

Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NOx33

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$$\Delta H^\circ(1) = \Delta H^\circ(2) = -39.6 \text{ kJ mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = 2.5 \times 10^{-22}$	290-293	Wahner et al., 1998	(a)
$k_2 = 1.8 \times 10^{-39} [\text{H}_2\text{O}]$			

Comments

- (a) NO_2 , N_2O_5 , and HNO_3 concentrations were monitored by in situ FTIR spectroscopy in a 250 m³ FEP-Teflon chamber. O_3 concentrations were monitored by UV absorption. The wall surface area was varied by placing extra Teflon sheets in the chamber. The N_2O_5 decay kinetics were found to have a second-order and a third-order gas-phase component and a contribution from reaction on the chamber walls. Rate coefficients were derived for the three decay channels by fitting the HNO_3 and N_2O_5 time-concentration profiles.

Preferred Values

Parameter	Value	T/K
$k_1/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$< 1 \times 10^{-22}$	280 – 300 K

Comments on Preferred Values

The values of k_1 and k_2 obtained by Wahner et al. (1998) are compatible with upper limits from earlier studies (Tuazon et al., 1983; Atkinson et al., 1986; Hjorth et al., 1987; Hatakeyama and Leu, 1989; Sverdrup et al., 1987; Mentel et al., 1996). Theoretical studies of this reaction (Hanway and Tao, 1998; Snyder et al., 1999; Voegele et al., 2003) substantiate the involvement of multiple water molecules on a qualitative level.

Recent measurements of NO₃ and N₂O₅ turnover lifetimes in the atmosphere (Aldener et al. 2006; Brown et al., 2006, 2009; Crowley et al., 2010) provide evidence that a gas-phase reaction between N₂O₅ and H₂O that irreversibly forms HNO₃ is not as rapid as calculated using the rate coefficients listed above. In ground based measurements, Brown et al., (2006) and Crowley et al. (2010) show that the sum of ($k_1 + k_2$) is a factor of ≈ 3 too high at temperatures of 280-290 K. Airborne measurements (at temperatures of 290 ± 5 K) of N₂O₅ turnover lifetimes close to one day enabled Brown et al. (2009) to conclude that the parameterisation of Wahner et al. (1998) leads to N₂O₅ loss rates which are occasionally a factor of >10 larger than those observed. An extremely low computed rate constant for hydrolysis also supports this observation (Alecú und Marshall, 2014). Brown (personal communication, 2009) reports no dependence on temperature within the small range covered.

Generally, only laboratory studies are considered in the evaluation of kinetic data. However, there are many problems associated with measurement of very slow reactions in closed (laboratory) systems and the separation of relative humidity dependent wall losses and true gas-phase processes in a reaction that takes place on a time scale of hours is non-trivial. In such cases, field observations can provide useful constraints. Until more laboratory or field data are available to better define the rate coefficient we do not recommend incorporation of this reaction in models of the atmosphere but set an upper limit of $1 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the bimolecular process only.

References

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