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PHOTO-OXIDATION OF SULPHANILAMIDE TO AZO AND AZOXY COMPOUNDS

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ABSTRACT

The second-order kinetics for the photochemical formation of azobenzene-4, 4-disulphonamide has been studied at pH 1-11 and at pH 7.0 in the presence of five antioxidants. The rate constants are not affected by changes in pH in the region of 5-9 at which the molecule is predominentiy in the unionised form. The rate of formation of azobenzene-4, 4'-disulphonamide is inhibited upto 80% by ascorbic acid. A scheme for the photo-oxidation of sulphanilamide to the azo and azoxy derivatives has been outlined.

Introduction

The photochemical formation of azobenzene-4, 4'-disulphonamide and azoxybenzene-4, 4'-disulphonamide on prolonged storage of sulphanilamide solutions (Clarke, 1965) and photodegradation of sulphacctamide solutions (Pandula, Racz and Pajor, 1969) has been reported. The photolysed sulphanilamide solutions assume yellow to intense orange-brown colour (Agyakawa and Haas, 1972) due to the presence of these compounds. Azo and azoxy derivatives have been identified as the photoproducts of sulphanilamide at pH 1-13 (Ahmad and Ahmad, 1981). In the present work an attempt has been made to study the phtochemical formation of azobenzene-4, 4'disulphonamide and to present a scheme for the photo-oxidation of sulphanilamide to azo and azoxy derivatives.

Materials and Method

Sulphanilamide was obtained from BDH and used as such. Azobenzene-4, 4'-disulphonamide and azoxybenzene-4, 4'-disulphonamide were prepared by the method of Seikel (Seikel, 1940) and recrystallised from 30% aqueous pyridine. Sulphanilamide solutions l0-'M) photolysed in a silica flask using a 30 watt Phillips UV tube (88% emission at 254nm) at pH 1-11 according to the method previously reported (Ahmad and Ahmad, 1983). Azobenzene-4, 4'-disulphonamide was determined by a two component spectrophotometric assay using the analytical wavelengths of 258nm and 320nm (Ahmad, 1978).

Table 1: Formation of Azobenzene-4,4' -disulphonamide Derivative of sulphanilamide in photolysed solutions.

pH	Second-order Rate
1	2.439 x 10^{4}
3	11.750x 10^{-4}
5	16.000 x 10^{-4}
7	15.000x10^{-4}
9	17.210 x 10^{-4}
11	15.000 x 10^{-4}
12	12.500 x 10^{-4}
13	5.952 x 10^{-4}

Results and Discussion

The gradual decrease in absorption at 258nm of sulphanilamide solutions during UV irradiation and simultaneous increase in absorption in the region of 280nm-380nm is in accordance with the absorption characteristics of azobenzene-4, 4'-disulphonamide (λ max 320nm) and azoxybenzene-4, 4'-disulphonamide (X max 336nm). The former compound, being the major product, absorbs strongly at 320nm, one of the wavelengths subsequently used for the spectrophotometric assay of azobenzene-4, 4'-disulphonamide in photolysed solutions. The apparent 2nd-order rate constants for the photoformation of azobenzene-4, 4'-disulphonamide are reported in Table-1. The rates do not appear to be affected by pH in the region of 5-9, whereas pH 5 (PK for NH, group, 2.36) and above pH 11 (PK, for SO_2NH_2 group 10.43) (Northey, 1948) the decrease in rate constants may be due to ionization of the molecule (Fig. 1).

Table 2: Formation of Azo derivative at pH 7.0 (Phosphate Buffer) in presence of Antioxidants.

Antioxidant	E°red(v)	Second-order Rate Constant (M^{-1} min: $^{-1}$)	Rate inhibition (%)
–		15.00 x 10^{-4}	0
Sodium sulphite	-0.92(11)	6.96 x 10^{-4}	54
Sodium thiosulphate	+0.10(12)	7.22 x 10^{-4}	52
Sodium metabisulphite		4.16 x 10^{-4}	72
Thiourea	+0.41(15)	3.38 x 10^{-4}	77
Ascorbic acid	+0.40(14)	2.98 x 10^{-4}	80

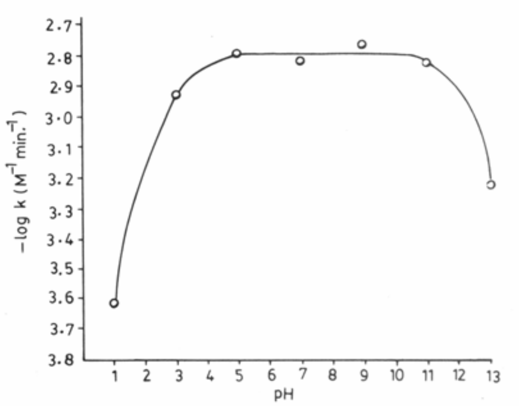

Fig. 1: pH dependency of the formation of Azo compound.

