A Kinetic Study of Aqueous-Phase Reactions of the Nitrate Radical ($NO_3\cdot$) with Aldehydes

A contribution to subproject CMD

Th. Umschlag[1], H. Herrmann[1,2] and R. Zellner[1]

[1]*Institut für Physikalische und Theoretische Chemie, Universität GH Essen, FB8, Universitätsstr. 5, D-45117 Essen, Germany*
[2]*Institut für Troposphärenforschung, Permoserstr. 15, D-04303 Leipzig, Germany*

Background

The influence of cloud and aerosol processes on the oxidation capacity of the gas-phase troposphere is still not well established. The aqueous particle phase may change the oxidation capacity by either uptake of radicals (lowering the gas phase oxidation capacity) or by heterogenous loss of reactive trace gases (thus enhancing the gas phase oxidation capacity). The kinetics of the degradation of aldehydes in the tropospheric aqueous phase with secondary radical oxidants like $NO_3\cdot$ is currently not well established. Also the influence of organic compounds on the aqueous phase free radical budgets is not well known. Due to high concentration of several aldehydes which were identified in various field experiments (Kawamura *et al.*, 1991; Graedel *et al.*, 1981), the concentration levels of the oxidants mentioned earlier might be significantly altered when reactions with aldehydes are taken into consideration. In the present study some important aldehydes were investigated in their reactivity to $NO_3\cdot$ radicals in aqueous solution.

Experimental

The kinetics of the reaction of $NO_3\cdot$ radical with aldehydes were studied by using a laser photolysis laser long-path absorption (LP-LPLA) apparatus. Only the main features are summarised here. An excimer laser (Lambda Physik LPX 100) operated at 351 nm (active medium XeF) with typical pulse energies of 60 mJ was used to photolyse peroxodisulfate anions to generate NO_3 radicals via the reaction of SO_4^{2-} with nitrate. Because the reaction of sulfate radical anions with nitrate is relatively slow ($k\ (I \rightarrow 0) = 5.0 \times 10^4\ L\ mol^{-1}s^{-1}$), nitrate is

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added in large excess: $[NO_3^-] = 0.1$ mol L^{-1}. A helium-neon laser operating at 632.8 nm is used as analysing light source. Details of the experimental setup have been described before (Herrmann *et al.*, 1995).

Results and discussion

In several studies the importance of aldehydes within biogenic and anthropogenic emission and also from automobile and biomass combustion was pointed out (Graedel and Weschler, 1981; Graedel *et al.*, 1986). Reactions between $NO_3\cdot$ and aldehydes in aqueous solution have been investigated by the application of the above mentioned experiment. The following rate coefficients were obtained ($T = 298$ K, pH = 3):

$NO_3\cdot + CHOCHO \rightarrow$ Prod. $k_3 = (1.1 \pm 0.9)\times 10^6\ M^{-1}s^{-1}$ (R3)

$NO_3\cdot + CH_3(CH_2)_2CHO \rightarrow$ Prod $k_4 = (2.5 \pm 0.7)\times 10^8\ M^{-1}s^{-1}$ (R4)

$NO_3\cdot + CCl_3CHO \rightarrow$ Prod. $k_5 = (1.6 \pm 0.4)\times 10^6\ M^{-1}s^{-1}$ (R5)

$NO_3\cdot + CH_3C(CH_2)CHO \rightarrow$ Prod. $k_6 = (2.7 \pm 0.4)\times 10^9\ M^{-1}s^{-1}$ (R6)

$NO_3\cdot + C_{10}H_{14}O \rightarrow$ Prod. $k_7 = (1.7 \pm 0.1)\times 10^9\ M^{-1}s^{-1}$ (R7)

The reaction of $NO_3\cdot$ radicals with aldehydes mainly follows H-atom abstraction in aqueous solution. For unsaturated aldehydes the reaction of the $NO_3\cdot$ radical via oxidation of the double bond becomes more important. All investigated aldehydes are in equlibrium with their hydrates. The available equilibrium constant K for butanal is $k_{\text{aldehyde}}/k_{\text{hydrate}} = 1.54$ (Le Hénaff, 1968), for chloral is $K = k_{\text{aldehyde}}/k_{\text{hydrate}} = 1\times 10^{-5}$ (Carey and Sundberg, 1995) for acetaldehyde is $K \approx 1$ (Vollhardt, 1988) and for formaldehyde K is $k_{\text{ald.}}/k_{\text{hyd.}} = 4.4\times 10^{-4}$ (Le Hénaff, 1968). Because of the mentioned equilibrium constants especially in case of chloral and formaldehyde the observed rate coefficients must be assigned to the reaction of the hydrate with the $NO_3\cdot$ radical.

Influence of temperature on the rate coefficients of the reaction of the $NO_3\cdot$ *radical with several aldehydes*

Temperature dependent measurements of the Arrhenius expressions for the reactions (3), (6), and (7) were carried out. The pre-exponentional factors and the energies of activation obtained are summarised in Table 1.

