IONOSPHERIC RESEARCH

Scientific Report 391

THE REACTION OF H₂O₂ WITH NO₂ AND NO

by

David Gray, Eduardo Lissi, and Julian Heicklen

March 29, 1972

The research reported in this document has been sponsored by the National Aeronautics and Space Administration under Grant NGL 39-009-003 and in part by the National Science Foundation under Grant No. GP-5611.

IONOSPHERE RESEARCH LABORATORY

University Park, Pennsylvania
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<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
</tr>
<tr>
<td>INTRODUCTION</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
</tr>
<tr>
<td>Materials</td>
</tr>
<tr>
<td>REACTION OF H₂O₂ WITH NO₂</td>
</tr>
<tr>
<td>REACTION OF NO WITH HONO₂</td>
</tr>
<tr>
<td>REACTION OF H₂O₂ WITH NO</td>
</tr>
<tr>
<td>CONCLUSION</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
</tr>
<tr>
<td>REFERENCES</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
</tr>
</tbody>
</table>
ABSTRACT

The reactions of NO and NO₂ with H₂O₂ have been examined at 25°C. Reaction mixtures were monitored by continuously bleeding through a pinhole into a monopole mass spectrometer. NO₂ was also monitored by its optical absorption in the visible part of the spectrum. Reaction mixtures containing initially 1.5 - 2.5 torr of NO₂ and 0.8 - 1.4 torr of H₂O₂ or 1 - 12 torr of NO and 0.5 - 1.5 torr of H₂O₂ were studied.

In the NO₂ - H₂O₂ system the overall reaction was

\[(1 + \alpha) \text{H}_2\text{O}_2 + 2\text{NO}_2 + 2\text{HONO}_2 + \alpha\text{H}_2\text{O} + (\alpha/2) \text{O}_2\]

The reaction was probably heterogenous and followed the rate law

\[-d[\text{H}_2\text{O}_2]/dt = k[\text{NO}_2][\text{H}_2\text{O}_2]^n\]

where n was between zero and one. Assuming that n=1, an upper limit for the homogeneous rate coefficient is \(1 \times 10^{-18}\) cm³/molecule-sec.

The H₂O₂ - NO reaction was complex. There was an induction period followed by a marked acceleration in reactant removal. The final products of the reaction, NO₂, probably H₂O, and possibly HONO₂ were produced mainly after all the H₂O₂ was removed. The overall stoichiometry in the presence of excess NO was

\[\text{H}_2\text{O}_2 + \text{NO} \rightarrow \text{H}_2\text{O} + \text{NO}_2\]

The initial induction period gives an upper limit to the homogeneous gas-phase reaction coefficient of \(5 \times 10^{-20}\) cm³/molecule-sec for the reaction

\[\text{NO} + \text{H}_2\text{O}_2 \rightarrow \text{HONO} + \text{HO}\]

The HO radical presumably is removed via

\[\text{HO} + \text{NO} \rightarrow \text{HONO}\]
The HONO intermediate was shown to disproportionate to NO$_2$ + NO + H$_2$O in a relatively slow first order reaction. The acceleration in H$_2$O$_2$ removal after the NO - H$_2$O$_2$ reaction is started is caused by NO$_2$ catalysis:

\[
\text{NO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{HONO}_2 + \text{HO}
\]

\[
\text{HONO}_2 + \text{NO} \rightarrow \text{HONO} + \text{NO}_2
\]

The latter reaction was demonstrated in separate experiments in which NO was added to HONO$_2$ (in the presence of NO$_2$, O$_2$, and H$_2$O). A minor part of the catalysis may also be caused by HONO via:

\[
\text{HONO}^* + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{HO}
\]

where HONO$^*$ must have retained sufficient energy to overcome the 12 kcal/mole endothermicity of the reaction.
INTRODUCTION

The reaction of H₂O₂ with NO and NO₂ has been postulated as a possible means of H₂O₂ removal in the upper atmosphere. No direct measurements of the rate coefficients have been reported, though Nicolet¹ has pointed out that the reactions will be important if their rate coefficients exceed 10⁻¹⁵ cm³/sec. Since the same gases are also constituents in polluted urban atmospheres, such reactions could also be occurring there too. Therefore we have studied these systems at 25°C and this paper reports our findings.

