Absorption Spectra of Unstable Colored Intermediates from Picryl Chloride by the Action of Sodium Hydroxide

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In a previous paper[1], it was reported that on treatment of an aqueous solution of picryl chloride with a drop of aqueous solution of sodium hydroxide, a red solution was instantaneously formed and in a few minutes changed into a yellow solution which showed a spectrum closely resembling a spectrum of picric acid. At room temperature the red color faded away so fast that its spectrum could not be measured. It has, however, been found that the red solution containing a small quantity of ethanol is relatively stable. An attempt has, therefore, been made to measure the spectrum of the red solution prepared by adding a sodium hydroxide solution to an aqueous picryl chloride solution containing a small quantity of ethanol, together with spectra of colored solutions of picryl chloride in ethanol and in acetone in the presence of sodium hydroxide. These spectra have been compared to investigate a solvent effect on them.

Experimental

Picryl chloride of Tokyo Kasei Co. guaranteed grade was recrystallized twice from methanol-water; m. p. 82.5°C (lit. 83°C). Commercial pure picric acid was recrystallized three times from water; m. p. 122.6°C (lit. 122.5°C). Commercial guaranteed ethanol and acetone were fractionally distilled after usual treatments. The spectra of the solutions were measured with a Hitachi EPU-2 spectrophotometer at room temperature. Path length of absorption celles was 1 cm.

Results and Discussion

Absorption Spectra of the Red-Colored Solution in Water Containing a Small Quantity of Ethanol. — The orange aqueous solution of picryl chloride was made by pipetting 1 cc. of an aqueous sodium hydroxide solution and 5 cc. of ethanol into 1 cc. of a paleyellow ethanolic solution of picryl chloride and diluting the solution with water to 25 cc. The orange solution changed into a paleyellow solution by addition of a dilute aqueous solution of hydrochloric acid immediately after the preparation. When it was allowed to stand at room temperature, the orange solution changed gradually into a yellow solution. The spectra of the orange solution are shown in Fig. 1. Picryl chloride in water, in ethanol and in acetone dose not show an absorption maximum in a range of wavelengths from 300 mμ to 600 mμ[1]. The orange solution gives absorption bands at about 360, 416 and 490 mμ immediately after the preparation, but an only intense absorption band at about 397 mμ when the solution is allowed to stand at room temperature for more than six hours.

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[1] T. Abe, This Bulletin, 32, 339 (1959).

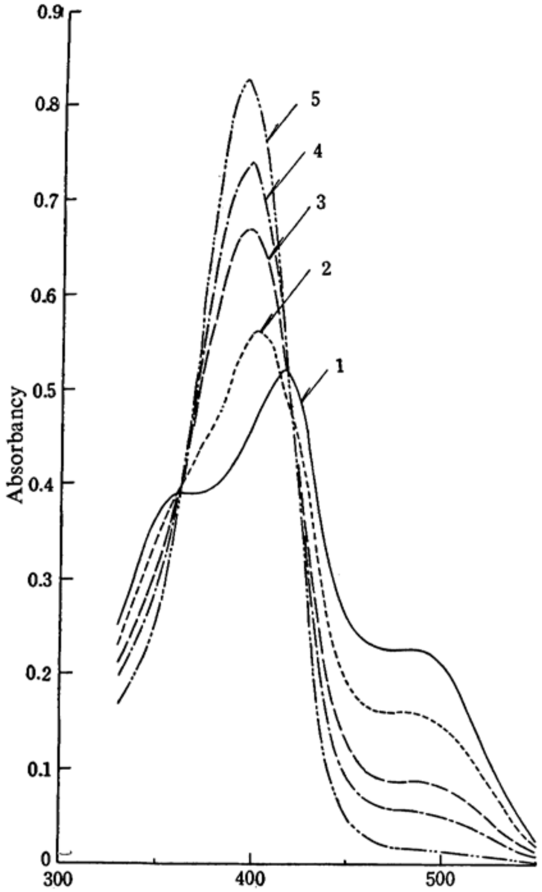

Fig. 1. Absorption spectra of picryl chloride (3.15×10^{-5} mol.) in water containing ethanol (24% by volume) in the presence of sodium hydroxide (0.377 N) at room temperature.
1 immediately after the preparation,
2 after 2.5 hr.,
3 after 6 hr.,
4 after 9 hr.,
5 after 20 hr.

