Liquid Phase Oxidation of Nitrous Acid by Hydrogen Peroxide

HANS T. KARLSSON

Department of Chemical Engineering, Lund Institute of Technology, Box 740, S-220 07 Lund, Sweden

The liquid phase oxidation of nitrous acid by hydrogen peroxide was investigated in a pH-stat. The results have revealed that the overall reaction includes a series of reactions and several intermediates. Nitrous acid decomposes to nitrogen oxide which in turn is oxidized to nitrogen dioxide by hydrogen peroxide. The dimer of nitrogen dioxide reacts with water to form the end product, i.e. nitric acid.

Nitrous acid is an important link in the complex aqueous chemistry of nitrogen oxides. If alkali is not present in the solution, nitrous acid decomposes into a variety of nitrogen oxides; alkali acts as a stabilizer due to nitrite ion formation. Hydrogen peroxide is thought to be an efficient species for oxidizing nitrous acid to nitric acid. Such an option is beneficial in air pollution control, not only because environmental impacts from nitrogen oxides are eliminated, but also because nitric acid can be recovered as a useful by-product.

At least two hydrogen peroxide based processes for control of air pollution by nitrogen oxides have been developed. Hydrogen peroxide can be used to enhance the absorption of nitrogen oxides in a wet scrubber. Secondly, the release of nitrogen oxides to the ventilation gas in steel pickling can be suppressed by adding hydrogen peroxide to the pickling bath.

The present study was undertaken to obtain kinetic data for the liquid phase oxidation of nitrous acid by hydrogen peroxide. Furthermore, an in-depth analysis of the chemistry was made to outline the reaction mechanism.

THEORY

If sodium nitrite is added to a water solution, complete dissociation is obtained:

\[ \text{NaNO}_2 \rightleftharpoons \text{Na}^+ + \text{NO}_2^- \]  

(a)

Hydrogen ions present in the solution produce nitrous acid by shifting the following equilibrium reaction to the right:

\[ \text{H}^+ + \text{NO}_2^- \rightleftharpoons \text{HNO}_2 \]  

(b)

From equilibrium data given by Skoog et al.,\(^3\) it can be inferred that the conversion of nitrite to nitrous acid is greater than 90 % at pH values below 2.3.

Hydrogen peroxide oxidizes the nitrous acid according to the following overall reaction:

\[ \text{HNO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} \]  

(c)

It is assumed that this reaction obeys an \( m \)-, \( n \)-th-order rate expression of the following form:

\[ r_c = -k_c(\text{HNO}_2)^m(\text{H}_2\text{O}_2)^n \]  

(1)

where the parentheses indicate aqueous phase concentration.

If a concentrated solution of sodium nitrite is added to the reaction mixture, the concentration of nitrous acid attains the following steady state value:

\[ (\text{HNO}_2) = (\text{H}^+) \_0 - (\text{H}^+) \]  

(2)

where \((\text{H}^+)\) is given from the measured steady state pH value, and \((\text{H}^+)\_0\) is the corresponding
value before one starts to add nitrite to the solution.

The concentration of hydrogen peroxide can be calculated from the amount of this species charged to the solution, minus the amount consumed by reaction. The reaction rate can be estimated from the rate of added sodium nitrite solution and the concentration of the feed.

Thus the rate constant and the reaction orders can be obtained from steady state experiments by varying the concentrations of hydrogen peroxide and nitrous acid, i.e. hydrogen ion.

EXPERIMENTAL

Equipment. The experiments were performed by utilizing a pH-stat equipment (Radiometer). Hydrogen peroxide, water and nitric acid were charged to a glass beaker in desirable amounts. The pH-value of the solution was measured by an electrode connected to the pH-stat and the solution of sodium nitrite was added by an autoburette to obtain a preset pH value of the solution. The pH-stat adjusts the feed rate of the nitrite solution by a control loop based on a signal from the pH electrode.

The amount of nitrite fed to the solution was followed by continuously recording a signal from the burette on a strip chart recorder. The reaction rate was simply estimated by calculating the slope of the curve obtained on the strip chart numerically, and by multiplying by a calculated correction factor.

Procedure. The test runs were performed isothermally at 25 °C by cooling the glass beaker. Each experiment was run to completion, in order to allow a material balance calculation. It was found that the hydrogen peroxide was consumed stoichiometrically in all test runs with a deviation of roughly 5%.

Preliminary experiments were performed in the absence of hydrogen peroxide to determine if any appreciable amount of nitrous acid was decomposed with subsequent stripping of nitrogen oxides; such a competing reaction path will lead to an overestimation of the reaction rate. However, negligible amounts of nitrite solution had to be added to the reaction mixture in order to maintain a constant pH value over an extended period of time. Thus, stripping of nitrogen oxides has a negligible impact on the result. This conclusion was further supported by the material balances.

