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Mechanism of the Color Reaction of Active Methylene Compounds with 1,3,5-Trinitrobenzene Derivatives. IV.[1] Color Reaction of Picric Acid and Acetone under the Janovsky Conditions[2]

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Color reaction of picric acid with acetone in an aqueous alkaline solution under the Janovsky conditions was investigated. Two main coloring matters responsible for the observed colors were prepared separately and their chemical structures were determined as a Meisenheimer compound (I-2Na) and a bicyclic compound (II-Na), respectively, as shown in Chart 2 and 3. The correlation between the coloring matters and their roles in the reaction were discussed by comparing the spectral behavior of them with the spectral changes of the reaction mixture.

In the previous paper of this series,[4] it was shown that sodium salts of Meisenheimer type, bicyclic type and tetracyclic type anions were formed as the main coloring matters of the reaction of acetone with 1,3,5-trinitrobenzene (TNB) under the spot test procedure.[5]

Although it has been known that the colorations of picric acid and acetone in alkaline media vary with time from red-orange to yellow[6,7] and the principal reaction might be expressed by Chart 1,[6] the coloring matters responsible for the observed colors have not been isolated.

During the course of study on the mechanism of the color reaction of acetone with picric acid under the spot test procedure,[5] it was found that a bicyclic type compound was formed along with a Meisenheimer type compound.[2]

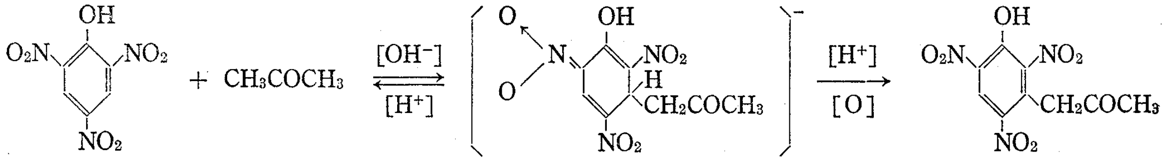

Chart 1

The present paper describes the preparations and structural characterizations of the coloring matters, the Meisenheimer type compound and the bicyclic type compound, formed in the Janovsky reaction[8] of acetone with picric acid, and discusses their roles in the reaction by comparing their absorption spectral behavior with the reaction mixture.

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1) Part III: K. Kohashi, Y. Ohkura, and T. Momose, *Chem. Pharm. Bull.* (Tokyo), 21, 118 (1973).

2) This forms "Organic Analysis LXXXVII." A part of this paper was presented at "Communications to the Editor" in T. Kabeya, K. Kohashi, Y. Ohkura, and T. Momose, *Chem. Pharm. Bull.* (Tokyo), **19**, 645 (1971). Part LXXXVI: 1).

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4) K. Kohashi, Y. Ohkura, and T. Momose, *Chem. Pharm. Bull.* (Tokyo), **18**, 2151 (1970); **19**, 2065 (1971).

5) T. Momose, Y. Ohkura, and K. Kohashi, *Chem. Pharm. Bull.* (Tokyo), **11**, 301 (1963).

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7) T. Abe, *Bull. Chem. Soc. Japan*, **34**, 21 (1960).

8) J.V. Janovsky and L. Erb, *Ber.*, **19**, 2155 (1886); J.V. Janovsky, *ibid.*, **24**, 971 (1891). For reviews, see T. Nambara, *Bunseki Kagaku*, **13**, 184 (1964); E. Buncel, A.R. Norris, and K.E. Russell, *Quart. Rev.*, **22**, 123 (1968).

Absorption Spectra of Reaction Mixtures of Picric Acid and Acetone under the Janovsky Conditions[8]

Absorption spectrum of an alkaline reaction mixture of picric acid with acetone under the Janovsky conditions described in the legend of Fig. 1 changed with time (Fig. 1). The intensity of the absorption maximum at 395 nm increased to become maximum after 60 min (Fig. 1, 1—6) and was kept constant for several hours. On the other hand, the maximum at 485 nm increased in intensity and reached maximum after 5 min (Fig. 1, 3), and then decreased to disappear after 60 min (Fig. 1, 4—6).

