Substituent Effects on the Ultraviolet Absorption Spectrum of 1,3,5-Trinitrobenzene in Some Solvents

By Takehiro ABE

(Received August 22, 1958)

The near ultraviolet absorption spectrum of 1,3,5-trinitrobenzene shows an intense band at 223 mμ and two shoulders at about 300 and 340 mμ in ethanol[1,2]. The maximum absorption band has a shorter wavelength of 223 mμ and a greater molar absorbancy than that of nitrobenzene[2], which has been interpreted by Nagakura and Tanaka[3], in terms of the intramolecular charge transfer.

In the present paper, an attempt has been made to investigate the effects of four substituents on the spectra of 1,3,5-trinitrobenzene in some solvents. The ultraviolet absorption spectra of 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrotoluene (TNT), picryl chloride (PC), 2,4,6-trinitrophenylmethylnitramine (Tetryl) and picric acid (PA) have been compared in solvents like water, water-sodium hydroxide, ethanol, benzene and acetone, together with the solvent effects upon the spectra of PC, Tetryl and PA. The spectra of TNB and TNT, measured in the previous work[2], have been used here.

Experimental

Materials.—Trinitrobenzenes of commercial extra pure grade were purified by recrystallizing several times. PC: m. p. 82.5°C, Tetryl: m. p. 129.9°C, PA: m. p. 122.6°C. Commercial guaranteed solvents were fractionally distilled after usual treatments.

---

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

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

[3] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, 22, 236 (1954).

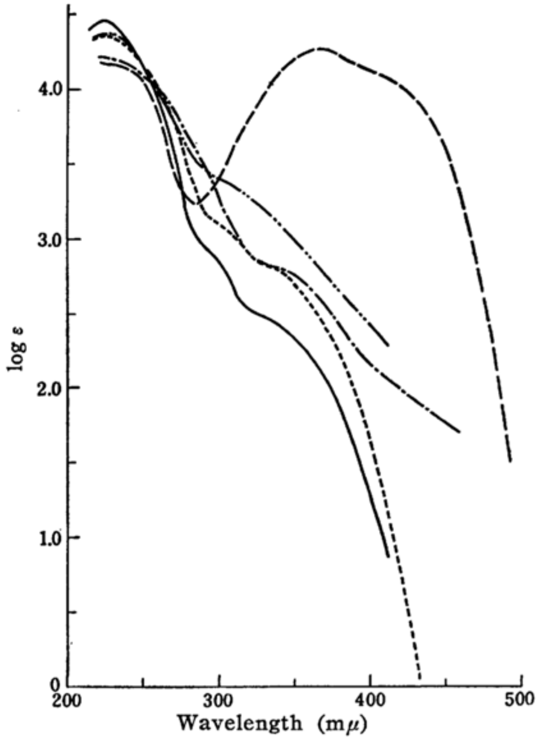


Fig. 1. Absorption spectra of TNB (——), TNT (------), PC (—·—), Tetryl (—··—) and PA (— —), all in ethanol.

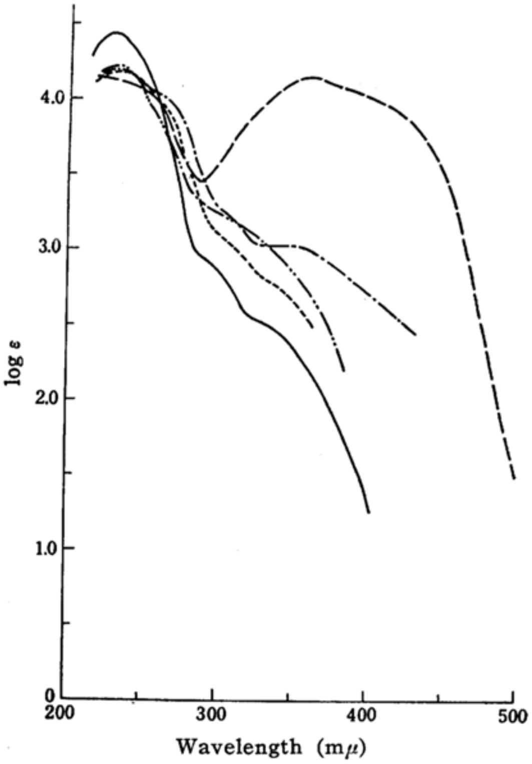


Fig. 2. Absorption spectra of TNB (——), TNT (------), PC (—·—), Tetryl (—··—) and PA (— —), all in water.

