

# Kinetics of Aqueous Phase Reactions Relevant for Atmospheric Chemistry

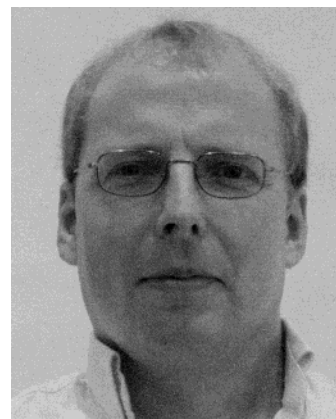
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## 1. Introduction

The present review intends to critically assess recent developments in atmospheric aqueous phase chemistry with special emphasis on radical kinetics, which is regarded as a long-term issue in atmospheric research. The present paper should be regarded as a follow-up of the reviews by Zellner and Herrmann<sup>1</sup> and the assessment of Huie<sup>2</sup> of the same year. Hence, the present paper intends to cover the period of 1996 to the time of writing, i.e., early 2003. Since 1996, some focused overviews have been published such as assessments in the I&S volume of IGAC for both aerosol and cloud chemistry.<sup>3</sup> The freely available online NIST Standard Reference Database 40<sup>4</sup> is a very useful tool because it contains kinetic data for thousands of radical reactions from studies prior to 1996. Solution phase photochemical studies are of interest for both tropospheric chemistry and more technical applications such as water treatment. Here,

the photochemistry of the nitrate anion has been reviewed by Bolton and co-workers.<sup>5</sup> A more detailed understanding of the processes governing the so-called effective quantum yields in aqueous solution for processes of interest of atmospheric chemistry together with an adequate data collection is highly desirable and is subject to another review.<sup>6</sup> Hence, photochemical processes will not be treated explicitly in the present overview.

It could be speculated that solution phase reactions might, to a certain extent, occur in nonaqueous media, such as within particles consisting of organic liquids. However, apart from such an idea almost no process data or systematic studies exist at this time and hence the present overview is also restricted to aqueous phase reactions.

The matrix for atmospheric reactions in liquids is subject to huge variations with regard to its key properties, an overview of which is given in Table 1 for tropospheric systems.

In the tropospheric system, solution reactions might occur in the droplets of fog, clouds, and rain at low ionic strengths. For aerosols, the temperature range is the same, but ionic strength is drastically

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**Table 1. Size, Liquid Water Content (LWC), pH, and Ionic Strength of Atmospheric Water-Containing Particles**

particle or drop	radius $r/\mu\text{m}$	LWC $\text{cm}^3 \text{m}^{-3}$	pH	ionic strength $I/\text{mol L}^{-1}$	remarks and refs
rain	150–1500	0.1–1	4–5	$(0.67\text{--}3.81) \times 10^{-5}{}^a$	$r$ , LWC, and $I$ after Seinfeld and Pandis [7]
remote cloud	~1–25	0.05–3	4–6	$(0.75\text{--}7.5) \times 10^{-4}$	LWC after Seinfeld [8] $r$ and LWC after Seinfeld and Pandis [7] pH and $I$ after Collett and Herckes [9]
remote cloud	3.5 – > 16.5 <sup>b</sup>	< 0.6 <sup>b</sup>	3.5–6 <sup>b</sup>	$(0.001\text{--}1.7) \times 10^{-1}{}^{b,c}$	Bower et al. [10]
continental cloud	1–15 <sup>d</sup>	0.2–0.35 <sup>d</sup>	3.9–4.6 <sup>d</sup>	$5 \times 10^{-4}{}^{d,e}$	Wobrock et al. [11]
polluted cloud	~1–25	0.05–3	2–5	$(0.5\text{--}1.0) \times 10^{-2}$	$r$ and LWC after Seinfeld and Pandis [7] pH and $I$ after Collett and Herckes [9]
polluted fog	~1–20	0.02–0.5	3–7	$(0.07\text{--}4) \times 10^{-2}$	$r$ and LWC after Seinfeld and Pandis [7] pH and $I$ after Collett and Herckes [9]
marine aerosol	0.005–5	$(0.01\text{--}1) \times 10^{-3}{}^f$	1–9	6.1 <sup>g</sup>	radius after Kim et al. [12] ionic strength after Sander and Crutzen [13] pH after Keene et al. [14] LWC after von Glasow and Sander [15]
marine aerosol	0.07–1.38 <sup>h</sup>	$9.46 \times 10^{-6}{}^{f,h,i}$	–0.2 <sup>h</sup>	$j$	Li et al. [16]
haze	~0.1–0.5	$10^{-5}\text{--}10^{-4}{}^f$	1–8 (1.5–2.5) <sup>k,l</sup>	$\approx 1$ <sup>g</sup>	Seinfeld [8]
urban aerosol	$\leq 10$ <sup>m</sup>	$(2.5\text{--}4) \times 10^{-5}{}^{f,m,n}$	3.4–3.7 <sup>m,o</sup>	8.0–18.6 <sup>g,m,o</sup>	Stelson and Seinfeld [17]
urban aerosol	0.07–1.38 <sup>h</sup>	$7.6 \times 10^{-7}{}^{f,h,i}$	–1.2 <sup>h</sup>	$j$	Li et al. [16]

<sup>a</sup> Ionic strength in rain droplets in remote areas of the world,  $6.7 \times 10^{-6} \text{ mol L}^{-1}$  at Poker Flat, Alaska, and  $3.8 \times 10^{-5}$  at Amsterdam Island, Indian Ocean. <sup>b</sup> Parameters for the given case study, measurement on the island of Tenerife in June–July 1997. <sup>c</sup> Ionic strength calculated for the cloud event which took place between the seventh and eighth of July, 23.00–08.00, polluted case. <sup>d</sup> Clouds strongly influenced by industries and other human activities, parameters for the given case study in 1990 at Kleiner Feldberg, Germany. <sup>e</sup> Calculated ionic strength, considering the median concentration of different components measured in cloudwater during the experiment. <sup>f</sup> The liquid water content (LWC) values for aerosol particulate matter depend on relative humidity. <sup>g</sup> The ionic strength is dependent upon the relative humidity. <sup>h</sup> Parameters for the given case study, measurements in southern California, 1994. <sup>i</sup> Calculated from given pH and  $\text{H}^+$  concentration. <sup>j</sup> The ionic strength is not specified. <sup>k</sup> In regions of high sulfate content, the haze pH can be even lower than one. <sup>l</sup> In parentheses, the pH value for haze in Tel Aviv, Israel, for particles in the size range 0.4–0.9  $\mu\text{m}$ , Ganor et al.<sup>18</sup> <sup>m</sup> Parameters for this given case study, measurements in the Los Angeles area in 1973. <sup>n</sup> LWC when  $x_{\text{Pb}} = 0$ ,  $x_{\text{Ca}} = 0$ ,  $x_{\text{Na}} = 0$ ,  $x_{\text{K}} = 0$ , and  $x_{\text{Mg}} = 0$  in mol/1000 g of  $\text{H}_2\text{O}$  and the sum of electrolyte concentration is between 15 and 25  $\mu\text{g m}^{-3}$ . <sup>o</sup> pH and Ionic strength when  $x_{\text{Pb}} = 0$ ,  $x_{\text{Ca}} = 0$ ,  $x_{\text{Na}} = 0$ ,  $x_{\text{K}} = 0$ , and  $x_{\text{Mg}} = 0$  in mol/1000 g of  $\text{H}_2\text{O}$ .

increased. With regard to ionic strengths accessible in ground-based measurements, a very wide range is covered as can be seen from the data of Table 1. Whereas chemical conversion in the droplets of haze, clouds, and rain might be treated as chemical reactions in dilute electrolytes, this is no longer true for aerosol particles where very high ionic strengths can be reached. It is a standing demand that aqueous phase kinetic laboratory studies for the application in atmospheric chemistry offer practical solutions to treat kinetics at elevated ionic strengths. A specific approach for the treatment of ionic strength effects in reactions of neutral species with ions is suggested in section 3.7 of this contribution.

In the free troposphere, because of the decrease of the water vapor mixing ratio, the aerosol water content is thought to further decrease, possibly leading to even higher ionic strength as encountered in boundary layer particles. This trend continues into the upper troposphere. Higher clouds are mixed phase clouds and hence contain ice, the interfacial layers of which under certain conditions should be regarded as quasi-liquid.<sup>19</sup> Hence, potentially, reactions at the interface of ice particles in higher tropospheric clouds might occur, which possibly could be treated in terms of solution chemistry. Finally, in the stratosphere, solution or liquid phase chemistry refers to reactions in the quasi-liquid layers of solid

particles but to bulk chemistry in liquid particles as well. As a consequence, aqueous phase kinetic studies of relevance for atmospheric chemistry should not be restricted to room temperature measurements but should cover a wider range of temperature as it is encountered in the troposphere and ranges from significantly supercooled aqueous cloud droplets to temperatures around room temperature.

Within the above matrices, a wide variety of reactions may take place contributing to the conversions of atmospheric constituents. Aqueous atmospheric particles may take up soluble gases as well as intermediates from the surrounding gas phase or dissolve material from particles directly. Aqueous phase reactions have the potential to convert these substances to stable products, which, in the tropospheric case, could be easily identified when the aqueous particles are removed from the atmosphere. A classical example of this is the oxidation of sulfur (IV) in the atmosphere. Furthermore, aqueous reaction may lead to the production of less-soluble products that could be released back to the gas phase and hence change gas-phase composition and oxidation potential. The most prominent example for this is halogen activation from aqueous particles and, near ground, possibly, other aqueous surfaces. Aqueous phase reactions in the atmosphere also contribute to the conversion of organic compounds. Generally,

water solubility should increase during the gas-phase oxidation of a given VOC and at a certain stage removal to aqueous particles might become more feasible than further gas-phase oxidation steps. For such oxidation processes, the need for multiphase VOC degradation schemes arises, including proper description of phase transfer and particle phase conversion, where aqueous phase processes constitute at least an important subset. The aqueous phase part of a given scheme may then be able to describe and explain the formation of products, the formation of which in a pure gas-phase reaction scheme would not be effective. However, in current multiphase mechanisms, the treatment of organic compounds is still very restricted as further discussed in section 4. Hence, the present review is trying to assess available kinetic information of interest for the further development of atmospheric organic multiphase chemistry.

The overview to be given is arranged as follows. First, some recent new experimental approaches are summarized. A short treatment of recent information on complex reactions is followed by reviews on reactions of the most important radical oxidants, i.e., OH, NO<sub>3</sub>, the chlorine-containing radicals (Cl/Cl<sub>2</sub><sup>-</sup>), SO<sub>x</sub><sup>-</sup> (*x* = 3, 4, 5), radical interconversions and a treatment of ionic strength effects in aqueous solution. This is followed by some remarks on the current status of atmospheric multiphase models and a summary and outlook. For the reported errors stated in this review, the reader is referred to the original literature. As far as data originating from our own laboratory, statistical errors are given for a confidence interval of 0.95.

## 2. Recent Experimental Developments

### 2.1. Surface and Bulk Radical Reactions

Just recently the idea has been put forward that reactions at the water–air interface of deliquescent particles and cloud droplets might proceed with elevated reaction rates due to local enrichment of certain reactive species, such as chloride anions at the interface.<sup>20</sup> This enrichment has been observed as a result of high level *ab initio* calculations that have been performed for the case of sea salt aerosol with ionic strengths of about 6 mol L<sup>-1</sup>, cp. ref 21 and references therein. Even more recently, however, such enrichment processes have been investigated by Jungwirth and Tobias,<sup>22</sup> who found that especially chloride does not seem to be enriched whereas Br<sup>-</sup> and I<sup>-</sup> seem to be enriched at the interface.

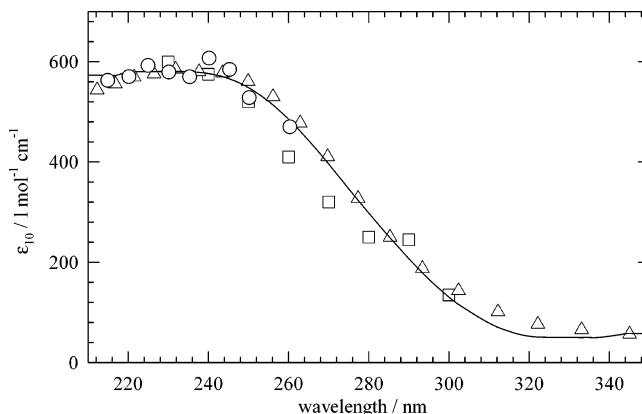
A promising approach to study both bulk as well as interfacial reaction has been put forward by the group of George.<sup>23</sup> Briefly, a droplet of a diameter of some millimeters sitting on a platform can be irradiated by an excimer laser to produce radicals that are monitored by time-resolved UV/VIS spectroscopy through the droplet. Additionally, and this represents the main new feature of the experiment, the droplet is irradiated by a UV/VIS broadband light source such as a xenon lamp and the light diffusely reflected by the droplet is collected and fed to a monochromator/photomultiplier combination. The first studies of

the dichloride radical anion (Cl<sub>2</sub><sup>-</sup>) reaction with ethanol as a test system indicate that the reaction at the surface appears to be nearly three times faster than the bulk reaction. Further studies are required to more exactly quantify up to which depth into the droplet the surface and the surface layer are actually probed by this technique developed.

The relative importance of surface processes is also dependent on the actual surface-to-volume ratio of a particle ensemble in a given air volume. However, potentially, when enhanced reaction rates at aqueous surfaces could be experimentally proven for more systems, not only chemical processes in the bulk of atmospheric particles but also interfacial processes may need to be considered, e.g., in spatially resolved particle chemistry models.

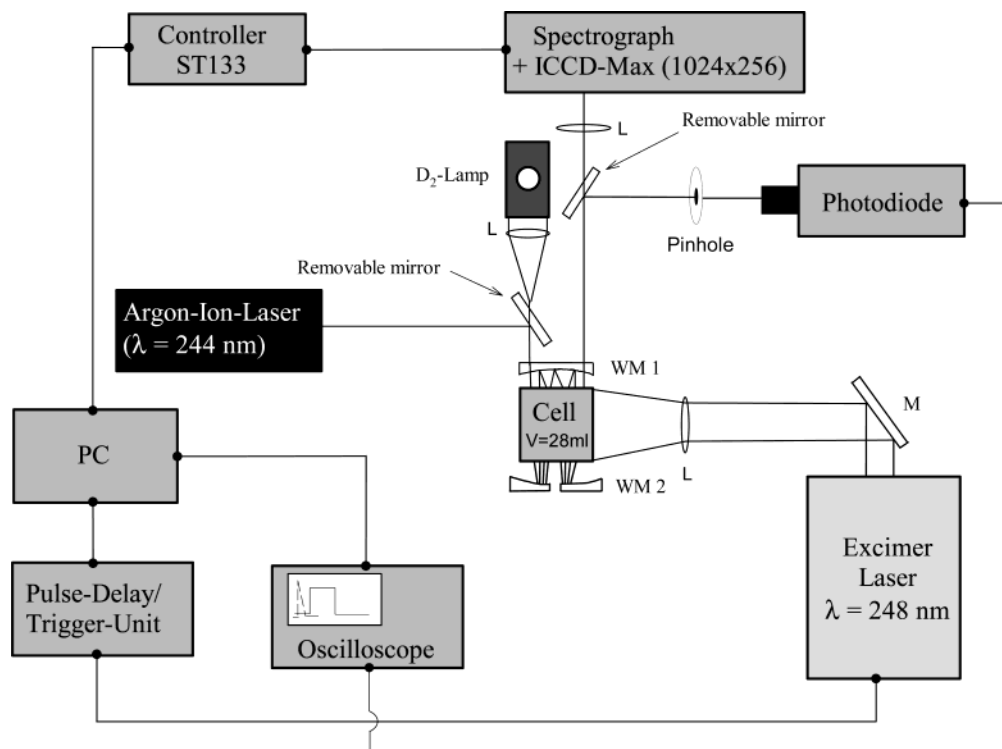
### 2.2. Recently Developed Techniques for the Investigation of OH Reactions in Solution

In this section, recently developed techniques for the kinetic investigation of OH reactions in solution are shortly reviewed. The OH absorption spectrum in aqueous solution is much different from its absorption spectrum in the gas phase. In fact, in aqueous solution the maximum absorption is found around  $\lambda = 235$  nm; see Figure 1.



**Figure 1.** Absorption spectra of OH in aqueous solution. (—): Hesper and Herrmann (2003),<sup>24</sup> (□): Jayson et al. (1973),<sup>25</sup> (○): Nielsen et al. (1976),<sup>26</sup> (△): Thomsen et al. (2001).<sup>27</sup>

This leads to the idea to use an internally frequency-doubled Ar<sup>+</sup>-laser to directly monitor the absorption of OH at  $\lambda = 244$  nm. However, when organic substances are investigated, the decay of absorption of OH is overlapped by the rising absorption of the organic radicals, or, in the presence of oxygen, the organic peroxy radicals. Hence, to derive the rate constant for the reaction of OH with an organic substrate RH in the presence of oxygen, the observed intensity vs time profile has to be numerically treated accordingly. This method has been applied for the investigation of other OH reactions with organics in the past, but not in the presence of oxygen and not by application of the laser light source mentioned. The method requires the knowledge of the absolute absorption coefficient at  $\lambda = 244$  nm for the peroxy radical formed. The method and its application are described in more detail elsewhere<sup>24,28</sup> and a schematic of the setup is shown in Figure 2.



**Figure 2.** Schematic setup of the laser photolysis-long path absorption (LP-LPA) experiment used for spectroscopic and direct kinetic investigations of OH.<sup>24</sup>

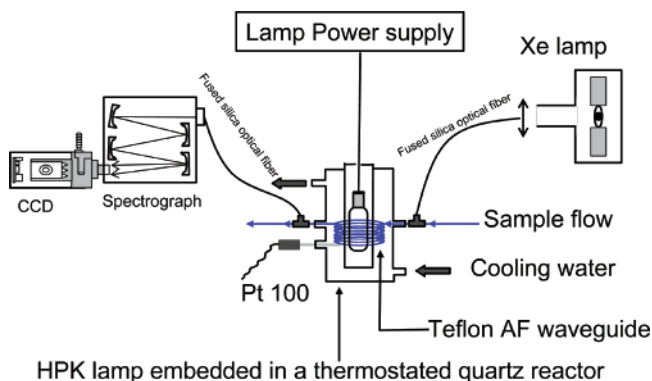
**Table 2. Spectroscopic Data of Peroxyl-Radicals in Aqueous Solution**

parent compound	formula	exp technique	pH	$\lambda_{\max}$ (nm)	$\epsilon_{10}$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	refs
Alkanes						
methane	CH <sub>4</sub>	<i>a</i>	6.0	255	1100	[29]
ethane	C <sub>2</sub> H <sub>6</sub>	<i>a</i>	6.0	255	1250	[29]
propane	C <sub>3</sub> H <sub>8</sub>	<i>a</i>	6.0	255	1273	[29]
Alcohols						
methanol	CH <sub>3</sub> OH	<i>a</i>	6.0	244	970	[30]
ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	<i>a</i>	6.0	250	1180	[30]
2-propanol	(CH <sub>3</sub> ) <sub>2</sub> CHOH	<i>b</i>	5.8	248	1060	[24]
		<i>b</i>	6.0	250	1180	[30]
1-butanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	<i>b</i>	5.8	260	1126	[24]
2-butanol	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>3</sub>	<i>b</i>	5.8	260	1180	[24]
Carbonyl Compounds						
propionaldehyde	CH <sub>3</sub> CH <sub>2</sub> CH(O)	<i>b</i>	6.0	260	1110	[24]
butyraldehyde	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(O)	<i>b</i>	5.9	263	1490	[24]
acetone	CH <sub>3</sub> C(O)CH <sub>3</sub>	<i>b</i>	6.0	217	712	[24]
				300	510	
2-hydroxy-3-butanone	CH <sub>3</sub> CH(OH)COCH <sub>3</sub>	<i>b</i>	5.8	236	945	[24]
Hydroxycarboxylic Acids						
tartronic acid	HOOCCH(OH)COOH	<i>b</i>	1.5	224	1160	[24]
tartronate (dianion)	[OOCCH(OH)COO] <sup>2-</sup>	<i>b</i>	9.0	219	8470	[24]
D,L-malic acid	HOOCCH <sub>2</sub> CH(OH)COOH	<i>b</i>	1.5	248	2235	[24]
D,L-maleate (dianion)	[OOCCH <sub>2</sub> CH(OH)COO] <sup>2-</sup>	<i>b</i>	9.0	214	6830	[24]
Dicarboxylic Acids						
glutaric acid	HOOC(CH <sub>2</sub> ) <sub>3</sub> COOH	<i>b</i>	2.0	224	1818	[24]
glutarate (dianion)	[OOC(CH <sub>2</sub> ) <sub>3</sub> COO] <sup>2-</sup>	<i>b</i>	9.0	234	3885	[24]
adipic acid	HOOC(CH <sub>2</sub> ) <sub>4</sub> COOH	<i>b</i>	2.0	234	1680	[24]
adipate (dianion)	[OOC(CH <sub>2</sub> ) <sub>4</sub> COO] <sup>2-</sup>	<i>b</i>	9.0	250	3845	[24]
pimelic acid	HOOC(CH <sub>2</sub> ) <sub>5</sub> COOH	<i>b</i>	2.0	244	1560	[24]
pimelate (dianion)	[OOC(CH <sub>2</sub> ) <sub>5</sub> COO] <sup>2-</sup>	<i>b</i>	9.0	260	3770	[24]
suberic acid	HOOC(CH <sub>2</sub> ) <sub>6</sub> COOH	<i>b</i>	2.0	255	1470	[24]
suberate (dianion)	[OOC(CH <sub>2</sub> ) <sub>6</sub> COO] <sup>2-</sup>	<i>b</i>	9.0	262	3330	[24]

<sup>a</sup> Laser flash photolysis at 193 nm of H<sub>2</sub>O as OH source. <sup>b</sup> Laser flash photolysis at 248 nm of H<sub>2</sub>O<sub>2</sub> as OH source.

