REACTION KINETICS AND CATALYSIS LETTERS, Vol. 2, No. 3, 257-263 (1975)

FORMATION AND CATALYTIC PROPERTIES OF WATER-SOLUBLE PHOSPHINE COMPLEXES

F. Joó and M. T. Beck

Institute of Physical Chemistry, Kossuth Lajos University,
H 4010 Debrecen

Received November 11, 1974

Using sulfonated triphenylphosphine, a number of water-soluble platinum metal - phosphine complexes were prepared. Some of them show a pronounced reactivity towards small molecules and the ruthenium compound catalyzes the hydrogenation of ketocarboxylic acids.

Используя сульфонированный трифенилфосфин, были приготовлены несколько водорастворимых комплексов между металлической платиной и фосфином. Некоторые из них обладают явной реакционностью по отношению к малым молекулам. Соединения рутения катализируют гидрирование кетокарбоксильных кислот.

INTRODUCTION

Water-soluble phosphine complexes are of importance for two main reasons:

1) The extensive phosphine chemistry in non-aqueous media has led to very important discoveries in the field of homogeneous catalysis /1, 2/. With water as solvent, analogous catalytic systems may throw more light on certain fundamental biochemical processes, e. g. the activation of small molecules (N_2, O_2, CO_2).

2) The comparison of the ability of a given metal to form complexes with ligands having various donor atoms requires phosphorus containing ligands too. For several reasons these experiments are usually carried out in aqueous solutions.

The latter field has been thoroughly explored /3–10/, and reviewed by Bjerrum /11/. On the other hand, the catalytic properties of water-soluble transition metal phosphine complexes have not been investigated. Recently interest has been arising in this direction, however, Chatt and co-workers have failed to discover catalytically active compounds among the water-soluble hydroxymethylphosphine complexes of Rh, Pd and Pt /12/.

We now report the results of a study of the catalytic properties of transition metal complexes containing diphenylphosphinobenzene-m-sulfonic acid (Dpm), the most widely used water-soluble phosphine ligand.

EXPERIMENTAL

Dpm was prepared according to the procedure of Ahrland et al. /3/, and was purified by the recrystallization of its Ba-salt from water.

Most of the experiments were carried out in 0.1 M HCl. The Ru(III) and Rh(III) stock solutions in 0.1 M HCl were left to stand for months before use.

Ultraviolet spectra were recorded on a Hitachi Perkin-Elmer 139 spectrophotometer, using cells which could be filled under the required atmosphere. Hydrogenations were followed using and automated apparatus of Nagy and Simándi /13/.

TLC of the lactic acid – pyruvic acid solutions was carried out on Merck precoated cellulose plates, using ethanol: ammonia: water = 80 : 4 : 16 as solvent system.

RESULTS AND DISCUSSION

On addition of Dpm to acidic aqueous solutions of Pt(IV), Rh(III), Ru(III), Ir(IV), Co(II), Ni(II), Fe(II), Fe(III), Cu(II) or Cd(II), changes of colour or – in some cases – precipitation occurred. Addition of solid $NaBH_4$ did not result in deposition of metals and only the Co–TPM and Fe–TPM compounds could be reduced to metal after a longer period. On the other hand, in the absence of the phosphine, in all but one case (Ir) metallic precipitates formed immediately. Consequently, these transition metal ions form complexes with Dpm, in their initial oxidation state and / or in the lower oxidation states arising as a result of reduction with $NaBH_4$. Complexation stabilizes the lower oxidation states of the central ions and hinders reduction to the metal.

We have studied in detail the chemical behaviour of the systems containing Ru–Dpm complexes /14, 15/. The phosphine has been found to reduce Ru(III) to Ru(II) at a conveniently measurable rate. The UV spectrum of the reduced species was not affected by the gas atmosphere in which the reaction was carried out (Ar, N_2, O_2, CO_2).

