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PHOTOLYSIS OP NITRIC ACID VAPOR

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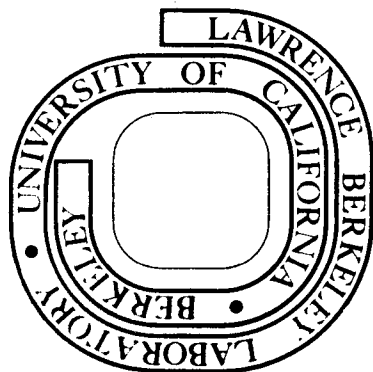
Harold S. Johnston and Shih-Ger Chang

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Photolysis of Nitric Acid Vapor

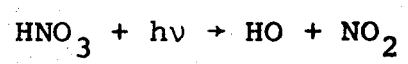
by

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Abstract

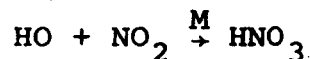
The primary reaction in the photolysis of nitric acid vapor by ultraviolet radiation is



and the primary quantum yield is one. This article gives strong experimental evidence in favor of these two conclusions for the wavelength region 255 to 315 nm, and somewhat less direct experimental evidence for the wavelengths 200-255 nm. The photolysis of nitric acid vapor in laboratory apparatus is subject to several unwanted side reactions, and conditions must be carefully selected to eliminate the effect of such reactions.

Introduction

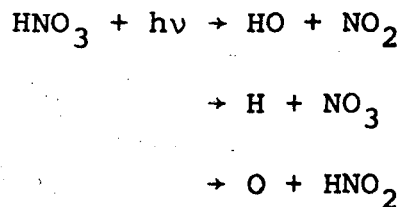
Nitric acid has been observed in the stratosphere by Murcray et al.¹ It is presumably formed from hydroxyl radicals and nitrogen dioxide



and it may also be formed by gaseous dinitrogen pentoxide abstracting water from aqueous sulfuric acid droplets



The maximum mole fraction of nitric acid vapor is found between 20 and 24 km. The decreasing mole fraction above the maximum is probably caused by the photolysis of nitric acid vapor. Recently the absorption spectrum of nitric acid vapor has been obtained.² However, quantitative modelling calculations of the photolysis of nitric acid in the stratosphere require knowledge of the products of the primary photochemical reaction and the quantum yield as a function of wave length. The primary products could be



Berces and Forgeteg³ reported a quantum yield of about 0.1 at 265 nm, but their conclusions involved assumed values of other rate constants that have since been shown by Morris and Niki⁴ to be in error by several orders of magnitude. The purpose of this study was to identify the primary products and obtain the

primary quantum yield for the photolysis of nitric acid vapor by ultraviolet radiation.

Experimental Conditions

Materials.--Anhydrous nitric acid was prepared by vacuum distillation from a 50-50 slurry of concentrated sulfuric acid and sodium nitrate. The high temperature should not exceed 30°C in order to avoid the thermal decomposition of liquid nitric acid to form nitrogen dioxide, and the low temperature should not be below -40°C to avoid distillation of water from the concentrated sulfuric acid. The pure nitric acid was completely colorless, and it remained pure indefinitely when stored at Dry Ice temperature and in the dark. The oxygen (Matheson, research grade) was passed through traps at Dry Ice temperature. Carbon monoxide (Matheson UHP grade) was passed through a five-foot long column of activated charcoal on glass wool in order to remove iron carbonyl.

Apparatus.--The glass vacuum apparatus was of conventional design. Stopcocks were lubricated with Kel-F stopcock grease, which is inert to nitric acid, or were of the non-lubricated variety with a Teflon plug and Viton o-rings. Pressures were measured by a Pace Transducer, which we calibrated against an oil manometer. The reaction cells were cylindrical, 100 mm in length, and 35 mm in diameter. Two grease-free stopcocks with Viton o-rings were sealed to the cell with quartz-to-glass graded seals. The silica windows were fused to the cell.

Several different light sources were used: a 50 watt deuterium arc at 200 and 215 nm with a Bausch and Lomb high intensity grating monochromator; a 200 watt high pressure mercury arc with the same monochromator; a 1600 watt xenon arc with a 500 mm Bausch and Lomb monochromator.

Light intensities were measured by two methods: (1) potassium ferrioxatate actinometry^{5,6} and (2) a Hewlett-Packard 8330-A Radiant Fluxmeter. The intensities obtained by these two methods were in good agreement, but all quantitative data (except that at 200 and 215 nm) are based on the chemical actinometry. The optical band width (full width at half maximum) was 2.2 nm at 300 nm, 6.5 nm at 290 nm, 2.5 nm at 255 nm, and 6.5 nm below 225 nm.

Procedure.--Three types of runs were carried out: (1) with pure nitric acid alone, (2) with nitric acid plus carbon monoxide, and (3) with nitric acid plus carbon monoxide and oxygen. Nitrogen dioxide in the cell was measured by stopping the photolysis, by transferring the reaction cell to a Beckman DU or a Cary 14 spectrophotometer, and by measuring optical density at 405 nm ($\sigma = 6.24 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$, compare Figure 1). The carbon dioxide produced was measured in a Consolidated Electronics Corporation 21-110 high resolution mass spectrometer. Appropriate blanks were measured with no photolysis. Most runs were carried to only very small degrees of conversion (one or two per cent), and thus it was not practicable to follow the course of the reaction in terms of disappearance of HNO_3 or of CO. The course of the reaction was followed from time to time by optical analysis of NO_2 formed; or it was followed by ending the run, freezing out the nitric acid, and analyzing the CO and CO_2 with the mass spectrometer. All runs were made at 25°C.

Results and Discussion

The photolysis of nitric acid vapor was studied at 25°C with initial nitric acid pressures between 5 and 40 torr. During the course of the photolysis at 40 torr HNO_3 , it was noticed that liquid droplets (presumably aqueous nitric acid) condensed out on the walls of the reaction cell, and all runs at 40 torr have been rejected. At 5 torr HNO_3 the rate of formation of products was exceedingly slow. Most runs were made at 15 or at 30 torr.

Photolyses were carried out at wavelengths between 200 and 315 nm. The absorption spectrum of NO_2 , HNO_3 , and N_2O_5 is given as Figure 1. At all wave lengths the absorption cross sections of N_2O_5 is substantially greater than that of HNO_3 , and thus secondary photolysis of N_2O_5 is a complicating feature of certain experiments. The absorption spectrum of NO_2 occurs in two bands, above and below 250 nm. Between about 250 and 400 nm the product of the photolysis of NO_2 is NO and ground-state oxygen atoms, $\text{O}(^3\text{P})$. Below 250 nm the product of the photolysis of NO_2 is NO and an excited singlet oxygen atom, $\text{O}(^1\text{D})$.⁷ The excited singlet oxygen atom reacts very rapidly with H_2O , H_2 , CH_4 , etc.⁸ and presumably it would react very rapidly with HNO_3 . On the other hand the ground state oxygen atom, $\text{O}(^3\text{P})$, reacts very slowly (if at all) with nitric acid vapor.⁴ Thus the reactions following the secondary photolysis of the product NO_2 are quite different above and below 250 nm. Most runs were made at 255 nm (where the cross section for light absorption by HNO_3 is greater than

that for NO_2) or at 290 or 300 nm (where the cross section of NO_2 greatly exceeds that of HNO_3). Only a few runs were made below 250 nm, where $\text{O}(^1\text{D})$ enters the mechanism.

