Visible and Ultraviolet Absorption Spectra of 1,3,5-Trinitrobenzene in Water in the Presence of Sodium Hydroxide

By Takehiro ABE

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In the previous paper[1,2], the author has reported an absorption spectrum of a red-colored solution produced by adding a few drops of sodium hydroxide solution into an aqueous solution of 1, 3, 5-trinitrobenzene. In the present paper, an attempt has been made to investigate the interaction of 1, 3, 5-trinitrobenzene with hydroxyl ion in detail by measuring the absorption spectra of the colored solution at various concentrations of sodium hydroxide, together with an effect of hydrochloric acid on the colored solution.

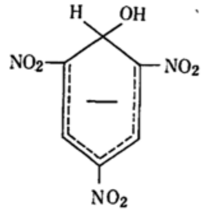
Experimental

Commercial pure 1, 3, 5-trinitrobenzene was purified by recrystallizing three times from methanol-water; m. p. 123.1°C. Each colored solution of trinitrobenzene and sodium hydroxide in water was freshly prepared by adding an aqueous solution of sodium hydroxide into an aqueous solution of trinitrobenzene before each measurement. The spectra of the solution were measured with a Hitachi Model EPU-2 spectrophotometer at 25°C or at room temperature. Path length of absorption cells was 1 cm.

Results and Discussion

Absorption Spectra of Trinitrobenzene in Water at Various Concentrations of Sodium Hydroxide (Fig. 1).—As Fig. 1 shows, the aqueous solutions of trinitrobenzene in the presence of sodium hydroxide show absorption bands at 260, 300 and 400~500 mμ. The absorption curve of the colored solution with a sodium hydroxide concentration of 0.393 N resembles that of the red complex between trinitrobenzene and ammonium hydroxide in water[3]. The visible absorption curves of the colored solutions of trinitrobenzene and sodium hydroxide in water are different from that of the solution in acetone, which shows absorption bands at two regions of 450 and 510~590 mμ[4]. The visible absorption curves appreciably resemble that obtained by Caldin et al.[5,6] for the colored solution of trinitrobenzene and ethoxide ion in ethanol, for which a different absorption curve has been obtained by Foster[7].

The color produced by the reaction of trinitrobenzene with sodium hydroxide in water seems to be due to the following structure which is the same as that presented by Meisenheimer[8] for the red product of trinitrobenzene with sodium ethoxide, although the question pointed out in the previous paper[2] still remains.



The structures of Meisenheimer's type have recently been supported for the colored products of many polynitro aromatic hydrocarbons with alkalies[2-4,6,7,9-13].

The absorbances of the visible absorption bands increase with the increasing concentration of sodium hydroxide below the sodium hydroxide concentration, about 0.6 N, but reversely decrease above the sodium hydroxide concentration. The color finally disappears at very high concentration of sodium hydroxide. On the other hand, the bands at 260 and 300 mμ, observed distinctly above the sodium hydroxide concentration, about 0.4 N, become intense, as the sodium hydroxide

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[1] T. Abe, This Bulletin, **31**, 904 (1958).
[2] T. Abe, ibid., **32**, 339 (1959).
[3] T. Abe, ibid., **32**, 997 (1959).
[4] T. Abe, ibid., **32**, 778 (1959).
[5] E. F. Caldin and G. Long, *Proc. Roy. Soc.*, **A228**, 263 (1955).
[6] J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, **1956**, 2528.
[7] R. Foster, *Nature*, **183**, 1042 (1959).
[8] J. Meisenheimer, *Ann.*, **323**, 214, 241 (1902).
[9] D. L. Hamick and R. Foster, *J. Chem. Soc.*, **1954**, 2153.
[10] R. Foster, *Nature*, **175**, 746 (1955).
[11] S. Nagakura, S. Oosawa and H. Tsubomura, presented at the Symposium on Electron States of Molecules, Kyoto, October, 1958.
[12] S. Nagakura and S. Oosawa, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.
[13] J. F. Bunnett and J. J. Randall, *J. Am. Chem. Soc.*, **80**, 6020 (1958).

