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Determination of uptake coefficients ClO radicals with surfaces of sea salts depend on the ozone concentration

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Sea salt aerosols represent an unlimited halogen reservoir. The ClO radical plays a critical role in stratospheric destruction of ozone. The present work was aimed to study the interaction of ClO radicals with KBr, NaCl and NaBr crystal films using discharge flow reactor with modulated molecular beam mass spectrometer. The experimental values of ClO uptake coefficient ku on KBr, NaCl and NaBr, which are important components of sea salts, were determined. Investigation of uptake coefficients ClO radicals with surfaces of sea salts were carried out. Reaction of chlorine atoms with ozone has been used as a source of ClO radicals. Objective: Uptake coefficients of ClO radicals. Sea salt: NaCl, NaBr, and KBr. Source of ClO: Cl + O_3 => ClO + O_2, k = 1.2 • 10-11 cm3 molecule-1 s-1. Determination O_3: 1.Photoabsorption; 2. Titration NO + O_3 => NO_2 + O_2. 3. Ionization Cross Section (ICS) ICS O_3/ ICS O_2 = 1.5.

The reactive surfaces were prepared by coating the inner surface of the reactor by spray depositing thin films using a constant output atomizer. Salt surface is the geometrical area: Surface composition: pure NaCl, NaBr, KBr, film deposition. Study of the heterogeneous processes of the halogen containing radical was carried out in the temperature range 240 - 370 K and at a total pressure 1-10 mbar using the discharge-flow technique. The reactants were detected by molecular beam mass spectrometers with electron impact detectors. Uptake coefficient measurements were obtained using an MS 7303 quadrupole mass spectrometer. Uptake coefficients were calculated from the first-order decay of the radical signal as a function of the injector position over the salt crystallites. The uptake coefficients radicals ClO on the surface of NaCl, KBr, NaBr were determined (3.7 ± 1.5) •10-4, (12.3 ± 3.6) • 10-4, (9.6 ± 5.7) • 10-4, respectively.

Table 1 represents the kinetics of ClO consumption on NaBr surface at T = 295K. This data gave ku = (14.3 ± 0.95) • 10-4. Under the regular experimental conditions with ozone concentration of
4.6 `[U+F0B4]` 1013 molecule cm-3, the average value of ku obtained for NaBr was higher than that for KBr and NaCl, ku = (12.3 ± 3.6) • 10-4. It can be noted that the scattering of the data in the experiments with NaBr was rather low. The experimental error did not exceed 30%, that is sufficiently lower than that for KBr (∼60 %), and for NaCl (∼40 %).

One must be careful when determining ku at high concentrations of ozone ku depends on its concentration in a reactor. It was found that even small changes in ozone concentration resulted in a noticeable change of the ClO uptake. The ku dependence on the concentration of ozone was investigated. The ozone concentration was varied by the change of the fraction of the O_3/O_2 mixture flow from the ozonizer directed to the reactor. The increase of ozone concentration from 1.45 • 1013 to 2.52 • 1014 molecules cm−3 resulted in a significant decrease of the ku value from 9.3 •10−4 up to 0.4 • 10−4 (Table 1). A possible explanation of this phenomenon is the occupation of the active sites of the injector surface by ozone molecules.

Table 1. Dependence of ClO uptake coefficient ku on KBr surface on ozone concentration
at T = 292 K.

ku /10-4	[O_3]/1013 molecule cm-3
7,14	1,45
9,33	1,92
7,11	2,64
6,72	3,18
6,12	3,66
5,23	4,7
7,82	4,74
2,35	6,73
1,98	8,54
2,94	10,1
0,85	15,16
0,39	25,22

It can be assumed that a strong ku dependence on ozone concentration exists also at lower O_3 concentrations typical for real atmospheric altitudes.