80. *A Spectrophotometric Study of Hexanitrodiphenylamine. Part I. The Molecular and Ionic Forms in Dioxan.*

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Hexanitrodiphenylamine, in its yellow and its red form, was investigated potentiometrically and spectrophotometrically in dioxan solution. It was found to be a strong acid, and its red form is an anion of an *aci*-nitro-acid. The potassium salt, which is insoluble in water, was studied in dioxan solution and found to be a simple salt.

2 : 2′ : 4 : 4′ : 6 : 6′-HEXANITRODIPHENYLAMINE, also known as dipicrylamine, is used as a precipitant for potassium.[1] Treadwell and Hepenstrick [2] determined its solubility and dissociation constant in water, and Schroeder *et al.*[3] investigated its absorption spectra in absolute ethyl alcohol but did not discuss the results.

The possibility of the existence of tautomeric forms of aromatic nitro-compounds was discussed by Hantzsch and Lister,[4] but the problem is still under discussion.[5] Feigl [6] discusses the different forms of aromatic nitro-compounds, and in particular hexanitrodiphenylamine, postulating the existence of *baso-* and *aci*-forms. In addition he suggests the possibility that the potassium salt is an inner complex salt on the basis of its slight solubility in water, its stability against mineral acids, and its solubility in organic nitro-compounds.

Our object was to study the *baso-* and *aci*-forms of the amine, their conditions of existence, and their relationship to each other and to the potassium salt. Part II will deal with these interrelationships in various organic solvents.

EXPERIMENTAL

Reagents.—The hexanitrodiphenylamine was an Eastman Kodak Reagent for laboratory use, and was not recrystallized. The potassium and sodium hydroxides used were " Baker's Analyzed " C.P. reagents. Dioxan (B.D.H.) was not further purified before use. Absolute ethyl alcohol was used.

0·01M-Solutions of hexanitrodiphenylamine were prepared by dissolving the yellow crystals in dioxan. Fresh solutions were always used since these solutions are unstable, becoming appreciably orange in 24 hr., and consequently unsuitable for measurements. Solutions of 0·1M- and 0·01M-potassium and sodium hydroxide were prepared by diluting a 1·0M-solution in absolute ethyl alcohol with dioxan.

Apparatus.—A Beckman Model G pH-Meter in conjunction with a glass–calomel electrode system, and a Beckman Model DU Spectrophotometer with a hydrogen lamp and matched 10 mm. quartz cells were used. Measurements in the visible range were made by using a tungsten lamp and 10-mm. Beckman glass cells.

Procedure.—The potentiometric titrations were carried out by titrating 30 ml. of 0·01M-amine with 0·1M-potassium hydroxide in increments of 0·01 ml. from a microburette of 5 ml. capacity, whose tip dipped into the solution. The solution was mechanically stirred. It took several seconds for the readings of the pH meter to become constant.

For the spectrophotometric measurements the reference solution had the same solvent composition as the measured solution.

Results.—Determination of dissociation constant. Fig. 1 shows the potentiometric titration curve of a dioxan solution of hexanitrodiphenylamine with potassium hydroxide : it is typical for the titration of a strong acid with a strong base. The apparent pK_a is 0·35 ($K_{(\text{app.})a.}$ = 0·46), which is of the same order of magnitude as that of picric acid in water.

Effect of neutralization on absorption curves. The absorption curves in the presence of

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[1] Kolthoff and Bendix, *Analyt. Chem.*, 1939, **11**, 94; Amdur, *ibid.*, 1942, **14**, 731; Cotton, *ibid.*, 1945, **17**, 734; Welcher, " Organic Analytical Reagents," Vol. IV, Van Nostrand Co., New York, 1948, p. 8.

[2] Treadwell and Hepenstrick, *Helv. Chim. Acta*, 1949, **32**, 1903.

[3] Schroeder, Wilcox, Trueblood, and Dekker, *Analyt. Chem.*, 1951, **23**, 1740.

[4] Hantzsch and Lister, *Ber.*, 1910, **43**, 1685.

[5] *E.g.*, see reviews by Ferguson, " Electronic Structures of Organic Molecules," Prentice Hall Inc., New York, 1952; Baker and Taylor, " Sidgwick's Organic Chemistry of Nitrogen," Oxford Univ. Press, 1942.

[6] Feigl, " Chemistry of Specific, Selective, and Sensitive Reactions," Academic Press Inc., 1949, p. 282.

potassium hydroxide are shown in Fig. 2: the alkali causes a shift from the yellow to the red which effectively reaches its maximum when the stoicheiometrical quantity of potassium hydroxide needed to neutralize the hexanitrodiphenylamine present has been added. In dioxan solution this shift is from 430 to 560 mμ at an extinction value of 1·0. A similar effect of the same order of magnitude was observed when using sodium hydroxide instead of potassium hydroxide.

