A KINETIC AND MECHANISTIC STUDY OF BrO_x/HO_x CROSS REACTIONS INFLUENCING BROMINE PARTITIONING AND OZONE BUDGET IN THE STRATOSPHERE.

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Bromine is a considerably more effective ozone destroyer than chlorine on a per atom basis. The efficiency of bromine in depleting ozone strongly depends on the bromine partitioning between its active forms and its major reservoir species, HBr. Current model calculations of HBr concentrations in the stratosphere underestimate those recently measured. The disagreement between model calculations and observations may result from uncertainties in reaction rates for HBr formation and consumption. In this respect, the kinetics and mechanism of the following reactions have been investigated at 1 Torr total pressure and in the temperature range 230-355K using the discharge flow mass spectrometric technique: $OH + BrO \rightarrow HO_2 + Br$ (1a), $OH + BrO \rightarrow HBr + O_2$ (1b), $HO_2 + BrO \rightarrow HOBr + O_2$ (2a), $HO_2 + BrO \rightarrow HBr + O_3$ (2b), $HO_2 + Br \rightarrow HBr + O_2$ (3), $OH + HBr \rightarrow Br + H_2O$ (4). The data to be reported include in particular branching ratio of reactions 1b and 2b, and measurements of temperature dependence of the rate constants of reactions (1)-(4). Atmospheric implications of these experimental data will be discussed.