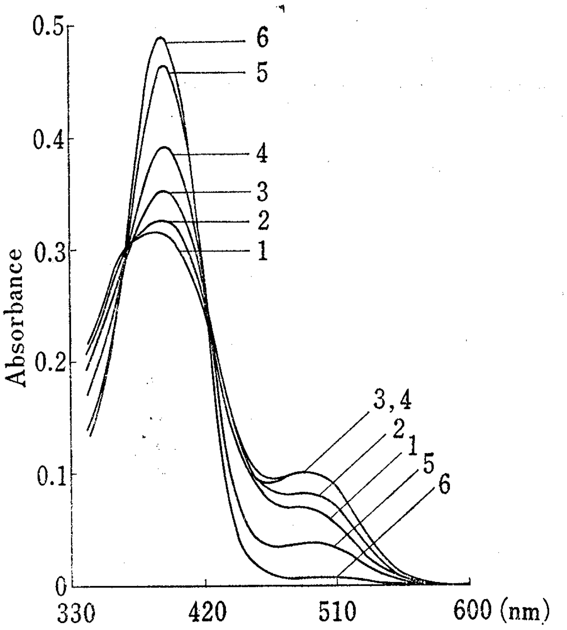

Fig. 1. Spectral Change of Alkaline Reaction Mixture of Picric Acid with Acetone under Janovsky Conditions

To 2.0 ml of acetone solution of picric acid (5×10^{-5} M), 2.0 ml of H_2O and 1.0 ml of aq. 0.1 M NaOH were successively added. The solution was kept for the periods (1; immediately, 2; 2, 3; 5, 4; 10, 5; 30, 6; 60 min) at room temperature (about 25°).
The spectra were measured against H_2O.

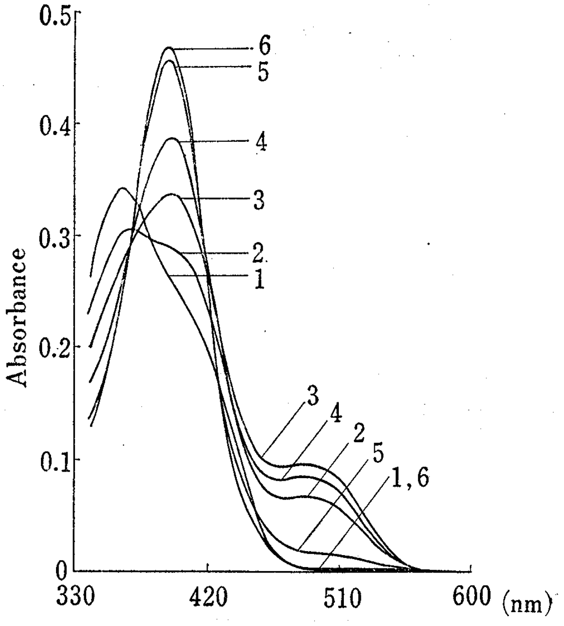

Fig. 2. Absorption Spectra of Neutralized Reaction Mixtures of Picric Acid with Acetone under the Janovsky Conditions

To 2.0 ml of acetone solution of picric acid (5×10^{-5} M), 1.0 ml each of H_2O and aq. 0.1 M NaOH were successively added. The solution was neutralized with 1.0 ml of aq. 1.5% $NaH_2PO_4\cdot2H_2O$ after standing at room temperature (about 25°) for 1; immediately, 2; 2, 3; 5, 4; 10, 5; 30, 6; 60 min.
The spectra were measured against H_2O.

The above spectral change, however, could be stopped at every period in the course of the reaction by neutralizing the reaction mixture with sodium dihydrogen phosphate. The spectra of the neutralized solutions, depicted in Fig. 2, seemingly were close similar to spectral change of the alkaline solution shown in Fig. 1. In this case, the shape of absorption band was clearly affected in the region around 350 nm by unreacted picrate anion in an earlier stage of the reaction (Fig. 2, 1—2). The spectra did not change for a long time indicating that the coloring matters produced in the Janovsky reaction were stable also in the neutral solution.

