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MECHANISM OF THE FORMATION OF PINK WATER

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TNT solutions in distilled and Picatinny Lake water were photolyzed at 365 nm wavelength. This wavelength is close to the one that gave the maximum product of the sunlight intensity and the TNT absorption coefficient. Results for both waters were the same except that photolysis in Picatinny Lake water had progressed further for the same photolysis time. For short photolysis times, the main features of the differential spectra were a shoulder at 310 nm and bands at ~ 290 nm and 500 nm. The last is probably responsible for the

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pink color of the solution. For longer photolysis times the band at 500 nm changed drastically to a broad absorption with shallow bands at $\sim$475 and $\sim$450 nm indicating that photolyses of the products were occurring.

The ultraviolet spectral characteristics suggested a nitrosocompound, while the visible spectra at long photolysis times indicated the presence of a phenolic compound.

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INTRODUCTION

The object of this study was to determine the factors that affect the formation of "Pink Water" in order to prevent its occurrence. "Pink Water" is the name given to the ground water when the sun photolyzes the effluent waste water from TNT manufacturing and loading plants. Of particular importance are the possible toxic effects of the photolytic products of α-TNT. The pink color itself is only a cosmetic problem.

It is only recently that a substantial effort has been made to study the "Pink Water" problem. The mechanism for the production and the properties of the compound or compounds responsible for the pink color are not known yet. It is interesting to note that some of the same/similar photolytic products from α-TNT in water have been identified in the thermal decompostion and in the manufacture of α-TNT (Ref 1,2,3). These products may be present in military grade TNT. However, there appears to be very little work on the formation of "Pink Water" from effluents, which can be produced from various sources. Water containing nitrobodies is produced in manufacturing from spills, overflowing, wash waters, condensate from the red water concentrator, distillates from the acid recovery unit, and dust scrubbers in the drying house. In addition, nitrobody water is produced in TNT and Composition B loading facilities when shells are improperly loaded and subsequently steamed out. Another factor that must be considered is the stream into which the nitrobody effluent is deposited. Here, various inorganic and organic substances are present which may affect the course of the photolytic reaction. It is also expected that nitrates, nitrites, sulfates, and sulfites are present in the water effluents of TNT plants.

It has been shown that azoxy compounds were found when an aqueous TNT solution was exposed to sunlight. These compounds are present only in trace amounts in laboratory irradiations (Ref 1). The presence of various substances in the water, both effluent and stream, could cause significant differences. For example, RDX markedly accelerates the photolytic decomposition of TNT in CH_3CN (RDX and nitroso compounds also catalyze thermal decomposition) (Ref 2).

EXPERIMENTAL PROCEDURES

Materials

The TNT (Eastman Kodak Company) was purified by the method described by Gey, Dalbey, and Dolah (Ref 4). Distilled water and Picatinny

Lake water were used to make 3×10^{-4} M stock solutions. Working solutions of 3×10^{-5} M were chosen since they gave good overall spectra without absorption washout, although absorption at the wavelength region of the sun was not ideal.

Photolyses

The apparatus assembled for the photolytic experiments consisted of an Oriel 200 watt high pressure Xe-Hg lamp and a Bausch and Lomb high intensity monochromator with both slit-widths at the maximum 6 mm (overall bandwidth of 30 nm). A standard 1 cm pathlength quartz absorption cell with $\sim$ 3 ml of 3×10^{-5} M TNT was placed behind the exit slit. A Beckman DK-2 spectrophotometer was employed for spectral analyses.

The Hg wavelength of 365 nm was chosen for the initial study. This was done as an expediency to shorten the photolysis time in the first experiments since the 365 nm line is the highest intensity closest to the 330-335 nm region which gives the maximum product of the sunlight intensity and the TNT absorption coefficient. It appears that this approach has not been taken previously.

Photolyses were done at four 6 1/2-hour intervals. In order to study the sensitivity of the photolytic processes to the nature of the solvent and for spectral comparison purposes here and with the authors' previous work of TNT in cyclohexane (Ref 5), photolyses were also performed in distilled water at 254 nm by placing the Beckman cell in front of a low pressure mercury quartz pencil lamp (Spectronics Corporation). A Corning CS 9-54 filter was used to eliminate any 185 nm light which might affect the water. Photolyses were performed at both 5 minute and 15 minute intervals.

Thin Layer Chromatography

Thin layer chromatographic analyses were performed on the photolyzed solutions using Baker silica gel IB-F sheets, Eastman Chromagram chamber plate set, solvent developer, and ethylenediamine-dimethylsulfoxide (1-5) as a visualization reagent for colorless compounds.

RESULTS AND DISCUSSION

Ultraviolet Absorption Spectrum of TNT in Water and the Wavelength of Maximum Sun Effectiveness

Figure 1(a) shows the spectrum of TNT in distilled water with λ_{max} at 232.5 nm with an $\epsilon = 19000$. This is to be compared with the work of Kamlet, Hoffsommer, and Adolph who obtained $\varepsilon = 19200$ at λ_{max} = 227 nm for TNT in methanol (Ref 6). With cyclohexane as the solvent $\varepsilon = 23000$ at λ_{max} = 224.5 nm (Ref 5). The bathochromic shift of λ_{max} in going from nonpolar to polar solvents is characteristic of $\pi \rightarrow \pi^*$ transitions.

