Visible Absorption Spectra of 1, 3, 5-Trinitrobenzene and its Derivatives in Aqueous Alkaline Acetone

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In a previous short communication¹⁾ it was reported that when an acetone solution of 1, 3, 5-trinitrobenzene was treated with aqueous sodium hydroxide intense 460 and weak 510~590 mμ bands appeared and when ammonia water was applied an intense 505 mμ band came out. In the present work, the same spectroscopic investigation has been made on similar reactions of aqueous sodium hydroxide and of aqueous ammonia with 1, 3, 5-trinitrobenzene derivatives of 1, 3, 5-trinitrobenzene, 2, 4, 6-trinitrotoluene, tetryl (2, 4, 6-trinitrophenylmethylnitramine) and picryl chloride, in acetone.

Expermental

Commercial extra pure grade trinitro compounds and commercial grade acetone were purified by the same methods as in the previous paper²⁾. Sodium hydroxide and ammonia water (ca. 28%) of commercial grade were used without further purification. Each colored solution was made pipetting 1 cc. of an aqueous alkaline solution into 1 cc. of acetone solution of each trinitro compound and diluting the resulting solutions with acetone to 25 cc. Spectra of all the colored solutions were measured, using a Hitachi EPU-2 spectrophotometer at room temperature. The length of the absorption cells was 1 cm.

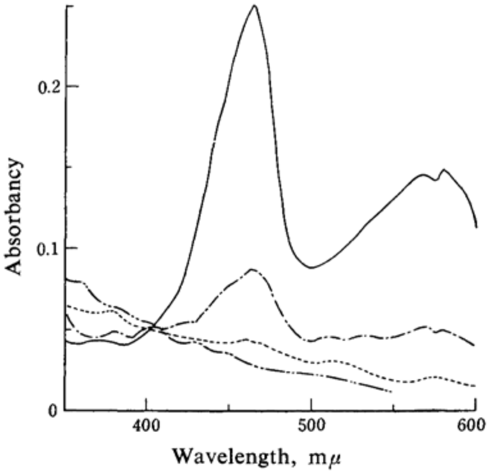

Fig. 1. Absorption spectra of 1,3,5-trinitrobenzene (1.06×10^{-5} M) in acetone (containing 4% water by volume) in the presence of sodium hydroxide (4.16×10^{-2} N) at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 2 hr.
4 —··— After 5 hr.

Results and Discussion

Absorption Spectra of the Trinitro Compounds in Aqueous Acetone Containing Sodium Hydroxide (Figs. 1-4).—When dilute aqueous solutions of sodium hydroxide are added, all the

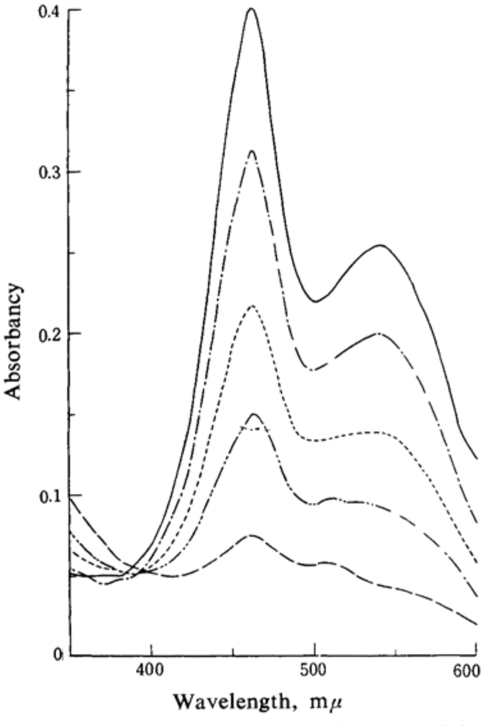

Fig. 2. Absorption spectra of 2,4,6-trinitrotoluene (1.68×10^{-5} M) in acetone (containing 4% water by volume) in the presence of sodium hydroxide (4.16×10^{-2} N) at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 2 hr.
4 —··— After 3 hr.
5 — — — After 5 hr.

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1) T. Abe, This Bulletin, 32, 778 (1959).
2) T. Abe, ibid., 32, 339 (1959).

