

CATALYSIS BY METAL COMPLEXES. III.*,**

HYDROSILYLATION OF OLEFINS CATALYZED
BY $\text{Co}_2(\text{CO})_8$ AND $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$

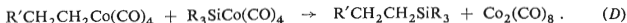
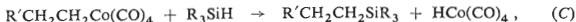
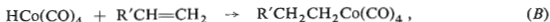
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Relative rate constants of the $\text{Co}_2(\text{CO})_8$ - and $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ -catalyzed additions of propyl-ethoxysilanes of the type $(n\text{-C}_3\text{H}_7)_{3-n}(\text{C}_2\text{H}_5\text{O})_n\text{SiH}$ ($n = 0-3$) to 1-hexene and of the $\text{Co}_2(\text{CO})_8$ catalyzed additions of ethylchlorosilanes of the type $(\text{C}_2\text{H}_5)_{3-n}\text{Cl}_n\text{SiH}$ ($n = 0-3$) to 1-heptene were determined. The $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ -catalyzed competition addition of couples of the ethylchlorosilanes differing by one chlorine atom in their molecule to 1-heptene yielded only the products of hydrosilylation of the silane having a greater number of chlorine atoms bonded to silicon. Mechanism of these reactions is discussed.

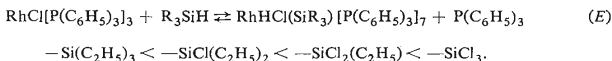
The addition of the Si—H bond across the multiple bond of unsaturated compounds can be effected by many methods. Such as thermal dissociation of the Si—H bond, radical additions, the reactions catalyzed by tertiary amines, chloroplatinic acid, or by platinum on charcoal are sufficiently known¹⁻³. Although most of hitherto studies were concerned mainly with practical aspects, during the last few years hydrosilylation has received attention also from the theoretical point of view of homogeneous catalysis⁴⁻⁹. Chloroplatinic acid, dicobalt octacarbonyl, and tris-(triphenylphosphino)rhodium chloride are the best known hydrosilylation catalysts. Mechanism of the chloroplatinic acid-catalyzed hydrosilylation of olefins, as suggested by Chalk and Harrod⁴, involves reduction of chloroplatinic acid by organosilicon hydride to Pt(II), coordination of an olefin, oxidative addition of the hydride to give a Pt(IV) complex with hydrogen and a silyl group as ligands, addition of hydrogen to the coordinated olefin to form an alkylplatinum complex and reductive elimination of an alkylsilane, accompanied by coordination of another molecule of the olefin. Hydrosilylation of olefins catalyzed by dicobalt octacarbonyl is thought to proceed as follows^{5,10,11}



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No evidence of the reaction (C) has been however observed⁹. Hydrosilylation catalyzed by $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ likely proceeds *via* formation of the penta-coordinated rhodium complexes III (Equation (E))^{6,7}. Complexes of this type were isolated⁷ and their stability was found to increase in the order



However, whether during hydrosilylation the olefin inserts into the Rh—H or Rh—Si bond is not still clear. As quantitative data on the reactivity of the individual hydrosilylation components that could provide valuable information concerning the mechanism of these reactions are very scarce, we decided to pay attention to this problem. We have recently found¹² that the rate of the chloroplatinic acid-catalyzed hydrosilylation of olefins with trichlorosilane depends above all on the electron density on the double bond of an olefin. The effect of structure of some silicon hydrides on the platonic acid — catalyzed hydrosilylation has been discussed¹³.

With the aim to extend this study to other homogeneous hydrosilylation catalysts, in the present work we determined relative rate constants of the $\text{Co}_2(\text{CO})_8$ — and $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ — catalyzed additions of ethylchlorosilanes of the type $(\text{C}_2\text{H}_5)_{3-n}\text{Cl}_n\text{SiH}$ ($n = 0-3$) and propylethoxysilanes of the type $(n-\text{C}_3\text{H}_7)_{3-n} \cdot (\text{C}_2\text{H}_5\text{O})_n\text{SiH}$ ($n = 0-3$) to olefins, using the method of competition reactions.

EXPERIMENTAL

Compounds used. Benzene, thiophene free (Lachema, Brno), was dried over a molecular sieve (type 4A). Octacarbonyl dicobalt (Alfa Inorganics), 1-heptene, and 1-hexene (both supplied by Fluka) were used without further purification. Tris(triphenylphosphine)rhodium chloride was prepared by a reaction of triphenylphosphine with rhodium(III) chloride in ethanol¹⁴. The preparation and physical properties of the ethylchlorosilanes, propylethoxysilanes and hydrosilylation products were reported in a previous work¹³.

