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Compounds of β-Cyclodextrin and Organosilicon Oligomers

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ABSTRACT

Products of hydrolysis and condensation of organosilicon monomers in the presence of β-cyclodextrin (cycloheptaamylose β-CD) were studied by IR, NMR, MS, and x-ray methods. It was established that when an aqueous solution of β-CD is treated with dimethyldichlorosilane (DMDCS), diphenyldichlorosilane (DFDCS), methylphenyldichlorosilane (MFDCS), or with a mixture of the DMDCS and DFDCS, crystalline compounds of cyclodextrin with appropriate siloxane oligomers are formed: β-CD·MSO (69% yield by weight), β-CD·FSO (6.0% yield by weight), β-CD·MFSO (16%) yield by weight), β-CD·(MSO + FSO) (22-63% yield by weight). The content of the obtained products showed: β-CD:MSO = 1 mole of β-CD:2 $(CH_3)_2SiO$ elements; β-CD:FSO = 1 mole of β-CD:0.57 mole of $(C_6H_5)_2SiO$; β-CD:MFSO = 1 mole of β-CD:0.87 mole of $(CH_3)\ (C_6H_5)SiO$. Contents of β-CD·(MSO + FSO) depend on the starting monomer mixture. It is suggested that nonchemical bonds between β-CD molecules and siloxane elements occur. The topological structure of the obtained substances is analyzed. Analogous compounds are not formed with methyltrichlorosilane, triphenylchlorosilane, diethoxydichlorosilane, dimethyldimethoxysilane, dimethyldiacetoxysilane, or silica tetrachloride. Compounds with β-cyclodextrin are not formed from already formed siloxane oligomers. In the processes described above, linear dextrins show a total lack of activity. Methylsiloxanes bound with β-CD have a cyclic structure, while phenyl ones probably have a linear structure.

INTRODUCTION

Since the appearance of the first publications announcing the synthesis of topological compounds [1, 2], some workers have been seeking possibilities of obtaining such compounds in various branches of organic chemistry.

The paper presented here covers one of the stages of research on the synthesis of polymeric topological compounds based on Schardinger's cyclic dextrins and organosilicon monomers. The authors are making attempts to develop research results on the synthesis of polymeric topological compounds, using inclusion compounds as intermediate substances in the snythesis.

It is well known that Schardinger's cyclic dextrins form inclusion compounds with numerous organic substances. Such adducts are very easily formed with different chlorohydrocarbon halides [3]. It seemed of interest to study the possibility of forming adducts of cyclic dextrins with organosilicon halides, which could be a future basis for synthesis of polymeric topologs containing cyclodextrin molecules. Although a different topological structure is considered here, that is, a structure which is formed from organosilicon compounds and cyclodextrin molecule, it might be useful to recall that in 1953 the possibility that topological structures may occur in pure siloxane polymers had already been raised [4].

In our research on the possibility of forming adducts there was one attractive unknown, namely, the behavior of organosilicon monomers included in inclusion compounds with β-cyclodextrin in the presence of water. Water plays an important part in the formation of inclusion compounds [5] and probably cannot be eliminated from the medium of reaction. The common way of obtaining inclusion compounds is by the action of a specific, usually organic, substance on an aqueous solution of cyclic dextrins. A crystalline sediment of the inclusion compound is formed. In the case of organosilicon monomers, the presence of water in the medium must cause immediate hydrolysis of the chlorine substituent and condensation of the obtained silanols together with the formation of products which have increased molecular weight. The possibility that silicon halides may react with hydroxyl groups of cyclodextrin and form chemical compounds with Si–O–C bonds in the presence of water is remote, yet it cannot be completely eliminated. Under the conditions of the experiment, other chemical reactions of significant yield between cyclodextrin and organosilicon monomers are eliminated.

