



Laser-based Studies for OH Reactions with Oxygenated Species in the Troposphere

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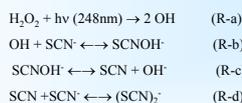
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Motivation

Free radicals such as OH, NO₃, Cl/Cl₂, Br/Br₂, play an important role in the chemistry of the aqueous tropospheric particle phase. The OH radical has the highest oxidation capacity toward organic and inorganic compounds in both the tropospheric gas and aqueous phase i.e. in clouds droplets, fog, rain and the aqueous aerosols, hence is the most important radical in the troposphere. Organic compounds subject to the oxidation by OH in the tropospheric multiphase system may be of biogenic or anthropogenic origin. With regards to the latter recently oxygenated compounds became of interest because of their application as solvents and fuel additives. Due to their volatility, these compounds are emitted either directly or indirectly into the atmosphere. In this study the rate constants of the OH radical reactions with different organic compounds have been investigated in aqueous solution, under different conditions as a contribution to the MOST project.

Experimental

A laser-photolysis long path absorption (LP-LPA) set-up (Fig.1) was used for kinetic studies of OH radical reactions. The kinetic investigations of the OH radical were carried out by competition kinetics using thiocyanate (SCN⁻) as reference substance. The formation of the OH radicals was initiated by excimer laser flash photolysis of hydrogen peroxide operated at λ=248 nm.



The product (SCN)₂⁻ radical anion is the strongly absorbing reaction product with peak absorbance at 475 nm. Therefore the analysis light was emitted by a cw-laser at λ=473 nm. In this study we applied the temperature dependent rate constant on reaction (R-b) reported by Chin and Wine (k_{R,b} = 1.24 · 10¹⁰ M⁻¹ s⁻¹ at 298 K) as reference data set. The results presented in this study are in good agreement with the available literature data (Table 1) indicating that under the experimental conditions applied in the present study the use of thiocyanate and the application of the kinetic reference data set of Chin and Wine is suitable.

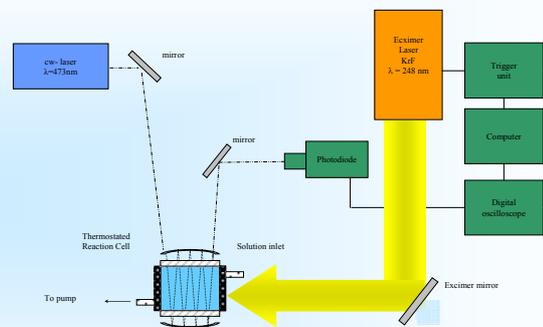


Figure 1: Laser-photolysis long-path absorption laser apparatus (LP-LPLA) set-up for kinetic investigations

Results and Discussion

Reaction of OH with Acetone, Methyl Ethyl Ketone, Acetylacetonone, Isobutyraldehyde, Ethyl Formate

Due to the low boiling point of acetone (328 K) the reactivity of OH with acetone was investigated in the temperature range between 278K and 318K. The obtained rate constant is shown in Table 1.

$$k(T) = (2.8 \pm 0.4) \cdot 10^{11} \exp((-2200 \pm 1300)/T) \text{ M}^{-1} \text{ s}^{-1} \quad \text{(Eq-1)}$$

Table 1: Observed rate constants for the reaction of OH with organic compounds

Compound	Formula	k _{OH} (M ⁻¹ s ⁻¹)
Acetone	CH ₃ COCH ₃	(2.1 ± 0.6) · 10 ¹⁰ (this study)
		(1.7 ± 0.5) · 10 ¹⁰ (Monod et al., 2002)
2-Butanone	CH ₃ COCH ₂ CH ₃	(1.5 ± 0.7) · 10 ⁹ (this study)
		1.8 · 10 ⁹ (George et al., 2002)
Acetylacetonone	CH ₃ COCH ₂ CH ₂ COCH ₃	(7.6 ± 1.1) · 10 ⁹ (this study)
Isobutyraldehyde	(CH ₃) ₂ CHCHO	(2.9 ± 1.0) · 10 ⁹ (this study)
Ethyl Formate	HCOOC ₂ H ₅	(3.2 ± 0.8) · 10 ⁹ (this study)
		3.9 · 10 ⁹ (Adams et al., 1965)

The obtained rate constant for the reaction of OH with 2-butanone as well as for the reaction of OH with acetone is presented in Table 1. The measurements were performed in a temperature range between 278 K and 328 K and the following Arrhenius equation was obtained:

$$k(T) = (1.2 \pm 0.2) \cdot 10^{13} \exp((-2800 \pm 1200)/T) \text{ M}^{-1} \text{ s}^{-1} \quad \text{(Eq-2)}$$

Obviously, 2-butanone is reacting much faster as expected from the C-H bond strengths of the α-H-atoms. This effect is found as well in the measurements of the group of George (see Table 1).

