BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 51 (2), 645—646 (1978)

The Solvent Extraction of Thallium(I) as a Dibenzo-18-crown-6 Complex with the Picrate Ion

Tatsuya SEKINE, Hiroji WAKABAYASHI, and Yuko HASEGAWA

Departmeut of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 162

(Received August 5, 1977)

Synopsis. The solvent extraction of thallium(I) with dibenzo-18-crown-6 (DBC) as the picrate into chloroform and benzene was measured at 25 °C. The extraction was nearly the same as that of potassium(I) and much better than rubidium(I); this tendency was mainly attributed to the difference in the stability of the DBC complexes in the aqueous phase. Thallium(III) was extracted only poorly.

The solvent extraction of alkali metal ions with various macrocyclic polyethers of different ring sizes was employed in the early work on these compounds as a measure of the stability of the complexes of the metal ions with them.[1,2] It was found that, among the alkali metal ions, 18-crown-6 polyethers extracted potassium(I) most effectively; this was explained in terms of the size of K^+ being the most favorable fit for the 18-crown-6 polyether rings. The relationship between the extractability and the stability of the macrocyclic polyether complexes was further considered statistically.[3-5] It was assumed that metal ions trapped in the ring were not hydrated or that they were hydrated similarly.[5]

The extraction of metal ions with macrocyclic polyethers has been further studied by several inorganic chemists with regard to alkali metal ions[4-7] and alkaline earth ions,[4] and the extraction equilibria as well as the nature of the complexes have been discussed in details. Furthermore, extraction with macrocyclic polyethers has been used in the substoichiometric determination of sodium(I)[8] and the separation of strontium(II) from macro amounts of calcium(II).[9]

In the present study, we have measured the solvent extraction of thallium(I) as a dibenzo-18-crown-6 (DBC) complex with the picrate ion into benzene and chloroform. The results were compared with previous data on alkali metal ions obtained under similar conditions.[6]

Experimental

All the procedures were performed at 25±0.3 °C. The DBC was obtained from the Aldrich Co., U.S.A., and was recrystallized several times from chloroform. The other reagents were of an analytical grade. The lithium picrate solution was prepared from lithium hydroxide and picric acid. The standard thallium(I) solution was prepared from thallium(I) nitrate, the concentration being checked by a colorimetric method.[10] A 5-ml portion of an aqueous solution containing lithium picrate and 1×10^{-4} mol dm^{-3} of thallium(I) (pH about 3.3) and the same volume of benzene or chloroform containing a certain amount of DBC were placed in a stoppered glass tube and agitated mechanically until the distribution equilibrium was attained. The two phases were then centrifuged off, and the thallium(I) in the organic phase was back-extracted with 0.1 mol dm^{-3} perchloric acid. The amount of thallium thus back-extracted and that remained in the aqueous phase was measured by an atomic absorption method. The distribution ratio was defined by means of the following equation and was calculated from the experimental data:

$$D = [\mathrm{Tl(I)}]_{\mathrm{org,total}}/[\mathrm{Tl(I)}]_{\mathrm{total}}. \tag{1}$$

Results and Discussion

In the following statistical treatment, a unipositive metal ion, DBC, and a picrate ion are denoted by M^+, E, and A^-, respectively, and the chemical species in the organic and aqueous phases by the subscript "org" and by the lack of any subscript respectively. Then the following equilibrium constants may be defined:

$$\beta_1 = [\mathrm{ME}^+][\mathrm{M}^+]^{-1}[\mathrm{E}]^{-1}, \tag{2}$$

$$K_{\mathrm{ex0}} = [\mathrm{ME}^+\mathrm{A}^-]_{\mathrm{org}}[\mathrm{M}^+]^{-1}[\mathrm{E}]_{\mathrm{org}}^{-1}[\mathrm{A}^-]^{-1}, \tag{3}$$

$$K_{\mathrm{ex}} = [\mathrm{ME}^+\mathrm{A}^-]_{\mathrm{org}}[\mathrm{ME}^+]^{-1}[\mathrm{A}^-]^{-1}, \tag{4}$$

$$K_{\mathrm{d}} = [\mathrm{E}]_{\mathrm{org}}[\mathrm{E}]^{-1}. \tag{5}$$

Thus,

$$K_{\mathrm{ex}} = K_{\mathrm{ex0}}K_{\mathrm{d}}\beta_1^{-1} \text{ or } K_{\mathrm{ex0}} = K_{\mathrm{ex}}\beta_1 K_{\mathrm{d}}^{-1}. \tag{6}$$

The distribution ratio may generally be written as

$$D = ([\mathrm{ME}^+\mathrm{A}^-]_{\mathrm{org}} + [\mathrm{ME}^+]_{\mathrm{org}})([\mathrm{M}^+] + [\mathrm{ME}^+])^{-1}. \tag{7}$$

However, since the dissociation of the ion-pair in the non-polar solvents may be negligible, and since $[\mathrm{ME}^+]$ was found to be much smaller than $[\mathrm{M}^+]$ under the conditions of the present work, as will be seen, Eq. 7 is written in the present paper as

$$D = K_{\mathrm{ex0}}[\mathrm{E}]_{\mathrm{org}}[\mathrm{A}^-]. \tag{8}$$

The distribution ratio as a function of the DBC concentration showed a straight line with a slope of 1, as is seen from Fig. 1; that as a function of the picrate ion also showed a straight line with a slope of 1 in the picrate concentration range from 10^{-3} to 10^{-2} mol dm^{-3}, although it deviated slightly from the line above this range.

The equilibrium constants obtained from these data are listed in Table 1, together with those from the literature.