The only previous work is that of Tyler,¹ who examined the reaction between NO and H₂O₂ at 297-473°C in the presence of excess N₂. Though no quantitative results were obtained, he concluded that the initial reaction produced HO or HO₂ or both, and that these were removed via

\[ \text{HO} + \text{H₂O₂} \rightarrow \text{H₂O} + \text{HO₂} \]

\[ \text{HO₂} + \text{NO} \rightarrow \text{HO} + \text{NO₂} \]

\[ \text{HO} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M} \]
EXPERIMENTAL

All the experiments were carried out in a 10 cm cylindrical quartz cell having optically flat windows at both ends. The gases to be introduced into this cell were stored in glass bulbs connected to a conventional Hg-free gas handling system. The hydrogen peroxide was stored in a blackened glass finger to prevent any photodecomposition. Pressures of all reactants were measured on a dibutyl phthalate manometer. This vacuum system could be pumped to a working pressure of less than one micron as measured on a Veeco thermocouple guage.

The course of the reaction was followed by means of a G.E. 600 monopole mass spectrometer. A very small pinhole, made by drawing out a piece of glass tubing into a fine short capillary, was inserted into the center of the cell through a side arm. This tube terminated at the entrance to the ion chamber of the mass spectrometer. Decomposition of hydrogen peroxide on the stainless steel surfaces of the spectrometer was eliminated in this manner. This pinhole was sufficiently small that the high pressure differential required for the normal working of the spectrometer was realized. Working with a cell pressure of up to 15 torr the mass spectrometer chamber was maintained at a pressure of approximately $6 \times 10^{-7}$ torr. At these pressures the loss of reactants was less than 2% in one hour.

The mass spectrometer was evacuated using a Veeco 400 series high speed pumping station incorporating a high capacity rotary and a 4-inch oil diffusion pump. Pressures in the chamber were measured with a Bayard Alpert type ion guage controlled by a Veeco R 93A ultra stable ionization guage circuit.
This pinhole bleed system provided continuous sampling of the gas mixture in the cell during the course of the reaction. By scanning the suitable mass range, the peak heights of the reactants and products relative to argon as standard were obtained. The output from the collector of the electron multiplier in the monopole mass spectrometer was fed into the input of a Keithley 416 high speed picoammeter. The 3V f.s. output from this was fed via a potential divider into a fast response 1 mV. recorder.

All reactants except the \( \text{H}_2\text{O}_2 \) were calibrated using argon as a standard in the following way. A gas was introduced into the cell and its pressure was read on the D.B.P. manometer. The cell stopcock was closed and the whole vacuum line evacuated to less than one micron. The argon was introduced into the whole line to a certain pressure greater than the previously added gas, the cell stopcock was opened and the final pressure reading on the manometer was measured. The difference of these two readings gave the added pressure of argon. A mass spectrum of the added gas peak and the argon peak was taken and the ratio of the peak heights was obtained. The procedure was repeated for various ratios and a graph of ratio of added gas pressure to argon pressure against ratio of peak heights was plotted.

The \( \text{H}_2\text{O}_2 \) could not be calibrated in this way since some \( \text{H}_2\text{O} \) was always present. Therefore calibrations were done in two other ways utilizing the stoichiometry of chemical reactions. In one method \( \text{H}_2\text{O}_2 \) was photolyzed with 2139A radiation to completion as determined by the disappearance of the mass spectral peak at m/e 34. The \( \text{O}_2 \) produced was measured and was presumed equal to \( \frac{1}{2} \) the initial \( \text{H}_2\text{O}_2 \) pressure, since the photochemical decay of \( \text{H}_2\text{O}_2 \) follows the stoichiometry²
\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow \text{H}_2\text{O} + (1/2) \text{O}_2 \]

Scattered results were obtained by this method. A more reproducible method was to react a large excess of NO\textsubscript{2} with H\textsubscript{2}O\textsubscript{2} ([NO\textsubscript{2}]/[H\textsubscript{2}O\textsubscript{2}] > 3), which produced HONO\textsubscript{2} as the sole product. The stoichiometric eqn. presumably is

\[ \text{H}_2\text{O}_2 + 2\text{NO}_2 \rightarrow 2\text{HONO}_2 \]

From the NO\textsubscript{2} consumed both the H\textsubscript{2}O\textsubscript{2} and HONO\textsubscript{2} were calibrated. The calibrations for H\textsubscript{2}O\textsubscript{2} from the two methods agreed, but since the latter method was more reproducible, it was used.

