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THE REACTION OF H_2O_2 WITH NO_2 AND NO

by

David Gray, Eduardo Lissi, and Julian Heicklen

March 29, 1972

IONOSPHERE RESEARCH LABORATORY

University Park, Pennsylvania

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ABSTRACT

The reactions of NO and NO_2 with H_2O_2 have been examined at 25°C.
Reaction mixtures were monitored by continuously bleeding through a pin-
hole into a monopole mass spectrometer. NO_2 was also monitored by its
optical absorption in the visible part of the spectrum. Reaction mixtures
containing initially 1.5 - 2.5 torr of NO_2 and 0.8 - 1.4 torr of H_2O_2 or
1 - 12 torr of NO and 0.5 - 1.5 torr of H_2O_2 were studied.

In the NO_2 - H_2O_2 system the overall reaction was

$$(1 + \alpha) \ H_2O_2 + 2NO_2 \rightarrow 2HONO_2 + \alpha H_2O + (\alpha/2) \ O_2$$
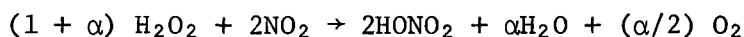
The reaction was probably heterogenous and followed the rate law

$$-d[H_2O_2]/dt = k[NO_2][H_2O_2]^n$$

where n was between zero and one. Assuming that n=1, an upper limit
for the homogeneous rate coefficient is 1×10^{-18} cm^3/molecule-sec.

The H_2O_2 - NO reaction was complex. There was an induction period
followed by a marked acceleration in reactant removal. The final pro-
ducts of the reaction, NO_2, probably H_2O, and possibly $HONO_2$ were pro-
duced mainly after all the H_2O_2 was removed. The overall stoichiometry
in the presence of excess NO was

$$H_2O_2 + NO \rightarrow H_2O + NO_2$$
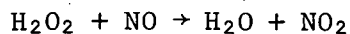
The initial induction period gives an upper limit to the homogeneous
gas-phase reaction coefficient of 5×10^{-20} cm^3/molecule-sec for the
reaction

$$NO + H_2O_2 \rightarrow HONO + HO$$
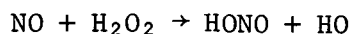
The HO radical presumably is removed via

$$HO + NO \rightarrow HONO$$
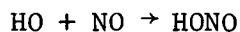
The HONO intermediate was shown to disproportionate to $NO_2 + NO + H_2O$ in a relatively slow first order reaction. The acceleration in H_2O_2 removal after the $NO - H_2O_2$ reaction is started is caused by NO_2 catalysis

$$NO_2 + H_2O_2 \rightarrow HONO_2 + HO$$

$$HONO_2 + NO \rightarrow HONO + NO_2$$
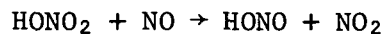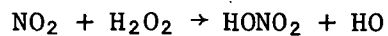
The latter reaction was demonstrated in separate experiments in which NO was added to $HONO_2$ (in the presence of NO_2, O_2, and H_2O). A minor part of the catalysis may also be caused by HONO via

$$HONO^* + H_2O_2 \rightarrow H_2O + NO_2 + HO$$
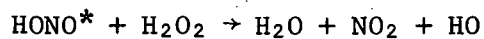
where $HONO^*$ must have retained sufficient energy to overcome the 12 kcal/mole endothermicity of the reaction.

INTRODUCTION

The reaction of H_2O_2 with NO and NO_2 has been postulated as a possible means of H_2O_2 removal in the upper atmosphere. No direct measurements of the rate coefficients have been reported, though Nicolet[1] has pointed out that the reactions will be important if their rate coefficients exceed 10^{-14} cm^3/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,[1a] who examined the reaction between NO and H_2O_2 at 297-473°C in the presence of excess N_2. Though no quantitative results were obtained, he concluded that the initial reaction produced HO or HO_2 or both, and that these were removed via

$$HO + H_2O_2 \rightarrow H_2O + HO_2$$

$$HO_2 + NO \rightarrow HO + NO_2$$

$$HO + NO + M \rightarrow HONO + M$$
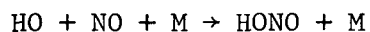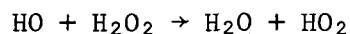
EXPERIMENTAL