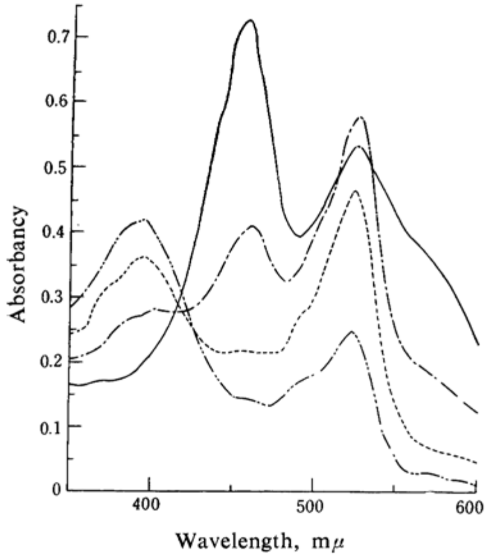


Fig. 3. Absorption spectra of tetryl (3.95×10^{-5} M) in acetone (containing 4% water by volume) in the presence of sodium hydroxide (4.16×10^{-2} N) at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 2 hr.
4 —··— After 4 hr.

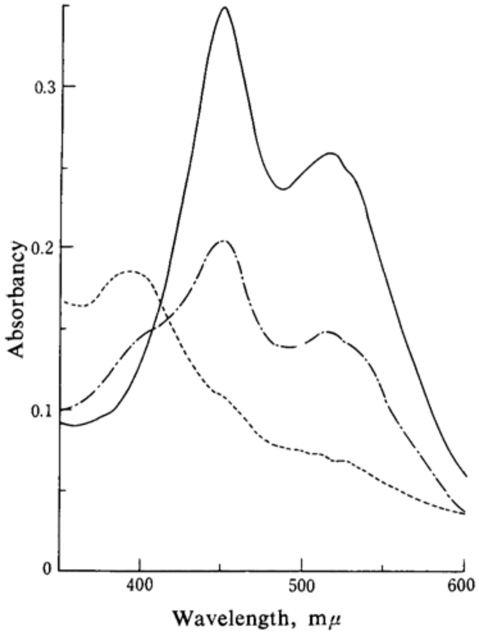


Fig. 4. Absorption spectra of picryl chloride (1.73×10^{-5} M) in acetone (containing 4% water by volume) in the presence of sodium hydroxide (4.16×10^{-2} N) at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 3 hr.

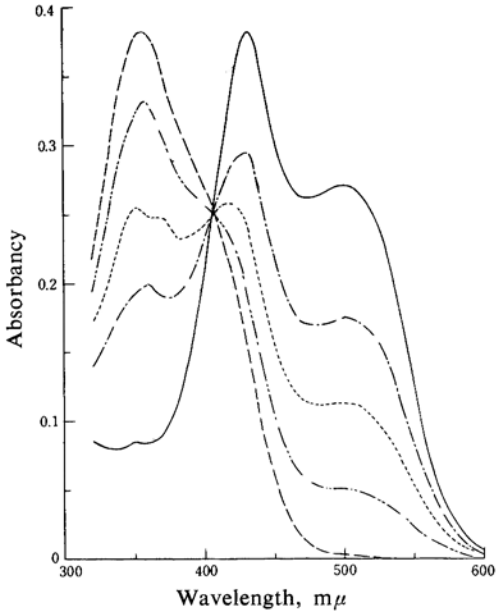
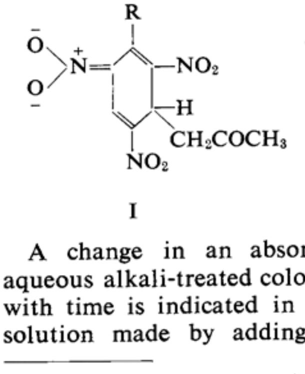


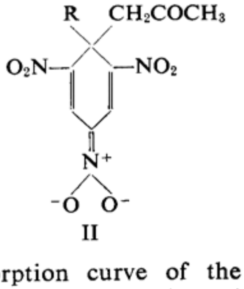
Fig. 5. Absorption spectra of tetryl in water containing sodium hydroxide at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 2 hr.
4 —··— After 4 hr.
5 ——— After a day

acetone solutions of these trinitro compounds initially show similar absorption curves 1. The analogy among the absorption curves 1 in Figs. 1–4 is not in perfect accord with Kimura's results³⁾. He reported that a spectral pattern of a colored solution produced by treating trinitrobenzene with sodium hydroxide in a mixture of acetone and methanol (50% by volume) was different from patterns similarly made from trinitrotoluene and picryl chloride, and that the former was due to structure I while the latter ones were due to both structures I (mainly) and II.



