

SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS.
PART IV.⁽¹⁾

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One of the authors⁽²⁾ has already written on the tautomeric changes of some hydroxyazo-compounds and given them three different formulas according to their conditions.

We have now studied more in detail about the influences of methyl-group on these hydroxyazo-compounds, for as we have seen in a previous

(1) Read before the Chemical Society of Japan, June 11, 1927.

(2) Uemura, Yokojima and Tan, This journal, 1 (1926), 260.
Uemura, Yokojima and Endo, *ibid.*, 2 (1927), 10 & 48.

paper,⁽¹⁾ benzeneazo-p-cresol and p-nitrobenzeneazo-p-cresol have two absorption bands while the other compounds have but one. We have thought this was perhaps due to the methyl-group in the two above-mentioned hydroxy-azo-compounds. In the present paper, we shall describe tolueneazo-cresols.

Experimental.

1. **o-Tolueneazo-o-cresol**,⁽²⁾ Cc1ccc(N=Nc2cc(O)cc(C)c2)cc1

The neutral solution of this compound is light yellow and by adding KOH-solution it becomes yellowish orange even a concentrated (0.5 N.) alkaline solution. We may assign A(azo)-form⁽³⁾ to the neutral solution and R(red)-form⁽³⁾ to the alkaline.

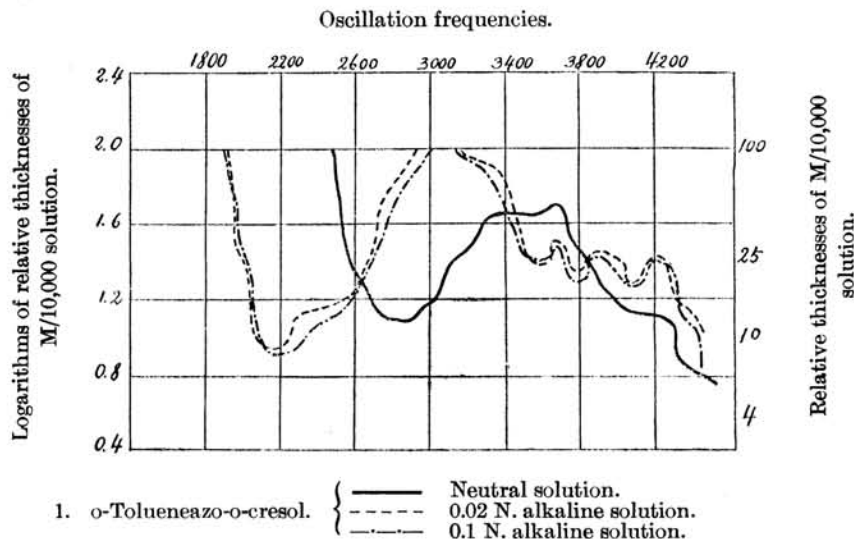


Fig. 1.

2. **m-Tolueneazo-o-cresol**,⁽⁴⁾ Cc1ccc(N=Nc2cc(O)cc(C)c2)cc1

The absorption curve of this compound (Fig. 2) is almost the same type as that of No. 1 compound. The colour change of this solution through alkali is also nearly the same as that of No. 1. When we compare the neutral solution curve of this compound with that of p-hydroxyazobenzene,⁽⁵⁾

(1) This journal, **1** (1926), 262 & 265.

(2) Noetting and Werner, *Ber.*, **23** (1890), 3259.

(3) This journal, **1** (1926), 261.

(4) Jacobson, *Ann.*, **287** (1895), 185.

(5) This journal, **1** (1926), 262.

a considerably hyperchromic effect can be recognised, and the corresponding curve of benzeneazo-o-cresol⁽¹⁾ almost coincides with that of this compound. It seems to us that, although the methyl-group has a hyperchromic effect, yet it is still negligible against an already methylated compound.

