SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS.⑴
PART I.

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Introduction. The authors have studied on the relation between the colour of hydroxyazo-compounds and their chemical constitution by the spectrochemical method.

Hewitt,⑵ Baly,⑶ and Sircar⑷ already chemically investigated some hydroxyazo-compounds with regard to their chemical constitution, and

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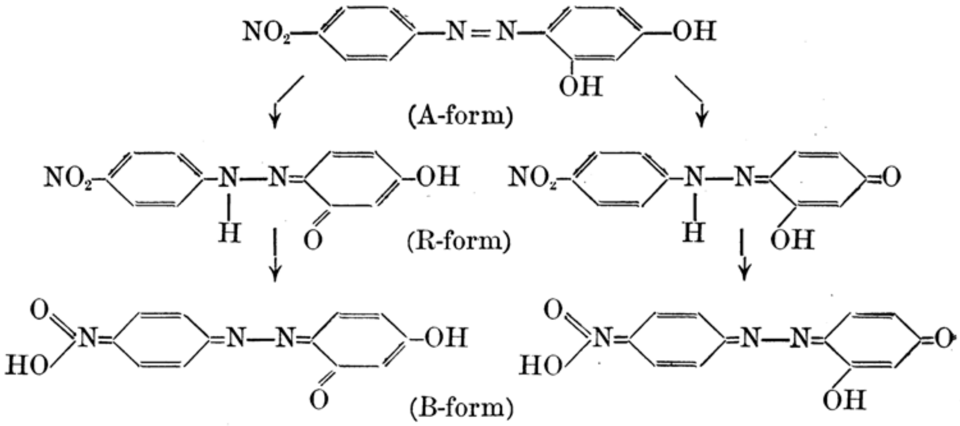
⑴ Read before the Chemical Society of Japan, October 9, 1926.

⑵ Hewitt and Mitchell, *J. Chem. Soc.*, 91 (1907), 1251.
Hewitt and Fox, *J. Chem. Soc.*, 93 (1908), 333.
Hewitt and Thomas, *J. Chem. Soc.*, 95 (1909), 1292.
Hewitt and Thole, *J. Chem. Soc.*, 95 (1909), 1393; 97 (1910), 511.

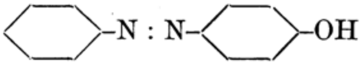
⑶ Baly, Tuck, and Marsden, *J. Chem. Soc.*, 97 (1910), 1497.

Tuck⁽¹⁾ did it spectrochemically. They all recognised the tautomeric changes in these compounds. K. Suitsu⁽²⁾ recently observed three different colours of para-red (p-nitrobenzeneazo-β-naphthol) by changing conditions, and he respectively assigned the azo-, monoquinonoid- and diquinonoid-form to the three tautomers. We also have been able to observe the remarkable analogy in many simpler hydroxyazo-compounds and have then given the following forms respectively :



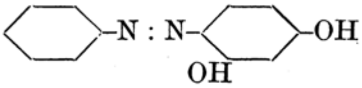
Experimental.

1. p-Hydroxyazobenzene,⁽³⁾



A dilute neutral alcoholic solution of the substance is yellow, and changes into a deeper shade by adding a KOH-solution. As the absorption curve of its N/10000 solution shows, the bathochromic and hyperchromic influences are easily observed by the addition of alkali (Fig. 1). We give A-form to the neutral solution and R-form to the alkaline.

2. Benzeneazoresorcinol,⁽⁴⁾



Bathochromic and hyperchromic effects due to alkali are also seen in Fig. 2, and the curve analogous to that of No. 1 compound (Fig. 1) was obtained. A- and R-forms can then be respectively assigned to neutral and alkaline solutions.

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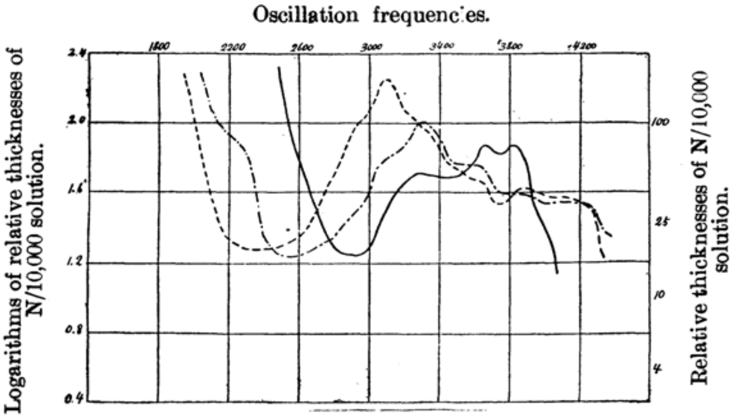
(1) Tuck, *J. Chem. Soc.*, **91** (1907), 449; **95** (1909), 1809.

