

## Free Radical ( $\text{NO}_3^\cdot$ , $\text{SO}_4^{\cdot-}$ , $\text{Cl}_2^{\cdot-}$ ) Oxidation Reactions of VOCs and their Degradation Products in the Atmospheric Aqueous Phase

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(Removal and Interconversions of Oxidants in the Atmospheric Aqueous Phase, Part 2)

### 1. Introduction

The influence of cloud and aerosol processes on the oxidation capacity of the tropospheric gas phase is still not well elucidated. The aqueous particle phase may change this entity by either uptake of radicals (lowering the gas phase oxidation capacity). Main objectives of this work were to determine the rate constants for the reaction of the  $\text{NO}_3^\cdot$ -radicals,  $\text{Cl}_2^{\cdot-}$ -radical anions and  $\text{SO}_4^{\cdot-}$ -radical anions with several organic compounds in aqueous solution. These compounds are key organic tropospheric compounds which are transferred from the gas phase into the tropospheric aqueous phase, i.e. into droplets of clouds, fog, rain and also in the aqueous phase of aerosols. Currently oxidation processes of organic key substances are not well described for reactions in aqueous solution. Due to high concentrations of aldehydes, terpenes, sulfur containing compounds and aromatic substances identified in various field experiments [1, 2] the concentration levels of the oxidants mentioned earlier may be significantly altered when reactions of the above compounds in aqueous solution are taken into consideration. The work was divided into three different parts. First the kinetic investigations of the reactions of  $\text{NO}_3^\cdot$ -radical with sulfur containing organics, i.e. with dimethylsulfoxide (DMSO), dimethylsulfone ( $\text{DMSO}_2$ ), with the aldehydes glyoxal, butanal and, trichloroacetaldehyde, with the isoprenes and terpenes isoprene,  $\alpha$ -pinene, R-(+)-limonene and with the products of the isoprene and terpene degradation methacrolein and pinonealdehyde.

In a second part the rate constants of the reactions of the  $\text{Cl}_2^{\cdot-}$ -radical anion with the sulfur containing organics dimethylsulfoxide, dimethylsulfone, methanesulfonic acid, methanesulfinic acid, with the aldehydes glyoxal, butanal and, trichloroacetaldehyde and with the substituted aromatics benzoic acid, phenol, 5-methyl-2-nitrophenol and 2,4-dinitrophenol have to be studied in aqueous solution.

The third part of the project was ascribed to the kinetic study of the reactions of the  $\text{SO}_4^{\cdot-}$ -radical anion with the sulfur containing organics dimethylsulfoxide, dimethylsulfone, methanesulfonic acid,

methanesulfinic acid and also the reactions with the substituted aromatics benzoic acid, phenol and 5-methyl-2-nitrophenol.

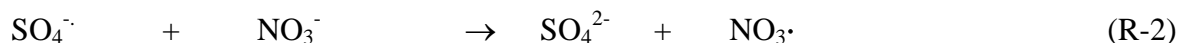
To quantify the influence of temperature to the rate constants of the reaction of the  $\text{NO}_3\cdot$  radical with glyoxal, methacrolein and pinonealdehyde and the  $\text{Cl}_2\cdot^-$  radical anion with glyoxal T-dependent measurements were carried out. Additionally investigations of ionic strength effects for the reactions of  $\text{NO}_3\cdot^-$ -radical with butanal and trichloroacetaldehyde were performed.

## 2. Experimental

The kinetics of the reactions of the  $\text{NO}_3\cdot^-$ -radical with the above mentioned substances were performed using a laser-photolysis long-path laser-absorption apparatus (LP-LPLA). Details of the experimental setup have been fully described before [8] and therefore only the most important details are summarised here. An excimer laser (Lambda Physik LPX 100) operating at  $\lambda = 351 \text{ nm}$  (active medium XeF) with typical pulse energies of 50 mJ was used to photolyse peroxydisulfate anions ( $[\text{S}_2\text{O}_8^{2-}] = 3 \cdot 10^{-2} \text{ M}$ ):



