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METAL CHELATE EXCHANGE IN THE ORGANIC PHASE—III*

EXTRACTION AND EXCHANGE CONSTANTS OF DITHIZONATES AND OXINATES

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Summary—Reactions between dithizonates and oxinates of Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Co(II), Ni, Pd, In, Ga and Bi in chloroform have been studied spectrophotometrically. From the exchange constants determined, the extraction constants of metal dithizonates or metal oxinates have been calculated. By this method extraction constants of many metal chelates can be calculated which are difficult to determine by studies of distribution between aqueous and chloroform phases.

IN PARTS I and II[1,2] the exchange reaction between metal dithizonates and diethyldithiocarbamates in the organic phase has been studied in order to find the composition and the extraction constants of metal diethyldithiocarbamates. The present paper deals with the investigation of the exchange reaction between metal dithizonates, $M(HDz)_N$, and oxine, HOx, or between metal oxinates MOx_N and dithizone H_2Dz. The exchange reaction can be generally described[1,2] by the equation

$$M(HDz)_N + N\,HOx = MOx_N + N\,H_2Dz \qquad (1)$$

The exchange constant of reaction (1) is given by

$$E_{M(HDz)_N} = \frac{[MOx_N][H_2Dz]^N}{[M(HDz)_N[HOx]^N} = \frac{K_{MOx_N}}{K_{M(HDz)_N}} \qquad (2)$$

where K_{MOx_N} and $K_{M(HDz)_N}$ denote the extraction constants of metal oxinates and dithizonates respectively,* and the concentrations refer to the organic phase.

Because the extraction constants of metal dithizonates are generally much higher than those of metal oxinates, it is necessary to use a great excess of oxine for the investigation of the exchange reaction (1). The exchange constants were determined by methods similar to those described previously.[1,2]

EXPERIMENTAL

Reagents

Unless otherwise stated, all reagents were of analytical reagent grade.

Chloroform. Twice distilled.

Dithizone. Purified by solvent extraction with chloroform.[3,4]

Oxine. Reagent grade, not further purified.

Metal dithizonates. Prepared as previously described.[1,2]

Metal oxinates. Solutions of metal oxinates containing excess of oxine were prepared by

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* Part II—*Talanta*, 1968, **15**, 505.

equilibrating equal volumes of an aqueous $10^{-4}M$ solution of metal ion and $0{\cdot}10M$ oxine solution in chloroform under the conditions for quantitative extraction (in the case of gallium and indium only $0{\cdot}0010M$ oxine solution was used). The organic phase was separated and filtered and the concentration of the metal oxinate determined spectrophotometrically at 380–400 nm.[3] Thallium(I) is only partially extracted by oxine solution even at high pH.[3] For this reason the concentration of thallium(I) oxinate extracted was determined (after subsequent dilution) by the exchange reaction with an excess of dithizone. The ionic strength of the aqueous solution was about 0·1 and the temperature 20–25°.

RESULTS AND DISCUSSION

Thallium

To determine the exchange constant $E_{\mathrm{TlHDz-HOx}}$, known amounts of thallium(I) dithizonate in chloroform were mixed with a known amount of oxine in the same solvent. The equilibrium concentration of thallium(I) dithizonate and dithizone was determined by the mixed colour method at 505 and 605 mm. The equilibrium concentration of thallium(I) oxinate formed is equal to the equilibrium concentration of dithizone; the concentration of oxine ($0{\cdot}1$–$0{\cdot}01M$) is practically unchanged by equilibration, for the concentration of thallium oxinate formed is $10^{-5}M$. The mean value of $\log E_{\mathrm{TlHDz-HOx}} = -5{\cdot}00 \pm 0{\cdot}04$. Practically the same value ($\log E_{\mathrm{TlHDz-HOx}} = -4{\cdot}92 \pm 0{\cdot}04$) has been found from the investigation of the exchange reaction between thallium(I) oxinate and dithizone.