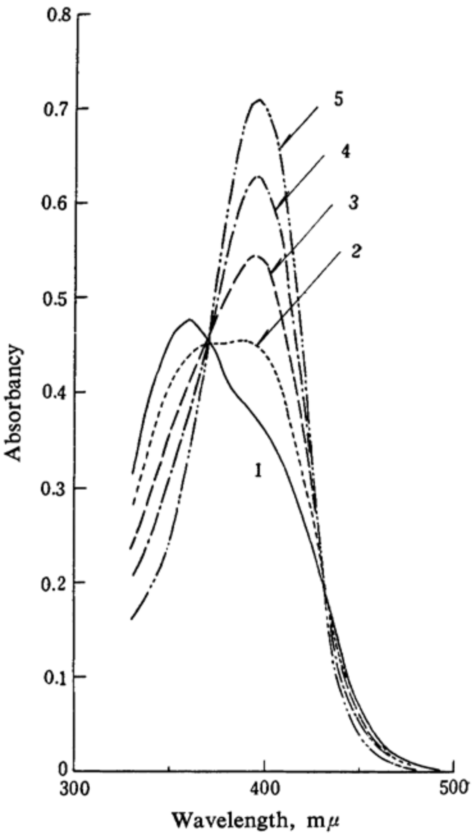

Fig. 2. Absorption spectra of picric acid (3.12×10^{-5} mol.) in water containing ethanol (24% by volume) in the presence of sodium hydroxide (0.377 N) at room temperature.
1 immediately after the preparation,
2 after 2 hr.,
3 after 5 hr.,
4 after 9 hr.,
5 after 20 hr.

Spectra of a solution of picric acid under the same condition in which the orange aqueous solution of picryl chloride was prepared, are indicated in Fig. 2. The solution of picric acid shows absorption bands at about 360 and 400 mμ, due to picrate anion, immediately after the preparation. However, when it is allowed to stand for many hours, the solution gives a 396 mμ band similar to the absorption curves 3-5 in Fig. 1. On addition of an aqueous hydrochloric acid solution, the 396 mμ band of the solution of picric acid disappears, as indicated in Fig. 3. Neither a spectrum of an aqueous picric acid solution (3.12×10^{-5} mol.) only in the presence of sodium hydroxide of 0.377 N nor a spectrum of an aqueous picric acid solution (3.12×10^{-5} mol.) containing only 24% ethanol by volume changed at all, although the solutions were allowed to stand at room temperature for more than ten hours. The intense 396 mμ bands in Fig. 2 closely resemble those of aqueous concentrated sodium hydroxide solutions of picric acid[2]. Both of the latter also disappeared when hydrochloric acid was added to the solutions. Accordingly, the 396 mμ bands in Fig. 2 may be due to a complex between picric acid and sodium hydroxide.

From the above results, the 397 mμ band of the solution in Fig. 1 can be considered to be due to picric acid produced from picryl chloride, in water containing both ethanol and sodium hydroxide. The 360 mμ band of the absorption curve 1 in Fig. 1 appears to be

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[2] T. Abe, *Nature*. **187**, 234 (1960).

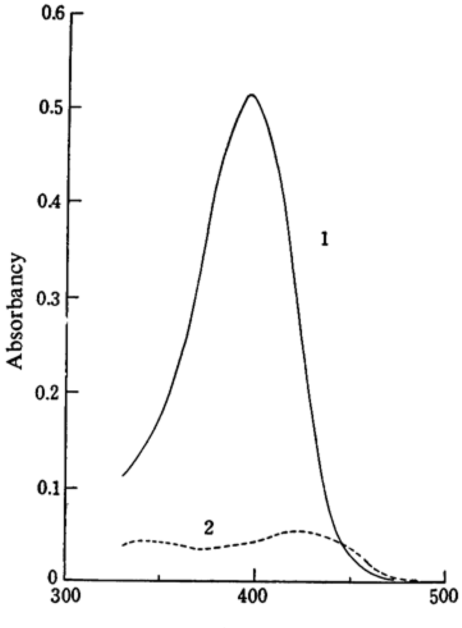
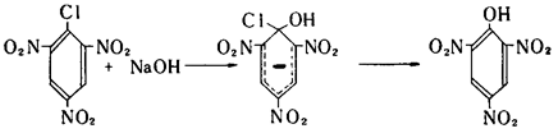