First kinetic results have been obtained and are considered in the respective section of this review (see below). Recently, a number of peroxy radicals have been investigated and their UV/VIS absorption spectra were measured by means of a laser-photolysis-

long path broadband CCD<sup>28</sup> or, in the former version,<sup>29</sup> diode array absorption experimental setup. The main spectral properties of organic peroxy radicals obtained in recent studies are summarized in Table 2.



HPK lamp embedded in a thermostated quartz reactor

**Figure 3.** Schematic setup of the liquid core waveguide (LCW) micro-flowtube experiment. Reproduced from ref 33 with permission. Copyright 2003 PCCP Owner Societies.

The data now available on organic peroxy radicals may serve as a basis for the further kinetic studies and the elucidation of the chemical mechanisms following the initial attack of OH radicals toward organic substrates in aqueous solution.

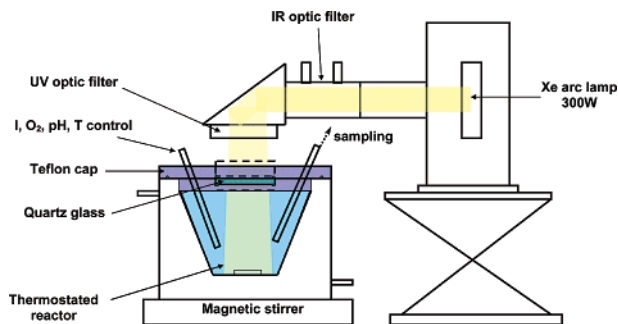
Finally, it should be noted that the method of following the rise of the absorption of organic peroxy radicals and the simultaneous decay of OH establishes a direct method that does not rely on kinetic reference data which are required for any kind of competition kinetic studies. Therefore, this method is also attractive for the study of ionic strength dependences (see section 3.7 of this review) because the respective I-dependence of the competition reference reaction does not need to be known.

A much-applied competition kinetic system for the study of OH reactions in aqueous solution is the thiocyanate system which has been described by Chin and Wine.<sup>31,32</sup> This competition kinetic system is applied in a novel technique introduced by the group of George,<sup>33</sup> which, in contrast to previous applications, makes use of a Teflon waveguide to achieve long optical path lengths. A schematic of this setup is shown in Figure 3.

The material Teflon AF 2400 has a refraction index smaller than the one of water and, furthermore, is transparent for UV light with a transmission of the waveguide of about 90% for wavelengths above  $\lambda = 300$  nm. Hence, a tube made of that material filled with a liquid can serve as a lightguide and can be exposed to a UV source for radical generation. Huge optical path lengths are readily available without complex optical setups. First rate constants for reactions of OH with oxygenated organics in aqueous solution have been obtained<sup>33</sup> and are also considered in this review in section 3.2.

### 2.3. Aqueous Solution Product Studies

Some recent studies have been performed to not solely investigate single rate constants of elementary reaction, but also to study the degradation or conversion of key organic compounds of atmospheric interest in more detail, especially considering the identification and quantification of reaction products. To this end, Monod and co-workers have suggested an "aqueous phase simulation chamber", the schematic of which is shown in Figure 4.



**Figure 4.** Schematic setup of static photoreactor equipped with a continuous UV-Vis irradiation source. Reproduced from ref 55 by permission of Anne Monod, Laboratoire de Chimie et Environnement, France.

This setup makes use of a conventional xenon lamp to mimic tropospheric irradiance conditions and has been applied to study the oxidation of methanol by OH in aqueous solution in much detail.<sup>34</sup>

An alternative approach combining excimer laser photolysis and HPLC for the study of products in the interaction of OH/NO<sub>2</sub>/NO<sub>3</sub> with phenols in aqueous solution is shown schematically in Figure 5.

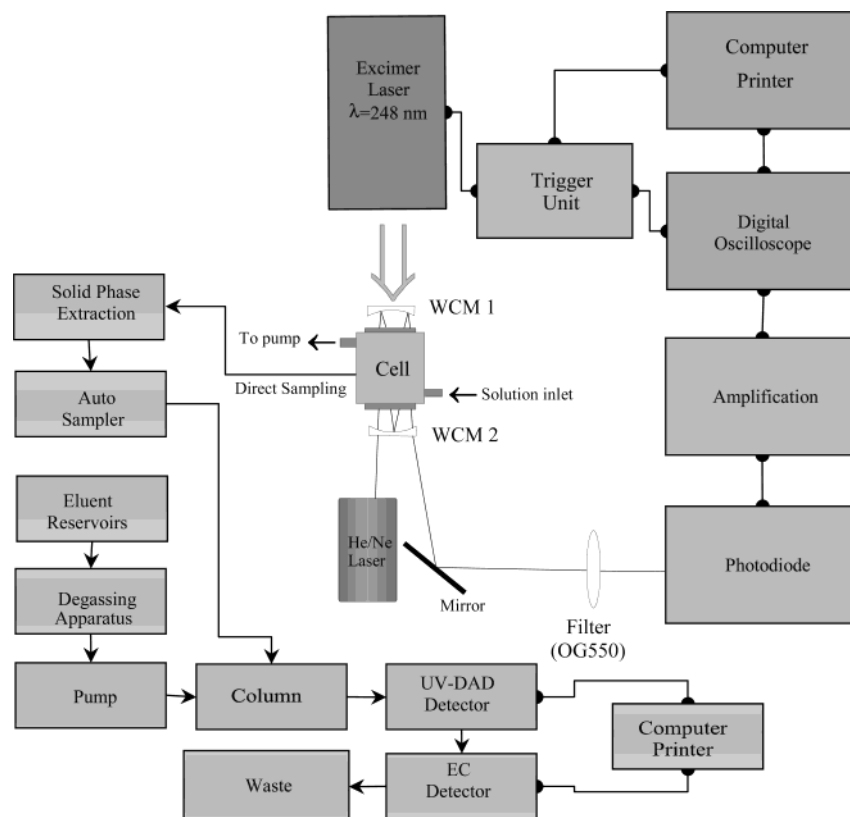
In this laser photolysis-long path absorption/high performance liquid chromatography-electrochemical detector and UV detector (LP/LPA/HPLC-ED-UV) experiment, radicals are produced by laser photolysis of adequate precursors. The resulting initial concentrations of OH, NO<sub>2</sub>, and NO<sub>3</sub> following photolysis of nitrate anions at  $\lambda = 248$  nm equal some nanomoles per liter ( $10^{-9}$  mol L<sup>-1</sup>). Following photolytic initiation, nitrate radicals can be monitored in a time-resolved manner. Finally, an aliquot of the photolyzed solution is transferred to a solid-phase extraction. The organic eluent is then analyzed for the various organic reaction products by means of high performance liquid chromatography (HPLC). By means of the combined experiment, it has been demonstrated to perform a product study following a single excimer laser photolysis shot for nitrophenol formation in a study of the interaction of OH/NO<sub>2</sub>/NO<sub>3</sub> with phenol.<sup>35</sup>

The latter two approaches extend atmospheric aqueous phase studies of radical-induced conversions beyond pure kinetic studies and show possibilities to better elucidate reaction mechanisms, especially for the oxidation of organics by free radicals, which appears to be a key issue for the further development of aerosol and cloud chemistry mechanisms; see section 4 of this contribution.

## 3. Chemical Subsystems

### 3.1. Complex System Studies: Sulfur(IV) Oxidation

As much emphasis during the last years has been laid on the study on radical reactions in aqueous solution, chemical conversions initiated by conventional, nonradical oxidants such as ozone, hydrogen peroxide, or even just oxygen in the presence of transition metal ions (TMIs) have also been studied in much detail during the late years. A wealth of kinetic and mechanistic data and many valuable



**Figure 5.** Experimental setup (LP-LPA/HPLC-ED-UV) for product analysis used for the  $\text{NO}_3$  single-shot experiment. Reproduced with permission from ref 35. Copyright 2002 PCCP Owner Societies.

references can be found in the volumes derived from activities within the EUROTRAC-II project, and here especially from the subactivity Chemical Mechanism Development (CMD).<sup>36–39</sup> Further summaries are again found in the IGAC I&S volume.<sup>3</sup>

The system that is mostly treated is the conversion of S(IV) to S(VI); see also Herrmann et al.<sup>40</sup> Studies from 1996 on have focused much on the effects of transition metal ions as well as organic substances. Many of the studies in this area are descriptive in their nature and, sometimes, far from elucidating a reaction mechanism based on its elementary reaction steps. This is sometimes due to the complexity of the systems studied. However, current multiphase models (see also section 4) almost exclusively describe solution chemistry by combinations of elementary reactions which hinders the implementation of empirical complex rate laws or qualitative findings in such schemes.

The reader is referred to the section by Grgić et al. of the CMD final report<sup>41</sup> for a comprehensive overview on current studies of S(IV) conversion and the effects of transition metal ions and organic constituents as well. More data on dark reactions are summarized in a contributions to the IGAC I&S volume.<sup>3</sup> Some broader considerations of S(IV) conversions in clouds have also recently been presented.<sup>40</sup>

The role of the metal ions Mn(II), Fe(II), and Fe(III) in the catalysis of the conversion of S(IV) has been investigated over the last years in a series of studies by Grgić and co-workers.<sup>42,43</sup> These recent investigations continue the former studies performed in the course of the HALIPP project.<sup>44</sup> Apparently,

the role of metal ions in the oxidation of S(IV) should be properly represented in aqueous phase chemical mechanisms.

The groups of Grgić and of Pasiuk-Bronikowska have spent a lot of effort to investigate the role of organic constituents which might be found in tropospheric aerosols and cloudwater in the oxidation of S(IV).<sup>45–48</sup> As a result of the cited studies, these authors differentiate between two groups of organic scavengers. Group 1 consists of aromatics and terpenes with a double bond as well as an OH function. Group 2 consists of compounds with an intact  $\alpha$ -pinene skeleton. For the compounds of group 1, it is suggested that radical derived from the cited parent compound groups are able to oxidize S(IV) by secondary electron transfer reactions. For the terpenes of group 2, it is suggested that they mainly show an inhibiting effect of S(IV) oxidation.

It should be noted that the complex system of S(IV) oxidation has also been used to study the influence of elevated electrolyte concentrations. Several findings up to the year 2000 have been summarized before.<sup>3</sup> More recent studies have been performed by the groups of Pasiuk-Bronikowska<sup>49</sup> and of Grgić.<sup>50,51</sup> Following the summary of Grgić et al.<sup>41</sup> as a result of these studies, the salt effect can lead to both increased or decreased reaction rates. On one hand, this might be due to a kinetic salt effect of either sign in some of the reactions involved. On the other hand, effects are caused by the modification of the transition metal ion speciation in the presence of higher electrolyte concentration by complexation. A sulfoxy radical scavenging by the supporting electrolytes such as NaCl,  $\text{NaNO}_3$ , and  $\text{Na}_2\text{SO}_4$  is restricted to

reactions of  $\text{SO}_4^-$  with chloride and nitrate because of thermochemical reasons.

As stated before, many findings in studies of S(IV) oxidation are still of a qualitative nature and should be substantiated by corresponding studies of the elementary reactions involved. A mechanism based upon both complex system studies as well as studies of elementary reactions in isolated subsystems should then be able to quantitatively explain the chemical behavior of the system. The basic S(IV) oxidation mechanism suggested by Warneck and co-workers<sup>52,53</sup> as a major outcome of the European HALIPP activity still remains a good starting point for the further quantitative description of S(IV) oxidation.

### 3.2. Hydroxyl Radical and Organic Peroxyl Radicals

Table 3 summarizes the results of recent studies of OH reaction kinetics in aqueous solution. For the full details of the cited studies, the reader is referred to the original publications.

It is interesting to note that many of the rate constants listed in Table 3 have been derived by means of competition kinetics applying the thiocyanate system mentioned before when photochemical initiation is applied. Some reactions of OH toward the same substrates have been studied by more than one experimental method. The agreement of the different investigations of the reaction of OH with acetone and 2-butanone can be regarded reasonable and may serve as an intercomparison of the different methods applied. The results shown in Table 3 also reflect the motivation of the studies the table is based on. George et al.<sup>33</sup> introduced their lightguide technique and have been motivated to study oxygenated organics, but also compounds such as *N*-methyl pyrrolidone, which are technically applied as solvents and may undergo complex tropospheric chemical conversion. A study of substituted ethers as alternative fuel oxygenates by Mezyk et al. is carried by a possible development of remediation techniques but the parameters obtained are also of direct use for atmospheric chemistry.<sup>59</sup> Another study dealing with ether oxidation by OH was performed by Janik et al.<sup>64</sup> and contains valuable mechanistic details. Driven again by the development of remediation techniques, Hardison et al. investigated the reaction of OH with *tert*-butyl formate (TBF).<sup>62</sup>

Ervens et al.<sup>54</sup> studied OH reactions which are considered in an update of the multiphase mechanism CAPRAM; see section 4. Hesper and Herrmann<sup>24</sup> validated the above-mentioned laser-based technique for measuring OH rate constants in their study. The Marseille group applied their photoreactor for the study of carbonyl compounds of interest for atmospheric chemistry.<sup>55</sup> The Leeds group investigated the OH-induced oxidation of glyoxal,<sup>58</sup> the reactivity of some terpenic compound with OH<sup>66</sup> (and also  $\text{SO}_4^-$ , cf. section 3.5), and the oxidation of hydroxymethanesulfonate ( $\text{HMS}^-$ ) by OH<sup>73</sup> and again also by  $\text{SO}_4^-$ ; see also section 3.5. Out of these studies especially the investigation of the glyoxal oxidation and the  $\text{HMS}^-$  degradation are of importance for atmospheric liquid-phase chemistry. The study of

Flyunt et al.<sup>61</sup> yields very interesting kinetic information as well as mechanistic details on the reaction of OH with methanesulfinic acid, a compound that is expected to occur in marine atmospheric particles resulting from DMS and its subsequent atmospheric oxidation; see also Sehested and Holcman.<sup>78</sup>

Besides these studies which are either directly motivated by atmospheric chemistry or the results of which can directly be applied to atmospheric chemistry, there are many more aqueous phase kinetic data available for reactions of OH with organics and especially aromatic compounds. Here, Schuler and Albarran studied the reactions of OH with benzene and toluene.<sup>69</sup> Dong et al. studied the reaction with 2-chlorophenol<sup>71</sup> and Bonifačić et al. studied the reaction with 2,4,5-trichlorophenol.<sup>73</sup> Mohan<sup>67</sup> investigated the reactions of OH with a series of substituted ortho-iodobenzenes, i.e.,  $\text{C}_6\text{H}_4\text{-XI}$  with X = H, Br,  $\text{CH}_3$ , and  $\text{CF}_3$ . Shoute and Mittal<sup>68</sup> communicate the rate constants of the reactions of OH with four perfluoroaromatic carbonyl compounds and Zona et al. investigated the OH reactions with phenoxyacetic acid and 2,4-dichlorophenoxyacetic acid.<sup>70</sup> D'Angelantonio et al. studied the reaction of OH with furfural.<sup>72</sup> Aguila et al. investigated the reactions of OH with organophosphorus reactants<sup>60</sup> and Williams et al. studied the reaction of OH with a series of chloracetones.<sup>63</sup> The rate constants for the reactions of OH with trichloroethanol at two different pH are available from a study of Alfassi et al.<sup>65</sup> These results are also listed here because some of the data might be of interest in atmospheric chemistry.

Some few reactions of OH with inorganic reactants were also studied over the last years. Johnson et al.<sup>75</sup> investigated the reactions of OH with hydroxylamine ( $\text{NH}_2\text{OH}$ ) and monochloramine ( $\text{NH}_2\text{Cl}$ ). The study of Poskrebyshev et al.<sup>77</sup> is discussed in more detail in section 3.6.1 in view of other findings now available. Finally, Mezyk<sup>76</sup> studied the reaction of OH with iodate ( $\text{IO}_3^-$ ).

As can be seen from this overview, a wealth of kinetic data has been obtained for the reactions of OH with nonaromatic organic compounds. For a considerable fraction of the reactions T-dependent rate constants are also now available. On the basis of the kinetic results listed in Tables 3 and 4 a listing of the bond dissociation energies for the weakest C–H bond of the organic substrate and the rate constant per abstractable H atom has been generated. The rate constant per abstractable H 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. The assumption behind this treatment is that a given radical is predominantly reacting with these most easily abstractable H atoms. The bond dissociation energies listed are mostly based upon Benson's incremental method<sup>79</sup> and hence are gas-phase bond dissociation energies with an uncertainty of  $\pm 2$  kcal/mol or  $\pm 8$  kJ/mol.

The use of gas-phase bond dissociation energies to establish Evans-Polanyi-type correlations has been applied for the aqueous phase H-abstraction reaction of the radicals  $\text{NO}_3$ <sup>80</sup> or  $\text{Cl}_2$ <sup>81</sup> and, more recently, for