Preparations and Structural Characterizations of the Coloring Matters

When an ethanolic solution of sodium ethoxide[9] was added to an acetone solution of picric acid with stirring and the mixture was kept stirring at 0—5° for 2 hr, red precipitates were gradually separated out. The compound, recrystallized from ethanol, showed no melting point and exploded when ignited or heated rapidly. The data of elemental analyses were

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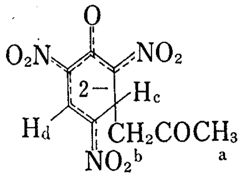
[9] Coloring matters could not be isolated successfully from the aqueous sodium hydroxide solution of picric acid and acetone.

consistent with the formula of $C_9H_7O_8N_3Na_2$. The infrared (IR) spectrum showed absorptions at 1700 cm^{-1} (CO), 1332, 1220, and 743 cm^{-1} (NO_2^-).[10] From these data and the nuclear magnetic resonance (NMR) spectral assignments, a structure of the compound was determined as disodium salt of the Meisenheimer type anion I (I-2Na), as shown in Chart 2.



I

Chart 2

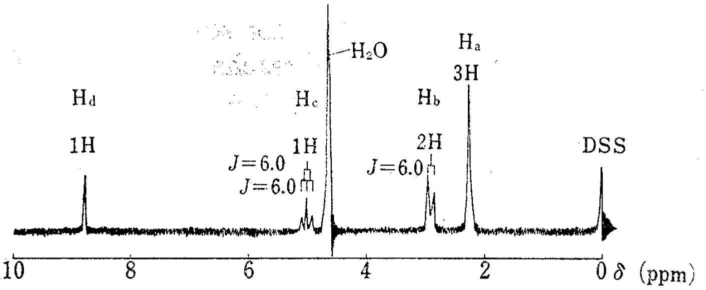


Fig. 3. NMR Spectrum of I-2Na (in D_2O)

J is expressed in Hz.

The NMR spectrum of I-2Na in D_2O is shown in Fig. 3. The signal pattern was similar to that of the Meisenheimer type compound derived from TNB and acetone.[4,11]

A singlet at δ (ppm) 8.74 (1H) was assigned to the proton Hd on the TNB ring system. The value of chemical shift was consistent with that of the corresponding proton in the 1,3,5-trinitrocyclohexadienide systems of the Meisenheimer type anions, which appeared in a range of δ 8.3—8.9.[12] The triplet at δ 4.99 (1H, $J=6.0$ Hz) could be assigned to the proton Hc coupled to the methylene protons Hb, which appeared as a doublet at δ 2.86 (2H, $J=6.0$ Hz). The singlet at δ 2.25 (3H) was assigned to the methyl protons of acetonyl group.

Visible absorption spectrum of I-2Na in aqueous solution shown in Fig. 5, a was similar to those of the reaction mixtures of picric acid and acetone shown in the curve 3 or 4 of Fig. 2. This suggested that I-2Na corresponded to one of the coloring matters produced in an earlier stage of the reaction.

The bicyclic type compound was first obtained as piperidinium salt of mp 106° by treating aqueous picric acid with acetone in the presence of piperidine as described in Experimental. The data of the elemental analyses were consistent with the formula of $C_9H_7O_8N_3 \cdot 2(C_5H_{12}N)$. The NMR spectrum of the piperidinium salt was almost the same as that of the bicyclic compound derived from TNB and acetone[4] except for the intense signals due to the protons of piperidinium cation (δ 1.55 and 2.90 (CH_2) and 8.00 (N^+–H_2)). A structure of the bicyclic anion was assumed to be a dianion IIa shown in Chart 5. The compound, dipiperidinium salt of IIa (IIa-2Pip), was easily converted to a sodium salt by treating it with a mixture of acetic anhydride and anhydrous sodium acetate at room temperature as described in Experimental.

The IR spectrum of the compound showed absorptions at 3436 cm^{-1} (OH), 1728 cm^{-1} (CO), 1560 and 1322 cm^{-1} (NO_2), and 1300, 1278, and 774 cm^{-1} (NO_2^-).[10] The data of the elemental analyses were consistent with the formula of $C_9H_8O_8N_3Na$, indicating that the compound was monosodium salt. The NMR spectrum of the compound shown in Fig. 4 also resembled that of the bicyclic compound derived from TNB and acetone[4] except that a singlet ascribable to hydroxyl proton, which disappeared on adding D_2O, was observed at δ 18.04, instead of a dinitropropenide proton of the bicyclic compound derived from TNB and acetone which appeared as a singlet at δ 8.51.[4] The results of spin-decoupling shown in Fig. 4 were entirely identical with those of the bicyclic compound described in the previous

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[10] K. Nakanishi, "IR Absorption Spectroscopy (Practical)," Nankodo, Tokyo, 1960, p. 94.