According to standard literature methods, using the Na-salt of Dpm instead of PPh_3, we have attempted to prepare compounds analogous to some well known phosphine complexes. In some cases the non-aqueous solvent could be replaced by water and the compounds formed precipitated upon adding solid NaCl to the solutions.

Following the method of Stephenson and Wilkinson for the preparation of $RuCl(PPh_3)_4$ /2/, a light brown compound of the composition $RuCl_2(Dpm)(H_2O)$. C_2H_5OH can be obtained from ethanolic solutions. This compound can also be isolated from an aqueous solution by the salting-out technique.

Cis- and trans-$RuCl_2(CO)_2(PPh_3)_2$ can be obtained by bubbling CO through ethanolic solutions of hydrated $RuCl_3$ followed by the addition of PPh_3 /2/. By the same method, we have isolated a white, Dpm-containing compound. According to its IR spectrum (ν_{CO} 2 000 cm^{-1} and 2 060 cm^{-1}) and elemental analysis, this complex can be formulated as cis-$RuCl_2(CO)_2(Dpm) \cdot C_2H_5OH$. Using water instead of ethanol as solvent, a light yellow compound precipitated, which turned light brown upon drying in air. Its IR spectrum also shows bands at 2 000 and 2 060 cm^{-1}.

Robinson and Uttley have prepared $RuH(CH_3COO)(PPh_3)_3$, an effective catalyst for the hydrogenation of terminal olefins /16/. Similarly, we have obtained a yellow compound which shows the ν_{Ru-H} vibration at 2 000 cm^{-1}.

The Dpm analogue of $RhCl(PPh_3)_3$ can also be prepared following the method of Osborne /1/. The orange-yellow compound cannot be obtained from water but ist aqueus solutions are only slowly oxidized in air.

HYDROGENATION EXPERIMENTS

We have studied the hydrogen uptake of solutions having different [Dpm]/[Ru] ratios. The detailed mechanism of hydrogenation has not yet been clarified. The basic observations are as follows.

Upon bubbling H_2 of atmospheric pressure through solutions with $[Dpm]/[Ru] = 5$, significant hydrogen consumption can be observed above 30 °C. Below this temperature no hydrogenation occurs. Similarly, solutions with $[Dpm]/[Ru] < 1$ composition do not adsorb hydrogen.

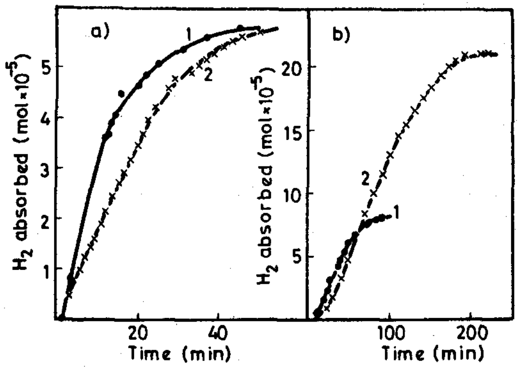

Fig. 1. Kinetic curves for the "self-hydrogenation" of a Ru–Dpm solution (a), and pyruvic acid hydrogenation catalyzed by Ru–Dpm (b). a) Dpm: 9×10^{-5} M, Ru(III): 1×10^{-5} M; b) Dpm: 5×10^{-5} M, Ru(III): 1×10^{-5} M; $Ch_3COCOONa$: 1×10^{-3}; Temperature: 60.0 ± 0.1 °C; 1) with UV irradiation 2) without UV irradiation

At the beginning of the hydrogenation the yellow colour of the solution quickly turns red. This colour is retained during the reaction, the solution becomes light green only at the end of the process. The red intermediate can be salted out. When wet, it is sensitive to air and gives a green oxidation product. Neutral aqueous solutions of the red product react with CO_2, giving an unidentified gelatinous orange-yellow precipitate.