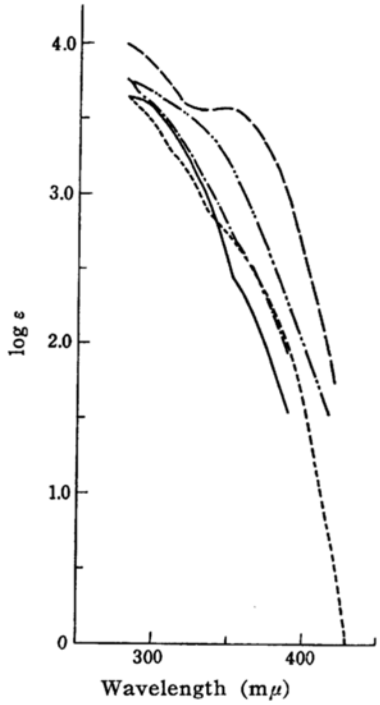


Fig. 3. Absorption spectra of TNB (——), TNT (------), PC (—·—), Tetryl (—··—) and PA (— —), all in benzene.

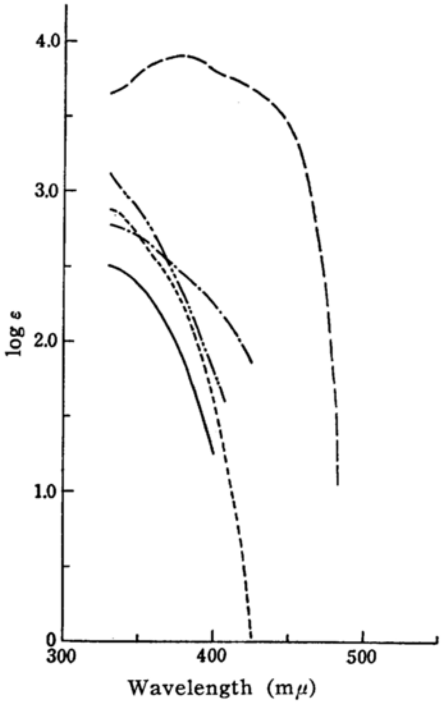


Fig. 4. Absorption spectra of TNB (——), TNT (------), PC (—·—), Tetryl (—··—) and PA (— —), all in acetone.

Spectra.—The spectra of the solution were measured with a Hitachi Model EPU-2 spectrophotometer at room temperature. Path length of absorption cells was 1 cm.

Results and Discussion

Spectra of Trinitrobenzenes in Some Solvents.—*In ethanol* (Fig. 1).—By substituting a group like $-CH_3$, $-Cl$, $-N(CH_3)NO_2$ or $-OH$, the 223 mμ band of TNB shifts to the red and its molar absorbancy decreases in the following order: TNB> Tetryl> TNT> PC> PA. Molar extinction coefficients of 300 and 340 mμ bands of the substituted trinitrobenzenes are greater than those of TNB, except those of PA that gives intense absorption bands at 350∼450 mμ.

In the previous paper[2], it has been described that a benzene nucleus of polynitro-substituted benzene possesses some positive charge owing to the strong electron-attracting nature of nitro groups, and that the greater this positive charge, the greater becomes the blue shift of the maximum absorption band of the nitro compound. A benzene nucleus of each derivative of TNB possesses a less positive charge than that of TNB, because the electron of the $-CH_3$, $-Cl$, $-N(CH_3)NO_2$ or $-OH$ substituent can migrate to some extent toward the benzene nucleus in the direction opposite to the electron migration of the nitro groups, as indicated in Fig. 5. It is, therefore, known that the maximum absorption bands of the substituted trinitrobenzenes, benzene nuclei of which possess less positive charges than that of TNB, shift to the red with decreasing molar absorbancies, compared with the band of TNB.

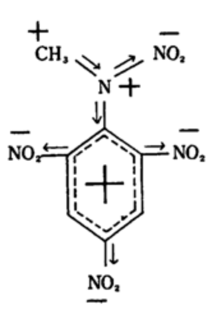


Fig. 5. Charge distribution of Tetryl.

In water (Fig. 2).—The substituted trinitrobenzenes show similar spectra as in ethanol, but give their maximum absorption bands at longer wavelengths and the smaller molar absorbancies in water than in ethanol. Both in ethanol and in water the molar absorbancies of their maximum absorptions are in the following order: TNB> Tetryl> TNT> PC> PA.

In benzene (Fig. 3).—The molar absorbancy of the 350 mμ shoulder of each substituted TNB is greater than that of TNB. Especially PA shows intense bands in this region.

