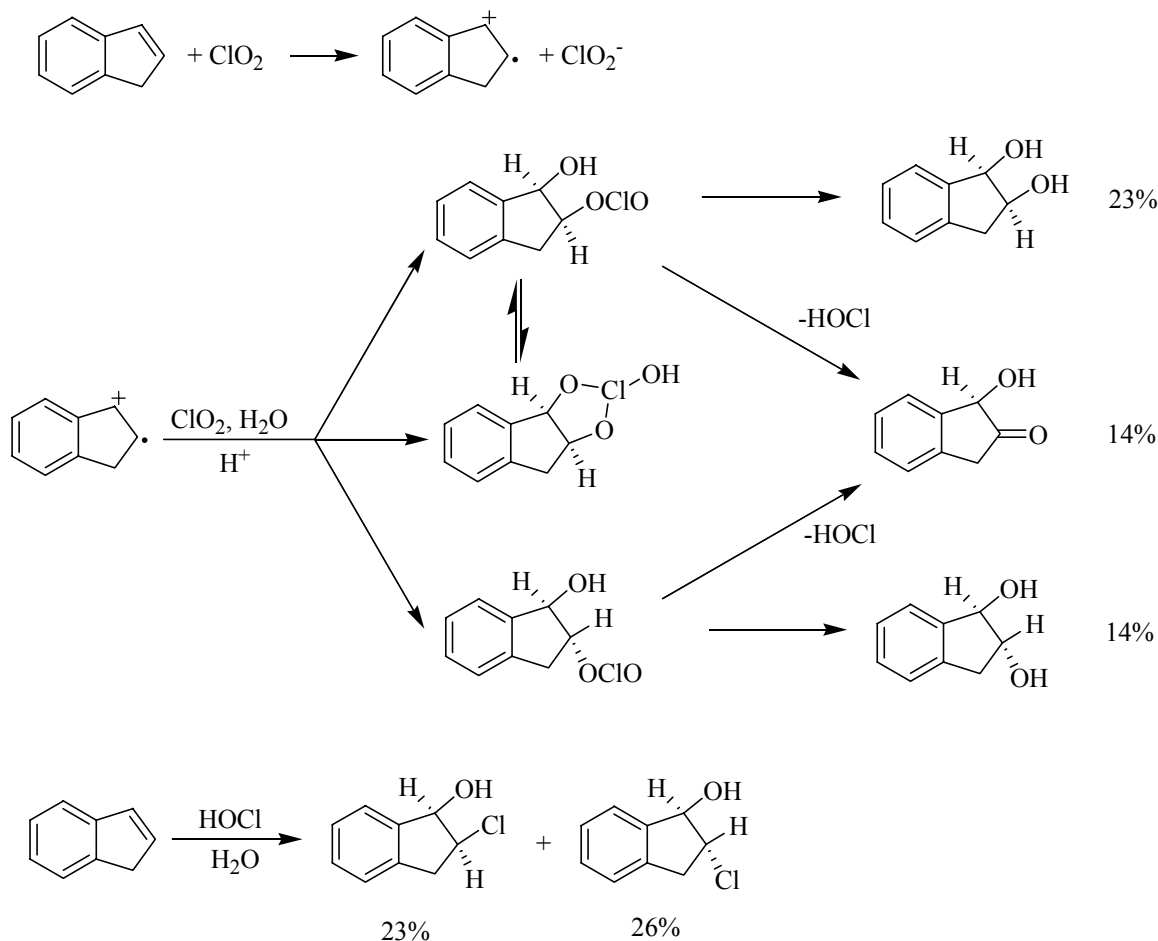
Chlorine-containing products are formed by the addition of hypochlorous acid at the C=C double bond. The major source of HOCl is believed to be disproportionation of chlorite ions in acid media:

$$2ClO_2^- + H^+ \Rightarrow HOCl + ClO_3^-$$
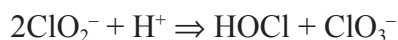
Thus sound evidence has been obtained to prove that the first stage of olefin reactions with chlorine dioxide is an electron transfer. Formation and decomposition of chlorous acid ethers ROClO were often postulated to be the next stages of this reaction, but reliable proof of this has not been obtained. Regrettably, today we have no experimental data on liquid-phase reactions of chlorine dioxide with alkyl radicals or on alkyl chlorites as possible intermediates of these reactions. For the gas phase, it was shown [1] that the reaction of chlorine dioxide with the methyl radical leads to the methoxyl and ClO radicals.

G2(MP2) and B3LYP/6-311++(3df,3p) quantum-chemical calculations [72] indicated that recombination of an alkyl radical (e.g., CH₃˙) with ClO₂ leads to methyl chlorite CH_3OClO, the latter being ~20-25 kcal·mole⁻¹ more favorable than chlorylmethane CH_3ClO_2. Decomposition of methyl chlorite into formaldehyde and hypochlorous acid is energetically favorable; the cyclic transition state of this reaction has a low activation enthalpy (6 kcal·mol⁻¹) and negative activation entropy (-2.5 cal·mol⁻¹·K⁻¹). The methyl chlorite molecule that formed in the gas phase possesses enough energy to dissociate into CH_3O and ClO, but it cannot dissipate the energy into the medium and decomposes according to the radical mechanism, which is preferable from the entropy viewpoint in agreement with experiment [1]. Thus the important role of alkyl ethers of chlorous acid in reactions of ClO_2 with hydrocarbons is confirmed by theoretical calculations.
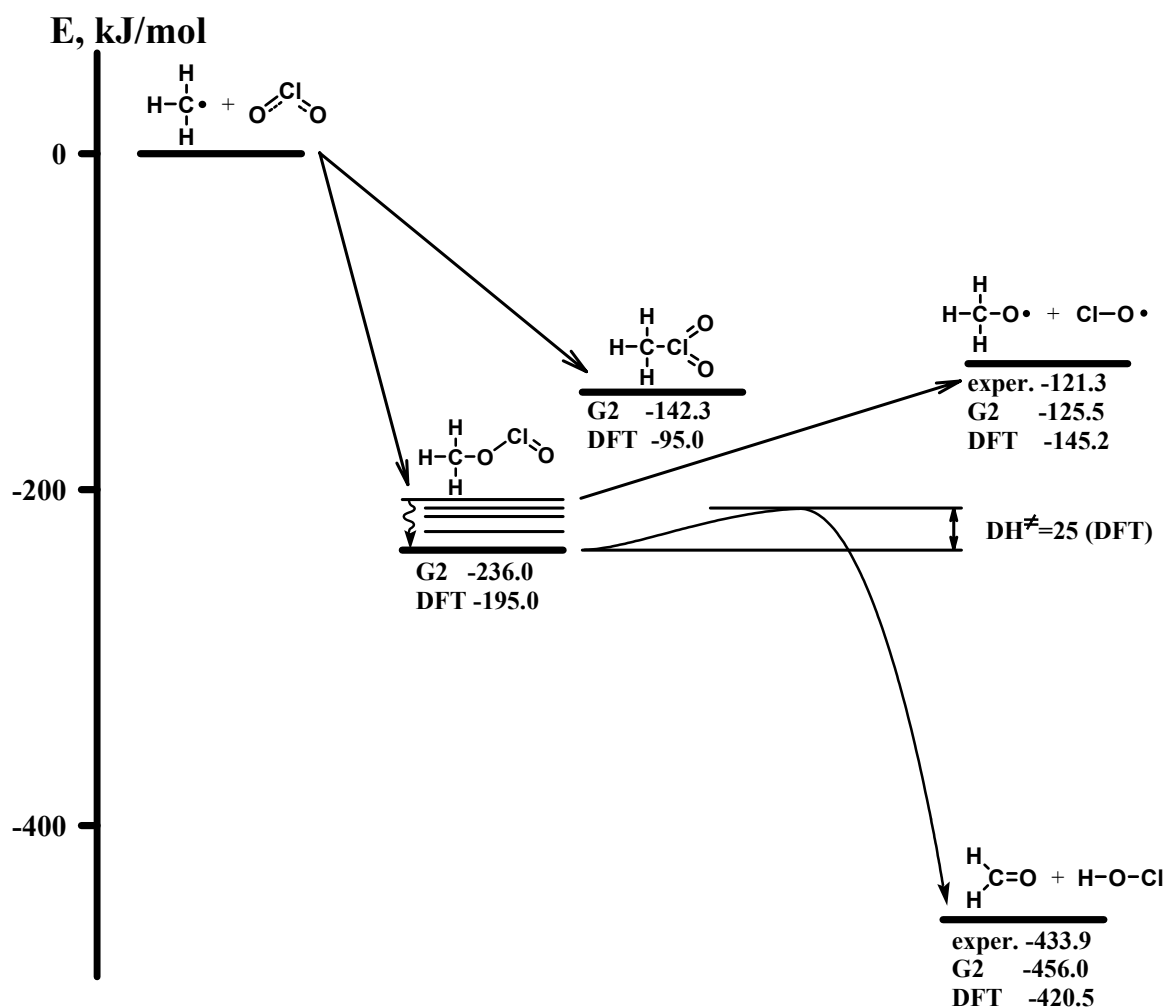
Fig. 2. Energetically diagram of the pathways of the reaction chlorine dioxide with methyl radical at 25 K. (Enthalpy data given both from literature and calculated by G2(MP2) – G2 and B3LYP/6-311++(3df,3p) – DFT methods [67]).

