Rate Constants for the OH Reactions with Oxygenated Organic Compounds in Aqueous Solution

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ABSTRACT: The kinetics of the oxidation of functionalized organic compounds of atmospheric relevance by the hydroxyl radical (OH) was measured in the aqueous phase. Competition kinetics, using the thiocyanate anion (SCN⁻) as competitor, was applied using both a laser flash photolysis long path absorption (LP-LPA) setup and a Teflon AF waveguide photolysis (WP) system. Both experiments were intercompared and validated by measuring the rate coefficients for the reaction between OH and acetone where values of $k_1 = (1.8 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ were obtained with the WP system, which agrees very well with the rate constant of $k_1 = (2.1 \pm 0.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ determined before by LP-LPLA [1]. The following temperature dependencies of the rate constants (M⁻¹ s⁻¹) for the reactions of OH with ketones, dicarboxylic acids, and unsaturated compounds were obtained in Arrhenius' form: Reaction of OH with: methylisobutyl ketone (MIBK): $k_2 = (1.0 \pm 0.1) \times 10^{12} \exp(\frac{-1572 \pm 583}{T})$, N-methyl pyrrolidone (NMP): $k_3 = (1.8 \pm 0.2) \times 10^{11} \exp(\frac{-1062 \pm 808}{T})$, malic acid (pH = 1): $k_4 = (7.9 \pm 0.8) \times 10^{10} \exp(\frac{-1575 \pm 787}{T})$, maleate monoanion (pH = 4.3): $k_5 = (2.9 \pm 0.4) \times 10^{11} \exp(\frac{-1701 \pm 1204}{T})$, maleate dianion (pH = 9): $k_6 = (1.2 \pm 0.2) \times 10^{11} \exp(\frac{-1449 \pm 1193}{T})$, mesoxalic acid (pH = 1): $k_7 = (3.8 \pm 0.8) \times 10^{10} \exp(\frac{-1588 \pm 1524}{T})$, triethyleneglycol divinyl

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ether (DVE-3): $k_9 = (2.3 \pm 0.1) \times 10^{13} \exp(\frac{-2179 \pm 346}{T})$ methacrolein: $k_{10} = (3.0 \pm 0.1) \times 10^{13} \exp(\frac{-2289 \pm 168}{T})$. The E_a/A values are given with full precision to avoid rounding errors. Equations were derived from the regression line of the Evans–Polanyi plot in the form activation energy (E_a) versus bond dissociation energy (BDE) and from the regression line for the region $380 \le BDE \le 412 \text{ kJ} \text{ mol}^{-1}$ of the Evans–Polanyi plot in the form log k_{H} versus BDE. Both equations can be used as a tool for predicting unknown rate coefficients and activation energy for the reactions of OH with different organics in the aqueous phase. © 2009 Wiley Periodicals, Inc. Int J Chem Kinet 41: 309–326, 2009

INTRODUCTION

Free radicals such as OH, NO₃, Cl, and Br are key compounds in many (if not all) atmospheric reaction cycles producing, among other, ozone, acidity, or even particles. In the troposphere, the hydroxyl radical (OH) is the most important daytime oxidant. This radical is the key oxidant involved in the self-cleaning capacity of the atmosphere and in the transformation of primary pollutants into secondary species. It is important to underline that this is the case for the gaseous environment found not only in the troposphere but also in the condensed phase such as cloud droplets, deliquescent particles, and hydrometeors.

Oxidation kinetics and mechanisms in the aqueous phase have been the focus of many studies over the last years (e.g., see the recent review by Herrmann [1] and references therein) where a large amount of data has been compiled. However, a careful inspection of these studies reveals that most of the work has focused either on very simple molecules with just a few carbon atoms and only one functional group or, on the other hand, the complex molecules such as aromatic compounds. In between these families, however, there is only little information about the reactivity of OH toward ketones, hydroxyketones, aldehydes, or dicarboxylic acids. For these species there is a clear need for further research, considering that oxygenated species may more widely be used as "new" solvents, in a huge number of industrial processes including cleaning and degreasing applications, paints, pharmaceutical process synthesis, polymer disposal agents, and adhesives [2], the technical application of which will result in increased emissions into the atmosphere.

Also, a number of organic compounds may be produced in situ in the atmosphere. For instance, the OH oxidation of aldehydes and ketones both in the gas phase and in the aqueous phase leads to the accumulated acidity in the aqueous phase. Among these, the carboxylic acids containing four carbon atoms (e.g., malic acid) form important contributions to the organic mass increase (organic mass production) in tropospheric particles following precursor transfer from the gas phase [3]. To better understand the atmospheric multiphase oxidation process of oxygenated organic compounds, in the present study the attention was focused on the temperature dependencies of the rate constants for the reactions of OH radicals with various oxygenated compounds such as ketones, dicarboxylic acids, aldehydes, and some unsaturated compounds. Aqueous phase kinetics was investigated using laser flash photolysis and a Teflon AF waveguide photolysis (WP) system in the two contributing laboratories, both applying the competition kinetics method based on the thiocyanate anion (SCN⁻) system.

The aim of this study is not only to provide rate coefficients but also to strengthen already existing [4,5] correlations based on the Evans–Polanyi relationship as a tool for predicting unknown rate coefficients and associated activation parameters in the aqueous phase.

EXPERIMENTAL

Competition Kinetics Method

Because the OH radical in aqueous solution absorbs only weakly in the deep UV region of the spectrum with a small extinction coefficient of $\varepsilon \sim 600 \text{ Lmol}^{-1} \text{ cm}^{-1}$ at $\lambda_{max} \sim 235 \text{ nm}$ [1] and due to the overlapping of the organic peroxyl radicals formed in parallel to the OH decay, an OH radical absorption measurement is difficult. Hence, the concentration of OH was not directly determined but derived from the titration reaction resulting from the competition reaction of the OH with SCN⁻, which produces (SCN⁻₂) radical anions.

$$H_2O_2 + hv \rightarrow 2OH$$
 (R-A)

$$OH + SCN^- \rightarrow OH^- + SCN$$
 (R-B)

$$SCN + SCN^- \leftrightarrow (SCN)_2^-$$
 (R-C)

$$(\text{SCN})_2^- \rightarrow \text{products}$$
 (R-D)

(R-B) competes with

$$OH + RH \rightarrow products$$
 (R-E)

Therefore, adding any organics to an aqueous solution containing the chemicals given in the reaction sequence (R-A) to (R-D) will lower the yield of $(\text{SCN})_2^-$ and such changes will allow the determination of the ratio of $k_{\text{B}}/k_{\text{E}}$ (see below).

For this competition kinetics system the temperature dependent rate constant reported by Chin and Wine has been applied as a reference: In $k(T) = (29.614 \pm 0.636) - (1900 \pm 190)/T$ [M⁻¹ s⁻¹] [6]. The competition kinetic system based on SCN⁻ as a competitor for the study of OH reactions in aqueous solution has already been applied and discussed in some previous studies [4,5,7,8].

Note that a recent study [9] has questioned this reference value while a second one has validated it and even extended its application to various ionic strengths [10]. In this context, it has been decided to derive all rate coefficients by using the reference rate coefficient reported by Chin and Wine [6] as the latter has been widely used as mentioned before [4,5,7,8]. Where data for comparison exist, the results obtained in the present work are in good agreement with the kinetic data from those previous studies and various available kinetic data from the literature demonstrate that the use of thiocyanate as a competitor and the use of the kinetic reference data set of Chin and Wine are appropriate for the experimental conditions applied in the present work.

To improve the reliability of the kinetic data (and hence of any correlations making use of them), the kinetics was derived by two different experimental approaches as described in the following.

