AIP The Journal of Chemical Physics

The Absorption Coefficient of Nitrogen Pentoxide in the Ultraviolet and the Visible Absorption Spectrum of NO3

Ernest J. Jones and Oliver R. Wulf

Citation: The Journal of Chemical Physics **5**, 873 (1937); doi: 10.1063/1.1749956
View online: http://dx.doi.org/10.1063/1.1749956
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/5/11?ver=pdfcov
Published by the AIP Publishing

NOVEMBER, 1937 JOURNAL OF CHEMICAL PHYSICS VOLUME 5

The Absorption Coefficient of Nitrogen Pentoxide in the Ultraviolet and the Visible Absorption Spectrum of NO_3

ERNEST J. JONES AND OLIVER R. WULF
Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

(Received August 9, 1937)

Absorption spectrograms have been made of the gaseous system $N_2O_5-O_3$ during the decomposition of the ozone and into the subsequent decomposition of the N_2O_5, placing these in time such that one was taken when the system consisted essentially of only N_2O_5 and oxygen. From such spectrograms as the last mentioned, the absorption coefficient, α_{10}, of N_2O_5 has been measured over the wave-length range 3800–2850A. The value rises steadily from approximately 0.002 at the first wave-length to approximately 0.52 at 2850A. The absorption coefficient curve continues to rise to shorter wave-lengths and qualitative observations indicated no maximum as far as 2400A. No absorption which could be attributed to N_2O_5 could be observed in the 4500A region. Absorption spectrograms of NO_3 in the visible are given. In a study using low dispersion of the influence of oxygen on the absorption spectrum of NO_2, no noticeable effect was observed.

INTRODUCTION

IN the course of studies of the absorption spectra of the nitrogen oxides in progress in this laboratory, the authors have made observations on the system nitrogen pentoxide-ozone in the gas phase. In the presence of appreciable amounts of N_2O_5, ozone, even of low concentration, decomposes with a measurable rate at ordinary temperatures.[1] Over the period of its decomposition there exists in the mixture a higher oxide of nitrogen which is believed to be NO_3.[2] This decreases in concentration with the ozone, the concentration of the N_2O_5 remaining essentially constant. At the time of complete disappearance of the ozone, nitrogen pentoxide and oxygen alone are present. Following this, nitrogen dioxide makes its appearance as a product of the N_2O_5 decomposition which at ordinary temperatures also proceeds with a measurable rate. The thermal decomposition of N_2O_5 makes it difficult to introduce pure N_2O_5 alone into an absorption cell and to obtain absorption spectra[3] of the gas, without some NO_2 having made its appearance during these operations. Since NO_2 itself absorbs in the visible and ultraviolet, its presence is not desired while measuring the absorption of N_2O_5. Oxygen which is present at all times in such a mixture, possesses no interfering absorption.

In a suitable absorption cell containing originally nitrogen pentoxide and ozone there is thus the opportunity to observe both the absorption of the higher oxide when relatively large amounts of ozone are present, and the absorption of nitrogen pentoxide at that point in time when the ozone has completely decomposed and before nitrogen dioxide has yet made its appearance. Using a cylindrical absorption cell of 2 meters length to intensify the absorption of the NO_3 which is present at very low concentration, the authors have obtained photographs of the NO_3 spectrum, and have studied the absorption of nitrogen pentoxide, making quantitative measurements of the intensity of the latter over a range of wave-lengths in the ultraviolet, working at the above-mentioned point in time when the tube contained only nitrogen pentoxide and oxygen. In the course of the work observations were also made relative to the influence of oxygen on the absorption of NO_2.

EXPERIMENTAL

The 2 meter absorption cell, made of 3 cm diameter Pyrex tubing, was equipped with quartz windows attached through graded seals, and was made part of a closed system in which the gases were circulated by means of a water-cooled glass

[1] Tolman and White, J. Am. Chem. Soc. **47**, 1240 (1925); Nordberg, Science, **42**, 580 (1929); Schumacher and Sprenger, Zeits. f. physik. Chemie, **136**, 77 (1928); **B2**, 267 (1929); Sprenger, Zeits. f. Elektrochem. **37**, 674 (1931).

