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14. **Michiya Kimura**: Reaction between Polynitrobenzene and Active Methylene Groups. IV.[1] Reaction between 1-Substituted 2,4,6-Trinitrobenzene and Acetone.

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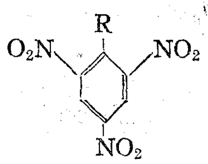
In the previous paper[1] it was shown that the colored substances obtained from *sym*-trinitrobenzene and methyl ketones in alkaline medium were isolated in a pure state and their chemical structures had been elucidated. In the present paper, the product and the reaction mechanisms of 1-substituted *sym*-trinitrobenzenes with acetone are discussed.

The substituted trinitrobenzenes employed in this study were picric acid, picryl chloride, phenyl picrate, trinitroanisole, trinitrophenethole, trinitrotoluene, trinitrobenzoic acid, ethyl trinitrobenzoate, picramide, picryl benzoate, picrylaniline, diethylpicramide, β-picrylethanol, and β-picrylethyl acetate. Acetone was used as the active methylene agent as well as a solvent in the reaction.

Table I. Maximum Absorptions of the Color Reaction between 1-R-2,4,6-Trinitrobenzene and Acetone in Alkaline Medium



R	λ_{max} I (mμ)	λ_{max} II (mμ)	Type
H	465	560	A
OC_6H_5	445	530	〃
COOH	465	535	〃
$COOC_2H_5$	460	555	〃
OH	410	485	B
OCH_3	445	500～520	〃
OC_2H_5	445	500～520	〃
Cl	450	520～530	〃
CH_3	460	500～530	〃
CH_2CH_2OH	465	520～540	〃
$CH_2CH_2OCOCH_3$	465	500～530	〃
NH_2	430(?)	—	
NHC_6H_5	faint coloration		
$N(C_2H_5)_2$	425(?)	—	
$OCOC_6H_5$	no maximum in the visible range		

Wave lengths at absorption maxima of each of the colored solution obtained from these substituted trinitrobenzenes and acetone are shown in Table I. Almost the same results were obtained when the measurements were carried out with the colored compounds which were separated from the solutions by paper chromatography employing 5% aq. sodium sulfate solution as the developer and by the subsequent elution with

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[1] M. Kimura: J. Pharm. Soc. Japan, **73**, 1219(1953).

dilute methanol. They give characteristic spectra having two absorption maxima in the visible range. The shape of spectra might be divided into two types, type A and type B, the latter having less distinct absorption in the second maximum, as shown in Fig. 1.

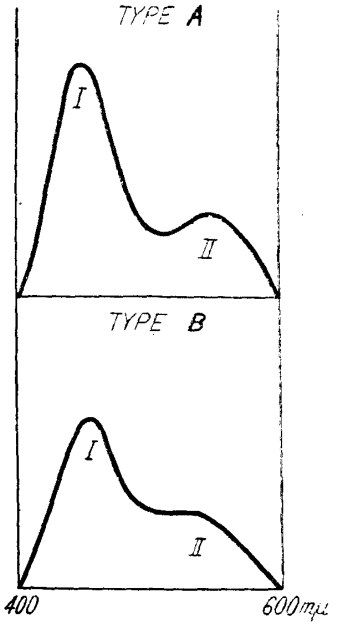
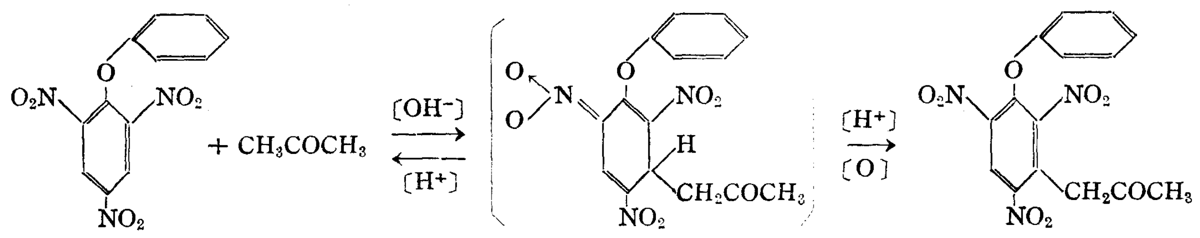


Fig. 1.