In acetone (Fig. 4).—The molar absorbancies of the 340 mμ shoulders of the substituted trinitrobenzenes are greater than that of TNB. In addition to this shoulder, PA shows intense bands at 370∼440 mμ. In all solvents the molar absorbancies of the 340 mμ bands of the trinitrobenzenes increase in the order of TNB, TNT, PC, Tetryl and PA, except the absorbancies of PC in water and in acetone.

It has been found that the visible absorption bands of TNB in acetone, indicated in the previous paper[2], are owing to the action of visible light on the trinitrobenzene used, because TNB that gives no visible absorption bands in acetone as shown in Fig. 4, shows such visible absorption spectra as indicated in the previous paper, after being irradiated by an usual incandescent lamp for a long time.

Solvent Effects on the Spectra of PC, Tetryl and PA (Figs. 1∼4).—PC, Tetryl and PA give greater molar absorbancies of absorption bands near 300 mμ in benzene than in ethanol or in water. These great absorbancies in benzene seem probably to be due to formations of molecular complexes between the trinitrobenzenes and benzene, as TNB and TNT form complexes with benzene[2,4].

The absorption curves of PC and Tetryl in ethanol are not so closely resemble those in water as the curves of TNB and TNT. Only the 350 mμ band of PC exceptionally gives a greater molar absorbancy in water than in ethanol.

PA shows similar absorption curves in all three solvents like ethanol, water and acetone. This similarity seems to show that PA dissociates in negative ion not only in water, but also in ethanol and in acetone, losing a proton, because PA is known to be strongly acidic in water.

Spectra of Trinitrobenzenes in Aqueous Sodium Hydroxide Solution (Figs. 6∼8).—In Fig. 6, visible absorption spectra of

---

[4] G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **59**, 184 (1955).

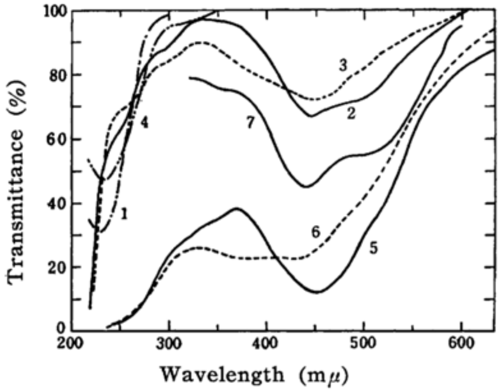


Fig. 6. Absorption curves of:
1. An aqueous solution of TNB;
2. A solution measured immediately after a few drops of 2 N sodium hydroxide solution were added into the solution (1);
3. A solution obtained by boiling the solution (2);
4. An aqueous solution of TNT;
5. A solution measured immediately after a few drops of 2 N sodium hydroxide solution were added into the solution (4);
6. A solution obtained by boiling the solution (5);
7. An aqueous solution of Tetryl, in which a few drops of 2 N sodium hydroxide solution were added.

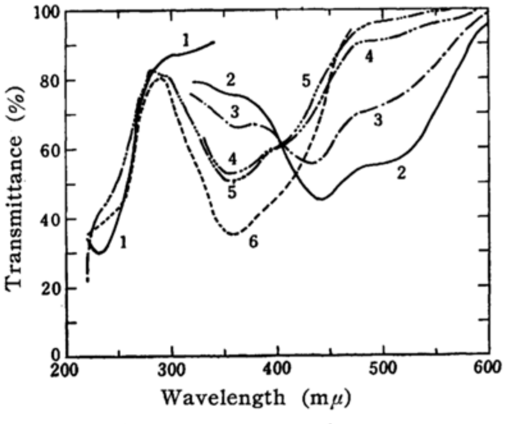


Fig. 7. Absorption curves of:
1. An aqueous solution of Tetryl;
2. A solution measured immediately after a few drops of 2 N sodium hydroxide solution were added into the solution (1);
3. A solution obtained by standing the solution (1) for about half an hour;
4. The solution (2) after an hour and forty minutes;
5. The solution (2) after two hours and a half;
6. An aqueous solution of PA.

