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Halogen monoxides

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Abstract. The results of studies of the properties of OF, ClO, BrO and IO radicals are summarised. The methods of radical generation, spectroscopic and thermodynamic characteristics as well as some of their reactions are considered. Similar data for dichlorine trioxide are given. The bibliography includes 182 references.

I. Introduction

In the present review a group of radicals XO (where X is a halogen atom) is considered, which includes oxygen monofluoride OF and oxides ClO, BrO, IO, which are usually referred to as halogen monoxides. The interest of scientists in these radicals arose in the late 1970s – early 1980s, mainly due to the discussion of their role in the process of ozone stratospheric destruction. In the past two decades, spectroscopic properties of these radicals and the kinetics of their reactions with some other small molecules that are of great interest for the atmospheric chemistry were investigated along with the theoretical studies. The behaviour of halogen monoxides in troposphere and stratosphere is discussed in detail in a review.[1] Several papers [2,3] are dedicated to the tetraatomic (X_2O_2) and triatomic (HOX) oxygen-containing halogen compounds. The gas-phase reactions of inorganic halogen-containing molecules, including halogen monoxides, are discussed in a review.[4]

II. Oxygen monofluoride

1. Generation of OF radicals

For the first time, OF radicals were observed in condensed phase.[5] Radicals were generated by irradiation of a mixture of oxygen difluoride mixtures with nitrogen or argon deposited on caesium bromide at 4 K with a high-pressure mercury lamp. Later, these radicals were detected by laser magnetic resonance in the gas phase.[6] For the generation of radicals, a microwave discharge in carbon tetrafluoride was applied (10 – 30 W); in this case, oxygen atoms result from etching of quartz reactor walls.[6] DC glow discharge in a mixture of $CF_4 - O_2$ proved to be ineffective for the preparation of OF radicals.[7] In addition to the matrix photolysis of oxygen difluoride OF radicals can also be formed in the reaction of alkali metals or magnesium with oxygen difluoride in the cryogenic environment.[8]

The reaction of fluorine atoms with ozone at 298 K has been applied as a method for radical generation [9–11]

$$F + O_3 \longrightarrow OF + O_2, \quad (1)$$

which was subsequently often used as the source of radicals (see *e.g.* Refs 12 – 17). Fluorine atoms are obtained by the dissociation of molecular fluorine in a microwave discharge. This reaction is rather fast: at room temperature, k_1 is equal to 1.3×10^{-11} (in the excess of F atoms over O_3, Ref. 11) or 6.2×10^{-12} cm^3 molecule^{-1} s^{-1} (in the excess of O_3 over F atoms, Ref. 17). The value of $k_1 = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (298 K) and the temperature dependence $k_1 = 2.2 \times 10^{-11} \exp(-230/T)$ cm^3 molecule^{-1} s^{-1} in the 250 – 365 K range are recommended.[18] The reaction of fluorine atoms with ozone molecules in argon matrix (15 K) leads to the formation of $FO - O_2$ complex, which decomposes upon photolysis and yields isolated OF radicals.[19]

Heterogeneous thermal decomposition of oxygen difluoride at 473 – 523 K in stainless steel reactor was used for the generation of OF radicals.[17,20–22] Thermal dissociation of oxygen difluoride was investigated in a number of papers (see Ref. 23). Reactions of OF_2 with H, N, O and F atoms proceed slowly and cannot be used as an effective source of OF radicals.[24]

OF radicals were obtained [25] by the reaction of atomic fluorine with nitric acid vapour in Teflon flow reactor in the excess of atomic fluorine:

$$F + HNO_3 \longrightarrow NO_3 + HF,$$

$$F + NO_3 \longrightarrow + NO_2.$$

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The reaction of fluorine with oxygen in a microwave discharge can also be used as a source of OF radicals although it was shown to be inefficient.[25]

2. Spectroscopic and thermodynamic characteristics

Vibrational frequencies (cm^{-1}) for the diatomic OF radical in an argon matrix at 16 K are given below.

Species	Raman spectrum [8]	IR spectrum [26]
^{16}OF	1028.9	1028.6
^{18}OF	998.4	997.7

For OF radical in the gas phase, the values of frequency $\nu_0 = 1033.4182\ cm^{-1}$ and rotational constant $B_e = 1.05955\ cm^{-1}$ were obtained, as well as the equilibrium interatomic distance $r_e = 1.35789$ Å.[6] These values have been refined later,[7] 14 transitions from the ground state $^2\Pi_{3/2}$ were observed; the values $\nu_0 = 1033.4829\ cm^{-1}$ and $B_e = 1.05289\ cm^{-1}$ have been reported. Using a high-resolution infrared Fourier spectrometer, transitions from the states $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ have been detected and the following parameters have been obtained: $\nu_0 = 1032.9648\ cm^{-1}$ (vibrational constant $\omega_e = 1053.42\ cm^{-1}$), $B_e = 1.05869\ cm^{-1}$; and a more precise value of $r_e = 1.35412$ Å.[15] The chemiluminescence of vibrationally excited OF radicals in the ground state generated in the reaction of F atoms with ozone has been studied with the use of infrared Fourier spectroscopy,[16] and the following values have been reported $\omega_e = 1052.994\ cm^{-1}$ and $B_e = 1.0587\ cm^{-1}$.

OF radicals have a very small dipole moment, which hinders their detection by means of EPR methods and microwave spectroscopy. In an early paper,[27] for the value of $r_e = 1.321$ Å the dipole moment was estimated as -0.361 D (polarity O^+F^-). Later, it was established that this value had been overestimated. The experimental value of the dipole moment for OF turned out to be the lowest among those for the diatomic heteropolar molecules being equal to only -0.0043 D for the ground state of OF.[28] The calculated values -0.0089 D (Ref. 29) and -0.0006 D (Ref. 30) are close to the experimental one.

The vertical ionisation potential calculated for OF radicals is equal to 13.1 ± 0.3 eV.[27] Experimentally, the vertical (U_v) and adiabatic (U_{ad}) ionisation potentials have been estimated by means of photoelectron spectroscopy (vacuum UV, HeI radiation) [13] and photoionisation mass spectrometry.[25,31]

U_v/eV	U_{ad}/eV	Ref.
–	12.79	31
13.08	12.77	13
–	12.78 ± 0.03	25

Compared to neutral OF radicals, $FO^+(X^3\Sigma^-)$ ions have shorter interatomic distance ($r_e = 1.234$ Å) and higher vibration frequency ($\omega_e = 1300\ cm^{-1}$).[13]

The adiabatic electron affinity of OF radicals is equal to 2.272 eV (according to data from photoelectron spectroscopy).[32] The anion $FO^-(^1\Sigma^+)$ is characterised by interatomic distance $r_e = 1.516$ Å and vibrational constant $\omega_e = 769\ cm^{-1}$ (Ref. 32). The calculated value of adiabatic electron affinity of OF radicals is equal to 2.08 ± 0.2 eV.[33] Using calculations for $FO^-(^1\Sigma^+)$ anion the following values were obtained: $r_e = 1.54$ Å and $\omega_e = 750\ cm^{-1}$ (Ref. 33).

For the dissociation energy (D) of the O–F bond, the following experimental estimations are available:

D/kcal mol^{-1}	Ref.
55 ± 5	8
51.5 ± 4	9
51 ± 3	27
58.1 ± 4.1	34
52.5	16

Calculations with the application of Gaussian-2 programme package [30] gave the values of dissociation energy close to the listed ones, being equal to 50.5 and 51.1 kcal mol^{-1}.

The enthalpy of formation of OF radicals is close to 26 kcal mol^{-1}. *Ab initio* calculations [35] of the isodesmic reaction

$$OF + HOH \longrightarrow HO + HOF$$

have given the value of $\Delta_f H^\circ_0(OF) = 27.8 \pm 1$ kcal mol^{-1}. The following values have been estimated by mass spectrometry: $\Delta_f H^\circ_0(OF) = 26.1 \pm 2.3$ (Ref. 31) and $\Delta_f H^\circ_{298}(OF) = 26.1 \pm 1.9$ kcal mol^{-1} (Ref. 25); the value $\Delta_f H^\circ_{298}(OF) = 26$ kcal mol^{-1} was recommended.[18] For OF^+ ions the corresponding calculated value is equal to $\Delta_f H^\circ_{298}(OF^+) = 320$ kcal mol^{-1} (Ref. 25).

