過氧硫酸氫根離子氧化碘分子的反應動力學

李少榕¹  邱瑞妙²

摘 要

過氧硫酸氫根離子氧化碘分子成碘酸根離子的反應，依擬一級動力學的方式(過氧硫酸氫根離子過量)，在 25°C、pH 值範圍為 2.71-3.62 的水溶液中完整地被探討。碘分子消失的速率分別與過氧硫酸氫根離子及碘分子的濃度成比，且水溶液中的 pH 值增加反應速率增快。此反應的反應速率定律式為：

$$-\frac{d[I_2]}{dt} = k[H_2SO_5][I_2]$$

其中 $k = \frac{k[H^+]}{[H^+]+K_{a1}} + \frac{k_2K_a}{[H^+]+K_{a2}}$，$K_a$ 是 $H_2SO_5$ 的第二解離常數，$k_1 = 0.57 M^{-1}s^{-1}, k_2 = 3.01 \times 10^6 M^{-1}s^{-1}$。

關鍵詞：動力學、過氧硫酸氫根離子、碘分子

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1 義守大學化工系副教授
2 聯華林德氣體工業股份有限公司工程師
A Kinetic Study of Lodine Molecule Oxidation by Aqueous Hydrogen Peroxymonosulfate

Shao-yung Lee* Jui-miao Chiu**

Abstract

This study investigated the peroxymonosulfate oxidation of iodine to iodate under pseudo-first-order conditions (with excess HSO$_5^-$) in buffered aqueous solutions at pH 2.71–3.62 at 25 °C. The rates of iodine decay are first order in both iodine and peroxymonosulfate ion concentrations and increase rapidly with increasing pH. The reaction can be described with the following rate law: $-\frac{d[I_2]}{dt} = k[HSO_5^-][I_2]$, where

\[
k = \frac{k_1[H^+]}{[H^+] + K_{a_2}} + \frac{k_2K_{a_2}}{[H^+] + K_{a_2}},
\]

$K_{a_2}$ is the second dissociation constant of H$_2$SO$_5$, $k_1 = 0.57$ M$^{-1}$s$^{-1}$, and $k_2 = 3.01 \times 10^6$ M$^{-1}$s$^{-1}$.

Keywords: Kinetics, peroxymonosulfate, iodine

* Associate Professor, Department of Chemical Engineering, I-Shou University.
** Engineer, Linde Lienhwa Industrial Gases Co., Ltd.
1. Introduction

The oxidation of halide ions with peroxo compounds has been extensively investigated [1–4]. The proposed reaction mechanisms are the followings:

\[ \text{ROOH} + X^- \rightarrow \text{RO}^- + \text{HOX} \quad \text{(slow)} \quad (1) \]

\[ \text{HOX} + \text{H}^+ + X^- \rightarrow \text{X}_2 + \text{H}_2\text{O} \quad \text{(fast)} \quad (2) \]

The reactivity of the hydroperoxides for the oxidation of the bromide ion is $\text{H}_2\text{O}_2 < \text{H}_2\text{PO}_4^- < \text{CH}_3\text{COOOH} < \text{HSO}_5^- < \text{H}_3\text{PO}_5$ [2]. Recently, Régimbal et al. found that the second-order rate constant for the oxidation of iodide with peroxynitric acid, which is shown in reaction (3), was $890 \text{ M}^{-1}\text{s}^{-1}$ [5]. The reaction rate was

\[ \text{HOONO}_2 + \text{I}^- \rightarrow \text{NO}_3^- + \text{HOI} \quad (3) \]

independent of the hydrogen ion concentration at pH 1.2-4.9. They also concluded that the reactivity of the peroxymonosulfate ion oxidation of iodide follows the same pattern as that observed when using peroxynitric acid, both qualitatively and quantitatively. The kinetics of the redox reactions of the peroxymonosulfate ion with halides were found to follow a two-electron process, and the second-order rate constant for the oxidation of iodide was $1400 \text{ M}^{-1}\text{s}^{-1}$ [6]. However, the reaction of $\text{H}_2\text{O}_2$ with iodine to form iodide at low concentration of hydrogen ion was also observed [7]. Therefore, the decomposition of hydrogen peroxide would be catalyzed in the presence of an iodine or iodide ion at pH~5. The oxidation of iodine to iodate with evolution of oxygen was also observed under certain conditions during the

\[ \text{I}_2 + 11 \text{HOOH} \rightarrow 2 \text{IO}_3^- + 3 \text{O}_2 + 2 \text{H}^+ + 10 \text{H}_2\text{O} \quad (5) \]

iodate-catalyzed decomposition of hydrogen peroxide [8].