Aromatic hydrocarbons

Reactions of ClO_2 with aromatic and especially polycyclic aromatic hydrocarbons (PAH) were investigated in view of chlorine dioxide applications to drinking water treatment and sewage disposal where the PAH disposal problem is especially acute. It was shown that benzene is unreactive with chlorine dioxide in dilute aqueous solutions (pH = 7) [36] or in pure form [2]. The simplest alkyl-substituted benzenes such as toluene, ethylbenzene, xylenes, and diphenylmethane are not oxidized with chlorine dioxide under "drinking water purification" conditions (pH = 7, [ArH] = $3 \cdot 10^{-8}$ M, [ClO_2] = $3 \cdot 10^{-5}$ M) or in the absence of molecular chlorine vapors [36]. It was reported [65] that pure toluene is oxidized with a minor excess of ClO_2 to form mainly chlorinated products (50-55°C).

6.6%   0.4%

2.6%   0.6%   0.5%
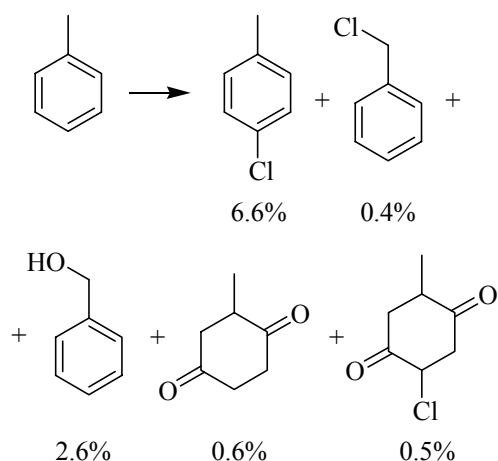
In dilute aqueous solutions (pH = 7), ClO_2 fails to oxidize naphthalene, fluorine, fluoranthene, and phenanthrene. On the other hand, benz(*a*)pyrene, anthracene, benz(*a*)anthracene, pyrene, and benz(*e*)-

pyrene are readily oxidized by chlorine dioxide under the same conditions [4,73].

Oxidation of polycyclic aromatic hydrocarbons mainly forms quinoid products, but scarcely any chloro derivatives. Thus anthraquinone [4,73,74], as well as monohydroxyanthracene [73], were found among the products of anthracene oxidation:
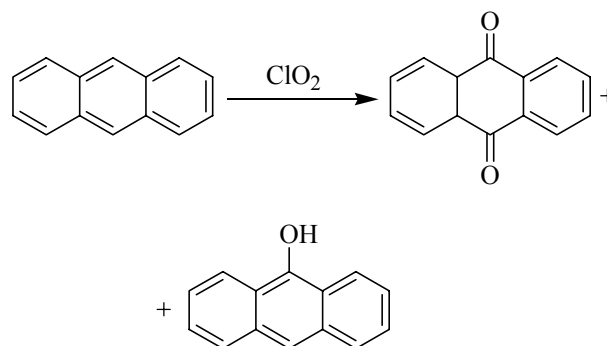
Phenanthrene was reported to react with chlorine dioxide at reasonably high concentrations in carbon tetrachloride, forming diphenic acid and 10,10-dichloro-9-phenanthrone [75].

In reactions with polycyclic aromatic hydrocarbons, the reaction kinetics obeys the first-order kinetic law for both reagents [4,73]; the rate constants correlate with the half-wave oxidation potentials of PAHs and with the energies of their highest occupied molecular orbitals [4].

The one-electron mechanism suggested [4] for oxidation of aromatic hydrocarbons with chlorine dioxide was experimentally confirmed by Handoo and co-workers [76]. Oxidation with chlorine dioxide in a mixture of dichloromethane and trifluoroacetic acid (TFAA) yielded a number of radical cations of several PAHs and other compounds with low ionization potentials:

$$ ArH + ClO_2 \xrightarrow{\text{CH}_3\text{COOH - CH}_2\text{Cl}_2} ArH^{+\bullet} + ClO_2^{-} $$
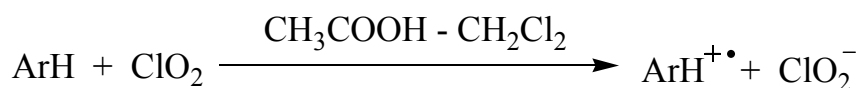
ArH:
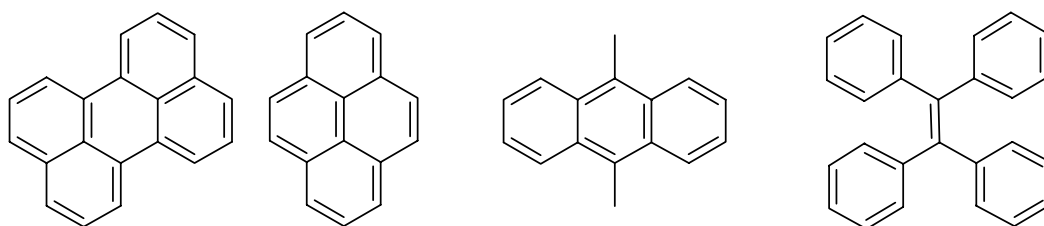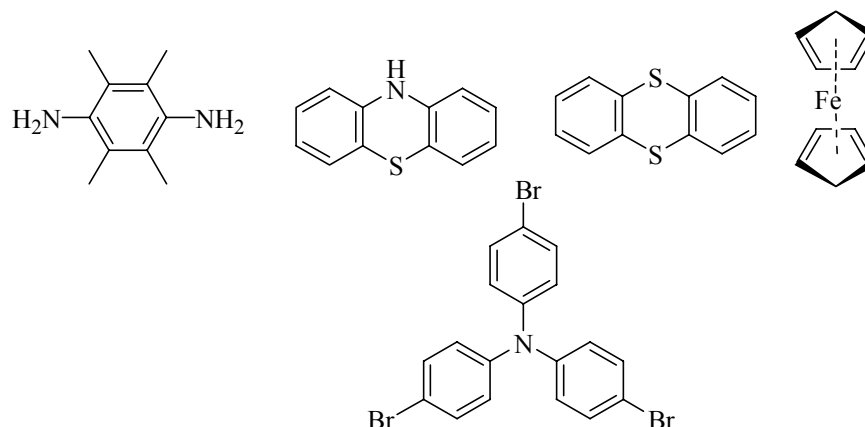
The radical cations formed are stabilized in the presence of TFAA, which makes possible their experimental observation by means of EPR and electron spectroscopy.

Interaction of fullerene C_{60} with chlorine dioxide was investigated in [77]. The brown precipitate formed in this reaction exhibits paramagnetic properties. The EPR spectrum of the precipitate is an asymmetric singlet ($g = 2.0029$, $\Delta H_{pp} = 0.2$ mT) assigned to the fullerenyl radical cation. Precipitation is accompanied by chemiluminescence in the visible and IR regions of the spectrum. The reaction is characterized by high stoichiometry: chlorine dioxide completely reacts with C_{60} until the molar ratio $[ClO_2]_0$: $[C_{60}]_0 = 60:1$ has been achieved.

In NMR and electron spectroscopy studies, it was found [78] that chlorine dioxide forms complexes with a number of aromatic compounds. The equilibrium constants and thermodynamic parameters of complexations have been determined. The ionization potentials of arenes were correlated with the equilibrium constants. The complexes formed were assumed to be charge transfer complexes.

