Kinetic Study of the Reaction of $NO_3\cdot$ Radicals with Benzoic Acid, substituted Benzoic Acids and their Nitration Products in Aqueous Solution

A contribution to subproject CMD / APP

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1. Background

Emissions of benzene and toluene from traffic or from industry result in the formation of phenol or cresols and ring fragmentation products. Phenols are known to be formed in the atmosphere by the OH-initiated atmospheric oxidation of aromatic hydrocarbons. In various field experiments phenols, benzoic acids and their nitration products have been identified in rain water, cloud droplets and fog [1, 2, 3]. Benzoic acid and 4-methylbenzoic acid were found in automobile, road dust and boilers emissions [4]. As an additional source of 4-methylbenzoic acid asphalt emission was identified [4].

Organic aerosols formed by gas phase photochemical reactions have been identified both in urban and rural areas. These compounds are carboxylic acids (benzoic acid), polysubstituted phenols and nitrophenols derived from aromatic hydrocarbons degradation [4].

The complexities introduced by aromatic and polyfunctional organic compounds are enormous and much research is required to elucidate the rates and mechanisms involved.

In aqueous solution nitroaromatic compounds may be formed via direct nitration by NO_2^+ [5] and also by degradation reactions with $NO_3\cdot$ radicals.

Additionally nitroaromatic compounds are known to have toxic effects on plants and humans. Because of this kinetic invstigations of the reaction of NO3· radicals with these compounds are of importance for understanding biochemical processes. In the present study some important aldehydes were investigated in their reactivity to $NO_3\cdot$ radicals in aqueous solution.

2. Experimental Set-up

The kinetics of the reactions of the $NO_3^{\cdot}$-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 λ = 248 nm (active medium KrF) with typical pulse energies of 150 mJ was used to photolyse nitrate anions (NO_3^-) containing acidic aqueous solution. A helium-neon laser operating at 632.8 nm is used as the analysing light source. To increase the detection limit the laser light is folded through the cell 28 times by means of a White mirror configuration resulting in a total pathlength of 168 cm.

3. Results and Discussion

Reactions between $NO_3\cdot$ and different aromatic compounds in aqueous solution have been investigated by the application of the above mentioned experiment. The following rate coefficients were obtained (T = 298 K, pH = 0).

$NO_3\cdot$ + C_6H_5COOH $\rightarrow$ Prod. $k_1 = (6.5 \pm 1.3) \cdot 10^7\ M^{-1}s^{-1}$ (R-1)
$NO_3\cdot$ + $3\text{-}NO_2\text{-}C_6H_4COOH$ $\rightarrow$ Prod $k_2 = (2.0 \pm 0.6) \cdot 10^7\ M^{-1}s^{-1}$ (R-2)
$NO_3\cdot$ + $4\text{-}CH_3\text{-}C_6H_4COOH$ $\rightarrow$ Prod. $k_3 = (6.0 \pm 0.1) \cdot 10^8\ M^{-1}s^{-1}$ (R-3)
$NO_3\cdot$ + $4\text{-}CH_3\text{-}3\text{-}NO_2\text{-}C_6H_3COOH$ $\rightarrow$ Prod. $k_4 = (3.3 \pm 0.4) \cdot 10^7\ M^{-1}s^{-1}$ (R-4)

3.1 Influence of ionic strength on the rate constant of the reaction of $NO_3\cdot$ with benzoic acid

In further studies the effect of ionic strength was studied at T = 298 K, pH = 1 and between ($0.29 \leq [NaClO_4] \leq 3.0$) M. From these experiments the following values for the limiting rate constants for zero ionic strength (k_1 ($I \rightarrow 0$)) and for high ionic strength (k_1 ($I \rightarrow \infty$)) are derived: $k_{1\,(I \rightarrow 0)} = 5.3\cdot10^7\ M^{-1}\ s^{-1}$ and $k_{1\,(I \rightarrow \infty)} = 1.2\cdot10^8\ M^{-1}\ s^{-1}$.

An increase of ionic strength results from I✹0 M to I = 3 M in a rate constant increase by a factor of 2.3. 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 ‘secondary kinetic salt effect’ as presented by Debye and McAulay [6]. The present results represent the first study of ionic strength effect on the rate of reaction for (R-1). No literature data are currently available for comparison.

3.1 Influence of temperature on the rate constant of the reaction of $NO_3\cdot$ with 4-methylbenzoic acid

The effect of temperature on the reaction of $NO_3\cdot$ radicals with 4-methylbenzoic acid was studied in the temperature range of [288 K ≤ T ≤ 328K] at pH = 0. Within these experiments the following activation parameters for reaction (R-3) were obtained.

