

Rate Constants for the Reactions of NO_3^\cdot and $\text{SO}_4^{\cdot-}$ Radicals with Oxalic Acid and Oxalate Anions in Aqueous Solution

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Abstract: Rate constants for the reactions of NO_3^\cdot and $\text{SO}_4^{\cdot-}$ radicals with oxalic acid and oxalate anions in aqueous solution have been measured using pulse radiolysis and laser flash photolysis.

Keywords: NO_3^\cdot , $\text{SO}_4^{\cdot-}$, oxalates, aqueous phase rate constants.

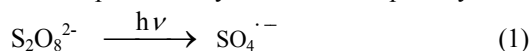
NO_3^\cdot and $\text{SO}_4^{\cdot-}$ radicals have been suggested as important intermediates in aqueous phase atmospheric chemistry. Particularly, at night, NO_3^\cdot radical takes over from $\cdot\text{OH}$ radical as the dominant oxidant in the troposphere, and the diurnal impact of $\cdot\text{OH}$ and NO_3^\cdot are complementary¹. $\text{SO}_4^{\cdot-}$ is an important chain carrier in the oxidation of SO_2 in acid rain chemistry². Previous studies of the reactions of NO_3^\cdot and $\text{SO}_4^{\cdot-}$ with oxygenated volatile organic compounds in aqueous phase have mainly dealt with alcohols³. More recently, Buxton *et al.* measured the rate constants for reactions of NO_3^\cdot and $\text{SO}_4^{\cdot-}$ with some esters⁴. However, for the reactions of NO_3^\cdot and $\text{SO}_4^{\cdot-}$ with oxalic acid and oxalate anions, no data have been reported so far. The low molecular weight dicarboxylic acids, such as oxalic acid, are an important class of organic compounds in the marine rains. Oxalic acid, the smallest diacid, is the most abundant, comprising 50 % of the total diacids. Dicarboxylic acids are also found in the arctic aerosol⁵. The concentration of oxalate in fog water is significant and it is suggested that the oxalate anion plays a potentially important role in the photochemistry of atmospheric droplets⁶. In order to assess the importance of the chemical degradation of oxalic acid and oxalate anions through reaction with NO_3^\cdot and $\text{SO}_4^{\cdot-}$, reliable reaction rate coefficient data is needed. Accordingly, we report herein the reactions of NO_3^\cdot and $\text{SO}_4^{\cdot-}$ with oxalic acid and oxalate anions at room-temperature.

When measuring the rate constant for the reaction of NO_3^\cdot with oxalic acid and oxalic anions, NO_3^\cdot was produced by pulse radiolysis of N_2O saturated 2.0 mol/L HNO_3 solutions and argon saturated 1.0 mol/L NaNO_3 solutions, respectively. Pulse radiolysis was carried out using single pulses of 2.5 MeV electrons from a Van de Graaff accelerator as reference⁷. The pulse radiolysis cell had a triple-pass optical system with a path-length of 7.0 cm. Dosimetry was carried out using O_2 -saturated solutions of 10^{-2}

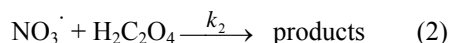
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mol/L KSCN taking $G\epsilon[(\text{SCN})_2^{\cdot-}]$ at 475 nm to be $2.59 \times 10^{-4} \text{ m}^2 \text{ J}^{-1} \cdot \text{s}^{-1}$.

$\text{SO}_4^{\cdot-}$ radicals were produced by the laser flash photolysis of $\text{S}_2\text{O}_8^{2-}$ solution:

