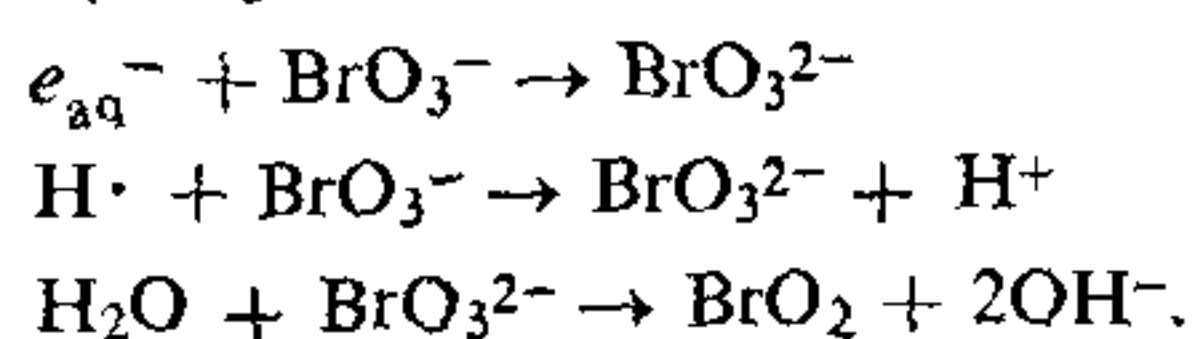## REDOX REACTION INDUCED BY ENERGY STORED IN IRRADIATED CRYSTALS

WE had reported earlier the occurrence of a number of radiation-induced redox reactions together with appropriate mechanisms, consistent with the G values observed[1-6]. These are reactions which, though thermodynamically possible, do not occur at room temperature except under radiation activation. A result of interest recently observed in this laboratory refers to the utilization of the energy stored in irradiated sodium chloride in inducing a redox reaction[7]. Thus when $1 \cdot 6$ g of AR grade NaCl irradiated by γ from ^{60}Co to a dose of the order of 2×10^{19} eV/g was added to 5 ml of an aqueous solution containing the redox mixture at pH $6 \cdot 5$ (1 M $NaBrO_3$ + 1 mM NaI) (*which mixture is otherwise stable*), about 10% of the I^- was found to be oxidized to IO_3^- and another 17% to I_2. In the process BrO_3^- is reduced to Br^-.

In explaining *aquoluminescence* (AL) (*i.e.*, emission of faint light during the dissolution of irradiated crystals[8]), we had suggested that the electrons released from traps due to the destruction of crystal structure, instantly react with water to form hydrated electrons (e_{aq}^-). Some of these reacting with the holes lead to the emission of AL[8,9]. In the present case the primary product (e_{aq}^-) reacts with the solute BrO_3^- present in excess, resulting in the formation of Br(IV) species (BrO_3^{2-} or BrO_2), the reactions being[10]

$$e_{aq}^- + BrO_3^- \rightarrow BrO_3^{2-}$$
$$H \cdot + BrO_3^- \rightarrow BrO_3^{2-} + H^+$$
$$H_2O + BrO_3^{2-} \rightarrow BrO_2 + 2OH^-.$$

At the same time, the hole species ($Cl \cdot$ or $Cl_2^{-\cdot}$) present in the irradiated crystal reacts with I^- to form I_2

$$Cl \cdot + I_{aq}^- \rightarrow Cl_{aq}^- + 0 \cdot 5 I_2.$$
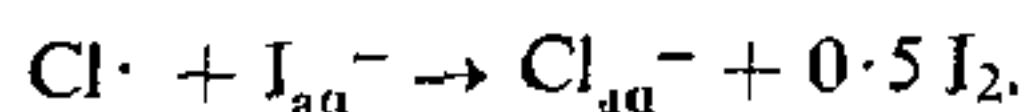
The Br(IV) species oxidizes I_2 to IO_3^-

$$BrO_3^{2-} + 0 \cdot 5 I_2 \rightarrow Br^- + IO_3^-.$$
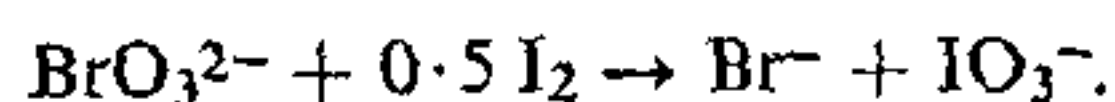
Under these conditions, as may be expected, AL is quenched as the primaries e_{aq}^- and holes are used up in the above redox reactions. The observed oxidation yields of 10% IO_3^- and 17% I_2, by the indirect transfer of energy stored in the irradiated crystal, lends support to the mechanisms postulated earlier both for AL and for radiolytic redox reaction between bromate and iodide ions.

