Kinetics of oxidation of nitrite by peroxomonosulphate

Madhu Sharma, D. S. N. Prasad & K. S. Gupta
Atmospheric Chemistry Laboratory, Department of Chemistry
University of Rajasthan, Jaipur 302 004, India
Received 24 October 1991; accepted 12 March 1992

Rate studies on peroxomonosulphate-nitrite reaction show that the reaction obeys the rate equation,

\[ \frac{-d[HSO_5^-]}{dt} = \frac{k_0K_a + k_1[H^+] + k_2K_a[H^+]^2}[PMS][NO_2^-]_h}{(K_a + [H^+])} \]

where \( K_a \) is the dissociation constant of HNO_2. Values of \( k_0, k_1 \) and \( k_2K_a \) are 0.14, 0.31 and \( 6.4 \times 10^2 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\), respectively at 25°C. A comparison with oxidation of HSO_3\(^-\) by peroxomonosulphate shows that, in atmosphere, NO_2\(^-\) will not be able to compete with HSO_3\(^-\).

Concentration of peroxomonosulphate (PMS) has been predicted to be only one order of magnitude less than that of H_2O_2 in remote marine and continental clouds. PMS radical is formed in the first propagation step of the metal ion catalysed atmospheric oxidation of SO_2. Moreover, PMS ion is reported to be formed as an intermediate in surface catalysed autoxidation of aqueous SO_2 in suspensions of several metal and non-metal oxides. Besides sulphur dioxide, oxides of nitrogen are other important acid rain precursors. A recent modelling exercise by Luria and Sievering has shown that HNO_2 in atmosphere, may be present to the extent of 0.1-0.4 parts per trillion by volume. Reaction of NO_2\(^-\) with S(IV) (refs 10-12) is considered to be one of the paths contributing to atmospheric acid precipitation. In remote marine and continental clouds, both nitrite and sulphur(IV) may compete for PMS. The kinetics of oxidation of S(IV) by PMS have been studied recently. It was, therefore, of interest to study the oxidation of nitrite by PMS in order to compare the relative reactivities of NO_2\(^-\) and PMS in the pH region of interest to atmospheric situations. Previously, a preliminary investigation on kinetics of nitrite-PMS reaction has been made.

Experimental
Oxone (Aldrich), which is a triple salt (2KHSO_5.KHSO_4.K_2SO_4), was the source of peroxomonosulphate. Sodium nitrite (BDH, AnalaR) and all other chemicals of reagent grade were used. Iodometric assay revealed the PMS content in the triple salt to be around 85%. Sodium nitrite solutions were standardised cerimetrically and only fresh solutions were used. Acetate buffer was used for maintaining the pH of reaction mixtures. The reactions were initiated by mixing temperature equilibrated solution of sodium nitrite with the solution of PMS containing buffer and maintained at the same temperature (±0.1°C). For following the kinetics, the nitrite was decomposed by addition of sulphamic acid to the aliquots. Now potassium iodide was added and the liberated iodine was titrated against standard sodium thiosulphate solution using starch as an indicator. The duplicate rate measurements were reproducible within ±5%.

Stoichiometry
The stoichiometry was determined by keeping [PMS] in some, and [nitrite] in other experiments, in excess and the unreacted PMS was determined iodometrically and unreacted nitrite was determined cerimetrically. Both the methods of stoichiometric measurements led to Eq. (1). The product nitrate was detected by usual qualitative tests as well as by appearance of a peak in the visible spectrum of final product solution at 302 nm.

Results
The kinetic results of [PMS] and [nitrite] variations are consistent with the experimental rate law (2),

\[ \frac{-d[PMS]}{dt} = k_{obs}[PMS][NO_2^-]_h \]

where \([PMS]_h\) and \([NO_2^-]_h\) represent the analytical concentrations of PMS and nitrite respectively. From the kinetic runs in which \([NO_2^-]_h\) was in excess over \([PMS]_h\), the pseudo-first order rate constants, \( k_{obs} \) (Table 1), were obtained by using Eq. (3),

\[ \frac{-d[PMS]}{dt} = k_{obs}[PMS] \]

where \( k_{obs} = [NO_2^-]_h \).

In some kinetic runs, \([PMS]_h\) and \([NO_2^-]_h\) were either equal or comparable and, the values of second or-
der rate constants are in good agreement with those derived from $k_{obs}$. On increasing pH the rate of reaction decreases and tends to attain a limiting value at pH > 5 (Table 1). The variation of ionic strength (0.1-1.0 mol dm⁻³) with sodium perchlorate did not affect the rate of the reaction.

**Discussion**

The first dissociation constant of peroxomono­sulphate is reported to be high ($pK_1 < 0$) and the second dissociation constant to be low ($pK_2 = 9.8$) (ref. 16). Thus, in the pH range of 2.0-7.01 used in this study, PMS will be present largely as HSO₅⁻.

The observed [H⁺] dependence is thus most likely related to involvement of nitrite ion and its various protonated forms, as shown in the following Scheme 1.

