Russian Chemical Reviews **73** (6) 609 – 619 (2004) © 2004 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2004v073n06ABEH000879

Oxy acids of halogens HOHal

I V Nikitin

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Abstract. The key methods for the synthesis of the acids HOF, HOCl, HOBr and HOI are considered. The results of investigations of the structures and properties of these acids are described. Possible participation of the HOHal acids in the destruction of stratospheric ozone is discussed. The bibliography includes 207 references.

I. Introduction

The aim of this review is to characterise a group of relatively little-known triatomic compounds of general formula HOHal belonging to the group of oxy acids of halogens. There are several types of oxy acids of halogens; however, only the triatomic acids HOHal are known for all halogens including fluorine, which forms hypofluorous acid. It is customary to use the suffix 'vatistaya' when naming the HOHal acids in the chemical literature written in Russian; its English equivalent is the suffix 'ous', which is used throughout the text of the review. Sometimes the compounds in question are called halogen hydroxides.

All the HOHal acids are unstable. They display a powerful oxidising action. The 'eldest' is hypochlorous acid, HOCl, whose salts have been known since the late 18th or early 19th century ('eau de Javelle', 'eau de Labarraque'). Salts of hypochlorous acid, *e.g.*, bleaching powder, calcium hypochlorite and sodium hypochlorite have found wide applications in the home and in industry as oxidants, bleaching agents, degassing agents and disinfectants. The chemistry of aqueous solutions of hypochlorous acid and its salts had been well studied by the mid-twentieth century. The acids of general formula HOHal have attracted considerable attention since the synthesis of hypofluorous acid and mainly in connection with the development of atmospheric chemistry. Possible involvement of halogen-containing small molecules† in the catalytic cycles of destruction of stratospheric ozone gave an impetus to investigations on the spectroscopic characteristics, photochemistry and reactivity (in particular, under conditions that simulate stratospheric conditions) of these species. Studies on the properties of hypofluorous acid and other hypohalous acids HOHal have also been reported. These new data are complementary to scarce information on these acids available from books on inorganic chemistry and handbooks.

I V Nikitin Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-096) 576 40 09. Tel. (7-096) 522 35 70.
E-mail: led@icp.ac.ru

Received 2 October 2003
Uspekhi Khimii **73** (6) 662 – 672 (2004); translated by A M Raevskiy

II. Hypofluorous acid

Hypofluorous acid has long been considered a 'non-existent' compound [2] though its synthesis does not require hard-to-access starting compounds or unusual equipment.

Production of hypofluorous acid in the form of a complex with HF in the course of photolysis of a mixture of H_2O with F_2 in a low-temperature nitrogen matrix at 14 and 20 K was detected by IR spectroscopy in 1968.[3] The first synthesis of HOF was reported in 1971.[4]

HOF is synthesised from gaseous fluorine and liquid water or ice by bubbling fluorine through water one time at 223 – 233 K. Sometimes the reaction of fluorine with water is carried out in a recirculating system.

$$F_2 + H_2O \longrightarrow HOF + HF.$$

In spite of low reaction rate and low yield of HOF, the amount of the acid thus obtained can vary from several tens to several hundreds of milligrams.[2] The by-products of the reaction are oxygen difluoride, OF_2, and oxygen. It was assumed [5,6] that oxygen difluoride is produced in the reaction

$$F_2 + HOF \longrightarrow OF_2 + HF.$$

Later on, this assumption was confirmed experimentally. Using tracers (^{18}O and ^{18}F), it was shown that the OF_2 molecule contains one fluorine atom from the hypofluorous acid molecule and one fluorine atom from the F_2 molecule.[7] The reaction of fluorine with D_2O gave deuterated hypofluorous acid.

Noteworthy is that oxygen difluoride is not an anhydride of hypofluorous acid (no acid is produced upon dissolution of this compound in water). This differentiates OF_2 from dichlorine monoxide which gives hypochlorous acid upon dissolution in water.

Photolysis of a mixture of H_2O with F_2 in argon matrix produces HOF in the form of a complex with HF.[3] A thorough study of photolysis of $H_2O - F_2$ mixtures in solid argon at 12 K revealed the formation of complexes HF – HOF, FH – FOH and FH – OHF, the first-mentioned complex being the most stable.[8]

† The review [1] concerns tetraatomic compounds of halogens Hal_2O_2, which are of interest for atmospheric chemistry.

Hypofluorous acid is stable at the boiling temperature of liquid nitrogen but decomposes into HF and O_2 (sometimes, explosively) on heating. The half-life of HOF is $\sim$30 min at room temperature;[2] however, it increases to $\sim$3 h in a passivated IR spectroscopic cell.[9] The melting temperature of HOF is 156 K while its boiling temperature is somewhat lower than room temperature. The vapour pressure of HOF is at most 1 Torr at 194 K and nearly 5 Torr at 209 K (more accurate vapour pressure measurements are impossible because of the decomposition of the acid).[4]

The HOF molecule is a slightly asymmetrical prolate rotor characterised by the rotational constants $A_0 = 585\,628.93$, $B_0 = 26\,757.53$ and $C_0 = 25\,514.10$ MHz (see Refs 10, 11) and by the parameter $\kappa = 2[B-1/2(A+C)]/(A-C) = -0.9955$. The rotational constant values were repeatedly refined (see Refs 9, 12, 13). The rotational constants of the $H^{16}OF$ molecule are as follows: $A_e = 19.663796$, $B_e = 0.9003148$ and $C_e = 0.8608167$ cm^{-1}.[13]

An X-ray diffraction study [14] showed that the single crystal of HOF belongs to the orthorhombic crystal system. The lattice constants are $a = 4.075$, $b = 5.040$ and $c = 5.939$ Å; the space group is $P2_12_12_1$. The single crystal was grown by slow cooling of the HOF sample down to 113 K. Table 1 lists the experimental (obtained by X-ray analysis [14] and microwave spectroscopy [10, 11]) and calculated [15] bond lengths and bond angles in the HOF molecule.

Table 1. Bond lengths and bond angles in the HOF molecule.

Method	r(O–F) /Å	r(O–H) /Å	HOF angle /deg	Ref.
X-Ray analysis	1.442	0.78	101	14
Microwave	1.442	0.964	97.2	10
spectroscopy	1.442	0.966	96.78	11
TZP CCSD [a]	1.4356	0.9664	97.72	15

[a] *Ab initio* calculations using the Triple-Zeta-Plus-Polarisation Coupled Cluster Method with Single and Double Excitations.

The HOF molecule has a large dipole moment, $\mu_{exp} = 2.23 \pm 0.10$ D.[16] *Ab initio* calculations gave the values of 2.18 D (see Ref. 17) and 2.032–2.182 D (see Ref. 15).

Hypofluorous acid forms no associates in the gas phase (at least at pressures below 160 Torr) [18] but undergoes association in the condensed phase. Initially, it was hypothesised [18, 19] that the HOF molecules are linked together through O–H...F bridges; however, this assumption was rejected.[20] Taking into account the fact that the oxygen atom in the HOF molecule bears a larger negative charge compared to the fluorine atom owing to withdrawal of the electron density from the hydrogen atom, one could expect the formation of O–H...O bridges. It was reported [20] that in self-association of hypofluorous acid involving O–H...O bridges the HOF molecules form zig-zag chains or large cycles, $(HOF)_n$.[20] An X-ray diffraction study [14] confirmed the presence of nearly linear bridges O–H...O [O–H...O 163°, r(H...O) = 2.895 Å] in the single crystal of HOF (Fig. 1).