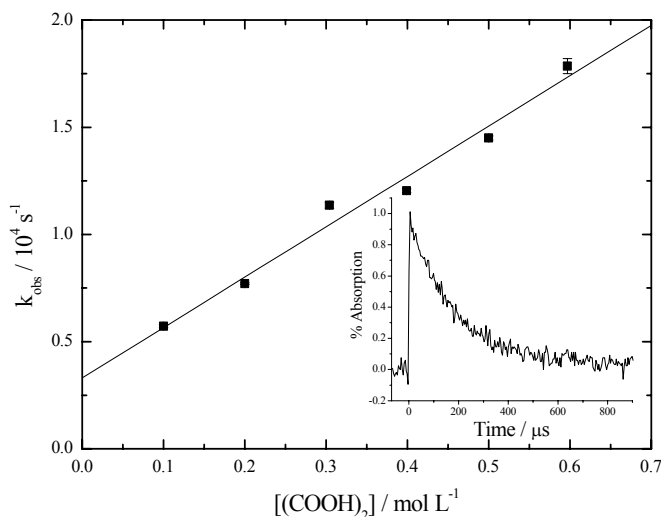


Laser flash photolysis was carried out using single pulses of photolysing light from a Lambda Physik Excimer Multigas laser operating at 248 nm. The system produces optimum output of 200 mJ per pulse with a pulse half-width of 14 ns. The optical pathlength of the cell was 1 cm. To improve signal quality, recorded traces were an average of four separate flashes to freshly flushed samples. The reactions of NO_3^{\cdot} and $\text{SO}_4^{\cdot-}$ radicals were monitored by following the decay of their absorbances at 630 and 450 nm, respectively. All the kinetics experiments were carried out under pseudo-first-order conditions with $[\text{oxalates}] \gg [\text{radicals}]_0$ at ambient temperature. All errors are reported as 2σ from linear regression fits. A typical trace for the reaction of NO_3^{\cdot} with $\text{H}_2\text{C}_2\text{O}_4$ is shown in reaction (2),

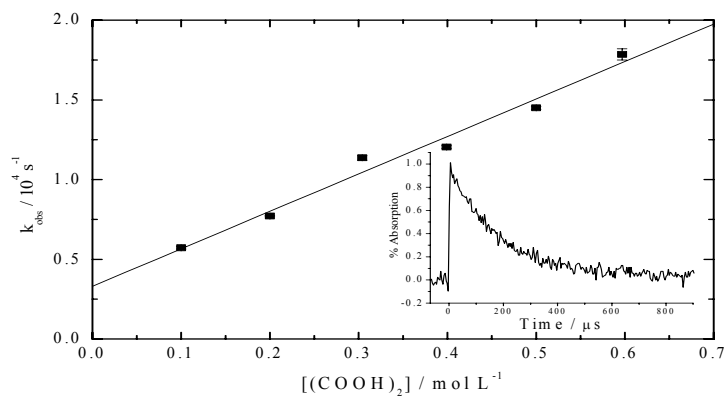


A plot of k_{obs} against $[(\text{COOH})_2]$ (**Figure 1**) produced $k_1 = (2.4 \pm 0.2) \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$. At the moment, no literature value is available for comparison.

Figure 1 Dependence of k_{obs} for the reaction of $\text{NO}_3^{\cdot} + \text{H}_2\text{C}_2\text{O}_4$ on $[\text{H}_2\text{C}_2\text{O}_4]$

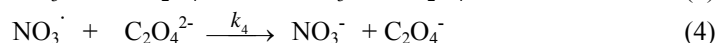
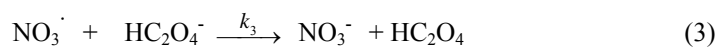


Time-absorbance trace for the reaction of NO_3^{\cdot} with $\text{H}_2\text{C}_2\text{O}_4$, $[\text{HNO}_3] = 2.0 \text{ mol/L}$, $[(\text{COOH})_2] = 0.1 \text{ mol/L}$, $\text{pH} < 0$, N_2O saturated, $\lambda = 630 \text{ nm}$, Dose = 1.4 Gy.

Figure 2 Dependence of k_{obs} for the reaction of $\text{NO}_3^\cdot + \text{C}_2\text{O}_4^{2-}$ on $[\text{C}_2\text{O}_4^{2-}]$ 

Time-absorbance trace for the reaction of NO_3^\cdot with $\text{C}_2\text{O}_4^{2-}$, $[\text{NaNO}_3] = 1.0 \text{ mol/L}$, $\text{pH} = 3.0$, $[\text{C}_2\text{O}_4^{2-}] = 7 \text{ mmol/L}$, Ar saturated, $\lambda = 630 \text{ nm}$, Dose = 9.5 Gy .

The inset to **Figure 2** presents a typical trace for the decay of NO_3^\cdot monitored at 630 nm for the reactions of NO_3^\cdot with oxalates, HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$, reaction (3) and (4):

