158. *A Study of the Reaction of Some Nitrosoamines with α-Naphthylamine Hydrochloride.*

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The colorimetric reaction between aromatic *N*-nitrosoamines and α-naphthylamine hydrochloride takes place by the liberation of the nitroso-group and its reaction with α-naphthylamine hydrochloride to give the blue-violet hydrochloride of 4-amino-1 : 1′-azonaphthalene.

The reaction is suitable for the quantitative determination of these nitrosoamines and suggests a possible means of investigating their acid denitrosation.

The presence of nitro-groups in the aromatic nucleus of the nitrosoamine molecule causes a marked decrease in the velocity of the decomposition.

The blue-violet colour produced when *N*-nitroso-*N*-ethylaniline reacts with α-naphthylamine in alcoholic hydrochloric acid was noted by Lecorche and Jovinet (*Mém. Poudres*, 1928, **23**, 147). A similar reaction takes place with many other aromatic nitrosoamines, and the object of the present investigation was to establish the mechanism of the reaction. The results obtained have shown that under certain conditions the reaction is suitable for the colorimetric determination of these compounds.

N-Nitroso-*N*-ethylaniline and its 2-nitro-, 3-nitro-, 4-nitro-, 2 : 4-dinitro-, and 2 : 4 : 6-trinitro-derivatives were selected for study. The intensity of colour produced by each of these compounds under selected conditions of test was measured with a " Spekker " photoelectric absorptiometer and determined as a function of the time of heating at 60°. The depth of colour increased with time and finally reached a maximum and almost constant value (Fig. 1), except with the trinitro-compound which gave only a faint colour after 6 hours at 60°.

The maximum colour intensities at different concentrations are shown graphically (Fig. 2). In each case a straight-line relationship was demonstrated within the normal range of the absorptiometer. Comparison of the slopes of these graphs gives a direct estimate of the relative amount of colour produced from 1 mg. of each of the nitrosoamines. The slopes are in the following ratio :

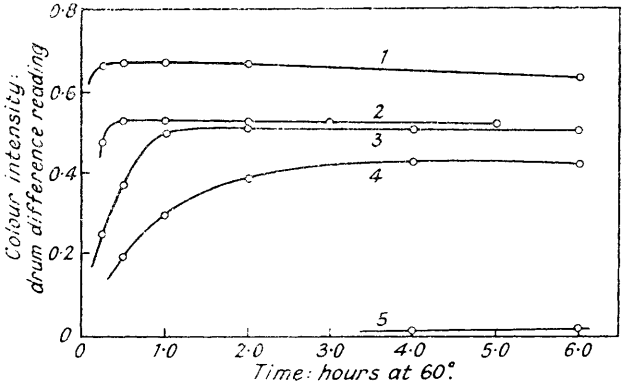
N-nitroso-*N*-ethylaniline : mononitro-derivatives : dinitro-derivatives = 1·62 : 1·28 : 1·00

and are thus almost exactly proportional to the reciprocal molecular weights (*i.e.*, 1·60 : 1·30 : 1·00). This result suggests that the agent producing the colour is nitrous acid, which would be liberated from the nitrosoamines in just this proportion. By treatment of dilute alcoholic solutions of sodium nitrite with α-naphthylamine and alcoholic hydrochloric acid in the same way, solutions of identical tint were produced, the slope of the colour intensity–concentration curve being roughly proportional to the reciprocal of the molecular weight of sodium nitrite.

The action of nitrous acid upon an excess of α-naphthylamine would be expected to produce either 1 : 1′-diazoaminonaphthalene or 4-amino-1 : 1′-azonaphthalene. The dye obtained from the nitrosoamines had indicator properties, being red-brown in alkaline solutions and blue-violet in acid solution, and was identified as 4-amino-1 : 1′-azonaphthalene.

FIG. 1.

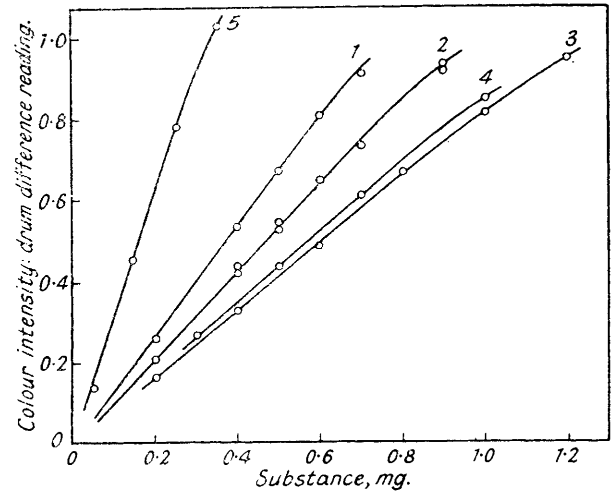
Rates of development of colour at 60° (*as measured by " Spekker " absorption*).