Introduction of the gas mixtures into the cell for an experiment was conducted in a similar manner. Firstly, the hydrogen peroxide-water mixture was thoroughly degassed and then allowed to expand into the cell. The stopcock on the cell was closed and the line evacuated. A measured pressure of argon was then introduced into the cell containing the hydrogen peroxide-water mixture, and the line evacuated once more. After a mass spectrum of the mixture was taken to determine the initial concentration, a certain known amount of either NO or NO\textsubscript{2} was added to the cell in a similar manner. Then mass spectra of the mixture were determined at frequent intervals to determine the concentration of reactants during the course of the reaction.

The concentration of NO\textsubscript{2} was also monitored using its absorption of light above 3600\textsubscript{A}. The light source was an Hg resonance lamp in combination with a Corning 5-60 filter to eliminate wavelengths below 3500\textsubscript{A}. The light was monitored with a RCA 935 phototube and a 1 mV recorder to measure the voltage drop across a known variable resistor. To avoid any photolysis effects a very small beam of light was used.
The same results were obtained by chopping this beam or allowing continuous illumination proving that any photolysis is negligible.

Materials

Hydrogen peroxide: pure 90% solution obtained by the courtesy of E. I. DuPont Nemours Ltd. Apart from constant outgassing this solution was used unpurified.

NO₂: prepared in situ on the vacuum line from pure NO and O₂. It was repurified before every use by additional oxygen. It contained no measurable N₂O or NO impurity.

NO: obtained from Matheson Co. The NO was distilled from liquid argon. It contained no measurable impurity.

Argon: obtained from Air Products Ltd.
Several runs were done in the presence of 2.5 - 3.0 torr of Ar with initial reactant pressures of 1.5 - 2.5 torr of NO₂ and 0.8 - 1.4 torr of H₂O₂, and [NO₂]/[H₂O₂] ratios of 1.2 - 2.7. The reaction was extremely rapid and one of the reactants was at least 90% consumed in 1-3 min. Higher pressures of H₂O₂ could not be used because its vapor pressure at room temperature is about 1.5 torr. Higher pressures of NO₂ were not used because the reaction became too rapid to follow. Lower initial pressures of reactants were not used since then the reaction could not be followed to a significant percent because of limits in detectability.

The major product of the reaction was HONO₂, as determined from the growth of the mass spectral peaks at m/e 46 and 63. The peak at m/e 63 was very small and barely detectable. However the peak at m/e 46 first decayed and then grew during the reaction even though NO₂ (parent m/e = 46) was being consumed. Small amounts of O₂ were also produced in runs for low [NO₂]/[H₂O₂] ratios as determined from the growth of the mass spectral peak at m/e 32. There was no evidence for the production of H₂O or NO, though both would have been difficult to detect, and they could have been produced as minor products.

During each run H₂O₂ and HONO₂ were monitored by their mass spectral peaks at m/e 34 and 46, respectively. In order to monitor HONO₂, the fraction of the 46 peak due to NO₂ had to be taken into account. Thus values early in a run could not be obtained because of the large correction required. The NO₂ was monitored optically. In each run the NO₂ and H₂O₂ were consumed in a ratio of about 2 to 1. The HONO₂ produced was proportional to the NO₂ consumed. From mass balance considerations,
we assume that the constant of proportionality is one, since absolute calibrations were not made for HONO$_2$. The overall reaction can be represented as

$$(1 + \alpha)\text{H}_2\text{O}_2 + 2\text{NO}_2 \rightarrow 2\text{HONO}_2 + \alpha\text{H}_2\text{O} + (\alpha/2)\text{O}_2$$

where $\alpha < 1$.