An IR spectroscopic study of photochemical reactions of hypofluorous acid in low-temperature matrices revealed the formation of dimers, $(HOF)_2$, and, probably, other oligomers of HOF.[21] It was concluded [21] that the HOF molecules form dimers $(HOF)_2$ linked through the O–H...O bridge (acyclic dimer). *Ab initio* calculations [22] showed that the O–H...O bridge in the dimer is stronger than the O–H...F bridge. Other *ab initio* calculations [23] revealed two stable $(HOF)_2$ structures differing in orientation of the constituent HOF molecules, namely, a linear structure of C_1 symmetry (molecules are linked together through both O–H...O and O–H...F bridges) and a cyclic structure of C_2 symmetry (here, molecules form dimers involving two O–H...F bridges). The linear structure is more stable, though the energy of the cyclic structure is only 0.35 kcal mol^{-1} higher.

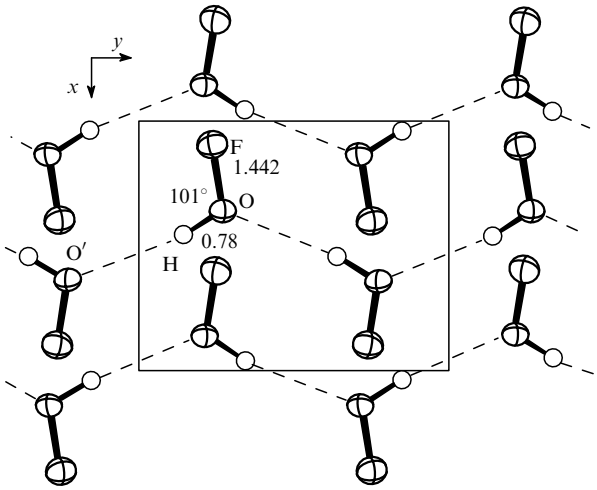


Figure 1. Crystal structure of HOF.[14]

The vibrational spectrum of HOF molecules has been thoroughly studied [9, 13, 18, 19, 21, 24, 25] (see Table 2).

Gaseous hypofluorous acid is characterised by intense absorption in the region $\lambda < 300$ nm; no pronounced absorption maximum is observed.[21] According to calculations,[26] the absorption spectrum of HOF exhibits two maxima, one in the region $\lambda < 200$ nm and the other in the region $\lambda > 200$ nm.

The ^1H and ^{19}F NMR spectra of hypofluorous acid were recorded [27] shortly after the pioneering synthetic study. The chemical shift of the F atom is 403 ppm (171 K) or 402 ppm (193 K) relative to gaseous fluorine at 298 K. The proton chemical shift is −16.0 ppm (193 K) or −12.1 ppm (293 K) relative to gaseous methane at 298 K. Fast proton exchange between HOF and HF present in the sample was demonstrated for the liquid phase.

The mass spectrum of HOF exhibits a peak of a molecular ion.[4] Photoionisation of hypofluorous acid at $\lambda = 77.5$ nm produces HOF^+, OH^+ and O^+ ions with the relative intensities of 100, 37 and 44 arbitrary units, respectively.[28] The first ionisation potential of the HOF molecule is 12.71 ± 0.01 eV [28] and nearly coincides with the adiabatic ionisation potential (12.69 ± 0.03 eV) determined from the HeI photoelectron spectrum of hypofluorous acid.[29] GAUSSIAN-2 (G2)‡ calculations [30] of the adiabatic ionisation energy of HOF gave a value of 12.71 eV.

The enthalpy of formation of hypofluorous acid determined in the study on photoionisation of HOF is -22.8 ± 1 (0 K) or -23.5 ± 1 kcal mol^{-1} (298 K).[28] A more accurate value is $\Delta H^\circ(HOF) = -19.9$ kcal mol^{-1} (0 K);[32] however, it was refined [33] and a new value of −19.5 kcal mol^{-1} (0 K) was reported. The results of some calculations very closely approach the experimental value of the enthalpy of formation of HOF (Table 3).

The adiabatic bond dissociation energy, $D_0(HO-F)$, of HO–F (50.4 kcal mol^{-1}) [28] was then recalculated. The refined $D_0(HO-F)$ value is 47.5 kcal mol^{-1} (see Ref. 32). Table 3 lists the bond dissociation energies reported in different studies. The atomisation energy of HOF obtained from G2 calculations [31] is 149.7 kcal mol^{-1}.

Proton affinity calculations for the HOF molecule were carried out for protonation at the O atom and at the F atom [routes (1) and (2), respectively].

$$HOF + H^+ \longrightarrow H_2OF^+ \quad (1)$$

‡ For G2 calculations, see Ref. 31.

Table 2. Main vibrational frequencies of HOF molecule.

Method	Spectrum recording conditions	ν /cm^{-1}			Ref.
		ν_1 (O–H, stretching vibration)	ν_2 (bending vibration)	ν_3 (O–F, stretching vibration)	
IR spectroscopy	gas phase	3578.5	1354.8	889.0	24
	low-temperature matrix	3537.1	1359.0	886.0	25
	the same	3572	1350	888	21
	HOF film, 78 K	3370	1397	885	19
High resolution FT-IR spectroscopy	H^{16}OF	3577.92580	1353.40466	889.07974	9, 13
Raman spectroscopy	77 K	3359	–	884	18

Table 3. Enthalpies of formation of HOF molecule (kcal mol^{-1}) and bond dissociation energies (kcal mol^{-1}) in the HOF molecule.

Computational method	ΔH°(HOF) (T /K)	D_0(HO–F)	D_0(H–OF)	Ref.
GAUSSIAN 1 (G1) [a]	–19.9 (0)	47.5	–	32
Refined values	–19.5 (0)	47.3	97.0	33
G2	–21.1 (298)	48.1	–	30
Quantum-chemical calculations				
B3LYP	–20.43±1.92 (298.15)	45.91	95.00	34
B3PW91	–20.35±1.34	46.20	115.05	34
CCSD(T)	(298.15)	45.77	98.17	34

[a] For G1 calculations, see Ref. 35.

and

$$HOF + H^+ \longrightarrow HOFH^+. \quad (2)$$

The former process was found to be preferred (Table 4).[30, 36–39] The O–F interatomic distance in the $HOFH^+$ and H_2OF^+ molecules is respectively longer and shorter than in the HOF molecule.[30, 36] According to G2 calculations, protonation of HOF at the oxygen atom is 18 kcal mol^{-1} more energetically favourable than protonation at the F atom.[34] (Protonation of other HOHal acids at the oxygen atom is also more energetically favourable.[30])

The possibility of using hypofluorous acid as the starting reagent in the synthesis of other compounds was studied by Appelman and co-workers.[2, 5, 6, 40–42] shortly after the synthesis of HOF. Hypofluorous acid appeared to be an excellent donor of oxygen atoms; however, the short lifetime of HOF at temperatures close to room temperature hampers the wide use of this compound.

Table 4. Proton affinity energy of the HOF molecule (298 K).

