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Rate Constants for the Reactions of the NO₃ Radical with HCOOH/HCOO⁻ and CH₃COOH/CH₃COO⁻ in Aqueous Solution Between 278 and 328 K

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Abstract. The kinetics of the aqueous phase reactions of NO₃ radicals with HCOOH/HCOO⁻ and CH₃COOH/CH₃COO⁻ have been investigated using a laser photolysis/long-path laser absorption technique. NO₃ was produced via excimer laser photolysis of peroxydisulfate anions (S₂O₈²⁻) at 351 nm followed by the reactions of sulfate radicals (SO₄²⁻) with excess nitrate. The time-resolved detection of NO₃ was achieved by long-path laser absorption at 632.8 nm.

For the reactions of NO₃ with formic acid (1) and formate (2) rate coefficients of $k_1 = (3.3 \pm 1.0) \times 10^5$ l mol⁻¹ s⁻¹ and $k_2 = (5.0 \pm 0.4) \times 10^7$ l mol⁻¹ s⁻¹ were found at $T = 298$ K and $I = 0.19$ mol/l. The following Arrhenius expressions were derived: $k_1(T) = (3.4 \pm 0.3) \times 10^{10} \exp[-(3400 \pm 600)/T]$ l mol⁻¹ s⁻¹ and $k_2(T) = (8.2 \pm 0.8) \times 10^{10} \exp[-(2200 \pm 700)/T]$ l mol⁻¹ s⁻¹. The rate coefficients for the reactions of NO₃ with acetic acid (3) and acetate (4) at $T = 298$ K and $I = 0.19$ mol/l were determined as: $k_3 = (1.3 \pm 0.3) \times 10^4$ l mol⁻¹ s⁻¹ and $k_4 = (2.3 \pm 0.4) \times 10^6$ l mol⁻¹ s⁻¹. The temperature dependences for these reactions are described by: $k_3(T) = (4.9 \pm 0.5) \times 10^9 \exp[-(3800 \pm 700)/T]$ l mol⁻¹ s⁻¹ and $k_4(T) = (1.0 \pm 0.2) \times 10^{12} \exp[-(3800 \pm 1200)/T]$ l mol⁻¹ s⁻¹. The differences in reactivity of the anions HCOO⁻ and CH₃COO⁻ compared to their corresponding acids HCOOH and CH₃COOH are explained by the higher reactivity of NO₃ in charge transfer processes compared to H atom abstraction. From a comparison of NO₃ reactions with various droplets constituents it is concluded that the reaction of NO₃ with HCOO⁻ may present a dominant loss reaction of NO₃ in atmospheric droplets.

Key words: Droplet chemistry, acid/base pairs, NO₃ radicals, reaction mechanisms, radical reactions, pH-dependence.

1. Introduction

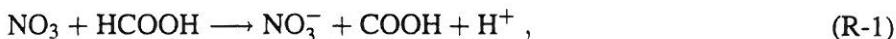
In atmospheric gas phase chemistry the NO₃ radical is known to be a strong nighttime oxidant (Wayne, 1991). The most important atmospheric source of the radical is the reaction between NO₂ and O₃ (Burrows *et al.*, 1985; Wayne, 1991), viz.



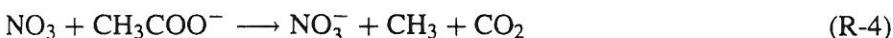
The maximum concentration of NO₃ is reached at night when no photolysis of the radical takes place. NO₃ may be scavenged from the gas phase into the liquid phase of droplets of clouds, rain and fog (Chameides, 1986). Being a strong oxidizing agent, NO₃ may initiate oxidation processes in the atmospheric aqueous phase like the conversion of S(IV) species (Chameides, 1984; Exner *et al.*, 1992) or

the transformation of organic compounds (Chameides, 1986). In contrast to the study of Chameides (1986), the role of NO_3 in aqueous phase chemistry has been questioned by Mozurkewich (1986) based on the theoretical prediction of a low solubility of the nitrate radical in water. Clearly, further experimental investigations on both the sticking coefficient and the Henry's Law constant of NO_3 appear to be necessary. Nevertheless, in order to assess the role of NO_3 in aqueous phase chemistry quantitatively, the reactivity of the NO_3 radical has to be examined.

It is generally accepted that the dissolved mineralic acids HNO_3 and H_2SO_4 are responsible for the acidification of atmospheric droplets (Granat, 1972) and that the amount of acids is influenced by free radical reactions (Chameides and Davis, 1982; Graedel and Goldberg, 1983). Moreover, in remote areas formic acid and, to a smaller amount, acetic acid have been identified as important components of acid rain (Galloway *et al.*, 1982). Because these acids are also commonly found in droplet water (Graedel and Weschler, 1981; Keene and Galloway, 1986), the reactions of NO_3 with formic acid and acetic acid have been investigated in this work. These reactions can be described by a H-abstraction mechanism leading to nitrate anions and carboxylic radicals, viz.



The present work differs in two important aspects from other studies of NO_3 reactions reported in the literature. Firstly, the very low ionic strength of $I = 0.19 \text{ mol/l}$, as applied under the present experimental conditions, allows to determine rate coefficients close to zero ionic strength, whereas in most of the previous investigations the ionic strength varied between $I = 2-6 \text{ mol/l}$ (Martin *et al.*, 1964; Pikaev *et al.*, 1974; Neta and Huie, 1986; Shastri and Huie, 1990; Katsumura *et al.*, 1991). This is important because it has been shown that the rate of reaction between neutral species and ions depends on ionic strength (Exner *et al.*, 1992). Secondly, kinetic measurements can be carried out in the alkaline region, as opposed to the very acidic solutions of concentration HNO_3 , $\text{K}_2\text{Ce}(\text{NO}_3)_6$ or $\text{K}_2\text{Ce}(\text{NO}_3)_6/\text{HNO}_3$ mixtures used in other investigations (Martin *et al.*, 1964; Dogliotti and Hayon, 1967; Pikaev *et al.*, 1974; Neta and Huie, 1986; Shastri and Huie, 1990; Katsumura *et al.*, 1991). Thus, we are able to report the first determination of the reactions of NO_3 with the anions HCOO^- and CH_3COO^- . The rate coefficients derived for these reactions are more than two orders of magnitude larger compared to the rate coefficients of the corresponding acids. Hence, we suggest an electron transfer mechanism for these reactions, viz.

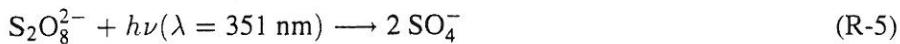


The results reported in this paper are of fundamental interest to atmospheric chemistry. Because of the high concentration of $\text{HCOOH}/\text{HCOO}^-$ of up to 5×10^{-6}

mol/l in atmospheric droplets (Church *et al.*, 1991) and the fast rate coefficients for the reactions with NO₃ the acid/base pair HCOOH/HCOO⁻ contributes to a rapid aqueous phase removal of NO₃. Since the rates of acid and corresponding anion differ considerably, the pH-dependence of the rate coefficients should be taken into consideration in atmospheric aqueous phase chemistry.