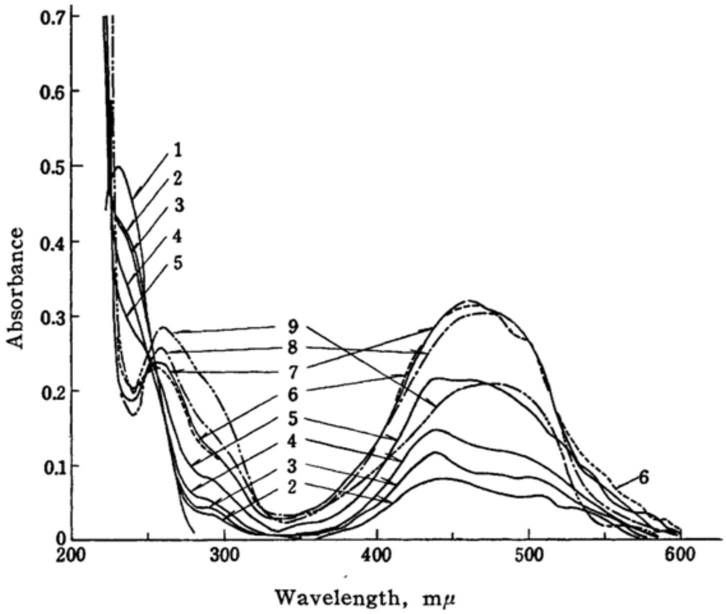
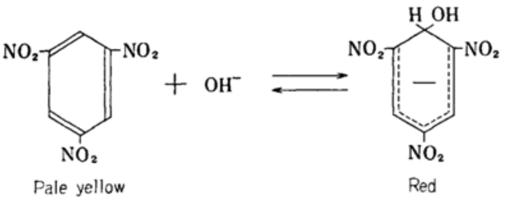
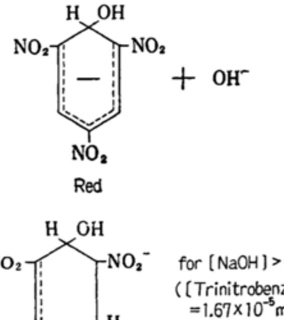


Fig. 1. Absorption spectra of 1, 3, 5-trinitrobenzene (1.67×10^{-5} mol.) in water containing various concentrations of sodium hydroxide at 25°C (path length of cells, 1 cm.). Concentrations of sodium hydroxide:
1) 0; 2) 5.89×10^{-2} N; 3) 7.86×10^{-2} N; 4) 1.18×10^{-1} N; 5) 1.97×10^{-1} N; 6) 3.93×10^{-1} N; 7) 5.89×10^{-1} N; 8) 9.60×10^{-1} N; 9) 1.92 N.

concentration increases. The 260 and 300 mμ bands, as mentioned below, can not be ascribed to a product produced by a further reaction of the colored species, and disappear by addition of an acid. From the above results, the absorption bands may be interpreted as follows. The decrease in the absorbances of the visible absorption bands, considered to be due to [Trinitrobenzene·OH]$^-$, seems to lead to the suggestion that interaction of [Trinitrobenzene·OH]$^-$ with hydroxyl ion results in the formation of [Trinitrobenzene·2OH]$^{2-}$ above the sodium hydroxide concentration, about 0.4 N. The increase in the absorbances of the 260 and 300 mμ bands can be explained by attributing these bands to [Trinitrobenzene·2OH]$^{2-}$. Accordingly, the following reactions may possibly be expected for the interaction of trinitrobenzene with sodium hydroxide in water.

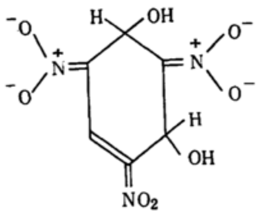


(1)



(2)

The pK values of 1, 3, 5-trinitrobenzene solution were determined by Schaal[14] by ultraviolet absorption measurement in an ethylenediamine-water mixture of a known



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[14] R. Schaal, *Compt. rend.*, **239**, 1036 (1954).

acidity function, with the result of $pK_1=14.40$ and $pK_2=18.00$. The two pK values may support the formations of [Trinitrobenzene·OH]$^-$ and [Trinitrobenzene·2OH]$^{2-}$. Schaal also supposed the formation of the following complex for the pK_2.