In the present paper we are trying to find an answer to three main questions: (1) Do organosilicon monomers form inclusion compounds with cyclodextrin: If so, what monomers? (2) What occurs after the reaction with water? (3) Do chemical bonds of the type –C–O–Si– occur between dextrin and silicon compounds during the experiment?

RESULTS AND DISCUSSION

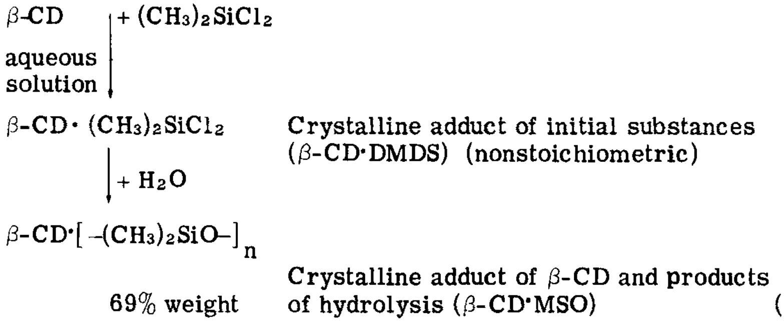
β-Cyclodextrin (CD) (cycloheptaglucan) was used as cyclic dextrin. The following silane derivatives were used as silicon compounds: dimethyldichlorosilane (DMDCS), methyltrichlorosilane (MTCS), diphenyldichlorosilane (DFDCS), methylphenyldichlorosilane (MFDCS), phenyltrichlorosilane (FTCS), dimethyldimethoxysilane, dimethyldiacetoxysilane, diethoxydichlorosilane, and silicon tetrachloride.

Method of Obtaining Compounds

An aqueous solution of β-cyclodextrin was shaken at room temperature with an appropriate monomer or with a solution of this monomer in ethyl acetate. The precipitates remaining after filtration were rinsed successively with water, acetone, ethyl acetate, acetone, and water. Water dissolved the free cyclodextrin while the organic solvents removed monomeric compounds of silicon uncombined with cyclodextrin and products of their condensation (their total solubility in chosen solvents had been confirmed in earlier tests). After rinsing, the precipitates were studied further, either directly or after recrystallizing from water.

Compounds of β-Cyclodextrin with Products of Hydrolysis (MSO) of Dimethyldichlorosilane (β-CD·MSO)

During stirring of dimethylchlorosilane with β-cyclodextrin solution, a crystalline product of reaction precipitates immediately. The obtained compounds are probably formed according to the scheme shown in Eq. (1). The product of reaction is formed with the yield of 69% by weight in relation to the initial β-CD. The product is a nonmelting, fine crystalline powder insoluble in water at room temperature, and completely soluble in DMF, DMSO, and in boiling water. The IR spectrum (Fig. 1) shows marked similarity to the



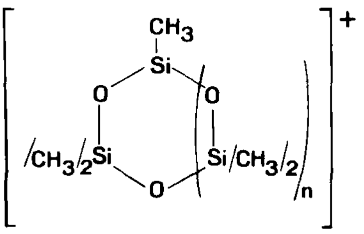
(1)

FIG. 1. IR spectrum of β-CD·MSO.

spectrum of β-CD [6]. At the same time it shows absorption bands characteristic of methylsiloxanes at 1270, 810, and 780 cm^{-1} [7].

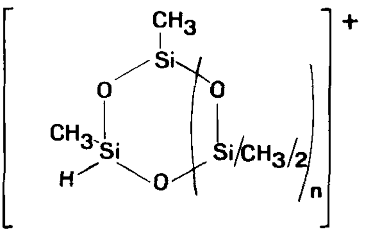
In the NMR spectrum signals with quantitative ratio of protons corresponding to pure β-CD appear; signals of protons from methyl groups of silicone are apparent in the δ0 area. According to the literature [8], they are shifted by 0.08 in relation to standard signals $(CH_3)_4Si$. No signals of OH group in the molecule of siloxane have been observed. According to the correlative formula [9] it should occur at $\delta = 5.4$. Although there can be various reasons for the lack of such a signal in the spectrum, in our case it is related to the cyclic structure of siloxane compounds (MSO) present in adducts with β-CD.

