



Aqueous Phase Reactions with Selected Oxygenated Organic Compounds

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Motivation

The degradation of volatile organic compounds (VOCs) in the troposphere leads to the formation of a range of secondary pollutants such as ozone, peroxyacyl nitrates, and secondary organic aerosols. They are emitted either directly in the atmosphere from solvents and fuel additives, and are also formed in the tropospheric oxidation of all hydrocarbons. Both in the gas phase and in aqueous phase the OH radical is the most important day oxidizing agent responsible for the atmospheric degradation of the oxygenated VOCs. In this work, the temperature dependent rate constants of the OH radical reactions with different (VOCs) have been investigated in aqueous solution as a contribution to the MOST project.

Experimental

A laser-photolysis long path absorption (LP-LPLA) 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 OH radicals in the aqueous phase are produced by excimer laser flash photolysis of hydrogen peroxide at $\lambda=248\text{nm}$. 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 $\lambda=473\text{nm}$. In this study we applied the temperature dependent rate constant reported by Chin and Wine ($k_R = 1.24 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 298 K) as reference data set.

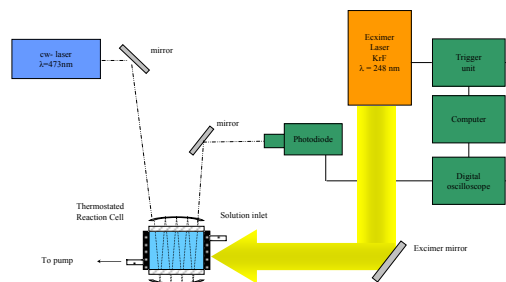


Figure 1: Laser-photolysis long-path absorption laser apparatus (LP-LPLA) set-up for kinetic investigations

Results and Discussions

The reactions of OH radical with acetone, methyl ethyl ketone, acetylacetone, isobutyraldehyde, ethyl formate, and diacetyl have been investigated as a function of temperature in the range between 278K and 348 K. The preexponential factors and activation energies obtained are summarized together with the literature data in the Table 1. The similar preexponential factors indicate that the reactions investigated proceed through the same reaction pathway.

Table 1: Pre-exponential factors (A), activation energy (E_A) and bond dissociation energies (BDE) for H-abstraction reactions of the OH radical in aqueous solution

N ^o	Reactant	A (l/mol s)	E _A (kJ/mol)	BDE ^{a)} (kJ/mol)	Symbol
1	acetone	$(3.4 \pm 0.4) \cdot 10^{11}$	(18 ± 11)	411	■
2	acetone	$(8.4 \pm 0.4) \cdot 10^{10}$	(16 ± 3)	411	▲
3	acetone	$(2.1 \pm 0.3) \cdot 10^{11}$	(17 ± 8)	411	▼
4	acetone	$(6.6 \pm 0.2) \cdot 10^{10}$	(16 ± 3)	411	◆
5	tert-butanol	$(3.3 \pm 0.1) \cdot 10^{10}$	(10 ± 3)	410	●
6	acetylacetone	$(1.1 \pm 0.1) \cdot 10^{11}$	(12 ± 5)	401	■
7	ethyl formate	$(1.8 \pm 0.1) \cdot 10^{10}$	(10 ± 4)	396	●
8	MEK	$(5.1 \pm 0.6) \cdot 10^{11}$	(15 ± 8)	386	●
9	MEK	$(6.6 \pm 4.9) \cdot 10^9$	(4 ± 0.3)	386	○
10	ethanol	$(1.0 \pm 0.1) \cdot 10^{11}$	(10 ± 5)	389	■
11	1-propanol	$(5.6 \pm 0.6) \cdot 10^{10}$	(8 ± 6)	385	■
12	1-butanol	$(1.0 \pm 0.1) \cdot 10^{11}$	(8 ± 1)	385	▲
13	2-propanol	$(6.1 \pm 0.3) \cdot 10^{10}$	(8 ± 2)	381	▲
14	2-butanol	$(7.4 \pm 0.3) \cdot 10^{10}$	(8 ± 3)	381	▲
15	propionaldehyde	$(2.6 \pm 0.1) \cdot 10^{11}$	(11 ± 3)	366	▲
16	butyraldehyde	$(8.1 \pm 0.3) \cdot 10^{10}$	(8 ± 3)	361	▲
17	isobutyraldehyde	$(3.0 \pm 0.1) \cdot 10^{10}$	(6 ± 3)	358	●

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 OH radical reactions in aqueous solution have been plotted against the bond dissociation energy of the weakest abstractable C-H bond (Figure 1).

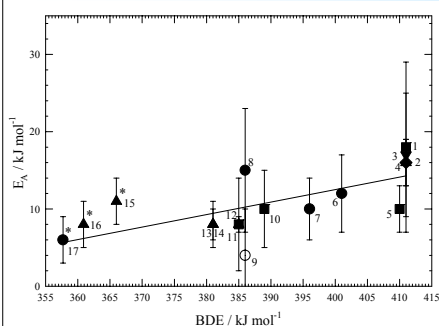


Figure 1: Evans-Polanyi plot in the form of activation energy (E_A) vs. bond dissociation energy (BDE). Numbering refers to the numbers of Table 1. (*): Data for mixtures of hydrated and unhydrated aldehydes.