**Table 3. Kinetic Data for Hydroxyl Radical (OH) Reactions in Aqueous Solution**

reactant <sup>a</sup>	formula	exp techn	pH	$k_{298K}$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$A$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$E_A$ (kJ mol <sup>-1</sup> )	refs
OH + Nonaromatic Organic Compounds							
methanol (1)	CH <sub>3</sub> OH	<i>d</i>		$(1.3 \pm 0.4) \times 10^9$			[33]
ethanol (2)	CH <sub>3</sub> CH <sub>2</sub> OH	<i>e</i>	5	$(2.1 \pm 0.1) \times 10^9$	$(1.02 \pm 0.1) \times 10^{11}$	10 ± 5	[54]
		<i>d</i>		$(1.9 \pm 0.5) \times 10^9$			[33]
1-propanol (3)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	<i>e</i>	5	$(3.2 \pm 0.2) \times 10^9$	$(5.6 \pm 0.6) \times 10^{10}$	8 ± 6	[54]
2-propanol (4)	(CH <sub>3</sub> ) <sub>2</sub> CHOH	<i>f</i>	5.8	$(2.1 \pm 0.2) \times 10^9$	$(6.1 \pm 0.3) \times 10^{10}$	8 ± 2	[54]
1-butanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	<i>f</i>	5.8	$(4.1 \pm 0.8) \times 10^9$	$(1.0 \pm 0.1) \times 10^{11}$	8 ± 1	[54]
2-butanol (5)	C <sub>4</sub> H <sub>9</sub> OH	<i>f</i>	5.8	$(3.5 \pm 0.4) \times 10^9$	$(7.4 \pm 0.3) \times 10^{10}$	8 ± 3	[54]
<i>tert</i> -butyl alcohol (6)	(CH <sub>3</sub> ) <sub>3</sub> COH	<i>e</i>		$(5.0 \pm 0.6) \times 10^8$	$(3.3 \pm 0.1) \times 10^{10}$	10 ± 3	[54]
acetaldehyde (7)	CH <sub>3</sub> CH(O)	<i>e</i>		$3.6 \times 10^9$			[54]
propionaldehyde	CH <sub>3</sub> CH <sub>2</sub> CH(O)	<i>f</i>	6.0	$(2.8 \pm 0.3) \times 10^9$	$(2.6 \pm 0.1) \times 10^{11}$	11 ± 3	[24]
butyraldehyde	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(O)	<i>f</i>	5.9	$(3.9 \pm 1.0) \times 10^9$	$(8.1 \pm 0.3) \times 10^{10}$	8 ± 3	[24]
acetone (8)	CH <sub>3</sub> C(O)CH <sub>3</sub>	<i>f</i>	6.0	$(1.3 \pm 0.1) \times 10^8$	$(8.4 \pm 0.4) \times 10^{10}$	16 ± 3	[24]
		<i>b</i>		$(1.7 \pm 0.7) \times 10^8$			[55]
		<i>c</i>		$(1.3 \pm 0.5) \times 10^8$	$6.6 \times 10^{10}$	15 ± 4	[55]
		<i>d</i>		$1.8 \times 10^8$	$(2.1 \pm 0.3) \times 10^{11}$	17 ± 8	[56]
		<i>e</i>	6	$(2.1 \pm 0.6) \times 10^8$	$(2.8 \pm 0.4) \times 10^{11}$	18 ± 11	[57]
ethyl formate	CH <sub>3</sub> CH <sub>2</sub> OC(O)H	<i>e</i>	6	$(3.2 \pm 0.8) \times 10^8$	$(1.8 \pm 0.1) \times 10^{10}$	10 ± 4	[57]
dimethyl carbonate	(CH <sub>3</sub> ) <sub>2</sub> CO <sub>3</sub>	<i>d</i>		$(5.1 \pm 2.2) \times 10^7$			[33]
2-butanone (9)	CH <sub>3</sub> C(O)CH <sub>2</sub> CH <sub>3</sub>	<i>d</i>		$1.8 \times 10^9$	$(4.1 \pm 0.3) \times 10^{14}$	31 ± 6	[33]
		<i>e</i>	6	$(1.5 \pm 0.7) \times 10^9$	$(1.2 \pm 0.1) \times 10^{13}$	23 ± 10	[57]
2-hydroxy- 3-butanone	CH <sub>3</sub> CH(OH)C(O)CH <sub>3</sub>	<i>f</i>	5.8	$(2.9 \pm 1.0) \times 10^9$	$(2.9 \pm 0.1) \times 10^{11}$	11 ± 3	[24]
isobutyraldehyde	(CH <sub>3</sub> ) <sub>2</sub> CHC(O)H	<i>e</i>	6	$(2.9 \pm 1.0) \times 10^9$	$(3.0 \pm 0.1) \times 10^{10}$	6 ± 3	[57]
<i>n</i> -methyl pyrrolidone	(C <sub>3</sub> H <sub>6</sub> C(O)N)(CH <sub>3</sub> )	<i>d</i>		$(6.9 \pm 1.2) \times 10^9$			[56]
diethyl carbonate	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> CO <sub>3</sub>	<i>d</i>		$(7.9 \pm 3.2) \times 10^8$			[33]
acetonylacetone	CH <sub>3</sub> C(O)C <sub>2</sub> H <sub>4</sub> C(O)CH <sub>3</sub>	<i>e</i>	6	$(7.6 \pm 1.1) \times 10^8$	$(5.1 \pm 0.1) \times 10^{11}$	16 ± 8	[57]
		<i>c</i>		$(2.2 \pm 0.3) \times 10^9$			[55]
		<i>c</i>		$(2.0 \pm 0.2) \times 10^9$	$1.1 \times 10^{11}$	10 ± 2	[55]
methyl isobutyl ketone (mibk)	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> C(O)CH <sub>3</sub>	<i>d</i>		$(1.6 \pm 0.3) \times 10^9$	$(1.4 \pm 0.4) \times 10^{14}$	24 ± 20	[55]
oxalate (dianion)	(COO <sub>2</sub> ) <sub>2</sub> <sup>2-</sup>	<i>e</i>	8	$(1.6 \pm 0.6) \times 10^8$	$(4.6 \pm 0.5) \times 10^{14}$	36 ± 10	[54]
oxalate (monoanion)	[C <sub>2</sub> O <sub>4</sub> H] <sup>-</sup>	<i>e</i>	3	$(1.9 \pm 0.6) \times 10^8$	$(2.5 \pm 0.1) \times 10^{12}$	23 ± 4	[54]
glyoxylate (monoanion)	HC(O)COO <sup>-</sup>	<i>e</i>	8	$(2.8 \pm 1.0) \times 10^9$	$(8.1 \pm 0.6) \times 10^{15}$	36 ± 8	[54]
glyoxylic acid	HC(O)COOH	<i>e</i>	1	$(3.6 \pm 0.2) \times 10^8$	$(8.1 \pm 0.4) \times 10^9$	8 ± 3	[54]
glyoxal	HC(O)C(O)H	<i>g</i>	2–6	$(1.1 \pm 0.04) \times 10^9$		13 ± 1	[58]
malonate (monoanion)	HOOCCH <sub>2</sub> COO <sup>-</sup>	<i>e</i>	5	$(3.6 \pm 0.7) \times 10^8$	$(3.2 \pm 0.5) \times 10^9$	11 ± 5	[54]
malonate (dianion)	[OOCCH <sub>2</sub> COO] <sup>2-</sup>	<i>e</i>	9	$(8.0 \pm 3.0) \times 10^7$	$(2.1 \pm 0.6) \times 10^{14}$	38 ± 19	[54]
pyruvic acid	CH <sub>3</sub> C(O)COOH	<i>e</i>	0	$(1.2 \pm 0.4) \times 10^8$	$(1.0 \pm 0.1) \times 10^{12}$	23 ± 4	[54]
pyruvate	CH <sub>3</sub> C(O)COO <sup>-</sup>	<i>e</i>	6	$(7.0 \pm 2.0) \times 10^8$	$(1.3 \pm 0.1) \times 10^{12}$	19 ± 4	[54]
methylglyoxal	CH <sub>3</sub> C(O)C(O)H	<i>e</i>	4.5	$(1.1 \pm 0.2) \times 10^9$	$(2.9 \pm 0.3) \times 10^{11}$	13 ± 6	[54]
propionic acid (11)	CH <sub>3</sub> CH <sub>2</sub> COOH	<i>e</i>	1.5	$(3.1 \pm 0.5) \times 10^8$	$(7.6 \pm 0.9) \times 10^{11}$	19 ± 8	[54]
propionate (monoanion)	CH <sub>3</sub> CH <sub>2</sub> COO <sup>-</sup>	<i>e</i>	7.4	$(7.2 \pm 0.4) \times 10^8$	$(3.2 \pm 0.2) \times 10^{11}$	15 ± 4	[54]
succinic acid	HOOC(CH <sub>2</sub> ) <sub>2</sub> COOH	<i>e</i>	1.5	$(1.1 \pm 0.1) \times 10^8$	$(8.0 \pm 1.0) \times 10^9$	11 ± 6	[54]
succinate (monanion)	HOOC(CH <sub>2</sub> ) <sub>2</sub> COO <sup>-</sup>	<i>e</i>	7.8	$(5.0 \pm 0.5) \times 10^8$	$(5.0 \pm 0.4) \times 10^{10}$	11 ± 5	[54]
d,l-malic acid	HOOCCH <sub>2</sub> CH- (OH)COOH	<i>f</i>	1.5	$(7.1 \pm 1.3) \times 10^8$			[24]
d,l-maleate (dianion)	[OOCCH <sub>2</sub> CH(OH)- COO] <sup>2-</sup>	<i>f</i>	9.0	$(8.4 \pm 1.0) \times 10^8$			[24]
dimethyl- malonate	CH <sub>3</sub> O(O)CCH <sub>2</sub> C(O)- OCH <sub>3</sub>	<i>d</i>		$(2.7 \pm 0.9) \times 10^8$			[33]
glutaric acid	HOOC(CH <sub>2</sub> ) <sub>3</sub> COOH	<i>f</i>	2.0	$(6 \pm 2) \times 10^8$			[24]
glutarate (dianion)	HOOC(CH <sub>2</sub> ) <sub>3</sub> COO <sup>-</sup>	<i>f</i>	9.0	$(1.0 \pm 0.2) \times 10^9$			[24]
dimethyl- succinate	CH <sub>3</sub> O(O)C(CH <sub>2</sub> ) <sub>3</sub> C(O)- OCH <sub>3</sub>	<i>d</i>		$(5.3 \pm 2.9) \times 10^8$			[33]
adipic acid	HOOC(CH <sub>2</sub> ) <sub>4</sub> COOH	<i>f</i>	2.0	$(1.7 \pm 0.3) \times 10^9$			[24]
adipate (dianion)	[OOC(CH <sub>2</sub> ) <sub>4</sub> COO] <sup>2-</sup>	<i>f</i>	9.0	$(2.4 \pm 0.2) \times 10^9$			[24]
pimelic acid	HOOC(CH <sub>2</sub> ) <sub>5</sub> COOH	<i>f</i>	2.0	$(2.4 \pm 0.7) \times 10^9$			[24]
pimelate (dianion)	[OOC(CH <sub>2</sub> ) <sub>5</sub> COO] <sup>2-</sup>	<i>f</i>	9.0	$(2.9 \pm 0.8) \times 10^9$			[24]



Table 3 (Continued)

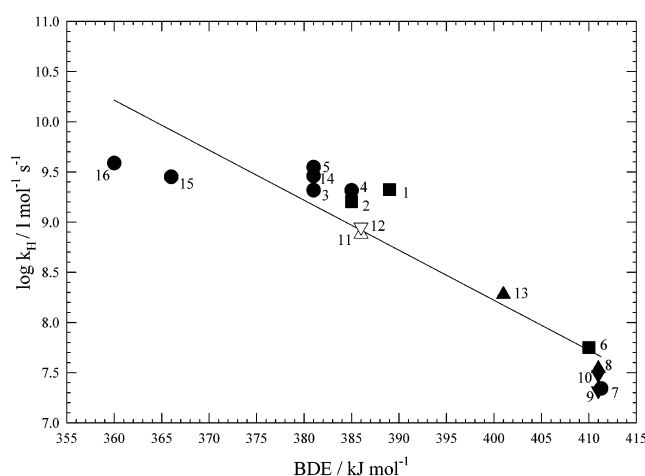
reactant <sup>a</sup>	formula	exp techn	pH	$k_{298K}$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$A$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$E_A$ (kJ mol <sup>-1</sup> )	refs
NO <sub>3</sub> + Amino Acids (cont'd)							
suberic acid	HOOC(CH <sub>2</sub> ) <sub>6</sub> COOH	<i>f</i>	2.0	$(5.0 \pm 0.4) \times 10^9$			[24]
suberate (dianion)	[OOC(CH <sub>2</sub> ) <sub>6</sub> COO] <sup>2-</sup>	<i>f</i>	9.0	$(5.8 \pm 0.3) \times 10^9$			[24]
<i>tert</i> -butyl-ether	(CH <sub>3</sub> ) <sub>3</sub> COC(CH <sub>3</sub> ) <sub>3</sub>	<i>g</i>		$(1.81 \pm 0.09) \times 10^9$			[59]
diisopropyl-ether	(CH <sub>3</sub> ) <sub>2</sub> HCOCH(CH <sub>3</sub> ) <sub>2</sub>	<i>g</i>		$(2.49 \pm 0.12) \times 10^9$			[59]
methyl- <i>tert</i> - amyl-ether	CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> OCH <sub>3</sub>	<i>g</i>		$(2.37 \pm 0.12) \times 10^9$			[59]
trimethyl- phosphonate	(CH <sub>3</sub> ) <sub>3</sub> PO <sub>3</sub>	<i>g</i>		$(2 \pm 1) \times 10^8$			[60]
diethyl-methyl- phosphonate	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (CH <sub>3</sub> )PO <sub>3</sub>	<i>g</i>		$(6 \pm 1) \times 10^8$			[60]
methanesulfinic acid	HO <sub>2</sub> SC(NH)NH <sub>2</sub>	<i>g</i>		$5.3 \times 10^9$			[61]
<i>tert</i> -butyl formate	(CH <sub>3</sub> ) <sub>3</sub> COC(O)H	<i>g</i>		$(5.23 \pm 0.07) \times 10^8$ at 295 K			[62]
chloroacetone	CH <sub>3</sub> C(O)CH <sub>2</sub> Cl	<i>g</i>		$(1.69 \pm 0.05) \times 10^8$			[63]
1,1-dichloroacetone	CH <sub>3</sub> C(O)CHCl <sub>2</sub>	<i>g</i>		$(8.8 \pm 0.4) \times 10^7$			[63]
1,1,1-trichloro- acetone	CH <sub>3</sub> C(O)CCl <sub>3</sub>	<i>g</i>		$(3.3 \pm 0.1) \times 10^7$			[63]
2,4-dimethoxy- pentane	CH <sub>3</sub> CH(OCH <sub>3</sub> )CH <sub>2</sub> - CH(OCH <sub>3</sub> )CH <sub>3</sub>	<i>g</i>		$3.7 \times 10^9$			[64]
trichloroethanol	CCl <sub>3</sub> CH <sub>2</sub> OH	<i>g</i>	6.6	$1.5 \times 10^8$			[65]
		<i>g</i>	11.4	$1.9 \times 10^9$			[65]
tetrahydrofuran (10)	C <sub>4</sub> H <sub>8</sub> O	<i>d</i>		$(3.8 \pm 1.0) \times 10^9$			[33]
<i>cis</i> -verbenol	(C <sub>5</sub> H <sub>5</sub> CO)CH <sub>2</sub> (CH <sub>3</sub> ) <sub>3</sub>	<i>g</i>	4	$(6.8 \pm 0.5) \times 10^9$			[66]
methacrolein	CH <sub>2</sub> CCH <sub>3</sub> C(O)H	<i>g</i>	4	$(8.0 \pm 0.7) \times 10^9$			[66]
OH + Aromatic Organic Compounds							
2-iodotoluene	IC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	<i>g</i>	6	$1.7 \times 10^9$			[67]
2-bromo-1-iodo benzene	IC <sub>6</sub> H <sub>4</sub> Br	<i>g</i>	6	$9 \times 10^8$			[67]
iodobenzene	C <sub>6</sub> H <sub>5</sub> I	<i>g</i>	6	$2.9 \times 10^9$			[67]
2-iodobenzene	IC <sub>6</sub> H <sub>2</sub> F <sub>3</sub>	<i>g</i>	6	$8 \times 10^8$			[67]
trifluoride							
2,3,4,5,6-penta- fluoro- acetophenone	C <sub>6</sub> F <sub>5</sub> C(O)CH <sub>3</sub>	<i>g</i>	7	$(1.5 \pm 0.3) \times 10^9$			[68]
2,3,4,5,6-penta- fluoro- benzaldehyde	C <sub>6</sub> F <sub>5</sub> C(O)H	<i>g</i>	7	$(2.0 \pm 0.3) \times 10^9$			[68]
2,3,4,5,6-penta- fluoro- benzoic acid	C <sub>6</sub> F <sub>5</sub> COOH	<i>g</i>	0.6	$(1.1 \pm 0.2) \times 10^9$			[68]
2,3,4,5,6-penta- fluoro- benzoate	C <sub>6</sub> F <sub>5</sub> COO <sup>-</sup>	<i>g</i>	9	$(1.1 \pm 0.3) \times 10^{10}$			[68]
benzene	C <sub>6</sub> H <sub>6</sub>	<i>g</i>		$7.8 \times 10^9$			[69]
toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	<i>g</i>		$8.1 \times 10^9$			[69]
2,4-dichloro- phenoxy- acetic acid	HOCCCH <sub>2</sub> OC <sub>6</sub> H <sub>3</sub> (Cl) <sub>2</sub>	<i>g</i>		$(6.6 \pm 0.5) \times 10^9$			[70]
phenoxyacetic acid	C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> COOH	<i>g</i>		$(10 \pm 1) \times 10^9$			[70]
2,4-dichloro- phenol	HOC <sub>6</sub> H <sub>3</sub> (Cl) <sub>2</sub>	<i>g</i>		$(7.1 \pm 0.5) \times 10^9$			[70]
2-chlorophenol	HOC <sub>6</sub> H <sub>4</sub> Cl	<i>g</i>		$1.0 \times 10^9$			[71]
furfural	(C <sub>3</sub> H <sub>3</sub> OC)CH(O)	<i>g</i>		$(4.7 \pm 0.8) \times 10^9$			[72]
2,4,5-trichloro- phenol	HOC <sub>6</sub> H <sub>3</sub> (Cl) <sub>3</sub>	<i>g</i>		$(1.4 \pm 0.3) \times 10^8$			[73]
OH + Inorganic Compounds							
hydroxymethane- sulfonate ion	HOCH <sub>2</sub> SO <sub>3</sub> <sup>-</sup>	<i>g</i>		$(3.0 \pm 0.3) \times 10^8$			[74]
monochloramine	NH <sub>2</sub> Cl	<i>g</i>	neutral	$(2.8 \pm 0.2) \times 10^9$			[75]
hydroxylamine	NH <sub>2</sub> OH	<i>g</i>	basic	$(8.5 \pm 0.4) \times 10^9$			[75]
	NH <sub>3</sub> OH <sup>+</sup>	<i>g</i>	acid	$\leq 5 \times 10^7$			[75]
iodate	IO <sub>3</sub> <sup>-</sup>	<i>g</i>		$(1.08 \pm 0.48) \times 10^5$ at 295 K $k_f = (8.6 \pm 1.3) \times 10^7$		26.5 ± 2.8	[76]
nitric acid	HNO <sub>3</sub> <sup>b</sup>	<i>g</i>	1.0 to 0.0	$k_b = (3 \pm 1) \times 10^2$ $K_{eq} = (2.8 \pm 0.4) \times 10^5$			[77]

<sup>a</sup> Reactant numbers in parentheses refer to the plot  $k(Cl)$  versus  $k(OH)$ , Figure 9. <sup>b</sup> Static photoreactor/photolysis of H<sub>2</sub>O<sub>2</sub> for OH. <sup>c</sup> Static photoreactor/Fenton for OH. <sup>d</sup> Teflon waveguide system/photolysis of H<sub>2</sub>O<sub>2</sub>. <sup>e</sup> Laser photolysis long path absorption apparatus/photolysis of H<sub>2</sub>O<sub>2</sub> (competition kinetic, referent compound SCN<sup>-</sup>). <sup>f</sup> Laser photolysis long path absorption apparatus/photolysis of H<sub>2</sub>O<sub>2</sub> (direct method, following the build-up of peroxy-radicals). <sup>g</sup> Pulse radiolysis technique. <sup>h</sup> See also Table 9.

**Table 4. Data for the Evans-Polanyi Plots for H-Abstraction Reactions of OH in Aqueous Solution**

no.	reactant	$k_{\text{H}}$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$\log k_{\text{H}}^a$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$E_{\text{A}}$ (kJ mol <sup>-1</sup> )	BDE <sup>b</sup> (kJ mol <sup>-1</sup> )	refs	symbols
1	ethanol	$1.1 \times 10^9$	9.02	(10 ± 5)	(389 ± 4)	[54]	■
2	1-propanol	$1.6 \times 10^9$	9.20	(8 ± 6)	(385 ± 8)	[54]	■
3	2-propanol	$2.1 \times 10^9$	9.32	(8 ± 2)	(381 ± 4)	[24]	●
4	1-butanol	$2.1 \times 10^9$	9.32	(8 ± 1)	(385 ± 8)	[24]	●
5	2-butanol	$3.5 \times 10^9$	9.55	(8 ± 3)	(381 ± 8)	[24]	●
6	<i>tert</i> -butyl alcohol	$4.8 \times 10^8$	7.75	(10 ± 3)	410	[54]	■
7	acetone	$2.2 \times 10^7$	7.34	(16 ± 3)	(411.3 ± 7.5)	[24]	●
8	acetone	$3.5 \times 10^7$	7.54	(18 ± 11)	(411.3 ± 7.5)	[57]	▲
9	acetone	$2.2 \times 10^7$	7.34	(15 ± 4)	(411.3 ± 7.5)	[55]	▼
10	acetone	$3.0 \times 10^7$	7.48	(17 ± 8)	(411.3 ± 7.5)	[33]	▼
11	2-butanone	$7.5 \times 10^8$	8.88	(23 ± 9)	386	[57]	△
12	2-butanone	$9.0 \times 10^8$	8.95	(31 ± 6)	386	[33]	▽
13	acetonylacetone	$1.9 \times 10^8$	8.28	(16 ± 8)	401	[57]	▲
14	acetoin (3-hydroxy-2-butanone)	$2.9 \times 10^9$	9.46	(11 ± 3)	(381 ± 8)	[24]	●
15	propanal	$2.8 \times 10^9$	9.45	(11 ± 3)	(366 ± 8)	[24]	●
16	butanal	$3.9 \times 10^9$	9.59	(8 ± 3)	360	[24]	●

<sup>a</sup>  $k_{\text{H}}$  - rate constant per abstractable hydrogen atom. <sup>b</sup> BDE - bond dissociation energy of the weakest C-H bond.