[2] Hautefeuille and Chappuis, Ann. de l'école norm. sup. series 2, **11**, 137 (1882); series 3, **1**, 103 (1884); Compt. rendus acad. sci. **92**, 80 (1881); **94**, 1111 (1882); Warburg and Leithäuser, Ann. d. Physik **20**, 743 (1906); **23**, 209 (1907); Schumacher and Sprenger, Zeits. f. angew. Chemie **42**, 697 (1929); Sprenger, Zeits. f. Elektrochem. **37**, 674 (1931).

[3] Urey, Dorsey and Rice, J. Am. Chem. Soc. **51**, 3190 (1929); Dutta and Sen Gupta, Proc. Roy. Soc. **A139**, 397 (1933).

plunger-type pump. The system, which was entirely of glass, consisted of the following elements in series, given in order and in the direction of the circulation of the gas mixture: the circulating pump, a water-cooled ozonizer of conventional form, a portion of glass tubing which could be heated by means of a resistance winding, two U-type traps, the absorption tube with an inlet and outlet tube at opposite ends, the system finally closing again at the circulating pump. The plunger or piston of the pump was operated magnetically by means of a surrounding solenoid, the current in which was varied periodically about 4 times per second by a multivibrator vacuum tube circuit. The latter was installed after mechanical interruption of the current had produced local radio disturbance. An all-glass pressure gauge of a twisted hollow ribbon type was used in reading pressures, its direct motion being amplified mechanically to the motion of a small mirror which threw a spot of light on a graduated scale after the manner of galvanometer practice.

The apparatus whose volume was approximately 1500 cc was filled with the desired amount of nitrogen pentoxide by first slowly admitting air to the evacuated system over liquid-air surfaces to remove water and carbon dioxide. By operating the ozonizer and condensing the resulting nitrogen oxides by means of one of the U-traps cooled in a dry-ice alcohol bath, an amount of nitrogen pentoxide, known roughly from the pressure drop, was collected. The remaining air was then pumped from the system with a Hyvac oil pump, and the system sealed. Oxygen was next admitted to a pressure of about 600 mm Hg through a break-off valve, and the system again sealed. With nitrogen pentoxide frozen out in the dry-ice alcohol trap, the oxygen constantly circulating in the system could be partially converted to ozone, after which the nitrogen pentoxide could be evaporated into this gas. Care was necessary here to evaporate in such a way as to distribute the N_2O_5 uniformly throughout the circulating gas. Nonuniformity of the distribution was a source of error in the work, and special effort was made to minimize this.

As soon as the evaporation was complete there existed the condition of highest NO_3 in the system, the tube being visually blue, due in a small measure to the absorption of ozone but chiefly to the absorption of NO_3. At this time satisfactory spectrograms could be had of the NO_3 spectrum. With time the NO_3 and ozone steadily decreased, the contents of the tube finally passing through a colorless stage, directly followed by the appearance of brown fumes of NO_2. It was at this point of absence of both ozone and NO_2 at which plates were taken to make a spectrophotometric determination of the intensity of absorption of N_2O_5 in the ultraviolet. After the N_2O_5 decomposition was complete, the system was in a stable condition, the nitrogen being in the form of NO_2 and N_2O_4. The system could be returned to the initial condition as often as desired by holding the $NO_2-N_2O_4$ mixture in one of the cold traps until sufficient ozone had been made by the ozonizer, and then carefully evaporating the oxides of nitrogen into the gas stream where they were converted by the ozone to N_2O_5. The N_2O_5 could then be frozen out and the oxygen strengthened in ozone content by reozonizing. Thus as many runs as desired could be made with a single filling of gas.

Results

A number of spectrograms were made of the absorption of NO_3, and since so far as the authors are aware no photograph of the spectrum has hitherto been published, a set of these are reproduced in Fig. 1. The first strip above the wave-length scale is the spectrum of the source, a tungsten filament lamp. The several strips above this are spectra taken consecutively, reading upward, as the N_2O_5 was evaporated from the cold trap into the circulating oxygen-ozone mixture as described above. In the second, third, and fourth strip (*a*, *b*, and *c* respectively) the strongest of the ozone bands can be noticed as broad absorption faintly overlying that of NO_3 which increases in this order. In the fifth strip (*d*) the evaporation is complete, the ozone has already been reduced somewhat, and the NO_3 is at its maximum concentration. The following strips show the decrease of NO_3 accompanying the decomposition of ozone, and in the last and top strip (*i*) finally the appearance of NO_2. These spectra were taken with a large Steinheil 3-prism glass spectrograph using an Eastman spectro-