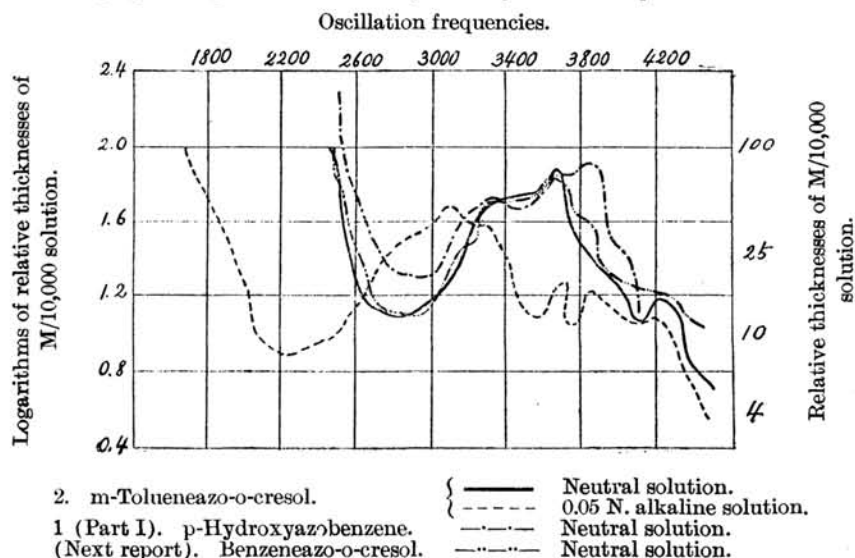


Fig. 2.

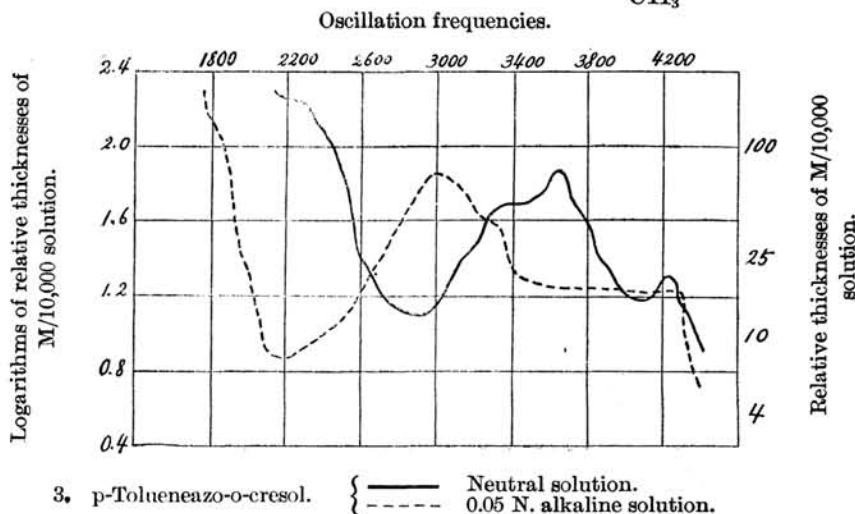
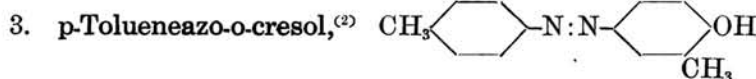


Fig. 3.

(1) Details about this compound will appear in the next report.

(2) Noetting and Werner, *Ber.*, 23 (1890), 3261.

this indicates the no position influence of the methyl-group in the toluene ring. As for the colour change, these compounds in solution are about the same as in No. 4 compound.

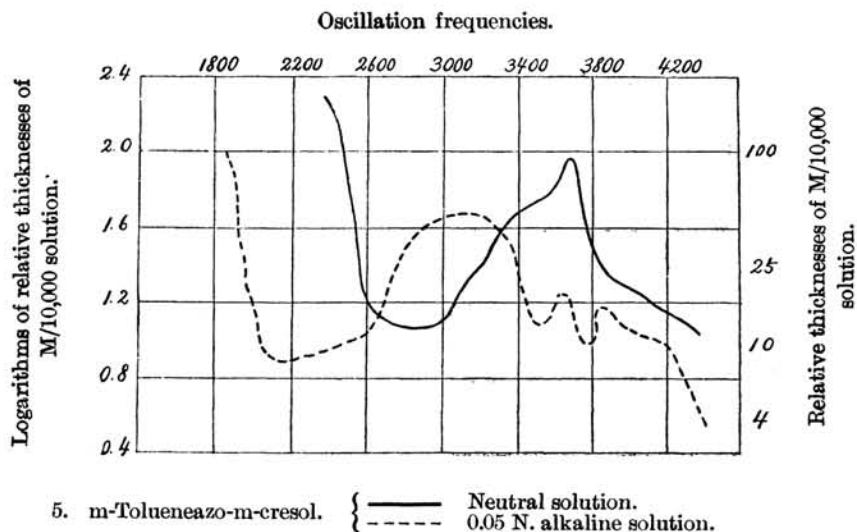


Fig. 5.