Laser Flash Photolysis Long-Path Absorption Setup

A laser photolysis long-path absorption (LP-LPA) setup [1,4,5] was used for indirect kinetic studies of OH radical reactions. This experimental setup has been described in detail previously and only a brief summary is given here. The formation of the OH radicals was initiated by photolysis of hydrogen peroxide by an excimer laser (Lambda LPX 100) operated at $\lambda = 248$ nm using KrF as active medium. The mean energy of the excimer laser was about 150 mJ measured with an energy monitor.

The time dependency of the concentration of the $(SCN)_2^-$ radical was monitored using a combination of a high-pressure Hg-Xe lamp ($\lambda = 436$ nm) and a monochromator/photomultiplier unit (Zeiss PMQ 2/ Hamamatsu PMT 1P 28). The emitted analytical light has been adjusted via White cell optics [11] for 12 passes resulting in an absorption path length of 84 cm

in the reaction cell. The amplified electrical signal was transferred to a digital oscilloscope (Gould 9500A) connected to a PC controlling the experiment. The errors stated here are statistical errors for a confidence interval of 95% derived from linear regression analysis of the experimental data.

Teflon Waveguide Photolysis System

The Teflon WP system has been detailed in two previous studies [7,8]. Basically, in WP system a "windowless" reaction cell is applied, which can be created by using a liquid-core waveguide (henceforth called LCW) made of Teflon AF-2400. The highly flexible Teflon AF-2400 tubing was loosely coiled (~4 cm diameter) and placed in a thermostated reactor close to a photolytic source, that is, an HPK lamp (Cathodeon, 150 W). The OH radicals were generated by photolysis of water dissolved H_2O_2 within the LCW. The generated OH radicals then react with the organic compounds under study, which are also water dissolved. The concentration of OH radicals in the aqueous phase was not directly measured but derived according to the reactions (R-A) to (R-E) as described above.

To probe the $(SCN)_2^-$ concentration in the LCW tube, the output of a 75 W xenon lamp was focused onto the entrance of a 200 μ m diameter-fused silica optical fiber held inside the LCW tube. The light leaves the solid optical fiber and is conducted to the other end of the liquid waveguide. There, another fused silica optical fiber (placed in the liquid) collects most of the transmitted light and leads it to a spectrograph (Andor, Shamrock) coupled to a charge-coupled device (CCD) camera (Andor Technology). The CCD camera monitors the evolution of the UV–visible spectrum as a function of wavelength and time within the LCW. The $(SCN)_2^-$ anion spectra were recorded in the wavelength range from 350 to 750 nm, but the kinetics was derived from absorbance changes at 465 nm.

Aqueous solutions of the organic reactant and the radical precursors were continuously pumped into the LCW, which was hence used as a microflowtube. In all cases, the liquid passed through the LCW in less than 0.5 s. Under these experimental conditions, steady state was obtained within the LCW and verified experimentally (see a previous study [7]) and theoretically using numerical simulations of the chemistry within the LCW.

For both experiments, the following relationship describes the relation between the absorbance of $(SCN)_2^-$ in the presence and absence of added organics:

$$\frac{1}{Abs} = \frac{1}{Abs_0} \left(1 + \frac{k_E[\text{RH}]}{k_B[\text{SCN}^-]} \right)$$
(1)

In this equation, Abs is the absorbance of the $(SCN)_2^-$ anion at a known concentration of the organic compound RH and Abs_0 is the maximum $(SCN)_2^-$ anion absorbance in the absence of the reactant RH. Therefore, given the absorbancies, k_B and the concentration of the reactant RH, the rate coefficient k_E can be determined.

Therefore, by means of the two experiments described above any changes in the absorbance of the $(SCN)_2^-$ anion as a function of the organics content of the solution can be measured allowing the determination of the ratio k_E/k_B . Knowing the rate coefficient k_B for the reference reaction (R-B), allows the calculation of the unknown rate constant k_E .

Materials

All the organic compounds used in this study were purchased from Sigma Aldrich (Seelze, Germany) (purity \geq 99%) except DVE-3, which was provided from BASF (Ludwigshafen, Germany).

Prior to the measurements, the LP-LPA system was cleaned by continuous flowing (15 min) of ultrapure MilliQ water through the tank, tubing, and the reaction cell.

The WP system was cleaned with continuous flowing (10–15 min) of ultrapure MilliQ water throughout the Teflon WP system.

RESULTS AND DISCUSSION

In this section, a report will be first given on all the kinetics measurements performed for a number of oxygenated compounds, before discussing possible structure–reactivity relationships.

Reactions of OH with Ketones

Ketones are an important class of compounds that are either directly emitted by industrial/commercial applications or can be formed in the atmosphere by oxidation and photochemical reactions.

Acetone

The reaction of OH with acetone was investigated at 298 K in aqueous solution using the two experimental techniques.

$$OH + CH_3COCH_3 \rightarrow H_2O + CH_3COCH_2$$
 (R-1)

The measured data are compiled in Table I in comparison with preexisting data. First of all, it can be seen that the data obtained within this study do agree quite remarkably validating the experimental approach.

The measured rate coefficients do also compare reasonably with most of the previous measurements. The very good agreement between the rate constants from this study with the one from Ervens et al. [5] represents an additional validation for the two complementary experimental systems applied in this study.

As can be seen from Table I, the reaction of OH with acetone was studied over a wide range of experimental methods since this compound is one of the most abundant carbonyls in the atmosphere. Following the rate constants for the reactions of OH with acetone as a function of temperature is out of scope since they were previously studied, and the corresponding activation parameters were reported [5]. Studies focusing on the gas-phase reactions suggested that (R-1) may proceed by two mechanisms, through an H-abstraction mechanism or by addition via intermediate H-bonded complexes [20-25]. The recent kinetic and product studies for the reactions of OH with acetone in the aqueous phase [18] identified reaction products that correspond (i) to the oxidation of the weakest C-H bond into a carbonyl function and (ii) to the oxidation of the weakest C-H bond into a hydroxyl group. Accordingly, the main reaction pathway is still C-H oxidation through an H-abstraction process (as depicted by (R-1)) and not addition on the carbonyl function.

Methyl Isobutyl Ketone

Methyl isobutyl ketone (MIBK) is widely used as a solvent, a denaturant, in dry cleaning operations and in the synthesis of methyl isobutyl carbinol [26]. On the other hand, MIBK could be an important atmospheric organic compound because of its ozone production potential [27]. As a consequence, the reaction of OH with MIBK was also investigated at the 298 K and the rate constant is presented in Table I and compared with the literature.

$$OH + (CH_3)_2 CHCH_2 COCH_3 \rightarrow$$
$$H_2O + (CH_3)_2 CHCHCOCH_3 \qquad (R-2)$$

