

# Reactivity Study of Br-atoms with Tropospherically Important Oxygenated Organic Compounds in Aqueous Solution

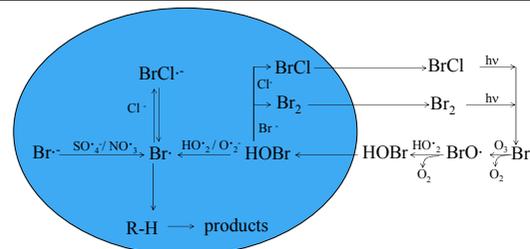
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## Motivation

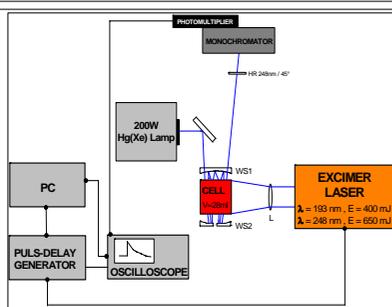
The oxidative capacity of the atmosphere determines the life time and ultimate fate of atmospheric trace species and it is controlled by the presence of highly reactive radicals [1]. Among the highly reactive radicals, halogen and halogen containing radicals (Cl, Br, BrCl, Br<sub>2</sub>) are of current research interest since these compounds may react rapidly with atmospheric trace compounds such as ozone and hydrocarbons [2]. The primary and secondary products of the oxidation reaction of the above radicals with hydrocarbons might be toxic to human, plants, animals, and materials. Model calculation suggests that the particles are the main source of halogen and related species in marine boundary layer [3]. The halogen (Cl, Br) can be formed in aqueous phase either radical conversion processes or the direct transfer from gas phase. Figure 1 shows the possible coupling between Br-atom activation and aqueous phase Br-atom chemistry.



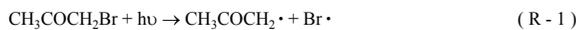
**Figure 1** : Possible coupling between Br-atom activation and aqueous phase Br-atom chemistry

## Experimental and generation of Br-atoms in aqueous solution

Br-atoms in aqueous solution have been generated by photolysis of bromoacetone (R-1) by an excimer laser (Lambda Physik Compex 200) operating at  $\lambda = 248$  nm. The reactivity of Br-atoms with tropospherically relevant organic compounds in aqueous solution have been studied using a Laser Photolysis - Long Path Absorption (LP-LPA) method. A high pressure mercury xenon lamp (200W, Hamamatsu) has been used as an analytical light. The decay of Br-atoms (R-2) is followed by using its absorption at  $\lambda = 297$  nm which is close to the absorption maxima of Br-atoms [5]. The schematic diagram of the experimental set-up is shown in the Figure 2. The experimental set-up is fully thermostated which allow us to study the temperature dependency study.



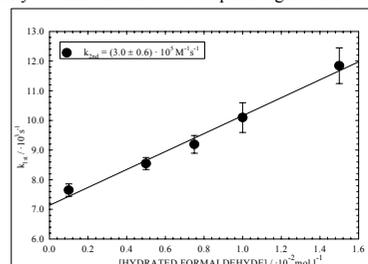
**Figure 2** : Experimental set-up of Laser Photolysis - Long Path Absorption Technique (LP-LPA)



## Results and discussions

### Br-kinetics:

The direct decay kinetics of Br-atoms with some tropospherically important organic compounds has been determined at  $T = 298\text{K}$  under pseudo first order condition at five different reactant concentrations. Normally 64 time-resolved absorption signals for each  $k_{1st}$  and 8 such  $k_{1st}$  were determined for each concentration and averaged. The second order rate coefficient is evaluated by plotting the observed  $k_{1st}$  for five different reactant concentrations. The regression line of the plot gives the second order rate coefficient for the reaction of Br-atom with organic compound in aqueous solution. As an example, a typical plot for evaluation 2<sup>nd</sup> order rate coefficient for the reaction of Br-atom with formaldehyde is shown in Figure 3.



**Figure 3**: Plot of measured  $k_{1st}$  versus [reactant] for the reaction of Br with hydrated formaldehyde at  $T = 298\text{K}$ .

**Table 1**: Observed second order rate constants for H-atom abstraction reactions of Br-atoms with different organics at  $T = 298\text{K}$  and bond dissociation energy of the weakest C-H bond

