IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation
Data Sheet HI13; V.A1.13

The citation for this datasheet is: Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J., Atmos. Chem. Phys., 10, 9059-9223, 2010; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.
This datasheet last evaluated: June 2014; last change in preferred values: June 2014

HO_2NO_2 + Ice → products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Uptake coefficients: γ, γ_0			
$\gamma_{ss} = 0.15 \pm 0.10$	193	Li et al., 1996	CWFT-MS (a)
K_{linC} (cm)			
3.74×10^{-12} exp(7098/T)	230-253	Ulrich et al., 2012	CWFT-CIMS (b)

Comments

(a) The ice was prepared by vapour deposition, resulting in films between 13 and 160 µm thick. p(HNO_4) was varied between 1.6 x 10^{-5} mbar and 6 x 10^{-4} mbar. HNO_4 was produced by mixing NO_2BF_4 with H_2O_2 at 273 K. H_2O_2, the main impurity, was partially retained in a cold trap at 258 K. During the experiments, H_2O_2, HNO_3 and NO_2 were less than 20% of HNO_4. The HNO_3 impurity was quantitatively adsorbed onto the ice film and therefore did not interfere with PNA detection. Saturation of the uptake on ice was observed at > 100 monolayers. Evaporation of PNA and HNO_3 was observed in temperature programmed desorption experiments. HNO_3 was obviously originating from uptake of HNO_3 as an impurity from the PNA source. It was concluded that no decomposition of PNA occurs on ice.

(b) ~10 µm thick ice films were prepared by freezing liquid water in a quartz tube at 258 K. HO_2NO_2 was produced online by irradiating a $NO_2/H_2O/CO/O_2/N_2$ mixture at 172 nm. HONO and H_2O_2 formed as byproducts were reduced in a Ti(IV) denuder by 94% and 96%, respectively; HNO_3 evolving from the latter was trapped in a cold trap at 252 K. HO_2NO_2 was detected by CIMS as NO_4^-(HF) at m/z 98 using SF_6^- as reagent ions, Typical concentrations of HO_2NO_2 in the CWFT were 9.7×10^{10} molecules cm^{-3}, with CO at 1.6×10^{16} molecules cm^{-3}, NO_2 at 4×10^{11} molecules cm^{-3}, HONO at 1×10^{9} molecules cm^{-3}, HNO_3 at 9×10^{9} molecules cm^{-3} and H_2O_2 at 1×10^{11} molecules cm^{-3} in the CWFT. The partition coefficient given in the table was obtained from integration of breakthrough curves, which always showed complete recovery. Analysis in adsorption and desorption mode yielded consistent results.

Preferred Values

Parameter	Value	T/K
γ	no recommendation	
K_{linC} (cm)	5.5×10^{-12} exp(7000/T)	230-253
Reliability		
Δ(E/R) / K	500	230-253

Comments on Preferred Values

Studies with HO_2NO_2 are inherently difficult due to the problems associated with preparing HO_2NO_2 in a form suitable for flow tube experiments. Li et al. (1996) used a batch method that led to substantial amounts of byproducts, notably including large concentrations of HNO_3. The ice film was therefore likely transformed into an HNO_3 solution or NAT. In addition, during the course of their experiments in which they observed irreversible uptake, the HO_2NO_2 partial pressures were possibly high enough to allow for formation of hydrates as suggested by the authors. We therefore make no recommendation for the uptake coefficient based on their study.

Ulrich et al. (2012) worked at substantially lower HO_2NO_2 concentrations by using an online photolysis method and successfully suppressed H_2O_2 and HNO_3 enough to keep their equilibrium coverages below 20% of a monolayer. The experiment was not designed to determine adsorption kinetics. HO_2NO_2 showed reversible adsorption behaviour, decomposition to HONO did not occur over the timescales of their experiments. Application of a coadsorption model to account for the presence of H_2O_2 and HNO_3 did not lead to significant changes in K_{linC}. Nevertheless, in view of the single study, our recommendation for K_{linC} carries a substantial uncertainty in E/R.