Peroxymonosulfurous acid ($\text{H}_2\text{SO}_5$) is a strong acid with $pK_{a1} < 0$ [9,10]. Peroxymonosulfate, a mono-substituted derivative of $\text{H}_2\text{O}_2$, is a powerful oxidant and is often used in swimming pools, spa shocks, and disinfection methods. The oxidation of amino acids by peroxymonosulphate has also been extensively studied [11]. This mono-substituted derivative of $\text{H}_2\text{O}_2$ is often more reactive than $\text{HOOH}$, even though its reduction potential is only slightly higher ($E^{\circ}_{\text{HSO}_5^-/\text{HSO}_4^-} = 1.82 \text{ V}; E^{\circ}_{\text{H}_2\text{O}_2/\text{H}_2\text{O}} = 1.78 \text{ V}$) [9,12-13]. However the oxidation of iodine with other peroxo compounds is not well known [6]. In order to understand the oxidation of iodine with peroxymonosulfate ion, we studied the stoichiometry and rate of the reaction. We also investigated the effect of hydrogen ion concentration on the reaction.

2. Experimental

Materials. A commercially prepared salt containing peroxymonosulfate ion is available from Du Pont Co. as a white granular powder under the trade name of oxone (2KHSO$_5$·KHSO$_4$·K$_2$SO$_4$). The purification of oxone to yield KHSO$_5$·H$_2$O was achieved by modifying Appleman’s method [14–15]. All the other chemicals purchased were reagent grade and used directly without further purification. Peroxymonosulfate solution were standardised by iodometric titration. Formic acid buffer was used
Kinetics. UV-visible spectra and single-wavelength absorbance vs. time data were acquired by employing a Hitachi 3000 or HP 8453 spectrophotometer. The temperature was controlled at ±0.5 °C by maintaining the water circulation from a constant-temperature bath through the jacket of the cell holder. All kinetic measurements were performed using formate adjusted to \( \mu = 1.0 \) M. A Millipore Milli-Q SP system was used in all the kinetic measurements to purify the water.

3. Results and Discussion

Rate constants. The colour immediately changed to yellow-brown in a clear solution of potassium iodide upon addition of excess potassium peroxymonosulfate. Intense absorption at \( \lambda = 462 \) nm (\( \epsilon_{462} = 975 \) M\(^{-1}\)cm\(^{-1}\)) [16] and no significant absorption at \( \lambda = 351 \) nm (\( \epsilon_{351} = 2.6 \times 10^4 \) M\(^{-1}\)cm\(^{-1}\)) [4] indicated the complete conversion of iodide to iodine. The absorption at 462 nm then decreased as a function of time, and a clear solution was eventually obtained. It is noteworthy that no gas product was observed during the reaction. Therefore, the kinetics of the reaction of iodine with peroxymonosulphate was monitored by the absorption change at 462 nm. All the rate measurements were performed under pseudo-first-order conditions with a 10-fold or greater excess of peroxymonosulfate ion. A typical kinetic trace is shown in Fig. 1. The plots of \( \ln(A_t-A_\infty) \) vs. time gave a good linear

![Figure 1. Kinetic trace at \( \lambda = 462 \) nm for the reaction of HSO\(_5^–\) with I\(_2\).](image)

\( \text{pH} = 3.22, T = 25 \) °C, \( \mu = 1.0 \) M, \( [\text{HSO}_5^-] = 3.85 \times 10^{-2} \) M.
relation for at least 2-3 half-lives. The pseudo-first-order rate constant was proportional to the concentration of peroxymonosulfate at constant pH, as shown in Fig. 2. Consequently, the reaction rate law corresponding to the decreased absorption process is

$$\frac{d[I_2]}{dt} = k[HSO_5^-][I_2]$$

(7)

**Hydrogen ion concentration effect.** This reaction was also studied at various pH conditions under pseudo-first-order conditions. The second order rate constants at various pH conditions are listed in Table 1.

