

THE NATURE OF HYDROSILYLATION CATALYST FROM CHLOROPLATINIC ACID AND POLYSTYRENE SUBSTITUTED BY DIMETHYLAMINOMETHYL GROUPS*

M. MEJSTŘÍKOVÁ, R. ŘEŘIČHA and M. KRAUS

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Praha - Suchbát*

Received January 22nd, 1973

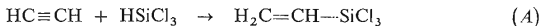
Sorption of chloroplatinic acid on a styrene-divinylbenzene copolymer containing $-\text{CH}_2\text{N}(\text{CH}_3)_2$ groups and successive activation of this precursor by heating in a stream of acetylene gave rise to the catalyst for hydrosilylation of acetylene. Up to the platinum content 6 per cent the active catalyst is not obtained, which is likely due to the fact that the precursor contains platinum in two forms. One form is the surface trialkylammonium hexachloroplatinate, the other is probably a hydridochloroplatinum complex. The activation consists in reduction of Pt(IV) to metallic platinum and Pt(II) complexes. The latter ones are probably precursors of catalytically active species, metallic platinum is little active.

In present effort in "heterogenization" of homogeneous complex catalysts by their fixation to organic polymer supports with suitable groups (*e.g.*¹⁻⁶), the attention has also been paid to hydrosilylation catalysts⁷⁻¹⁰. One type is formed from chloroplatinic acid and polymers containing diphenylphosphine, dimethylamine or nitrile groups and is suitable for effecting additions of compounds of the type HSiX_3 (where X is a halogen, alkyl or an alkoxy) to alkenes, alkadienes and alkynes, in both the liquid and gaseous phase^{9,10}. It is widely assumed that the structure and mechanism of the action of complex catalysts with macromolecular ligands are identical with or very similar to the properties of corresponding homogeneous catalysing complexes. It is evident, however, that in addition to the expected effects of the texture (*i.e.* the number and size of pores) of polymeric component^{11,12}, spatial arrangements of functional groups (ligands) on the surface of the polymer may lead to significant differences. There are some indications in literature¹³ that the analogy between catalytic properties of the soluble and insoluble metal complexes may not be too close. For that reason an investigation of the structure of complex catalysts fixed to polymers is topical.

This work is devoted to the study of the nature of a hydrosilylation catalyst which is formed from chloroplatinic acid and a styrene-divinylbenzene copolymer bearing dimethylaminomethyl groups. This catalyst is active in various additions of silicon

* Part XV in the series Catalysis by Metal Complexes; Part XIV: This Journal 39, 123 (1974).

hydrides to unsaturated compounds; in the present work all activity tests have been carried out, however, using the reaction



at 100°C with the reactants in gaseous phase.

EXPERIMENTAL

Polymeric supports. Three polymeric supports were used. *A.* Ball macroreticular copolymer of styrene and divinylbenzene (20%) bearing $-\text{CH}_2\text{Cl}$ groups (Research Institute of Synthetic Resins and Lacquers, Pardubice) and containing 16.8% Cl was suspended in toluene and then gaseous dimethylamine was slowly introduced into the suspension. A total of 56 g of the amine was absorbed per 100 g of the copolymer. The mixture was then allowed to stand at room temperature for 20 h. The product was separated by filtration, washed successively with methanol, dilute hydrochloric acid, water, dilute ammonia and water until negative test on the presence of chloride ions. The dry product contained 4.9 w.% Cl (corresponds to 62% conversion), 3.4% N and its surface area (BET) was 115 m²/g. *B.* The commercial macroreticular resin, Amberlyst A-21 (Rohm & Haas) used was chemically equivalent to the support A and contained 5.9% N. The catalysts prepared from supports A and B did not differ in their properties. *C.* Noncross-linked polystyrene was chloromethylated by the action of chloromethyl methyl ether in 1,2-dichloroethane and then it was converted into the amine by the action of dimethylamine in benzene solution (90% conversion), analogously to preparation A. In preparing thin layers of the polymer on potassium bromide plates, a gellous, about 2% solution in benzene was used.

