Heterogeneous and homogeneous hydrogenation of styrene and stilbene chromium tricarbonyl complexes

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Heterogeneous hydrogenation of the styrene and stilbene chromium tricarbonyl complexes by molecular hydrogen on skeletal nickel and palladium on carbon as catalysts was studied. As compared to styrene and stilbene, their arene chromium tricarbonyl analogs are hydrogenated considerably more slowly, which is related, most likely, to strong adsorption of the π -complexes on the catalyst surface. For the homogeneous hydrogenation of these complexes using a H₂PtCl₆—SnCl₂—LiBr system, styrene and η^6 -styrene chromium tricarbonyl are reduced with a high rate, whereas stilbene and its chromium tricarbonyl complex are hydrogenated very slowly. A possibility of reduction of the unsaturated arene chromium tricarbonyl complexes by sodium borohydride in the presence of cobalt(11) chloride as a catalyst was shown.

Key words: arene chromium tricarbonyl complexes, homogeneous and heterogeneous hydrogenation, catalysis, Raney nickel, palladium on carbon, hexachloroplatinic acid, cobalt(II) chloride, sodium borohydride.

Reactivity of the double bond in the arene chromium tricarbonyl complexes of alkenes is insufficiently studied.¹ In particular, the effect of the chromiumtricarbonyl group on the properties of the double bond in the α -position toward the π -bonded arene cycle remains unclear. The approach to this question can be found in the study of the reaction behavior of the double bond in characteristic reactions of alkenes, for instance, in hydrogenation. The reduction with hydrogen in the presence of catalysts occurs rapidly, the hydrogenation procedure is simple, and few by-products are formed.²

Styrene and stilbene chromium tricarbonyl π -complexes of the general formula R—CH=CH—PhCr(CO)₃ (R = H, Ph) were chosen for the study. These compounds were reduced in a setup for alkene hydrogenation with hydrogen³ at room temperature. The catalysts were skeletal nickel,⁴ palladium on carbon,⁵ the platinum—tin catalyst for homogeneous hydrogenation,⁶ and a CoCl₂—NaBH₄ system⁷ capable of reducing alkene without use of molecular hydrogen.

The results obtained for the hydrogenation of noncoordinated compounds on the heterogeneous catalysts (Ni, Pd/C) agree with literature data.^{8,9} The hydrogenation reactions of free ligands are characterized by a linear dependence of the conversion on the duration of the process in the initial regions, although their slope ratios, half-lives, and reaction rates are different. The half-lives in the series oct-1-ene < styrene < stilbene are related as 1:3:7. This order of changing the reactivity is caused by double bond activation due to conjugation with the phenyl rings. However, compared to the non-coordinated compounds (Fig. 1), the arene chromium tricarbonyl complexes are hydrogenated with a low initial rate, which is probably associated with the strong adsorption of the π -complexes on the catalyst surface. To confirm this assumption, we carried out experiments with different additives introduced into the reaction mixture. The additives were benzene, chromium hexacarbonyl, bis(η^6 -benzene)chromium, and η^6 -toluene chromium tricarbonyl, *i.e.*, compounds containing the same structural fragments as styrene and stilbene chromium tricarbonyls.

As can be seen from the presented curves (Fig. 2), benzene and $bis(\eta^6$ -benzene)chromium exert a very weak effect on the hydrogenation of oct-1-ene and stilbene, respectively, whereas the chromium carbonyl complexes substantially retard the hydrogenation of oct-1-ene. Especially strong retardation is observed for additives of the arene chromium tricarbonyl complexes, probably, due to their stronger chemisorption on the catalyst surface.

This is also favored by the results of competitive hydrogenation of stilbene and η^6 -stilbene chromium tricarbonyl. As can be seen from the data in Fig. 3, when the solution simultaneously contains equimolar amounts of these compounds, η^6 -stilbene chromium tricarbonyl is predominantly activated, whereas stilbene is reduced with hydrogen much more slowly. It can be assumed that the arene chromium tricarbonyl complexes occupy the most part of the active catalyst surface, while the free stilbene ligands

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Fig. 1. Dependence of the conversion (*C*) of olefins and the arene chromium tricarbonyl complexes on the duration of the reaction on the catalysts Raney nickel (*a*) and palladium on carbon (*b*): stilbene (*1*), styrene (*2*), oct-1-ene (*3*), stilbene chromium tricarbonyl (*4*), and styrene chromium tricarbonyl (*5*); T = 18.5 °C.