The reaction between MIBK and OH may correspond to an H-abstraction either at the secondary carbon atom or at the tertiary carbon atom of the butyl group. To identify the weakest bond in an H-abstraction process, Benson's incremental method [28] was applied. The calculated bond dissociation energy (BDE)

| Compound | $k [\mathrm{L} \mathrm{mol}^{-1} \mathrm{s}^{-1}]$ | Experiment Type | Analytical Technique | Source of OH | Reference Compound | pН | Ref. |
|---------------------------------|--|--------------------|-------------------------|-----------------------------|--------------------------------------|-----|-----------|
| Acetone | 8.3×10^{7} | PR | UV–vis abs | $e_{30}^{-} + N_2O$ | Ι- | 7 | [12] |
| | 9.7×10^{7} | PR | UV-vis abs | $e_{aq}^{-} + N_2O$ | SCN ⁻ | 6–7 | [13] |
| | 1.4×10^8 | PR | UV-vis abs | $e_{aq}^{-} + N_2O$ | [Fe(CN) ₆] ⁴⁻ | | [14] |
| | 1.3×10^{8} | PR | UV-vis abs | $e_{aq}^{-} + N_2O$ | ABTS ²⁻ | 6 | [15] |
| | $(1.3 \pm 0.1) \times 10^8$ | LFP | UV-vis abs | $H_2O_2 + h\nu$ (248 nm) | Absorption/time profile at 244 nm | 6 | [16] |
| | $(1.7\pm0.5)\times10^8$ | СР | Chromatography | Photo–Fenton reaction | CH ₃ OH | 2 | [17] |
| | $(2.1\pm0.6)\times10^8$ | FP | UV–vis abs | $H_2O_2 + h\nu$ (248 nm) | SCN^{-} | 6 | [5] |
| | $(1.8\pm0.4)\times10^8$ | FP | UV–vis abs | $H_2O_2 + h\nu$ (248 nm) | SCN- | 6–7 | This work |
| Methyl isobutyl | $(2.1\pm0.5)\times10^9$ | СР | Chromatography | Photo–Fenton reaction | 2-Propanol | 2 | [18] |
| ketone | $(4.6 \pm 1.6) \times 10^9$ | FP | UV–vis abs | $H_2O_2 + h\nu$ (248 nm) | SCN ⁻ | 6–7 | This work |
| <i>N</i> -Methyl pyrrolidone | $(3.1 \pm 1.0) \times 10^9$ | СР | Chromatography | Photo–Fenton reaction | MIBK | 2 | [19] |
| pjilondone | $(4.9 \pm 2.3) \times 10^9$ | FP | UV–vis abs | $H_2O_2 + hv$ (248 nm) | SCN ⁻ | 6–7 | This work |

Table IThe Rate Constants for the Reactions of OH with Acetone, Methyl Isobutyl Ketone, and N-Methyl Pyrolidone,in Aqueous Solution, at 298 K

PR = pulse radiolysis; LFP = laser flash photolysis; FP = flash photolysis; CP = continuous photolysis.

of 376 kJ mol⁻¹indicates that the weakest bond corresponds to the tertiary carbon atom (for more details see section on OH correlations).

Reaction (R-2) was studied as a function of temperature over the range from 278 to 318 K. The corresponding Arrhenius equation is

$$k_{2} = (1.0 \pm 0.1) \times 10^{12} \\ \times \exp\left(\frac{-1572 \pm 583}{T}\right) M^{-1} s^{-1}$$
 (2)

The measured rate coefficients for R-2 are summarized in Table I.

N-Methyl Pyrrolidone

N-Methyl pyrrolidone (NMP) is suggested to be used as a solvent in a wide variety of commercial applications. It may be released to the troposphere as a fugitive emission during its production or in the effluent of industrial processes [29].

The reaction of OH with NMP has been investigated in the temperature range between 278 and 308 K.



The rate coefficients for this reaction are listed in Table I and are described by the following Arrhenius equation:

$$k_{3} = (1.8 \pm 0.2) \times 10^{11} \\ \times \exp\left(\frac{-1062 \pm 808}{T}\right) M^{-1} s^{-1} \qquad (3)$$

The Arrhenius plots for the reactions of OH with MIBK and NMP are shown in Fig. 1.

The oxidation of NMP initiated via H-abstraction by OH occurs preferentially at the α -carbon atom [30]. This pathway leads to succinimide through the formation of *N*-methyl succinimide and 2-pyrrolidone, respectively.

The kinetics and mechanisms of (R-3) in the aqueous phase were studied earlier by Monod and coauthors [19] suggesting three H-abstraction reactions, (i) at the methyl group; (ii) at the CH₂ group adjacent to the imine function, and (iii) at the other CH₂ groups of the ring. Pathway (iii), which is more speculative,



Figure 1 Arrhenius plot for the reaction of OH with MIBK (\bigcirc) and NMP (\blacktriangle).

suggests that this reaction proceeds via a ring opening mechanism, leading to the formation of *N*-methyl-4-aminobutanoic acid. The associated rate coefficients at 298 K are summarized in Table I and compared with the literature available data.

From the comparison it can be seen that both rate constants, obtained in this study and the one from Monod and coauthors [19] are in good agreement within the statistical error.

Reactions of OH with Dicarboxylic Acids

Experimental observations have shown that dicarboxylic acids are commonly found in snow, rain, cloud droplets, fog, and aerosols both in urban, rural, marine, remote, and polar areas [31]. Ervens et al. [32] in their cloud parcel model coupled to an aqueous chemistry model have shown that dicarboxylic acids $(\leq C6)$ can be efficiently produced by tropospheric multiphase oxidation. The formation and accumulation of dicarboxylic acids in aqueous solution is also observed in the aqueous phase model CAPRAM 3.0 recently developed by Herrmann et al. [3]. As dicarboxylic acids may affect the hygroscopic behavior of the aerosols [32,33], it is especially important to understand their condensed phase chemistry. Some observations have demonstrated that the presence of a double bond (mesoxalic acid) or a hydroxyl group (malic acid) in the C4 dicarboxylic acids could increase the water solubility, and thus enhance the decrease of surface tension in concentrated solutions in comparison to the C4- α , ω -dicarboxylic acid (e.g., succinic acid) [33].

The LP-LPA setup has been used to study the reactivity of OH with dicarboxylic acids such as malic and mesoxalic acids at different pH values and temperatures.

Malic Acid

Table II presents the resulting kinetic data for the reaction between OH and malic acid at 298 K, compared with available literature data.

At pH = 1, the reaction proceeds as follows:

In Table II, it can be seen that the measured rate constant is about two times lower compared with the previously reported data. The reason for this is unclear at present. The reaction of OH with the dianion form of malic acid was investigated at pH = 9:

OH +
$$^{-}$$
OOCCH(OH)CH₂COO $^{-} \rightarrow$
H₂O + $^{-}$ OOCC(OH)CH₂COOH $^{-}$ (R-5)

At this pH, there is a good agreement with the rate constant determined by Hesper [16], but still some discrepancy with the data obtained by Logan [35]. This

| Malic acid | pH | $k [L \text{mol}^{-1} \text{s}^{-1}]$ | Reference Compound | Experiment Type | Ref. |
|---------------|-----|--|--|--------------------|-----------|
| Undissociated | 2 | $6.4 	imes 10^8$ | OH + 5-MeU Absorption/time | γ-R | [34] |
| | 1.5 | $(7.1 \pm 1.3) \times 10^8$ | profile at 244 nm | LFP | [16] |
| | 1 | $(3.6 \pm 1.6) \times 10^8$ | $OH + SCN^{-}$ | LFP | This work |
| Dianion | 9 | $(8.4 \pm 1.0) \times 10^8$ | Absorption/time profile at 244 nm OH | LFP | [16] |
| | 9 | 2.3×10^{9} | Ferrocenylbutyrate ion | PR | [35] |
| | 9 | $(8.5 \pm 1.1) \times 10^8$ | $OH + SCN^{-}$ | LFP | This work |
| Monoanion | 4.3 | $(9.7\pm2.5)\times10^8$ | $OH + SCN^{-}$ | LFP | This work |

Table II The Rate Constants for the Reactions of OH with Malic Acid at Different pH, in Aqueous Solution, at 298 K

PR = pulse radiolysis; LFP = laser flash photolysis, γ -R = gamma radiolysis (p K_a = 3.44 and 5.11) [36].