The mass spectra of the adducts provide evidence for the cyclic structure of siloxane (Fig. 2). Intensive peaks occur with values of m/e = 133, 207, 281, corresponding to ions of structure I, and m/e = 193, 267, 341 (sometimes), corresponding to ions II [10, 11], that is, ions of cyclic dimers, trimers, and tetramers. Weak signals of higher oligomers (m/e = 355, 415) are also apparent in the spectra. Literature data [10, 11] for mass spectra of cyclic siloxanes were



n=1,2,3, . . .

I



n=1,2,3, . . .

II

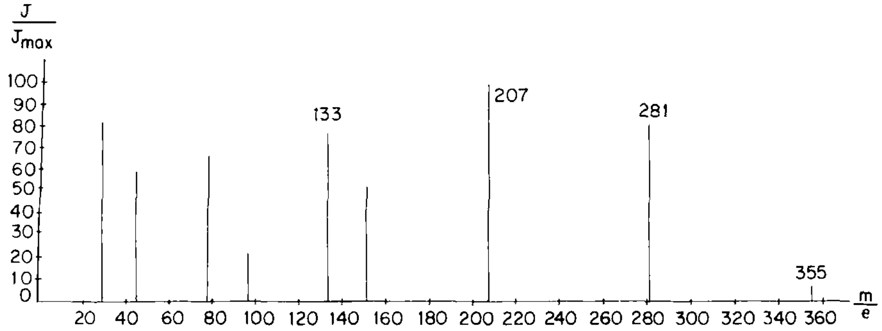


FIG. 2. Mass spectrum of β-CD•MSO.

checked on standards for apparatus on which the analyzed spectra had been recorded.

The absence of peaks characteristic of a product of condensation having a linear structure (147, 221, 295) in the mass spectra should be stressed [10, 11]. The absence of peaks of chlorine ions in the spectra proves the occurrence of complete hydrolysis of DMDCS.

β-CD•MSO are not completely stable compounds; still they retain some degree of stability even in an aqueous solution at boiling point and can be crystallized from it. Crystallized adducts do not differ significantly from products rinsed with solvents (IR, NMR, MS). Under the influence of boiling water, β-CD•MSO adducts undergo an irreversible dissociation together with formation of silicon oil and free cyclodextrin.

The quantitative composition of adducts does not change under the influence of an organic solvent. The formation of cyclic siloxanes in β-CD•DMDCS adducts is the proof for the absence of chemical bonds between β-CD and MSO in β-CD adducts. Control tests have been carried out the main idea of determining the reaction of DMDCS with dextrins which have a linear structure. (They are incapable of forming inclusion compounds.) No compounds of dextrin with siloxane oligomers have been observed in the products of reaction.

The nonchemical character of bonds between β-CD and MSO is derived also from x-ray studies. The β-CD MSO diffraction patterns with respect to d values are identical with those of typical inclusion compounds, e. g., β-CD with a mixture of methyl methacrylate and vinylidene chloride.

The chemical modification of cyclodextrin with siloxane groups would have to lead to changes in the crystalline structure of the compound. The absence of these changes can only result from the fact that in the β-CD (methyl methacrylate + vinylidene chloride) and β-CD·MSO compounds, the same element, common for all, is that fragments of chemically unchanged β-cyclodextrin form a crystalline net.