Fig. 2. Effect of additives on the conversion of olefins on the catalyst palladium on carbon: stilbene + bis(benzene)chromium (1), oct-1-ene + benzene (2), oct-1-ene + chromium hexacarbonyl (3), and oct-1-ene + toluene chromium tricarbonyl (4); T = 18.5 °C.

are hydrogenated on a few number of remaining active sites.



Fig. 3. Dependence of the conversion (*C*) of the components of an equimolar mixture of stilbene (*I*) and stilbene chromium tricarbonyl (*2*) on the duration of the reaction on the catalyst palladium on carbon; T = 18.5 °C.

To avoid chemisorption of the arene chromium tricarbonyl complexes on the solid catalyst surface, we carried out the homogeneous hydrogenation of free and coordinated olefins using the H_2PtCl_6 —SnCl₂ system⁶ by a procedure proposed¹⁰ for the homogeneous hydrogenation of Dewar hexamethylbenzene.

For homogeneous catalytic alkene hydrogenation on the platinum—tin mixed catalyst, hydrogen addition differs strongly from that observed in the case of heterogeneous hydrogenation. As can be seen from the data in Fig. 4, *a*, styrene is characterized by the highest hydrogenation rate, whereas stilbene is hydrogenated very slowly. This can be explained by the fact that the hydrogenation on the heterogeneous catalysts involves adsorption of hydrogen and olefin on a number of catalytic sites and steric factors are insignificant. For homogeneous catalysis hydrogen and olefin are accommodated on one transition metal atom. The stilbene ligand containing two bulky phenyl groups represents considerable steric hindrance for stilbene coordination on a metal atom, which certainly reflects the process rate.

 η^6 -Styrene chromium tricarbonyl is rapidly hydrogenated on this catalyst. The reaction affords ethylbenzene chromium tricarbonyl, which was isolated from the reaction mixture in 87% yield. Its physicochemical characteristics (melting point, IR spectrum, *etc.*) correspond completely to the substance prepared by us using the direct synthesis from ethylbenzene and chromium hexacarbonyl. All attempts to hydrogenate η^6 -stilbene chromium tricarbonyl on this catalytic system failed.

We hydrogenated the unsaturated arene chromium tricarbonyl complexes using hydride inorganic reducing agents. It is known,⁷ for example, that the complex obtained from cobalt(π) salts and sodium borohydride easily reduces alkenes in a high yield and with a very high selectivity.



Fig. 4. Dependence of the conversion (*C*) of olefins and the arene chromium tricarbonyl complexes on the $H_2PtCl_6-SnCl_2-LiBr$ mixed catalyst (*a*) and CoCl₂-NaBH₄ system (*b*) on the duration of the reaction: styrene (*1*), oct-1-ene (*2*), styrene chromium tricarbonyl (*3*), and stilbene (*4*); *T* = 18.5 °C.

Our studies showed that the CoCl₂—NaBH₄ system in isopropyl alcohol (Fig. 4, *b*) is most efficient for the hydrogenation of styrene, oct-1-ene, and η^6 -styrene chromium tricarbonyl, whereas sterically hindered stilbene is hydrogenated very slowly (3% dibenzyl are formed for 5 h), and η^6 -stilbene chromium tricarbonyl is not virtually reduced under these conditions.

Despite some restrictions, all the three procedures used by us can be applied for the hydrogenation of the unsaturated arene chromium tricarbonyl complexes. The hydrogenation on the heterogeneous metallic catalysts occurs very slowly, whereas homogeneous hydrogenation, although being rather rapid in the case of terminal olefins, is hardly suitable for the reduction of olefins with sterically hindered double bonds.

Thus, the most convenient procedure for the hydrogenation of η^6 -styrene chromium tricarbonyl is its homogeneous reduction with molecular hydrogen on the H₂PtCl₆-SnCl₂-LiBr complex system.

