

Laser-based Laboratory Investigations of halogene-containing Compounds Reactions in aqueous Phase

Contribution to subproject: CMD-APP

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Summary

A laser flash photolysis experiment has been used to investigate the BrCl⁻ radical anion. The equilibrium constant for the reaction



has been measured for the first time by treating spectroscopical data with a fitting program (Specfit 32).

A method to study the kinetics of bromine atom in the aqueous phase has been developed. Bromine atoms have been generated by 248 nm excimer-laser photolysis of aqueous solutions containing bromoacetone.

The results obtained can be used in modelling studies and may be helpful for a better understanding of tropospheric aqueous phase chemistry.

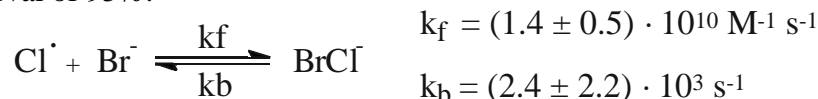
Introduction

Tropospheric particles may release halogen atoms into the gas phase (Vogt and Crutzen, 1996). Model calculations suggest that halogen-atoms and related species could play a role not just in the gas-phase but also in cloud water and, possibly, in aerosol particles (Herrmann et al., 2000).

Results

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. 1) 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. 1) was applied to everyone of the 4 sets of data and the results were averaged for a confidence interval of 95%:



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.

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 (Fig. 2).

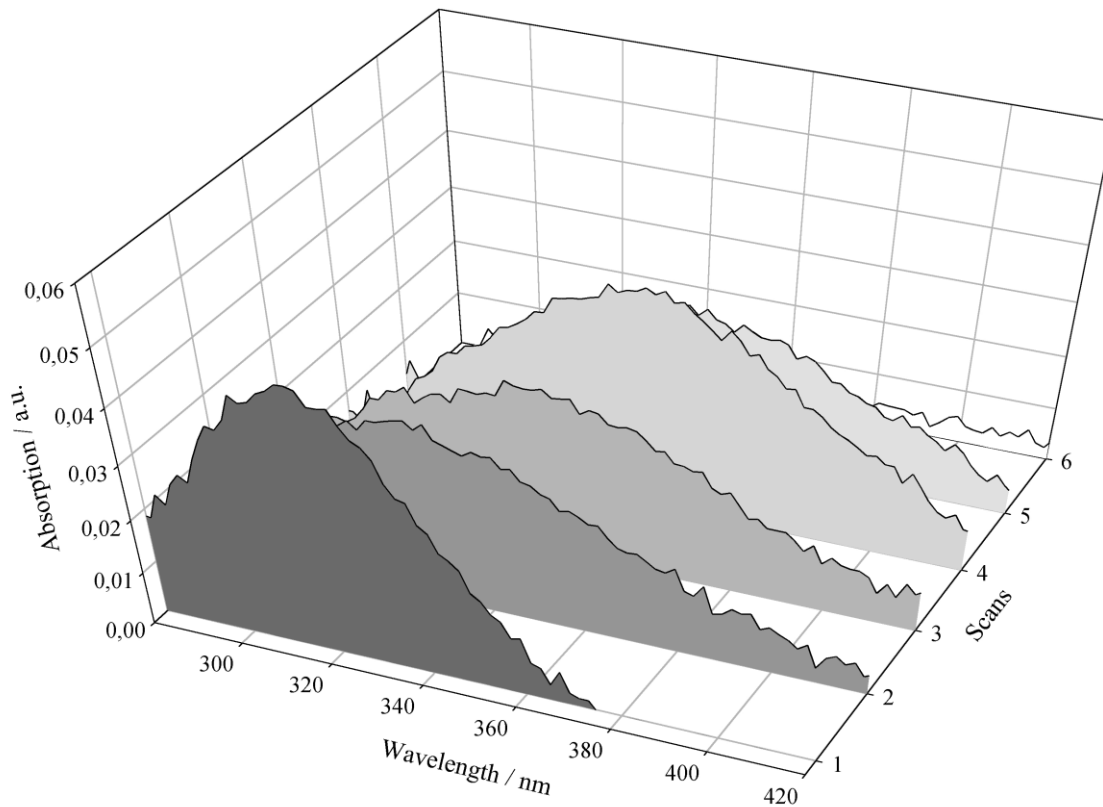


Figure 1: Spectroscopic characterization of the BrCl^\cdot radical system ($[\text{Br}^\cdot] = 1 \cdot 10^{-5} \text{ M}$) from the absorption maximum of chlorine atom ($0.8 \mu\text{s}$ delay time) until the complete decay of BrCl^\cdot (2.31 ms delay time).