$$k(T) = (1.6 \pm 0.3) \cdot 10^{12} \cdot \exp[-(2400 \pm 500)\ K / T]$$

$$E_a = (20 \pm 4)\ kJ\ mol^{-1}$$

$$\Delta H^{\neq} = (17 \pm 4)\ kJ\ mol^{-1}$$

$$\Delta G^{\neq} = (23 \pm 9)\ kJ\ mol^{-1}$$

$$\Delta S^{\neq} = -(20 \pm 4)\ J\ mol^{-1}\ K^{-1}$$

Figure 1 shows possible reaction pathways of the $NO_3\cdot$ radical with aromatic compounds in aqueous solution. In general there are five different pathways on which the reaction of the $NO_3\cdot$ radical with aromatics can occur in aqueous solution. Because of the weak H-bond for the H-CH_2-bond of 357 kJ mol^{-1} (calculated from [11]) the predominant reaction pathway for the reaction of $NO_3\cdot$ with 4-methylbenzoic acid is assigned to the reaction via H-atom abstraction at the methyl group. The reactions of the $NO_3\cdot$ radical with benzoic acid and 3-nitrobenzoic acid may possible occur via direct electron transfer or addition-elimination at the aromatic system.

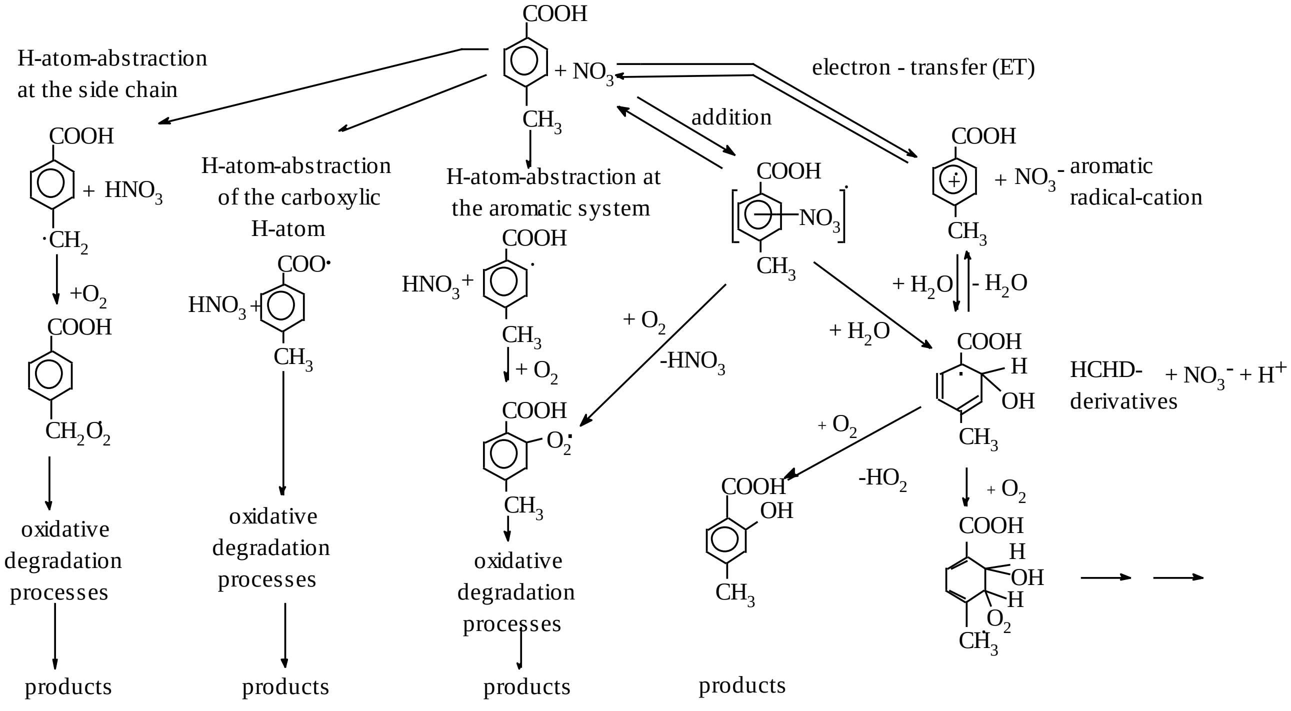

Fig. 1: Posssible reaction pathways for the recation of the $NO_3\cdot$ radical with aromatic compounds in aqueous solution.

4. Implications

The nitrate radical (NO_3) may be transferred into the tropospheric aqueous phase from the gas phase. Modelling studies [9, 10] on tropospheric heterogeneous systems have included various aqueous phase reactions of NO_3 and demonstrated far-reaching implications of its tropospheric aerosol [9] as well as cloud droplet chemistry [7].

As is seen from the derived rate constants the reaction of the $NO_3\cdot$ radical with benzoic acid and their nitration products proceeds very fast. Therefore these reactions might be of importance for tropospheric cloud and aerosol chemistry. At daytime the in-situ oxidation of aromatic hydrocarbons may be dominated by the reaction of ·OH with the aromatics. At night, however the reaction of the $NO_3\cdot$ radical with these compounds might be an additional pathway in the nitration of aromatic compounds in aqueous solution, besides the nitration of aromatics by the nitronium cation (NO_2^+). Beside these nitration reactions H-atom abstractions reaction attached importance for the reaction of $NO_3\cdot$ radicals with aromatic compounds in aqueous solution.

5. References

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