Other substances. Chloroplatinic acid (Safina Works, Prague) contained in solid state 38.3% Cl and 38.7% Pt (this corresponds to Cl : Pt = 5.5 : 1). Bis(benzyltrimethylammonium)hexachloroplatinate¹⁴ was prepared from aqueous solutions of the amine and chloroplatinic acid by evaporating to dryness (m.p. 192°C).

Testing of catalyst activity was carried out in all-glass flow apparatus equipped with automatic control of reactor temperature, the feeding of trichlorosilane by means of a mechanical feeder and with drying of acetylene and the nitrogen used to flushing the apparatus. The acetylene from pressure cylinder was passed through concentrated sulphuric acid and through the tube filled with solid sodium hydroxide, activated carbon and a molecular sieve. Liquid hydrosilylation products were separated from unreacted acetylene by cooling to -40°C and were analysed by gas chromatography on apparatus equipped with flame ionisation detector, using hydrogen as a carrier gas, 130°C oven temperature and 5% silicone elastomer E 301 on ground unglazed tiles as support. Standard conditions for testing: 100°C, feed rates 6.53 g/h (HSiCl₃) and 45 ml/min (C₂H₂), weighed amount of the catalyst 0.2 g.

Infrared spectra (4000–300 cm⁻¹) were recorded with double-beam spectrometers Zeiss (Jena), Model UR-20, and Beckman IR-7 with the CsI prism/grating optics, the ultraviolet spectra were recorded with a Beckman DK-2A double-beam spectrophotometer.

RESULTS AND DISCUSSION

Organic polymers containing diphenylphosphine, amine or nitrile groups sorb chloroplatinic acid from aqueous solution. The polymers with dimethylaminomethyl

groups differ from the others in that ascertainable catalytic activity for hydrosilylation is displayed by the preparations with platinum content higher than 6 per cent. The activity then steeply and practically linearly increases with platinum content, whereas *e.g.* in the case of the nitrile polymers the active catalysts are already those containing less than 1 per cent of platinum. This difference has to be connected with a specific interaction of the platinum with the polymer component of the catalyst. Even the preparations containing platinum enough (*i.e.* from 6 to 18.5%) do not catalyze hydrosilylation instantaneously, but they require activation, which is apparent *e.g.* from induction period and from the time dependence of the conversion. We found that the activating component in our case is acetylene, and not a silicon hydride. We therefore activated catalysts by their heating in a stream of acetylene at temperatures above 80°C, most at 130°C, for 1 h. From the necessity of activation it follows that the preparation obtained by impregnation of the polymer by chloroplatinic acid differs in its character from the active substance. For that reason we studied separately the character of this precursor and of the catalyst.

After introducing the polymer with dimethylaminomethyl groups to the aqueous solution of chloroplatinic acid, the liquid decolorizes, and as far as the solution

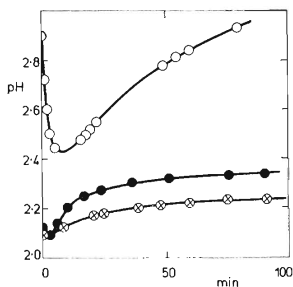


FIG. 1

Changes in pH during the Sorption of Chloroplatinic Acid on Polymer A

○ Polymer particles >0.7 mm, chloroplatinic acid conc. 0.43 g/l, final platinum content 6.5% ● particles <0.2 mm, 1.2 g/l chloroplatinic acid, 18% Pt; ⊙ particles >0.7 mm, 1.2 g/l chloroplatinic acid, 18% Pt.

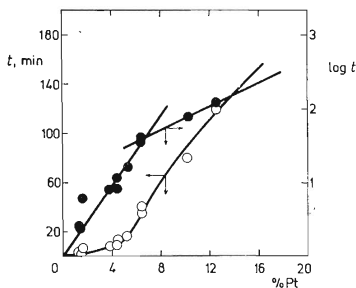


FIG. 2

Time of Discolouration of the Solution during the Sorption of Chloroplatinic Acid on Polymer A in Dependence on the Platinum to Support Ratio

The experiments were arranged so that such amounts of the polymer and chloroplatinic acid were added to 200 ml of H₂O as to form 2.5 g of the precursor with the platinum content recorded on the ordinate.

