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SHORT COMMUNICATIONS

KINETICS AND MECHANISM OF THE DIAZO COUPLING REACTION OF 1-ARYL-3,3-DIETHYLTRIAZINES WITH β-NAPHTHOL IN NON-AQUEOUS ACID SOLUTIONS

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ABSTRACT. Rates of reaction of 1-aryl-3,3-diethyltriazines with β-naphthol in acid media to yield azo dyes have been measured in dimethylformamide solution at 25°. For a series of four acids of different acid strengths, pseudo-first-order rate constants were obtained, and the reaction was found to be follow third order kinetics, first order in triazine, and second order in acid. The kinetic results support a mechanism in which the slow step is bimolecular decomposition of the protonated triazine, TH^+, with an acid, HA, to the coupling entity, the diazonium ion, D^+, which reacts rapidly with β-naphthol to produce the azo dye.

INTRODUCTION

The preparation of 1-aryl-3,3-diethyltriazines, and a proposed mechanism for the diazo coupling reaction of the substrate (**1**) with β-naphthol, has recently been described [1]. The investigation was extended to involve a new variety of acids in non-aqueous solvents of varied character. Dimethylformamide (DMF) was used in this study. The moderately high dielectric constant (36.7 at 25°), and its aprotic nature make it particularly useful for acid-base studies, and a good solvent for a wide range of polar and nonpolar organic compounds [2 - 5]. Moreover, azoic dyes are readily stripped in pure form from the fibre by DMF [6].

Coupling of 1-aryl-3,3-diethyltriazines (**1a-j**) with β-naphthol in dimethylformamide solution and in the presence of acids resulted in almost quantitative yields of the azo dyes (**2a-j**) [1]. The diazo coupling reaction of the triazines (**1**) with β-naphthol in DMF was monitored spectrophotometrically at the absorbance maximum of the corresponding dye (**2**) [1]. Since acids accelerate the production of color, the effects of 2-hydroxybenzoic, 2,6-dihydroxybenzoic, hydrochloric, and picric acids on the reaction rate were examined at 25°.

RESULTS AND DISCUSSION

Satisfactory first-order rate constants were obtained for the reaction of the triazines (**1**) [1] with β-naphthol in four acids of varying acidity using DMF as a protophilic solvent. The concentration of acids ranged from 0.01 to 2 M on going from picric to 2-hydroxybenzoic acid and kinetic studies were carried out at five different concentrations for each acid with all the triazines examined (**1a-j**) [1]. The kinetic behaviour conformed accurately to the rate law:

$$- d\,[T]\,/\,[T]\,dt = k_{obs} = k_{cat}\,[HA]^2 \qquad (1)$$

Consequently, catalytic coefficients, k_{cat}, could be evaluated as slopes of plots of k_{obs} *versus* $[HA]^2$.

It is worth nothing that for each compound, the catalytic rate ratios

$$(k_{cat})_{HA}\,/\,(k_{cat})_{2\text{-hydroxybenzoic acid}}$$

are: 1, 220, 330, 2090 for 2-hydroxybenzoic, 2,6-dihydroxybenzoic, hydrochloric, and picric acid, respectively. Consequently, it was possible to construct a Brønsted plot for this reaction. The mathematical expression of these linear correlations satisfies the equation

$$\log k_{cat} = \alpha \log k_a + C \qquad (2)$$

A constant value of $0.5 + 0.02$ for the Brønsted parameter, α, was estimated from the good fit of the log k_{cat} *versus* log k_a [7] correlations. This moderate magnitudes of α [8,9] leads to the conclusion that decomposition of each of the triazines in acid media exhibits general acid catalysis.

The dependence of the rate of reaction upon the square of the acid concentration, the fact that electron-withdrawing substituents in the benzenediazo residue of substrates decrease the values of k_{obs} [1], and the linear relationship between values of k_{cat} and k_a are compatible with the following scheme (Equations 3-5):

$$ArN_2N(C_2H_5)_2 + HA \rightleftharpoons ArN_2N^+H(C_2H_5)_2 + A^- \qquad (3)$$

$$ArN_2N^+H(C_2H_5)_2 + HA \rightarrow ArN_2^+ + (C_2H_5)_2NH_2^+A^- \qquad (4)$$

$$ArN_2^+ + \beta\text{-}HOC_{10}H_7 + A^- \rightarrow ArN_2C_{10}H_6(OH)\text{-}\beta + HA \qquad (5)$$

The rate of reaction is represented by Equation (6), where k_2 is the rate constant for the slow step.

$$Rate = \frac{k_1k_2\;[T]\;[HA]^2}{k_{-1} + k_2\,[HA]} \qquad (6)$$

If $k_{-1} > k_2\,[HA]$, the reaction becomes second order in acid, and the experimental first-order rate constant (k_{obs}) is given by Equation (7).

$$k_{obs} = K\,[HA]^2 \qquad (7)$$

where

$$K = \frac{k_1k_2}{k_{-1}} = k_{cat}$$

The predicted rate equation (Equation (1)) for reactions (3) - (5) is in agreement with experiment.

EXPERIMENTAL

Materials. The ten triazines used in this investigation were prepared, purified and standardized by the procedure described earlier [1]. β-Naphthol was available in pure form from a previous study [1]. Spectrophotometric grade DMF (Jansen Chimica) was further dried and purified according to literature procedure [10]. The purified solvent was used within 48 h. 2-Hydroxybenzoic and picric acids [11] as well as hydrochloric acid [12, 13], were used as described previously. 2,6-Dihydroxybenzoic acid, obtained from Jansen Chimica, was recrystallized from water and dried under vacuum at 70 °[14].

Kinetic measurements. Rates of reaction were determined by spectrophotometric analysis for azo dyes using a Bausch and Lomb spectronic 21 UVD spectrophotometer. The technique used in the present study is the same as previously reported [1]. Reactions were studied under pseudo-first-order conditions, with β-naphthol and acids in excess.

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