OXIDATION OF INDIGOCARMINE, ISATIN AND 5-NITRO-ISATIN BY CHLORAMINE-T AND DICHLORAMINE-T

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Abstract

Indigocarmine undergoes a four electron oxidation per mole with chloramine-T in mineral acids and pH 1 buffer media while aqueous solutions of the compound are oxidized by a solution of dichloramine-T in glacial acetic acid. The products are isatin sulphonate and *p*-toluene sulphonamide and an approximate estimate of the former has been carried out by a spectrophotometric method. 5-Nitro-isatin and isatin can be oxidized by CAT and DCT respectively with a two electron change per mole and volumetric methods have been proposed for their estimation in solution.

Introduction

CHLORAMINE-T (CAT) and recently dichloramine-T (DCT) have been successfully employed for estimating a variety of compounds[1,2]. A detailed investigation of the oxidation of indigocarmine and 5-nitro-isatin with CAT has now been carried out. The communication further reports the estimation of indigocarmine and isatin with DCT. Since the oxidation was not instantaneous back titration procedures have been developed.

Materials and Methods

About 2 mM solutions of indigocarmine (E'Merck), isatin (Ward Blenkinsop) and 5-nitro-isatin (Aldrich Chemical Co.) in the appropriate solvents were prepared. Standard buffer systems were employed. Chloramine-T (May and Baker) was purified by the method of Morris *et al.*[3] and its decinormal solution was standardized by the iodometric method. Dichloramine-T was prepared and purified by the method of Jacob and Nair[1] and its decinormal solution in glacial acetic acid was prepared and standardized as above. Beckman DB spectrophotometer was used for optical density measurements.

Table I gives a typical set of results for the oxidation of indigocarmine with CAT in 30 minutes. It is seen from the table that the rate of oxidation is fairly rapid and stoichiometric with a 4-electron change per mole, in mineral acids and pH 1 buffer media. The rate increases with an increase in pH, reaches a maximum of nearly 8-electron change at pH 5 and then decreases. Hence the standard estimation was carried out at pH 1 by adding aliquots of indigo carmine solution in this buffer to a measured excess of 0·1N CAT followed by iodometric back titration of the latter after 30 minutes.

Oxidation of Indigocarmine with DCT :

Preliminary studies revealed that the rate of oxidation of aqueous indigocarmine solutions with DCT was independent of the dilution. Oxidation beyond the 4-electron change per mole was not noticed, even after 1–2 hours.

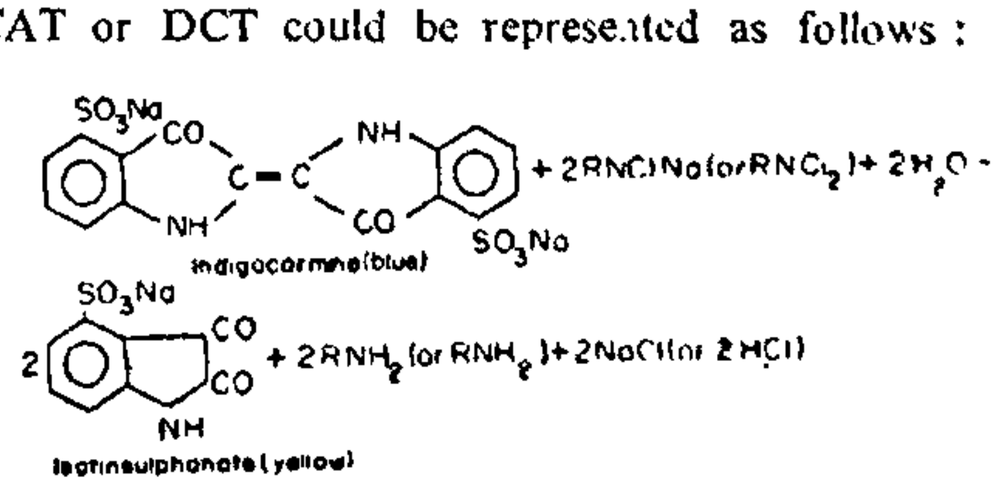
Table I

Extent of oxidation of indigocarmine with chloramine-T

Medium	CAT/Indigo	Medium	CAT/Indigo
1·0 NH_2SO_4	2·001	pH 1·0	2·007
0·1 NH_2SO_4	2·005	pH 2·2	2·197
1·0 NHCl	1·982	pH 3·0	2·273
0·1 NHCl	2·000	pH 4·0	3·348
1·0 $NHClO_4$	1·888	pH 5·0	3·910
		pH 6·0	3·318
		pH 7·0	2·968
		pH 8·0	1·862

Indigocarmine taken = 0·02 m mole ; CAT taken = 1·0 m mole. Time = 30 min. ; Temperature = 26° C. CAT/Indigo = moles of CAT per mole indigocarmine oxidation.

