

KINETICS OF HYDROSILYLATION OF TERT-BUTYLPHENYLKETONE
 BY DIPHENYLSILANE CATALYSED
 BY $[\text{Rh}(1,5\text{-COD})(-)\text{-DIOP}]^+\text{ClO}_4^-$ *

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Kinetic analysis of the title reaction has been made by the method of initial reaction rates. On the basis of the rate data, kinetic isotope effect and spectroscopic study of the reaction of the organosilicon hydride with the catalyst, the reaction model was proposed involving the following steps: the displacement of the diene by reaction with the silicon hydride to form a rhodium-arene complex in an induction period of the hydrosilylation, the oxidative addition of the organosilicon hydride to the rhodium-arene complex, followed by the interaction of the ketone with the silyl-hydridorhodium (*III*) species in the rate determining step. The process is characterized by the following activation parameters: $\Delta U^\ddagger = 54.5 \pm 8.5 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -88 \pm 25 \text{ J mol}^{-1} \cdot \text{K}^{-1}$. The significant role of the entropic factor was supported by the analysis of the temperature dependence of the asymmetric efficiency of the catalyst.

Enantioselective hydrosilylation of ketones is a convenient route to the synthesis of optically active alcohols (for recent review see ref.¹). The cationic rhodium complexes containing DIOP as a chiral ligand are effective in the addition of the Si—H bond of organosilicon hydrides to the C=O bond^{2,3}. The asymmetric efficiency of $[\text{Rh}(1,5\text{-COD})(-)\text{-DIOP}]^+\text{BF}_4^-$ was found to be comparable to that of a neutral Rh-DIOP complex² and some relations between the structure of prochiral ketones and optical bias have been reported³. However, the course of the enantioselective hydrosilylation has not been examined in detail.

Continuing our study of the hydrosilylation of keto compounds catalysed by chiral rhodium complexes^{4,5} we were interested in the kinetics of this reaction. Hydrosilylation of tert-butyl phenyl ketone by diphenylsilane catalysed by (1,5-cyclooctadiene) $[(-)\text{-}2,3\text{-O-cyclohexylidene-}2,3\text{-dihydroxy-}1,4\text{-bis(diphenylphosphino)butane}]$ rhodium perchlorate ($[\text{Rh}(1,5\text{-COD})(-)\text{-DIOP}]^+\text{ClO}_4^-$) was chosen as a model reaction. The results obtained are discussed in the present work.

* Part LXII in the series Catalysis by Metal Complexes; Part LXI: This Journal 45, 2219 (1980).

EXPERIMENTAL

Chemicals

Benzene (Lachema, Brno) was dried over sodium, distilled in the presence of sodium or calcium(II) hydride and stored under argon. (—)-2,3-O-Cyclohexylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane[(—)-DIOP] was from laboratory stock. Its preparation was reported elsewhere⁵; m.p. 118.5–120°C, $[\alpha]_D^{20} = -19.65^\circ$ ($c = 0.6$, benzene). ¹H-NMR spectrum (δ , ppm): 7.4–7.0 m (20 H arom.), 3.90 m (2=CH), 2.31 d (4 CH₂), 1.2–1.0 m (10 CH₂, cyclohexyl). [Rh(1,5-COD)(—)-DIOP]⁺ClO₄⁻ was obtained in 96% yield from [Rh(acac).(1,5-COD)] (ref.⁶) and (—)-DIOP according to the procedure reported⁷ for the isopropylidene analogue. For C₄₂H₄₈ClO₆P₂Rh (849.2) calculated: 59.41% C, 5.70% H; found: 58.81% C, 5.82% H. ¹H-NMR spectrum (δ , ppm): 8.0–7.2 m (20 H arom.), 4.65 and 4.45 two broad singlets (2 + 2 = CH), 2.75 m (H₂CP); 3.55 m (2 HCO), 2.27 and 1.73 two multiplets (4 + 4 CH₂ in 1,5-COD), 1.40–1.05 m (10 H, CH₂ in cyclohexyl).

Tert-butyl phenyl ketone was obtained in 55% yield by the reaction of pivaloyl chloride with phenylmagnesium bromide⁸ as a colourless liquid boiling at 90–92/1.33 kPa, n_D^{20} 1.5090 (ref.⁸ n_D^{20} 1.5060). The product was chromatographically pure. ¹H-NMR spectrum (δ , ppm): 1.26 s (9 H, —C(CH₃)₃), 7.45–7.33 m (2 H in position 3 of the phenyl groups), 7.80–7.38 m (2 H in position 2 and 1 H in position 4 of the aromatic ring).

Diphenylsilane. To 120 g of 70% toluene solution of NaAlH₂(OCH₂CH₂OCH₃)₂ diluted with 300 ml of benzene were added 90 g (0.41 mol) of diphenyldichlorosilane, the reaction mixture was refluxed for 20 min and then allowed to stand overnight. After decomposition of the mixture with 220 ml of 20% H₂SO₄, the organic layer was separated, washed successively with aqueous sodium carbonate solution and water, and dried over anhydrous calcium(II) chloride. The solvents were evaporated on a rotatory evaporator under reduced pressure and the residue was distilled *in vacuo* to give 62 g (0.34 mol, 83% yield) of chromatographically pure product, b.p. 126–127°C/1.5 kPa, n_D^{20} 1.5780 (reported⁹ n_D^{20} 1.5795). ¹H-NMR spectrum (δ , ppm): 7.66–6.88 m (10 H arom.), 4.88 s (2 H, —SiH₂).