The hydrogenation of the Ru-system has been followed at constant pressure. The amount of absorbed hydrogen indicates that the phosphine is also reduced, in addition to the metal ion: in a typical experiment 5.88×10^{-5} M H_2 was taken up by a mixture of 1.0×10^{-5} M Ru(III) and 5.0×10^{-5} M Dpm. It is a point of interest that intense UV irradiation roughly doubles the rate of the reaction (Fig. 1). The total amount of absorbed hydrogen, however, remains unchanged. The rate of hydrogenation decreases exponentially with increasing hydrogen ion and chloride ion concentration.

The Rh–Dpm system also absorbs molecular hydrogen at moderate temperatures. In contrast to the Ru–Dpm system, however, in some cases metal deposition is observed. This reaction was not investigated further.

The Ru–Dpm system catalyzes the hydrogenation of pyruvic acid to lactic acid. During the hydrogenation the catalyst itself is also reduced. The totally reduced form of the Ru-complex, however, is inactive. The conversion for pyruvic acid is 15–35% depending on the pyruvic acid : Ru ratio. The number of catalytic cycles, however, is always about 30. The reaction starts with a pronounced induction period and its rate is about 50% lower than the overall rate of the "self-hydrogenation" of the catalyst. UV irradiation lowers the conversion to a few per cent. This means that irradiation accelerates the hydrogenation of the catalytically active intermediate(s) to inactive product(s), but does not influence the rate of the pyruvic acid hydrogenation significantly (Fig. 1).

Preliminary experiments show that the Ru–Dpm system catalyzes the hydrogenation of 2-ketoglutaric acid, too. The main features of this reaction are similar to those of pyruvic acid hydrogenation.

For the purpose of systematic investigations we have prepared a series of Ru–Dpm compounds having also keto-carboxylic acid ligands in addition to the phosphine. The acids were added to the solutions of Ru–Dpm, containing a sixfold excess of the phosphine and, after reduction by the latter, the compounds formed were salted out with solid NaCl. The following acids were used: pyruvic, 2-ketocaproic, oxalic, oxaloacetic and 2-ketoglutaric acid. The characterization and investigation of these compounds is in progress.

ACKNOWLEDGEMENT

The authors express their gratitude to their students, Mr. I. Végvári and Mr. Z. Tóth for participating in a phase of the experimental work.

REFERENCES

1. J. A. Osborne, F. H. Jardine, J. F. Young, G. Wilkinson: J. Chem. Soc. (A) 1711 (1966)
2. T. A. Stephenson, G. Wilkinson: J. Inorg. Nucl. Chem., 28, 945 (1966)
3. S. Ahrland, J. Chatt, N. R. Davies, A. A. Williams: J. Chem. Soc., 276 (1958)
4. B. Salvesen, J. Bjerrum: Acta Chem. Scand., 16, 735 (1962)
5. G. Wright, J. Bjerrum: Acta Chem. Scand., 16, 1262 (1962)
6. R. George, J. Bjerrum: Acta Chem. Scand., 22, 497 (1968)
7. C. J. Hawkins, Ö. Monsted, J. Bjerrum: Acta Chem. Scand., 24, 1059 (1970)
8. C. J. Chang, J. Bjerrum: Acta Chem. Scand., 26, 815 (1972)
9. M. Meier: Dissertation Nr. 3988, E. T. H., Zürich 1967
10. S. Ahrland, J. Chatt, N. R. Davies: Quart. Rev., 12, 265 (1958)
11. J. Bjerrum: Magy. Tud. Akad. Kém. Tud. Oszt. Közl., 41, 67 (1974)
12. J. Chatt, G. J. Leigh, R. M. Slade: JCS Dalton Transactions, 2021 (1973)
13. F. Nagy, L. Simándi: Acta Chim. Acad. Sci. Hung., 38, 213 (1963)
14. F. Joó, M. Beck: Magy. Kém. Folyóirat, 79, 189 (1973)
15. M. T. Beck, F. Joó, Z. Tóth, I. Végvári: Proc. 5th Conference on Coordination Chemistry (Smolenice, Czechoslovakia, 1974), p. 11
16. S. D. Robinson, M. F. Uttley: JCS Dalton Transactions, 1912 (1973)