

Heterogeneous Reactions of NaCl (s) with $\text{HNO}_3(\text{g})$, $\text{N}_2\text{O}_5(\text{g})$, and $\text{ClONO}_2(\text{g})$ over a Temperature Range 223-296 K

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The heterogeneous reactions of $\text{HNO}_3 + \text{NaCl} \rightarrow \text{HCl} + \text{NaNO}_3$ (1), $\text{N}_2\text{O}_5 + \text{NaCl} \rightarrow \text{ClONO}_2 + \text{NaNO}_3$ (2), and $\text{ClONO}_2 + \text{NaCl} \rightarrow \text{Cl}_2 + \text{NaNO}_3$ (3) were investigated over a temperature range 223-296 K in a flow reactor interfaced with a quadrupole mass spectrometer. Partial pressures of HNO_3 , N_2O_5 , and ClONO_2 in the range 10^{-8} - 10^{-5} Torr were used. Granule sizes and surface roughness of the NaCl substrates were determined by using a scanning electron microscope, and in separate experiments, surface areas of the substrates were measured by using BET analysis of gas-adsorption isotherms. Both electron-impact ionization and chemical ionization sources coupled to mass spectrometers were used to monitor the reactants and products. For dry NaCl substrates, the reaction probability measurements based on the decay rates of the reactants and the growth rates of products are summarized as follows:

Temperature	$\gamma(1)$	$\gamma(2)$	$\gamma(3)$
296 K	1.5(-2)	<1.0(-4)	4.6(-3)
223 K	1.3(-2)	<1.0(-4)	6.7(-3)

In order to mimic the conditions encountered in the lower stratosphere, the effect of water vapor pressures between 5×10^{-5} and 3×10^{-4} Torr was also studied. With added **1120**, the mechanism for reaction (1) does not change much; however, the hydrolysis of N_2O_5 and ClONO_2 become significant in comparison to reactions (2) and (3). The implications of this result for the enhancement of hydrogen chloride in the stratosphere after the El Chichon volcanic eruption and for the marine troposphere will be discussed.

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