All the experiments were carried out in a 10 cm cylindrical quartz
cell having optically flat windows at both ends. The gases to be intro-
duced 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 6×10^{-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 H_2O_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 H_2O_2 could not be calibrated in this way since some H_2O was always present. Therefore calibrations were done in two other ways utilizing the stoichiometry of chemical reactions. In one method H_2O_2 was photolyzed with 2139A radiation to completion as determined by the disappearance of the mass spectral peak at m/e 34. The O_2 produced was measured and was presumed equal to 1/2 the initial H_2O_2 pressure, since the photochemical decay of H_2O_2 follows the stoichiometry[2]

$$H_2O_2 + h\nu \rightarrow H_2O + (1/2)\ O_2$$
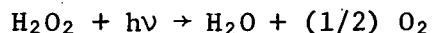
Scattered results were obtained by this method. A more reproducible

method was to react a large excess of NO_2 with H_2O_2 ($[NO_2]/[H_2O_2]>3$),

which produced $HONO_2$ as the sole product. The stoichiometric eqn.

presumably is

$$H_2O_2 + 2NO_2 \rightarrow 2HONO_2$$
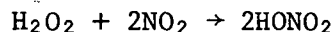
From the NO_2 consumed both the H_2O_2 and $HONO_2$ were calibrated. The cali-

brations for H_2O_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 contain-

ing 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_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_2 was also monitored using its absorption

of light above 3600A. The light source was an Hg resonance lamp in

combination with a Corning 5-60 filter to eliminate wavelengths below

3500A. 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.

NO_2: prepared _in situ_ on the vacuum line from pure NO and O_2. It was repurified before every use by additional oxygen. It contained no measurable N_2O 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.

REACTION OF H_2O_2 WITH NO_2

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 NO_2 and 0.8 - 1.4 torr of H_2O_2, and $[NO_2]/[H_2O_2]$ 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 H_2O_2 could not be used because its vapor pressure at room temperature is about 1.5 torr. Higher pressures of NO_2 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 $HONO_2$, 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 NO_2 (parent m/e = 46) was being consumed. Small amounts of O_2 were also produced in runs for low $[NO_2]/[H_2O_2]$ ratios as determined from the growth of the mass spectral peak at m/e 32. There was no evidence for the production of H_2O or NO, though both would have been difficult to detect, and they could have been produced as minor products.

During each run H_2O_2 and $HONO_2$ were monitored by their mass spectral peaks at m/e 34 and 46, respectively. In order to monitor $HONO_2$, the fraction of the 46 peak due to NO_2 had to be taken into account. Thus values early in a run could not be obtained because of the large correction required. The NO_2 was monitored optically. In each run the NO_2 and H_2O_2 were consumed in a ratio of about 2 to 1. The $HONO_2$ produced was proportional to the NO_2 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

$$(1 + \alpha)H_2O_2 + 2NO_2 \rightarrow 2HONO_2 + \alpha H_2O + (\alpha/2)O_2 \qquad 1$$
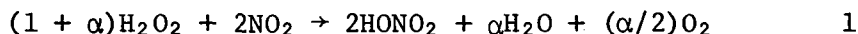
where $\alpha < 1$.

The pressures in a typical run are plotted vs reaction time in Fig. 1. The NO_2 and H_2O_2 decay rapidly, the H_2O_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 presssures were stabilized and the stoichiometry in eqn. 1 was satisfied ($-\Delta[H_2O_2]$ = 1.3 torr, $-\Delta[NO_2]$ = 1.55 torr, $\Delta[O_2]$ = 0.25 torr, and $\Delta[HONO_2]$ = 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_2O_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_2O_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_2O_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 $\alpha \ll 1$ for most runs. (The run in Fig. 1 had a large α because it had one of the

lowest initial ratios for $[NO_2]_o/[H_2O_2]_o$. 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 H_2O_2 pressure. The data were badly scattered, but both plots indicated zero order dependence on $[H_2O_2]$ at high H_2O_2 pressures (>0.5 torr). At lower H_2O_2 pressures, both reactant decays were dependent on $[H_2O_2]$. The dependence seemed to approach first-order at low enough H_2O_2 pressures.