Diphenylsilane-d₂. To a suspension of 4.2 g (0.1 mol) of LiAlD₄ (98.5% purity on deuterium) in 200 ml of dry benzene, 50 g (0.19 mol) of diphenyldichlorosilane were dropwise added, the reaction mixture was refluxed for 1 h under stirring and then allowed to cool for 2 h. The product was isolated as in the case of diphenylsilane. A total of 33 g of chromatographically pure (C₆H₅)₂.SiD₂ was obtained (93% yield). ¹H-NMR spectrum (δ , ppm): 7.65–6.55 m (10 H, arom.), 4.83 s (approx. 3% of —SiH₂ or —SiHD impurity). The estimated amount of the not fully deuterated silane is based on comparison of strong signals of aromatic protons with a weak signal of Si—H bond and is likely laden with relatively large experimental error.

1-Phenyl-1-diphenylsiloxy-2,2-dimethylpropane. A Schlenk flask placed in a thermostated silicone oil bath was charged with 15 ml of 2 · 10⁻³ mol/l benzene solution of [Rh(1,5-COD).(—)-DIOP]⁺ClO₄⁻ and 1.84 g (10 mmol) of (C₆H₅)₂SiH₂ were added at room temperature. After 30 min, 1.62 g (10 mmol) of tert-butyl phenyl ketone were added and the reaction mixture was maintained at the above temperature for 6 h and then set aside overnight. The half of the solvent volume was evaporated *in vacuo*, the residue was diluted by twofold volume of dry n-hexane and evaporated *in vacuo* after precipitation of the catalyst. Distillation of the residue yielded 1.5 g (4.3 mmol, 43% yield) of C₆H₅C(OSiH(C₆H₅)₂)/C(CH₃)₃, b.p. 195–196°C/13.3 Pa. ¹H-NMR spectrum (δ , ppm): 7.70–6.90 m (15 H, arom.), 5.26 s (1 H, SiH), 4.30 s (1 H, —CHOSi).

1-Phenyl-2,2-dimethylpropanol was obtained in 87% yield by the reduction of tert-butylphenyl ketone with LiAlH_4 in diethyl ether in the form of colourless low-melting crystals (b.p. $92\text{--}93^\circ\text{C}$: 1.33 kPa). According to gas chromatographic analysis, the product was contaminated by less than 1% of the starting ketone.

Hydrosilylation

Procedure. Hydrosilylation reactions were carried out in 15 ml-Schlenk tubes which were topped with two layer exchangeable silicon rubber cover connected to the neck of the tube by means of a plastic screw. The tubes were placed in a thermostated bath, the temperature of which was maintained constant within 0.1°C . In each experiment, the closed tubes were repeatedly (at least three times) evacuated to approx. 10 Pa and filled with argon (*via* side tube equipped with three-way valve). Individual components were introduced *via* hypodermic syringes purged several times with argon. First, the tube was charged with the solvent, the amount of which was so that the final volume be 10 ml. The catalyst was weighed with the precision of ± 0.2 mg, dissolved in benzene to 10^{-2} mol/l solution. Freshly prepared solutions were used for each set of measurements. Diphenylsilane and tert-butylphenyl ketone were injected as such or were used as 1 mol/l benzene solutions. For the range of concentrations of individual components see Results and Discussion.

Kinetic measurements were carried out at $15\text{--}35^\circ\text{C}$ in benzene. The tube was charged successively with the solvent, the catalyst solution and diphenylsilane. Tert-butyl phenyl ketone was added after 30 min and this moment was regarded as the beginning of the reaction. The course of the reaction was followed by removing samples at fixed time intervals. Concentrations of the reaction components were chosen such that these intervals be 3–5 min for the fastest reaction. This allowed to make simultaneously 3–5 experiments. The samples removed (50 to 100 μl) were immediately solvolysed by twofold volume of the appropriate agent (see the next paragraph). The mixture after solvolysis was analysed on the content of 1-phenyl-2,2-dimethylpropanol formed quantitatively from 1-phenyl-1-diphenylsiloxy-2,2-dimethylpropane by solvolysis.

Analysis of reaction mixture. The determination of the solvolysis product, 1-phenyl-2,2-dimethylpropanol, and unreacted starting ketone was made gas chromatographically using Chrom 4 instrument equipped with a flame ionisation detector; 3.7 m column (3 mm i.d.) packed with 9% Apiezon L on Chromaton N (0.20–0.25 mm particle size), column temperature 195°C , injection port temperature $220\text{--}230^\circ\text{C}$, hydrogen flow rate 25 ml/min, 1.0 μl samples. The amount of both compounds was determined from the corresponding peak areas with the aid of calibration which was made before the analysis of each set of kinetic measurements. The error in analysis did not exceed 4 rel.%. Prior to the analysis, the samples of the reaction mixture were solvolysed. As shown earlier⁴, solvolysis of silyl ethers formed by hydrosilylation of keto compounds is a general acid-base reaction. The applicability and reproducibility of this process depends on the type of the catalyst⁴. In our case the best results were obtained by using 0.5 mol/l ammonium fluoride in 90% aqueous methanol (the error did not exceed 4 rel.%).

