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Equilibrium and Enthalpy Measurements on the Complex Formation between Silver(I) and Tri- and Dialkylphosphines and Tributylstibine in Pyridine Solution

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Abstract

The stabilities and the heats of formation of silver(I) tributylphosphine, tricyclohexylphosphine, dicyclohexylphosphine, and tributylstibine complexes have been determined in pyridine, by means of potentiometric and calorimetric measurements. Three mononuclear complexes are formed with tributylphosphine, while only two mononuclear complexes are formed with the other ligands, within the ranges of concentration available. All complexes are formed in strongly exothermic reactions, while the entropy changes are negative. The stabilities of the silver(I) phosphine complexes show a strong correlation with some physical parameters of the ligands, such as the dipole moments, and the acid constants in aqueous solution, and the electronic parameters, ν, determined IR-spectroscopically in the $Ni(CO)_3L$ complexes, L = phosphine or phosphite, in dichloromethane. The stabilities of the trialkylphosphine complexes are higher than the triphenylphosphine complexes, and the stabilities of alkylphosphines are in the order (primary) < secondary < tertiary phosphines.

Introduction

Soft metal ions such as silver(I) form strong complexes with ligands coordinating through a group V atom [1] in the order $N \ll P \gg As > Sb > Bi$ [2]. Group V donor atoms in XR_3 compounds are denoted as weak π-acids [3], *i.e.* a metal–ligand bond will only have a low degree of π-bonding. A comparison of the complex formation abilities of different phosphines to silver(I) will indicate if there is a significant degree of π-bonding in Ag–P bonds. The complex formation constants will also be compared with the dipole moments of the ligands. A previous study on the solvation of the mercury(II) halides has shown that solvents with identical donor atoms and similar configuration, e.g. OR_2, SR_2 and NR_3, R = H or alkyl group, have solvation abilities to soft acceptors proportional to the dipole moment of the solvent [4]. If R is an electron withdrawing group such as phenyl, the solvation properties can be weaker than expected from the dipole moment. It is therefore possible that the stability constants of the silver(I)–phosphine systems are proportional to the dipole moments of the phosphine ligands if the contribution of π-bonding in the Ag–P bond can be neglected. Furthermore, the stability constants will also be compared with the basicity of the phosphines in aqueous solution [5, 6], and the electronic parameter ν determined in $Ni(CO)_3PR_3$ complexes in dichloromethane [7, 8].

The complex formation between silver(I) and triphenyl amine, phosphine, arsine, stibine and bismuthine has previously been determined in DMSO [9] and pyridine [10], and the silver(I) tri-n-butyl amine and phosphine complexes in DMSO [11]. The stability constants are found to be about ten to the power of two lower in pyridine than in DMSO due to stronger solvation of silver(I) in pyridine [10]. When electron withdrawing groups are coordinated to the group V donor atom, the complexes will be substantially weaker, e.g. the first silver(I)–triphenylphosphine complex is approximately 500 times weaker than the corresponding tri-n-butylphosphine complex in DMSO [11]. This effect is independent of the solvent used if the difference in solvation of the ligands is similar in all solvents.

Experimental

Chemicals

Silver(I) and tetraethylammonium perchlorates, and pyridine (all Fluka) were of analytical grade. The silver(I) perchlorate was dried at 80 °C over P_2O_5 under vacuum. The tetraethylammonium perchlorate was dried at 80 °C and stored over silica

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gel. The pyridine was stored in dark bottles over 3 Å molecular sieves. Tri- and dicyclohexyl-, tributylphosphine and tributylstibine (all Strem) were used without further purification. These were stored in sealed ampoules over N_2 and Ar atmosphere to prevent oxidation.

Solutions

The solutions were prepared by weighing out the salts or ligands prior to dissolving them in pyridine. The tetraethylammonium concentration was set to 0.1 M in all solutions by the perchlorate salt. According to low stability of the ligand solutions, they were freshly prepared every day. No decomposition of the ligands could however be noticed during a titration.