2. Experimental Section

The experimental apparatus developed for direct kinetic studies of NO₃ in aqueous solution combines radical generation via laser photolysis and long-path laser absorption for radical detection. The experimental set-up is shown schematically in Figure 1. An excimer laser (Lambda Physik) was used as a photolysis light source operating at a wavelength of 351 nm (active medium XeF) with typical pulse energies of 50 mJ. The photolytic dissociation of peroxodisulfate anions (S₂O₈²⁻) (usually [S₂O₈²⁻] = 3 × 10⁻² mol/l) leads to the formation of sulfate radicals from which, in the presence of nitrate anions, the corresponding NO₃ radicals are generated, viz.



For laser pulse energies of 50 mJ NO₃ concentrations of typically 3 × 10⁻⁷ mol/l were obtained. Because reaction (6) is relatively slow ($k_6 = 9.0 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ at $I = 0.19 \text{ mol/l}$, Exner *et al.*, 1992) nitrate ions were added in large excess ([NO₃⁻] = 0.1 mol/l).

The reaction cell consisted of a glass cylinder with an inner diameter of 50 mm and an inner length of 60 mm. It could be thermostated by a heater/cooler combination allowing temperature dependent measurements in the range of 278–358 K. Plane plates of fused silica were used as front windows of the cell. A helium-neon laser (Spindler und Hoyer 35-2, typical output energy 2 mW) operated at 632.8 nm served as an analysis light source. This laser line is located near the NO₃ absorption maximum of 635 nm (Herrmann *et al.*, 1991). The light beam was passed into a White-cell optics consisting of two dielectrically coated mirrors. In all experiments the White-cell was adjusted for 32 passes giving an optical path length of 192 cm. Under these conditions the detection limit of NO₃ was about 5 × 10⁻⁸ mol/l. Since the two laser beams were passed through the cell coaxially they were separated by a set of optical elements consisting of a lens ($f = 100 \text{ mm}$), a prism, a small aperture and a cut-off-filter. For light detection a sensitive silicon photodiode (Hamamatsu S 1722-02) was used, the electrical output of which was intensified by a fast amplifier (Burr-Brown OPA 606) and then fed to a digital storage oscilloscope (Gould 4035). The oscilloscope was connected to an IBM-AT-compatible computer. It triggered the photolysis laser and also was used to

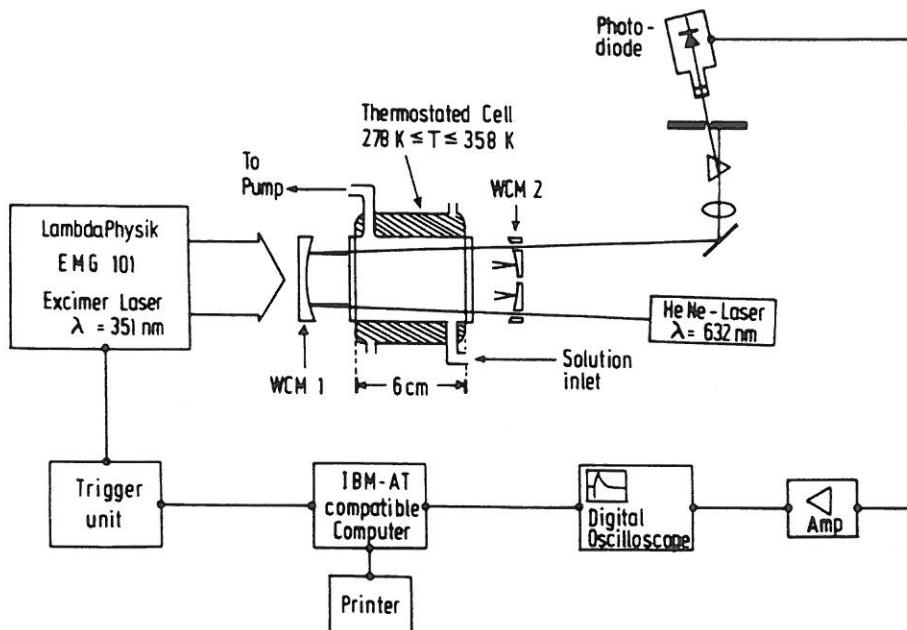


Fig. 1. Schematic representation of laser photolysis/long-path laser absorption experimental arrangement.

average a variable number of experiments. Normally 8 experiments were averaged using a repetition rate of 1 Hz.

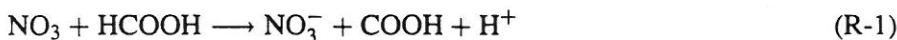
The reagents $\text{K}_2\text{S}_2\text{O}_8$, KNO_3 , HCOOH , H_2SO_4 (Fluka) and CH_3COOH , NaOH (Merck) were of analytical grade (p.a.) and used as received. All solutions were freshly prepared employing double distilled water from a quartz distilling apparatus. pH values were adjusted with H_2SO_4 and NaOH .

3. Results and Discussion

3.1. THE REACTIONS OF NO_3^- WITH HCOOH AND HCOO^-

3.1.1. $\text{NO}_3^- + \text{HCOOH}$

The reaction of NO_3^- with formic acid is known to take place via H-abstraction from the carbon atom to form the organic radical and nitrate (Neta *et al.*, 1988), viz.



Abstraction of H from the carbon site of HCOOH appears to be preferred over abstraction from the acidic site because of the much higher strength of the O—H

TABLE I. Rate coefficients for the reaction of NO₃ with formic acid as a function of temperature, pH = 0.5

T(K)	$k/10^5 \text{ l mol}^{-1} \text{ s}^{-1}$
278	(1.8 ± 0.2)
288	(2.4 ± 0.4)
298	(3.3 ± 1.0)
308	(5.3 ± 0.8)
318	(7.1 ± 0.9)
328	(12 ± 2)

bond (D(O—H) = 465 kJ/mol) in comparison to the C—H bond (D(C—H) = 415 kJ/mol).

In the presence of molecular oxygen the intermediate COOH produced is expected to form HO₂ and CO₂:



The rate coefficient of reaction (1) has been determined at pH = 0.5 by varying the formic acid concentration between 2.5×10^{-3} mol/l and 1×10^{-2} mol/l. At constant temperature the first-order rate constants are linearly dependent on concentration (Figure 2). From the slope of the straight line at T = 298 K a rate constant of $k_1 = (3.3 \pm 1.0) \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ was obtained. The results at all other temperatures are summarized in Table I and presented in Figure 3. In Arrhenius form the following expression is obtained:

$$k_1(T) = (3.4 \pm 0.3) * 10^{10} \exp[-(3400 \pm 600)/T] \text{ l mol}^{-1} \text{ s}^{-1},$$

$$E_A = (28 \pm 5) \text{ kJ/mol}$$

The intercepts in Figure 2 may be due to a temperature dependent electron transfer reaction between NO₃ and S₂O₈²⁻. However, it may also be possible that a reaction of NO₃ with water, albeit endothermic, takes place. Currently, investigations on both processes are under way in our laboratory (Exner *et al.* (1993)).

