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Oxygen compounds of halogens X_2O_2 (X is a halogen atom)

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Abstract. The results of studies on the structure and properties of the O_2F_2, Cl_2O_2, Br_2O_2 and I_2O_2 molecules and the FOO, ClOO and BrOO radicals obtained mainly in the past decade are surveyed. The bibliography includes 173 references.

I. Introduction

Compounds of the general formula X_2O_2 pertain to the class of high-energy compounds. Representatives of this class are thermally unstable and are characterised by low binding energies. Some of them are the most potent inorganic oxidants.

In my book [1] published in 1986 and devoted to the oxygen compounds of halogens, compounds with the general formula X_2O_2 were represented by only dioxygen difluoride O_2F_2. Moreover, it was mentioned that this compound has no Cl-, Br- and I-analogues. Such a conclusion was drawn based on the fact that in the mid-80's, the works which admitted the existence of Cl_2O_2 were few, and virtually none dealt with Br_2O_2 and I_2O_2. However, in recent studies on atmospheric chemistry it was reported that halogen oxides X_2O_2 (and halogen atoms, particularly, those of chlorine and bromine) are involved in depletion of stratospheric ozone. This fact has attracted the attention of researchers to these compounds, and new information appeared on this class of compounds, which allowed the X_2O_2 oxides to be characterised in more detail. Thus, this review supplements the book.[1]

It should be noted that, as for other halogen – oxygen compounds, the distinctions between the structures and properties of X_2O_2 oxides override their similarities.

II. Dioxygen difluoride and related compounds

1. Dioxygen difluoride

Dioxygen difluoride exists only at low temperatures (m.p. = 119 K, b.p. = 216 K). It was obtained for the first time in 1933 by Ruff and Menzel [2] upon action of an electric discharge on a fluorine – oxygen mixture. The most probable mechanism of O_2F_2 formation is as follows:

$$F + O_2 \longrightarrow O_2F,$$

$$F + O_2F \longrightarrow O_2F_2.$$

Inasmuch as the synthesis of O_2F_2 was described in detail in the book,[1] this issue will not be discussed here.

Jackson [3] established the structure of the O_2F_2 molecule in 1962 by using the method of microwave spectroscopy (MW). The dioxygen difluoride molecule was shown to represent spatially skewed chains of atoms F – O – O – F with C_2 symmetry. This structure was confirmed later by electron diffraction (ED).[4] Table 1 shows the bond lengths (r) and bond and torsion angles in the O_2F_2 molecule.

Being formally close to the hydrogen peroxide structure, the molecular structure of dioxygen difluoride, however, differs substantially in its details. For instance, the O – O bond length in the H_2O_2 molecule is 1.48 Å, which is close to that of a single bond, whereas the bond length in the O_2F_2 molecule suggests a double-bond nature, being similar to the bond length in the O_2 molecule and the O_2^+ cation (1.208 and 1.12 Å, respectively, according to the data from Ref. 7). Thus, the following resonance structure was proposed for the O_2F_2 molecule:

$$F^-O{=}O^+F \longleftrightarrow FO^+{=}OF^-.$$

Calculations of the structure of O_2F_2 molecules by the local density functional (LDF) [5] method provided good agreement with the experimental [5] data: the calculated O – O and O – F bond lengths differed from those found experimentally by no more than 0.01 and 0.015 Å, respectively (see Table 1). The geometrical parameters of the FOOF molecule calculated using the Becke – Perdew – Wang B3PW91 functional [6] fit less the experimental data, and the Hartree – Fock theory usually applied in calcula-

Table 1. Geometrical parameters of the O_2F_2 molecule.

Parameter	Experimental data		Quantum-chemical calculations	
	MW [3]	ED [4]	LDF [5]	B3PW91 [6]
r(O – O) /Å	1.217(3)	1.216	1.215 [a]	1.222
r(O – F) /Å	1.575(3)	1.586	1.562 [a]	1.523
F – O – O /deg.	109.5	109.2	110.5 [a]	109.2
FOO/OOF /deg.	87.5	88.1	88.4 [a]	88.1
Rotation barriers /kcal mol^{-1}	30		36 – 42	

[a] A mean value is given (averaged from nine values calculated using different Gaussians).

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tions of geometrical parameters of molecules gave unsatisfactory results for dioxygen difluoride (see Ref. 5).

According to calculations,[5] the internal rotation barrier in the O_2F_2 molecule is $\sim 36-42$ kcal mol^{-1}, which exceeds substantially the value of 30 kcal mol^{-1} suggested by Jackson [3], the value of 20.83 kcal mol^{-1} determined by the CNDO/2 method [1] and the energy of the O–F bond dissociation equal to 20 kcal mol^{-1} (see Ref. 8).

Vibrational spectra (IR and Raman) of dioxygen difluoride samples in both solid state and solution are described in the book,[1] and the IR spectrum of gaseous O_2F_2 was measured with an IR Fourier spectrometer in a multipass cell at 175 K (Ref. 9). The O_2F_2 molecule is characterised by six normal vibrational modes active in the IR spectrum, *viz.*, O–O stretching (ν_1), O–F stretching symmetrical (ν_2) and antisymmetrical (ν_5), O–O–F bending symmetrical (ν_3) and antisymmetrical (ν_6) and also torsion (ν_4) modes. The most intense absorption bands were obtained at 1210 (ν_1) and 615 cm^{-1} ($\nu_2 + \nu_5$ combination). The ν_1 frequency in the spectrum of gaseous O_2F_2 is 100 cm^{-1} lower as compared with the spectrum of matrix-isolated O_2F_2. The IR spectral band of gaseous O_2F_2 observed at 1490 cm^{-1} was attributed to O–O stretches of the O_2F radicals present in equilibrium with O_2F_2. It was noted [9] that the half-life of O_2F_2 at a temperature below 180 K exceeds 2 h.

An experimental value for the enthalpy of formation of dioxygen difluoride $\Delta H^\circ_{298}(O_2F_2) = 4.73\pm0.30$ kcal mol^{-1} first determined in 1959 [10] was never refined. It should be noted that this quantity was calculated by different methods (Table 2) in quite a number of studies (see, *e.g.*, Refs 6, 11–15). In 1996, Chase [11] tabulated the recommended thermodynamic constants for oxygen halides (NIST–JANAF) based on spectroscopic and thermodynamic data published up to 1994 inclusive, and the value of 4.6±0.2 kcal mol^{-1} was proposed for the enthalpy of formation of dioxygen difluoride. Later, this value was argued against by Kieninger *et al.*[6] who calculated the thermodynamic characteristics of oxygen fluorides by the density functional method. Using the B3PW91 functional, they have obtained good agreement between experimental and calculated enthalpies of formation of the OF, O_2F and OF_2 molecules (the largest deviation was observed for the OF molecule and amounted to ~ 0.6 kcal cm^{-1} at 0 K). However, the same calculation method gave overestimated values for the enthalpies of formation of O_2F_2, namely, 7.3 kcal mol^{-1} (at 298 K) and 9.0 kcal mol^{-1} (at 0 K).[6] The value for 298 K exceeded the recommended one [11] by 64%. At the same time, the high value of 9.0 kcal mol^{-1} did not differ dramatically from the values $\Delta H^\circ_0(O_2F_2) = 8.2$ kcal mol^{-1} estimated [14] by using the B3LYP functional and $\Delta H^\circ_0(O_2F_2) = 8.7\pm0.2$ kcal mol^{-1} calculated in Ref. 15. Although the difference in experimental and calculated enthalpies of formation of the FOOF molecules cannot be called a dramatic one, however, further studies should be performed in order to refine the experimental value for the enthalpy of formation of FOOF.

Table 2. The enthalpy of formation of the FOOF molecule calculated by different methods.

T/K	ΔH° /kcal mol^{-1}	Ref.
298.15	4.6 [a]	11
	4.5	12
	5.0	13
	7.3	6
0	9.0	6
	8.2	14
	8.7	15

[a] This value is included in the recommended NIST–JANAF Thermochemical Table.

Dioxygen difluoride is a strong oxidative-fluorinating agent, which reacts over a wide range of low temperatures.

Thus, fluorination of ClF_3 by O_2F_2 occurs at 195 K to give chlorine pentafluoride in a quantitative yield.[16] All the other methods of ClF_5 synthesis require much higher temperatures and pressures.[17] Xenon is fluorinated by an excess of O_2F_2 to give a mixture of XeF_2 and XeF_4 at 153–195 K, repeated treatment producing pure xenon tetrafluoride.[18] Fluorination of actinides by O_2F_2 can be carried out at ambient and lower temperatures.[19]

Due to low O–F binding energy, the dioxygen difluoride molecules and O_2F radicals behave as more efficient sources of the fluorine atoms as compared with molecular fluorine and rank below krypton difluoride only.[20]

Synthesis of dioxygenyl salts in the reaction of O_2F_2 with fluorine-containing Lewis acids is among the most important preparative reactions of dioxygen difluoride.[1] Here, dioxygen difluoride is a source of O_2F radicals, which react with Lewis acids to give salts, *e.g.*, $O_2^+AsF_6^-$.

$$O_2F_2 \longrightarrow O_2F + F,$$

$$O_2F + AsF_5 \longrightarrow O_2^+AsF_6^-.$$

The radicals O_2F can be obtained from this salt by thermolysis

$$O_2^+AsF_6^- \longrightarrow O_2F + AsF_5$$

and used, *e.g.*, for the preparation of electronically excited and vibrationally excited ClF, BrF and IF molecules in their ground electronic states, which are employed in various spectroscopic studies (see Ref. 17 and references cited therein).

2. The O_2F radicals

The O_2F radicals are formed upon a low-temperature impact (photolysis, radiolysis, *etc.*) on systems containing fluorine and oxygen. Following stabilisation in low-temperature matrices, they can be studied by various spectral techniques.

