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Journal of Molecular Catalysis A: Chemical 104 (1996) 293–297

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Cyclodextrin modification of the hydrosilylation reaction

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Received 31 January 1995; accepted 2 July 1995

Abstract

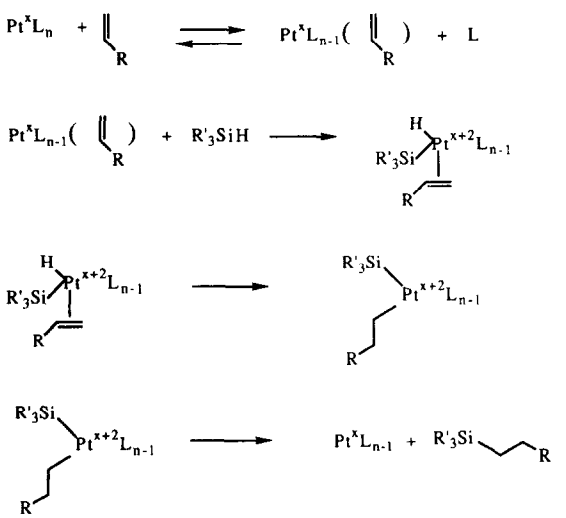
Beta-cyclodextrin (BCD) has an accelerating rate on the platinum-catalyzed hydrosilylation reaction. The addition of triethoxysilane to styrene was 45% complete after 0.5 h at 50°C but in the presence of BCD the reaction was 100% complete after 0.5 h at 50°C. Other conditions were explored as well. The platinum-catalyzed reactions of triethoxysilane and triethylsilane to vinyltrimethylsilane were accelerated by the presence of BCD. Platinum catalysts studied were Karstedt's catalyst, a Pt^0 complex with divinyltetramethyldisiloxane ($M^{vi}M^{vi}$) in xylene and Lamoreaux' catalyst, a mixture of Pt^{II} and Pt^{IV} complexes in octanol.

Keywords: Hydrosilylation; Cyclodextrin

1. Introduction

The hydrosilylation reaction is one of the most efficient methods for forming Si–C bonds [1,2]. Catalysts for hydrosilylation have been reported for metals in groups 8, 9 and 10 but platinum is the most active. It is not uncommon for a reaction to be catalyzed by as little as 10 ppm Pt with complete conversion to product achieved under 100°C in a few hours.

The mechanism of hydrosilylation is a complicated one and is under continued investigation. Chalk and Harrod's mechanism was based on standard steps of organometallic chemistry, Scheme 1, and is likely for platinum catalysts with inhibiting ligands such as phosphines [1]. There is evidence that for highly active catalysts an alternative mechanism is operative [3–7]. An example of a highly active platinum hydrosilylation catalyst is Karstedt's catalyst. Karstedt's catalyst is prepared from the reaction of divinyltetramethyldisiloxane ($M^{vi}M^{vi}$) with H_2PtCl_6 which gives a Pt^0 complex containing silicon–vinyl ligands, Scheme 2 [8,9]. Recently Lappert and



Scheme 1.

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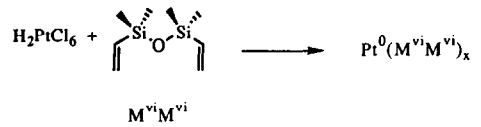
SSDI 1381-1169(95)00147-6



Scheme 2.

co-workers solved the three-dimensional crystal structure for the product of $Pt(COD)_2$ (COD = 1,5-cyclooctadiene) with $M^{vi}M^{vi}$, a compound closely related to Karstedt's catalyst [10,11]. The mechanism of hydrosilylation for catalysts like Karstedt's proceeds through intermediates where the Pt–vinyl bonds have been replaced by Pt–Pt and Pt–Si linkages [12]. Thus a trigger for high activity are those conditions which favor rapid loss of the ligands on the initial Pt catalyst precursor [4].