<table>
<thead>
<tr>
<th>$K_\text{a}$</th>
<th>$K_\text{b}$</th>
<th>$K_\text{c}$</th>
<th>$K_\text{d}$</th>
</tr>
</thead>
</table>

| HNO₂ | K⁺ NO₃⁻ + H⁺ |
| HNO₂ + H⁺ | K⁺ NO⁺ + H₂O |
| NO₂⁻ + HSO₅⁻ | k₁ NO₃⁻ + SO₄²⁻ + H⁺ |
| HNO₂ + HSO₅⁻ | k₂ NO₃⁻ + SO₄²⁻ + 2H⁺ |
| NO⁺ + HSO₅⁻ + H₂O | k₂ NO₃⁻ + SO₄²⁻ + 3H⁺ |

Scheme 1

Scheme 1 leads to the rate law (4).

$$k = \frac{k_0 K_a + k_1 [H^+] + k_2 K_2 [H^+]^2}{[K_a + [H^+]]} \quad \ldots \ (4)$$

Dissociation constant, $K_a$, of HNO₂ is reported to be $5.1 \times 10^{-4}$ and so in the pH range 5-7, nitrite will be almost wholly present as NO₂⁻. Hence the rate of reaction in this region can be ascribed to mainly NO₂⁻-HSO₅⁻ reaction and contributions from $k_1$ and $k_2$ paths may be ignored. On this basis second order rate constants determined in pH region 5-7 may be taken equal to $k_0$.

On rearranging Eq. (4) becomes Eq. (5).

$$\frac{k(K_a + [H^+]) - k_0 K_a}{[H^+]} = k_1 + k_2 K_2 [H^+] \quad \ldots \ (5)$$

The plot of left hand side of Eq. (5) against $[H^+]$ was linear (Fig. 1) and from the intercept and slope the

![Fig. 1—The effect of $[H^+]$ on the rate of nitrite-peroxomono­sulphate reaction at $I = 1.0 \text{ mol dm}^{-3}$](image)
values of \( k_1 \) and \( k_2K_2 \) were determined. These values together with \( k_0 \) are given in Table 2 which also includes energies and entropies of activation for \( k_0 \), \( k_1 \) and \( k_2K_2 \).

The value of equilibrium constant, \( K_2 \), is reported\(^{17}\) to be \( 3 \times 10^{-7} \). From the \( k_2K_2 \) value, \( k_2 \) is estimated to be \( 2.1 \times 10^9 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) at 25°C. This value of \( k_2 \) suggests the reaction of NO\(^+\) with HSO\(_3^-\) to be diffusion controlled. The reaction of NO\(^2-\) and H\(_2\)O\(_2\) has also been studied in the [H\(^+\)] range of 0.1-1.0 mol dm\(^{-3}\). Using the same \( K_2 \) value, from the data of Benton and Moore\(^{18}\), the value of \( k_2 \) for NO\(^+\) and H\(_2\)O\(_2\) reaction is estimated to be \( 5 \times 10^9 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\). Thus, both NO\(^+\)-H\(_2\)O\(_2\) and NO\(^+\)-HSO\(_3^-\) reactions are diffusion controlled and take place at nearly the same rates. Incidentally, Betterton and Hoffmann\(^{13}\) found a similar behaviour of HSO\(_3^-\) and H\(_2\)O\(_2\) towards HSO\(_3^-\).

It is of interest to compare the results of this study with those of Edwards and Mueller\(^{14}\). \( k \) (25°C) and \( E_a \) values of 0.14 dm\(^3\) mol\(^{-1}\) s\(^{-1}\) and 11.0 kcal/mol compare favourably with those (0.31 dm\(^3\) mol\(^{-1}\) s\(^{-1}\) and 13.2 kcal/mol) of earlier workers\(^{14}\). In the previous study the main contributing path to the overall rate was NO\(^2-\)-HSO\(_3^-\) reaction as their study was done in the high pH range. In the present case, two additional paths manifest themselves in the low pH region. In atmosphere, both H\(_2\)O\(_2\) and HSO\(_3^-\) may compete for oxidising nitrite. A comparative rate analysis carried out by Edwards and Mueller\(^{14}\) has shown HSO\(_3^-\) to be several orders of magnitude more reactive than H\(_2\)O\(_2\) in the pH range of interest to atmospheric chemists. Thus, if both HSO\(_3^-\) and H\(_2\)O\(_2\) are present, NO\(^2-\) will be preferentially oxidised by HSO\(_3^-\).

A comparison of the rates of oxidation of S(IV) and nitrite ion by PMS is in order. At pH 2.08, Betterton and Hoffmann\(^{13}\) determined the overall second order rate constant to be \( 4.11 \times 10^4 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) at 5°C. In the present reaction at the same pH value but at 25°C the overall second order rate constant has a value of 4.38 dm\(^3\) mol\(^{-1}\) s\(^{-1}\). It is therefore concluded that, in atmosphere, HSO\(_3^-\) will oxidise HSO\(_3^-\) at a rate much faster than NO\(^2-\).

**Acknowledgement**

The work was supported by Indo-US Subcommission and UGC research projects.

**References**


---

**Table 2—The values of \( k_0 \), \( k_1 \) and \( k_2K_2 \) at different temperatures**

<table>
<thead>
<tr>
<th>Rate constants (dm(^3)mol(^{-1}) s(^{-1}))</th>
<th>Temperature, °C</th>
<th>( E_a ) (kJ mol(^{-1})K(^{-1}))</th>
<th>( \Delta S^* ) (J mol(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_0 )</td>
<td>25</td>
<td>0.14</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.19</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.26</td>
<td>47</td>
</tr>
<tr>
<td>( k_1 )</td>
<td>25</td>
<td>0.31</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.50</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.95</td>
<td>85</td>
</tr>
<tr>
<td>( k_2K_2 )</td>
<td>640</td>
<td>780</td>
<td>870</td>
</tr>
</tbody>
</table>