contained initially less than equivalent amount of platinum, the sorption is complete within 30–90 min. This is accompanied by the change in pH of the solution, which first decreases and then again increases (Fig. 1). This indicates that we do not deal here with a simple process. The form of the curves in Fig. 1 depends on the concentration of the solution and on the particle size of the polymer, and also on the polymer to chloroplatinic acid molar ratio used. If we take the time when the yellow colour of the solution disappears (this corresponds to platinum concentration less than 1 mg/l) for the total time of the reaction and plot it in dependence on the resulting content of platinum in the precursor (Fig. 2), we obtain the dependence which indicates the different course of sorption at the amounts of platinum corresponding to more than five per cent of platinum in the polymer. Maximum amount of platinum which could be sorbed on our supports, irrespective of the excess of chloroplatinic acid used, was 18.5 per cent.

From the composition of the starting copolymer it follows that the nitrogen to platinum ratio equals at maximum saturation approximately to three to one. This contrasts with sorption capacity of the copolymer with regard to sulphuric acid, which corresponded to the nitrogen to sulphate ions ratio equaling to 1.9. To ascertain whether the low exchange capacity of the copolymer with respect to chloroplatinic acid is not due to its hydrolysis, experiments were made with aqueous solutions of the acid which was hydrolysed¹⁵ by setting aside the solutions for 50 h under UV light. Then, the amount sorbed and catalytic activity were the same as in the previous case. As the majority of pores of the support are of 200–600 Å size and their surface is hence sufficiently accessible, and since hydrochloric and chloroplatinic acids do not differ substantially in the size of their anions, the reason of different stoichiometry of the sorption cannot be sought for in different steric requirements. The different sorption capacity of sulphate and hexachloroplatinate anions can be however accounted for by different strength of both acids. A certain number of the amino groups of the polymer are in the form of hydrochlorides, from which they are released only by the stronger acid, in our case by sulphuric acid. Chloroplatinic acid is comparable in acidity with hydrochloric acid, so that in equilibrium state the polymer contains the basic groups in the form of the salts of hydrochloric acid and of chloroplatinic acid in comparable amounts. On impregnation of the copolymers and on their drying, hydrochloric acid is partly released. In dry precursors the chlorine to platinum ratio is close to five.

Chloroplatinic acid can be released again from the polymer by washing with hydrochloric acid. On eluting the column of the precursor with concentrated hydrochloric acid, we were able to remove 60 per cent of the initial content of platinum (at maximum). With precursors containing less than 8% Pt, the extent of the elution was considerably lesser than with the samples with the higher content. We find here a similar break as we observed on the dependence of activity on the composition and of the sorption rate on the composition (Fig. 2). The location of this break is not

the same, it lies however within the range of from 5 to 8% Pt. This all indicates that platinum is bound at least in two forms.

This hypothesis is confirmed also by the infrared spectra (Fig. 3). In the spectra of the precursors (H_2PtCl_6 + support A, B or C) there is a broad band in the 2700 to 2450 cm^{-1} region, which is characteristic of alkylammonium cations^{16,17}. In the region above 300 cm^{-1} one observes the single band at 335 cm^{-1} , which is typical for a group, the central platinum atom of which is symmetrically surrounded by chlorine atoms¹⁸. The same patterns also find in the spectrum of bis(benzyl-dimethylammonium)hexachloroplatinate, which was used by us as a monomer model of precursors. On the basis of these results we consider the trialkylammonium salt of chloroplatinic acid on the surface of polymer supports to be proved and regard it to be one of the presumed forms of coordinately bound platinum.