3. Reactions of OF radicals

It was suggested [9] that the decomposition of OF radicals occurring as the disproportionation results in the appearance of fluorine atoms and oxygen molecules

$$OF + OF \longrightarrow 2F + O_2 \qquad (2)$$

with the rate constant in the range of $2 \times 10^{-12} - 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (298 K). Mass-spectrometric investigation of reactions of diatomic radicals carried out by the same authors gave the following value for k_2: $(8.5 \pm 2.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (298 K).[12] This reaction was concluded [20] to be the main channel of disproportionation while the contributions of other channels yielding $F + O_2F$, $F_2 + O_2$ or O_2F_2 are insignificant. The rate constant for the reaction

$$OF + OF \longrightarrow \text{products}$$

in the temperature range 300–435 K increases from $(1.0 \pm 0.2) \times 10^{-11}$ to $(1.4 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Ref. 20).

The reaction of OF radicals with hydrogen atoms was investigated at 300 K in flow environment by electric discharge.[36] Both possible reaction channels

$$OF + H \xrightarrow{a} F + OH \qquad OF + H \xrightarrow{b} O + HF$$

are exothermic. The rate constant $k = k_a + k_b = (2.4 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and the fraction of channel b, $k_b/(k_a + k_b) = 0.34 \pm 0.02$, have been evaluated. At the same time, the reaction rate constant for OF radicals with molecular hydrogen does not exceed 1.0×10^{-17} cm^3 molecule^{-1} s^{-1} at 300 K.[22] Calculations [37] show that this reac-

tion has a high activation barrier estimated as 17.5 kcal mol^{-1}. The reaction of hydrogen atom abstraction by OF radical from HO_2 radical with the formation of HOF and O_2 also has a rather high activation energy (9.3 or 8.5 kcal mol^{-1}).[38]

Reactions of OF radicals with oxygen or nitrogen atoms at room temperature proceed at the same rate as with the hydrogen atoms.[21] Of two exothermic reaction channels with nitrogen atoms

$$OF + N \begin{cases} \longrightarrow NO + F \\ \longrightarrow NF + O \end{cases}$$

the former is preferable.

OF radicals react with NF_2 radicals obtained by the thermal decomposition of tetrafluorohydrazine

$$OF + NF_2 \longrightarrow 2F + NOF$$

at high rate[39] ($k = 3.8 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 300 K).

The negative temperature dependence of the rate constant of the reaction

$$OF + NO \longrightarrow F + NO_2$$

has been established in the range of 300–845 K, which suggests the formation of the excited intermediate complex FONO and its subsequent fragmentation.[22] Calculations[40] show that upon the reaction of OF radicals with the hydroxyl radicals the formation of HOOF peroxide as an intermediate product is possible.

The activation energy for the reaction

$$OF + H_2O \longrightarrow OH + HOF$$

is estimated[41] as 25.7 kcal mol^{-1}, while for the reaction of OF radicals with methane at 300 K this value is equal to 12.1 ± 2 kcal mol^{-1}.[42] OF radicals react with ozone molecules very slowly. At stratospheric temperature (220 K) the rate constant for this reaction does not exceed 4×10^{-19} cm^3 $molecule^{-1}$ s^{-1} (Ref. 43). Oxygen monofluoride has a lower reactivity as compared to atomic fluorine or hydroxyl radicals.[37]

III. Chlorine monoxide. Dichlorine trioxide

Numerous studies are devoted to chlorine monoxide, some earlier results are given in reviews.[23,44] In the 1930s, ClO radicals were considered as an intermediate product of Cl_2O decomposition. For the first time, the bands of ClO radicals were observed by flame emission spectroscopy.[45]

1. Generation of ClO radicals

In order to obtain radicals, one can use photochemical or plasmochemical treatment, *e.g.* photolysis of dichlorine monoxide, chlorine dioxide, a mixture of chlorine with oxygen or ozone or microwave discharge in a mixture of chlorine with oxygen. It is possible to generate ClO radicals by the reaction of chlorine atoms obtained upon microwave discharge with dichlorine monoxide, chlorine dioxide, ozone or oxygen. The reaction of oxygen atoms with chlorine or chlorine dioxide also yields ClO radicals.It was concluded that reactions of chlorine atoms with ozone or chlorine dioxide ensure good yield of ClO radicals, while reactions

$$O + Cl_2O \longrightarrow 2ClO$$

and

$$H + ClO_2 \longrightarrow OH + ClO$$

give very low yields of chlorine monoxide.[46] The recommended[18] value of the rate constant for the reaction

$$Cl + OClO \longrightarrow ClO + ClO$$

at 298 K is equal to 5.8×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Fast reaction

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (3)$$

results from the direct attack of chlorine atom on the terminal oxygen atom of the ozone molecule without formation of the asymmetric ClO_3 complex.[47] The temperature dependence of the rate constant for this reaction is described by two Arrhenius-type equations:[48]

$$k_3 = 1.19 \times 10^{-11} \exp\left(\frac{-33}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$
$$T = 189 - 269 \text{ K};$$

$$k_3 = 2.49 \times 10^{-11} \exp\left(\frac{-233}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$
$$T = 269 - 385 \text{ K}.^{48}$$

At the same time, ClO radicals, similar to oxygen monofluoride, react with ozone very slowly. The order of magnitude of the maximum value of the rate constant for this reaction is in the range $10^{-15} - 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} (Refs 49 and 50).

Upon photolysis ($\lambda = 308$ nm) of chlorine nitrate, vibrationally excited ClO radicals are formed.[51] Photolysis of dichlorine monoxide leads to the cleavage of the Cl–O bond with the formation of ClO radicals and Cl atoms.[52] This channel is the only one at $\lambda = 308$ nm and the main at $\lambda = 248$ nm. The formed radicals partly dissociate at $\lambda = 248$ nm, while at $\lambda = 193$ nm the coherent dissociation of Cl_2O occurs yielding Cl_2 and O atoms.

The reaction of fluorine atoms with dichlorine monoxide was also used[53] to obtain ClO radicals

$$F + Cl_2O \longrightarrow ClF + ClO.$$

2. Spectroscopic and thermodynamic characteristics

The electronic state $^2\Pi_{3/2}$ of the diatomic radical ClO is about 320 cm^{-1} lower in energy than $^2\Pi_{1/2}$. At room temperature ~15% of radicals are in $^2\Pi_{1/2}$ state.[54]

The absorption maximum for chlorine monoxide in UV range is observed at 275.1 nm (band 12,0) with the section $\sigma = 6.81 \times 10^{-18}$ cm^2 (Ref. 55). In continuum, this section decreases from 5.04×10^{-18} cm^2 at 260 nm to 2.22×10^{-18} cm^2 at 240 nm.[55] The absorption section at 275.2 nm decreases upon temperature increase from 9.70×10^{-18} cm^2 at 220 K to 7.84×10^{-18} cm^2 at 400 K.[56]

Using microwave spectrum of ClO, the vibrational constant was calculated: $\omega_e = 854.1$ cm^{-1} (Ref. 57). From the high-resolution Fourier-transform infrared spectrum for ^{35}ClO and ^{37}ClO, the values of ω_e have been estimated, which

are equal to 853.72446 and 846.45538 cm^{-1}, respectively.[58] The rotational constants B_e for ^{35}ClO and ^{37}ClO are equal to 0.623459 and 0.6129003 cm^{-1}, respectively.[54]

The values of internuclear distance $r_e(Cl-O)$ obtained in various experiments do not virtually differ.

$r_e(Cl-O)$ /Å	Ref.
1.56965	59
1.56954	60
1.56959	57

In the excited state $A^2\Pi$ the internuclear distance increases up to 1.858 Å.[59] The dipole moment of $ClO(^2\Pi_{3/2})$ radicals in the ground vibrational state is equal to 1.2974 D.[61]

The adiabatic and vertical ionisation potentials of ClO radicals were determined by means of photoelectron spectroscopy [62] and photoionisation mass spectrometry.[53, 63]

Initial state	U_{ad}	U_v	Ref.
$^2\Pi_{3/2}$	10.87	11.0	62
$^2\Pi_{1/2}$	10.83	10.96	62
$^2\Pi_{3/2}$	10.88	–	53
$^2\Pi_{3/2}$	10.85	–	63

The equilibrium internuclear distance in ClO^+ ($X^3\Sigma^-$) ion was estimated at 1.480 Å.[62] The ClO radicals have high electron affinity (2.276 eV).[64]

The enthalpy of formation of chlorine monoxide $\Delta_f H^\circ_{300}(ClO) = 24.4$ kcal mol^{-1}.[65] Using semiempirical calculations [30] the value $\Delta_f H^\circ_0(ClO) = 24.72$ kcal mol^{-1} was obtained. The energy of bond dissociation in ^{35}ClO radical is equal to 63.427 kcal mol^{-1}.[66]

3. Reactions of ClO radicals

Photodissociation of ClO radicals at $\lambda = 248$ nm occurs by the dominating (97%) channel [67]

$$ClO \longrightarrow Cl(^2P_{3/2}) + O(^1D_2).$$

At room temperature the bimolecular reaction ClO + ClO proceeds by three channels [55]

$$ClO + ClO \xrightarrow{a} Cl_2 + O_2$$
$$ClO + ClO \xrightarrow{b} Cl + ClOO$$
$$ClO + ClO \xrightarrow{c} Cl + OClO$$

with rate constant $k = k_a + k_b + k_c = (2.2 \pm 0.6) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}; the ratio of the channels $k_a : k_b : k_c = 0.29 : 0.50 : 0.21$.[18]

At low temperature of the stratosphere the trimolecular reaction predominates

$$ClO + ClO + M \rightleftharpoons Cl_2O_2 + M,$$

resulting in the formation of Cl_2O_2 dimer.[55, 68, 69] Rate constants for some of the reactions of ClO radicals are given in Table 1.