Spectroscopic measurements. Electron absorption spectra of catalyst solutions were measured with Specord UV-VIS spectrophotometer in the 330–600 nm region, using approx. $1 \cdot 10^{-4}$ mol/l concentrations and 0.5–1 cm glass cells. These were closed by special teflon stopcocks composed of two parts mutually connected by thin brass screws. In both parts were 1 mm holes. The packing of both segments was made of silicone rubber and could be exchanged. This modification made it possible to wash the cells with argon and to ensure inert atmosphere for measurements. The applicability of these cells was verified by measuring the spectra of $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$

which is known to be very sensitive to minute amounts of oxygen. Recorded spectra did not change with time and were in good agreement with literature data¹⁰.

Catalyst solutions for measurements were prepared in Schlenk tubes by the already described procedure and injected to the cells with the aid of hypodermic syringes. Prior introducing the samples, the cells were purged with argon for 15 min. In spectroscopic investigation of the reaction of the catalyst with diphenylsilane, the organosilicon hydride was added to the catalyst solution prepared in Schlenk tube and the reaction mixture so obtained was transferred into cells. This procedure ensured more accurate feeding of the known amount of the silicon hydride, although the first record of the spectrum could be made after 1—1.5 min after mixing the components.

¹H-NMR spectra of starting compounds and products were recorded on Tesla BS 467 (60 MHz) spectrometer, using 25% solutions in CCl₄ and hexamethyldisiloxane as internal reference. The spectrum of the rhodium complex was measured with Tesla BS 487 A (80 MHz) instrument, using saturated solutions of the complex in CH₃COCD₃ or in CDCl₃ at 25°C and the same reference compound as in the previous case.

IR spectra of rhodium complexes were recorded on UR-20 (Zeiss, Jena) spectrophotometer in the 3600—700 cm⁻¹ region, using KBr pellets. The spectrum of diphenylsilane was obtained *in substantia* (thin films).

Determination of the optical purity of 1-phenyl-2,3-dimethylpropanol. Parallel to kinetic measurements, analogical experiments were carried out under the same conditions except that the larger amounts of the starting compounds were used, in order to obtain approx. 10 mmol of the product. This was isolated by the procedure reported earlier⁴. For determination of optical purity the alcohol was dissolved in benzene. Its concentration was close to the value for which the specific rotation $[\alpha]_D^{20} = +25.9\%$ is reported in the literature¹¹. Since the samples contained unreacted tert-butylphenyl ketone, the allowance was made for its amount which was determined by gas chromatographic analysis.

Treatment of kinetic data. Kinetic analysis was made by the method of initial reaction rates. Because of the complexity of the system, kinetic equations were analysed in their differential forms. Since reaction models of catalytic reactions generally lead to kinetic equations with several parameters, each involving the catalyst, some simplifying assumptions are necessary. In this work, an attempt was made to divide the catalytic cycle to single steps and these then analysed separately. Simplified forms of kinetic equations so obtained were applied to experimental reaction rates; the linear dependence of reciprocal reaction rate r on a given parameter was verified, the other parameters being constant. The verification was made by linear regression. Although this approach is not strictly exact from statistical point of view (reciprocal reaction rate is random quantity and its distribution does have to be necessarily normal), it turned out to be sufficient for our purposes. For kinetic equations derived on the basis of proposed reaction models see Results and Discussion.

RESULTS AND DISCUSSION

For purposes of kinetic study we have chosen tert-butyl phenyl ketone as a model compound. It exhibits suitable reactivity, is not enolizable and does not form therefore a silylenol ether which yields the starting ketone *via* solvolysis^{2,5}. The latter fact would be inevitable complication of the course of the hydrosilylation of ketones having hydrogen in the α position.

Preliminary experiments showed that the reaction of tert-butyl phenyl ketone with diphenylsilane in the presence of $[\text{Rh}(1,5\text{-COD})(-)\text{-DIOP}]^+\text{ClO}_4^-$ is characterized by an induction period. In order to obtain information about the nature of processes taking place during this period, we examined first the interaction of the complex with diphenylsilane by electron spectroscopy.

As shown in Fig. 1, the electron absorption spectrum of benzene solution of the rhodium complex exhibits a band with maximum at 443 nm ($\epsilon_{443} = 2.45 \cdot 10^3$). Similarly to the solid, the dissolved complex is not sensitive to oxygen and does not undergo any decomposition reaction. The addition of the organosilicon hydride leads to colour changes of the solution (from red to lemon yellow). Time changes of the spectrum are illustrated in Figs 2 and 3 and involve a decrease in the absorbance of the 443 nm band with simultaneous formation of a new band having maximum at 347 nm. In further stage of the reaction the intensity of this band decreases, an absorption band at 395 nm being formed. These changes are not instantaneous, which shows that the reaction proceeds at a measurable rate. The rate of these changes depends on diphenylsilane concentration, while the resulting absorbance at 395 nm is independent of this factor.

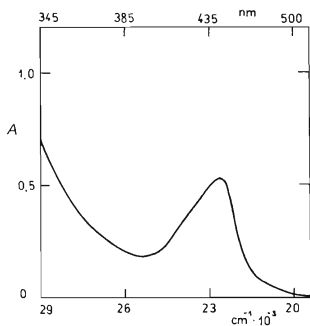


FIG. 1

1 Electron Absorption Spectrum of $[\text{Rh}.(1,5\text{-COD})(-)\text{-DIOP}]^+\text{ClO}_4^-$ in Benzene (Rh concn. = $4.3 \cdot 10^{-4}$ mol/l, $\lambda_{\text{max}} = 443$ nm, $\epsilon_{443} = 2.45 \cdot 10^3$).