Absorption Curves of the Color Reaction between 1-R-2,4,6-Trinitrobenzene and Acetone in Alkaline Medium

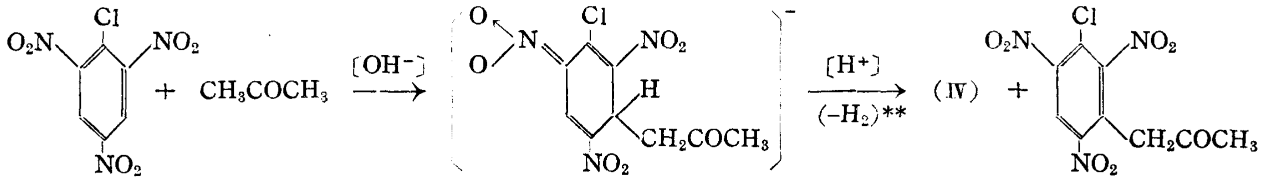
Phenyl picrate (I) and picryl chloride (IV), which give the absorption of type A and B, respectively, were taken as examples for studying the color reaction with acetone. Both of the colored substances from the above reagents and acetone were not isolated in a pure state but only in amorphous form owing to their hygroscopic and unstable properties. They are freely soluble in water, alcohol, and acetone, hardly soluble in less polar solvents such as benzene and ether, and are rather stable in neutral or weak alkaline medium. The paper chromatography of the substances gave only a single spot, accompanying another faint spot only in the case of far larger amount of the sample used, so they seemed to be pure enough for the present study.

The colored substance derived from phenyl picrate decomposes instantly into the parent substances in yield of ca. 70% of the theoretical amount, when it is treated with mineral acids. In the presence of some hydrogen peroxide the acidified solution does not give any phenyl picrate, but a colorless crystalline compound of m.p. 154.5° (corr.). This substance is easily soluble in benzene and acetone, slightly in ethanol. It colors gradually on standing to dark violet and by alkaline solution to red, finally to brown. The paper chromatography gives a single orange-colored spot at Rf 0.4 by using 1% aq. potassium hydroxide solution as the developer. It gives a *p*-nitrophenylhydrazone of m.p. 198~199°(decomp.) and an oxime of m.p. 178°(decomp.). The analytical data well coincide with the structure (III). The reaction process would reasonably be indicated as follows :