The reaction rate of ClO with NO_3 does not depend on the temperature in the range of 210–353 K. The reaction proceeds by two channels:[72]

Table 1. Rate constants for the reactions involving ClO radicals (298 K).

Reaction	$k \times 10^{11}$ /cm^3 $molecule^{-1}$ s^{-1}	Ref.
$ClO + O \longrightarrow Cl + O_2$	3.90	70
$ClO + SO \longrightarrow SO_2 + Cl$	3.22	71
$ClO + NO_3 \longrightarrow$ products	0.05	72
$ClO + BrO \longrightarrow$ products	1.29	56
$ClO + OH \longrightarrow$ products	1.46	73
	2.44	74
$ClO + HO_2 \longrightarrow$ products	0.6	75
	0.7	76

$$ClO + NO_3 \longrightarrow ClOO + NO_2 \text{ (main)}$$
$$ClO + NO_3 \longrightarrow OClO + NO_2$$

In the reaction of ClO and OH radicals, HO_2 radicals are formed as the main product.

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

The contribution of the channel

$$ClO + OH \longrightarrow HCl + O_2$$

is equal to $7 \pm 3\%$ at 207–298 K.[73]

The reaction of ClO and HO_2 radicals proceeds almost entirely by the single channel

$$ClO + HO_2 \longrightarrow HOCl + O_2.$$

The contribution of the channel

$$ClO + HO_2 \longrightarrow HCl + O_3$$

does not exceed 1%–5%.[76–78] In the temperature range of 215–298 K, the rate constant for the reaction $ClO + HO_2$ is described by the expression [76]

$$k = (7.1 \pm 0.4) \times 10^{-12} \exp\left(\frac{-16 \pm 17}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Ab initio calculations show [79] that this reaction proceeds both by a multistage mechanism and by the direct proton detachment. A small probability of formation of HCl and ozone molecules upon reaction of ClO and HO_2 radicals was also confirmed by the calculations.[80]

For the reaction of ClO and BrO radicals

$$ClO + BrO \xrightarrow{a} ClOO + Br$$
$$ClO + BrO \xrightarrow{b} OClO + Br$$
$$ClO + BrO \xrightarrow{c} O_2 + BrCl$$

at 298 K the constants ratio was established [81] $k_b : k = 0.48$ and $k_{a+c} : k = 0.48$ ($k = k_a + k_b + k_c$).

4. Dichlorine trioxide

The reaction of ClO radicals with chlorine dioxide leads to dichlorine trioxide (chlorine sesquioxide):

$$ClO + OClO + M \longrightarrow Cl_2O_3 + M.$$

The rate constant for this trimolecular reaction at 226 K is equal to $(2.8 \pm 2.2) \times 10^{-31}$ cm^6 molecule^{-2} s^{-1} (Ref. 82).

For the first time, the possibility of the existence of this oxide was mentioned in 1936.[83] In 1967, the synthesis of compound with the empirical formula $ClO_{1.5 \pm 0.1}$ or Cl_2O_3 was described [84]. Dichlorine trioxide was obtained by UV irradiation of gaseous chlorine dioxide placed in a flask with its lower half kept at 228 K. Two decades later, a number of investigations on the properties of this compound were carried out.

The UV absorption spectrum of Cl_2O_3 formed in low-temperature photolysis ($\lambda = 350$ nm) of gaseous mixtures containing OClO was recorded;[85] the authors came to a conclusion that Cl_2O_3 is less stable than the chlorine monoxide dimer Cl_2O_2. Gas phase photolysis of mixtures of chlorine dioxide with oxygen and nitrogen at 249–300 K yields Cl_2O_3 or chlorine perchlorate Cl_2O_4 or a mixture of Cl_2O_3 and Cl_2O_4 depending on experimental conditions.[86] Dichlorine trioxide is also formed in the photolysis of OClO dimer isolated in an argon matrix.[87] The formation of Cl_2O_3 upon flash photolysis of a solution of chlorine dioxide in CCl_3F was reported.[88]

The IR spectrum of Cl_2O_3 has absorption bands at 1225 (the most intensive one), 1057, 740 and 560 cm^{-1} (Ref. 89). The absorption maximum in the UV spectrum of Cl_2O_3 was found at 265 nm (Ref. 85) or 267 nm (Ref. 89). For the absorption section, the following estimates were made:

$\sigma \times 10^{17}$ /cm^2	Ref.
1.86	85
1.80	89
1.60	90
1.76	91

Dichlorine trioxide is in fact chlorine chlorate ClOCl(O)O. Non-planar molecule of Cl_2O_3 has rotational constants $A = 8629.1968$, $B = 2106.40979$, $C = 1776.12211$ MHz (for ^{35}Cl isotope) and large internuclear distance $ClO-ClO_2$ (1.775 Å) [92] (the calculated value [93] is 1.815 Å). The results of calculations [93–97] confirm that the most stable isomer of Cl_2O_3 has the structure of chlorine chlorate. According to calculations with the use of Gaussian-2 programme package,[97] the isomers of Cl_2O_3 are arranged in the following order of relative stability (the point group of symmetry is given in parentheses): ClOCl(O)O > ClOOOCl (C_2) > ClOOOCl (C_s) > $ClClO_3$ (C_{3v}) > cyclo-ClOOCl(O) > ClOOClO.

The enthalpy of formation for Cl_2O_3 according to different experimental results [85, 90, 98] and calculations [93, 95, 97] is in the range 32.3–38.2 kcal mol^{-1} (0 K). Dichlorine trioxide is an unstable molecule: the energy of dissociation for $ClO-ClO_2$ bond is ~11 kcal mol^{-1} (Ref. 90) (according to calculations,[99] it is 8.59 kcal mol^{-1}). The half-life period of Cl_2O_3 in the antarctic stratosphere environment was estimated [88] as 50 s, while the lifetime of Cl_2O_3 is predominantly determined by the rate of its thermal decomposition rather than the rate of photolysis.[91] According to other data,[100] the lifetime of Cl_2O_3 at the temperature of lower stratosphere is about 10^3 s.

IV. Bromine monoxide

BrO radicals were detected in 1938 using the flame spectrum of ethyl bromide and later using flame spectra of methyl bromide.[101] Later, these radicals were detected by EPR [102] and mass spectrometry.[103]

1. Generation of BrO radicals

Bromine monoxide radicals are generated in the reaction of bromine atoms with ozone or of oxygen atoms with molecular bromine. Bromine atoms are usually obtained upon dissociation of bromine molecules in a microwave discharge (see *e.g.* Refs 104–107), although in order to obtain BrO radicals glow discharge (60 Hz) in a mixture of bromine with oxygen can also be used.[108] As a source of atomic bromine thermal dissociation of molecular bromine [109] and the reaction [107]

$$Cl + C_2H_3Br \longrightarrow C_2H_3Cl + Br.$$

were also used.