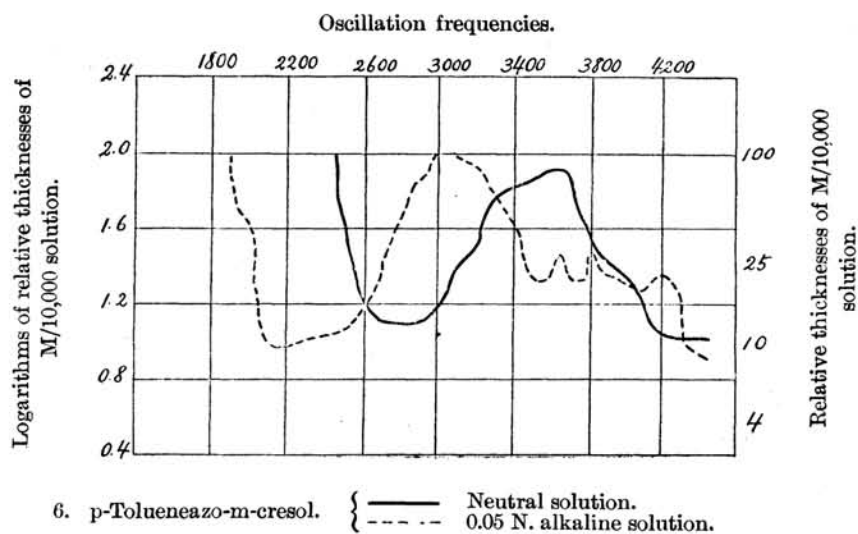
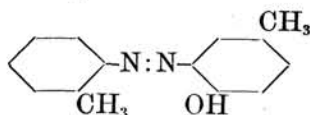


Fig. 6.

7. o-Tolueneazo-p-cresol,⁽¹⁾



(1) Noelting and Werner, *Ber.*, 23 (1890), 3263.

This compound has a hydroxyl-group in an ortho position with respect to the azo-group in cresol ring and has two absorption bands as is to be expected, and two bands more obvious can be also observed in the alkaline solution (Fig. 7). When we compare this absorption curve with that of benzeneazo-p-cresol,⁽¹⁾ the slight bathochromic and hyperchromic influences can be seen, and this is probably an effect of the methyl-group in the toluene ring. As the absorption curve of o-hydroxyazobenzene cannot yet been obtained, we are not here in a position perfectly to ascertain our point of issue like in the case of No. 2 compound.

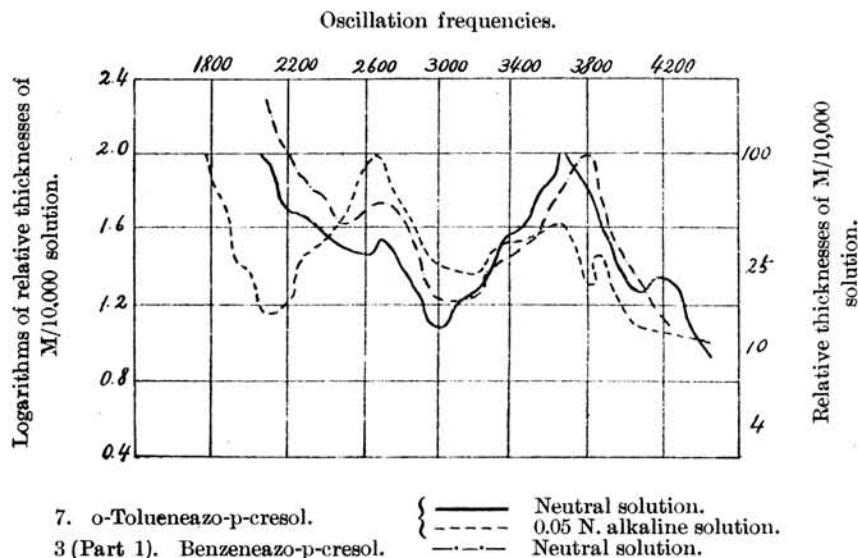
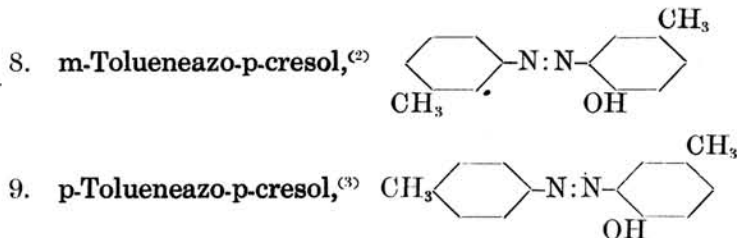


Fig. 7.