Potentiometric Measurements

The measurements were performed by an automated potentiometric titration system described elsewhere [12]. The electrodes were made of thick silver foil with a total area of about 2 cm^2. The set up included five Ingold vessels, where two were used for measurement electrodes, two for reference electrodes and the fifth as a salt bridge connection. The measurements were performed at 25.0 ± 0.1 °C. The vessels initially contained 10.0 ml silver(I) C_M mM solution; titrations, with $C_M = 5$, 10 and 24 mM have been performed. Ligand solutions of C_L mM were added in portions to the silver(I) solutions. Solutions with C_L ranging from 6.6 to 23.5 mM were used. The potentials were measured with an HP3478A digital multimeter used as a potentiometer. The input resistance over the potentiometer was at least 1000 times larger than the resistance over an electrode. All measurements were carried out in a glove box containing 3 Å molecular sieves and phosphorous pentoxide to remove traces of water. The stability constants β_j were calculated by the least-squares computer program EMK [13].

Calorimetric Measurements

The measurements were performed in an automated titration calorimeter system described previously [14]. The reaction vessel initially contained 40 ml silver(I) perchlorate solution with initial concentrations, C_M, ranging from 5 to 16 mM. To these solutions aliquots of ligand solution were added to a total volume of 60 ml. If the complex formation was not completed, 20 ml was withdrawn and the titration was continued. In the titrations performed, the total ligand concentration ranged from 0 to 65 mM. The heats of dilution of silver(I) and the ligands were determined, and corrections for these were applied if necessary. All measurements were carried out at 25.000 ± 0.002 °C. The least squares computer program KALORI was employed for the calculations of the overall enthalpy changes [13].

Results

The overall stability constants, obtained from the potentiometric measurements, are given in Table I. Silver(I) forms three complexes with tri-n-butylphosphine already at fairly low free ligand concentrations; on the other hand, silver(I) forms only two complexes with tri- and dicyclohexylphosphine and tri-n-butylstibine in pyridine solution. The stabilities of the stepwise complexes are in the order $K_1 > K_2 > K_3$, which means that every complex has a certain range where it predominates. The stepwise stability constants, K_j, are given in Table III, and the complex formation functions are given in Fig. 1.

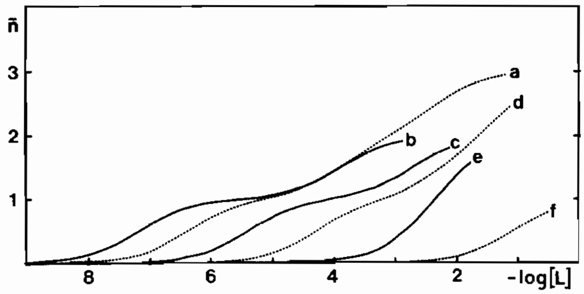

Fig. 1. The complex formation curves of the silver(I) XR_3 systems in pyridine, $XR_3 = P(C_4H_9)_3$ (a); $P(C_6H_{11})_3$ (b); $P(C_6H_{11})_2H$ (c); $P(C_6H_5)_3$ (d). $Sb(C_4H_9)_3$ (e); $Sb(C_6H_5)_3$ (f). Ionic medium 0.1 M Et_4NClO_4.

TABLE I. Overall Stability Constants [β_j (M^{-j})] for the Complex Formation Between Silver(I) and Ligands Donating Through N, P and Sb, in Pyridine Solution at 25 °C. Medium 0.1 M Et_4NClO_4. The Limits of Error Refer to Three Standard Deviations; NP Denotes the Number of Observations (emfs measured) for Each System

