

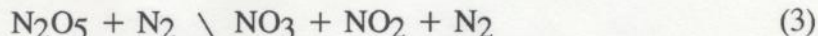
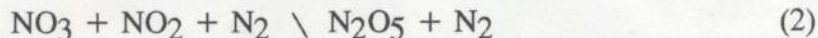
Studies of the NO₂-NO₃-N₂O₅ System

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The nitrate radical, NO₃, through its reactions involving NO₂ and N₂O₅,



is important in controlling the levels of active nitrogen and the partitioning of NO and NO₂ in both the troposphere and the stratosphere. Measurement of NO₃ in the atmosphere have not been successfully reconciled with attempts to model its concentration. This suggests that some fundamental rate and/or spectroscopic parameters may not be known with sufficient accuracy today. The Atmospheric Kinetics and Photochemistry group (including G.S. Tyndall, J.J. Orlando, C.A. Cantrell, R.E. Shetter) within NCAR have redetermined the cross sections of each of these molecules, equilibrium constant for (1) and the rate coefficients for both the formation (2) and decomposition (3) of N₂O₅ as a function of pressure and temperature.



These rate data, combined with previous measurements over a more limited temperature and pressure range, provide a more complete data set which can be used to define the falloff characteristics of the rate coefficients k_2 and k_3 in atmospheric modeling. Comparisons of the ratio of rate coefficients k_2/k_3 at a given pressure and temperature with measured values of K_1 allow a check in the consistency of the present data.

Isotopes in Stratospheric Ozone

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Observations have shown that stratospheric ozone is isotopically heavier than it would be if it contained only statistical proportions of ¹⁶O, ¹⁷O and ¹⁸O.

Attempts to predict and/or explain the isotopic ratios have failed; no model accounts for the observed enrichments of heavy oxygen despite a growing number of studies from theory and laboratory experiments. An explanation of the isotopic data is desirable even if it would not greatly alter our views of stratospheric photochemistry. I will review what is known and attempt to isolate several likely possible mechanisms whose investigation could resolve the problem.