CHEMISTRY LETTERS, pp. 1075-1078, 1981.

SYNERGISTIC EFFECT OF TRIOCTYLPHOSPHINE OXIDE AND DIBENZO-18-CROWN-6 ON THE EXTRACTION OF SILVER(I) AS PICRATE

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Solvent extraction of silver(I) with dibenzo-18-crown-6 (E) as ion-pairs with picrate ion (A^-) into chloroform was found to be synergistically enhanced by trioctylphosphine oxide (TOPO). This was concluded to be due to an adduct formation of the cationic silver(I) complex with TOPO, $AgE(topo)_2{}^+$, in this organic solvent.

In a previous study it was found that the solvent extraction of silver(I) with dibenzo-18-crown-6 (DBC) as picrate is somewhat higher into benzene than into chloroform and this was explained in terms of interactions of the π-donor with the silver(I) in the complex.1) The solvent effect has been further studied and trioctylphosphine oxide (TOPO) in chloroform was found to enhance the extraction of the above complex synergistically and this has been concluded to be due to an adduct formation of the silver(I)-DBC complex with the n-donor, TOPO.

The DBC used was recrystallized several times from benzene and the TOPO from hexane. Chloroform was washed with deionized water just before the use. A portion of an aqueous solution containing 7.2×10^{-3}M (M ≡ mol dm^{-3}) lithium picrate and 1×10^{-4}M silver nitrate and being adjusted at pH 4.5 and the same volume of chloroform containing a certain amount of DBC and/or TOPO were placed in a stoppered glass tube and agitated mechanically until the distribution equilibrium was attained. After centrifuging, the silver(I) in the organic phase was back-extracted with 3M nitric acid. The amount of silver thus back-extracted and that remained in the aqueous phase was measured by an atomic absorption method. The distribution ratio defined by means of the following equation was calculated from the experimental data:

$$D = [Ag(I)]_{org,total}/[Ag(I)]_{aq,total}$$

The distribution ratio in the absence of both DBC (E) and TOPO (T) is written as,

$$D_{0,0} = [Ag^+A^-]_{org}/[Ag^+] = Kex_{0,0}[A^-] \qquad (1)$$

where A^- is picrate ion and $\mathrm{Kex}'_{0,0} = [Ag^+A^-]_{org}[Ag^+]^{-1}[A^-]^{-1}$. The distribution ratio in the presence of DBC but no TOPO can be written as;

$$D_{E,0} = ([Ag^+A^-]_{org} + [AgE^+A^-]_{org})/[Ag^+] = (\mathrm{Kex}_{0,0} + \mathrm{Kex}_{1,0}[E]_{org})[A^-] \tag{2}$$

where $\mathrm{Kex}_{1,0} = [AgE^+A^-]_{org}[Ag^+]^{-1}[E]_{org}{}^{-1}[A^-]^{-1}$ (cf. ref. (1)).

While that in the presence of TOPO but no DBC may be written as;

$$\begin{aligned} D_{0,T} &= ([Ag^+A^-]_{org} + \Sigma[AgT_m{}^+A^-]_{org})/[Ag^+] \\ &= \mathrm{Kex}_{0,0}(1 + \Sigma\beta_{m(org)}[T]_{org}{}^m)[A^-] \end{aligned} \tag{3}$$

where $\beta_{m(org)} = [AgT_m{}^+A^-]_{org}[Ag^+A^-]_{org}{}^{-1}[T]_{org}{}^{-m}$.

In the presence of both, mixed species containing DBC and TOPO may be extracted and then;

$$D_{E,T} = ([Ag^+A^-]_{org} + [AgE^+A^-]_{org} + \Sigma[AgT_m{}^+A^-]_{org} + \Sigma[AgET_n{}^+A^-]_{org})/[Ag^+] \tag{4}$$

Hence

$$\begin{aligned} &[D_{E,T} - \mathrm{Kex}_{0,0}[A^-](1 + \Sigma\beta_{m(org)}[T]_{org}{}^m)]\times\mathrm{Kex}_{1,0}{}^{-1}[E]_{org}{}^{-1}[A^-]^{-1} \\ &= 1 + \Sigma\beta_{n(org)}[T]_{org}{}^n \end{aligned} \tag{5}$$

where $\beta_{n(org)} = [AgET_n{}^+A^-]_{org}[AgE^+A^-]_{org}{}^{-1}[T]_{org}{}^{-n}$.