Reactions	k_{forward} (1)	k_{backward} (2)	Reference
$\text{Cl} + \text{Br}^\cdot \rightleftharpoons \text{BrCl}^\cdot$	Variable	Variable	
$2 \text{BrCl}^\cdot \rightarrow \text{Products}$	Variable		
$\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{ClOH}^\cdot + \text{H}^+$	$3.4 \cdot 10^3 \text{ M}^{-1} \text{ s}^{-1}$	$2.1 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	(1)Wicktor, 2000.
$\text{ClOH}^\cdot \rightleftharpoons \text{OH} + \text{Cl}^\cdot$	$6.1 \cdot 10^9 \text{ s}^{-1}$	$4.3 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$	(2)Klänning and Wolff,1985.
$\text{OH} + \text{Chloroacetone} \rightarrow \text{Prod}$	$1.3 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$		(1)Wolfenden et al., 1982
$\text{ClOH}^\cdot + \text{Br}^\cdot \rightleftharpoons \text{BrCl}^\cdot + \text{OH}^\cdot$	$1.9 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$	$2.7 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$	*(1)(2)Fornier de Violet, 1981
$\text{Cl} + \text{Chloroacetone} \rightarrow \text{Prod}$	$1.3 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$		(1) Buxton et al., 2000.

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

Table 1: Reactions present in the model.

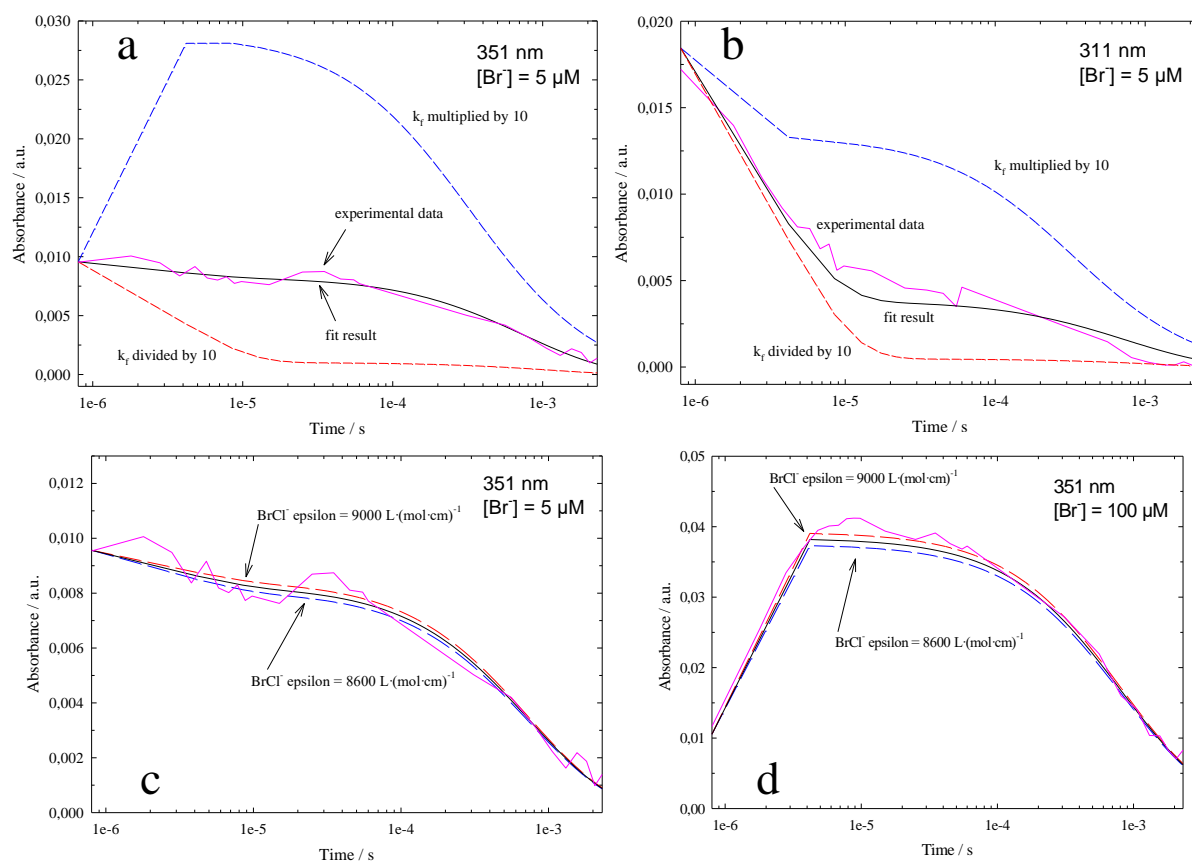
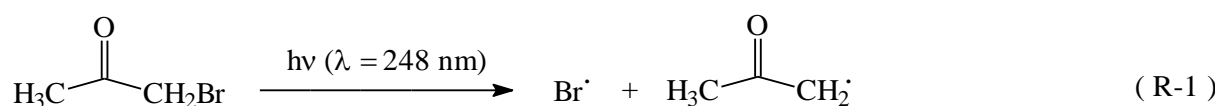


Figure 2: Comparison between measured data, fit results and data obtained varying the value of k_f (figures a, b) and using different BrCl^- epsilon values (figures c, d). The data are plotted as single wavelength time profiles.