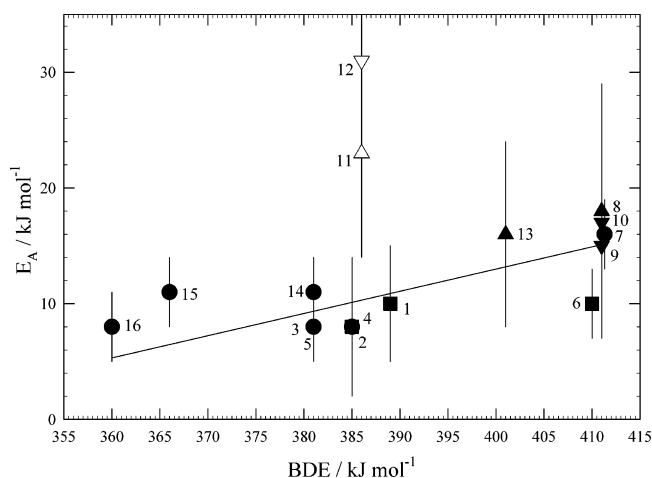
**Figure 6.** Evans-Polanyi plot in form of  $\log(k_{\text{H}})$  vs bond dissociation energy (BDE). Numbering refers to the numbers of Table 4. (●): Hesper and Herrmann (2003),<sup>24</sup> (■): Ervens et al. (2002),<sup>54</sup> (▲, △): Gligorovski and Herrmann (2002),<sup>57</sup> (▼): Poulain et al. (2002),<sup>55</sup> (▽): George et al. (2003).<sup>33</sup>

OH<sup>54</sup> as well as Cl.<sup>82</sup> This method is hence assuming that the aqueous phase hydration of both reaction educts and products is energetically identical within a series of reactions of a given radical. Despite this limitation, the currently available results lead to statistically significant correlations and may be used to estimate rate constants for H-abstraction reactions of small radicals in aqueous solution when measured data are not available.

By means of the data of Table 4 the Evans-Polanyi plots shown in Figure 6 in the form  $\log k_{\text{H}} = f(\text{BDE})$  and, in Figure 7, in the form  $E_{\text{A}} = f(\text{BDE})$  result.

It has to be mentioned that the C-H bond dissociation energies for the compounds ethyl formate and isobutyl methyl ketone could not be properly assessed and hence these compounds were not considered for the plots of Figures 6 and 7 at this stage. The regression line given in Figure 6 corresponds to the expression:

$$\log(k_{\text{H}}/\text{L mol}^{-1} \text{ s}^{-1}) = (28 \pm 4) - (0.05 \pm 0.01)\text{BDE}/\text{kJ mol}^{-1} \quad (\text{I})$$



**Figure 7.** Evans-Polanyi plot in form  $E_{\text{A}}$  vs bond dissociation energy (BDE). Numbering refers to the numbers of Table 4. (●): Hesper and Herrmann (2003),<sup>24</sup> (■): Ervens et al. (2002),<sup>54</sup> (▲, △): Gligorovski and Herrmann (2002),<sup>57</sup> (▼): Poulain et al. (2002),<sup>55</sup> (▽): George et al. (2003).<sup>33</sup>

with  $n = 16$  and  $r = 0.93$ . As can be seen, there is a reasonable correlation between the C-H bond dissociation energy of the weakest bond in the organic substrates and the measured rate constant per abstractable H atom in the reaction with OH in aqueous solution. There are no obvious deviations of results, indicating that the experiments employed are working without severe systematical errors.

Recently, a similar regression has been established considering H-abstraction reactions of OH in aqueous solution considering also the anions of dicarboxylic acids (DCA).<sup>54</sup> From that study the expression

$$\log(k_{\text{H}}/\text{L mol}^{-1} \text{ s}^{-1}) = (25 \pm 8) - (0.04 \pm 0.02)\text{BDE}/\text{kJ mol}^{-1} \quad (\text{II})$$

with  $n = 23$  and  $r = 0.70$  was derived. When monoanions of DCAs are considered, the possibility exists that electron transfer may also contribute to the observed rate constant. While such contributions cannot be fully ruled out, the agreement between the correlations (I) and (II) is a very good indicator that also the assumption that the DCA monoanions predominately react by H-abstraction can be re-

garded as valid. To better assess possible contributions of electron-transfer reactions, better thermochemical data are needed. Currently, to the author's knowledge, no reliable one-electron redox potential is available for the DCA mono- and dianions, preventing a better assessment of electron-transfer reaction contributions.

The data of Table 4 were used to obtain the Evans-Polanyi plot presented in Figure 7. The regression line in Figure 7 corresponds to

$$E_A / \text{kJ mol}^{-1} = -(52 \pm 33) + (0.16 \pm 0.08)\text{BDE} / \text{kJ mol}^{-1} \quad (\text{III})$$

with  $n = 16$  and  $r = 0.75$ . The  $p$ -value for the slope is  $p_m = 0.002$ . The data points obtained for 2-butanone (points 11 and 12) have not been included in the regression. Obviously, 2-butanone reacts much faster than expected from the C–H bond strengths of the  $\alpha$ -H atoms. This effect is found in the measurement of the group of George,<sup>33</sup> but also, however to a lesser extent, in a very recent measurement from our own laboratory.<sup>57</sup> The reason for this behavior is unclear.

In the recent study by Ervens et al.,<sup>54</sup> a correlation similar to eq V has been established. Under consideration of a OH reaction with several monoanions of DCAs, these authors found the following:

$$E_A / \text{kJ mol}^{-1} = -(102 \pm 49) + (0.29 \pm 0.12)\text{BDE} / \text{kJ mol}^{-1} \quad (\text{IV})$$

with  $n = 21$  and  $r = 0.73$ . As in the case of the relations (I) and (II), again a reasonable agreement is found, indicating that H-abstraction seems to be the dominating reaction pathway in reactions of OH with DCA anions.

Many of the OH data summarized here have up to now not been applied in atmospheric multiphase models. A further effort of mechanism extension is required to extend coverage of organic conversions for the description of cloud and aerosol chemistry beyond treatment of compounds with just one or two C atoms. It should be noted, however, that for the further construction of chemistry modules not only knowledge about the radical initiation steps but also data about the subsequent steps involving organic peroxy radicals are urgently required; see also refs 1 and 2. To this end, determination of OH reaction rate constants can only be a first step which needs to be followed by the characterization of the spectroscopic properties of the corresponding peroxy radicals, cf. Table 2, their chemical behavior, subsequent reaction kinetics, and product yields; see also section 2.2 and 2.3. Very valuable information of the reactivity and reaction mechanisms of organic peroxy radicals in aqueous solution is given in the monograph by von Sonntag<sup>83</sup> and the recent compilation edited by Alfassi.<sup>84</sup>

### 3.3. Nitrate Radical

Over the last few years, rate constants of reactions of the nitrate radical ( $\text{NO}_3$ ) in aqueous solution have been measured for formic acid/formate, a number of

esters, phenols, benzoic acids, and amino acids, which extends former studies as summarized before.<sup>85</sup> In addition, several reactions have been reinvestigated. The more recent kinetic data for  $\text{NO}_3$  reactions in aqueous solution are summarized in Table 5.

The determination of the rate constant for the reaction of  $\text{NO}_3$  with formate and formic acid by Buxton et al.<sup>86</sup> confirms the previously available data by Exner et al.<sup>93</sup> The rate coefficients for the reactions with the esters listed are first measurements where no data for comparison currently exist.

Aqueous phase reaction rate constants of  $\text{NO}_3$  can be derived from concentration decay measurements of this radical in the gas phase in a wetted wall reactor. In such studies, the solution contains varying concentrations of anions which undergo electron-transfer reactions with  $\text{NO}_3$  after its uptake. A series of such studies has been performed in the laboratory of Ravishankara.<sup>90,94,95</sup> By means of this method reaction rate coefficients are accessible which cannot be easily determined by conventional solution phase kinetic experiments. It should be mentioned that the experimental conditions have to be chosen in a such a manner that the observed concentration decays are predominately due to removal of the species of interest by chemical reaction in the solution phase and that mass transport in either phase as well as mass accommodation are not the rate-limiting steps in the system.

The two most prominent reasons for difficulties in conventional aqueous phase studies motivating an indirect measurement in a multiphase flowtube are (i) the interaction of the reactant to be studied with the ( $\text{NO}_3$ ) radical precursor, which, in most cases in the past was of a heavily oxidizing nature, or (ii) an overlap of product absorption with the absorption of the radical of interest (here  $\text{NO}_3$ ). A prominent example of a  $\text{NO}_3$  aqueous phase rate coefficient measurement by a wetted wall experiment is for the reaction of  $\text{NO}_3$  with iodide in aqueous solution<sup>90</sup> which has not been determined before. The value determined generally appears to be consistent with the data of the reactions of  $\text{NO}_3$  with chloride and bromide and is listed in Table 5.

In addition to the data listed in Table 5, Imamura et al.<sup>96</sup> performed a study determining the rate constants of a series of electron-transfer reactions of  $\text{NO}_3$  in aqueous solution by means of the above-mentioned wetted-wall experiment. These authors determined rate coefficients which are strongly different from the rate constants that were determined before by Exner et al.<sup>93,97</sup>

Table 6 gives an overview of these data and the resulting differences. It has been speculated that the reason for the discrepancies might be a different reaction rate constant for the reaction of  $\text{NO}_3$  with chloride. Hence, the data of Imamura et al.<sup>96</sup> were also scaled with the more recently available forward rate constant for the reaction of  $\text{NO}_3$  with the chloride anion,<sup>98</sup> which is by far higher than all data that have been determined by other authors; see also section 3.6.2. For comparison, the original data published by Imamura et al.<sup>96</sup> based on the reference rate constant given by Exner et al. are listed together with rate

**Table 5. Kinetic Data for Nitrate Radical (NO<sub>3</sub>) Reactions in Aqueous Solution**

reactant	formula	exp techn	pH	$k_{298}$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$A$ (mol L <sup>-1</sup> s <sup>-1</sup> )	$E_A$ (kJ mol <sup>-1</sup> )	refs
NO <sub>3</sub> + Nonaromatic Organic compounds							
formic acid	HCOOH	<i>b</i>	6–7	$(3.3 \pm 1.0) \times 10^4$ <sup>e</sup>			[86]
formate	HCOO <sup>-</sup>	<i>b</i>	6–7	$(4.2 \pm 0.1) \times 10^7$ <sup>e</sup>			[86]
methyl formate	CH <sub>3</sub> OC(O)H	<i>b</i>	6–7	$(3.5 \pm 0.3) \times 10^6$ <sup>e</sup>			[86]
ethyl formate	CH <sub>3</sub> CH <sub>2</sub> OC(O)H	<i>b</i>	6–7	$(4.7 \pm 0.3) \times 10^6$ <sup>e</sup>			[86]
methyl acetate	CH <sub>3</sub> C(O)OCH <sub>3</sub>	<i>b</i>	6–7	$<10^4$ <sup>e</sup>			[86]
ethyl acetate	CH <sub>3</sub> CH <sub>2</sub> OC(O)CH <sub>3</sub>	<i>b</i>	6–7	$<10^4$ <sup>e</sup>			[86]
NO <sub>3</sub> + Phenols							
phenol	C <sub>6</sub> H <sub>5</sub> OH	<i>a</i>	0	$(1.9 \pm 0.3) \times 10^9$	$(1.4 \pm 0.2) \times 10^{12}$	17 ± 4	[87]
2-methylphenol	HOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	<i>a</i>	0	$(1.1 \pm 0.2) \times 10^9$	$(7.9 \pm 0.4) \times 10^{12}$	22 ± 7	[87]
4-methylphenol	HOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	<i>a</i>	0	$(8.2 \pm 0.3) \times 10^8$	$(3.8 \pm 0.2) \times 10^{15}$	38 ± 4	[85] [87]
2-ethylphenol	HOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>3</sub>	<i>a</i>	0.5	$(6.7 \pm 0.4) \times 10^8$	$(9.5 \pm 0.3) \times 10^{11}$	18 ± 2	[88]
2-methoxyphenol	HOC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	<i>a</i>	0.5	$(1.1 \pm 0.1) \times 10^8$	$(2.3 \pm 0.2) \times 10^{12}$	25 ± 4	[88]
4-methoxyphenol	HOC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	<i>a</i>	0.5	$(6.6 \pm 1.8) \times 10^8$			[85] [87]
2-hydroxyphenol	HOC <sub>6</sub> H <sub>4</sub> OH	<i>a</i>	0.5	$(5.6 \pm 0.8) \times 10^8$	$(3.7 \pm 0.5) \times 10^{15}$	39 ± 9	[88]
4-hydroxyphenol	HOC <sub>6</sub> H <sub>4</sub> OH	<i>a</i>	0.5	$(1.6 \pm 0.6) \times 10^9$			[85] [87]
2-nitrophenol	HOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	<i>a</i>	0.5	$(2.3 \pm 0.4) \times 10^7$			[88]
4-nitrophenol	HOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	<i>a</i>	0	$(7.1 \pm 0.4) \times 10^7$			[87]
2,4-dinitrophenol	HOC <sub>6</sub> H <sub>3</sub> (NO <sub>2</sub> ) <sub>2</sub>	<i>a</i>	0	$(5.3 \pm 0.6) \times 10^7$			[87]
2-phenylphenol	HOC <sub>6</sub> H <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> )	<i>a</i>	0.5	$(2.4 \pm 0.4) \times 10^8$			[88]
2-chlorophenol	HOC <sub>6</sub> H <sub>4</sub> Cl	<i>a</i>	0.5	$(2.9 \pm 0.3) \times 10^8$			[88]
4-chlorophenol	HOC <sub>6</sub> H <sub>4</sub> Cl	<i>a</i>	0.5	$(1.0 \pm 0.4) \times 10^9$			[88]
2-bromophenol	HOC <sub>6</sub> H <sub>4</sub> Br	<i>a</i>	0.5	$(2.7 \pm 0.1) \times 10^8$			[88]
4-bromophenol	HOC <sub>6</sub> H <sub>4</sub> Br	<i>a</i>	0.5	$(1.7 \pm 0.2) \times 10^9$			[88]
2-fluorophenol	HOC <sub>6</sub> H <sub>4</sub> F	<i>a</i>	0.5	$(5.5 \pm 0.4) \times 10^8$			[88]
2-cyanophenol	HOC <sub>6</sub> H <sub>4</sub> CN	<i>a</i>	0.5	$(3.1 \pm 0.3) \times 10^8$			[88]
4-aminophenol	HOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<i>a</i>	0.5	$(8.1 \pm 0.3) \times 10^8$			[88]
4-ethoxyphenol	HOC <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> CH <sub>3</sub>	<i>a</i>	0.5	$(8.0 \pm 0.4) \times 10^8$			[88]
2-nitro-4-methylphenol	HOC <sub>6</sub> H <sub>3</sub> (NO <sub>2</sub> )CH <sub>3</sub>	<i>a</i>	0	$(1.0 \pm 0.1) \times 10^8$			[87]
2,6-dinitro-4-methylphenol	HOC <sub>6</sub> H <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	<i>a</i>	0	$(1.4 \pm 0.2) \times 10^8$			[87]
NO <sub>3</sub> + Benzoic Acids							
benzoic acid	C <sub>6</sub> H <sub>5</sub> COOH	<i>a</i>	0	$(6.5 \pm 1.3) \times 10^7$	$(4.9 \pm 0.2) \times 10^9$	13 ± 2	[85] [87]
4-hydroxybenzoic acid	HOCC <sub>6</sub> H <sub>4</sub> OH	<i>a</i>	1	$(5.0 \pm 1.3) \times 10^8$			[85] [87]
3-nitrobenzoic acid	HOCC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	<i>a</i>	0	$(2.0 \pm 0.6) \times 10^7$			[87]
4-nitrobenzoic acid	HOCC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	<i>a</i>	1	$(2.0 \pm 0.9) \times 10^7$			[85] [87]
4-cyanobenzoic acid	HOCC <sub>6</sub> H <sub>4</sub> CN	<i>a</i>	1	$(2.7 \pm 1.5) \times 10^7$			[85] [87]
4-methoxybenzoic acid	HOCC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	<i>a</i>	1	$(6.9 \pm 3.2) \times 10^8$			[85] [87]
4-methylbenzoic acid	HOCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	<i>a</i>	0	$(6.0 \pm 0.8) \times 10^8$	$(1.6 \pm 0.3) \times 10^{12}$	20 ± 4	[87]
3-nitro-4-methylbenzoic acid	HOCC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	<i>a</i>	1	$(3.3 \pm 0.4) \times 10^7$			[87]
NO <sub>3</sub> + Inorganic Compounds							
chlorate anion	ClO <sub>3</sub> <sup>-</sup>	<i>a</i>		$k_f = (9.0 \pm 1.2) \times 10^3$ $k_b = (8.3 \pm 1.0) \times 10^2$ $K = 42 \pm 6$			[89]
iodide anion	I <sup>-</sup>	<i>c</i>		$(4.6 \pm 0.5) \times 10^9$ <sup>f</sup>			[90]
chloride	Cl <sup>-</sup>	<i>b</i>		$k_f = (3.5 \pm 0.5) \times 10^8$ $K = 3.5 \pm 0.5$			[91]
NO <sub>3</sub> + Amino Acids							
β-phenylalanine	HOOCCH(NH <sub>2</sub> )-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>d</i>		$(3.1 \pm 0.1) \times 10^7$			[92]
histidine	HOOCCH(NH <sub>2</sub> )-CH <sub>2</sub> C <sub>3</sub> N <sub>2</sub> H <sub>3</sub>	<i>d</i>		$(1.5 \pm 0.2) \times 10^7$			[92]
arginine	HOOCCH(NH <sub>2</sub> )(CH <sub>2</sub> ) <sub>3</sub> -NHC(NH <sub>2</sub> )(NH)	<i>d</i>		$(6.5 \pm 0.3) \times 10^6$			[92]
glutamine	HOOCCH(NH <sub>2</sub> )(CH <sub>2</sub> ) <sub>2</sub> -C(O)NH <sub>2</sub>	<i>d</i>		$(2.2 \pm 0.1) \times 10^5$			[92]
leucine	HOCC <sub>3</sub> H <sub>10</sub> NH <sub>2</sub>	<i>d</i>		$(2.1 \pm 0.4) \times 10^5$			[92]
proline	HOCC <sub>4</sub> NH <sub>4</sub>	<i>d</i>		$(1.6 \pm 0.2) \times 10^5$			[92]
threonine	HOOCCH(NH <sub>2</sub> )-CH(CH <sub>3</sub> )OH	<i>d</i>		$(1.1 \pm 0.1) \times 10^5$			[92]
serine	HOOCCH(NH <sub>2</sub> )CH <sub>2</sub> OH	<i>d</i>		$(5.8 \pm 0.3) \times 10^4$			[92]
valine	HOOCCH(NH <sub>2</sub> )CH(CH <sub>3</sub> ) <sub>2</sub>	<i>d</i>		$(5.2 \pm 0.5) \times 10^4$			[92]
hydroxyproline	HOCC <sub>4</sub> NH <sub>7</sub> OH	<i>d</i>		$(5.1 \pm 0.4) \times 10^4$			[92]
aspartic acid	HOOCCH(NH <sub>2</sub> )-CH <sub>2</sub> COOH	<i>d</i>		$(3.5 \pm 0.2) \times 10^3$			[92]
2-aminobutyric acid	HOOCCH(NH <sub>2</sub> )CH <sub>2</sub> CH <sub>3</sub>	<i>d</i>		$(3.4 \pm 0.3) \times 10^3$			[92]
alanine	HOOCCH(NH <sub>2</sub> )CH <sub>3</sub>	<i>d</i>		$(1.7 \pm 0.1) \times 10^3$			[92]
glycine	HOOCCH <sub>2</sub> NH <sub>2</sub>	<i>d</i>		$(1.5 \pm 0.2) \times 10^3$			[92]

<sup>a</sup> Laser flash photolysis. <sup>b</sup> Pulse radiolysis. <sup>c</sup> Wetted-wall flow tube. <sup>d</sup> Flash photolysis. <sup>e</sup> At  $T = 292 \pm 1$  K. <sup>f</sup> At  $T = 273 \pm 1$  K.

**Table 6. Comparison of Rate Constants for NO<sub>3</sub> Reactions with Anions at 273 K Determined by Means of a Wetted-Wall Technique and Corresponding Literature Data**

reactant	$k_a^a$ L mol <sup>-1</sup> s <sup>-1</sup>	$k_b^b$ L mol <sup>-1</sup> s <sup>-1</sup>	$k_c$ L mol <sup>-1</sup> s <sup>-1</sup> direct studies	ratios of rate constants	
				$k_c/k_a$	$k_c/k_b$
HSO <sub>3</sub> <sup>-</sup>	$2.9 \times 10^7$	$3.2 \times 10^8$	$7.2 \times 10^8$ [97]	24.8	2.3
SO <sub>3</sub> <sup>2-</sup>	$1.8 \times 10^7$	$2.0 \times 10^8$	$2.6 \times 10^8$ [97]	14.4	1.3
HCOO <sup>-</sup>	$1.4 \times 10^5$	$1.6 \times 10^6$	$2.6 \times 10^7$ [93]	185.5	16.3
			$2.5 \times 10^7$ [86] <sup>c</sup>	178.6	15.6
CH <sub>3</sub> COO <sup>-</sup>	$1.1 \times 10^5$	$1.2 \times 10^6$	$9.1 \times 10^5$ [93]	8.3	0.75
OH <sup>-</sup>	$2.1 \times 10^6$	$2.3 \times 10^7$	$4.1 \times 10^7$ [97]	20.5	2.3

<sup>a</sup>  $k_a$  is the rate constant obtained by Imamura et al.<sup>96</sup> using the rate constant for the reaction of NO<sub>3</sub> with Cl<sup>-</sup> given by Exner et al.<sup>97</sup> as the reference. <sup>b</sup> After Imamura et al.<sup>96</sup> based on Buxton et al.<sup>98</sup> Estimated using the rate constant for the reaction of NO<sub>3</sub> with Cl<sup>-</sup> ( $k_{292\text{ K}} = 3.4 \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup> obtained by Buxton et al.<sup>98</sup>) derived for  $T = 273$  K using a correcting factor  $f = k(273\text{ K})/k(292\text{ K})$  using the T-dependence of Exner et al., 1992.<sup>97</sup> <sup>c</sup> Estimated for  $T = 273$  K using a correcting factor  $f = k(273\text{ K})/k(292\text{ K})$  using the T-dependence of Exner et al., 1994.<sup>93</sup>

constants that were calculated by applying the rate constant for the reaction of NO<sub>3</sub> with chloride determined at  $T = 292$  K and the T-dependence of Exner et al.<sup>97</sup> as other T-dependences have not been provided up to now.

