# *Visible and Ultraviolet Absorption Spectra of Red Complexes of 1,3,5-Trinitrobenzene and its Derivatives with Ammonium Hydroxide*

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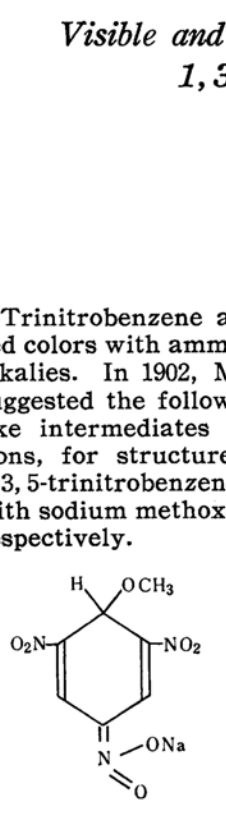
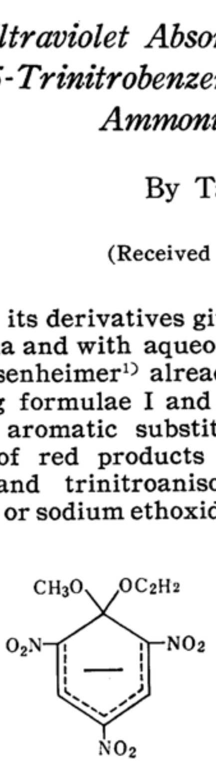
(Received February 10, 1959)

Trinitrobenzene and its derivatives give red colors with ammonia and with aqueous alkalies. In 1902, Meisenheimer[1] already suggested the following formulae I and II like intermediates in aromatic substitutions, for structures of red products of 1,3,5-trinitrobenzene and trinitroanisole with sodium methoxide or sodium ethoxide, respectively.



I



II

By means of the infrared or visible absorption spectra for the red complex of trinitroanisole Meisenheimer's structure II has recently been supported by Hammick and Foster[2,3], by Caldin et al.[4,5], and by Nagakura and Tsubomura[6]. In the previous papers[7,8] the present author also reported the visible absorption spectra of the red colors produced by trinitrobenzene, trinitrotoluene, and tetryl in dilute aqueous solutions of sodium hydroxide. These red colors were reversibly decolorized by addition of weak acids. All the above spectra have been measured directly for the red solutions prepared by adding alkaline solutions into solutions of the nitro compounds, and consequently have been subjected to be influenced by alkalies in the solutions, giving no precise molar absorbancies. In the present study, an attempt has, therefore, been made to determine molar extinction coefficients for the spectra of the red complexes of 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene, tetryl, and picryl chloride with ammonium hydroxide without the effect of alkali.

## Experimental

**Solvents.**—All commercial guaranteed solvents were fractionally distilled after usual treatments.

**Preparation of the Red Complexes of the Nitro Compounds with Ammonium Hydroxide.**—A red-colored solution was prepared by

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[1] J. Meisenheimer, *Ann.*, **323**, 205, 214, 241 (1902).

[2] D. L. Hammick and R. Foster, *J. Chem. Soc.*, **1954**, 2153.

[3] R. Foster, *Nature*, **175**, 746 (1955).

[4] E. F. Caldin and G. Long, *Proc. Roy. Soc.*, **A228**, 263 (1955).

[5] J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, **1956**, 2528, 2540, 2546.

[6] S. Nagakura and H. Tsubomura, Personal Communication; at the Symposium on Electonic States in Tokyo on May 17, 1958.

[7] T. Abe, This Bulletin, **31**, 904 (1958).

[8] T. Abe, ibid., **32**, 339 (1959).

adding a little of guaranteed ammonia water (28%) into a solution made by dissolving each of the nitro compounds into acetone. This red solution was evaporated slowly at room temperature by a vacuum pump to remove acetone, ammonia and water, and a dark red residue was obtained. However, the red substance obtained by evaporation not at room temperature but on a water bath gives an absorption curve illustrated in Fig. 1, which is very different from that indicated in Fig. 2, possibly owing to the further reaction. After being washed with a small quantity of acetone to remove the nitro compound contained, the red substance was dried again at room temperature by a vacuum pump. The powdered dark red product obtained is considered to be the colored complex of the nitro compound with ammonium hydroxide, which is more soluble in water than in acetone, while the nitro compound readily dissolves in acetone but not easily in water. By the above procedure, the red complex of picryl chloride could be obtained easily, although the red color produced by picryl chloride with sodium hydroxide in water disappeared in a few minutes[8].