Cyclodextrins are cyclic, doughnut-shaped oligomers of glucopyranose sugars and are given the prefixes α, β or γ on the basis of rings containing 6, 7 or 8 glucopyranose sugars [13]. Modification of the rate of organic reactions by cyclodextrins is a well known phenomenon [13–15]. Cyclodextrins have a hydrophobic interior and a hydrophylic exterior and therefore have been used as enzyme models [16]. The kinetics of the cleavage of aryl alkanolates is retarded and/or accelerated with cyclodextrins [17]. Cyclodextrins also accelerate the rate of electrocatalytic oxidation of NADH by ferrocene carboxylic acid [18]. Extensive work has appeared on improved acylation rates caused by cyclodextrins [19–21].

So-called host–guest complexes of cyclodextrin and some platinum and palladium compounds have recently been reported [22]. These host–guest complexes have been employed as latent hydrosilylation catalysts [23,24]. The latent catalysts are inactive at ambient temperature and active at elevated temperature. In this case the cyclodextrin sequesters the platinum compound, preventing catalysis. At higher temperature the guest compound is released and catalysis proceeds. In the present paper several cases are reported where addition of cyclodextrin has an accelerating effect on the hydrosilylation reaction. To our knowledge, no reports have appeared where cyclodextrin moderates the hydrosilylation reaction.

2. Experimental

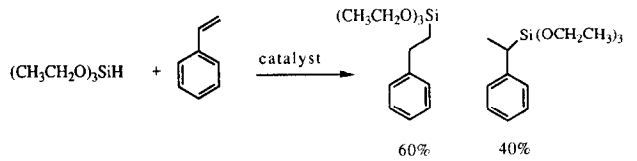
Cyclodextrins were obtained from American Maize Company and used as received. Silicon compounds were obtained from Hüls (now UTI) and styrene was obtained from Aldrich Chemical and distilled before use. Karstedt's catalyst was obtained from GE Silicones and can be prepared as reported [26]. Lamoreaux catalyst was obtained from GE Silicones and is prepared as reported [25] by heating H_2PtCl_6 in 1-octanol and then subjecting the mixture to vacuum stripping to remove low molecular weight species. Platinum analyses were carried out by dissolving the samples within a Teflon® dish[1], evaporating with an IR lamp and then dissolving the sample in HNO_3 and HF and analyzing for Pt by inductively coupled plasma vs. a $Pt(acac)_2$ standard. ^1H NMR spectra were recorded on a GE QE-300 instrument at 300.15 MHz, all shifts, δ, relative to TMS = 0. ^{195}Pt NMR spectra were recorded on a Varian XL 300 NMR spectrometer at 64.12 MHz, all shifts, δ, relative to $Na_2PtCl_6 = 0$. ^{29}Si NMR was also carried out on the Varian XL 300 instrument at 59.3 MHz using TMS = 0 as the internal standard. NMR spectra of BCD were recorded in $(CD_3)_2SO$, dried with molecular sieves; all other NMR spectra were recorded in $CDCl_3$. Gas chromatographic (GC) analysis was carried out using a Hewlett Packard Model 5890 instrument coupled to a Model 3393 integrator. A 1.52 m OV 101 column was employed and a thermal conductivity detector was used.

Analysis of the reaction products were described previously for products of Scheme 3 [6], products of Eqs. (1) and (2) [27].

2.1. Typical hydrosilylation reaction, reaction in Scheme 3

$(EtO)_3SiH$ (4.45 g, 27 mmol), styrene (2.82 g, 27 mmol) and Karstedt catalyst solution (10

[1] Teflon® is a trademark of DuPont Company.



Scheme 3.

