BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (5), 1651—1652 (1975)

The Back-extraction Behavior of Chelate Compounds. II.* Some Aspects of the Secondary Dithizonate of Copper

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(Received November 18, 1974)

Synopsis. The behavior of secondary copper dithizonate in carbon tetrachloride, chloroform, 1,2-dichloroethane, benzene, monochlorobenzene, *o*-dichlorobenzene, and nitrobenzene has been investigated by a kinetic study of the back-extraction of the copper ion in order to clarify the extraction mechanism and to ascertain the chemical form of this chelate.

Dithizone (diphenylthiocarbazone, H_2Dz) forms an extractable, colored chelate with about twenty metals by replacing one or both hydrogen atoms, yielding the primary and the secondary dithizonate.[1,2] The primary dithizonate of copper ($Cu^{II}(HDz)_2$ type)[3] is formed in an acidic solution and appears as red-purple, while a secondary complex of a yellow-brown color ($Cu^{II}Dz$,[3] $Cu^{I}(HDz)$,[4,6] or $Cu^{II}_2(Dz)_2$[5] type) is formed in a basic solution or in the presence of a deficit of dithizone. The extraction mechanism and the structure of the secondary dithizonate of copper have not yet been fully elucidated.[1-6]

Experimental

The secondary dithizonate of copper in an organic solvent containing no free dithizone was prepared around pH 11 under the so-called substoichiometric conditions by adding an excess of copper ions over the equivalent amount of dithizone. After the phase separation, the organic phase was shaken with the same volume of an acidic aqueous solution adjusted to a desired pH with 0.1 M acetic acid. The aqueous phase was separated from the organic phase by centrifugation, and then the pH was checked again. The concentration of copper ions back-extracted into the aqueous solution was determined by atomic absorption spectrophotometry. The amount of the initial secondary complex was also determined by atomic absorption spectrophotometry after all the copper has been extracted into 6 M hydrochloric acid. All the extractions were carried out in a thermostatic room at 20 °C.

Results and Discussion

The change in the absorption spectra in the course of the back-extraction of the secondary copper dithizonate in carbon tetrachloride at pH 3.0 was determined; the results are shown in Fig. 1(a), in which No. 1 is the spectrum before the back-extraction. The spectra gradually change to No. 2, that of the primary copper dithizonate after a few hours' shaking; there are two isosbestic points—at 497 and 615 nm. The spectrum of dithizone in carbon tetrachloride is also shown in Fig. 1(a) (No. 3). Moreover, an extraction reaction between the primary complex in carbon tetrachloride and copper ions took place at pH 3.0; the change in the absorption spectrum of the secondary and primary complexes with the shaking time were determined at 450 nm and 550 nm respectively. The results are shown in Fig. 1(b). From these results, it is clear that the extraction equilibrium between the secondary copper dithizonate and the primary copper dithizonate in carbon tetrachloride is reversible under the present conditions:

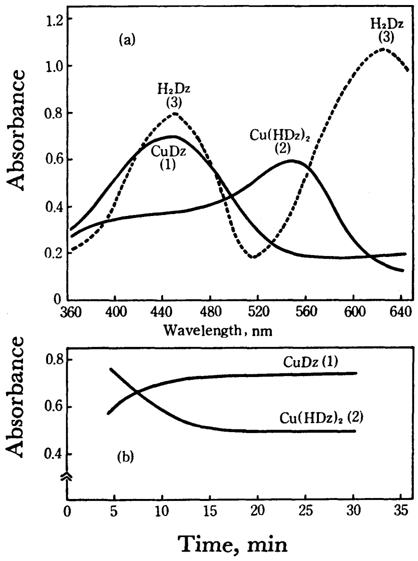

Fig. 1. (a) The change of the absorption spectra of copper dithizonate in carbon tetrachloride with the formation of $Cu(HDz)_2$ from CuDz by back-extraction at pH 3.0
(1) $(CuDz)_{initial}=3.3\times10^{-5}$ M (2) $Cu(HDz)_2=2.5\times10^{-5}$ M (3) $H_2Dz=4.0\times10^{-5}$ M
(b) The change of the absorbance of CuDz at 450 nm and $Cu(HDz)_2$ at 550 nm in carbon tetrachloride by the formation of CuDz from $Cu(HDz)_2$ and Cu^{2+} at pH 3.0
$(Cu(HDz)_2)_{initial}=5\times10^{-5}$ M, $(Cu^{2+})_{initial}=5\times10^{-5}$ M
(1) CuDz (2) $Cu(HDz)_2$

$$2CuDz + 2H^+ \rightleftharpoons Cu(HDz)_2 + Cu^{2+} \qquad (1)$$

Fig. 2(a) shows that the amount of copper ions increased in an aqueous phase with the shaking time in the relation of a hyperbolic curve, when the reaction was performed in carbon tetrachloride. The following two relations have been found to hold from the results after the determination of copper ions.

$$(Cu(HDz)_2)_0 = (Cu^{2+}) \qquad (2)$$

For the remaining secondary dithizonate,

$$\begin{aligned}(CuDz)_0 &= (CuDz)_{initial} - (Cu(HDz)_2)_0 - (Cu^{2+})\\ &= (CuDz)_{initial} - 2(Cu^{2+}) \qquad (3)\end{aligned}$$

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* T. Honjo, K. Ameno, M. Horiuchi, and T. Kiba, This Bulletin, **47**, 1799 (1974), Part I.