An Equilibrium Constant for the Colored Reaction of Trinitrobenzene with Hydroxyl Ion.—In the previous paper[2] the author has found that the red-colored species of 1,3,5-trinitrobenzene and 2,4,6-trinitrotoluene with sodium hydroxide in water are more stable than those of picryl chloride and 2,4,6-trinitrophenylmethylnitramine (Tetryl). The colored solution of trinitrobenzene and ethoxide ion has been found by Caldin and Long[5] and by Foster[7] to obey Beer's law. An attempt has, therefore, been made to obtain the equilibrium constant K for the colored reaction 1 of trinitrobenzene with sodium hydroxide in water from the result in Fig. 1.

As $[\mathrm{NaOH}] \gg [\mathrm{Trinitrobenzene}]$ in the present measurements, Benesi and Hildebrand's equation[15] can be written as

$$\frac{l\,[\mathrm{Trinitrobenzene}]}{d}=\frac{1}{\varepsilon K}\cdot\frac{1}{[\mathrm{NaOH}]}+\frac{1}{\varepsilon} \tag{3}$$

Here l represents the path length of absorption cells (1 cm.) and d and ε are respectively an absorbance and a molar extinction coefficient for the colored species. Fig. 2 is obtained by plotting [Trinitrobenzene]/d against 1/[NaOH]. Although the colored species of trinitrobenzene and hydroxyl ion is comparatively stable, it slowly reacts with hydroxyl ion, as mentioned below. Moreover, the molar extinction coefficient of the colored species may be affected by the concentration of sodium hydroxide, since the absorption curves of the red complexes of trinitrobenzenes with ammonium hydroxide are apt to be greatly influenced with any solvent, as shown in the previous paper[3]. As Fig. 2 shows, [Trinitrobenzene]/d, however, is nearly proportional to 1/[NaOH] below the sodium hydroxide concentration, about 0.6 N. The linearities of Benesi and Hildebrand's plots indicate the formation of the 1 : 1 colored complex between trinitrobenzene and hydroxyl ion, because Benesi and Hildebrand's Eq. 3 is derived for the 1 : 1 complex. Therefore, the visible absorption bands are undoubtedly owing to the formation of [Trinitrobenzene·OH]$^-$. Deviations of the plots from the linearities above the sodium hydroxide concentration, about 0.6 N can be interpreted to be owing to the formation of [Trinitrobenzene·2OH]$^{2-}$ according to reaction 2. By Eq. 3 the intercept at 1/[NaOH] = 0 and the ratio of the intercept to slope give $1/\varepsilon$ and $1/\varepsilon K$, respectively. From the best straight line for the 450 mμ absorption band, it is possible to find $\varepsilon_{450}=3.5\times10^4$ and $K=2.7$ at 25°C. The value of 3.5×10^4 is larger than the molar extinction coefficient of 9.4×10^3 for the maximum absorption band (at 480 mμ) of the red complex of trinitrobenzene with ammonium hydroxide in water[3]. The equilibrium constant of 2.7 is very much smaller as compared with that (2.4×10^3) obtained by Caldin and Long[5] for the color reaction of trinitrobenzene with ethoxide ion in ethanol at 25°C.

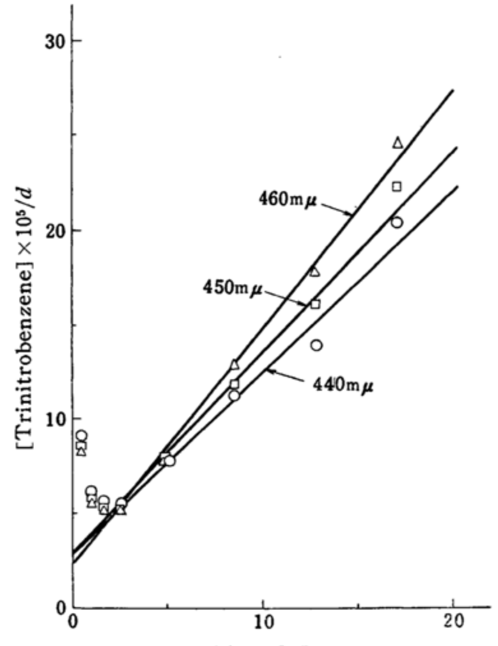

Fig. 2. Benesi and Hildebrand's relation for the result in Fig. 1.

