Laser-based Kinetic and Spectroscopic Investigations of Halogene-containing Oxidants in the Aqueous Phase

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

Additionally the equilibrium reaction between chlorine atom and bromide have been investigated for the first time.
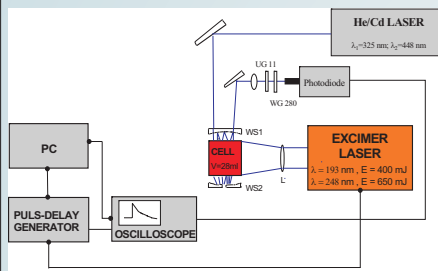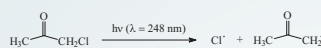
Chlorine Atom Kinetics

Fig 2: LP-LPLA apparatus for kinetic investigations.

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

$$H_3C-\underset{O}{\overset{\parallel}{C}}-CH_2Cl \xrightarrow{h\nu\ (\lambda=248\ nm)} Cl^\cdot + H_3C-\underset{O}{\overset{\parallel}{C}}-CH_2^\cdot$$

For the kinetic studies a recently developed laser-photolysis-longpath-laser-absorbance apparatus (LP-LPA) was used.

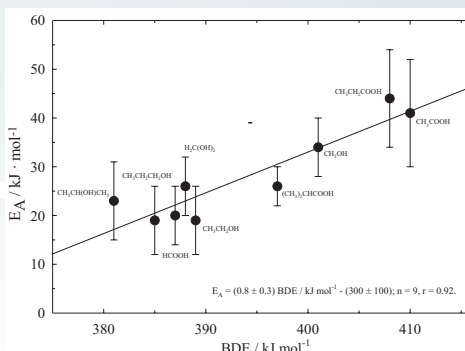The reaction cell with an inner width of 40 mm and an inner length of 35 mm could be thermostated, allowing temperature dependent measurements in the range from 278 K to 328 K.

In order to avoid the accumulation of reaction products the cell was designed as a flow system.

The Cl atom absorption was measured directly using the 325 nm output of an Helium Cadmium Laser. The time-resolved Cl atom absorption profiles were monitored by a photodiode and then transferred into a digital oscilloscope.

Fig. 3: Bell-Evans-Polanyi plot for H-abstraction reactions of Cl atom in aqueous phase.

$E_A = (0.8 \pm 0.3)$ BDE / kJ mol^{-1} - (300 ± 100); n = 9, r = 0.92.

Fig. 4: Plot of log k vs I_{eff} for the reactions of $Cl_{(aq)}$ with methanol and Hydrated Formaldeyde. The I_{eff} dependence parameters are also reported.

Table 1. Observed rate constants at 298K and activation energies for the reaction with Cl atom in aqueous solution; BDE of the weakest C-H bond. * values approximated to the calculated BDEs of, respectively, acetic acid and Isobutanol (C2). (1): Lide and Frederikse, 1994; (2): Benson, 1976; (3): Singleton et al., 1989.

Compound	k_{2nd} (298K) / M^{-1} s^{-1}	E_A / kJ mol^{-1}	BDE / kJ mol^{-1}
2-Propanol	$(3.2 \pm 0.7)\ 10^9$	23 ± 8	381 (1)
1-Propanol	$(2.2 \pm 0.4)\ 10^9$	19 ± 7	385 (2)
Ethanol	$(2.2 \pm 0.3)\ 10^9$	19 ± 7	389 (1)
Methanol	$(1.0 \pm 0.1)\ 10^9$	34 ± 6	401 (2)
Hydrated Formaldehyde	$(1.4 \pm 0.3)\ 10^9$	26 ± 6	388 (2)
Acetic Acid	$(1.0 \pm 0.2)\ 10^8$	41 ± 11	410 (3)
Propionic Acid	$(1.2 \pm 0.3)\ 10^9$	44 ± 10	410 (2)*
Isobutyric Acid	$(1.7 \pm 0.3)\ 10^9$	26 ± 4	397 (2)*
Formic Acid	$(2.8 \pm 0.3)\ 10^9$	20 ± 6	387 (2)

According to the principle of Evans and Polanyi there is a correlation between the activation energy and the enthalpy for reactions that follow the same chemical mechanism (Evans and Polanyi, 1938):

$$E_A = A + B \cdot H_X \qquad (I)$$

To test whether the reactions of $Cl_{(aq)}$ with organic compounds do follow the same reaction mechanism (H-atom-abstraction), the activation energies for the reaction of $Cl_{(aq)}$ with some organic compounds were measured and plotted against the bond dissociation energy.

