Visible Absorption Spectra of Colored Solutions Produced by Adding Alkali to Nitro-, Dinitro-, and Trinitro-substituted Benzenes in Acetone

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In the course of my visible absorption studies on the color reactions of polynitrobenzenes with alkali, it has been found that nitrobenzene, *o*-, *m*-, and *p*-dinitrobenzene, and 1,3,5-trinitrobenzene, all in acetone give intense absorption bands at the visible region when they are treated with a few drops of dilute aqueous solution of sodium hydroxide at room temperature, as shown in Fig. 1. Dinitrobenzenes slowly yield reddish-violet colors. Trinitrobenzene at once gives a red color, while a red color can be observed by standing the nitrobenzene solution containing sodium hydroxide (in a brown desiccator to avoid light) for a long time. These red colors show the maximum

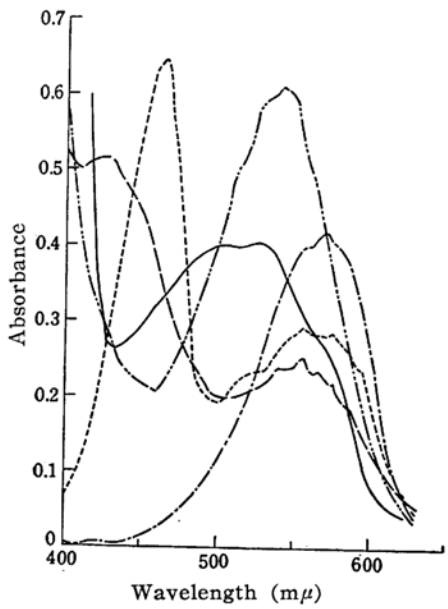

Fig. 1. Absorption spectra of the colored solutions produced by adding a few drops of dilute sodium hydroxide solution to nitrobenzene (——), *o*-dinitrobenzene(—·—), *m*-dinitrobenzene (—··—), *p*-dinitrobenzene (—···—), and 1,3,5-trinitrobenzene (----), in acetone at room temperature.

absorption bands at longer wavelengths as compared with the maximum absorption bands observed for the solutions that are obtained by adding sodium hydroxide into aqueous solutions of polynitrobenzenes[1]. There is no simple relation between numbers of nitro group and the positions of the absorption maxima, although the aromatic nitro compounds show the absorption bands at longer wavelengths in the aqueous solutions of sodium hydroxide as the number of nitro group increases[1].

The absorption curve of the red-colored solution produced by treating trinitrobenzene in acetone with sodium hydroxide solution, giving the intense maximum absorption band at about 460 mμ and several bands at 510~590 mμ, is greatly different from that of the red complex of trinitrobenzene with ammonium hydroxide[2]. Fig. 2 shows the absorption curves of the red solutions produced by adding a few drops of dilute sodium hydroxide solution, of dilute calcium hydroxide solution, or of concentrated ammonia water into the acetone solutions of 1,3,5-trinitrobenzene. It may be known from Fig. 2 that the absorption curves of the colored solutions produced by treating with strong alkalies (sodium hydroxide and calcium hydroxide) is different from that of the red solution obtained by addition of a weak alkali (ammonia). The maximum absorption band of the red complex of trinitrobenzene with ammonium hydroxide lies at the longer wavelength in acetone than in ethanol and in water[2].

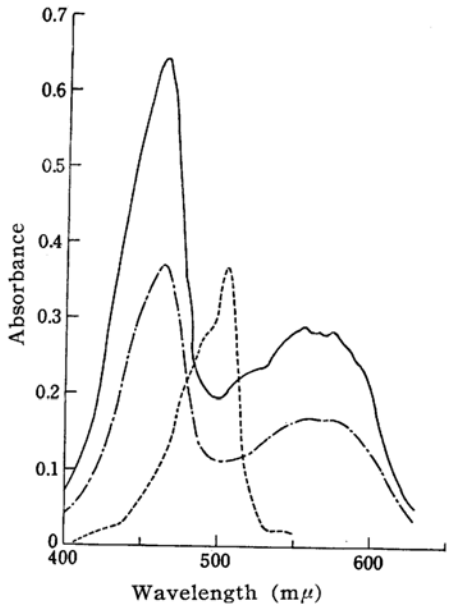

Fig. 2. Absorption spectra of the colored solutions produced by adding a few drops of dilute sodium hydroxide solution (——), of dilute calcium hydroxide solution (—·—), and of concentrated ammonia water (----) to 1,3,5-trinitrobenzene in acetone at room temperature.

Although weak alkali and strong alkali give different absorption curves, all the above red colors seems possibly to be owing to formation of the same transition complexes of Meisenheimer's type as the intermediates presented for the color reactions of trinitrobenzenes and dinitrobenzens with alkalies[1-8].

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