

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.18 HET_SL_18

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HOI + H₂SO₄ → Products

Experimental Data

Parameter	Temp./K	Reference	Technique/Comments
<i>Accommodation coefficients: α</i>			
> 0.3 (>58 wt.% H ₂ SO ₄)	253	Holmes et al., 2001	CWFT-MS (a)
<i>Experimental uptake coefficients: γ</i>			
$1 \times 10^{-5} \exp\{(1700 \pm 200) / T\}$	195-252	Allanic and Rossi, 1999	Knudsen-MS (a)
> 4×10^{-2} (>58 wt.% H ₂ SO ₄)	253	Holmes et al., 2001	CWFT-MS (a)

Comments

- (a) HOI (at concentrations $<10^{10}$ molecule cm⁻³) was formed in the reaction of O(³P) with C₃H₇I. The uptake to >58 wt % H₂SO₄ was continuous and its size independent of the HOI concentration. No evidence for formation of iodine containing products was observed. The surface concentration of H₂SO₄ could have been much greater than the initial value of 58 wt.% as the bulk gas-flow was not humidified.
- (b) HOI (at approximate concentrations of $\sim 10^{10}$ molecule cm⁻³) was formed in the reaction of O(³P) with C₂H₅I. 40 – 70 wt.% H₂SO₄ solutions were kept at temperatures between 195 and 252 K. The gas-phase H₂O flow was adjusted to prevent surface concentration changes. The uptake coefficients displayed a negative temperature dependence, with the parameters in the Table derived from an unweighted fit to the datapoints reported at each temperature.

Preferred Values

none

Comments on Preferred Values

Both Allanic and Rossi (1999) and Holmes et al (2001) found the uptake of HOI to H₂SO₄ solutions to be continuous (i.e. non-saturating), suggestive of very high solubility, possibly enhanced by protonation to form H₂OI⁺. The continuous uptake could also be caused by the presence of impurities in the HOI source reacting with HOI in/on H₂SO₄.

Allanic and Rossi observed the immediate formation of I₂ as gas-phase product, albeit at a yield which was estimated to account for less than 50 % of the HOI taken up. In contrast, Holmes et al. report no gas-phase iodine containing products. It is conceivable that the products observed by Allanic and Rossi were formed on surfaces other than H₂SO₄ in their Knudsen reactor. The single datapoint of Holmes et al. at 253 K does not fit with the trend in γ with temperature

observed by Allanic and Rossi, but is too high. This may reflect enhanced uptake to very concentrated H_2SO_4 surfaces which may have been present in the Holmes et al, experiments. On the other hand, Allanic and Rossi (1999) did not observe a change in HOI uptake coefficient when the H_2O partial pressure above an initially 70 wt.% H_2SO_4 solution was increased by a factor of 4.

Upon adding NaCl to the H_2SO_4 solution, Holmes et al. (2001) observed ICl formation with 100 % yield, suggesting that dissolved HOI (or H_2OI^+) reacts efficiently with halide ions.

The accommodation coefficient presented by Holmes et al (2001) was derived from observation of pressure dependent values of γ on H_2SO_4 solutions of largely unknown composition and thus no recommendation is made.

References

Allanic, A. and Rossi, M.J.: J. Geophys. Res. 104, 18689-18696, 1999.

Holmes, N. S., Adams, J. W., and Crowley, J. N.: Phys. Chem. Chem. Phys, 3, 1679-1786, 2001.