Reaction (1) has been examined in two former studies. Dogliotti and Hayon (1967) found a value of $(2.1 \pm 0.1) \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ (T = 297 K, pH = 0.65) using flash photolysis of K₂Ce(NO₃)₆. From a pulse radiolytic investigation Neta and Huie (1986) obtained an upper limit of $1 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ at T = 295 K and pH < 0. Whereas the former study is within experimental uncertainty in agreement with the present work, the result from the latter study is more than a factor of 3 lower. A possible resolution of this difference may be obtained by further pH-dependent measurements extending to pH < 0.

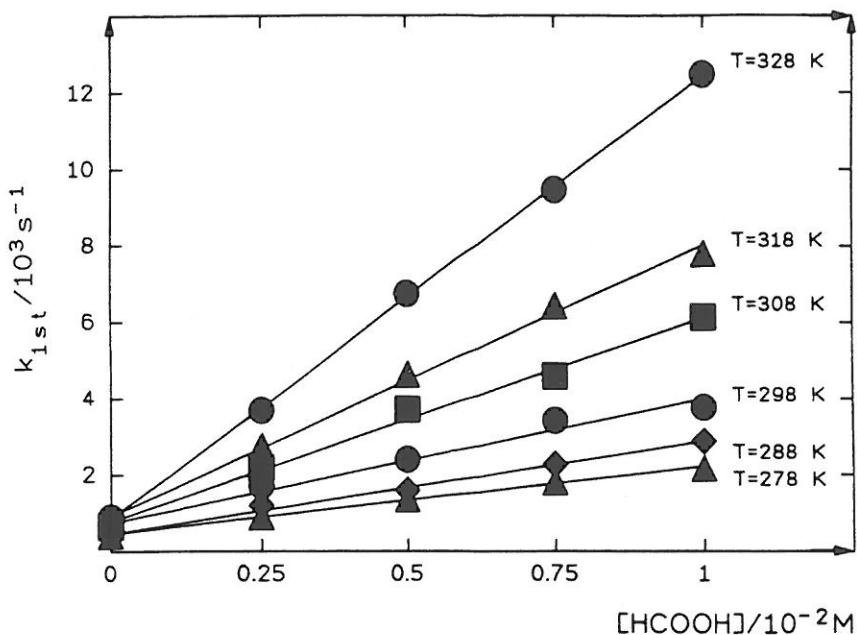


Fig. 2. First-order rate coefficients as a function of formic acid concentration and temperature for the reaction of NO_3 with HCOOH .

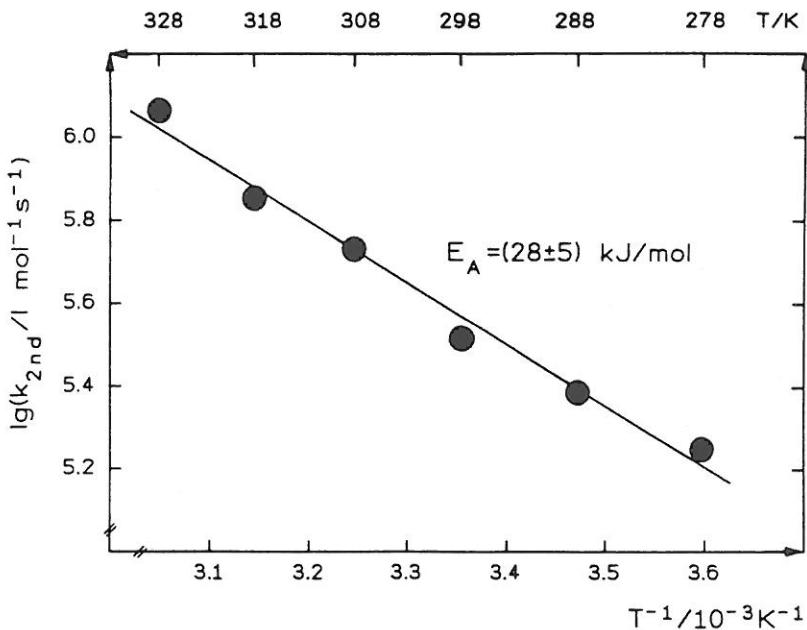
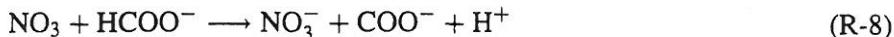


Fig. 3. Arrhenius plot for the reaction of NO_3 with HCOOH .

3.1.2. NO₃ + HCOO⁻

The reaction between NO₃ and formate can be described by two different reaction mechanisms, hydrogen abstraction (8) and electron transfer (2), viz.



Arguments, however, are put forward which suggest the dominance of reaction (2).

The reaction of NO₃ with formate has been investigated in the temperature interval 278–308 K at pH = 9.0. The pH was adjusted with NaOH. Buffer solutions could not be used because the reaction between NO₃ and the buffer system reduced the yield of NO₃ below the detection limit of our apparatus. Moreover, the thermal decomposition of S₂O₈²⁻ (Kolthoff and Miller, 1951; Steudel, 1974) decreases the pH value of the solution so that at temperatures higher than 308 K measurements under stable pH conditions were not possible.

TABLE II. Rate coefficients for the reaction of NO₃ with formate as a function of temperature, pH = 9.0, I = 0.19 mol/l

T(K)	k/10 ⁷ l mol ⁻¹ s ⁻¹
278	(2.7 ± 0.5)
288	(3.6 ± 0.7)
298	(5.0 ± 0.4)
308	(5.8 ± 0.6)

Because of the high reactivity of formate and in order to obtain reasonable time-resolved signals the HCOO⁻ concentration had to be reduced compared to the formic acid study. The observed pseudo-first-order rate constants as a function of formate concentration and temperature are shown in Figure 4. Contrary to the second-order plot for reaction (1) larger intercepts at all temperatures were measured, which is due to the additional contribution of the temperature dependent reaction of NO₃ with hydroxide (OH⁻) at pH = 9.0 (Exner *et al.*, 1992).

