Dyes and Pigments **12** (1990) 173–177

Studies on the Diazotization of Aromatic Amines with Glycol Nitrite

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(Received 15 November 1988; accepted 9 January 1989)

ABSTRACT

A new method for the diazotization of aromatic amines in a non-aqueous system is presented. The process is a modification of the known Knoevenagel's method and consists of treating solutions or dispersions of amine sulphates in ethylene glycol with glycol nitrite.

1 INTRODUCTION

There is a growing interest in the synthesis of some azo dyes in non-aqueous systems, particularly in the synthesis of disperse dyes and pigments, where the change of reaction medium can lead to the formation of new crystalline dye forms with improved performance properties. Coupling in non-aqueous systems is associated with the need to use non-aqueous diazo salts. Such an approach can be partly realized by using for the coupling process stable salts or the diazoamino compounds used as components in azoic dyes. However, the use of such compounds is restricted, since the diazo salts of many amines cannot be separated from an aqueous solution in this form and the commercially available products contain considerable amounts of inorganic salts often environmentally hazardous e.g. zinc chloride.

The known diazotization methods for amines in organic solvents are of theoretical or laboratory significance and are not used on a commercial scale. Typical of these is the method of Griess,[1] who in 1866 discovered the diazotization process by passing nitrogen oxides through an ethanolic solution of picramic acid. Griess's method was later modified by

Dyes and Pigments 0143-7208/90/$03·50

Knoevenagel,[2,3] who used alkyl nitrites instead of nitrogen oxides. In this process, ethanolic solutions of amine hydrochloride or amine sulphate are treated with, for example, butyl or amyl nitrite. The reaction is often used in laboratories to separate solid diazonium salts.[4] Also described has been the diazotization of some amines in systems such as glacial acetic acid, acetate, benzene, chloroform, DMF and formamide.[5]

It seemed of interest therefore, to examine the use of glycol nitrite for the diazotization of amines in ethylene glycol, to investigate the diazonium compounds thus obtained and to use them for the synthesis of dyes and pigments.

2 EXPERIMENTAL[6]

Aniline (**I**) and its derivatives such as 4-methyl- (**II**), 4-chloro- (**III**), 4-nitro- (**IV**), 2,5-dichloro- (**V**), 2-chloro-4-nitro- (**VI**), 4-chloro-2-nitro- (**VII**), 2-methoxy-4-nitro- (**VIII**), 4-methoxy-2-nitro- (**IX**), 4-methyl-2-nitro- (**X**) and 2,4-dinitro-aniline (**XI**) were used for diazotization.

Glycol nitrite used as a diazotizing agent was prepared by dropping concentrated sulphuric acid in a stoichiometric quantity at 15°C into a dispersion of sodium nitrite in excess ethylene glycol. Precipitated $NaHSO_4$ was filtered off and the solution was found to be approx. 10% glycol nitrite in ethylene glycol. The process is illustrated by eqn (1).

$$\begin{aligned}&HOCH_2CH_2{-}OH + NaNO_2 + H_2SO_4 \rightarrow\\&\qquad HOCH_2CH_2{-}ONO + NaHSO_4 + H_2O \qquad (1)\end{aligned}$$

The glycol nitrite content in ethylene glycol was determined by titration of a known weight of pure 4-chloroaniline with the prepared solution. The diazotization of aromatic amines was carried out at 20–30°C by dropping stoichiometric quantities of glycol nitrite into the solution or dispersion of amine in ethylene glycol in the presence of sulphuric acid used in some excess. The excess was found experimentally to eliminate the formation of diazoamine compounds. The process of diazotization of amines is illustrated by eqn (2):

$$\begin{aligned}&ArNH_2 + H_2SO_4 + ON{-}OCH_2CH_2OH \rightarrow\\&\qquad ArN_2^+HSO_4^- + HOCH_2CH_2OH + H_2O \qquad (2)\end{aligned}$$

The diazotization process was controlled with potassium iodide–starch paper after diluting a reaction sample with a small amount of water. At the same time the process was controlled by means of a test with sodium acetate, viz. a sample was diluted with a small amount of 10% sodium acetate and