A series of photolyses was carried out at 290 nm radiation, 30 torr pure HNO_3 , and the progress of the reaction was followed by light absorption by NO_2 . The results are given in Figure 2 where the logarithm of concentration of NO_2 is plotted against the logarithm of photons absorbed per cm^3 . The initial nitric acid concentration is indicated at the top of the figure. The primary quantum yield ϕ is defined as

$$\phi = \frac{\text{number of molecules of } \text{HNO}_3 \text{ destroyed}}{\text{number of photons absorbed by } \text{HNO}_3} \quad (1)$$

The quantum $\phi(x)$ with respect to some product x is defined as

$$\phi(x) = \frac{\text{number of molecules of } x \text{ formed}}{\text{number of photons absorbed by } \text{HNO}_3} \quad (2)$$

If NO_2 were produced with a quantum yield of one, the experimental points would lie on the 45 degree line given on the figure; points above the line would correspond to a quantum yield greater than one; and points below the line correspond to quantum yields less than one. The first four experimental points represent quantities of NO_2 which are less than one per cent of the initial HNO_3 and the quantum yield for formation of NO_2 is about 0.1, in rather close agreement with the results of Berces and Forgeteg.³ Our interpretation of the results, however, is quite different from that of Berces and Forgeteg.

These experimental results were interpreted by a model of 41 reactions (Table 1) carried out by the complete Gear routine,⁹

modified for this photochemical study (Lawrence Livermore Laboratory and Dr. Gary Whitten of this laboratory). This discussion focuses on the dominant reactions to give the reader a qualitative understanding of what is involved; quantitative conclusions are based on the integration of the full set of reactions. From the Gear integration of the 33 homogeneous reactions under the conditions of Figure 2, it was seen that for the first few experimental points, the predominant product is not NO_2 , but N_2O_5 :



Berces and Forgeteg³ looked for N_2O_5 in their reaction cells but found none. We have observed repeatedly that N_2O_5 reacts fairly rapidly with water on the walls of reaction cells to produce nitric acid



where W signifies a reaction on the walls of the cell. The net result of these four reactions is to return all photolysis products back to the starting material; all quantum yields are zero by this four-step mechanism.

The observed quantum yield of NO_2 is about 0.1, however. This formation of products occurs by way of:

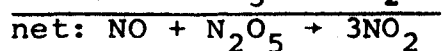
(a) The photolysis of N_2O_5



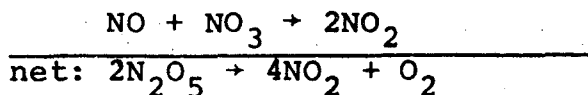
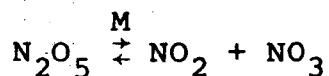
(b) The photolysis of NO_2 and by its reaction with oxygen atoms



(c) The fast reaction of NO with N_2O_5 which occurs via the mechanism



(d) The thermal decomposition of N_2O_5



These numerous, relatively slow, secondary reactions (4) compete with the reconversion of N_2O_5 to HNO_3 by reaction (3d), giving the small observed quantum yield of about 0.1.

The detailed calculations of the homogeneous reactions show that N_2O_5 decreases precipitously during the course of the photolysis in Figure 2. Because of the great speed of the reaction of NO with N_2O_5 , these two species are incompatible with each other. The photolysis of NO_2 (compare Figure 1) forms NO which destroys N_2O_5 . At the midpoint of the observed points in Figure 2, N_2O_5 has been reduced to a very low level, the back reaction (3d) no longer occurs, and the slope of the line

(log NO₂ vs. log photons absorbed) is one, which means the quantum yield for formation of NO₂ is one. However, late in the reaction, the slope is much greater than one; NO₂ is being produced much faster than nitric acid is being photolyzed. According to the detailed mechanism and in terms of homogeneous reactions, nitric oxide exceeds NO₂ after 10¹⁷ photons have been absorbed per cm³. As noted by Smith,¹⁰ NO reacts at a moderate rate with nitric acid as a heterogeneous reaction on the walls of the reaction cell

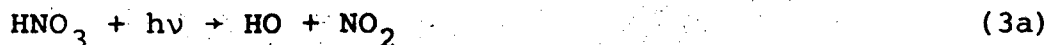


The rapid increase in NO₂ during the last half of the observed points in Figure 2 results from the photolysis of NO₂ (reactions 4b, c) to form NO and the reaction of this NO with nitric acid.

These considerations show that the direct photolysis of pure nitric acid vapor is an unsuitable method for obtaining the primary quantum yield. During the early stages of the reaction the results are dominated by a heterogeneous reaction (3d) that gives a quantum yield of NO₂ much less than the primary quantum yield, and during late stages of the reaction the results are dominated by another heterogeneous reaction (5) that gives a (differential) quantum yield of NO₂ formation that is much greater than unity.

It is well known that carbon monoxide reacts rapidly with hydroxyl radicals to produce carbon dioxide.¹¹ Thus the formation of carbon dioxide gives a sensitive method to detect the rate of production of HO, presumably the rate of the primary photochemical

process



For this discussion we assume this primary quantum yield to be one. To the extent that the hydroxyl radical reacts with nitric acid



the quantum yield for formation of carbon dioxide is zero

$$\phi_a(\text{CO}_2) = 0$$

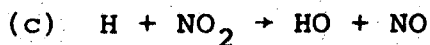
The reaction of the hydroxyl radical with carbon monoxide



contributes unit quantum yield to carbon dioxide formation

$$\phi_b(\text{CO}_2) = 1$$

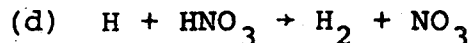
What happens to the hydrogen atom determines the total quantum yield of CO_2 . If the hydrogen atom reacts with nitrogen dioxide



the quantum yield is two

$$\phi_{bcb}(\text{CO}_2) = 2$$

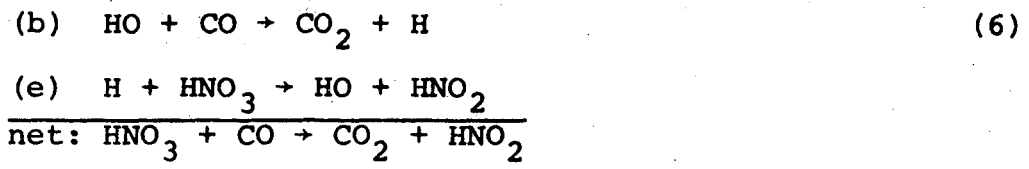
If the hydrogen atom reacts with nitric acid to form H_2



the total quantum yield of CO_2 is one

$$\phi_{bd}(\text{CO}_2) = 1$$

If the hydrogen atom reacts with nitric acid to form HO, there is a chain reaction that produces carbon dioxide



In this case the quantum yield could be indefinitely large

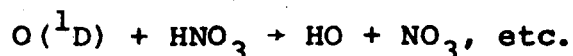
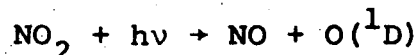
$$\Phi_{be}(\text{CO}_2) \gg 1$$

Berces, Forgeteg, and Marta¹² interpreted their data on added CO in terms of a primary quantum yield of 0.1 and a chain length of reactions be up to 17. The rate constant that they required for reaction e was $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Morris and Niki⁴ attempted to measure this rate constant, but they were unable to detect it. From the sensitivity of their experiment, they found that reactions e plus d must be at least 10 times and probably 100 times slower than the value used by Berces, Forgeteg, and Marta.¹² Thus, the predominant mechanism is bcb, and the quantum yield for formation of CO₂ at small degrees of conversion of HNO₃ is expected to approach two for a great excess of carbon monoxide over nitric acid.