If the extraction constant of thallium(I) dithizonate $\log K_{\mathrm{TlHDz}}$ is taken to be $-3{\cdot}8$,[3] the extraction constant of thallium(I) oxinate $\log K_{\mathrm{TlOx}} = -3{\cdot}8 - 4{\cdot}96 = -8{\cdot}76$. This value is in fair agreement with the value $\log K_{\mathrm{TlOx}} = -9{\cdot}5$ estimated from the work of Schweitzer and Norton.[5]

Silver

The addition of oxine ($0{\cdot}1M$ solution) to silver dithizonate in chloroform does not displace an observable amount of dithizone, *i.e.*, the exchange constant $\log E_{\mathrm{AgHDz-HOx}} \ll -8$.

Copper

The exchange reaction between copper dithizonate and oxine or copper oxinate and dithizone yields the same value of the exchange constant ($\log E_{\mathrm{Cu(HDz)_2-HOx}} = -7{\cdot}27 \pm 0{\cdot}03$; mean of 20 results). If the extraction constant $\log K_{\mathrm{CuOx_2}}$ is taken to be 1·40 or 1·70,[3] the extraction constant $\log K_{\mathrm{Cu(HDz)_2}} = 8{\cdot}7$–$9{\cdot}0$. The published value[3] of $\log K_{\mathrm{Cu(HDz)_2}} = 6{\cdot}5$ for chloroform seems to be too small in comparison with the value[3] 10·5 for carbon tetrachloride as a solvent. For this reason the extraction of copper ($10^{-5}M$) from $0{\cdot}05M$ sulphuric acid by dithizone solution in chloroform has been investigated. It has been found that the extraction equilibrium can be reached only after several hours' shaking. From these experiments $\log K_{\mathrm{Cu(HDz)_2}}$ (corrected for the formation of copper sulphate complexes) is 8·5, which is in agreement with the value obtained from the exchange constant.

Zinc

The results of the investigation of the exchange reaction between the zinc chelates and the organic reagents used are given in Table I. The mean value is $\log E_{\mathrm{Zn(HDz)_2-HOx}} = -7{\cdot}20 \pm 0{\cdot}02$. If $\log K_{\mathrm{Zn(HDz)_2}}$ is[3] 0·6–1·0 the value of $\log K_{\mathrm{ZnOx_2}}$ will be $-6{\cdot}2$ and $-6{\cdot}6$. From Chou's results[6] $\log K_{\mathrm{ZnOx_2}} = -6{\cdot}2$, which is in agreement with our results.

TABLE I.—DETERMINATION OF EQUILIBRIUM CONSTANT $E_{Zn(HDz)_2-HOx}$

−log of original concentration				−log of equilibrium concentration				log
$[ZnOx_2]$	$[H_2Dz]$	$[Zn(HDz)_2]$	$[HOx]$	$[ZnOx_2]$	$[H_2Dz]$	$[Zn(HDz)_2]$	$[HOx]$	$E_{Zn(HDz)_2-HOx}$
		5·04	1·70	5·50	5·20	5·22	1·70	7·28
		5·04	1·52	5·39	5·09	5·29	1·52	7·24
		5·04	1·40	5·31	5·01	5·36	1·40	7·17
		5·03	2·00	5·67	5·37	5·14	2·00	7·27
		5·03	1·70	5·50	5·20	5·22	1·70	7·28
		5·03	1·52	5·37	5·07	5·28	1·52	7·19
		5·03	1·40	5·31	5·01	5·34	1·40	7·19
		5·03	1·22	5·20	4·90	5·40	1·22	7·08
4·30	4·62		2·30	4·42	6·11	4·94	2·30	7·10
4·30	4·62		1·82	4·41	5·70	4·96	1·82	7·21
4·30	4·62		1·60	4·40	5·49	4·98	1·60	7·20
4·30	4·62		1·45	4·39	5·33	5·01	1·45	7·14
4·30	4·62		1·34	4·38	5·23	5·04	1·34	7·12
4·60	4·64		1·82	4·82	5·56	5·00	1·82	7·30
4·60	4·64		1·45	4·78	5·23	5·09	1·45	7·25
4·60	4·64		1·35	4·76	5·13	5·11	1·35	7·21
4·60	4·64		1·26	4·75	5·05	5·15	1·26	7·17
							Average =	7·20 ± 0·02