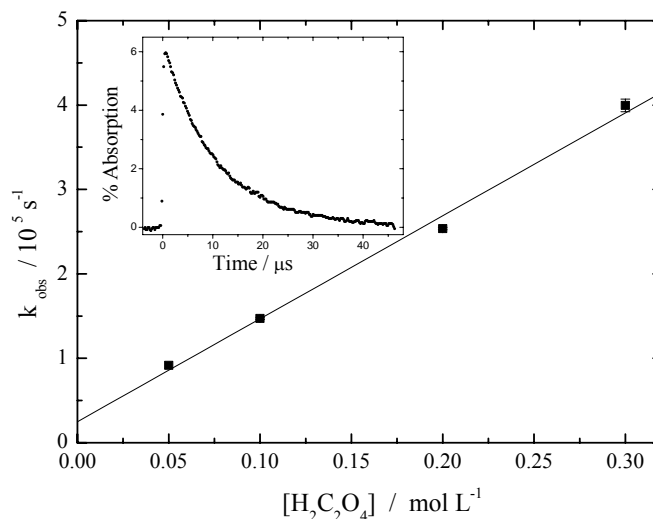


The variation of k_{obs} with $[\text{C}_2\text{O}_4^{2-}]$ is shown in **Figure 2** and gave the following rate constants: $k_a = (7.6 \pm 0.2) \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ ($\text{pH} = 3$), and $k_b = (2.2 \pm 0.1) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ ($\text{pH} = 7$). Where k_a and k_b are the rate constants for the reaction of NO_3^\cdot with oxalates at $\text{pH} = 3$ and 7 , respectively. Based on the equilibria of oxalic acid in water, the molar fraction of $\text{H}_2\text{C}_2\text{O}_4$, HC_2O_4^- , and $\text{C}_2\text{O}_4^{2-}$ were calculated, so that the rate constants for NO_3^\cdot with the different forms of oxalates ($\text{H}_2\text{C}_2\text{O}_4$, HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$) can be obtained as follows (in $\text{L mol}^{-1} \text{ s}^{-1}$):

$$k(\text{NO}_3^\cdot + \text{H}_2\text{C}_2\text{O}_4) = (2.4 \pm 0.2) \times 10^4; \quad k(\text{NO}_3^\cdot + \text{HC}_2\text{O}_4^-) = (7.8 \pm 0.7) \times 10^7$$

$$k(\text{NO}_3^\cdot + \text{C}_2\text{O}_4^{2-}) = (2.2 \pm 0.1) \times 10^8$$

The inset to **Figure 3** represents a typical trace for the decay of $\text{SO}_4^{\cdot-}$ monitored at 450 nm for the reactions of $\text{SO}_4^{\cdot-}$ with $\text{H}_2\text{C}_2\text{O}_4$. At room temperature ($292 \pm 2 \text{ K}$), the observed first-order rate constants are linearly dependent on the concentrations (see **Figure 3**). The rate constants of reaction has been determined to be $(1.2 \pm 0.1) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$. Followed the same procedure described above, the rate constants (in $\text{L mol}^{-1} \text{ s}^{-1}$) for the reactions of $\text{SO}_4^{\cdot-}$ with three different forms of oxalates were calculated: $k(\text{SO}_4^{\cdot-} + \text{H}_2\text{C}_2\text{O}_4) = 1.4 \times 10^5$, $k(\text{SO}_4^{\cdot-} + \text{HC}_2\text{O}_4^-) = 3.0 \times 10^6$ and $k(\text{SO}_4^{\cdot-} + \text{C}_2\text{O}_4^{2-}) = 5.6 \times 10^6$.

Figure 3 Dependence of k_{obs} for the reaction of $\text{SO}_4^{\cdot-} + \text{H}_2\text{C}_2\text{O}_4$ on $[\text{H}_2\text{C}_2\text{O}_4]$ 

Time-absorbance trace for the reaction of $\text{SO}_4^{\cdot-}$ with oxalic acid at 450 nm: $[\text{S}_2\text{O}_8^{2-}] = 10 \text{ mmol/L}$, $\text{pH} = 1.0$, Ar saturated, $[\text{H}_2\text{C}_2\text{O}_4] = 0.05 \text{ mol/L}$, 248 nm laser light.

The trend for the reactions of oxalates with $\text{SO}_4^{\cdot-}$ are similar to it reacted with NO_3^{\cdot} . The reaction of $\text{SO}_4^{\cdot-}$ and NO_3^{\cdot} with $\text{C}_2\text{O}_4^{2-}$ is fastest, and that with $\text{H}_2\text{C}_2\text{O}_4$ is slowest.

For most of reactions in water, *e.g.*, the reactions of alcohols, OH radical normally has largest rate constant. The $\text{SO}_4^{\cdot-}$ radical also exhibits a higher reactivity than NO_3^{\cdot} . However, the reaction of NO_3^{\cdot} with $\text{C}_2\text{O}_4^{2-}$, NO_3^{\cdot} is nearly 40 times more reactive than $\text{SO}_4^{\cdot-}$ and OH . The high reactivity of NO_3^{\cdot} with $\text{C}_2\text{O}_4^{2-}$ suggests that reaction with NO_3^{\cdot} would represent the major oxidation route for $\text{C}_2\text{O}_4^{2-}$ in the aqueous phase.

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