The temperature dependences of observed rate constants are shown in Figure 2 for the compounds investigated in this study.

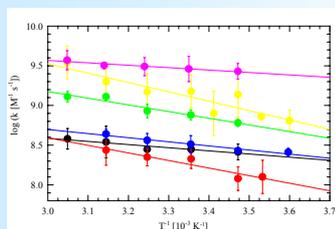


Figure 2: Arrhenius plot for the reactions of OH with: ● isobutyraldehyde, ● 2-butanone, ● acetylacetonone, ● ethyl formate, ● acetone

Acetylacetonone is reacting with OH by H atom abstraction i. e. the same mechanism is assumed for the all compounds investigated in this study. The bond dissociation energy's of the weakest extractable H atom in this study were calculating based upon Benson's incremental method.

$$k(T) = (5.1 \pm 0.1) \cdot 10^{11} \exp((-1900 \pm 1000)/T) \text{ M}^{-1} \text{ s}^{-1} \quad \text{(Eq-3)}$$

Isobutyraldehyde is very reactive as might be expected from the chemistry of the aldehydes. The hydrogen atom in α position is the weakest bonded H-atom in the molecule because the resulting alkyl radical is stabilized by inductive and resonance effects.

$$k(T) = (3.0 \pm 0.1) \cdot 10^{10} \exp((-720 \pm 360)/T) \text{ M}^{-1} \text{ s}^{-1} \quad \text{(Eq-4)}$$

For a given ester group, the rate constants increase with increasing chain length of the acid, i.e butyrate>propionate>acetate. Ethyl Formate is more reactive than might be expected from the general trend, but this is explained by the presence of an α hydrogen atom with its resultant effect on the reducing properties of the molecule (Adams et al., 1965).

$$k(T) = (1.8 \pm 0.1) \cdot 10^{10} \exp((-1200 \pm 500)/T) \text{ M}^{-1} \text{ s}^{-1} \quad \text{(Eq-5)}$$

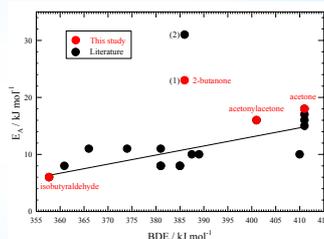


Figure 3: Plot of the activation energies vs. BDE

In order to understand if the reactions studied do follow an H-abstraction mechanism by forming the most stable alkyl-radical, the measured activation energies for hydroxyl radical reactions in aqueous solution have been plotted against the bond dissociation energy of the weakest C-H bond. Due to the missing increments upon Benson's method the bond dissociation energy for weakest C-H bond in the ethyl formate is not determined and hence is not plotted. The data points obtained for 2-butanone (Point 1 and 2) have not been included into the regression. The correlation found here (Eq-6) indicates that H-abstraction seems to be main reaction pathway in reactions of OH with different organic compounds.

$$E_a = (51 \pm 26) + (0.16 \pm 0.07) \cdot \text{BDE} \text{ (kJmol}^{-1}) \quad \text{(Eq-6)}$$

$$n=19; r=0.77$$

The logarithm of the rate constants per abstractable H atom were plotted against the BDE's. Assuming an H abstraction mechanism it can be concluded that molecules with a smaller C-H bond dissociation energy are more reactive. This behaviour of aldehydes is shown in Figure 4. The dashed line presenting the diffusion limit and the plateau observed is still unclear. The correlation found here is presented in following equation:

$$\log(k_H/\text{M}^{-1}\text{s}^{-1}) = (34 \pm 3) - (0.06 \pm 0.01) \cdot \text{BDE} \quad \text{(Eq-7)}$$

$$n=19; r=0.98 \text{ for } 380 \leq \text{BDE} \leq 412 \text{ (kJ mol}^{-1})$$

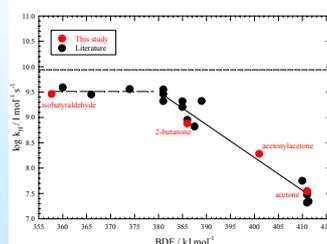


Figure 4: Plot of the log k_H vs. BDE

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Summary and Conclusion

The kinetic investigations contribute to fill existing gaps with regard to OH radical reaction kinetics in aqueous solution. In contrast to most existing studies the rate constants have been investigated as a function of temperature. Considering available temperature dependent values both from literature studies and from the present study, it was shown that correlation exist between the activation energy and the bond dissociation energy. The kinetic data obtained from this study will be implement in the tropospheric multiphase model (CAPRAM 2.4 (MODAC mechanism)).