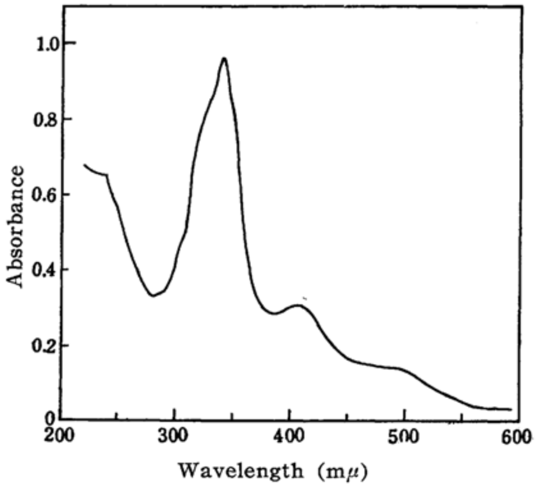

Fig. 1. An absorption spectrum of the red complex of trinitrotoluene with ammonium hydroxide, obtained by evaporation on a water bath, in water.

**Spectra.**—The spectra of the solutions were measured with a Hitachi quartz spectrophotometer, Model EPU-2 at room temperature. The path length of absorption cells was 1 cm.

Trinitrobenzene forms with sodium methoxide a red product of the empirical composition, trinitrobenzene · $CH_3ONa \cdot 1/2H_2O$[9] and with sodium hydroxide a red one having the empirical composition, trinitrobenzene · NaOH[10], respectively. In the present work, the red complexes of the nitro compounds with ammonium hydroxide are assumed to have compositions of nitro compound·$NH_4OH$ in calculating molar extinction coefficients for their spectra. This point is returned to below.

## Results and Discussion

**The Spectra of the Red Complexes of the Nitro Compounds with Ammonium Hydroxide in Water** (Fig. 2).—An absorption spectrum for the red complex of trinitrotoluene is similar to that for the complex of trinitrobenzene, showing an intense absorption maximum band at about 475 mμ, although a whole molar absorbancy for the former is slightly greater than that for the latter. This similarity implies that both the red complexes are structurally analogous. The red complex of tetryl also shows an analogous absorption curve with those of trinitrobenzene and trinitrotoluene, giving a weaker absorption maximum at about 490 mμ as compared with those for the latter. Only the red complex of picryl chloride shows an intense absorption maximum band at about 420 mμ as compared with those for the other complexes, and a weak band clearly at about 330 mμ. The 330 mμ band seems possibly to be attributed to the complex, although it has not been decided whether the band is due

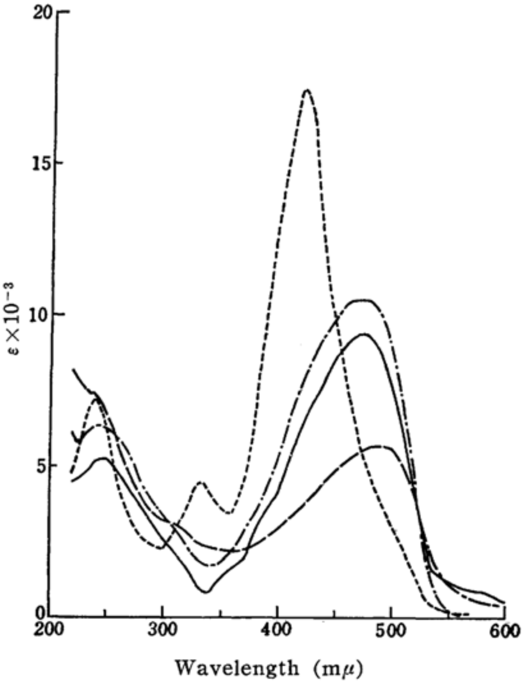

Fig. 2. Absorption spectra of the red complexes of trinitrobenzene (——), trinitrotoluene (—-—), tetryl (— —), and picryl chloride (----) with ammonium hydroxide, all in water.

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[9] L. de Bruyn and van Leent, *Rec. trav. chim.*, **14**, 150 (1895).

[10] Giua, *Gazz. chim. ital.*, **45**, II, 351 (1915).

to the complex itself or to picric acid formed by the further reaction[8], because the band lies at the wavelength close to that of the maximum for the picrate ion. All these red complexes give distinct bands at about 240 mμ.

