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THE FORMATION OF SILVER—ARENE COMPLEXES IN LIQUID ANHYDROUS HYDROGEN FLUORIDE

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Summary

In anhydrous hydrogen fluoride the silver ion forms strong complexes with arenes of composition Ag^+: ar = 1 : 1, 1 : 2 and 1 : 3. The stoichiometries and formation constants of the complexes formed were evaluated by argentometric titrations.

Introduction

The silver ion forms a wide range of complexes with arenes, in the solid state and in solution [1]. Most of the solid complexes described in the literature show Ag^+: arene (ar) ratios in the range 1 : 2 to 2 : 1. Only three compounds with ratios 1 : 3 are known, i.e., $Ag(mesitylene)_3PF_6$, $Ag(acenaphthylene)_3BF_4$ and $Ag(pyrene)_3BF_4$ while $Ag(fluoranthrene)_4BF_4$ is the only 1 : 4 complex reported. The actual number of arene molecules coordinated to the silver ion in these complexes, is unknown however, as their crystal structures have not been determined.

Structural studies of several silver—arene complexes [1,2] show the following common features: (1) the silver ion is coordinated to one or two arenes, (2) each arene is bonded to one "double bond" of an aromatic ring and (3) the silver ion is located almost perpendicular to the plane of the aromatic ring above (or below) the mid-point of the two bonded carbon atoms. When two arenes are bonded to the silver atom the coordinated "double bonds" form an angle with the silver atom of ca. 180°. If the donation of electrons from one "double bond" is regarded as equivalent to that from a unidentate ligand, it is possible to envisage the coordination of three or even four arenes to a single silver ion.

Studies of complex-formation between Ag^+ and arenes in aqueous solutions [1] show that complexes of very low stability with Ag : ar ratios 1 : 1, 2 : 1, and possibly 3 : 1 are formed. No complexes with more than one arene per silver ion have been observed in this medium.

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Many silver salts with weakly coordinating anions, e.g. $AgPF_6$, are soluble in arenes forming silver complexes for which bond energies of ca. 200 kJ/mol have been postulated [3]. The high solubility of AgF in AHF * solutions is significantly enhanced by the addition of arenes. Thus, one additional mol of AgF dissolves on addition of 3 [4] or 4 [5] mols of arene. This increase in solubility has been attributed to the formation of silver—arene complexes in AHF, although direct evidence for the formation and composition of these complexes has not been reported.

It has been recently shown [6] that the silver ion is less solvated in AHF than in water and that, as a consequence, this ion shows enhanced coordinating tendency in the former solvent. Since this can be expected to apply also to silver—arene complexes, these were investigated in AHF.

Experimental

Apparatus, materials and general techniques used for the verification of argentometric titrations in AHF have been described elsewhere [6]. AHF solutions or suspensions (usually around 50 ml) containing 0.01—0.05 M arene and 0.2—0.25 M of KF per litre as an inert electrolyte, were titrated with ~0.5 M AgF solutions in AHF (method A). Alternatively solutions ~0.01 M AgF in AHF containing ~0.25 M KF were titrated by adding arenes in known amounts with a syringe (method B). Since fluoride ion is the "strong base" in AHF, KF containing solutions are termed "alkaline" AHF solutions. Stability constants were calculated with the program GVARI on a CDC 6500-6400 computer.

Results and discussion

Monocyclic arenes of low basicity, e.g., benzene or toluene, dissolve to some extent in AHF without being protonated. Benzene, the most soluble, dissolves to form approximately 0.2 M solutions on saturation at 0°C. During the course of a titration of an arene solution with AgF (method A) the initial ratio of Ag^+ to arene will be only low and consequently the silver—arene complexes $Agar_x^+$ formed will be those with the highest values of x. As the titration proceeds the "degree of argentation", $m = [Ag]_{complexed}/[ar]_{total}$ increases and complexes with lower values of x are formed. The formation of 1 : 1 complexes of relatively low stabilities cannot be detected by this technique. However, the titration of a solution of AgF with an arene (method B) allows the determination of the ratio of the values of the stability constants for the 1 : 1 (K_1) and the 1 : 2 (β_2) complexes and thus, in conjuction with data from method A, the calculation of K_1. Some representative argentation curves are shown in Fig. 1.