In addition, the wavelength at which the product of the sun intensity times the TNT extinction coefficient is a maximum has been determined. Figures 2(a) and 2(b) are plots of sun intensity times extinction coefficient ($I\varepsilon$) vs. wavelength at two locations (Cleveland, Ohio and Tucson, Arizona, respectively) where sun intensity data were readily available (Ref 7). It can be seen that the wavelength at maximum $I\varepsilon$ is in the 330-335 nm region.

Photolyses in Distilled Water

Figure 1(b) shows the spectrum of TNT after photolysis for 6 1/2 hours at 365 nm. The amount of photolysis amounted to ∿ 12%. It can be seen by comparison with Figure 1(a) that transmission has increased (absorption decreased) in the λ_{max} region, while transmission has decreased (absorption increased) at the higher wavelengths to the right. By taking differential spectra, using the original unirradiated solution as reference instead of water, the TNT in the photolyzed solution is compensated, for the most part, if photolysis is not excessive. In this way it is possible to detect products more absorbing than TNT in regions away from λ_{max} of TNT. Figures 3(a) and 4(a) represent the differential spectra after 6 1/2 hours of irradiation. It can be seen that there is an inflection at ∿ 310 nm and bands at ∿ 290 and 500 nm. The latter is responsible for the slight pinkish color of the solution.

The shoulder at 310 and the band at 290 nm are similar to those obtained previously with cyclohexane as solvent both by continuous (253.7 nm) and flash photolysis (Ref 5). Due to the lack of detailed analytical studies of the complex TNT in cyclohexane photolysis solutions, only comparisons with the simpler o-nitrotoluene in n-heptane solutions (which also had similar bands and was studied in more detail) can be made (Ref 5). With the latter solution, o-nitrosotoluene was established as the product. It was believed that the TNT bands were also due to a nitrosocompound, as is here with the aqueous solutions. In cyclohexane, no photolyzed TNT bands at 500 nm were present and the solution remained colorless (extensive photolysis and long pathlengths gave yellowish solutions).

As far as is known, no other workers have observed nitrosocompounds in the photolysis of TNT, although they have been observed in the photolyses of some other nitrocompounds. This may be due to the much larger TNT conversions than obtained here, which cause the nitrosocompound to be one of the predominant photolytic species present in the solution. The photolysis of products in addition to the TNT accounts for the large number of compounds usually found in photolyzed TNT solutions. The same explanation may also account for the unsuccessful attempts to extract the photolysis products with benzene. Spectral analysis indicated that little, if any, material was extracted. This is in contrast to the results reported by Burlinson, Kaplan, and Adams where 20% by weight of the photolyzed TNT was extracted with benzene after 60-70% conversion of the TNT (Ref 1). The three most prevalent compounds detected were 4,6-dinitroanthanil, 2,4,6-trinitrobenzaldehyde, and 2,4,6-trinitrobenzonite.

Figures 3 (b) and 4 (b) represent the spectra after an additional 6 1/2 hours irradiation. The UV bands deepened and the 290 band shifted to 285 nm. Some of this shift may be caused by over-compensation of the TNT by the reference, as indicated previously. The visible spectrum has changed drastically. Now, there appeared to be almost flat absorption from 360 to 500 nm with slight bands at ∿ 475 nm and ∿ 450 nm. The solution had a definite pink color. The change in spectral characteristics indicates photolysis of the initial products.

Further 6 1/2 hour irradiations of the solution tended to produce smaller changes--the third irradiation gave results that were very little different from those of the second. The small changes in spectra can be explained by the significant depletion of the TNT and products readily photolyzible at 365 nm by the time the second irradiation was completed.

Unequivocal identification of products will eventually consist, for the most part, of synthesizing those compounds that are suspected to be photolysis products. However, the types of products present may be determined from simpler compounds at hand by using the fact that, in general, chromophoric groups will have similar spectra in whatever compound they are present.

As indicated previously, the spectral characteristics of the photolysis in the UV suggested a nitrosocompound. Consideration of the absorption in the visible region after prolonged irradiation suggests a phenolic compound as a product. With this in mind, spectra were taken of compounds at hand, such as o-nitrosotoluene (Fig 5), p-nitrosophenol (Fig 6), and picric acid (Fig 7). The ultraviolet spectra stongly suggest the presence of a nitrosocompound. The visible spectra suggest a phenolic compound is possible. The 500 nm band present at low irradiation levels has not yet been identified.

Photolyses in Picatinny Lake Water

Photolyses of TNT solutions in Picatinny Lake water at 365 nm were performed. This water had a greater absorption than distilled water -the transmission varied almost linearly from ∿ 100% at 700 nm to ∿ 72% at 220 nm. The results of the photolyses were substantially those with distilled water except that the Picatinny Lake water photolyses had progressed further for a given time than those with distilled water. This might be explained by the absorption of radiation by the impurities in the lake water which subsequently transfer this energy to the TNT giving additional reaction. Such an energy transfer mechanism is well known (Ref 8).

Photolysis at 254 nm using a Spectroline quartz pencil lamp was also done. The overall spectral characteristics of the products were similar, but not identical, to those at 365 nm.

In none of the photolyses were there any significant dark reactions.