Fig. 3. Absorption spectra of solutions obtained by adding 2 cc. of water and 2 cc. of an aqueous hydrochloric acid solution (6.24 N), respectively, to 5 cc. of the solution of Fig. 2, stood for 25 hr.
1 water,
2 hydrochloric acid.

due to picric acid that changes later into the complex giving the 397 mμ band. Therefore, the 416 and 490 mμ bands of the curve 1 in Fig. 1 can be considered to be due to an labile intermediate that appears in the process of the substitution reaction of picryl chloride (I) to picric acid (III). This intermediate may be expected to be the same addition product II of Meisenheimer's type as presented for many colored products of polynitrobenzene derivatives with alkalies[1-15].



I II III

(red-colored)

The absorption curve 1 at 416 and 490 mμ in Fig. 1 closely resembles those of red aqueous solutions of 1, 3, 5-trinitrobenzene, 2, 4, 6-trinitrotoluene and tetryl in the presence of sodium hydroxide[1,7]. The intense 416 mμ band lies at the wavelength close to that of the maximum for an aqueous solution of a red complex obtained from an acetone solution of picryl chloride in the presence of ammonia water[6].

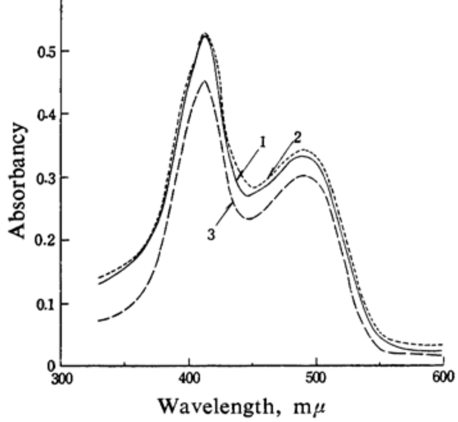


Fig. 4. Absorption spectra of picryl chloride (1.77×10^{-5} mol.) in ethanol (containing 4% water by volume) in the presence of sodium hydroxide (4.16×10^{-2} N) at room temperature.
1 immediately after the preparation,
2 after 2 hr.,
3 after 20 hr.

Absorption Spectra of the Red-Colored Solution in Ethanol.—The orange ethanolic solution of picryl chloride was made by pipetting 1 cc. of an aqueous sodium hydroxide solution into an ethanolic picryl chloride solution and diluting the solution to 25 cc. As indicated in Fig. 4, the orange ethanolic solution shows two absorption maxima at about 412 and 490 mμ close to those of the bands for the orange aqueous solution of picryl chloride. Yellow crystals began to precipitate from the orange ethanolic solution allowed to stand at room temperature for two hours. As shown in Fig. 4, the part of the solution gives the absorption maxima at the same wavelengths.

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3) J. Meisenheimer, *Ann.*, **323**, 205, 214, 241 (1902).
4) R. Foster and D. LL. Hammick, *J. Chem. Soc.*, **1954**, 2153; R. Foster, *Nature*, **176**, 746 (1955); **183**, 1042 (1959).
5) J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, **1956**, 2528.
6) T. Abe, This Bulletin, **32**, 997 (1959).
7) T. Abe, ibid., **33**, 41 (1960).
8) R. C. Farmer, *J. Chem. Soc.*, **1959**, 3425.
9) R. C. Farmer, ibid., **1959**, 3430, 3433.
10) M. Kimura, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **73**, 1219 (1953); M. Kimura and M. Thoma, ibid., **78**, 1401 (1958).
11) M. Kimura, *Pharm. Bull.* (*Japan*), **3**, 75 (1955).
12) M. Akatsuka, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **80**, 378, 384, 390 (1960).
13) S. Nagakura, S. Oosawa and H. Tsubomura, presented at the Symposium on Electronic States of Molecules, Kyoto, October, 1958.
14) S. Nagakura and S. Oosawa, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.
15) S. Nagakura and S. Oosawa, presented at the 13th same Meeting, Tokyo, April, 1960.