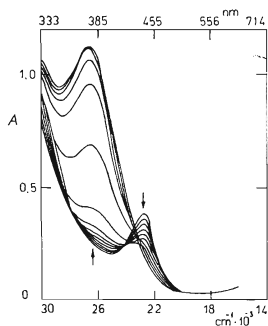


FIG. 2

Time Changes of the Spectrum of the Cationic Rhodium Complex Due to Its Reaction with Diphenylsilane — Formation of an Arene-Rhodium Complex

Rh concn. = $4.0 \cdot 10^{-4}$ mol/l, $(\text{C}_6\text{H}_5)_2 \cdot \text{SiH}_2 = \text{concn. } 0.25$ mol/l, 30°C , benzene, time intervals 30 s.

Before entering into a discussion of the observed spectral changes, some facts concerning the related interaction of hydrogen with the studied rhodium complex should be mentioned. In a NMR study of the reactivity of $[\text{Rh}(1,5\text{-COD}(-)\text{-DIOP})^+ \cdot \text{ClO}_4^-]$, Chaloner and Brown¹² reported that hydrogenation of the complex in methanol leads to $[\text{Rh}(-)\text{-DIOP}(\text{CH}_3\text{OH})_n]^+ \text{ClO}_4^-$ ($n = 2-3$) which does not undergo the oxidative addition of hydrogen to yield the corresponding dihydridorhodium complex $[\text{RhH}_2(-)\text{-DIOP}]^+ \text{ClO}_4^-$ in detectable amounts, *i.e.* the reaction usual for analogous rhodium complexes containing monodentate tertiary phosphines as ligands. The relevant changes in the electron spectrum of the complex after hydrogenation are demonstrated by curve 2 in Fig. 4. It is evident that the displacement of the cyclooctadiene ligand by its hydrogenation does not lead to a significant shift of absorption maximum but only to a decrease in the absorbance ($\epsilon_{444} = 1.3 \cdot 10^3$). The addition of benzene to the solution of the complex in methanol after hydrogenation or the interaction of hydrogen with the complex dissolved in benzene result in the formation of a new band with absorption maximum at 374 nm ($\epsilon_{374} = 2.9 \cdot 10^3$), which situation is illustrated on the latter case as an example in Fig. 5. A simi-

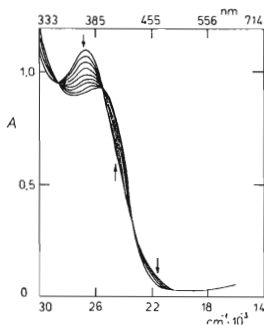


FIG. 3

The Reaction of the Cationic Rhodium Complex with Diphenylsilane — the Second Stage of the Reaction

For conditions see Fig. 2.

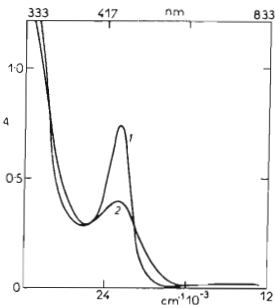


FIG. 4

Electron Absorption Spectrum of the Cationic Rhodium Complex in Methanol (curve 1) and After its Reduction with Hydrogen ($p_{\text{H}_2} = 0.11$ kPa) (curve 2)

Temperature 30°C, Rh concn. = $6.2 \cdot 10^{-4}$ mol/l, 0.5 cm cell; 1 $[\text{Rh}(1,5\text{-COD}) \cdot (-)\text{-DIOP}]^+ \text{ClO}_4^-$, $\lambda_{\text{max}} = 443$ nm, $\epsilon_{443} = 2.40 \cdot 10^3$; 2 $[\text{Rh}(\text{CH}_3\text{OH})_n(-)\text{-DIOP}]^+ \cdot \text{ClO}_4^-$ ($n = 2-3$, ref.¹³), $\lambda_{\text{max}} = 444$ nm, $\epsilon_{444} = 1.3 \cdot 10^3$.

lar bathochromic shift has been observed also on adding other substances having aromatic ring, such as toluene, xylene or diphenyldimethylsilane. We believe that the 374 nm band can be ascribed to a rhodium-arene complex. In the light of the recent report by Pluth and coworkers¹³ on the isolation of $[\text{Rh}(\text{C}_6\text{H}_6)(\text{diphos})]^+ \cdot \text{BF}_4^- \cdot \text{C}_6\text{H}_6$ after hydrogenation of $[\text{Rh}(\text{diene})(\text{diphos})]^+ \text{BF}_4^-$ in benzene and the analogous formation of $[\text{Rh}(\text{L-L})(\text{CH}_3\text{OH})_n]^+ \text{X}^-$ complexes by hydrogenation in methanol, this assumption is not unreasonable. The identity of this band with that initially formed by the reaction of the complex with diphenylsilane further indicates that in the first stage the interaction of diphenylsilane results in the displacement of the coordinated cyclooctadiene (likely by its hydrosilylation) to form the rhodium-arene complex, which then undergoes the oxidative addition to form a silylhydridorhodium(III) complex. This situation is visualized by equations (A) and (B).