The correction of all data by Imamura still does not lead to a fully consistent set of rate constants when compared to the former measurements of Exner et al.<sup>93,97</sup> However, the discrepancies become much smaller. This might indicate that the reaction of NO<sub>3</sub> with chloride might be significantly faster than previously thought. Further investigations are necessary here; see section 3.6.2.

Apparently, the application of a wetted wall reactor for the indirect determination of NO<sub>3</sub> radical rate constants in aqueous solution is a very promising technique but still needs further detailed characterization including the best possible characterization of the kinetic data of the reference reaction to be applied. Very recently, Poskrebyshev et al.<sup>91</sup> investigated the reaction of NO<sub>3</sub> with chloride as Buxton et al.<sup>98</sup> did in 1999. These radical conversion reactions are treated in more detail in section 3.6.2.

A variety of NO<sub>3</sub> reactions with substituted phenols have been studied to better understand a possible role of NO<sub>3</sub> in aqueous phase production of nitrophenols from phenols, or, more generally, the formation of nitroaromatics from aromatics in the presence of NO<sub>x</sub> and aqueous particles in the troposphere.

A number of NO<sub>3</sub> reaction rate constants for p-substituted phenols has been published.<sup>87</sup> More recently, a number of rate constants for the reactions of the corresponding o-substituted<sup>88</sup> phenols has also been determined as can be seen from Table 5. Benzoic acids have been found in urban rainwater, and hence the possibility exists that these compounds may, to a certain extent, be degraded in cloud droplets and aqueous aerosol particles, which has been the motivation to also study the reactivity of these compounds with NO<sub>3</sub>.<sup>87</sup>

From the data obtained for the reactions of NO<sub>3</sub> with the substituted phenols and benzoic acids, it can be explored whether the measured rate constants are related to the electron density of the aromatic system. If this is the case, electron transfer from the aromatic system may significantly contribute to the measured rate constant. Regardless of the exact mechanism, the logarithm of the measured rate constant should be a function of the Hammett parameter  $\sigma_p^+$  for the

para-substituted compounds and  $\sigma_o^+$  for the ortho-phenols. The latter parameter is related to the well established  $\sigma_p^+$  data (cf. Leffler and Grunwald<sup>99</sup> or Hansch et al.<sup>100</sup>) by the expression

$$\sigma_o^+ = 0.66\sigma_p^+ \quad (\text{V})$$

as it has been suggested by Jonsson et al.<sup>101</sup>

The resulting plots are shown in Figure 8. In part A of the figure the regression of the six points with the largest  $\sigma_o^+$  leads to

$$\log(k_{2\text{nd}}/\text{L mol}^{-1} \text{ s}^{-1}) = 8.83 - 2.03 \sigma_o^+ \quad (\text{VI})$$

with  $n = 6$  and  $r = 0.77$  for  $\sigma_o^+ \geq -0.1$  and the limiting value of

$$\log(k_{2\text{nd}}^{\text{limit}}/\text{L mol}^{-1} \text{ s}^{-1}) = 8.52 \text{ or } k_{2\text{nd}}^{\text{limit}} = 3.3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \quad (\text{VII})$$

For the para-substituted phenols the following parameters result:

$$\log(k_{2\text{nd}}/\text{L mol}^{-1} \text{ s}^{-1}) = 9.36 - 1.65 \sigma_p^+, n = 5, r = 0.92 \quad (\text{VIII})$$

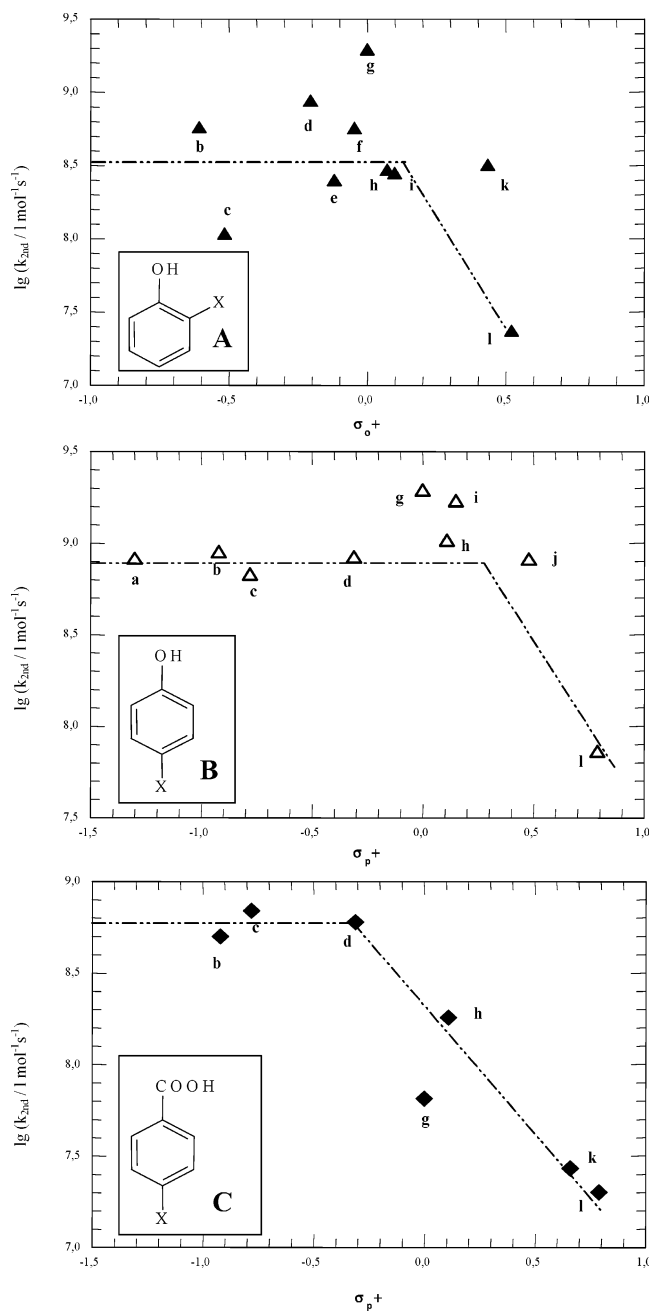
$$\log(k_{2\text{nd}}^{\text{limit}}/\text{L mol}^{-1} \text{ s}^{-1}) = 8.895 \text{ or } k_{2\text{nd}}^{\text{limit}} = 7.9 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \quad (\text{IX})$$

Finally, for the p-substituted benzoic acids the result is

$$\log(k_{2\text{nd}}/\text{L mol}^{-1} \text{ s}^{-1}) = 8.22 - 1.21 \sigma_p^+, n = 5, r = 0.92 \quad (\text{X})$$

$$\log(k_{2\text{nd}}^{\text{limit}}/\text{L mol}^{-1} \text{ s}^{-1}) = 8.77 \text{ or } k_{2\text{nd}}^{\text{limit}} = 5.9 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \quad (\text{XI})$$

As can be seen, in all three cases, about the same limiting rate constant  $k_{2\text{nd}}^{\text{limit}}$  is reached which is found at least in the region of mixed reaction control. Obviously, a saturation behavior is observed, even if the diffusion limit for the reaction of NO<sub>3</sub> with the hydroxyphenols or the hydroxybenzoic acids is calculated to be  $k_{\text{diff}} = 7.5 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> and  $k_{\text{diff}} = 7.6 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup> applying the Smoluchowski equation.<sup>102,103</sup>



**Figure 8.** Hammett-plot for the reaction of nitrate radical with (A) ortho-, (B) para-substituted phenols, and (C) para-substituted benzoic acids, where X- is (a)  $-\text{NH}_2$ ; (b)  $-\text{OH}$ ; (c)  $-\text{OCH}_3$ ; (d)  $-\text{CH}_3$ ; (e)  $-\text{C}_6\text{H}_5$ ; (f)  $-\text{F}$ ; (g)  $-\text{H}$ ; (h)  $-\text{Cl}$ ; (i)  $-\text{Br}$ ; (j)  $-\text{OC}_2\text{H}_5$ ; (k)  $-\text{CN}$ ; (l)  $-\text{NO}_2$  (See Table 5).

The obtained eqs VI–XI may be applied for the prediction of rate constants for reactions of the nitrate radical with the given substituted aromatic compounds in aqueous solution.

The electronic effect of the substituents could influence (i) reactions occurring according to an electron-transfer mechanism by changing the electron density of the aromatic ring as well as (ii) influence the OH bond strengths of the phenolic moiety in the case of the ortho- and para-substituted phenols.

Hence, in the case of the substituted phenols, both electron transfer for the ring as well as abstraction of the phenolic H is possible, whereas the observed

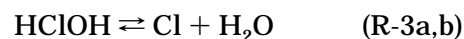
behavior in the case of the substituted benzoic acids indicates that electron transfer is the dominating mechanism. Therefore, in the plots of Figure 8, in the region of about  $\sigma_p^+ < 0.2$  H-abstraction, both from the phenolic and the substituent group, is competing with electron transfer for the phenols substituted with electron-donating groups. At higher  $\sigma_p^+$  electron transfer is suggested to be the predominant mechanism. In particular, the 2-cyanophenol has very high bond dissociation energy for the phenolic H atom ( $371.3 \text{ kJ mol}^{-1}$ <sup>104</sup>), which results in an only small contribution ( $< 7\%$ ) of the H-abstraction channel to the observed rate constant.

In conclusion of this treatment of recent studies of reactions of  $\text{NO}_3$  with organic compounds in solution, it should be mentioned that Venkatachalapathy and Ramamurthy<sup>92</sup> studied the reaction of  $\text{NO}_3$  with amino acids in acidic aqueous solution by means of flash photolysis.

### 3.4. Chlorine-Containing Radicals

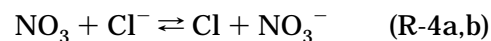
Table 7 summarizes recent data obtained for reactions of the chlorine atom and the dichloride radical anion in aqueous solution.

It has been speculated that reactions of chlorine atoms might play a role in tropospheric aqueous phase chemistry. However, recent modeling with an extended version<sup>109</sup> of the CAPRAM 2.4<sup>110</sup> mechanism indicates that Cl even in marine particles is formed in rather low concentrations. Cl atoms as a reactive species in cloud droplets and aerosols could only be formed as secondary radicals from precursor radicals of higher oxidizing power. Hence, Cl formation can only follow the OH pattern during daytime or the formation of  $\text{NO}_3$  at night. As it is known, OH in tropospheric aqueous particles results from both the direct phase transfer from the gas phase as well as in situ formation by a variety of different thermal and chemical sources. Daytime formation of Cl atoms will be strongly influenced by the presence of possible reactants other than chloride anions. In strongly polluted aqueous particles, OH will be scavenged by inorganic and organic reactants, preventing the effective formation of Cl from the series of equilibria which has been before in detail<sup>1,111,105</sup> and very recently<sup>107</sup> discussed, i.e.,



It should be noted again that this reaction sequence can only lead to the production of Cl when protons are present in a concentration high enough to make the formation of HClOH and its subsequent decomposition possible.

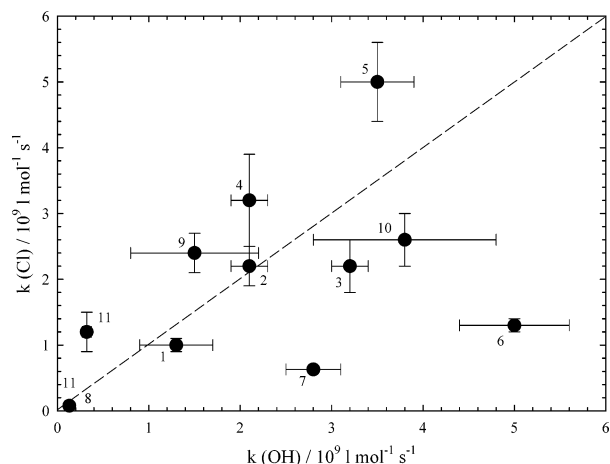
During nighttime Cl will only be formed in significant amounts from the reaction of  $\text{NO}_3$  with chloride, viz.



**Table 7. Kinetic Data for Reactions of Aqueous Phase Chlorine-Containing Radicals (Cl and Cl<sub>2</sub><sup>-</sup>)**

reactant <sup>a</sup>	formula	exp techn	pH	$k_{298K}$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$A$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$E_A$ (kJ mol <sup>-1</sup> )	refs
<b>Cl + Organic Compounds</b>							
methanol (1)	CH <sub>3</sub> OH	<i>b</i>	5.4	(1.0 ± 0.1) × 10 <sup>9</sup>	(7.9 ± 0.3) × 10 <sup>14</sup>	34 ± 6	[82]
		<i>c</i>		(1.0 ± 0.2) × 10 <sup>9</sup>		12 ± 2	[105]
ethanol (2)	CH <sub>3</sub> CH <sub>2</sub> OH	<i>b</i>	5.4	(2.2 ± 0.3) × 10 <sup>9</sup>	(4.6 ± 0.4) × 10 <sup>12</sup>	19 ± 7	[82]
				(1.7 ± 0.3) × 10 <sup>9</sup>		15 ± 2	[105]
1-propanol (3)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	<i>b</i>	5.4	(2.2 ± 0.4) × 10 <sup>9</sup>	(5.0 ± 0.4) × 10 <sup>12</sup>	19 ± 7	[82]
2-propanol (4)	(CH <sub>3</sub> ) <sub>2</sub> CHOH	<i>b</i>	5.4	(3.2 ± 0.7) × 10 <sup>9</sup>	(2.8 ± 0.3) × 10 <sup>13</sup>	23 ± 8	[82]
				(1.5 ± 0.1) × 10 <sup>9</sup>		17 ± 1	[105]
2-butanol (5)	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>3</sub>	<i>b</i>	5.4	(5.0 ± 0.6) × 10 <sup>9</sup>			[82]
<i>tert</i> -butyl alcohol (6)	(CH <sub>3</sub> ) <sub>3</sub> COH	<i>b</i>	5.4	(6.2 ± 0.3) × 10 <sup>8</sup>		21 ± 2	[105]
				(1.5 ± 0.1) × 10 <sup>9</sup>			[82]
hydrated formaldehyde	CH <sub>2</sub> (OH) <sub>2</sub>	<i>b</i>	5.4	(1.4 ± 0.3) × 10 <sup>9</sup>	(4.7 ± 0.3) × 10 <sup>13</sup>	26 ± 6	[82]
				(1.4 ± 0.1) × 10 <sup>9</sup>			[105]
acetaldehyde (7)	CH <sub>3</sub> CH(O)	<i>b</i>		(6.3 ± 0.4) × 10 <sup>8</sup>		15 ± 2	[105]
propionaldehyde	C <sub>2</sub> H <sub>5</sub> CH(O)	<i>b</i>		< 5 × 10 <sup>6</sup>			[105]
acetone (8)	CH <sub>3</sub> C(O)CH <sub>3</sub>	<i>b</i>	5.5	(7.8 ± 0.7) × 10 <sup>7</sup>			[82]
2-butanone (9)	CH <sub>3</sub> C(O)C <sub>2</sub> H <sub>5</sub>	<i>b</i>	5.4	(2.4 ± 0.3) × 10 <sup>8</sup>			[82]
formic acid	HCOOH	<i>b</i>	1	(2.8 ± 0.3) × 10 <sup>9</sup>	(8.9 ± 1.4) × 10 <sup>12</sup>	20 ± 6	[82]
				(1.3 ± 0.1) × 10 <sup>8</sup>		9 ± 1	[105]
formate	HCOO <sup>-</sup>	<i>b</i>	6	(4.2 ± 0.5) × 10 <sup>9</sup>		16 ± 2	[105]
acetic acid	CH <sub>3</sub> COOH	<i>b</i>	1	(1.0 ± 0.2) × 10 <sup>8</sup>	(1.3 ± 0.1) × 10 <sup>15</sup>	41 ± 11	[82]
				(3.2 ± 0.2) × 10 <sup>7</sup>		8 ± 1	[105]
acetate	CH <sub>3</sub> COO <sup>-</sup>	<i>b</i>	6	(3.7 ± 0.4) × 10 <sup>9</sup>		14 ± 2	[105]
propionic acid (11)	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	<i>b</i>	1	(1.2 ± 0.3) × 10 <sup>9</sup>	(6.4 ± 0.6) × 10 <sup>16</sup>	44 ± 10	[82]
isobutyric acid	C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> H	<i>b</i>	1	(1.7 ± 0.3) × 10 <sup>9</sup>	(5.7 ± 0.3) × 10 <sup>13</sup>	26 ± 4	[82]
diethyl ether	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	<i>b</i>	5.8	(1.3 ± 0.1) × 10 <sup>9</sup>			[82]
methyl- <i>tert</i> -butyl ether	CH <sub>3</sub> OC <sub>4</sub> H <sub>9</sub>	<i>b</i>	5.4	(1.3 ± 0.1) × 10 <sup>9</sup>			[82]
methyl formate	CH <sub>3</sub> CO <sub>2</sub> H	<i>c</i>	4	(2.0 ± 0.1) × 10 <sup>7</sup>			[86]
ethyl formate	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	<i>c</i>	4	(7.2 ± 0.2) × 10 <sup>7</sup>			[86]
methyl acetate	CH <sub>3</sub> C(O)OCH <sub>3</sub>	<i>c</i>	4	(1.4 ± 0.1) × 10 <sup>7</sup>			[86]
ethyl acetate	C <sub>2</sub> H <sub>5</sub> C(O)OCH <sub>3</sub>	<i>c</i>	4	(8.0 ± 0.7) × 10 <sup>7</sup>			[86]
tetrahydrofuran (10)	C <sub>4</sub> H <sub>8</sub> O	<i>b</i>	5.4	(2.6 ± 0.4) × 10 <sup>9</sup>			[86]
methyl chloride	CH <sub>3</sub> Cl	<i>b</i>	5.4	(2.3 ± 0.5) × 10 <sup>8</sup>			[86]
methylene chloride	CH <sub>2</sub> Cl <sub>2</sub>	<i>b</i>	5.4	(4.7 ± 0.3) × 10 <sup>6</sup>			[86]
benzene	C <sub>6</sub> H <sub>6</sub>	<i>c</i>	2.5–3	6.0 × 10 <sup>9</sup>			[106]
<b>Cl + Inorganic Compounds</b>							
nitrite anion	NO <sub>2</sub> <sup>-</sup>	<i>c</i>		(5.0 ± 0.2) × 10 <sup>9</sup>			[105]
azide anion	N <sub>3</sub> <sup>-</sup>	<i>c</i>		(5.2 ± 0.4) × 10 <sup>9</sup>			[105]
nitrate anion	NO <sub>3</sub> <sup>-</sup>	<i>c</i>		(1.0 ± 0.1) × 10 <sup>8</sup>			[105]
chlorate anion	ClO <sub>3</sub> <sup>-</sup>	<i>c</i>		(5.0 ± 0.1) × 10 <sup>8</sup>			[105]
sulfate anion	SO <sub>4</sub> <sup>2-</sup>	<i>c</i>		(1.7 ± 0.2) × 10 <sup>8</sup>			[105]
hydrogen carbonate anion	HCO <sub>3</sub> <sup>-</sup>	<i>c</i>		(2.4 ± 0.5) × 10 <sup>9</sup>			[105]
thiocyanate anion	SCN <sup>-</sup>	<i>c</i>		(5.3 ± 0.3) × 10 <sup>9</sup>			[105]
hydrogen sulfite anion	HSO <sub>3</sub> <sup>-</sup>	<i>c</i>		(2.8 ± 0.3) × 10 <sup>9</sup>			[105]
water	H <sub>2</sub> O	<i>b</i>	2	$k_f = (3.6 ± 0.2) × 10^3$ $k_b = (2.6 ± 0.6) × 10^{10}$ $K = (1.4 ± 0.3) × 10^{-7}$			[107]
chloride	Cl <sup>-</sup>	<i>b</i>		$k_f = (7.8 ± 0.8) × 10^9$ $k_b = (5.2 ± 0.3) × 10^4$ $s^{-1}$ $K = (1.4 ± 0.2) × 10^5$ $M^{-1}$			[107]
hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	<i>b</i>		(2.0 ± 0.3) × 10 <sup>9</sup>			[107]
<b>Cl<sub>2</sub><sup>-</sup> + Organic Compounds</b>							
methanol	CH <sub>3</sub> OH	<i>b</i>	4	(5.1 ± 0.3) × 10 <sup>4</sup>	(5.1 ± 0.9) × 10 <sup>12</sup>	46 ± 13	[81]
ethanol	C <sub>2</sub> H <sub>5</sub> OH	<i>b</i>	4	(1.2 ± 0.2) × 10 <sup>5</sup>			[81]
				(1.8 ± 0.3) × 10 <sup>5</sup>			[23]
1-propanol	C <sub>3</sub> H <sub>7</sub> OH	<i>b</i>	4	(1.0 ± 0.1) × 10 <sup>5</sup>			[81]
2-propanol	C <sub>3</sub> H <sub>7</sub> OH	<i>b</i>	4	(1.9 ± 0.3) × 10 <sup>5</sup>			[81]
hydrated formaldehyde	CH <sub>2</sub> (OH) <sub>2</sub>	<i>b</i>	4	(3.6 ± 0.5) × 10 <sup>4</sup>	(7.9 ± 0.7) × 10 <sup>10</sup>	36 ± 5	[81]
acetone	CH <sub>3</sub> C(O)CH <sub>3</sub>	<i>b</i>	4	(1.4 ± 0.1) × 10 <sup>3</sup>			[81]
formic acid	HCOOH	<i>b</i>	0	(8.0 ± 1.4) × 10 <sup>4</sup>	(2.0 ± 0.1) × 10 <sup>10</sup>	37 ± 2	[81]
formate	HCOO <sup>-</sup>	<i>b</i>	5.8	(1.3 ± 0.3) × 10 <sup>6</sup>			[81]
acetic acid	CH <sub>3</sub> COOH	<i>b</i>		(1.5 ± 0.8) × 10 <sup>3</sup>		41 ± 11	[81]
diethyl ether	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	<i>b</i>	4	(4.0 ± 0.2) × 10 <sup>5</sup>			[81]
methyl- <i>tert</i> -butyl ether	CH <sub>3</sub> OC <sub>4</sub> H <sub>9</sub>	<i>b</i>	4	(7.0 ± 1.0) × 10 <sup>4</sup>			[81]
tetrahydrofuran	C <sub>4</sub> H <sub>8</sub> O	<i>b</i>	4	(4.8 ± 0.6) × 10 <sup>5</sup>			[81]
benzene	C <sub>6</sub> H <sub>6</sub>	<i>c</i>	2.5–3	1.2 × 10 <sup>10</sup>			[106]
<b>Cl<sub>2</sub><sup>-</sup> + Inorganic Compounds</b>							
water	H <sub>2</sub> O	<i>b</i>		$k[H_2O] < 100$ s <sup>-1</sup>			[107] [108]
hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	<i>b</i>		(1.4 ± 0.2) × 10 <sup>6</sup>			[107] [108]