Oxygen-containing compounds

Alcohols

The available data on reactions of chlorine dioxide with alcohols are very scarce. It was reported that ethanol and 1,3-butanediol react with an excess of chlorine dioxide in rather stringent conditions (pH = 1, 70 , 80°C), forming a mixture of aldehydes and carboxylic acids [2-4]. Glucose [4] (pH = 2) is oxidized at the $-CH_2OH$ group, which is transformed into aldehyde or carboxyl group without ring cleavage.

The kinetics of ClO_2 reactions with alcohols in aqueous media was investigated in [38,39,79]. Most detailed studies were performed on oxidation of methanol [38] and 2-propanol [39]; it was found that this is a first-order reaction for both alcohol and ClO_2. The rate constants were determined from the initial rates and increase with the ionic strength of the solution. The effects of inorganic salts were investigated, and it was found that the reaction is accelerated by chlorides, nitrates, and potassium bromide, but retarded by sodium hydrophosphate. When water is replaced by D_2O, an isotope effect is observed: $kH_2O/ kD_2O = 1.59$ for CH_3OH and 1.78 for $(CH_3)_2CHOH$; this is probably associated with an isotope exchange between deuterowater and the $-OH$ group of the alcohol. The rate constant depends on pH in a complex manner. In the range pH = 3.0-5.9, the rate constant decreases, but increases dramatically in the range pH = 6.3-6.7; this was attributed [38,39,79] to the reaction of the RO^- anion with chlorine dioxide. Further, the reaction rate again decreases [39]. The activation energy of oxidation of monohydric alcohols decreases in the series [79] (E_A, kJ/mol):

$$H_3C-OH > \wedge OH > \wedge\wedge OH >$$

$$64.4 \qquad 61.10 \qquad 56.1$$

$$> \wedge\wedge\wedge OH > \text{(2-methyl-1-propanol, OH)} >$$

$$51.9 \qquad 46.2$$

$$> \text{(tert-butanol, OH)} \approx \text{(2-butanol, OH)}$$

$$44.8 \qquad 43.9$$
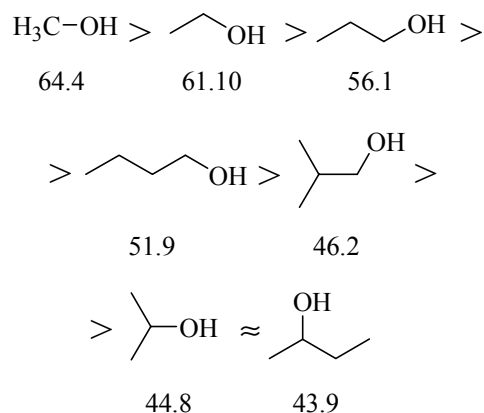
The reaction mechanism, postulating a transfer of the hydride ion at the first stage, is discussed in [38,39]:
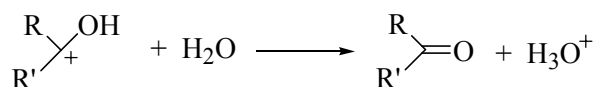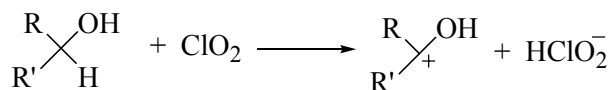
The products are the corresponding ketones and chloroketones [38,39].

Kuchin *et al.* [80] recently suggested using chlorine dioxide for preparative oxidation of allyl alcohols, in particular, terpene alcohols:
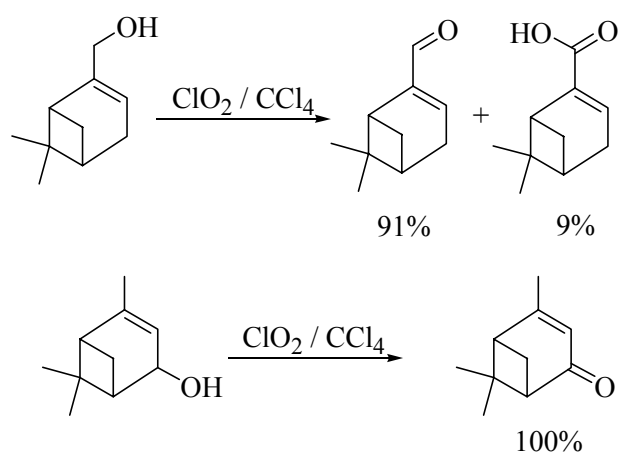
It was shown [81] that 3,4-dimethoxyacetophenone is the primary product of the reaction of ClO_2 with 1-(3,4-dimethoxyphenyl)ethanol at pH = 8. When pH = 4, acetophenone is not formed, and the products are chlorinated compounds and ring oxidation products. The primary isotope effect $k_{(H)}/k_{(D)} = 2.05$ at pH = 8, but it is absent when pH = 4. According to the suggested mechanism, at high values of pH ClO_2 reacts with benzyl alcohols via the ClO_2-benzyl alcohol complex.

The kinetics of oxidation of propan-2-ol, 2-methylpropan-1-ol, butan-1-ol, butan-2-ol, 3-methylpentan-1-ol, heptan-4-ol, decan-2-ol, cyclohexanol, and borneol with chlorine dioxide in heptane, tetrachloromethane, benzene, 1,4-dioxane, chlorobenzene, ethyl acetate, 1,2-dichloroethane, and acetonitrile was investigated spectrophotometrically [40]. For all indicated alcohols, the reaction rate is described by the second-order equation $w = k[ROH] \cdot [ClO_2]$. Rate constants have been measured (10÷60°C), and activation parameters of the oxidation reaction have been determined (Table 2).

The oxidation products have been identified, and their yields have been determined. The alcohol reacts completely when the ratio of alcohol to chlorine dioxide is 1:2 mol/mol. Oxidation of the primary alcohol butan-1-ol leads to the corresponding aldehyde. Oxidation of the primary alcohols 2-methylpropan-1-ol and 3-methylpropan-1-ol gives carbonyl compounds along with chlorinated alcohols – 2-methyl-2-chloropropan-1-ol and 3-methyl-3-chloropentan-1-ol, and chlorinated aldehydes – 2-methyl-2-chloroproanal and 3-methyl-3-chloropentanal. Secondary alcohols are oxidized into ketones.

The following reaction scheme is suggested:

Table 2
Activation parameters of the oxidation of alcohols with chlorine dioxide at T = 30ºC

Alcohol	log A	E_a	$\Delta H^{\neq}$	$\Delta G^{\neq}$	$S^{\neq}$,
		kJ·mol⁻¹			J·mol⁻¹·K⁻¹
Propan-2-ol	5.0	53.4	50.9	98.6	-157.2
2-Methylpropan-1-ol	6.2	60.7	58.2	99.0	-134.7
Butan-1-ol	3.0	43.5	41.0	98.5	-189.8
Butan-2-ol	2.2	35.0	32.5	96.5	-211.2
3-Methylpentan-1-ol	3.1	42.1	39.6	98.5	-194.5
Heptan-4-ol	8.4	73.0	70.5	98.9	-93.7
Heptan-4-ol	3.7	43.7	41.2	96.6	-183.0
Cyclohexanol	7.2	62.6	60.1	95.0	-115.5
Borneol	4.2	42.5	40.0	92.7	-173.9
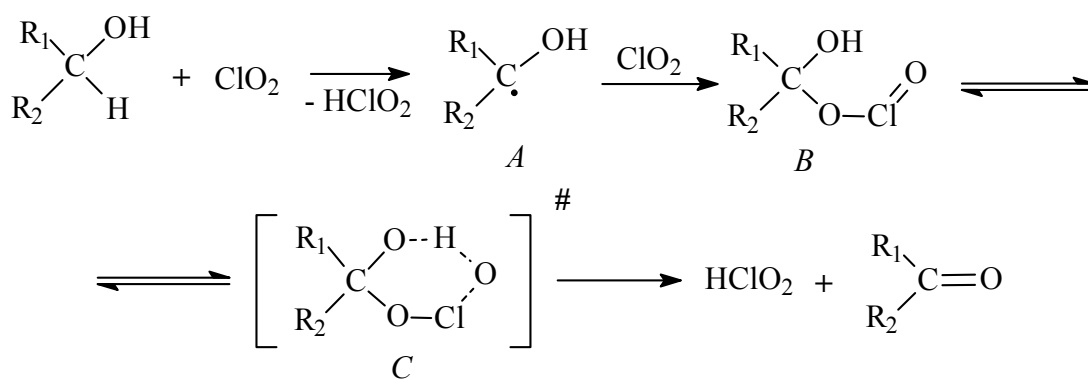
1,3-Dioxacycloalkanes