difference can be partly explained by the use of different reference compounds. In the study of Logan [35] a reference reaction of OH + ferrocenylbutyrate ion with the rate constant of 1.6×10^{10} L mol⁻¹ s⁻¹ was used. The reaction between OH radical and the monoanion form of malic acid was investigated at pH 4.3:

$$OH + HOOCCH(OH)CH_2COO^- \rightarrow$$
$$H_2O + HOOCC(OH)CH_2COO^- (R-6)$$

However, under these conditions the different anionic forms of the acid may coexist. Therefore, determining the rate coefficient for the monoanion only requires some correction of the raw data. This can be achieved by considering the two dissociation constants for malic acid ($pK_a = 3.44$ and 5.11) [36], which allow the speciation of the various forms of the acids. In the region where the monoanion form of malic acid exists with a fraction of about 80%, the undissociated form and the dianion are present with 13% and 8%, respectively. Hence, the obtained rate constant of (8.9 ± 2.2) × 10⁸ L mol⁻¹ s⁻¹ was properly corrected correspondingly to the dissociation constants of malic acid ($pK_a = 3.44$ and 5.11) [36] and by help of the following equation:

$$k_{\rm obs} = 0.8 \ k({\rm HA}^-) + 0.13 \ k({\rm H}_2{\rm A}) + 0.08 \ k({\rm A}^{2-})$$
(4)

where k_{obs} is the measured rate constant for the reaction of OH with the monoanion form at pH = 4.3, $k(H_2A)$ is the rate constant observed for the reaction of OH with malic acid at pH = 1, $k(A^{2-})$ is the rate constant obtained for the reaction of OH with the dianion form of malic acid at pH = 9, and $k(HA^{-})$ is the rate

coefficient for the monoanion. All data are listed in Table II.

In addition, the temperature dependence was investigated from 288 to 328 K, at pH = 1, pH = 4.3, and pH = 9 (see Table III).

The rate constants for the reaction of OH with maleate (pH = 4.3) at different temperatures were again corrected according to the reported dissociation constants of malic acid $pK_a = 3.44$ and 5.11 [36], assuming that the pK_a values do not change in the temperature range studied here as *T*-dependences of the mentioned pK_a values were not available.

As stated in our previous study [5], the rate coefficients for the reactions of OH with undissociated acids are lower than those of their corresponding anions. This trend is also confirmed in the present study for (R-5) and (R-6). The possible explanation for such trends may arise from an electron transfer contribution to the observed rate constants for anions.

The measured Arrhenius equations for the reactions of OH with the undissociated malic acid, monoanion, and dianion are presented with Eqs. (5)-(7),

Table IIIThe Observed Rate Constants for theReactions of OH with Malic Acid at Different pH andTemperatures in Aqueous Solution

| Т | pH = l | pH = 4.3 | pH = 9 |
|---------------------------------|---|---|---|
| (К) | k [L mol ⁻¹ s ⁻¹] | k [L mol ⁻¹ s ⁻¹] | k [L mol ⁻¹ s ⁻¹] |
| 288 298 308 318 328 | $\begin{array}{c} (3.6\pm0.8)\times10^8\\ (3.6\pm1.6)\times10^8\\ (4.7\pm0.1)\times10^8\\ (5.6\pm1.2)\times10^8\\ (6.7\pm1.9)\times10^8\end{array}$ | $(8.3 \pm 3.6) \times 10^{8}$ $(9.7 \pm 2.5) \times 10^{8}$ $(1.0 \pm 0.2) \times 10^{9}$ $(1.6 \pm 0.5) \times 10^{9}$ $(1.6 \pm 0.4) \times 10^{9}$ | $\begin{array}{c} (8.3\pm1.1)\times10^8\\ (8.5\pm1.1)\times10^8\\ (9.9\pm2.8)\times10^8\\ (1.1\pm0.2)\times10^9\\ (1.6\pm0.4)\times10^9\end{array}$ |



Figure 2 Arrhenius plot for the reaction of OH with malic acid: undissociated (\bigcirc), monoanion (\blacksquare), and dianion (\triangle).

respectively.

$$k_4 = (7.9 \pm 0.8) \times 10^{10} \\ \times \exp\left(\frac{-1575 \pm 787}{T}\right) \mathrm{M}^{-1} \mathrm{s}^{-1}$$
(5)

$$k_5 = (2.9 \pm 0.4) \times 10^{11} \\ \times \exp\left(\frac{-1701 \pm 1204}{T}\right) \mathrm{M}^{-1} \mathrm{s}^{-1}$$
(6)

$$k_{6} = (1.2 \pm 0.2) \times 10^{11} \\ \times \exp\left(\frac{-1449 \pm 1193}{T}\right) \mathrm{M}^{-1} \mathrm{s}^{-1}$$
(7)

Figure 2 shows the corresponding plots for these Arrhenius equations.

Mesoxalic Acid

The reaction of OH radical with mesoxalic acid

$$OH + HOOC(CO)COOH \rightarrow products$$
 (R-7)

has been investigated in aqueous solution at pH = 1. The dissociation constants of mesoxalic acid are $pK_a = 1.6$ and 3.9 as reported by Schuchmann et al. [37]. At pH = 1, we measured a rate constant of $k_7 = (1.8 \pm 0.3) \times 10^8$ L mol⁻¹ s⁻¹.

The same reaction has been studied by pulse radiolysis by Schuchmann et al. [37] at pH=3 and the reported rate constant is $k_7 = 5.7 \times 10^7$ L mol⁻¹ s⁻¹. Obviously the rate constant from this study is somewhat different than the rate constant measured by Schuchmann et al., which arise due to the different pH values of the solution. The hydration constant of mesoxalic acid is reported in the literature [37] to be $K_{\text{Hydr}} = 10^2 =$ [hydrate form]/[carbonyl form] at 298 K and pH = 1.7, indicating that the hydrated form is predominant. However, for the dianion, the carbonyl form is as abundant as 10% at 293 K [37]. The obtained rate constant for the reaction of OH with the hydrated form of mesoxalic acid at pH = 9 (dianion)

$$OH + OOCC(OH)_2COO^- \rightarrow products (R-8)$$

is $k_8 = (2.2 \pm 0.6) \times 10^9$ L mol⁻¹ s⁻¹. A rate constant of $k_8 = 1.0 \times 10^8$ L mol⁻¹ s⁻¹ has been reported by Schuchmann et al. [37] measured by pulse radiolysis at pH = 9. Accordingly, there is a large discrepancy of about one order of magnitude between both studies that is still unclear to the authors.

The reactions of OH with mesoxalic acid were investigated in the temperature range between 288 and 328 K, only at pH = 1. The measured rate coefficients for the undissociated acid at different temperatures are summarized in Table IV. In this case the rate constants were not corrected since the pK_a value for this acid enables exclusive existence of its dianion form at pH = 9.

Table IVThe Observed Rate Constants for theReactions of OH with Mesoxalic Acid at DifferentTemperatures in Aqueous Solution at pH = 1

| T (K) | k (Mesoxalic Acid) [L mol ⁻¹ s ⁻¹] |
|-------|---|
| 288 | $(1.7 \pm 0.8) \times 10^8$ |
| 298 | $(1.8 \pm 0.3) \times 10^8$ |
| 308 | $(1.8 \pm 0.7) \times 10^8$ |
| 318 | $(3.0 \pm 0.9) \times 10^8$ |
| 328 | $(3.1 \pm 0.4) \times 10^8$ |
| | |



Figure 3 Arrhenius plot for the reaction of OH with mesoxalic acid, at pH = 1.

The Arrhenius plot corresponding to Eq. (8) is shown in Fig. 3.

$$k_7 = (3.8 \pm 0.8) \times 10^{10}$$

 $\times \exp\left(\frac{-1588 \pm 1524}{T}\right) \mathrm{M}^{-1} \mathrm{s}^{-1}$ (8)

In aqueous solutions, the mesoxalate dianion is in equilibrium with its hydrate [37]. The carbonyl form is present with 10% at 293 K and the ratio [hydrate form]/[carbonyl form] increases linearly with temperature. Therefore, the reaction of OH with mesoxalic acid dianion was not studied in an extended temperature range due to the lack of data for the *T*-dependence of K_{Hydr} for the mesoxalic acid dianion.