TABLE 1
Characteristics of the Diazotization of Aromatic Amines

Amine	$[ArNH_2]/[H_2SO_4]$	*Temperature* (°*C*)	*Water content* (%)	*Time* (*h*)	*Yield* (%)	*Decomposition after 24 h at 20°C* (%)
I Aniline	1:1·2	30	—	3	56·5	—
	1:1·2	30	—	8	64·15	—
	1:1·2	30	—	24	80·7	—
	1:1·2	30	12·5	2·5	95·7	—
II 4-Methylaniline	1:1·1	30	—	3	72·5	—
	1:1·1	30	—	8	80·2	—
	1:1·1	30	—	24	87·8	—
	1:1·1	30	12·5	2	95·3	—
III 4-Chloroaniline	1:1·5	25	—	1	70·9	—
	1:1·5	25	—	4	78·0	—
	1:1·5	25	—	24	87·0	—
	1:1·5	25	12·5	1·5	97·5	—
IV 2,5-Dichloroaniline	1:1·5	20	—	1	97·5	11·8
V 4-Nitroaniline	1:2	20	—	0·5	97·2	4·1
VI 2-Chloro-4-nitroaniline[a]	1:2	20	—	0·5	97·7	7·5
VII 4-Chloro-2-nitroaniline	1:2·5	20	—	0·5	97·7	6·7
VIII 2-Methoxy-4-nitroaniline	1:2	20	—	0·5	95·9	6·2
IX 4-Methoxy-2-nitroaniline	1:2	20	—	0·5	97·5	9·9
X 4-Methyl-2-nitroaniline	1:2	20	—	0·5	96·0	2·5
XI 2,4-Dinitroaniline[a]	1:3	20	—	1·5	94·7	36·6

[a] Process carried out in suspension.

the formation of a yellow dispersion of diazoamino compounds shows the presence of unreacted amine. A negative test result confirmed that the diazotization process was complete and thus allowed the diazotization time to be determined.

After diazotization, the solutions were coupled with a solution of the sodium salt of 2-naphthol in 50% ethanol. The medium used in this process ensured rapid coupling, and was also a good solvent for the unreacted compounds and impurities such as diazonium compounds. The insoluble pigments precipitated in this process were filtered, washed thoroughly with 50% ethanol, dried and weighed. Assuming that the coupling process was quantitatively complete, the yield of diazotization of particular amines was calculated. In the same way the content of diazonium salts in solutions stored for 24 h at 20°C was determined. The results were used to evaluate the stability of the glycol solutions of diazonium salts. The yield and conditions of the diazotization of various amines are given in Table 1.

The ethylene glycol used in the reactions was of pure grade from POCh Gliwice (Poland).

The optimum temperature for the diazotization process was fixed experimentally by measuring the time and yield of the diazotization at various temperatures. The parameters of amine diazotization are given in Table 1.

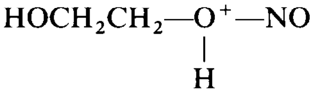
3 DISCUSSION OF RESULTS

As shown by the investigations, aniline (**I**) and amines with similar basicity (**II**, **III**) should be diazotized at 25–30°C. The remaining amines (**IV**–**XI**) with a basicity similar to that of 4-nitro- or 2,4-dinitro-aniline, are well diazotized at 20°C.

It was found that at low temperatures (0–10°C) the diazotization process was slow. The diazotization rate can be considerably increased by raising the temperature of diazotization, but there is a danger of decomposition of the diazonium salts. Detailed studies have shown that glycol solutions of diazonium salts have a relatively high stability. However, under these conditions, they undergo slow deamination, whilst analogous aqueous solutions undergo phenolic decomposition. This is in agreement with the mechanism of diazotization in which the concentration of a free amine is one of the factors controlling the reaction rate.

It has been found that the method is also suitable for the diazotization of some amines of very low basicity such as 2,4-dinitroaniline (**XI**) which are usually diazotized in concentrated sulphuric acid.

The observations show that the nitrosonium cation (^{+}NO) is probably the potential diazotizing agent, being in equilibrium with the protonated form of glycol nitrite,



$$HOCH_2CH_2\text{—}\underset{\displaystyle |\atop \displaystyle H}{O^+}\text{—}NO$$

This explains the facile diazotization of amines with a basicity as low as that of 2,4-dinitroaniline.

The reagents and conditions of the diazotization process make the method simple, safe and suitable for successful use under industrial conditions. The advantages result from the use of ethylene glycol as a medium in the synthesis of glycol nitrite as well as in the diazotization of aromatic amines. Ethylene glycol is an inexpensive, non-toxic, water-soluble solvent and is characterized by low decomposition during regeneration, and its possible residues are readily degradable in waste water.

At the same time the solution of glycol nitrite used as the diazotizing agent is not environmentally troublesome. Due to its very low volatility and dilution with ethylene glycol it does not possess such strong physiological properties as those of the more volatile butyl and amyl nitrites used in the method of Knoevenagel. The reagent is also water-soluble and can be easily removed and neutralized. It was also found that glycol nitrite in the form of solution in ethylene glycol is stable and does not decompose at 20°C for several weeks unless it is not fully neutralized.

From the point of view of dye technology, the process is suitable for the diazotization of many aromatic amines such as 4-nitroaniline and its derivatives, commonly used as diazo components in pigments and disperse dyes. The glycol solutions of diazonium salts were successfully used in the synthesis of organic pigments in organic solvents or their mixtures with water. The results of these experiments will be given in a separate publication.

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