Nitrate radicals are then generated via the consecutive reaction of the  $\text{SO}_4\cdot^-$ -radical anions with nitrate anions:



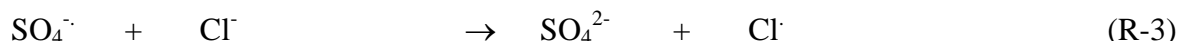
Because reaction (R-2) is slow ( $k_2 = (5.0 \pm 0.5) \cdot 10^4 \text{ M}^{-1}\text{s}^{-1}$  [8]) nitrate anions were added in large excess (i.g.  $[\text{NO}_3^-] = 0.1 \text{ M}$ ).

For the reactions with dimethylsulfoxide and dimethyl-sulfone  $\text{NO}_3\cdot^-$ -radical was generated via photolysis of nitrate anions ( $[\text{NO}_3^-] = 3 \cdot 10^{-2} \text{ M}$ ) at  $\text{pH} = 0$ . Using this technique the oxidation of the reactands DMSO and DMSO<sub>2</sub> by  $\text{S}_2\text{O}_8^{2-}$  and  $\text{NO}_3\cdot^-$  containing solution was prevented. The pH was adjusted by adding perchloric acid. In case of these experiments the excimer laser was operated at  $\lambda = 248 \text{ nm}$  (active medium KrF) with typical pulse energies of 150 mJ.

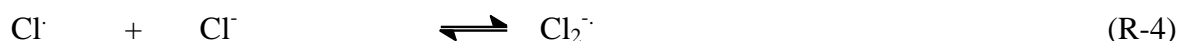
For the kinetic investigations with  $\text{Cl}_2\cdot^-$ -radical anions and additional spectroscopic investigations with  $\text{Cl}_2\cdot^-$ -radical anions and  $\text{SO}_4\cdot^-$ -radical anions a LP-LPLA / broadband-diodearray apparatus was used. Details of the experimental setup have been fully described elsewhere [8] and only deviations from the above mentioned experiment are summarised here. An excimer laser (Lambda Physik COMPex 200) operating at 248 nm (active Medium KrF) with typical pulse energies of 30 mJ was used to photolyse peroxydisulfate anions ( $[\text{S}_2\text{O}_8^{2-}] = 5 \cdot 10^{-4} \text{ M}$ ):



The sulfate radical anions then react with chloride to form chlorine atoms:



The  $\text{Cl}_2^{\cdot-}$  is formed then in the following equilibrium reaction with  $\text{Cl}^{\cdot}$  and  $\text{Cl}^{\cdot}$ .



In deviation to the above mentioned experimental setup for the study of  $\text{SO}_4^{\cdot-}$  radical anion kinetics a He/Cd-laser ( $\lambda_{\text{SO}_4^{\cdot-}} = 441.6 \text{ nm}$ ) was used as the analysing source.

### 3. Results and Discussion

The results for the kinetic investigations of  $\text{NO}_3^{\cdot-}$ -radical are summarised in Table 1. The obtained results for the reactions of reactions of the  $\text{SO}_4^{\cdot-}$ -radical anion are presented in Table 2 and the results for the  $\text{Cl}_2^{\cdot-}$ -radical anion are shown in Table 3.

