Tetrahedron Letters No.11, pp. 813-814, 1970. Pergamon Press. Printed in Great Britain.

SILVER OXIDE - PYRIDINE COMPLEXES

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(Received in USA 2 December 1969; received in UK for publication 26 January 1970)

Silver oxide can be dissolved in aqueous solutions of amines, giving water-soluble complexes of the general type AgL_nOH, where L is the ligand molecule.

In the literature there are very few examples of such solutions; this can be explained by the fact that many of the complexes undergo auto-oxidation, and some of the solutions cannot be stored for a long time.

Pyridine and homologs are known to complex silver nitrate and perchlorate, giving solid, crystalline complexes[1], but no attempt seems to have been made to obtain silver oxide complexes, probably because pure pyridine does not dissolve the pure oxide.

We tried to dissolve the silver oxide under a variety of conditions, and found that it is easily dissolved by pyridine when freshly precipitated from water solution of a silver salt, if the water is not removed. If the silver oxide was purified by washing the precipitated compound with water until only a slightly alkaline reaction remained in the washings, and then dried in an oven, it was much more difficult to dissolve. In pure pyridine, the oxide was insoluable but it dissolved slowly when enough water was added.

The presence of enough water was critical for the solution, and the silver oxide could be precipitated by alcohol, dioxane or other water-mixable solvents. During attempts to extract the complex with chloroform (a good solvent for silver nitrate- or silver perchlorate-pyridine complexes[2]), chloroform was oxidized and silver precipitated.

We could also obtain solutions of the following pyridine homologs complexed with silver oxide: 2-picoline, 3-picoline, 4-picoline, 2,4-lutidine, 2,6-lutidine, 3,5-lutidine, and 2,4,6-collidine. These complexes were obtained by mixing the pyridine homolog and water with pure silver oxide. With 2,4,6-collidine, as well as in other cases, we initially had 3 phases (collidine is only slightly soluble in water). After a few hours, complete solution took place.

The kinetics of solution of Ag_2O in the pyridine homologs was studied in a preliminary way by the time increase in conductance. During the first two minutes the increase in conductance is very clearly dependent on the nature of the substitutent located on the pyridine nucleus. The increase is faster for the more basic (more substituted) homologs; for isomeric compounds, it is slower for the 2 (6)-substituted ones, probably because the nitrogen lone pair of electrons is sterically hindered by the substituent. The rate of solubility of Ag_2O is in sequence Py $<$ 2-Me $<$ 3-Me $<$ 4-Me $<$ 2,4,6-triMe $<$ 2,6-diMe $<$ 2,4-diMe, where Me stands for picoline, diMe for lutadine, and triMe for collidine. The behavior of 2,4,6-collidine, more basic than the lutadines, but slower in dissolving Ag_2O, is explained by its lower solubility in water.

At the beginning, the silver oxide dissolves in water and is complexed by the pyridine homologs in an order that can easily be understood. Measurements on pure Ag_2O in water show that equilibrium saturation is obtained in about seven minutes.

From the second to approximately the seventh minute, the solution in water-pyridine homologs follows 3rd order kinetics of the type $dx = k(a - x)^3dt$. which becomes complex after the seventh minute by·concentration and side effects. All of them have a linear plot of χ^2 x time in that interval, showing that the kinetics of solution of Ag_2O in the seven pyridine homologs and water is determined by the same slow step. An analysis of the solution of silver oxide in pure water also shows 3rd order kinetics of the same type, and the conclusion is obvious that the rate-determining step is the Ag_2O in water, and the complexation is practically instantaneous.

All the complexes, in moderately dilute solution, behave as completely dissociated hydroxides and the solutions are strongly alkaline. By heating the solutions, metallic silver is slowly deposited.

The oxidizing properties of the complexes toward aldehydes and some organic acids was the subject of a previous communication[3]. At 30°C, all the complexes quantitatively oxidize formaldehyde in 30 minutes, but benzaldehyde does not react. At 60°C, 38% of the benzaldehyde is oxidized. With pyruvic acid at 95°C, the reactivity of the complexes is in the sequence of 2,6-diMe $>$ Py $>$ 2,4,6-triMe $>$ 2-Me $>$ 4-Me $>$ 3-Me, oxidizing from 81.7% (for 2,6-diMe) to only 14% (for 3-Me) of the acid in 30 minutes. Under the same conditions, lactic acid is recovered unchanged.

References

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