<sup>a</sup> Numbers in parentheses refer to the plot  $k(Cl) = f(k(OH))$  (Figure 9). <sup>b</sup> Laser flash photolysis at 248 nm. <sup>c</sup> Pulse radiolysis technique.



**Figure 9.** Plot  $k(\text{OH})$  vs  $k(\text{Cl})$  for different compounds. Numbering refers to the numbers of Table 7.

As already mentioned, the rate constants of (R-4a,b) are subject to discussion, cf. section 3.6.2.

To make the consideration of chlorine atom chemistry in atmospheric aqueous solution at all possible, Buxton et al.<sup>105</sup> and Wicktor et al.<sup>82</sup> investigated its reactions over the last several years. As can be seen from Table 7, the agreement of the room temperature data is very reasonable in most cases, but significant differences are observed with regard to the T-dependences studied. A more detailed discussion on this issue is given by Wicktor et al.<sup>82</sup>

The absolute values of the rate constants for the reaction of OH and of Cl against the same reactants are compared in Figure 9. Here, data from our laboratory have been used for the OH reactions<sup>24,54</sup> and the Cl reactions.<sup>82</sup>

As can be seen, there is no significant correlation resulting from the plot with a correlation coefficient of  $r = 0.5$ . Qualitatively, the reaction rate constants of both radicals are not strongly different where OH is somewhat more reactive than Cl. As a rough estimate, the same reactivity as the one for OH may be assumed for a given reactant if measured data are not available.

It should be noted that apparently some reactions of the dichloride radical anion do not occur by the direct reaction of  $\text{Cl}_2^-$  with the reactant but can be explained by the back dissociation of  $\text{Cl}_2^-$  into Cl and chloride and the subsequent reaction of the chlorine atom. However, this is not true for all reactions of  $\text{Cl}_2^-$ , and the rate coefficients as listed in Table 7 contain valuable kinetic information even when some  $\text{Cl}_2^-$  reactions do not occur directly; see Wicktor et al.<sup>82</sup>

Two very recent papers of Yu and Barker<sup>107,108</sup> contain information on the chemical reaction system developing following the formation of OH from  $\text{H}_2\text{O}_2$  photolysis and its reaction with chloride, i.e., (R-1). Both papers thoroughly consider available literature and confirm a number of previous studies. Among various other data, a rate constant for the reaction of Cl with  $\text{H}_2\text{O}_2$  is obtained. Finally, Alegre et al.<sup>106</sup> studied the reaction of both Cl and  $\text{Cl}_2^-$  with benzene in aqueous solution.

### 3.5. Sulfur-Oxy Radical Anions $\text{SO}_x^-$ ( $x = 3, 4, 5$ )

Studies of the reaction of the  $\text{SO}_x^-$  radical anions ( $x = 3, 4, 5$ ) are mainly motivated by the formation of all of these radicals in the oxidation of S(IV) in atmospheric liquid particles.<sup>44</sup> The initiation of the chain sequence involving all three species might occur thermally or by other radicals such as the primary species OH and  $\text{NO}_3$  or the secondary halogen containing radicals and radical anions.

Effective reactions of the sulfur-oxy radical anions with organics of either anthropogenic or biogenic origin might (i) interrupt the S(IV) oxidation chain and therefore enhance S(IV) lifetimes and transport ranges and (ii) contribute to the conversion or degradation of organics. Given this motivation, a variety of reactions of the sulfate radical anion ( $\text{SO}_4^-$ ) has been studied, the results of which are summarized in Table 8.

The reactants  $\alpha$ -pinene,  $\alpha$ -terpenol, *cis*-verbenol, verbenone, and myrtenal are terpenes that are emitted from coniferous trees and might be expected to undergo conversion reactions also in aqueous particles. However, the efficiency of such processes might be drastically reduced by a low aqueous phase solubility of the compound in question. Methacrolein is a degradation product of isoprene which is emitted in huge quantities from deciduous trees. The cited studies deliver rate constants for the reactions of the organic compounds with both  $\text{SO}_4^-$  as well as OH; see Table 3. In many cases also T-dependences for the rate constants are reported.<sup>66</sup>

The reactions of  $\text{SO}_4^-$  and  $\text{SO}_5^-$  with transition metal ions listed in Table 8 might also be of interest for atmospheric liquid-phase mechanism development because the redox cycling of the TMI is crucial for the  $\text{HO}_x$  budget in solution. There are new kinetic data for the reaction of both the sulfate radical anion as well as the peroxydisulfate radical anion with iron (II) and manganese (II).

Das<sup>121</sup> has recently studied the role of the peroxydisulfate radical anion in the chain oxidation of S(IV). A number of valuable rate constants have been determined in this study either experimentally or by fitting data to a complex mechanism.

### 3.6. Radical Interconversion Reactions

Radical interconversion might lead to a cascade of radical reactions within aqueous atmospheric particles starting from the generation of OH in the gas phase and OH formation in the liquid phase, e.g., by nitrate photolysis or thermal reactions such as the Fenton reaction between  $\text{H}_2\text{O}_2$  and Fe(II). Nitrate radicals will be produced solely in the gas phase and mainly from the reaction of  $\text{NO}_2$  with ozone. Other radicals as they are also discussed in this review may be referred to as secondary radicals and include the sulfur-oxy radical anions ( $\text{SO}_x^-$ ,  $x = 3, 4, 5$ ), the halogen-containing radicals ( $\text{X}/\text{X}_2^-$ ,  $\text{X} = \text{Cl}, \text{Br}$ ) and, the carbonate radical anion ( $\text{CO}_3^-$ ) which is not treated here.

#### 3.6.1. Reaction of $\text{NO}_3$ with Water

It has been repeatedly suggested that nitrate radicals might be converted into hydroxyl radicals by



**Table 8. Kinetic Data for Reactions of  $\text{SO}_x^-$  ( $x = 3, 4, 5$ ) Radical Anions in Aqueous Solution**

reactant	formula	exp techn	pH	$k_{298\text{K}}$ ( $\text{L mol}^{-1} \text{s}^{-1}$ )	$A$ ( $\text{L mol}^{-1} \text{s}^{-1}$ )	$E_A$ ( $\text{kJ mol}^{-1}$ )	refs
<b><math>\text{SO}_4^-</math> + Nonaromatic Organic Compounds</b>							
<i>tert</i> -butanol	$(\text{CH}_3)_3\text{COH}$	<i>b</i>	5–6	$(7.8 \pm 0.2) \times 10^5$			[112]
methyl formate	$\text{CH}_3\text{OC(O)H}$	<i>a</i>	3–5	$(8.1 \pm 0.1) \times 10^5$			[86]
ethyl formate	$\text{CH}_3\text{CH}_2\text{OC(O)H}$	<i>a</i>	3–5	$(5.2 \pm 0.3) \times 10^6$			[86]
methyl acetate	$\text{CH}_3\text{C(O)OCH}_3$	<i>a</i>	3–5	$(5.0 \pm 1.3) \times 10^4$			[86]
ethyl acetate	$\text{CH}_3\text{CH}_2\text{OC(O)CH}_3$	<i>a</i>	3–5	$(1.2 \pm 0.1) \times 10^6$			[86]
$\alpha$ -pinene	$\text{C}_{10}\text{H}_{16}$	<i>a</i>	4	$(3.1 \pm 0.1) \times 10^9$		$8.8 \pm 1.3$	[66]
$\alpha$ -terpenol	$\text{C}_{10}\text{H}_{18}\text{O}$	<i>a</i>	4	$(4.1 \pm 0.1) \times 10^9$		$13.4 \pm 0.6$	[66]
<i>cis</i> -verbenol	$(\text{C}_5\text{H}_5\text{CO})\text{CH}_2(\text{CH}_3)_3$	<i>a</i>	4	$(3.2 \pm 0.2) \times 10^9$		$10 \pm 1$	[66]
verbenone	$(\text{C}_5\text{H}_5\text{CO})\text{CH}_2(\text{CH}_3)_3$	<i>a</i>	4	$(1.6 \pm 0.1) \times 10^9$		$6.1 \pm 1$	[66]
myrtenal	$\text{C}_{10}\text{H}_{16}\text{O}$	<i>a</i>	4	$(1.9 \pm 0.1) \times 10^9$		$7.5 \pm 1$	[66]
methacrolein	$\text{CH}_2\text{C}(\text{CH}_3)\text{C(O)H}$	<i>a</i>	4	$(1.2 \pm 0.1) \times 10^9$			[66]
hydroxymethane sulfonate (hms)	$\text{CH}_2(\text{OH})\text{SO}_3\text{H}$	<i>b</i>		$(1.3 \pm 0.2) \times 10^6$			[74]
<b><math>\text{SO}_4^-</math> + Aromatic Organic Compounds</b>							
benzene	$\text{C}_6\text{H}_6$	<i>a</i>		$(6.4 \pm 2.5) \times 10^8$			[113]
methylbenzene	$\text{C}_6\text{H}_5\text{CH}_3$	<i>a</i>		$(1.3 \pm 0.6) \times 10^9$			[113]
1,4-dimethylbenzene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	<i>a</i>		$(2.7 \pm 0.9) \times 10^9$			[113]
4-methylphenol	$\text{HOC}_6\text{H}_4\text{CH}_3$	<i>a</i>		$(2.8 \pm 0.8) \times 10^9$			[113]
1,3,5-trimethylbenzene	$\text{C}_6\text{H}_3(\text{CH}_3)_3$	<i>a</i>		$(1.3 \pm 0.4) \times 10^9$			[113]
<b><math>\text{SO}_4^-</math> + Inorganic Compounds</b>							
chlorate ion	$\text{ClO}_3^-$	<i>a</i>		$k_f = (4.0 \pm 0.5) \times 10^6$ $k_b = (5 \pm 5) \times 10^5$			[89]
chloride	$\text{Cl}^-$	<i>b</i>	5–6	$k_f = (6.1 \pm 0.2) \times 10^8$ $k_b = (2.1 \pm 0.1) \times 10^8$ $K = (2.9 \pm 0.2)$ $3.6 \times 10^8$			[112]
peroxodisulfate ion	$\text{S}_2\text{O}_8^{2-}$	<i>b</i>	5–6	$< 1.5 \times 10^3$			[114]
peroxohydrogensulfate	$\text{HSO}_5^-$	<i>b</i>		$1.0 \times 10^6$			[112]
peroxosulfate	$\text{SO}_5^{2-}$	<i>b</i>		$1.0 \times 10^8$			[108]
<b><math>\text{SO}_4^-</math> + TMI</b>							
$\text{Fe}^{2+}$		<i>b</i>	3–5	$(4.6 \pm 0.2) \times 10^9$		$-(18 \pm 2)$	[115]
$\text{Mn}^{2+}$		<i>b</i>	3–5	$(1.4 \pm 0.01) \times 10^7$		$34 \pm 2$	[115] [116]
$\text{Cr}^{3+}$		<i>b</i>	3	$K = (7.6 \pm 1.9) \times 10^2$ <sup>c</sup> $k_{\text{ETR}} = (4 \pm 1) \times 10^4 \text{s}^{-1}$ <sup>d</sup>			[117]
			3.7	$K = (4.2 \pm 0.5) \times 10^3$ <sup>c</sup> $k_{\text{ETR}} = (6 \pm 1) \times 10^4 \text{s}^{-1}$ <sup>d</sup>			[117]
<b><math>\text{SO}_3^-</math> + TMI</b>							
$\text{Fe}^{2+}$		<i>b</i>	4	$K = (278 \pm 39)$ <sup>c</sup> $k_{\text{ETR}} = (3.05 \pm 0.32) \times 10^4 \text{s}^{-1}$ <sup>d</sup>			[118]
<b><math>\text{SO}_5^-</math> + Miscellaneous</b>							
$\text{Fe}^{2+}$		<i>a</i>	4.5	$(4.3 \pm 2.4) \times 10^7$			[119]
$\text{Mn}^{2+}$		<i>a</i>	4.5	$(4.6 \pm 1.0) \times 10^6$			[119]
hydroperoxyl radical	$\text{HO}_2$	<i>b</i>		$(1.7 \pm 0.1) \times 10^9$			[120]
peroxomonosulfate radical anion	$\text{SO}_5^-$	<i>b</i>	3.5–12	$(2.2 \pm 0.3) \times 10^8$			[121]
peroxomonosulfate radical anion	$\text{SO}_5^-$	<i>b</i>	3.5–12	$(2.1 \pm 0.3) \times 10^8$			[121]

<sup>a</sup> Laser flash photolysis at 248 nm. <sup>b</sup> Pulse radiolysis technique. <sup>c</sup> Stability constant of the complex, adduct formation is followed by electron transfer (ET). <sup>d</sup> Decay rate constant of the adduct formed by TMI and  $\text{SO}_4^-$  respectively  $\text{SO}_5^-$ .

the reaction of  $\text{NO}_3$  with water, i.e.,



This reaction, however, is endothermic with a gas-phase reaction enthalpy of  $\Delta H_R = +73.5 \text{ kJ mol}^{-1}$  and a corresponding solution phase value of the Gibbs free enthalpy of reaction of  $\Delta G_R = +51.4 \text{ kJ mol}^{-1}$ . Because highly different values for the rate constant of reaction (R-5a) have recently been published, we have also undertaken a study of this system by investigating the decay rates of  $\text{NO}_3$  when produced from different precursors in aqueous solution and monitored with the established long path laser absorption technique.<sup>93,97</sup> All results currently available on the reaction of  $\text{NO}_3$  with water are summarized in Table 9.

From the results of the investigation in our laboratory with the purest chemicals applied at the lowest possible concentration, i.e., at the photolysis of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  in 1 M  $\text{HNO}_3$  (Suprapur grade) at  $\lambda = 248 \text{ nm}$  a first-order decay of  $\text{NO}_3$  in aqueous solution with a rate constant of  $k_{\text{first}} = (52 \pm 2) \text{ s}^{-1}$  was measured. This decay rate is by far lower as it could be expected by the other studies available in the literature and summarized in Table 9. From this slowest decay of  $\text{NO}_3$  measured directly in water we hence derive a second-order rate coefficient of

$$k_5 \leq (0.90 \pm 0.04) \text{ L mol}^{-1} \text{ s}^{-1}$$

at  $T = 298 \text{ K}$  and  $I = 1 \text{ mol L}^{-1}$ . Even for this value contaminations cannot be ruled out and hence the

**Table 9. Radical Interconversion Reactions in Aqueous Solution**

reaction	$k_{2nd}$ (L mol <sup>-1</sup> s <sup>-1</sup> ) $K_{eq}$	ionic strength $I$ (mol L <sup>-1</sup> )	ref
R-5 $\cdot\text{OH} + \text{HNO}_3 \xrightleftharpoons[k_{5b}]{k_{5a}} \text{H}_2\text{O} + \text{NO}_3\cdot$	$k_{5a} = (8.6 \pm 1.3) \times 10^7$ <sup>a</sup>	$I \rightarrow 0$	[77]
	$k_{5b} = (3 \pm 1) \times 10^2$ <sup>a</sup>		
	$K_5 = (2.5 \pm 0.4) \times 10^8$ <sup>a</sup>		
	$k_{5a} = 5.3 \times 10^7$ <sup>a</sup>	0.2–1.5	[122]
	$k_{5b} = 5.3 \times 10^5$ <sup>a</sup>		
	$K_5 = 100$ <sup>a</sup>		
	$k_{5b} = (8.3 \pm 0.3)$ <sup>b</sup>	0.22	this work
	$k_{5b} = (12.1 \pm 0.3)$ <sup>c</sup>	0.22	
	$k_{5b} = (11.2 \pm 0.3)$ <sup>d</sup>	0.22	
	$k_{5b} = (8.2 \pm 0.2)$ <sup>e</sup>	0.22	
	$k_{5b} = (11.7 \pm 0.2)$ <sup>f</sup>	0.22	
	$k_{5b} = (5.2 \pm 0.5)$ <sup>g</sup>	0.22	
	$k_{5b} = (7.5 \pm 0.3)$ <sup>h</sup>	0.22	
	$k_{5b} = (5.9 \pm 0.2)$ <sup>i</sup>	0.22	
	$k_{5b} = (5.8 \pm 0.3)$ <sup>j</sup>	0.14	
$k_{5b} = (5.3 \pm 0.3)$ <sup>k</sup>	0.14		
$k_{5b} = (4.5 \pm 0.3)$ <sup>l</sup>	1.00		
$k_{5b} = (0.90 \pm 0.04)$ <sup>m</sup>	<b>1.00</b>		
$k_{5b} = 6$ <sup>n</sup>	0	[94]	
$k_{5b} = 1.5$ <sup>o</sup>	0		
$k_{5b} = 23^{+30-13}$ <sup>p</sup>	0–0.5		
$k_{5b} < 0.05$ <sup>p</sup>	$I \rightarrow 0$	[123]	
R-4 $\text{NO}_3\cdot + \text{Cl}^- \xrightleftharpoons[k_{4b}]{k_{4a}} \text{NO}_3^- + \text{Cl}^-$	$k_{4a} = (3.50 \pm 0.5) \times 10^8$	0.1–1	[91]
	$K_4 = 3.5 \pm 0.5$ <sup>q</sup>		
	$k_{4a} = (3.40 \pm 0.11) \times 10^8$ <sup>a</sup>	$I \rightarrow 0$	[98]
	$k_{4b} = (1.02 \pm 0.04) \times 10^8$		
	$K_4 = 3.33 \pm 0.24$		

<sup>a</sup> Experimental results fitted using a complex reaction mechanism. <sup>b</sup> LFP of KNO<sub>3</sub> (>99%)/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (>99%) at  $\lambda = 351$  nm; <sup>c</sup> LFP of NaNO<sub>3</sub> (>99%)/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (>99%) at  $\lambda = 351$  nm. <sup>d</sup> LFP of LiNO<sub>3</sub> (>99.5%)/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (>99%) at  $\lambda = 351$  nm. <sup>e</sup> LFP of NaNO<sub>3</sub> (>99%)/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (99.99%) at  $\lambda = 351$  nm. <sup>f</sup> LFP of NaNO<sub>3</sub> (>99%)/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (>99%) at  $\lambda = 351$  nm. <sup>g</sup> LFP of KNO<sub>3</sub> (>99.5%)/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (>99%) at  $\lambda = 351$  nm. <sup>h</sup> LFP of KNO<sub>3</sub> (>99%)/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (>99%) at  $\lambda = 351$  nm. <sup>i</sup> LFP of KNO<sub>3</sub> (>99.5%)/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (>99.99%) at  $\lambda = 351$  nm. <sup>j</sup> LFP of KNO<sub>3</sub> (>99.5%)/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (>99.99%) at  $\lambda = 248$  nm. <sup>k</sup> LFP of KNO<sub>3</sub> (>99%)/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (>99.99%) at  $\lambda = 248$  nm. <sup>l</sup> LFP of HNO<sub>3</sub> 0.02 M (Suprapur grade) at  $\lambda = 248$  nm. <sup>m</sup> LFP of  $3 \times 10^{-4}$  M (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> in 1 M HNO<sub>3</sub> (Suprapur grade) at  $\lambda = 248$  nm. <sup>n</sup> Estimated at 298 K. <sup>o</sup> Estimated at 273 K. <sup>p</sup> Derived from uptake coefficient ( $\gamma$ ) experimentally determined. <sup>q</sup> Where  $k_{4b} = (1.02 \pm 0.04) \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup> is adopted from Buxton et al.<sup>98</sup>

given rate constant still represents an upper limit. This upper limit of the rate constant is more than a factor of 6 smaller than the smallest value determined before by Rudich et al.<sup>94</sup> It is still larger than the value suggested by Thomas et al.<sup>123</sup> in a recently published uptake study, which might be due to remaining impurities NO<sub>3</sub> is able to react with.