A series of experiments was carried out with either 15 or 30 torr of HNO₃ and with various amounts of CO from 30 to 700 torr. The wavelength was 290 nm, and $(8.8 \pm 0.2) \times 10^{15}$ photons cm⁻³ were absorbed in each case. From Figure 2 this can be seen to be about one per cent of the nitric acid present at 30 torr and about 2 per cent at 15 torr. Thus these experiments represent initial conditions, and the effect of nitric oxide reacting with nitric acid was minimized. The ratio of CO₂/CO was measured on a mass spectrometer. The concentration of CO₂ produced as a function of initial carbon monoxide is given as Figure 3. At

large excess CO, the quantum yield approaches two, as expected from mechanism bcb. The quantum yield is less than two for small amount of CO, as expected from the competition of HNO₃ and CO for the available HO radical. These results strongly indicate that the primary quantum yield for the photolysis of nitric acid is one at 290 nm, since the quantum yield for formation of CO₂ becomes two with excess CO over HNO₃.

The most complicated condition is that of about equal HNO₃ and CO. In this case some N₂O₅ is formed, some NO₂ is formed, and the quantum yield for forming CO₂ is 0.4±0.1. This complicated condition was chosen for a study of the effect of wave length, Table 2. In the wavelength region where the photolysis of NO₂ leads to O(³P), the quantum yield of formation of CO₂ is around 0.3 to 0.4. At short wavelengths where photolysis of NO₂ leads to O(¹D), the quantum yield for formation of CO₂ is between 0.98 and 2.2. This increase in quantum yield appears to arise from

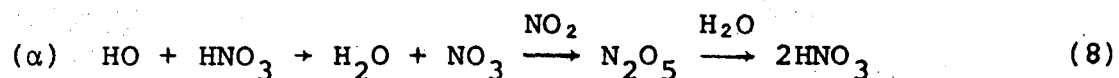


In view of the lack of rate constant for the O(¹D) reactions with HNO₃, it is not possible to do complete model calculations on this system. It was decided to work primarily on the relatively simple system where photolysis of NO₂ produces O(³P).

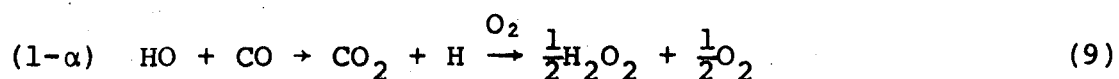
In the system with added CO, there is some ambiguity about the fate of the hydrogen atom, NO₂ is stripped down to NO, and the role of the heterogeneous reaction between NO and HNO₃ is

uncertain. If excess oxygen is added to the system, the hydrogen atom will be trapped to form HOO, the oxygen atom from the photolysis of NO₂ will add to molecular oxygen to form ozone, and both HOO and O₃ rapidly convert NO to NO₂, reducing the impact of the NO-HNO₃ reaction. From the values of the rate constants for H + NO₂ and H + O₂ + M, it can be seen that several hundred torr of oxygen are needed to suppress the reaction of H with NO₂. The optimum amount of carbon monoxide was found by varying CO from 23 to 400 torr at a constant 300 torr of O₂. The quantum yield for the formation of nitrogen dioxide is given by Figure 4, where the degree of dissociation of HNO₃ is one per cent. On this figure the quantum yield for formation of CO₂ from the situation with no added oxygen (Figure 3) is plotted against CO, and the quantum yield for forming NO₂ with 300 torr of oxygen is plotted on the same scale.

At small concentrations of CO there is a striking parallel between quantum yield to produce CO₂ and to produce NO₂. The reason for this parallelism is given in terms of the competition between HNO₃ and CO for the hydroxyl radical. The fraction of reaction of HO with HNO₃ is given as α



and the fractional reaction of HO with CO is



The quantum yield to form carbon dioxide is

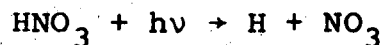
$$\phi(\text{CO}_2) = (1-\alpha) \quad (10)$$

The quantum yield to form nitrogen dioxide is

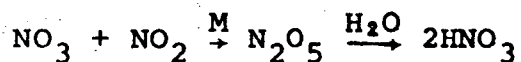
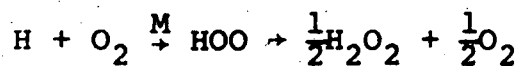
$$\phi(\text{NO}_2) = 1 - (\alpha) = (1-\alpha) = \phi(\text{CO}_2) \quad (11)$$

Thus to the first approximation, the quantum yields to form CO_2 and NO_2 are equal and in the limit of excess CO the quantum yield of NO_2 approaches the primary ϕ of HNO_3 . However, when HO reacts with HNO_3 , N_2O_5 is formed, and its reactions with NO, O, H, and $h\nu$ produce some additional NO_2 . These secondary reactions of N_2O_5 cause the initial yield of NO_2 to exceed that of CO_2 (Figure 4), and they lead to a quantum yield of NO_2 somewhat greater than one when CO is about 100 torr. However, when both CO and O_2 are about 300 to 400 torr, this exceedingly complicated system becomes surprisingly simple.

If the primary photolysis of nitric acid yielded a hydrogen atom

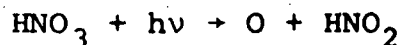


the added oxygen would remove the hydrogen atom and any NO_2 present would be converted to N_2O_5 and then to nitric acid:

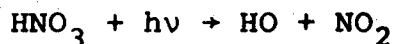


Even with added CO, the quantum yield both to produce NO_2 and to produce CO_2 would approach zero with excess oxygen. Thus the primary photochemical reaction is not to produce H and NO_3 .

If the primary photolysis of nitric acid yielded an oxygen atom and nitrous acid

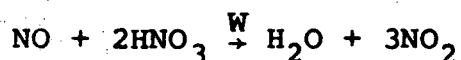


there would not be a large production of CO_2 . The primary photochemical reaction thus appears to be



Detailed calculations with a model of 37 homogeneous reactions showed that with 400 torr O_2 and 300 torr CO , there was only a very small contribution from N_2O_5 , NO , or HNO_2 both to the composition of the products and to the reaction rates. The quantum yield of NO_2 should be very close to the primary quantum yield of HNO_3 . The experimental data for various pressures of nitric acid (5, 15, and 30 torr) at 255 nm wavelength and with 400 torr O_2 and 300 torr CO are plotted on Figure 5. Also included is a comparison between 255 nm and 300 nm radiation for 15 and 30 torr HNO_3 . Results are plotted as photons absorbed by nitric acid vs. molecules of NO_2 formed. The line corresponds to unit quantum yield. The region above the line corresponds to quantum yield greater than one, and the region below the line corresponds to quantum yield less than one. Regardless of wavelength (255 or 300 nm) and regardless of initial pressure of nitric acid (5, 15, 30 torr), the experimental results are identical for nitric acid conversions of less than one per cent. For the cases with 15 torr HNO_3 , the quantum yield of NO_2 at 255 nm was one up to 2 per cent conversion of HNO_3 , and it became slightly higher than one (about 1.2) for 4 to 6 per cent conversion of HNO_3 ; but the quantum yield of NO_2 at 300 nm was one up to about 1.5 per cent conversion of HNO_3 and rapidly rose to two as the conversion of HNO_3 exceeded 2 per cent. From Figure 1 it can be seen that at 255 nm HNO_3 absorbs radiation about 1.5 times faster than NO_2 , but at 300 nm, NO_2 absorbs radiation 40 times

faster than HNO_3 . The rapid rise of NO_2 quantum yield above 2 per cent HNO_3 conversion at 300 nm comes from the photolysis of NO_2 and the subsequent reaction of nitric oxide with nitric acid



Since results at 255 and 300 nm agree very well below 1 per cent conversion of HNO_3 , it is reasonable to assume that this surface reaction is negligible under these conditions. Thus with added CO (which suppresses N_2O_5), added O_2 (which removes hydrogen atoms), and at low conversions, it appears that the quantum yield for formation of NO_2 is 1.0 between 255 and 300 nm.