The derived second-order rate coefficients are summarized in Table II and presented in Arrhenius form in Figure 5. At T = 298 K and I = 0.19 mol/l the rate coefficient of (R-2) was determined $k_2 = (5.0 \pm 0.4) \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$. In the temperature range 278–308 K the Arrhenius expression,

$$k_2(T) = (8.2 \pm 0.8) \times 10^{10} \exp[-(2200 \pm 700)/T] \text{ l mol}^{-1} \text{ s}^{-1},$$

corresponding to an activation energy of $E_a = (18 \pm 6) \text{ kJ/mol}$, is obtained.

For fast reactions and, hence, under the assumption of diffusion control, the activation energy in aqueous solution is mainly attributed to the temperature dependence of the viscosity of the solvent, which is about 15 kJ/mol (Wedler, 1987) for

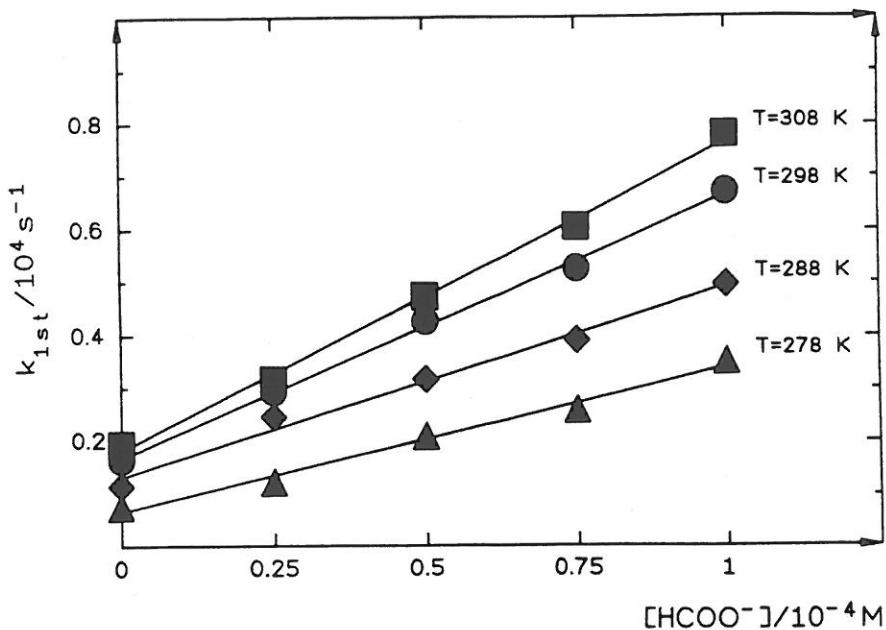


Fig. 4. First-order rate coefficients as a function of formate concentration and temperature for the reaction of NO_3 with HCOO^- , $I = 0.19 \text{ mol/l}$.

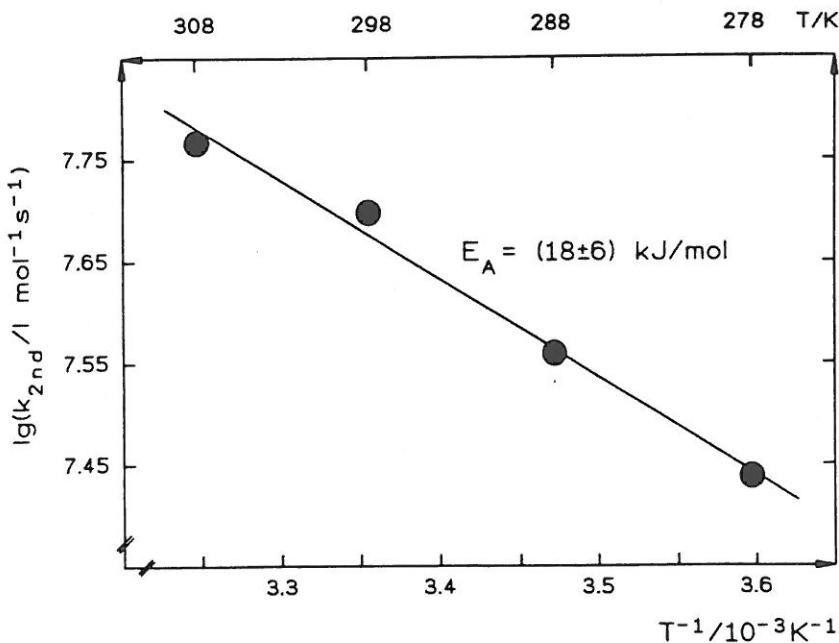


Fig. 5. Arrhenius plot for the reaction of NO_3 with HCOO^- , $I = 0.19 \text{ mol/l}$.

aqueous solutions. The observed rate constants for reaction (2) are in the lower limit of the diffusion control. As a consequence it appears likely that the measured activation energy does not include an additional barrier for a chemical activation process.

In comparison with the rate coefficient of NO₃ with formic acid a difference in the rate coefficients of more than two orders of magnitude is observed. Due to the fact that reaction (1) proceeds via hydrogen abstraction the significant deviation in rate constants is likely to be caused by different mechanisms, i.e., a one-electron transfer mechanism (reaction (2)). This is indirectly supported by the lack of an intrinsic activation barrier and the high redox potential of NO₃ of E° = 2.43/2.52 V (Stanbury, 1989; Wardman, 1989) which exceeds that of HCOO⁻/HCOO by 1.07/1.16 V.

A similar difference in reactivity has also been observed for the reaction of the sulfate radical anion (SO₄⁻) with HCOOH/HCOO⁻. Whereas for formic acid a rate coefficient of $4.6 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ was reported a corresponding value of $1.1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ for the reaction of SO₄⁻ with formate was found at zero ionic strength (Wine *et al.*, 1989).

3.1.3. pH Dependence of NO₃ + HCOOH/HCOO⁻

The pH values of atmospheric droplets vary over a wide range from pH = 2–7 for continental to pH = 7.8–8.3 for marine droplets (Graedel and Weschler, 1981). As a consequence both species (HCOOH and HCOO⁻) occur in the atmospheric aqueous phase and mixed second-order rate coefficients are expected. Therefore, the pH dependence has been examined in the pH interval between 0.5 and 9 in more detail. The obtained rate constants at T = 298 K are summarized in Table III and shown in Figure 6 together with the equilibrium mole fractions of HCOOH/HCOO⁻. The broken line represents the rate coefficients evaluated at each pH from the mole fractions and the kinetics for the reactions of NO₃ with HCOOH and HCOO⁻ exclusively (reaction (1) and (2)). Because of the reasonable agreement between measured and evaluated rate constants the mixed rate coefficients can be evaluated at each pH with sufficient confidence. The minor deviations of the measured data points in the range pH 2–4 appear to be due to experimental uncertainties in both the pH-values and the kinetic data.

As can be seen from Figure 6, formate is the most reactive species and shows a strong influence on the mixed rate coefficients at all pH values. Due to the high rate coefficient k_2 the mixed bimolecular rate constant has nearly reached its maximum at pH = 4.0, near the pK_a value.