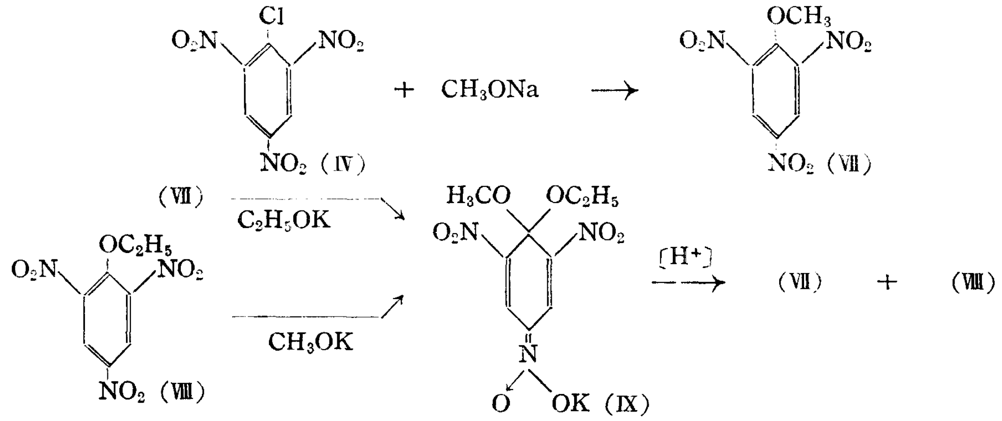
(I) m.p. 156°   (II)   (III) m.p. 154°

In the case of picryl chloride the reaction seems not so simple as that of phenyl picrate or trinitrobenzene.1) For the coloration of the reaction mixture it was necessary to add some amount of water or ethanol to the alkaline solution, from which a muddy precipitation of sodium chloride separated, while in the control test without acetone no chloride ion was detected. The paper chromatography of this alkaline solution gave several spots including a main reddish brown-colored one by employing water as the developer. The reddish brown spot was extracted with acetone and the substance obtained after being acidified with hydrochloric acid was subjected again to paper chromatography using 1% aq. potassium hydroxide solution as the developer. There were separated three spots, of which the two (Rf 0.0 and 0.7) were found to be identical with those of picryl chloride and picric acid, and another one (Rf 0.6) was found to be the anticipated condensation product (VI) as described below. It is worthy of note that, besides the above three substances, the existence of picrylacetone (XIII) was observed by its characteristic property during the process of development of chromatography.* The condensation product, m.p. 116~118°, gives reddish brown coloration with alkali and still possesses a chlorine atom, and its structure coincided with that of chloropicrylacetone, possibly the formula (VI). The yield of the product remained unchanged even in the presence of hydrogen peroxide. The principal reaction process would be presented as follows :



(IV) m.p. 83° (V) (VI) m.p. 116~118°

It has been known that picryl chloride transforms easily into methyl picrate (VII) in the presence of sodium methoxide,2) and methyl picrate is able to transform into ethyl picrate (VIII) by potassium ethoxide3) :



Consequently, it is not surprising that in the reaction of picryl chloride and acetone in alkaline medium, picrylacetone (XIII) and picric acid (XIV) are formed, by the following processes :

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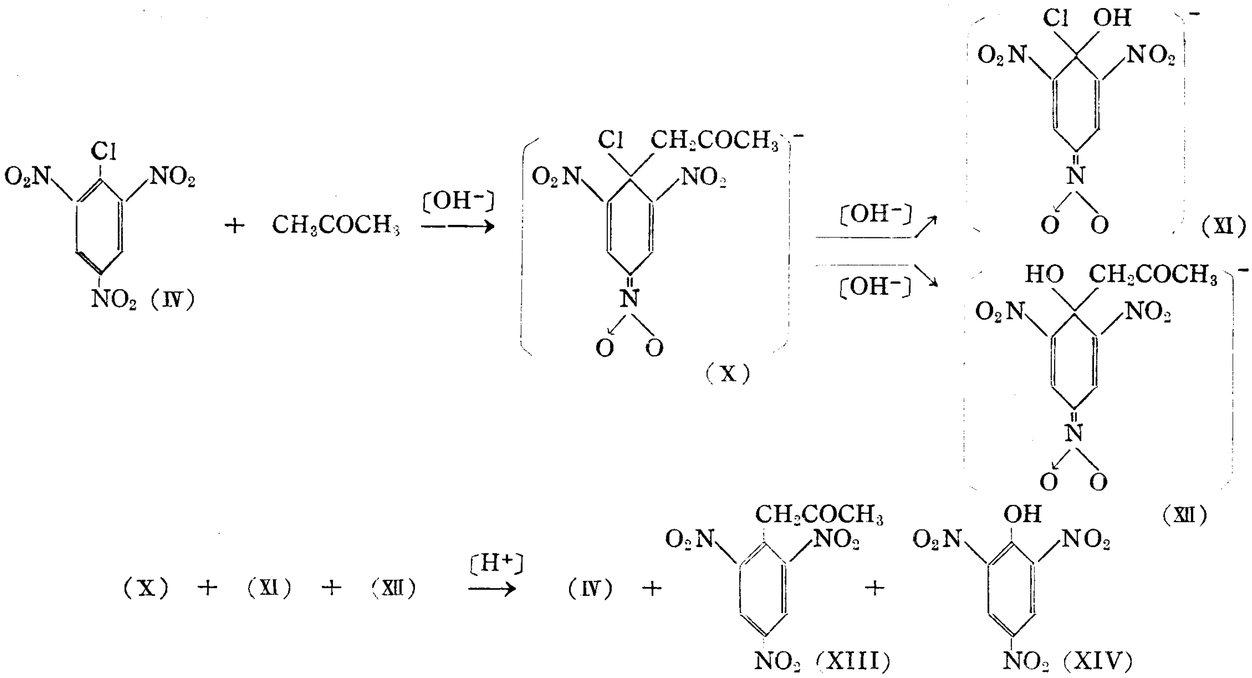
* In the paper chromatography, using 1% aq. potassium hydroxide as the developer, of the mother solution from which picryl chloride and the condensation product (VI) have been separated, a red spot appeared at first and then it began gradually to fade with the development, and finally disappeared.