[11] R. Foster and C.A. Fyfe, *J. Chem. Soc.* (*B*), **1966**, 53.

[12] R. Foster and C.A. Fyfe, *Rev. Pure and Appl. Chem.*, **16**, 61 (1966); M.J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

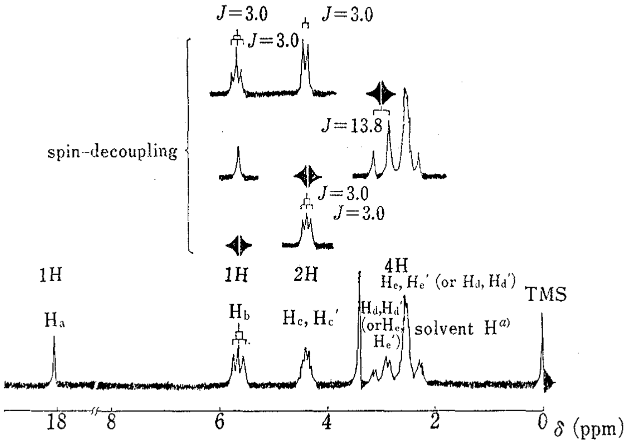
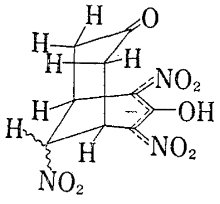


Fig. 4. NMR Spectrum of II-Na and Results of Spin-decoupling (in dimethylsulfoxide-d_6)

a) This signal might veil a part of the signals due to He and He' (or Hd and Hd').
J is expressed in Hz.



II

Chart 3

paper.[4] Thus, the compound was proved to be monosodium salt of bicyclic type anion II (II-Na), shown in Chart 3.

The absorption spectra of alkaline solutions of II-Na shown in Fig. 6, b_{3-6} were also similar to that of the reaction mixture in a prolonged reaction time shown in Fig. 1,6. Furthermore, the thin-layer chromatographic (TLC) separation of the reaction mixture[13] gave three main spots. One of them,[14] a yellow and larger spot located at *Rf* value of 0.52, was identified with the spot due to II-Na by the overlapping method in the development. The water extract of the spot showed an identical absorption spectrum to II-Na. These evidence indicated that II-Na was also produced as one of the main coloring matters in the Janovsky reaction.

Absorption Spectral Behavior of I-2Na and II-Na in Neutral and Alkaline Media[15]

An aqueous solution of I-2Na (4×10^{-5}M) had a pH value of 6.2 at 25° and showed the absorption band with three maxima at 238, 326, and 420 nm and a shoulder around 480 nm (Fig. 5,a). The maximum at 420 nm shifted to 413 nm and the shoulder around 480 nm slightly increased in intensity to form a maximum at 485 nm on adjusting the pH value of the solution to about 7—9 (Fig. 5,b). The spectra of these neutral and slightly alkaline solutions did not change for several hours at room temperature. This spectral behavior was similar to that of the neutralized reaction mixtures shown in Fig. 2.

When a higher concentrated sodium hydroxide solution was added, two maxima at 326 and 485 nm disappeared and the maximum at 413 nm shifted to 398 nm with increasing intensity (Fig. 5,c). The spectrum of the alkaline solution thus obtained returned partly to the initial band of I-2Na by the neutralization immediately after the addition of the alkali (Fig. 5,d). This observation might be explained as follows. By the addition of sodium hydroxide, the anion I was changed to other anions, one of which was reversibly returned to I by the neutralization. The reversible species was thought to be the anion Ia shown in Chart 4.

The other irreversible species might be thought to be the bicyclic type anion which showed a maximum at 398 nm in a higher alkaline concentration.

II-Na gave a slightly acidic solution of pH value of 5.7 at 25° when dissolved in water (4×10^{-5}M), and showed the spectrum with two maxima at 268 and 422 nm (Fig. 6,a). When

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13) TLC conditions: adsorbent, Wakogel B-5, 0.25 mm thickness; solvent system, ethanol–water–28% ammonia (10: 5: 1).