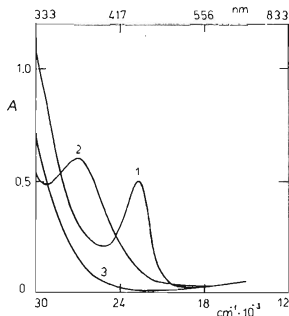
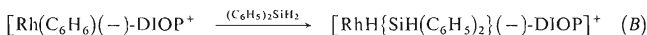
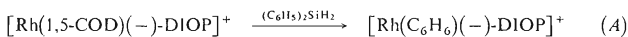


FIG. 5

The Spectrum of the Cationic Complex Before (curve 1) and After Its Reduction With Hydrogen (curve 2) in Benzene at 30°C and the Spectrum of the Reduced Complex After Exposure to Air Oxygen (curve 3)

0.5 cm cell, Rh concn. = $4.1 \cdot 10^{-4}$ mol/l, p_{H_2} = 0.11 kPa; 1 see Fig. 1, 2 $[\text{Rh}(\text{C}_6\text{H}_6) \cdot (-)\text{-DIOP}]^+ \text{ClO}_4^-$, λ_{max} = 374 nm, ϵ_{374} = $2.90 \cdot 10^2$.

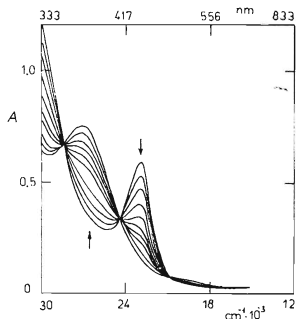


FIG. 6

Time Changes of the Spectrum of the Cationic Rhodium Complex Due to Its Reaction With Diethylmethylsilane in Benzene at 30°C

Rh concn. = $4.7 \cdot 10^{-4}$, $(\text{C}_2\text{H}_5)_2\text{CH}_3 \cdot \text{SiH}$ concn. = 0.22 mol/l, 0.5 cm cell, time intervals 7 min.

By contrast to the above dihydrosilane, only the first step of the reaction has been observed with monohydrosilanes (Eq. (A)). As shown in Fig. 6, the interaction of diethylmethylsilane with the rhodium complex leads to the corresponding rhodium-benzene complex. Furthermore, the reaction proceeds at a slower rate compared to the former case, in accordance with the expected lower reactivity of monohydrosilanes⁴.

The spectroscopic measurements further show that the reaction of diphenylsilane with the catalyst is complete after 15–20 min. This interval agrees well with the induction period observed. For that reason, in kinetic measurements the ketone was added to the solution of the catalyst and diphenylsilane after 30 min. Under these conditions the conversion curves did not exhibit induction period. This can be taken as the further support for the assumption about formation of a catalytically active species by the oxidative addition of organosilicon hydride in the first stage of the reaction.

Kinetic measurements were first centered on the determination of the reaction order in individual components. The dependence of the initial reaction rate r^0 on the catalyst concentration (c_{Rh}^0) is documented by the results presented in Table I. The linear dependence was confirmed by logarithmic treatment of these data. It holds

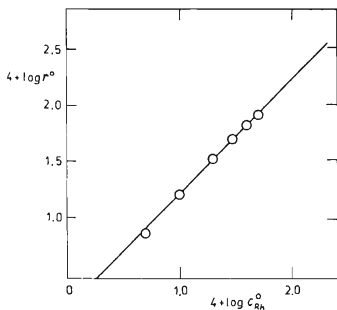


FIG. 7

Plot of $\log r^0$ vs $\log c_{\text{Rh}}^0$ for Hydrosilylation of Tert-Butyl Phenyl Ketone by Diphenylsilane Catalysed by $[\text{Rh}(1,5\text{-COD})(-)\text{-DIOP}]^+ \cdot \text{ClO}_4^-$ in Benzene at 25°C ($c_{\text{Kt}}^0 = c_{\text{Si}}^0 = 0.3 \text{ mol/l}$)

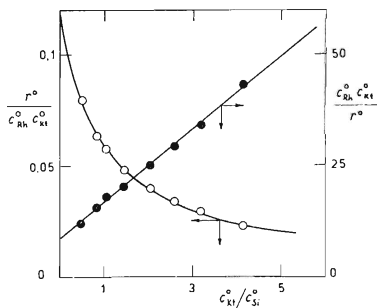


FIG. 8

Dependence of r^0 on $c_{\text{Kt}}^0/c_{\text{Si}}^0$ (Eq. (6)) for Hydrosilylation of Tert-Butyl Phenyl Ketone by Diphenylsilane

Reaction conditions see Table II, the curve corresponds to the expression $r^0/c_{\text{Rh}}^0 c_{\text{Kt}}^0 = 0.12/(1 + 0.99Y)$; \circ experimental data.

generally that $r = \text{const.} \cdot c_{\text{Kt}}^a \cdot c_{\text{Si}}^b \cdot c_{\text{Rh}}^c$. With constant ketone and organosilicon hydride concentrations (c_{Kt}^0 , c_{Si}^0) the following equation can be written for r^0 (Eq. (1)).

$$\log r^0 = \text{const.} + c \log c_{\text{Rh}}^0 \quad (1)$$

As found by linear regression (Fig. 7), the slope (c) has a value of 1.06, which proves the first order in the catalyst.