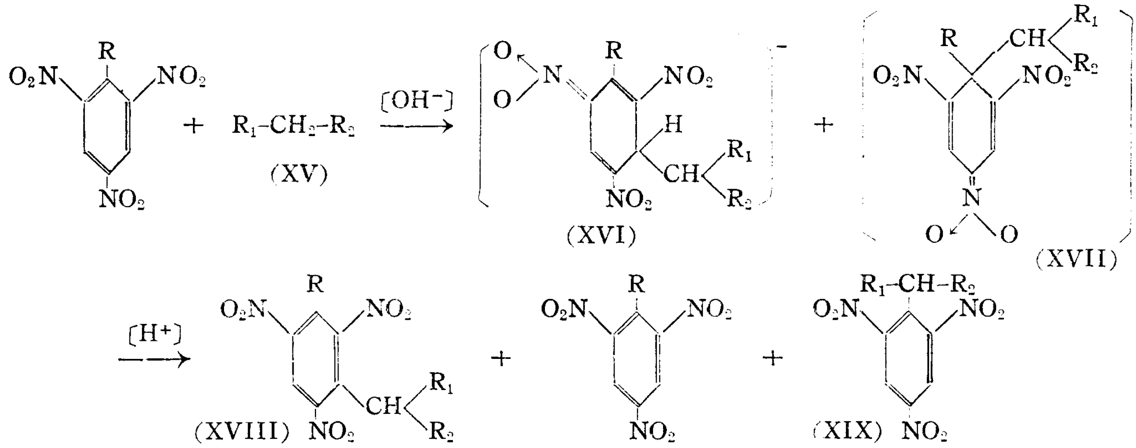
** The nitro groups may participate in this stage.

2) E. Chapman, A. G. Perkin, R. Robinson : J. Chem. Soc., **1927**, 3030.

3) J. Meisenheimer : Ann., **325**, 205(1903).



The mono-substituted *sym*-trinitrobenzenes, when they come into reaction with active methylene (XV) in alkaline medium, react in general at the two positions and the compounds of type A are considered to form addition product principally at 3-position (XVI), while the compounds of type B give both products at 1-(XVII) and 3-positions (XVI) (mainly). The relative tendency towards the formation of an adduct apparently depends on electromeric effect of the R residues, partly on the character of carbeniate ion of the active methylene groups employed in the reaction.



It should be emphasized again that the strong coloration of the reaction is attributed to the intermediate products of the quinoid forms (XVI and XVII), not to the final products of (XVIII) and (XIX), or their anions formed.

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Experimental*

***sym*-Trinitrobenzene Compounds**—Picric acid : Recrystallized from aq. EtOH, m.p. 122°.

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* All melting points are not corrected.

Picryl chloride: Prepared by the chlorination of picric acid with PCl_5, m.p. 83°(from EtOH).

Phenyl picrate[4]: Prepared in the aqueous solution of PhONa by adding picryl chloride, m.p. 156° (from benzene–EtOH).