TABLE III. Rate coefficients as a function of pH for the reaction of NO_3^- with $\text{HCOOH}/\text{HCOO}^-$, $T = 298 \text{ K}$

pH	$k/\text{l mol}^{-1} \text{s}^{-1}$
0.5	$(3.3 \pm 1.0) \times 10^5$
1.5	$(6.4 \pm 1.1) \times 10^5$
2.2	$(2.1 \pm 0.5) \times 10^6$
2.5	$(3.9 \pm 0.5) \times 10^6$
3.0	$(1.1 \pm 0.1) \times 10^7$
3.5	$(2.3 \pm 0.3) \times 10^7$
5.0	$(4.7 \pm 0.6) \times 10^7$
9.0	$(5.0 \pm 0.4) \times 10^7$

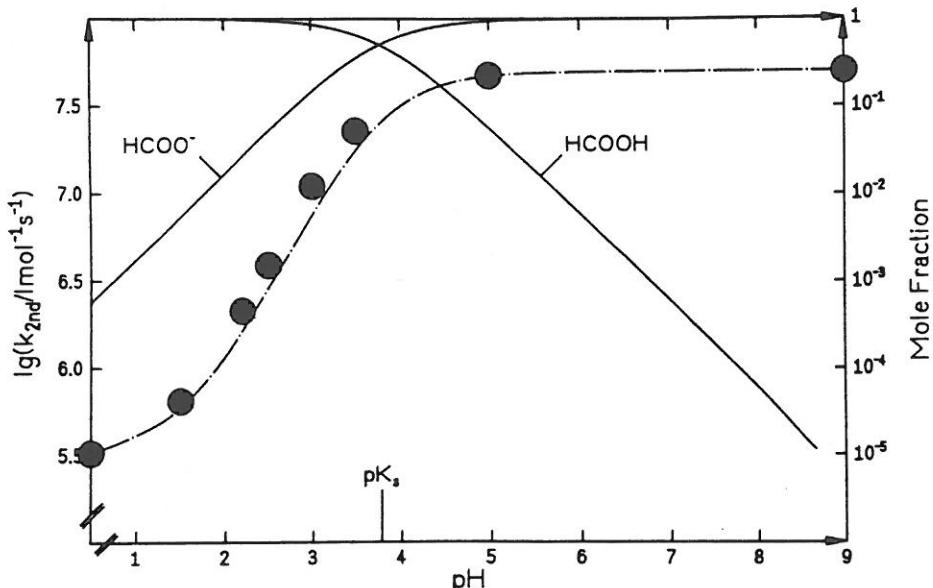
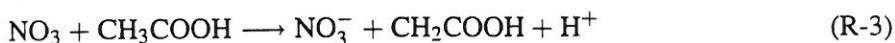


Fig. 6. Logarithmic plot of second-order rate coefficients (●) for the reaction of NO_3^- with $\text{HCOOH}/\text{HCOO}^-$ as a function of pH at $T = 298 \text{ K}$ together with the equilibrium mole fractions of the species (solid line) and the rate constants evaluated from the elementary reactions at pH = 0.5 and 9.0 (broken line).

3.2. THE REACTIONS OF NO_3 WITH $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$

3.2.1. $\text{NO}_3 + \text{CH}_3\text{COOH}$

The reaction of NO_3 with acetic acid which can be described as a hydrogen abstraction from the carbon atom, viz.



has been investigated at pH = 1.0.

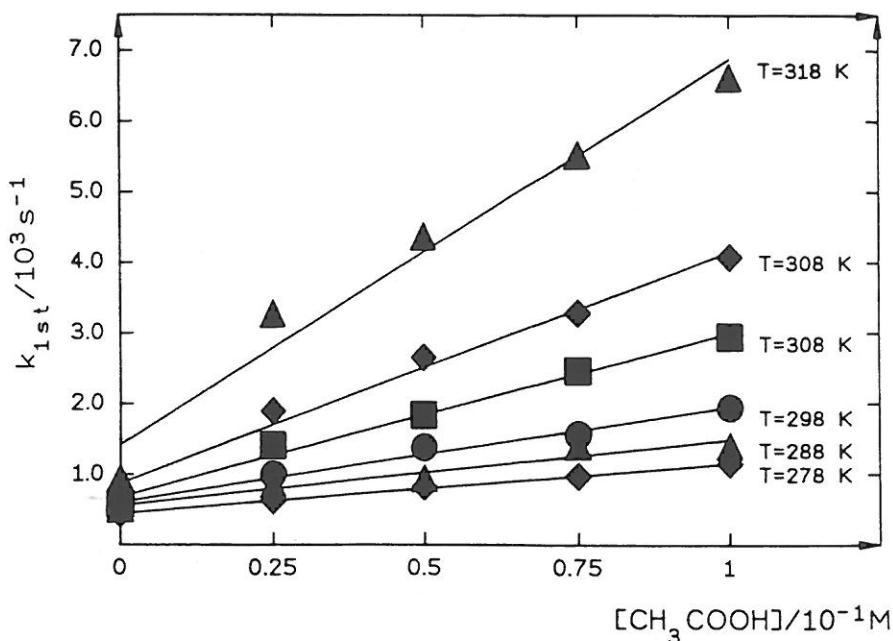


Fig. 7. First-order rate coefficients as a function of acetic acid concentration and temperature for the reaction of NO₃ with CH₃COOH.

The concentration of CH₃COOH was varied in the range of 2.5×10^{-2} mol/l to 1×10^{-1} mol/l. The observed first-order rate coefficients as a function of temperature and concentration are shown in Figure 7. The second-order rate constants derived from the plot are summarized in Table IV. At room temperature a value of $k_3 = (1.3 \pm 0.3) \times 10^4$ l mol⁻¹ s⁻¹ is found. From the Arrhenius plot (Figure 8) the following temperature dependence is obtained:

$$k_3(T) = (4.9 \pm 0.5) \times 10^9 \exp[-(3800 \pm 700)/T] \text{ l mol}^{-1} \text{ s}^{-1}$$

$$E_A = (31 \pm 6) \text{ kJ/mol}$$

To our knowledge, data on the temperature dependence of reaction (3) are currently not available in the literature.

