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

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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 $[M(HDz)_N]$ and α-benzoin oxime (HBo) in chloroform, can be expressed by Eq. (2)[1].

$$M(HDz)_n + nHBo = M(Bo)_n + nH_2Dz \quad \ldots (1)$$

$$E_{M(HDz)_n - HBo} = \frac{[M(Bo)_n][H_2Dz]^n}{[M(HDz)_n][HBo]^n} = \frac{K_{M(Bo)^n}}{K_{M(HDz)_n}} \quad \ldots (2)$$

where $K_{M(Bo)_n}$ and $K_{M(HDz)_n}$ 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 Es 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 *p*H meter PR 9405 L was used with Philips pV 9014 combination electrodes for *p*H measurements.

Unless otherwise stated, all reagents were of AR grade. Chloroform was purified before use. Dithizone (H_2Dz) was purified by recommended procedure[2] and its solution was prepared in chloroform. Solution (1.0×10^{-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 *p*H with chloroform solution (1.0×10^{-4} *M*) of dithizone for 15 min. The *p*H 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 (1.0×10^{-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 ($\lambda_{max} - 465$ nm; $\varepsilon = 29000$ dm^3 cm^{-1} 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 $E_{Ag(HDz)-HBo}$ of the reaction (3) is given by Eq. (4).

$Ag(HDz)$	$+ HBo$	$\rightleftharpoons Ag(Bo)$	$+ H_2Dz$
golden yellow	colourless	colourless	green

$\ldots (3)$

$$E_{Ag(HDz)-HBo} = \frac{[Ag(Bo)][H_2Dz]}{[Ag(HDz)][(HBo)]} \quad \ldots (4)$$

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.

$$C_1 \times 10^5 = 3.472 \times A_{\lambda_1} - 1.037\, A_{\lambda_2}$$

$$C_2 \times 10^5 = 2.615 \times A_{\lambda_2} - 0.0541 \times A_{\lambda_1}$$

Table 1—Experimental Conditions, Equilibrium Constants of Exchange Reaction (E) and Extraction Constants of Metal Dithizonates ($K_{M(HDz)_n}$) and Metal-α-Benzoin Oximates ($K_{M(Bo)_n}$

Sl No.	Metal ion used	*p*H used	λ_{max} (nm)	$\varepsilon_{\lambda max}$ ($dm^{-3}\ cm^{-1}\ mol^{-1}$)	log *E*	Lit value log $K_{M(HDz)_n}$	Ref.	log $K_{M(Bo)_n}$
1	Ag^+	2-3	465	29000	-2.06 ± 0.03	6.00	4	3.94
2	Tl^+	11-12	505	29250	-2.09 ± 0.02	−3.8	1	−5.89
3	Cd^{2+}	8.0	520	78000	-4.80 ± 0.05	0.5	6	−4.30
4	Zn^{2+}	7.0	530	85000	-3.54 ± 0.07	1.0	7	−2.54
5	Cu^{2+}	7.0	545	40200	-6.50 ± 0.06	8.7	1	2.2
6	Ni^{2+}	12.0	480	33500	-8.50 ± 0.06	2.46	1	−6.04
7	Co^{2+}	8.0	542	56800	-6.48 ± 0.05	−1.5	4	−7.98
8	Pd^{2+}	4-5	470	31000	-10.60 ± 0.04	>27.0	1	>16.4
9	Pb^{2+}	8.5	518	59500	-6.95 ± 0.08	−0.9	4	−7.85
10	Bi^{3+}	12-14	490	71400	-9.84 ± 0.05	5.30	8	−4.54
11	In^{3+}	8-9.5	515	100200	-8.15 ± 0.05	0.6	9	−7.55

where A_{λ_1} and A_{λ_2} are the absorbances at 465 and 605 nm of silver dithizonate respectively.

The equilibrium concentration of α-benzoin oxime was obtained from the difference between the original concentration of α-benzoin oxime and that utilized in the reaction. The amount of α-benzoin oxime used in the reaction was equivalent to the concentration of free dithizone liberated in the reaction. The concentration of Ag(Bo) was equivalent to the difference between the concentration of original silver dithizonate and that of silver dithizonate which remained at equilibrium as a result of the reaction.

Results and discussion

The reversibility of reaction (3) was studied by mixing silver-α-benzoin oximate to dithizone (see reaction 5). Equilibrium was reached within 4 to 5 min.

$$\underset{\text{colourless}}{Ag(Bo)} + H_2Dz \rightleftharpoons \underset{\text{green}}{Ag(HDz)} + \underset{\text{golden yellow}}{HBo} \quad \underset{\text{colourless}}{} \quad \ldots (5)$$

The $E_{Ag(Bo)-H_2Dz}$ of the reaction is given by Eq. 6)

$$E_{Ag(Bo)-H_2Dz} = \frac{[Ag(HDz)][HBo]}{[Ag(Bo)][H_2Dz]} \quad \ldots (6)$$

Dyer *et al.*[3] and Koroleff[4] reported log $K_{Ag(HDz)}$ equal to 5.8 and 6.0 respectively The log $E_{Ag(HDz)-HBo}$ determined by us as above is -2.06 ± 0.03. Hence

$$\log K^{CHCl_3}_{Ag(Bo)} = \log E + \log K^{CHCl_3}_{Ag(HDz)}$$
$$= -2.06 + 6.00$$
$$= 3.94$$

As in the case of silver, the extraction constants and equilibrium constants were also measured for the exchange involving Tl^+, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Pd^{2+}, Pb^{2+}, Bi^{3+} and In^{3+}. The results are given in Table 1. The literature values of log $K_{M(HDz)_n}$ are also included in Table 1.

To investigate the influence of organic solvents on the exchange constant the reaction between cadmium dithizonate and α-benzoin oxime in various solvents, viz. chloroform, benzene and chlorobenzene was investigated. The values of log $E_{Cd(HDz)_2-HBo}$ obtained in these solvents are -4.80 ± 0.05, -8.30 ± 0.10 and -8.82 ± 0.10 respectively. Thus organic solvents play an important role in the exchange reactions. The keto and enol tautomerism of the metal complexes are also solvent dependent. It is observed that chloroform is the most suitable solvent.

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