**Tab. 1:** Obtained rate constants for the reaction of  $\text{NO}_3^{\cdot-}$  with the above mentioned compounds.

Reaction	Reactand	$k_{2\text{nd}, 298 \text{ K}} / \text{M}^{-1} \text{ s}^{-1}$	pH
(R-5)	DMSO, $(\text{CH}_3)_2\text{SO}$	$(4.6 \pm 0.4) \cdot 10^8$	1.6
(R-6)	DMSO <sub>2</sub> , $(\text{CH}_3)_2\text{SO}_2$	$(1.8 \pm 0.2) \cdot 10^5$	1.6
(R-7)	Glyoxal, $\text{C}_2\text{H}_2\text{O}_2$	$(1.1 \pm 0.9) \cdot 10^6$	3.0
(R-8)	Butanal, $\text{CH}_3(\text{CH}_2)_2\text{CHO}$	$(2.5 \pm 0.7) \cdot 10^8$	3.0
(R-9)	Trichloroacetaldehyde, $\text{CCl}_3\text{CHO}$	$(2.5 \pm 0.4) \cdot 10^6$	3.0
(R-10)	isoprene	$(1.0 \pm 0.4) \cdot 10^9$	3.0
(R-11)	R-(+)-limonene	$(2.9 \pm 1.1) \cdot 10^9$	3.0
(R-12)	( $\alpha$ )-pinene	$(1.4 \pm 0.9) \cdot 10^9$	3.0
(R-13)	methacrolein	$(2.7 \pm 0.4) \cdot 10^9$	3.0
(R-14)	(-)-myrtenal	$(1.7 \pm 0.1) \cdot 10^9$	3.0

**Tab. 2:** Obtained rate constants for the reaction of  $\text{SO}_4^{\cdot-}$  with different compounds.

Reaction	Reactand	$k_{2\text{nd}, 298 \text{ K}} / \text{M}^{-1} \text{ s}^{-1}$	pH
(R-24)	DMSO, $(\text{CH}_3)_2\text{SO}$	$(1.5 \pm 0.5) \cdot 10^5$	5.8
(R-25)	DMSO <sub>2</sub> , $(\text{CH}_3)_2\text{SO}_2$	$(8 \pm 2) \cdot 10^4$	1.0
(R-26)	Methanesulfonic Acid, $\text{CH}_3\text{SO}_3\text{H}$	$(1.3 \pm 0.6) \cdot 10^4$	1.0
(R-27)	Benzoic Acid, $\text{C}_6\text{H}_5\text{COOH}$	$(1.6 \pm 0.4) \cdot 10^8$	5.8
(R-28)	5- $\text{CH}_3$ -2- $\text{NO}_2$ - $\text{C}_6\text{H}_3\text{OH}$	$(4.5 \pm 3.3) \cdot 10^5$	5.8

**Tab. 3:** Obtained rate constants for the reaction of  $\text{Cl}_2^{\cdot-}$  with the above mentioned compounds.

Reaction	Reactand	$k_{2\text{nd}, 298 \text{ K}} / \text{M}^{-1} \text{ s}^{-1}$	pH
(R-15)	DMSO, $(\text{CH}_3)_2\text{SO}$	Product absorption at the detection wavelength of $\text{Cl}_2^{\cdot-}$ makes kinetic investigation impossible.	5.8

(R-16)	DMSO <sub>2</sub> , (CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub>	(4.8 ± 0.6)·10 <sup>3</sup>	6.0
(R-17)	Methanesulfonic Acid, CH <sub>3</sub> SO <sub>3</sub> H	< 1200	1.0
(R-18)	Glyoxal, C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	(6.1 ± 0.4)·10 <sup>4</sup>	3.0
(R-19)	Butanal, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO	(1.6 ± 0.2)·10 <sup>6</sup>	5.8
(R-20)	Trichloroacetaldehyde, CCl <sub>3</sub> CHO	(1.8 ± 0.7)·10 <sup>4</sup>	3.0
(R-21)	Benzoic Acid, C <sub>6</sub> H <sub>5</sub> COOH	(5.0 ± 0.9)·10 <sup>4</sup>	1.0
(R-22)	5-CH <sub>3</sub> -2-NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> OH	(1.5 ± 0.1)·10 <sup>8</sup>	5.8
(R-23)	2,4-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> OH	(6 ± 3)·10 <sup>6</sup>	1.0

The influence of temperature on the rate constants on the reactions (R-7), (R-13), (R-14), (R-18) and (R-27) was studied in additional experiments. The results are presented in Table 4.

**Tab. 4:** Survey about the obtained energies of activation and pre-exponential factors for the above mentioned reactions.