**The Spectra of the Red Complexes in Ethanol** (Fig. 3).—These red comlexes in ethanol roughly show the similar spectra as in water. Both in ethanol and in water, the intense visible absorption bands for these complexes shift to the red in the order of picryl chloride, trinitrotoluene, trinitrobenzene, and tetryl with their molar absorbancies decreasing in the same order, except the molar absorbancy for picryl chloride in ethanol. The molar absorbancies for the 240 mμ bands increase in the order of trinitrobenzene, trinitrotoluene, picryl chloride, and tetryl. All the visible bands shift to the red and have greater molar absorbancies in ethanol as compared with those in water. Each of the wide visible bands for the red complexes of trinitrobenzene, trinitrotoluene, and tetryl in water is expected to consist of more than two absorption bands, because a shoulder is observed for the corresponding one in ethanol.

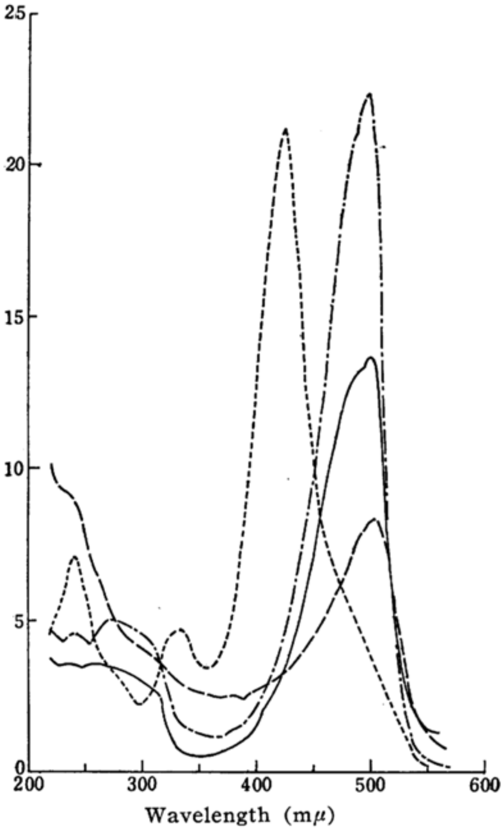
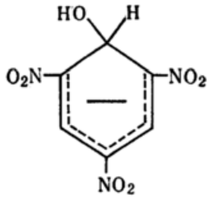
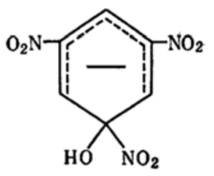


Fig. 3. Absorption spectra of the red complexes of trinitrobenzene (——), trinitrotoluene (—-—-), tetryl (— —), and picryl chloride (----) with ammonium hydroxide, all in ethanol.

The red complexes between these nitro compounds and ammonium hydroxide may be regarded as the same complexes as those of the nitro compounds with sodium hydroxide or sodium methoxide. Accordingly, the red complexes with ammonium hydroxide can be presumed to have compositions of nitro compound $\cdot$ $NH_4OH$ by analogy with the empirical compositions of trinitrobenzene $\cdot$ $CH_3ONa$[9], trinitrobenzene $\cdot$ NaOH[10], and trinitroanisole $\cdot$ $CH_3ONa$[11], as mentioned above. On standing in the cold with dilute aqueous solution of sodium hydroxide, 1, 3, 5-trinitrobenzene yields 3, 5-dinitrophenol[12] through a red intermediate. Considering only this reaction, the red intermediate seems to be more like the following structure IV than like the structure III presented by Meisenheimer, as mentioned in the previous paper[8].

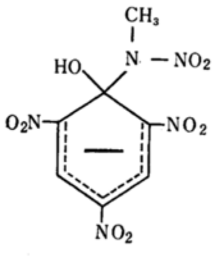


III



IV

The red color of the complex is certainly owing to transitions of its π-electrons. On the other hand, the complex of tetryl with sodium hydroxide finally produces a product indicating an absorption curve analogous to that for picric acid[8]. The red complex of tetryl with hydroxide anion is, therefore, expected to have Meisenheimer's structure V.



V

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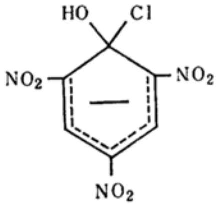
[11] Jackson, *Am. Chem. J.*, **20**, 448 (1898); **23**, 294 (1901).

[12] L. de Bruyn and van Leent, *Rec. trav. chim.*, **13**, 151 (1894).