On the other hand, a similar dependence of r^0 on the ketone concentration c_{Kt}^0 is more complicated, as indicated by the results given in Table II. The initial reaction rate does not increase linearly with the substrate concentration. The apparent fractional order of the reaction in this substance can likely be explained by a competitive equilibrium formation of the complex containing coordinated ketone. This situation is depicted in Scheme 1. Let us assume first that the rate determining step of the

TABLE I

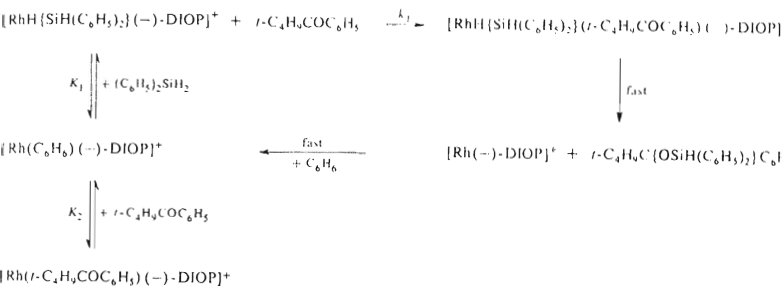
Dependence of Initial Reaction Rate r^0 ($\text{mol l}^{-1} \text{ s}^{-1}$) on Catalyst Concentration, c_{Rh}^0 (mol/l), for Hydrosilylation of Tert-Butyl Phenyl Ketone by Diphenylsilane Catalysed by $[\text{Rh}(1,5\text{-COD}) \cdot (-)\text{-DIOP}]^+ \text{ClO}_4^-$ in Benzene at 25°C ($c_{\text{Kt}}^0 = c_{\text{Si}}^0 = 0.3 \text{ mol l}^{-1}$)

c_{Rh}^0	$r^0 \cdot 10^5$	c_{Rh}^0	$r^0 \cdot 10^3$
5	0.75	30	5.30
10	1.67	40	7.09
20	3.50	50	8.65

TABLE II

Dependence of r^0 on tert-Butyl Phenyl Ketone Concentration c_{Kt}^0 , $c_{\text{Rh}}^0 = 2 \cdot 10^{-3} \text{ mol/l}$, the other conditions see Table I.

c_{Kt}^0	$c_{\text{Kt}}^0/c_{\text{Si}}^0$	$r^0 \cdot 10^5$	c_{Kt}^0	$c_{\text{Kt}}^0/c_{\text{Si}}^0$	$r^0 \cdot 10^5$
0.15	0.50	2.38	0.61	2.05	4.87
0.26	0.85	3.24	0.78	2.60	5.30
0.31	1.02	3.51	0.96	3.20	5.58
0.44	1.47	4.29	1.25	4.15	5.75



SCHEME 1

hydrosilylation is the reaction of the ketone to form the complex D. The reaction rate is then expressed by Eq. (2).

$$r^0 = k_1 c_C c_{K_1}^0 \quad (2)$$

The concentration of the species C can be expressed by means of the analytical concentration c_{Rh}^0 (Eq. (3)).

$$c_{\text{Rh}}^0 = c_A + c_B + c_C \quad (3)$$

The concentration c_D can be neglected since it should be very small compared to the concentrations of the other species (A–C). If the equilibria are established fast, then under the steady state condition c_C can be expressed by Eq. (4). By introducing this relation into Eq. (2)

$$c_C = \frac{K_1 c_{\text{Si}}^0 c_{\text{Rh}}^0}{1 + K_1 c_{\text{Si}}^0 + K_2 c_{K_1}^0} \quad (4)$$

one obtains Eq. (5) for the initial reaction rate r^0 .

$$r^0 = \frac{k_1 K_1 c_{\text{Si}}^0 c_{K_1}^0 c_{\text{Rh}}^0}{1 + K_1 c_{\text{Si}}^0 + K_2 c_{K_1}^0} \quad (5)$$

According to the spectroscopic measurements and $c_{\text{K}_1}^0$, $c_{\text{S}_i}^0$ concentrations used, $k_1 c_{\text{S}_i}^0$ and $K_2 c_{\text{K}_1}^0$ terms in the denominator of the equation are much greater than 1, which value could then be neglected. This simplification leads to Eq. (6) which can be linearised ($Y = c_{\text{K}_1}^0/c_{\text{S}_i}^0$, Eq. (7)). This relation has been used in the treatment of initial rate data.

$$r^0 = - \frac{dc_{\text{K}_1}}{dt} = \frac{k_1 c_{\text{K}_1}^0 c_{\text{Rh}}^0}{1 + K_2 c_{\text{K}_1}^0 / K_1 c_{\text{S}_i}^0}, \quad (6)$$

$$\frac{c_{\text{Rh}}^0 c_{\text{K}_1}^0}{r^0} = \frac{1}{k_1} + \frac{K_2}{k_1 K_1} Y. \quad (7)$$

Fig. 8 shows the experimental dependence $c_{\text{Rh}}^0 c_{\text{K}_1}^0 / r^0 = f(Y)$. Linear regression gave the following parameters: $K_2/K_1 = 0.99$ and $k_1 = 0.12 \text{ l mol}^{-1} \text{ s}^{-1}$. The treatment used allowed to separate the rate constant k_1 , and to determine the ratio of both equilibrium constants K_1 and K_2 .

In the reaction scheme discussed above, it was postulated that the rate determining step is the interaction of the ketone with the species C. It should be mentioned that the assumptions made in deriving the above kinetic relations do not exclude the possibility of the process which involves the formation of the product by transfer of hydrido and silyl ligands to the coordinated ketone in the species D as the rate determining step (this having been considered as fast in Scheme 1). It can be easily shown that this alternative leads to the relations which cannot be kinetically distinguished from the previous case¹⁴.