Reaction	Radical	Compound	A / L mol <sup>-1</sup> s <sup>-1</sup>	E <sub>a</sub> / kJ mol <sup>-1</sup>
(R-7)	NO <sub>3</sub> ·	Glyoxal	(1.0 ± 0.1) · 10 <sup>11</sup>	(28 ± 6)
(R-13)	NO <sub>3</sub> ·	Methacrolein	(2.3 ± 0.3) · 10 <sup>14</sup>	(28 ± 5)
(R-14)	NO <sub>3</sub> ·	(-)-Myrtenal	(3.6 ± 0.3) · 10 <sup>12</sup>	(38 ± 6)
(R-27)	SO <sub>4</sub> · <sup>-</sup>	Benzoic Acid	(3.3 ± 0.6) · 10 <sup>10</sup>	(14 ± 11)
(R-18)	Cl <sub>2</sub> ·	Glyoxal	(4.0 ± 0.3) · 10 <sup>9</sup>	(27 ± 4)

Finally the influence of ionic strength to selected reactions of the NO<sub>3</sub>· radical with aldehydes were investigated.

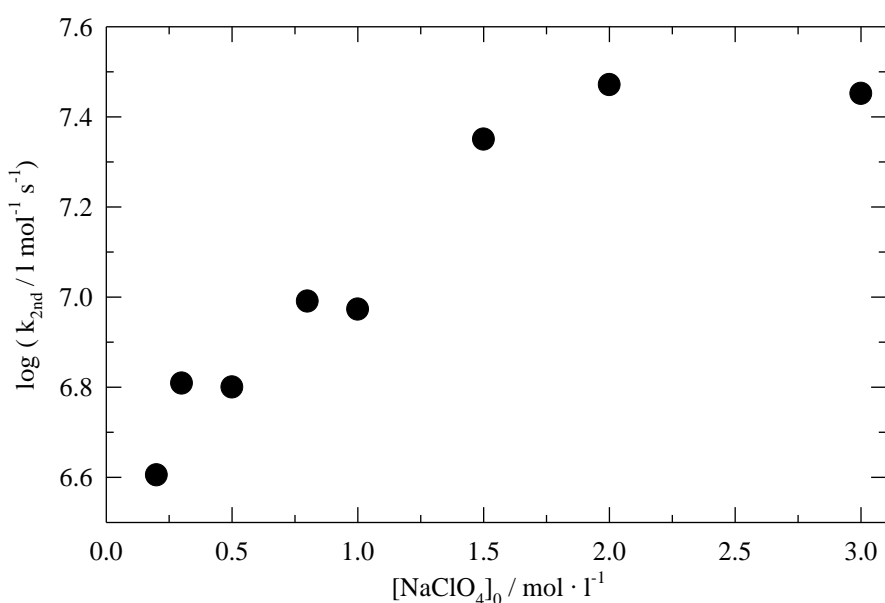
The influence of ionic strength on the reaction of NO<sub>3</sub>· radicals with butanal (R-8) was studied by varying the electrolyte concentration of NaClO<sub>4</sub> between (0.19 ≤ [NaClO<sub>4</sub>]<sub>0</sub> ≤ 3.0) M. The results of these investigation are presented in Figure 1. From Figure 1 the following values for the limiting rate constants for zero ionic strength (k<sub>8(I→0M)</sub>) and for high ionic strength (k<sub>8(I→∞)</sub>) are derived:

$$k_8(I \rightarrow 0 \text{ M}) = 4.5 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1} \text{ and } k_8(I \rightarrow \infty) = 3.0 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}.$$

An increase of ionic strength results from I→0 M to I = 3 M in a reaction rate coefficient increase by a factor of 6.7. Similar effects have been observed in other reactions of the nitrate radical with anions and also with neutral species. They may be attributed to an increase of the activity coefficients of the reactants in accordance with a theoretical prediction of this ‘primary kinetic salt effect (Type II)’ as presented by Debye and McAulay [4]. The present results represent the first

study of ionic strength effect on the rate of reaction of  $\text{NO}_3\cdot$  with butanal. Literature data are currently not available for comparison.