In the discussion of mechanism above, we have looked at the computer print-out for the complete 37-reaction model and have discussed only the major factors involved in each case. In addition to the major reactions discussed there are numerous other reactions giving an effect of a few per cent in one sense or another. In Figure 6 we plot an extensive run with 15 torr HNO_3 , 300 torr CO, 400 torr O_2 , and at 255 nm radiation. The curve is based on the complete model of 37 homogeneous reactions and on the assumption that the primary quantum yield for the photolysis of nitric acid is one. The points are observations at various stages of the reaction up to 7 per cent conversion of the original nitric acid. There is excellent agreement between calculated and observed results at the initial stage of conversion, at intermediate stages of conversion the observed points are

somewhat below the calculated curve, and at high degrees of conversion the observed points are somewhat above the calculated curve. These deviations are probably real effects due to surface reactions. The added CO almost completely suppresses N_2O_5 and the low quantum yield around 2×10^4 seconds is not due to the back reaction of N_2O_5 and H_2O . However, in this system large amounts of hydrogen peroxide are formed from the hydroperoxyl radicals



Hydrogen peroxide reacts with nitric oxide on surfaces to produce nitrogen dioxide¹³



Hydrogen peroxide decomposes directly on surfaces



Also, hydrogen peroxide reacts on surfaces with nitrogen dioxide to form nitric acid¹³



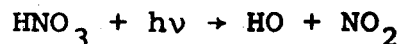
The low quantum yield around 2×10^4 seconds (Figure 6) could be due to this heterogeneous reaction, equation 16. The somewhat larger quantum yield after 6×10^4 seconds is probably due to the reactions indicated by equation 12.

With one heterogeneous reaction (16) giving a net quantum yield of zero and another set (12) giving a net quantum yield of 2 with respect to radiation absorbed by NO_2 , one asks whether the agreement between theory and experiment in Figure 6 could be

due to accidental balancing of these two opposing heterogeneous processes. However, this is not possible because the cross section for NO_2 absorption is too low. At the last point on the figure, NO_2 is about 7 per cent of the HNO_3 , and the absorption rate by NO_2 only 5 per cent of that of HNO_3 . Thus the maximum quantum yield of two (equation 12) for destruction of nitric acid from photolysis of NO_2 leads to an increase of the quantum yield by 10 per cent, which is about that observed.

Conclusions

The primary reaction in the photolysis of nitric acid vapor is



and the primary quantum yield is one. These statements are reasonably well established for radiation wavelengths between 255 and 315 nm, and there is strong (but inconclusive) evidence for these statements at wavelengths shorter than 255 nm. The difficulty below 250 nm is that the secondary photolysis of NO_2 produces $\text{O}(^1\text{D})$, and its reactivity towards HNO_3 is not known. The production of $\text{O}(^3\text{P})$ from the photolysis of NO_2 above 255 nm is of no consequence, but the production of nitric oxide at the same time leads to a serious heterogeneous reaction between NO and HNO_3 . Quantitative results are obtained only under conditions where this secondary reaction is effectively eliminated. The experimental condition with most nearly negligible side reactions was: 255 nm, the wavelength of minimum NO_2 absorption; degree of

reaction less than one percent; and added excess CO and O₂ to quench undesirable secondary reactions. A firm base line was established under these most favorable conditions, and it was then possible to extend the conclusions to other wavelengths and to other conditions.

Acknowledgement

This work was supported by the Climatic Impact Assessment Program by means of an interagency agreement between the Department of Transportation and the Atomic Energy Commission through the Inorganic Materials Research Division, Lawrence Berkeley Laboratory. We are grateful to Lawrence Livermore Laboratory for providing us with their Gear-B computer program, to Dr. Gary Whitten who adopted this program to the nitric acid problem, to Mr. R. Graham for the NO₂ and N₂O₅ spectra, and to Dr. Charles Koch for the mass spectra.

Table 1. Reactions considered, k at 298°K

| | | |
|-----|---|---------------------------|
| 1. | $\text{HNO}_3 \xrightarrow{h\nu} \text{HO} + \text{NO}_2$ | |
| 2. | $\text{HO} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ | 4.0×10^{-12} (a) |
| 3. | $\text{HO} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$ | 1.5×10^{-13} |
| 4. | $\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$ | 3.0×10^{-12} (a) |
| 5. | $\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$ | 0.10 (a) |
| 6. | $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{O}_2 + \text{NO}_2$ | 2.4×10^{-16} |
| 7. | $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$ | 0.87×10^{-11} |
| 8. | $\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}$ | |
| 9. | $\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$ | 9.1×10^{-12} |
| 10. | $\text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M}$ | 6.8×10^{-32} |
| 11. | $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ | 3.6×10^{-34} |
| 12. | $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ | 1.73×10^{-14} |
| 13. | $\text{HO} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ | 1.88×10^{-13} |
| 14. | $\text{H} + \text{NO}_2 \rightarrow \text{HO} + \text{NO}$ | 4.8×10^{-11} |
| 15. | $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HOO} + \text{M}$ | 5.6×10^{-32} |
| 16. | $\text{H} + \text{HNO}_3 \rightarrow \text{H}_2 + \text{NO}_3$ | $< 10^{-13}$ |
| | $\quad \quad \quad \rightarrow \text{HO} + \text{HNO}_2$ | $< 10^{-13}$ |
| 17. | $\text{HOO} + \text{NO} \rightarrow \text{NO}_2 + \text{HO}$ | 2×10^{-13} |
| 18. | $\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$ | 1.6×10^{-12} |
| 19. | $\text{HO} + \text{HOO} \rightarrow \text{H}_2\text{O} + \text{O}_2$ | 2×10^{-10} |
| 20. | $\text{HOO} + \text{HOO} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ | 3.3×10^{-12} |
| 21. | $\text{HO} + \text{HO} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$ | 8.6×10^{-31} |
| 22. | $\text{HO} + \text{NO} + \text{M} \rightarrow \text{HNO}_2 + \text{M}$ | 4.1×10^{-31} |
| 23. | $\text{HNO}_2 + \text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{NO} + \text{O}_2$ | 1.24×10^{-17} |
| 24. | $\text{H}_2\text{O}_2 + \text{HO} \rightarrow \text{H}_2\text{O} + \text{HOO}$ | 7.9×10^{-13} |

Table 1. Continued.