Trinitroanisole: Prepared in MeOH solution of picryl chloride by adding MeONa and then acidified with dil. HCl, m.p. 67°(from MeOH).

Trinitrophenethole: Prepared in abs. EtOH solution of picryl chloride by adding EtONa and then acidified with dil. HCl, m.p. 79~80°(from EtOH).

Trinitrotoluene: Prepared by the nitration of toluene, m.p. 80°(from EtOH).

Trinitrobenzoic acid: Recrystallized from Me_2CO–benzene, m.p. 224°(decomp.).

Ethyl trinitrobenzoate: Prepared according to Sudborough,[5] m.p. 158°(from EtOH).

Picramide: Prepared according to Borsche,[6] m.p. 183°(from AcOEt).

Picrylaniline: Prepared by dropping aniline into EtOH solution of picryl chloride, m.p. 178~179° (from EtOH).

Diethylpicramide: Prepared by dropping diethylamine into EtOH solution of picryl chloride, m.p. 166°(from benzene).

Picryl benzoate: Prepered by the method of Kym,[7] m.p. 163~164°(from benzene).

β-Picrylethanol: Prepared by the method of Vender,[8] m.p. 111~112°(from benzene).

β-Picrylethylacetone: Prepared by the method of Vender,[8] m.p. 98~99°(from EtOH).

Absorption Spectrum—About 1 mg. of the trinitrobenzene compound was dissolved in 0.5 cc. of acetone, 0.5 cc. MeOH (or water if needed) and a drop of 10% aq. NaOH were added consecutively to cause color reaction. $NaHCO_3$ was employed instead of NaOH when the colored substance was unstable, and the blind solution was favorably still colorless in some cases. The solution was shaken and allowed to stand at room temperature for about 15 mins. The absorption spectrum of the colored solution obtained was measured by the Beckman Model DU spectrophotometer. In order to separate the colored substance, the paper chromatography of the colored solution was successfuly carried out as follows: A paper strip, 2 cm. × 15 cm., was developed with water or 5% aq. Na_2SO_4. After cutting off the spot so formed, which was the same in color as the reaction solution, it was extracted with 50% MeOH. The absorption spectrum was also measured with this MeOH solution.

Preparation of the Colored Substances—a) From phenyl picrate: Five g. of phenyl picrate and 5 g. anhyd. K_2CO_3 were added to 50 cc. acetone, and the mixture was stirred vigorously at about 30°. The contents gradually began to show peculiar coloration and finally became extremely dark brownish purple. After stirring about 30 hrs., the solution was filtered to separate K_2CO_3 that still remained. The filtrate was condensed under a reduced pressure and the residue was extracted several times with a small amount of benzene in order to remove unreacted phenyl picrate. Hygroscopic black substance was obtained as a semi-solid.

b) From picryl chloride: A solution of EtONa, prepared by dissolving 0.4 g. of Na in 20 cc. abs. EtOH, was carefully added dropwise during about 2 hrs. into the solution of 5 g. of picryl chloride dissolved in 10 cc. acetone, under ice-cooling. The solution was condensed under a reduced pressure and the residue was treated with a small amount of benzene to remove unreacted picryl chloride. Hygroscopic black substance was obtained.

Degradation of the Colored Substances by Mineral Acids—a) Phenyl picrate: When treated with 10% HCl to pH 1~2 and allowed to stand at ordinary temperature, the aqueous solution of the colored substance, which was dark brownish purple at the beginning, became brown and muddy. The residue so formed was recrystallized form EtOH and identified as phenyl picrate by admixture with the authentic specimen. The yield was about 70% of the theoretical.

b) Picryl chloride: By treating the solution of the colored substance similarly to (a), it became brown in color and muddy. The benzene solution obtained by extracting the acidic solution was concentrated under a reduced pressure, the residue was dissolved in a large amount of petr. ether, and was submitted to fluid chromatography through alumina. The yellow effluent was concentrated and the oily residue, recrystallized from EtOH, was recognized as picryl chloride by the melting point, Rf value, and the coloration with alkali. When there were nothing to be removed into petr. ether, then acetone was employed as the second developing agent. The residue from concentration of the acetone effluent, was recrystallized from EtOH and colorless needles, m.p. 116~118°, were obtained. 0.4 g. of picryl chloride and 1.4 g. of the compound (VI) were thus obtained from 7 g. of picryl chloride employed for the preparation of the colored substance.