It should also be mentioned that as a result of forming chemical bonds between β-CD and MSO, insoluble crosslinked products would have to be formed in high yield in the process (69%). In relation to DMDCS, β-CD is at least a seven-functional compound (considering the possibility of reacting with primary OH groups only), and chemical reactions including both these compounds should invariably lead to crosslinked products. On presuming however that DMDCS reacts only within one molecule of β-CD, that is with two adjacent OH groups and not intermolecularly, giving uncrosslinked products, this would disagree with the results of research on the reaction carried out with different quantity of DMDCS in relation to β-CD. These results show that products with the same quantity of organosilicon elements are always formed: 2-mers $-Si(CH_3)_2-O-$ per β-CD molecule, regardless of the quantitive ratio of initial substrates. In such a case it would be difficult to explain why only four out of 21 OH groups which are present in the β-CD molecule take part in the chemical reaction (of 21, seven are primary OH groups). It is worth stressing that no increase of the siloxane content in the product isolated after a consecutive action of a new portion of dimethyldichlorosilane takes place. Such an increase would have been observed if a chemical reaction between the substrates had really taken place.

The final confirmation for the lack of Si–O–C bonds is that content of OH groups in the bound cyclodextrin does not differ from the content of these groups in pure β-CD.

The NMR spectra of eight samples showed a constant ratio of hydrogen atoms $(O_2H + O_3H):O_6H:C_1H$ of 2:1:1, with total agreement of chemical shifts with literature data [6].

The evidence for the lack of chemical bonds between β-CD and MSO in the reaction product seems to be sufficient. Thus the product should be included in the number of additive compounds.

β-CD·MSO is not, however, a typical inclusion compound which cyclic dextrins form with other substances. First of all, it irreversibly dissociates in water, and this means that the isolated siloxane part does not tend to re-form an inclusion compound with β-CD. These compounds are also not formed on treatment of the β-CD solution with siloxane oligomers containing cyclic oligomers which had been obtained separately without the help of β-CD. Thus the conclusion can be drawn that siloxane molecules which are formed with β-CD have been forced to stop in situ within the β-CD molecules where they had appeared as the result of an earlier formation of inclusion dimethyldichlorosilane compound. We can presume that molecules of cyclic methylsiloxane oligomers combine with β-CD molecules in a purely mechanical way and the compounds which are formed are rather of a topological character.

Compounds of β-Cyclodextrin with the Products of Hydrolysis of (MSO + FSO)

Analogously with reactions with pure dimethyldichlorosilane, crystalline compounds are formed with siloxane oligomers (β-CD)·MSO + FSO) on treatment of β-cyclodextrin with a mixture of DMDCS and diphenyldichlorosilane (DFDCS). Depending upon the content of the primary mixture of monomers, adducts are formed with different yields. Figure 3 shows that the yield of the process decreases with the increase of DFDCS content in the primary mixture and that pure DFDCS gives an adduct with a yield of 6.2% by weight, which is about ten times less than DMDCS (69%). It is worth noting that the yield of the process decreases still further when a phenyl group appears beside the methyl group within the molecule of the same monomer. An illustration of this is the example of methylphenyldichlorosilane which forms adducts with β-CD with smaller yield than a monomer mixture having the same ratio of methyl and phenyl groups (DMDCS 30% by weight + DFDCS 70% by weight).

Figure 4 shows the relationship between the content of β-CD·(MSO + FSO) adduct and the content of the primary mixture of monomers. As can be seen, the content of $-(C_6H_5)_2SiO-$ in the product initially increases together with the increase of DFDCS concentration in the monomer mixture. From the concentration of 30% upwards, this content maintains a constant level and is approximately equal to the content of this structural unit in the case of pure DFDCS (0.57 mole/mole of β-CD), whereas the content of $-(CH_3)_2SiO-$ units in the adduct increases continuously, reaching a value of 2.3 mole for pure DMDCS. Important characteristics of the formation of β-CD (MSO + FSO) adducts is the fact that according to the analysis of the mass spectra in intermediate β-CD·(DMDCS + DFDCS) adducts both monomers react separately, giving two kinds of oligomers: methylsiloxane