Recently, Bartlett and co-authors [20] reported the possibility of regenerating O_2F radicals from dioxygenyl salts at low temperature. Solvated O_2F radicals were formed from the salts ($O_2^+AsF_6^-$, $O_2^+SbF_6^-$) dissolved in anhydrous HF in the presence of an alkali-metal fluoride by the reaction

$$O_2^+ + F^- \longrightarrow O_2F.$$

A nonlinear O_2F radical represents a prolate asymmetrical rotor [21,22] with the rotational constants $A = 78.4301$, $B = 10.013935$ and $C = 8.855247$ GHz. The ground state of the O_2F radical is X^2A''; the energy of the $^2A'$ state exceeds that of the ground state by ~ 1.07 V (8630 cm^{-1}).[23] The asymmetrical OOF isomer is by 100 kcal mol^{-1} (according to Ref. 23) or 85 kcal mol^{-1} (according to Ref. 24) more stable than the symmetrical OFO isomer. In contrast to OOF, the OFO radical has never been observed experimentally.[23,25] In addition, as compared with the OFO^+ cation, the FOO^+ cation is more energetically favourable. The FOO^+ ion represents a charge-transfer complex $F(^2P)-O_2^+(^2\Pi_g)$ which dissociates readily to F and O_2^+ (see Ref. 26).

Internuclear distances r(O–O) and r(O–F) in the O_2F radical are 1.200 and 1.649 Å, repectively, and the F–O–O bond angle is 111.2°, which is somewhat larger [25] than in the FOOF molecule. An increase in the O–F bond length in the O_2F radical as compared with the O_2F_2 molecule agrees well with a decrease in the O–F bond strength when going from O_2F_2 to O_2F. The F–O_2F bond strength in dioxygen difluoride is ~ 19.6 kcal mol^{-1} at 0 K.[27] In the O_2F radical, the fluorine atom is less strongly bound to oxygen: the dissociation energy is 11.7±0.5 kcal mol^{-1} (0 K).[28] Virtually the same value 11.9±0.2 kcal mol^{-1} (0 K) was obtained in calculations [27] from the third law of thermodynamics when studying the thermodynamic properties of the F + O_2 reaction mixture.

Like peroxy radicals,[29] dioxygen monofluoride strongly absorbs in the UV range (200–300 nm). The absorption

maximum for the O_2F radical was shown [30] to lie at 206.5 nm (the absorption cross-section $\sigma = 1.35 \times 10^{-17}$ cm^2), at 215 or 220 nm.[27,28,31] At 298 K,[31] intense absorption of the O_2F radical was observed at 215 nm with the absorption cross-section $\sigma = 1.15 \times 10^{-17}$ cm^2 (for O_2F_2 molecules, $\sigma = 4.2 \times 10^{-18}$ cm^2).[31] At 300 K, the absorption maximum was observed at 220 nm, the absorption cross-section being equal to 1.3×10^{-17} cm^2 (Ref. 28) and 1.6×10^{-17} cm^2 (Ref. 27).

The IR spectrum of the O_2F radicals in the gas phase has been studied.[21,26,32,33] Using an IR Fourier spectrometer (resolution of 0.003 cm^{-1}) and a cell with an optical path of 100 m, the vibrational spectrum of the O_2F radical was obtained with the most intense absorption bands at 579.32 (ν_3), 940.22 ($\nu_2 + \nu_3$), 1142.46 ($2\nu_3$), 1486.93 (ν_1), 1495.60 ($\nu_2 + 2\nu_3$) and 2948.09 ($2\nu_1$).[21] All vibrational frequencies of gaseous O_2F appeared to be lower than those of matrix-isolated O_2F. The bending vibrational frequency ν_2 was in the range of 365–370 cm^{-1}. An attempt [9] to resolve the rotational structure of the O–O stretching band has failed; however, this structure was eventually resolved.[21] These results show that detachment of a fluorine atom from the O_2F_2 molecule results in a substantial increase in the O–O stretching mode frequency, the latter approaching a vibrational frequency of 1580 cm^{-1} for the O_2 molecule.

In spectrokinetic studies [28] of the equilibrium in the gas-phase reaction

$$F + O_2 \rightleftharpoons O_2F$$

in a temperature range of 295 to 359 K, the enthalpy of formation of the O_2F radical was found to be $\Delta H^\circ_{298}(O_2F) = 6.24 \pm 0.50$ kcal mol^{-1} (the radicals were generated by pulse irradiation of a gas mixture with electrons of 2 MeV energy). A kinetic study of the reaction of fluorine and oxygen atoms [31] gave a value of 5.49±0.40 kcal mol^{-1} (298 K). A later study [27] showed similar values for enthalpy (Table 3). Table 3 lists $\Delta H^\circ_0(O_2F)$ values calculated using B3LYP [14] and B3PW91 [6] functionals and the QCISD(T)/6-31G(*d,p*) method [34] (QCI is quadratic configuration interaction).

Generally, the O_2F radical behaves as a mere source of fluorine atoms rather than as a radical. Its relatively low reactivity is explained by the fact that abstraction of the F atom, which represents the active part of the radical, requires an activation energy of ~12.6 kcal mol^{-1} (Ref. 35). The O_2F radical is inert with respect to other peroxy radicals, whereas the HO_2 radical reacts quickly at room temperature with RO_2 with the rate constants lying within $(4-12) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Ref. 29).

Table 3. The enthalpy of formation of the O_2F radical.

T/K	ΔH°_{exp} /kcal mol^{-1}	ΔH°_{theor} /kcal mol^{-1}	Ref.
298	6.24 ± 0.50	–	28
	5.49 ± 0.40	–	31
	6.132	–	27
	–	5.93	34
	–	6.0	6
	–	6.1 ± 0.5 [a]	11
0	6.571	–	27
	–	7.2 ± 2.0	14
	–	8.9 ± 3.0	34
	–	6.5 ± 0.5 [a]	11

[a] This value is included in the recommended NIST–JANAF Thermochemical Table.

Solutions containing O_2F radicals are stable at temperatures ⩽223 K. They can be used for oxidative fluorination. For example, Au(III) is oxidised to Au(V)

$$2O_2F + AuF_4^- \longrightarrow AuF_6^- + 2O_2.$$

Similarly, the Ag(II) ions are oxidised to Ag(III), Ni(II) is oxidised to Ni(IV) and Pt(IV) is oxidised to Pt(V).

Controlled hydrolysis of a solution of a dioxygenyl salt in HF at 195 K represents a rare example of the chemical synthesis of ozone.[36]

$$2O_2^+AsF_6^- + 3H_2O \longrightarrow O_3 + O_2 + 2H_3O^+AsF_6^-.$$

The same result was obtained with other available and handy dioxygenyl salts, *viz.*, fluoroantimonates $O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$. It was assumed [36] that the reaction of dioxygenyl O_2^+ with a water molecule gives an O_2 molecule and an H_2O^+ cation, the latter decomposing with elimination of H^+. Hydroxyl formed upon the H_2O^+ decomposition reacts with O_2^+ producing protonated ozone $OOOH^+$, which transforms into ozone upon elimination of H^+.

The recent active studies on the properties of dioxygen difluoride and the O_2F radicals were partly associated with the hazards of atmospheric contamination by halogen-containing refrigerants and propellants that produce halogen atoms upon photolysis. The reactions of the fluorine atoms with methane, water and other hydrogen-containing compounds present in the atmosphere of Earth have low activation barriers [37] and result in HF, *i.e.*, stable reservoir molecules rained out of the atmosphere. However, the main mechanism for transformation of the fluorine atoms in the atmosphere is the reaction

$$F + O_2 + M \longrightarrow O_2F + M$$

(hereinafter M is any species), which produces the O_2F radicals. Moreover, due to a high oxygen concentration and a high rate of fluorine atom reaction with oxygen, the ratio of the equilibrium concentrations $[O_2F] : [F]$ in the stratosphere may exceed 10^4 (see Refs 35, 38, 39). The radicals O_2F in turn can take part in catalytic cycles of ozone destruction [36,38–41]

$$\begin{array}{l} O_2F + O_3 \longrightarrow OF + 2O_2 \\ OF + O_3 \longrightarrow O_2F + O_2 \\ \hline 2O_3 \longrightarrow 3O_2 \end{array} \qquad \begin{array}{l} O_2F + O \longrightarrow OF + O_2 \\ OF + O_3 \longrightarrow O_2F + O_2 \\ \hline O + O_3 \longrightarrow 2O_2 \end{array}$$

The efficiencies of the reactions of oxygen, water and methane with F atoms in the atmosphere depends on the altitude: at altitudes of 4–42 km, the reactions with oxygen resulting in O_2F_2 prevail; below 4 km and above 42 km, the reactions with H_2O and CH_4, which produce HF, are predominant.[42] At altitudes above 28 km, photolysis of O_2F proceeds actively, which inhibits accumulation of these radicals.[39]

The reaction of the F atoms with the oxygen molecules is not the only source of the O_2F radicals. The following reaction has been hypothesised: [43]

$$F + OClO \longrightarrow FOOCl \longrightarrow O_2F + Cl,$$

which, however, cannot play any noticeable role due to the lower chlorine dioxide content in the atmosphere as compared with oxygen.

Studies of certain reactions of the O_2F radicals at 295 K by means of pulse radiolysis coupled with UV absorption spectroscopy have shown [35] that the reactivity of the O_2F radical is relatively low, the upper limits of rate constants of its reactions with O_3, CH_4 and CO being 3.4×10^{-16}, 4.1×10^{-15} and 5.1×10^{-16} cm^3 molecule^{-1} s^{-1}, respectively.[35] Whence it follows that O_2F radicals pose no threat to the ozone layer.

