# Nitrous acid in the atmosphere and laboratory experiments on its photolysis

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(Manuscript received May 16; revised version August 16, 1973)

ABSTRACT

Low concentrations of nitrous acid in air were estimated by a differential absorption method. Over a three-month period, atmospheric concentrations at one location in southern England varied between 0.4 and 11 ppb while those of nitrogen dioxide varied between 4 and 21 ppb. The highest proportion of acid was found in air which had passed over the industrial regions of W. Europe. In the laboratory, concentrations of about 1 ppm of nitrous acid with less than 0.03 ppm of nitrogen dioxide were produced by blowing air over a shallow layer of very dilute acidified nitrite solution. Exposure of the vapour to the light from a pyrex-shielded mercury arc caused decomposition, with production of nitrogen dioxide. This decomposition was apparently prevented by some olefins. The experiments did not support the view that nitrous acid is a source of hydroxyl radicals in the atmosphere.

## Introduction

Colorimetric reagents for nitrogen dioxide cannot distinguish between this gas and nitrous acid. The two can however be separated physically because the latter is easily absorbed by water whereas the former is not, being too insoluble. Full advantage of this difference could not be taken however until an efficient absorbing reagent for nitrogen dioxide was available. A systematic search for such a reagent has recently been successful (Nash, 1970*a*) and it became possible for the first time to estimate with ease and accuracy the two principal reactive components of 'nitrous fumes' at high dilution in air.

## Collection and analysis

Arnold tubes were used because they are of a standard pattern, readily available in England and taking a conveniently small volume of collecting solution (4 ml). Two were placed in series, the first containing 0.1 N alkali which absorbed all of the nitrous acid and a small proportion of the nitrogen dioxide, and the second containing 0.1 N alkali with 0.004 M guaiacol (*o*-methoxy phenol, 0.05 % w/v) which collected nearly all of the remaining nitrogen dioxide and converted 73 % of it to nitrite ion (Nash, 1970*b*). After sampling for the appropriate time at 0.8 l/min the tubes were disconnected and 4 ml of modified Saltzman's reagent added to each. This reagent contained 25 g of oxalic acid, 5 g of sulphanilic acid and 20 mg of N-naphthyl ethylene diamine dihydrochloride, made up to 1 litre in distilled water. After 10 minutes for colour development the solutions were read on a Coleman spectrophotometer at 5 500 Å. Because of the above-mentioned partial collection of nitrogen dioxide in the first tube, a correction had to be made and the concentrations of the two gases in ppm calculated as follows:

| | |
|---|---|
| Nitrogen dioxide | $7.5\ R_2/V$ |
| Nitrous acid | $4.7\ (R_1 - 0.1\ R_2)/V$ |

Where $R_1$ and $R_2$ are the colorimeter readings from the first and second tubes respectively, and $V$ is the volume of air sampled in litres. The correction was determined by sampling air which had been completely freed from nitrous acid by bubbling through dilute alkali, but which still contained an adequate concentration of nitrogen dioxide (see below).

Table 1. *Concentrations in ppm attained after given times of forced evaporation from 1 litre of acidified sodium nitrite, surface area 0.4 m², at 10°C*

| | Time in minutes | | | Strength of solution |
|---|---|---|---|---|
| | 10 | 30 | 100 | |
| $HNO_2$ | 1.6 | 2.7 | 4.5 | 0.01 N |
| $NO_2$ | — | 0.05 | 0.11 | |
| $HNO_2$ | 8 | 14 | 22 | 0.1 N |
| $NO_2$ | 1.1 | 1.8 | 3.4 | |

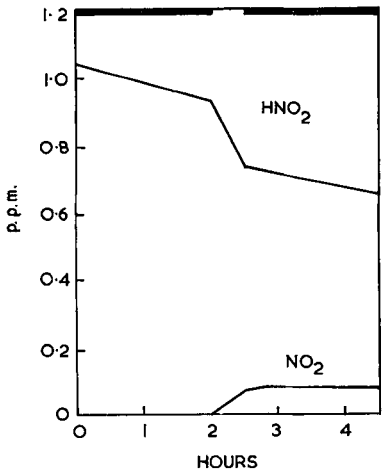


*Fig. 1.* Decay of nitrous acid vapour in chamber, and the production of nitrogen dioxide on irradiation. The period of irradiation in this and other Figures is represented by a break in the thick black line at the top.