	$(C_4H_9)_3N$	$(C_4H_9)_3P$	$(C_4H_9)_3Sb$	$(C_6H_{11})_3P$	$(C_6H_{11})_2PH$
β_1	<0.1	$(2.39 \pm 0.07) \times 10^6$	498 ± 30	$(1.55 \pm 0.08) \times 10^7$	$(2.51 \pm 0.06) \times 10^5$
β_2		$(1.75 \pm 0.06) \times 10^{10}$	$(5.12 \pm 0.58) \times 10^4$	$(1.25 \pm 0.14) \times 10^{11}$	$(1.32 \pm 0.07) \times 10^8$
β_3		$(3.72 \pm 0.22) \times 10^{12}$			
NP	118	437	230	214	442

TABLE II. Overall Enthalpy Changes [$\Delta H^\circ_{\beta j}$ (kJ mol^{-1})] for the Complex Formation Between Silver(I) and Ligands Donating Through P and Sb in Pyridine at 25 °C. Medium 0.1 Et_4NClO_4. The Limits of Error Refer to Three Standard Deviations; NP Denotes the Number of Aliquots for Each System

Ligand	$P(C_4H_9)_3$	$Sb(C_4H_9)_3$	$P(C_6H_{11})_3$	$P(C_6H_{11})_2H$
$-\Delta H_{\beta 1}$	67.0 ± 0.7	43.5 ± 1.6	67.9 ± 1.1	45.7 ± 0.7
$-\Delta H_{\beta 2}$	110.0 ± 1.0	64.7 ± 2.9	91.3 ± 1.4	76.6 ± 1.3
$-\Delta H_{\beta 3}$	148.3 ± 1.5			
NP	79	80	57	86

The overall enthalpy changes, $\Delta H^\circ_{\beta j}$, obtained from the calorimetric measurements are given in Table II, and the stepwise enthalpy changes, ΔH_j°, are given in Table III. The total heats evolved per mol silver(I), Δh_v, as a function of $\bar{n}$, are given in Fig. 2. The complete stepwise complex formation thermodynamics for some silver(I) amine, phosphine, arsine, stibine and bismuthine systems in pyridine, DMSO and aqueous solution are given in Table III.

Discussion

The stabilities of silver(I)–trialkylphosphine complexes are considerably higher than corresponding triphenyl complexes in all solvents studied, Table

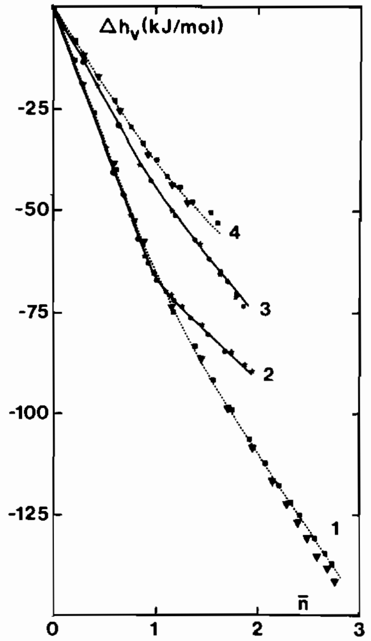

Fig. 2. Total molar enthalpy changes Δh_v as a function of the ligand number, $\bar{n}$, for the silver(I) XR_3 systems in pyridine; 1 = $P(C_4H_9)_3$; 2 = $P(C_6H_{11})_3$; 3 = $P(C_6H_{11})_2H$; 4 = $Sb(C_4H_9)_3$. The points refer to the value actually measured with initial values of C_M = 14 and 8 mM (squares and circles for C_M = 14 mM and stars and triangles for C_M = 8 mM). The solid curves have been calculated from the β_j and $\Delta H^\circ_{\beta j}$ values obtained (Tables I and II). Ionic medium 0.1 M Et_4NClO_4.