The reaction

$$O_2F + NO \longrightarrow \text{products} \qquad (1)$$

proceeds virtually completely by the channel

$$O_2F + NO \longrightarrow FNO + O_2,$$

probably, *via* an intermediate complex $ON-FO_2$. The rate constant for the reaction (1) is $(1.47 \pm 0.08) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The reaction

$$O_2F + NO_2 \longrightarrow \text{products} \quad (2)$$

proceeds at 295 K with the rate constant $k_2 = (1.05\pm0.15)\times10^{-13}$ cm^3 molecule^{-1} s^{-1} (Ref. 40). Kinetic studies of reactions (1) and (2) under continuous flow conditions using microwave electric discharge and mass spectrometry have confirmed their bimolecular mechanisms.[39] At a total pressure of 1 Torr, the following rate constants were obtained (cm^3 molecule^{-1} s^{-1}):

$$k_1 = (7.5\pm0.5)\times10^{-12}\exp\left(\frac{-688\pm377}{T}\right) \text{ at } 190\text{ K} < T < 298\text{ K}$$

and

$$k_2 = (3.8\pm0.8)\times10^{-11}\exp\left(\frac{-2042\pm456}{T}\right) \text{ at } 260\text{ K} < T < 315\text{ K}.$$

At room temperature, the upper limits of the rate constants for the reactions of O_2F with O_3 and CH_4 were 3×10^{-15} and 2×10^{-16} cm^3 molecule^{-1} s^{-1}, respectively.

3. Compounds HOOF and ClOOF

The HOOF and ClOOF molecules are of particular interest for atmospheric chemistry. A reaction of OF with OH may result in a compound HOOF, which is kind of hybrid between hydrogen peroxide and dioxygen difluoride. A non-empirical estimate[40] has shown that the HOO/OOF dihedral angle in a skewed HOOF molecule (the C_1 group of point symmetry) is $\sim83^\circ$ and the internuclear distance $r(O-O) = 1.339$ Å, these values being intermediate between those in H_2O_2 and O_2F_2 molecules. The HOOF molecule can be sufficiently stable and decomposes to F and HO_2 species. The enthalpy of HOOF formation can be estimated by using the following isodesmic reaction:

$$HOOF + HOH \longrightarrow HOOH + FOH$$

and was found to be 0.4±2 kcal mol^{-1} (at 0 K).

Chlorine fluorine peroxide ClOOF can be an intermediate in the reaction of radicals ClO + OF. An estimate[43] gave a value of 85.1° for the dihedral angle in the skewed ClOOF molecule. The enthalpy of formation of ClOOF at 300 K was assessed to be 36.8±2 kcal mol^{-1} (Ref. 43) and 18.5 kcal mol^{-1} (Ref. 13). The presence of a stronger bond F–O in the ClOOF molecule as compared with HOOF, allows one to assume that ClOOF decomposes to Cl and O_2F. Dissociation of ClOOF to F and ClO_2 is energetically less advantageous.[13,43] The peroxide ClOOF is by 18 kcal mol^{-1} more advantageous with respect to energy than the chlorite FOClO.[13]

III. Chlorine oxides Cl_2O_2

In contrast to fluorine which forms a single compound, *viz.,* dioxygen difluoride, chlorine oxides with the composition X_2O_2 are of greater diversity.

The first mention in the literature of a compound with the formula Cl_2O_2 dates back to 1949. In the ^{38}Cl radiotracer investigations of mechanisms of reactions of chlorine with chlorous acid, of the chloride ion with the chlorate ion and of chlorous acid disproportionation, each of these reactions was assumed[44] to involve an intermediate which had an asymmetrical structure of either $ClClO_2$ or ClOClO and decomposed to ClO_2.

Of all possible structures built of two chlorine atoms and two oxygen atoms which include three-membered and four-membered cycles, only chloryl chloride $ClClO_2$ (C_s symmetry), chlorine peroxide ClOOCl (C_2) symmetry) and chlorine chlorite ClOClO (C_1 symmetry) can exist. Among these isomers, ClOOCl is the most stable one. Chloryl chloride ranks higher in the energy scale as compared with chlorine peroxide (by 0.9–5 kcal mol^{-1} according to different estimates[45–48]) and chlorine chlorite (by 7–10 kcal mol^{-1}, see Refs 45–49).

An estimate[50] of the Gibbs energy for an equilibrium mixture of all Cl_2O_2 isomers in the ideal-gas state has shown that at low temperatures the ClOOCl isomer prevails, whereas at higher temperatures the fraction of $ClClO_2$ increases.

Temperature, K	100	200	300
Fraction of $ClClO_2$ in a mixture of Cl_2O_2 isomers (%)	0.4	8.8	21.6

The yield of chlorine chlorite at $T \leqslant 590$ K did not exceed 1%; however, its content in the mixture increased substantially with further increases in the temperature.

1. Chloryl chloride

Attempts to obtain chloryl chloride by the reaction of chloryl fluoride ClO_2F or chloryl perchlorate ClO_2ClO_4 with certain chlorine-containing compounds (NOCl, NO_2Cl, $AlCl_3$, BCl_3, HCl) were undertaken as early as in the 1950's (see, *e.g.*, Ref. 51), but resulted in formation of products of chloryl chloride decomposition, *viz*., ClO_2 and Cl_2 in a 2:1 ratio. Only in 1992, could the fluorine atom in ClO_2F be exchanged for a chlorine atom from $AlCl_3$, BCl_3 and HCl to give chloryl chloride in amounts sufficient for spectroscopic measurements; however, an attempt to isolate pure $ClClO_2$ has failed.[52] Chloryl chloride was synthesised by passing ClO_2F over $AlCl_3$ under a pressure of 0.1–1 mbar, the product being collected at 77 K.[52] The reactions of ClO_2F with BCl_3 and HCl also resulted in $ClClO_2$, while the reaction of ClO_2F with NOCl afforded predominantly NO_2Cl.

In a different preparation of $ClClO_2$, stoichiometric amounts of ClO_2F and HCl were mixed in a reactor and then the mixture was expanded into an absorption cell, the temperature in the reactor and the cell being kept at ~255 K.[53] Chloryl chloride was also formed in the reaction of photochemically generated chlorine atoms with chlorine dioxide and in the recombination of ClO radicals on ice.[54] At room temperature, with a $ClClO_2$ partial pressure of 1 mbar and a total gas pressure of 4 mbar, the $ClClO_2$ half-life is 1 min. Under stratospheric conditions, chloryl chloride is more stable, but easily undergoes photolysis.

The UV absorption spectrum of $ClClO_2$ in a neon matrix demonstrated two bands devoid of definite structures with maxima at 236 and 296 nm and half-widths of ~40 and ~45 nm, respectively.[52] The absorption maxima in the gas-phase $ClClO_2$ spectrum were at 231 ($\sigma = 1.3\times10^{-17}$ cm^2) and 296 nm ($\sigma = 1.5\times10^{-17}$ cm^2).

The IR spectra of matrix-isolated and gaseous $ClClO_2$ demonstrated six fundamentals $\nu_1-\nu_6$. Table 4 shows the vibrational frequencies for the matrix-isolated $^{35}Cl\,^{35}Cl\,^{16}O_2$ (neon matrix)[52] and compares them with the vibrational frequencies calculated by the CCSD/TZ2P method[47] (singles and doubles coupled-cluster). Geometrical parameters of the $ClClO_2$ molecule (Ref. 52) were later refined based on the rotational spectra[53,54] of chloryl chloride (Table 5). For comparison, Table 5 shows the geometrical parameters estimated by the MP2 method using 6-31G*

Table 4. Vibrational frequencies in the spectrum of the $ClClO_2$ molecule.

Frequency	Experimental data[52]	Calculations[a] using the CCSD/TZ2P method[47]	Mode
ν_1	1041.20	1039	Cl–O stretch, symmetric
ν_2	522.50	524	OClO bend
ν_3	440.43	459	ClClO bend, symmetric
ν_4	271.37	285	Cl–Cl stretch
ν_5	1216.37	1205	Cl–O stretch, antisymmetric
ν_6	251.40	254	ClClO bend, antisymmetric

[a] Of all the values calculated using the MP2, CCSD and CCSD(T) methods with TZ2P and TZ2Pf basis sets, the CCSD/TZ2P method provided the best agreement with experimental data.

Table 5. Geometrical parameters and dipole moment (μ) for the $ClClO_2$ molecule.

Parameter	Experimental data			Quantum-chemical calculations	
	IR [52]	MW [53]	MW [54]	MP2/6-31G* (see Ref. 46)	MP2/TZ2Pf (see Ref. 47) [a]
r (Cl–Cl) /Å	2.22	2.1966	2.1978	2.459	2.269
r (Cl–O) /Å	1.44	1.4367	1.4360	1.469	1.442
Cl–Cl–O /deg.	103.5	104.14	104.06	104.2	103.8
O–Cl–O /deg.	116.0	114.96	115.05	116.7	115.0
μ /D		1.570		3.378	2.20

[a] The values shown were calculated by the MP2/TZ2Pf method that provides the best agreement with experimental data.

(Ref. 46) and TZ2Pf (Ref. 47) basis sets. The internuclear distance Cl–Cl in a $ClClO_2$ molecule exceeds that in the Cl_2 molecule by almost 0.21 Å. Chloryl chloride molecules represent asymmetric prolate rotors with the rotational constants A = 9450.9218, B = 3588.0617 and C = 2787.9468 MHz (for $^{35}Cl^{35}Cl^{16}O_2$).

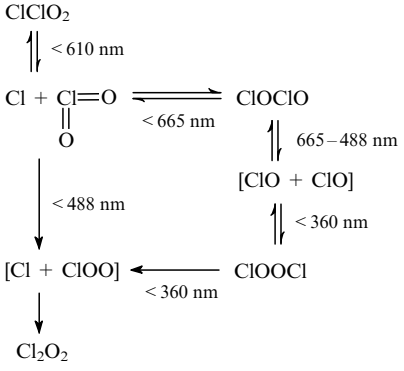
A non-empirical quantum-chemical calculation [46] of the enthalpy of formation carried out by the MP2 method using 6-31 + G(3*d*, 2*p*) and 6-31G* basis sets for the following isodesmic reaction:

$$ClClO_2 + HOCl \longrightarrow HOClO_2 + Cl_2$$

gave values of $\Delta H_0^\circ(ClClO_2)$ equal to 33.8 [MP2/6-31 + G(3*d*, 2*p*)] and 34.6 kcal mol^{-1} (MP2/6-31G*). The enthalpy of formation of $ClClO_2$ was also calculated [47] using the second-order Møller–Plesset perturbation theory and the CCSD and CCSD(T) methods with TZ2P and TZ2Pf basis sets. The CCSD(T)/TZ2P method gave a value of 35.1 kcal mol^{-1}, which is most similar to the experimental one.