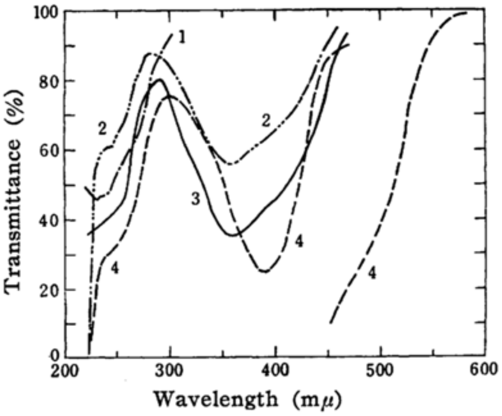


Fig. 8. Absorption curves of:
1. An aqueous solution of PC;
2. A solution in which a red color produced by adding a little of dilute sodium hydroxide solution into the solution (1), already discolored;
3. An aqueous solution of PA;
4. A solution obtained by adding a concentrated sodium hydroxide solution into the solution (3).

sodium hydroxide solutions of TNB, TNT and Tetryl are compared one another, and the absorption curves of the rather stable alkaline solutions of TNB and TNT, boiled to accelerate the rates of reactions between the trinitrobenzenes and alkali, are also indicated. The spectrum of TNB (curve 2) in sodium hydroxide solution closely resembles to that of Tetryl (curve 7). The spectrum of TNT (curve 5) in this solution also resembles them. These red colors are reversively decolorized by addition of weak acids.

On standing for two hours, the red color of the sodium hydroxide solution of Tetryl changes slowly to yellow, as described in Fig. 7. A spectrum of the yellow solution (curve 5) that yields no red color again by adding alkali, closely resembles that of PA (curve 6).

On treating an aqueous solution of PC with sodium hydroxide solution, a red color is produced and fades in a few minutes. By adding a concentrated solution of sodium hydroxide, a solution of PA at once gives a brownish orange color, which disappears in a moment. Absorption curves of yellow solutions to which these alkaline solutions of PC and PA change finally through red solutions, are given in Fig. 8. In a concentrated solution of sodium hydroxide, PA shifts a position of its maximum absorption band to the red by about 30 mμ, and shows a weak shoulder at about 500 mμ (curve 4).

From the above results, the red colors of the aqueous sodium hydroxide solutions of the substituted trinitrobenzenes are stable at room temperature in the following order: TNB and TNT> Tetryl> PC> PA. It is noticed that the substituted trinitrobenzenes that form the labile colors with sodium hydroxide, contain electron-donating substituents like $-N(CH_3)NO_2$, -Cl and -OH.

On boiling with dilute sodium hydroxide solution, TNB yields $3,3',5,5'$-tetranitroazoxybenzene and 3,5-dinitrophenol[5]. On standing in the cold with methanolic sodium methylate, TNB yields 3,5-dinitroanisol[6] and on boiling with alcoholic soda solution, it undergoes a partial reduction to form $3,3',5,5'$-tetranitroazoxybenzene[7]. The first product of the reaction of methanolic caustic alkali on TNB is a red crystalline addition product having the experimental composition, $TNB \cdot CH_3ONa \cdot 1/2H_2O$, isolated by Bruyn and Leent[8]. From these experimental results, the red product between TNB and sodium hydroxide seems probably to be an intermediate in the reaction of TNB to 3,5-dinitrophenol. The red products of TNT and Tetryl with sodium hydroxide may be also intermediates in their reactions. The transient colors of the sodium hydroxide solutions of PC and PA, absorption spectra of which have not been determined owing to their rapid discolorations, seem to be due to the same complexes as those of TNB, TNT and Tetryl. Actually, it has been reported that a methanol solution of TNT, treated with potassium methylate, yields a red product of an empirical composition, $TNT \cdot CH_3OK \cdot H_2O$[9]. A methanol solution of picryl chloride, treated with an excess of sodium methylate or of strong sodium hydroxide solution, also turns dark red and deposits red crystals of the empirical composition, trinitroanisol$\cdot NaOCH_3$[10]. The color reaction of sodium ethoxide with TNT and TNB in ethanol has been interpreted by Caldin and his co-workers[1,11] in terms of a proton-transfer reaction for TNT and in terms of an addition reaction for TNB.

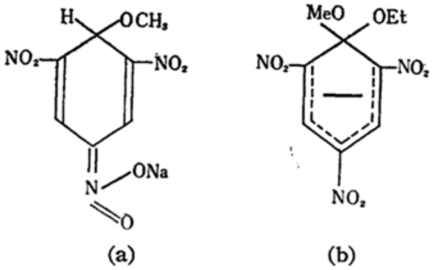
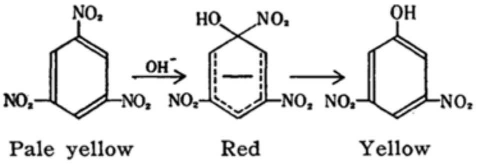


Fig. 9. Meisenheimer's structure for $TNB \cdot CH_3ONa$(a) and $TNA \cdot OEt^-$(b).