The second type of platinum complex was inferred from the existence of an additional band at 2080 cm^{-1} in the spectrum of precursors A and B (14–18% Pt). We found that the absorption at 2080 cm^{-1} increases with increasing intensity of the band in the 2700–2450 cm^{-1} region and that the ratio of maximum ab-

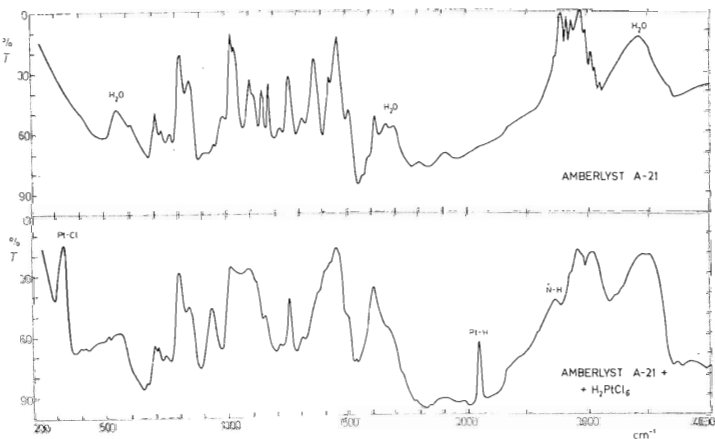


FIG. 3

The Infrared Spectrum of Support B and of the Precursor Formed from the Support (18% Pt) (KBr Pellets)

sorbances $2080\text{ cm}^{-1}/2700\text{ cm}^{-1}$ changes within the range from 0.05 to 0.20. At platinum contents less than 14%, the band at 2080 cm^{-1} likely present, is not discernible from the noise of the spectrum. This absorption is not connected with the alkylammonium salt, since it is absent in the spectra of the model monomer (about 29% Pt), benzyldimethylammonium chloride, and the starting amine. On the basis of the above mentioned facts we exclude the possibility that the absorption at 2080 cm^{-1} could originate from the $\text{N}^{(+)}\text{—H}$ bond vibrations and we assign it to the stretching vibration of the Pt—H bond (in defined compounds it occurs usually in the 2250 to 2000 cm^{-1} region).

This interpretation is further supported by the following facts. The band at 2080 cm^{-1} appears or its intensity increases in the spectra of the samples which were contacted with acetylene. Its form, intensity, half-band width, and, to a lesser extent, also the position of its maximum depend on temperature and on the duration of the contact with acetylene. Temperature itself did not exert effect on the spectrum. On heating precursor C or the model compound in vacuo up to 130°C , the band at 2080 cm^{-1} appeared only in the presence of acetylene in the cell. The intensity of this band increased with time and temperature (max. 165°C), the ratio of the intensities of Pt—H/N—H attained the values of from 0.2 to 1.0, the half-band width ($25 \pm 2\text{ cm}^{-1}$) was the same as with the precursor from polymers A and B which were not in contact with acetylene. In one case, when precursor (A + 18% Pt) was heated at 130°C in the presence of acetylene for 3 months, the ratio of the intensities increased to 1.4 and the half-band width was 47 cm^{-1} . The 2080 cm^{-1} band was always symmetrical, only with precursor C + acetylene at temperatures above 140°C there was a shoulder at the low wavenumber wing of the band. The positions of the band maximum occurred within the $2096\text{—}2080\text{ cm}^{-1}$ interval. The band corresponding to the Pt—H deformation vibration, occurring usually in the $845\text{—}815\text{ cm}^{-1}$ region, has never been detected in these spectra.

The above experiment, in which the precursor was in contact with acetylene for a long period of time, showed the complexity of this interaction. After three months, approximately 7 molecules of C_2H_2 were sorbed per one Pt atom. After this period, the sorption did not reach the equilibrium and further continued. The rate of acetylene sorption slightly increased with time. The rate of sorption increases in general also with temperature and content of platinum. We believe that we deal here in the main with slow polymerisation of acetylene. The appearances of the precursor do not change on contacting it with acetylene at ambient temperature. At the temperatures above 80°C its colour turns from orange to brown to black. The preparations active in hydrosilylation are of brown to black colour. The blackening is connected with the formation of metallic platinum, which forms even crystallites detectable by X-ray analysis. The platinum metal is very little active or even inactive in hydrosilylation of acetylene, as follows from the experiments in which we extracted from the active catalyst Pt^{II} and Pt^{IV} compounds by hydrochloric acid; the residue was inactive.