| | |
|---|-----------------------|
| 25. $\text{H}_2\text{O}_2 \xrightarrow{h\nu} \text{HO} + \text{HO}$ | |
| 26. $\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{HOO} + \text{HO}$ | 9.0×10^{-16} |
| 27. $\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{H}_2\text{O} + \text{O}_2$ | 9.0×10^{-16} |
| 28. $\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2 + \text{HOO}$ | 4.8×10^{-15} |
| 29. $\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{HO}$ | 4.8×10^{-15} |
| 30. $\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2$ | 6.1×10^{-17} |
| 31. $\text{N}_2\text{O}_5 \xrightarrow{h\nu} \text{O} + 2\text{NO}_2$ | |
| 32. $\text{O} + \text{HNO}_3 \rightarrow \text{HO} + \text{NO}_3$ | $< 2 \times 10^{-14}$ |
| 33. $\text{HO} + \text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2$ | 6.8×10^{-12} |
| 34. $\text{O} + \text{N}_2\text{O}_5 \rightarrow \text{O}_2 + 2\text{NO}_2$ | 2×10^{-13} |
| 35. $\text{HO} + \text{O} \rightarrow \text{H} + \text{O}_2$ | 4.2×10^{-11} |
| 36. $\text{HOO} + \text{H} \rightarrow \text{H}_2 + \text{O}_2$ | 1.3×10^{-11} |
| 37. $\text{HOO} + \text{H} \rightarrow \text{HO} + \text{HO}$ | 1.7×10^{-11} |
| 38. $\text{NO} + 2\text{HNO}_3 \rightarrow \text{H}_2\text{O} + 3\text{NO}_2$ | surface reaction |
| 39. $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$ | surface reaction |
| 40. $\text{H}_2\text{O}_2 + 2\text{NO}_2 \rightarrow 2\text{HNO}_3$ | surface reaction |
| 41. $\text{H}_2\text{O}_2 + \text{NO} \rightarrow \text{H}_2\text{O} + \text{NO}_2$ | surface reaction |

(a) A function of total gas concentration; this value refers to one atmosphere total pressure of $\text{CO} + \text{O}_2$.

Table 2. Effect of wave length on the quantum yield of formation of carbon dioxide with approximately equal nitric acid and carbon monoxide

| λ nm | photons absorbed 10^{16} cm^{-1} | HNO_3 torr | CO torr | $\phi(\text{CO}_2)$ | NO_2 PROD. |
|-----------------|--|------------------------|------------|---------------------|------------------------|
| 315 | 1.75 | 29 | 33 | 0.39 | $\text{O}(^3\text{P})$ |
| 300 | 0.55 | 26 | 26 | 0.43 | |
| 290 | 0.92 | 30 | 40 | 0.43 | |
| 290 | 2.33 | 30 | 28 | 0.25 | |
| 290 | 3.08 | 30 | 29 | 0.30 | |
| 280 | 0.83 | 27 | 24 | 0.26 | |
| 225 | 1.16 | 29 | 30 | 1.31 | $\text{O}(^1\text{D})$ |
| 215 | 2.25 | 30 | 18 | 2.2 | |
| 215 | 0.08 | 16 | 29 | 1.8 | |
| 215 | 0.72 | 15 | 28 | 1.0 | |
| 200 | 0.54 | 9 | 11 | 0.98 | |

References

1. D.G. Murcray, A. Goldman, F.H. Murcray, W.J. Williams, J.N. Brooks, and D.B. Barker, AIAA 11th Aerospace Science Meeting, Washington, D.C. January 10-12, 1973.
2. H.S. Johnston and R. Graham, J. Phys. Chem. 77, 62 (1973).
3. T. Berces and S. Forgeteg, Trans. Faraday Soc. 66, 633 (1970).
4. E.D. Morris, Jr. and H. Niki, J. Phys. Chem. 75, 3193 (1971).
5. G.G. Hatchard and C.A. Parker, Proc. Roy. Soc. A235, 518 (1956).
6. J.H. Baxendale and N.K. Bridge, J. Phys. Chem. 59, 787 (1955).
7. R. Simonaitis and J. Heicklen, Intern. J. Chem. Kin. 4, 529 (1972).
8. G. Paraskevopoulos, V.B. Symonds, and R.J. Cvetanovic, Canad. J. Chem. 50, 1838 (1972), and references cited there.
9. C.W. Gear, "The Automatic Integration of Stiff Ordinary Differential Equations", Proc. Int. Fed. Inform Proc. Cong. New York, Humanities Press, A-81 (1968).
10. J.H. Smith, J. Am. Chem. Soc. 69, 1741 (1947).
11. W.E. Wilson, Jr., J. Phys. Chem. Ref. Data 1, 535 (1972).
12. T. Berces, S. Forgeteg, and F. Marta, Trans. Faraday Soc. 66, 648 (1970).
13. D. Gray, E. Lissi, and J. Heicklen, J. Phys. Chem. 76, 1919 (1972).

Titles to Figures

- Fig. 1. The ultraviolet absorption spectra of HNO_3 , NO_2 , and N_2O_5 . $\ln I_0/I = \sigma NL$, where σ has units cm^2 , L cm, and N molecules cm^{-3} .
- Fig. 2. Photolysis of pure nitric acid vapor with 290 nm ultraviolet radiation. The straight line corresponds to unit quantum yield. The formation of NO_2 from pure HNO_3 occurs with a quantum yield much less than one.
- Fig. 3. Photolysis of nitric acid vapor in the presence of carbon monoxide with 8.7×10^{15} photons cm^{-3} absorbed by HNO_3 , 290 nm wavelength. The lower dashed line corresponds to a quantum yield for CO_2 of one; the upper dashed line corresponds to a quantum yield of two.
- Fig. 4. Photolysis of nitric acid vapor with added CO and with added CO and O_2 , 290 nm radiation. The quantum yield of CO_2 is in a system with added CO but no added O_2 . The quantum yield of NO_2 is in a system with added CO and with 300 torr O_2 . Note the parallelism between $\phi(\text{CO}_2)$ and $\phi(\text{NO}_2)$ below 100 torr of CO. With excess CO, the quantum yield of CO_2 approaches 2 and the quantum yield of NO_2 approaches one.
- Fig. 5. Photolysis of nitric acid vapor in the presence of excess CO and excess O_2 , at different wave lengths, and at different initial pressures of HNO_3 . The straight line corresponds to unit quantum yield.

Fig. 6. The build-up of NO_2 during one photolysis with excess CO and excess O_2 . The calculated curve is based on a mechanism of 33 homogeneous reactions as solved by the Gear program and on the assumption that $\phi(\text{HNO}_3)$ is one.