Computational method	Proton affinity energy /kcal mol^{-1}		Ref.
	protonation at the O atom	protonation at the F atom	
G2	135.2	116.8	30
	133.8	115.9	37
DFT/PW91 [a]	141.5	122.6	39

[a] *Ab initio* density functional calculations with the Perdew–Wang functional (PW91).

Photolysis of HOF in low-temperature matrices is thought to proceed as concerted elimination of HF to produce O(^{1}D) or O(^{3}P).[21]

$$HOF \xrightarrow{h\nu} O + HF.$$

In the case of non-inert matrices, the oxygen atoms enter in the reaction with the matrix molecules or with the dopant. For instance, photolysis of HOF in argon matrices doped with PF_3, AsF_3 or H_2O produces OPF_3, $OAsF_3$ or H_2O_2, respectively.

The possibility of using hypofluorous acid as oxidant has been thoroughly studied by Rozen and co-workers.[43–58] It was found that bubbling gaseous fluorine diluted with N_2 through a vigorously stirring mixture of acetonitrile with distilled water (usually, 10 : 1 or 20 : 1 by volume) at 263 or 258 K results in an oxidising solution with the oxidant concentration exceeding 1 mol litre^{-1}. Shortly after, it was established that the active component is the complex MeCN · HOF. The half-life of this complex is longer than 10 h at 273 K or 3 to 4 h at room temperature. This indicates that acetonitrile stabilises hypofluorous acid formed in the reaction of fluorine with water (HOF retains its oxidising properties).

^{19}F NMR and IR spectroscopies confirmed that HOF and acetonitrile form a rather stable 1 : 1 complex.[59] An X-ray diffraction study[60] of the complex MeCN · HOF carried out at 143 K revealed that the HOF and MeCN molecules are linked *via* a linear hydrogen bridge, O–H...N, 2.81 Å long (interatomic distance H...N is 1.71 Å).

Reactions involving the complex MeCN · HOF proceed under mild conditions at temperatures between 273 K and room temperature. A feature of these processes is their high rates (the reactions are completed in a few seconds to several minutes). In many cases, the product yields are as high as 90% to 100%. Often, compounds obtained using this complex cannot be synthesised by other methods.[54] Hydrogen fluoride formed as a by-product can be readily neutralised with calcium hydroxide.[56]

Complex MeCN · HOF is used for fast and efficient epoxidation of various olefins.[43, 45, 47, 49] The time taken to convert cyclooctene into epoxycyclooctane by the reaction with the complex MeCN · HOF at 273 K is shorter than 1 min; this also holds for the epoxidation of *trans*-stilbene.[45] Epoxidation of $C_4F_9CH=CH_2$ proceeds at a lower rate while sterically hindered $C_4F_9CH=CHC_4F_9$ does not enter into reaction.[47] Since the oxygen atom of the oxirane ring is supplied by the HOF molecule, it is possible to obtain epoxides containing tracers (^{17}O or ^{18}O isotopes) when using labelled water to synthesise HOF. This method allows the oxygen isotopes to be introduced into other compounds.[44–46, 48]

Reactions of anthracene and phenanthrene with MeCN · HOF produce quinones,[50] while pyrene, 2-acetylphenanthrene and 9-acetylphenanthrene are converted into epoxides.[57] Complex MeCN · HOF is used for the oxidation of aromatic amines[46] and aliphatic amines[48] to corresponding nitro compounds and for the oxidation of amino acid esters into nitrate esters.[51] The oxidation of AlkOMe ethers involves elimination of methanol, the ethers

with Alk = n-C_nH_{2n+1} being oxidised to acids (*via* aldehydes) while those with Alk = *sec*-C_nH_{2n+1} are oxidised to ketones and lactones.[54]

MeCN·HOF readily oxidises both aliphatic and aromatic sulfides to sulfones.[56] The reactions proceed at 198 K and involve an intermediate formation of sulfoxides that can be isolated in high yields.[56] Under these conditions, thiophenes are converted into corresponding *S*-dioxides.[52]

Thus, the complex MeCN·HOF is an efficient oxygen transfer agent. The oxidation reactions with participation of this complex proceed under mild conditions and in some cases at very high rates. The complex offers yet another remarkable advantage as a reactant, namely, no isolation, purification or other specific operations are needed when using it.

III. Hypochlorous acid

Traditionally, hypochlorous acid is synthesised by the reaction of chlorine with an aqueous suspension of yellow (red) mercury oxide or with moist mercury oxide powder.

$$HgO + 2Cl_2 + H_2O \longrightarrow 2HOCl + HgCl_2.$$

Hydrochloric acid formed in the reaction of chlorine with water (for the kinetics of hydrolysis of chlorine, see Ref. 61) reacts with mercury oxide, thus shifting the equilibrium in the reaction (3) to the right and giving an aqueous hypochlorous acid solution.

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl, \qquad (3, -3)$$

$$HgO + 2HCl \longrightarrow HgCl_2 + H_2O.$$

The reaction of chlorine with mercury oxide in the absence of water is known as a method for the synthesis of dichlorine monoxide. An approximate reaction equation has the form

$$2Cl_2 + HgO \longrightarrow Cl_2O + HgCl_2.$$

Being an anhydride of hypochlorous acid, Cl_2O is readily soluble in water, thus producing HOCl.

$$Cl_2O + H_2O \rightleftharpoons 2HOCl. \qquad (4, -4)$$

At room temperature, the equilibrium mixture $H_2O-Cl_2O-HOCl$ is stable over a period of a few hours.[62, 63] The equilibrium constant for the gas-phase reaction (4, −4) of hydrolysis of Cl_2O at room temperature ($K = 0.25$) calculated [62] in a study of the UV spectrum of HOCl appeared to be overestimated as compared to the results obtained in more recent studies.[63–66]

T/K	K	Method	Ref.
298	0.25	UV	62
298	0.082	UV	63
295 ± 3	0.068	IR	64
298	0.092 ± 0.011	LPMS-DFS [a]	65
298	0.10 ± 0.01	UV	66

[a] LPMS-DFS stands for Low-Pressure Mass Spectrometry–Discharge Flow System.

Hypochlorous acid is also synthesised by the reaction of aqueous sodium hypochlorite solution with aqueous solutions of magnesium sulfate heptahydrate or anhydrous $MgSO_4$.[67–70]

The acid HOCl was obtained in the reaction of hydrogen chloride with calcium hypochlorite powder.[71] The interaction between hydrogen fluoride diluted with N_2 and calcium hypochlorite powder also results in hypochlorous acid.[72, 73]

$$2HF + Ca(OCl)_2 \longrightarrow 2HOCl + CaF_2.$$

Gaseous HOCl is obtained by bubbling gaseous chlorine diluted with helium through an aqueous suspension of $CaCO_3$ (see Ref. 65).

$$2Cl_2 + H_2O + CaCO_3 \longrightarrow 2HOCl + CO_2 + CaCl_2.$$

The acid thus formed is immediately converted to the gas phase to prevent its decomposition into Cl_2O and H_2O. Sodium hydrocarbonate can be used instead of calcium carbonate; in this case, the reaction proceeds at a higher rate.[74]

The reaction of chlorine with concentrated hydrogen peroxide solution in alkali medium produces excited dioxygen in 100% yield.[75–77]

$$Cl_2 + H_2O_2 + 2OH^- \longrightarrow O_2(^1\Delta) + 2H_2O + 2Cl^-.$$

The main goal of investigations on the properties of HOHal acids carried out in the last decades is to study the behaviour of these compounds in the Earth's atmosphere and to establish their role in the destruction of stratospheric ozone.