Atomic oxygen is generated in a microwave discharge for its subsequent reaction with bromine molecules. Alternatively, BrO radicals are obtained directly in a mixture of bromine with oxygen (see, *e.g.*, Refs 110–116). Atomic oxygen can be obtained by photolysis of O_2 molecules.[105] Photolysis of $Br_2 + O_3$ or $Br_2 + O_2$ mixtures also yields BrO radicals:[106, 117–119]

$$Br_2 \xrightarrow{h\nu} 2\,Br, \quad Br + O_3 \longrightarrow BrO + O_2;$$

$$O_2 \xrightarrow{h\nu} 2\,O, \quad O + Br_2 \longrightarrow BrO + Br.$$

It was shown that the reaction products of bromine with oxygen in a microwave discharge stabilised at 6.5 K contained dibromine trioxide Br_2O_3.[120]

BrO radicals are formed by the laser irradiation ($\lambda = 193$ nm) of a mixture of Br_2 with N_2O and an inert gas (nitrogen).[121] In this case, the source of oxygen atoms is N_2O:

$$N_2O \xrightarrow{h\nu} O(^1D) + N_2,$$

Electronically excited atoms $O(^1D)$ are deactivated upon collision with the molecules of the inert gas:

$$O(^1D) + N_2 \longrightarrow O(^3P) + N_2.$$

The possible sources of atomic bromine in stratosphere are bromine-containing compounds such as CH_3Br, $CHBr_3$, CF_3Br, tetrabromobisphenol A that have passed through troposphere and underwent photolysis in stratosphere. The reaction of bromine atoms with ozone

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

proceeds quickly, its rate constant at 298 K is equal to 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} (Ref. 122). Bromine atom abstracts terminal oxygen atom from the ozone molecule with the formation of BrO and the oxygen molecule.[123] The contribution of the second possible reaction channel

$$Br + O_3 \longrightarrow BrO_2 + O$$

is insignificant.[123] A highly exothermic reaction of bromine atoms with ozone ($\Delta H = -30.8$ kcal mol^{-1}) leads to the formation of vibrationally excited BrO radicals. Their lifetime in stratosphere at the height of 40 km is estimated as 43 μs.[122]

2. Spectroscopic and thermodynamic characteristics

The recorded IR spectrum of BrO radicals in an argon matrix (10 K) has vibration frequency $\nu_0 = 729.9$ cm^{-1} (Ref. 104).

For ^{81}BrO radicals in the gas phase, vibrational constants ω_e were found to be 724 (Ref. 111) and 722.1 cm^{-1} (Ref. 124). In a later paper,[125] the vibration frequency value (723.4 cm^{-1}) for BrO radical in the gas phase was obtained. Using vibrational-rotational spectrum of BrO radicals in the ground electronic state $^2\Pi_{3/2}$, the following parameters were determined: $\omega_e = 725.69$ (^{79}BrO) and 724.18 cm^{-1} (^{81}BrO).[108] The application of high-resolution Fourier infrared spectroscopy to ν_0 of ^{79}BrO and ^{81}BrO afforded the values equal to 723.41420 and 721.92715 cm^{-1}, respectively.[126] The rotational constant B_0 of ^{81}BrO radical is equal to 12726.5 (Ref. 127) or 12771.513 MHz.[108] For the constant B_e, the values of 12833 (Ref. 110) and 12825.723 MHz (Ref. 111) were cited. The dipole moment of BrO ($^2\Pi_{3/2}$) is equal to 1.765 D for ^{79}BrO and 1.794 D for ^{81}BrO (the Stark method).[110] Using microwave spectrum of BrO the internuclear distance $r_e = 1.717$ Å was found.[110] Later, the values of 1.717263 (Ref. 111) and 1.72072 Å (Ref. 108) have been obtained for r_e.

BrO radicals absorb in the range of 290–355 nm ($A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ transition), excited radicals dissociate into $Br(^2P_{3/2})$ and $O(^1D)$.[128] At 338.4 nm (band 7,0), the absorption section is equal to 1.58×10^{-17} cm^2 at 298 K or 1.97×10^{-17} cm^2 at 228 K.[129]

Using the method of photoelectron spectroscopy the first ionisation potential of BrO was estimated to be 10.29 ± 0.01 eV.[130] The internuclear distance for the $BrO^+(X^3\Sigma^-)$ ion $r_e = 1.66 \pm 0.01$ Å and bond strength 3.97 ± 0.03 eV were estimated. Adiabatic ionisation potential for both ^{79}BrO and ^{81}BrO is equal to 10.46 ± 0.02 eV.[113] Further measurements[131] gave the ionisation potential of BrO equal to 10.48 ± 0.02 eV. Adiabatic electron affinity of BrO radicals is equal to 2.353 eV.[32] Internuclear distance in $BrO^-(^1\Sigma^+)$ ion is equal to 1.814 Å, vibrational constant $\omega_e = 575$ cm^{-1} (Ref. 32).

For the enthalpy of formation of BrO radicals the following value was found $\Delta_f H^\circ_{298}(BrO) = 30.4 \pm 0.5$ kcal mol^{-1} (Ref. 109). From studies on kinetics of the reactions Br + IO and I + BrO, $\Delta_f H^\circ_{298}(BrO)$ was estimated[107] as 28.6 ± 1.4 kcal mol^{-1}. According to data published elsewhere $\Delta_f H^\circ_0(BrO) = 32.0 \pm 0.4$ and $\Delta_f H^\circ_{298}(BrO) = 30.2 \pm 0.4$ kcal mol^{-1} (Ref. 129). In an earlier paper,[128] the dissociation energy from the ground state was found: $D_0(Br-O) = 55.2 \pm 0.6$ kcal mol^{-1}; the same value 55.2 ± 0.4 kcal mol^{-1} was obtained later.[129]

3. Reactions of BrO radicals

BrO radicals react with ozone very slowly:[132] at 343 K the rate constant for the reaction

$$BrO + O_3 \longrightarrow Br + 2O_2$$

is equal to 1.3×10^{-17} cm^3 $molecule^{-1}$ s^{-1}. At the same time, the reaction of BrO radicals with each other proceeds quickly:

$$BrO + BrO \xrightarrow{a} BrOO + Br \longrightarrow 2Br + O_2$$
$$BrO + BrO \xrightarrow{b} Br_2 + O_2$$

At 298 K, the rate constants $k_{a+b} = (3.2 \pm 0.5) \times 10^{-12}$ and $k_b = (4.7 \pm 1.5) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} were obtained.[133] The rate constant k_{a+b} does not depend on the buffer gas pressure at 298 K and is equal to $(2.75 \pm 0.50) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (Ref. 118), but at 220 K it increases from $(2.00 \pm 0.41) \times 10^{-12}$ (100 Torr) to $(3.10 \pm 0.30) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (400 Torr). The ratio $k_a : k_{a+b}$ changes from 0.84 at 298 K to 0.68 at 220 K. The values of k_{a+b} constant close to those mentioned above were also obtained in other investigations.[134–136] In Ref. 137 the following value of the rate constant is recommended $(2.75 \pm 0.35) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (298 K).

Ab initio calculations show[138] that recombination of BrO radicals can be exothermic (from 6.8 to 22.0 kcal mol^{-1}). The rate constants for some reactions involving bromine monoxide are given in Table 2.

Table 2. Rate constants for the reactions of BrO radicals (298 K).

Reaction	$k \times 10^{11}$ /cm^3 $molecule^{-1}$ s^{-1}	Ref.
BrO + ClO ⟶ products	1.13	139
	1.08	140
BrO + IO ⟶ products	6.9	121
	8.5	137
BrO + I ⟶ IO + Br	1.2	121
BrO + OH ⟶ products	7.5	115
	3.8	141
BrO + OD ⟶ products	3.7	142
$BrO + HO_2 \longrightarrow HOBr + O_2$	1.78	142
	2.0	143
	3.1	144

The interaction of BrO and ClO radicals proceed predominantly by channels *a* and *b*.

$$BrO + ClO \xrightarrow{a} Br + OClO$$
$$BrO + ClO \xrightarrow{b} Br + Cl + O_2$$
$$BrO + ClO \xrightarrow{c} BrCl + O_2$$

The formation of BrCl (channel *c*) occurs through excited intermediate BrOOCl, which eliminates BrCl.[139] Investigations[140] in the range of 234–406 K show that channel *a* dominates at lower temperature the contribution of channel *c* at room temperature being equal to 9%.

Bromine monoxide reacts more rapidly with the IO radicals, predominantly according to the equation:

$$BrO + IO \longrightarrow Br + OIO.$$

Other routes are also possible, which lead to the formation of Br + I + O_2, I + OBrO, IBr + O_2.[137]

The reaction of radicals BrO and OH probably occurs with the formation of a short-lived vibrationally excited HOOBr complex. Its decomposition yields HO_2 and Br atom:[115]

$$BrO + OH \longrightarrow HOOBr \longrightarrow HO_2 + Br.$$

The reaction

$$BrO + OH \longrightarrow HBr + O_2$$

is hindered by high activation energy.[115]

In the reaction of bromine monoxide with HO_2 radicals, the formation of HOOBrO intermediate is energetically favourable with its subsequent dissociation into HOBr and O_2. The energy barrier to the reaction is equal to 2.8 kcal mol^{-1} (Ref. 145).

Reaction of BrO radicals that are formed upon flash photolysis of ozone in the presence of bromine and dimethyl sulfide yields dimethyl sulfoxide almost quantitatively.[146]

The rate constant for the reaction

$$BrO + Me_2S \longrightarrow Br + Me_2SO$$

at 300 K is equal to 4.6×10^{-13} cm^3 molecule^{-1} s^{-1} (Ref. 119).