TABLE II.—DETERMINATION OF EQUILIBRIUM CONSTANT $E_{Pb(HDz)_2-HOx}$

−log of original concentration				−log of equilibrium concentration				log
$[PbOx_2]$	$[H_2Dz]$	$[Pb(HDz)_2]$	$[HOx]$	$[PbOx_2]$	$[H_2Dz]$	$[Pb(HDz)_2]$	$[HOx]$	$E_{Pb(HDz)_2-HOx}$
		4·87	2·70	5·95	5·65	4·90	2·70	6·95
		4·87	2·40	5·72	5·42	4·93	2·40	6·83
		4·87	2·30	5·68	5·38	4·94	2·30	6·90
		4·87	2·22	5·61	5·31	4·95	2·22	6·84
		4·87	2·10	5·58	5·28	4·97	2·10	6·97
		4·87	2·00	5·50	5·20	4·98	2·00	6·92
		4·87	2·00	5·52	5·22	4·99	2·00	6·97
		4·87	1·70	5·35	5·05	5·04	1·70	7·01
		4·87	1·70	5·35	5·05	5·05	1·70	7·00
		4·87	1·52	5·27	4·97	5·07	1·52	7·11
		4·87	1·52	5·28	4·97	5·08	1·52	7·10
		4·87	1·40	5·22	5·92	5·12	1·40	7·14
		4·72	2·00	5·43	5·13	4·80	2·00	6·89
		4·72	1·70	5·26	4·96	4·87	1·70	6·91
		4·72	1·40	5·12	4·82	4·94	1·40	7·02
		4·72	1·10	5·00	4·70	5·05	1·10	7·15
5·30		4·87	2·30	5·22	5·70	4·90	2·30	7·12
5·00		4·70	2·00	4·92	5·40	4·72	2·00	7·00
5·04	4·65		2·00	5·82	5·12	5·13	2·00	6·93
4·90	4·59		1·68	5·35	5·00	5·10	1·68	6·89
4·90	4·59		1·96	5·52	5·17	5·03	1·96	6·91
4·74	4·65		1·71	5·02	5·26	5·07	1·71	7·05
4·74	4·65		1·71	5·03	5·27	5·06	1·71	7·09
4·60	4·60		2·15	4·89	5·70	4·92	2·15	7·07
4·60	4·60		1·92	4·85	5·50	4·95	1·92	7·06
4·60	4·60		1·77	4·84	5·37	4·98	1·77	7·06
4·60	4·60		1·66	4·82	5·30	5·00	1·66	7·10
4·60	4·60		1·57	4·82	5·22	5·01	1·57	7·11
4·60	4·60		1·50	4·81	5·17	5·02	1·50	7·13
4·44	4·65		1·41	4·50	5·30	5·09	1·41	7·19
							Average =	7·02 ± 0·03

It is interesting to note that zinc is extracted by oxine solution as a complex of the type $ZnOx_2.2HOx$ ($\log K_{ZnOx_2.2HOx} = -2{\cdot}4$)[3] but in the exchange reaction only $ZnOx_2$ species appear to be involved, since if the experimental results are used to calculate the value of the equilibrium constant $[Zn(HOz)_2][HOx]^4/[ZnOx_2.2HOx][H_2Dz]^2$ the result $4{\cdot}04 \pm 0{\cdot}10$ is much less constant and individual values vary from 3·27 to 4·64.

Cadmium

The exchange constant for cadmium, $\log E_{Cd(HDz)_2-HOx} = 8{\cdot}48 \pm 0{\cdot}02$, has been determined in the same way as that for zinc. From the extraction constant of cadmium dithizonate ($\log K_{Cd(HDz)_2} = 0{\cdot}5$)[3] the extraction constant of cadmium oxinate ($\log K_{CdOx_2} = -8{\cdot}0$) has been calculated. This value can be difficult to determine by the conventional distribution technique because cadmium is extracted by oxine as a complex $CdOx_2.2HOx$.[3]

Lead

The mean value is $\log E_{Pb(HDz)_2-HOx} = -7{\cdot}02 \pm 0{\cdot}03$ (see Table II). This agrees well with the theoretical value (−7·14) calculated from the extraction constants[3] of lead dithizonate ($\log K_{Pb(HDz)_2} = -0{\cdot}9$) and lead oxinate ($\log K_{PbOx_2} = -8{\cdot}04$).