These methods show that complexes $x = 1, 2$ and 3 exist in AHF solutions. Computer-simulation of argentation curves shows that complexes with $x = 4$ are not present in solution in significant amounts. Furthermore, no evidence has been obtained for the presence of either species with $x < 1$ or of dinuclear species. A typical example of species-distribution on increasing the degree of argentation, that for m-xylene is shown in Fig. 2. Table 1 summarizes the values of

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* AHF = anhydrous hydrogen fluoride.

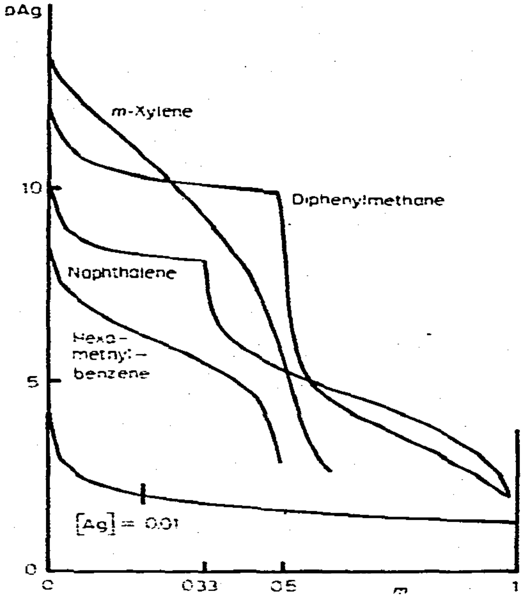

Fig. 1. Argentation curves. Degree of argentation $m = \frac{[\mathrm{Ag}]_t - [\mathrm{Ag}]_f}{[\mathrm{ar}]_t}$.

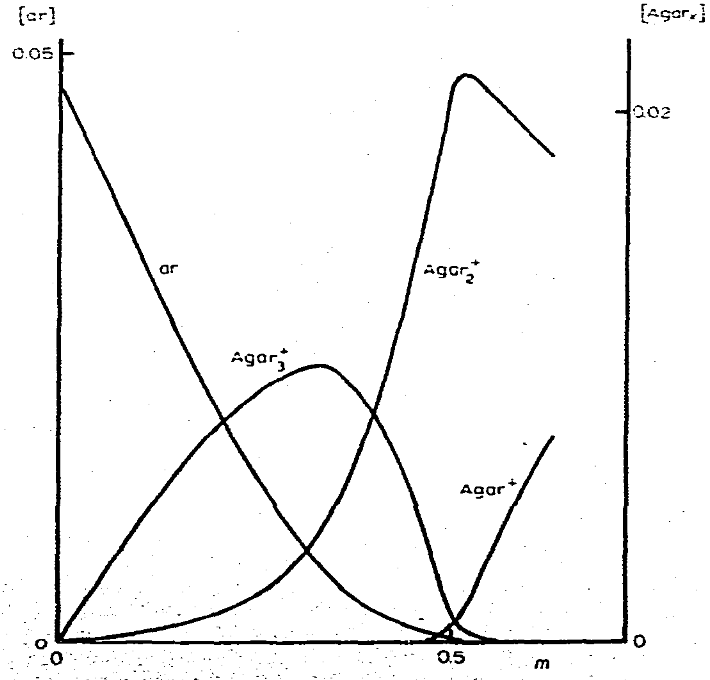

Fig. 2. Distribution of m-xylene on argentation ($[m\text{-Xylene}]_t = 0.0474$).

the stability constants for the reactions 1—3:

$$Ag^+ + \quad ar \rightleftharpoons Agar^+ \qquad K_I = [Agar]/([Ag][ar]) \tag{1}$$

$$Ag^+ + 2\,ar \rightleftharpoons Agar_2^+ \qquad \beta_2 = [Agar_2]/([Ag][ar]^2) \tag{2}$$

$$Ag^+ + 3\,ar \rightleftharpoons Agar_3^+ \qquad \beta_3 = [Agar_3]/([Ag][ar]^3) \tag{3}$$

Whereas in aqueous systems the values of log K_I for monocyclic arenes are ca. 0.5, they are ca. 5 in AHF. The stability constants obtained for the monocyclic arenes (see Table 1) show that the silver complexes become weaker on replacement of one hydrogen atom by a fluorine atom or a CF_3 group. In the latter case this substitution is sufficient to prevent the formation of the 1 : 3 complex. Furthermore, difluoro- and polyfluoro-arenes do not from silver complexes.