Procedure used. Hydrosilylations were carried out in sealed ampoules in an atmosphere of nitrogen at 80°C and 120°C, respectively. Relative rate constants were determined by the method of competition reactions¹⁵. The weight amounts of the individual reaction components were chosen so that the conversion of silane would not exceed 10%. The reaction products were analyzed on a Griffin D 6 gas chromatograph provided with a column (200 cm long and 0.4 cm across) filled with 5% silicone elastomer E 301 on grinded unglazed tiles (150°C column temperature, 40 ml per min hydrogen flow rate). By way of an example, a glass ampoule was first purged with nitrogen and then was charged with 0.745 g of tripropylsilane, 0.183 g of dipropylethoxysilane, 0.05 ml of 1-hexene, and 0.05 ml of $4 \cdot 10^{-3}\text{M}$ solution of $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ in benzene. The sealed ampoule was heated at 80°C for 2 hours. During this period, the content of the ampoule was occasionally shaken. The cooled reaction mixture was analyzed by gas chromatography. In case of the $\text{Co}_2(\text{CO})_8$ -catalyzed hydrosilylation by the propylethoxysilanes the catalyst was used as $1 \cdot 10^{-2}\text{M}$ benzene solution (0.1 ml); the hydrosilylations by ethylchlorosilanes were catalyzed by the solid catalyst ($1 \cdot 10^{-1}$ mmol). The relative rate constants summarized in Table I are averages of at least three measurements and were determined with relative error of $\pm 4\%$.

RESULTS AND DISCUSSION

The relative rate constants of the additions of propylethoxysilanes of the type $(n\text{-C}_3\text{H}_7)_{3-n}(\text{C}_2\text{H}_5\text{O})_n\text{SiH}$ ($n = 0-3$) to 1-hexene, catalyzed by $\text{RhCl}/(\text{C}_6\text{H}_5)_3/3$ and $\text{Co}_2(\text{CO})_8$ and carried out at 80°C , are given in Table I. A systematic increase in the magnitude of rate constants on going from tripropylsilane to triethoxysilane is in harmony with our earlier observation¹³ that the reactivity of a silicon hydride increases as the hydrogen of the Si—H bond becomes less hydridic (here undoubtedly due to $-I$ effect of the ethoxy groups).

However, as already pointed out¹³ steric similarity of n -propyl and ethoxy groups is not sufficient, especially when these groups are bonded to silicon, since -due to dative ($p-d$) π interaction between unshared electron pairs of the oxygen and vacant $3d$ -orbitals of silicon- the Si—O—C bond angles are larger, relative to the C—O—C bond angles, while the Si—C—C bond angles do not change. The lower reactivity of triethoxysilane, relative to diethoxypropylsilane, observed in the H_2PtCl_6 -catalyzed hydrosilylation¹³ has been accounted for by this factor. The above trend is less distinct when octacarbonyl dicobalt or tris(triphenylphosphine)rhodium (*I*) chloride are used as catalysts; only deviations from the otherwise additive character of the dependence of relative reactivity on degree of substitution can be observed. With octacarbonyl dicobalt, this "break" of additivity occurs already for propyl-diethoxysilane, while in case of tris(triphenylphosphine)rhodium(*I*) chloride for triethoxysilane. This difference can probably be attributed to steric effects, too. The fact that decrease in the reactivity along the series of silicon hydrides is not the same for all the catalysts used is not surprising, since difference in bond lengths and in spatial arrangement of the catalytically active intermediates should be expected. In case of platinum the complex formed is likely to be hexa-coordinated⁴, in case of rhodium it is penta-coordinated (complex *III*), with the structure of trigonal bipyramid having hydrogen in the basis⁵, and the presumed⁷ complex *II* should have

TABLE I

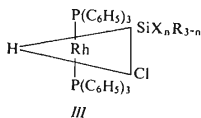
Relative Rate Constants of the Additions of Propylethoxysilanes to 1-Hexene Catalyzed by $\text{RhCl}/\text{P}(\text{C}_6\text{H}_5)_3/3$ (k_{rel}) and by $\text{Co}_2(\text{CO})_8$ (k'_{rel})

Compound	k_{rel}	k'_{rel}
$(n\text{-C}_3\text{H}_7)_3\text{SiH}^a$	1	1
$(n\text{-C}_3\text{H}_7)_2(\text{C}_2\text{H}_5\text{O})\text{SiH}$	5.4	27.5
$n\text{-C}_3\text{H}_7(\text{C}_2\text{H}_5\text{O})_2\text{SiH}$	28.4	59.5
$(\text{C}_2\text{H}_5\text{O})_3\text{SiH}$	42.8	119.0

$$^a k_{\text{rel}}(\text{C}_2\text{H}_5)_3\text{SiH} = 2.17.$$

the structure of distorted trigonal bipyramide with hydrogen in apical position¹⁶. The greater reactivity of triethylsilane (2·17), relative to tripropylsilane, observed in the $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ -catalyzed addition to 1-hexene, is likely the consequence of both the lesser +I effect and smaller steric effect of the triethylsilyl group, compared to the tripropylsilyl group.