(1) N-*Nitroso*-N-*ethylaniline*. (2) 4-*Nitro- and* 3-*nitro-derivatives*. (3) 2-*Nitro-derivative*. (4) 2 : 4-*Dinitro-derivative*. (5) 2 : 4 : 6-*Trinitro-derivative*.

FIG. 2.

Colour intensity–concentration curves (*after full colour development*).



(1) N-*Nitroso*-N-*ethylaniline*. (2) *Mononitro-derivatives*. (3) 2 : 4-*Dinitro-derivative*. (4) 4-*Amino*-1 : 1′-*azonaphthalene*. (5) *Sodium nitrite*.

From the colour intensity–concentration curve for solutions of 4-amino-1 : 1′-azonaphthalene in N/10-alcoholic hydrochloric acid was calculated the percentage of available nitrous acid in each of the nitrosoamines which is converted into this dye (see Table).

Compound (in N/10-alcoholic hydrochloric acid).	Available nitrous acid converted into the dye (%).
Sodium nitrite	85
N-Nitroso-*N*-ethylaniline	79
2-Nitro-derivative	77
3-Nitro-derivative	77
4-Nitro-derivative	77
2 : 4-Dinitro-derivative	78

It appears that (with dilute solutions in N/10-alcoholic hydrochloric acid) about 85% of free nitrous acid is converted into the dye, whereas with the nitrosoamines a little less than 80% of the available nitrous acid is converted. This discrepancy can be partly explained by the fact that the nitrosoamines are not quantitatively converted into the free bases. Thus from absorption measurements it appears that only 96% of the 4-nitro-derivative is recoverable as 4-nitro-*N*-ethylaniline. The fate of the remaining 4% of nitrosoamine and 15% of nitrous acid has not been determined.

Neber and Rauscher (*Annalen*, **1942**, **550**, 182) have shown that the Fischer–Hepp rearrangement of

N-nitrosoamines to their nuclear substituted isomers takes place in alcoholic hydrochloric acid through the intermediate formation of nitrosyl chloride. It is probable, therefore, that this is also the intermediate in the production of the colour with α-naphthylamine. It is significant that the use of sulphuric in place of hydrochloric acid reduces the intensity of the colour developed (after ½ hour at 60°) to about one quarter. However, the concentrations of nitrosoamine used in the present investigation were extremely small when compared with those used by the above workers.

Purely aliphatic nitrosoamines do not undergo this denitrosation in acid media. Thus solutions of dimethyl- and diethyl-nitrosoamine developed very little colour even after prolonged heating with α-naphthylamine and alcoholic hydrochloric acid. On the other hand, the rate of denitrosation of diphenylnitrosoamine was far greater than that of phenylethylnitrosoamine.

Since the reaction of nitrous acid with α-naphthylamine in N/10 alcoholic hydrochloric acid is very rapid, even at room temperature, the rate at which the dye is produced from the nitrosoamines is clearly a measure of the rate of their decomposition into the corresponding bases with the liberation of the nitroso-group. Assuming this denitrosation to be an electrophilic reaction involving the addition of a proton to the amino-nitrogen atom, the effect of aromatic substituents upon the rate of denitrosation is readily explained by the electronic theory. The aliphatic nitrosoamines do not react, owing to the polarisation by the nitroso-group which induces a positive charge on the amino-nitrogen atom. The introduction of the polarisable aromatic nucleus reduces this positive charge, enabling the proton addition to take place, while the introduction of electron-attracting nitro-groups into the aromatic nucleus again reduces the ease of proton addition. No doubt the marked decrease in reaction velocity which occurs when a nitro-group enters the *ortho* position is due to the introduction of a steric factor which considerably reduces the number of effective collisions of proton and nitrosoamine molecule.

The part played by ethyl alcohol in the reaction mechanism is not clear, but as the alcohol is diluted with water the reaction velocity decreases progressively until an alcohol content of about 65% w/w is reached. Further dilution causes an increase in the reaction velocity. This effect appears to be due to the change in pH of the solution which accompanies dilution, the pH being at a maximum for 65% alcohol.

The decomposition of nitrosoamines in acid media appears to be analogous to the decomposition of *N*-nitroamines under similar conditions. For example, in the presence of dilute mineral acid, the nitro-group in phenylmethylnitroamine readily splits off and migrates into the aromatic nucleus with the formation of *o*- and *p*-nitromethylanilines (Bamberger, *Ber.*, 1897, **30**, 1253). The dinitro- and trinitro-phenylmethylnitroamines are, however, far more stable.

EXPERIMENTAL.