Oxidation of various 1,3-dioxacycloalkanes with chlorine dioxide forms the corresponding glycol monoethers [82, 62]. Oxidation of asymmetric 1,3-dioxacycloalkanes leads to a 2:1 mixture of two isomeric ethers. Reactions of chlorine dioxide with cyclic acetals containing a phenyl substituent in the second position lead to benzaldehyde and benzoic acid. The oxidation reaction may be promoted by adding silica gel or a stable nitroxide (2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-3-oxide-1-oxyl) to the system [62]. It has been found that solvent polarity is inessential to the rate of oxidation of 1,3-dioxacycloalkanes by chlorine dioxide. 1,3-Dioxanes are more stable with chlorine dioxide than 1,3-dioxolanes. Reaction rate constants have been calculated, and activation parameters have been determined for the processes. According to the mechanism proposed for the reaction, chlorine dioxide attacks the C–H bond adjacent to the oxygen atom, forming an alkyl radical. Further oxidation of the resulting radical with chlorine dioxide forms the reaction products:
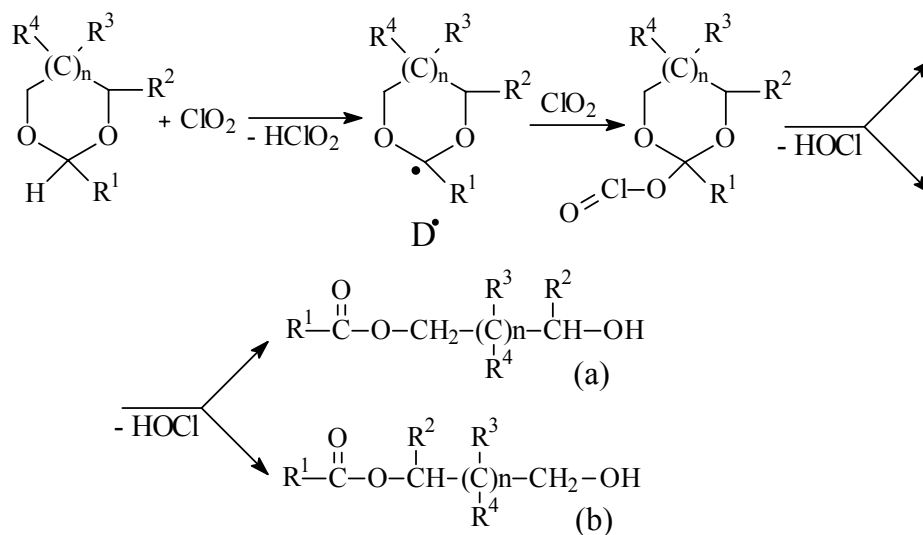
Accumulation of a mixture of isomeric ethers (a) and (b) during the oxidation of asymmetric cyclic acetals occurs due to the concurrent cleavage of the $C^2–O^3$ and $C^2–O^1$ bonds in the ring of alkylchlorite [62].

The formation of benzaldehyde and benzoic acid during the oxidation of cyclic acetals with a phenyl substituent in the second position is explained by the attack of ClO_2 at the C^4 atom. Curiously, the oxidation of 2-isopropyl-1,3-dioxolane with chlorine dioxide in $CHCl_3$ and CCl_4 forms 2-hydroxyethyl isobutyrate and 2-chloroethyl isobutyrate in a 1:1 mol/mol ratio [82]. When the reaction is carried out in methylene chloride, the chloro derivative is formed in small amounts if at all, the major product being 2 hydroxyethyl isobutyrate:
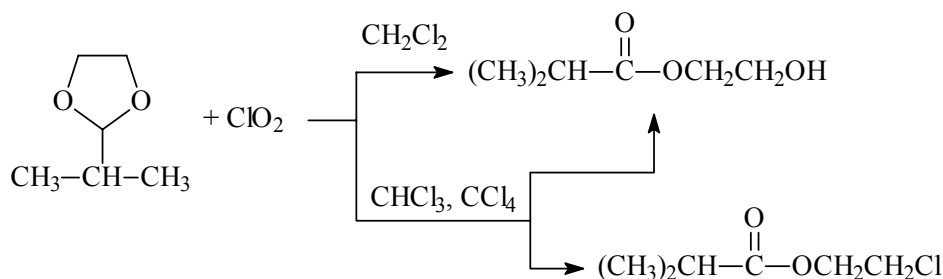
This is explained by the fact that the dioxolanyl radical is a strong nucleophile capable of reacting with both chlorine dioxide (with elimination of the oxygen atom) and solvent, leading to 2-hydroxyethyl isobutyrate and 2-chloroethyl isobutyrate, respectively. In CH_2Cl_2, the stability of the C–Cl bond is the highest ($D(H_2ClC–Cl) = 81$ kcal/mol [83]), and the dioxolanyl radicals preferably react with chlorine dioxide, ultimately giving 2-hydroxyethyl isobutyrate. In $CHCl_3$ and CCl_4, where the number of C–Cl bonds is larger and their stability is lower ($D(HCl_2C–Cl) = 77$ kcal/mol, $D(Cl_3C–Cl) = 73$ kcal/mol [83]), an additional competing reaction with the solvent leads to 2-chloroethyl isobutyrate.

Aldehydes and carboxylic acids

Benzaldehyde dispersed in water [84] reacts with chlorine dioxide with explosion. Other aldehydes and ketones such as acetaldehyde, *n*-butyrylaldehyde, and diacetyl are oxidized to the corresponding carboxy-lic acids in neutral aqueous solutions [85].

At the same time, it was reported [86] that ClO_2 is unreactive with hexanal and 2-methylbutanal at any pH and temperature. Carboxylic acids are mainly unreactive with ClO_2 unless they contain readily oxidizable functional groups [2,4].

Phenols

Along with oxidation of amines, oxidation of phenols in aqueous media is the best-studied section of organic chemistry of chlorine dioxide in view of the applications of ClO_2 to water purification [2,4,5, 87].

The major products of phenol oxidation with chlorine dioxide are *para*-benzoquinone and various chlorine-substituted *para*-benzoquinones [88,89]. Chlorophenols are oxidized to the corresponding quinones. With a large excess of ClO_2, quinone is oxidized with ring cleavage, forming dicarboxylic acids. The oxidation of phenols and chlorophenols may be represented by the following scheme [90]:
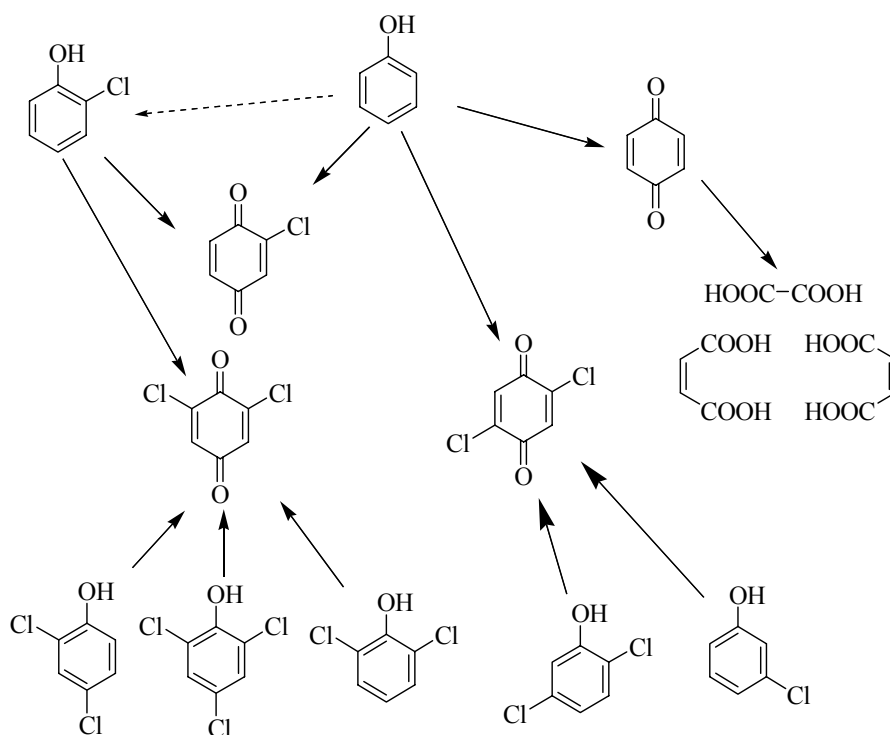
Chlorophenols were reported [4] to be the products of phenol oxidation in a lack of ClO_2.