Photolysis of matrix-isolated $ClClO_2$ caused its rearrangement into ClOClO and ClOOCl.[55] A more detailed study [56] has shown that the effect of light with a threshold wavelength of 610 nm on argon-matrix-isolated $ClClO_2$ results in immediate transformation of the latter into chlorine chlorite ClOClO without formation of any long-lived intermediates. A chlorine atom formed upon $ClClO_2$ dissociation can attack the ClO_2 residue either at the chlorine atom giving $ClClO_2$ or at the oxygen atom to give ClOClO. The action of light with a threshold wavelength of 665 nm on ClOClO causes its dissociation to either Cl and OClO (with subsequent regeneration of $ClClO_2$) or two ClO radicals (with subsequent regeneration of ClOOCl). A scheme of photolysis of argon matrix-isolated $ClClO_2$ has been described [56] and the wavelengths at which dissociation of Cl_2O_2 isomers takes place were specified (Scheme 1).

Scheme 1



By using narrow-band filters (665, 610 and 360 nm), all three isomers, *viz.*, ClOClO, $ClClO_2$ and ClOOCl, respectively, could be identified. The calculated [56] values of dissociation energies (E_{dis}) for chlorine chlorite and chloryl chloride were substantially lower than the photon energy, which points to the excessive energy of the photofragments.

Reaction	E_{dis} /kcal mol^{-1}
$ClOClO \longrightarrow 2\,ClO$	6
$ClOClO \longrightarrow Cl + OClO$	~9.5
$ClClO_2 \longrightarrow Cl + OClO$	~19

In the photolysis of neon matrix-isolated $ClClO_2$, only chlorine and oxygen are formed, and no photoisomerisation of $ClClO_2$ to ClOOCl takes place.

A study [57] of photoisomerisation of argon-matrix-isolated chlorine, bromine and iodine chlorites (XOClO, X = Cl, Br, I) obtained by addition of X atoms to OClO has shown that all three chlorites isomerised to the corresponding chloryl halides $XClO_2$. In turn, $ClClO_2$ and $BrClO_2$ were transformed into ClOClO and BrOClO; this process could be repeated many times until $XClO_2$ decomposed to oxygen and the halogen.

It was assumed [52] that chloryl chloride takes part in stratospheric ozone destruction (Scheme 2),[52] although one can simulate [46] a 'zero' cycle (Scheme 3), which does not result in ozone loss.[46]

Scheme 2

$$ClO + ClO + M \longrightarrow Cl_2O_2 + M$$
$$Cl_2O_2 \xrightarrow{h\nu} Cl + ClOO$$
$$ClOO + M \longrightarrow Cl + O_2 + M$$
$$2\,(Cl + O_3 \longrightarrow ClO + O_2)$$
$$2\,O_3 \longrightarrow 3\,O_2$$

Scheme 3

$$ClO + ClO + M \longrightarrow ClOClO + M$$
$$ClOClO \longrightarrow ClClO_2$$
$$ClClO_2 \xrightarrow{h\nu} Cl + OClO$$
$$OClO \xrightarrow{h\nu} O + ClO$$
$$Cl + O_3 \longrightarrow ClO + O_2$$
$$O + O_2 + M \longrightarrow O_3 + M.$$

For decades, the ClO radicals were the subject of spectroscopic and kinetic studies (the first works on this subject were carried out as far back as 20–30 years ago); however, little attention was paid to their dimerisation (self-reaction). The possibility of Cl_2O_2 formation upon recombination of the ClO radicals and further involvement of the Cl_2O_2 molecules in the presumed catalytic cycle of ozone depletion (see Scheme 2) were the reasons for the appearance of numerous publications devoted to recombination of the ClO radicals and properties of the dimer formed.

2. Chlorine peroxide

An IR spectroscopic study [58] of recombination of the ClO radicals generated at 220–240 K under continuous flow conditions by the reaction of Cl atoms with ozone has shown that chlorine peroxide ClOOCl, which can take part in the aforementioned catalytic cycle, is the dominant recombination product. Although it was soon shown [55, 59–62] that the IR spectral bands pertain most probably to dichlorine trioxide (chlorine sesquioxide Cl_2O_3), the main conclusion on the involvement of Cl_2O_2 in the catalytic cycle remained true.

When studying the spectrum of the ClO radical recombination products in the submillimetre range (415–435 GHz) at a temperature below 240 K, several Cl_2O_2 isomers and chlorine dioxide OClO were identified,[63] chlorine peroxide ClOOCl being the main product. The ClOOCl molecule has a chain structure with two equivalent chlorine atoms and two equivalent oxygen atoms (C_2

Table 6. Geometrical parameters and dipole moment (μ) for the chlorine peroxide molecule.

Parameter	Experimental data	Quantum-chemical calculations	
	MW [63]	MP2/6-31G* (see Ref. 46)	MP2/TZ2Pf (see Ref. 47)
r (Cl−O) /Å	1.7044	1.741	1.711
r (O−O) /Å	1.4259	1.420	1.407
Cl−O−O /deg.	110.07	109.0	108.9
ClOO/OOCl	81.03	85.0	83.0
μ /D	0.72	0.921	0.84

symmetry). Molecules of chlorine peroxide represent slightly prolate asymmetric rotors with the constants A = 13109.4463, B = 2409.7892 and C = 2139.6786 MHz.[63] Earlier,[64] the following constants were obtained: A = 12967, B = 2333 and C = 2085 MHz. Table 6 shows internuclear distances and bond angles for chlorine peroxide molecules (see also Ref. 65).

The calculated values of the internal rotational barrier for ClOOCl are as follows:

ClOOCl conformation	E /kcal mol^{-1}	
	data from Ref. 66	data from Ref. 67
cis	8.8	10.1
trans	4.9	5.4

According to Ref. 63, the dipole moment of a ClOOCl molecule is 0.72 D, although the value of 0.76 D was thought [67] to be the most reliable one for the dipole moment.

An IR spectrum of argon-matrix-isolated ClOOCl at 12 K demonstrated absorption bands at 752.6 (O−O, stretch), 649.8 and 647.6 cm^{-1} (Cl−O, stretches); [55] the absorption bands at 750 and 650 cm^{-1} were also present in the spectrum of gaseous chlorine peroxide.[60] In a later work,[56] the IR spectrum of ClOOCl isolated in an argon matrix was studied. For a molecule with an isotopic composition of $^{35}Cl^{16}O^{16}O^{35}Cl$, the frequencies 753.97 (ν_1), 543.0 (ν_2), 647.67 (ν_5) and 418.5 cm^{-1} (ν_6) were found and the values 310 (ν_3) and 127 cm^{-1} (ν_4) were calculated.

In the UV absorption spectrum of ClOOCl,[68] the absorption maximum was observed at 245 nm and the absorption cross-section (σ) was equal to 6.4×10^{-18} cm^2 (at 350 nm, the absorption cross-section was $<1\times10^{-19}$ cm^2). An adsorption maximum was also found [60] at 245 nm ($\sigma = 6.5\times10^{-18}$ cm^2), and measurable cross-section values could be obtained up to 410 nm. The fact that this UV spectrum pertained to chlorine peroxide was confirmed by calculations.[48] Later,[69] an UV spectrum of ClOOCl obtained by chlorine monoxide photolysis (λ = 254 nm) was studied; the absorption maximum was found at 244 nm ($\sigma = 6.4\times10^{-18}$ cm^2). The measurements were carried out at 195 K in the 200–400 nm range.

In a number of studies, the enthalpies of ClOOCl formation and energies of bond dissociation were calculated, which did not coincide completely but did not differ dramatically from one another. The enthalpy of ClO dimerisation found [68] from the temperature dependence of the equilibrium constant

$$K_{eq} = \exp\left(\frac{\Delta S_1^\circ}{R}\right)\exp\left(-\frac{\Delta H_1^\circ}{RT}\right)$$

for the reaction

$$ClO + ClO \rightleftharpoons Cl_2O_2,$$

was equal to -17 ± 0.7 kcal mol^{-1}. An experimental value of the enthalpy of ClOOCl formation (ΔH_{298}°) was equal to 31.3 ± 0.7 kcal mol^{-1}. A non-empirical calculation [46] of the enthalpy of ClOOCl formation carried out within the framework of the second-order Møller–Plesset perturbation theory with the 6-31+G(3*d*) and 6-31G* basis sets gave the values ΔH_0°(ClOOCl) = 35.7 (MP2/6-31 + G(3*d*) and 32.6 kcal mol^{-1} (MP2/6-31G*), and an estimate [47] obtained by the CCSD method was ΔH_0°(ClOOCl) = 34.2 kcal mol^{-1}. Using an experimental value of the heat of ClO formation and a calculated value of ΔH_0°(ClOOCl) with a correction made for T = 298 K, the energy of ClOOCl dissociation

$$ClOOCl \longrightarrow 2ClO,$$

was determined [47] to be D(ClO−OCl) = 14.9 kcal mol^{-1}. The fact that the enthalpy value of 34.2 kcal mol^{-1} calculated by using the isodesmic reaction

$$ClOOCl + H_2O \longrightarrow Cl_2O + HOOH$$

deviated from the experimental value may be due to an error introduced by determination of the heat of formation of Cl_2O.[47] Using another value for the heat of Cl_2O formation, the following parameters were obtained:[47] ΔH_0°(ClOOCl) = 32.7 kcal mol^{-1} and D(ClO−OCl) = 16.4 kcal mol^{-1}, which were in better agreement with the experimental data.