In these cases, we discover nearly the same absorption curves as that of No. 7 compound, that is, these compounds have two absorption bands in their solution. The bathochromic effect by the addition of alkali is remarkably observed in their absorption curves (Fig. 8 and Fig. 9). The neutral

(1) This journal, **1** (1926), 263.

(2) Jacobson and Piepenbrink, *Ber.*, **27** (1894), 2703.

(3) Obtained from p-toluidine and p-cresol.

solutions of these two compounds are yellow like No. 7 compound and become orange when they are alkaline.

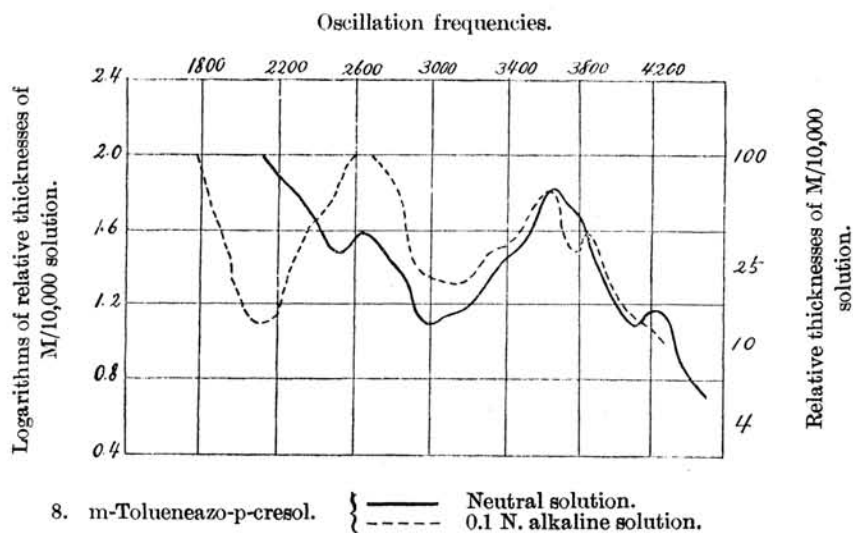


Fig. 8.

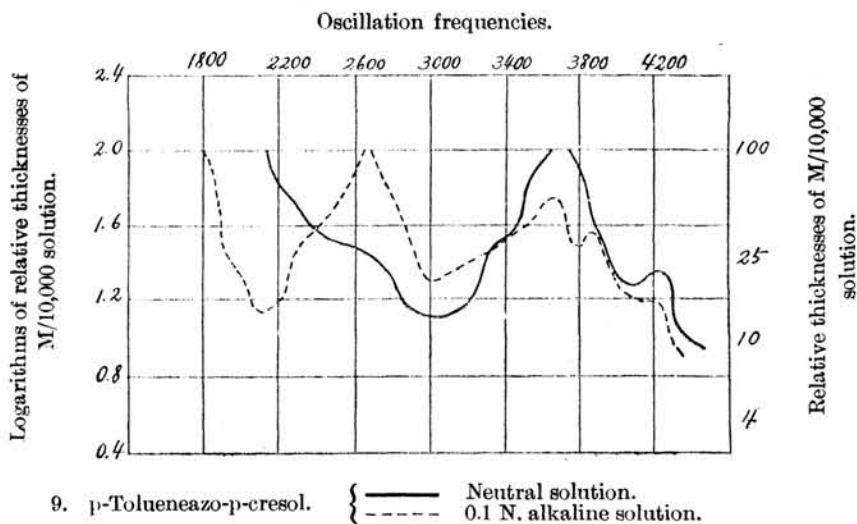


Fig. 9.

Summary.

(1) Tautomeric transformations may occur when the neutral solution of these tolueneazo-cresols change into the alkaline.

(2) The dilute neutral solution of these compounds is generally yellow and becomes deep yellow or orange when the solution is alkaline.

(3) We can respectively give A(azo)- and R(red)-forms⁽¹⁾ to these tautomers.

(4) There is one absorption band when hydroxyl-group in cresol ring takes para-position with regard to the azo-group, and two bands when ortho-position.

(5) The methyl-group has a hyperchromic influence, but when added to an already methylated compound, it ceases to be effective in the absorption curve.

(6) So far as the present studies are concerned, the methyl-group does not specially represent its influence with regard to the position.

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(1) loc. cit.