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STABILITY CONSTANTS OF COMPLEXES OF 2-HYDROXY-5-NITROPROPIOPHENONEOXIME WITH Ni(II), Co(II), Zn(II) AND Mn(II)

THIS communication reports the investigations of stability constants of complexes of 2-hydroxy-5-nitro-propiophenone oxime with Ni(II), Co(II), Zn(II) and Mn(II) by Calvin-Bjerrum technique as applied by Irving and Rossotti[1] at 40° ($\mu \simeq 0 \cdot 1$M $NaClO_4$) in water-dioxane (25 : 75 v/v) medium.

Experimental

2-Hydroxy-5-nitropropiophenone oxime was prepared by the aqueous ethanolic alkali method from ketone. Its stock solution was prepared by dissolving the required amount in purified dioxane[2] (S. Merck—technical grade). All solutions and pH-measurements were made as described earlier[3].

Three titrations, *viz.*, titration of (i) free perchloric acid, (ii) free perchloric acid plus the reagent and (iii) free acid plus the reagent plus the metal ion, were done against standard NaOH.

Results and Discussion

It was observed that $\bar{n}_H$ values did not fall into the range 0 to 1, indicating that either the hydrogen of oximino group did not dissociate or its dissociation overlapped the dissociation of phenolic hydrogen. Assuming the latter possibility an attempt was made to evaluate the two constants $^1K_1{}^H$ and $^1K_2{}^H$ by the method of least squares[4]. It gives a negative value for the product of $^1K_1{}^H \cdot {}^1K_2{}^H$, however $^1K_2{}^H$ is positive. Therefore, it was concluded that only the phenolic OH is dissociated. Thus 2-hydroxy-5-nitropropiophenoneoxime was considered monobasic and the $\bar{n}_H$ values accordingly were reduced by 1. The practical proton-ligand stability constant, log $^pK^H$, has been obtained as the Bjerrum half-integral value. The same has also been calculated at different points using the equation

$$\log {}^pK^H = B + \log \bar{n}_H / (1 - \bar{n}_H)$$

The average value of log $^rK^H$ (9.20) obtained by the pointwise calculation is in good agreement with the half-integral value (Table I).

TABLE I

Stability constants of bivalent complexes with
2-hydroxy-5-nitropropiophenoneoxime

(Temp. = $40 \pm 1^\circ$ C, $\mu \simeq 0.1$M NaClO$_4$)

Method Metal	Half-integral	Least squares	
H(I)	..	−18·88	log $^rK_1^H$.log $^rK_2^H$
	..	−10·02	log $^rK_1^H$
	9·21	8·86	log $^rK_2^H$
Ni(II)	11·74	11·74	log β_2
	6·17	5·64	log K_1
	5·57	6·10	log K_2
Co(II)	13·95	14·03	log β_2
	8·66	8·71	log K_1
	5·29	5·32	log K_2
Zn(II)	8·87	8·89	log β_2
	4·72	4·17	log K_1
	4·15	4·72	log K_2
Mn(II)	8·98	8·99	log β_2
	5·31	5·38	log K_1
	3·67	3·61	log K_2

In all the systems the highest values of $\bar{n}$ are more than 1, indicating that 1:1 and 1:2 complexes are formed. The log K_1 and log K_2 values were calculated by the methods of half-integral and least squares (Table I). The results, given in Table I, show that the order of stability is Zn < Co > Ni > Mn. It can be seen that the order is in agreement with Irving Williams order[5].