μl of a 5% Pt solution in xylene, 0.2 μmol Pt) were combined in a glass vial and optionally the vial was placed in a 50°C oil bath. In addition, the contents of the vial were stirred. The reaction above was repeated by adding BCD (0.25 g, 0.22 mmol). Reactions were analyzed by ^{1}H NMR and GC. All other reactions, Scheme 3 and Eqs. (1)–(2), were carried out in an analogous fashion. The above reaction within the presence of BCD was repeated with decane added (0.41 g, 3.6 mmol). When decane was present, no acceleration due to BCD was noted. The BCD from the reaction run in the presence of decane was recovered and analyzed by ^{1}H NMR which showed the presence of BCD resonances as well as resonances consistent with decane. The imputed decane resonances were absent from BCD recovered from reactions run without decane.

2.2. Second hydrosilylation example

$(EtO)_3SiH$ (4.45 g, 27 mmol), vinyltrimethylsilane (2.7 g, 27 mmol) and Lamoreaux catalyst (10 μl of a 3.6% Pt solution in octanol by weight) were combined as described above. No reaction was observed after heating to 50°C for 10 min as noted by GC analysis. If the reaction was repeated in the presence of BCD (0.1 g, 0.09 mmol), then 100% conversion to product occurred. The reaction without BCD present reached 100% conversion after 8 h.

2.3. Attempted encapsulation of $M^{vi}M^{vi}$ by BCD

BCD (1 g, 0.88 mmol) was dissolved in 30 ml of water by heating to about 50°C at which point divinyltetramethyldisiloxane (0.16 g, 0.87 mmol) was added. A white precipitate was obtained which was washed with CH_2Cl_2. No signal was observed by ^{29}Si NMR for the water soluble and CH_2Cl_2 soluble products.

2.4. Attempted reaction of Karstedt catalyst with BCD

BCD (0.5 g, 0.44 mmol) was combined with Karstedt's catalyst solution (10 ml of a 6.5% Pt by weight xylene solution, 3.07 mmol Pt) and the mixture was stirred at ambient temperature for 2 h. The mixture was then filtered and the solid BCD was recovered by filtration. The solution before addition of BCD had a Pt analysis of 6.65% and after analysis the filtrate had a Pt analysis of 6.5%. The recovered BCD was free of Pt and Si.

3. Results and discussion

The platinum-catalyzed hydrosilylation of styrene with $(CH_3CH_2O)_3SiH$ was investigated in the presence and absence of beta-cyclodextrin (BCD). Typically the products of hydrosilylation of styrene are composed of a mixture of isomers based on beta (60%) and alpha (40%) addition, Scheme 3 [6]. The reaction was run without solvent and in the presence of Karstedt's catalyst (0.01 mol% Pt). As shown in Table 1, dramatic

Table 1
Effect of cyclodextrin on hydrosilylation of styrene, Scheme 3

Cyclodextrin, mol.-%	Temperature, °C	Time, h	Total % conversion
None	50	0.5	45
BCD, 0.85	50	0.5[a]	100
None	ambient	17	50
BCD, 0.3	ambient	17	100
Me_2BCD, 0.3	ambient	17	70

[a] Reaction was over instantaneously upon addition of Pt.
BCD = beta-cyclodextrin, Me_2BCD = 14 of 21 OH groups of BCD methylated.

Table 2
Effect of cyclodextrin on the rate of hydrosilylation of trimethylvinylsilane

Reaction	BCD, mol.-%	Pt catalyst	Time, h	Total % conversion
7	0	Karstedt	0.4	63
7	0.33	Karstedt	0.2	100
7	0	Lamoreaux	24	0
7	0.33	Lamoreaux	0.2	100
8	0	Karstedt	3	59
8	0.28	Karstedt	3	71

increases in the rate of hydrosilylation were noted in the presence of cyclodextrin. The reaction run in the presence of BCD at 50°C was in fact over instantaneously after addition of the Si–H compound. The reaction mixture developed the characteristic exotherm and yellow color formation of Pt hydrosilylation immediately after addition of platinum while the reaction run without cyclodextrin did not develop the yellow color until after complete conversion was achieved. Analysis of the recovered BCD from the reaction showed the absence of Pt, styrene or Si of any kind. Thus the reaction was truly co-catalytic in BCD. Acceleration was also observed when BCD was replaced by dimethyl betacyclodextrin, Me_2BCD (Me_2BCD is BCD with 14 of the 21 OH groups methylated). Using 0.3 mol% Me_2BCD in place of BCD, after 17 h at 25°C, 70% conversion to products were obtained, cf. Table 1 above.