Formation and decomposition reactions of HOCl in the stratosphere have been the subject of scientific research since the 1980s. Most studies are concerned with the radical–radical reaction $ClO^{\bullet} + HO_2^{\bullet}$ and with hydrolysis of chlorine nitrate because both processes can produce HOCl.

Tentatively, a bimolecular reaction $ClO^{\bullet} + HO_2^{\bullet}$ results in the following products:[78, 79]

Reaction	Products	ΔH(298 K) /kcal mol^{-1}	Reaction channel
$ClO^{\bullet} + HO_2^{\bullet}$	$HOCl + O_2$	−46	(*a*)
	$HCl + O_3$	−15	(*b*)
	$ClOO^{\bullet} + OH^{\bullet}$	+2.9	(*c*)
	$OClO^{\bullet} + OH^{\bullet}$	+6.0	
	$HClO + O_2$	+17	

Hypochlorous acid is formed following route (*a*). At 210–300 K, the contribution of this channel to the overall reaction exceeds 95% while that of channel (*b*) is only 5 ± 2%.[79] Quantum-chemical calculations [80] also showed that route (*a*) is the most energetically favourable and that channel (*b*) is impracticable.§ The probability of a weakly endothermic reaction (*c*) is also low.

Hypochlorous acid is formed as a result of the reaction of radical $ClO^{\bullet}$ with the hydrogen atom of the radical $HO_2^{\bullet}$ and in a more complex way *via* decomposition of the cyclic intermediate OClOOH produced upon the attack of the Cl atom of the radical $ClO^{\bullet}$ on the terminal oxygen atom of the $HO_2^{\bullet}$ radical (see Refs 78, 79, 82–86). The former mechanism dominates at $T > 370$ K while the latter governs the reaction at temperatures below 270 K. The fast reaction $ClO^{\bullet} + HO_2^{\bullet} \longrightarrow HOCl + O_2$ is characterised by a rate constant of $(4.5-6.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.[78] Yet another estimate of the rate constant for this reaction is $(7.1 \pm 1.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 294 K.[81]

Chlorine nitrate is inert towards ozone; however, hydrolysis of $ClONO_2$ and its interaction with HCl which proceed on the surface of aerosol particles are followed by the formation of catalytically active molecules HOCl and Cl_2.[87, 88]

$$ClONO_2 + H_2O \longrightarrow HOCl + HNO_3,$$

$$ClONO_2 + HCl \longrightarrow Cl_2 + HNO_3.$$

The reaction of gaseous chlorine nitrate with water is very slow.[89] At the same time, hydrolysis of $ClONO_2$ adsorbed on the surface of aerosol particles proceeds at a much higher rate. This reaction was studied by many authors (see, *e.g.*, Refs 71, 89–112). The reaction rate is affected by several factors, namely, temperature, aerosol particle size, surface structure, $ClONO_2 : H_2O$ ratio, presence of unbound water. In type-I polar stratospheric clouds containing mainly nitric acid trihydrate, hydrolysis of chlorine nitrate proceeds at a lower rate compared to the process in type-II clouds (hexagonal ice Ih).[90] However, this reaction proceeds rapidly in water-enriched type-I clouds.[107] Solvation of $ClONO_2$

§ The contribution of channel (*b*) to the overall reaction $ClO^{\bullet} + HO_2^{\bullet}$ is at most 1%.[81]

causes a substantial decrease in the activation energy for the hydrolysis reaction.[105, 107, 109, 110]

Using a tracer technique, it was shown that hydrolysis of $ClONO_2$ on ice ($H_2{}^{18}O$) produces $H^{18}OCl$ rather than $H^{18}ONO_2$.[98] The presence of the ^{18}O isotope in the hypochlorous acid molecule indicates cleavage of the $Cl-ONO_2$ bond in the chlorine nitrate molecule upon hydrolysis. The positively charged chlorine atom (+0.08) in the $ClONO_2$ molecule appears to be more accessible to the attacking oxygen atom of the water molecule (−0.36) than the positively charged N atom (+1.34) shielded by oxygen atoms.[106]

One would assume that nucleophilic attack of the water molecule results in a reactive intermediate, H_2OCl^+, which can be rapidly hydrolysed in a sufficient amount of water.[89, 97, 106]

$$H_2O + ClONO_2 \longrightarrow H_2OCl^+ + ONO_2^-,$$

$$H_2O + H_2OCl^+ \longrightarrow H_3O^+ + HOCl.$$

However, another mechanism of hydrolysis was found to be preferred.

$$ClONO_2 + 3H_2O \longrightarrow HOCl\cdot NO_3^-\cdot H_3O^+\cdot H_2O.$$

This mechanism is 10 to 14 kcal mol^{-1} more energetically favourable.[107, 111] An IR spectroscopic study of the products of hydrolysis of $ClONO_2$ also gave no proofs of the formation of H_2OCl^+ ion (see Ref. 111). Hydrolysis of $ClONO_2$ on ice proceeds efficiently at 75–140 K.[105] At temperatures below 155 K, hypochlorous acid thus obtained is adsorbed on the surface of ice and then goes to the gas phase at 155–185 K.[104, 108] The measured enthalpy of adsorption of HOCl on ice is -8.5 ± 2 kcal mol^{-1}, which is close to the published experimental and calculated values (see Ref. 69). The HOCl molecule forms a hydrogen bond with the water molecule, thus acting as a proton donor.[103, 113]

Hypochlorous acid is also formed in the reaction of hydroxyl radicals with chlorine or dichlorine monoxide.

$$^{\bullet}OH + Cl_2 \xrightarrow{a} HOCl + Cl^{\bullet}$$
$$^{\bullet}OH + Cl_2 \xrightarrow{b} HCl + ClO^{\bullet}$$

$$^{\bullet}OH + Cl_2O \longrightarrow HOCl + ClO^{\bullet}. \quad (5)$$

The reaction with chlorine almost exclusively follows route *a*.[114] The rate constant for the reaction is 6.70×10^{-14} cm^3 $molecule^{-1}$ s^{-1} at 298 K (according to Ref. 114) and $(6.8 \pm 1.0) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 293 K (according to Ref. 115).

The rate constant for reaction (5) in the temperature interval 236–383 K is inversely proportional to temperature:[116]

$$k_5 = (1.7 \pm 0.8) \times 10^{-12} \exp\left(\frac{420 \pm 170}{T}\right) \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

At 298 K and a total pressure of 2 Torr, one has $k_5 = (7.4 \pm 0.6) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. Probably, a long-lived cyclic compound HOClOCl is formed as an intermediate product of this reaction.[116]

The reaction of hydroxyl radicals with chlorine dioxide also produces hypochlorous acid.[117]

$$^{\bullet}OH + OClO^{\bullet} \longrightarrow HOCl + O_2.$$

The microwave and IR spectra of HOCl have been the subject of numerous experimental and theoretical studies.[110, 118–137] Table 5 lists the bond lengths and bond angles in the HOCl molecule reported by different authors.