On the other hand, replacement of hydrogen atoms by CH_3 groups results in the formation of stronger complexes in the order: benzene < toluene < *m*-xylene. This sequence parallels qualitatively the order of increasing basicity of the arenes. A more quantitative relationship between the two sets of constants is not expected since the structure of the electronic Ag^+ complexes is markedly different from that of the H^+ complexes. This difference between the complexes of the two Lewis acids is seen in the case of mesitylene which has a higher basicity than *m*-xylene but lower Ag^+ stability constants. This effect is even more marked for hexamethylbenzene (see Table 1), where the extensive protonation even in basic AHF prevents the formation of the 1 : 3-complex. It is noteworthy that despite the "unconventional" bond-type between Ag^+ and arenes the values of K_I and K_{II} are about equal, as found for more standard ligands.

Although naphthalene, biphenyl, diphenylmethane and anthracene are sparingly soluble in AHF, suspensions of these arenes could be titrated by method A, the arenes dissolving on addition of Ag^+. In the case of naphthalene, dissolution is complete at a degree of argentation $m = 1/3$, indicating that the soluble species

TABLE 1

STABILITY CONSTANTS OF SILVER ARENE COMPLEXES[a]

ar	log K_I	log β_2	log β_3	log $\frac{[ar]}{[Har][F]}$ [b]	$-\log s$ [c]
Pentafluorobenzene	—[d]	—	—		
1-4-Difluorobenzene	—[d]	—	—		
ααα-Trifluorotoluene	2.60[e]	4.73	—		
Fluorobenzene	3.32	6.50	7.82		
Benzene	4.90	9.54	11.90	10.05	
Toluene	5.15	10.31	12.87	6.95	
m-Xylene	5.07	11.26	13.84	3.85	
Mesitylene[f]	4.47	10.01	11.61	1.05	
Hexamethylbenzene[f]	4.94	10.02	—	—0.8	
Biphenyl[g]	7.72	10.95	—	6.15	2.75
Diphenylmethane[g]	7.80	13.80	—		2.95
Naphthalene[h]	8.1	13.5	18.5	4.65	6.4
Anthracene[g]	~7—8[i]	~13—14[i]	—	3.8	

[a] 0°C, I = 0.23 ± 0.04 (KF). [b] Constants for the reaction: $Har^+ + F^- \xrightarrow{AHF} ar + HF$. Values taken from [7] and converted to the base log $[BF_4]/[BF_3][F] = 7.26$, see [8]. [c] s = solubility of ar in AHF in mol per litre at 0°C. [d] Complex not observed. [e] Errors, with a few exceptions, are less than ±0.1. [f] Values are corrected for protonation. [g,h] Sparingly soluble in AHF, dissolves on addition of Ag^+ under formation of (*g*) $Agar_2^+$, (*h*) $Agar_3^+$. [i] Formation of the 1 : 2 and 1 : 1 complex upon dissolution of anthracene occurs in the same pAg region, rendering evaluated data very imprecise.

formed is the 1 : 3 complex, while in the cases of biphenyl, diphenylmethane and anthracene the species formed are 1 : 2 complexes. The complexes with lower values of x are formed as the titration proceeds.

The K_I value for diphenylmethane is much larger than that for toluene even after correction for a statistical factor and this could be due to chelation. Biphenyl and naphthalene also show a similar effect when compared with benzene. In these cases, in addition to a possible chelating effect one may be observing the operation of electronic factors connected with conjugation. It is interesting to note that the log β_2 values of diphenylmethane and toluene also show the trends noted for K_I, presumably for the same reasons, while these difference are less marked in the case of biphenyl, for which the higher value corresponds approximately to the correction introduced by the statistical factor. Finally, the β_2 value for naphthalene is also large compared with the statistically corrected value calculated from benzene and again electronic factors may be responsible.

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