

Laser-based Kinetic Investigations of Cl Atom in Aqueous Solution



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1. Motivation

Tropospheric particles may release halogen atoms into the gas phase [1,2]. 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 [3,4].

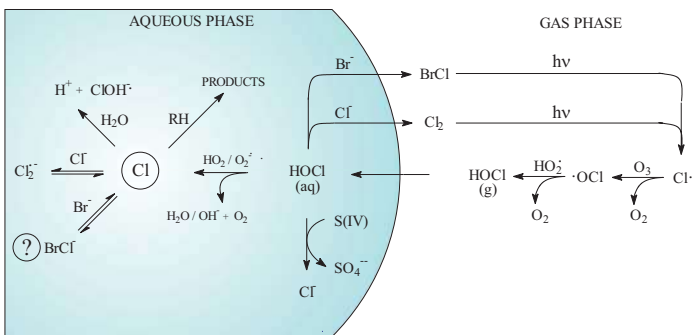
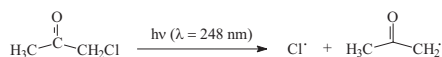


Fig. 1: Possible coupling between gas phase halogen activation and aqueous phase halogen chemistry.

2. Experimental

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



For the kinetic studies a recently developed laser-photolysis-longpath-laser-absorbance apparatus (LP-LPA) was used (Fig. 2). 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.

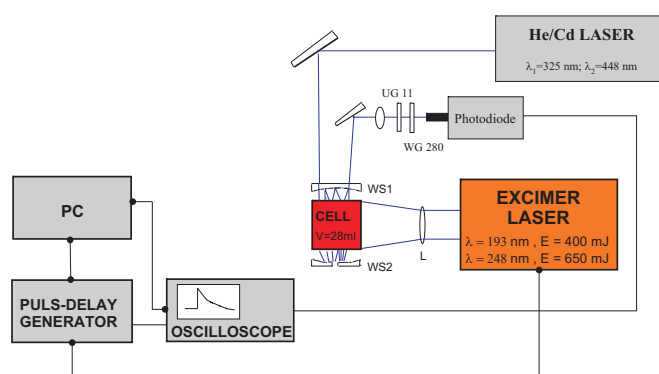


Fig. 2: Laser photolysis longpath laser absorption apparatus (LP-LPA).

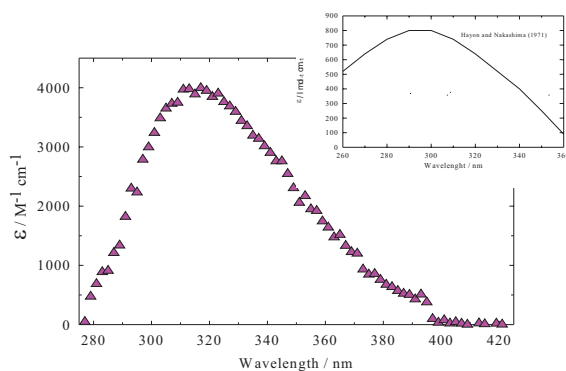


Fig. 3: Absorption spectra of Cl atom and acetyl radical normalized respectively with $\epsilon_{\text{max}}(\lambda, 320 \text{ nm}) = 3863 \text{ M}^{-1} \text{ cm}^{-1}$ [5, 6] and $\epsilon_{\text{max}}(\lambda, 295 \text{ nm}) = 800 \text{ M}^{-1} \text{ cm}^{-1}$.

3. Results and discussion

Several authors suggest that in the gas phase Cl atom reacts with alcohols via a H-abstraction mechanism; they concluded that no abstraction from the OH group was observed and that abstraction from the alkyl groups followed the thermodynamically favoured route by forming mainly the most stable hydroxyalkyl radical [8]. We have studied the reactivity of $\text{Cl}^\cdot_{(\text{aq})}$ with a number of organic compounds (including carboxylic acids) and a correlation between the strength of the C-H bond and the reaction rate was found suggesting that the previously described H-abstraction mechanism could occur also in the aqueous phase.