Oxidation of hydroquinone does not lead to any chlorinated products [89]:
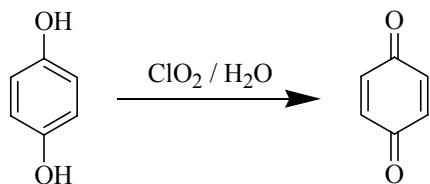
Detailed studies were performed on the oxidation products of more complex phenols: 2,6-dimethylphenol (2,6-xylenol) and 2,4,6-trimethylphenol (mesitol) [91]. The reaction of chlorine dioxide with 2,6-xylenol in a mixture of water and *tert*-butanol at pH = 5 yields quinone, epoxide, and a chloro derivative:
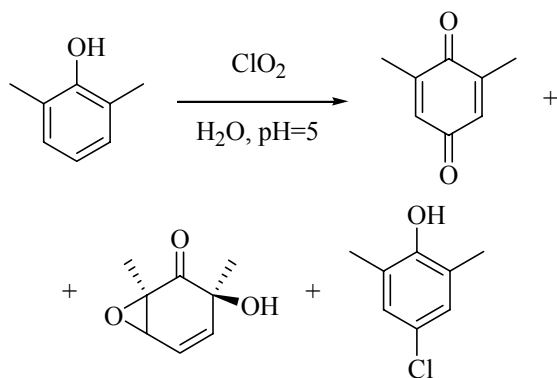
Oxidation of 2,6-xylenol in CCl_4 has also been studied. Under these conditions, the reaction is very slow and forms a tricyclic compound, which is a dimer of 6-chloro-2,6-dimethylcyclohexa-2,4-dien-1-one:
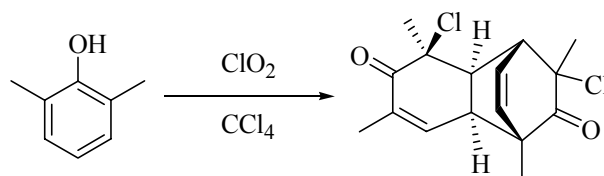
Mesitol is oxidized to epoxides and quinoid compounds:
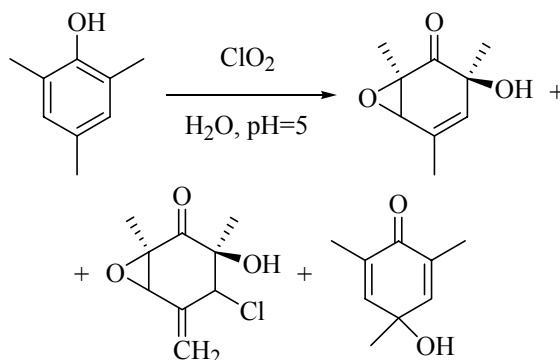
According to [88,89], for monoatomic phenols containing no *para*-substituents, as well as for hydroquinone, oxidation with chlorine dioxide does not destroy the ring and forms predominantly quinones and chloroquinones. Monoatomic phenols with *para*-substituents, as well as di- and triatomic phenols with hydroxyl groups in the *ortho*- or *meta*-positions are oxidized with ring cleavage, forming dicarboxylic acids.

It was reported [3] that 4-nitrophenol is oxidized to oxalic and fumaric acids, while 2,4-dinitrophenol and 2,4,6-trinitrophenol do not react with ClO_2. 4-Hydroxybenzaldehyde is quickly oxidized to 1,4-benzoquinone at pH ≤ 6 [3]. The reaction of ClO_2 with vanillin [3] leads to ring cleavage:
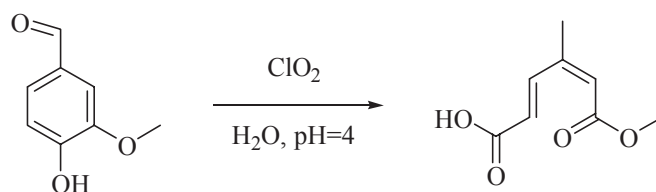
Vanillin alcohol is oxidized into two products:
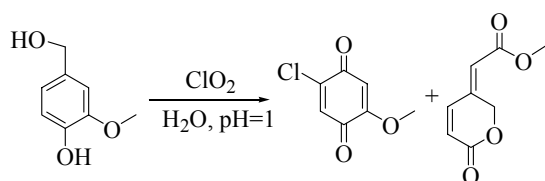
The first detailed investigation of the reaction kinetics of chlorine dioxide with phenols is reported in [92]. The reaction rate was found to increase with pH; it changes according to the equation:

$$w = \left\{ k_1 + \frac{k_2}{[H^+]} \right\} [ClO_2][PhOH]$$

When the ionic strength is unity (25°C, pH = 2), the constants k_1 and k_2 are $4.7 \cdot 10^{-1}$ $M^{-1} \cdot s^{-1}$ and $1.1 \cdot 10^{-3}$ $M^{-1} \cdot s^{-1}$, respectively (k_1 and k_2 are the rate constants of the reactions of chlorine dioxide with phenol and phenoxy anion, respectively). The observed kinetic tendencies suggest that concurrent reactions take place between chlorine dioxide and the undissociated and the dissociated forms of phenol [92]. The first stage of the reaction was assumed to be one-electron oxidation. This idea was further developed in [74]. In neutral and alkaline solutions, the reaction is governed by simpler kinetic law:

$$w = k[ClO_2][PhOH]$$

At 25°C and pH = 7, the rate constant k is in the range $(2-4) \cdot 10^4$ $M^{-1} \cdot s^{-1}$. The following mechanism of phenol oxidation with chlorine dioxide is proposed:
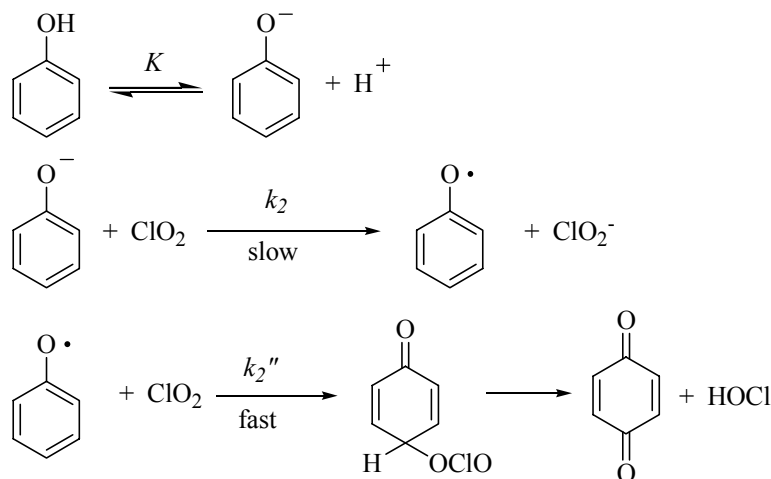
As in the case of the reactions of ClO_2 with olefins, formation of unstable intermediate ether ROClO is postulated; the latter quickly decomposes into hypochlorous acid HOCl, whose reactions subsequently form chlorinated products.

In further studies, absolute rate constants were determined for the reaction of chlorine dioxide with phenoxy anions and undissociated phenols (for the latter, the rate constants are millions of times lower than for the former), and the effect of the structure of phenol on its oxidation rate was investigated [33, 44,46,48,93]. In the most detailed study [33,87], it was found that the rate constants of the oxidation of the phenoxide ions with chlorine dioxide depend on the sum of the σ^- constants of the *ortho-*, *meta-*, and *para-*substituents (k, $M^{-1} \cdot s^{-1}$):

$$\lg k = (8.2 \pm 0.2) - (3.2 \pm 0.4) \sum \sigma^-_{o,m,p}$$

The one-electron mechanism of the oxidation is supported by the parabolic dependence of rate constant on the free energy in the course of the reaction, which is adequately described by Marcus' equation of electron transfer reaction theory [93]. Thus for the primary act of the reaction, the one-electron mechanism of oxidation may be considered to be reliably proven. Subsequent stages of this process, however, need further investigation.

