

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation
Data Sheet HI29; V.A1.29

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This datasheet last evaluated: January 2014; last change in preferred values: January 2009

ClO + ice → products

Experimental data

<i>Parameter</i>	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>			
$> 1.0 \times 10^{-2}$	190	Leu, 1988	CWFT-MS (a)
$\gamma_{ss} = (8 \pm 2) \times 10^{-5}$	183	Kenner, Plumb and Ryan, 1993	CWFT-MS (b)
$< 1.0 \times 10^{-4}$	213	Abbatt, 1996	CWFT-RF (c)
$> 1.0 \times 10^{-3}$	225	McKeachie et al., 2004	CWFT-UV/MS (d)

Comments

- (a) Flow tube reactor using electron-impact MS. The ice was condensed from the vapour phase onto the wall of the flow tube. ClO was produced by reacting Cl atoms with an excess of OClO or Cl₂O. The value given in the table is a lower limit. Cl₂ was not detected. The ClO concentration is not reported.
- (b) Fast flow reactor with electron-impact MS. A 4-7 μm thick ice film was deposited from water vapour. ClO was passed through the flow tube either continuously or in pulses. ClO was produced by microwave discharge of O₂ and Cl₂ in He or by first producing Cl atoms by microwave discharge of Cl₂ in He and reacting Cl with O₃. Both methods led to consistent observations of ClO uptake. The ClO pressure was about 6.3×10^{-6} mbar. Cl₂ could not be measured as product because of excess of Cl₂ present from the source. HCl could also not be measured due to a large background in the MS.
- (c) Coated wall flow tube at 1.3 mbar total pressure of He coupled to a resonance fluorescence (RF) detector. The ice film was prepared by coating a Pyrex tube with water followed by freezing. ClO was generated from the reaction Cl + O₃. Cl atoms were produced by microwave discharge of Cl₂ in He. For detection, ClO was reacted with NO, and Cl atoms detected by resonance fluorescence. The ClO concentrations used in this work were on the order of 4×10^{-6} mbar.
- (d) Coated wall flow tube coupled to either a UV-VIS absorption cell, EI-MS or resonance enhanced multiphoton time-of-flight MS (REMPI-TOF-MS). ClO was produced either via Cl + O₃, or via OClO + O to allow checking for interference of excess Cl₂, O₃, or OClO, separately. The ClO pressure was about 2×10^{-4} mbar. The ice film on a pyrex flow tube was prepared by spraying a mist into the precooled flow tube, or by vapour deposition from either He saturated with water or from laboratory air. The preparation of the film had no effect on the results. ClOOCl being the main target of this study, uptake of ClO to ice was inferred from the suppression of ClOOCl formation in presence of an

ice film. ClClO₂ and OCIO were detected as product when the ice film was evaporated after exposure to ClO. Separate experiments showed that ClOOCl was not measurably taken up by ice. The uptake coefficient reported in the table was estimated from the amount of OCIO recovered after different exposure times. The uptake coefficient seemed to increase with increasing ClO exposure time.

Preferred Values		
Parameter	Value	T/K
γ	$< 1 \times 10^{-4}$	180 - 220
<i>Reliability</i>		
$\Delta \log (\gamma)$	undetermined	

Comments on Preferred Values

There is substantial disagreement between the Kenner et al. (1993) and Abbatt (1996) studies on one hand, and the Leu (1988) and McKeachie et al. (2004) studies on the other hand. One of the reasons could simply lie in the ice preparation method leading to highly porous films in case of vapour deposition from the gas phase. However, Abbatt (1996) used a film frozen from solution and found low reactivity consistent with Kenner et al. (1993). The Leu (1988) study involved excess amounts of OCIO and Cl₂O present in the reactant mixture that, if they are reactive towards ice, could interfere with the ClO measurement using electron impact ionization MS, as noted by all three other authors. McKeachie et al. (2004) used the most selective detection scheme allowing for unequivocal detection of all involved species. They suggest that a complex in the gas phase (Francisco and Sander, 1995) initiates a disproportionation reaction at the ice surface leading to OCIO and ClClO₂ that remain on the ice. This would explain the induction behaviour observed in their experiment and the discrepancy to the Kenner et al. (1993) and Abbatt (1996) studies, which were both performed at nearly two orders of magnitudes lower pressures. McKeachie et al. also argue that the higher water vapour pressure at higher temperature promotes the abundance of the ClO·H₂O complexes. A significant retention of ClO on ice was excluded by Kenner et al. (1993) by measuring the arrival times of ClO pulses applied to the ice films, indicating that at low pressures the ClO surface coverage is low enough to prevent the secondary chemistry proposed by McKeachie et al. (2004). We therefore recommend the lower observed uptake coefficients as upper limits for ClO uptake at atmospherically relevant pressures.

References

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