14) Other two spots (*Rf*=0.89 and 0.56) were identified with those of sodium picrate and I-2Na, respectively. Kimura[6] also observed three main spots, corresponded to the picrate, probably I-2Na and II-Na, on the paper chromatogram of the Janovsky reaction mixture.

15) In acidic media, I-2Na and II-Na showed quite different spectra from those of the aqueous solutions. The descriptions on these spectra were omitted here, because they were not concerned with the present study. Recently, a new species was obtained by treating I-2Na with acetic acid. Its structural characterization and spectral behavior in acidic and alkaline media will be published in the near future.

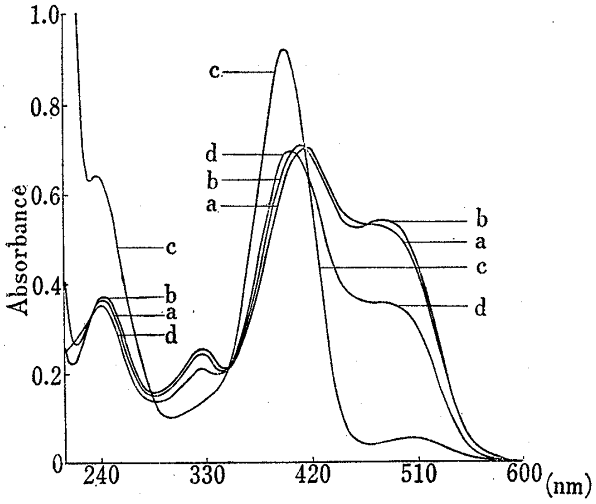
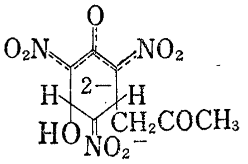


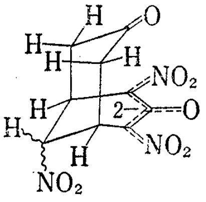
Fig. 5. Absorption Spectra of I-2Na in Neutral and Alkaline Solutions

a) 2.0 ml of aq. solution of I-2Na (1×10^{-4} M) was diluted with 3.0 ml of H_2O.
b) 2.0 ml of aq. solution of I-2Na in a) was diluted with 3.0 ml of a solution prepared by mixing 1.0 ml each of H_2O, aq. 0.4% NaOH and 2.0% $NaH_2PO_4\cdot2H_2O$ (pH 7.5).
c) To 2.0 ml of aq. solution of I-2Na in a), 1.0 ml each of H_2O, aq. 4.0% NaOH and H_2O were successively added. Immediately (20 sec) after that, the spectrum was measured.
d) Immediately (20 sec) after adding 1.0 ml each of H_2O and aq. 4.0% NaOH to 2.0 ml of aq. solution of I-2Na in a), the solution was neutralized with 1.0 ml of 4.0% H_3PO_4.
The spectra were measured against H_2O.



