Kinetic Investigation of Br-atoms with Tropospherically Important Organic Compounds in Aqueous Solution

K. Parajuli and H. Herrmann

Leibniz - Institut für Troposphärenforschung, Permoserstr. 15, 04318 Leipzig, Germany
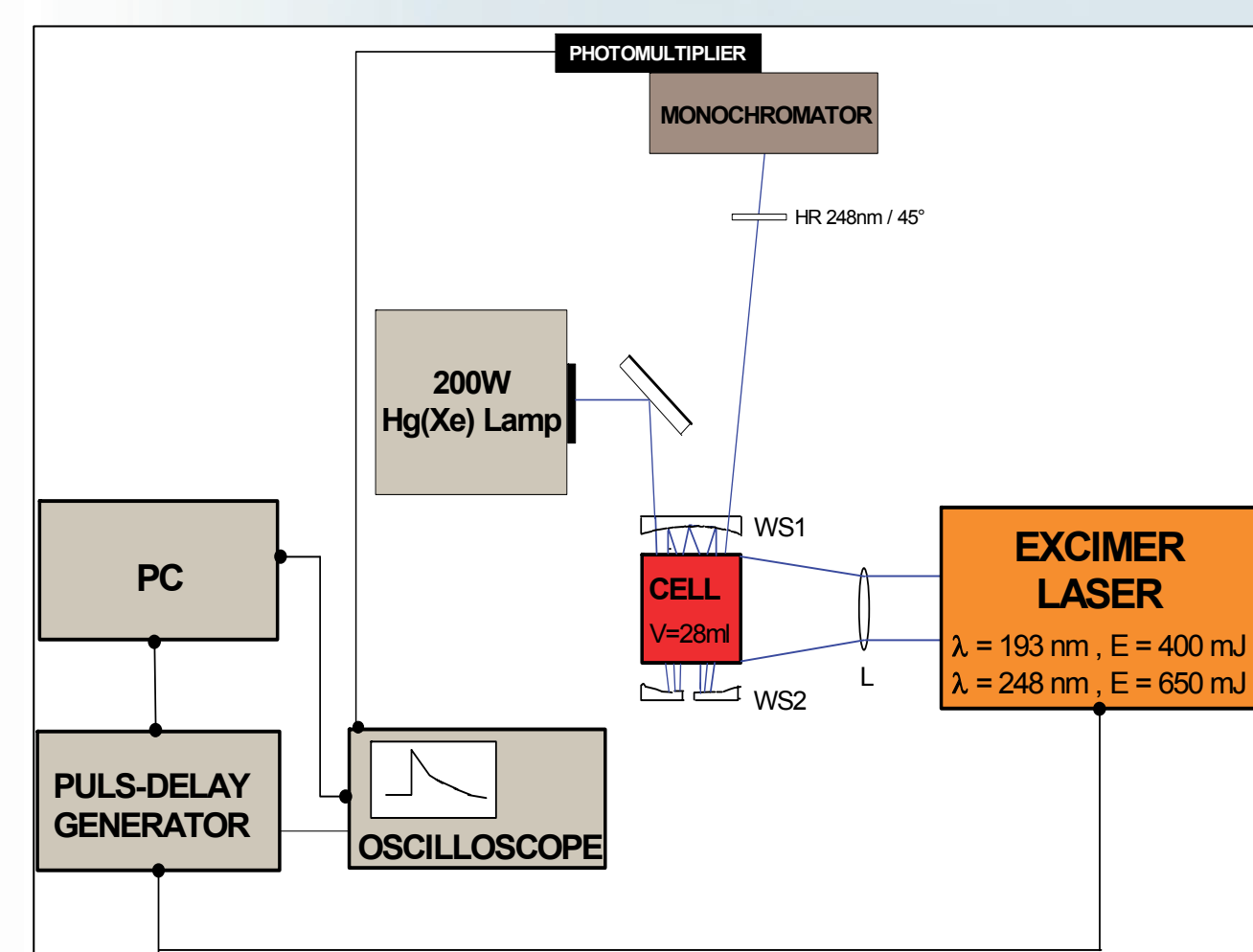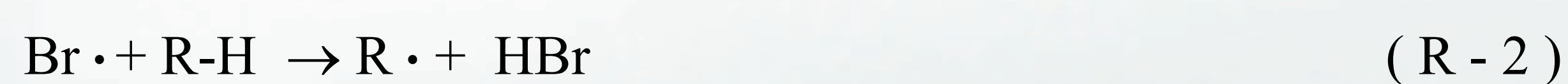
parajuli@tropos.de