The HOCl molecule is a nearly symmetrical prolate rotor characterised by the parameter $\kappa = -0.998$ (see Ref. 121) and rotational constants (for $HO^{35}Cl$) $A_e = 20.49760$, $B_e = 0.50735$ and $C_e = 0.49509$ cm^{-1} (see Ref. 133). CCSD(T)/TZ2P calculations[93] gave a value of 1.56 D for the dipole moment of the HOCl molecule.

Table 5. Experimental and calculated geometric parameters of the HOCl molecule.

Method	r(O–Cl) /Å	r(O–H) /Å	HOCl angle /deg	Ref.
Microwave spectroscopy	1.693	0.97	103	118
IR spectroscopy	1.6891	0.9643	102.96	126
IR spectroscopy	1.68897	0.96437	102.965	133
DFT/B3LYP/G-311G(3df)	1.700	0.965	103.4	138

Table 6 lists the main vibrational frequencies in the gas-phase high resolution IR spectra of hypochlorous acid.

Numerous studies (see, *e.g.*, Refs 26, 62, 63, 66, 74, 137, 139–146) concern the UV absorption spectrum and photolysis of gaseous HOCl. At room temperature, the absorption spectrum of the HOCl molecule in the region 200–380 nm exhibits two maxima at 242 and 304 nm [absorption cross sections, σ, are $(2.1 \pm 0.3) \times 10^{-19}$ and 0.61×10^{-19} cm^2, respectively].[66] A weak peak was also detected at 380 nm ($\sigma = 4 \times 10^{-21}$ cm^2); the long-wavelength absorption extends to 480 nm ($\sigma = 5.52 \times 10^{-23}$ cm^2).[146]

Table 6. Vibrational frequencies in the IR spectrum of the $HO^{35}Cl$ molecule.

Frequency	Numerical value /cm^{-1}	Assignment	Ref.
ν_1	3609.48013	O–H stretch	120
ν_2	1238.62460	bending vibration	125
ν_3	724.35807	Cl–O stretch	125

Photolysis of HOCl produces mainly $^{\bullet}OH$ and $^{\bullet}Cl$ radicals. Other decomposition channels ($O^{\bullet} + HCl$ or $H^{\bullet} + {}^{\bullet}OCl$) are of little importance or not involved.[140, 141, 144] Photodissociation of HOCl causes destruction of stratospheric ozone

$$HOCl + h\nu \longrightarrow {}^{\bullet}OH(^2\Pi) + Cl^{\bullet}(^2P)$$
$$^{\bullet}OH + O_3 \longrightarrow HO_2^{\bullet} + O_2$$
$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$
$$HO_2^{\bullet} + ClO^{\bullet} \longrightarrow HOCl + O_2$$

$$2\,O_3 \longrightarrow 3\,O_2$$

The lifetime of hypochlorous acid in the stratosphere under photolysis conditions is at most 30 min.[140, 146] The lifetime of HOCl in the mid-stratosphere (no photolysis) could be as long as ~600 h.[65]

The EI mass spectrum of HOCl exhibits peaks of molecular ions at m/e 52 and 54 (two isotopes, ^{35}Cl and ^{37}Cl).[70] The adiabatic and vertical ionisation energies determined from the HeI photoelectron spectrum of hypochlorous acid are 11.12 ± 0.01 and 11.22 ± 0.01 eV, respectively.[147] A photoionisation mass spectrometric study[148] of HOCl gave an adiabatic ionisation energy of 11.12 ± 0.01 eV, which coincides with the published value.[147] Using this value, Thorn *et al.*[148] calculated the enthalpy of formation of $HOCl^+$ [$\Delta H^\circ_{298}(HOCl^+) = 238.2 \pm 0.9$ kcal mol^{-1}]

and the proton affinity energy of ClO [$PA_{298}(ClO) = 151.8 \pm 0.9$ kcal mol^{-1}].

The enthalpies of formation of HOCl reported in the studies carried out at different times differ only slightly from one another (the ΔH_0° are given in parentheses).

ΔH_{298}(HOCl) /kcal mol^{-1}	−17.9	−18.0	−18.0	−18.4	−19.0	(−16.7)	(−17.2)
Ref.	64	63	65	149	67	150	32

QCISD(T)/6-311 + + G(3df,3pd)//QCISD(T)/6-311G(2d,2p) calculations [151] led to $\Delta H_{298}^\circ(HOCl) = -19.9 \pm 2$ kcal mol^{-1}. The values obtained later on using other computational methods are −18.2 (G2 calculations for 298 K) [30] and −17.5 kcal mol^{-1} [MP4/6-311 + G(d,p)].[138]

An exactly measured bond dissociation energy, $D_0(^{35}Cl-OH)$, is 55.15 kcal mol^{-1} (19290.3 ± 0.6 cm^{-1}).[152, 153] *Ab initio* G2 calculations gave $D_0(HO-Cl) = 55.2$ (see Ref. 30) and 55.25 kcal mol^{-1} (see Ref. 138). The result of density functional calculations [138] [B3LYP/6-31G(d) approximation], 55.24 kcal mol^{-1}, is also close to the experimental data. The H−OCl bond is stronger than the HO−Cl bond; the dissociation energy $D_0(H-OCl)$ is 93.8 kcal mol^{-1} (see Ref. 33) or 92.9 kcal mol^{-1} (see Ref. 154).

According to calculations, the HOCl isomer is 51.6 ± 1.2 kcal mol^{-1} (0 K) more stable than the HClO isomer.[155] The electron affinity energy of the HOCl molecule is low, namely, 0.27 eV (6.23 kcal mol^{-1}).[70] Protonation of HOCl at the oxygen atom ($HOCl + H^+ \longrightarrow H_2OCl^+$) is energetically more favourable compared to protonation at the chlorine atom ($HOCl + H^+ \longrightarrow HOClH^+$). The G2 calculated proton affinity energy is 153.4 kcal mol^{-1} in the former and 139 kcal mol^{-1} in the latter case (298 K).[30] The corresponding values obtained from density functional (PW91) calculations are 157.7 (298 K) and 140.1 kcal mol^{-1} (0 K).[39] Yet another computational study [156] also revealed that protonation at the oxygen atom is 16.2 kcal mol^{-1} energetically more preferable. The geometric parameters of the H_2OCl^+ ion calculated [110] at the B3LYP/6-311 + + G(d,p) level are as follows: $r(O-Cl) = 1.772$ Å, $r(O-H) = 0.984$ Å, the H−O−H angle is 123.9° and the H−O−Cl angle is 111.0°. The O−Cl bond length was also estimated at 1.78 Å.[157]

The reaction of hypochlorous acid with hydrogen chloride proceeding on the surface of ice or in sulfate aerosols can be a source of active chlorine in the stratosphere.[68, 71–73, 94, 96, 108, 158]

$$HOCl + HCl \longrightarrow Cl_2 + H_2O.$$

It is assumed [73] that protonation of HOCl is followed by the reaction of H_2OCl^+ ion with Cl^- producing Cl_2 and H_2O. Besides, HOCl can participate in the formation of active bromine monochloride following the reaction

$$HOCl + HBr \longrightarrow BrCl + H_2O.$$

Table 7. Rate constants for reactions involving HOCl (298 K).