N-Nitroso-*N*-ethylaniline and its 2-, 3-, and 4-nitro-derivatives were prepared in the normal manner by the treatment of hydrochloric acid solutions of the amines with sodium nitrite. The 2-nitro-nitrosoamine had m. p. 33·3—34·3°. Hempel (*J. pr. Chem.*, 1890, **41**, 167) gives m. p. 30°.

The method of Stoermer and Hoffman (*Ber.*, 1898, **31**, 2531) for the preparation of 2 : 4-dinitro-*N*-nitroso-*N*-ethylaniline gave rather poor yields. A satisfactory yield was obtained by the treatment of a solution of 2 : 4-dinitro-*N*-ethylaniline in concentrated sulphuric acid with sodium nitrite, the product being isolated by pouring the reaction mixture on crushed ice. For the removal of the last traces of unchanged dinitroamine the product was chromatographed using a 1 : 1 mixture of silica gel–celite as adsorbent and 10% of ethyl ether in light petroleum as developer (the nitrosoamine was more strongly adsorbed than the free amine under these conditions). After a final crystallisation from benzene–ligroin, small pale yellow platelets were obtained, m. p. 55·1—55·8°. Stoermer and Hoffman give 51·5—52·5°.

No record of 2 : 4 : 6-trinitro-*N*-nitroso-*N*-ethylaniline could be found in the literature. This compound was prepared by a method similar to that used for the preparation of the corresponding dinitronitrosoamine, final purification being effected by chromatography as before. After crystallisation from alcohol, pale yellow crystals were obtained, m. p. 73·0°. The *compound* gave a deep blue colour on treatment with diphenylamine in concentrated sulphuric acid. The presence of three nitro-groups and one nitroso-group was confirmed by titration of a small quantity with titanous sulphate [1 equiv. of titanous sulphate corresponded to 12·0 g. of the compound. $C_6H_2(NO_2)_3{\cdot}N(C_2H_5){\cdot}NO$ requires 11·88 g.].

4-Amino-1 : 1′-azonaphthalene was prepared by the method of Michaelis and Erdmann (*Ber.*, 1895, **28**, 2198), and had m. p. 175·5—176° (Found : C, 80·95; H, 5·13; N, 14·05; *M* (in benzene), 291. Calc. for $C_{20}H_{15}N_3$: C, 80·77; H, 5·09; N, 14·14%; *M*, 297·1).

Reagents.—Some batches of 95% alcohol or methylated spirits contained traces of impurities (possibly nitrites) which produced a small amount of colour when treated with α-naphthylamine and hydrochloric acid. In addition, certain impurities normally present in the alcohol interfere with the full colour development of the nitrosoamine under the specified conditions. All alcohol was therefore purified by distillation over lime through an efficient fractionating column (a column 4½ feet long and 2½ inches in diameter, packed with glass cuts proved satisfactory).

" AnalaR " α-Naphthylamine was recrystallised from boiling light petroleum (b. p. 40—60°). The product was dissolved in purified alcohol to give a 1% solution.

Dry hydrogen chloride was dissolved in purified alcohol to give a 2N-solution.

Rate of Development of Colour from the Nitrosoamines at 60°.—0·5 Mg. quantities of each of the nitrosoamines, dissolved in 5 ml. of purified alcohol, were placed in 100 ml. calibrated flasks. 80 Ml. of purified alcohol, 5 ml. of hydrochloric acid reagent, and 5 ml. of 1% α-naphthylamine solution were added to each. The flasks were kept in a water-bath at 60° ± 2° for various periods, after which they were transferred to a bath at 20° for 1 hour. A blank test with the reagents alone was included.

The solutions were then made up to 100 ml. and their extinctions (*i.e.*, difference in drum reading between blank and sample solutions) measured with the " Spekker " absorptiometer, using 1 cm. cells, a water-to-water setting of 1·00, and Ilford yellow-green filters No. 605.

The results obtained for the six nitrosoamines are given in a graph (Fig. 1) showing colour intensity (in terms of " Spekker " drum difference reading) plotted against time of colour development at 60°.

Construction of Colour Intensity–Concentration Curves.—The procedure described in the previous paragraph was applied to various quantities of each nitrosoamine, adopting the appropriate times for maximum colour development, as follows :

N-Nitroso-*N*-ethylaniline	30 minutes.		
4-Nitro-derivative	30 ,,	2-Nitro-derivative	3 hours.
3-Nitro-derivative	30 ,,	2 : 4-Dinitro-derivative	4 ,,

Curves were similarly obtained for sodium nitrite and 4-amino-1 : 1′-azonaphthalene (except that no heating at 60° was necessary for the development of the colour), using the same quantities of reagents. All these curves are shown in Fig. 2.