The pressures in a typical run are plotted vs reaction time in Fig. 1. The NO$_2$ and H$_2$O$_2$ decay rapidly, the H$_2$O$_2$ being consumed essentially at 4 minutes reaction time. Paralleling the reactant decay is the growth of O$_2$. However the HONO$_2$ growth showed a noticeable lag compared to reactant removal. Since the reaction was so rapid and there is evidence that the reaction proceeds on the vessel surface (see below) the HONO$_2$ lag might be partly attributed to the strong adsorption of HONO$_2$ to the reaction vessel. After about 15 minutes, the gas pressures were stabilized and the stoichiometry in eqn. 1 was satisfied ($-\Delta[\text{H}_2\text{O}_2] = 1.3$ torr, $-\Delta[\text{NO}_2] = 1.55$ torr, $\Delta[\text{O}_2] = 0.25$ torr, and $\Delta[\text{HONO}_2] = 1.50$ torr) with $\alpha \sim 0.4$.

A kinetic analysis was made from the curves of growth of several runs both by using integral rate expressions and rates measured from the slopes of the curves at different reactant pressures. Fig. 2 shows plots of the slopes of the reactant decay curves at fixed H$_2$O$_2$ pressures vs NO$_2$ pressure at the same time. The rates are first-order in [NO$_2$] within the scatter of the data. The results are essentially the same at 0.5 and 0.8 torr of H$_2$O$_2$. The slopes of the two curves give first-order rate coefficients of 1.57 and 0.71 min$^{-1}$ for the NO$_2$ and H$_2$O$_2$ decay, respectively. The ratio of these coefficients is 2.2. From eqn. 1, the expected ratio is $2/(1 + \alpha)$, which is approximately 2 since $\alpha << 1$ for most runs. (The run in Fig. 1 had a large $\alpha$ because it had one of the
lowest initial ratios for \([\text{NO}_2]_0/\text{[H}_2\text{O}_2]_0\). Also the slopes cannot be used too near the beginning or end of any run, because the experimental errors are large.) The discrepancy between the measured and expected ratios of slopes is within the experimental uncertainty.

Similar plots were made for the decay rates vs \(\text{H}_2\text{O}_2\) pressure. The data were badly scattered, but both plots indicated zero order dependence on \([\text{H}_2\text{O}_2]\) at high \(\text{H}_2\text{O}_2\) pressures (>0.5 torr). At lower \(\text{H}_2\text{O}_2\) pressures, both reactant decays were dependent on \([\text{H}_2\text{O}_2]\). The dependence seemed to approach first-order at low enough \(\text{H}_2\text{O}_2\) pressures.

The mechanism for reaction can be represented as

\[
\begin{align*}
\text{NO}_2 + \text{H}_2\text{O}_2 &\rightarrow \text{HO} + \text{HONO}_2 \\
\text{HO} + \text{NO}_2 &\rightarrow \text{HONO} \\
\text{HO} + \text{H}_2\text{O}_2 &\rightarrow \text{H}_2\text{O} + \text{HO}_2 \\
2\text{HO}_2 &\rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{HO}_2 &\rightarrow \text{•H} + \text{H}_2\text{O}_2 \\
\text{HO}_2 + \text{NO}_2 &\rightarrow \text{O}_2 + \text{HONO} \\
\text{HONO} + \text{HONO}_2 &\rightarrow \text{H}_2\text{O} + 2\text{NO}_2
\end{align*}
\]

The \(\text{HO}_2\) radical might also be removed via

\[
\text{HO}_2 + \text{NO}_2 \rightarrow \text{O}_2 + \text{HONO}
\]

The \text{HONO} would ultimately revert to \text{H}_2\text{O} and \text{NO}_2, possibly via

\[
\text{HONO} + \text{HONO}_2 \rightarrow \text{H}_2\text{O} + 2\text{NO}_2
\]

There is good evidence for \text{HONO} as an intermediate, since there is an induction period in \text{HONO}_2 production and since the \text{NO}_2 reached its ultimate value before all the \text{H}_2\text{O}_2 was consumed. (See Fig. 1.) The latter observation can be attributed to the fact that near the end of the run, \text{NO}_2 is being produced from \text{HONO} as fast as it is being removed by \text{H}_2\text{O}_2. In fact in some runs, \([\text{NO}_2]\) increased after the \text{H}_2\text{O}_2 was completely consumed.