Motivation

The reactivity of halogen and halogen containing radicals (Cl, Br, BrCl$^-$, Br$_2^-$) with organic compounds is of current research interest since these compounds may react rapidly with atmospheric trace compounds such as oxygenated organic compounds.The primary and secondary products of the oxidation reactions of the above radicals with organic compounds might have negative effect to human, plants, animals, and materials. The available kinetic data for the Cl-radical reactivity with several organic compounds indicates a reactivity comparable to OH radical [1]. However, in the case of Br reactivity; the kinetic data are quite sparse. Hence, in the present study the reactivity of Br-atoms towards the selected oxygenated organic compounds in qaueous slolution have been performed. Further the observed kinetic data can be implemented in the upcoming versions of tropospheric multiphase model so called Chemical Aqueous Phase Radical Mechanism (CAPRAM) for the better understanding of the tropospheric multiphase system.

Experimental

Fig 1 : Scheme of Laser Photolysis - Long Path Absorption Technique (LP-LPA) set-up.

Br-atoms in aqueous solution have been generated by photolysis of bromoacetone (R-1) operating at λ = 248 nm by an excimer laser. A high pressure mercury xenon lamp has been used as an analytical light. The decay of Br-atoms (R-2) is followed by using its absorption at λ = 297 nm which is close to the absorption maxima of Br-atoms [2].The kinetics of Br-atoms with organic compounds are determined under pseudo first order conditions. The experimental set up (figure 1) is fully thermostated which allow us to study the temperature dependency study in the temperature rang (288 – 328)K

$$CH_3COCH_2Br + h\upsilon \rightarrow CH_3COCH_2 \cdot + Br \cdot \qquad\qquad (R - 1)$$

$$Br \cdot + R\text{-}H \rightarrow R \cdot + HBr \qquad\qquad (R - 2)$$

Results and discussions

The second order rate constant at T = 298K together with thermodynamic parameters observed from T-dependent studies of the reactions of Br-atoms with selected organics are reported in the Table 1. From Table 1, one can see that to an increases 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. Further with increasing BDEs increasing activation energies are obtained. The observed negative entropies of activation suggest a highly ordered activated complex. Moreover, the nearly similar preexponential factors observed in the present study also reflects similar reaction mechanism of the investigated series of reactions of Br-atoms in aqueous solution.

Table 1: Observed second order rate constants at T = 298K, thermodynamic parameters for H-atom abstraction reactions of Br-atoms with different organics and bond dissociation energy of the weakest C-H bond