Ia

Chart 4



IIa

Chart 5

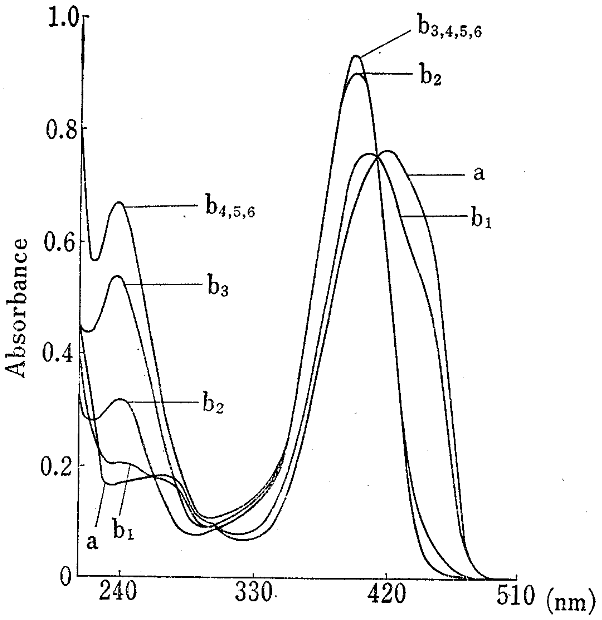


Fig. 6. Absorption Spectra of II-Na in Neutral and Alkaline Solutions

a) 2.0 ml of aq. solution of II-Na(1×10^{-4} M) was diluted with 3.0 ml of H_2O.
b) To 2.0 ml of aq. solution of II-Na in a), 2.0 ml of H_2O and 1.0 ml of variously concentrated NaOH solution (1; 4×10^{-4}, 2; 4×10^{-3}, 3; 5×10^{-2}, 4; 1×10^{-1}, 5; 1, 6; 5M) were added.
The spectra were measured against H_2O.

the pH value of the solution was adjusted to 7.2—7.5, these maxima shifted to 238 and 398 nm with increasing intensity (Fig. 6,b_2).

This spectrum was identical with those of IIa-2Pip in aqueous solution (pH 7.2), suggesting that the species present in the neutral solution was the dianion IIa shown in Chart 5.

When the aqueous solution was made alkaline with sodium hydroxide, the intensity of the maximum at 238 nm greatly increased and that of the maximum at 398 nm also slightly increased with increasing concentration of the alkali (Fig. 6, b_{3-6}), whereas in the case of the bicyclic compound derived from TNB and acetone, it was already observed that the intensity in the visible spectrum of its aqueous solution much decreased under such stronger alkaline conditions.[4] The difference of the spectral behavior between II-Na and the bicyclic compound derived from TNB and acetone suggested that the oxo-function sandwitched between two nitro groups in II might greatly contribute to stabilize the chromogenic group in an alkaline condition.[16]

The spectra (Fig. 6, b_{4-6}) were similar in shapes and maxima to those of I (Fig. 5,c), indicating that the species from II in the alkaline media had the same chromogenic group as that of Ia. Then, the species might be thought to be the trianion IIb shown in Chart 6.

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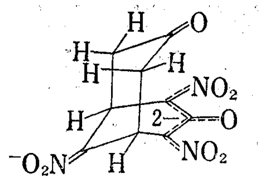
[16] The same spectral behavior as in II-Na was also observed in the aqueous reaction mixture of 2,4,6-trinitroanisole with a large amount of acetone in sodium hydroxide solution in a prolonged reaction time. The study on these phenomena is now going on.



IIb

Chart 6

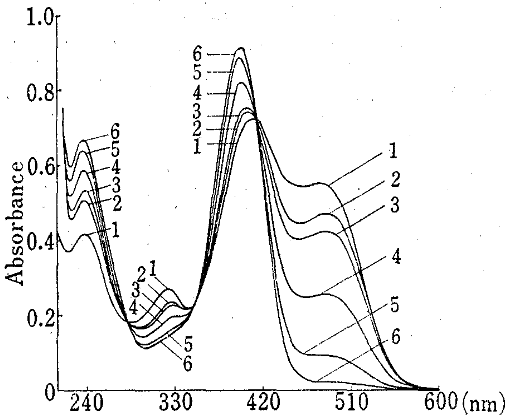


Fig. 7. Absorption Spectral Change of I-2Na in Alkaline Solution with Time

1) 2.0 ml of aq. solution of I-2Na(1×10^{-4} M) was diluted with a solution prepared by mixing 1.0 ml each of H_2O, aq. 0.4% NaOH and aq. 2.0% $NaH_2PO_4\cdot2H_2O$.
2, 3, 4, 5 and 6) To 2.0 ml of aq. solution of I-2Na in 1, 1.0 ml each of H_2O, aq. 0.4% NaOH were successively added. The solution was kept at room temperature (about 25°) for several periods (2; immediately, 3; 2, 4; 10, 5: 30, 6; 60 min), then diluted with 1.0 ml H_2O.
The spectra were measured against H_2O.

Therefore, the spectrum with the maximum at 398 nm (Fig. 5,c) was due to both anions Ia and IIb.

The spectrum of IIb (Fig. 6, b_{4-6}) returned reversibly to that of II (Fig. 6,a) through that of IIa (Fig. 6, b_2) when sodium dihydrogen phosphate was added to the alkaline solution.