However, there are two former investigations at room temperature using the flash photolysis of K₂Ce(NO₃)₆ or K₂Ce(NO₃)₆/HNO₃ mixtures. Dogliotti and Hayon (1967) found a value of $k_3 = 4.6 \times 10^4$ l mol⁻¹ s⁻¹ whereas Martin *et al.* (1964) obtained a rate constant of $k_3 = 2.3 \times 10^2$ l mol⁻¹ s⁻¹. As a consequence, there is a large discrepancy between all available studies. Jointly with the results of Dogliotti and Hayon the present data cast some doubt on the extremely low value measured by Martin *et al.*

TABLE IV. Rate coefficients for the reaction of NO_3 with acetic acid as a function of temperature, pH = 1.0

T(K)	$k/10^4 \text{ l mol}^{-1} \text{ s}^{-1}$
278	(0.71 ± 0.05)
288	(0.93 ± 0.20)
298	(1.3 ± 0.3)
308	(2.3 ± 0.4)
318	(3.3 ± 0.7)
328	(5.5 ± 1.5)

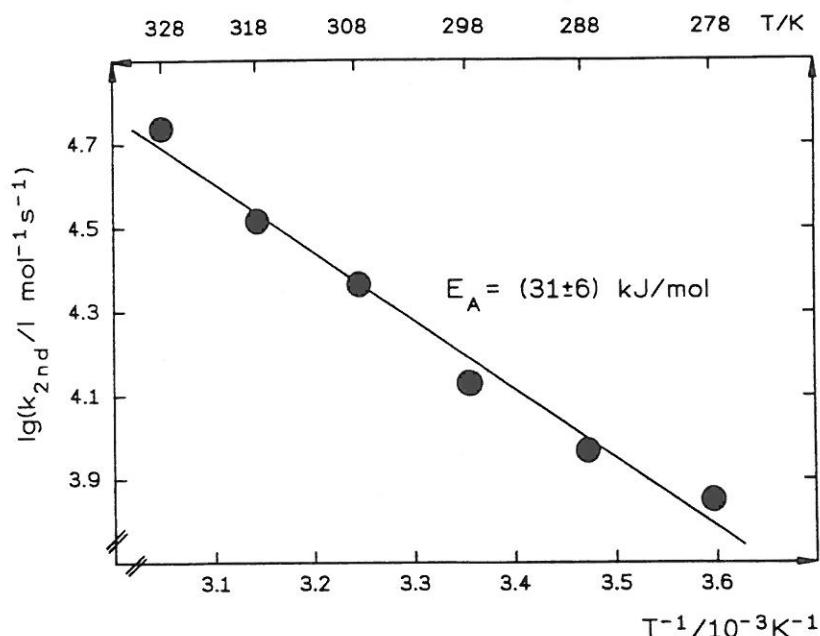
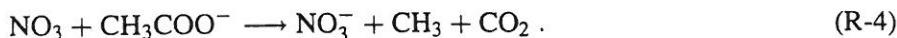


Fig. 8. Arrhenius plot for the reaction of NO_3 with CH_3COOH .

3.2.2. $\text{NO}_3 + \text{CH}_3\text{COO}^-$

Like for the reaction with formate, NO_3 may react with acetate via hydrogen abstraction or electron transfer. In the latter case a decarboxylation process may occur leading to CH_3 and CO_2 , viz.



The experiments for the study of this reaction were carried out at pH = 9.0 and $I = 0.19 \text{ mol/l}$. Due to the complications described in Section 3.1.2, the maximum

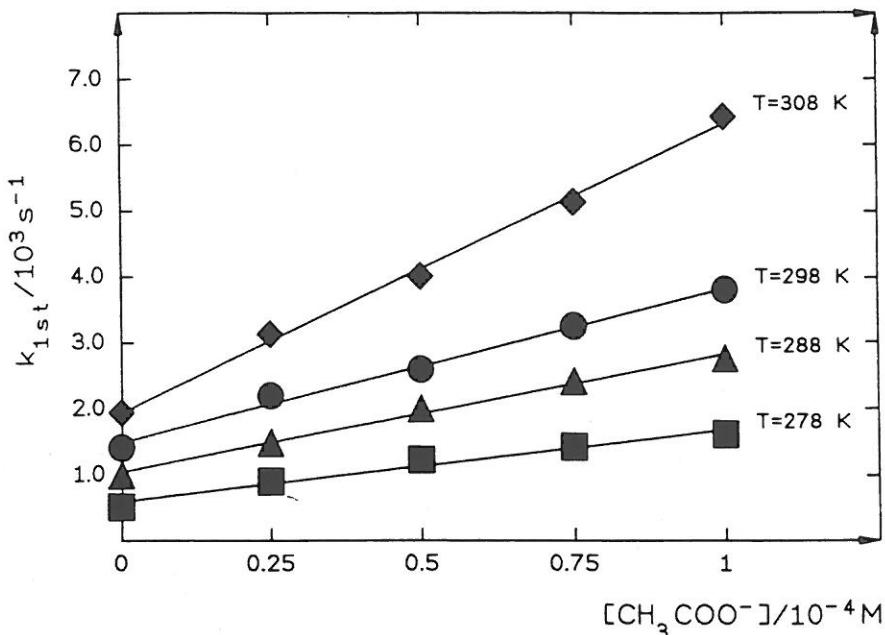


Fig. 9. First-order rate coefficients as a function of acetate concentration and temperature for the reaction of NO₃ with CH₃COO⁻, I = 0.19 mol/l.

TABLE V. Rate coefficients for the reaction of NO₃ with acetate as a function of temperature, pH = 9.0, I = 0.19 mol/l

T(K)	<i>k</i> /10 ⁶ 1 mol ⁻¹ s ⁻¹
278	(1.1 ± 0.3)
288	(1.8 ± 0.3)
298	(2.3 ± 0.4)
308	(4.4 ± 0.5)

temperature had to be reduced from 328 to 308 K. Similarly, the concentration of acetate was also reduced compared to the measurements with acetic acid.

The second-order rate coefficients which were derived from the plot of first-order rate constants as a function of concentration and temperature (Figure 9) are summarized in Table V. The temperature dependence for the reaction of NO₃ with acetate is represented in Figure 10. It corresponds to the Arrhenius expression

$$k_4(T) = (1.0 \pm 0.2) \times 10^{12} \exp[-(3800 \pm 1200)/T] \text{ mol}^{-1} \text{ s}^{-1}$$

with an activation energy of $E_A = (32 \pm 10)$ kJ/mol.

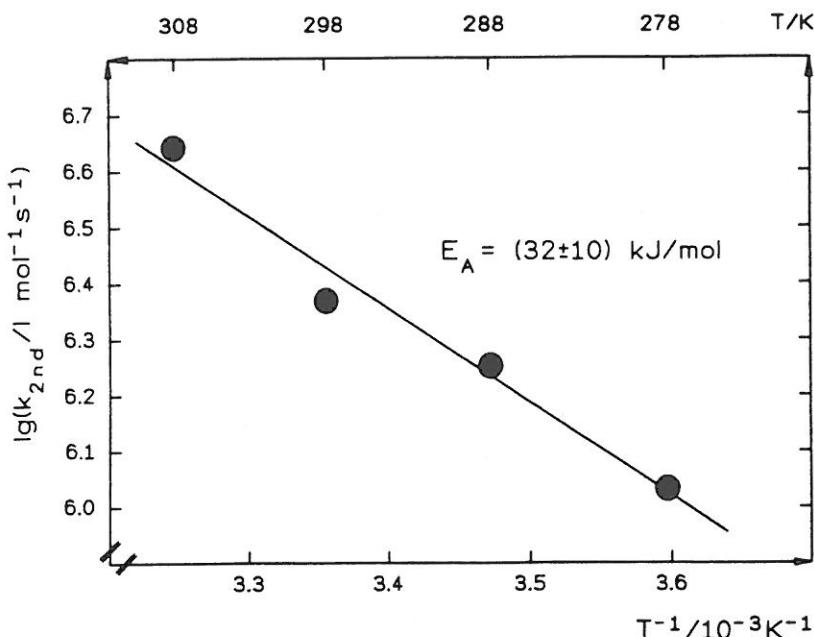


Fig. 10. Arrhenius plot for the reaction of NO_3 with CH_3COO^- , $I = 0.19 \text{ mol/l}$.