Although some very diffuse spots were obtained in the thin layer chromatography studies, including a reddish one, the results were not consistent. This was due to the fact that the 3 ml of 3×10^{-5} M TNT used in the Beckman cell contained 20 μg of TNT initially, which led to photolyzed products at the limits of detection. These results indicate the need for studies with larger quantities of solution in order to obtain sufficient products for TLC analyses.

SUMMARY

Photolyses of TNT in distilled and Picatinny Lake water, mostly at 365 nm, have been performed in order to serve as a basis for comparison and to simulate, to some degree, photolysis by natural radiation.

Spectral results indicate the presence of a nitroso- and phenolic compound as photolysis products. Results in distilled water and Picatinny Lake water were essentially the same except that the photolysis of the lake water had progressed further for a given time than that with distilled water. This was probably due to the absorption of radiation by the impurities in the lake water which gives additional reaction due to energy transfer to the TNT molecules.

The 500 nm absorption band, which accounts for the pink color of the photolyzed solutions, has not been identified as yet.

REFERENCES

1. (a) N. E. Burlinson, L. A. Kaplan, and C. E. Adams, "Photochemistry of TNT: Investigation of the 'Pink Water' Problem", NOLTR 73-172, 3 October 1973.

   (b) L. A. Kaplan, N. E. Burlinson, and M. E. Sitzman, "Photochemistry of the 'Pink Water' Problem, Part II", NOLTR 75-152, 21 November 1975.

2. W. P. Colman and F. C. Rauch, "Studies on Composition B", Final Report, American Cyanamid Co., Contract No. DAAA 21-70-0531, Picatinny Arsenal, February 1971.

3. J. A. Kohlbeck, C. D. Chandler, Jr., and R. L. Dickerson, "Final Engineering Report on Production Engineering Projects PE-238 and PE-289. AMCMS Code 4810.16.9960.2, Continuous TNT Characterization Study-Extension (PE-289) RAD 240.10, prepared by Radford Army Ammunition Plant, Hercules Incorporated, Radford, VA. for MTD, Picatinny Arsenal, May 1973.

4. W. A. Gey, E. R. Dalbey, and Van Dolah, J. Am. Chem. Soc., 78, 1803 (1956).

5. O. Sandus and N. Slagg, "Reactions of Aromatic Nitrocompounds I. Photochemistry", PATR 4385, Picatinny Arsenal, Dover, NJ, December 1972.