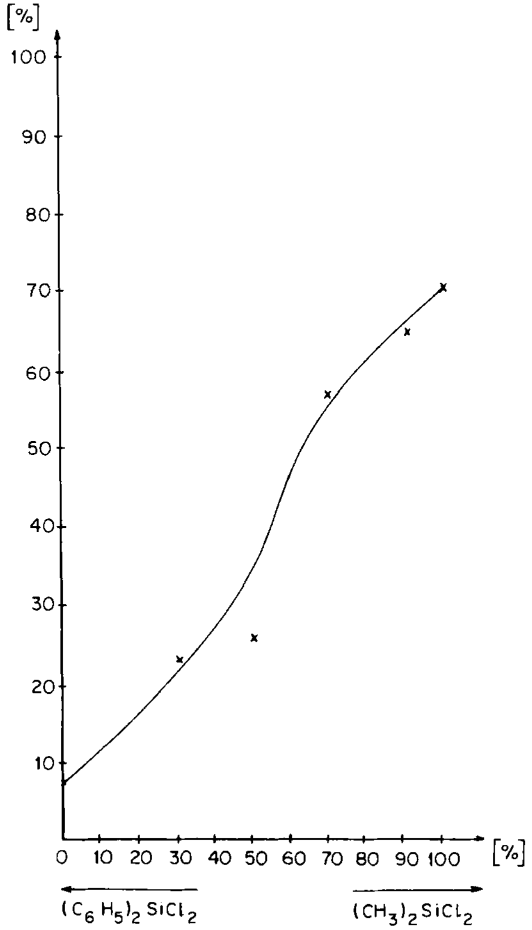


FIG. 3. Yield of reaction for different mixtures DMDCS and DFDCS.

(MSO) and phenylsiloxane (FSO). Mass spectra, which precisely correspond to the sum of spectra (peaks) for products obtained from pure monomers, are recorded for all mixtures. No new signals exist which could prove the presence of cocondensation products .

The mobility of the monomer in the net is probably not great, and does not allow contacts between molecules from two different monomers, which according to what had been said above are organized in blocks of the type AAA BBB AAA, where A and B are molecules of DMDCS and DFDCS, respectively.

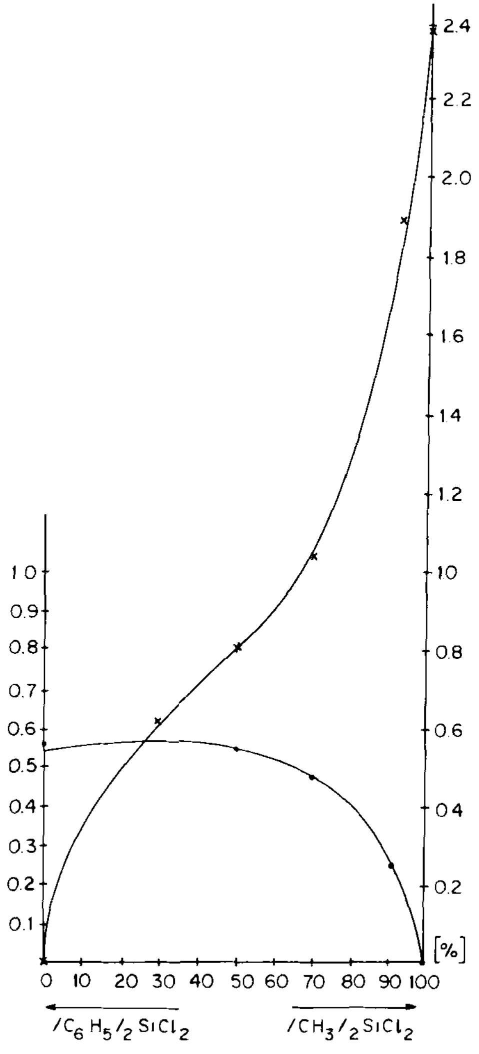


FIG. 4. Composition for the adduct β-CD·(MSO + FSO) depending on the compositions of the DMDCS and DFDCS mixture: (×) $(CH_3)_2SiO$–; (●) $(C_6H_5)_2SiO$–.