Reactions of OH with Unsaturated Compounds

Vinyl ethers are widely used as solvents in the industrial applications, as motor oil additives and for coatings (see e.g., website of BASF) [38]. Upon application they may partly be released into the atmosphere where they are available for atmospheric processing.

In this work, the reaction of OH with triethyleneglycol divinyl ether (DVE-3)

$$OH + H_2C = CH(OCH_2CH_2)_3OCH = CH_2 \rightarrow$$
products (R-9)

has been investigated in aqueous solution at 298 K using the LP-LPA setup. The obtained second-order rate constant for the reaction (R-9) is $k_9 = (1.6 \pm 0.2) \times 10^{10}$ L mol⁻¹ s⁻¹.

International Journal of Chemical Kinetics DOI 10.1002/kin

The reaction of OH with DVE-3 has been investigated in the temperature range between 288 and 328 K (Table V). The measured rate constants of this reaction are similar to the calculated diffusion rate constants for the corresponding temperature. In this case according to the kinetic theory [39] the investigated reactions are fully diffusion controlled reactions. Not surprisingly, the rate constant from this study is not significantly different compared with the one determined in the previous study by Moise et al., in 2005 [8], where a value of $k_9 = (4.8 \pm 2.4) \times 10^{10}$ L mol⁻¹ s⁻¹ was found.

From the temperature-dependent rate constants for this reaction, the following Arrhenius equation has been derived:

$$k_9 = (2.3 \pm 0.1) \times 10^{13} \\ \times \exp\left(\frac{-2179 \pm 346}{T}\right) \,\mathrm{M}^{-1} \,\mathrm{s}^{-1} \tag{9}$$

The corresponding Arrhenius plot is shown in Fig. 4.

Table VThe Observed Rate Constants for theReactions of OH with DVE-3 and Methacrolein atDifferent Temperatures in Aqueous Solution

| T (K) | k (DVE-3) [L mol ⁻¹ s ⁻¹] | k (Methacrolein) [L mol ⁻¹ s ⁻¹] |
|-------|---|--|
| 278 | _ | $(7.9 \pm 1.6) \times 10^9$ |
| 288 | $(1.2 \pm 0.2) \times 10^{10}$ | $(1.1 \pm 0.5) \times 10^{10}$ |
| 298 | $(1.6 \pm 0.2) \times 10^{10}$ | $(1.4 \pm 0.3) \times 10^{10}$ |
| 308 | $(2.1 \pm 0.2) \times 10^{10}$ | $(1.8 \pm 0.3) \times 10^{10}$ |
| 318 | $(2.4 \pm 0.7) \times 10^{10}$ | $(2.5 \pm 0.7) \times 10^{10}$ |
| 328 | $(3.1 \pm 1.8) \times 10^{10}$ | - |



Figure 4 Arrhenius plot for the reaction of OH with DVE-3 (○) and methacrolein (▲).

Methacrolein

Methacrolein is used in numerous pharmaceutical and agricultural applications. It is also produced in significant yields from the gas-phase reactions of isoprene [40] and directly emitted from vegetation [41]. Under atmospheric conditions, the major loss process for methacrolein in the gas phase is reaction with the OH radical [42]. In this work, the reactivity of OH with methacrolein, that is,

$$OH + H_2C = C(CH_3)CHO \rightarrow \text{products} (R-10)$$

has been investigated in aqueous solution at 298 K. This reaction proceeds by addition of the OH radical to the carbon atoms of the >C=C< double bond. The measured rate coefficient of $k_{10} = (1.4 \pm 0.3) \times 10^{10}$ L mol⁻¹ s⁻¹ is higher than the OH addition rate constant for the reaction of OH with acrolein of $k = 7.0 \times 10^9$ L mol⁻¹ s⁻¹ reported in the literature [43], which might be attributed to the enhancement of the reactivity of the >C=C< double bond due to the presence of a methyl group in methacrolein.

The kinetics of the reaction of OH with methacrolein has also been investigated as a function of temperature as summarized in Table V. Again, this reaction is shown to be fully diffusion controlled. The Arrhenius plot corresponding to Eq. (10) is shown in Fig. 4.

$$k_{10} = (3.0 \pm 0.1) \times 10^{13}$$

 $\times \exp\left(\frac{-2289 \pm 168}{T}\right) \mathrm{M}^{-1} \mathrm{s}^{-1}$ (10)

Mechanistic studies have shown that the gas-phase reactions of OH with methacrolein proceed via addition to the double bond (80% of the addition occurs at the carbon) and by H abstraction of the aldehyde group [44]. Since there are no available mechanistic data for (R-10) in the aqueous phase, it can be simply assumed that reaction of OH with methacrolein might proceed through the same mechanism as in the gas phase.

OH Reactivity Correlations

Evans–Polanyi Type Correlations: An Overview. The basic principle of the Evans and Polanyi [45] correlation relies on the relation between the activation energy (E_a) and the reaction enthalpy (ΔH_R^0) for a series of reactions:

$$E_a = E_0 + \alpha \,\Delta H_{\rm R}^0 \tag{11}$$

For reactions proceeding through the same mechanism (e.g., H-abstraction mechanism), the reaction enthalpy can be correlated to the BDE (C–H) of the weakest extractable bond:

$$\Delta H_{\rm R} \sim \rm BDE\,(\rm C-H) \tag{12}$$

Based on the Arrhenius equation, it emerges that BDE can also be correlated to the measured rate constants of the H-abstraction reactions:

$$\log k = \log A - \frac{E_a}{RT}$$
$$= \log A - \frac{E_0}{RT} - \frac{\alpha \text{BDE(C-H)}}{RT} \quad (13)$$

International Journal of Chemical Kinetics DOI 10.1002/kin

If " $n_{\rm H}$ " equivalent H atoms in the reactive molecule exist, all of them contribute to the same extent ($k_{\rm H}$) to the observed rate constant $k_{\rm obs}$:

$$k_{\rm obs} = n_{\rm H} \cdot k_{\rm H} \tag{14}$$

The combination of Eqs. (13) and (14) leads to a correlation between the logarithm of the rate constant per abstractable H atom (log $k_{\rm H}$ (M⁻¹ s⁻¹)) and BDE (C–H):

$$\log\left(\frac{k_{\rm obs}}{n_{\rm H}}\right) = \log k_{H}$$
$$= \log A - \frac{E_0}{RT} - \frac{\alpha \times \text{BDE}(\text{C-H})}{RT}$$
(15)

The rate constant per abstractable hydrogen atom is the ratio of the observed second-order rate constant and number of the identical most easily abstractable hydrogen atoms in the given molecule. Following this treatment it has to be assumed that the OH radical is predominantly reacting with the weakest abstractable H atom.

Comparison of Evans–Polanyi Correlations in the Form of log $k_{\rm H} = f(BDE)$ *Between the Aqueous Phase and Gas Phase.* Several studies suggest that the prevailing reaction mechanism between OH radical and saturated organic aliphatic compounds in the gas phase and in aqueous solution is the abstraction of the most loosely bonded hydrogen atom (e.g., see the reviews by Mellouki and coauthors [20], Herrmann [1], and references therein). In previous kinetic studies of OH radical reactions in aqueous solutions performed by Ervens et al. [5], Gligorovski and Herrmann [4], and Morozov et al. [46], the correlations between the BDE of the weakest C—H bond, activation parameters, and kinetic data have been established using the Evans–Polanyi equation.

Such correlations could further be strengthened by including the kinetic information from this study (Fig. 5).

Hence, the measured rate coefficients for the reactions of OH with acetone, MIBK, malic acid (pH = 1), maleate (monoanion, pH = 4.3), and maleate (dianion, pH = 9) were added to the Evans–Polanyi correlation previously developed by Gligorovski and Herrmann [4]. The measured value of the rate coefficient for the reactions of OH with NMP was excluded from these correlations due to the missing value of the BDE. The rate coefficients per abstractable hydrogen atoms ($k_{\rm H}$) and BDEs are summarized in Table VI.

