On some aromatic molecular complexes of silver perchlorate

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Summary: Some new aromatic molecular complexes of the electron donor-acceptor type, given by silver perchlorate with naphtalene, phenantrene, alpha- and beta-methylnaph talene, orto-, meta- and para-xylene and other aromatic hydrocarbons, were isolated in the solid state.

The preparative and analytical techniques used for their identification are described and their possible constitution is discussed.

Hill's studies [1] on the systems silver perchlorate - water - benzene (and respectively toluene) had already established, in 1922 and 1925, the existence of the solid complexes $AgClO_4 . C_6H_6$ and $AgClO_4 . C_7H_8$. No other silver aromatic hydrocarbon complexes have been till now isolated in the solid state.

Several investigations have been made, in the last eight years, on the argentation of aromatic hydrocarbons and some of their derivatives, specially by Andrews and Keefer [2] and Kofahl and Lucas [3], by measuring the solubility of the aromatic sustances in aqueous (or equimolecular methanol-water) solutions of silver nitrate mantained at constant ionic strength by addition of appropriate amounts of potassium nitrate. For most of the substances at least two equilibrium constants K_1 and K_2 were calculated, corresponding to the formation of two complexes with a ratio of silver ion to aromatic substance 1: 1 and 2 : 1. The K_2 constants have always very low values, of the order of about one tenth of the K_1 value, and their reliability depends on several assumptions regarding the properties of the aromatic substances and of the ions in solutions of different silver ion concentration. It might be interesting to investigate the composition of these complexes in the solid state.

We have, therefore, prepared some new solid silver perchlorate complexes of aromatic hydrocarbons. Because of the very high hygroscopicity of silver perchlorate and of its molecular complexes, all the manipulations were made in an atmosphere kept dry by means of phosphorus pentoxide. Silver perchlorate has to be completely dried up to constant weight at 115° over phosphorus pentoxide and all the reagents have to be carefully anhydrified in order to get analytically reliable results. The aromatic hydrocarbons were Eastman Kodak chemicals of the highest purity grade. The following techniques were used for the preparation and the identification of the complexes.

Naphtalene. Silver perchlorate and naphtalene are alternatively dissolved at room temperature in benzene up to the saturation with naphtalene. By adding an equal volume of ligroin the silver perchlorate – naphtalene complex is precipitated. If the solution is sufficiently concentrated in naphtalene no precipitation of the silver perchlorate – benzene complex occurs. Owing to the difficulty of washing the crystals with ligroin without decomposition, the Schreinemakers'method was used for the identification of the complex by analysing several solutions and their wet solid at the equilibrium. Fig. 1 shows a projection of the Schreinemakers' lines on the middle section of the tetrahedron silver perchlorate – naphtalene – benzene – ligroin. One line, as for phenanthrene, was obtained without ligroin, by crystallization of the complex from benzene solution. The complex has the composition 2 $AgClO_4$. Naphtalene.