In Figures 2c and 2d is shown the comparison between measured data and fit results using different extinction coefficients of BrCl^- radical anion. The highest fit's quality, in terms of sum of the squares of the distances between measured absorbance values and fit result absorbance values (calculated for all the delay times and wavelengths considered i.e. 25 delay times and 21 wavelengths), has been obtained for $\epsilon_{\text{BrCl}^-} = 8800 \text{ L} \cdot (\text{mol} \cdot \text{cm})^{-1}$.

Br atom kinetics

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 laser-photolysis-longpath-laser-absorbance apparatus (LP-LPA) has been used (Fig. 3). The Br atom absorption has been measured directly at 296 nm using the 200W output of a Hg(Xe) lamp and a monochromator coupled to a photomultiplier. All the experiments are carried out under pseudo-first order conditions. The time resolved Br atom decay traces are captured and averaged by a digital oscilloscope and then transferred to the PC to extract the first order rate constants.

The second order rate constants are extrapolated from the plot of measured k_{1st} vs concentration of the reactant (Fig. 4).

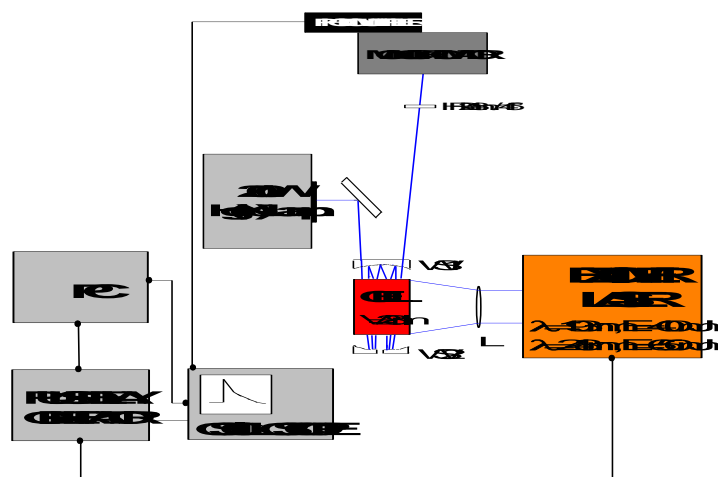


Figure 3: Laser Photolysis Longpath Laser Absorption equipment for kinetic investigations.

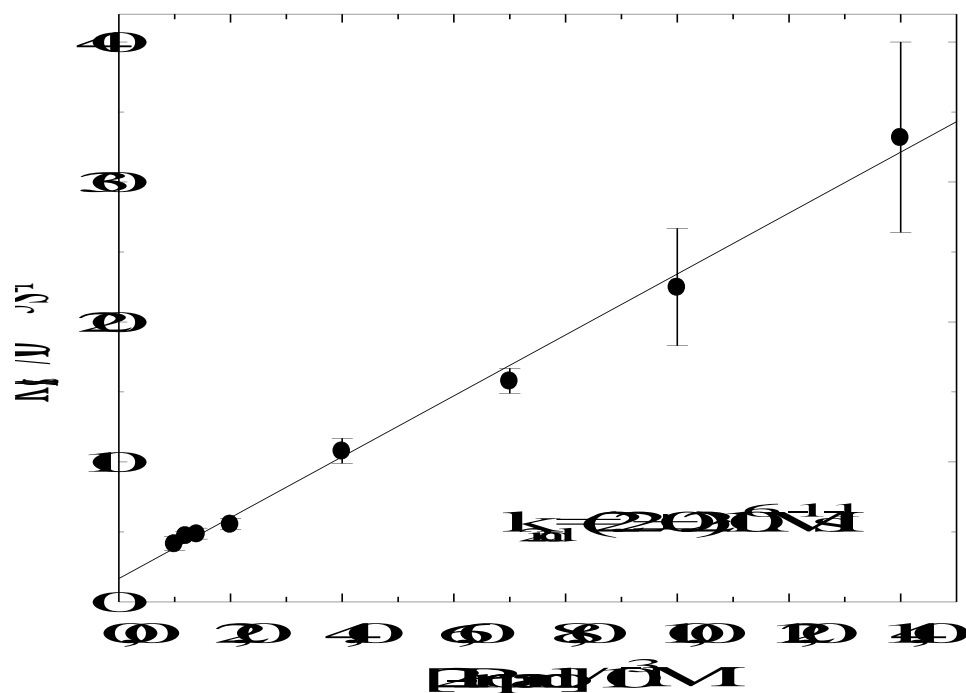


Figure 4: $k_{1st} = f([2\text{-Propanol}])$ for the reaction of Br atom with 2-Propanol; $T = 298\text{K}$, Ionic strength = 0, pH 5.5.

Conclusions

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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