**Table 1. The kinetic results for the reaction of peroxymonosulfate ion with iodine at various pH conditions.**

<table>
<thead>
<tr>
<th>pH</th>
<th>$10^2 \times [HSO_5^-]$, M</th>
<th>k, M$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.71</td>
<td>1.66–4.83</td>
<td>0.76 ± 0.03</td>
</tr>
<tr>
<td>2.89</td>
<td>1.67–4.88</td>
<td>1.16 ± 0.04</td>
</tr>
<tr>
<td>3.04</td>
<td>1.67–4.88</td>
<td>1.83 ± 0.06</td>
</tr>
<tr>
<td>3.22</td>
<td>1.64–4.47</td>
<td>1.88 ± 0.04</td>
</tr>
<tr>
<td>3.42</td>
<td>1.66–4.83</td>
<td>3.1 ± 0.1</td>
</tr>
<tr>
<td>3.46</td>
<td>1.36–4.96</td>
<td>3.3 ± 0.1</td>
</tr>
<tr>
<td>3.62</td>
<td>1.67–4.88</td>
<td>3.93 ± 0.07</td>
</tr>
</tbody>
</table>

* $T = 25 \, ^{\circ}C$, $\mu = 1.0 \, M$, buffer: formic acid.
From these data, it is apparent that this reaction would be faster in more basic aqueous solutions, which indicates that $SO_5^{2-}$ is the reactive species. The $K_{a2}$ of the peroxymonosulphate ion was $3.89 \times 10^{-10}$, as shown in equation (8).

$$HSO_5^- \rightarrow SO_5^{2-} + H^+$$

Therefore, a rate law that is consistent with the experimental data includes both $HSO_5^-$ and its conjugate base $SO_5^{2-}$, as shown in equation (9).

$$rate = k_1[HSO_5^-][I_2] + k_2[SO_5^{2-}][I_2]$$

$$= (k_1 \frac{[H^+]}{[H^+]} + k_2 \frac{K_{a2}}{[H^+]} + K_{a2})[HSO_5^-][I_2]$$

$$= k_1[H^+] + k_2K_{a2} + K_{a2}K_{a2}[H^+]$$

and

$$k = \frac{k_1[H^+]}{[H^+] + K_{a2}} + \frac{k_2K_{a2}}{[H^+] + K_{a2}}$$

The second-order rate constants associated with low and high pH correspond to $k_1$ and $k_2$, respectively. Therefore, when $[H^+] \gg K_{a2}$, i.e. when pH $< 7.4$

$$k \approx k_1 + k_2 \frac{K_{a2}}{[H^+]}$$

Thus, a linear plot of $k$ vs. $[H^+]^{-1}$ gives $k_2K_{a2}$ and $k_1$ from the slope and intercept, respectively. These rate constants were obtained from the intercept and slope of Fig. 3 as $k_1 = 0.57 \pm 0.19 \text{ M}^{-1}\text{s}^{-1}$ and $k_2 = (3.01 \pm 0.03) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. The basic form of

![Figure 3. Plot of $k$ vs. $[H^+]^{-1}$ for the reaction of peroxymonosulphate with iodine.](image)
SO\(_5^2\) is more reactive in this reaction, which agrees well with the role of SO\(_5^2\) in the oxidation of amino acids [17].

**Reaction stoichiometry.** Reaction stoichiometry was determined by spectrophotometric titration using a UV-visible spectrophotometer following an absorption band of iodine as a function of the reactants ratio and by interpolating the absorbance to a break point. The absorption of the iodine solution at \(\lambda = 462\) nm was examined after each addition of a small volume of fixed amount of peroxymonosulfate. A certain time interval was maintained between each addition to ensure completion of the reaction. The absorption was plotted against the moles of peroxymonosulfate in the solution to show the equivalence of peroxymonosulfate to iodine in the reaction. The results of these measurements at various pH show that 5.2 ± 0.4 moles of peroxymonosulfate are used per mole of I\(_2\). The final product of this reaction was obtained as a white precipitate. The UV spectrum of this product is consistent with that of the iodate ion. The iodate ion was also the final product in the reaction of iodide with ozone [18, 19] as well as in the reaction of iodine with hydrogen peroxide [7, 12]. This reaction was therefore proposed as

\[
5 \text{HSO}_5^- + \text{I}_2 + \text{H}_2\text{O} \rightarrow 5 \text{HSO}_4^- + 2 \text{IO}_3^- + 2 \text{H}^+
\]  

(12)

The rate-determining step of the reaction between the peroxymonosulfate ion and iodine should be the formation of IO\(^-\) (or I\(_2\)O) [6] based on the reduction potential of the hypo-iodite and the rate law of equation (6).

By comparing reaction (11) with (4), it is clear that the reactivity of the peroxymonosulfate ion is significantly different from that of hydrogen peroxide for the reaction with iodine.

4. Conclusions

The kinetic studies clearly show that there is a bimolecular reaction between peroxymonosulfate and iodine molecule in formate buffered aqueous solutions at low pH. The reaction rates are dependent on the pH of the aqueous solution. The reactivity of SO\(_5^2\) is much higher than that of HSO\(_5^-\) in the oxidation of iodine.

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**References**