The kinetics of oxidation of phenol, 3-methylphenol, 4-methylphenol, 4-*tert*-butylphenol, 2-cyclohexylphenol, 2,6-di-*tert*-butyl-4-methylphenol, and 2,4-dichlorophenol with chlorine dioxide in acetonitrile was investigated in [47,50]. Oxidation of phenol with chlorine dioxide was also studied using 2-methylpropanol, ethanol, 1,4-dioxane, acetone, ethyl acetate, dichloromethane, heptane, and tetrachloromethane as solvents. As medium polarity increases, the rate constant of phenol oxidation decreases. For the phenols under study, the rate of oxidation is described by a second-order equation $w = k[PhOH] \cdot [ClO_2]$. Rate constants have been measured (10-60°C), and the activation parameters of the oxidation reaction have been determined in the stated temperature range (Table 3).

The oxidation products have been identified, and the product yields have been determined. Full conversion of phenols was found to take place when the molar ratio of phenol to chlorine dioxide is 1:2, respectively. A relationship has been found between the reaction rate constant and the structure of the phenol. The reaction rate decreases with the increasing half-wave potential.

Table 3
Activation parameters of phenol oxidation with chlorine dioxide, T = 25°C

Phenol	Ln A	E_a	$\Delta H^{\neq}$	$\Delta G^{\neq}$	$S^{\neq}$, J·mol^{-1}·K^{-1}
		kJ·mol^{-1}			
Phenol	13	42	40	83	-145
3-Methylphenol	15	46	44	82	-129
4-Methylphenol	11	30	28	76	-160
4-Tert-butylphenol	15	46	43	81	-129
2-Cyclohexylphenol	14	44	42	82	-134
2,4-Dichlorophenol	16	53	51	86	-120

According to the scheme suggested for the reaction, the first (limiting) stage is an electron transfer from the phenol molecule to the chlorine dioxide molecule, forming the phenoxyl radical:
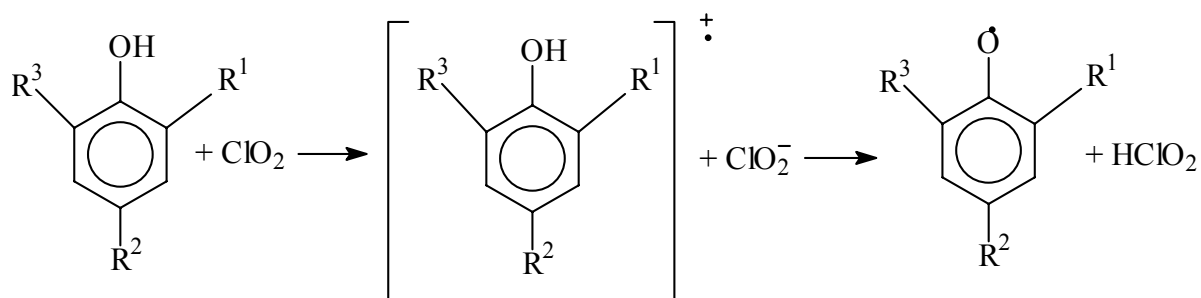
The phenoxyl radical is further oxidized by another chlorine dioxide molecule to quinone:
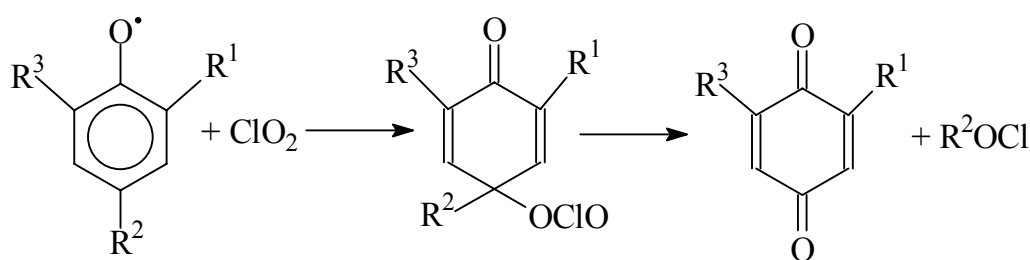
If R^2 = H, the resulting phenoxyl radicals can dimerize:
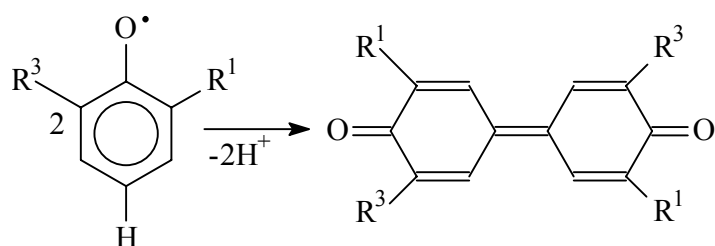
When R^2 = alkyl, quinols can form presumably according to the following scheme:
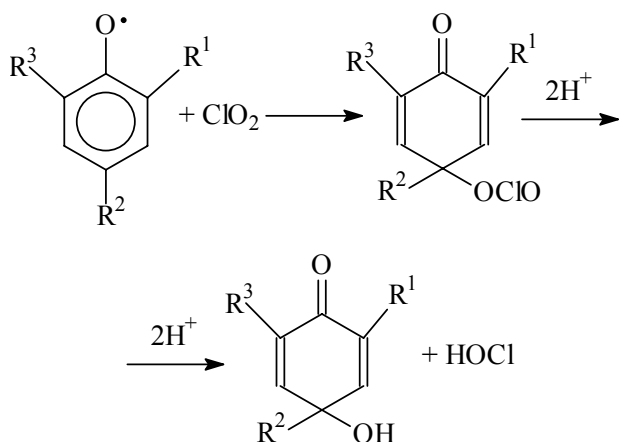
The formation of chloro derivatives in the oxidations of phenols with chlorine dioxide may be explained by chlorination of organic compounds by hypochlorous acid:
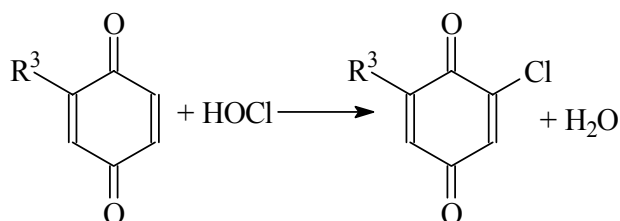

Sulfur-Containing Compounds

Selective oxidation of sulfides to sulfoxides and sulfones is one of challenges in organic chemistry. Sequential chemoselective oxidation of dialkyl sulfides to dialkyl sulfoxides and dialkyl sulfones and oxidation of dialkyl sulfoxides to dialkyl sulfones are treated in [94,95]. Oxidation was performed with gaseous ClO_2 or its aqueous solution. Conversion of the sulfide was 95-100%; yield 90-95% (sulfoxides) and 2-3% (sulfones) when the sulfide: chlorine dioxide ratio was 2:1. When the reagents were taken in an equimolar ratio, sulfones was the major reaction product:
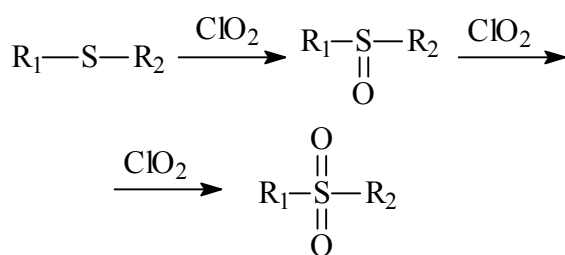
Liquid-phase oxidation of hydrogen sulfide, dibenzyl and dihexyl sulfides, and dipropyl and diisopropyl disulfides with chlorine dioxide in tetrachloromethane and toluene at 20°C led to the formation of paramagnetic species found by the spin probe method using MNP [96]. The mechanism of oxidation involves the initial generation of RS_nR^{+} radical cations and ClO_2^{-} ions and further intracellular transformation of these species, giving the $ClO^{.}$ radical:
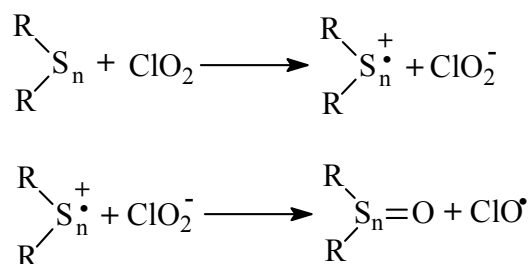

In the case of thiols, the major products of liquid-phase oxidation are the corresponding disulfides RSSR; these are oxidized into thiolsulfinates RS(O)SR and thiolsulfonates $RS(O_2)SR$ found as minor products of these reactions [63].