Time Dependence of Absorption Spectra of the Colored Solutions of Trinitrobenzene and Sodium Hydroxide in Water (Fig. 3).—On standing the colored solutions of trinitrobenzene and sodium hydroxide in water, the absorbances of the visible absorption bands gradually decrease, while an increase in absorbance can be observed at about 350 mμ. The 350 mμ band is probably due to a product in which [Trinitrobenzene·OH]$^-$ and [Trinitrobenzene·2OH]$^{2-}$ result.

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[15] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

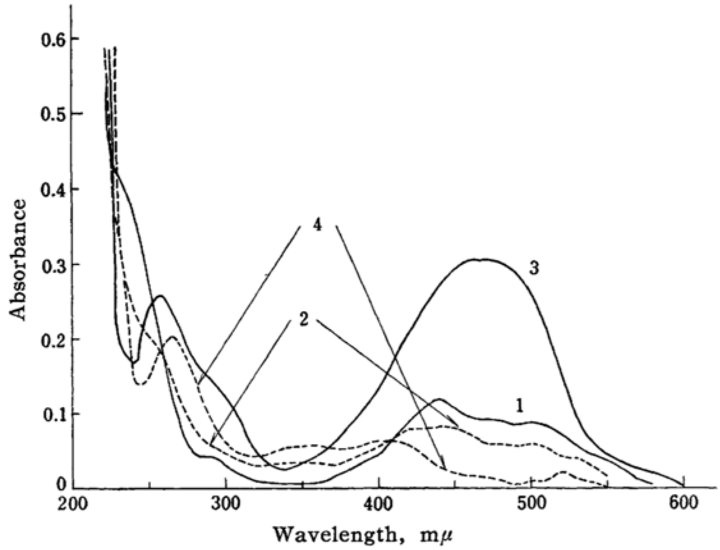

Fig. 3. Absorption spectra of the colored solutions of trinitrobenzene (1.67×10^{-5} mol.) and sodium hydroxide in water, stood for long hours (at room temperature).

1) A solution with a sodium hydroxide concentration, 7.86×10^{-2} N;

2) The same after two days;

3) A solution with a sodium hydroxide concentration, 9.60×10^{-1} N;

4) The same after a day.

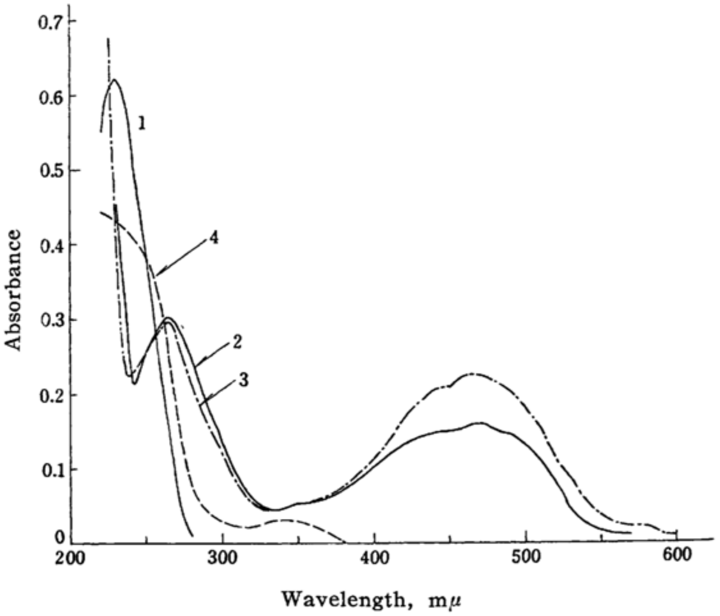

Fig. 4. An effect of hydrochloric acid on the spectrum of the colored solution of trinitrobenzene and sodium hydroxide in water (at room temperature).