I



II

A change in an absorption curve of the aqueous alkali-treated colored solution of tetryl with time is indicated in Fig. 5. The colored solution made by adding a drop of aqueous

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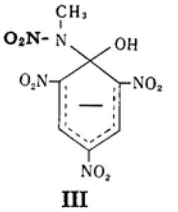
3) M. Kimura, *Pharm. Bull. (Japan)*, 3, 75 (1955).

sodium hydroxide solution (1 N) to a dilute aqueous solution of tetryl is decolorized at the highest measurable rate at room temperature among those of the four trinitro compounds. The decolorized solution shows an absorption curve 5 similar to that of picrate anion. It is well known that tetryl reacts with aqueous alkali to form picrate. Accordingly, as mentioned in the previous paper[2], a curve in Fig. 5 is expected to be due to Meisenheimer's intermediate III in the process of substitution reaction of tetryl to picric acid.



III

Recently such Meisenheimer's intermediates have been presented for many colored products of polynitrobenzene derivatives with alkalies*. From the close similarity of the absorption curves 1 in Figs. 1–4 with that 1 in Fig. 5 it seems likely that the curves 1 in Figs. 1–4 do not correspond to products such as I or II but do to such Meisenheimer's type complexes, III, formed between the trinitro compounds and sodium hydroxide.

When the colored solutions for Figs. 1–4 are allowed to stand for several hours, they become turbid. Their spectra can not, therefore, be measured thereafter. Figs. 3 and 4 suggest that both the colored species from tetryl and picryl chloride are gradually converted into a substance giving an absorption band at about 390 mμ. Picric acid in acetone also gives an absorption band at the same region in the presence of sodium hydroxide[4]. Accordingly, the colored species from tetryl and picryl chloride in acetone as well as in water are probably converted mainly into picric acid. On the other hand, the colored solutions of trinitrobenzene and trinitrotoluene do not have distinct bands at about 390 mμ even after decoloration, as indicated in Figs. 1 and 2. Therefore, those from trinitrobenzene and trinitrotoluene would undergo further complicated reactions like the reaction of trinitrobenzene with sodium carbonate in methanol, finally giving 3, 5-dinitroanisole through the formation of the Meisenheimer's intermediate[5].

Absorption Spectra of the Trinitro Compounds in Acetone Containing Ammonia Water (Figs. 6-9).—Figs. 6–9 show that colored solutions initially produced by additions of ammonia water to the acetone solutions of the trinitro compounds give absorption curves 1 similar to these for the colored solutions obtained by

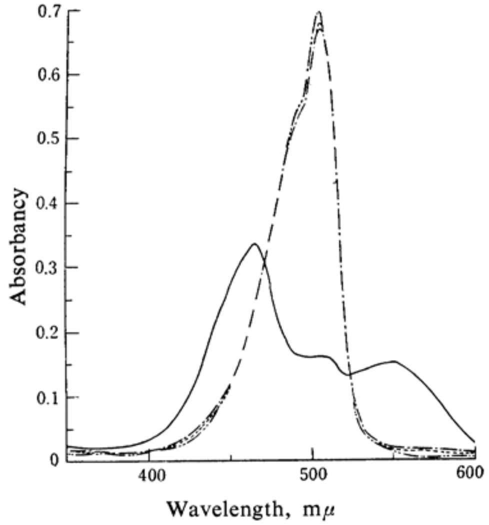


Fig. 6. Absorption spectra of 1,3,5-trinitrobenzene (1.23×10^{-5} M) in acetone (containing 4% water by volume) in the presence of ammonia (1.2%) at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 3 hr.
4 —··— After a day