Reaction	k /cm^3 molecule^{-1} s^{-1}	Ref.
HOCl + NO → products	1.0×10^{-17} (see [a])	159
HOCl + O_3 → products	4.0×10^{-16} (see [a])	159
HOCl + OH → H_2O + ClO	$(1.7-9.5) \times 10^{-13}$	160
HOCl + H → products	$(5.0 \pm 1.4) \times 10^{-12}$	160
HOCl + H → products	$(3.5 \pm 0.7) \times 10^{-12}$	67
HOCl + H → HCl + OH	$(6.7 \pm 2.1) \times 10^{-13}$ (see [a])	67
HOCl + Cl → products	$(1.4 \pm 0.37) \times 10^{-12}$	67
HOCl + Cl → Cl_2 + OH	$(3.4 \pm 1.5) \times 10^{-13}$	67
HOCl + F → products	$(4.9 \pm 0.6) \times 10^{-11}$	67
HOCl + F → ClF + OH	$(1.2 \pm 0.4) \times 10^{-11}$	67

[a] Given is the upper bound.

However, this reaction is of little importance because the concentration of hydrogen bromide in the atmosphere is at most 2 ppt (1 ppt = 10^{-12}).[69]

Table 7 lists the rate constants for some reactions involving HOCl calculated using the microwave discharge technique and mass spectrometry.

IV. Hypobromous acid

The first syntheses of solutions of hypobromous acid date back to the 1860s (cited according to Refs 161 and 162). Aqueous HOBr solutions are prepared by slowly adding liquid bromine to an aqueous solution of silver nitrate at room temperature.[161, 162] Subsequent vacuum distillation gives solutions with HOBr concentrations of about 0.2 mol litre^{-1}. Hypobromous acid is also formed in the reaction of bromine with an aqueous suspension of yellow mercury oxide (for hydrolysis of bromine, see Ref. 163). The reaction is conducted by passing water vapour and bromine through a column filled with mercury oxide supported by glass beads.[164, 165] Yet another procedure for the synthesis of hypobromous acid involves prolonged stirring of bromine in excess of water in the presence of Ag_2O powder.[33] The reaction was reported to proceed better in the presence of Ag_2O rather than mercury oxide.[33] A solution of HOBr was also prepared by the reaction of bromine with a 0.5 N solution of sulfuric acid in the presence of silver sulfate.[166]

By analogy with HOCl, hypobromous acid can be synthesised in the reaction of Br_2O with water.

$$Br_2O + H_2O \rightleftharpoons 2\,HOBr. \qquad (6, -6)$$

However, unlike a rather stable (at room temperature) Cl_2O, dibromine monoxide is stable only at temperatures below 233 K. It is produced by the reaction

$$2\,Br_2 + HgO \longrightarrow Br_2O + HgBr_2,$$

the yield of Br_2O being at most 1%–2%.[167, 168]

The rate constant for the reaction (6, −6) at 298 K is 0.02 (see Ref. 167) or 0.037 ± 0.004 (see Ref. 168).

HOBr for spectroscopic studies is obtained by fast exothermic reaction of $^\bullet$OH radicals with molecular bromine.

$$^\bullet OH + Br_2 \longrightarrow HOBr + Br^\bullet, \qquad (7)$$

The rate constant for reaction (7) is $k_7 = (4.2 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K (see Ref. 169). In the temperature range 262–303 K, reaction (7) proceeds barrierlessly or has a very low activation barrier (~1 kcal mol^{-1}).[115] A study of the UV absorption spectrum of gaseous HOBr revealed [170] that at room temperature more than 97% of the total amount of the $^\bullet$OH radicals generated by photolysis of H_2O_2 are consumed following route (7) and less than 3% of these radicals are consumed in the reaction

$$^\bullet OH + H_2O_2 \longrightarrow HO_2^\bullet + H_2O.$$

Similarly to the reaction $HO_2^\bullet + ClO^\bullet$, the radical–radical reaction $HO_2^\bullet + BrO^\bullet$ [reaction (8)] producing hypobromous acid should be taken into account in simulation of atmospheric processes resulting in the destruction of stratospheric ozone.

$$HO_2^\bullet + BrO^\bullet \longrightarrow HOBr + O_2 \qquad (8a)$$

$$HOBr + h\nu \longrightarrow Br^\bullet + {}^\bullet OH$$

$$Br^\bullet + O_3 \longrightarrow BrO^\bullet + O_2$$

$$^\bullet OH + O_3 \longrightarrow HO_2^\bullet + O_2$$

$$2\,O_3 \longrightarrow 3\,O_2$$

Reaction (8) mainly follows route (*a*), the contribution of reaction (8*b*)

$$HO_2^\bullet + BrO^\bullet \longrightarrow HBr + O_3 \qquad (8b)$$

is insignificant, namely, the rate constant ratio $k_{8b}:k_{8a}$ is at most 0.015 (at 233–298 K, according to Ref. 171) or 0.004 (at 298 K, according to Ref. 172). Different sources estimate the activation energy for reaction (8) at about -1 kcal mol^{-1}; however, the rate constants for this reaction obtained by different authors at 298 K are somewhat different, lying in the range $(1.4-3.4)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (see Ref. 173).

$k_8\times10^{11}$ /cm^3 molecule^{-1} s^{-1}	3.4 ± 1.0	3.3 ± 0.5	1.4 ± 0.3	2.0 ± 0.6	3.1 ± 0.8
Ref.	174	171	175	173	172

HOBr can be formed in the troposphere and in the lower stratosphere as a result of heterogeneous hydrolysis of bromine nitrate on sulfate aerosol particles and on polar stratospheric clouds.[176, 177]

$$BrONO_2 + H_2O \longrightarrow HOBr + HNO_3.$$

Hydrolysis of $BrONO_2$ in the dark causes accumulation of HOBr but in sunlight HOBr is rapidly photolysed; as a consequence, the lifetime of HOBr is $\sim$15 min in the lower stratosphere and a few seconds in the upper stratosphere.[177] Hydrolysis of $BrONO_2$ on ice produces Br_2O as the secondary product.[162, 178]

$$BrONO_2 + HOBr \longrightarrow Br_2O + HNO_3.$$

The HOBr molecule is a nearly symmetrical prolate rotor characterised by the parameter $\kappa = -0.99936$. The dipole moment of the HOBr molecule is 1.384 D.[179]

The geometric parameters extracted from the pure rotation spectrum of HOBr are as follows:[179] $r(O-Br) = 1.834$ Å, $r(O-H) = 0.961$ Å and the H–O–Br angle is 102.3°. The rotational constants (for HO^{79}Br) are as follows: $A = 613\,677.34$, $B = 10\,576.60290$ and $C = 10\,383.05728$ MHz.

The frequencies in the IR spectrum of the HOBr molecule are listed in Table 8.[180, 181]

Table 8. Vibrational frequencies in the IR spectrum of the HOBr molecule.