## Experimental chamber

All of the experimental atmospheres were prepared in a 22 m³ chamber with aluminium walls, ceiling and floor. There were high-capacity centrifugal fans in both input and output trunking for rapid ventilation between tests. Fresh air was taken in directly from outside (rural situation, southern England) and because of the relatively high concentrations of $NO_x$ used, little interference was expected from pollution: experiments were restricted to times of clean westerly winds.

## Generation of nitrous fumes

It was already known (Nash, 1968) that $NO_x$ consisting mainly of nitrous acid vapour could be found over dilute acidified solutions of nitrite. Preliminary tests in the chamber showed that the proportion of nitrous acid was greatest when the solution was in a shallow layer with air blown rapidly over the surface. It was found convenient to use large photographic trays, 32 cm by 42 cm by 7 cm deep, with 300 to 600 ml of solution in each. Up to 10 such trays could be placed on the floor of the chamber, according to the experiment, and three electric fans could be adjusted so as to blow air across the surface of the solution. The latter was made up immediately before each experiment by adding 6 N sulphuric acid to the dilute nitrite so as to bring the pH to about 2. This procedure ensured that practically all of the nitrite ion was converted to the free acid (pK 3.4). In other experiments it was established that hydrogen ion itself did not influence the decomposition of the acid in solution, which probably followed the expected bimolecular route.

Tests were done with nitrite of different strengths, using one litre of solution distributed among three trays, and Table 1 shows how the concentration of nitrous acid and of nitrogen dioxide increased with time. With still weaker solutions of nitrite, 0.001 M, it was found that a concentration of about 1 ppm of nitrous acid was attained in 30 minutes with the nitrogen dioxide not exceeding 3 pphm. This degree of contamination was considered tolerable and most of the photolysis experiments were done using similar atmospheres.

## Photolysis of nitrous acid vapour

Nitrous acid has a slow 'natural' decay rate in the chamber, which is greatly accelerated by irradiation. The kind of result obtained and illustrated in Fig. 1 is representative of several experiments, in which the nitrogen dioxide remained below the level of measurement until irradiation was started.

Addition of olefin to the air of the chamber was often effective in preventing decomposition during irradiation. This was so with 1-butene (Fig. 2) and with cyclohexene (Fig. 3). In the latter experiment the nitrogen dioxide concentration was measured before and after addi-

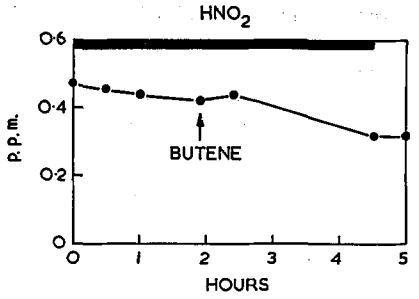


*Fig. 2.* Prevention of photolytic decomposition of nitrous acid by 10 ppm-1-butene. Arrow indicates addition of olefin.

tion of the olefin, and it may be seen that the concentration attained on irradiation in the absence of olefin was unchanged by irradiation in its presence. Not all olefins behave in this manner, as in several tests using ethyl vinyl ether, an olefin having a double bond conjugated with oxygen, no effect at all was discernible. Carbon monoxide had a slight effect at 100 ppm but none at 10 ppm.

## Photolysis of nitrogen dioxide

Nitrous acid in the atmosphere is probably formed from nitrogen dioxide, and it was therefore of interest to re-investigate the reported slow conversion of one to the other in the air of a smaller chamber (Nash, 1968) and to find the effect of irradiation on this process.

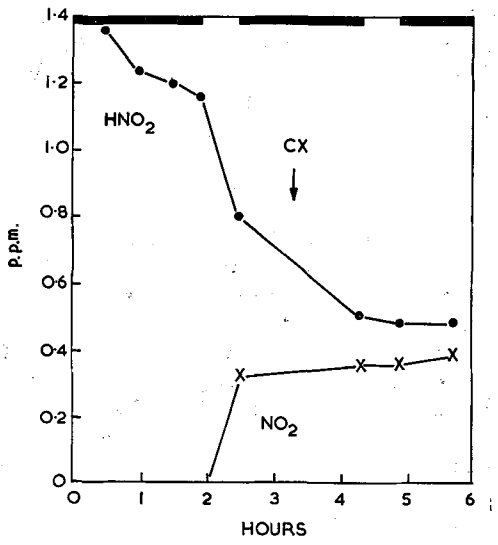


*Fig. 3.* Photolysis of nitrous acid with production of nitrogen dioxide (first period of irradiation) compared with the absence of such photolysis after addition of 10 ppm cyclohexene (second period of irradiation). Arrow indicates addition of olefin.