According to an estimate,[58] dissociation of chlorine peroxide ClOOCl to ClO + ClO requires ~16.7 kcal mol^{-1}, whereas the dissociation to Cl + ClOO requires more than 19 kcal mol^{-1}. The value of ΔH_0°(ClOOCl) was calculated [70] to be 33 ± 2 kcal mol^{-1}. In a kinetic study [71] devoted to reactions of ClOOCl thermal decomposition and ClO dimerisation, the energy of the O−O bond dissociation (18.1 kcal mol^{-1}) was calculated and the enthalpy of ClOOCl formation (30.5 ± 0.7 kcal mol^{-1}) was determined. Apparently, without introducing a huge error, one can assume the dissociation energies of Cl−OOCl and ClO−OCl bonds to be 21 and 18 kcal mol^{-1}, respectively.[69, 72]

Thus, the molecule of chlorine peroxide differs sharply from the FOOF molecule in the bond strength: the O−O bond in ClOOCl is much weaker as compared with that in FOOF. Ionisation of ClOOCl makes this bond still weaker: for an ionic dimer $ClOOCl^+$, the values $D_{298}(ClO-OCl^+)$ = ~11.5 ± 4.3 kcal mol^{-1} and $\Delta H_{298}^\circ(ClOOCl^+)$ = 287.5 ± 2.9 kcal mol^{-1} were found.[73]

3. The ClOO and OClO radicals

It was assumed [58] that the photolysis of ClOOCl in the polar stratosphere results in the formation of Cl atoms and ClOO radicals. An investigation [74] confirmed this assumption. It was found that it is these products that were formed upon laser pulse photolysis of chlorine peroxide (λ = 308 nm, 235 K) with a primary quantum yield of 1.03 ± 0.12. The photodissociation of ClOOCl to Cl atoms and ClOO radicals was also mentioned in Ref. 68; however, the possibility of another dissociation channel resulting in two ClO radicals [56] cannot be ruled out. In contrast to Cl atoms, ClO radicals do not catalyse the ozone destruction; hence, the ratio of the dissociation products [Cl] : [ClO] is important when assessing the ozone-depletion effect of ClOOCl. Experiments [75] on the ClOOCl photolysis (λ = 248 and 308 nm) have shown that irradiation mainly cleaves the stronger Cl−O bond, the [Cl] : [ClO] ratio being 0.88 : 0.12 (248 nm) and 0.90 : 0.10 (308 nm). Mass-spectrometric studies failed to detect the intermediate ClOO that forms in the Cl−O bond scission, because of its fast dissociation. Photolysis of chlorine peroxide at λ = 308 nm resulted in its dissociation to Cl atoms and O_2 molecules, whereas photolysis at 248 nm produced in addition ClO, O and ClOO.[76]

Abstraction of a chlorine atom from the ClOOCl molecule results in a ClOO radical, which is an isomer of the well-known chlorine dioxide OClO. The possibility of existence of the ClOO radical as an intermediate product in the pulse photolysis of chlorine–oxygen mixtures was reported by Porter and Wright [77] as far back as the early 1950's. The ClOO radical was by 3–4 kcal mol^{-1} energetically more favourable as compared with the OClO radical, the former being very reactive, however, in contrast, chlorine dioxide was stable at room temperature and

could exist as a radical for an indefinitely long period without any sign of dimerisation. Association of OClO with the formation of weakly bound dimers was observed only in the solid state.[78,79] Both ClO_2 isomers can be involved in the stratospheric ozone destruction, which explains the attention they have attracted in recent years (photochemistry of chlorine dioxide is the subject of numerous studies, see, *e.g.*, Refs 80–111). Experiments on OClO photolysis most frequently used radiation with wavelengths of 365–368 nm; the absorption of OClO begins at ~510 nm.

Photolysis of OClO can result in both dissociation of the molecule and its photochemical isomerisation. A model of concerted isomerisation of the OClO molecule which proceeds *via* ClOO isomers in the lower excited state $^2A'$ was proposed. From this state, the radical ClOO can either emit a photon and pass to the ground state $^2A''$ with the energy 25–30 kcal mol^{-1} lower than the energy of the $^2A'$ state or dissociate. The ground state $^2A''$ of ClOO radicals obtained by photoisomerisation of chlorine dioxide and stabilised in an aluminosilicate matrix at 77 K was confirmed by analysis of the ESR spectrum.[81]

Decomposition of photo-excited OClO molecules results in Cl atoms and O_2 molecules. Chlorine atoms can destroy ozone. Decomposition of OClO can proceed by a different pathway, namely, with ClO and O formation. The latter species can regenerate ozone; however, dimerisation of ClO is preferable. Dimerisation of ClO and photoisomerisation of OClO result in the formation of ClOOCl or ClOO which destroy ozone. The direction of OClO reactions, *viz.,* isomerisation or dissociation, and the mechanisms of these processes depend strongly on the photolysis conditions. In low-temperature inert matrices, chlorine dioxide transforms almost completely to the ClOO isomer. The ClOO radicals represent the only photoproduct upon photolysis of OClO in an amorphous ice matrix (360 nm, 80 K).[100] Photolysis of OClO at 150 K also produced ClOO together with $ClClO_2$. The latter was formed in the reaction of Cl atoms with chlorine dioxide.[97,103] Chloryl chloride was also observed among the photolysis products of thin OClO films either condensed at 100 K (up to 70 monolayers) or adsorbed on ice (0.5–2 monolayers).[105]

Photolysis of aqueous and other solutions of chlorine dioxide results in the formation of chlorine atoms. The quantum yield and the mechanism of Cl atom formation were the subjects of a discussion. Thus it was assumed [97] that chlorine dioxide is first isomerised to ClOO, which is decomposed to Cl and O_2. On the other hand, it was supposed [89] that nearly 90% of excited OClO molecules dissociate to O and ClO in an aqueous solution at room temperature at $\lambda = 365$ nm and only 10% of the molecules isomerise to ClOO, the latter decomposing to Cl and O_2 (the rate constant is $\sim 6.7 \times 10^9$ s^{-1}). However, the possibility of chlorine atom formation as the primary photoproduct has not been ruled out

$$OClO \xrightarrow{h\nu} Cl(^2P_u) + O_2(^1\Delta_g).$$

According to data from Ref. 98, the 10% yield of Cl atoms comprised 9.5% of Cl obtained upon ClOO decomposition and 0.5% of Cl formed upon direct photodissociation. The same conclusion was made by the authors [110,111] who studied photolysis of an aqueous solution of chlorine dioxide at $\lambda = 400$ nm. They have found that nearly 90% of excited OClO molecules dissociate to ClO and O with subsequent recombination of these fragments. In this process, the quantum yield of the Cl atoms was about 10%, of which 2% were formed upon decomposition of ClOO and 8% were formed upon dissociation. They managed to observe ClOO radicals with a lifetime of ~4 ns.

Chang and Simon [104] assumed that a 'hot' ClOO isomer formed upon pholysis of OClO undergoes relaxation in 9 ps and then dissociates. Irradiadion of ClOO with light with a wavelength of 365 nm increased the yield of Cl atoms owing to the photolysis of vibrationally excited ClO radicals formed by the dominant photodissociation channel [108]

$$OClO \longrightarrow ClO + O.$$

A femtosecond spectroscopic study of the photolysis of an aqueous solution of OClO has shown that ClO and O fragments quickly recombine to give vibrationally excited OClO which relaxed to the ground state in 10 ps. Irradiation of OClO with light with $\lambda = 400$ nm produced only Cl and O_2 as the photolysis products with a quantum yield of 0.07±0.03.[106,107]

Gas-phase photoisomerisation of OClO molecules seems to be highly unlikely.[90,101]

In the UV spectrum, the absorption maximum of ClOO radicals was found at 248 nm [$\sigma = (3.4\pm0.3) \times 10^{-17}$ cm^2, 298 K] (Ref. 112) and at 246 nm [$\sigma = (2.98\pm0.23) \times 10^{-17}$ cm^2, 191 K] (Ref. 113).

An IR spectrum of ClOO radicals generated by either photoisomerisation of argon-matrix-isolated OClO or the reaction of Cl atoms with oxygen molecules at 17 K demonstrated the following vibrational frequencies: 1442.8 (ν_1), 408.3 (ν_2), 192.4 (ν_3) cm^{-1} and an overtone of 375.6 cm^{-1} ($2\nu_3$) (C_s point symmetry group).[95] IR-Fourier spectra measured for eight neon-matrix-isolated ClOO radicals with different isotope compositions contained all fundamental frequencies, four overtones and five combined frequencies.[79] For example, the spectrum of $^{35}Cl\,^{16}O\,^{16}O$ radicals contained the frequencies 1438.56 (ν_1), 413.73 (ν_2), 201.38 cm^{-1} (ν_3) (antiharmonicity-corrected frequencies were 1477.8, 432.4 and 214.8 cm^{-1}). The O–O stretch frequency for the ClOO radical (1477.8) was close to that for the O_2F radical (1487 cm^{-1}).

The exact values of geometrical parameters for ClOO radicals are unknown. Based on IR spectra measured during the photolysis of a $Cl_2 + O_2$ mixture at 4 K, estimates were made [114] for bond lengths and bond angles in a ClOO radical (Table 7). For this radical, the following values were proposed:[115] r(O–O) = 1.31 Å and r(O–Cl) = 1.835 Å. Noticeably different geometrical parameters of ClOO radicals were calculated by different methods, *viz*., by the high-level nonempirical CMRCI (contracted multireference configuration interaction) method,[116] by using the MP2 theory with different basis sets [117] and by means of the density functional theory (DFT) [118] (see Table 7). According to calculations,[116] the dipole moment of ClOO is 1.113 D.

Table 7. Bond lengths and bond angle in the ClOO radical.