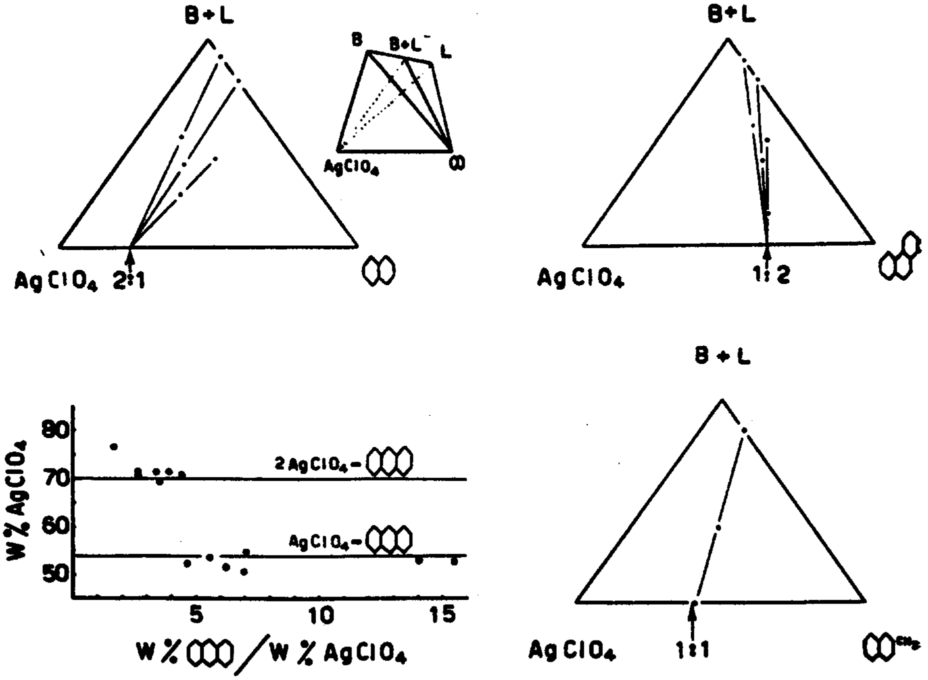

FIG. 1.

Phenanthrene. The silver perchlorate – phenanthrene complex was prepared and identified with the same method used for naphtalene and has the composition $AgClO_4$. 2 Phenanthrene.

Anthracene. Anthracene is little soluble in benzene and in toluene, but using toluene as solvent at 30° it is possible to avoid the precipitation of the silver perchlorate – toluene complex, as this complex decomposes at 25°. By addition of ligroin (about 3-4 times of the volume of toluene) the anthracene complex crystallizes very slowly. Several preparations were made from solutions having a progressively higher ratio of anthracene to silver perchlorate and crystals were analysed in the dry state. In fig. 1 the silver perchlorate content found in the solid is put in ordinate whilst the ratio Anthracene/$AgClO_4$ of the original solution in toluene is put in abscissa. Between A/Ag ratios of 2,5-4,5 very fine, long and yellow needles are formed which correspond to the composition 2 $AgClO_4$. Anthracene. Between A/Ag ratios of 4,5-7,5 needles are formed which are shorter and thicker and of a different color in mass; they correspond to a composition of $AgClO_4$. Anthracene. At greater A/Ag ratios of 14-15, obtained by using ligroin containing anthracene, very beautiful prismatic crystals are obtained which have the same composition $AgClO_4$. Anthracene.

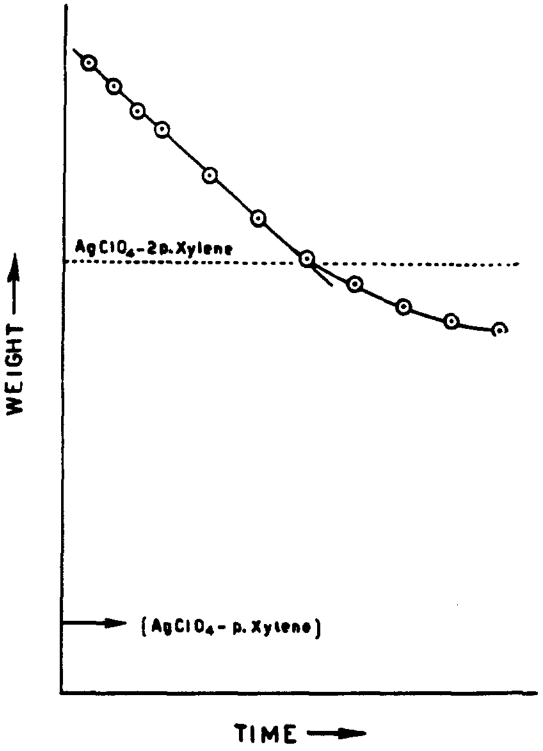

Fig. 2.

β-methylnaphtalene. The complex was prepared with the naphtalene method and identified by analysing at the equilibrium the liquid, the wet solid and the dry crystals. The complex has the composition $AgClO_4$. β-methylnaphtalene.

In the preceding determinations the samples were analysed both for their silver and hydrocarbon content.