(2) Suitsu and Okuma. *J. Soc. Chem. Ind. Japan*, **29** (1926), 132.

(3) Beilstein, " Handbuch der Organischen Chemie," IV (1899), 1407.

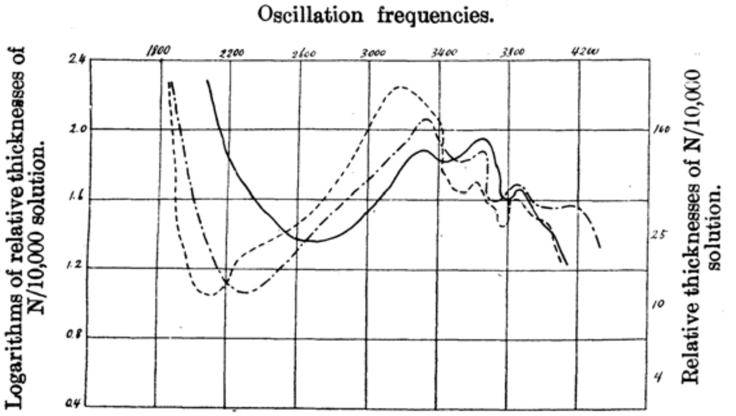
(4) Ibid., IV (1899), 1441.



1. p-Hydroxyazobenzene. { —— Neutral Solution. / - - - - 0.9 N. Alkaline Solution.

4. p-Nitrobenzeneazophenol. -·-·- Neutral Solution.

Fig. 1.

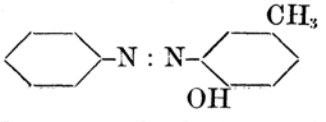


2. Benzeneazoresorcinol. { —— Neutral Solution. / - - - - 0.9 N. Alkaline Solution.

5. p-Nitrobenzeneazoresorcinol. -·-·- Neutral Solution.

Fig. 2.

3: Benzeneazo-p-cresol,(1)



By adding KOH, the yellow neutral solution of this compound changes into red, but not blue. Two absorption bands (Fig. 3) can be observed in its neutral solution and they become clearer when we add KOH to it. We can give A-form to the yellow solution and R-form to the red one.

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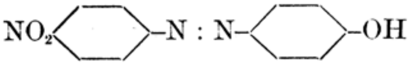
(1) Beilstein, "Handbuch der Organischen Chemie," IV (1899), 1420.

4. p-Nitrobenzeneazophenol,⁽¹⁾



This substance undergoes quite the same change in colour as the above-mentioned compounds and like them cannot obtain blue tautomer. Hewitt⁽²⁾ once gave B-form to the red solution of this compound, but according to our examination we can only give R-form to this red solution, for we can ascertain that the curve of this alkaline solution coincides to that of the red one of m-nitrobenzeneazoresorcinol (No. 6 compound) which cannot take B-form (Fig. 4).

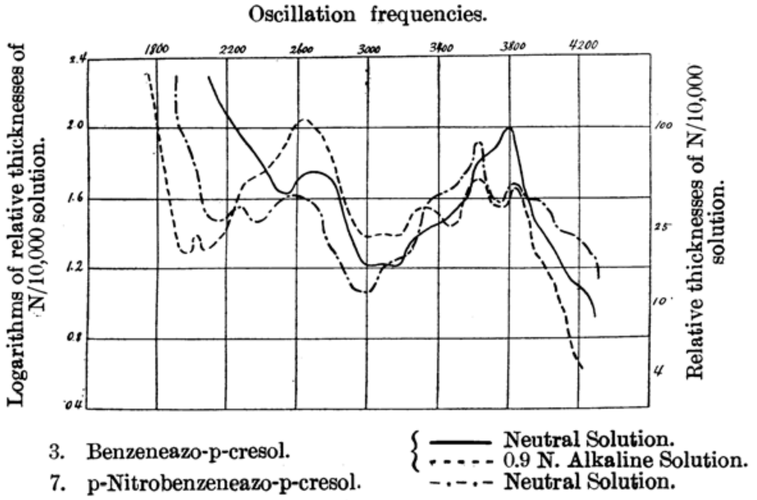


Fig. 3.