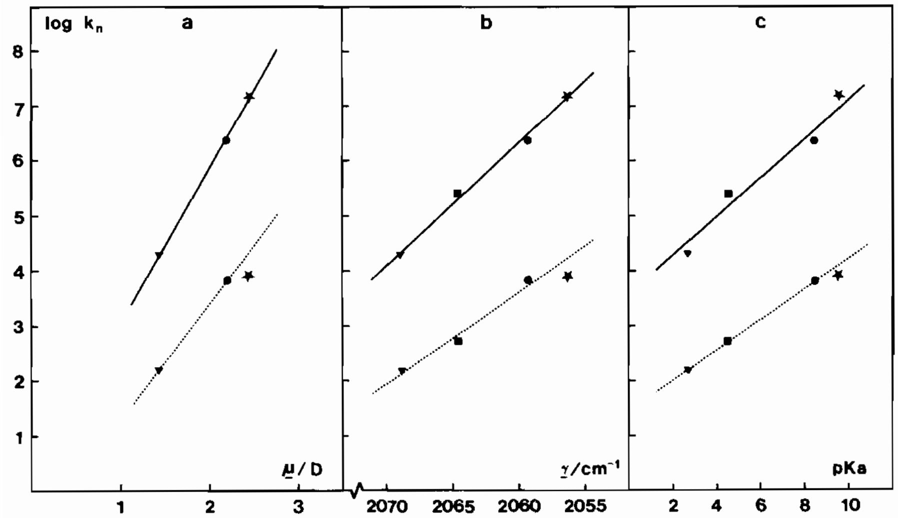

Fig. 3. The stability constants of the silver(I)–phosphine complexes in pyridine, log K_1, (solid) and log K_2 (dotted), plotted against the dipole moment (a), the electronic parameter ν from $Ni(CO)_3PR_3$ complexes in dichloromethane (b), and the basicity in aqueous solution (c) of the phosphine ligands. PR_3 = $P(C_6H_{11})_3$ (stars); $(C_4H_9)_3$ (circles); $P(C_6H_{11})_2H$ (squares); $P(C_6H_5)_3$ (triangles).

TABLE III Equilibrium Constants [K_j (M^{-1})] and thermodynamic functions [ΔG_j°, ΔH_j° (kJ mol^{-1}), ΔS_j° (J mol^{-1} K^{-1})] for the Stepwise Formation of Complexes between Silver(I) and Organic Ligands Coordinating Through Group V Donors in Pyridine, Dimethylsulfoxide and Aqueous Solutions at 25 °C

	Pyridine, 0 1 M Et_4NClO_4									
	$N(C_6H_5)_3$	$P(C_6H_5)_3$	$As(C_6H_5)_3$	$Sb(C_6H_5)_3$	$Bi(C_6H_5)_3$	$N(C_4H_9)_3$	$P(C_4H_9)_3$	$Sb(C_4H_9)_3$	$P(C_6H_{11})_3$	$P(C_6H_{11})_2H$
$\log K_1$	–	4.31	1.44	1.09	–	–	6.38	2.70	7.19	5.40
$\log K_2$		2.14	–	–			3.87	2.01	3.91	2.72
$\log K_3$		1.14					2.33	–	–	–
K_1/K_2		148	–	–			325	4.85	1913	480
K_2/K_3		10.2					34.6	–	–	–
$-\Delta G_1^\circ$		24.6	8.2	6.2			36.4	15.4	41.0	30.8
$-\Delta G_2^\circ$		12.2					22.1	11.5	22.3	15.5
$-\Delta G_3^\circ$		6.5					13.3	–	–	–
$-\Delta H_1^\circ$		34.4	15.6	11.6			67.0	43.5	67.9	45.4
$-\Delta H_2^\circ$		22.0					43.0	18.3	23.4	31.2
$-\Delta H_3^\circ$		16.1					38.4	–	–	
ΔS_1°		–33	–25	–18			–103	–94	–90	–49
ΔS_2°		–33					–70	–31	–4	–53
ΔS_3°		–32					–84	–	–	
$-\Delta G_{\beta 3}^\circ$		43.3					71.8	–	–	
$-\Delta H_{\beta 3}^\circ$		72.5					148.3	–	–	
$\Delta S_{\beta 3}^\circ$		–98					–257	–	–	