From the samples which after the reaction with acetylene showed the band at 2080 cm^{-1} we attempted to extract the presumed second form of platinum to water or to dichloromethane. We obtained always a yellow to brown solution; the UV spectra of both dilute extracts gave ill-defined curves with the absorbancy monotonously increasing from 360 nm to 250 nm and with several superimposed distinct maxima. The IR spectrum of the dichloromethane extract showed only three weak absorption bands located in the $400\text{--}300\text{ cm}^{-1}$ region. Qualitative analysis of these extracts and of the extracts of active catalysts by hydrochloric acid confirmed by colour tests^{19,20} the presence of Pt(II) and Pt(IV).

The samples of the catalysts after the extraction were re-examined by IR spectroscopy in KCl pellets. It was found that the spectrum is identical with the spectrum before the reaction and contains hence the band corresponding to the Pt—H bond. In the case of the model compound after the reaction with acetylene, the species containing the Pt—H bond is abstracted to dichloromethane solution, similarly as the starting model compound.

As to the structure of the compound containing Pt—H bond, we presume that it is a hydridochloroplatinum complex, which may be formed in two ways. The first one involves the more probable formation of an acid alkylammonium salt, the anion $(\text{HPtCl}_6)^-$ of which may be formulated as $\text{PtCl}_4(\text{ClHCl})^-$. The formation of the bihalide ion would release two coordination sites in PtCl_4 , which is octahedral²¹. One, or both coordination sites may be then occupied by hydridic ligand. However, the origin of the hydrogen is difficult to explain, since the Pt—H band appears also in the spectra of the samples which were not exposed to acetylene. The second possibility is intramolecular electrophilic substitution of the aromatic ring under the formation of Pt-ring σ -bond²². This reaction proceeds with about 22% conversion between benzyldimethylamine and K_2PtCl_4 (ref.²³). The residual chlorine ligands may be displaced by hydrogen from the *ortho* position of the benzene ring²². The use of this assumption in our case is also difficult, since it requires the presence of Pt(II), which again cannot be presumed in the samples which were not in contact with acetylene, although they do contain the Pt—H bond. The same can be said also about another reported Pt(II) complex^{24,25} which is formed from H_2PtCl_6 and tert-butylacetylene in 2-propanol. One chlorine atom is displaced by $\text{C}\equiv\text{C}\text{—Pt}$ (hence acetylide), the other in the *trans* position by the molecule of 2-propanol. This possibility can be discarded here, too, especially for that reason that the alkynes bonded in complexes have $\nu(\text{C}\equiv\text{C})$ at lower wavenumbers than the free alkynes. In our case of acetylene (1973 cm^{-1}), the spectra of the catalysts did not show, however, any band in the $1970\text{--}1600\text{ cm}^{-1}$ region.

Finally, it is noteworthy to mention yet another interaction of the polymeric support with an active component; in several cases in which precursor A was heated in a stream of acetylene to 130°C , we observed sublimation of a white substance which was confirmed to be ammonium chloride. We believe this compound is the

product of degradation of the support by the action of the metallic platinum formed from chloroplatinic acid by its reduction.

Summarizing, the fixation of chloroplatinic acid to the polymeric support with dimethylaminomethyl groups is accompanied by complex transformations of the platinum compound, and in part also of the support. The ineffectiveness of the preparations with low platinum content should be ascribed to the effect of the functional groups of the polymer, since the supports with cyanomethyl groups are active already when containing low Pt concentrations. The catalytically active component proper is very likely a Pt(II) compound which is formed by the reduction by acetylene of chloroplatinic acid or of the surface substances formed from it. This was confirmed, among others, also by introducing some ammo-Pt(II) complexes on suitable supports. The so obtained preparations were found to be effective catalysts.

We thank Mrs J. Lněničková for technical assistance with recording the spectra and Mr Z. Žitný for testing the catalysts. The collaboration of Dr D. Tomanová during sorption measurements is gratefully acknowledged.

Note added in proof: While this work was submitted to publication, we carried out preliminary experiments with Cope's salt²³ (see Discussion) heated to 100–160°C in acetylene. A new weak absorption appeared in the IR spectrum near 2090 cm⁻¹ already after 1 hour heating at 100°C, *i.e.* transformation of Cope's salt into a hydridocomplex is possible.