Experimental

Synthesis of organometallic compounds and all procedures with them were carried out under purified argon. Styrene, oct-1-ene, and stilbene were commercially purchased (analytical purity grade). η^6 -Styrene chromium tricarbonyl was prepared by the Rausch method,¹¹ and η^6 -stilbene chromium tricarbonyl was synthesized by the direct reaction of stilbene with chromium hexacarbonyl.¹² All solvents used were dried and purified directly before use. The catalysts, *viz.*, skeletal nickel,¹³ palladium on carbon,¹⁴ and platinum—tin for homogeneous hydrogenation,¹⁰ were prepared according to earlier published procedures.

Compounds were hydrogenated in a setup described for alkene reduction with hydrogen.⁴ Gas chromatographic analysis was carried out on a Tsvet-500 M instrument with a dumped packing column (15% Apiezon L on Chromaton N-AW-DMCS, column length 2 m, rate of the carrier gas (helium) 26 mL min⁻¹, flame-ionization detector).

Heterogeneous hydrogenation. The catalyst (0.1 g, Raney Ni or Pd/C) and ethyl acetate (25 mL) were introduced under argon into a reaction flask equipped with a magnetic stirrer and injection of gaseous hydrogen. The reaction mixture was maintained at a constant temperature for 15 min purging hydrogen from the Kipp apparatus, then the magnetic stirrer was switched on, and an unsaturated compound (1.0 mmol) dissolved in ethyl acetate (10 mL) was syringed into the flask through the side neck. The reaction course was monitored by the volume of absorbed hydrogen measured with a gas burette. These data referred to normal conditions were used to calculate the conversion and yields of the reaction products. The reaction mixture obtained after hydrogenation was filtered, and its composition was determined by gas chromatography. Before analysis the arene chromium tricarbonyl complexes were decomplexated by crystalline iodine. The hydrogenation products were identified by retention times in the chromatographic column.

Homogeneous hydrogenation on the Pt/Sn catalyst. To prepare a solution of the catalyst, H₂PtCl₆·6H₂O (0.13 g, 0.25 mmol), LiBr (0.39 g, 0.45 mmol), and ethyl acetate (10 mL) were introduced under argon into a round-bottom three-necked flask equipped with a magnetic stirrer, a dropping funnel, and a tube for gas injection. Then a solution of tin chloride (0.29 g, 1.5 mmol) in ethyl acetate (15 mL) was added dropwise with stirring from the dropping funnel. The solution turned stramineous-colored and then red-colored after the flask was filled with molecular hydrogen. Stirring was continued for 1 h, and then olefin (1.0 mmol) was syringed into the catalyst solution. The reaction course was monitored by the amount of absorbed hydrogen. After the end of reduction, the reaction mixture was hydrolyzed with 30 mL of 2 M HCl, and the organic layer was separated, washed with water, dried, evaporated, and analyzed by gas chromatography. In the case of the unsaturated arene chromium tricarbonyl complexes, viz., η^6 -styrene and n^6 -stilbene chromium tricarbonyls, the evaporation of the organic layer and sublimation *in vacuo* gave n⁶-ethylbenzene chromium tricarbonyl (69.5% yield, m.p. 47 °C (cf. Ref. 15: m.p. 48-49 °C)) and n⁶-dibenzvl chromium tricarbonvl (73.1% vield. m.p. 97.5 °C (cf. Ref. 16: m.p. 98-100 °C)), respectively.

Reduction by the $CoCl_2$ -NaBH₄ system. A solution of NaBH₄ (0.76 g, 20 mmol) in isopropyl alcohol (10 mL) was

introduced into a round-bottom three-necked flask equipped with a magnetic stirrer, a dropping funnel, and a tube for gas injection. A solution of CoCl₂ (0.26 g, 10 mmol) in the same solvent was added from a dropping funnel to this solution for 1 h at ~20 °C under argon. Upon mixing the reactants, the solution darkened and molecular hydrogen evolved. Stirring was continued for 1 h, and the solution turned black and a precipitate formed. Then alkene under study (2.0 mmol) was introduced into the vigorously stirred mixture under argon with a microsyringe through the silicone plug. To monitor the course of the reaction, samples were taken at different stages and analyzed by chromatography. After the end of reduction (3-7 h), the reaction mixture was poured into 3 M HCl. The aqueous layer was extracted with ether. The ethereal layer was washed with water and dried above anhydrous Na₂SO₄. After ether was evaporated, the resulting product was identified.

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