V. Iodine monoxide

The emission spectrum of IO radicals, which are formed in the flame of methyl iodide mixed with oxygen, was observed for the first time in 1937.[128] The absorption spectrum of radicals generated by flash photolysis of a mixture of iodine with oxygen was obtained in 1957.[128] IO radicals were registered also by mass spectrometry with the use of molecular beam analyser.[103]

1. Generation of IO radicals

IO radicals can be obtained in several ways, *e.g.*, by the reaction of oxygen atoms O(^{3}P) with iodine,[147–150] laser flash photolysis of ozone in the presence of iodine[151] or flash photolysis of N_2O mixtures with iodine and nitrogen.[152] The addition of ozone into the flow reactor in the preparation of IO radicals from oxygen and iodine by microwave discharge greatly increases the concentration of radicals probably due to the reaction of ozone with iodine atoms.[150] Methyl iodide[101] or CF_3I[149, 153, 154] can serve as sources of iodine for the generation of IO radicals. The dissociation energy of the C—I bond in CF_3I is equal to 53.8 kcal mol^{-1} (Ref. 155). At 295 K, the rate constant for the reaction

$$O + CF_3I \longrightarrow IO + CF_3$$

is equal to $(5.8 \pm 1.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Ref. 156). The reaction of iodine atoms with chlorine dioxide proceeds by the only channel and yields two radicals:[148]

$$I + OClO \longrightarrow IO + ClO.$$

Excited oxygen atoms O(^{1}D) formed upon ozone photolysis react with HI yielding IO radicals:[157, 158]

$$O + HI \longrightarrow IO + H.$$

The main source of iodine in the atmosphere is phytoplankton and seaweed outputs. Iodine-containing compounds undergo photolysis by solar radiation, which reaches the surface of Earth, with the formation of atomic iodine. The most stable among iodine-containing compounds in troposphere is HI (its lifetime is $\sim 1-2$ h) although its reaction with hydroxyl radicals yields iodine atoms:[158, 159]

$$HI + OH \longrightarrow H_2O + I.$$

Reactions of iodine atoms with hydrogen-containing molecules are endothermic and do not proceed at low temperatures. At the same time, their reaction with ozone leads to the destruction of ozone in the troposphere:[160]

$$I + O_3 \longrightarrow IO + O_2.$$

The rate constant for this reaction in the temperature range of 240–370 K is described by the equation

$$k = (2.3 \pm 0.7) \times 10^{-11} \exp\left(\frac{-860 \pm 100}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and does not depend on the pressure in the range 30–200 Torr.[161] Yet another rate constant value at 298 K was obtained[162] $(1.20 \pm 0.10) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. This value was also recommended in an independent study.[161]

The concentration of IO radicals can be estimated by the titration of the mixture with nitrogen oxide

$$IO + NO \longrightarrow I + NO_2$$

with subsequent mass-spectrometric determination of NO_2 formed.[149]

2. Spectroscopic and thermodynamic characteristics

The vibrational constant ω_e of IO radicals in an argon matrix at 20 K is equal to 688 cm^{-1}.[101] Using vibrational-rotational spectrum of radicals in the ground state $X^2\Pi_{3/2}$, the following values were found: $\omega_e = 681.6$ cm^{-1}, $B_e = 0.34021$ cm^{-1} and $r_e = 1.8877$ Å.[147] The same value r_e was earlier obtained[163] from the microwave spectrum. A higher energy state of $X^2\Pi_{1/2}$ radicals is characterised by the values $\omega_e = 658$ cm^{-1} and $r_e = 1.887$ Å.[164] *Ab initio* calculations[165] of IO($X^2\Pi$) radicals gave the following values; $\omega_e = 664$ cm^{-1} and $r_e = 1.894$ Å.

The absorption spectrum of iodine monoxide in the UV region (340–470 nm) shows a pronounced vibrational structure in the range of 400–470 nm. The absorption section of the IO radicals at 427.2 nm (band 4,0) is equal to 3.1×10^{-17} (Ref. 151) or 2.8×10^{-17} cm^2 (Ref. 152). The section does not depend on temperature and is equal to 3.6×10^{-17} cm^2 in the range of 203–373 K.[166] At 435.6 nm (band 3,0), $\sigma = 5.9 \times 10^{-17}$ cm^2 (Ref. 167), at 445.0 nm (band 2,0), $\sigma = 7.3 \times 10^{-17}$ cm^2 (Ref. 156).

Among all halogen monoxides IO radicals have the highest dipole moment (2.45 D).[30]

Iodine monoxide, like other halogen monoxides has high electron affinity which is equal to 2.378 eV.[64, 164] The vibrational constant ω_e for IO^- anions is equal to 581 cm^{-1}, the equilibrium internuclear distance is 1.929 Å.[64, 164]

The adiabatic potential of IO ionisation was measured[163] by mass spectrometry and estimated[30, 165] by *ab initio* calculations.

U_{ad}/eV	Ref.
9.735	168
9.8	30
9.60	165

For IO^+ ions in the ground state formed as the result of a transition $IO^+(X^3\Sigma^-) \leftarrow IO(X^2\Pi_{3/2})$ the constants $\omega_e = 764$ cm^{-1} and $B_e = 0.357$ cm^{-1}, as well as the internuclear distance $r_e = 1.824$ Å were calculated.[165] The proton affinity of IO radicals was estimated as 180 kcal mol^{-1} (Ref. 168).

The dissociation energy of I—O bond was evaluated in a series of investigations:

D_0(I—O)/kcal mol^{-1}	Ref.
42 ± 5	128
53 ± 3	169
54	168
50	170

The value reported in Ref. 128 seems to be underestimated. The calculated[30] value of the dissociation energy is equal to

53.6 ± 1.0 kcal mol^{-1}. The bond strength in IO^- anion decreases to 37.9 kcal mol^{-1} as compared to the neutral radical while in IO^+ cation it increases to 68.7 kcal mol^{-1} (Ref. 30). The recommended values are $D_0(I-O^-) = 39.9$ and $D_0(I-O^+) = 72.3$ kcal mol^{-1} (Ref. 171).

For the enthalpy of formation of iodine monoxide, the calculated [170] value $\Delta_f H^\circ_0(IO) = 34.6$ kcal mol^{-1}. In the experimental study [168] this was estimated as $\Delta_f H^\circ_0(IO) = 30.6 \pm 1.0$ kcal mol^{-1}. A similar value [$\Delta_f H^\circ_0(IO) = 31.0 \pm 1.0$ kcal mol^{-1}] was also reported.[30] In the investigation of kinetics of IO reactions, the enthalpy of formation was found $\Delta_f H^\circ_{298}(IO) = 27.7 \pm 1.2$ kcal mol^{-1} (Refs 148 and 149).

3. Reactions of IO radicals

Photolysis of iodine monoxide during the day time under solar radiation (410–470 nm) is the main process leading to the disappearance of IO in the troposphere.[151, 152] Upon photolysis of IO, oxygen atoms $O(^3P)$ are formed with quantum yield 0.91 ± 0.19.[172]

IO radicals quickly react with each other. A number of papers is devoted to the investigation of kinetics of this reaction (see *e.g.* Refs 151, 152, 154, 156, 166, 173 and 174). Thus it was found [166] that the reaction rate at 250–320 K does not depend on temperature and has the constant of $(9.9 \pm 1.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Similar values of constant at 295 K was found:[154, 156] $(8.2 \pm 1.3) \times 10^{-11}$ and $(1.0 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Investigation of IO recombination obtained in different reaction systems at different pressures afforded the values of rate constants at 295–298 K in the range from $(5.3 \pm 0.3) \times 10^{-11}$ to $(10 \pm 3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Ref. 175). In the flash photolysis of iodine mixtures with ozone, the rate constant for recombination of IO radicals was obtained $(7.6 \pm 1.1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (298 K).[175] The main products of this reaction are OIO and dimer I_2O_2, in the troposphere the latter prevailing.[154, 175]

Iodine monoxide, like other halogen monoxides, reacts very slowly with ozone. The rates for both reaction channels were estimated separately:[176]

$$IO + O_3 \xrightarrow{a} IO_2 + O_2$$
$$IO + O_3 \xrightarrow{b} I + 2O_2$$

$k_a \leqslant 2.3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (323 K) and $k_b \leqslant 1.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (292 K).

