

A Laser Flash Photolysis Kinetic Investigation of Br-Atoms in Aqueous Solution

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Motivation

The reactions of halogen atoms with organic compounds are in the focus of current research as these atoms could affect the budget of ozone and hydrocarbons [1]. Model calculations suggest that halogen atoms and related species could also play an important role not only in gas phase but also in cloud water and in aerosol particles [2]. In Figure 1 the possible coupling between "halogen activation and aqueous phase halogen chemistry" is shown. Recently the concentration of halogen containing radicals such as Cl and Br have been calculated by Herrmann et. al [3] in different marine scenarios shows that the concentration of Br-atom is at least ten times higher than the Cl-atom concentration. In literature, the kinetic data are available for Cl-atoms with various organics and shows the comparable reactivity as OH radical [4]. However, in the case of Br reactivity, the kinetic data is quite sparse and needs to fulfil the existing kinetic gap in the aqueous tropospheric multiphase chemistry for better understanding of the heterogeneous multiphase chemistry.

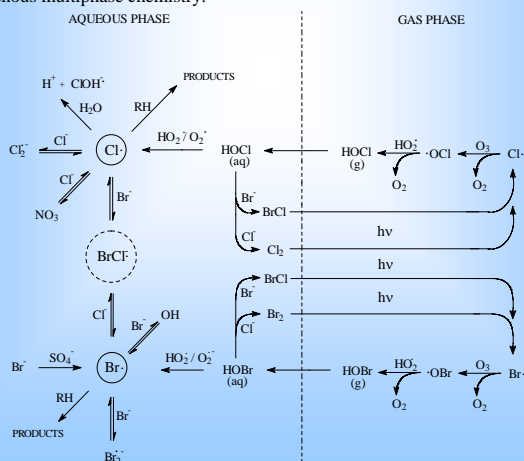


Figure 1: Possible coupling between halogen activation and aqueous phase halogen chemistry

Experimental

The direct decay kinetics of Br-atoms with tropospheric relevant compounds in aqueous solution have been studied using a laser photolysis long path absorption (LP-LPA) technique. The schematic diagram of the technique is shown in Figure 2.

Br kinetics

Br-atoms have been generated by photolysis of bromoacetone (R-1) at $\lambda = 248 \text{ nm}$ by an excimer laser (Lambda Physik, Compex 200). The decay of free radical reactant concentration ($\text{Br}\cdot$) is followed by using its absorption of UV-light from Hg / Xe lamp at $\lambda = 297 \text{ nm}$ which is comparable to the absorption maximum of Br atom.

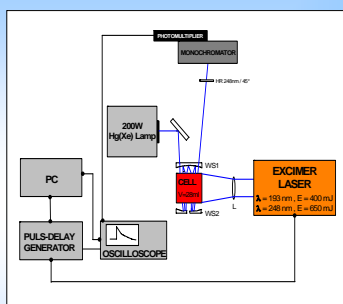
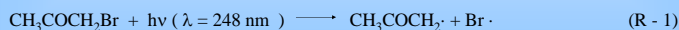


Figure 2: Experimental set-up of laser photolysis long path absorption (LP-LPA) experiment

Results and Discussions

Reactivity of Br atoms with organics

To see the reactivity of Br-atoms with different organics, the following compounds (Table 1) have been chosen according to Bond Dissociation Energy (BDE) of the weakest (R-H) bond. The decay kinetics of Br-atoms are measured under pseudo first order condition at five different reactant concentrations. Usually 64 time-resolved absorption signals were averaged for each k_{1st} and 8 such k_{1st} were determined for each concentration and averaged.

The plot of k_{1st} versus reactant concentrations gives the second order rate constant. Figure 2 shows a typical plot of k_{1st} versus reactant concentrations for the reaction of Br with 2-propanol at room temperature. The slope of regression line of the plot gives the second order rate constant.

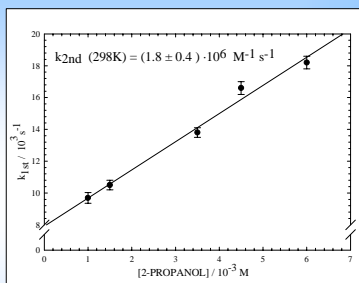


Figure 3: Plot of measured k_{1st} versus [reactant] for the reaction of Br with 2-propanol at $T = 298 \text{ K}$

Hydrogen abstraction reactions

Like other radicals (OH, Cl) the reactions of Br with most of the saturated aliphatic organics in aqueous solution are suggested to proceed via the abstraction of the most loosely bound hydrogen atoms present in the organic molecule.