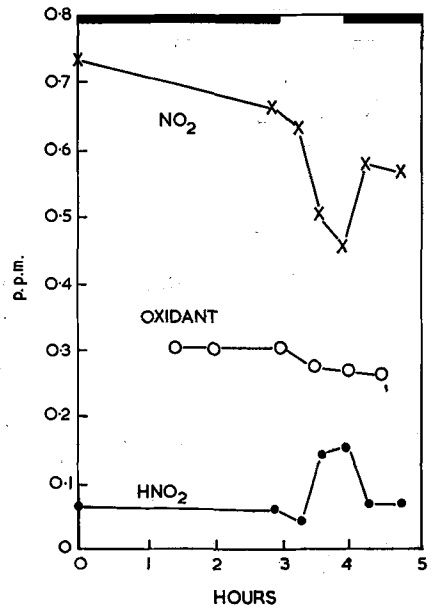


*Fig. 4.* Effect of irradiation on nitrogen dioxide containing some nitrous acid impurity, at a relative humidity of 50 %.

An atmosphere containing initially about 1 ppm of nitrogen dioxide was produced by blowing a dilution in dry oxygen into the chamber. Sampling with series Arnold tubes was then carried out at intervals, as in the nitrous acid experiments. The results of one test at 50 % relative humidity are shown in Fig. 4. Total oxidant was measured by phenolphthalin (Haagen-Smit & Brunelle, 1958) which is sensitive to nitrogen dioxide; the figures are arbitrary and intended for comparative purposes only.

It may be seen that, in spite of the precautions taken to exclude moisture from the vessel holding the initial high concentration of nitrogen dioxide, a certain amount of nitrous acid appeared at once in the chamber, and remained practically unchanged until the lamp was put on. A loss of nitrogen dioxide on irradiation is indicated not only by the points for nitrogen dioxide but also by those for total oxidant.

In a second experiment at a higher relative humidity there seemed to be a steady conversion

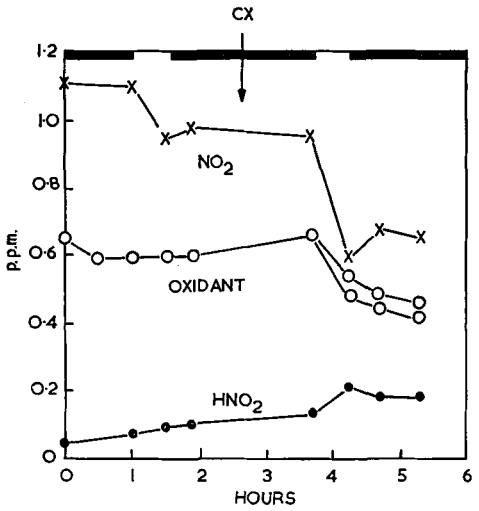


*Fig. 5.* Irradiation of nitrogen dioxide, first without and then with 10 ppm cyclohexene, and the gradual production of nitrous acid, at a relative humidity of 80 %. Arrow indicates addition of olefin.

of nitrogen dioxide to nitrous acid in the dark, which was accelerated by irradiation, especially in the presence of olefin. In this experiment (Fig. 5) there were two periods of irradiation, first without olefin and second after addition of 10 ppm of cyclohexene. The double oxidant plot on the right of the figure represents the increased reading obtained on standing the phenolphthalin solution for one hour after sampling. As nitrogen dioxide alone does not produce such an increase some other oxidant must have been responsible.

## Nitrous acid in the atmosphere

Using the same procedure as in the laboratory experiments, samples of from 2 to 4 hours duration were taken of outside air in the period around mid-day on various occasions from October 1972 to January 1973. The results are given in Table 2. On only one occasion, the first, did the nitrous acid concentration exceed that of the nitrogen dioxide. Trajectory analysis showed that this particular batch of air had passed over the industrial regions of W. Europe.

## Volatility

By comparing the rate of rise of nitrous acid concentration in the chamber with the rate of rise of relative humidity, in experiments similar to those whose results are given in Table 1, it was deduced that the volatility of nitrous acid at 10°C is about 35 times that of water.