Effect of added water on the absorption curves. The effect of added water on the partial spectrum of a dioxan solution is shown in Fig. 3 : the water causes a shift of the absorption curve towards longer wavelengths, the maximum effect (from 430 to 550 mμ) being substantially achieved with 20% of water. With more than 70% of water, hexanitrodiphenylamine is precipitated.

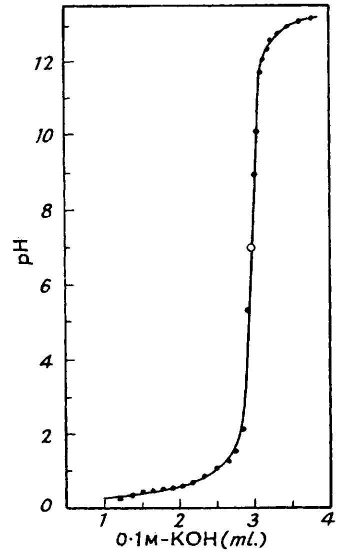


FIG. 1. *Potentiometric titration curve of* 30 *ml. of* 0·01M-*hexanitrodiphenylamine with* 0·1M-*potassium hydroxide in dioxan.*

FIG. 2. *Effect of added potassium hydroxide on the absorption curves of hexanitrodiphenylamine.*

Composition : 0·01M-Hexanitrodiphenylamine (2 ml.), 0·01M-potassium hydroxide (*x* ml.), dioxan [(18 — *x*) ml.].

Percentage neutralisation : 1, 0; 2, 20; 3, 40; 4, 60; 5, 80; 6, 100; 7, 200; 8, 300%.

FIG. 3. *Effect of added water on the absorption curves of hexanitrodiphenylamine.*

Composition : 0·01M-Hexanitrodiphenylamine (2 ml.), water (*x* ml.) dioxan [(18 — *x*) ml.].

Concentration of water (%) : 1, 0; 2, 10; 3, 20; 4, 30; 5, 40; 6, 50; 7, 60; 8, 70%.

FIG. 3.

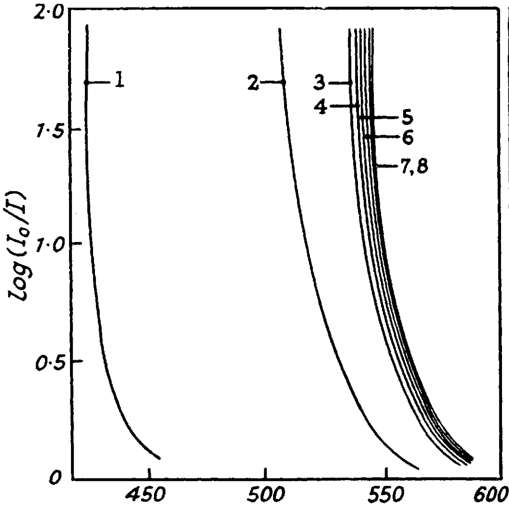
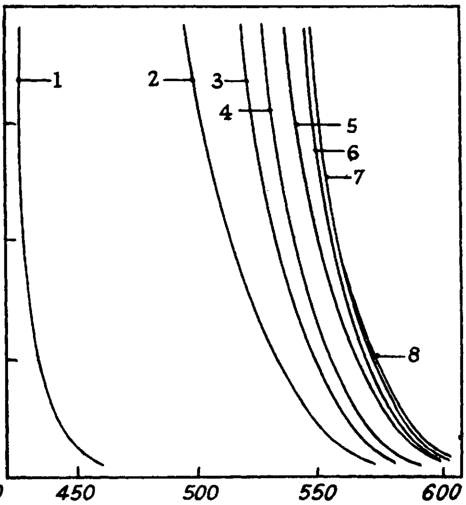


FIG. 2.



Ultraviolet absorption spectra. Fig. 4 shows the absorption spectra from 250 mμ to 520 mμ of the amine under different conditions. As can be seen, the minimum which occurs in curve (1) at 345 mμ has moved to roughly 300 mμ in curves (2) and (3), and the maximum at 355 mμ has shifted to 415 mμ. Although the amount of amine is the same in all three experiments, it is obvious that the absorbance is very roughly twice as large in (2) and (3) as in (1). No measurements could be made at wavelengths below 250 mμ, since dioxan itself absorbs strongly.

Effect of acids and electrolytes on colours. Qualitative tests were made to detect the influence of various acids and electrolytes on the yellow and the red form of hexanitrodiphenylamine in dioxan. Addition of concentrated sulphuric, nitric, hydrochloric, or acetic acid to the yellow form caused no change. Addition of lithium, sodium, or potassium nitrate solution to a yellow amine solution caused immediate formation of a deep red colour (the salt solutions were in 1 : 3 ethanol–dioxan—a blank test gave no colour change). On the addition of water to an acidified yellow solution the red form did not appear before the precipitation of the yellow solid took place. The red solution in dioxan, which had been prepared by adding a little sodium nitrate to the yellow solution, became yellow on the addition of concentrated hydrochloric acid. Glacial acetic acid had no effect on the colour.