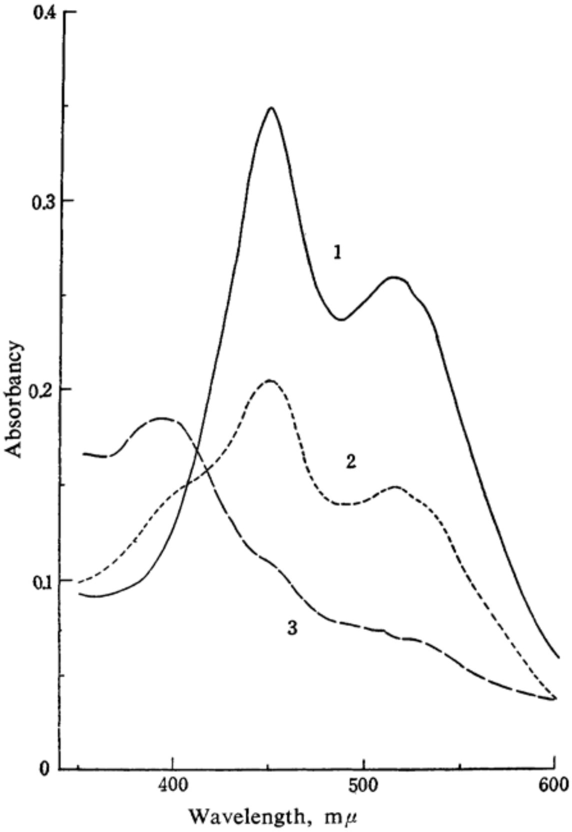


Fig. 5. Absorption spectra of picryl chloride (1.73×10^{-5} mol.) in acetone (containing 4% water by volume) in the presence of sodium hydroxide (4.16×10^{-2} N) at room temperature.
1 immediately after the preparation,
2 after 1 hr.,
3 after 3 hr.

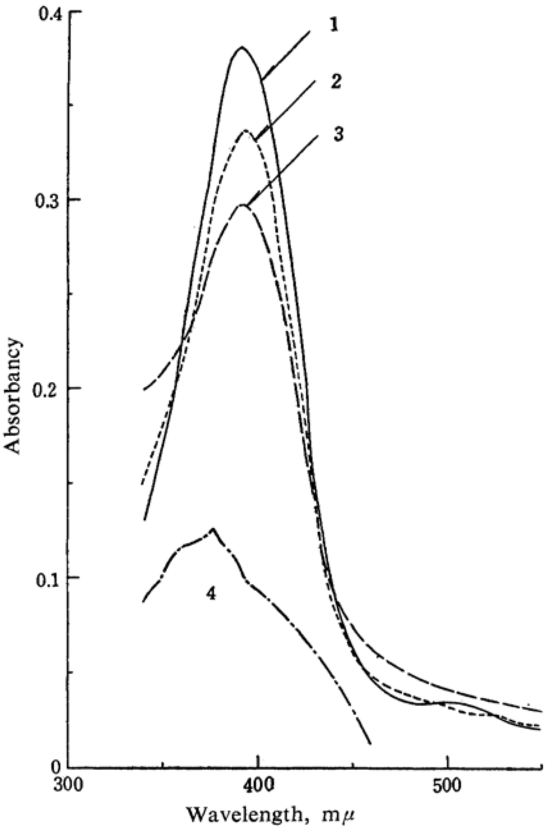


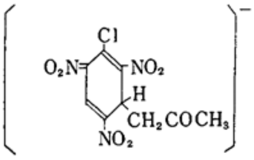
Fig. 6. Absorption spectra of picric acid (1.81×10^{-5} mol.) in acetone (containing 4% water by volume) in the presence of sodium hydroxide (4.16×10^{-2} N) at room temperature.
1 immediately after the preparation,
2 after 1 hr.,
3 after 3 hr.,
4 a solution of picric acid (1.81×10^{-5} mol.) in acetone.