The extraction behavior of silver(I) as picrate is summarized as follows.

i) Silver(I) is extractable with DBC as picrate as reported previously, the $\mathrm{Kex}_{1,0}$ is $10^{3.3,\ 1)}$, i.e., under the conditions of the present study where $[A^-]$ is 7.2×10^{-3} M and $[E]_{org}$ is 8×10^{-3}M, the $D_{E,0}$ is $10^{-0.9}$. The extraction in the absence of DBC is very poor. When the aqueous phase contains 7.2×10^{-3}M lithium picrate, the $D_{0,0}$ is found in the present study to be $10^{-2.5}$ and thus $\mathrm{Kex}_{0,0}$ is tentatively obtained to be $10^{-0.4}$.

ii) TOPO extracts silver(I) as picrate in the absence of DBC. Figure 1 gives the $D_{0,T}$ as a function of the TOPO concentration when $[A^-]$ is 7.2×10^{-3}M by the open circles. By a curve-fitting method,[2] the

Table 1. Summary of adduct formation constants of Ag(I) complexes with TOPO in chloroform at 25°C.

	$\log\beta_{1(org)}$	$\log\beta_{2(org)}$
$AgT_m{}^+A^-$	2.5	3.5
$AgET_n{}^+A^-$	---	2.1
$Ag(tta)T_l$[3]	3.58	4.20
$Ag(cap)T_k$[3]	2.73	4.26

tta: thenoyltrifluoroacetonate
cap: caproate
T : trioctylphosphine oxide (TOPO)
E : dibenzo-18-crown-6 (DBC)

data are analyzed and the value of $\beta_{1(org)}$ and $\beta_{2(org)}$ are obtained as given in Table 1. The solid lines are the asymptotes of the normalized curve which is denoted as, $X = \log v$, $Y = \log(1 + pv + v^2)$.

iii) An addition of TOPO to the extraction system of Ag^+ with DBC as picrate enhances the distribution ratio as shown by the closed circles in Fig. 1 where $[A^-]$ and $[E]_{org}$ are 7.2×10^{-3}M and 8×10^{-3}M. The enhancement is partly due to an extraction of silver ion as picrate with TOPO but it is also due to extractions of mixed species of silver(I) containing both DBC and TOPO as picrates. Figure 2 gives the $\log(D_{E,T} - D_{0,T})/(D_{E,0} - D_{0,0})$ vs. $\log[T]_{org}$ plot (when [dbc] and $[A^-]$ are constant, $D_{0,T}$ at each TOPO concentration corresponds to $Kex_{0,0}[A^-](1 + \Sigma\beta_{m(org)}[T]_{org}{}^m)$ and $(D_{E,0} - D_{0,0})$ is $Kex_{1,0}[E]_{org}[A^-]$. cf. Eq. (5)). By the curve-fitting, the data were analyzed and the constant for the extraction of the $AgET_2{}^+A^-$ species is determined, but the $AgET^+A^-$ species is not confirmed within the experimental accuracy. The broken lines are the asymptotes of the normalized curve which is denoted as, $X = \log v$, $Y = \log(1 + v^2)$. The equilibrium constants are listed in Table 1 together with the adduct