In further studies the influence of ionic strength on the reaction of the  $\text{NO}_3\cdot$  radical with chloral was studied between  $(0.19 \leq [\text{NaClO}_4]_0 \leq 2.0) \text{ mol l}^{-1}$ . From these investigations the following values for the limiting rate constants for zero ionic strength ( $k_{\text{chloral}} (\text{I} \rightarrow 0 \text{ mol l}^{-1})$ ) and for high ionic strength ( $k_{\text{chloral}} (\text{I} \rightarrow \infty)$ ) were determined:  $k_{\text{chloral}} (\text{I} \rightarrow 0 \text{ mol l}^{-1}) = 1.1 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{chloral}} (\text{I} \rightarrow \infty) = 2.5 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . For these studies literature data are currently not available for comparison.



**Fig. 1:** Ionic strength effect in the reaction of nitrate radicals with butanal in aqueous solution ( $T = 298 \text{ K}$ ,  $\text{pH} = 3$ )

The reaction of the  $\text{Cl}_2\cdot^-$ -radical anion with dimethylsulfoxide (DMSO) occurs formally via the addition of a chlorine atom to the DMSO to form a  $\text{DMSOCl}\cdot^-$ -radical. While it is not clear, whether there is direct addition of a chlorine atom from  $\text{Cl}_2\cdot^-$ -radical anion or if first the dimethylsulfoxide radical cation ( $\text{DMSO}^+$ ) is formed, which then reacts with chloride to give the  $\text{DMSOCl}\cdot^-$ -radical. For the reaction of the  $\text{Cl}_2\cdot^-$ -radical with DMSO Asmus et al. measured a value of  $1.2 \cdot 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$  [5] which is in great discrepancy to the value found in our laboratory of  $(4.5 \pm 0.7) \cdot 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$ . Therefore spectroscopic investigations were done, showing that immediately after photolysis a species is formed absorbing in the same region as the  $\text{Cl}_2\cdot^-$ -radical anion. The observed absorption is

probably caused by the DMSOCl<sup>·</sup>-radical for which Asmus reported a maximum of absorption at 390 nm [5]. Additional experiments to measure the reaction of Cl<sub>2</sub><sup>·-</sup>-radical with DMSO via build-up kinetics of the product DMSOCl<sup>·</sup>-radical at 550 nm have shown that the DMSOCl<sup>·</sup>-radical is formed too fast for the used apparatus to get a second order rate constant. This is a hint that the reaction is very fast. Therefore we commend to use the rate constant measured by Asmus et al. for modelling studies although the reason for the discrepancies between Asmus value and our value are not clear at the moment.

For the reaction of the SO<sub>4</sub><sup>·-</sup>-radical anion with DMSO there are similar discrepancies between the obtained rate constant and literature value published by Kishore et al. [5]. In the present work a rate constant for reaction (R-24) of  $k_{24}=(1.5 \pm 0.5) \cdot 10^5 \text{ M}^{-1} \cdot \text{s}^{-1}$  was found while Kishore et al. reported a value of  $2.7 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ . But in difference to the Cl<sub>2</sub><sup>·-</sup>-radical anion case no species is formed absorbing at the analysis wavelength of 445 nm. Spectroscopic investigations have shown an absorber formed during the reaction with an absorption maximum at about 310 nm which is probably the DMSO<sup>·+</sup>-radical cation as reported by Kishore [5]. Tests whether DMSO can be oxidized directly by S<sub>2</sub>O<sub>8</sub><sup>2-</sup> showed only a little loss of DMSO that cannot explain the difference between Kishore's and our value. For modelling studies the obtained value of the Asmus' group should be used although the discrepancy between the data are not clear up to now.