Further tests were made to check the decomposition rate of hydrogen peroxide. Only small amounts were found to decompose at the pertinent concentration levels.

A total of 20 experiments were made under controlled conditions. The concentration of hydrogen peroxide was screened from 0.4 to 3.1 % by weight (115 to 920 mol m\(^{-3}\)). The steady state pH value was set below 2.3, and the concentration of nitrous acid was varied tenfold from about 5 to 50 mol m\(^{-3}\).

RESULTS

Four series of data points were obtained, with constant concentration of hydrogen peroxide within each series. The data points are displayed in Fig. 1, as the reaction rate as a function of the concentration of nitrous acid. The plot reveals four straight lines with about equal slopes, but with intercepts increasing with the level of hydrogen peroxide. By rewriting eqn. (1) on a logarithmic form:

\[
\log(-r_c) = \log[k_c(H_2O_2)^m] + n \log(HNO_2)
\]

it can be concluded that the findings are consistent with the suggested rate expression. Eqn. (3) predicts a straight line with a slope equaling the reaction order in nitrous acid. Furthermore, the intercept, corresponding to the first term of the right hand side, should increase with increasing concentration of hydrogen peroxide.

![Figure 1. The reaction rate as a function of the concentration of nitrous acid at 25 °C.](image)

Each series of data points can, of course, be evaluated separately by simple least-square fits. However, based on the findings, a modified type of fit is more appropriate, in which case the slope is equal for all series. Such an approach is outlined in the Appendix.

By applying the procedure given in the Appendix, a slope of 1.35 was obtained. This value is equal to the reaction order with respect to nitrous acid. For convenience, justified later, it was rounded off to n=4/3. Based on this value, four straight lines have been inserted in Fig. 1.

In the limiting case (HNO₂)=1 mol m⁻³, eqn. (3) is condensed to:

\[ \log(-r_e) = \log(k_e) + m \log(H₂O₂) \]  

(4)

By plotting the intercepts from Fig 1, obtained by extrapolating down to (HNO₂)=1 mol m⁻³, the reaction order with respect to hydrogen peroxide can be obtained as shown in Fig. 2. The straight line was obtained from a simple least-square fit, yielding a slope of 0.685. This value was rounded off to m=2/3. The rate constant was calculated from the intercept to give a value of \( k_e = 1.56 \times 10^{-3} \) mol⁻¹ m³ s⁻¹.

**REACTION MECHANISM**

It was hypothesized that nitrous acid is inert with respect to oxidation by hydrogen peroxide directly. It was further alleged that the overall oxidation is a result of a reaction mechanism involving a series of reactions and several intermediates.

In the first step, nitrous acid is decomposed to nitric oxide and nitrogen dioxide according to the following two reactions:

2 HNO₂ ⇌ N₂O₃ + H₂O  \hspace{1cm} (d)

N₂O₃ ⇌ NO + NO₂  \hspace{1cm} (e)

Andrew et al.⁴ studied the overall of these two reactions. They pointed out that the reactions are instantaneous and attain equilibrium in all points of the solution. It can clearly be concluded from work by Komiyama et al.⁷ that N₂O₃ is an actual intermediate in the decomposition of nitrous acid.

It is well known from Sherwood et al.,⁵ among others, that nitrogen dioxide reacts instantaneously to form a dimer:

2 NO₂ ⇌ N₂O₄  \hspace{1cm} (f)

The produced dimer is a reactive species. It reacts with water to form the end product, i.e. nitric acid, and to regenerate some nitrous acid:

N₂O₄ + H₂O → HNO₃ + HNO₂  \hspace{1cm} (g)

In order to make the reactions proceed at steady state, the nitric oxide must be oxidized to nitrogen dioxide:

NO + H₂O₂ → NO₂ + H₂O  \hspace{1cm} (h)

The reaction mechanism is summarized in Fig. 3. The rate expressions for reactions (g) and (h) can be written, respectively:

![Fig. 3. Reaction mechanism for oxidation of nitrous acid by hydrogen peroxide.](image)
\[ r_g = -k_g (\text{N}_2\text{O}_4) \]  \hspace{1cm} (5)  
\[ r_h = -k_h (\text{NO}) (\text{H}_2\text{O}_2) \]  \hspace{1cm} (6)

The first rate expression has been verified by a large number of investigators during the last decades, for instance by Komiyama et al. The second rate expression was suggested by Baveja et al. and was later verified for low concentrations of nitrogen oxide.