6. M. J. Kamlet, J. C. Hoffsommer, and H. G. Adolph, J. Am. Chem. Soc., 84, 3925 (1962).

7. L. R. Koller, Ultraviolet Radiation, John Wiley and Sons, Inc. New York (1952), p. 124, 125.

8. J. B. Birks, "Photophysics of Aromatic Molecules", John Wiley and Sons, Ltd., London (1970), Chapter 11.

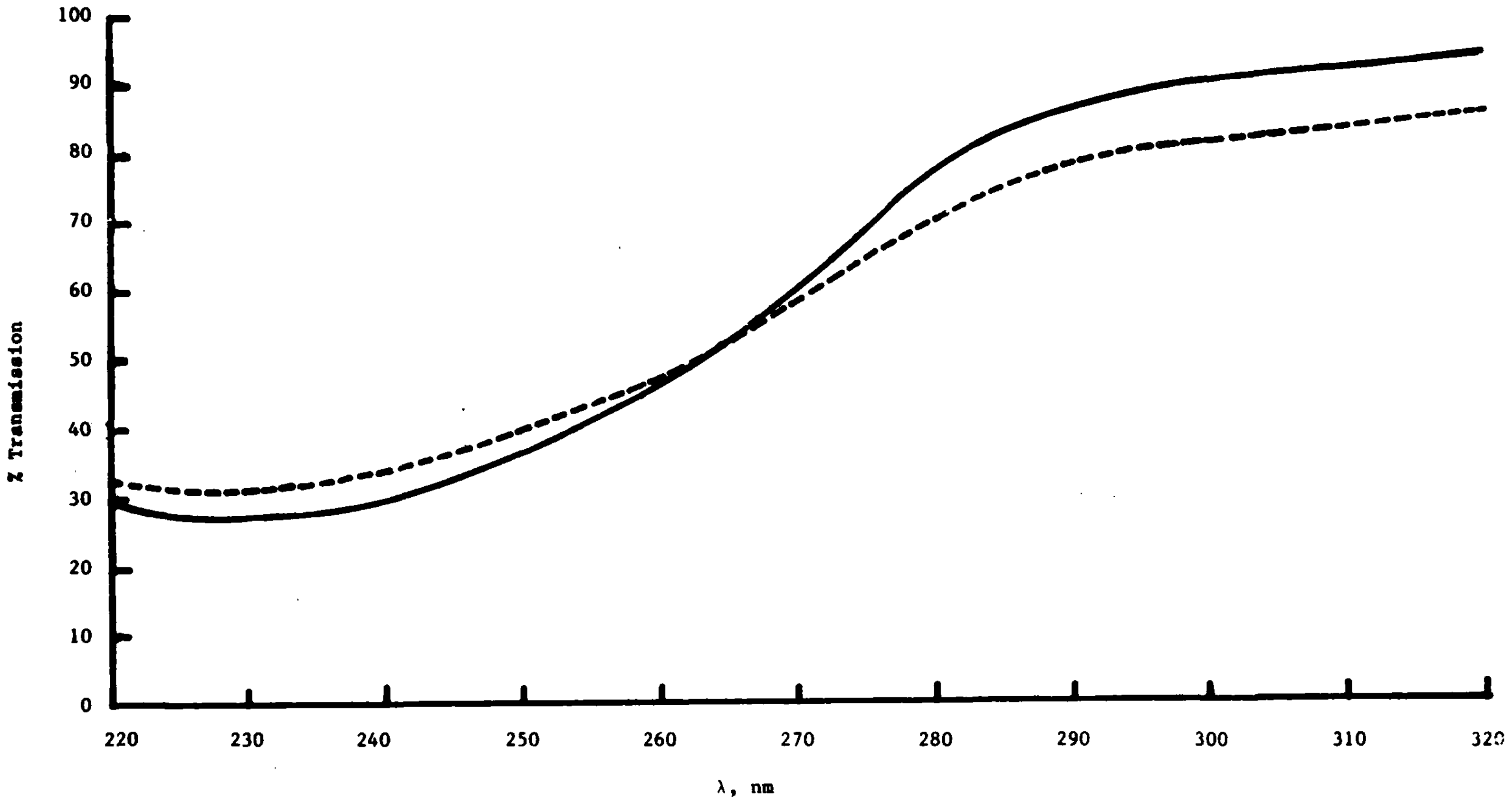

Fig 1 Spectrum of 3 X 10^{-5}M TNT in Water

(a) Solid Line. Unphotolyzed Solution