Other reactions can also participate. For example reaction 2 could be accompanied by
$$H_2O_2 + NO_2 \rightarrow HO_2 + HONO$$

However this reaction followed by reaction 5 is equivalent to reaction 6, and need not be considered separately. Another possible reaction is

$$HO + HONO_2 \rightarrow H_2O + NO_3$$

This reaction probably occurs to some extent near the end of the reaction when [HONO$_2$] is relatively large; the NO$_3$ would either react with NO$_2$ to produce N$_2$O$_5$ or with itself to produce 2NO$_2$ + O$_2$. For simplicity we shall ignore the reaction between HO and HONO$_2$.

Reaction 3 has been reported previously and is rapid. The ratio $k_3/k_4$ can be estimated from the expression

$$\frac{-6d[H_2O_2]/dt}{d[O_2]/dt} = 2 + \frac{k_3[NO_2]}{k_4[H_2O_2]}$$

where $\beta$ is 1/2 if reaction 6 is negligible; 1, if reaction 5 is negligible; or otherwise, between 1/2 and 1. The ratio $k_3/k_4$ is estimated from the rates in Fig. 1 to be between 2 and 8, though this may be the ratio of rate coefficients on the wall rather than in the gas phase. Since $k_4$ is $8.0 \times 10^{-13}$ cm$^3$/molecule sec at 25°C, $k_3$ exceeds $10^{-13}$ cm$^3$/molecule sec.

Reaction 2 is rate controlling and is first-order in [NO$_2$]. Since it is less than first-order in [H$_2$O$_2$], it presumably occurs on the wall, the reaction involving gas-phase NO$_2$ and adsorbed H$_2$O$_2$ following the Langmuir adsorption isotherm

$$[H_2O_2]_{ads} = \frac{a[H_2O_2]}{1 + a[H_2O_2]}$$

where $a$ is some constant.

The rate law would then be first-order in [H$_2$O$_2$] if $1 \gg a[H_2O_2]$, zero-order in [H$_2$O$_2$] if $1 \ll a[H_2O_2]$, and appear to have an intermediate order at intermediate H$_2$O$_2$ pressures, viz
\[-d[H_2O_2]/dt = k[N_2O][H_2O_2]^n\]

The rate coefficient \( k \) was found to be between 1 and 2 torr\(^{-1} \) min\(^{-1} \) assuming \( n=1 \) or 0.71 min\(^{-1} \) assuming \( n=0 \). The former rate constant, which is an upper limit to the gas-phase reaction, becomes \((0.5 - 1) \times 10^{-18} \text{ cm}^3/\text{molecule-sec.}\)
REACTION OF NO WITH HONO$_2$

The reaction of NO with HONO$_2$ has been reported by Smith$^5$ who found the stoichiometry to be

$$2\text{HONO}_2 + \text{NO} \rightarrow 3\text{NO}_2 + \text{H}_2\text{O}$$

though the rate law was exceedingly complex. We have reexamined this reaction by adding NO to the HONO$_2$ produced in the reaction of H$_2$O$_2$ and excess NO$_2$. In each case the H$_2$O$_2$ was consumed prior to the addition of NO, but NO$_2$, O$_2$, and H$_2$O were present. The results of such an experiment are shown in Fig. 1, where 2.0 torr of NO was added after 20 minutes. The 1.5 torr of HONO$_2$ was converted to 2.4 torr of NO$_2$ and the above stoichiometry was confirmed. The most reasonable reaction sequence is