The BDEs for the malic acid and MIBK were estimated by Benson's method [28].

For the regression line through the aqueous-phase data points in Fig. 5 for the region $380 \le BDE \le 412$ kJ mol⁻¹ the following equation holds:



Figure 5 Comparison of the Evans–Polanyi plots in the form of log ($k_{\rm H}$) versus BDE between aqueous phase (O), this work, (\bullet), and gas phase (Δ). Numbering refers to the numbers in Table VI.

| Aqueous Phase | | | | Gas Phase | | | | |
|---------------|---------------------|--|---|-----------|---|---|------|---------------------------------|
| No. | Reactant | $ \frac{\circ k_H}{(298 \text{ K})} $ (L mol ⁻¹ s ⁻¹) | $ log k_H (298 K) (L mol-1 s-1) $ | Ref. | $\frac{\Delta k_H}{(298 \text{ K})}$ (L mol ⁻¹ s ⁻¹) | $ \begin{array}{c} \text{Log } k_{\text{H}} \\ \text{(298 K)} \\ \text{(L mol^{-1} s^{-1})} \end{array} $ | Ref. | BDE^a (kJ mol ⁻¹) |
| 1 | Acetone | 3.0×10^{7} | 7.48 | This work | 8.9×10^{7} | 7.95 | [48] | 411 |
| 2 | tert-Butanol | 5.3×10^{7} | 7.73 | [5] | 5.4×10^{7} | 7.73 | [49] | 410 |
| 3 | Acetonylacetone | 1.9×10^{8} | 8.28 | [4] | 2.2×10^8 | 8.35 | [50] | 401 |
| 4 | Ethyl formate | 3.3×10^{8} | 8.52 | [4] | 5.2×10^{8} | 8.72 | [50] | 396 |
| 5 | Ethanol | 1.0×10^{9} | 9.02 | [5] | 1.1×10^{9} | 9.06 | [51] | 389 |
| 6 | MEK | 7.5×10^{8} | 8.88 | [4] | 1.0×10^{9} | 9.00 | [52] | 386 |
| 7 | Malic acid | 3.6×10^{8} | 8.56 | This work | _ | _ | _ | 386 |
| 8 | Maleate (monoanion) | 9.7×10^{8} | 8.99 | This work | _ | _ | _ | 386 |
| 9 | Maleate (dianion) | 8.5×10^{8} | 8.93 | This work | _ | _ | _ | 386 |
| 10 | 1-Propanol | 1.6×10^{9} | 9.20 | [16] | 1.7×10^{9} | 9.23 | [53] | 385 |
| 11 | 1-Butanol | 2.1×10^{9} | 9.32 | [16] | 4.7×10^{9} | 9.67 | [53] | 385 |
| 12 | 2-Propanol | 2.1×10^{9} | 9.32 | [16] | 3.3×10^{9} | 9.52 | [51] | 381 |
| 13 | 2-Butanol | 3.5×10^{9} | 9.55 | [16] | 4.9×10^{9} | 9.69 | [54] | 381 |
| 14 | MIBK | 2.3×10^{9} | 9.36 | This work | 4.2×10^{9} | 9.63 | [42] | 376 |
| 15 | Acetaldehyde | 2.4×10^9 | 9.38 | [47] | $1.0 	imes 10^{10}$ | 10.00 | [55] | 374 ^a |
| 16 | Valeraldehyde | 3.9×10^{9} | 9.59 | [18] | $1.6 	imes 10^{10}$ | 10.20 | [56] | 372 |
| 17 | Propionaldehyde | 2.8×10^9 | 9.45 | [16] | $1.2 	imes 10^{10}$ | 10.07 | [42] | 366 |
| 18 | Butyraldehyde | 3.9×10^9 | 9.59 | [16] | $1.4 	imes 10^{10}$ | 10.16 | [56] | 361 |
| 19 | Isobutyraldehyde | 2.9×10^9 | 9.46 | [4] | $1.1 	imes 10^{10}$ | 10.02 | [57] | 358 |

Table VI Rate Constants Per Most Easily Abstractable Hydrogen Atom (k_H) in the Aqueous Phase and in the Gas Phase

^aRefs. [58] and [59].

$$\log (k_{\rm H} ({\rm M}^{-1} {\rm s}^{-1})) = (30 \pm 4) -(0.06 \pm 0.01) \times \text{BDE} (\rm kJ \, mol^{-1})$$
(16)

with n = 14 and r = 0.95.

The attack of OH radical on dicarboxylic acids is directed primarily to the C–H bonds at different positions. The corresponding mono and dianions are reacting faster, which probably comes from the difference in the inductive effect of –COOH and –COO[–] groups and the electrophilic nature of the OH radical.

Although electron transfer may contribute to the observed rate constant of OH-oxidation of anions such as maleate (monoanion) and maleate (dianion), H-abstraction seems to be the dominating reaction pathway also for these species.

In case of aldehydes, as discussed in the previous study [4], the number of most easily abstractable equivalent H atoms is n = 1 in both forms, the aldehyde and in its corresponding diol form. Therefore, the rate constant per abstractable H atom ($k_{\rm H}$) is equal to the observed rate constant in both cases. The rate constants for the reaction of OH with the equilibrium mixtures of aldehydes and their hydrates are considered for the correlation shown in Fig. 5.

On the other hand, the BDEs applied in the present correlation are those for the unhydrated aldehydes.

In this plateau (Fig. 5) formed by the aldehydes, we added the rate constants values for the reactions of OH with MIBK from this study and valeraldehyde from the literature [18]. In the BDE range from 358 to 376 kJ mol⁻¹, the rate constant corresponds to $\bar{k}_{\rm H} = 3.0 \times 10^9 \,\mathrm{L \, mol^{-1} \, s^{-1}}$. The formation of the plateau by aldehydes in both phases indicates that the reaction mechanism for these compounds toward OH radical is not a H-abstraction but probably addition to the >C=O double bond or formation of the hydrogenbonded complexes followed by H-abstraction [20]. However, the existence of hydrogen-bonded complexes is less probable in the aqueous phase, since all the compounds are already bonded to water molecules in the first solvation shell (see next section). To the best of the authors knowledge the existence of such a plateau remains unclear.

This regression line found here may be used to estimate rate constants at 298 K for H-abstraction reactions of the OH radical in aqueous solution when measured kinetic data are not available.

The same series of reactions in the gas phase were plotted and compared with the corresponding one in the aqueous phase in Fig. 5. Identical plateau formed by the group of aldehydes and MIBK is observed for the gas-phase data as well. In the BDE range between 358