At room temperature a second-order rate constant of $(2.3 \pm 0.4) \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ is determined. To our knowledge, kinetic data on this reaction are not available in the literature.

Similar to the reaction of NO_3 with $\text{HCOOH}/\text{HCOO}^-$ the rate coefficients for the reaction of NO_3 with acetic acid and acetate differ by a factor of 180, with acetate being the most reactive species. Again, arguments are presented which suggest the dominance of reaction (4) i.e. decarboxylation, compared to the H atom abstraction reaction (9).

Indirect support for reaction (4) being an electron process comes from two investigations of the reaction of the sulfate radical anion with acetate. In these, a one-electron transfer process has been found (Gilbert *et al.*, 1972; Chawla and Fessenden, 1975). The generation of the methyl radical could be monitored by using an electron spin resonance technique. From this result and because of the similar reactivity in electron transfer reactions of sulfate and nitrate radicals (Exner *et al.*, 1993) a one-electron transfer mechanism with a direct decarboxylation process is assumed for the reaction of NO_3 with CH_3COO^- .

The analogy of NO_3 and SO_4^{2-} can also be seen by comparison of the reaction rate constants of the radicals with acetic acid and acetate. For the reaction of SO_4^{2-} with $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ rate coefficients of $1.4 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ and $3.7 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ were obtained (Wine *et al.*, 1989), which only differ by a factor of 1.1 and 1.6, respectively, from the rate constants for NO_3 measured here.

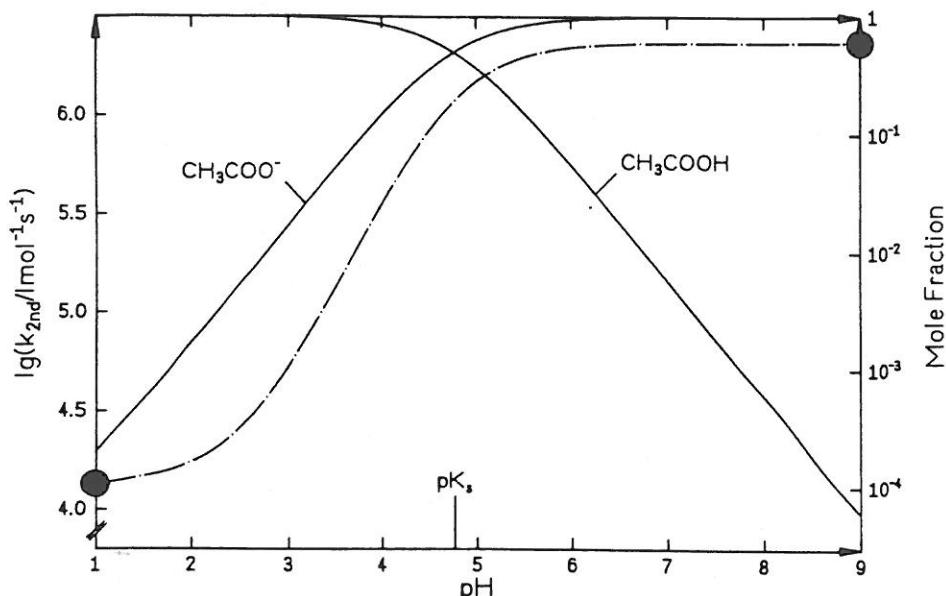


Fig. 11. Logarithmic plot of second-order rate coefficients (broken line) evaluated from the elementary reactions of NO₃ with CH₃COOH and CH₃COO⁻ (●) as a function of pH at T = 298 K together with the equilibrium mole fractions of the species (solid line).

The pH dependence of the reaction of NO₃ with CH₃COOH/CH₃COO⁻ was evaluated using the rate coefficients of the two elementary reactions and the mole fractions of the species in the pH interval between 1.0 and 9.0. The result is shown in Figure 11 (broken line) together with the mole fractions (solid line) and the measured second-order rate coefficients at pH 1.0 and 9.0. As can be seen from the plot, even at low pH values reaction (4) increases the mixed rate coefficients between NO₃ and CH₃COOH/CH₃COO⁻, although the mole fractions of CH₃COO⁻ are still very small compared to the corresponding acid. With increasing pH the net rate coefficient increases nearly parallel with the mole fraction of acetate.

3.3. REACTIVITY TRENDS

The rate coefficients obtained for the electron transfer reactions of NO₃ with formate and acetate differ by a factor of twenty-two and are dependent on the redox potential of the reagents. The larger rate constant for formate (k_2) is associated with a low redox potential of HCOO⁻/HCOO (1.36 V, Wardman, 1989) whereas the smaller rate constant for acetate (k_4) is associated with a higher value for the CH₃COO⁻/CH₃COO redox potential (2.41 V, Wine and Chameides, 1989). In comparison with other one-electron transfer reactions of the NO₃ radical (Table VI) a linear relationship between the logarithm of rate constants and the redox potentials of the reagents is apparent (Figure 12).

TABLE VI. Rate coefficients for selected electron transfer reactions of the NO_3 radical, $T = 298 \text{ K}$

Species	E°/V	$\lg(k/\text{mol}^{-1}\text{s}^{-1})$
$\text{HCOO}^-/\text{HCOO}$	1.36 ^a	7.70 ^c
$\text{CH}_3\text{COO}^-/\text{CH}_3\text{COO}$	2.41 ^c	6.40 ^c
Cl^-/Cl	(2.5 ± 0.2) ^b	7.0 ^d
OH^-/OH	(1.9 ± 0.1) ^b	7.94 ^d
$\text{HSO}_3^-/\text{SO}_3^-$, H^+	0.84 ^a	9.13 ^d
$\text{SO}_3^{2-}/\text{SO}_3^-$ *	0.63 ^a	8.48 ^d

Rate constant obtained at $T = 278 \text{ K}$, ^a Stanbury (1989), ^b average values taken from Wardman (1989), ^c Wine and Chameides (1989), ^d Exner *et al.* (1992), ^e this work.