In order to obtain further information concerning this possibility we made analogous experiments with the deuterated analogue, diphenylsilane- d_2 . Provided that the rate determining step is not the interaction of ketone with species C (Scheme 1), but the hydrogen transfer within coordination sphere to the ketone, one can expect the occurrence of kinetic isotope effect.

The primary kinetic isotope effect depends generally on the strength of the bond cleaved in the rate determining step. The limiting $k_{\text{H}}/k_{\text{D}}$ ratio is reported to be expressed by the relation¹⁵ $k_{\text{H}}/k_{\text{D}} = \exp \{ (hc/2kT) \Delta \bar{\nu} \}$, where $\Delta \bar{\nu}$ is the difference in the frequencies of X—H and X—D stretching vibrations. For the Rh—H and Rh—D bonds this difference amounts to $400 - 500 \text{ cm}^{-1}$ (refs^{16,17}), which leads to $k_{\text{H}}/k_{\text{D}} = 3 - 4$. This rate difference is large enough to ensure the use of this method as a tool for distinguishing discussed models. The results obtained with diphenylsilane- d_2 are presented in Table III and in Fig. 9. The value of the rate constant k_1 is only by approx. 7% lower than in the case of diphenylsilane reaction and does not exceed much the experimental error. This provides support for the reaction model proposed in Scheme 1.

It is worth mentioning that in the case of the deuterated analogue, the K_2/K_1 ratio is by 18% higher compared to the value found for diphenylsilane. Since K_2 should have the same value for both cases, this increase results from the lowering of the K_1 value. This is in agreement with the fact that for equilibria kinetic effect takes place in both directions, *i.e.* in both the formation and dissociation of the species C (Scheme 1). As $\Delta\bar{v}$ for Si—H and Si—D bonds is greater ($600-700\text{ cm}^{-1}$) compared to the corresponding difference for rhodium bonds one can expect that the rate of the cleavage of Si—D would be slower than the cleavage of the Rh—D bond. This would result in the lower K_1 value for diphenylsilane- d_2 , in accordance with the experimental results.

TABLE III

Dependence of r^0 on c_{Kt}^0 for Hydrosilylation of Tert-Butyl Phenyl Ketone by Diphenylsilane- d_2
 $c_{Rh}^0 = 2 \cdot 10^{-3}$ mol/l, $c_{Si}^0 = 0.3$ mol/l, benzene, 25°C.

c_{Kt}^0	c_{Kt}^0/c_{Si}^0	$r^0 \cdot 10^5$	c_{Kt}^0	c_{Kt}^0/c_{Si}^0	$r^0 \cdot 10^5$
0.15	0.50	2.05	0.65	2.15	4.06
0.27	0.90	3.10	0.80	2.65	4.39
0.32	1.05	3.13	0.98	3.27	4.56
0.46	1.52	3.58	1.21	4.03	4.66

TABLE IV

Temperature Dependence of r^0 for Hydrosilylation of Tert-Butyl Phenyl Ketone by Diphenylsilane
 $c_{Rh}^0 = 2 \cdot 10^{-3}$ mol/l, $c_{Si}^0 = 0.3$ mol/l, benzene.

Temp., °C	c_{Kt}^0/c_{Si}^0	$r^0 \cdot 10^5$	Temp., °C	c_{Kt}^0/c_{Si}^0	$r^0 \cdot 10^5$
15	0.50	1.49	30	0.50	2.21
	1.00	2.57		1.05	3.81
	1.55	3.58		1.50	4.30
	2.10	4.16		2.00	4.86
	2.60	4.80		2.70	5.39
20	0.55	1.87	35	0.50	3.33
	1.00	2.85		1.05	4.54
	1.50	3.69		1.45	4.89
	2.05	4.40		2.05	5.04
	2.60	4.95		2.55	5.13

The temperature dependence of the rate data is represented by the results summarized in Table IV and plotted against Y (Eq. (7)) in Fig. 10. The temperature region used in these measurements was relatively narrow, due to the lower reproducibility of kinetic data at higher temperatures (see *e.g.* data for 35°C). Calculated rate constant k_1 and K_2/K_1 ratios are listed in Table V. The former values were used to estimate the activation parameters of the reaction. From the Arrhenius plot, the following values were obtained:

$$\Delta U^\ddagger = 54.5 \pm 8.5 \text{ kJ mol}^{-1} \quad \text{and} \quad \Delta S^\ddagger = -88 \pm 25 \text{ J mol}^{-1} \text{ K}^{-1}.$$

TABLE V

Temperature Dependence of Rate Constants k_1 ($l \text{ mol}^{-1} \text{ s}^{-1}$) and the Ratio of Equilibrium Constants K_2/K_1 (Scheme 1) for Hydrosilylation of *tert*-Butyl Phenyl Ketone by Diphenylsilane Catalysed by $[\text{Rh}(1,5\text{-COD})(-)\text{-DIOP}]^+\text{ClO}_4^-$

Temp., °C	$k_1 \cdot 10^2$	K_2/K_1
15	5.80 ± 0.17	0.34
20	7.00 ± 0.08	0.46
25	11.95 ± 0.25	0.99
30	13.55 ± 0.75	1.16
35	26.60 ± 2.50	2.72

TABLE VI

Temperature Dependence of Optical Yield ρ of (R)-(+)-1-Phenyl-2,2-Dimethylpropanol Obtained by Hydrosilylation of *tert*-Butyl Phenyl Ketone by Diphenylsilane Catalysed by $[\text{Rh}(1,5\text{-COD})(-)\text{-DIOP}]^+\text{ClO}_4^-$

$$c_{\text{Rh}}^0 = 2 \cdot 10^{-3} \text{ mol/l}, \quad c_{\text{KI}}^0/c_{\text{Si}}^0 = 0.3 \text{ mol/l, benzene.}$$

Temp., °C	ρ , %	$\ln P^a$
15	53.1	1.18
20	47.1	1.05
25	43.1	0.93
30	38.8	0.82
35	34.3	0.71
40	27.3	0.56
50	22.1	0.45

^a Eq. (9).

