The Mechanism of Reactive NO₃ Uptake on Dry NaX (X=Cl, Br)

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(Received: 3 August 1998; in final form 31 March 1999)

Abstract. A simple kinetic mechanism of nitrate radicals uptake on dry sea-salt NaCl, NaBr surfaces is proposed. The mechanism includes adsorption/desorption equilibrium and unimolecular decomposition of the adsorbed complex:

\[ \text{NO}_3(g) + \text{NaX}(s) \rightarrow (\text{NO}_3\text{-NaX})(s); \quad (\text{NO}_3\text{-NaX})(s) \rightarrow \text{NaNO}_3 + \text{X}(s) \]

Two techniques were used: the matrix isolation ESR and mass spectrometry. The uptake coefficient (\(\gamma\)) is found to be dependent on exposure time of salt to NO\(_3\) for raw coating. The initial (\(\gamma(\rightarrow 0)\)) is higher than the observable steady-state (\(\gamma_\text{obs}\)) at room temperature. \(\gamma_\text{obs}\) is independent of [NO\(_3\)] at low [NO\(_3\)] \(= 3 \times 10^7 - 10^{11} \text{ cm}^{-3}\), but it is inversely proportional to [NO\(_3\)] at concentrations higher than \(10^{12} \text{ cm}^{-3}\). At temperatures above 100 °C, \(\gamma_\text{obs}\) becomes independent of [NO\(_3\)] in a wider range of [NO\(_3\)]. An increased number of dislocations is supposed to exist in the case of raw coating. Due to a wide spread of the surface sites binding energy with the ionic lattice near dislocations, the part of surface complexes has lower binding energy and "burns" more rapidly. That burning determines the transition from \(\gamma(\rightarrow 0)\) down to \(\gamma_\text{obs}\).

The kinetic parameters and elementary rate coefficients are obtained. The recommended \(\gamma\) for low atmospheric NO\(_3\) concentration are in the range of 0.002 ± 0.04 for NaCl and 0.1-0.3 for NaBr depending on a mechanism of the \(\gamma(\rightarrow 0)\) relaxation.

Key words: atmospheric aerosol particles, NO\(_3\) heterogeneous reaction, reaction mechanism, uptake coefficient.

1. Introduction.

Heterogeneous reactions of nitrogen containing minor constituents are well known to be important in both the stratosphere and the troposphere. During the past decade a number of laboratory studies of the reactions of NO\(_2\), N\(_2\)O\(_5\), HNO\(_3\), ClNO\(_2\) with different aerosol materials has been carried out. Reactions of these species with NaCl and NaBr proceed via displacement of chloride and bromide followed by release of the halogen containing products to the gas phase.

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Special attention was paid to the reaction of $\text{N}_2\text{O}_3 + \text{NaX} \rightarrow \text{NaNO}_3 + \text{XNO}_2$, ($X = \text{Cl, Br}$) (Finlayson-Pitts et al., 1989; Zetzsche and Behnke, 1992; Fenter et al., 1996). A photolyzable product XNO$_2$ formed in this reaction results in halogen atom generation via photolysis of XNO$_2$. Atomic chlorine is an active agent in initiation of oxidation processes, while the bromine is more effective in ozone destruction. The detailed study of ClINO$_2$ generation in the reaction of gaseous $\text{N}_2\text{O}_3$ with NaCl aqueous solution and its decay has been recently carried out (Behnke et al., 1997; Frenzel et al., 1998).

Possible presence of chlorine and its remarkable contribution to the oxidizing capacity of the marine boundary layer (MBL) and coastal regions has been demonstrated in field observations (Pszenny et al., 1993; Singh et al., 1996) and modeling (Sander and Crutzen, 1996; Vogt et al., 1996). Direct observation of BrO in the arctic troposphere during polar sunrise shows its correlation with surface ozone depletion (Hausmann and Platt, 1994). Besides $\text{N}_2\text{O}_3$ reactions, those of the nitrate radical with sea-salt

$$\text{NO}_3 + \text{NaX} \rightarrow \text{NaNO}_3 + \text{X}$$
$$\rightarrow \text{NaNO}_3 + \frac{1}{2}\text{X}_2$$
could be also a source of halogen in the troposphere. For example, in the tropics under MBL conditions ($T = 300 \text{ K}$, $\text{NO}_3 = 10$-20 ppt) the night-time equilibrium NO$_3$ concentration is about two orders of magnitude higher than [N$_2$O$_3$]. Thus one might expect that the NO$_3$ reaction with sea-salt would essentially contribute to the halogen activation of the troposphere during the night (Platt et al., 1984).

It is pertinent to note that NO$_3$ reaction can be a non photolytic source of halogen atoms (Seisel et al., 1997). Besides possible importance in halogen activation of the troposphere, the NO$_3$ reaction with sea-salt aerosol might be an efficient sink of NO$_3$ in MBL (Seisel et al., 1997; Rudich et al., 1996). Note that NO$_3$ itself is responsible for a large part of the oxidizing potential of the troposphere at night (Wayne et al., 1991).

Recently the reactive uptake of nitrate radicals by aqueous solutions of NaCl and NaBr was studied (Rudich et al., 1996). The uptake coefficient ($\gamma$) does not depend on the [NO$_3$] in the (0.2-1) x 10$^{12}$ cm$^{-3}$ range. It grows almost directly proportional to the square root of the Cl$^-$ and Br$^-$ ion concentrations. For typical sea-salt ionic composition ([Cl$^-$] = 1 M, [Br$^-$] = 5 x 10$^{-3}$ M) the total uptake coefficient reaches 10$^{-2}$. A higher $\gamma = (4.9 \pm 3) x 10^{-3}$ for dry NaCl was measured by Seisel et al., (1997). The uptake coefficient independence on NO$_3$ concentration in a wider range of (3 x 10$^{10}$-10$^{15}$) cm$^{-3}$ was confirmed by Seisel et al. (1997).

The authors (Seisel et al., 1997; Rudich et al., 1996) conclude that in the marine environment, the rate of NO$_3$ consumption in the heterogeneous reaction with sea-salt aerosols is comparable with the main gaseous NO$_3$ sink in reaction with dimethyl sulfide (DMS).

This paper describes the results of the kinetic mechanism studies of NO$_3$ consumption in the reaction with dry NaCl and NaBr salts. Other studies dealing