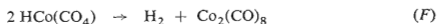
In an attempt to determine the relative rate constants of the $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ -catalyzed addition of the hydrides $(\text{C}_2\text{H}_5)_{3-n}\text{Cl}_n\text{SiH}$ ($n = 0-3$) to 1-heptene carried out under the same conditions as were used in the addition of the propylethoxysilanes (80°C and 2 h) no hydrosilylation products have been obtained. This is not surprising, since it has already been found^{7,17} that the addition of trichlorosilane proceeded with difficulty when this catalyst was used. For this reason we attempted to determine relative reactivities of these compounds at a higher temperature (120°C), using couples of the silicon hydrides differing in each case by one chlorine atom (*e.g.* the couple triethylsilane–diethylchlorosilane). In all runs, only products of the addition of the chlorosilane having a greater number of chlorine atoms have been found. On the basis of these experiments the reactivity order seems to be at least $(\text{C}_2\text{H}_5)_3\text{SiH}$ 1, $(\text{C}_2\text{H}_5)_2\text{ClSiH}$ 2 · 10², $(\text{C}_2\text{H}_5)\text{Cl}_2\text{SiH}$ 4 · 10⁴, Cl_3SiH 8 · 10⁶ (the chromatograph used could detect substances in amount greater than 0·5 w. %). This increase of the reactivity is however too high, in the light of both the interrelations between the structure and reactivity of silicon hydrides¹³ and the fact that preparative hydrosilylations⁷ with triethylsilane and trichlorosilane (60°C and 6 days) yielded the respective products in 60% and 8% yield, respectively.



We believe these results can be explained in the following way. The Si—Rh bond in complexes *III* (which are formed during hydrosilylation by reaction (*E*)) is strengthened by a Rh—Si back donation (which is made easier by the presence of electro-negative substituents at silicon). This increases the stability of these complexes to such an extent that at 80°C they do not react to form catalytically active intermediates. Such reaction proceeds however at 120°C. It seems reasonable to suppose that the silyl-substituted complexes, whose stability increases in the order $-\text{Si}(\text{C}_2\text{H}_5)_3 < < -\text{SiCl}(\text{C}_2\text{H}_5)_2 < -\text{SiCl}(\text{C}_2\text{H}_5) < -\text{SiCl}_3$ (the temperature of decomposition⁷ 103°C, 142°C, 158°C, 168°C), may undergo exchange reactions of their silyl ligands which would probably result in the formation of the complex substituted by the silyl ligand having a greater number of chlorine atoms since this is more stable. This assumption is not improbable since silyl ligands in complexes of this type are known

to undergo exchange reactions relatively easily⁸. The fact that we have always found in the reaction mixtures only the products of the addition of the silane having a greater number of chlorine atoms might indicate that this exchange is fast and practically quantitative before the complex *III* is attacked by an olefin.

The addition of the chloro-substituted silicon hydrides to 1-heptene catalyzed by 0.1 ml of 0.01M benzene solution of $\text{Co}_2(\text{CO})_8$ gave very low yields of hydrosilylation products, which made analysis of the reaction mixture by gas chromatography impossible. Only after the concentration of the catalyst had been increased by about two orders of magnitude (*i.e.* when c. $1 \cdot 10^{-1}$ mol of the catalyst had been used) satisfactory yields were obtained. It is noteworthy that similar concentration of the catalyst has also been used by MacDiarmid⁹. However, it is difficult to speak here of hydrosilylation as homogeneous reaction, since a certain amount of the catalyst remains undissolved. In this case differences in the reactivity of individual members of the series are relatively small (Cl_3SiH 1, $(\text{C}_2\text{H}_5)\text{Cl}_2\text{SiH}$ 1.3, $(\text{C}_2\text{H}_5)_2\text{SiSiH}$ 1.5, $(\text{C}_2\text{H}_5)_3\text{SiH}$ 1.6). Furthermore, it should be stressed that, besides reactions (A)–(D) that describe the course of hydrosilylation, reactions (F) and (G) may proceed as well.



I

The formed complex *I*, whose stability increases on going from trialkylsilyl to trichlorosilyl group¹⁸, is ineffective in hydrosilylation. Therefore, reactions (F) and (G) must be suppressed by excess of an olefin¹⁹, which increases the rate of reaction (B). However, in the determination of relative rate constants by the method of competition reactions it is necessary to use excess of silicon hydrides so that side reaction (A) (the rate of which increases with increasing number of electronegative groups bonded to silicon) prevails over reaction (B) which is, however, the necessary step in hydrosilylation mechanism.

In conclusion it can be said that our results support current views on the course of homogeneously catalyzed hydrosilylation (Equations (A)–(E), (F) and (G)) *i.e.* that the reaction proceeds *via* formation of the transition metal–hydrogen bond, followed by insertion of an olefin into this bond.

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