Because significant deviations of $\ln k_1$ values from the straight line obtained by the least square method, the above values are of semiquantitative nature. Nevertheless, the relatively small activation energy and the great activation entropy indicate that the latter significantly contribute to the activation free energy, specifying thus a process with the highly arranged transition state. This is not surprising in that it is a prerequisite for stereospecific course of the reaction. Further information concerning this aspect has been obtained by the study of the asymmetric efficiency of the catalyst. The temperature dependence of the optical bias is presented in Table VI. According to the Curtin-Hammett principle¹⁸, the ratio of both enantiomers

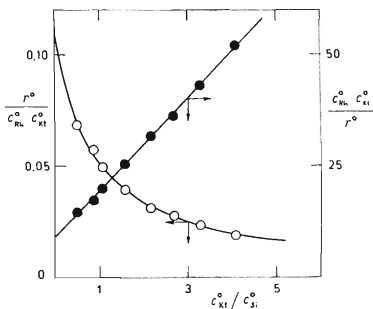


FIG. 9

Dependence of r_0 on c_{Kt}^0/c_{Si}^0 (Y) for Hydro-silylation of tert-Butyl Phenyl Ketone by Diphenylsilane- d_2

For conditions see Table II, the curve corresponds to the expression $r_0/c_{Rh}^0 c_{Kt}^0 = 0.11/(1 + 1.17Y)$, points are experimental data.

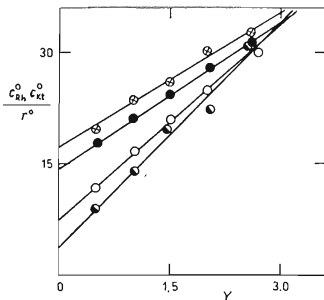


FIG. 10

Temperature Dependence of Reciprocal Initial Reaction Rate on Y (Eq. (7)) for Hydro-silylation of tert-Butyl Phenyl Ketone by Diphenylsilane in the Presence of $[Rh(1,5-COD)(-)-DIOP]^+ ClO_4^-$

Reaction conditions see Table IV; \odot 15°C, \bullet 20°C, \circ 30°C, \oplus 35°C.

formed (P) depends on the difference in free energies of the corresponding diastereoisomeric transition states ΔF^\ddagger , which can be expressed by Eq. (8).

$$P = k^R/k^S = \exp \{(\Delta F_S^\ddagger - \Delta F_R^\ddagger)/RT\} . \quad (8)$$

The relation can be rewritten to the expression (9) where ϱ is the optical yield of the reaction.

$$\ln P = \ln \{(100 + \varrho)/(100 - \varrho)\} = \Delta \Delta U^\ddagger/RT - \Delta \Delta S^\ddagger/R \quad (9)$$

The linear regression of these data (Table VI, the value for 50°C was not included) leads to the following values: $\Delta \Delta U^\ddagger = -18.0 \text{ kJ mol}^{-1}$ and $\Delta \Delta S^\ddagger = -52.3 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$, demonstrating again the importance of the entropic factor.

The value of the optical yield at 50°C deviates from the dependence, indicating an increased asymmetric effectiveness of the catalyst, in contrast to the observed trend. This likely results from the participation of the hydrosilylation product, $t\text{-C}_4\text{H}_9[\text{OSiH}(\text{C}_6\text{H}_5)_2]\text{C}_6\text{H}_5$ on the course of the reaction. It is known that diarylalkoxysilanes are unreactive at room temperature², producing however diaryldialkoxysilanes at elevated temperatures. A similar situation has been observed in the case of hydrosilylation of acetophenone with diethylsilane. Whereas the reaction leads exclusively to the monoalkoxysilane $\text{C}_6\text{H}_5(\text{CH}_3)\text{CHOSiH}(\text{C}_6\text{H}_5)_2$ at room temperature, at 50°C the dialkoxy derivative $[\text{C}_6\text{H}_5(\text{CH}_3)\text{CHO}]_2\text{Si}(\text{C}_2\text{H}_5)_2$ is formed, too.

This fact does not influence kinetic results discussed earlier, since in this case, the low conversion of the starting ketone ensured that the concentration of such a product is low. However, on determining optical yields, the addition was allowed to proceed to higher conversions (50–60%), so that the reaction of the ketone with the hydrosilylation product cannot be neglected. This process should be more stereoselective, resulting thus in the higher optical yield of the alcohol, as found experimentally.

Summarizing, the results obtained in this study are not at variance with the proposed reaction model (Scheme 1) involving the oxidative addition of organosilicon hydride, followed by the reaction of ketone with the silyl(hydrido)rhodium(III) species in the rate determining step of the hydrosilylation.

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