Parameter	Experimental data	Quantum-chemical calculations		
	IR [114]	CMRCI [116]	MP2 [117]	DFT [118]
r(O–O) /Å	1.23	1.201	1.174–1.247	1.2154
r(Cl–O) /Å	1.83	2.139	1.923–2.203	1.9286
Cl–O–O /deg.	110	115.7	114.1–118.6	115.74

In a kinetic study of the reaction of Cl atoms with O_2 molecules and the following equilibrium:

$$Cl + O_2 + O_2 \rightleftharpoons ClOO + O_2$$

(181–200 K, oxygen pressure of 15–40 Torr), the rate constant for $Cl + O_2$ association was found to be $(8.9\pm2.9) \times 10^{-33}$ cm^6 molecule^{-2} s^{-1} (186.5±5.5 K).[115] According to this study,[115] the equilibrium constant (K_{eq}) of the reaction $Cl + O_2$ is 18.9 atm^{-1} (185.4 K). A similar value ($K_{eq} = 20.4$ atm^{-1}) was found at the same temperature in a different study.[112] The enthalpy of formation of ClOO radical was found [112] to be ΔH°_{298}(ClOO) = 23.4±0.5 kcal mol^{-1}; calculations [119] gave the value of 24.2±2 kcal mol^{-1}. In experimental studies,[112,115] calculations according to the third law of thermodynamics gave the following values for the dissociation energy D_0(Cl–OO): 4.76±0.49 (Ref. 115) and 4.83±0.05 kcal mol^{-1} (Ref. 112). The calculated value of D_0(Cl–OO) was 4.0±2 kcal mol^{-1} (see Ref. 119). Quantum-chemical calculations using the density func-

tional method showed that the dissociation energy of the ClO−O bond is 62.4 kcal mol^{-1}. Thus, it is evident that the ClOO radical has a strong O−O bond and a weak Cl−OO bond and in this respect resembles the FOO radical. A rather weak Cl−O bond allows us to consider the ClOO radical as an O_2 molecule with a 'chaperon', *viz.,* a chlorine atom.[120]

4. Compound HOOCl

Substitution of a hydrogen atom for a chlorine atom in chlorine peroxide gives HOOCl. This compound has not yet been isolated, however, it is of interest for atmospheric chemistry. Reactions Cl + HO_2 and ClO + OH can result in the formation of HOOCl. The reaction of Cl with HO_2 probably produces an excited HOOCl molecule with the lifetime at 298 K estimated as 1 ns.[121] HOOCl molecules can decompose by three channels, *viz.,* to Cl + HO_2, HCl + O_2 and OH + ClO. A study[122] of the Cl + HO_2 reaction under continuous flow conditions at 250–420 K and a pressure of 0.9–1.5 Torr have shown that in this temperature range its rate constant depends little on the temperature and is equal to $(4.2\pm0.7)\times10^{-11}$ cm^3 molecule^{-1} s^{-1}. At 298 K, the reaction proceeds by roughly 20% by the channel

$$Cl + HO_2 \longrightarrow OH + ClO.$$

At 243–298 K, the reaction of OH and ClO radicals largely proceeds by the channel

$$OH + ClO \longrightarrow HO_2 + Cl,$$

probably, with the formation of an excited HOOCl intermediate.[123] The other reaction channel

$$HO + ClO \longrightarrow HCl + O_2,$$

is realised to a small degree due to the high energy barrier associated with rearrangement of the intermediate.

The probability of stabilisation of excited HOOCl molecules is low under both atmospheric and laboratory conditions.[124] However, a non-empirical calculation using the CCSD(T)/TZ2P method has shown[125] that the thermal stability of HOOCl even exceeds that of ClOOCl; hence, when studying atmospheric processes, one must bear in mind the possibility of the existence of HOOCl. In the same work,[125] geometrical parameters of the HOOCl molecule were estimated [r(O−O) = 1.443 Å, r(Cl−O) = 1.746 Å, r(H−O) = 0.968 Å, bond angles Cl−O−O and O−O−H were 108.6° and 100.6°, respectively, the dihedral angle ClOO/OOH was 98.1°] as well as the dipole moment (1.74 D). The enthalpy of HOOCl formation was shown to be 1.5±1 or 0.2±1 kcal mol^{-1}. The calculated frequencies of HOOCl harmonic vibrations ω_1–ω_6 were 3744, 1399, 835, 633, 392 and 361 cm^{-1}, respectively. The skewed structure of HOOCl was also confirmed by calculations.[126] It was also found[126] that the HOOCl isomer is most stable among the isomers of the general formula $HClO_2$, the energies of branched Y-shaped $HClO_2$ and a chain HOClO (chlorous acid) forms exceeding the energy of the HOOCl form by 51.0 and 8.3 kcal mol^{-1}, respectively. The calculated[126] enthalpies of formation of HOOCl, HOClO and $HClO_2$ molecules were 1.6, 11.9 and 56.2 kcal mol^{-1}, respectively [according to other estimates,[13] ΔH°_{300}(HOOCl) = −0.1 kcal mol^{-1}]. The geometrical parameters of the HOOCl molecule calculated using the MP2/6-31G(*d,p*) method [r(O−O) = 1.408 Å, r(O−Cl) = 1.751 Å][116] were similar to those found in Ref. 125.

5. Chlorine chlorite and $Cl_2O_2^+$ cation

In studies of disproportionation of chlorine-containing compounds, it was assumed that chlorine chlorite ClOClO can be an intermediate in these reactions.[127] Apparently, chlorine chlorite is the intermediate[128] in the reaction

$$O + ClOCl \longrightarrow ClO + ClO.$$

A mass-spectrometric study[73] of ClO dimers has shown that several Cl_2O_2 isomers exist, of which ClOClO is the least stable.

Table 8. Calculated values of bond lengths and bond and torsion angles for the ClOCl′O′ molecule.

Parameter	Quantum-chemical calculations	
	MP2/6-31G* (see Ref. 46)	CCSD/TZ2P[47]
r(Cl−O) /Å	1.713	1.717
r(O−Cl′) /Å	1.909	1.739
r(Cl′−O′) /Å	1.512	1.517
Cl−O−Cl′ /deg.	109.7	111.6
O−Cl′−O′ /deg.	116.8	112.4
ClOCl′/OCl′O′ /deg.	67.1	76.6

According to different estimates,[13,46,47] the enthalpy of ClOClO formation is 40.8–44.3 kcal mol^{-1}. Table 8 shows the results of quantum-chemical calculations[46,47] of geometrical parameters for the ClOClO isomer.

Salts that involve $Cl_2O_2^+$ as a cation have been synthesised.[129] A reaction of hexafluoroantimonate $O_2^+SbF_6^-$ with chlorine in anhydrous HF at 195–233 K gave $Cl_2O_2^+SbF_6^-$; the addition of antimony pentafluoride to the same reactants resulted in the formation of $Cl_2O_2^+Sb_2F_{11}^-$. Black-violet crystals of both salts precipitated when the solutions were cooled to 193 K. Structural studies showed that the salts contain the $Cl_2O_2^+$ cations shaped as flat trapezia in which the 'chlorine part' is spaced at 2.425 Å from the 'oxygen part', which amounts to ~75% of the sum of the van der Waals radii of Cl and O. The internuclear distances Cl−Cl and O−O were 1.916 and 1.185 Å, respectively. In the Raman spectrum of the $Cl_2O_2^+Sb_2F_{11}^-$ salt, an O−O stretch was observed at 1534 cm^{-1} and Cl−Cl stretches were found at 586 and 593 cm^{-1}. Despite the apparent weakness of the cation structure, the salts are sufficiently stable: $Cl_2O_2^+SbF_6^-$ decomposes at 273 K, and $Cl_2O_2^+Sb_2F_{11}^-$ is stable up to 313 K. The dissociation energy of the $Cl_2O_2^+$ cation

$$Cl_2O_2^+ \longrightarrow Cl_2^+ + O_2$$

is equal to 12.8 kcal mol^{-1}. The formation of $Cl_2O_2^+$ cations occurs as a result of chlorine oxidation by a dioxygenyl cation.

$$Cl_2 + O_2^+ \longrightarrow Cl_2^+ + O_2 \longrightarrow [Cl_2\cdots O_2]^+.$$

IV. Bromine and iodine oxides

1. Bromine oxides

Currently, bromine oxides remain insufficiently explored compounds despite the growing interest in them.[130] Probably, this is associated with their low stabilities. Only bromide monoxide Br_2O, bromine bromate $BrOBrO_2$ and bromic anhydride $O_2BrOBrO_2$ have been characterised in most detail. Despite being known since the 1930s, BrO_2 has probably never been obtained in pure form. Moreover, a substance with this molecular formula is believed to be in fact either a mixture of Br_2O_3 and Br_2O_5 (see Ref. 130) or bromine perbromate $BrOBrO_3$ (Ref. 131).

The oxide Br_2O_2 has never been isolated either. However, this was probably observed[132] in the IR spectroscopic studies of the products of atomic–molecular reactions of bromine and oxygen in solid argon. Moreover, it is most probable that this oxide is an intermediate in the recombination of the BrO radicals.

A study of disproportionation of the BrO radicals generated by photolysis of either bromine–ozone or bromine–oxygen mixtures

$$BrO + BrO \longrightarrow BrOOBr^* \longrightarrow BrOO + Br, \qquad (3a)$$

$$BrO + BrO \longrightarrow BrOOBr^* \longrightarrow \left[\begin{array}{c} O-O \\ / \quad \backslash \\ Br\text{------}Br \end{array}\right]^{\neq} \longrightarrow Br_2 + O_2, \qquad (3b)$$

A

has shown[133] that reaction (3) is of the second order. The branching ratio for reactions (3a) and (3) k_{3a}/k_3 was equal to

Table 9. Geometrical parameters of the BrOOBr molecule calculated by different methods.