| No. | Reactant | A [L mol ^{-1} s ^{-1}] | $E_{\rm a}[{\rm kJ}~{\rm mol}^{-1}]$ | Ref. |
|-----|----------------------------------|--|--------------------------------------|-----------|
| 1 | Acetone | $(3.4 \pm 0.4) \times 10^{11}$ | (18 ± 11) | [4] |
| 2 | Acetone | $(8.4 \pm 0.4) \times 10^{10}$ | (16 ± 3) | [16] |
| 3 | Acetone | $(2.1 \pm 0.3) \times 10^{11}$ | (17 ± 8) | [60] |
| 4 | Acetone | $(6.6 \pm 0.2) \times 10^{10}$ | (16 ± 3) | [17] |
| 5 | Acetone | _ | (12 ± 4) | [18] |
| 6 | tert-Butanol | $(3.3 \pm 0.1) \times 10^{10}$ | (10 ± 3) | [5] |
| 7 | Acetonylacetone | $(1.1 \pm 0.1) \times 10^{11}$ | (12 ± 5) | [4] |
| 8 | Ethyl formate | $(1.8 \pm 0.1) \times 10^{10}$ | (10 ± 4) | [4] |
| 9 | Ethanol | $(1.0 \pm 0.1) \times 10^{11}$ | (10 ± 5) | [5] |
| 10 | Ethanol | _ | (7 ± 1) | [18] |
| 11 | MEK | $(5.1 \pm 0.6) \times 10^{11}$ | (15 ± 8) | [4] |
| 12 | MEK | $(6.6 \pm 4.9) \times 10^9$ | (4 ± 0.3) | [60] |
| 13 | MEK | _ | (13 ± 3) | [18] |
| 14 | 1-Propanol | $(5.6 \pm 0.6) \times 10^{10}$ | (8 ± 6) | [5] |
| 15 | 1-Propanol | _ | (7 ± 2) | [18] |
| 16 | 1-Butanol | $(1.0 \pm 0.1) \times 10^{11}$ | (8 ± 1) | [16] |
| 17 | 2-Propanol | $(6.1 \pm 0.3) \times 10^{10}$ | (8 ± 2) | [16] |
| 18 | 2-Butanol | $(7.4 \pm 0.3) \times 10^{10}$ | (8 ± 3) | [16] |
| 19 | Propionaldehyde | $(2.6 \pm 0.1) \times 10^{11}$ | (11 ± 3) | [16] |
| 20 | Butyraldehyde | $(8.1 \pm 0.3) \times 10^{10}$ | (8 ± 3) | [16] |
| 21 | Isobutyraldehyde | $(3.0 \pm 0.1) \times 10^{10}$ | (6 ± 3) | [4] |
| 22 | MIBK | $(1.0 \pm 0.1) \times 10^{12}$ | (13 ± 5) | This work |
| 23 | MIBK | 1.3×10^{11} | 10 | [18] |
| 24 | Malic acid $(pH = l)$ | $(7.9 \pm 0.8) \times 10^{10}$ | (13 ± 7) | This work |
| 25 | Maleate monoanion ($pH = 4.3$) | $(2.9 \pm 0.4) \times 10^{11}$ | (14 ± 10) | This work |
| 26 | Maleate dianion $(pH = 9)$ | $(1.2 \pm 0.2) \times 10^{11}$ | (12 ± 10) | This work |

and 374 kJ mol⁻¹ the rate constant for the gas-phase reactions with aldehydes and MIBK is best represented by $\bar{k}_{\rm H} = 1.2 \times 10^{10}$ L mol⁻¹ s⁻¹. The correlation found in the gas phase is much alike to the one in the aqueous phase for the BDE between 380 and 412 (kJ mol⁻¹) and corresponds to the following equation:

$$\log (k_{\rm H} ({\rm M}^{-1} {\rm s}^{-1})) = (32 \pm 4)$$
$$- (0.06 \pm 0.01) \times {\rm BDE}$$
(17)

with n = 10; r = 0.98

Evans–Polanyi Correlation in the Form of $E_a = f(BDE)$: Comparison Between the Aqueous Phase and Gas Phase. This form of Evans–Polanyi plot has also been previously developed by Ervens et al. [5] and further confirmed by Gligorovski and Herrmann [4] in 2004 for the H-abstraction reactions of OH with saturated organic compounds. The aforementioned correlation was expanded with the E_a values from this study. Using the available E_a data set for the OH reactions in the gas phase a comparative analysis is undertaken.

In Tables VII and VIII E_a for the reactions of OH with different organic compounds are listed for the aqueous phase and gas phase, respectively.

The regression line for the aqueous phase represented in Fig. 6 corresponds to

$$E_{a} (kJ mol^{-1}) = -(42 \pm 31) + (0.14 \pm 0.08) \times BDE (kJ mol^{-1})$$
(18)

with n = 26 and r = 0.58

The correlation found here might be used to estimate activation energies for H-abstraction reactions of OH radical reactions in aqueous solution. The potential user of the correlation Eq. (18) has to be aware of the uncertainties of the derived activation energies.

The equation derived from the regression line for the reactions of OH in the gas phase corresponds to

$$E_{a} (kJ mol^{-1}) = -(58 \pm 18) + (0.15 \pm 0.05) \times BDE (kJ mol^{-1})$$
(19)

with n = 25 and r = 0.79

The very similar slopes in both plots presented in Fig. 6 indicate that the same reaction mechanism

| No. | Reactant | A [L mol ^{-1} s ^{-1}] | $E_{\rm a}$ [kJ mol ⁻¹] | Ref. |
|-----|------------------|--|-------------------------------------|------|
| 1 | Acetone | 1.7×10^{9} | (6.3 ± 1.6) | [61] |
| 2 | Acetone | $(7.5 \pm 1.4) \times 10^8$ | (4.6 ± 0.5) | [62] |
| 3 | Acetone | 1.3×10^{9} | (5.7 ± 0.8) | [63] |
| 4 | Acetone | $(1.0 \pm 0.3) \times 10^9$ | (5.0 ± 0.6) | [64] |
| 5 | tert-Butanol | $(2.0 \pm 1.0) \times 10^9$ | (2.6 ± 1.3) | [65] |
| 6 | tert-Butanol | $(1.6 \pm 0.3) \times 10^9$ | (2.2 ± 1.1) | [66] |
| 7 | Acetonylacetone | $(9.0 \pm 2.6) \times 10^8$ | $-(3.7 \pm 0.7)$ | [50] |
| 8 | Ethyl formate | $(3.4 \pm 0.7) \times 10^8$ | $-(1.1\pm0.5)$ | [67] |
| 9 | Ethanol | 2.5×10^{9} | (0.6 ± 1.7) | [61] |
| 10 | Ethanol | $(4.5 \pm 1.9) \times 10^9$ | (2.0 ± 0.9) | [68] |
| 11 | Ethanol | 4.2×10^{9} | (2.0 ± 0.8) | [63] |
| 12 | MEK | $(9.1 \pm 1.7) \times 10^8$ | (0.5 ± 0.5) | [62] |
| 13 | MEK | 7.8×10^{8} | (0.2 ± 1.7) | [61] |
| 14 | MEK | $(1.4 \pm 0.7) \times 10^9$ | (1.4 ± 1.0) | [64] |
| 15 | 1-Propanol | 2.8×10^{9} | $-(0.6 \pm 0.8)$ | [61] |
| 16 | 1-Butanol | 3.2×10^{9} | $-(1.2 \pm 1.7)$ | [61] |
| 17 | 2-Propanol | 1.6×10^{9} | $-(1.6 \pm 1.7)$ | [61] |
| 18 | Propionaldehyde | 3.1×10^{9} | $-(3.4 \pm 1.7)$ | [61] |
| 19 | Butyraldehyde | $(3.6 \pm 1.5) \times 10^9$ | $-(3.4 \pm 2.1)$ | [61] |
| 20 | Isobutyraldehyde | $(4.4 \pm 1.1) \times 10^9$ | $-(3.2\pm0.6)$ | [69] |
| 21 | Isobutyraldehyde | $(4.1 \pm 0.2) \times 10^9$ | $-(3.3 \pm 1.0)$ | [70] |
| 22 | Isobutyraldehyde | 9.5×10^{9} | $-(2.6 \pm 1.2)$ | [71] |
| 23 | Valeraldehyde | $(6.0 \pm 1.1) \times 10^9$ | $-(2.5 \pm 0.5)$ | [69] |
| 24 | Valeraldehyde | $(3.8 \pm 0.1) \times 10^9$ | $-(3.8 \pm 0.9)$ | [70] |
| 25 | MIBK | $(4.6\pm0.8)\times10^8$ | $-(6.9 \pm 0.4)$ | [62] |

Table VIIIPreexponential Factors and Activation Energies for H-Abstraction Reactions of OH Radical in the GasPhase



Figure 6 Comparison of Evans–Polanyi plot in the form of E_a versus BDE: aqueous phase (\bullet), this work (\circ), and gas phase (\blacktriangle). Numbering refers to the numbers in Table VII for the aqueous-phase and Table VIII for the gas-phase data. For BDE see Table VI.

