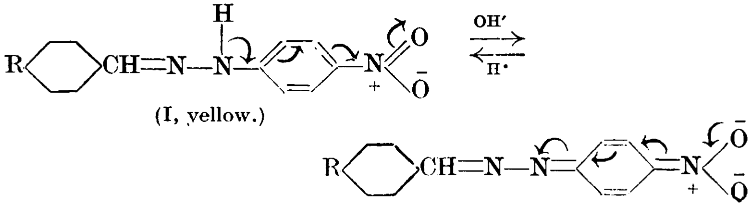
XXXIII.—*Colour and Constitution. Part IV. The Absorption Spectra of Nitrophenylhydrazones in Alcohol and in Alcoholic Potassium Hydroxide.*

By HERBERT HENRY HODGSON and KENNETH ERNEST COOPER.

THE presence of a nitro-group in the ortho- or para-position in a phenylhydrazone induces incipient ionisation of the imino-hydrogen. That the treatment of such hydrazones with hydroxyl ions renders the ionisation actual, with the consequent formation of a quinonoid structure, was suggested by Chattaway and Clemo (J., 1923, **123**, 3041) to explain the resulting intense colorations, and their view is supported by the fact that no such colours are produced in the absence of either the imino-hydrogen or the *o*- or *p*-nitro-group.



(I, yellow.)

(II, magenta.)

It has been suggested (*Brit. Assoc. Reports*, 1922, 298) that the combination of two atoms involving a loss of energy ε results in a compound capable of absorbing light of frequency $\varepsilon = h\nu$. We suspected that the colour of the ions represented by formula (II) might bear a relation to the energy changes involved in the ionisation of the imino-hydrogen by the action of the hydroxyl ions. The greater the initial degree of incipient ionisation, the less will be the energy required for the ionisation and the lower, it is presumed, will be the frequency of the radiation absorbed by the ion. The present investigation records the influence of a series of substituents (R in I) whose effects upon the ease of ionisation are known. The combined direct and inductive effect (Allan, Oxford, Robinson, and Smith, J., 1926, 401; Cooper and Ingold, J., 1927, 836; Ingold and Vass, J., 1928, 417) places the groups in the following order.*

$$\mathrm{R} = \underleftarrow{\mathrm{O}(-),\ \mathrm{CH_3},}\qquad \underrightarrow{\mathrm{NMe_2},\quad \mathrm{OMe},\quad \mathrm{Cl},\quad (+)\mathrm{NMe_3}\{\overset{(-)}{\mathrm{O}}\mathrm{H}}$$

Inhibiting ionisation. Enhancing ionisation.

The results (Fig. 1) are in agreement with the above series, and although the differences are small, as would be expected from the distance these effects have to travel, they are definite.

p-Substituted benzaldehyde-*p*-nitrophenylhydrazones in alcoholic KOH.

R	(+)NMe$_3${$\bar{\mathrm{O}}$H	Cl	OMe	NMe$_2$	CH$_3$	O(−)
Head of band...	580	565	550	545	542	530
Curve (Fig. 1)	I	II	III	IV	V	VI

The order of the absorption curves of the hydrazones without the addition of alkali is, on the other hand, entirely different (Fig. 2). It is significant that the maximum looseness of the electronic

---

* The tautomeric effect of these groups will have little or no influence, for in the process of ionisation no demand is made for a negative charge (compare the ionisation constants of substituted acids; Ingold and Shaw, J., 1927, 2923).

structure produced by the introduction of the NMe_2 group, with its mobile unshared electrons, is accompanied by the maximum wave-length, and the maximum tightening of the system by the $(+)NMe_3$ with the minimum wave-length. This is in agreement with the known effects of salt formation on the absorption of aniline and phenol (Baly and Collie, J., 1915, **107**, 1338).

p-Substituted benzaldehyde-*p*-nitrophenylhydrazones in alcohol.

R	NMe_2	OH and OMe	Cl	CH_3	$(+)NMe_3Cl(-)$
Head of band	460	415	400	400	395
Curve (Fig. 2)	IV	VI and III	II	V	I

FIG. 1.