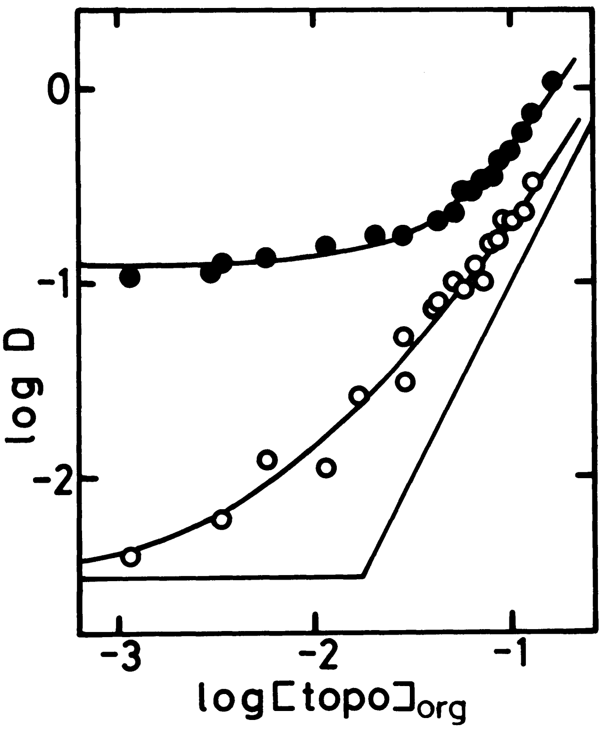

Fig. 1. The extraction of Ag(I) with DBC and/or TOPO as picrates.

aq. phase: 7.2×10^{-3}M lithium picrate

org. phase: ● in the presence of 8×10^{-3}M DBC

○ in the absence of DBC

The solid curves are $\log D = \log(10^{-2.5}(1+10^{2.5}\times[T]_{org}+10^{3.5}[T]^2_{org}) + 10^{-0.9}(1+10^{2.1}[T]^2_{org}))$ for ● (cf. Eq. (4)) and $\log D = -2.5 + \log(1+10^{2.5}[T]_{org}+10^{3.5}[T]^2_{org})$ for ○ (cf. Eq. (3)).

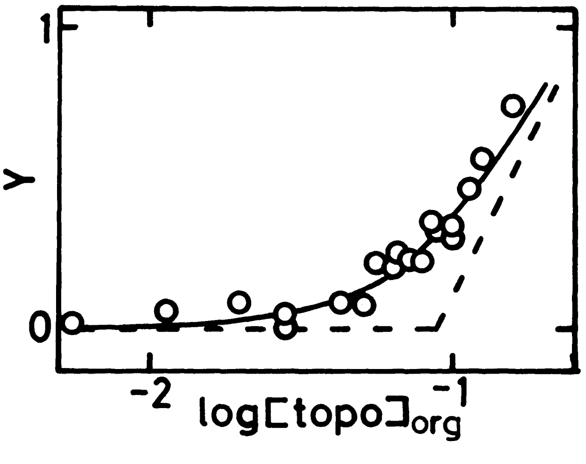

Fig. 2. The synergistic effect of DBC and TOPO on the extraction of Ag(I)-picrate. The solid curve is: $Y=\log(1+10^{2.1}[T]^2_{org})$ Cf. Eq. (5).

formation constants of Ag(I)-thenoyltrifluoroacetonate or caproate complex with TOPO.[3] ($\beta_{k(org)} = [AgRT_k]_{org}[AgR]_{org}^{-1}[T]_{org}^{-k}$ where R is tta$^-$ or caproate ion). Lithium(I)-DBC complex is observed to form hardly adducts with TOPO.

As seen from Table 1 and also Fig. 1, the adduct formation constant of silver(I)-DBC complex with TOPO is lower than that of uncomplexed silver(I) which is extracted as ion-pairs with a picrate ion into chloroform and also much lower than those of silver(I) caproate or thenoyltrifluoroacetonate complex with TOPO in chloroform.

Adduct formation of metal-DBC complexes in organic solvents with n-donors such as TOPO does not seem to have ever been reported.

References

1) Y. Hasegawa, N. Iizima, and T. Sekine, J. Inorg. Nucl. Chem., 43, 633 (1981).

2) F. J. C. Rossotti and H. Rossotti, "The determination of stability constants in solution", McGraw-Hill, New York (1961).

3) T. Sekine and Y. Takahashi, Bull. Chem. Soc. Jpn., 46, 1183 (1973).

(Received May 11, 1981)