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SPECTROPHOTOMETRIC DETERMINATION OF CINCHONINE BY SOLOCHROME GREEN V 150

THE trace analysis of cinchonine is of interest to toxicologists, forensic and analytical chemists. Very few spectrophotometric methods exist for the determination of cinchonine. Celap *et al*[1] described an elaborate method for its determination based on the development of molybdenum blue but the method is not sensitive and accurate. Spacu and Ianu[2] reported the chronic thiocyanate method, wherein the alkaloid is precipitated by potassium chromium thiocyanate and the precipitate is dissolved in acetone aud analysed spectrophotometrically. The method is indirect and far less sensitive than the present method. Palumbo and Sacca[3] determined cinchonine by cis–aconitic acid in acetic anhydride. For the direct spectrophotometric determination of alkaloids, the acid dye[4–8] extraction methods are reported; these methods are relatively rapid, convenient and sensitive. A survey of the literature revealed that only one acid dye, bromothymol blue has been reported so far for the determination of cinchonine[9]. The author, in his investigations on the use of the acid dyes of Solochrome series, found Solochrome Green V 150 having the following formula,
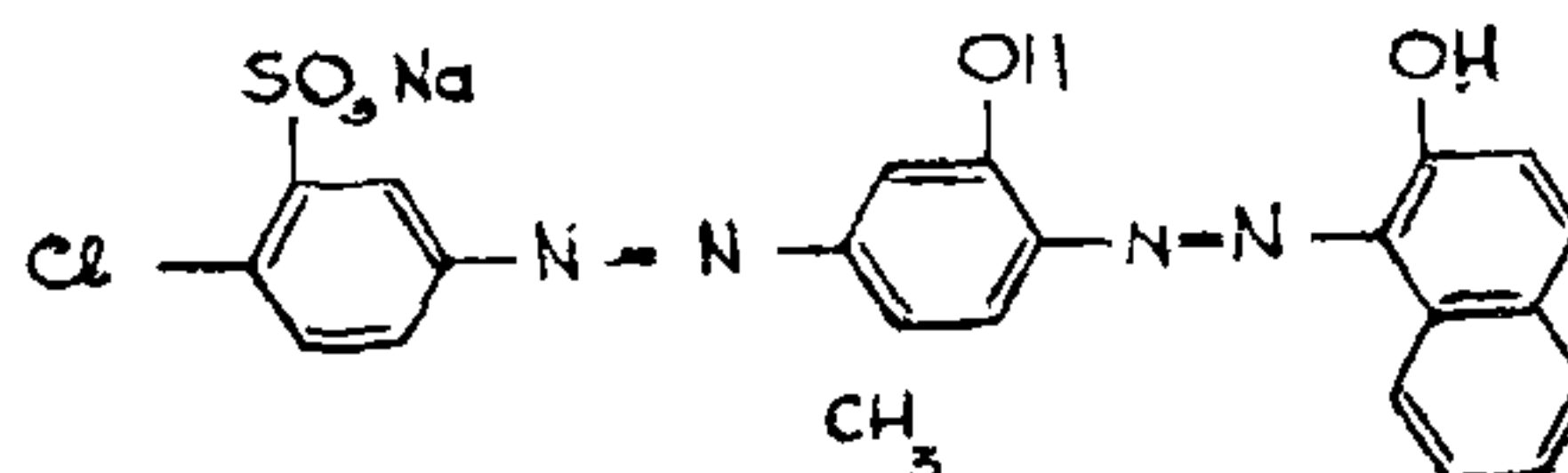
to be extremely sensitive in the determination of alkaloids and proposed methods for strychnine[10], brucine[11] and opium alkaloids[12]. The present report gives a method for the determination of chnchonine by the extraction of the ion pair formed with Solochrome Green V 150 into chloroform and measuring the chloroform extract spectrophotometrically at 510 nm. The dye is not extracted by chloroform under the experimental conditions. The method is more sensitive than bromothymol blue method, lower limit of determination being 0·54 micrograms per ml. The interference of the commonly associated materials has been checked.

Experimental

Bausch and Lomb spectronic–20 spectrophotometer was used for the absorbance measurements. Clarke and Wallpole buffers were used. Solochrome Green V 150 (C.I. No. 26925) was supplied by Imperial Chemical Industries Limited, Calcutta, India. Standard sample of cinchonine (Koch–Light, England) was used. All other chemicals used were of analytical grade.