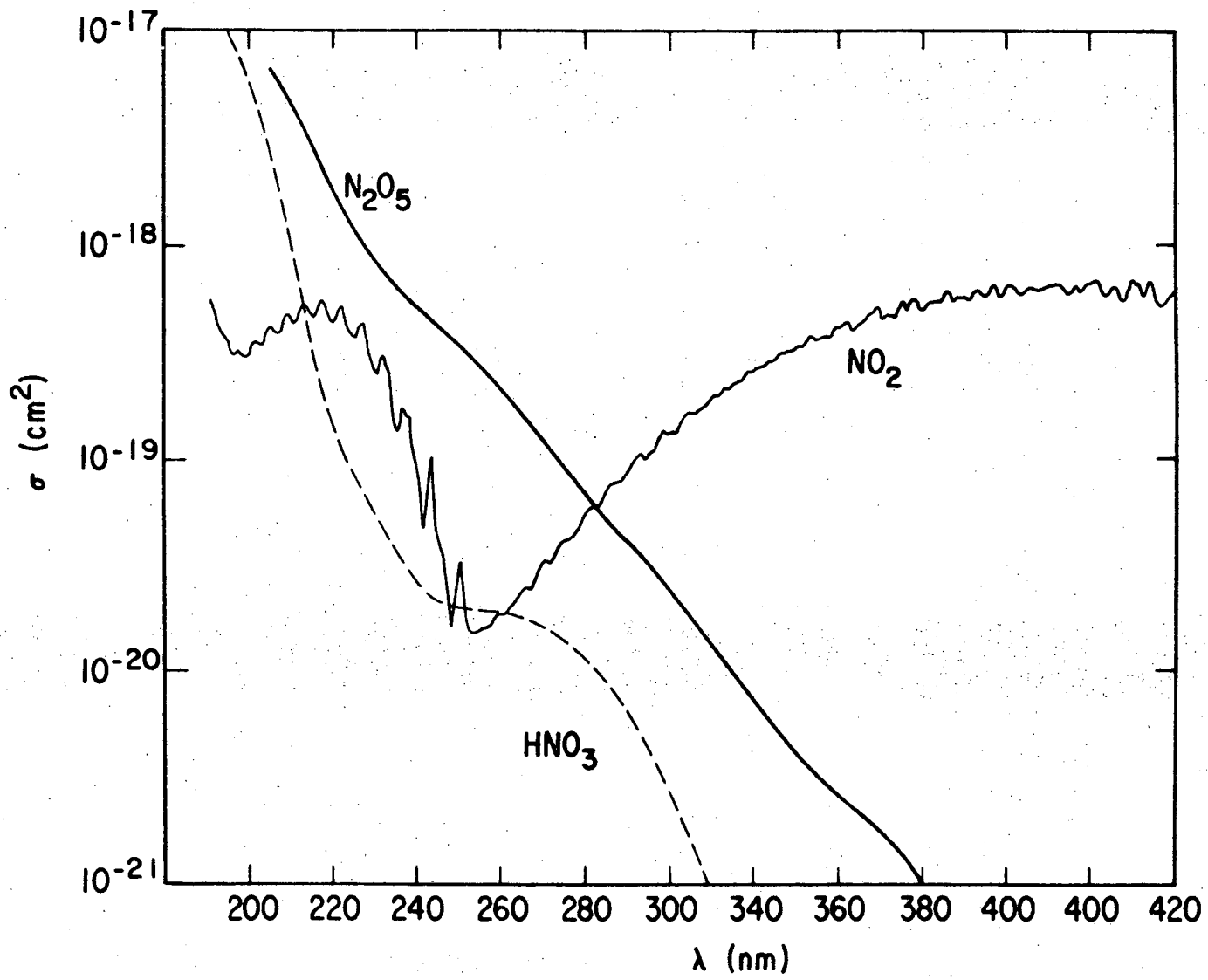
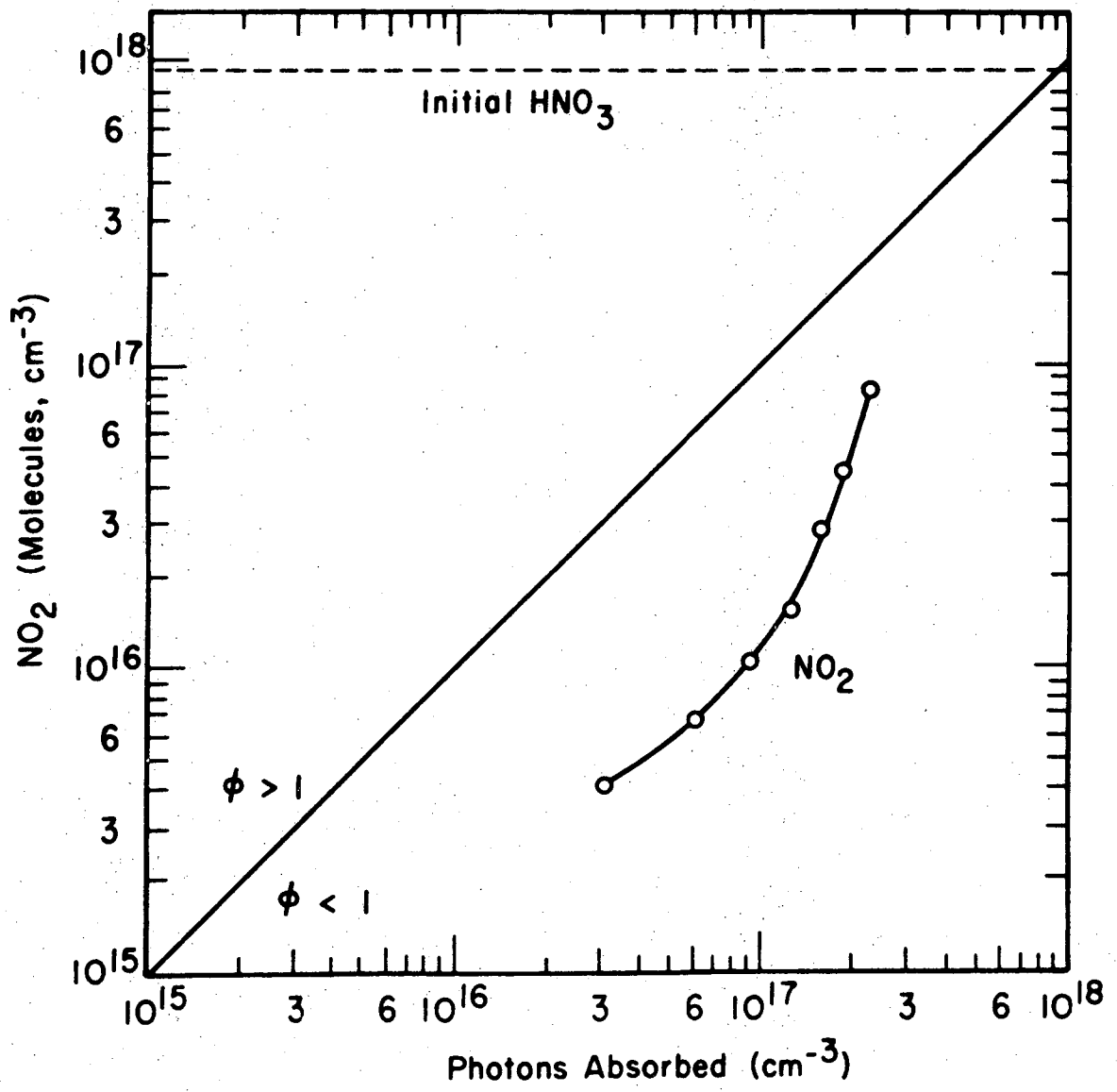


Fig. 1

XBL 737-6391

PHOTOLYSIS OF PURE NITRIC ACID VAPOR (290 nm Radiation)



XBL 737-6394

Fig. 2

PHOTOLYSIS OF NITRIC ACID VAPOR IN THE PRESENCE OF CO.
(290 nm Radiation)