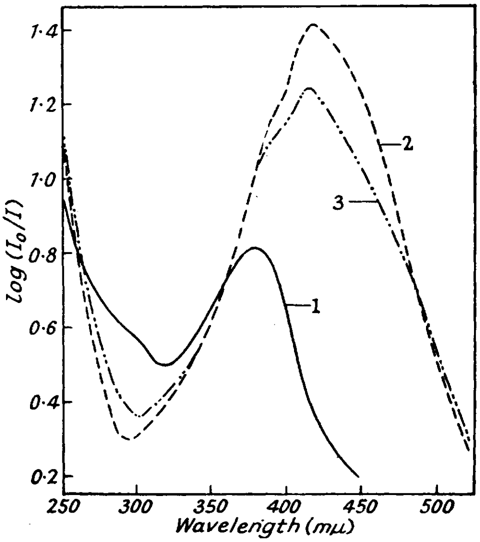
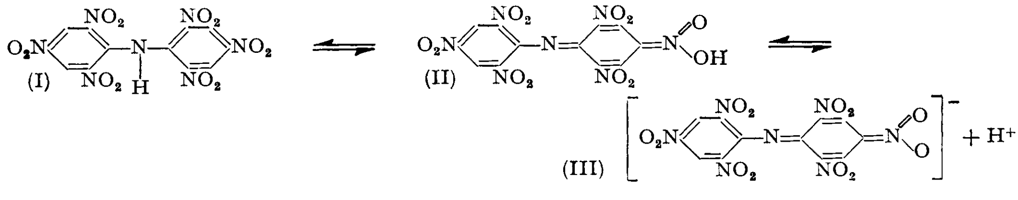


FIG. 4. *Absorption spectra of hexanitrodiphenylamine* (5×10^{-5}M).

1, In dioxan; 2, in 3 : 7 v/v water–dioxan; 3, in dioxan in presence of $1{\cdot}5 \times 10^{-4}$M-potassium hydroxide.

Discussion

On the basis of the work of Hantzsch and Lister[4] and in accordance with the suggestion of Feigl,[6] it can be assumed that hexanitrodiphenylamine exists in two forms (I; yellow) and (II; red). As seen from the determination of the dissociation constant, form (II) is a strong acid, dissociating into the ionized form (III) which will be the stable form. Therefore, it appears that (I) is the yellow crystalline form that is synthesized, being insoluble in water but readily soluble in non-polar solvents, whilst (III) is the red form, being an *anion* whose sodium salt is very soluble in water and in organic solvents. The intense colour is doubtless derived from the continuous system of conjugated double bonds, and from the possibility of ionic resonance existing in the anion, since both *para*-nitro-groups and all four *ortho*-nitro-groups are equivalent as far as each can become the *aci*-nitro-group. This effect would cause the stabilization and deepening of the colour.



According to Brönsted's definition of acids and bases, structure (I) can only be stable in the absence of proton-acceptors, which is the case with dioxan, it being too weak a proton-acceptor to effect the ionization of hexanitrodiphenylamine. The conversion into the red form requires a proton-acceptor. The experiments in which water was added to the yellow dioxan solution, changing it gradually to red, show that even water (a weak proton-acceptor) is sufficiently strong to cause the dissociation of structure (I) to (III). This dissociation is complete, if it is assumed that hydroxyl ions effect complete ionization, since the shift caused by the addition of 20% of water is substantially equal to the shift caused by the addition of hydroxyl ions, which are very strong proton-acceptors. The fact that so weak a proton-acceptor as water can cause complete dissociation is additional proof of the strength of the amine as an acid. Concerning its stability in water, Ungnade [7] found that polar solvents, such as water, would tend to stabilize polar quinonoid resonance forms such as anions of structure (III).

Naturally, in the presence of acids the concentration of the anion is repressed. All mineral acids convert the red into the yellow form, but acetic acid in dioxan is apparently too weak. However, the presence of neutral electrolytes, such as the alkali-metal nitrates, provides sufficiently strong proton-acceptors for the conversion into the anion structure (III) to take place.

The similarity of the spectrum of hexanitrodiphenylamine in 30% water in dioxan to its spectrum in the presence of an excess of potassium hydroxide in dioxan seems to suggest that the same anion is present in both solutions. Likewise the shift in the partial spectrum is of the same order of magnitude in both cases (Figs. 2 and 3). These facts make it reasonable to assume that the solution of the potassium salt contains the same free anions as does the acid, and that the potassium is not bound to the anion in an inner complex. The neutralization of a strong base, such as potassium hydroxide, with a strong acid, such as hexanitrodiphenylamine, would be expected to give a fully ionized salt, which the potassium salt of hexanitrodiphenylamine appears to be.

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[7] Ungnade, *J. Amer. Chem. Soc.*, 1953, **75**, 432.