Liquid hydrocarbons. Silver perchlorate was dissolved in the liquid hydrocarbon, the complex precipitated with ligroin or crystallized directly from the saturated solution by cooling, isolated and analysed only for its silver content. *α-methylnaphtalene* gave, by precipitation with ligroin the complex $AgClO_4$. α-methylnaphtalene. *o-xylene* gave, either by precicipitation with ligroin or by direct crystallization, only the complex $AgClO_4$.

2 o-xylene. *m-xylene* gave, by precipitation with ligroin, the complex $AgClO_4$ m-xylene, and, by direct crystallization, the complex $AgClO_4$. 2 m-xylene. *p-xylene* gave, by direct crystallization, the complex $AgClO_4$. 2 p-xylene. Because of its greater instability on evaporation of the solvent, this complex was identified by a progressive drying of the crystals, weighting the sample at measured intervals of time and analysing it at the end of the experiment. As fig. 2 shows, the evaporation of the absorbed liquid gives a straight line. The beginning of the decomposition of the complex (and its composition) is indicated by the point at which the straight line becomes a curve.

The interaction between the aromatic ring and the silver ion is of the electron donor-acceptor type, in which the aromatic molecules funtion as electron donors by sharing their π electrons with the silver ion, which functions as electron acceptor by a process comparable to Lewis acid-base interaction. The silver ion – aromatic hydrocarbons complexes can be described in terms of a resonance hybrid structure involving a no-bond structure (Ar, Ag^+) and a bonded structure (Ar^+-Ag) [2] [4].

The crystal structure of the silver perchlorate-benzene complex, determined by Rundle and Goring [5], shows that each silver is bonded to two carbons of each of two rings with *Ag-C* distances of 2,6 *A*, leading to an electron density of about 0,15 electron pair per bond by Pauling's rule and radii. The ClO_4 ion presumably remains attached to the Ag^+ or Ag^+, *Bz* ions, but in a relatively passive role. The location of silver ion relatively to one benzene ring is between and above two carbon atoms. The line which connects the silver ion to the center of the carbon-carbon bond makes an angle of 100° with the plane of the benzene ring.

In the case of the non substituted polycyclic hydrocarbons in which some carbon-carbon bonds have a higher character of double bond it is possible to admit that silver is preferentially bonded to these positions. The 2:1 silver perchlorate complexes with naphtalene and anthracene have the composition which can be predicted by admitting that they have a lattice structure, similar to that of the $n : n$ benzene complex, formed by alternated planes of hydrocarbon molecules and silver perchlorate molecules, in which silver ions are bonded, from both sides of the plane of the molecule in a $2\,n : n$ solid complex, to the four carbon-carbon bonds 1-2, 3-4, 5-6, 7-8 which have total bond orders of 1,84 for naphtalene and 1,81 for anthracene, as obtained from the bond lengths, 1,361 and 1,366 *A* given by Cruickshank [6] by using the bond order-length curve calculated by the *MO* method and given by Coulson [7]. For the 1 : 1 anthracene complex, even if it is already very well characterized analytically and morphologically, other investigations are necessary in order to better define its properties and its relations with the other complex. For phenanthrene the

9-10 carbon-carbon bond, for its higher total bond order, is the position to which the silver ion of the 1 : 2 complex may be attached.

In the case of methyl substituted hydrocarbons it was already shown by Andrews and Keefer [2] that, notwithstanding that each successive methyl substitution increases the basicity of the aromatic nucleus, it increases also the steric effect opposing the silver complex formation in aqueous solution. This steric hindrance has also the effect of diminishing the ratio between silver perchlorate and aromatic molecules in the solid complexes, as it is shown by the 1:1 ratio of the α – and β-methylnaphtalene complexes instead of the 2 : 1 ratio obtained for the naphtalene complex and by the pre dominant 1 : 2 ratio of the xylene complexes instead of the 1 : 1 ratio of the benzene and toulene complexes (this latter very unstable as it decomposes at 25°). The 1:1 m-xylene complex is perhaps due to the fact that the methyl substitution in meta position reinforces, by superposed induction effects, the same positions of the benzene ring.

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