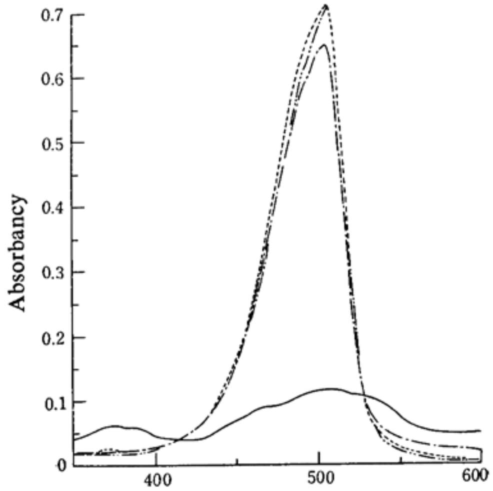


Fig. 7. Absorption spectra of 2,4,6-trinitrotoluene (1.68×10^{-5} M) in acetone (containing 4% water by volume) in the presence of ammonia (1.2%) at room temperature.

1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 3 hr.
4 —··— After a day

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* For example, see Ref. 4.

[4] T. Abe, This Bulletin, 34, 21 (1961).

[5] P. T. Izzo, *J. Org. Chem.*, 24, 2026 (1959).

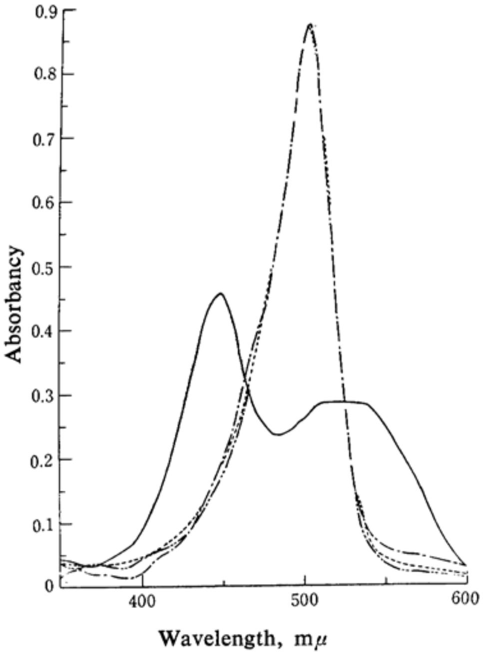

Fig. 8. Absorption spectra of tetryl (2.00×10^{-5} M) in acetone (containing 4% water by volume) in the presence of ammonia (1.2%) at room temperature.
1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 3 hr.
4 —··— After a day

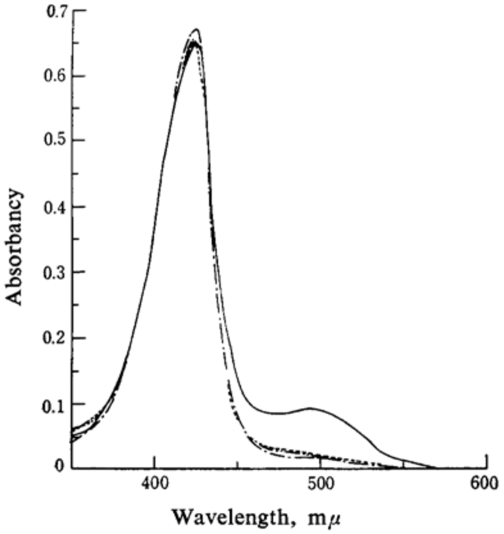

Fig. 9. Absorption spectra of picryl chloride (1.65×10^{-5} M) in acetone (containing 4% water by volume) in the presence of ammonia (1.2%) at room temperature.
1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 3 hr.
4 —··— After a day