Parameter	Quantum-chemical calculations		
	BLYP, SVWN and B3LYP [139]	MP2, CCSD(T), B3LYP [140]	MP2/6-31 + G(2*d*) [141]
r(O – O) /Å	1.264 – 1.335	1.359 – 1.410	1.4068
r(Br – O) /Å	1.922 – 2.082	1.861 – 1.900	1.8861
Br – O – O /deg.	113.3 – 115.6	109.6 – 112.6	111.46
BrOO/OOBr /deg.	79.2 – 85.6	82.2 – 84.6	84.75

0.84±0.03 (at 298 K). According to the data from Ref. 134, the branching ratio k_{3b}/k_3 is equal to 0.12±0.04. The vibrationally excited intermediate BrOOBr* either dissociates to BrOO and Br or passes to a more stable state and then dissociates to Br_2 and O_2 *via* a four-centred complex **A**.

Studies of the kinetics and mechanism of the self-reaction of the BrO radicals generated by pulse photolysis of bromine – ozone mixtures at 220 and 298 K and a pressure of different gases of 75 – 600 Torr have revealed [135] absorption at 312 nm, which was not reported earlier. The absorption at 220 K was attributed to the Br_2O_2 dimer. The rate constant for reaction (3) was equal to $(2.75\pm0.50)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K independent of pressure and changed from $(2.00\pm0.41)\times10^{-12}$ (100 Torr) to $(3.10\pm0.30)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (400 Torr) at 220 K. In the same work, the pressure-independent ratios $k_{3a}/k_3 = 0.84$ (298 K) and 0.68 (220 K) were found. Estimates [135] have shown that the lifetime of Br_2O_2 does not exceed 1 min in the stratosphere at 195 K.

In a kinetic study,[136] the absence of the OBrO radical among the products of the BrO + BrO reaction was reported. Apparently, the metastable intermediate BrOBrO the decomposition of which would have given OBrO either was not formed at all or quickly isomerised to BrOOBr. For reaction (3), the following rate constants were found (cm^3 molecule^{-1} s^{-1}): [136] $k_3 = (2.98\pm0.42)\times10^{-12}$, $k_{3a} = (2.49\pm0.42)\times10^{-12}$, $k_{3b} = (4.69\pm0.68)\times10^{-13}$ at 298 K and 760 Torr (oxygen as the buffer gas). These values are similar to those obtained in a different study.[135] According to data from Ref. 137, in the temperature range of 204 – 388 K, the rate constant for reaction (3) depends on the temperature in the following way:

$$k_3 = (1.70\pm0.45)\times10^{-12}\exp\left(\frac{215\pm50}{T}\right).$$

At 298 K, $k_3 = (3.51\pm0.35)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. When simulating the atmospheric processes, it is recommended (bearing in mind the results of previous studies) to use the value

$$k_3 = (1.50\pm0.46)\times10^{-12}\exp\left(\frac{230\pm100}{T}\right)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}.$$

A detailed study [138] of the kinetics and mechanism of the self-reaction of BrO radicals in the temperature range of 220 – 298 K has shown that at $T < 250$ K a new reaction channel appears

$$BrO + BrO + M \rightleftharpoons Br_2O_2 + M. \qquad (3c)$$

At 222 K, the rate constants k_{3c} and k_{-3c} are equal to 8.2×10^{-32} cm^6 molecule^{-2} s^{-1} and 2.5×10^{-18} cm^3 molecule^{-1} s^{-1}, respectively. The equilibrium constant is 1.937×10^5 (235 K) and 1.26×10^6 atm^{-1} (222 K). An enthalpy change in the reaction

$$BrO + BrO \longrightarrow Br_2O_2$$

was estimated to be -14 ± 0.02 kcal mol^{-1}.

The absorption maximum in the UV spectrum of the Br_2O_2 dimer was found at 305 nm, the cross-section $\sigma = 1.4\times10^{-17}$ cm^2 (at 350 nm, the cross-section was 1.28×10^{-17} cm^2).[138]

Like Cl_2O_2, compound Br_2O_2 can exist in several isomeric forms. Among three possible isomers of Br_2O_2, bromine peroxide BrOOBr is the most stable.[139, 140] A calculation [139] using BLYP, SVWN and B3LYP density functionals have shown that the energies of $BrBrO_2$ and BrOBrO isomers are higher than that of the BrOOBr isomer by 8.4 and 11.3 kcal mol^{-1}, respectively. Table 9 shows the results of quantum-chemical calculations [139 – 141] of geometrical parameters for the bromine peroxide molecule. Depending on the calculation method, the internuclear distance *r*(O – O) varies from 1.264 to 1.410 Å, and *r*(Br – O) varies from 1.861 to 2.082 Å, the bond angle Br – O – O varies from 109.6 to 115.6° and the torsion angle BrOO/OOBr varies from 79.2 to 85.6°. The vibrational spectrum of the BrOOBr molecule was also calculated.[139 – 141] The frequencies of O – O stretches (1103, 1046 and 878 cm^{-1}) obtained [139] by three different methods differ substantially from the calculated frequencies 746 cm^{-1} (Ref. 140) and 737 cm^{-1} (Ref. 141).

The enthalpy of BrOOBr formation was estimated [13] to be 41 kcal mol^{-1} (300 K). Calculated within the framework of different approximations, the enthalpies of BrOOBr, $BrBrO_2$ and BrOBrO formation at 0 K are, correspondingly, 46.1, 52.9 and 54.8 kcal mol^{-1} (Ref. 139) and 44±1, 57±6 and 56±4 kcal mol^{-1} (Ref. 140).

It was shown [142] that the reaction of bromine atoms with O_2 molecules in an argon matrix at 10 K gives BrOO radicals. The frequency of 1487.0 cm^{-1} in the IR spectrum of the BrOO radicals was assigned to the O – O stretch. In a recent study [143] which analysed the IR spectrum of argon-matrix-isolated BrOO radicals with different isotope compositions at 17 K, the frequencies of 1485.1, 1444.0 and 1402.3 cm^{-1} were attributed to the O – O stretches in Br ^{16}O ^{16}O, Br ^{16}O ^{18}O and Br ^{18}O ^{18}O, respectively. Non-empirical calculations using the QCISD(T) method [144] gave the frequencies of the Br – O stretch (450 cm^{-1}) and the Br – O – O bend (261 cm^{-1}).

Like its chlorine analogue, the BrOO radical is more stable than its symmetrical isomer OBrO by approximately 5 kcal mol^{-1} (Ref. 145) or 17 – 18 kcal mol^{-1} (Ref. 146).

By using five different density functionals, the internuclear distances Br – O and O – O and the Br – O – O bond angle were calculated [146] for the BrOO radical in its ground state $^2A''$ (Table 10). In the other studies,[144, 145] higher values were obtained for the Br – O bond length and lower values were found for the O – O bond length.

Table 10. Geometrical parameters of the BrOO radical.

Parameter	Quantum-chemical calculations			
	BHLYP [146]	BP86 [146]	QCISD(T) [144]	[UMP/2, CCSD(T)] [145]
r(Br – O) /Å	2.178	2.150	2.302	2.291
r(O – O) /Å	1.253	1.242	1.232	1.214
Br – O – O /deg.	118	118		116.4

According to estimates,[147] the strength of the Br – O bond is ~1 kcal mol^{-1}. A later estimate [145] gave practically the same value, *viz.*, 1.2 – 1.7 kcal mol^{-1}. Dissociation of BrOO radicals to BrO and O requires more than 50 kcal mol^{-1} (Ref. 145). The enthalpy of BrOO formation is 35.1 kcal mol^{-1} (300 K).[13]

Irradiation of BrOO radicals isolated in a solid argon matrix at 275 nm resulted in reversible photoisomerisation to give OBrO.[143] If the matrix also contained oxygen, photolysis of BrOO produced O_3 and BrO. Apparently, in this case a reaction of excited BrOO radicals with oxygen molecules proceeds.[148]

Contamination of the atmosphere of Earth with bromine-containing compounds proceeds both in a natural way and as a result of human activities. Methyl bromide is the main source of stratospheric bromine. Its content in the atmosphere was recently assessed to be ~ 10 ppt (1 ppt = 10^{-12}).[149] The lifetime of CH_3Br in the atmosphere is less than two years, it readily photolyses in the lower stratosphere. It was concluded[150] that, of all possible bromine-involving catalytic cycles of ozone depletion, the cycle with the reaction BrO + ClO as the rate-determining step (Scheme 4) is the most efficient.

Scheme 4

$$\mathrm{BrO + ClO \longrightarrow Br + ClOO}$$

$$\mathrm{ClOO + M \longrightarrow Cl + O_2 + M}$$

$$\mathrm{Br + O_3 \longrightarrow BrO + O_2}$$

$$\mathrm{Cl + O_3 \longrightarrow ClO + O_2}$$

$$\mathrm{2\,O_3 \longrightarrow 3\,O_2}$$

This cycle is particularly remarkable due to the fact that the loss of two radicals that are inactive with respect to ozone results in appearance of very reactive bromine and chlorine atoms.[151] The contribution of such a cycle into the halogen-controlled ozone depletion can reach 20% – 25%.[152] Many studies were devoted to the BrO + ClO reaction (*e.g.*, see Refs 153 – 161 and references therein).