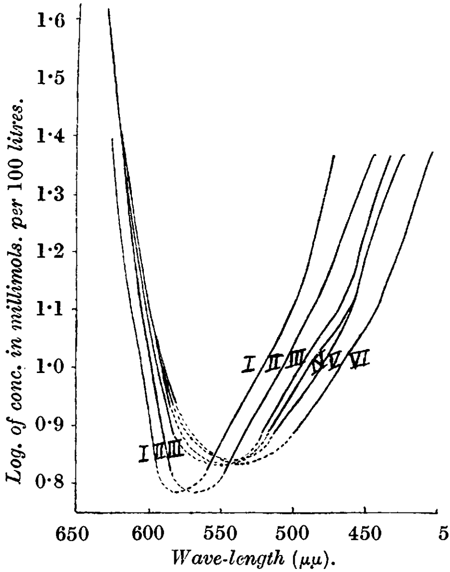
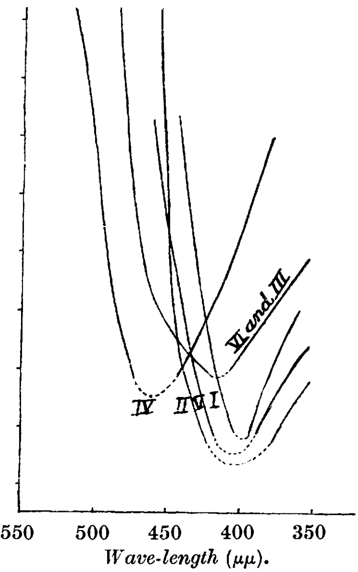


FIG. 2.



The order of the effect of substituents in this series, *viz.*, $NMe_2 > OMe > Cl = CH_3 > +NMe_3$, is in accordance with the well-known bathochromic effect of the amino- and the hydroxyl group as compared with the uncertain effects of chlorine in the dyes.

The nitrophenylhydrazones were chosen in preference to the nitrobenzaldehydephenylhydrazones because they require much less alkali to effect complete ionisation and produce their characteristic colours (Hodgson and Beard, J., 1927, 2382). That the absorption band is characteristic of the ion will be shown in a future paper (private communication from Mr. Handley).

EXPERIMENTAL.

Benzaldehyde-p-*trimethylammonium iodide*, prepared by refluxing a slight excess of methyl iodide with *p*-dimethylaminobenzaldehyde for 6 hours, crystallised from water in colourless plates, m. p. 152° (Found: I, 43·8. $C_{10}H_{14}ONI$ requires I, 43·6%).

Benzaldehyde-p-*trimethylammonium chloride* p-*nitrophenylhydrazone* was obtained by warming theoretical quantities of the two components in acetic acid for 10 minutes and diluting the solution with water (5 vols.); after recrystallising from hydrochloric acid and then from alcohol, it melted at 196° (Found: Cl, 10·9. $C_{16}H_{19}O_2N_4Cl$ requires Cl, 10·6%).

p-*Hydroxybenzaldehyde*-p-*nitrophenylhydrazone*, recrystallised from alcohol, had m. p. 262° (Found: N, 16·5. $C_{13}H_{11}O_3N_3$ requires N, 16·3%).

Absorption spectra were photographed with an iron arc through 1 cm. thickness of solutions of concentration $2M/10,000$, $2M/15,000$, $2M/20,000$, and $2M/25,000$ and of intermediate concentrations when necessary. The concentration of alkali for the curves in Fig. 1 was approximately 200 mols. of potassium hydroxide per mol. of hydrazone, largely in excess of that required to produce the desired band and destroy the band of the hydrazone. All solutions were kept in well-stoppered bottles, since they easily oxidised in the air in the presence of alkali.

We wish to record our thanks to the Department of Scientific and Industrial Research for a grant which has enabled one of us (K.E.C.) to take part in this research, and to Prof. C. K. Ingold, F.R.S., and Prof. E. C. C. Baly, F.R.S., for the very kind interest they have shown in this work.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, July 13th*, 1928.]