1) A solution obtained by adding 2 cc. of water into 2 cc. of an aqueous solution of trinitrobenzene (4.18×10^{-5} mol.);

2) A solution obtained by adding 2 cc. of water into 2 cc. of a colored solution of trinitrobenzene (4.18×10^{-5} mol.) and sodium hydroxide (2.88 N);

3) A solution obtained by adding 2 cc. of a 1.77 N aqueous solution of hydrochloric acid into 2 cc. of the same colored solution as in 2);

4) A solution obtained by adding 2 cc. of a 3.55 N aqueous solution of hydrochloric acid into 2 cc. of the same colored solution as in 2).

The 260 and 300 mμ bands and the visible absorption bands may, therefore, be considered to be due to intermediates, that is, [Trinitrobenzene·OH]$^-$ and [Trinitrobenzene·2OH]$^{2-}$ in the reaction of trinitrobenzene with hydroxyl ion to the product giving the 350 mμ band. The absorbances of the visible absorption bands decrease faster in the colored solution with a high sodium hydroxide concentration than in that with a low sodium hydroxide concentration. This suggests that sodium hydroxide plays an important role for the further decoloration reaction of [Trinitrobenzene·OH]$^-$, as mentioned in the previous paper[3].

An Effect of Hydrochloric Acid on the Spectrum of the Colored Solution of Trinitrobenzene and Sodium Hydroxide (Fig. 4).—It has been reported by Caldin and Long[5], by Nagakura and Oosawa[12], and by the author[2] that the colored solutions formed on adding alkalies to solutions of aromatic polynitrocompounds are reversibly decolorized by the addition of acids. As Fig. 4 shows, when 2 cc. of 1.77 N aqueous solution of hydrochloric acid is added to the colored solution with a sodium hydroxide concentration, 2.88 N, in which reaction 2 is expected to occur according to the appearance of the distinct 260 mμ band, the absorbances of the visible absorption bands increase, while that of the 260 mμ band slightly decreases. This seems to be due to a reverse reaction of [Trinitrobenzene·2OH]$^{2-}$ to [Trinitrobenzene·OH]$^-$ by addition of hydrochloric acid. If a higher concentrated solution of hydrochloric acid is added to the colored solution, the visible absorption bands disappear and a weak absorption band can be observed 350 mμ. The 350 mμ bands seems to be due to the final product of the reaction between trinitrobenzene and hydroxyl ion, as mentioned above. From the above results, [Trinitrobenzene·2OH]$^{2-}$ may be considered to change into [Trinitrobenzene·OH]$^-$ reversibly by the addition of an acid.

Summary

(1) Absorption spectra of the colored solutions of 1,3,5-trinitrobenzene and various concentrations of sodium hydroxide in water have been measured at 25°C. The colored solution shows absorption bands at 260, 300 and 440∼500mμ. The absorbances of the visible absorption bands increase below the sodium hydroxide concentration, about 0.6 N, but decrease above the sodium hydroxide concentration, as the concentration of sodium hydroxide increases. On the other hand, the 260 and 300 mμ bands, observed above the sodium hydroxide concentration, about 0.4 N, increase their absorbances with an increase in concentration of sodium hydroxide. These lead to the suggestion that the visible absorption bands are due to [Trinitrobenzene·OH]$^-$ and the 260 and 300 mμ bands are due to [Trinitrobenzene·2OH]$^{2-}$.

(2) Below the sodium hydroxide concentration, about 0.6 N, Benesi and Hildebrand's equation holds for the colored solutions, giving an equilibrium constant of 2.7 for the reaction between trinitrobenzene and hydroxyl ion in water at 25°C.

(3) On keeping the colored solution to stand for long hours, the 260 and 300 mμ bands and the visible absorption bands decrease their absorbances, while an absorption band appears at about 350 mμ.

(4) When an aqueous solution of hydrochloric acid is added into the colored solution with a high concentration of sodium hydroxide, the absorbances of the visible absorption bands increase. The 260 mμ band and the visible absorption bands disappear by adding a solution of hydrochloric acid, enough to neutralize the sodium hydroxide contained in the solution. By the addition of acids, [Trinitrobenzene·OH]$^-$ and [Trinitrobenzene·2OH]$^{2-}$ seem to change into trinitrobenzene reversibly.

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Department of Chemistry
Defense Academy
Yokosuka