S.N.	Reatants	BDE (kJmol^{-1})	$k_{2nd(298K)}$ (M^{-1}s^{-1})	A (l mol^{-1}s^{-1})	E_A (kJmol^{-1})	$\Delta G^{\neq}$ (kJmol^{-1})	$\Delta H^{\neq}$ (kJmol^{-1})	$\Delta S^{\neq}$ (JK^{-1}mol^{-1})
1	isobutanal	358	$(1.0 \pm 0.2)\cdot10^8$	$(6.7 \pm 2.2)\cdot10^8$	5 ± 17	28 ±100	3 ± 9	-(84 ± 28)
2	butanal	361	$(1.0 \pm 0.2)\cdot10^8$	$(4.7 \pm 0.6)\cdot10^9$	10 ± 7	28 ± 24	7 ± 6	-(68 ± 9)
3	propanal	366	$(5.7 \pm 2.0)\cdot10^7$	$(1.1 \pm 0.01)\cdot10^9$	7 ± 3	29 ±15	5 ± 2	-(80 ± 5)
4	ethanal	374	$(3.5 \pm 0.7)\cdot10^7$	$(2.0 \pm 0.4)\cdot10^{10}$	15 ±11	30 ± 27	13 ± 9	-(56 ± 10)
5	2-propanol	381	$(1.8 \pm 0.4)\cdot10^6$	$(7.8 \pm 1.2)\cdot10^{10}$	26 ±10	37 ± 20	24 ± 9	-(45 ± 7)
6	2-butanol	381	$(1.5 \pm 0.2)\cdot10^6$	$(2.0 \pm 0.1)\cdot10^9$	18 ± 4	38 ± 11	15 ± 3	-(75 ± 6)
7	diethyl ether	384	$(1.3 \pm 0.7)\cdot10^6$					
8	1-propanol	385	$(3.8 \pm 0.4)\cdot10^5$	$(8.1 \pm 1.1)\cdot10^7$	13 ± 6	41 ± 24	11 ± 5	-(102 ±13)
9	THF	385	$(1.9 \pm 0.4)\cdot10^6$					
10	formic acid	387	$(7.7 \pm 1.2)\cdot10^5$	$(1.6 \pm 0.2)\cdot10^9$	19 ± 8	39 ± 24	16 ± 7	-(77 ± 12)
11	hydrated formaldehyde	388	$(3.0 \pm 0.6)\cdot10^5$	$(4.9 \pm 0.9)\cdot10^{10}$	30 ± 12	42 ± 25	27 ± 11	-(49 ± 9)
12	ethanol	390	$(8.2 \pm 0.7)\cdot10^5$	$(1.3 \pm 0.2)\cdot10^9$	19 ± 8	39 ± 22	16 ± 7	-(78 ± 11)
13	ethyl formate	395	$(9.3 \pm 3.7)\cdot10^4$	$(1.0 \pm 0.2)\cdot10^{11}$	35 ± 12	45 ± 23	32 ± 11	-(43 ± 8)
14	methanol	401	$(4.1 \pm 2.0)\cdot10^4$	$(2.7 \pm 0.3)\cdot10^9$	28 ± 7	47 ± 18	25 ± 6	-(73 ± 9)

Fig 3: Plot of logk$_H$ (OH) vs logk$_H$ (Br) for different compounds

H-abstraction mechanism:

An Evans-Polanyi plot [3] in the form of E$_A$ vs BDE is shown in Figure 2. From the regression line of the plot 2, the empirical equation (E-1) has been extrapolated. The reasonable correlation coefficient of the regression line of the plot 2 indicates that the same reaction mechanism applies for the investigated organic compounds and it is suggested to be H-abstraction mechanism.

Fig 2: Evans –Polanyi plot in the form of E$_A$= f (BDE). Numbering refers to Table 1.

$$E_A / kJmol^{-1} = (207 \pm 95) + (0.59 \pm 0.25) \cdot BDE / (kJmol^{-1})$$
[with n = 12; r = 0.85]   (E-1)