Iodine monoxide reacts with hydrogen-containing molecules slowly as well. At room temperature the rate constants of IO reactions with ethylene or propylene is less than 2×10^{-16} cm^3 molecule^{-1} s^{-1}, for the reaction with methanethiol the rate constant is equal to 6.6×10^{-16} cm^3 molecule^{-1} s^{-1} (Ref. 177). Dimethyl sulfide appearing in the troposphere upon ocean emissions, is slowly oxidised to dimethyl sulfoxide on IO treatment

$$IO + Me_2S \longrightarrow I + Me_2SO.$$

According to different data,[167, 177–179] at 298 K the rate constant of this reaction is in the range from 2.5×10^{-13} to 8.8×10^{-15} cm^3 molecule^{-1} s^{-1}. However, the reaction of iodine monoxide with hydroperoxyl radicals proceeds quickly yielding HOI as the only iodine-containing product:

$$IO + HO_2 \longrightarrow HOI + O_2.$$

This reaction has negative activation energy:

$k = 9.3 \times 10^{-12} \exp\left(\frac{680}{T}\right)$ cm^3 molecule^{-1} s^{-1},
$T = 274-373$ K [180]

or

$k = (2.2 \pm 0.6) \times 10^{-11} \exp\left(\frac{400 \pm 80}{T}\right)$ cm^3 molecule^{-1} s^{-1},
$T = 273-353$ K.[179]

An important source of atomic iodine apart from the photodissociation of IO is its reaction with nitrogen oxide proceeding by the only channel, which yields I and NO_2. This reaction has a small negative activation energy (Table 3).

Table 3. Temperature dependence of rate constant for the reaction $IO + NO \longrightarrow I + NO_2$.

$k \times 10^{11}$/cm^3 molecule^{-1} s^{-1}	T/K	Ref.
$(6.9 \pm 1.7) \times 10^{-12} \exp\left(\frac{328 \pm 71}{T}\right)$	242–359	159
$(1.02 \pm 0.31) \times 10^{-11} \exp\left(\frac{185 \pm 70}{T}\right)$	240–370	161
$(1.03 \pm 0.09) \times 10^{-11} \exp\left(\frac{210 \pm 80}{T}\right)$	293–366	181
$(8.3 \pm 2.3) \times 10^{-12} \exp\left(\frac{269 \pm 85}{T}\right)$	273–353	179

Reaction of iodine monoxide with chlorine monoxide leads to several products. Using mass spectrometry, is was shown [149] that the most probable channel of this reaction is the formation of chlorine dioxide.

$$IO + ClO \longrightarrow I + OClO$$
$$IO + ClO \longrightarrow I + Cl + O_2$$
$$IO + ClO \longrightarrow ICl + O_2$$

In the temperature range of 200–362 K the rate constant of the reaction

$$IO + ClO \longrightarrow \text{products}$$

is described by the equation

$$k = (5.1 \pm 1.7) \times 10^{-12} \exp\left(\frac{280 \pm 80}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and is equal to $(1.29 \pm 0.27) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.[153] A larger constant value, $(2.62 \pm 0.57) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 295 K, was found in another work.[182]

* * *

The material presented in this review confirms the interest of scientists in halogen monoxides — simplest oxygen-containing compounds of halogens. Investigation of these radicals can shed light on many chemical processes occurring in the atmosphere, in particular, on the mechanism of ozone decomposition in the stratosphere, and will be also useful for establishing the mechanisms of oxidation and halogenation reactions.

References

1. R P Wayne, G Poulet, P Biggs, J P Burrows, R A Cox, P J Crutzen, G D Hayman, M E Jenkin, G Le Bras, G K Moortgat, U Platt, R N Schindler *Atmos. Environ.* **29** 2677 (1995)
2. I V Nikitin *Usp. Khim.* **71** 99 (2002) [*Russ. Chem. Rev.* **71** 85 (2002)]
3. I V Nikitin *Usp. Khim.* **73** 662 (2004) [*Russ. Chem. Rev.* **73** 609 (2004)]
4. R Atkinson, D L Baulch, R A Cox, J N Crowley, R F Hampson, R G Hynes, M E Jenkin, M J Rossi, J Troe *Atmos. Chem. Phys.* **7** 981 (2007)
5. A Arkell, R R Reinhard, L P Larson *J. Am. Chem. Soc.* **87** 1016 (1965)
6. A R W McKellar *Can. J. Phys.* **57** 2106 (1979)
7. A R W McKellar, C Yamada, E Hirota *J. Mol. Spectrosc.* **97** 425 (1983)
8. L Andrews, J I Raymond *J. Chem. Phys.* **55** 3078 (1971)
9. M A A Clyne, R T Watson *Chem. Phys. Lett.* **12** 344 (1971)
10. H G Wagner, J Warnatz, C Zetzsch *Angew. Chem., Int. Ed. Engl.* **10** 564 (1972)
11. H G Wagner, C Zetzsch, J Warnatz *Ber. Bunsen-Ges. Phys. Chem.* **76** 526 (1972)
12. M A A Clyne, R T Watson *J. Chem. Soc., Faraday Trans. 1* **70** 1109 (1974)
13. J M Dyke, N Jonathan, J D Mills, A Morris *Mol. Phys.* **40** 1177 (1980)
14. G W Ray, R T Watson *J. Phys. Chem.* **85** 2955 (1981)
15. J B Burkholder, P D Hammer, C J Howard, A R W McKellar *J. Mol. Spectrosc.* **118** 471 (1986)
16. P D Hammer, A Sinha, J B Burkholder, C J Howard *J. Mol. Spectrosc.* **129** 99 (1988)
17. Yu R Bedzhanyan, E M Markin, Yu M Gershenzon *Kinet. Katal.* **33** 744 (1992) [a]
18. R Atkinson, D L Baulch, R A Cox, R F Hampson Jr, J A Kerr, M J Rossi, J Troe *J. Phys. Chem. Ref. Data* **26** 521 (1997)
19. E Ya Misochko, A V Akimov, C A Wight *J. Phys. Chem. A* **103** 7972 (1999)
20. Yu R Bedzhanyan, E M Markin, Yu M Gershenzon *Kinet. Katal.* **33** 753 (1992) [a]
21. Yu R Bedzhanyan, E M Markin, G G Politenkova, Yu M Gershenzon *Kinet. Katal.* **33** 998 (1992) [a]
22. Yu R Bedzhanyan, E M Markin, Yu M Gershenzon *Kinet. Katal.* **34** 7 (1993) [a]
23. I V Nikitin *Khimiya Kislorodnykh Soedinenii Galogenov* (Chemistry of Oxygen Compounds of Halogens) (Moscow: Nauka, 1986)
24. Yu R Bedzhanyan, E M Markin, E O Kirakosyan, Yu M Gershenzon *Kinet. Katal.* **34** 788 (1993) [a]
25. Z Y Zhang, S-C Kuo, R B Klemm, P S Monks, L J Stief *Chem. Phys. Lett.* **229** 377 (1994)
26. L Andrews *J. Chem. Phys.* **57** 51 (1972)
27. P A G O'Hare, A C Wahl *J. Chem. Phys.* **53** 2469 (1970)
28. A R W McKellar *J. Mol. Spectrosc.* **101** 186 (1983)
29. S R Langhoff, C W Bauschlicher Jr, H Partridge *Chem. Phys. Lett.* **102** 292 (1983)
30. M P McGrath, F S Rowland *J. Phys. Chem.* **100** 4815 (1996)
31. J Berkowitz, P M Dehmer, W A Chupka *J. Chem. Phys.* **59** 925 (1973)
32. M K Gilles, M L Polak, W C Lineberger *J. Chem. Phys.* **96** 8012 (1992)
33. P Haaland *Chem. Phys. Lett.* **176** 287 (1991)
34. D H Levy *J. Chem. Phys.* **56** 1415 (1972)
35. Y Zhao, J S Francisco *Chem. Phys. Lett.* **167** 285 (1990)
36. Yu R Bedzhanyan, E M Markin, Yu M Gershenzon *Kinet. Katal.* **33** 1004 (1992) [a]
37. J S Francisco *J. Chem. Phys.* **100** 2896 (1994)
38. J S Francisco *J. Chem. Phys.* **96** 3348 (1992)
39. Yu R Bedzhanyan, Yu M Gershenzon, V B Rozenshtein *Kinet. Katal.* **31** 1474 (1990) [a]
40. J S Francisco *J. Chem. Phys.* **98** 2198 (1993)
41. J S Francisco, Y Su *Chem. Phys. Lett.* **215** 58 (1993)
42. J S Francisco, Y Su *Chem. Phys. Lett.* **215** 417 (1993)
43. Yu R Bedzhanyan, E M Markin, S D Il'in, Yu M Gershenzon *Khim. Fiz.* **16** (5) 84 (1997) [b]
44. J J Renard, H I Bolker *Chem. Rev.* **76** 487 (1976)
45. G Pannetier, A G Gaydon *Nature (London)* **161** 242 (1948)
46. D K Bulgin, J M Dyke, N Jonathan, A Morris *J. Chem. Soc., Faraday Trans. 2* **75** 456 (1979)
47. J Zhang, Y T Lee *J. Phys. Chem. A* **101** 6485 (1997)
48. J M Nikovich, K D Kreutter, P H Wine *Int. J. Chem. Kinet.* **22** 399 (1990)
49. M S Zahniser, F Kaufman, J G Anderson *Chem. Phys. Lett.* **37** 226 (1976)
50. M Trainer, M Helten, D Knapska *J. Chem. Phys.* **79** 3648 (1983)
51. G S Tyndall, C S Kegley-Owen, J J Orlando, J G Calvert *J. Chem. Soc., Faraday Trans.* **93** 2675 (1997)
52. C M Nelson, T A Moore, M Okumura, T K Minton *J. Chem. Phys.* **100** 8055 (1994)
53. R P Thorn Jr, L J Stief, S-C Kuo, R B Klemm *J. Phys. Chem.* **100** 14178 (1996)
54. A G Maki, F J Lovas, W B Olson *J. Mol. Spectrosc.* **92** 410 (1982)
55. F G Simon, W Schneider, G K Moortgat, J P Burrows *J. Photochem. Photobiol. A* **55** 1 (1990)
56. S P Sander, R R Friedl *J. Phys. Chem.* **93** 4764 (1989)
57. R K Kakar, E A Cohen, M Geller *J. Mol. Spectrosc.* **70** 243 (1978)
58. J B Burkholder, P D Hammer, C J Howard, A G Maki, G Thompson, C Chackerian Jr *J. Mol. Spectrosc.* **124** 139 (1987)
59. J A Coxon, W E Jones, E G Skolnik *Can. J. Phys.* **54** 1043 (1976)
60. T Amano, E Hirota, *J. Mol. Spectrosc.* **66** 185 (1977)
61. D Yaron, K Peterson, W Klemperer *J. Chem. Phys.* **88** 4702 (1988)
62. D K Bulgin, J M Dyke, N Jonathan, A Morris *Mol. Phys.* **32** 1487 (1976)
63. M Schwell, H-W Jochims, B Wassermann, U Rockland, R Flesch, E Rühl *J. Phys. Chem.* **100** 10070 (1996)
64. M K Gilles, M L Polak, W C Lineberger *J. Chem. Phys.* **96** 8012 (1992)
65. M A Grela, A J Colussi *J. Phys. Chem.* **100** 10150 (1996)
66. J A Coxon, D A Ramsay *Can. J. Phys.* **54** 1034 (1976)
67. H F Davis, Y T Lee *J. Phys. Chem.* **100** 30 (1996)
68. M Trolier, R L Mauldin III, A R Ravishankara *J. Phys. Chem.* **94** 4896 (1990)
69. A Horowitz, J N Crowley, G K Moortgat *J. Phys. Chem.* **98** 11924 (1994)
70. L Goldfarb, J B Burkholder, A R Ravishankara *J. Phys. Chem. A* **105** 5402 (2001)
71. J Brunning, L J Stief *J. Chem. Phys.* **84** 4371 (1986)
72. P Biggs, M H Harwood, A D Parr, R P Wayne *J. Phys. Chem.* **95** 7746 (1991)
73. J B Lipson, M J Elrod, T W Beiderhase, L T Molina, M J Molina *J. Chem. Soc., Faraday Trans.* **93** 2665 (1997)
74. C S Kegley-Owen, M K Gilles, J B Burkholder, A R Ravishankara *J. Phys. Chem. A* **103** 5040 (1999)
75. F C Cattell, R A Cox *J. Chem. Soc., Faraday Trans. 2* **82** 1413 (1986)
76. G P Knight, T Beiderhase, F Helleis, G K Moortgat, J N Crowley *J. Phys. Chem. A* **104** 1674 (2000)
77. T J Leck, J-E L Cook, J W Birks *J. Chem. Phys.* **72** 2364 (1980)
78. M Finkbeiner, J N Crowley, O Horie, R Mmller, G K Moortgat, P J Crutzen *J. Phys. Chem.* **99** 16264 (1995)
79. D Buttar, D M Hirst *J. Chem. Soc., Faraday Trans.* **90** 1811 (1994)
80. N Kaltsoyannis, D M Rowley *Phys. Chem. Chem. Phys.* 419 (2002)
81. R R Friedl, S P Sander *J. Phys. Chem.* **93** 4756 (1989)
82. A D Parr, R P Wayne, G D Hayman, M E Jenkin, R A Cox *Geophys. Res. Lett.* **17** 2357 (1990)
83. F H C Edgecombe, R G W Norrish, B A Thrush *Proc. R. Soc. London, Ser. A* **233** 24 (1957)
84. E T McHale, G von Elbe *J. Am. Chem. Soc.* **89** 2795 (1967)
85. G D Hayman, R A Cox *Chem. Phys. Lett.* **155** 1 (1989)

