KINETIC STUDIES OF HALOGEN CONTAINING RADICALS IN THE AQUEOUS PHASE

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INTRODUCTION

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.
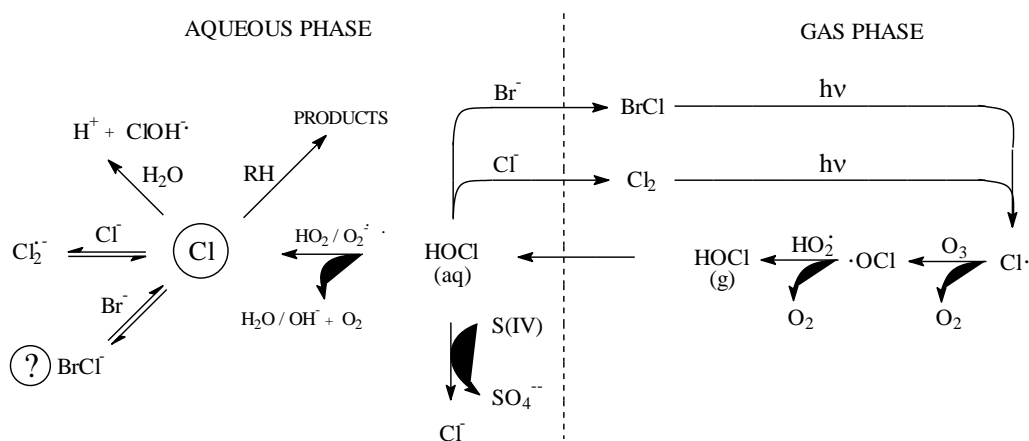

Figure 1. Possible coupling between gas phase and aqueous phase halogen chemistry.

METHODS

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

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

The reaction cell with an inner diameter of 40 mm and an inner length of 350 mm could be thermostated, allowing temperature dependent measurements in the range from 278 K to 318 K. To avoid 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 in a digital oscilloscope.

CONCLUSIONS

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): $E_a = A + B \cdot \Delta H_r$. The activation energies for the reaction of $Cl_{(aq)}$ with different organic compounds (including carboxylic acids) were measured and plotted against the bond dissociation energies and the following correlation was found: $E_A = (0.84 \pm 0.32)$ BDE / $kJ \cdot mol^{-1} - (301 \pm 126)$; n = 9, r = 0.92.

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)

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.

The ionic strength dependence for the reaction of $Cl_{(aq)}$ with methanol and hydrated formaldehyde was measured and, for both compounds, a negative correlation between log k_{2nd} and I_{eff} was found. This correlation can be quantified using a relation by Debye and McAulay (Debye and McAulay, 1925): log k / $M^{-1} s^{-1}$ = $k_{I=0}$ + ß · I_{eff} (in which ß is the kinetic salt coefficient and can be extrapolated from the plot of k_{2nd} against I_{eff}).

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

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