The paper²⁶ proving existence of bis(trimethylamine)protium cation appeared. The complex ion is characterized by a very strong IR band at 2100 cm⁻¹ (half-band width about 500 cm⁻¹) which was assigned²⁶ to the N—H—N stretching vibration. Irrelevance of this species to the spectra of our catalysts (dimethylaminomethyl groups + H₂PtCl₆) is clear from comparison of the band shapes: the half-band width of our band near 2080 cm⁻¹ never exceeded 50 cm⁻¹. Moreover, existence of the mentioned cation requires absence of moisture, which was not our case. Therefore, we prepared a series of surface salts of the support B with the following acids the procedure for H₂PtCl₆ cf. Experimental): HCl, HBr, HClO₄, CH₃COOH, H₂SO₄, H₃PO₄. In each case, only the absorption between 2800–2400 cm⁻² (characteristic for ammonium salts) was observed.

REFERENCES

1. Manassen J.: *Proc. XX Int. Congr., Chemistry Days 1969, Industrial Catalysis*, p. 42. Editrice di Chimica, Milano 1970.
2. Manassen J.: *Platinum Met. Rev.* 15, 142 (1971).
3. Kraus M.: *Chem. listy* 66, 1281 (1972).
4. Kohler N., Dawans F.: *Rev. Inst. Franc. Petrole* 27, 105 (1972).
5. Whitehurst D. D., Haag W. O.: Paper No 30 presented on 5th Int. Congr. Catal., West Palm Beach 1972.
6. Allum K. G., Hancock R. D., McKenzie S., Pikhethly R. C.: Paper No 31 presented on 5th Int. Congr. Catal., West Palm Beach 1972.
7. Čapka M., Svoboda P., Černý M., Hetflejš J.: *Tetrahedron Letters* 1971, 4787.
8. Čapka M., Svoboda P., Kraus M., Hetflejš J.: *Chem. Ind. (London)* 1972, 650.

9. Bažant V., Čapka M., Hetflejš, J., Kraus M., Svoboda P.: Czechoslov. Pat. Appl. 7462—71.
10. Kraus M., Hetflejš J., Čapka M., Bažant V.: Czechoslovak Pat. Appl. 2103—72.
11. Grubbs R. H., Kroll L. C.: J. Am. Chem. Soc. *93*, 3062 (1971).
12. Dietzmann I., Tomanová D., Hetflejš J.: This Journal *39*, 123 (1974).
13. Heinemann H.: Chem. Technol. *1*, 286 (1971).
14. Ende E.: Arch. Pharm. *247*, 363 (1909).
15. Böll M.: Ann. Phys. *9*, 29 (1914).
16. Nakanishi K., Goto T., Ohashi M.: Bull. Chem. Soc. Japan *30*, 403 (1957).
17. Davidson C. M., Jameson R. F.: Trans. Faraday Soc. *61*, 133 (1965).
18. Kelly D. A., Good M. L.: Spectrochim. Acta A *28*, 1529 (1972).
19. Young R. S.: Analyst *76*, 49 (1951).
20. Koch O. G., Koch-Dedic G. A.: *Handbuch der Spurenanalyse*, p. 774. Springer, Berlin 1964.
21. Cook P. M., Dahl L. F., Dieherhoof D. W.: J. Am. Chem. Soc. *94*, 5511 (1972).
22. Parshall G. W.: Accounts Chem. Res. *3*, 139 (1970).
23. Cope A. C., Friedrich E. C.: J. Am. Chem. Soc. *90*, 909 (1968).
24. Puchnarevič V. B., Suščinskaja S. P., Voronkov V. K., Ponomareva S. M., Trofimov B. A., Voronkov M. G.: Ž. Obšč. Chim. *42*, 1068 (1972).
25. Voronkov M. G., Puchnarevič V. B., Suščinskaja S. P., Kopylova L. I., Trofimov B. A.: Ž. Obšč. Chim. *42*, 2687 (1972).
26. Masri F. N., Wood J. L.: J. Mol. Struct. *14*, 217 (1972).

Translated by J. Hetflejš.