The adsorption enthalpy derived from the Arrhenius plot by Ulrich et al. was 59±5 kJ mol^{-1}. In view of the large solubility in water, the comparatively small K_{linC} values may be related to the low acidity of HO_2NO_2 (pKa = 5.85).

References

Li, Z., Friedl, R.R., Moore, S.B. and Sander, S.P.: J. Geophys. Res. 101, 6795-6802, 1996.

Ulrich, T., Ammann, M., Leutwyler, S., and Bartels-Rausch, T.: Atmos. Chem. Phys., 12, 1833-1845, 2012.

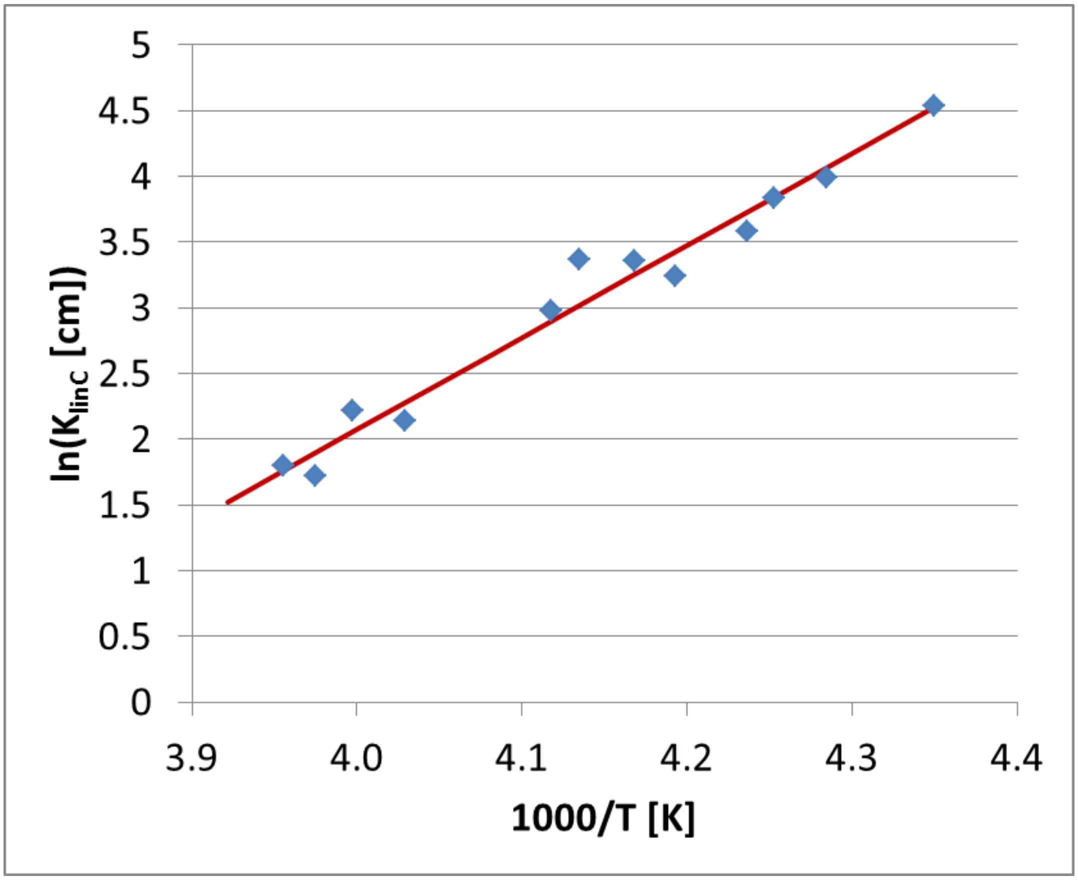

Figure 1: Arrhenius plot of Ulrich et al. (2012) data (blue symbols), with recommendation (red line).