Reactivity comparison of Br-atoms reactions with OH radical in aqueous solution:
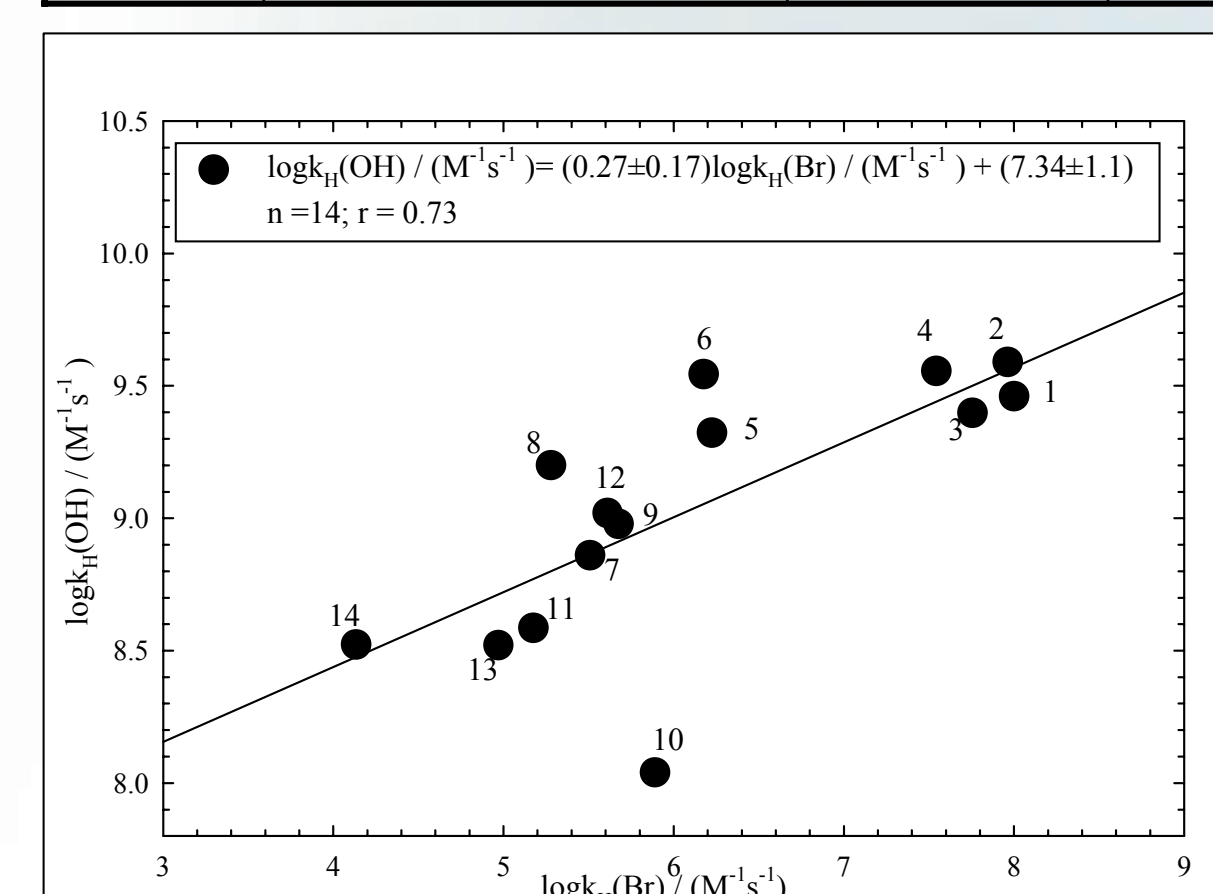
Since both Br and OH radicals are supposed to follow the same reaction mechanism at least for the compounds investigated in present study, a reactivity correlation between these two radicals is expected. Therefore the reactivity comparison of Br-atoms with OH radical is done by plotting logk$_H$ (OH) vs logk$_H$ (Br) (where k$_H$ = k$_{2nd}$ / n and n = the number of most loosely bonded C-H bond present in the organic compounds). Second order rate constants (k$_{2nd}$) for OH radical with the selected organics are taken from the available literatures [4, 5, 6]. Figure 3 represents the comparison of reactivity of Br-atoms with OH reactivity with similar set of organic compounds. The numbering in the plot 3 refers to Table 1. From the figure 3 the following empirical equation (E-2) has been extrapolated.
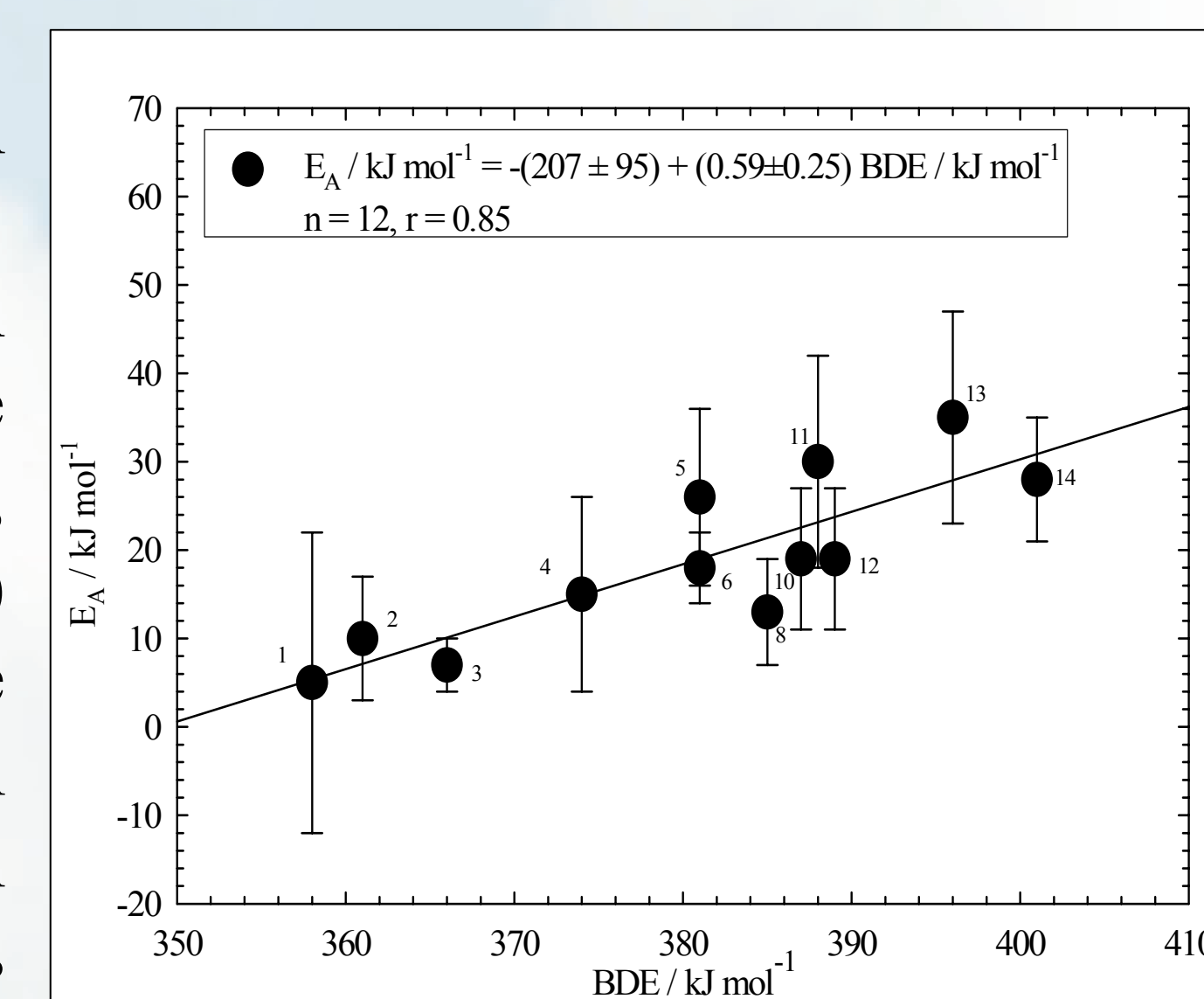
$$logk_H (OH) / (M^{-1}s^{-1}) = (0.27 \pm 0.17)\, logk_H (Br) / (M^{-1}s^{-1}) + (7.34 \pm 1.1) \qquad [\text{with } n = 14; r = 0.73] \qquad (E-2)$$

The significance of such equation is that one can use the regression equation to estimate the reactivity of Br-atoms toward any H-abstraction reaction if reactivity of the reaction with OH radical is known. However the potential user must be aware of the uncertainty of the observed results.

Conclusions and outlook

•A good correlation between E$_A$ (kJ mol^{-1}) and BDE (kJ mol^{-1}) of the investigated organic reactants suggest that at least for the reactions of Br-atom investigated in the present study proceed through H-abstraction mechanism.

•The correlation between logk$_H$(OH) and logk$_H$(Br) obtained in this study can be used to estimate the unknown rate constant of Br-atoms with other organics and vice versa.

•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.

•Whenever there is halogen radical (Cl, Br) in tropospheric aqueous phase, the formation of the BrCl$^-$ radical anion is possible. Therefore in the future, spectroscopic and kinetic investigations of this radical anion will be performed.

References

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