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Table 1: Survey of the determined activation energies

Reaction	Compound	A [$l\ mol^{-1}\ s^{-1}$]	E_a [$kJ\ mol^{-1}$]
(R3)	Glyoxal	$(1.0 \pm 0.1) \times 10^{11}$	(28 ± 6)
(R6)	Methacrolein	$(2.3 \pm 0.3) \times 10^{14}$	(28 ± 5)
(R7)	(-)-Myrtenal	$(1.0 \pm 0.1) \times 10^{13}$	(22 ± 9)

Influence of ionic strength on the rate coefficients of the reaction of the $NO_3\cdot$ radical with butanal and chloral

The influence of ionic strength on the reaction of $NO_3\cdot$ with butanal (R4) was studied by varying the electrolyte concentration of $NaClO_4$ between $(0.19 \leq [NaClO_4]_0 \leq 3.0)$ mol l^{-1}. The results obtained are presented in Fig. 1.

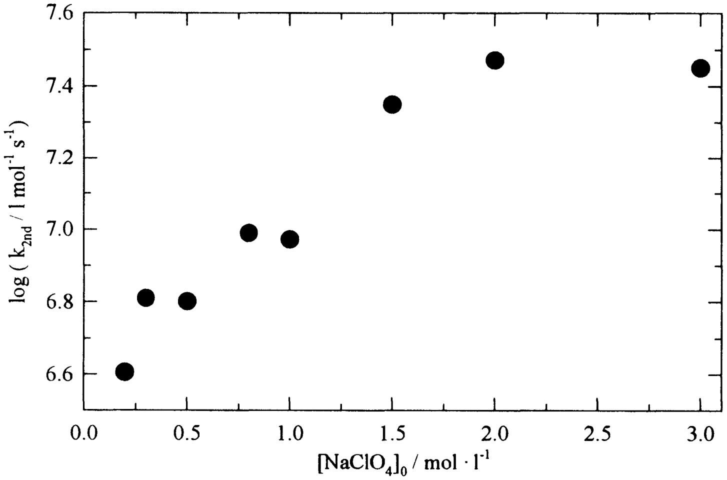

Fig. 1: Ionic strength effect in the reaction of nitrate radicals with butanal in aqueous solution (T = 298 K, pH = 3)

From Fig. 1 the following values for the limiting rate constants for zero ionic strength ($k_{4\,(I \to 0\,M^{-1})}$) and for high ionic strength ($k_{4\,(I \to \infty)}$) are derived:

$k_4\ (I \to 0\ mol\ L^{-1}) = 4.5 \times 10^6\ M^{-1}\ s^{-1}$ and $k_4\ (I \to \infty) = 3.0 \times 10^7\ M^{-1}\ s^{-1}$

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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 acitivity coefficients of the reactants in accordance with a theoretical prediction of this 'primary kinetic salt effect (Type II)' as presented by Debye and McAulay (1925). The present results represent the first study of ionic strength effect on the rate of reaction of $NO_3\cdot$ with butanal. Literature data are currently not available for comparison.

In further studies the influence of ionic strength on the reaction of the $NO_3\cdot$ radical with chloral was studied between $(0.19 \leq [NaClO_4]_0 \leq 2.0)$ mol L^{-1}. From these investigations the following values for the limiting rate constants for zero ionic strength ($k_{5\,(I \rightarrow 0\,mol\,l^{-1})}$) and for high ionic strength ($k_{5\,(I \rightarrow \infty)}$) were determined:

$$k_5\,(I \rightarrow 0\ \text{mol}\ L^{-1}) = 1.1 \times 10^6\ M^{-1}\ s^{-1} \quad \text{and} \quad k_5\,(I \rightarrow \infty) = 2.5 \times 10^7\ M^{-1}\ s^{-1}$$

For these studies literature data are currently not available for comparison.

Implications

The nitrate radical ($NO_3\cdot$) may be transferred into the tropospheric aqueous phase from the gas phase. Modelling studies (Dentener *et al.*, 1993, Herrmann *et al.*, 1997) on tropospheric heterogeneous systems have included various aqueous phase reactions of $NO_3\cdot$ and demonstrated far-reaching implications of its tropospheric aerosol (Dentener *et al.*, 1993) as well as cloud droplet chemistry (Herrmann and Zellner, 1998).

Because they are generally water soluble, 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 (Graedel *et al.*, 1981). NO_3 reactions with aldehydes within the tropospheric aqueous phase may represent an important sink for this radical.

In the present study it has been shown that the reactions of NO_3 with unsaturated aldehydes proceed extremely fast in aqueous solution.

In daytime the *in-situ* formation of carboxylic acids may be dominated by the oxidation of aldehydes with $\cdot OH$ radicals. At night, however the reaction of the $NO_3\cdot$ radical with these compounds might be an important source in aqueous solution for carboxylic acid formation.

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