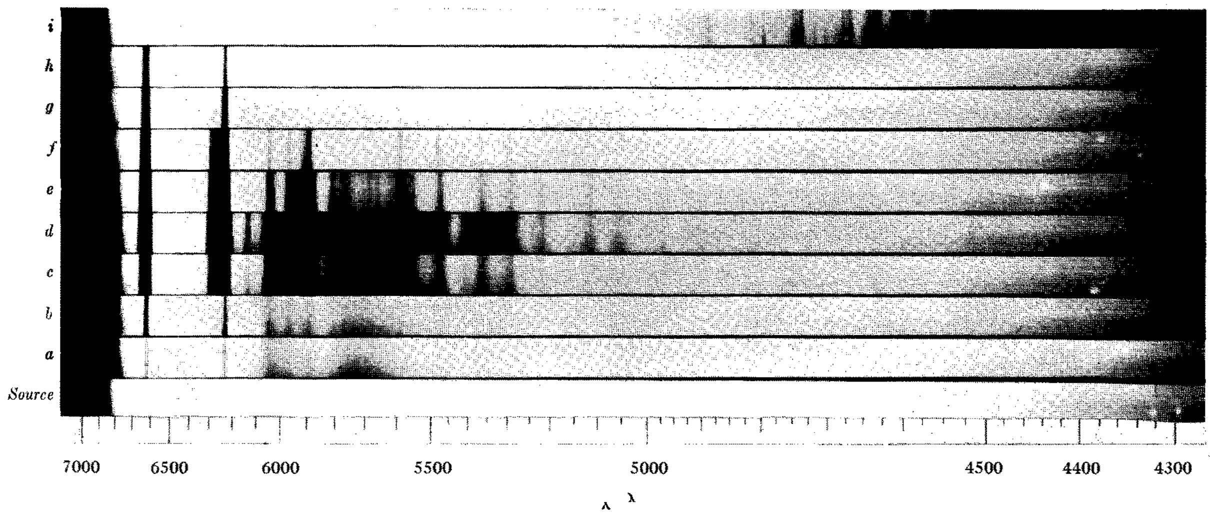

FIG. 1. The absorption of NO_3, overlain with weak ozone absorption in *a*, *b*, *c*. The absorption of NO_2 shows in *i*. The apparent relative intensity differences within the NO_3 spectrum between different strips is probably to be accounted for by the diffuse ozone absorption overlying certain of these. The wave-length, λ, is given in angstroms. Maximum N_2O_5 pressure roughly 80 mm Hg; maximum O_3 pressure roughly 50 mm Hg.

scopic I–F plate. The wave-length scale was constructed from neon and mercury lines which were also taken on the plates. As might be expected for the case of such a molecule, the absorption spectrum of NO_3 appears complicated. From the fine structure that appears at some points it would not be surprising if higher dispersion were to show considerably more detail as is the case with NO_2. All the prominent absorption maxima agree satisfactorily in position with those recorded by Warburg and Leithäuser, who state that their pictures were taken on a Rowland grating, but do not describe the grating further. Insofar as qualitative observations were made in the present work on the rate of the disappearance of ozone and NO_3, they are in accord with the results of Schumacher and Sprenger.[1] Sprenger[1] concludes from his kinetic measurements that with an N_2O_5 pressure of 20 mm Hg and an O_3 pressure of 100 mm Hg, the NO_3 pressure is about 0.02 mm Hg at 20°C. The quantitative light absorption measurements reported by Sprenger at two wave-lengths lead with this concentration to very high values of the absorption coefficient of NO_3 in the strongest of the absorption maxima. While not given in the ordinary form by Sprenger, from his data one finds a value of roughly $\alpha_{10}=500$ at the absorption maximum in the vicinity of 6650A, expressed in the conventional units, per cm of the pure gas at 0°C and one atmosphere. While high, this is probably not excessive for such a molecule composed of four atoms and possessing rather sharp narrow regions of absorption such as are evident in Fig. 1. The absorption is, however, somewhat unusual for an inorganic molecule at such long wave-lengths. An exploratory plate taken with the Eastman spectroscopic type *N* showed that absorption bands of NO_3 could be detected to approximately 7100A.