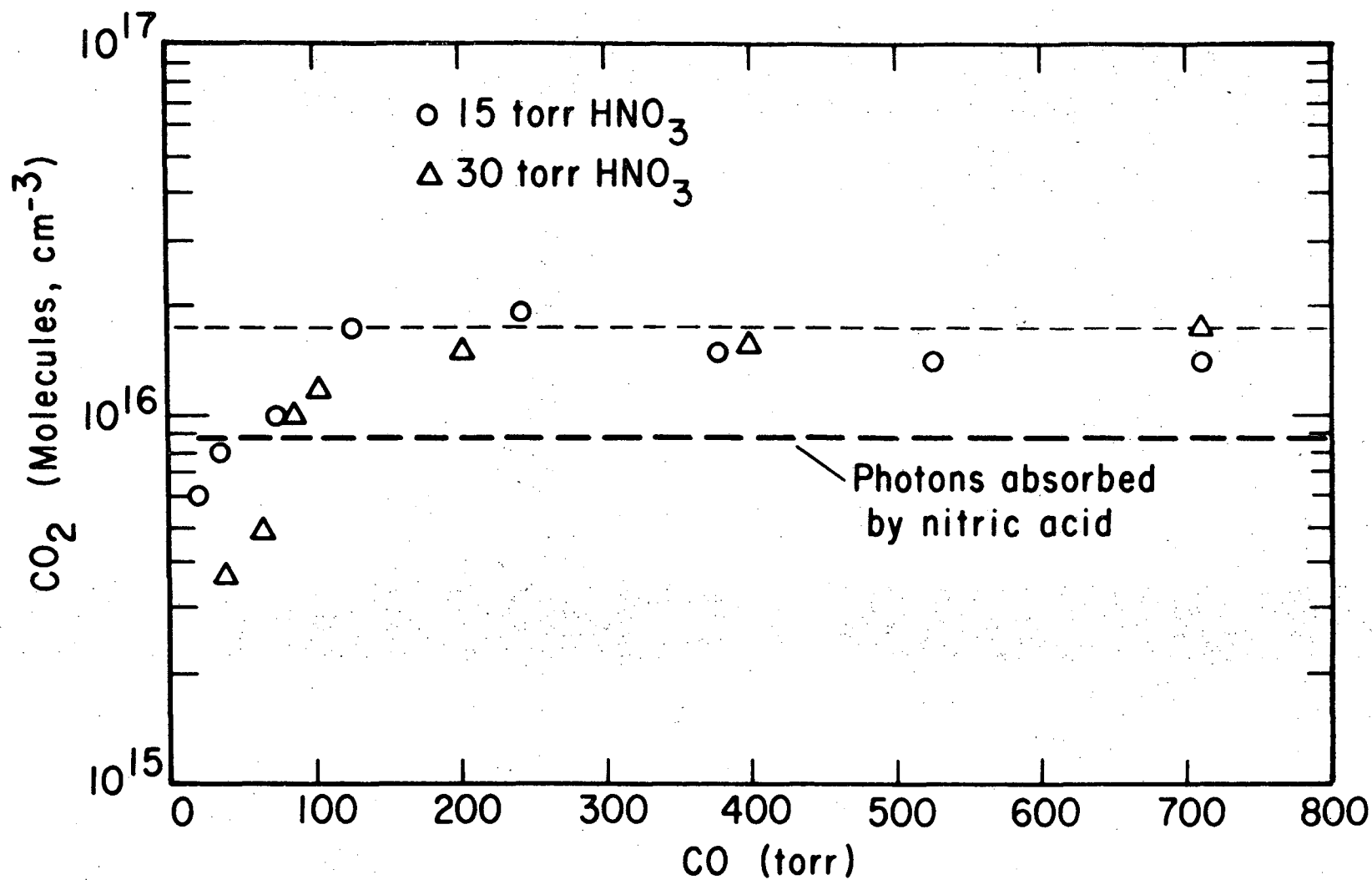


Fig. 3

XBL 737-6396

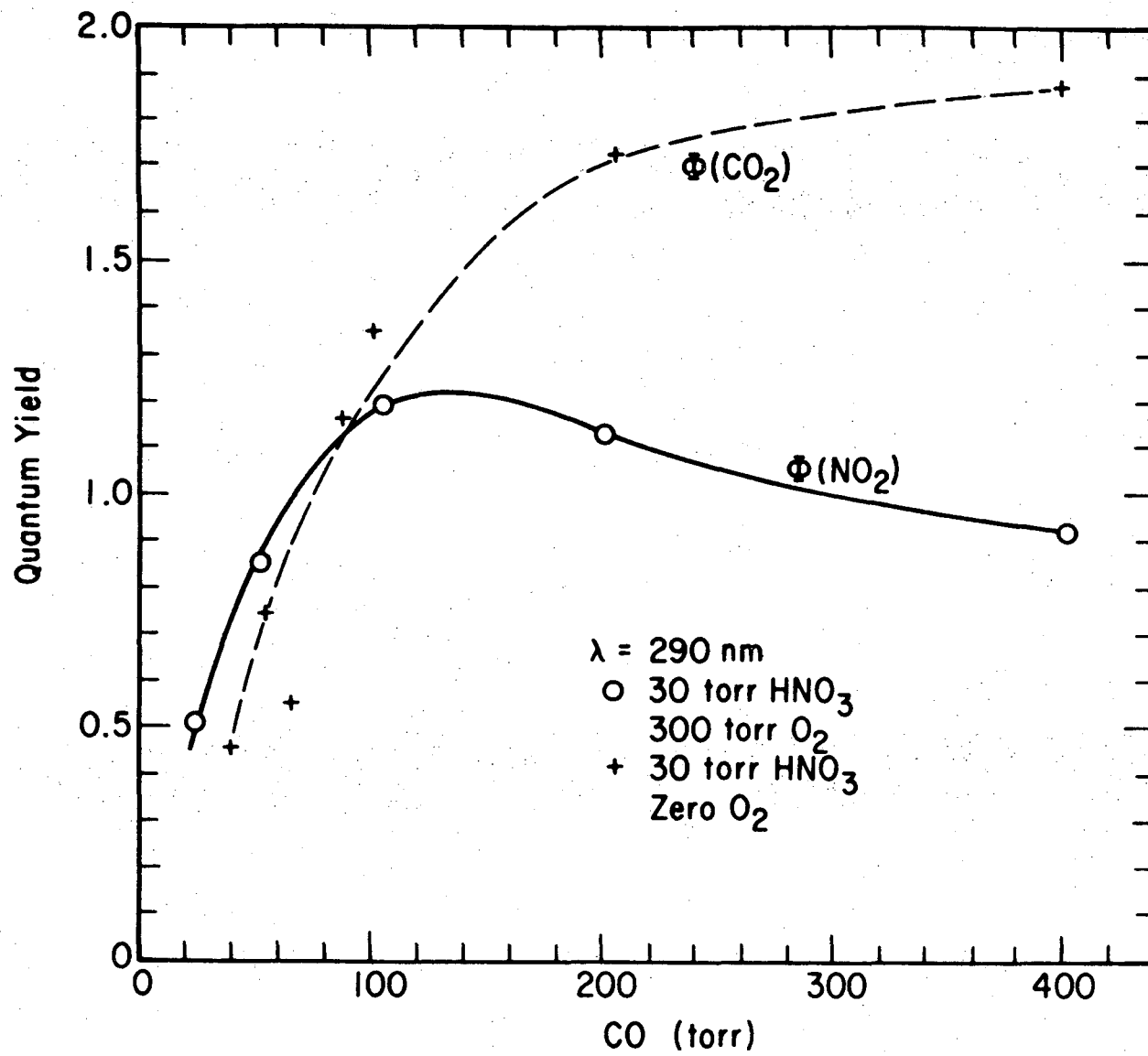
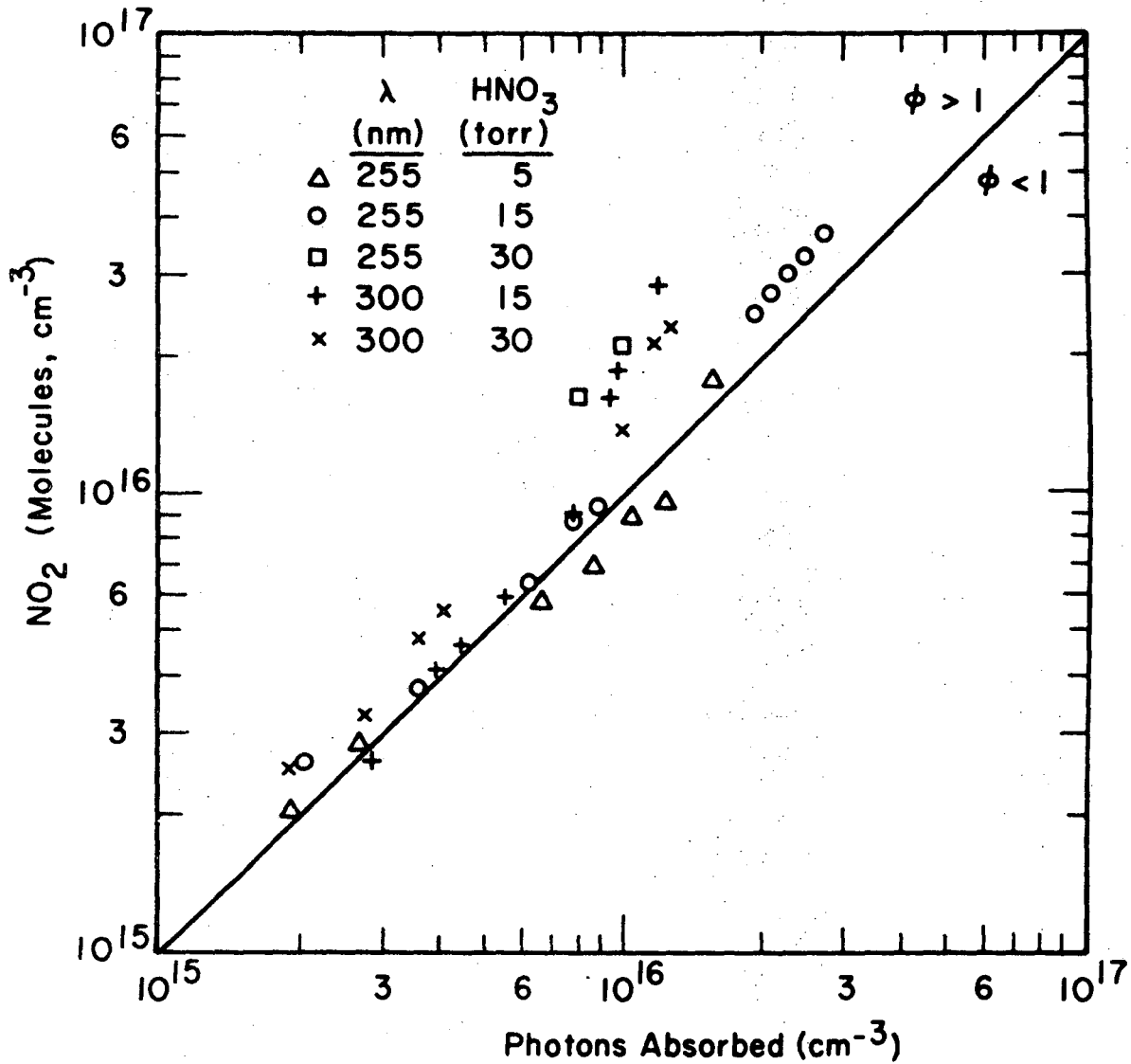