Absorption Spectral Change of I-2Na in Alkaline Solution with Time

When the alkaline solution of I-2Na was left standing at room temperature (25°), the spectrum of I-2Na (Fig. 7, 1) changed with time (Fig. 7, 2—6) and did not return to that of the initial neutral solution by the neutralization (*cf.*, Fig. 1 and 2). The spectrum of I-2Na after standing for 60 min under the same alkaline conditions as described in the legend of Fig. 1 was almost identical in shape and maximum with those of II-Na dissolved in a similar alkaline solution (Fig. 6, b_{4-6}) and also the reaction mixture in the reaction time of 60 min (Fig. 1, 6).

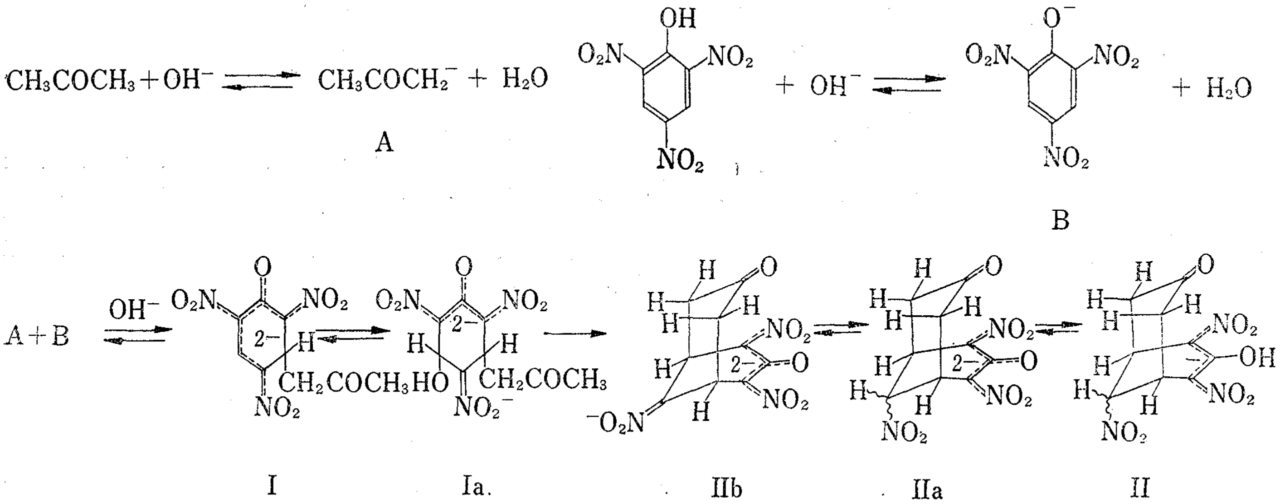


Chart 7

When the alkaline solutions were neutralized at every minute of standing periods in the alkaline medium, stable intermediate spectra, which might be considered to be two component spectra due to I (Fig. 5,b) and II (Fig. 6,b_2), were observed. The change of spectra with time was close similar to those of the reaction mixtures (Fig. 1 and 2) except for overlap of the spectra caused by unreacted picrate ion (*cf.*, Fig. 2, 1), which caused the intensities of the spectra in the shorter wave length region to make higher than that of the corresponding spectrum of I-2Na shown in Fig. 5b.

Reaction Schema of Picric Acid with Acetone under the Janovsky Conditions in Aqueous Medium

On the basis of the spectral behavior of I-2Na and II-Na (Fig. 5 and 6) and the comparison of the spectral change of I-2Na with time (Fig. 7) with those of the reaction mixtures (Fig. 1 and 2), the color reaction of picric acid with acetone under the Janovsky conditions might be explained as follows (Chart 7).

When sodium hydroxide was added to an aqueous acetone solution of picric acid, picrate and acetonate anions, formed instantaneously from the reactants, combined to produce the anion I, which was responsible for the orange-red color observed in the earlier stage of the reaction (Fig. 1, 3). Under the alkaline conditions of the Janovsky reaction described in the legend of Fig. 1, the anion I was immediately changed to the trianion Ia, which was gradually transformed into the bicyclic type anion IIb.