$$R = C_2H_5, C_3H_7, HOCH_2CH_2$$

The rate constants and activation parameters of this reaction have been measured. The structure of thiol was found to affect the reaction kinetics. The constant k changes slightly when the hydrocarbon radical is lengthened, but replacement of the alkyl radical by an aromatic one (phenyl, 2 methylphenyl) increases the rate constant by an order of magnitude or more. From the Taft equation $\lg k = \lg k_0 + \rho^* \sigma^*$ it was found that $\rho^* = 1.41 \pm 0.29$, $\lg k_0 = 0.71 \pm 0.12$, $r = 0.94$. The positive sign of the coefficient ρ^* indicates that electron-accepting substituents accelerate the reaction. It was found that the solvent affects the rate of thiol reactions with chlorine dioxide, obeying Laidler-Eyring and Coppell-Palm equations. The following mechanism was suggested for the oxidation:

$$HClO_2^{+\cdot} + ClO_2^- \longrightarrow HClO_2 + ClO_2$$

$$RS^\cdot + RS^\cdot \longrightarrow RSSR$$
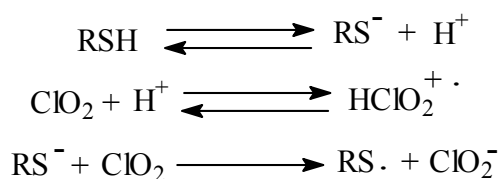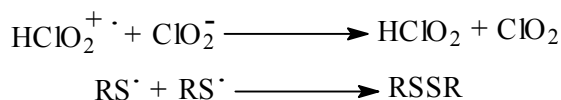
The oxidation of concentrates of saturated gamma-ketosulfides was investigated in [97]. A mixture of gamma-ketosulfoxides, sulfones, and sulfochlorides is formed. The ratio of these products depends on the composition of the starting gamma-ketosulfides.

Nitrogen-Containing Compounds

Amines

For aliphatic (primarily, tertiary and secondary) amines, the products of oxidation in aqueous solutions, as well as the reaction kinetics and intermediates, were examined in a series of works [52,53,55,59, 98-101]. Based on the data obtained, a mechanistic model has been suggested for the process. In this model [53], chlorine dioxide reacts with tertiary amines according to the one-electron oxidation mechanism at the first (reversible) stage of the reaction:
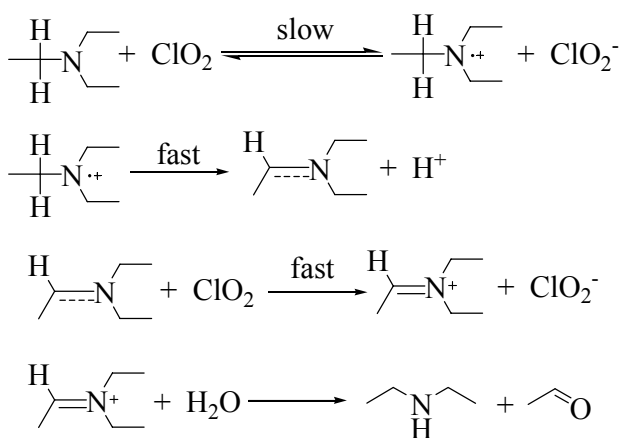
In the case of primary and secondary amines, having a benzyl hydrogen atom, the first (irreversible) stage is elimination of the hydrogen atom by chlorine dioxide:
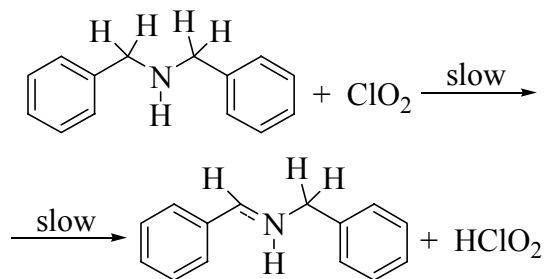

The radical formed at this stage reacts further with another chlorine dioxide molecule according to the scheme shown above. For any amine, both one-electron oxidation and hydrogen elimination generally take place [53], the efficiency of the process depending on the structure of the amine. Thus in the case of hydrogen elimination, the degree of oxidation is 25% for benzyl-tert-amine and 73% for benzylamine [53].

The model proposed for the reaction is supported by the following experimental facts.

- The reaction obeys the first-order kinetic law for both reagents, two ClO_2 molecules reacting per amine molecule [58]. Tertiary amines react with chlorine dioxide very quickly; secondary and especially primary amines react much more slowly, and ammonia does not react with ClO_2 at all [52].
- For tertiary and secondary amines, the oxidation rate decreases as the concentration of the ClO_2^- ion increases; in the case of secondary amines, there is another rate component, which is independent of the concentration of ClO_2^- ions. The first component relates to the reversible reaction, forming ClO_2^- [53].
- For benzyldimethylamines with substituents in the aromatic ring, the rate constant of oxidation depends linearly on the σ constants of substituents according to the Hammett equation [53]. The reaction rate was correlated to the electrochemical oxidative potentials of amines [99].
- The oxidation of benzyldimethylamines is nonselective and leads to the products of elimination of both benzyl and methyl groups [52].
- Replacement of α hydrogen atoms by deuterium in tertiary amines leads to a weak (probably, secondary) isotope effect ($k_H/k_D = 1.3$); for secondary amines, the isotope effect is much more significant, $k_H/k_D \geq 5.0$ [53].
- Oxidation of triethylenediamine led to the corresponding radical cation [49,100].

Thus oxidation of amines with chlorine dioxide leads to successive elimination of alkyl groups, forming aldehydes. In the case of amines with an $-NR_2$, $-OH$, or oxo group in the β-position, bond cleavage takes place between the α and β carbon atoms. Thus the reaction of triethylenediamine with chlorine dioxide yields piperazine [98]:
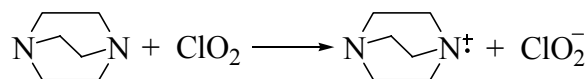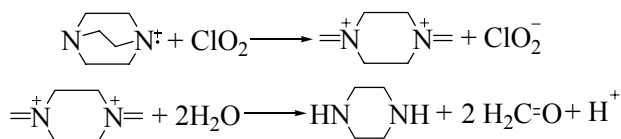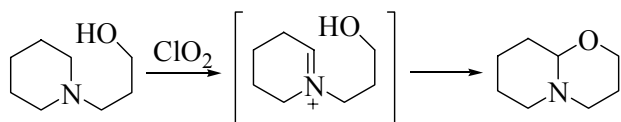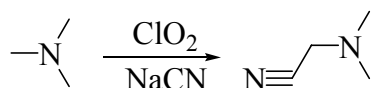
N-Methylpiperidine forms piperidine; the latter, in turn, is slowly oxidized to 2,3,4,5-tetrahydropyridine, which is further trimerized [3]:
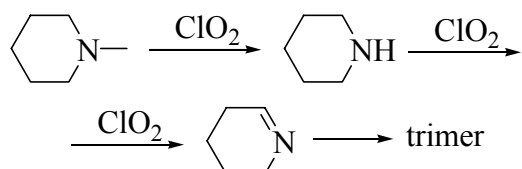
One of the synthetic applications of chlorine dioxide is preparation of bicyclic aminoethers [102]:


Reactions of tertiary amines in the presence of NaCN afford α cyano-substituted tertiary amines [102]:

Nitroxides

When ClO$_2$ reacted with hindered secondary amines from piperidine and imidazoline series in organic solvents and on silica gel surface, the reaction mixtures contained nitroxides [72,103]. The low yields of nitroxides are due to their secondary reactions with chlorine dioxide, leading to oxoammonium salts via the stage of formation of ClO$_2$ complexes with nitroxides. Complexes of chlorine dioxide with piperidine and imidazoline stable nitroxides, as well as complexes with nitroxides having aromatic substituents, were identified by spectrophotometry (from the appearance of a new band in the spectrum) (Fig. 3):

R= -H(**1**), -OH(**2**), =O(**3**),
   -OCH$_3$(**4**), -NHC(O)CH$_3$(**5**)   (**6**)

(**7**)
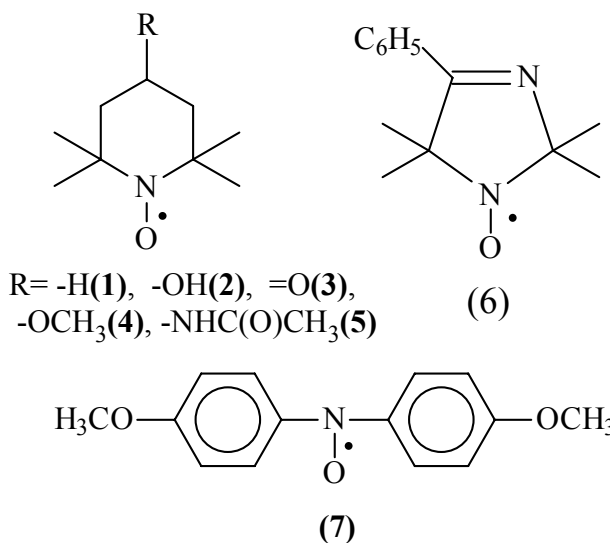
The maxima of the absorption bands of the complexes are at 460-490 nm for radicals (**1**) - (**5**), at 438 nm for radical (**6**), and at 590 nm for (**7**). In polar solvents, λ$_{max}$ is shifted to the long-wave region (bathochromic shift), as typically observed for charge transfer complexes (Table 4).