Cobalt

From the investigation of the reaction between cobalt(II) oxinate and dithizone the value $\log E_{Co(HDz)_2-HOx} = -5{\cdot}86 \pm 0{\cdot}04$ has been determined. This value cannot be verified by the investigation of the reaction between cobalt(II) dithizonate and oxine because of the extremely slow reaction rate. The same effect has been observed in the exchange reaction between cobalt(II) dithizonate and diethyldithiocarbamic acid.[2]

Nickel

Equilibrium in the exchange reaction between nickel dithizonate and oxine or between nickel oxinate and dithizone is reached very quickly. The mean value (from 20 experiments) of $\log E_{Ni(HDz)_2-HOx}$ is $-4{\cdot}64 \pm 0{\cdot}03$. The extraction constant of nickel oxinate $\log K_{NiOx_2}$ is −2·18 and therefore the extraction constant of nickel dithizonate $\log K_{Ni(HDz)_2}$ should be 2·46. The extraction constant determined by distribution between chloroform and acetate solution (concentration not stated) is $\log K_{Ni(HDz)_2} = -2{\cdot}9$.[3,4] Because of the formation of nickel acetate complexes and the very slow rate of extraction of nickel by dithizone solution in acidic medium the real value of $\log K_{Ni(HDz)_2}$ must be much higher and needs to be verified.

Palladium

The addition of oxine to palladium dithizonate solution in chloroform results in a negligible displacement of dithizone. The value $\log E_{Pd(HDz)_2-HOx}$ is < -12 and thus $\log K_{Pd(HDz)_2}$ is >27 ($\log K_{PdOx_2} \sim 15$)[3].

Indium

From the investigation of the exchange reaction between indium oxinate and dithizone or between indium dithizonate and oxine only an approximate value

$\log E_{\mathrm{In(HDz)_3-HOx}} \sim 0$ can be determined. The published data for $\log K_{\mathrm{InOx_3}}$ are 0·89 and 1·35;[3] therefore $\log K_{\mathrm{In(HDz)_3}}$ must be of the same order.

Gallium

Only the reaction between gallium oxinate and dithizone can be investigated because gallium dithizonate cannot be prepared in a pure state. The equilibrium concentration of gallium dithizonate formed was determined from the decrease of the absorption of dithizone at 505 nm. The mean value of $\log E_{\mathrm{Ga(HDz)_3-HOx}}$ is ~ 5. If the extraction constant of gallium oxinate is $\log K_{\mathrm{GaOx_3}} = 3{\cdot}72$,[3] the extraction constant of gallium dithizonate $\log K_{\mathrm{Ga(HDz)_3}}$ should be $-1{\cdot}3$ which is in agreement with extraction results.[7]

Bismuth

The mean value (20 experiments) of the exchange constant is $\log E_{\mathrm{Bi(HDz)_3-HOx}} = -9{\cdot}11 \pm 0{\cdot}04$. The value of $\log K_{\mathrm{BiOx_3}}$ is $-1{\cdot}2$,[3] and thus $\log K_{\mathrm{Bi(HDz)_3}} = 7{\cdot}9$. The two available published values, 5·2 and 8·7, differ markedly.[3,4]

CONCLUSIONS

The values of the equilibrium constants of the exchange reactions in chloroform are summarized in Table III. From the results obtained it can be seen that the equilibrium constants can be accurately determined. Equilibrium is reached very quickly and in most cases the exchange reactions are completely reversible, *i.e.*, the same value of the exchange constant is obtained by the investigation of the reaction between metal dithizonate and oxine or between metal oxinate and dithizone.

TABLE III.—EQUILIBRIUM CONSTANTS OF EXCHANGE REACTION, E, AND EXTRACTION CONSTANTS OF METAL DITHIZONATES, $K_{\mathrm{M(HDz)}_N}$ AND OF OXINATES, K_{MOx_N}