86. F Zabel *Ber. Bunsen-Ges. Phys. Chem.* **95** 893 (1991)
87. H S P Müller, H Willner *J. Phys. Chem.* **97** 10589 (1993)
88. A J Colussi, R W Redmond, J C Scaiano *J. Phys. Chem.* **93** 4783 (1989)
89. J B Burkholder, J J Orlando, C J Howard *J. Phys. Chem.* **94** 687 (1990)
90. J B Burkholder, R L Mauldin III, R J Yokelson, S Solomon, A R Ravishankara *J. Phys. Chem.* **97** 7597 (1993)
91. M H Harwood, D M Rowley, R A Freshwater, R A Cox, R L Jones *J. Chem. Soc., Faraday Trans.* **91** 3027 (1995)
92. R R Friedl, M Birk, J J Oh, E A Cohen *J. Mol. Spectrosc.* **170** 383 (1995)
93. W-K Li, K-C Lau, C Y Ng, H Baumgärtel, K-M Weitzel *J. Phys. Chem. A* **104** 3197 (2000)
94. R Flesh, B Wassermann, B Rothmund, E Rühl *J. Phys. Chem.* **98** 6263 (1994)
95. J Clark, J S Francisco *J. Phys. Chem. A* **101** 7145 (1997)
96. K H Kim, Y K Han, Y S Lee *J. Mol. Struct. (THEOCHEM)* **460** 19 (1999)
97. R S Zhu, M C Lin *J. Chem. Phys.* **118** 8645 (2003)
98. S Abramowitz, M W Chase Jr *Pure Appl. Chem.* **63** 1449 (1991)
99. A Beltrán, J Andrés, S Noury, B Silvi *J. Phys. Chem. A* **103** 3078 (1999)
100. S P Sander, R R Friedl, Y L Yung *Science* **245** 1095 (1989)
101. A Loewenschuss, J C Miller, L Andrews *J. Mol. Spectrosc.* **80** 351 (1980)
102. A Carrington, D H Levy *J. Phys. Chem.* **71** 2 (1967)
103. M Kaufman, C E Kolb *Chem. Instrum.* **3** 175 (1971)
104. D E Tevault, N Walker, R R Smardzewski, W B Fox *J. Phys. Chem.* **82** 2733 (1978)
105. S P Sander, G W Ray, R T Watson *J. Phys. Chem.* **85** 199 (1981)
106. A Wahner, A R Ravishankara, S P Sander, R R Friedl *Chem. Phys. Lett.* **152** 507 (1988)
107. Y Bedjanian, G Le Bras, G Poulet *Chem. Phys. Lett.* **266** 233 (1997)
108. J E Butler, K Kawaguchi, E Hirota *J. Mol. Spectrosc.* **104** 372 (1984)
109. D W Toohey, J G Anderson *J. Phys. Chem.* **92** 1705 (1988)
110. T Amano, A Yoshinaga, E Hirota *J. Mol. Spectrosc.* **44** 594 (1972)
111. E A Cohen, H M Pickett, M Geller *J. Mol. Spectrosc.* **87** 459 (1981)
112. G Poulet, M Pirre, F Maguin, R Ramaroson, G Le Bras *Geophys. Res. Lett.* **19** 2305 (1992)
113. P S Monks, L J Stief, M Krauss, S C Kuo, B B Klemm *Chem. Phys. Lett.* **211** 416 (1993)
114. M J Elrod, R F Meads, J B Lipson, J V Seeley, M J Molina *J. Phys. Chem.* **100** 5808 (1996)
115. D J Bogan, R P Thorn, F L Nesbitt, L J Stief *J. Phys. Chem.* **100** 14383 (1996)
116. J C Hansen, Y Li, J S Francisco, Z Li *J. Phys. Chem. A* **103** 8543 (1999)
117. F Danis, F Caralp, J Masanet, R Lesclaux *Chem. Phys. Lett.* **167** 450 (1990)
118. R L Mauldin III, A Wahner, A R Ravishankara *J. Phys. Chem.* **97** 7585 (1993)
119. Y Nakano, M Goto, S Hashimoto, M Kawasaki, T J Wallington *J. Phys. Chem. A* **105** 11045 (2001)
120. O Gálvez, A Zoermer, A Loewenschuss, H Grothe *J. Phys. Chem. A* **110** 6472 (2006)
121. B Laszlo, R E Huie, M J Kurylo, A W Miziolek *J. Geophys. Res. D* **102** 1523 (1997)
122. Y Ninomiya, S Hashimoto, M Kawasaki, T J Wallington *Int. J. Chem. Kinet.* **32** 125 (2000)
123. J Zhang, T-T Miau, Y T Lee *J. Phys. Chem. A* **101** 6922 (1997)
124. M Barnett, E A Cohen, D A Ramsay *Can. J. Phys.* **59** 1908 (1981)
125. B J Drouin, C E Miller, H S P Müller, E A Cohen *J. Mol. Spectrosc.* **205** 128 (2001)
126. J J Orlando, J B Burkholder, A M R P Bopegedera, C J Howard *J. Mol. Spectrosc.* **145** 278 (1991)
127. A R W McKellar *J. Mol. Spectrosc.* **86** 43 (1981)
128. R A Durie, D A Ramsay *Can. J. Phys.* **36** 35 (1958)
129. D M Wilmouth, T F Hanisco, N M Donahue, J G Anderson *J. Phys. Chem. A* **103** 8935 (1999)
130. S J Dunlavey, J M Dyke, A Morris *Chem. Phys. Lett.* **53** 382 (1978)
131. R P Thorn Jr, L J Stief, T J Buckley, R D Johnson III, P S Monks, R B Klemm *J. Phys. Chem. A* **103** 8384 (1999)
132. O V Rattigan, R A Cox, R L Jones *J. Chem. Soc., Faraday Trans.* **91** 4189 (1995)
133. I T Lançar, G Laverdet, G Le Bras, G Poulet *Int. J. Chem. Kinet.* **23** 37 (1991)
134. I Bridier, B Veyret, R Lesclaux *Chem. Phys. Lett.* **201** 563 (1993)
135. D M Rowley, M H Harwood, R A Freshwater, R L Jones *J. Phys. Chem.* **100** 3020 (1996)
136. M H Harwood, D M Rowley, R A Cox, R L Jones *J. Phys. Chem. A* **102** 1790 (1998)
137. Y Bedjanian, G Le Bras, G Poulet *J. Phys. Chem. A* **102** 10501 (1998)
138. Z Li, G-R Jeong *Chem. Phys. Lett.* **340** 194 (2001)
139. G Poulet, I T Lançar, G Laverdet, G Le Bras *J. Phys. Chem.* **94** 278 (1990)
140. A A Turnipseed, J W Birks, J G Calvert *J. Phys. Chem.* **95** 4356 (1991)
141. Y Bedjanian, V Riffault, G Le Bras, G Poulet *J. Phys. Chem. A* **105** 6154 (2001)
142. Z Li, R R Friedl, S P Sander *J. Chem. Soc., Faraday Trans.* **93** 2683 (1997)
143. J M Cronkhite, R E Stickel, J M Nikovich, P H Wine *J. Phys. Chem. A* **102** 6651 (1998)
144. Y Bedjanian, V Riffault, G Poulet *J. Phys. Chem. A* **105** 3167 (2001)
145. S Guha, J S Francisco *J. Phys. Chem. A* **103** 8000 (1999)
146. T Ingham, D Bauer, R Sander, P J Crutzen, J N Crowley *J. Phys. Chem. A* **103** 7199 (1999)
147. J P Bekooy, W L Meerts, A Dymanus *J. Mol. Spectrosc.* **102** 320 (1983)
148. Y Bedjanian, G Le Bras, G Poulet *J. Phys. Chem.* **100** 15130 (1996)
149. Y Bedjanian, G Le Bras, G Poulet *J. Phys. Chem. A* **101** 4088 (1997)
150. P O Wennberg, J W Brault, T F Hanisco, R J Salawitch, G H Mount *J. Geophys. Res. D* **102** 8887 (1997)
151. R E Stickel, A J Hynes, J D Bradshaw, W L Chameides, D D Davis *J. Phys. Chem.* **92** 1862 (1988)
152. B Laszlo, M J Kurylo, R E Huie *J. Phys. Chem.* **99** 11701 (1995)
153. A A Turnipseed, M K Gilles, J B Burkholder, A R Ravishankara *J. Phys. Chem. A* **101** 5517 (1997)
154. W J Bloss, D M Rowley, R A Cox, R L Jones *J. Phys. Chem. A* **105** 7840 (2001)
155. X Wang, Z Tian, T Shi, X Shi, D Yang, Q Zhu *Chem. Phys. Lett.* **380** 600 (2003)
156. D B Atkinson, J W Hudgens, A J Orr-Ewing *J. Phys. Chem. A* **103** 6173 (1999)
157. G Inoue, M Suzuki, N Washida *J. Chem. Phys.* **79** 4730 (1983)
158. M Alagia, N Balucani, P Casavecchia, G G Volpi *J. Phys. Chem. A* **101** 6455 (1997)
159. E P Daykin, P H Wine *J. Phys. Chem.* **94** 4528 (1990)
160. D Davis, J Crawford, S Liu, S McKeen, A Bandy, D Thornton, F Rowland, D Blake *J. Geophys. Res. D* **101** 2135 (1996)
161. A A Turnipseed, M K Gilles, J B Burkholder, A R Ravishankara *Chem. Phys. Lett.* **242** 427 (1995)
162. S N Buben, I K Larin, N A Messineva, E M Trofimova *Khim. Fiz.* **9** 116 (1990) [b]
163. S Saito *J. Mol. Spectrosc.* **48** 530 (1973)
164. M K Gilles, M L Polak, W C Lineberger *J. Chem. Phys.* **95** 4723 (1991)
165. P Hassanzadeh, K K Irikura, R D Johnson III *J. Phys. Chem. A* **101** 6897 (1997)
166. M H Harwood, J B Burkholder, M Hunter, R W Fox, A R Ravishankara *J. Phys. Chem. A* **101** 853 (1997)