The spectrograms of the N_2O_5 absorption were taken on Eastman III–O plates using a Hilger E2 quartz spectrograph, working at the point mentioned above, when all ozone and NO_3 had disappeared and before NO_2 had begun to appear. The procedure consisted in taking a series of exposures throughout a time interval of which this point was approximately the middle. In this way the plates usually contained exposures still showing ozone absorption as well as exposures in which the ozone absorption had disappeared but the NO_2 absorption had made its appearance. Between these there usually existed, however, an exposure which was sufficiently free of either of these to be representative of the absorption of N_2O_5 alone. The extent to which this ideal condition was actually approached in the particular exposure chosen on each plate as the one upon which to make quantitative measurements, depended upon the care which had been exercised in avoiding nonuniform distribution of the N_2O_5 during evaporation into the circulating oxygen-ozone mixture and in the proper placing of the exposure in time during the decomposition. Since ozone in small amounts does not absorb appreciably in the range 3300–3800A, and since NO_2 in small amounts does not absorb appreciably in the range 2800–3300A, it was realized that for measurements in the 2800–3300A region it was safer to lean slightly in the direction of being a little past the ideal point in the decomposition, while for the 3300–3800A region it was safer to use an exposure which if anything may have had a trace of ozone yet remaining.

On each of the plates a series of exposures was made for the purpose of plate calibration, using five screens of known transmission. These and the exposure chosen for the measurement of the N_2O_5 absorption were measured with a recording densitometer and the reduction of light intensity caused by the absorption of the N_2O_5 computed in the conventional way. The results of these measurements are shown in Fig. 2. They come from five different plates, two of which were taken at an N_2O_5 concentration of 98 mm Hg at room temperature, roughly 25°C. The open and closed circles in the figure lying at 3500A and above represent respectively the measurements of these two plates. The three other plates were taken at a pressure of 4.5 mm Hg and constitute the principal portion of the results, shown in Fig. 2 from 3500–2800A. The triangles and squares represent points determined by two somewhat different methods of measurement and are scattered among these three plates.

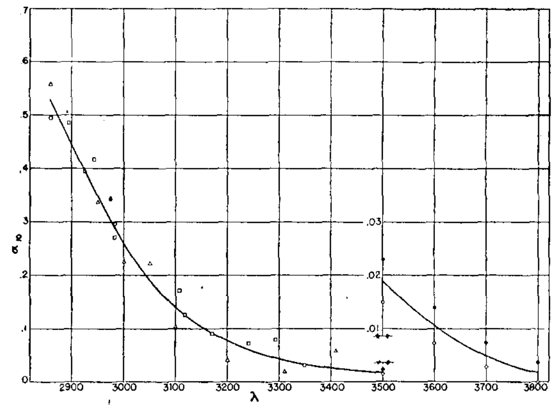

FIG. 2. Absorption coefficient of N_2O_5, α_{10}, given in the units per cm of pure gas at 0°C and one atmosphere and plotted against the wave-length, λ, in angstroms.

The determination of the higher pressure of nitrogen pentoxide was made by noting the pressure change upon the condensation and upon the evaporation of the solid and also by the pressure change during the N_2O_5 decomposition to $NO_2-N_2O_4$. As a result of these measurements the pressure was found to be 98 mm Hg at room temperature, which was taken as 25°C, and the value is probably good within ±5 percent.

The determination of the lower pressure of nitrogen pentoxide was made by three different methods: by noting the actual pressure change in the gas phase decomposition, making correction for the $NO_2-N_2O_4$ equilibrium in the resulting mixture; by observing the pressure change during the condensation of the $NO_2-N_2O_4$ mixture when all the oxide was in this form; and by determining the pressure change on either the condensation or evaporation of the N_2O_5 as such. Throughout these measurements at the low pressure correction was made for the influence of room temperature on the pressure of the gas in the cell and for the influence of changing barometric pressure on the readings of the pressure gauge with which the pressure measurements were made. The value 4.5 mm Hg was chosen as a result of these measurements, and is believed to be correct within ±5 percent.