(hydrogen abstraction) occurs in the gas phase and in the aqueous phase. Yet one can notice the higher dispersion of the data in the aqueous phase in comparison with the gas phase. The latter probably comes from the limited temperature range in the aqueous phase $(3^{\circ}C-80^{\circ}C)$.

Moreover, one can notice the negative temperature dependence for the reaction of the OH radical with 1propanol, 1-butanol, 2-propanol, acetonylacetone, and ethyl formate and with the aldehydes performed in the gas phase. This observation suggests the possibility that those reactions and especially those of the aldehydes with OH in general do proceed through an addition-elimination mechanism [72], since many addition reactions of OH show overall negative temperature dependence. Atkinson [73] postulated that the reactions of OH with aldehydes proceed via overall Hatom abstraction, although the initial reaction possibly involves the OH radical addition to the >C=O function. However, it is not clear why a hydrogen abstraction reaction presents negative E_a and why the overall OH addition to the double bond does not occur. Singleton and Cvetanovic [74] propose a complex mechanism and explain the occurrence of these negative activation energies as being due to the reversible formation of a loosely bound prereactive complex that is formed without an E_a , followed by a second reaction, which is irreversible, and whose transition-state energy is lower than the energy of the separated reactants. In the recent review of Mellouki et al., [20], the reaction pathway of aldehydes toward OH in the gas phase is regarded unclear. The authors in this review consider all the possibilities: the reaction can proceed via H-atom abstraction, addition to the >C=O double bond or initial formation of a hydrogen-bonded complex followed by H-atom abstraction.

Smith and Ravishankara [23] concluded that the dynamics of the reactive encounters between OH and aldehydes is affected by the hydrogen bond that is formed between them and that this could be the reason for the negative temperature dependencies manifested in those reactions.

Aloisio and Francisco [21] performed ab initio calculations by run of the program GAUSSIAN 94 and have demonstrated the presence of hydrogen bond adducts formed in the reactions of OH with aldehydes in the gas phase. Furthermore, they are giving the complete picture of the structure and energetics of the complexes involving OH radical and the carbonylcontaining molecules.

Despite the aforementioned theoretical observations for the reactions of OH with carbonyl compounds in the gas phase, it is still not clear why the reaction of OH with acetone, for instance, which is known to have

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a non-Arrhenius behavior, does not show a negative temperature dependence for the overall reaction.

In the aqueous phase the formation of H-bonded complex can be hindered due to the already existing hydrogen bond between the water molecules and the organic compounds. The presence of hydrogen bonds between the water molecules and the organics may influence their reactivity [75]. For instance, the ab initio calculations performed by Vassilev et al. [76] have revealed that OH radical in the first solvation shell is characterized with three H-bonded water molecules leading to enlargement of its effective size [77].

It should be noted that the negative temperature dependencies for the above mentioned reactions have not been observed in the aqueous phase. The latter can be due to the limited range of temperature studied or different reaction pathways compared to the gas phase. Monod et al. [18] speculated that although the overall mechanism in both phases can be the abstraction of the hydrogen atom, different reactivity of the OH radical in both phases comes from the different intermediary steps.

Finally in a very recent paper by Monod and Doussin [77], a structure–activity relationship was developed for the estimation of OH rate constants in aqueous solution as an alternative approach to the Evans– Polanyi correlations presented in this study.

Atmospheric Implications

Oxidation processes of organic compounds both in the gas phase and in the aqueous phase lead to less volatile organics, for example, dicarboxylic acids. As shown in several studies dicarboxylic acid is ubiquitous in tropospheric particles [78–81]. The addition of their formation and decay mechanisms into models can help to clarify the composition of the organic matter in atmospheric particles. Such interpretations could be of particular interest because the composition of particles can have influence on their hygroscopic behavior, that is, the ability to act as cloud condensation nuclei [82–84]. Furthermore, the degradation processes might influence the acidity [82] and the radiative properties [85] of the atmospheric particles.

The rate constant data obtained in the present study contribute to a better definition of the tropospheric lifetimes of the studied ketones, dicarboxylic acids, and unsaturated compounds that react predominantly with the OH radical.

A remote scenario, which was chosen as a standard scenario in CAPRAM 3.0 [1], corresponds to OH concentration of 1.3×10^{-13} mol L⁻¹ in the aqueous phase. By using this value, first-order loss processes

| Reactant | First-Order Loss Process in the Aqueous Phase (s^{-1}) | First Order Loss Process in the Gas Phase (s^{-1}) |
|------------------------------|--|--|
| Acetone | 2.3×10^{-5} | 3.2×10^{-5} [61] |
| <i>N</i> -Methyl pyrrolidone | $6.4 	imes 10^{-4}$ | |
| Methyl isobutyl ketone | $6.0 	imes 10^{-4}$ | 4.8×10^{-4} [61] |
| Methacrolein | 1.8×10^{-3} | 1.2×10^{-3} [86] |
| DVE-3 | 2.1×10^{-3} | |
| Malic acid | 4.7×10^{-5} | |
| Mesoxalic acid | 2.3×10^{-5} | |

Table IX The First-Order Loss Rates in $|s^{-1}|$ for OH Radical Reactions in the Aqueous Phase and in the Gas Phase

OH concentration in the aqueous phase (remote scenario) 1.3×10^{-13} M [3].

OH concentration in the gas phase (standard scenario) 6.0×10^{-14} M [27].

of the organics under study toward OH reaction were calculated.

Concerning a typical gas phase OH concentration of 1×10^6 molecule cm⁻³ it is possible to roughly estimate the impact of OH radical on the reactant's budget (Table IX). In Table IX the first-order loss processes for the reactions of OH with the organics under study in the aqueous phase and in the gas phase are compared. Note that although the gas-phase kinetic data set is larger than the aqueous phase, the rate constants for the reactions of OH with NMP, MIBK, DVE-3, and malic acid gas-phase data are not available. Hence, the comparison was not possible in these cases.

In Table IX it can be seen that the first-order loss processes are of comparable magnitude in both phases at 298 K, which comes from the respective rate constants discussed in the previous sections of this article.

CAPRAM 3.0 [1], the latest development of CAPRAM series includes a description of the chemistry of oxygenated organic compounds that are used as solvents and fuel additives such as NMP, MIBK, and DVE-3. It has been shown that these compounds or their respective oxidation products might play a role in the tropospheric aqueous phase in a close interaction with their respective gas-phase chemistry.

CONCLUSION

Rate constants for the reactions of OH with ketones, dicarboxylic acids, and unsaturated compounds in aqueous solution have been determined.

The obtained rate constants and the activation parameters were used to improve the already established Evans–Polanyi correlations in the form of log $(k_{\rm H}) = f({\rm BDE}), E_{\rm a} = f({\rm BDE})$. Correlations Eqs. (16) and (18) were provided for the prediction of second-order rate constants and activation energies for the reaction of OH with organic compounds reacting by H-abstraction mechanism. The correlations presented in this study cover a lack in the literature and they are in good agreement with previous studies [4,5].

For ketones and dicarboxylic acids considered in this study it was possible to describe the observed rate constants in view of a H-abstraction mechanism acting during the oxidation process.

On the other hand, the reactions of OH with methacrolein and DVE-3 are proceeding by addition–elimination mechanism, which is clearly diffusion controlled.

To cover a wider range of situations encountered in the atmosphere, further experimental and modeling investigations are needed to understand the overall aqueous-phase chemistry.

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