

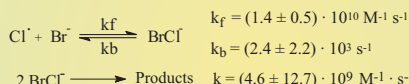
Fig. 1: Coupling between gas-phase halogen activation and aqueous-phase halogen chemistry.

Motivation

Tropospheric particles may release halogen atoms into the gas phase (Vogt and Crutzen, 1996). Model calculations suggest that halogen-atom and related species could play a role not just in the gas phase but also in cloud water and, possibly, in aerosol particles. Therefore kinetic and spectroscopic data are necessary. The reactivity of chlorine atoms with a number of organic compounds was studied. Recently a method to investigate bromine atom kinetics has been developed. Additionally the equilibrium reaction between chlorine atom and bromide has been investigated for the first time.

BrCl⁻ Radical Anion

The BrCl⁻ radical anion was generated through the equilibrium reaction between chlorine atom and bromide. The K_{eq} have been measured by treating spectroscopical data with a specific computer program (Specfit 32). The spectroscopic measurements (Fig. 2-3) were performed considering the wavelength interval from 295 nm to 395 nm. Spectra were taken at 25 different delay times from 0.8 μs (chlorine atom's maximum) to 2.3 ms (complete decay of BrCl⁻). The experiment was repeated 4 times using each time a different [Br⁻]. The same reaction model (Tab. 2) was applied to each of the 4 sets of data and the results were averaged (errors for a confidence interval of 95%):



The quality of the fit and the sensibility of the model have been tested by comparing the experimental absorption time profiles with artificial time profiles at fixed wavelengths. The order of magnitude of the rate constants obtained in this work is comparable to the corresponding literature values relative to Cl₂⁻ and Br₂⁻ radical anions.

Tab. 1: Kinetic data for Cl₂⁻ and Br₂⁻.

Reactions	$k_{forward} / \text{M}^{-1} \text{s}^{-1}$	$k_{backward} / \text{s}^{-1}$	K_{eq} / M^1	References
$\text{Cl} + \text{Cl} \rightleftharpoons \text{Cl}_2$	$8.5 \cdot 10^9$	$6.0 \cdot 10^9$	$1.4 \cdot 10^0$	Buxton et al., 1998
	$2.1 \cdot 10^{10}$	$1.1 \cdot 10^9$	$1.9 \cdot 10^0$	Jayson et al., 1973
	$6.5 \cdot 10^9$	//	//	Kläning and Wolff, 1985
$2 \text{Cl}_2 \rightarrow \text{Products}$	$1.2 \cdot 10^9$	//	//	Huie et al., 1990
	$8.7 \cdot 10^9$	//	//	Zellner et al., 1996
$\text{Br} + \text{Br} \rightleftharpoons \text{Br}_2$	$1.2 \cdot 10^{10}$	$1.9 \cdot 10^9$	$6 \cdot 10^0$	Merenyi and Lind, 1994
	$1.1 \cdot 10^{10}$	//	//	Treinin and Hayon, 1975
	//	//	$1.2 \cdot 10^0$	Kosanic, 1993
$\text{Br} + \text{Br} \rightleftharpoons \text{Br}_2$	$2.4 \cdot 10^{10}$	//	//	Feraudi, 1993
$2 \text{Br}_2 \rightarrow \text{Products}$	$1.9 \cdot 10^9$	//	//	D'Angelantonio et al., 1988

Tab. 2: Reactions and absorbing species present in the model.

Reactions	$k_{forward}$ (1)	$k_{backward}$ (2)	Reference
$\text{Cl} + \text{Br}^- \rightleftharpoons \text{BrCl}^-$	Variable	Variable	//
$2 \text{BrCl}^- \rightarrow \text{Products}$	Variable	//	//
$\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{ClOH} + \text{H}^+$	$3.4 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$2.1 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	(1)Wicktor, 2000, (2)Kläning and Wolff, 1985.
$\text{ClOH} \rightleftharpoons \text{OH} + \text{Cl}$	$6.1 \cdot 10^9 \text{ s}^{-1}$	$4.3 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$	(1)Wicktor, 2000, (2)Kläning and Wolff, 1985
$\text{OH} + \text{Chloroacetone} \rightarrow \text{Products}$	$1.3 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$	//	(1)Wolffenden et al., 1982
$\text{ClOH} + \text{Br}^- \rightleftharpoons \text{BrCl}^- + \text{OH}^-$	$1.9 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$2.7 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$	*(1)Fornier de Violet, 1981
$\text{Cl} + \text{Chloroacetone} \rightarrow \text{Products}$	$1.3 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$	//	(1)Buxton and Bydder, 2000.