$$\text{HONO}_2 + \text{NO} \rightarrow \text{HONO} + \text{NO}_2$$

$$\text{HONO}_2 + \text{HONO} \rightarrow \text{H}_2\text{O} + 2\text{NO}_2$$

It is surprising that reaction 11 proceeds so readily since it is exactly thermal neutral. Perhaps this reaction is more complex than indicated, especially since Smith found the rate to be at least partly heterogeneous and to be catalyzed by NO$_2$. Of course the fact that one of the products of reaction 11 (HONO) is removed by further reaction shifts the equilibrium far to the right.
The reaction of H$_2$O$_2$ with NO is slower than with NO$_2$, but is considerably more complex. Reactions were run in the presence of 1-2 torr of Ar with initial NO pressures, [NO]$_0$, from 1-12 torr; initial H$_2$O$_2$ pressures, [H$_2$O$_2$]$_0$, from 0.5 - 1.5 torr; and [NO]$_0$/[H$_2$O$_2$]$_0$ ratios of 1-10. A typical reaction time history is shown in Fig. 3. There is an induction period followed by a more rapid reaction. The products are NO$_2$ and probably HONO$_2$, both of which appear after considerable induction periods. In fact, the H$_2$O$_2$ is almost entirely consumed before NO$_2$ was observed, either optically or by mass spectral analysis. There was no evidence for O$_2$ production, though it may have been produced in small amounts. H$_2$O was probably also produced, though it was difficult to detect because of the large background peak in the mass spectrometer. No serious effort was made to look for this presumed product. When the reaction was completed the NO$_2$ produced equalled the H$_2$O$_2$ consumed in each run as determined from optical measurements. In Fig. 3, where the final values have not quite been reached, the NO$_2$ is also shown as computed from the mass spectral peak at m/e 46, assuming that all the 46 peak can be attributed to NO$_2$. Clearly in the later stages of the runs, an additional compound, HONO$_2$, must also be present. Since the sensitivities of the peak at m/e 46 for both NO$_2$ and HONO$_2$ are similar, the difference (~0.3 torr) can be considered to be HONO$_2$. Another interesting feature in the optical NO$_2$ curve is the plateau observed at about 4 minutes in the optical measurement. This occurred in all runs and apparently is not an artifact. The discrepancy with the mass spectral peak (which did not occur in every run) is due to the inaccuracy of the mass spectral analysis at low NO$_2$ pressures. Neglecting the HONO$_2$ production, the overall
stoichiometry for the reaction is

\[ \text{H}_2\text{O}_2 + \text{NO} \rightarrow \text{H}_2\text{O} + \text{NO}_2 \]  

It is clear from the long time lag in \( \text{NO}_2 \) production that some intermediate must be produced as a precursor to \( \text{NO}_2 \) formation. Undoubtedly, this precursor is HONO, which probably would not be detected in our system. The nitrites and nitrates have almost no mass spectral parent or parent-minus-one peaks. For HONO\(_2\), the parent peak (m/e 63) is <1% of the 46 peak, and no 62 peak was observed at all. Therefore in HONO, the peaks at m/e 46 and 47 are also probably undetectably small. The major expected peak at m/e 30 of course corresponds to NO, one of the reactants.

The initial slow decay of \( \text{H}_2\text{O}_2 \) corresponds to the attack of NO on \( \text{H}_2\text{O}_2 \),

\[ \text{NO} + \text{H}_2\text{O}_2 \rightarrow \text{HONO} + \text{HO} \]  

Assuming that this reaction occurs entirely in the gas-phase gives an upper limit to the gas-phase rate constant of 0.10 torr\(^{-1}\) min\(^{-1}\) or \(5.2 \times 10^{-20}\) cm\(^3\)/molecule-sec.

The acceleration in the rate must be due to catalysis by either HONO or \( \text{NO}_2 \), or both. Of course, \( \text{NO}_2 \) reacts more rapidly than NO with \( \text{H}_2\text{O}_2 \), so that reaction 2 would occur if any \( \text{NO}_2 \) were present. The resulting HONO\(_2\) would react with NO to regenerate the \( \text{NO}_2 \), and HONO\(_2\) would be only a minor product of the reaction. The \( \text{NO}_2 \) reaction sequence would be

\[ \text{NO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{HO} + \text{HONO}_2 \]  
\[ \text{HONO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HONO} \]  
\[ \text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O} \]  
\[ \text{HO} + \text{NO} \rightarrow \text{HONO} \]
HO₂ + NO → HO + NO₂

Figure 4 shows the early time portion of Fig. 3 for the H₂O₂ decay and NO₂ growth. Also plotted are the decay rates of H₂O₂ as a function of reaction time. As the NO₂ accumulates, -d[H₂O₂]/dt increases, reaching a maximum at the plateau in the [NO₂] curve. Then both -d[H₂O₂]/dt and [H₂O₂] drop as the reaction between NO₂ and H₂O₂ passes out of the regime zero-order in [H₂O₂].

About 70% of the acceleration in the H₂O₂ decay can be accounted for by the NO₂ - H₂O₂ reaction, as estimated from our results discussed earlier. Perhaps within the uncertainty of our measurements, all the enhancement is due to NO₂. However, if not, then some of the acceleration may also be due to catalysis by HONO. A possible reaction step is

\[ \text{HONO}^* + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{HO} \]

where HONO* is excited HONO. Reaction 16 is 12 kcal/mole endothermic and could only occur if the HONO retained some of the excess energy of formation in reaction 14.