(b) Dashed Line. Solution Photolyzed at 365nm for 6 1/2 hours

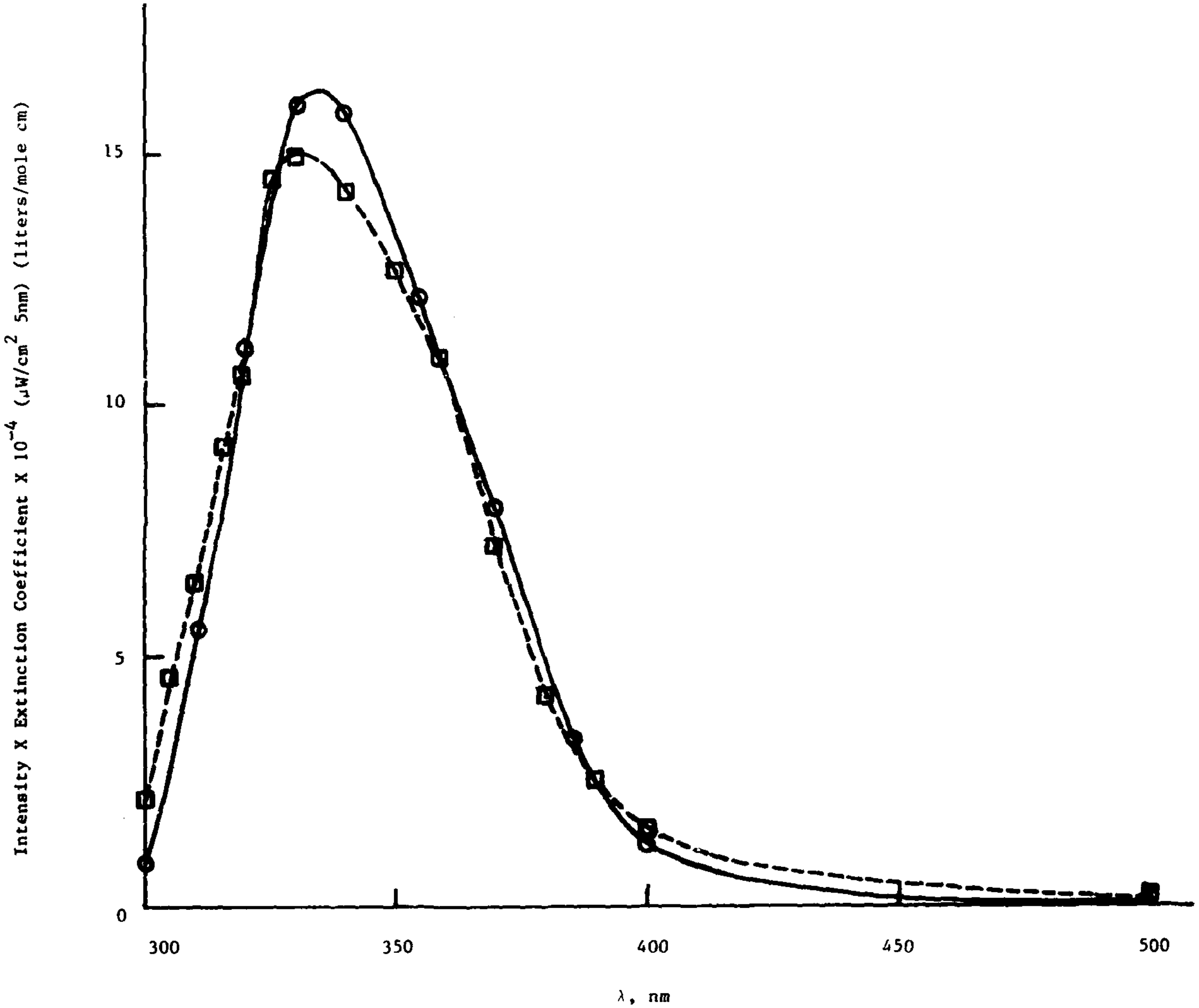

Fig 2 Sun Intensity X TNT Extinction Coefficient as a function of Wavelength

(a) —○— Cleveland, Ohio. Sunlight & Skylight

(b) —□— Tucson, Arizona. Sun at Zenith

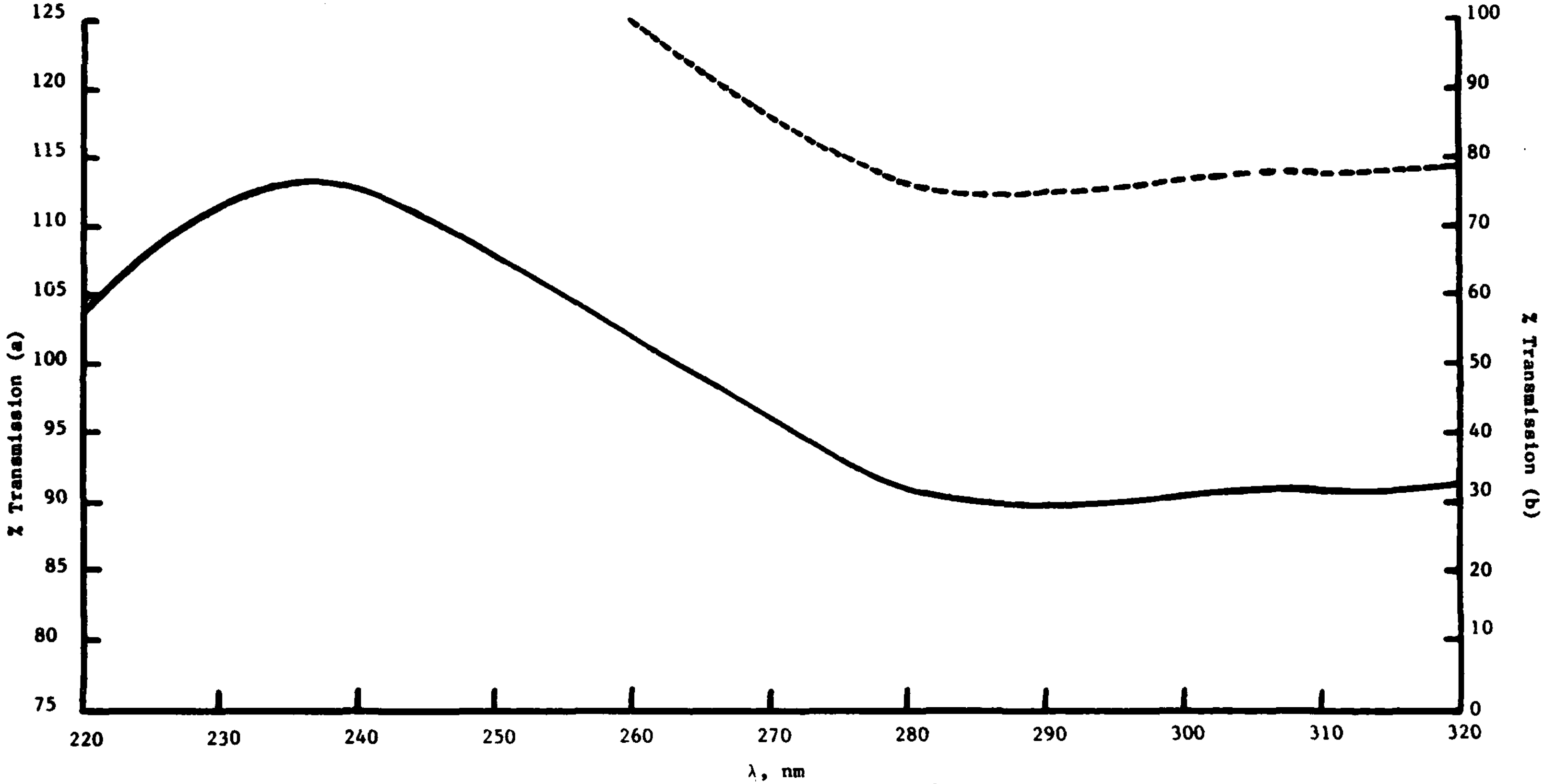

Fig 3 Ultraviolet Differential Spectra of 3 X 10^{-5} M TNT in Water Photolyzed at 365nm. References are Unphotolyzed Solutions