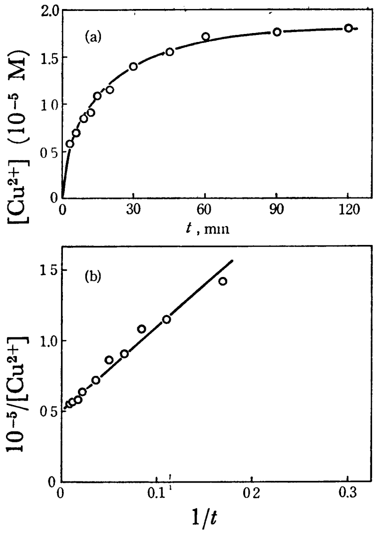

Fig. 2. The effect of the reaction time on stripping of Cu^{2+} from CuDz in carbon tetrachloride at pH 2.93. $(CuDz)_{initial}=8.6\times10^{-5}$ M

where ( ) and $(\ )_0$ designate the concentration of chemical species in the aqueous and the organic phase respectively. The term of $(CuDz)_{initial}$ indicates the concentration of the secondary dithizonate at the start of the reaction. The kinetic study of the reaction shows that the increasing rate of the copper ion in the aqueous phase is the pseudo-second order reaction.

$$d(Cu^{2+})/dt = k(CuDz)_0^2 \tag{4}$$

$$d(Cu^{2+})/dt = k\{(CuDz)_{initial}-2(Cu^{2+})\}^2 \tag{5}$$

$$1/(Cu^{2+}) = 1/\{k(CuDz)_{initial}^2 t\} + 2/(CuDz)_{initial} \tag{6}$$

This equation shows that the reciprocal of the concentration of the copper ion is proportional to the reciprocal of the reaction time, that is, the shaking time, *t*. As is shown in Fig. 2(b), the $1/(Cu^{2+})$ *vs.* $1/t$ plot is linear at pH 2.93. This fact indicates that the treatment of the back-extraction mechanism of the secondary copper dithizonate in carbon tetrachloride is valid. The back-extraction of the secondary copper dithizonate in other solvents, such as 1,2-dichloroethane, benzene, monochlorobenzene, *o*-dichlorobenzene, and nitrobenzene, was also investigated by shaking a solution of them with an aqueous solution of pH 2.90—2.95. In the case of the complex in a chloroform solution, the back-extraction at pH 1.46 was examined because a distinct back-extraction reaction in the pH region mentioned above was observed. The wavelengths of the maximum absorptions of the secondary dithizonate in the seven solvents against the dielectric constants of the solvents are given in Table 1, together with those of dithizone. The plots of $1/Cu^{2+}$ *vs.* $1/t$ obtained with these solvents are shown in Fig. 3. This shows that the primary complex which had been formed by Reaction (1) acted with a proton to effect the following reaction:

$$Cu(HDz)_2 + 2H^+ \rightleftarrows 2H_2Dz + Cu^{2+} \tag{7}$$

Dithizone was released as a matter of course. The solvents showing the break in the line have relatively high dielectric constants. This fact is compatible with the general rule that the polar solvents have stronger effects on the solutes than the non-polar solvents. It is clear from these results that the extraction equilibrium between the secondary copper dithizonate and the primary dithizonate is reversible and that the secondary copper dithizonate is of the $Cu^{II}Dz$ type.

TABLE 1. THE DIELECTRIC CONSTANT, ε, OF THE ORGANIC SOLVENTS AND THE WAVELENGTH OF THE ABSORPTION MAXIMUM, λ_{max}, OF THE SECONDARY COPPER DITHIZONATE AND DITHIZONE IN THESE SOLVENTS

Solvent	ε	λ_{max}, nm		
		CuDz	H_2Dz	
Carbon tetrachloride	2.24	450	450	627
Chloroform	4.81	448	441	610
1,2-Dichloroethane	10.36	450	450	620
Benzene	2.28	454	454	627
Monochlorobenzene	5.62	454	457	629
o-Dichlorobenzene	9.93	458	457	629
Nitrobenzene	34.82	448	441	610

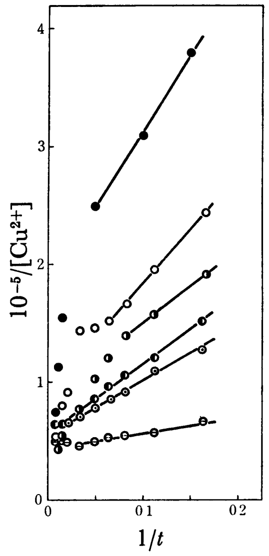

Fig. 3. The effect of the reaction time on stripping of Cu^{2+} from CuDz in various organic solvents at pH 2.90—2.95.

Solvent	$(CuDz)_{initial}$	pH
—●— chloroform	4.9×10^{-5} M	1.46
—○— 1,2-dichloroethane	9.5×10^{-5} M	2.92
—◐— benzene	7.7×10^{-5} M	2.90
—⊙— monochlorobenzene	9.7×10^{-5} M	2.90
—⊖— *o*-dichlorobenzene	8.0×10^{-5} M	2.90
—◑— nitrobenzene	5.5×10^{-5} M	2.95

References

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