The equilibrium reactions can be represented by equilibrium constant expressions of the following forms:

\[ \frac{(\text{N}_2\text{O}_3)}{(\text{HNO}_2)^2} = K_d \]  \hspace{1cm} (7)  
\[ \frac{(\text{NO})(\text{NO}_2)}{(\text{N}_2\text{O}_3)} = K_e \]  \hspace{1cm} (8)  
\[ \frac{(\text{N}_2\text{O}_4)}{(\text{NO}_2)^2} = K_f \]  \hspace{1cm} (9)

By a simple material balance, the pH values can be related to the concentrations of the various species:

\[ (\text{H}^+)_o - (\text{H}^+) = (\text{HNO}_2) + (\text{NO}_2) + (\text{NO}) + 2(\text{N}_2\text{O}_4) + 2(\text{N}_2\text{O}_3) \]  \hspace{1cm} (10)

This relationship is rather cumbersome to work with. However, by assuming that the concentration of nitrous acid is much greater than the concentrations of all other species, the following approximate equation is pertinent:

\[ (\text{H}^+)_o - (\text{H}^+) = (\text{HNO}_2) \]  \hspace{1cm} (11)

By this simplification, the concentration of nitrous acid can be calculated from observables explicitly.

If pseudo steady state is assumed, which is a reasonable approach at low concentrations, the following useful connection emerges:

\[ r_c = r_g = r_h \]  \hspace{1cm} (12)

By rearranging eqn. (5) through (9), (11) and (12), and by successively eliminating all species except nitrous acid, the reaction rate expression takes the following form:

\[ K_d K_e (-) \hspace{1cm} \text{Andrew et al.:}^4 1.3 \times 10^{-6}, \text{ and Nonhebel:}^6 1.5 \times 10^{-6}. \]
\[ K_f (\text{mol}^{-1} \text{m}^3) \hspace{1cm} \text{Andrew et al.:}^4 \text{ Sherwood et al.:}^5 \text{ Nonhebel:}^6 \text{ Komiyama et al.:}^7 \text{ Wendel et al.:}^9 \text{ and Kramers et al.:}^{10} 13-73. \]
\[ k_g (s^{-1}) \hspace{1cm} \text{Andrew et al.:}^4 48, \text{ Wendel et al.:}^9 290, \text{ Kramers et al.:}^{10} 415, \text{ Gerstacker:}^{11} 490, \text{ Komiyama et al.:}^7 591 \text{ and Nonhebel:}^6 670. \]
\[ k_h (\text{mol}^{-1} \text{m}^3 \text{s}^{-1}) \hspace{1cm} \text{Baveja et al.:}^8 \text{ and Karlsson:}^1 0.57. \]
\[ K_e (\text{mol} \text{m}^{-3}) \hspace{1cm} \text{Sherwood et al.:}^5 0.22. \]

\[ r_c = -(k_h K_d K_e)^{2/3} (k_g K_f)^{1/3} (\text{H}_2\text{O}_2)^{2/3} (\text{HNO}_2)^{4/3} \]  \hspace{1cm} (13)

It is concluded then, that this expression is equivalent to eqn. (1), with \( k_c \) replaced by:

\[ k_c = (k_h K_d K_e)^{2/3} (k_g K_f)^{1/3} \]  \hspace{1cm} (14)

From the experimental findings it was shown that the reaction orders with respect to hydrogen peroxide and nitrous acid were 2/3 and 4/3, respectively, which is consistent with the theoretical expression, \textit{i.e.} eqn. (13).

DISCUSSION

Table 1 lists kinetic rate constants and equilibrium constants for the reactions involved in the detailed mechanism previously outlined. Data for \( K_f \) and \( k_g \) cover a wide range, mainly because solubility data for \( \text{N}_2\text{O}_4 \), obtained in the literature, appear to be rather unreliable.

The data allow a theoretical prediction of the rate constant for reaction (c) by utilizing eqn. (14). By inserting the extreme values in eqn. (14), the following limits can be obtained:

\[ 7.0 \times 10^{-4} < k_c < 3.3 \times 10^{-3} \text{ (mol}^{-1} \text{ m}^3 \text{s}^{-1}) \]

while the experimentally determined rate constant is $k_c = 1.56 \times 10^{-3} \text{ mol}^{-1} \text{ m}^3 \text{ s}^{-1}$.

All experimental data points have been plotted in Fig. 4 as the reaction rate as a function of $(\text{HNO}_2)^{4/3}(\text{H}_2\text{O}_2)^{2/3}$, along with the fitted curve. The dashed lines represent the limits for the predicted values based on the adapted literature data.