The real value of  $k_5$  may still be considerably smaller. When the Evans-Polanyi type correlation for H-abstraction reactions of the nitrate radical in aqueous solution which has been developed and described before,<sup>85</sup> i.e.,

$$\log(k_{\text{NO}_3}^{\text{H}}(\text{aq})/\text{mol}^{-1} \text{ s}^{-1}) = (-0.084 \pm 0.014)\text{BDE} / \text{kJ mol}^{-1} + (38.5 \pm 5.6) \quad (\text{XII})$$

with  $r = 0.89$  and  $n = 37$  is applied, a rate constant of only  $k_5 = 4.7 \times 10^{-4}$  L mol<sup>-1</sup> s<sup>-1</sup> results, given the O–H bond dissociation energy of H<sub>2</sub>O as (bond dissociation energy) BDE (H<sub>2</sub>O) = 498 kJ mol<sup>-1</sup>.<sup>124</sup> It is concluded that a recently postulated efficient conversion of NO<sub>3</sub> into OH radicals in atmospheric aqueous systems<sup>78</sup> suppressing a NO<sub>3</sub> aqueous phase

chemistry cannot be of importance in view of the experimental findings discussed here and in line with thermochemistry.

### 3.6.2. Reaction of NO<sub>3</sub> with Chloride

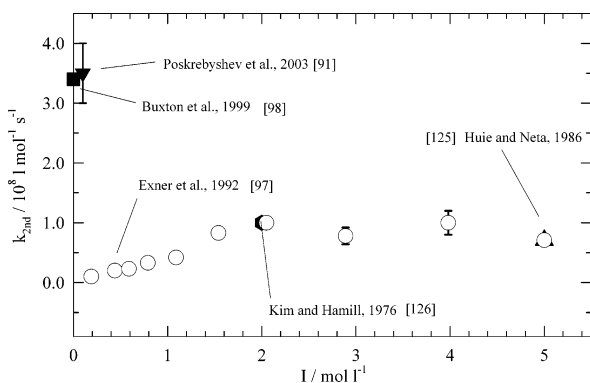
Recent kinetic data on the equilibrium reaction between NO<sub>3</sub> and Cl are also summarized in Table 9. A coherent picture on the rate coefficient of the forward reaction seemed to exist a few years ago, when the initial discrepancy between the measurements of Exner et al.<sup>97</sup> and the former measurements of Neta and Huie<sup>125</sup> and Kim and Hamill<sup>126</sup> was attributed to the different ionic strengths applied in the experiments. More recently, Buxton et al.<sup>98</sup> have suggested that the forward reaction rate constant  $k_{4a}$  is much higher than previously thought. This situation is graphically represented by the data shown in Figure 10 where the forward rate constant  $k_{4a}$  is plotted as a function of ionic strength.

As can be seen, the most recent data point exceeds the former data points obtained from direct measurements at low ionic strength by about a factor of 35 and is also much higher than the data obtained earlier in pulse radiolysis experiments. However, the study by Buxton needs to be regarded as thoroughly

**Table 10. Ionic Strength Effects**

radical	reactant	$k_{(I=0)}$ (uncorrected) (L mol <sup>-1</sup> s <sup>-1</sup> )	$k_{(I=\infty)}$ (uncorrected) (L mol <sup>-1</sup> s <sup>-1</sup> )	$k_{(I=0)}$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$k_{(I=\infty)}$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$b$ (L mol <sup>-1</sup> )	$I_{\text{eff}}$ (L mol <sup>-1</sup> )	ref	symb
OH	acetone			$(2.0 \pm 0.5) \times 10^8$	$(4.4 \pm 0.8) \times 10^8$	$(0.13 \pm 0.16)$	0–1.94	[128]	●
	2-propanol			$(2.1 \pm 0.2) \times 10^9$	$(4.4 \pm 0.3) \times 10^9$	$(0.22 \pm 0.12)$	0–2.11	[24]	▲
	2-butanol			$(3.5 \pm 0.4) \times 10^9$	$(6.3 \pm 0.8) \times 10^9$	$(0.25 \pm 0.15)$	0–2.11	[24]	▼
NO <sub>3</sub>	chloride <sup>a,b</sup>	$(9.1 \pm 0.9) \times 10^6$ $(3.40 \pm 0.11) \times 10^{8c}$	$(9.1 \pm 1.0) \times 10^7$	$(8.2 \pm 0.2) \times 10^6$	$(8.8 \pm 1.0) \times 10^7$	$(0.82 \pm 0.17)$ $(0.24 \pm 0.001)^c$	0.18–2.6	[85] [129]	△
	formate	$(3.6 \pm 1.0) \times 10^7$	$(2.3 \pm 0.3) \times 10^8$	$(4.2 \pm 0.2) \times 10^7$	$(2.3 \pm 0.3) \times 10^8$	$(0.61 \pm 0.45)$	0.18–2.4	[85] [129]	○
	oxalic acid			$(1.4 \pm 0.4) \times 10^8$	$(2.0 \pm 0.4) \times 10^8$	$(0.22 \pm 0.17)$	0.18–3.1	[85] [129]	□
	acetaldehyde			$(1.8 \pm 0.6) \times 10^6$	$(7.8 \pm 0.4) \times 10^6$	$(0.28 \pm 0.18)$	0.18–3.1	[85] [129]	●
	benzoic acid			$1.5 \times 10^7$	$1.2 \times 10^8$	$(0.50 \pm 0.97)$	1.3–3.1	[87]	■
	phenol			$4.1 \times 10^8$	$2.6 \times 10^9$	$(0.41 \pm 0.23)$	1.14–2.8	[87]	▲
Cl	hydrated form-aldehyde			$(1.4 \pm 0.3) \times 10^9$	$(9.8 \pm 0.5) \times 10^8$	$-(0.14 \pm 0.07)$	0–1.83	[82]	●
	methanol			$(1.0 \pm 0.1) \times 10^9$	$(3.5 \pm 0.9) \times 10^8$	$-(0.33 \pm 0.07)$	0–1.83	[82]	■
Cl <sub>2</sub> <sup>-</sup>	hydrated form-aldehyde	$(3.6 \pm 0.1) \times 10^4$	$(1.9 \pm 0.5) \times 10^4$	$(3.7 \pm 0.1) \times 10^4$	$(2.0 \pm 0.5) \times 10^4$	$-(0.11 \pm 0.27)$	0.1–2.62	[81]	○
	methanol	$(5.5 \pm 0.2) \times 10^4$	$(1.8 \pm 0.9) \times 10^4$	$(5.8 \pm 0.3) \times 10^4$	$(1.9 \pm 0.9) \times 10^4$	$-(0.35 \pm 0.58)$	0.1–2.62	[81]	□

<sup>a</sup> Imamura et al.<sup>96</sup> did observe only a much smaller effect on the rate constant upon addition of NaNO<sub>3</sub> at concentrations of [NaNO<sub>3</sub>] = 0, 0.11, and 1.0 mol L<sup>-1</sup>. <sup>b</sup> Poskrebyshev et al.<sup>91</sup> did not observe a significant effect upon the second-order rate constant upon addition of 2 mol L<sup>-1</sup> NaClO<sub>4</sub>. <sup>c</sup> Experimental results fitted using a complex reaction mechanism; the method of I-adjustment is subject to discussion, see text.



**Figure 10.** Ionic strength dependence for the forward reaction of NO<sub>3</sub> with Cl<sup>-</sup>.

conducted. The equilibrium constant obtained is consistent with one-electron reduction potentials of  $E^\circ(\text{Cl}/\text{Cl}^-) = 2.41$  V as suggested by Stanbury<sup>127</sup> and of  $E^\circ(\text{NO}_3/\text{NO}_3^-) = 2.44$  V, which is somewhat lower than the respective value earlier suggested by Stanbury but appears highly feasible.

The discussion of Buxton et al.<sup>98</sup> about possible reasons for the discrepancy to the earlier measurements by Exner et al.<sup>97</sup> should be substantiated by a reexamination of the equilibrium (R-4a,b) extending the range of chloride concentrations, by another direct study of the reverse reaction (R-4b) and, finally, by consideration of the stated findings on the reaction of NO<sub>3</sub> with water. Reasons for the discrepancies toward the older pulse-radiolytic studies still remain unclear as stated already by Buxton and co-workers.

### 3.7. Studies of Ionic Strength Effects in Radical Reactions

Whereas many aqueous phase kinetic data are available for diluted electrolyte solutions which might be used for the description of chemical reactions in the droplets of clouds and fog, the available kinetic data describing reactions of atmospheric relevance

at higher electrolyte concentrations as encountered in deliquescent aerosol particles are much more sparse. These aspects are discussed in the IGAC I&S volume.<sup>3</sup>

A sum parameter describing the overall charge-weighted ion concentration of an electrolyte solution is ionic strength (I) defined as:

$$I = \frac{1}{2} \sum_{i=1}^n c_i Z_i^2 \quad (\text{XIII})$$

Where  $c_i$  and  $Z_i$  are the concentration in mol L<sup>-1</sup> and the charge of the ion  $i$ , respectively.

As in experimental studies often the ionic strength of a solution is adjusted by the addition of an electrolyte such as NaClO<sub>4</sub>, and at elevated concentrations the effect of incomplete dissociation of these salts has to be considered. Hence, the real ion content of such an electrolyte solution is given by the so-called effective ionic strength ( $I_{\text{eff}}$ ), which can be calculated for a 1:1 electrolyte, here in the form of a sodium salt NaX, as follows:

$$I_{\text{eff}} = -\frac{1}{2K_{\text{Ass}}} + \sqrt{\frac{0.25}{K_{\text{Ass}}^2} + \frac{1}{K_{\text{Ass}}}[\text{NaX}]_0} \quad (\text{XIV})$$

where  $K_{\text{Ass}}$  is the ion association equilibrium constant for the reaction (R-6):

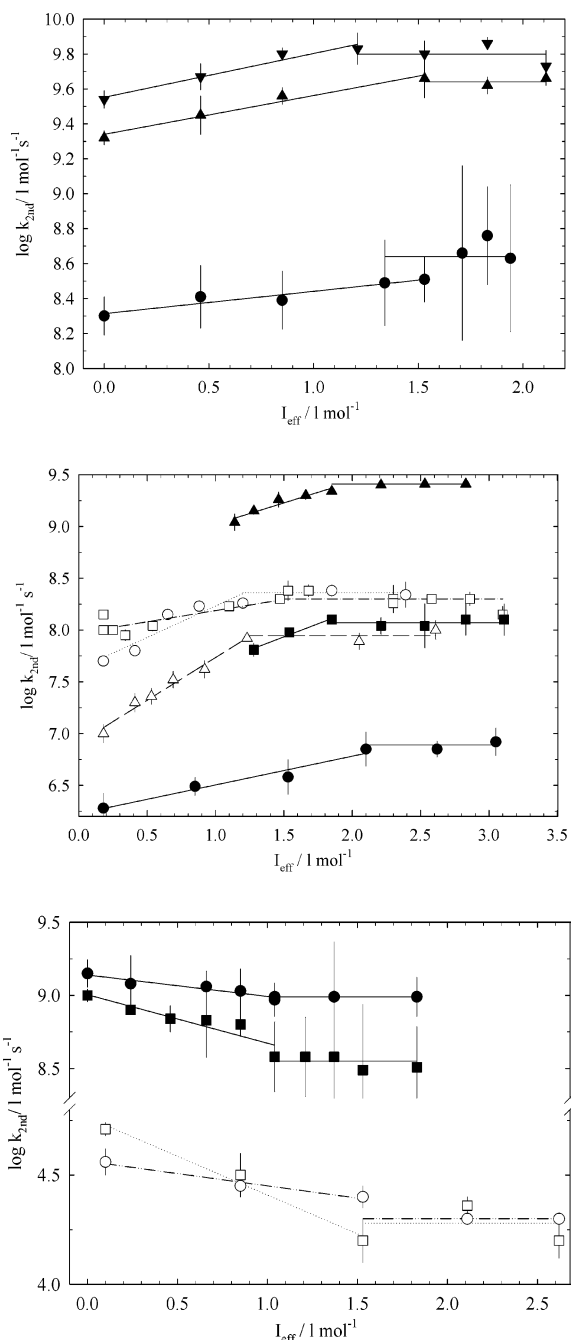


Data on  $K_{\text{Ass}}$  are discussed later in this section. Some most important values are summarized in Table 11.

Over the last several years, dependences of the rate coefficients of reactions of OH, NO<sub>3</sub>, and Cl mainly with organic substances have been investigated. The results of these studies are summarized in Table 10 and graphically represented in Figure 11 in a plot of the logarithm of the observed rate constants versus effective ionic strength.

**Table 11. Ion Association Equilibrium Constants<sup>a</sup>**

ion associations equilibrium	$K$ (L mol <sup>-1</sup> )	remarks	refs
Anionic Reactants			
Na <sup>+</sup> + Cl <sup>-</sup> ⇌ NaCl	0.16	average of literature values	[147–149]
Na <sup>+</sup> + HCOO <sup>-</sup> ⇌ HCOONa	0.11	calc. after Fuoss [150]	
Na <sup>+</sup> + CH <sub>3</sub> COO <sup>-</sup> ⇌ CH <sub>3</sub> COONa	0.14	calc. after Fuoss [150]	
Radical Anions			
Na <sup>+</sup> + Cl <sub>2</sub> <sup>-</sup> ⇌ NaCl <sub>2</sub>	0.18	calc. after Fuoss [150]	
Electrolytes for I-Adjustment			
Na <sup>+</sup> + ClO <sub>4</sub> <sup>-</sup> ⇌ NaClO <sub>4</sub>	0.20		[151]
Na <sup>+</sup> + NO <sub>3</sub> <sup>-</sup> ⇌ NaNO <sub>3</sub>	1.73	average of literature values	[152] [153]

<sup>a</sup>  $T = 298$  K.

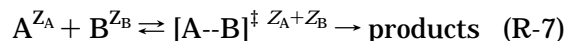
**Figure 11.** Ionic strength dependencies: (top) (OH): (▼): 2-BuOH,<sup>24</sup> (▲): 2-PrOH,<sup>24</sup> (●): acetone.<sup>128</sup> (middle) (NO<sub>3</sub>): (▲): phenol,<sup>87</sup> (■): benzoic acid,<sup>87</sup> (●): acetaldehyde,<sup>85,129</sup> (Δ): chloride,<sup>85,129</sup> (○): formate,<sup>85,129</sup> (□): oxalic acid.<sup>85,129</sup> (bottom) (Cl: filled symbols<sup>82</sup>, Cl<sub>2</sub><sup>-</sup>: open symbols<sup>81</sup>): (●): hydr. formaldehyde,<sup>81</sup> (■): methanol.<sup>81</sup>

In all of the radical reactions, the effect of ionic strength follows a saturation curve leading to higher observed rate coefficients with increasing effective ionic strengths for both the reactions between an anion and a neutral species but also for the reactions between two neutral species. It has to be noted that for reactions of the dichloride radical anion with neutral reactants, i.e., methanol and hydrated formaldehyde, a decrease of the observed rate constant with increasing ionic strength is observed.<sup>81</sup>

Primary kinetic salt effects are observed when the reaction rate constant of a given reaction is changed by the influence of the ionic medium. This might apply to three classes of reactions, i.e., (a) ion–ion reactions, (b) reactions of an ion with a neutral molecule, and (c) reactions between two neutral species.

For clarity, it is suggested to address the kinetic salt effect occurring in ion–ion reactions as primary kinetic salt effect (type I) and the corresponding effect in reactions under participation of an uncharged species as primary kinetic salt effect (type II). This is to clearly separate these effects from the so-called secondary kinetic salt effect which usually describes the dependence of a solution phase equilibrium constant on the nature of the electrolyte.

If two species carrying the respective charges  $Z_A$  and  $Z_B$  react with each other according to



an activated complex with the charge  $Z^\ddagger = Z_A + Z_B$  is formed. According to transition state theory<sup>130</sup> and after Brønsted<sup>131,132</sup> and Bjerrum<sup>133</sup> the following expression for the rate constant is obtained:

$$k = k(I=0) \frac{\gamma_A \gamma_B}{\gamma_\ddagger} \quad (\text{XV})$$

with  $k$  being the observed rate constant and  $k(I=0)$  the rate constant at infinite dilution.  $\gamma_i$  are the activity coefficients for the species A and B ( $\gamma_A$ ,  $\gamma_B$ ) and for the activated complex ( $\gamma_\ddagger$ ). The term  $\gamma_A \gamma_B / \gamma_\ddagger$  is addressed as kinetic activity factor according to Brønsted. Taking the logarithm of eq XV results in

$$\log k = \log k(I=0) + \log \gamma_A + \log \gamma_B - \log \gamma_\ddagger \quad (\text{XVI})$$

Primary kinetic salt effects are occurring because the electrolyte composition of the solution influences all

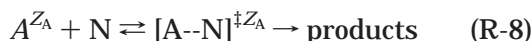
three activity coefficients occurring in eq XVI. For ion–ion reactions in diluted solutions, it is in most cases assumed that the dependences of all three  $\gamma$  can be expressed by the Debye–Hückel limiting law or its extensions, e.g., the expression suggested by Davies,<sup>134</sup> which consist of a two-term expression for  $\log \gamma_i$ , one of which is linear in  $I$ :

$$\log \gamma_i = -Z_i^2 A_{\text{DH}} \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (\text{XVII})$$

where  $A_{\text{DH}} = (e^2/4\pi\epsilon_r\epsilon_w k_B T)^{3/2} (2N_A/\pi^2)^{1/2}$  is the so-called Debye–Hückel constant or prefactor.

As all of the systems to be treated refer to reactions with at least one neutral reactant, primary kinetic salt effects of type I will not be further considered here.

For the systems of interest here, an ion A with the charge  $Z_A$  reacts with a neutral reactant N, i.e.,



As discussed before,<sup>1,85</sup> Debye and McAulay<sup>135</sup> derived an expression for the activity coefficient  $\gamma_i$  of a neutral species in solution when the activity coefficient of this neutral species is influenced by the ionic atmosphere surrounding the solute molecule:

$$\log \gamma_i = \alpha \frac{e^2}{\epsilon_w r k_B T} \sum c_j z_j^2 = bI \quad (\text{XVIII})$$

with  $\alpha$ : experimental constant,  $e$ : elementary charge,  $\epsilon_w$ : dielectric constant of water,  $k_B$ : Boltzmann constant,  $T$ : temperature,  $r$ : radius of the ion,  $c_j$ : concentration of supporting electrolyte ions,  $z_j$ : charge of supporting electrolyte ions,  $b$ : kinetic salting coefficient, and  $I$ : ionic strength.

It should be added that the classical study by Debye and McAulay was refined in the 1960s by treatments such as those of Long and McDevit<sup>136</sup> and Conway et al.<sup>137</sup> Activity coefficients for neutral species might be derived from solubility measurement; see Shoor and Gubbins and references therein.<sup>138</sup> Solubilities are often expressed in terms of Setchenow coefficients; see Bockris et al.<sup>139</sup> Despite from empirical gas solubility data such as summarized by Fogg and Sangster,<sup>140</sup> salting coefficients might be obtained from the so-called “scaled particle theory” as introduced by Masterton and Lee.<sup>141</sup> In turn, solubility may be estimated based on property–solubility or structure–solubility relationships and, finally, by means of group contribution approaches; see the monograph by Reinhard and Drehfal<sup>142</sup> for an overview.