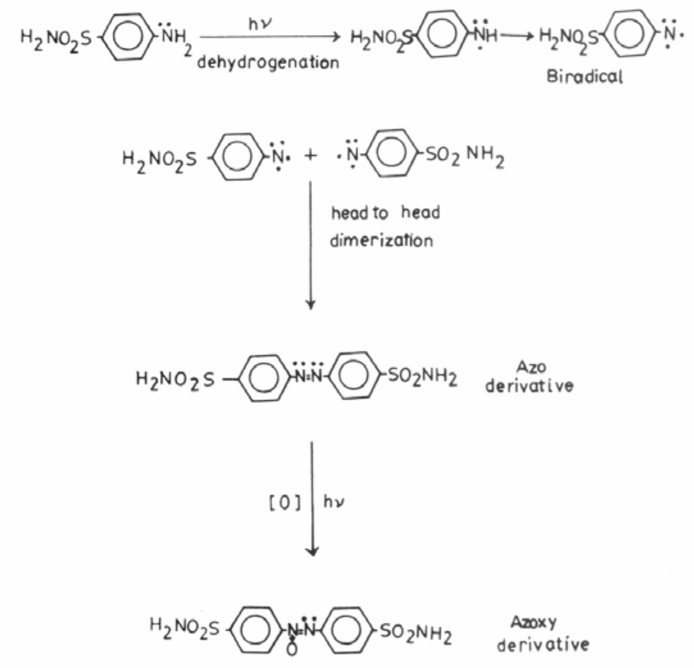

Fig. 2: Photolysis of Sulphanilamide to Azobenzene-4, 4’-disulphonamide and Azoxybenzene-4, 4’disulphonamide.

In order to observe the effect of certain antioxidants (0.01%) on the rate of formation of azobenzene-4, 4'-disulphonamide at pH 7.0 the photolysis was carried out in the presence of sodium sulphite, sodium thiosulphate, thiourea and ascorbic acid. The 2nd-order rate constants for these reactions are reported in Table-2. It may be concluded that the action of the antioxidants increases in the order of their increasing redox potentials and is in general agreement with the photolysis pattern of sulphanilamide under the same experimental conditions (Ahmad and Ahmad, 1983). The corresponding rates of inhibition for these antioxidants arc 52%, 54%, 72%, 77% and 80%. On the basis of the kinetic results and spectral characteristics of photolysed solutions a scheme for the photo formation of azobenzene-4, 4'-disulphonamide and azoxybenzene-4, 4'-disulphonamide may be formulated (Fig. 2).

Sulphanilamide on absorption of radiation is excited to the singlet state which may be deactivated by the emission of fluorescence/heat or else may be transformed to the triplet state. The triplet state may lose hydrogen atom to the solvent to form a biradical. The biradicals could undergo head to head dimerization to form azobenzene-4, 4'-disulphonamide which is photochemically oxidised to azoxybenzene-4. 4'-disulphonamide. The proposed pathway for the photolysis of sulphanilamide to azo and azoxy derivatives is analogous to the radical mechanism suggested by Ginsburg (Ginsburg, 1967) for the oxidation of aniline to azobenzene. The mechanism is in accordance with the second-order formation of azobenzene-4, 4'-disulphonamide.

Some of the mechanistic implications in this reaction may be explained on the basis of the participation of certain radicals e.g. C_6H_5NH in the photolysis of sulphanilamide as detected by spin trapping studies (Chignell, Kalyanaraman, Sik and Mason, 1981).The probability of the dehydrogenation at the aromatic NH, is higher on the grounds of the bond energy of NH bond (85 Kcal/mole) compared with that of the C-N bond (175 Kcal/ mole) (Weast, 1968) which remains intact in the formation of azobenzene-4, 4'-disulphonamide.

The azo compounds undergo many coupling rearrangement and dictation reactions (Zollinger, 1961; Tedder, 1970) and may react with tissue constituents in eye causing irrepairable damage. It is, therefore, extremely important to take necessary measures to control the photo-oxidation of sulphanilamide by using appropriate antioxidants as sulphanilamide is a product of photolysis of sulphacemmide in eye-drop preparations.

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