The reactions of the NO<sub>3</sub><sup>·</sup>-radical and the Cl<sub>2</sub><sup>·-</sup>-radical anion with aldehydes proceeds via H-atom abstraction. For the observed rate constants it is important to note that all aldehydes are in equilibrium with their hydrates. For further discussions it is important to know the equilibrium constants for these processes. So the observed rate constants may differ from the „real“ value for the reactions of the mentioned radicals with the unhydrated aldehydes. The observed rate constants for the reactions of the free radicals NO<sub>3</sub><sup>·</sup> and Cl<sub>2</sub><sup>·-</sup> with aldehydes have to be ascribed to the reactions of NO<sub>3</sub><sup>·</sup> and Cl<sub>2</sub><sup>·-</sup> with both, the unhydrated aldehyde RCHO as well as the hydrated form RCH(OH)<sub>2</sub>. However since the C-H-bond energies in the diols are expected to be significantly higher than in the unhydrated aldehydes, the observed rate constants will mainly be due to the reactions with the aldehydes in their unhydrated form. For unsaturated aldehydes (e.g. methacrolein) the reaction of the NO<sub>3</sub><sup>·</sup> radical via oxidation of the double bond becomes more important as it could be seen from the higher second order rate constant.

The reactions of the SO<sub>4</sub><sup>·-</sup> and Cl<sub>2</sub><sup>·-</sup> radical anions with benzoic acid probably occur via electron transfer because all H-atoms of this compound are bonded very strong. Because of the very high rate

constants for the reactions of the  $\text{Cl}_2^{\cdot-}$ -radical anion and the  $\text{SO}_4^{\cdot-}$ -radical anion with 5-methyl-2-nitrophenol these reactions should probably occur via electron transfer. The relatively low rate constants for the reaction of the  $\text{Cl}_2^{\cdot-}$ -radical anion with 2,4-dinitrophenol is a hint that this reaction occurs via H-atom abstraction of the phenolic H-atom. Because of the two nitro groups of the 2,4-dinitrophenol the electron density is diminished and therefore the bond energy of the phenolic H-atom is lower than in phenol.

#### **4. Implications**

Kinetic Data, including temperature- and ionic strength dependent data, have been obtained for reactions of the free radicals  $\text{NO}_3$ ,  $\text{SO}_4^{\cdot-}$  and  $\text{Cl}_2^{\cdot-}$  with the key substance group compounds as listed earlier. These radicals might be transferred into the tropospheric aqueous phase from the gas phase. Modelling studies [6] on tropospheric heterogeneous systems have included various aqueous phase reactions of these radicals and demonstrated far-reaching implications of its tropospheric aerosol [6] as well as cloud droplet chemistry [7].

Studies on the aromatic compound show that free radicals are reacting fast with these substrates. The same is also true for the reactions with unsaturated compound such as isoprene, terpenes and their oxidation products. These results indicate that multiphase oxidation of biogenic organic compound might occur on wet aerosols of biogenic origin.

Because of their generally water solubility aldehydes are present in atmospheric aqueous systems. Aldehydes will undergo oxidation via the abstraction of H-atoms leading to the formation of the corresponding carboxylic acid [2].  $\text{NO}_3$  reactions with aldehydes within the tropospheric aqueous phase might represent an important sink for this radical.

#### **5. References**

- 1.: K. Kawamura, I. R. Kaplan in 'Organic Chemistry of the Atmosphere' pp. 233, CRC Press 1991
- 2.: T.E. Graedel, C.J. Weschler in Reviews of Geophysics and Space Physics; 3 Vol. 19, No. 4, 505-539, (1981).
- 3.: H.-W. Jacobi, Dissertation Thesis, Essen (1996).
- 4.: P. Debye and J. McAulay, Physik. Z. **26**, 22 (1925).
- 5.: K. Kishore and K.-D. Asmus; J. Chem. Soc. Perkin Transl. **2**, 2079-84 (1989).
- 6.: F. J. Dentener and P.J. Crutzen, J. Geophys. Res. **98**, 7149 (1993).
- 7.: H. Herrmann and R. Zellner, in N-Centered Radicals, Ed. Z.B. Alfassi, Wiley, New York, in Press.
- 8.: H. Herrmann, M. Exner, H.-W. Jacobi, A. Reese and R. Zellner; Faraday Discuss. **100**, 129 (1995).

#### **6. Acknowledgements**

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