	DMSO, 0.1 M NH_4ClO_4							Water, $NaClO_4$		
	$N(C_6H_5)_3$	$P(C_6H_5)_3$	$As(C_6H_5)_3$	$Sb(C_6H_5)_3$	$Bi(C_6H_5)_3$	$N(C_4H_9)_3$	$P(C_4H_9)_3$	$(C_2H_4OH)P(C_2H_5)_2$[a]	$(p\text{-}C_6H_4SO_3)P(C_6H_5)_2$[b]	$As(m\text{-}C_6H_4SO_3)_3^{3-}$[c]
$\log K_1$	0.19	6.58	3.56	3.16	0.80	2.10	9.28	11.83	8.15	4.96
$\log K_2$		4.15	1.81	1.45		1.23	6.63	9.02	5.95	1.7
$\log K_3$		2.44	1.31	1.45		–	3.91	4.86	5.40	–
K_1/K_2		269	56	51		7.4	450	646	158	1820
K_2/K_3		52	3.2	1.0		–	520	1.45×10^4	3.55	–
$-\Delta G_1^\circ$	1.1	37.6	20.3	18.1	4.6	12.0	53.0	67.5	46.5	28.3
$-\Delta G_2^\circ$		23.7	10.4	8.3		7.0	37.8	51.5	34.0	10
$-\Delta G_3^\circ$		13.9	7.5	8.3		–	22.3	27.7	30.8	–
$-\Delta H_1^\circ$	1	51.8	34.5	32.1	0.5			80.6	71	31

$-\Delta H_2^\circ$	38.1	19.4	8.6			69.0	50.6	17
$-\Delta H_3^\circ$	36.3	44.5	57.1			38.1	64	–
ΔS_1°	−48	−48	−47	14		−44	−82	−9
ΔS_2°	−48	−30	−1			−59	−56	−23
ΔS_3°	−75	−124	−164			−35	−111	–
$-\Delta G_{\beta 3}^\circ$	72.5	38.1	34.6		113.1	146.7	111.3	–
$-\Delta H_{\beta 3}^\circ$	126.2	98.4	97.8			187.7	195	–
$\Delta S_{\beta 3}^\circ$	−171	−202	−212			−138		–

[a] 1.0 M KNO_3. [b] 0.1 M. [c] 0.5 M.

III. This is due to a higher electron density on the phosphorous atom in trialkylphosphines, than in triphenylphosphine, because of the electron withdrawing effect of the phenyl groups. A decreasing donor property is generally observed when phenyl or other electron withdrawing groups are bonded to the donor atom [4]. This effect is independent of the solvent used. The higher stability of corresponding complexes in DMSO than in pyridine due to stronger solvation of the silver(I) ion in pyridine has been discussed previously [10].

Previous studies have indicated that the solvation and complex formation abilities towards soft electron acceptors for compounds with the same donor atom and similar configuration are proportional to its dipole moment [4]. The dipole moment of the phosphines are in the order primary < secondary ⩽ tertiary [15, 16]. The stabilities of the silver(I)–phosphine complexes are therefore expected to increase in the same order which is indeed found, as shown in Table III [15, 17]. Furthermore, very good correlation between the dipole moments of the phosphines and the obtained stability constants, Fig. 3a, confirms the relationship between the ability to form complexes with a soft electron acceptor and the dipole moment of the ligand if no backbonding is present.