It may be seen from these data that the extraction of thallium(I) is much better than that of rubidium(I) and nearly the same as that of potassium(I), which is extracted most effectively with 18-crown-6 polyethers among the alkali metal ions.

By separate experiments, it was found that the extraction of thallium(III) was much poorer than that of thallium(I). For example, the distribution ratio of the former into chloroform, was $10^{-1.14}$ when $[\mathrm{E}]_{\mathrm{org}}$ was 1×10^{-2} mol dm^{-3} and $[\mathrm{A}^-]$ was 7.5×10^{-3} mol dm^{-3}, and under identical conditions the distribution ratio

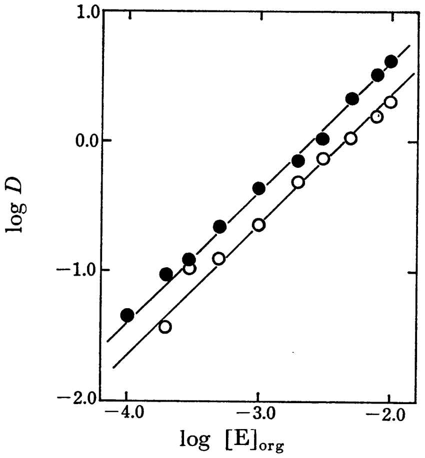

Fig. 1. Extraction curves of thallium(I) complex with DBC as picrate into chloroform (●) and benzene (○). The aqueous phase contained 7.4×10^{-3} mol dm^{-3} of lithium picrate and was at pH about 3.3. The straight lines are calculated by introducing the values of K_{ex0} in Table 1 and the above picrate concentration into Eq. 8.

Table 1. Summary of constants

Metal ion	Na^+	K^+	Rb^+	Cs^+	Tl^+	Remarks
Diameter (nm)	0.19	0.27	0.29	0.33	0.29	Ref. 11
log K_{ex0} into $CHCl_3$	—	—	—	—	4.74[a)]	
log K_{ex0} into C_6H_6	2.2	4.65	3.75	3.07	4.49[a)]	
log β_1	1.2	1.7	1.1	0.8	1.5	Ref. 11
log K_{ex} into C_6H_6[b)]	3.9	5.9	5.6	5.2	5.9	

a) Present work, others taken from Ref. 6.

b) $\log K_{ex}=\log K_{ex0}K_d\beta_1^{-1}$ in which $\log K_d=2.9$ (Ref. 6) was employed.

of thallium(I) was $10^{0.62}$.

The apparent tendency of the extraction given by K_{ex0} in Eq. 3 for different metal ions is affected by both the stability and the extractability of the complex in the aqueous phase, as may be seen from Eq. 6. The value of K_{ex}, which represents the latter property of the complex, should be affected by the molar volume of the extracted species and also by the interactions of the complex, probabaly mainly by those of the central metal ion, with water molecules and/or solvent molecules. The molar volumes of the extractable complexes of different metal ions with the same polyether should be rather similar to each other. Thus, when the K_{ex} values of metal ions with the same macrocyclic polyether are different, it is probably due to the difference in the hydration of the complex if no special interactions with the solvent molecules are to be expected.

As may be seen from Table 1, the value of K_{ex} of thallium(I) is similar to that of potassium(I) and not very much different from rubidium(I). Thus, the difference in the extractability of these three ions into benzene may be attributed mainly to the difference in the stability of the complex. The fact that the stability of the thallium(I) complex with 18-crown-6 polyethers is very similar to that of the corresponding potassium(I) complexes has already been pointed out.[11,12)]

Since thallium(I) is much more effectively extracted with DBC than thallium(III), the separation of thallium in these oxidation states may be achieved by extraction with this reagent, and, since this tendency is the inverse of that observed in many other extraction systems, it should be useful for such purposes as to separate a small amount of thallium(I) from a large amount of thallium(III).

The authors are very grateful to Dr. Yasuyuki Takeda of the Department of Chemistry, Chiba University, for his valuable discussion and experimental aid in the early stage of this work.

References

1) C. J. Pedersen, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **27**, 1305 (1968); *J. Am. Chem. Soc.*, **92**, 391 (1970).

2) G. Eisenman, S. Ciani, and G. Szabo, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **27**, 1289 (1968).

3) H. K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 4684 (1971).

4) J. Rais, M. Kyrs, and L. Kadlecova, Proc. Int. Solvent Extraction Conf., 1974, Soc. Chem. Ind., London (1974), p. 1705.

5) P. R. Danesi, H. Meider-Gorican, R. Chiarizia, V. Capuano, and G. Scibona, Proc. Int. Solvent Extraction Conf., **1974**, Soc. Chem. Ind. London (1974), p. 1764; *J. Inorg. Nucl. Chem.*, **37**, 1479 (1975).

6) A. Sadakane, T. Iwachido, and K. Toei, *Bull. Chem. Soc. Jpn.*, **48**, 60 (1975).

7) T. Iwachido, M. Kimura, and K. Toei, *Chem. Lett.*, **1976**, 1101.

8) J. W. Mitchell and D. L. Shanks, *Anal. Chem.*, **47**, 642 (1975).

9) T. Kimura, K. Iwashima, T. Ishimori, and H. Hamaguchi, *Chem. Lett.*, **1977**, 563.

10) H. Goto, Y. Kakita, and N. Ichinose, *Nippon Kagaku Zasshi*, **88**, 640 (1967).

11) E. Shchori, N. Nae, and J. Jagur-Grodzinski, *J. Chem. Soc. Dalton Trans.*, **1975**, 2381.

12) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).