Table 2. *Concentrations in ppb of nitrous acid and of nitrogen dioxide in the air of rural southern England (Porton)*

| Date | Nitrous acid | Nitrogen dioxide |
|---|---|---|
| 5.10.72 | 11 | 6.5 |
| 6.10.72 | 4 | 13 |
| 9.10.72 | 3.5 | 4.5 |
| 15.12.72 | 5 | 12 |
| 19.12.72 | 3.2 | 17.5 |
| 20.12.72 | 1.2 | 4 |
| 4.1.73 | 2.6 | 12 |
| 5.1.73 | 2 | 8 |
| 10.1.73 | 11 | 21 |
| 12.1.73 | 3.2 | 13 |
| 19.1.73 | 0.8 | 5.5 |
| 22.1.73 | 0.4 | 4 |
| 23.1.73 | 1 | 10.5 |

## Discussion

It may be seen from Figs. 4 and 5 that some nitrous acid is apparently formed very rapidly when nitrogen dioxide is introduced into the chamber. Bimolecular vapour-phase hydrolysis can hardly be important at such high dilution, but some kind of monomolecular hydrolysis might have occurred on the walls of the chamber, with adsorption of the resulting free radical:

$$NO_2 + H_2O \text{ (adsorbed)} \rightarrow HNO_2 + OH \text{ (adsorbed)}$$

The high volatility of the acid would be consistent with such a mechanism. The same kind of reaction could occur in polluted atmospheres on the surface of particles.

The presence of measurable concentrations of nitrous acid in the atmosphere reopens the question of its possible reactions. The idea that the acid is a source of hydroxyl radicals seems to have gained some measure of acceptance (Kerr et al., 1972). However, while photolytic production of hydroxyl radicals and nitric oxide can explain the observed breakdown under irradiation (Figs. 1 and 3) by the successive reactions

$$HNO_2 \rightarrow HO + NO; \quad HO + HNO_2 \rightarrow H_2O + NO_2$$

it cannot explain the inhibiting effect of olefin (Figs. 2 and 3) which could prevent the second of these reactions but not the first. The observed effect of olefin could be explained by supposing that irradiation produced an activated nitrous acid molecule, capable of decomposing a second inactive molecule. The function of the olefin would then be to deactivate by collision. Some support for this idea comes from the observed ineffectiveness of ethyl vinyl ether in preventing photolytic decomposition, which is difficult to explain on the free-radical hypothesis as this olefin is particularly reactive e.g. towards ozone. Loss of activity as regards collision deactivation is however not unreasonable as conjugation with oxygen would have a large effect on the double-bond vibration frequency.

Nitrous acid may still be important in the free-radical chemistry of the atmosphere, as its ready oxidation to nitrogen dioxide makes it likely that it would be an efficient radical scavenger.

With regard to nitrous acid solutions, mathematical analysis shows that the figures given in Table 1 are consistent with bimolecular decomposition if we assume that the resulting nitrogen dioxide is evolved rapidly because of its relatively high volatility and low solubility. Knowing the volume of the chamber it is also possible to estimate the decomposition rate constant: this came to 0.022 $l^2$ $mole^{-2}$ $min^{-1}$ at 10°C, but no great accuracy is claimed for this figure.

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## АЗОТНАЯ КИСЛОТА В АТМОСФЕРЕ И ЛАБОРАТОРНЫЕ ЭКСПЕРИМЕНТЫ ПО ЕЕ ФОТОЛИЗУ

Методы дифференциального поглощения было найдено, что концентрации азотной кислоты в воздухе низки. В течение трехмесячного периода ее концентрация в атмосфере в одном месте в южной части Англии варьировала между $0{,}4 \cdot 10^{-9}$ и $11 \cdot 10^{-9}$, в то время как концентрация двуокиси азота менялась между $4 \cdot 10^{-9}$ и $21 \cdot 10^{-9}$. Наибольшая пропорция кислоты была найдена в воздухе, прошедшем над индустриальными районами Западной Европы. В лаборатории концентрации азотной кислоты около $10^{-6}$ и менее чем $3 \cdot 10^{-8}$ двуокиси азота получались при продувании воздуха над мелким слоем очень разбавленного окисленного раствора нитрита. Освещение паров светом ртутной дуги, экранированной пирексом, вызывало разрушение кислоты с получением двуокиси азота. Это разрушение заметно предотвращалось некоторыми олефинами. Эти эксперименты не поддерживают мнение, что азотная кислота является источником радикалов гидроксила в атмосфере.