The Nature of Zolon Red

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Pyrazolone Dye, Zolon Red

Zolon red is an acid dye obtained in the enol form as the stable condensation product of glutaconic aldehyde with two molecules of 1-phenyl-3-methylpyrazol-5-one. Silver(I) replaces the hydroxylhydrogen of the dye to give deep blue precipitate of silver-zolon red compound.

Introduction

Pyridine and pyrazolone reagents had long been used for the detection and estimation of micro amounts of cyanides and ammonia [1-3]. The procedure involves the production of a blue dye by the interaction of pyridine and pyrazolone in the presence of chloramine T and sodium cyanide. Initially glutaconic aldehyde is formed by the opening of pyridine ring of pyridinium cyanide chloride which reacts with two molecules of 1-phenyl-3-methylpyrazol-5-one to give a blue dye which obeys the Beer-Lambert Law. The solution of the blue dye known as zolon blue was found to be unstable and could be converted to a red dye by boiling for short period in aqueous alkali [4]. The red dye to which the name zolon red was given forms coloured precipitates not only with silver(I), mercury(II) and copper(I) [4] but also with mercury(I) and palladium(II). Analytical application of zolon red as a gravimetric, spectrophotometric and extracting reagent for silver have been investigated [5-6]. The structure was assigned to zolon red [7] which represents the keto form of the condensation product of glutaconic aldehyde with two molecules of 1-phenyl-3-methylpyrazol-5-one. This work describes the nature of zolon red in detail and provides evidences in favour of enol form of the structure 4.

Experimental

Preparation of zolon blue

9.0 g of 1-phenyl-3-methylpyrazol-5-one was mixed with 2.0 ml pyridine to form a paste and then diluted with a solution of 1.25 g sodium cyanide in 125 ml water. The suspension so produced was treated with 7.0 g chloramine T in 125 ml water dropwise and with constant stirring. A red colour

Fig. 1. Tautomeric forms of zolon blue-zolon red systems.

was produced which immediately turned to blue paste. The stirring was continued for 20-30 min until the test made by placing a drop of the reaction mixture on filter paper gave a blue spot. However, due to unstability of the blue dye a trace of red ring might be observed around the central blue spot. The blue dye so obtained smelled like pyridine and was soluble in water. It was recrystallised with acetone and dried over phosphorus pentoxide.

Analysis for $C_{25}H_{22}N_4O_2$

Calcd C 73.17 H 5.37 N 13.65,
Found C 72.68 H 5.36 N 14.09.

Preparation of zolon red

First the blue dye was prepared, as described above, filtered and washed with 50 ml water. The dye was transferred into a beaker and a paste was made with a minimum amount of water. Then a solution of 10 g anhydrous sodium carbonate in 125 ml water was added and the mixture was boiled. The colour changed from blue to purple to red. The boiling was continued until a drop of the reaction

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mixture on filter paper gave a red orange spot. A thick red product was obtained on cooling which was filtered with suction and washed twice with 50 ml water. The red compound was dissolved in 300 ml water and reprecipitated by adding a slight excess of 10% hydrochloric acid. The red dye was filtered and washed well with water. It was recrystallised with methanol and acetone and dried over phosphorus pentoxide. Yield 2.50 g; m.p. 212 °C (decomposes to a black mass).

Analysis for $C_{25}H_{22}N_4O_2$

Calcd	C 73.17	H 5.37	N 13.65,
Found	C 72.87	H 5.36	N 13.85.

Molecular weight

Molecular weight of zolon red in methanol was determined on Hitachi Perkin-Elmer Model 115 Molecular Weight Apparatus. Benzil (molecular weight 210.23) was used for calibration. Molecular weight found 820.20, calculated for $C_{25}H_{22}N_4O_2$ 410.0.

Stoichiometry of reaction of zolon red with silver(I)

Three samples of 25 ml 10^{-2} M, 2.5×10^{-4} moles, of silver nitrate were buffered with 0.1 M sodium acetate and treated with 0.0513, 0.1026 and 0.2050 g of zolon red in minimum ethanol to give silver(I): zolon red ratio of 1:0.5, 1:1 and 1:2, respectively. The mixture was shaken, allowed to stand for 30 min in the dark and then filtered. The precipitates were washed well with water. Excess of silver(I) was determined in the filtrates and washings by cyanide method [8]. About half of the unreacted silver, 1.26×10^{-4} moles, were present in the filtrate containing, silver(I): zolon red ratio 1:0.5. No silver was detected in the other two samples.