S.N.	Reactants	BDE (kJmol <sup>-1</sup> )	n <sub>H</sub>	k <sub>2nd(298K)</sub> (M <sup>-1</sup> s <sup>-1</sup> )	k <sub>H</sub> = k <sub>2nd(298K)</sub> / n <sub>H</sub> (M <sup>-1</sup> s <sup>-1</sup> )	logk <sub>H</sub> (M <sup>-1</sup> s <sup>-1</sup> )
1	isobutanal	(358 ± 8)	1	(1.0 ± 0.2) · 10 <sup>8</sup>	(1.0 ± 0.2) · 10 <sup>8</sup>	8
2	butanal	(361 ± 8)	1	(1.0 ± 0.2) · 10 <sup>8</sup>	(1.0 ± 0.2) · 10 <sup>8</sup>	8
3	propanal	(366 ± 8)	1	(5.7 ± 2.0) · 10 <sup>7</sup>	(5.7 ± 2.0) · 10 <sup>7</sup>	7.76
4	ethanal	(374 ± 2)	1	(3.5 ± 0.7) · 10 <sup>7</sup>	(3.5 ± 0.7) · 10 <sup>7</sup>	7.54
5	2-propanol	(381 ± 4)	1	(1.8 ± 0.4) · 10 <sup>6</sup>	(1.8 ± 0.4) · 10 <sup>6</sup>	6.26
6	2-butanol	(381 ± 8)	1	(1.5 ± 0.2) · 10 <sup>6</sup>	(1.5 ± 0.2) · 10 <sup>6</sup>	6.18
7	diethyl ether	(384 ± 2)	4	(1.3 ± 0.7) · 10 <sup>6</sup>	(3.3 ± 0.2) · 10 <sup>5</sup>	5.51
8	1-propanol	(385 ± 4)	2	(3.8 ± 0.4) · 10 <sup>5</sup>	(1.9 ± 0.2) · 10 <sup>5</sup>	5.28
9	THF	(385 ± 4)	4	(1.9 ± 0.4) · 10 <sup>6</sup>	(4.8 ± 0.1) · 10 <sup>5</sup>	5.68
10	formic acid	(387 ± 8)	1	(7.7 ± 1.2) · 10 <sup>5</sup>	(7.7 ± 1.2) · 10 <sup>5</sup>	5.89
11	hydrated formaldehyde	(388 ± 8)	2	(3.0 ± 0.6) · 10 <sup>5</sup>	(1.5 ± 0.3) · 10 <sup>5</sup>	5.18
12	ethanol	(389 ± 4)	2	(8.2 ± 0.7) · 10 <sup>5</sup>	(4.1 ± 0.3) · 10 <sup>5</sup>	5.61
13	ethylformate	(395 ± 8)	1	(9.3 ± 3.7) · 10 <sup>4</sup>	(9.3 ± 3.7) · 10 <sup>4</sup>	4.97
14	methanol	(401 ± 8)	3	(4.1 ± 2.0) · 10 <sup>4</sup>	(1.4 ± 0.7) · 10 <sup>4</sup>	4.14

### References

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In Table 1, observed second order rate coefficient for the reaction of Br-atoms with the different organic compounds investigated in this study at  $T = 298\text{K}$  are summarised together with the BDEs of the most loosely bonded C-H bond of the organic compounds. From the Table 1 one can see that to an increase of the BDE corresponds to a decrease of the observed rate constant. This indicates that the Br reactivity at least for the organic compounds investigated in this study are highly BDE dependent.

### H - abstraction reaction mechanism:

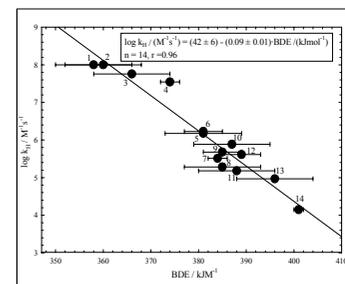
According to Evans-Polanyi [6], for H - abstraction reactions, a proportional relationship exists between the logarithm of observed rate constant per abstractable hydrogen atom and the bond dissociation energy (BDE) of the weakest C-H bond of the organic compound i.e.

$$\log k_H \sim \text{BDE (C-H)} \rightarrow \text{Evans - Polanyi}$$

Therefore the logarithm of observed rate coefficients per abstractable hydrogen atom are plotted as a function of BDE and the Figure 4 is compiled. The rate coefficient per abstractable hydrogen atom have been evaluated by dividing the observed second order rate constant with the number of mostly loosely bonded hydrogen atom present in the organic compound. The numbering in the Figure 4 referring to the Table 1. From the regression line of the Figure 4 following empirical equation has been extrapolated.

$$\log k_H / (\text{M}^{-1}\text{s}^{-1}) = (42 \pm 6) - (0.09 \pm 0.01) \cdot \text{BDE} / (\text{kJ mol}^{-1}) \quad [n = 14; r = 0.96]$$

The high correlation coefficient of the regression line indicates that the same reaction mechanism applies for the investigated organic compounds and it is suggested to be H-abstraction mechanism. Further, the regression equation obtained in the present study can be used to estimate the unknown rate coefficient for H-abstraction reactions Br-atoms if the BDE of the organic compound is known and vice versa. However, the potential user must be aware of the uncertainty of the result obtained.



**Figure 4**: Evans-Polanyi plot in the form of  $\log k_H$  vs (BDE)

### Conclusions / outlook

- The direct decay kinetics of Br-atoms with different tropospherically relevant organics at room temperature have been determined in aqueous solution.
- A good correlation has been found between  $\log k_H / (\text{M}^{-1}\text{s}^{-1})$  and  $\text{BDE} / (\text{kJ mol}^{-1})$  of the studied organic reactants. The correlation obtained in this study can be used to estimate the second order rate constant of hydrogen abstraction reactions of Br-atoms with other organics.
- The kinetic data obtained from this study can be implemented in the tropospheric multiphase model so called Chemical Aqueous Phase Radical Mechanism CAPRAM in forthcoming versions.
- In the future the reactivity of Br-atom with some organic / inorganic anions will be studied.
- Whenever there is halogen radical (Cl, Br) in tropospheric aqueous phase, the formation of the BrCl<sup>-</sup> radical anion is possible. Therefore in the future, some spectroscopic and kinetic investigations of this radical anion will be performed.