Strohmeier [7] and later Tolman [8] have proposed that phosphorous donor ligands can be ranked in an electronic series. The electronic parameter ν is based on the A_1 ν(CO) stretching frequency of the carbonyl group in the $Ni(CO)_3L$ complexes in dichloromethane, where L is a phosphine or a phosphite. The ν(CO) stretching frequency increases with decreasing electron donor property of the phosphine. The reason for the decrease in ν(CO) stretching frequency is that there are more electrons available for the antibonding π-orbital of the CO groups [18]. Nickel, with the formal oxidation state 0 in the $Ni(CO)_3L$ complexes, is regarded as a soft electron acceptor and has acceptor properties similar to silver(I). There is a very good correlation between the ν values of the phosphines and the stabilities of the silver(I)–phosphine complexes in pyridine, Fig. 3b. All the studied silver(I)–phosphine complexes except the second di- and tricyclohexylphosphine complexes are slightly less stable than predicted from the ν value. This is most probably due to sterical hindrance of the already coordinated ligand when the second complex is formed. The cone angle of tricyclohexylphosphine is large [19]. The cone angle of dicyclohexylphosphine has not been reported but one can assume that it is close to that of tricyclohexylphosphine. From a steric point of view it is reasonable to believe that the $Ag(P(C_6H_{11})_3)_2^+$ and $Ag(P(C_6H_{11})_2H)_2^+$ complexes are linear with pyridine molecules only in the second coordination sphere. The bulky cyclohexyl groups from different ligand molecules in the second silver(I) complexes may come in contact with each other, which destabilizes the second complex thermodyamically and also weakens the Ag–P bonds.

There is also a linear correlation between the stabilities of the silver(I)–phosphine complexes in pyridine and the basicity of the phosphines in aqueous solution [5, 6], Fig. 3c. The P–H bond in PHR_3^+ ions has a high degree of σ-character and no π-bonding is present.

These correlations between the stabilities of silver(I)–phosphine complexes in pyridine and physical parameters of phosphines show that only electrostatic and σ-bonding are involved in the bonding between silver(I) and different kind of phosphines. The contribution of π-bonding in these bonds can certainly be neglected. The first rate correlation between stability constants and physical parameters of the phosphines make predictions of stabilities of silver(I)–phosphine, and probably also phosphite, complexes unusually accurate, if one or several of the physical parameters discussed above is known.

The free energies of complex formation correlate well with the heats of complex formation for the silver(I)–XR_3 systems, X = P, As or Sb; R = C_6H_5, C_4H_9, C_6H_{11} or H, independent of solvent used, Table III and Fig. 4. This shows that the difference in bond strength between a ligand and a solvent molecule is proportional to the stability of the formed complex. This strongly indicates that the complexes are formed in substitution reactions.

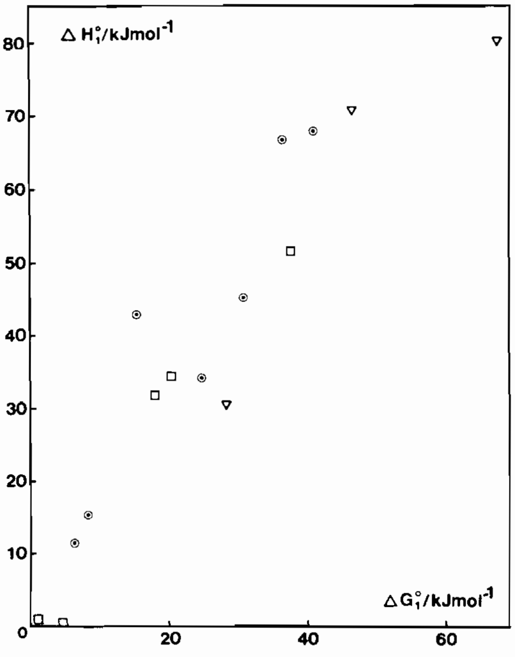

Fig. 4. The relationship between free energy and heat of complex formation for the first silver(I)–XR_3 complexes, X = N, P, As, Sb and Bi) and R = H, C_6H_5 and alkyl groups, in pyridine (circles with dot), dimethylsulfoxide (open squares) and aqueous solution (open triangles). The numerical values of ΔG_1° and ΔH_1°, are given in Table III.