HONO is known to disproportionate to H₂O, NO, and NO₂. After the H₂O₂ is completely removed this reaction should have no complications and obey a simple rate law. All of the runs were analyzed for that portion where the H₂O₂ was already completely consumed. None fitted a second-order law, and all gave satisfactory first-order plots, as shown in Fig. 5. Thus HONO removal must occur on the wall

\[ \text{HONO} \rightarrow \text{HONO}_{\text{ads}} \]

\[ \text{HONO}_{\text{ads}} + \text{HONO} + \text{H}_2\text{O} + \text{NO} + \text{NO}_2 \]

with reaction 17 rate determining. The slopes in Fig. 5 give \( k_{17} = 0.30 - 0.45 \text{ min}^{-1} \).
CONCLUSION

The reaction scheme in the $\text{H}_2\text{O}_2 - \text{NO} - \text{NO}_2$ system has been elucidated, and is at least partly heterogeneous. The homogeneous reactions of NO and NO$_2$, with H$_2$O$_2$ are too slow to be of importance in the upper atmosphere. However, in polluted urban atmospheres, the heterogeneous reactions may be of considerable importance in the conversion of NO to NO$_2$ especially in the presence of particulates which could act as surfaces on which the reactions proceed.
ACKNOWLEDGMENT

The authors wish to thank Drs. H. A. Wiebe and R. Simonaitis for their help. This work was supported by NASA Grant NGL-009-003 and NSF Grant No. GP-5611 for which we are grateful.
REFERENCES


LIST OF FIGURES

Fig. 1. Plots of pressures vs time in the reaction of NO$_2$ with H$_2$O$_2$ at 25°C. [NO$_2$]$_0$ = 1.85 torr, [H$_2$O$_2$]$_0$ = 1.3 torr, [Ar] = 2.8 torr. The NO$_2$ was monitored optically; the O$_2$, H$_2$O$_2$, and HONO$_2$, by their mass spectral peaks at m/e 32, 34, and 46, respectively. For HONO$_2$, corrections due to the NO$_2$ contribution were made. After 20 minutes 2.0 torr of NO was added. Note break in abscissa between 8 and 18 min.

Fig. 2. Plots of the slopes of reactant decay curves vs the NO$_2$ pressure in the reaction of NO$_2$ with H$_2$O$_2$ at 25°C during the course of several runs when the H$_2$O$_2$ pressure was 0.5 or 0.8 torr.

Fig. 3. Plots of pressure vs reaction time in the reaction of H$_2$O$_2$ with NO at 25°C. [NO]$_0$ = 2.0 torr, [H$_2$O$_2$]$_0$ = 1.5 torr, [Ar] = 2.7 torr. The excess NO$_2$ from the mass spectral determination reflects the presence of HONO$_2$. The NO pressure could not be monitored after measurable amounts of NO$_2$ were produced because the NO$_2$ mass spectral peak at m/e 30 interfered. Note break in abscissa between 15 and 22 min.

Fig. 4. Early time history for H$_2$O$_2$ decay and NO$_2$ growth in run depicted in Fig. 3. Also plotted is the slope of the H$_2$O$_2$ decay curve.

Fig. 5. Semilog plots of [NO$_2$]$_f$ - [NO$_2$] vs t-t$_0$ in the reaction of NO with H$_2$O$_2$ at 25°C for several runs. [NO$_2$]$_f$ is the final [NO$_2$] concentration and t$_0$ is a time after the H$_2$O$_2$ has been consumed.
Figure 4: Graph showing the rate of reaction versus pressure and time. The equation $\frac{d[H_2O_2]}{dt}$ is plotted with symbols indicating different data points.

- RATE, Torr/min.
- TIME, min.
- PRESSURE, Torr

Symbols:
- $\Delta$
- $\bigcirc$
- $\square$
- $\nabla$
- $\bigtriangleup$

Equation: $H_2O_2$ and $NO_2$ treatment.

- 0.5
- 0.4
- 0.3
- 0.2
- 0.1
- 0.0

- 5
- 4
- 3
- 2
- 1

- 1.6
- 1.2
- 0.8
- 0.4
- 0.0