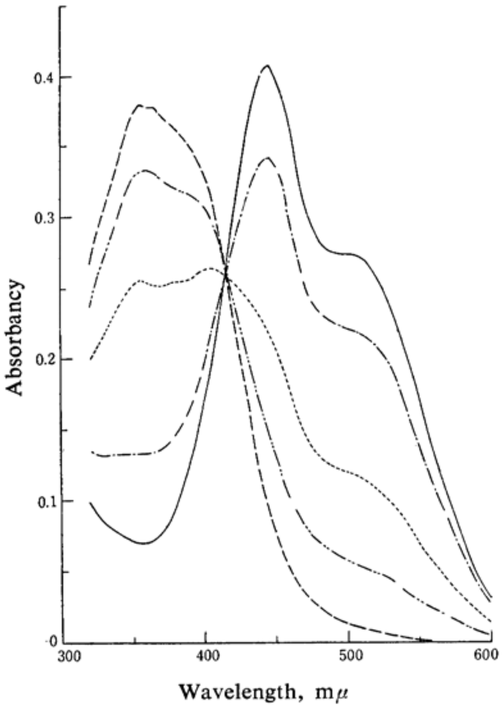

Fig. 10. Absorption spectra of tetryl in water containing ammonia at room temperature.
1 ——— Immediately after the preparation
2 —·—· After 1 hr.
3 ------ After 4 hr.
4 —··— After 8 hr.
5 ——— After a day

the addition of sodium hydroxide, except in the case of the solution from trinitrotoluene, and that the initially produced colored solutions change to the other solutions having different stable intense bands. The absorption curve 1 in Fig. 7 is the only one which does not correspond to the curve 1 in Fig. 2, but does to the curve[6,7] for a colored solution formed from trinitrotoluene in ethanol by the action of sodium ethoxide. Caldin et al.[6,7] have suggested a proton-transfer reaction. Miller and Wynne-Jones[8] also observed that a mixture of trinitrobenzene with diethylamine in acetone or in ethanol produced at first an intensely colored solution having absorption maxima at 470, 515 and 570 mμ and that the solution changed after a considerable period to that having an absorption band only at 515 mμ.

One can see from Fig. 10 that both ammonia water and sodium hydroxide react identically

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

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

[8] R. E. Miller and W. F. K. Wynne-Jones, ibid.. **1959**, 2375.

with tetryl in water. From the similarity of the absorption curves 1 in Figs. 1–5 and 10, the absorption curves 1 in Figs. 6, 8 and 9 are perhaps due to the colored intermediates such as III, except for the case of trinitrotoluene. These initially formed colored intermediates may further react to produce a stable colored species giving the final absorption curves 4 in Figs. 6–9. The stable colored species were provisionally considered to be Meisenheimer's intermediates in the previous paper⁹⁾. However, it has not yet been proved that the stable colored species are converted further into picric acid. Therefore, at present one can not conclude that they are the Meisenheimer's intermediates. Kimura¹⁰⁾ reported that a darkish purple substance obtained by adding sodium bicarbonate to the acetone solution of trinitrobenzene was a product similar to II.

Summary

The visible absorption spectra of the colored solutions produced by adding aqueous sodium hydroxide solution or ammonia water to the acetone solutions of 1, 3, 5-trinitrobenzene and its derivatives (2, 4, 6-trinitrotoluene, tetryl and picryl chloride) were measured at room temperature in order to investigate the difference of the chemical actions between stong-alkaline sodium hydroxide and weak-alkaline ammonia water.

These trinitro compounds in acetone containing sodium hydroxide show spectra similar to that of the aqueous sodium hydroxide solution of tetryl. The spectrum of this aqueous colored solution is considered to be due to an intermediate of the Meisenheimer type in the process of the substitution reaction of tetryl to picric acid. Consequently, all the spectra of the colored solutions from the trinitro componds are also probably due to the intermediates of the Meisenheimer type.

Each colored solution of the trinitro compounds in acetone containing ammonia water initially shows the same spectrum as that with sodium hydroxide, except for the case of trinitrotoluene, and changes to the other colored solution having an intense and stable band entirely different from the initial spectrum. The initially formed colored solutions of these trinitro compounds, except the solution from trinitrotoluene, may also be due to the Meisenheimer intermediates.

The author is particularly indebted to Professor Yōkan Nomura for helpful discussions.

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9) T. Abe, This Bulletin, 32, 997 (1959).

10) M. Kimura, *J. Pharm. Soc Japan* (*Yakugaku Zasshi*), 73, 1219 (1953).