The bond dissociation energies were taken from literature when available. However, many of the BDEs have not been experimentally measured. Therefore, they have been estimated using a Benson's incremental method for the gas phase species. The regression line represented in Figure 1 corresponds to:

$$E_A = (-52 \pm 34) + (0.16 + 0.09) \cdot \text{BDE} \text{ (kJmol}^{-1}\text{)}$$

$n = 17; r = 0.69$

According to Evans and Polanyi there are correlation between ($k_{H1} = k_{obs}/n$) and BDE of the weakest C-H bond, where k_{obs} is the observed rate constant at 298 K and n represents the number of identical most easily abstractable H atoms. To this end, the same series of oxygenated VOCs for H abstraction reactions of OH radical in both gas phase and aqueous phase were plotted in form of k_{H1} versus BDE (Figure 2). The rate constants per abstractable hydrogen atom k_{H1} for both gas phase and aqueous phase corresponding to Figure 2 are presented in Table 2.

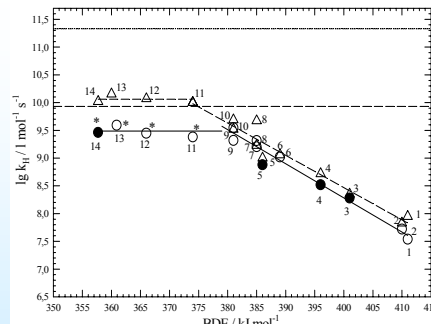


Figure 2: Comparison of the Evans-Polanyi plots in the form of $\lg(k_{H1})$ vs. bond dissociation energy (BDE) between (○): Aqueous phase, (●): This work and (Δ): Gas phase. Numbering refers to the numbers of Table 2.

For $380 \leq \text{BDE} \leq 412 \text{ kJ mol}^{-1}$ the correlation found corresponding to the kinetic data in the aqueous phase can be expressed by the following equation:

$$\lg(k_{H1} / \text{M}^{-1} \text{s}^{-1}) = (33 \pm 3) - (0.06 \pm 0.01) \cdot \text{BDE} / \text{kJmol}^{-1} \quad n = 10; r = 0.99$$

The dotted line in Figure 2 represents the number of bimolecular collisions. In the BDE range between 358 and 374 kJ mol⁻¹ the rate constant for the reactions with a series of aldehydes is best represented by $k_{H1} = 1.2 \cdot 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. The correlation found in the gas phase is identical to that of the aqueous phase and for BDE between 375 and 412 (kJ mol⁻¹) is represented by following equation:

$$\lg(k_{H1} / \text{M}^{-1} \text{s}^{-1}) = (32 \pm 4) - (0.06 \pm 0.01) \cdot \text{BDE} / \text{kJmol}^{-1} \quad n = 11; r = 0.98$$

Table 2: Rate constants per abstractable hydrogen atom (k_{H1}) in the aqueous phase and in the gas phase

N ^o	Reactant	Aqueous Phase		Gas Phase		BDE (kJ/mol)
		$k_{H1}(298\text{K})$ (l mol ⁻¹ s ⁻¹)	$\lg k_{H1}$ (298K) (l mol ⁻¹ s ⁻¹)	$k_{H1}(298\text{K})$ (l mol ⁻¹ s ⁻¹)	$\lg k_{H1}$ (298K) (l mol ⁻¹ s ⁻¹)	
1	acetone	$3.5 \cdot 10^7$	7.54	$8.9 \cdot 10^7$	7.95	411
2	tert-butanol	$5.3 \cdot 10^7$	7.73	$5.4 \cdot 10^7$	7.73	410
3	acetylacetone	$1.9 \cdot 10^8$	8.28	$2.2 \cdot 10^8$	8.35	401
4	ethyl formate	$3.3 \cdot 10^8$	8.52	$5.3 \cdot 10^8$	8.72	396
5	MEK	$7.5 \cdot 10^8$	8.88	$1.0 \cdot 10^9$	9.00	386
6	ethanol	$1.0 \cdot 10^9$	9.02	$1.1 \cdot 10^9$	9.06	389
7	1-propanol	$1.6 \cdot 10^9$	9.20	$1.7 \cdot 10^9$	9.23	385
8	1-butanol	$2.1 \cdot 10^9$	9.32	$4.7 \cdot 10^9$	9.67	385
9	2-propanol	$2.1 \cdot 10^9$	9.32	$3.3 \cdot 10^9$	9.52	381
10	2-butanol	$3.5 \cdot 10^9$	9.55	$4.9 \cdot 10^9$	9.69	381
11	acetaldehyde	$2.4 \cdot 10^9$	9.38	$1.0 \cdot 10^{10}$	10.00	374
12	propionaldehyde	$2.8 \cdot 10^9$	9.45	$1.2 \cdot 10^{10}$	10.07	366
13	butyraldehyde	$3.9 \cdot 10^9$	9.59	$1.4 \cdot 10^{10}$	10.16	361
14	isobutyraldehyde	$2.9 \cdot 10^9$	9.46	$1.1 \cdot 10^{10}$	10.02	358

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Summary and Conclusions

The kinetic investigations contribute to fulfill existing gaps with regard to OH radical reaction kinetics in aqueous solution. The rate constants were investigated as a function of temperature. The Evans Polanyi correlations are presented in both the forms E_A vs. BDE (r = 0.69) and in the form $\lg k_{H1}$ vs. BDE (r = 0.99) considering literature data for the rate constants at 298 K and for the activation energies indicating that the reactions of the OH radical with oxygenated compounds proceed via an H-abstraction mechanism. The obtained correlations might be used for the prediction of rate constants and to estimate activation energies for H-abstraction reactions of OH radical in aqueous solution.

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