Table 4

Characteristics of chlorine dioxide complexes with nitroxides of varying structure (T = 20°C, measurement error up to 15%, E$_T^N$ is the medium polarity parameter [104])

Radical	Solvent	E$_T^N$	λ$_{max}$, nm	K, M^{-1}	$\Delta H°$, kJ·mol^{-1}	$\Delta S°$, J·mol^{-1}·K^{-1}	$\Delta G°$, kJ·mol^{-1}
1	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
	Sulfuric 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	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

Table 4

Continued

| Radical	Solvent	E_T^N	λ_{max}, nm	K, M^{-1}	$\Delta H°$, kJ·mol^{-1}	$\Delta S°$, J·mol^{-1}·K^{-1}	$\Delta G°$, kJ·mol^{-1}
2	Tetrachloromethane	0.052	474.1	23.9	-33.1	-57.1	-16.4
	Dichloromethane	0.309	485.4	5.6	-42.8	-130.3	-4.6
	Toluene	0.099	473.2	12.7	-44.8	-126.1	-7.8
	Sulfuric ether	0.117	476.6	13.5	-24.6	-61.0	-6.7
3	Acetone	0.355	467.3	6.8	-30.4	-88.0	-4.6
	Acetonitrile	0.460	481.5	1.4	-23.7	-78.2	-0.8
	Sulfuric 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	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	-42.8	-131.2	-4.4
	Dichloromethane	0.309	480.8	4.6	-36.4	-107.6	-4.9
	Toluene	0.099	474.1	3.2	-45.0	-141.2	-3.6
	Sulfuric ether	0.117	470.6	7.7	-54.8	-164.8	-6.5
	Heptane	0.012	465.3	6.2	-34.5	-107.7	-2.9
5	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	Heptane	0.012	438.4	0.8	-29.7	-103.3	0.6
7	Dichloromethane	0.309	568.2	693	–	–	–
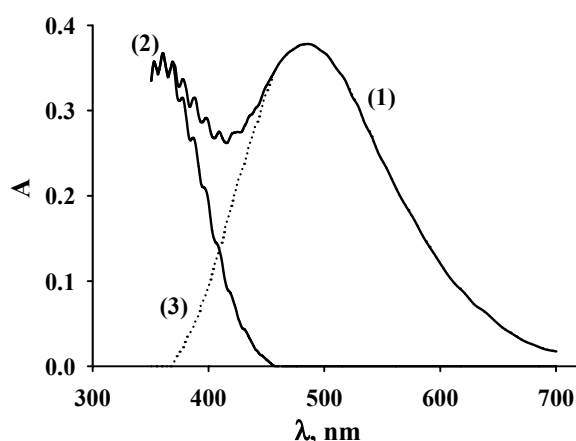
Fig. 3. Electronic absorption spectrum of complex 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) with chlorine dioxide (diethyl ether, 20°C): (1) mixture [TEMPO] = 3·10^{-2} M and [ClO$_2$]=1.4·10^{-3} M, compensation solution [TEMPO] = 3·10^{-2} M, (2) solution [ClO$_2$]=1.4·10^{-3} M, (3) spectrum of complex, obtained by subtracting spectrum (2) from spectrum (1).

The spectral data for the complexes and the thermodynamic parameters of complexation were found to depend on medium polarity and on the structure of the starting nitroxide.

The nature of chemical binding in ClO$_2$ complexes with model nitroxides (H$_2$NO, dimethyl and *tert*-butylnitroxide) was investigated by the NBO method in terms of density functional theory (B3LYP/cc pVTZ) [68]. The main donor-acceptor interactions are electron density transfer from the lone electron pair of the $>$ N–O$^.$ oxygen to the antibonding orbital of chlorine dioxide n(O) $\rightarrow$ σ*(Cl–O) and the reverse charge transfer from the lone electron pair of the ClO$_2$ oxygen to the antibonding σ*(C–H) orbital. Further stabilizing effect is provided by the n(Cl) $\rightarrow$ σ*(N–O) interaction. The geometry of the ClO$_2$ complex of TEMPO, obtained using a simpler basis set, B3LYP/3-21G*, is shown in Fig. 4.
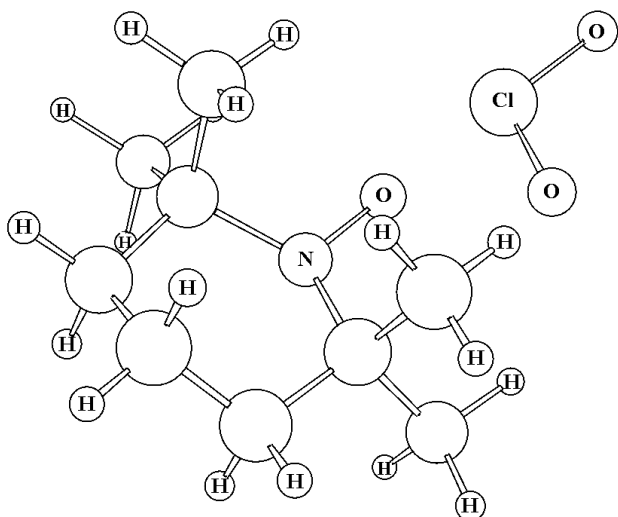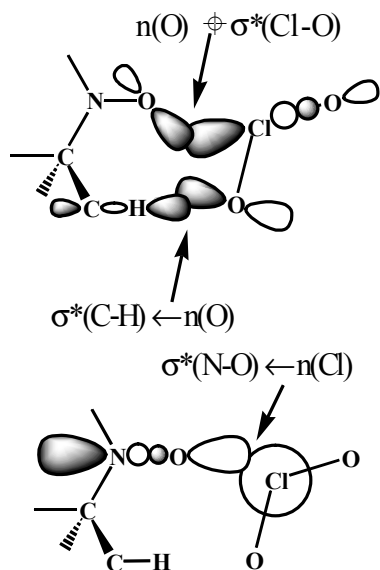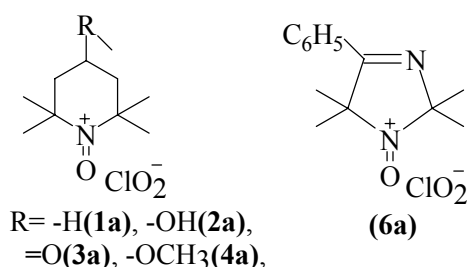
Fig. 4. Structure of complex chlorine dioxide with radical (**1**), calculated by B3LYP/3-21G* method.

Donor-acceptor interactions in the piperidine nitroxide complex of ClO$_2$ may be schematically represented as follows:

The nitroxide complex of ClO$_2$ subsequently undergoes transformation into the corresponding oxoammonium salt [103]:

R= -H(**1a**), -OH(**2a**),
=O(**3a**), -OCH$_3$(**4a**),

(**6a**)

The stability of the complex depends on the temperature and solvent, as well as on the nature and concentration of the nitroxide. The reaction is accelerated when the complex is irradiated with light corresponding to the maximum of the absorption band.

Note that oxoammonium salts are intermediates in catalytic oxidative systems involving nitroxides [105]. Therefore, studies of nitroxide complexation with chlorine dioxide bring new insights into the mechanism of this process.

Conclusions

Thus from our literature analysis it is clear that chlorine dioxide may be used for oxidation of organic compounds from various classes. At the same time, wide application of chlorine dioxide as reagent in organic synthesis is restrained by the lack of data on the kinetics and mechanism of reactions involving chlorine dioxide, as well as data on the product yields and composition, temperature and solvent effects, and catalysts.

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