All silver(I)–phosphine and stibine complexes are formed in strongly exothermic reactions. The entropy changes are negative for all complexes formed in this study, Table III and Fig. 5. This means that the complexes are strongly enthalpy stabilized, as in all previous studied silver(I)–XR_3 complexes, X = P, As, Sb, independent of solvent [9–11, 20, 21]. The decrease in $-\Delta H_j^\circ$ for each consecutive step in the phosphine system, Table III and Fig. 5, certainly reflects a successive weakening of the Ag–P bond as the number of coordinated phosphines increases. This is shown in a series of solid state structures containing $AgCl((PC_6H_5)_3)_n$, n = 1–3, complexes [22–25].

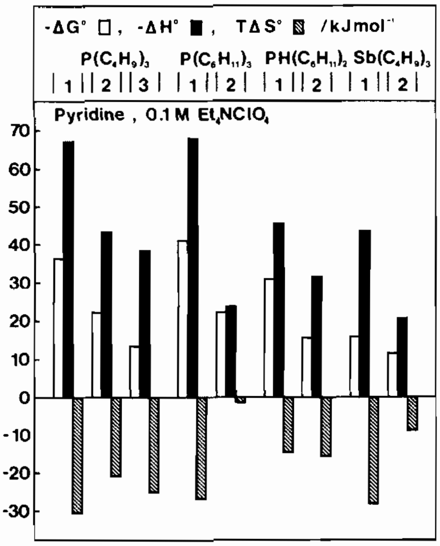

Fig. 5. Changes of free energy (white), enthalpy (black), and entropy (hatched) for the consecutive steps of the silver(I)–XR_3 systems in pyridine at 25 °C.

In the silver(I)–tributylphosphine and –dicyclohexylphosphine systems the change in entropy is similar for all steps, which indicates that the complexes are formed in substitution reactions and that no extensive desolvation accompanied by a coordination switch takes place at a certain step [10]. The substantially larger negative $T\Delta S_{\beta 3}^\circ$ value for the tributylphosphine than for the triphenylphosphine system is explained by the fact that tributylphosphine is much more strongly coordinated to silver(I) than triphenylphosphine. The solvation has been quantified for triphenylphosphine but not for tributylphosphine [26]. However, extensive studies on PPh_4^+, NPh_4^+ and NBu_4^+ ions have been reported [27–29]. These show that the solvation of tetraalkylammonium ions, and certainly also of corresponding phosphonium ions, is only about 50% of the solvation of the tetraphenylammonium ion for the solvents studied, dimethylsulfoxide, *N,N*-dimethylformamide and hexamethylentriphosphoric amide. The negative $T\Delta S^\circ_{\beta 3}$ value for the tributylphosphine complex means that the tributylphosphine molecules lose a lot of freedom when they coordinate to silver(I). Tributylphosphine loses more freedom upon the complex formation than triphenylphosphine because of stronger complex formation and weaker solvation. The freedom the solvate molecules gain when they are desolvated upon the complex formation can never make up for the loss of the ligand.

The entropy changes in the silver(I)–tricyclohexylphosphine and –tributylstibine systems show a different pattern from the previously studied systems in pyridine with $T\Delta S^\circ_2 \gg T\Delta S^\circ_1$, Table III. This indicates a larger desolvation at the formation of the second complex compared with the first one. A configuration change from tetrahedral to linear followed by a substantial desolvation of silver(I) most probably takes place when the $Ag(P(C_6H_{11})_3)_2^+$ complex is formed as discussed above. On the other hand coordination switch does not take place when the $Ag(Sb(C_4H_9)_3)_2^+$ complex is formed. A structural study of this complex has shown that the initial tetrahedral configuration around silver(I) remains in this complex, with two antimony atoms strongly coordinated and two pyridines loosely coordinated to silver [30]. It is possible that the strength of the solvate bonds decreases markedly when the second stibine complex is formed, causing an increase in the entropy.

Acknowledgement

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