(a) Solid Line - Left Ordinate. Photolyzed for 6 1/2 hours

(b) Dashed Line - Right Ordinate. Photolyzed for 13 hours

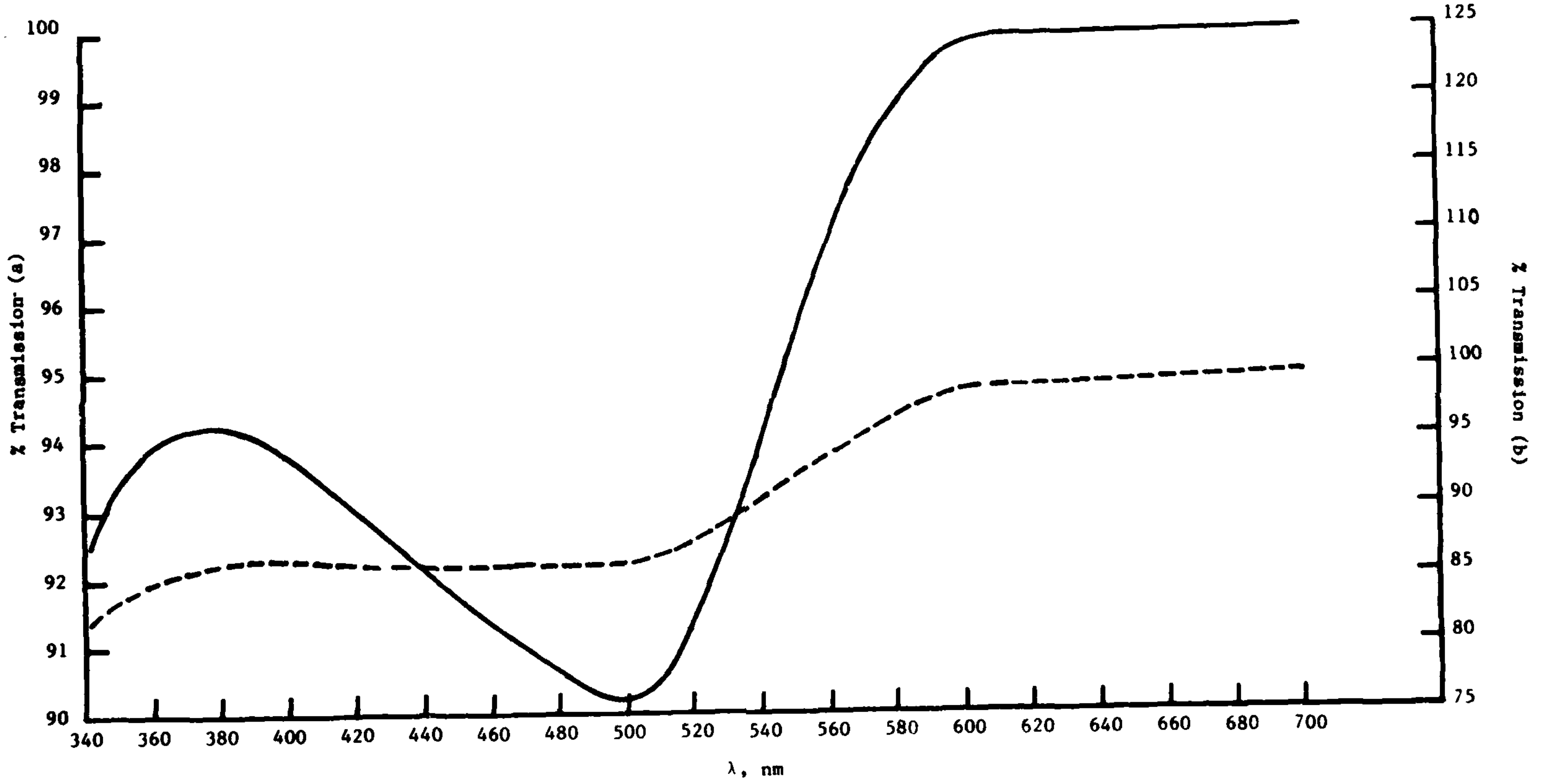

Fig 4 "Visible" Differential Spectra of 3×10^{-5}M TNT in Water Photolyzed at 365nm. References are Unphotolyzed Solutions

(a) Solid Line - Left ordinate. Photolyzed for 6 1/2 hours
(b) Dashed Line - Right ordinate. Photolyzed for 13 hours