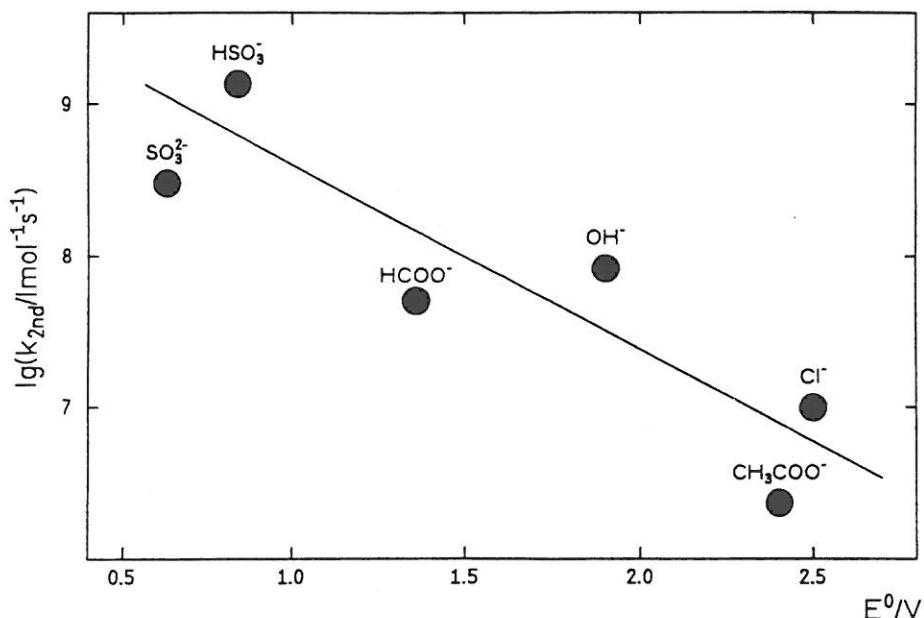


Fig. 12. Logarithmic plot of second-order rate coefficients for electron transfer reactions of the NO_3 radical with selected reactants as a function of their redox potentials.

On the other hand it may be expected that the reactions of NO_3 with acetic and formic acid, which occur via a hydrogen abstraction mechanism, depend on the dissociation energy of the corresponding C—H bonds. The rate constant per abstractable hydrogen atom is $k_1 = 3.3 \times 10^5 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_3 = 4.3 \times 10^3 \text{ mol}^{-1} \text{ s}^{-1}$ for HCOOH and CH_3COOH , respectively. The corresponding bond strengths are 387 and 410 kJ/mol as estimated by the method of Benson (Benson, 1976; Reid *et al.*, 1987). Apparently there is a tendency of small bond dissociation energies to correlate with high rate constants for hydrogen abstraction reactions by

TABLE VII. Rate coefficients, concentrations and first order loss rates for reactions of NO₃ radicals with different atmospheric droplet ionic constituents, T = 298 K

Species	<i>k</i> /l mol ⁻¹ s ⁻¹	Concentration range/mol × l ⁻¹	Loss rate / s ⁻¹
Cl ⁻	1.0 × 10 ⁷ ^b	1 × 10 ⁻⁷ –5 × 10 ⁻⁴ ^c	1–1000
HCOO ⁻	5.0 × 10 ⁷ ^a	3 × 10 ⁻⁷ –5 × 10 ⁻⁶ ^c	15–250
HSO ₃ ⁻	1.4 × 10 ⁹ ^b	7 × 10 ⁻⁸ –2 × 10 ⁻⁹ ^d	3–100
CH ₃ COO ⁻	2.3 × 10 ⁶ ^a	2 × 10 ⁻⁸ –3 × 10 ⁻⁶ ^c	0.05–7

^a This work, ^b Exner *et al.* (1992), ^c Church *et al.* (1991), ^d Graedel and Weschler (1981).

the nitrate radical and vice versa. This is further supported by studies of a number of other H-abstraction reactions the results of which will be published elsewhere (Exner *et al.*, 1993).

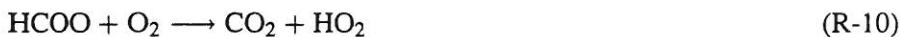
3.4. ATMOSPHERIC IMPLICATIONS

In order to assess the importance of the reactions of the NO₃ radical with HCOOH/HCOO⁻ and CH₃COOH/CH₃COO⁻ for atmospheric aqueous phase chemistry, the pseudo-first order loss rates of the nitrate radical were evaluated. In addition, the electron transfer reactions of NO₃ with Cl⁻ and HSO₃⁻ which have been identified as important atmospheric aqueous phase reactions (Exner *et al.*, 1992) were also taken into consideration. The measured species concentrations and the kinetic data which were used are summarized in Table VII.

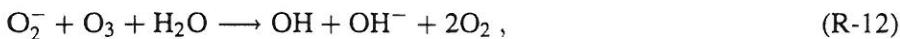
A comparison of the results obtained shows that the reaction with formate, viz.



may represent a more important sink for the nitrate radical within droplets of clouds and rain than the reaction with the S (IV) species HSO₃⁻. Since in the presence of O₂ reaction (2) is followed by



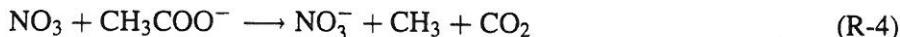
the produced intermediate HO₂ can react with ozone as well as undergo a self reaction, which in each case leads to the formation of OH radicals, viz.



Hence, the interconversion of NO_3 into HO_2 may significantly contribute to the destruction of O_3 within atmospheric cloud water, a matter very recently discussed in the literature (Lelieveld and Crutzen, 1991).

As a consequence of the above arguments it can be concluded that reaction (2) plays an important role in atmospheric aqueous phase processes especially at high pH values as found in the marine environment. However, even at the natural pH of 5.6, this reaction should be included in atmospheric modelling studies. At still lower pH values, as typically found in droplets of urban origin, the net reaction rate constants become smaller, so that the importance of the reaction of NO_3 with $\text{HCOOH}/\text{HCOO}^-$ is decreased. Because of the small loss rates of NO_3 below a pH value of 2 the controlling influence of the formic acid/formate system of the NO_3 concentration within droplets can be neglected.

The evaluated rate for NO_3 loss via reaction



is relatively small, due to the moderately slow rate constant for this reaction compared to other NO_3 reactions listed in Table VII. Therefore the influence of acetate on NO_3 removal within tropospheric droplets is negligible. On the other hand the methyl radical formed in reaction (4) will add molecular oxygen and the resulting methylperoxy radical may initiate further oxidation processes within droplets. The relevance of this process can only be assessed on the basis of other generation processes of CH_3O_2 , i.e. uptake from the gas phase, which presently cannot be quantified.

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