However, Figs. 2 and 3 indicate that the spectra for the red complex of trinitrobenzene resemble those for the red complex of tetryl, as in the case of the red complexes with sodium hydroxide[8]. This similarity between their spectra can be explained by assuming the structure III for the red complex of trinitrobenzene, since the structure IV is hardly expected to be able to give the similar spectra as those for structure V owing to difference between their $\pi$-electron systems. In dilute aqueous solution of sodium hydroxide, picryl chloride finally gives an absorption curve analogous to that of picric acid after the red coloration[8], as in the case of tetryl. The red complex of picryl chloride with ammonium hydroxide is, therefore, expected to have the structure VI such as that for tetryl.



VI

Figs. 2 and 3, though not decisive, appear to be in favor of Meisenheimer's structures such as III, V and VI for all the above red complexes with ammonium hydroxide. Their structures are, however, to be determined hereafter by means of X-rays and infrared spectroscopy.

The difference between the spectra for the red complexes of tetryl and picryl chloride, which both seem to have the same $\pi$-electron structures indicated in V and VI, can be interpreted in terms of hyperconjugation of $-Cl$ and $-N(CH_3)NO_2$ to their $\pi$-electron systems.

**Effect of Sodium Hydroxide on the Spectrum of the Red Complex of 2, 4, 6-Trinitrotoluene with Ammonium Hydroxide in Water** (Fig. 4).—As the concentration of sodium hydroxide increases, the molar absorbancy for the spectrum of the red complex of trinitrotoluene with ammonium hydroxide decreases in water, and the decolorization of the red color becomes faster. On the other hand, all these red complexes of the nitro compounds are very stable both in water and in ethanol in absence of alkali. The negative ion $OH^-$ is, therefore, considered to play an important role for the further decolorization reaction of the red complex. At a low concentration of sodium hydroxide, 0.103 N, the red complex of trinitrotoluene shows an absorption curve similar to that for trinitrotoluene in an aqueous solution of sodium hydroxide[7,8]. This leads to the suggestion that the absorption curves for the red complexes of the nitro compounds, reported in the previous papers[7,8], are somewhat affected by sodium hydroxide.

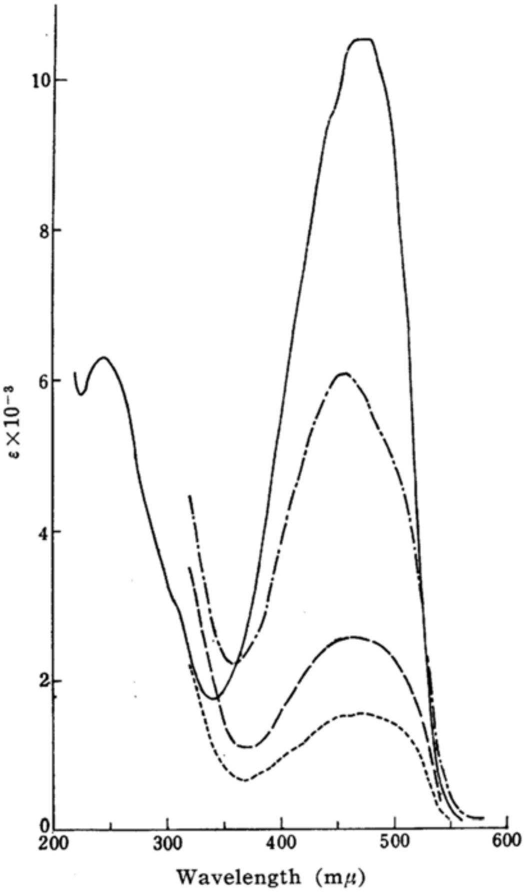


Fig. 4. Absorption spectra of the red complex of trinitroluene with ammonium hydroxide ($4.96 \times 10^{-5}$ M) in water (——) and in aqueous sodium hydroxide solution (0.103 N: —·—, 0.516 N: — —, 1.03 N: ----).

## Summary

The red complexes of trinitrobenzene, trinitrotoluene, tetryl and picryl chloride with ammonium hydroxide, regarded as intermediates in aromatic substitutions, were obtained. Each of these red complexes roughly shows a similar spectrum

both in water and in ethanol. All their visible bands, however, shift to the red and have greater molar absorbancies in ethanol as compared with those in water. The red complex of trinitrobenzene shows an absorption curve analogous to that for the complex of tetryl, although they yield different products after further reactions. As the concentration of sodium hydroxide increases, the molar absorbancy for the spectrum of the red complex of trinitrotoluene decreases in water, probably owing to the action of $OH^-$.

The author is particularly indebted to Professor Y. Nomura for his suggestion and encouragement throughout this work. Thanks are also due to Dr. S. Maeda for the use of the spectrophotometer.

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