As seen in Fig. 2, continuous absorption due to N_2O_5 has been followed as far as 3800A. The only other substance in the present system which might lead to absorption at such long wave-lengths is NO_2, and as was remarked above, the effort was made to choose an exposure before the time when the system contained pure N_2O_5 and oxygen, in order to avoid the possibility of having NO_2 absorption present, even though some ozone absorption showed, since the ozone absorption does not extend with appreciable strength to such wave-lengths. To wave-lengths shorter than 2800A the intensity of absorption increases rapidly, and our qualitative observations disclosed no tendency for the absorption to pass through a maximum as far as 2400A.

Kondratiew and Polak[4] have reported that oxygen effected a change in the absorption spectra of NO_2 in the region of its first predissociation.

[4] Kondratiew and Polak, Zeits. f. Physik 76, 386 (1932).

Later they[5] state that a further study of their plates, taken on a small grating spectrograph, did not substantiate their earlier findings. In the interim between the appearance of these two papers the present authors attempted a study of the effect of admitting oxygen to NO_2, and using a small glass Hilger spectrograph could detect no change in the absorption spectra of NO_2. Thus the negative results are in accord, though in view of the complicated structure of the NO_2 spectrum it might be unwise to conclude that under conditions of high resolution no effect would be found.

Discussion

As remarked above, the value of the absorption coefficient, as given by the measurements of Sprenger in the strongest of the absorption maxima of NO_3, is very high. It is interesting to consider whether there is any obvious reason for this very strong electronic transition at such long wave-lengths, and the resultant blue color, in the NO_3 molecule. The NO_3 absorption lies in much the same position as does the visible absorption of ozone[6] and the gross intensity distribution with wave-length in the two absorptions is very similar, but the transition in ozone is extremely weak. The material in the NO_3 spectrum also appears much sharper than the diffuse bands of O_3. It does not seem reasonable to imagine any connection between the two spectra, since the three oxygen atoms in NO_3 will certainly not be ozone-like. The oxide N_2O_3 or a polymer of this is deep blue in the liquid state, as is well known. This absorption in the red was not however observed by Melvin and Wulf[7] in the path lengths which they used in studying gaseous N_2O_3, and it may be that the color is actually due to a higher polymer. One is reminded also of the intense blue color frequently characteristic of monomeric organic nitroso compounds[8] although it is not evident that there exists an analogous structure in the molecule NO_3. Since the molecule NO_3 contains an odd number of electrons, the general fact that it is highly colored is not surprising.

In the present work the continuous absorption of nitrogen pentoxide has been observed to somewhat longer wave-lengths than in the work either of Urey, Dorsey and Rice[3] or Dutta and Sen Gupta.[3] In agreement with the work of the former, we have not found the other absorption reported by Dutta and Sen Gupta at longer wave-lengths in the vicinity of 4500–4000A, this in spite of the fact that our effective path lengths were sufficient to follow the main continuous absorption to considerably longer wave-lengths than was the case in either of these two other researches. The nature of the dissociation process corresponding to this continuous absorption is, of course, not surely known, but if we compute the heat of dissociation of nitrogen pentoxide into N_2O_4 and normal oxygen atom, using the data given by Bichowsky and Rossini,[9] we find

$$N_2O_5 = N_2O_4 + O(^3P_2) - 61{,}160 \text{ cal.}$$

which corresponds to a wave-length of closely 4660A or about 2.65 volts. There is still a wide margin between the wave-length at which the absorption has been observed and that corresponding to the above process, and hence this process may indeed represent the actual dissociation. It seems probable that the continuous absorption could be observed still further to the red in longer paths than we have employed, as is frequently the case in dealing with continuous absorption of this character. It is notoriously difficult to fix the beginning of such absorption. An excited oxygen atom would not be an admissible product, apparently, since the first excited state $O(^1D_2)$ is about 2 volts or 45,000 calories higher, which would place the beginning of dissociation corresponding to this process at about 2800A.

[5] Kondratiew and Polak, Physik. Zeits. Sowjetunion **4**, 766 (1933).
[6] Wulf, Proc. Nat. Acad. **6**, 507 (1930).
[7] Melvin and Wulf, J. Chem. Phys. **3**, 755 (1935).
[8] See, for example, Baly and Desch, J. Chem. Soc. **93**, 1747 (1908).
[9] *Thermochemistry of Chemical Substances*, (Rheinhold Publ. Corp., 1936).