Frequency	Numerical value /cm^{-1}	Assignment	Ref.
ν_1	3614.903	O–H stretch	180
ν_2	1162.570	bending vibration	181
ν_3	620.18	O–Br stretch	181

The absorption spectrum of gaseous HOBr in the region 200–420 nm was first studied by Orlando and Burkholder[167] who reported two structureless bands with maxima at nearly 280 nm [absorption cross section, σ, is $(3.1\pm0.4)\times10^{-19}$ cm^2] and at nearly 350 nm [$\sigma = (6.1\pm1.0)\times10^{-20}$ cm^2]. Later on, the third band at about 440 nm ($\sigma\approx9\times10^{-21}$ cm^2) was detected.[164] *Ab initio* calculations[182] substantiated the possibility for HOBr to absorb in the visible region with a maximum at 477 nm. According to another study,[170] at 295 K the spectrum of HOBr exhibits three broad bands with maxima at 284, 351 and 457 nm and the corresponding absorption cross sections σ of $(25.0\pm1.2)\times10^{-20}$, $(12.4\pm0.6)\times10^{-20}$ and $(2.3\pm0.2)\times10^{-20}$ cm^2. The absorption of HOBr in the long-wavelength region must have a strong effect on the rate of photolysis of the acid.[183] Laser photolysis of HOBr at 363 nm produces Br($^2P_{3/2}$) atoms with a quantum yield greater than 0.95.[161] No HBr was found among the products of photolysis.

The adiabatic ionisation energy of HOBr is 10.62 ± 0.04 (according to Ref. 184), 10.638 ± 0.03 eV (photoionisation mass spectrometry data[33]) and 10.642 ± 0.005 eV (photoelectron spectroscopy data[185]). G2 calculations[186] gave nearly the same ionisation energy, *viz*., 10.65 eV.

Earlier, the enthalpy of formation of HOBr was estimated at -19 ± 2 kcal mol^{-1}. However, this value appeared to be strongly overestimated compared to the results obtained more recently. In particular, a new value of the enthalpy of formation of HOBr reported in an experimental study[184] is $\Delta H^\circ_{298} = -9$ kcal mol^{-1} while the results of study[33] are $\Delta H^\circ_0 \geqslant -10.93\pm0.42$ and $\Delta H^\circ_{298} \geqslant -13.43\pm0.42$ kcal mol^{-1}. The ΔH°_{298} values determined in spectroscopic investigations are -11 (see Ref. 167) and -14.3 ± 0.9 kcal mol^{-1} (see Ref. 187). G2 calculations gave $\Delta H^\circ_{300} = -14.2\pm1.6$ (see Ref. 188) and $\Delta H^\circ_{298} = -13.9$ kcal mol^{-1} (see Ref. 30). More recent density functional calculations[138] at the B3LYP/6-311G(3df,3pd) level led to $\Delta H^\circ_{298} = -14.8$ kcal mol^{-1}. Two recommended[154] values of the enthalpy of formation of HOBr are -11.9 ± 0.3 (0 K) and -14.5 ± 0.3 kcal mol^{-1} (298 K).

The HOBr isomer is more stable than the 'hypervalent' isomer HBrO (the enthalpy of HOBr → HBrO conversion calculated for 0 K is 56.3 kcal mol^{-1}).[189]

The bond dissociation energies in the hypobromous acid molecule are $D_0(HO-Br) = 48.45\pm0.42$ kcal mol^{-1} and $D_0(H-OBr) = 94.2$ kcal mol^{-1}.[33] G2 calculations gave the following results: $D_0(HO-Br) = 48.8$ (see Ref. 30) and 49.5 kcal mol^{-1} (see Ref. 154) and $D_0(H-OBr) = 95.5$ kcal mol^{-1} (see Ref. 154).

The proton affinity energy of HOBr in the case of protonation at the oxygen atom

$$HOBr + H^+ \longrightarrow H_2OBr^+$$

is estimated at 162.0 (298 K)[30] or 161.5 kcal mol^{-1} (see Ref. 190).

Decomposition channels of hypobromous acid in the atmosphere involve photolysis and the interaction with ground-state elemental oxygen O(^{3}P)[191]

$$HOBr + O \longrightarrow BrO^\bullet + {}^\bullet OH. \qquad (9)$$

Tracer (^{18}O isotope) experiments followed by mass spectrometric analysis of reaction products showed that elemental oxygen interacts with the bromine atom of the HOBr molecule (HOBr + ^{18}O ⟶ Br^{18}O$^\bullet$ + $^\bullet$OH).[161] At 298 K, the rate constant for reaction (9) is $(2.5\pm0.4)\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, being nearly 200 times higher than the rate constant for analogous reaction involving HOCl.[191] In the temperature range 233–423 K the rate constant can be calculated by the equation[192]

$$k_9 = (1.4\pm0.5)\times10^{-10}\exp\left(-\frac{430\pm260}{T}\right)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

Reactions of HOBr with F(^{2}P) and Cl(^{2}P) atoms proceed even more rapidly. At 298 K, the rate constants for these reactions are $k(F) = (2.0\pm0.7)\times10^{-10}$ and $k(Cl) = (1.1\pm0.7)\times10^{-10}$ cm^3 molecule^{-1} s^{-1} (see Ref. 191).

Gas-phase titration of HOBr with chlorine atoms revealed that the reaction exclusively follows one of the two possible channels, namely, route *a*.[161]

$$HOBr + Cl \xrightarrow{a} BrCl + {}^\bullet OH$$
$$HOBr + Cl \xrightarrow{b} BrO^\bullet + HCl$$

Heterogeneous reactions

$$HOBr + HBr \longrightarrow Br_2 + H_2O,$$
$$HOBr + HCl \longrightarrow BrCl + H_2O$$

can also proceed in the atmosphere on the surface of ice at $T < 228$ K. These reactions produce photochemically active Br_2 and BrCl.[166, 193] The interaction of HOBr with the surface of ice prepared by freezing aqueous NaBr solutions at 233 or 248 K results in the formation of Br_2; if ice contains NaCl, BrCl is formed. In the presence of both NaBr and NaCl, BrCl is the only gaseous product at 233 K but raising the temperature to 248 K causes the formation of Br_2 and BrCl.[194]

V. Hypoiodous acid

The main source of atmospheric iodine is methyl iodide liberated by algae and phytoplankton, but small amounts of ethyl iodide are also present in the atmosphere.[195] Photolysis of iodides produces elemental iodine, which then reacts with ozone

$$I^{\bullet} + O_3 \longrightarrow IO^{\bullet} + O_2.$$

Radical $IO^{\bullet}$ can react with radical $HO_2^{\bullet}$, thus resulting in hypoiodous acid

$$IO^{\bullet} + HO_2^{\bullet} \longrightarrow HOI + O_2. \quad (10)$$

Under photolysis conditions, HOI regenerates the iodine atoms or enters in the reaction with nitrogen oxide, which also leads to regeneration of elemental iodine [196]

$$IO^{\bullet} + NO \longrightarrow I^{\bullet} + NO_2.$$

Hypoiodous acid is the most abundant inorganic compound of iodine in the troposphere at heights below 8 km. It is of great importance for tropospheric chemistry, especially in marine areas.[197] However, the presence of HOI in the stratosphere and its active role in the catalytic cycle of ozone destruction cannot be ruled out.[198]

Unlike HOF, HOCl and HOBr which are produced in the reactions of corresponding halogens with water, large amounts of hypoiodous acid can hardly be obtained by the reaction of iodine with water. It is a common practice to perform *in situ* synthesis of HOI using some other reactions when carrying out spectroscopic studies of the acid.