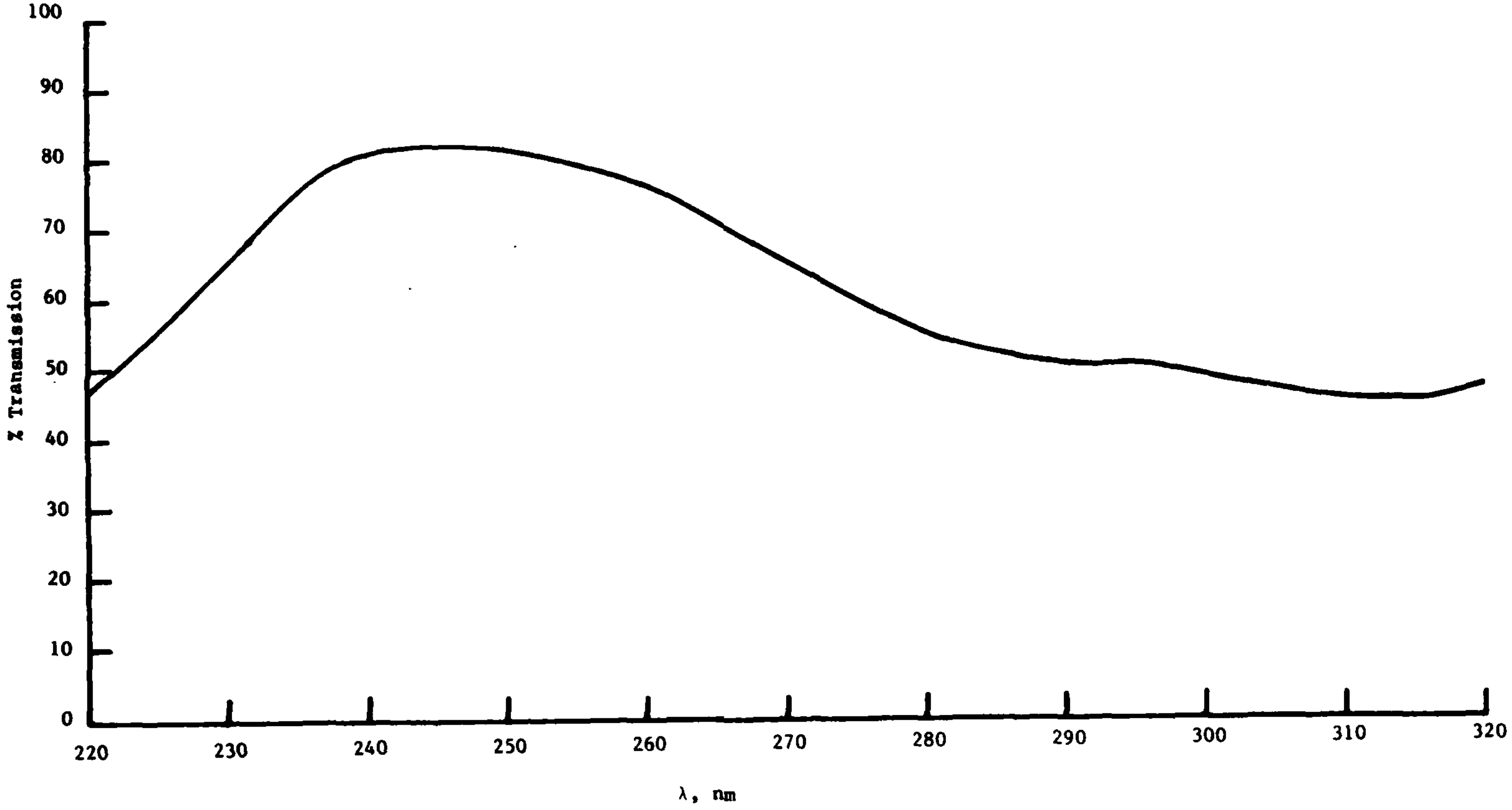

Fig 5 Spectrum of o-Nitrosotoluene in Water

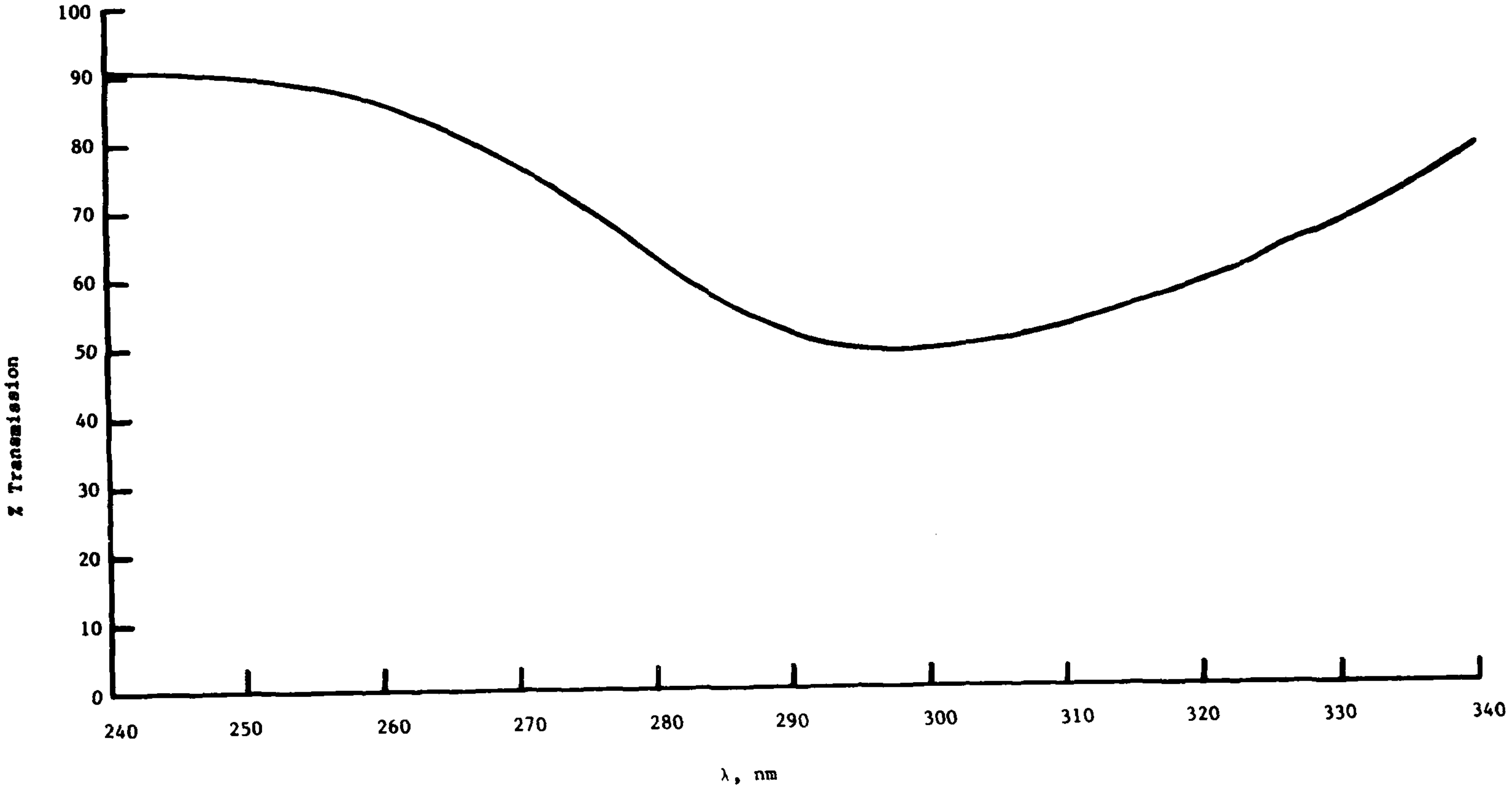

Fig 6 Spectrum of p-Nitrosophenol in water