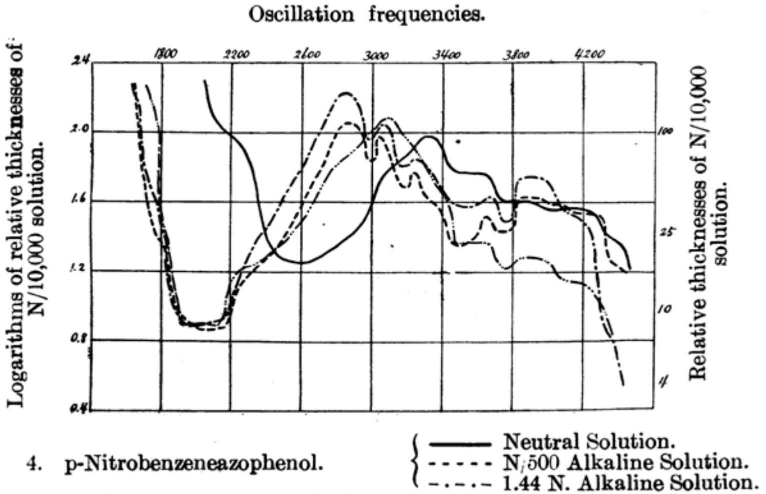


Fig. 4.

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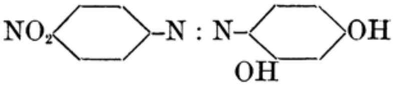
(1) Ibid., IV (1899), 1410.

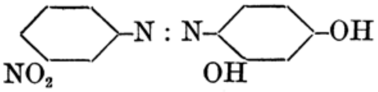
(2) Hewitt and Mitchell, *J. Chem. Soc.*, 89 (1906), 17.

5. p-Nitrobenzeneazoresorcinol,(1)

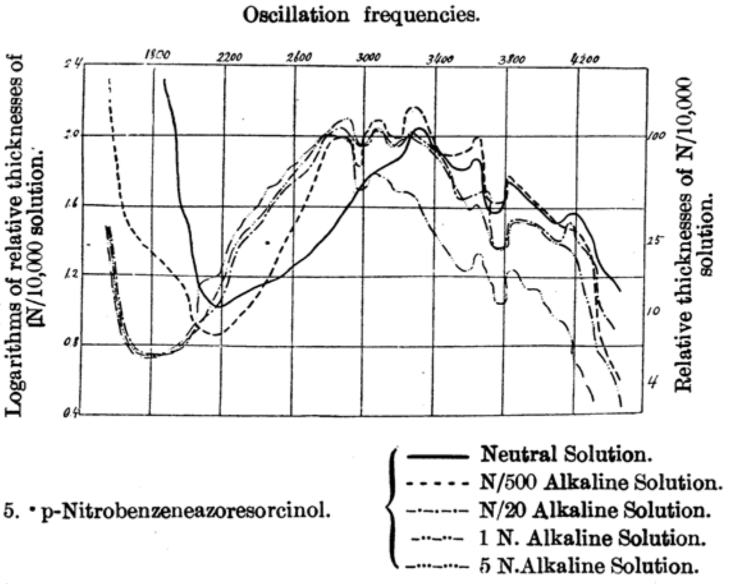


The reddish yellow neutral solution becomes red when it is N/500 alkaline solution, and bluish violet by adding a stronger alkali. Then we may respectively assign A-, R- and B-forms to these three tautomers (Fig. 5).

6. m-Nitrobenzeneazoresorcinol,(2)



The curve of N/500 alkaline solution of No. 5 compound and that of the alkaline solution of this substance nearly coincide and, therefore, this substance has A- and R-forms (Fig. 6). This compound has no B-form, for the nitro-group, in this substance takes the meta-position with respect to the azo-group, and cannot, of course, be of the isonitroform. As the three compounds (No. 2, No. 5 and No. 6), already described, have two hydroxyl-groups (ortho and para with respect to the azo-group), we may suppose two cases of tautomeric changes, but cannot yet definitely say whether it is the hydrogen atom in para hydroxyl that moves or the one in the ortho hydroxyl.