Other hydrosilylation reactions were accelerated by BCD in the presence of Pt. Two model reactions were monitored for acceleration by BCD; the reaction of Eq. (1) and that in Eq. (2). As shown below in Table 2, BCD accelerated the reactions in Eqs. (1) and (2). As with the styrene reaction, the reactions run in the presence of BCD had immediate yellow color formation upon the addition of the Si–H compound.

$$(CH_3CH_2O)_3SiH + (CH_3)_3SiCH{=}CH_2 \xrightarrow{\text{Pt catalyst}} (CH_3)_3SiCH_2CH_2Si(OCH_2CH_3)_3 \quad (1)$$

$$(CH_3CH_2)_3SiH + (CH_3)_3Si(CH{=}CH_2) \xrightarrow{\text{Pt catalyst}} (CH_3CH_2)_3SiCH_2CH_2Si(CH_3)_3 \quad (2)$$

Several experiments were designed to determine the origin of the acceleration by cyclodextrin. An attempt was made to make a cyclodextrin complex with $M^{vi}M^{vi}$. It was reasoned that cyclodextrin might encapsulate $M^{vi}M^{vi}$ and thereby hasten the onset of reaction. However, all attempts to make a beta-cyclodextrin $M^{vi}M^{vi}$ complex failed. Recovered cyclodextrin from the above experiments was free of silicon as determined by elemental analysis. In another experiment Karstedt's catalyst solution was stirred with cyclodextrin at ambient temperature. The xylene solution before and after addition of cyclodextrin had the same Pt analysis. Furthermore, the recovered cyclodextrin was free of both $M^{vi}M^{vi}$ (no Si by elemental analysis and no $M^{vi}M^{vi}$ by ^1H NMR) and Pt (as determined by elemental analysis).

Hydrosilylation experiments were also carried out with Lamoreaux's catalyst [25]. Lamoreaux's catalyst was described in the 1960's and is the product of H_2PtCl_6 with octanol. ^{195}Pt NMR analysis suggests that Lamoreaux catalyst is a complex mixture of Pt compounds with Pt^{IV} and Pt^{II} species present where the identity of the ligands is unknown. As shown in Table 2, cyclodextrin had a dramatic accelerating effect on reactions catalyzed by Lamoreaux's catalyst. For Eq. (1), triethoxysilane addition to trimethylvinylsilane, no conversion to product occurred at ambient temperature in the presence of Lamoreaux's catalyst after 24 h. When a small amount of cyclodextrin was present, the Lamoreaux-catalyzed reaction was rapid and exothermic. Conversion of starting material was monitored by gas chromatography during the reactions.

Decane was employed as an internal standard when monitoring reactions by gas chromatography. When decane was not present, cyclodextrin had the accelerating effect. However, when decane was present, no acceleration by cyclodextrin was noted. The results with and without decane suggest that decane might be blocking the guest cavity of cyclodextrin and that the blocked guest cavity could not accelerate the reaction. Addition of cyclodextrin hastens the formation of the characteristic yellow color in platinum catalyzed

hydrosilylation reactions. The yellow color formation has been associated with colloid and/or formation of active catalytic species [4,6,12]. Thus the action of BCD may be to accelerate the formation of the these active Pt species responsible for catalysis.

Acknowledgements

Mr. Paul Donahue carried out some of the NMR measurements. Dr. Matthew Romberger, American Maize Co., donated the cyclodextrins used in this work and participated in many helpful discussions.

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