Fig. 4

XBL 737-6393

0000590739

PHOTOLYSIS OF NITRIC ACID VAPOR IN THE PRESENCE OF
300 TORR CO AND 400 TORR O₂.



XBL737-6395

Fig. 5

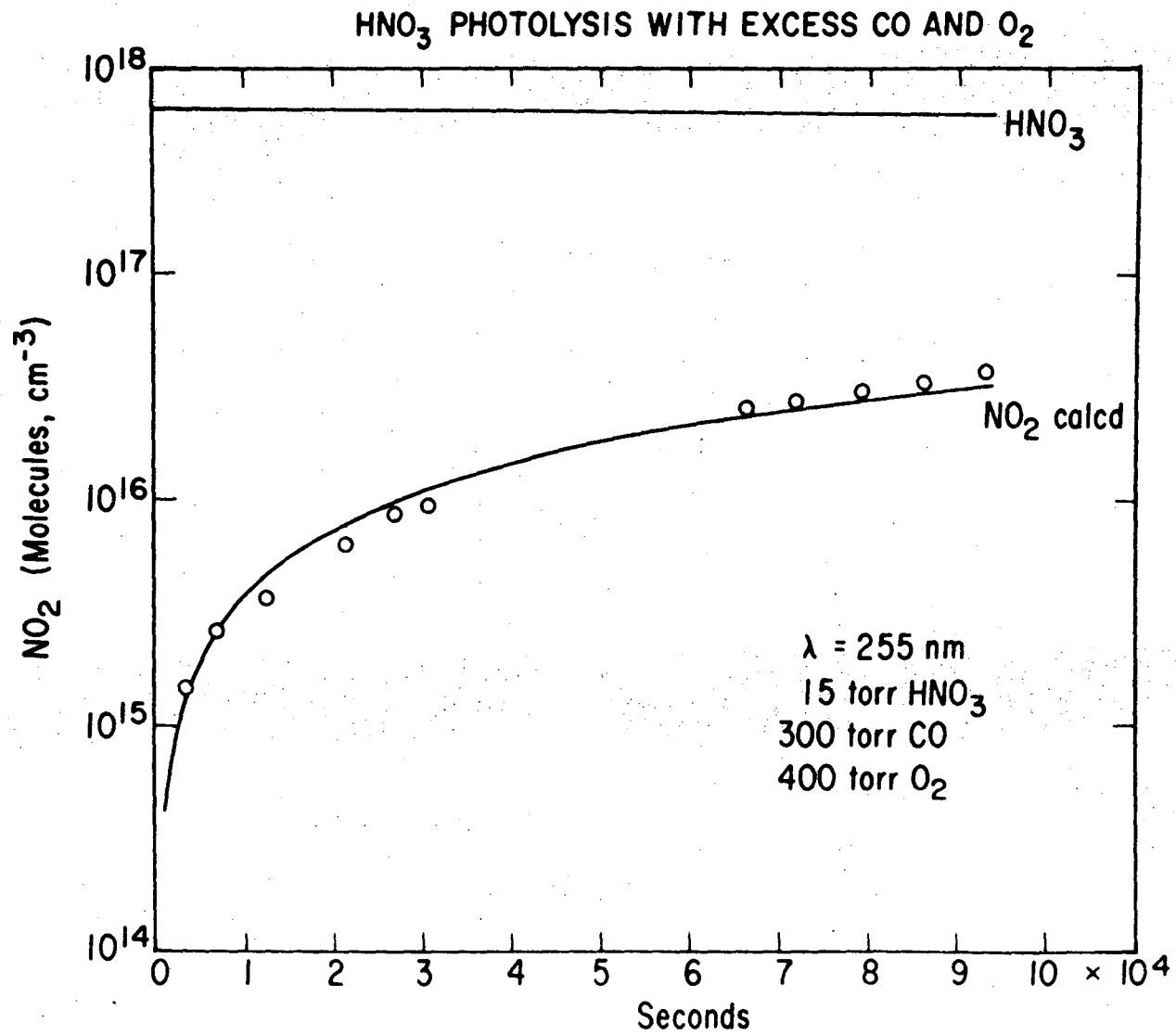


Fig. 6

XBL 737-6392

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