The ionic strength dependence for the reaction rate of $Cl_{(aq)}$ with methanol and hydrated formaldehyde is reported in Figure 4. The ionic strength was modified using sodium perchlorate according to: $I = 0.5 \cdot c_i \cdot z_i^2$; the dissociation constant of NaClO$_4$ in water ($K_{sol} = 0.2$ M^{-1}) was also considered. The negative correlation between log k_{2nd} and I_{eff} can be explained by a type II kinetic salt-effect (Herrmann, 1997). This correlation can be quantified using a relation by Debye and McAulay (Debye and McAulay, 1925):

$$\log k / M^{-1} s^{-1} = k_{I=0} + \beta \cdot I_{eff}$$

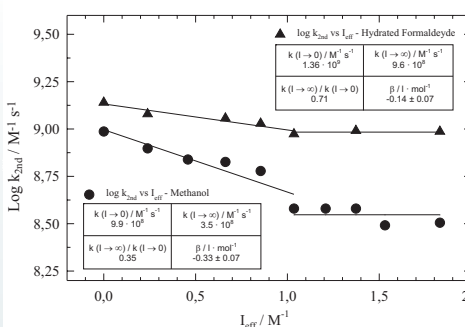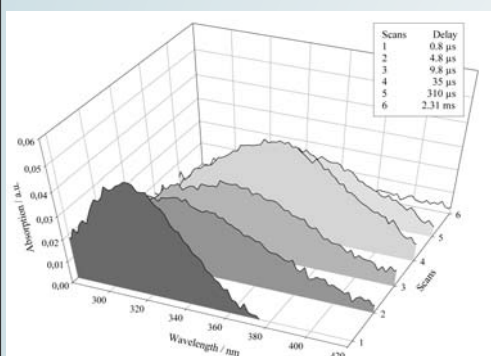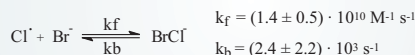## BrCl$^-$ Radical Anion

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

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 measurement (Fig. 5) was repeated 4 times using each time a different [Br$^-$]. The same reaction model was applied to everyone of the 4 sets of data and the results were averaged with for a confidence interval of 95% :

$$Cl^\cdot + Br^- \underset{kb}{\overset{kf}{\rightleftharpoons}} BrCl^-$$

$k_f = (1.4 \pm 0.5) \cdot 10^{10}$ M^{-1} s^{-1}
$k_b = (2.4 \pm 2.2) \cdot 10^3$ s^{-1}

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. 6: Comparison between measured data, fit results and data obtained varying the value of k$_f$. The data are plotted as single wavelength time profiles.
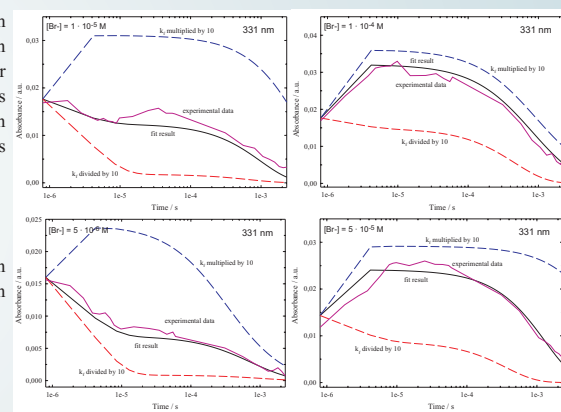
Summary and Conclusion

The reactivity of chlorine atom have been investigated with an excimer-laser-photolysis experiment. All rate constants measured in this work are in the order of magnitude of 10^9 M^{-1} s^{-1} and therefore Cl atom might be involved in the oxidation of organics in clouds and, possibly, in aerosol particles.

The equilibrium Cl + Br$^-$ <==> BrCl$^-$ have been studied for the first time.

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

Acknowledgements

References

Benson S.W. (1976), *Thermochemical Kinetics*, 2. Aufl., Wiley, New York.

Debye P. and J. McAulay (1925). Das elektrische Feld der Ionen und die Neutralsalzwirkung, *Physik Zeitschr.* **26**, 22-29.

Evans M.G. and M. Polanyi (1938). Inertia and driving force of chemical reactions, *Trans. Faraday Soc.* **34**, 11-29.

Herrmann H. (1997). Photochemische Bildung, Spektroskopie und Kinetik freier Radikale in wäßriger Lösung, *Habilitationsschrift*, Universität Essen.

Lide, D.R., H.P.R. Frederiksen (editor) (1994), *CRC Handbook of chemistry and Physics*, 75. Aufl., CRC Press, Boca Raton.

Singleton, D.L. G. Paraskevopoulos, R.S. Irwin (1989), Rates and mechanisms of the reactions of hydroxyl radicals with acetic, deuterated acetic, and propionic acids in the gas phase, *J. Am. Chem. Soc.*, **111**, 5248-5251.

Vogt R., P.J. Crutzen, R. Sander (1996), A mechanism for Halogen Release from Sea-Salt Aerosol in the Remote Marine Boundary Layer, *Nature* **383**, 327-330.