It was reported by Farmer[8] that on treatment of picryl chloride with methanolic potash, Meisenheimer's anion of [Picryl chloride·OCH_3]$^-$ was produced. It was reported by Nagakura and Oosawa[15] that when methoxide ion was added to a methanolic solution of chloro-dinitrobenzene, a red color appeared immediately and soon disappeared, and that chloro-dinitrobenzene was almost completely converted into dinitroanisole. The visible absorption curves in Fig. 4 would be due to Meisenheimer's product II. These absorption curves do not resemble that (showing an intense absorption band at about 425 mμ) of an ethanolic solution of the red complex obtained from the acetone solution of picryl chloride in the presence of ammonia water[6].

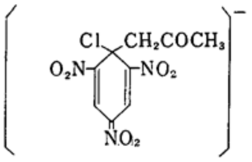
Absorption Spectra of the Red-Colored Solution in Acetone.—The reddishorange solution of picryl chloride in acetone was made by pipetting 1 cc. of an aqueous sodium hydroxide solution into an acetone solution of picryl chloride and diluting the solution to 25 cc. As indicated in Fig. 5, the reddishorange solution gives two absorption maximum bands at longer wavelengths of about 450 and 515 mμ, as compared with the orange aqueous solution in Fig. 1 and the orange ethanolic solution in Fig. 4. When allowed to stand, the reddishorange solution gradually changed into a decolorized solution giving a band at about 390 mμ. About three hours after the preparation the reddishorange solution became turbid. The spectra of the solution could not, therefore, be measured after that time.

Spectra of a solution of picric acid under the same condition as when the reddishorange solution was prepared, are indicated in Fig. 6. The solution of picric acid showed an intence band at about 390 mμ immediately after the preparation and also became turbid after about three hours. Absorbancy of the 390 mμ band decreases as the solution is allowed to stand.

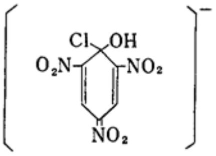
Kimura[11] reported that picryl chloride in a mixture of acetone and methanol (50% by volume) gave an intense 450 mμ band and weak 520∼530 mμ ones, and stated that the following four products were responsible for the color, where the product IV was predominant.



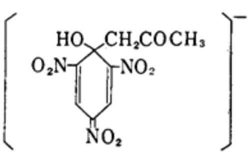
IV



V



VI



VII

The color reactions of trinitrobenzene derivatives with alkalies, however, occur instantaneously at room temperature even in the absence of acetone[1-9,13-15]. The absorption curve 1 in Fig. 5 closely resembles that of 1 in Fig. 1. In addition, the 360 mμ band of the absorption curve 3 in Fig. 5 seems to be due to picric acid produced in comparison with the absorption curves 1-3 in Fig. 6. Accordingly, the curve 1 in Fig. 5 would be due to the product II described above.

The curve (1) in Fig. 5 closely resembles that of a red solution prepared by adding a drop of aqueous sodium hydroxide solution to 1, 3, 5-trinitrobenzene in acetone[16].

Summary

The red solution prepared by adding sodium hydroxide to an aqueous picryl chloride solution containing a small quantity of ethanol, was relatively stable even at room temperature. The red solution showing the two bands at about 416 and 490 mμ, changed into the yellow solution showing the band similar to that of picric acid under the same condition. Accordingly, the 416 and 490 mμ bands may be due to the intermediate of Meisenheimer's type in the process of the substitution reaction of picryl chloride to picric acid.

In the presence of sodium hydroxide, picryl chloride in ethanol as well as in acetone finally gave the absorption bands analogous to that of picric acid in water containing ethanol. The red solutions in ethanol and in acetone, therefore, would be due to the same intermediate.

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[16] T. Abe, This Bulletin, 32, 778 (1959).