For a reaction of the type of (R-8), the activated complex has the same charge as the only participating charged reactant.

Equation XVI now modifies to

$$\log k = \log k(I=0) + (b_A + b_N - b_i)I/\text{mol L}^{-1} \quad (\text{XIX})$$

where  $b = \alpha e^2/\epsilon_w r k_B T = (b_A + b_N - b_i)$ , with  $b_A$  being the prefactor in a possible linear term in the descrip-

tion of the  $I$  dependence of the activity coefficient of the ion A. Such term is found in the Davies equation given above with  $b_A = -0.3$ . If the Debye–Hückel limiting law is used without extensions, then  $b_A = b_i = 0$ . According to eq XIX, for both the cases of primary kinetic salt effects of type II, i.e., reaction of one ion with a neutral species or a reaction between two neutral species, the logarithm of the observed rate constant should show a linear dependence on the ionic strength  $I$ . The slope derived from a plot  $\log k = f(I)$  then leads to the so-called kinetic salting coefficient  $b \equiv b_A + b_N - b_i$ . The kinetic salting coefficient might be compared with the thermodynamic salting coefficient for a neutral reactant which might be experimentally determined or theoretically calculated, e.g., by means of the so-called scaled particle theory.<sup>141,143</sup> If the kinetic salting coefficient for a reaction of a neutral species N and its thermodynamic salting coefficient for the same supporting electrolyte are in reasonable agreement, this indicates that the  $I$ -dependence of the rate constant for the reaction in question is dominated by the change in the activity coefficient of the neutral reactant N.

In case the kinetic and the thermodynamic salting coefficient deviate from each other, this means that other factors than only the change of the activity coefficient of the neutral reactant N influence the observed reaction rate constants. These factors include three thermodynamic possibilities:

- (i) Possible changes of the activity coefficient for the activated complex which differ from the change of the activity coefficient of the participating ion A;
- (ii) Ion pairing of the reactant ion;
- (iii) Ion pairing of the activated complex.

Effects (ii) and (iii) might lead to effect (i). Kinetically, these effects might correspond to

(iv) a change in reactivity because of changes in reaction barrier height because of ion–ion interaction, dipole–ion interaction, or ion pairing of the activated complex.

(v) a change of reactivity from the original ionic reactant to an ion-paired reactant.

Following a more qualitative discussion,<sup>85</sup> ionic strength effects in reactions of a neutral species and an ion might be deconvoluted kinetically following the suggestion of Olson and Simonson<sup>144</sup> into four elementary reactions, i.e., the equilibrium between the ion and its respective ion-pair and the two reactions of the neutral species with the ion and the ion-pair, here for a single-charged reactant anion  $A^-$ , the neutral reactant N and the supporting electrolyte cation, here, e.g.,  $\text{Na}^+$ :



with  $k_{\text{ip}}$  being the second-order rate constant of the ion-pair reaction, and  $k_{\text{nip}}$  being the second-order rate constant of the non ion-pair reaction. It should be

noted that the anion might be a radical anion such as  $\text{Cl}_2^-$  as well as a reactant ion such as formate.

The equilibrium constant for (R-10) is the association or ion pair stability constant  $K_{ip}$ , i.e.:

$$K_{ip}[\text{L mol}^{-1}] = \frac{[\text{NaA}]}{[\text{Na}^+][\text{A}^-]} \quad (\text{XX})$$

Data for  $K_{ip}$  can either be taken from the literature, e.g., from the IUPAC data compilations,<sup>145,146</sup> or they can be calculated by means of the Fuoss-Eigen equation:

$$K_{ip} = \frac{4\pi N_A r_{12}^3}{3000} \exp(-w(r)/k_B T) \quad (\text{XXI})$$

where  $N_A$ : Avogadro's number, with

$$w(r) = \frac{Z_1 Z_2 e^2}{\epsilon r_{12}(1 + \beta r_{12} I^{1/2})} \quad (\text{XXII})$$

and

$$\epsilon = \epsilon_w + 2\delta^*[\text{NaClO}_4] \quad (\text{XXIII})$$

with  $k_B$ : Boltzmann-constant,  $\beta$ : Debye-Hückel parameter,  $\beta(I=0, T=298 \text{ K}) = 3.29 \times 10^{-7} \text{ mol}^{-1/2} \text{ cm}^{-1}$ ,  $\epsilon_w$ : dielectric constant of water ( $\epsilon_w = 78.5$ ),  $\epsilon$ : dielectric constant of the electrolyte solution, and  $\delta^*$ : mean coefficient of dielectric constant extenuation of anion and cation of the electrolyte (here for  $\text{NaClO}_4$ ).  $r_{12}$ ,  $e$ , and  $k_B$  are to be used in the cgs-system here.

The ion association constant data applicable for the systems of Table 10 where ion-pairing can occur are listed in Table 11.

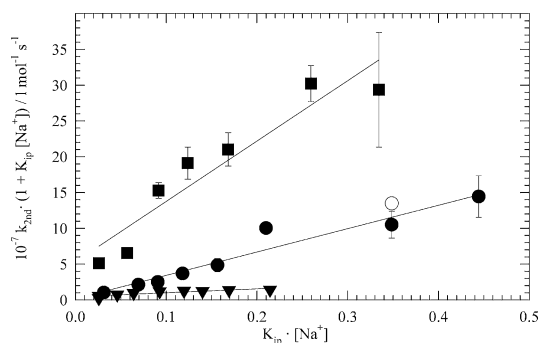
According to Olson und Simonson<sup>144</sup> the observed rate constant for a system such as (R-9)/(R-10)/(R-11) is

$$k_{\text{exp}} = \frac{k_{\text{nip}}}{1 + K_{ip}[\text{Na}^+]} + \frac{k_{ip} K_{ip}[\text{Na}^+]}{1 + K_{ip}[\text{Na}^+]} \quad (\text{XXIV})$$

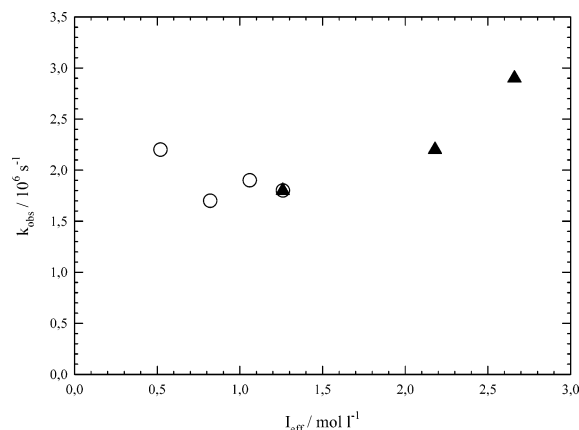
It follows from this expression that a plot of  $k_{\text{exp}}(1 + K_{ip}[\text{Na}^+])$  against  $K_{ip}[\text{Na}^+]$  leads to a straight line with the intercept  $k_{\text{nip}}$  and the slope  $k_{ip}$ . Hence, the reactions of  $\text{NO}_3$  with chloride, formate, and acetate and the reactions of  $\text{Cl}_2^-$  with methanol and hydrated formaldehyde were treated accordingly. The plots for the nitrate radical reactions are shown in Figure 12.

The results of the analysis for all three  $\text{NO}_3$  reactions and two  $\text{Cl}_2^-$  reactions are summarized in Table 12.

As can be seen from Table 12, the observed rate constants could be deconvoluted into  $k_{ip}$  and  $k_{\text{nip}}$ . Together with the respective ion association constants from Table 11, the ionic strength dependence of each of the five reactions can be fully described by a pure kinetic model consisting of four elementary reactions over a wide range of ionic strengths. It has to be mentioned here that the ionic strength effect on the rate constant of the reaction of  $\text{NO}_3$  with chloride is subject to discussion in the literature.<sup>91,96,98</sup>



**Figure 12.** Plot after Olson-Simonson for the primary kinetic salt effects (type II) in reactions of  $\text{NO}_3$  with anions,  $T = 298 \text{ K}$ . (●):  $\text{NO}_3$  + chloride, (○): data point from ref 126, (■):  $\text{NO}_3$  + formate, (▼):  $\text{NO}_3$  + acetate.



**Figure 13.** Effect of incomplete electrolyte dissociation in the study of Buxton et al.<sup>98</sup>

**Table 12. Analysis Results for the Primary Kinetic Salt Effect (type II) of Reactions with  $\text{NO}_3^-$  and  $\text{Cl}_2^-$ <sup>a</sup>**

reactant	main electrolyte	$k_{\text{nip}}$ ( $\text{L mol}^{-1} \text{ s}^{-1}$ )	$k_{ip}$ ( $\text{L mol}^{-1} \text{ s}^{-1}$ )	$r$
$\text{NO}_3^-$				
$\text{Cl}^-$	$\text{NaClO}_4$	$(1.7 \pm 19.4) \times 10^6$	$(3.3 \pm 0.9) \times 10^8$	0.97
$\text{HCOO}^-$	$\text{NaClO}_4$	$(5.3 \pm 6.2) \times 10^7$	$(8.4 \pm 3.3) \times 10^8$	0.95
$\text{CH}_3\text{COO}^-$	$\text{NaClO}_4$	$(4.5 \pm 2.9) \times 10^6$	$(5.5 \pm 2.5) \times 10^7$	0.89
$\text{Cl}_2^-$				
$\text{CH}_3\text{OH}$	$\text{NaClO}_4$	$(4.6 \pm 2.2) \times 10^4$	$(5.4 \pm 7.3) \times 10^4$	0.81
$\text{H}_2\text{C}(\text{OH})_2$	$\text{NaClO}_4$	$(3.7 \pm 0.3) \times 10^4$	$(2.2 \pm 0.9) \times 10^4$	0.97

<sup>a</sup>  $T = 298 \text{ K}$ .

Whereas Buxton et al.<sup>98</sup> obtained a significantly smaller kinetic salting coefficient than Exner et al.,<sup>97</sup> Imamura et al.<sup>96</sup> and very recently Poskrebyshev<sup>91</sup> et al. did not observe significant effects of ionic strength on this rate constant. Different explanations for this discrepancy are discussed in Buxton et al.<sup>98</sup> and Poskrebyshev et al.<sup>91</sup> The comment of the latter authors that possible impurities in  $\text{NaClO}_4$  are responsible for the effect observed by Exner et al. cannot be regarded valid as only the intercept in the plots of  $k_{\text{first}}$  against  $[\text{Cl}^-]$  would be affected and not the slope of the plots from which the second-order rate coefficients are derived.

A methodical problem in the study of Buxton et al.<sup>98</sup> is that ionic strength was not adjusted by  $\text{NaClO}_4$  only but either just by  $\text{NaNO}_3$  or by varying fractions of  $\text{NaClO}_4$  and  $\text{NaNO}_3$  as well while intending to keep the overall ionic strength at  $I = 4 \text{ mol}$

**Table 13. Effect of Incomplete Electrolyte Dissociation in the Study of Buxton et al.<sup>98</sup>**

electrolyte	added electrolyte (mol L <sup>-1</sup> )		$I_{\text{eff}}$ (mol L <sup>-1</sup> )	$k_{\text{obs}}^a$ (s <sup>-1</sup> )	sym
	NaNO <sub>3</sub>	NaClO <sub>4</sub>			
NaNO <sub>3</sub>	1.0		0.52	$2.2 \times 10^6$	○
	2.0		0.82	$1.7 \times 10^6$	○
	3.0		1.06	$1.9 \times 10^6$	○
	4.0		1.26	$1.8 \times 10^6$	○
NaNO <sub>3</sub> + NaClO <sub>4</sub>	1.0	3.0	2.66	$2.9 \times 10^6$	▲
	2.5	1.5	2.18	$2.2 \times 10^6$	▲
	4.0		1.26	$1.8 \times 10^6$	▲

<sup>a</sup> Obtained from Figure 6 in Buxton et al.<sup>98</sup>

L<sup>-1</sup>. However, incomplete dissociation of these salts has not been considered by these authors. With the ion association constants of Table 11 the initial concentrations used by Buxton et al.<sup>98</sup> could be corrected and the real effective ionic strengths were derived and are listed in Table 13.

As can be seen from the corrected data, when  $I$  is adjusted by NaNO<sub>3</sub> only, the range of real, effective ionic strengths covered decreases from  $1.0 \leq I \leq 4.0$  as intended by the authors to just  $0.52 \leq I_{\text{eff}} \leq 1.26$ . The combination of both electrolytes not only reduces the range of effective ionic strengths covered but also reverses the order of the data points leading to an increase of the observed first-order rate constant with  $I_{\text{eff}}$ . Overall, the added electrolytes seem to have an enhancing influence on the observed rate constant in the system different from the author's original statement. In view of these considerations, it is suggested that the data treatment of the  $I$ -dependent measurements of Buxton et al.<sup>98</sup> should be revised.

The approach outlined here for the treatment of primary kinetic salt effects (type 2) might help to describe effects that might become important in many atmospheric liquid particles which might not be easily considered as dilute aqueous solutions. It should be added that at present no data on primary kinetic salt effects (type 2) for reactions of OH with anions are available.

Because the description of the dependence of just a single observed reaction rate constant on a single varying electrolyte concentration requires the same effort as the study of the  $T$ -dependence of that reaction, the collection of a wider basis of measured ionic strength dependencies would be an enormous effort. Furthermore, it has been observed that the kinetic salt effects observed are also dependent on the type of electrolyte actually present in solution.<sup>98,154</sup> When applied to a single ion pairing mechanism, the kinetic model outlined here hence needs to be regarded a first approximation because it considers the nature of the supporting electrolyte only for its main ions. For complex ionic electrolytes as encountered in liquid atmospheric particles, multiple equilibria and reaction such as the sequence (R-9)/(R-10)/(R-11) could occur making a more detailed treatment very complicated.

Therefore, even the description of some of the most important radical reactions in an  $I$ -dependent manner in a more advanced aerosol model would first require a very significant amount of laboratory work. On the other hand, the treatment of reactions just by the application of the rate constants measured in

diluted solutions might introduce not accountable errors into aerosol models as some of them are currently applied. A resolution of this dilemma does unfortunately not seem to be readily available.

#### 4. Model Development

The ultimate goal of the determination of spectroscopic, kinetic, and mechanistic parameters for atmospheric processes in liquids is the use of the results in atmospheric multiphase models. To this end, parameters as reviewed here are used in constructing aqueous phase chemical mechanisms. Mechanisms of higher complexity occurred in the literature early with the studies of Chameides and Davis (1982),<sup>155</sup> Graedel and Goldberg (1983)<sup>156</sup> and Schwartz (1984)<sup>157</sup> followed by studies from the Hoffmann group in 1983<sup>158,159</sup> and 1986<sup>160,161</sup> and further refined by Jacob.<sup>162</sup> Somewhat later, these studies were followed by the study of Lelieveld and Crutzen (1991),<sup>163</sup> which fostered increased attention to the question of how clouds may be involved in tropospheric photochemistry. A complex reaction mechanism was put forward by Möller and Mauersberger in 1995.<sup>164</sup> Aerosol particles may significantly change gas-phase composition as has been demonstrated by Sander and Crutzen in 1996<sup>13</sup> for sea salt halogen activation. This topic is still intensively treated; see von Glasow et al.<sup>165,166</sup> and Herrmann et al.<sup>109</sup> for recent studies and references therein. Walcek et al.<sup>167</sup> demonstrated in 1997 that the effect of a given aqueous phase mechanism on gas phase composition is highly dependent on the actual gas-phase composition with regards to NO<sub>x</sub> and VOCs. This is especially true for the question if at all and to what extend the presence of aqueous droplets influences the gas phase concentration of ozone. These authors also studied the effect of aqueous phase composition and especially the effects of dissolved copper and iron on HO<sub>2</sub> and ozone.

Using a box model, Lelieveld and Crutzen<sup>163</sup> obtained decreasing ozone concentrations when cloud chemistry was considered. This effect was mainly due to lower ozone production rates in the gas phase. In addition, the decomposition of ozone in the liquid phase via the reaction with O<sub>2</sub><sup>-</sup> was identified as a direct loss process. Dentener and Crutzen (1993)<sup>168</sup> found comparable results considering aerosol chemistry, however, with smaller ozone reductions. More recently, Matthijsen et al. (1995)<sup>169</sup> showed that the destruction of ozone within the droplets is further reduced, when transition metal ions (TMI) such as iron and copper are included in the aqueous phase chemical mechanism, because HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> concentrations are strongly decreased in reactions with dissolved TMI. On the other hand, separation of HO<sub>2</sub> from the gas into the aqueous phase reduces ozone production via the reaction of NO with HO<sub>2</sub>. Liang and Jacob<sup>170</sup> in 1997 concluded that cloud chemistry perturbs ozone levels by less than 3% even in the tropics. Possible effects and uncertainties of the impact of cloud chemistry on tropospheric ozone have been recently discussed in a critical review by Jacob.<sup>171</sup>

It should be noted that many of the more recent mechanisms carry, in some cases, much more detail but still follow the basic philosophy of the first pioneering studies. Following the studies cited so far, the so-called chemical aqueous phase radical mechanism (CAPRAM) has been developed in its initial version CAPRAM 2.3,<sup>172</sup> which has very recently been extended and updated to CAPRAM 2.4.<sup>110</sup> A special mechanism is treating halogen chemistry as it might occur in marine aerosols and clouds and is coupling the nonradical halogen producing reactions to an extensive scheme of radical chemistry including halogen containing radicals.<sup>109</sup>

This mechanism is continuously further developed, and the respective material is available over the Internet.<sup>173</sup> Modifications or special applications of CAPRAM are available through the very recent studies of Leriche et al.<sup>174,175</sup> or Williams et al.<sup>176</sup>

Clearly, mechanism such as those mentioned here should be further extended, especially in areas where current coverage is incomplete. Whereas the inorganic conversions seem to be quite well understood, even the largest mechanisms do treat organic chemistry only up to compounds with two carbon atoms. An extension here is urgently needed and first efforts in this direction have been undertaken.<sup>177</sup> In the organic chemistry extension module applied by Ervens and Herrmann many reaction rate constants, especially for the reactions of the OH radical, which have been just recently determined and have been reviewed in the present contribution, were used to extend the organic chemistry module of CAPRAM to also begin to cover the chemistry of C<sub>3</sub> and C<sub>4</sub> organic compounds. It is interesting to note that such mechanism extensions will lead to the description of concentration–time profiles of many more compounds which can be measured in tropospheric aerosol and cloud field studies than was possible before. Further work in this respect is required and has to be based on the results of thoroughly conducted laboratory investigations as well as of correlations with extrakinetic data resulting from such studies.

## 5. Conclusion

Results of studies of liquid phase reaction have been reviewed in the present contribution which in part will lay the groundwork for further chemical mechanism construction for tropospheric cloud and aerosol chemistry models. On the basis of the single experimental data, it has been shown that correlations could be developed which actually enable the prediction of rate constants. Examples are the Evans-Polanyi type correlations for H-abstraction reactions of OH discussed here, those for other radicals available from literature, or the Hammett-type correlation for the reaction of NO<sub>3</sub> with substituted phenols. In view of the enormous complexity of the mixture of organic compounds in atmospheric aerosols and clouds, special attention should be paid to the development of such simple models and correlations.

In view of the wide range of electrolyte concentrations encountered in liquid atmospheric particles (cf. Table 1), a simple model has been suggested in the

present contribution to account for primary kinetic salt effects in reactions involving an ion and a neutral species. The ion-pairing model could lead a way to describe aqueous phase atmospheric chemical conversion involving most reactive and short-lived intermediates in dependence of the electrolyte medium which is then represented here by its main ions.

Further extension of the organic chemistry in tropospheric multiphase mechanisms will also lead to the question of how far such mechanisms are able to describe real atmospheric systems especially with regard to their organic chemistry when coupled to adequate physical and microphysical cloud and aerosol models. To, on one hand, validate chemical mechanisms and, on the other hand, interpret results from the field, so-called hill capped cloud or orographic cloud passage experiments have been performed before and are described in the literature for the 1990 Kleiner Feldberg cloud experiment<sup>178</sup> and the 1993 Great Dunn Fell cloud experiment.<sup>179</sup> A similar experiment is currently performed and analyzed in an ongoing German project (FEBUKO, see ref 180) with special emphasis on (i) assessing the budgets of organic particle constituents and (ii) to better understand the conversions of organic compounds in a complex multiphase system comprising the gas phase, aerosol particles and cloud droplets as encountered in the passage of an air parcel over a cloud-capped mountain. The better characterization of particle and cloud droplet composition will also lead the way for further laboratory investigations including liquid-phase kinetic studies.

Complex multiphase field experiments as well as advanced laboratory studies coupled by state-of-the-art multiphase modeling should be further conducted in the future with special emphasis on the processing of organic compounds by aerosols and clouds. This should lead to a better understanding of the role of liquid-phase reactions in atmospheric chemistry.

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