Table 1 shows the measured second order rate constants of the compounds investigated at room temperature and the corresponding bond dissociation energy of the compounds.

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 R-H bond

Organics	BDE (kJ mol ⁻¹)	$k_{2nd, 298K}$ (M ⁻¹ s ⁻¹)	n_H	$k_H = k_{2nd, 298K} / n_H$ (M ⁻¹ s ⁻¹)	log k_H (M ⁻¹ s ⁻¹)
Methanol	(401±1) ⁽⁶⁾	(4.1 ± 1.9) 10 ⁴	3	(1.4 ± 0.6) 10 ⁴	4.15
Ethanol	(389±4) ⁽⁶⁾	(2.2 ± 0.4) 10 ⁵	2	(1.1 ± 0.2) 10 ⁵	5.04
Formic acid	(387±8) ⁽⁶⁾	(7.7 ± 1.2) 10 ⁵	1	(7.7 ± 1.2) 10 ⁵	5.89
1-Propanol	(385±8) ⁽⁶⁾	(3.8 ± 0.4) 10 ⁵	2	(1.9 ± 0.2) 10 ⁵	5.28
2-Propanol	(381±4) ⁽⁶⁾	(1.8 ± 0.4) 10 ⁶	1	(1.8 ± 0.4) 10 ⁶	6.26
Ethanal	(374±2) ⁽⁷⁾	(3.5 ± 0.7) 10 ⁷	1	(3.5 ± 0.7) 10 ⁷	7.54
Propanal	(366±8) ⁽⁸⁾	(5.7 ± 1.1) 10 ⁷	1	(5.7 ± 1.1) 10 ⁷	7.76
Butanal	(360±8) ⁽⁸⁾	(9.2 ± 0.7) 10 ⁷	1	(9.2 ± 0.7) 10 ⁷	7.96

Evans - Polanyi correlation

Evans and Polanyi [5] empirically has found a linear relationship between the logarithm of the rate constant per abstractable hydrogen atom and BDE of the weakest (R-H) bonds of the organics.

$$\ln k = \ln A - E_A / RT \quad \rightarrow \text{Arrhenius equation} \quad (\text{I})$$

$$\Rightarrow \ln k \sim E_A \quad (\text{II})$$

$$E_A \sim \text{BDE (R-H)} \quad \rightarrow \text{Evans and Polanyi} \quad (\text{III})$$

Hence from Equation (II) and Equation (III)

$$\ln k \sim \text{BDE (R-H)} \quad (\text{IV})$$

The Equation (IV) shows the logarithm of the rate constant is proportional to the BDE of the weakest R-H bond of the organics. Therefore, the logarithm of the rate constants of the reactions of Br per equivalent abstractable hydrogen atom as a function of bond dissociation energy (BDE) are plotted in Figure 4.

As can be seen in the figure, the observed rate constant is increasing with decreasing the bond dissociation energy of the organics studied presently. A good correlation has been found between $\log k_H$ (M⁻¹ s⁻¹) and BDE (kJ mol⁻¹) of the measured organics (Figure 4). From the Figure, the following empirical equation has been extrapolated.

$$\log k_H (\text{M}^{-1} \text{s}^{-1}) = (45 \pm 11) - (0.1 \pm 0.03) \cdot \text{BDE (kJ mol}^{-1}) \quad [n = 8; r = 0.96]$$

The correlation found here confirms that, at least for the compounds investigated, the hydrogen abstraction is the main reaction pathway for Br-atoms.

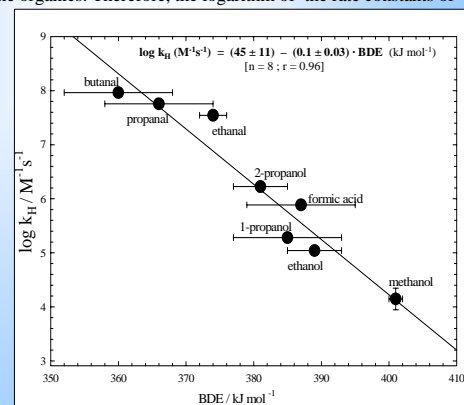


Figure 4: Plot of $\log k_H$ versus bond dissociation energy (BDE) for H-abstraction reactions of Br with number of saturated aliphatic organics at $T = 298 \text{ K}$.

Conclusions and 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 $\log k_H$ (M⁻¹ s⁻¹) and BDE (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 will be implemented in the tropospheric multiphase our model CAPRAM in updated version.
- Further investigations of Br-atoms reactivity toward other tropospheric relevant compounds (inorganic and organic compounds) will be performed.

References

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