Analysis of solid silver-zolon red compound

0.02336 g of solid silver-zolon red compound was dissolved in concentrated nitric acid and evaporated to dryness. The residue was treated with water, filtered and washed. Filtrate and washings were mixed with 25 ml 0.104 M KCN and back titrated the excess of cyanide with 0.05 M standard silver nitrate solution. It required 25.10 ml of silver nitrate. Amount of silver in silver-zolon red compound was calculated.

Silver calculated for $AgC_{25}H_{21}N_4O_2$ 20.87, found 20.67.

Potentiometric titrations

25 ml of 10^{-3} M portions of zolon red in ethanol were titrated potentiometrically against 10^{-2} M NaOH and 10^{-2} M $AgNO_3$ solutions using D-812 Weilheim direct reading pH meter.

Spectroscopic studies

1. NMR spectra were recorded on Varian T-60 NMR Spectrometer. Solutions were prepared in deuterated, d_6 -dimethylsulphoxide. TMS was used

as standard. All chemical shifts are reported in δ values.

2. Infrared spectra of zolon blue, zolon red and silver-zolon red in Nujol mull were obtained with Perkin-Elmer 257 Infrared Spectrophotometer.

3. Electronic absorption spectra of zolon blue, zolon red and silver-zolon red in ethanol were taken on Unicam SP 500 Spectrophotometer.

Discussion

The blue and red dye have identical molecular formulas and the two isomers could be represented by the four most likely tautomeric forms as shown in Fig. 1.

Zolon Blue, even in vacuum and in the dark, slowly changes to red. The red dye, therefore, seems to be the most stable form of zolon blue-zolon red systems. The red dye decomposes to a black mass at its melting point (212 °C). It is sparingly soluble in water, chloroform and carbon tetrachloride but readily dissolves in alcohols, acetone, ether and dimethylsulphoxide. 98 mg zolon red in 100 ml ethanol give a saturated solution of orange colour. Zolon red forms a dimer in methanol and might be in other solvents perhaps through hydrogen bond which results in a molecular weight (820.20) twice that expected (410.0) for $C_{25}H_{22}N_4O_2$.

Potentiometric titration of the red dye with sodium hydroxide has indicated zolon red, which would be referred as HZR, is a weak acid with a single dissociable hydrogen ion. It has a pK_a value 3.80 as found by spectrophotometric determination. Silver(I) is not completely precipitated by HZR unless sodium acetate buffer is used. Stoichiometry of reaction of HZR with silver(I) buffered with sodium acetate indicated the formation of a deep blue, black when dry, 1:1 species which dissolves in alcohols and acids. The analysis of silver in the dried product has confirmed the stoichiometry of the reaction and formation of silver-zolon red in the ratio 1:1 [7].

The pH 3.90 of zolon red slowly dropped when 25 ml 10^{-3} M solution was titrated potentiometrically with 10^{-2} M aqueous silver nitrate. The pH became constant (pH 2.20) after 2.70 ml silver(I) had been added. This observation supports the view that zolon red is an acid which dissociates and forms insoluble compound with silver(I) according to the following reactions.

Further the solubility of silver-zolon red compound in acids and incomplete precipitation of silver(I) unless sodium acetate buffer is used suggests that the reaction between silver(I) and zolon red is reversible

The dissociated hydrogen ions are removed in presence of acetate buffer and equilibrium of the above reaction is shifted towards right resulting complete precipitation of silver(I).