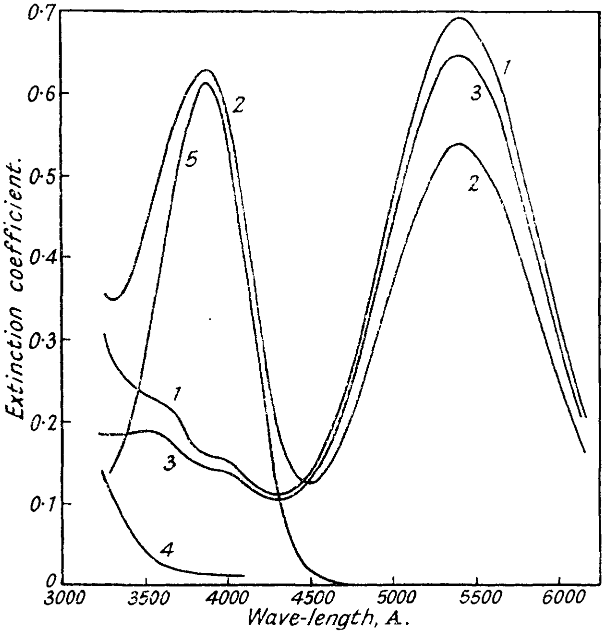
Effect of Variation of the Concentration of the Reagents.—In order to select the optimum conditions for the colour reaction, experiments were carried out in which the concentrations of hydrochloric acid and α-naphthylamine were varied. Concentrations lower than those selected failed to produce a full colour development in the times chosen.

Stability of the Coloured Solutions.—The coloured solutions resulting from the reactions studied were quite stable when stored in the dark. No significant change was detected during one week, but on prolonged storage a slight fading of the colour was noticed.

Constitution of the Dye.—(*a*) After treating 0·2 g. of sodium nitrite and 0·3 g. of *N*-nitroso-*N*-ethylaniline severally with α-naphthylamine under the selected conditions, small quantities of the resulting dye (as the free base) were isolated and identified by m. p. in admixture with 4-amino-1 : 1′-azonaphthalene. *N*-Ethylaniline was isolated from the products of the second reaction.

FIG. 3.

Absorption curves.



(1) *Solution derived from* 0·5 *mg. of* N-*nitroso*-N-*ethylaniline.*
(2) *Solution derived from* 0·5 *mg. of the* 4-*nitro-derivative.*
(3) *Solution of* 4-*amino*-1 : 1′-*azonaphthalene in* N/10-*alcoholic* HCl.
(4) 0·05 *G. of* α-*naphthylamine in* 100 *ml. of* N/10-*alcoholic* HCl.
(5) 0·5 *Mg. of* 4-*nitro*-N-*ethylaniline in* 100 *ml. of* 95% *alcohol.*

(*b*) Absorption curves were obtained over the range 3250—6500 A. for the following solutions (see Fig. 3) :

(i) That obtained by treating 0·5 mg. of *N*-nitroso-*N*-ethylaniline in alcoholic hydrochloric acid with α-naphthylamine under the selected conditions.

(ii) That obtained by the similar treatment of 0·5 mg. of the 4-nitro-derivative.

(iii) 4-Amino-1 : 1′-azonaphthalene in 0·1N-alcoholic hydrochloric acid.

(iv) A blank solution containing 0·05 g. of α-naphthylamine in 100 ml. of 0·1N-alcoholic hydrochloric acid.

(v) 0·5 Mg. of 4-nitro-*N*-ethylaniline in 100 ml. of 95% alcohol.

The solution of the hydrochloride of 4-amino-1 : 1′-azonaphthalene shows a maximum at 5400—5420 A. and two plateaux at 3250—3500 A. and 3750—4000 A. Both solutions (i) and (ii) show the maximum at 5400—5420 A. and the solution derived from the *N*-nitroso-*N*-ethylaniline (i) shows the two plateaux (although modified by the rise in absorption from 4000 to 3250 A. caused by the presence of the α-naphthylamine). In solution (ii) the plateaux are completely obscured by the maximum which this solution shows at 3850—3870 A. This corresponds to the maximum shown by the solution of 4-nitro-*N*-ethylaniline in 95% alcohol. The relative heights of the latter maxima (after correction for the absorption shown by the dye at this wave-length) indicate that 96% of the 4-nitronitrosoamine has been converted into 4-nitro-*N*-ethylaniline.

The absorption curves were obtained with a Beckman Quartz Photoelectric Spectrophotometer, using a tungsten filament lamp as light source and slit widths such that the sensitivity control was set at three turns from its clockwise limit.

The author desires to express his thanks to the Director of Scientific Research, Admiralty, for permission to publish this paper.

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[*Received, February* 11*th*, 1946.]