2. Compounds BrOOCl, BrOClO and HOOBr

The class of compounds covered by this review also involves BrOOCl and BrOClO. These can form as intermediates in the BrO + ClO reaction

$$\mathrm{BrO + ClO \longrightarrow BrOOCl \longrightarrow Br + Cl + O_2}, \quad (4a)$$

$$\mathrm{BrO + ClO \longrightarrow BrOClO \longrightarrow Br + OClO}, \quad (4b)$$

$$\mathrm{BrO + ClO \longrightarrow \left[\begin{array}{c} O-O \\ / \quad \backslash \\ Br\text{------}Cl \end{array}\right]^{\neq} \longrightarrow BrCl + O_2} \quad (4c)$$

A

It was found[154, 156] that the rate constant for reaction (4) is $(8.2\pm1.0)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} and does not depend on the temperature in the range of 241 – 408 K. In the same studies, the following branching ratios were found: $k_{4a}/k_4 = 0.45\pm0.10$, $k_{4b}/k_4 = 0.55\pm0.10$ and $k_{4c}/k_4 < 0.02$. The presence of channel (4c) was concluded by Toohey and Anderson,[155] and the formation of BrCl in considerable amounts was experimentally observed,[157, 158, 160, 161] which suggests that this channel makes a substantial contribution to reaction (4). Using the gas-discharge technique and mass spectrometry and a combination of pulse photolysis and UV absorption spectroscopy, the value $k_4 = (1.29\pm0.16)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (298 K) and the ratio $k_{4c}/k_4 = 0.08\pm0.03$ were obtained.[158, 159] Like many other bimolecular radical – radical reactions, reaction (4) is characterised by an inverse temperature dependence. Thus the following values were obtained for the rate constant of reaction (4) in the temperature range of 220 – 400 K (cm^3 molecule^{-1} s^{-1}):

$$k_4 = (4.70\pm0.50)\times10^{-12}\exp\left(\frac{320\pm40}{T}\right) \text{ (Ref. 158)}$$

and

$$k_4 = (6.1\pm1.2)\times10^{-12}\exp\left(\frac{240\pm60}{T}\right) \text{ (Ref. 159)}.$$

Values of rate constants for reaction (4) similar to the aforementioned values,[158, 159] were found in the studies devoted to the kinetics of this reaction and involving mass-spectrometric detection of the products:[160] $k_4 = (1.13\pm0.15)\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_{4b}/k_4 = 0.43\pm0.10$ and $k_{4c}/k_4 = 0.12\pm0.04$ (298 K). Thus, the BrO + ClO reaction proceeds with formation of two intermediates, *viz.*, BrOClO which gives OClO [channel (4b)] and BrOOCl which either decomposes to Br, Cl and O_2 [channel (4a)] or rearranges to the four-centred state **A** with subsequent elimination of BrCl [channel (4c)].

A calculation[140] has shown that, of the mixed oxides $XX'O_2$ (X = Br and X′ = Cl), the peroxide BrOOCl is the most stable; the enthalpy of its formation was found to be 39 ± 2 kcal mol^{-1} (0 K)[140] or 38.9 kcal mol^{-1} (0 K).[139] In an earlier work,[155] the geometrical parameters of the BrOOCl molecule were estimated: r(Br – O) = 1.8 Å, r(Cl – O) = 1.7 Å, r(O – O) = 1.2 Å and the BrOO/OOBr dihedral angle was $\sim 70^\circ$. A calculation[140] using the MP2 perturbation theory gave the following values: r(Br – O) = 1.859 Å, r(Cl – O) = 1.710 Å, r(O – O) = 1.412 Å, bond angles Br – O – O and Cl – O – O were both equal to 109° and the dihedral angle was 84.5°. The values close to those mentioned above were also obtained in calculations using the B3LYP density functional.

It was assumed[162] that the reaction of the BrO radical with hydroxyl involves the formation of a short-lived vibrationally excited complex HOOBr. The main and probably the only channel of this reaction is

$$\mathrm{BrO + OH \longrightarrow [HOOBr] \longrightarrow Br + HO_2}.$$

The rate constant for this reaction was estimated to be $(7.5\pm4.2)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K and 1 Torr.[162] The enthalpy of HOOBr formation was determined to be 5 kcal mol^{-1} (298 K)[162] which is similar to the value of 4.2 kcal mol^{-1} (300 K)[13] and to the calculated[139] value of 8.6 kcal mol^{-1} (0 K). The formation of the HOBrO intermediate in the BrO + OH reaction cannot be ruled out either; however, isomerisation of HOOBr to HOBrO is hindered due to the high energy barrier.[163]

3. Iodine oxides

An assumption of the existence of I_2O_2 and its hydrate $H_2I_2O_3$ as intermediates in the reaction of the iodate ions with the iodide ions in an acidic medium was put forward back in 1930 (see Ref. 164). In a study devoted to the mechanism of this reaction,[164] the following scheme of I_2O_2 formation (in the IIO_2 form) was proposed:

$$\mathrm{H^+ + IO_3^- \rightleftharpoons HIO_3},$$

$$\mathrm{HIO_3 + H^+ + I^- \rightleftharpoons IIO_2 + H_2O},$$

$$\mathrm{I^- + IIO_2 \longrightarrow I_2 + IO_2^-}.$$

By analogy with the recombination of ClO and BrO radicals, one can assume that the reaction IO + IO also proceeds with the formation of I_2O_2 dimers as the intermediates, although the evidence of their existence is still insufficient.

When studying the recombination of IO radicals generated upon photolysis of CH_3I in the presence of ozone at 303 K at an atmospheric pressure (N_2 and O_2 as the diluent gases), the formation of the I_4O_9 aerosol was observed, which deposited on reactor walls as a yellow-white film.[165] It was assumed[165, 166] that, at first, the bimolecular self-reaction of the IO radicals proceeds

$$\mathrm{IO + IO \longrightarrow I_2O_2}.$$

The I_2O_2 formed reacts with I to give IO_2

$$\mathrm{I + I_2O_2 \longrightarrow I_2 + IO_2},$$

and the latter transforms into amorphous I_4O_9.

The IO + IO reaction was studied by a combination of pulse photolysis and UV absorption spectroscopy in the temperature range of 250 – 373 K at a pressure of 650 Torr (nitrogen as the

diluent gas).[167] The rate constant for this reaction is independent of the temeprature and has the following form:

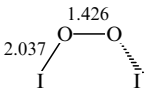
$$k = 1.73 \times 10^{-12} \exp\left(\frac{1020 \pm 200}{T}\right).$$

At 298 K, its value was $(5.6\pm1.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The rate constant at 300 K was determined [168] to be $(6.6\pm2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Later,[169] the rate constant $k = (8\pm1.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was measured at room temperature and a pressure of 60–600 Torr.

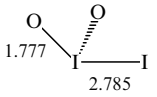
It was concluded [170] that I_2O_2 dimers can form in the self-reaction of the IO radicals, although this possibility has never been confirmed in spectroscopic studies. According to certain data,[170] the rate constant for this reaction is temperature-independent in the range of 220–320 K and is equal to $(9.9\pm1.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

A non-empirical calculation using the QCISD(T)/6-311+G(3*df*) basis set [171] has shown that all I_2O_2 isomers are unstable with respect to the elements at 298 K.

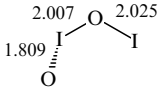
Below, four possible isomers of I_2O_2 are shown as well as the calculated bond lengths (in Å) in them



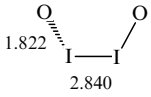
IOOI (C_2)



IIO_2 (C_s)



IOIO (C_1)



OIIO (C_2)

In this family, the IIO_2 isomer is the most stable (in contrast to the corresponding chlorine and bromine analogues). The stability of I_2O_2 isomers decreases in the following sequence: [171] IIO_2 > IOIO > IOOI > OIIO. In the IIO_2 molecule, the internuclear distance r(I–O) = 1.777 Å [calculated using the MP2/6-311+G(3*df*) method] is the shortest distance as compared with the other I_2O_2 isomers, and the frequency of the I–O stretch is the highest (about 960 cm^{-1}). The lifetime of IIO_2 with respect to its decomposition to I and OIO at room temperature was estimated to be ~4 s. The geometrical parameters of iodine peroxide molecules IOOI were also calculated: [171] r(I–O) = 2.037 Å, r(O–O) = 1.426 Å, the bond angle I–O–O and the torsion angle IOO/OOI were equal to 110 and 86°, respectively. The frequency of the I–O stretch was ~510 cm^{-1}. Using the following isodesmic reaction

$$IOOI + 2H_2O \longrightarrow 2HOI + H_2O_2$$

the enthalpy of IOOI formation was calculated to be 37.5 kcal mol^{-1} (at 298 K).[171] As suggested by the authors of this work,[171] OIO may be among the products of the IO + IO reaction.

Apparently, IOO radicals are still less stable as compared with ClOO radicals.[171, 172]

The reaction of IO and ClO radicals at 298 K and the total pressure of 1 Torr was studied by mass spectrometry [173]

$$IO + ClO \longrightarrow I + OClO, \quad (5a)$$

$$IO + ClO \longrightarrow I + Cl + O_2, \quad (5b)$$

$$IO + ClO \longrightarrow ICl + O_2. \quad (5c)$$

For reactions (5), the rate constant $k_5 = (1.1\pm0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and the branching ratios $k_{5a}/k_5 = 0.55\pm0.03$, $k_{5b}/k_5 = 0.25\pm0.02$ and $k_{5c}/k_5 = 0.20\pm0.02$ were found.[173] The value $k_5 = (1.29\pm0.27) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (298 K) was also obtained.[172]

The channel

$$IO + ClO \longrightarrow Cl + OIO$$

was assumed to be highly improbable.

The most important source of iodine in the atmosphere is methyl iodide, which is liberated by algae and phytoplankton of the ocean and is rapidly photolysed in the troposphere. Iodine compounds can get to the stratosphere as a result of convection. Nuclear stations can also be a source of atmospheric contamination with iodine. The activity of iodine in the atmosphere is associated particularly with the absence of a photolytically stable reservoir of iodine-containing molecules.

* * *

Until recently, insufficient attention has been paid, for very clear reasons, to halogen–oxygen compounds X_2O_2, with the exception of dioxygen difluoride. The interest which has been aroused in these and related compounds was associated with the problem of stratospheric ozone depletion. The use of traditional and advanced methods for studying the properties of unstable compounds, as well as theoretical calculations of different levels allowed certain characteristics of both existing and imaginary compounds with the general formula X_2O_2 to be obtained. In this review, an attempt is undertaken to draw their 'portraits' based on the data taken from literature sources in which these compounds are discussed. The work dealing with other oxygen compounds of halogens are beyond the scope of this survey.

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