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 (C_2)

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

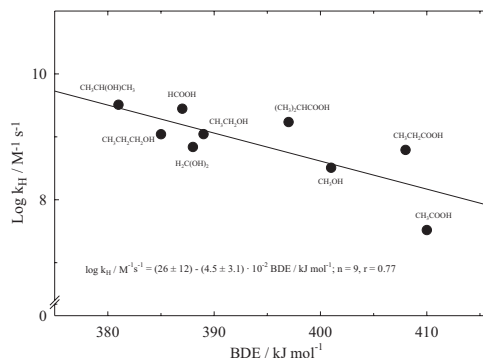


Fig. 4: The logarithm of the measured rate constant, divided by the number of the equivalent abstractable H-atoms, is plotted against the bond dissociation energy. The correlation equation obtained from the plot could be used to estimate reaction rates from extrakinetical data (i.e. BDE).

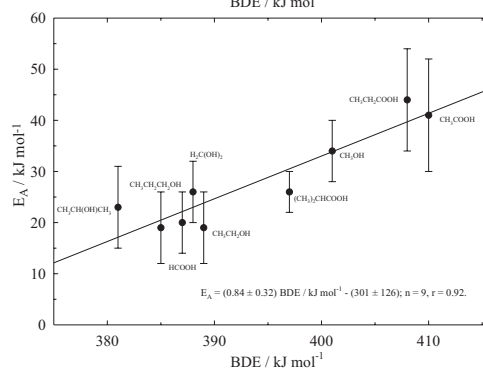


Fig. 5: Bell-Evans-Polanyi plot for H-abstraction reactions of Cl atom in aqueous phase. This plot indicates that $\text{Cl}^\cdot_{(\text{aq})}$ reacts with the compounds listed in table 1 via a H-atom-abstraction mechanism. The activation energies, calculated for each compound from its Arrhenius plot, were plotted against the BDE.

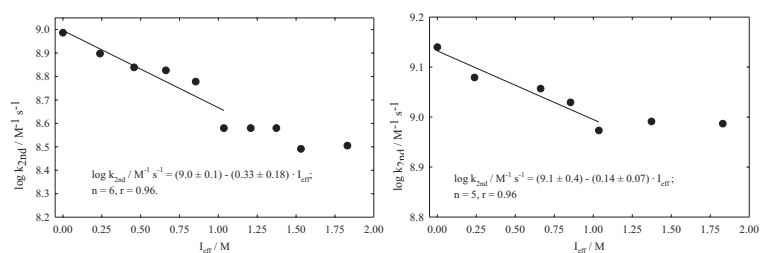


Fig. 6-7: Ionic strength dependence for the reaction rate of $\text{Cl}^\cdot_{(\text{aq})}$ with methanol (Fig. 6, left) and hydrated formaldehyde (Fig. 7, right). The ionic strength was modified using sodium perchlorate according to: $I = 0.5 \cdot \sum c_i \cdot z_i^2$; the dissociation K of NaClO_4 in water ($K_{\text{sol}} = 0.2 \text{ M}^{-1}$ [7]) was also considered. The negative correlation between $\log k_{2nd}$ and I_{eff} can be explained by a type II kinetic salt-effect [12]. This correlation can be quantified using a relation by Debye and McAulay [13]: $\log k / \text{M}^{-1} \text{s}^{-1} = k_{I=0} + \beta \cdot I_{\text{eff}}$ (in which β is the kinetic salt coefficient and can be extrapolated from the plot).

4. Conclusion and outlook

All the rate constants measured in this work are in the order of magnitude of $10^9 \text{ M}^{-1} \text{s}^{-1}$ and therefore the role of Cl atom could be significant. The results obtained can be used in modelling studies and may be helpful for a better understanding of tropospheric aqueous phase chemistry.

5. Acknowledgement

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