5. • p-Nitrobenzeneazoresorcinol.

Fig. 5.

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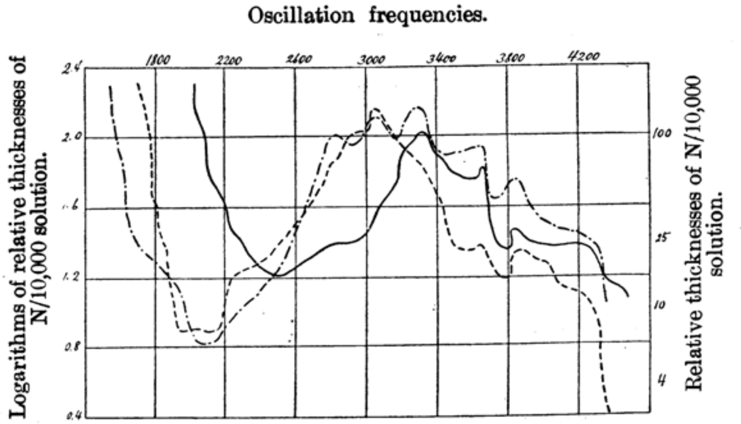
(1) Beilstein, "Haudbuch der Organischen Chemie," IV (1899), 1442.

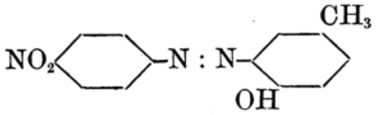
(2) Obtained from m-nitraniline and resorcinol.



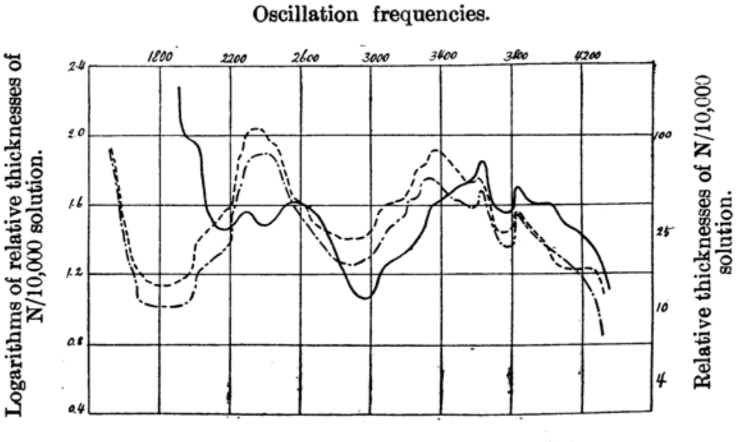
6. m-Nitrobenzeneazoresorcinol. { —— Neutral Solution.
- - - - - 2 N. Alkaline Solution.
5. p-Nitrobenzeneazoresorcinol. - · - · - N/500 Alkaline Solution.

Fig. 6.

7. p-Nitrobenzeneazo-p-cresol,(1)



The yellow neutral solution changes into red and instantly into violet by adding KOH. N/1000 alkalien solution shows already a bluish violet shade. The curve of this compound (Fig. 7) has two absorption bands like that of



7. p-Nitrobenzeneazo-p-cresol. { —— Neutral Solution.
- - - - - N/1000 Alkaline Solution.
- · - · - 0.9N. Alkaline Solution.

Fig. 7.

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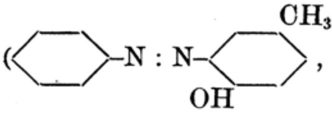
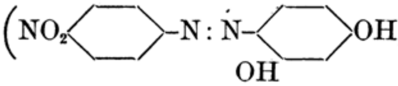
(1) Beilstein, " Handbuch der Organischen Chemie," IV (1899), 1041.

No. 3 compound (, in Fig. 3). The absorption curve of 1 N. alkaline solution of No. 5 compound ( in Fig. 5) to which was assigned B-form, nearly coincides to that of 0.9 N. alkaline solution of this compound, which is only more hypochromic than the former, and we have given A- and B-forms to this compound according to the condition. Of course, we may recognise the existence of R-form which is very unstable.

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