Reaction	$\log E$*	$\log K_{\mathrm{M(HDz)}_N}$	$\log K_{\mathrm{MOx}_N}$
$\mathrm{TlHDz + HOx = TlOx + H_2Dz}$	$-4{\cdot}96 \pm 0{\cdot}04$	$(-3{\cdot}8)$[3,4]	$-8{\cdot}76$
$\mathrm{AgHDz + HOx = AgOx + H_2Dz}$	$\leqslant -8$		
$\mathrm{Cu(HDz)_2 + 2HOx = CuOx_2 + 2H_2Dz}$	$-7{\cdot}27 \pm 0{\cdot}03$	8·7–9·0	(1·4–1·7)[3]
$\mathrm{Zn(HDz)_2 + 2HOx = ZnOx_2 + 2H_2Dz}$	$-7{\cdot}20 \pm 0{\cdot}02$	(0·6–1·0)[3]	$-(6{\cdot}2–6{\cdot}6)$
$\mathrm{Cd(HDz)_2 + 2HOx = CdOx_2 + 2H_2Dz}$	$-8{\cdot}48 \pm 0{\cdot}02$	(0·5)[3,4]	$-8{\cdot}0$
$\mathrm{Hg(HDz)_2 + 2HOx = HgOx_2 + 2H_2Dz}$	$\leqslant -14$		
$\mathrm{Pb(HDz)_2 + 2HOx = PbOx_2 + 2H_2Dz}$	$-7{\cdot}02 \pm 0{\cdot}03$	$-1{\cdot}02$	$(-8{\cdot}04)$[3]
$\mathrm{Co(HDz)_2 + 2HOx = CoOx_2 + 2H_2Dz}$	$-5{\cdot}86 \pm 0{\cdot}04$		
$\mathrm{Ni(HDz)_2 + 2HOx = NiOx_2 + 2H_2Dz}$	$-4{\cdot}64 \pm 0{\cdot}03$	2·46	$(-2{\cdot}18)$[3]
$\mathrm{Pd(HDz)_2 + 2HOx = PdOx_2 + 2H_2Dz}$	< -12	>27	(15)[3]
$\mathrm{In(HDz)_3 + 3HOx = InOx_3 + 3H_2Dz}$	~ 0	~ 1	(0·9–1·3)[3]
$\mathrm{Ga(HDz)_3 + 3HOx = GaOx_3 + 3H_2Dz}$	~ 5	$\sim -1{\cdot}3$	(3·72)[3]
$\mathrm{Bi(HDz)_3 + 3HOx = BiOx_3 + 3H_2Dz}$	$-9{\cdot}11 \pm 0{\cdot}04$	7·9	$(-1{\cdot}2)$[3]

* The errors quoted are the standard errors of the means.

The value $1/N \log E_{\mathrm{M(HDz)}_N-\mathrm{HOx}}$ measures the relative affinity of the chelating agents for the metal investigated. Metals with a positive value for $1/N \log E_{\mathrm{M(HDz)}_N-\mathrm{HOx}}$ have a greater higher affinity for oxine than dithizone (*e.g.*, gallium); a negative value denotes the affinity is higher towards dithizone (*e.g.*, mercury, silver).

When the extraction constant of one metal chelate (dithizonate or oxinate) is known the extraction constant of the second metal chelate can be readily calculated even when conventional distribution measurements cannot be used because of hydrolysis or complexation in the aqueous phase, decomposition of the reagent or the chelate formed, or slowness of equilibration. Thus in the present paper the extraction constants of dithizonates of copper, lead, nickel, indium, gallium and bismuth and the extraction constants of oxinates of thallium(I), zinc and cadmium have been determined. There was no evidence of the formation of the mixed type of complex, M(Ox)(HDz).

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Zusammenfassung—Die Reaktion zwischen Dithizonaten und Oxinaten von Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Co(II), Ni, Pd, In, Ga und Bi in Chloroform wurden spektrophotometrisch untersucht. Aus den ermittelten Austauschkonstanten wurden die Extraktionskonstanten der Metalldithizonate bzw. -oxinate berechnet. Auf diese Weise kann man Extraktionskonstanten vieler Metallchelate berechnen, die durch Untersuchung der Verteilung zwischen wäßriger und Chloroformphase schwierig zu bestimmen sind.

Résumé—On a étudié spectrophotométriquement les réactions entre les dithizonates et les oxinates de Ag, Tl(I), Cu(II), Zn, Cd, Hg(II), Pb, Co(II), Ni, Pd, In, Ga et Bi en chloroforme. Des constantes d'échange déterminées, on a calculé les constantes d'extraction des dithizonates ou oxinates métalliques. Par cette méthode, on peut calculer les constantes d'extraction de nombreux chélates métalliques qu'il est difficile de déterminer par des études de partage entre phases aqueuse et chloroformique.

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