It was proposed [199] to synthesise hypoiodous acid in the reaction of hydroxyl radicals with iodine (HONO can be used as a source of $^{\bullet}OH$ radicals). The rate constant for the reaction $^{\bullet}OH + I_2$ is $(2.1 \pm 1.0) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (294 K).[199] A fast reaction

$$^{\bullet}OH + I_2 \begin{cases} \xrightarrow{a} HOI + I \\ \xrightarrow{b} IO + HI \end{cases}$$

was also proposed as a possible source of HOI.[200] The rate constant for this reaction is 1.6×10^{-10} cm^3 molecule^{-1} s^{-1} (298 K). It should be noted that channel (*b*) plays an insignificant role because $k_b : k_a < 0.01$.[200]

Hypoiodous acid is produced by photolysis (254 nm) of gaseous mixtures $I_2-H_2O_2$, $CH_3I-H_2O_2$ and $CH_2I_2-H_2O_2$.[197] The IR spectra of all these systems exhibit two absorption bands centred at 3620 and 1068 cm^{-1} and assigned to the stretching (O–H) and bending vibrations of the HOI molecule, respectively.[197] Photolysis of H_2O_2 followed by the reaction of $^{\bullet}OH$ radicals with iodine was also used to obtain HOI.[201, 202]

HOI can also be synthesised in the reactions of microwave discharge generated hydroxyl radicals with iodine or CF_3I and in the reactions of C_2H_5I with O(^{3}P).[198] Reactions of O(^{3}P) with two-carbon and longer alkyl iodides, *e.g.*,

$$C_2H_5I + O \longrightarrow HOI + C_2H_4,$$

$$C_3H_7I + O \longrightarrow HOI + C_3H_6,$$

produce excited (vibrationally hot) HOI molecules.[203] A study on the mechanisms of these reactions using ethyl iodide isotopomers CH_3CD_2I and CD_3CH_2I showed that attack of the O(^{3}P) atom on the I atom followed by hydrogen abstraction from the methyl group results in the formation of HOI.[204] The reaction with methyl iodide containing only one carbon atom yields no hypoiodous acid.

Similarly to HOCl and HOBr, hypoiodous acid can be synthesised in the radical–radical reaction (10). The first study on the kinetics of this reaction was reported in 1991.[205] The rate constant, k_{10}, for the reaction was estimated at $(6.4 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K. Another k_{10} value available in the literature [206] is $(1.03 \pm 0.13) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (298 K). The absence of ozone among the reaction products was demonstrated; this indicates an insignificant contribution of the channel

$$IO^{\bullet} + HO_2^{\bullet} \longrightarrow HI + O_3$$

to the overall reaction.

The temperature dependence of the rate constant for reaction (10) reported for the temperature range $T = 274-373$ K in a recent kinetic study [207] is described by the equation

$$k_{10} = 9.3 \times 10^{-12} \exp\left(\frac{680}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

At 298 K, the k_{10} value is $(9.7 \pm 2.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. An inversely proportional temperature dependence ($T = 273-353$ K) of the rate constant for reaction (10) was also reported in another study [197]

$$k_{10} = (2.2 \pm 0.6) \times 10^{-11} \exp\left(\frac{400 \pm 80}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The authors [197] concluded that the $IO^{\bullet}$ and $HO_2^{\bullet}$ radicals react exclusively to produce HOI and O_2.

The lack of simple methods for synthesis of HOI and the instability of the acid (its lifetime in an IR spectroscopic cell is only 1–2 min at room temperature [197]) strongly hamper studies on the structure and chemical properties of this acid.

The HOI molecule is a symmetrical prolate rotor characterised by the rotational constants $A_0 = 20.935$, $B_0 = 0.27894$ and $C_0 = 0.27507$ cm^{-1} and by the parameter $\kappa = -0.9996$.[203] The vibrational frequencies of HOI are $\nu_1 = 3625.84$, $\nu_2 = 1068$ and $\nu_3 = 575$ cm^{-1}.[203] The internuclear distance, r(O–I), is 1.991 Å, the distance r(O–H) is assumed to be 0.9643 Å (by analogy with the corresponding distances in the HOCl and HOBr molecules) and the angle H–O–I is 105.4°. Another set of geometric parameters of the HOI molecule is as follows: r(O–H) ≈ 0.96 Å, r(O–I) ≈ 1.959–1.995 Å and the angle H–O–I is 102.4°.[33] MultiConfiguration Self-Consistent Field (MCSCF) calculations [137] gave r(O–H) = 1.0078 Å, r(O–I) = 2.1044 Å and an H–O–I angle of 103.73°.

The absorption spectrum of gaseous HOI in the region 278–494 nm has been studied at 298 K.[201, 202] The spectrum exhibits two broad bands with absorption maxima at 340.4 and 406.4 nm [absorption cross sections, σ, are $(3.85 \pm 0.4) \times 10^{-19}$ and $(3.30 \pm 0.3) \times 10^{-19}$ cm^{-2}, respectively][201] or at 338.4 and 404.8 nm ($\sigma = 3.99 \times 10^{-19}$ and 2.85×10^{-19} cm^{-2}, see Ref. 202). Compared to HOCl and HOBr, the absorption bands of gaseous HOI are more intense and shifted towards the long-wavelength region.[202] The reaction $O + C_2H_5I$ used as a source of HOI provided evidence for the formation of oxide I_2O that can be a product of the reaction $2HOI \rightarrow I_2O + H_2O$.[202]

Photolysis of HOI (355 nm, 295 K) produces $^{\bullet}OH$ radicals with a quantum yield close to unity.[201] The lifetime of HOI in the troposphere in sunlight was estimated at a few minutes.[201, 202]

The adiabatic ionisation energy of HOI predicted [33] based on the analysis of trends in the changes in the properties of OHal and HOHal (Hal = F, Cl, Br) is the lowest among the HOHal compounds (9.71–9.80 eV). The experimental ionisation energy (9.81 ± 0.02 eV) [198] is close to the predicted [33] value. G2 calculations led to a value of 9.89 eV.[30]

According to an early estimation,[199] the enthalpy of formation of HOI lies in the range from −18.4 to −24.4 kcal mol^{-1} (more recently,[206] the average value, -21.4 ± 3.0 kcal mol^{-1}, was recommended). Revision [33] of these results led to a considerably different enthalpy of formation of HOI lying between −8 and −9 kcal mol^{-1} (*cf.* $\Delta H_0^{\circ} = -10.7$ and $\Delta H_{298}^{\circ} = -11.7$ kcal mol^{-1} obtained from G2 calculations [30]). Yet another pair of recommended enthalpy values is as follows: $\Delta H_0^{\circ} = -13.2$ and $\Delta H_{298}^{\circ} = -14.3$ kcal mol^{-1}.[154]

The calculated bond dissociation energies are D_0(HO–I) = 43–44 and D_0(H–OI) = 94.5–95.2 kcal mol^{-1}.[33] G2 calculations [30] gave a value of

45.3 kcal mol^{-1} for D_0(HO—I). The bond dissociation energies recommended in another study,[154] D_0(HO—I) = 48.2 and D_0(H—OI) = 93.7 kcal mol^{-1}, differ only slightly from those listed above.

* * *

The main goal of the studies on the properties of gaseous hypochlorous, hypobromous and hypoiodous acids is to establish their role in the destruction of stratospheric ozone. Hypofluorous acid, which also belongs to this group of oxy acids of halogens, is of little importance for atmospheric processes; however, this compound is of interest for preparative chemistry.

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