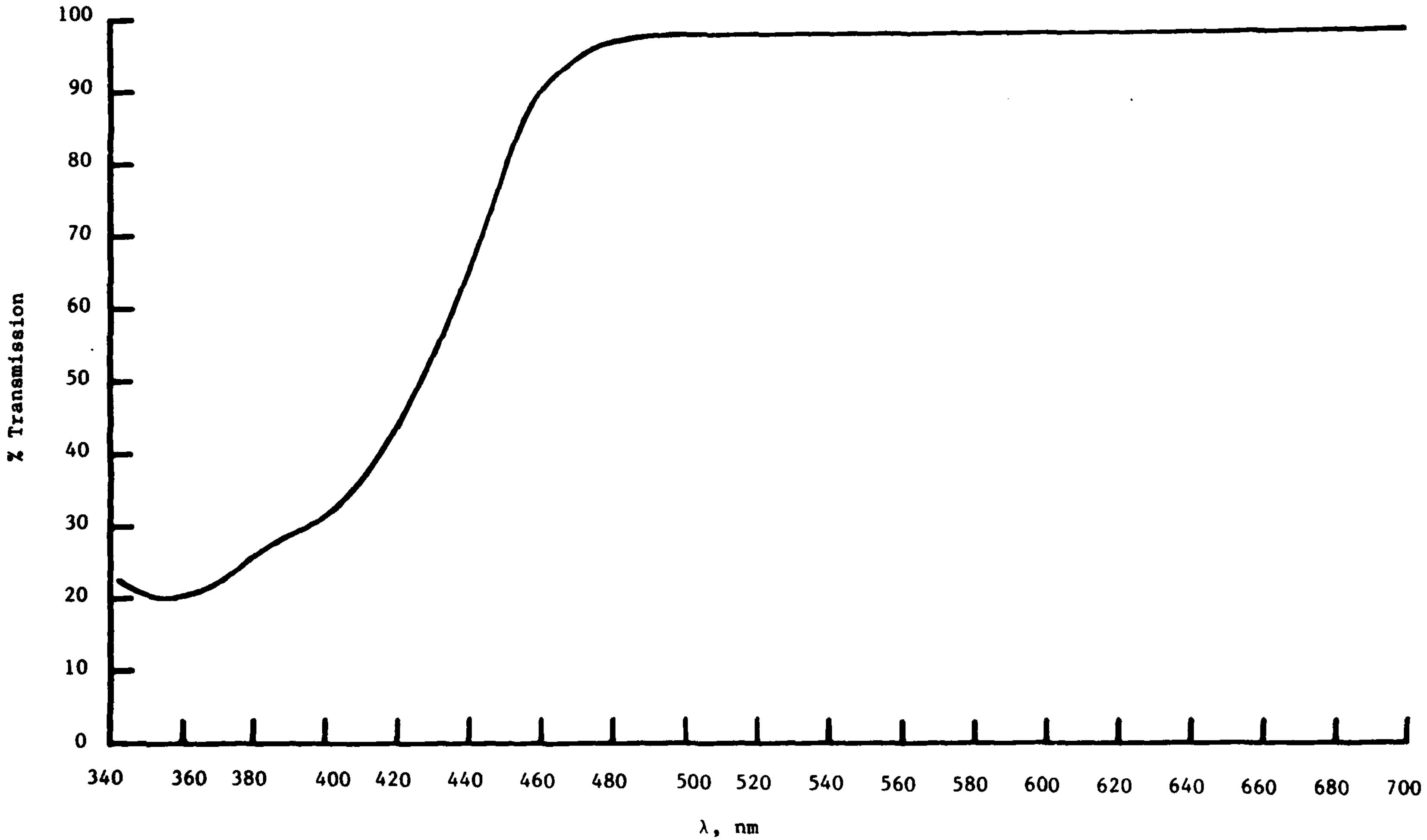

Fig 7 Spectrum of Picric Acid in water

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