The mechanism for reaction can be represented as

$$NO_2 + H_2O_2 \rightarrow HO + HONO_2 \qquad\qquad 2$$

$$HO + NO_2 \rightarrow HONO_2 \qquad\qquad 3$$

$$HO + H_2O_2 \rightarrow H_2O + HO_2 \qquad\qquad 4$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad\qquad 5$$

The HO_2 radical might also be removed via

$$HO_2 + NO_2 \rightarrow O_2 + HONO \qquad\qquad 6$$

The HONO would ultimately revert to H_2O and NO_2, possibly via

$$HONO + HONO_2 \rightarrow H_2O + 2NO_2 \qquad\qquad 7$$

There is good evidence for HONO as an intermediate, since there is an induction period in $HONO_2$ production and since the NO_2 reached its ultimate value before all the H_2O_2 was consumed. (See Fig. 1.) The latter observation can be attributed to the fact that near the end of the run, NO_2 is being produced from HONO as fast as it is being removed by H_2O_2. In fact in some runs, $[NO_2]$ increased after the H_2O_2 was completely consumed.

Other reactions can also participate. For example reaction 2 could be accompanied by

$$H_2O_2 + NO_2 \rightarrow HO_2 + HONO$$
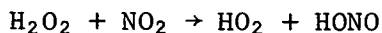
However this reaction followed by reaction 5 is equivalent to reaction 6, and need not be considered separately. Another possible reaction is

$$HO + HONO_2 \rightarrow H_2O + NO_3$$
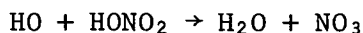
This reaction probably occurs to some extent near the end of the reaction when [$HONO_2$] is relatively large; the NO_3 would either react with NO_2 to produce N_2O_5 or with itself to produce $2NO_2 + O_2$. For simplicity we shall ignore the reaction between HO and $HONO_2$.

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

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

where β 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 8.0×10^{-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_2O_2], it presumably occurs on the wall, the reaction involving gas-phase NO_2 and adsorbed H_2O_2 following the Langmuir adsorption isotherm

$$[H_2O_2]_{ads} = \frac{a[H_2O_2]}{1 + a[H_2O_2]} \qquad\qquad 8$$

where a is some constant.

The rate law would then be first-order in [H_2O_2] if $1 \gg a[H_2O_2]$, zero-order in [H_2O_2] if $1 \ll a[H_2O_2]$, and appear to have an intermediate order at intermediate H_2O_2 pressures, viz

$$-d[H_2O_2]/dt = k[NO_2][H_2O_2]^n \qquad\qquad 9$$

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 $(0.5 - 1)$ x 10^{-18} cm^3/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

$$2HONO_2 + NO \rightarrow 3NO_2 + H_2O \qquad\qquad 10$$

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

$$HONO_2 + NO \rightarrow HONO + NO_2 \qquad\qquad 11$$

$$HONO_2 + HONO \rightarrow H_2O + 2NO_2 \qquad\qquad 7$$
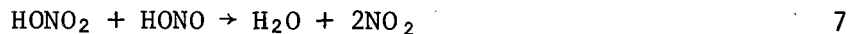
It is surprising that reaction 11 proceeds so readily since it is exactly thermal neutral. Perhaps this reaction is more complex than indicated, especially since Smith found the rate to be at least partly heterogeneous and to be catalyzed by NO$_2$. Of course the fact that one of the products of reaction 11 (HONO) is removed by further reaction shifts the equilibrium far to the right.

