

Ligand exchange equilibria of metal complexes-I: Ligand exchange of metal dithizonates with α -benzoin oxime in chloroform

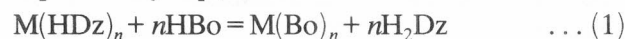
C K Bhaskare* & (Miss) S G Kawatkar

Department of Chemistry, Shivaji University, Kolhapur 416 004

Received 7 September 1987; revised 15 March 1988; accepted 8 July 1988

Ligand exchange reactions between dithizonates of Ag^+ , Tl^+ , Cd^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Pd^{2+} , Pb^{2+} , Bi^{3+} and In^{3+} with α -benzoin oxime in chloroform have been studied spectrophotometrically. From the exchange constants so determined the extraction constants of metal- α -benzoin oximates have been calculated.

The equilibrium constant of the exchange reaction (see Eq. 1) between metal dithizonate $[\text{M}(\text{HDz})_n]$ and α -benzoin oxime (HBo) in chloroform, can be expressed by Eq. (2)¹.



$$E_{\text{M}(\text{HDz})_n - \text{HBo}} = \frac{[\text{M}(\text{Bo})_n][\text{H}_2\text{Dz}]^n}{[\text{M}(\text{HDz})_n][\text{HBo}]^n} = \frac{K_{\text{M}(\text{Bo})_n}}{K_{\text{M}(\text{HDz})_n}} \quad \dots (2)$$

where $K_{\text{M}(\text{Bo})_n}$ and $K_{\text{M}(\text{HDz})_n}$ are the extraction constants of metal- α -benzoin oximates and metal dithizonates respectively, and E is the equilibrium constant. Thus from Eq. (2) it is possible to determine E if values of extraction constants are known for any exchange reaction or if E is known the unknown extraction constant of one metal chelate can be determined if the extraction constant of other metal chelate is known. Presently we have measured the E s of the ligand exchange reactions and from the literature values of extraction constants of metal dithizonates, the extraction constants of metal- α -benzoin oximates have been determined.

Experimental

The absorbances were measured on a Beckman model DU 2 UV spectrophotometer using 10 mm matched pair of silica cuvettes. Philips pH meter PR 9405 L was used with Philips pV 9014 combination electrodes for pH measurements.

Unless otherwise stated, all reagents were of AR grade. Chloroform was purified before use. Dithizone (H_2Dz) was purified by recommended procedure² and its solution was prepared in chloroform.

Solution ($1.0 \times 10^{-2} M$) of α -benzoin oxime (HBo) was also prepared in chloroform.

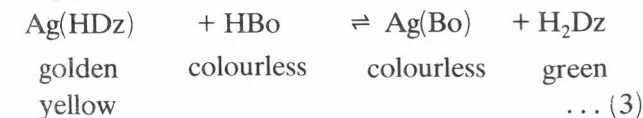
Metal dithizonates were prepared by shaking excess of aqueous solution of the metal salt at desired pH with chloroform solution ($1.0 \times 10^{-4} M$) of dithizone for 15 min. The pH values of these solutions were adjusted using 0.1 M sulphuric acid or 0.1 M sodium carbonate. The coloured dithizonate layers were washed with little water and the chloroform layers were transferred through a plug of cotton wool to dry amber coloured bottles. Many dithizonates are photochromic, hence these were not exposed to direct sunlight.

α -Benzoin oximates were prepared as follows: Metal salts in ethanol were refluxed for several hours with ethanolic solution of α -benzoin oxime. The solid products obtained were recrystallized from ethanol, successively washed with water and ethanol and dried over P_2O_5 . The α -benzoin oximates of silver, thallium (ous), cadmium, zinc, copper, nickel and cobalt were prepared by this method. Solid complexes of palladium, lead, bismuth and indium could not be prepared.

Solutions of metal- α -benzoin oximates ($1.0 \times 10^{-3} M$) were prepared by dissolving appropriate amount of these in chloroform (100 ml).

In the following is described a typical procedure for determining E .

To a certain amount of silver dithizonate ($\lambda_{\text{max}} - 465 \text{ nm}$; $\epsilon = 29000 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$) various known amounts of α -benzoin oxime were added. α -Benzoin oxime displaced dithizone and the equilibrium was reached within a few minutes. It was necessary to use 100-fold excess of α -benzoin oxime for studying the exchange reaction. The $E_{\text{Ag}(\text{HDz}) - \text{HBo}}$ of the reaction (3) is given by Eq. (4).



$$E_{\text{Ag}(\text{HDz}) - \text{HBo}} = \frac{[\text{Ag}(\text{Bo})][\text{H}_2\text{Dz}]}{[\text{Ag}(\text{HDz})][\text{HBo}]} \quad \dots (4)$$

Equilibrium concentrations of all the species involved, viz. C_1 of silver dithizonate and C_2 of free dithizone were determined using mixed colour method which gave the following equations.

$$\begin{aligned} C_1 \times 10^5 &= 3.472 \times A_{\lambda_1} - 1.037 A_{\lambda_2} \\ C_2 \times 10^5 &= 2.615 \times A_{\lambda_2} - 0.0541 \times A_{\lambda_1} \end{aligned}$$