By evaluating the reliability of the literature data, it was concluded that the true data should generate a line between the one obtained from the present experiments and the upper limit.

Check of approximations. The literature data allow a check of the accuracy of the approximate equation describing the concentration of nitrous acid, i.e. eqn. (11). Using the most unfavorable data, the following set of information is obtained:

\[
\begin{align*}
(\text{NO}_2) & < 5.6 \times 10^{-3} \text{ (HNO}_2) \\
(\text{NO}) & < 4.4 \times 10^{-3} \text{ (HNO}_2) \\
2(\text{N}_2\text{O}_3) & < 6.8 \times 10^{-4} \text{ (HNO}_2) \\
2(\text{N}_2\text{O}_4) & < 2.0 \times 10^{-2} \text{ (HNO}_2)
\end{align*}
\]

By simply adding these values, it can be concluded that the concentration of nitrous acid is never overpredicted by more than 3 %. However, the maximal errors given above do not appear simultaneously. Hence, the error is even smaller than 3 %. As the experimental conditions are altered, the error drops drastically.

The assumption concerning reactions (d) and (e) can be checked by writing the actual reaction rate for the overall reaction as:

\[
r_{de} = -k_{de}'(\text{HNO}_2)^2 + k_{de}^-\text{(NO)(NO}_2)
\]

If considering that:

\[
 r_{de} \approx r_c
\]

the following condition must be met to allow the assumption that reactions (d) and (e) are instantaneous:

\[
-r_c \ll k_{de}'(\text{HNO}_2)^2
\]

By utilizing eqn. (1), this can be rewritten to:

\[
\frac{k_{de}'}{k_c} \gg \left( \frac{(\text{H}_2\text{O}_2)}{(\text{HNO}_2)} \right)^{2/3}
\]

A conservative estimate is given from the largest value of the right hand side, i.e. 150. From data by Komiyama et al., $k_{de}'$ can be estimated to 27 mol$^{-1}$ m$^3$ s$^{-1}$ at 25 °C. Hence, $k_{de}'/k_c = 1.8 \times 10^4 >> 150$.

**APPENDIX**

**Simultaneous least square fit of a number of series of data points.** Eqn. (3) can be written in a simplified form:

\[
Y = aX + b
\]  

(A1)

$p$ series of experiments are made, with $q_j$ data points in series number $j$. $b$ is unique for each series and attains a constant value within each series, but varies from one series to another. The slope, $a$, has the same value for all data points.

The square sum of the total error including all data points can be written:

\[
S = \sum_j \sum_i (aX_{ij} + b_j - Y_{ij})^2
\]  

(A2)

The best fit is defined by:

\[
\frac{dS}{da} = 0
\]  

(A3)
which leads to:

\[ a \sum_j \sum_i X_{ij}^2 + \sum_j (b_j \sum_i X_{ij}) - \sum_j \sum_i (X_{ij}Y_{ij}) = 0 \]  \hspace{1cm} (A4)

For each series:

\[ S_j = \sum_i (aX_{ij} + b_j - Y_{ij})^2 \]  \hspace{1cm} (A5)

with the following condition:

\[ \frac{dS_j}{db_j} = 0 \]  \hspace{1cm} (A6)

which leads to:

\[ a \sum_i X_{ij} + b_j q_j - \sum_i Y_{ij} = 0 \]  \hspace{1cm} (A7)

The intercept for each series is:

\[ b_j = \left( \sum_i Y_{ij} - a \sum_i X_{ij} \right)/q_j \]  \hspace{1cm} (A8)

This can be rewritten as:

\[ \sum_j (b_j \sum i X_{ij}) = \sum_j \left[ \left( \sum_i Y_{ij} \right) \sum_i \left( X_{ij}/q_j \right) \right] \]

\[ -a \sum_j \left[ \left( \sum_i X_{ij} \right)^2/q_j \right] \]  \hspace{1cm} (A9)

The second term of eqn. (A4) can now be eliminated to give the slope explicitly:

\[ a = \frac{\sum_j \sum_i (X_{ij}Y_{ij}) - \sum_j \left[ \left( \sum_i Y_{ij} \right) \sum_i \left( X_{ij}/q_j \right) \right]}{\sum_j \sum_i X_{ij}^2 - \sum_j \left[ \left( \sum_i X_{ij} \right)/q_j \right] \left( \sum_i \left( X_{ij}/q_j \right) \right]} \]  \hspace{1cm} (A10)

From a known value of \( a \), \( b_j \) can be calculated explicitly by eqn. (A8).

REFERENCES


Received August 13, 1982.