*Values for the reaction $\text{BrOH} + \text{Br}^- \rightleftharpoons \text{Br}_2 + \text{OH}^-$

Absorbing Species	λ_{max} (nm) (1)	ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$) (2)	Reference
Cl	320	4000	(1)This work, (2)Kläning and Wolff, 1985
BrCl ⁻	352	8800	(1)This work, (2)Jayson et al., 1973 (*Cl ₂ ⁻ ϵ_{max})
ClOH ⁻	350	3700	(1)Kläning and Wolff, 1985

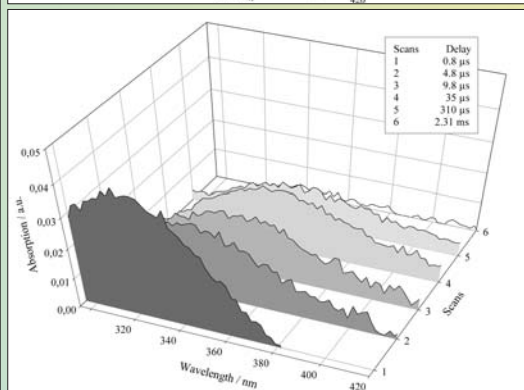
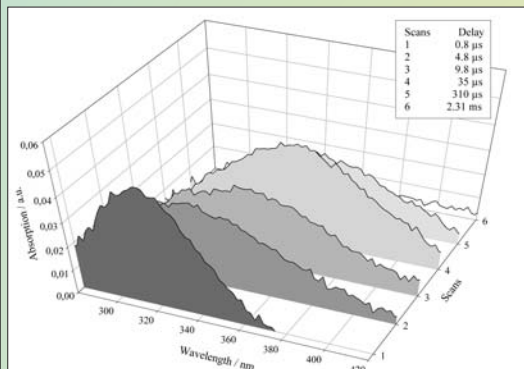


Fig. 2-3: Spectroscopic characterization of the BrCl⁻ radical system ([Br⁻] = 1 · 10⁻⁵ M and [Br⁻] = 5 · 10⁻⁶ M respectively) from the absorption maximum of chlorine atom (0.8 μs delay time) until the complete decay of BrCl⁻ (2.31 ms delay time).

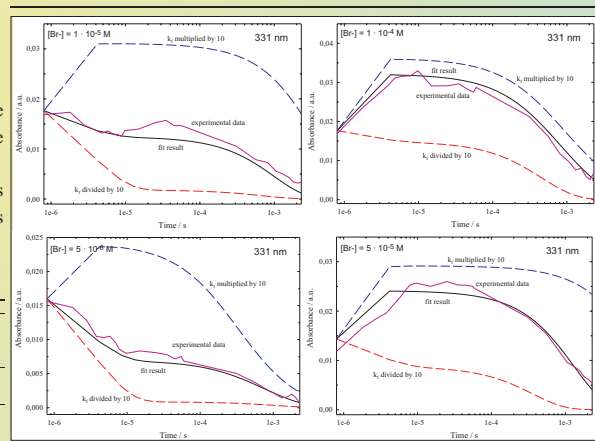


Fig. 4: Comparison between measured data, fit results and data obtained varying the value of k_f . The data are plotted as single wavelength time profiles.

Bromine Atom Kinetics

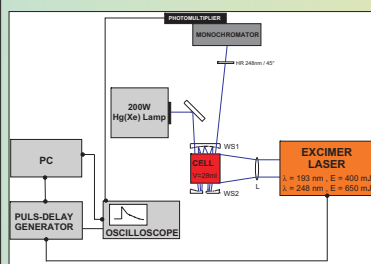


Fig. 5: Laser photolysis longpath laser absorbance equipment for kinetic investigations.

Bromine atoms were generated by excimer-laser-photolysis at 248 nm of aqueous solutions containing bromoacetone as precursor according to:



For the kinetic studies a recently developed laser-photolysis-longpath-laser-absorbance apparatus (LP-LPA) is used (Fig. 5). The Br atom absorption is measured directly at 296 nm using the 200W output of a Hg(Xe) lamp and a monochromator coupled to a photomultiplier. The time resolved Br atom decay traces are transferred to a digital oscilloscope.

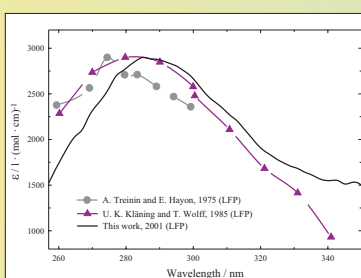


Fig. 6: Absorption spectrum of bromine atom in aqueous phase.

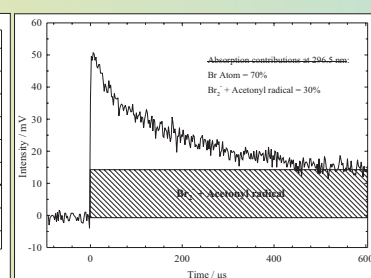


Fig. 7: Time resolved absorption trace of bromine atom at 296 nm. [2-Propanol] = 1 · 10⁻³ M.

Summary and Conclusion

The BrCl⁻ radical anion has been spectroscopically characterized. The equilibrium reaction $\text{Cl} + \text{Br}^- \rightleftharpoons \text{BrCl}^-$ has been investigated for the first time. A method to study the kinetics of bromine atom in the aqueous phase has been found and developed. The results obtained can be used in modelling studies and may be helpful for a better understanding of tropospheric aqueous phase chemistry.

Acknowledgements

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