A yellow color observed at an intermediate time was due to Ia and IIb (Fig. 1, 5 and Fig. 5,c). When the alkaline solution was neutralized at this stage, various colors due to I and IIa were observed because Ia returned to I, and IIb changed to IIa (Fig. 2, 4—5). However, the alkaline reaction mixture standing for 60 min showed a yellow color due to only IIb (Fig. 1, 6), and the neutralized solution showed the band due to IIa (Fig. 2, 6).

Experimental[17)]

Preparation of I-2Na——To the solution of picric acid (2.0 g) in $(CH_3)_2CO$ (20 ml), EtONa, prepared by dissolving Na (0.46 g) in abs. EtOH (15 ml), was added dropwise over a period about 1.5 hr with stirring under ice-water cooling. Red precipitates were filtered, washed with abs. EtOH several times and recrystallized from EtOH containing a small amount of AcOH to give red prisms. Yield, 2.6 g. *Anal.* Calcd. for $C_9H_7O_8N_3Na_2$: C, 32.63; H, 2.11; N, 12.69; Na, 13.90. Found: C, 32.90; H, 2.54; N, 12.81; Na, 13.85. $\lambda_{max}^{H_2O}$ nm (ε): 238 (9300), 326 (6200), and 420 (18500).

Preparation of IIa-2Pip——To the solution of picric acid (2.0 g) in $(CH_3)_2CO$ (20 ml) and H_2O (10 ml), piperidine (2.0 ml) was added. After standing at 50° for 2 hr, the solvent was removed *in vacuo* and the residue was recrystallized from EtOH to give yellow needles, mp 106° (uncorr.). Yield, 1.4 g. IR ν_{max}^{KBr} cm^{-1}: 3310 (OH),[18)] 1720 (CO), 1543 and 1325 (NO_2), 1318, 1239, and 774 (NO_2^-).[12)] NMR (in dimethylsulfoxide-d_6) δ (ppm): 1.55 (broad singlet, piperidine CH_2), 2.90 (broad singlet, piperidine CH_2 adjacent to N), 8.00 (broad singlet, piperidinium N^+-H_2), 2.35 (doublet, $J=3.0$ Hz), 4.30 (2H, poorly resolved quartet), 5.63 (1H, triplet, $J=3.0$ Hz). *Anal.* Calcd. for $C_{19}H_{31}O_8N_5$: C, 49.93; H, 6.84; N, 15.33. Found: C, 50.12; H, 7.23; N, 15.16. $\lambda_{max}^{H_2O}$ nm (ε): 238 (7400) and 398 (22100).

Preparation of II-Na from IIa-2Pip——To the solution of IIa-2Pip (1.0 g) in Ac_2O (10 ml), the solution of NaOAc (0.5 g) in AcOH (1.0 ml) was added. After standing at about 25° for 1 hr, the separated crystals were filtered and recrystallized from H_2O to give yellow needles. It showed no melting point and exploded when ignited or heated rapidly. Yield, 0.5 g. *Anal.* Calcd. for $C_9H_8O_8N_3Na$: C, 34.95; H, 2.61; N, 13.59; Na, 7.44. Found: C, 35.38; H, 2.95; N, 13.71; Na, 7.07. $\lambda_{max}^{H_2O}$ nm (ε): 268 (4400) and 422 (19800).

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17) Absorption spectra were measured by a Shimadzu Recording Spectrophotometer SV-50A or a Hitachi 124 Spectrophotometer in a cell of 10 mm optical length. pH values were measured by a Hitachi-Horiba pH Meter M-7. Samples were dissolved in the distilled water free from carbon dioxide. IR spectra were measured by a Koken DS-301 or a Nihonbunko DS-701G IR Spectrophotometer in KBr pellet. NMR spectra were measured by a JEOL C-60H NMR Spectrometer. Solutions were prepared immediately prior to use. All chemical shifts expressed as δ values were measured in ppm from sodium dimethylsilapentanesulfonate (DSS) or tetramethylsilane (TMS) as internal standard.

18) Although a structure of the dianion IIa was expressed as shown in Chart 5, it might be assumed from the signal of hydroxyl group in the IR spectrum that IIa-2Pip in crystalline form had another structure as shown in Chart 8. Studies on the relation between these structures are now going on.

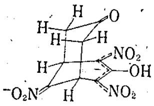

Chart 8