REACTION OF H_2O_2 WITH NO

The reaction of H_2O_2 with NO is slower than with NO_2, but is con-
siderably more complex. Reactions were run in the presence of 1-2 torr
of Ar with initial NO pressures, $[NO]_o$, from 1-12 torr; initial H_2O_2
pressures, $[H_2O_2]_o$, from 0.5 - 1.5 torr; and $[NO]_o/[H_2O_2]_o$ ratios of 1-10.
A typical reaction time history is shown in Fig. 3. There is an induc-
tion 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_2O_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_2O
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 com-
pleted the NO_2 produced equalled the H_2O_2 consumed in each run as deter-
mined 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 com-
pound, $HONO_2$, 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 ($\sim$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

$$H_2O_2 + NO \rightarrow H_2O + NO_2 \qquad\qquad 12$$

It is clear from the long time lag in NO_2 production that some intermediate must be produced as a precursor to 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 H_2O_2 corresponds to the attack of NO on H_2O_2,

$$NO + H_2O_2 \rightarrow HONO + HO \qquad\qquad 13$$

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 5.2×10^{-20} cm^3/molecule-sec.

The acceleration in the rate must be due to catalysis by either HONO or NO_2, or both. Of course, NO_2 reacts more rapidly than NO with H_2O_2, so that reaction 2 would occur if any NO_2 were present. The resulting $HONO_2$ would react with NO to regenerate the NO_2, and $HONO_2$ would be only a minor product of the reaction. The NO_2 reaction sequence would be

$$NO_2 + H_2O_2 \rightarrow HO + HONO_2 \qquad\qquad 2$$

$$HONO_2 + NO \rightarrow NO_2 + HONO \qquad\qquad 11$$

$$HO + H_2O_2 \rightarrow HO_2 + H_2O \qquad\qquad 4$$

$$HO + NO \rightarrow HONO \qquad\qquad 14$$
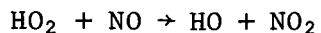
$$HO_2 + NO \rightarrow HO + NO_2 \qquad\qquad 15$$

Figure 4 shows the early time portion of Fig. 3 for the H_2O_2 decay and NO_2 growth. Also plotted are the decay rates of H_2O_2 as a function of reaction time. As the NO_2 accumulates, $-d[H_2O_2]/dt$ increases, reaching a maximum at the plateau in the $[NO_2]$ curve. Then both $-d[H_2O_2]/dt$ and $[H_2O_2]$ drop as the reaction between NO_2 and H_2O_2 passes out of the regime zero-order in $[H_2O_2]$.

About 70% of the acceleration in the H_2O_2 decay can be accounted for by the $NO_2 - H_2O_2$ reaction, as estimated from our results discussed earlier. Perhaps within the uncertainty of our measurements, all the enhancement is due to NO_2. However, if not, then some of the acceleration may also be due to catalysis by HONO. A possible reaction step is

$$HONO^* + H_2O_2 \rightarrow H_2O + NO_2 + HO \qquad\qquad 16$$
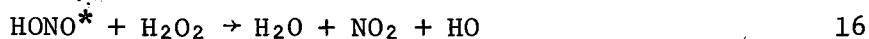
where HONO* is excited HONO. Reaction 16 is 12 kcal/mole endothermic and could only occur if the HONO retained some of the excess energy of formation in reaction 14.

HONO is known to disproportionate to H_2O, NO, and NO_2. After the H_2O_2 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 H_2O_2 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

$$HONO \xrightarrow{wall} HONO_{ads} \qquad\qquad 17$$

$$HONO_{ads} + HONO \rightarrow H_2O + NO + NO_2 \qquad\qquad 18$$
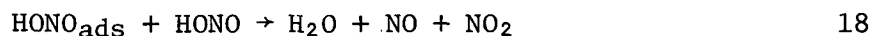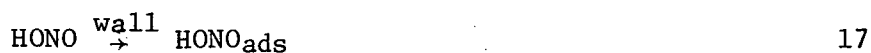
with reaction 17 rate determining. The slopes in Fig. 5 give $k_{17} = 0.30 - 0.45$ min^{-1}.

CONCLUSION

The reaction scheme in the H_2O_2 – NO – NO_2 system has been elucidated, and is at least partly heterogeneous. The homogeneous reactions of NO and NO_2, with H_2O_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

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LIST OF FIGURES

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5