The presence of dissociable hydrogen is confirmed by the NMR spectra of zolon red which shows four types of proton resonances, one multiplet and three sharp singlets. The integral indicates that the multiplet between δ values of 7.00–8.00 corresponds to ten protons of the two phenyl groups in zolon red. The five-proton singlet at $\delta = 4.40$ is assigned to the five protons of the system, $\text{>C=CH-CH=CH-CH=CH-}$, and the six-proton singlet at $\delta = 2.30$ is assigned to the six protons of the two methyl groups in the structure of zolon red. A sharp one-proton singlet at $\delta = 2.06$ can be assigned to either the proton of the >NH group or to the proton of the -OH group in the structures **3** and **4**, respectively. The presence of this signal in the NMR spectrum, therefore, eliminates the possibility of the structure **1** and **2** for zolon red. The singlet at $\delta = 2.06$ disappears when the sample solution is shaken with a few drops of deuterium oxide and is absent in the NMR spectrum of zolon blue. This observation further supports the elimination of structure **1** and **2** and suggests forms **3** or **4** are possible structures for zolon red since the >NH proton and the -OH proton could equally be replaced by deuterium.

The absence of >NH group and the presence of -OH group in the structure of zolon red is confirmed by infrared spectrum. The peak frequencies of zolon blue, zolon red and silver-zolon red compound in the infrared spectra are recorded in Table I.

The blue dye does not show any absorption in the -OH and >NH stretching region if the spectrum is taken within two days of its preparation. However, after two days weak bands appear in the -OH and >NH regions and become more prominent after four days although the dye still looks blue. The blue dye completely changes to red after two weeks and the spectrum becomes identical with the spectrum of zolon red. The appearance of bands in the -OH

Table I. Wave numbers (cm^{-1}) of peak frequencies.

Zolon blue	Zolon red	Silver-zolon red
650	650	650
665	660	665
690	690	695
752	758	752
815	830	820
992	1005	998
1020	1030	1022
1115	1120	1120
1200	1195	1195
1232	1240	1245
1310	1335	1335
—	1495	—
—	1560	1550
1595	1595	1595
—	3410	—

and >NH regions after two days in the blue dye is due to contamination with red dye because zolon blue is unstable and changes to zolon red which is the stable form of zolon blue-zolon red systems. Structures **1** and **2**, therefore, may represent zolon blue but are ruled out for zolon red. The broad absorption at 3410 cm^{-1} and a strong at 1495 cm^{-1} in the infrared spectrum of red dye are assigned -OH stretching and -OH bending vibrations respectively. These vibrations disappear in silver-zolon red compound which suggests that the hydroxyl-hydrogen is replaced by silver. The >NH stretching frequencies do occur in $3300\text{--}3500 \text{ cm}^{-1}$ region and the imino-hydrogen could equally be replaced by silver but the >NH peaks are usually sharper. Further the absorption at 1560 cm^{-1} in zolon red and 1550 cm^{-1} in silver-zolon red compound which are assigned >C=O stretching in >C=O-H group, are not in favour of structures **3** having >NH group. Structures **1**, **2** and **3** represent only one type of carbonyl group, >C=O whereas structure **4** is expected to show two types of C=O stretching frequencies because of >C=O and >C=O-H groups. Zolon red does exhibit a peak at 1560 cm^{-1} which is retained in silver-zolon red compound at 1550 cm^{-1} . Infrared spectra, therefore, favours structure **4** for zolon red because of the presence of -OH group. The presence of -OH group rather >NH group in zolon red should not be surprising as most of the pyrazolone dyes *e.g.*, Eriochrome red B and xylene yellow 3 G contain -OH groups in their structures.

The wave lengths of maximum absorption of solutions of zolon blue, zolon red and silver-zolon red compound in ethanol in the ultraviolet and

visible regions are recorded in Table II. Zolon red and silver-zolon red form orange and redpurple solutions respectively in organic solvents but both show maximum absorption at 255 nm and 520 nm in the electronic absorption spectra. The structure of silver-zolon red compound has not been investigated. However, it seems the silver compound is formed by ions association like silver acetate (AgOOCH_3) because complexes of silver(I) are not well known for oxygen ligands. The change of colour

Table II. The wave lengths (nm) of maximum absorption.

Compound	Colour of the solution	Max
Zolon blue	Blue	250, 625
Zolon red	Orange	255, 520
Silver-zolon red	Redpurpule	255, 520

of zolon red, when it reacts with silver(I), from orange to red-purple in solution and intense blue in solid is perhaps due to charge transfer transitions involving the ion pair, Ag ZR^- .

Conclusion

This work on the basis of chemical and spectroscopic studies supports the presence of hydroxyl group in the structure of zolon red and suggests it to be the enol form of the tautomers. Zolon red, therefore, should be best represented by structure 4.

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