Some typical results of analyses are shown in Table II. The stoichiometry of oxidation of indigocarmine by CAT or DCT could be represented as follows :



Here R = *p*-CH_3-$C_6H_4SO_2$.

The presence of *p*-toluene sulphonamide (PTS) in the reaction products was detected by paper chromatography[3]. Isatin sulphonate formed had a λ_{max}

TABLE II

Estimation of indigocarmine, 5-nitro-isatin and isatin

Oxidant CAT				Oxidant DCT			
Indigocarmine		5-Nitro-isatin		Indigocarmine		Isatin	
Taken (mg)	Found (mg)	Taken (mg)	Found (mg)	Taken (mg)	Found (mg)	Taken (mg)	Found (mg)
7·99	8·05	3·51	3·44	4·76	4·85	3·32	3·35
9·59	9·53	4·91	4·91	9·52	9·54	3·98	3·99
11·99	12·07	5·61	5·73	14·27	14·31	4·65	4·62
13·59	13·56	7·02	7·05	16·17	16·02	4·98	4·99
15·99	15·95	8·42	8·35	17·12	17·17	5·31	5·37
17·51	17·51	9·83	9 83	20·93	20 99	5 98	5·99
19·99	19·98	10·53	10·49	23·79	23·65	6·64	6·62
27·98	28·03	11·93	11·96	25·69	25 57	..	..
..	..	12·63	12·61	..	..	..	..
..	..	14·04	14·10	..	..	..	..

at 410 nm ($\log \epsilon = 2·8$) and hence was estimated by a spectrophotometric procedure. As pure isatin sulphonate was not available, the indigocarmine was oxidised with KIO_3 to get isatin sulphonate[4] for preparing the calibration curve. The results are shown in Table III.

It is interesting to note that the rate of oxidation of indigocarmine by CAT is fastest in the pH range 4–5. This behaviour could probably be attributed to the high rate of disproportionation of monochloramine-T present at this pH to DCT and PTS as suggested by Higuchi *et al.*[5]

Oxidation of Isatins.—Extensive investigations showed that definite stoichiometric oxidation corresponding to a 2-electron change per mole could be obtained for aqueous solutions of isatin with DCT and ethanolic solutions of 5-nitro-isatin with CAT.

Oxidation of isatin with DCT.—The procedure is similar to the oxidation of indigo carmine with DCT, but required a water content of 30–50% in the reaction mixture and an oxidation period of 75 minutes.

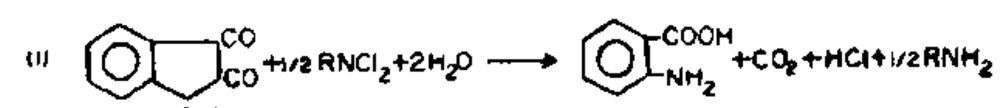
Oxidation of 5-nitro-isatin with CAT.—Add aliquots (0·02–0·08 m mole) of a solution of 5-nitro-isatin prepared in 95% ethanol to a known excess (~1·0 m mole) of 0·1 N CAT. Shake the mixture occasionally and after 5 minutes add 10 ml of $2NH_2SO_4$ and 10 ml of 20% KI and titrate against standard thiosulphate. Run a blank with CAT solution alone.

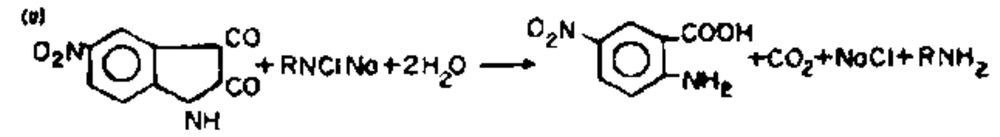
TABLE III

Spectrophotometric estimation of isatin sulphonate ($\lambda_{max} = 410$ nm)

Oxidant CAT		Oxidant DCT	
Weight of isatin sulphonate		Weight of isatin sulphonate	
Calculated mg.	Found mg	Calculated mg	Found mg
1·54	1·59	1·09	1·19
2·59	2·64	3·27	3·44
4·13	4·01	3·82	3·88
5·17	5·18	4·98	5·23
6·20	6·18	5·45	5·68
10·33	10·31	6·54	6·72

The stoichiometry of the above oxidations is as follows :

(i) 

(ii) 

The presence of anthranilic acid ($R_f = 0·278$) in the reaction mixture was detected by paper chromatography, with butanol-ammonia (4 : 1 V/V) solvent and ethanolic ferric chloride as spray reagent[6].

Some typical results of analyses are given in Table II. The results are accurate within 0·5%.

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