167. Y Nakano, S Enami, S Nakamichi, S Aloisio, S Hashimoto, M Kawasaki *J. Phys. Chem. A* **107** 6381 (2003)
168. Z Zhang, P S Monks, L J Stief, J F Liebman, R E Huie, S-C Kuo, R B Klemm *J. Phys. Chem.* **100** 63 (1996)
169. D S A G Radlein, J C Whitehead, R Grice *Nature (London)* **253** 37 (1975)
170. B Ruscic, J Berkowitz *J. Chem. Phys.* **101** 7795 (1994)
171. P Hassanzadeh, K K Irikura *J. Phys. Chem. A* **101** 1580 (1997)
172. T Ingham, M Cameron, J N Crowley *J. Phys. Chem. A* **104** 8001 (2000)
173. M E Jenkin, R A Cox *J. Phys. Chem.* **89** 192 (1985)
174. S P Sander *J. Phys. Chem.* **90** 2194 (1986)
175. J C Gómez Marttn, P Spietz, J P Burrows *J. Phys. Chem. A* **111** 306 (2007)
176. I K Larin, D V Nevozhai, A I Spasskii, E M Trofimova, L E Turkin *Kinet. Katal.* **40** 487 (1999) [a]
177. F Maguin, A Mellouki, G Laverdet, G Poulet, G Le Bras *Int. J. Chem. Kinet.* **23** 237 (1991)
178. I Barnes, V Bastian, K H Becker, R D Overath *Int. J. Chem. Kinet.* **23** 579 (1991)
179. G P Knight, J N Crowley *Phys. Chem. Chem. Phys.* 393 (2001)
180. J M Cronkhite, R E Stickel, J M Nikovich, P N Wine *J. Phys. Chem. A* **103** 3228 (1999)
181. S N Buben, I K Larin, N A Messineva, E M Trofimova *Khim. Fiz.* **15** (5) 116 (1996) [b]
182. I K Larin, N A Messineva, D V Nevozhai, A I Spasskii, E M Trofimova *Kinet. Katal.* **41** 346 (2000) [a]

[a] — *Kinet. Catal. (Engl. Transl.)*
[b] — *Russ. J. Phys. Chem. B (Engl. Transl.)*