A structure of the red product of $TNB \cdot CH_3ONa$ was presented by Meisenheimer[12], as indicated in Fig. 9 (a). His structure seems to be doubtful in the following point. If the red product between TNB and sodium hydroxide has such a structure as given in Fig. 9 (a), PA may be produced from it at the end of the reaction, while 3,5-dinitrophenol is experimentally obtained as mentioned above. The absorption band of PA is not found also in the spectrum (curve 3) of the boiled alkaline solution of TNB in Fig. 6. It has been, by Nagakura[13], suggested to the present author that TNB should react with sodium hydroxide as follows:



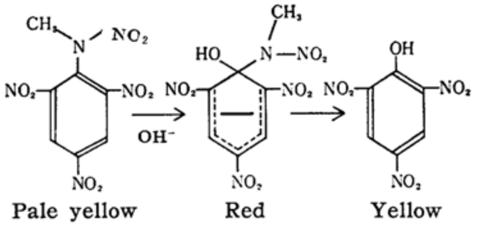
It was suggested also by Meisenheimer[14] that a red product between 2,4,6-trinitroanisol (TNA) and sodium ethoxide had the probable constitution indicated in Fig. 9(b). In this case, he isolated as solids the products of the reaction of TNA with potassium ethoxide and of 2,4,6-trinitrophenetole with potassium methoxide, obtained a mixture containing trinitrophenetole on decomposing each of these solids with dilute sulfuric acid, and concluded that both red products consisted of the potassium salt of the anion (Fig. 9(b)). The structure presented by Meisenheimer for the complex between TNA and ethoxide ion, has been recently supported by Hamick and Foster[15,16], and by Nagakura and Tsubomura[13,17], who

---

[5] L. de Bruyn and van Leent, *Rec. trav. Chim.*, **13**, 151 (1894).
[6] L. de Bruyn, ibid., **9**, 208 (1890).
[7] L. de Bruyn and van Leent, ibid., **13**, 148 (1894).
[8] L. de Bruyn and van Leent, ibid., **14**, 150 (1895).
[9] A. Hantzsch and H. Kissel, *Ber.*, **32**, 3140 (1899).
[10] Jackson, *Am. Chem. J.*, **20**, 448 (1898); **23**, 294 (1901).
[11] J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, **1956**, 2528, 2540, 2546.
[12] J. Meisenheimer, *Ann.*, **323**, 214, 241 (1902).
[13] S. Nagakura, Private communication.
[14] J. Meisenheimer, *Ann.*, **323**, 205 (1902).
[15] D. L. Hamick and R. Foster, *J. Chem. Soc.*. **1954**, 2153.
[16] R. Foster, *Nature*, **175**, 746 (1955).
[17] H. Tsubomura, Private communication.

have succeeded in measuring an energy of activation for a decomposition reaction of a red complex of 2,4-dinitroanisol and hydroxyl ion to dinitrophenol.

In the reaction of Tetryl with sodium hydroxide PA seems to be finally produced through an intermediate, as indicated below, because the final absorption curve (5) of the reaction closely resembles that of PA (6) in Fig. 7. Although the red products of TNB and Tetryl with alkali finally yield the different substances, that is, 3,5-dinitrophenol and PA, respectively, the resemblance between their spectra (curves 2 and 7 in Fig. 6) suggests that the structure of the red product of TNB may be similar to that of the red product of Tetryl. This is, thus, considered to support Meisenheimer's structure, since the resemblance of their spectra can be interpreted by assuming his structures in Fig. 9 (a), although the question pointed out above remains still.



Summary

(1) In ethanol and in water the maximum absorption bands of the substituted trinitrobenzenes are observed at longer wavelengths and possess smaller molar absorbancies than 1,3,5-trinitrobenzene, a benzene nucleus of which possesses some greater positive charge than those of the derivatives.

(2) Picric acid shows similar absorption curves in solvents like ethanol, water and acetone. This similarity seems to show that picric acid dissociates in all solvents.

(3) On treating the trinitrobenzenes with aqueous sodium hydroxide solution, the red colors are produced. The colors given by the trinitrobenzenes having substituents like $-N(CH_3)NO_2$, -Cl and -OH, are labile, while those produced from trinitrobenzene and 2,4,6-trinitrotoluene are rather stable. The spectrum of the red color of trinitrobenzene closely resembles that of Tetryl.

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

Department of Chemistry
Defense Academy
Yokosuka, Kanagawa