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4) C. L. Jackson, R. B. Earle: Am. Chem. J., **29**, 213(1907).

5) J. J. Sudborough: J. Chem. Soc., **67**, 600(1895).

6) W. Borsche: Ber., **56**, 1939(1923).

7) O. Kym: *Ibid.*, **32**, 1428(1899).

8) V. Vender: Gazz. chim. ital., **45**, II, 97(1915).

Degradation of the Colored Substances in the Presence of Hydrogen Peroxide—a) Phenyl picrate: To the conc. aq. solution of the colored substance, 30% H_2O_2 was added to the final concentration of about 3%, and AcOH was also added to keep the solution at pH 1~2. After adding a small amount of $FeSO_4$ and stirring under cooling with ice-water, the solution became brown and muddy, which was then extracted with benzene. The benzene extract was recrystallized into colorless plates, m.p. 154°, from EtOH. 0.5 g. of this substance was obtained from 3 g. of phenyl picrate employed for the preparation of the colored substance.

b) Picryl chloride: Both picryl chloride and the compound (VI) of m.p. 116~118° always formed when treated similarly as in (a).

α-(1-Phenoxy-2,4,6-trinitrophenyl)acetone (III)—The compound of m.p. 154° described above, melted at 130~145° in the mixed fusion with the authentic phenyl picrate (m.p. 156°). It gave a *p*-nitrophenylhydrazone as yellow needles of m.p. 198~199°(decomp.), when treated in EtOH solution of *p*-nitrophenylhydrazine with AcOH on a steam bath. Oxime, faint yellow needles of m.p. 178°(decomp.), was derived when heated in EtOH solution with hydroxylamine hydrochloride for about 10 mins. on a steam bath. *Anal.* Calcd. for $C_{15}H_{11}O_8N_3$: C, 49.3; H, 3.1; N, 11.6; mol. wt., 361. Found: C, 49.9; H, 3.4; N; 12.0; mol. wt. (Rast), 325.

α-(1-Chloro-2,4,6-trinitrophenyl)acetone (VI)—m.p. 116~118°. It was inactive to the ketone reagents. It still possessed Cl atom as evidenced by the following tests: (1) The product formed by fusion with metallic Na was dissolved in water and then filtered. After boiling the aq. solution with HNO_3 for 10 mins., aq. $AgNO_3$ solution was added. The white precipitate formed, which gradually became dark on standing. (2) MeOH solution was boiled with 10% NaOH and then acidified with HNO_3. White precipitate formed on the addition of $AgNO_3$. *Anal.* Calcd. for $C_9H_6O_7N_3Cl$: C, 35.6; H, 2.0; N, 13.9; mol. wt., 303. Found: C, 36.1; H, 2.2; N, 14.2; mol. wt. (Rast), 287.

Summary

1) The absorption spectra were measured of the color reaction between each of the fourteen 1-substituted 2,4,6-trinitrobenzene compounds and acetone in the presence of alkali. The typical absorption curves are shown in Fig. 1.

2) Phenyl picrate and picryl chloride were selected from among these nitro compounds as examples. When the colored substances, formed by the reaction between each of these two compounds and acetone in alkaline medium, were acidified in the presence of hydrogen peroxide, the trinitrobenzene compounds (III) and (VI) were respectively formed. From this result, the structures (II and V) of these colored substances were determined.

3) The colored substances derived from 1-substituted 2,4,6-trinitrobenzene compounds of type A were assumed to form principally the structure of (XVI), while the compounds of type B give both structures of (XVI) (mainly) and (XVII).

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