According to mass spectra, methylsiloxane oligomers present in the adducts have an exclusively cyclic structure, analogously to adducts obtained from pure DMDCS. This confirms the lack of chemical bonds between β-CD and –$(CH_3)_2SiO$– structural units in the adducts.

Most probably however, there are linear structures in phenylsiloxane compounds. NMR spectra show signals at δ values which according to the correlative formula [9] are characteristic of OH end groups for methylphenylsiloxane oligomers (6.69 δ) and for phenylsiloxane oligomers (7.02 δ).

The formation of cyclic oligomers with dimethyldichlorosilane and of linear oligomers with monomers containing phenyl substituents is a situation reverse to normal polycondensation of organosilicon monomers. According to the literature [12], phenyl monomers display greater tendencies for cyclization than monomers with methyl substituents. The reverse situation which occurs is probably due to spheric limitations occurring inside the canal of the inclusion β-CD compound.

After examining a molecular model (of the space-filling type), it is evident that at least the hexaphenyltrisiloxane ring does not fit into the canal. The information mentioned above proves that the sequence, in which the formation of the final products occurs, is as presented on the scheme, that is: first the inclusion compound of the chloro derivative of the organosilicon compound is formed; then, under the specific conditions of the crystal system with β-cyclodextrin, hydrolysis of chlorine substituents occurs, followed by the condensation of the formed diols.

Such a course of reaction would explain the fact that methyl and phenyl oligomers are formed separately from a mixture of monomers as well as the fact that copolycondensates are absent in the products of reaction.

The β-CD·(MSO + FSO) adducts in crystalline form are not a simple mixture of β-CD·MSO and β-CD·FSO adducts, but probably form a system of their own.

Although x-ray diffraction diagrams of the adduct obtained from a mixture of 70% of DMDCS and 30% of DFDCS and of products obtained from pure DMDCS and DFDCS separately are identical and do not prove the thesis, yet x-ray diffraction diagrams of adducts obtained from the formed mixture differ from those of adducts obtained with pure monomers and they are not the sum of reflections appearing in the diffraction diagrams of β-CD·MSO and β-CD·FSO adducts.

The general characteristic feature of β-CD·(MSO + FSO) in crystalline form is the great stability in comparison to β-CD·MSO and β-CD·FSO adducts. Dissociation of mixed systems occurs only after heating for 1 hr with water while for example β-CD·FSO dissociates completely immediately after reaching the boiling point of water. Dissociation of β-CD·(MSO + FSO) under the influence of hot water also occurs irreversibly as in the case of adducts obtained from pure monomers. β-CD·(MSO+ FSO) adducts are not formed as the result of action of separately obtained products of common hydrolysis and condensation of the mixture of DMDCS and DFDCS monomers. It can be thus assumed that in this case also we are dealing with compounds of a rather topological structure.

Attempts at Synthesis of β-Cyclodextrin Products with Other Organosilicon Monomers.

The studied monomers, with the exception of dimethyldichlorosilane and diphenyldichlorosilane, also form adducts of β-cyclodextrin organosiloxane type with methylphenyldichlorosilane. The remaining monomers, that is, methyltrichlorosilane, triphenylchlorosilane, diethoxydichlorosilane, dimethyldimethoxysilane, dimethyldiacetoxysilane, silica tetrachloride, give condensation products which do not contain β-CD molecules.

The ability of individual monomers to form adducts with β-CD probably depends on many factors. In light of the achieved results the most important of those factors seems to be the following: (1) that the monomer belong to a group of compounds which display a general tendency to form inclusion compounds with cyclodextrins, for example, the halogen derivative compounds; (2) that the rate of monomer hydrolysis and condensation is moderate, commensurable with the rate of adduct formation; (3) that the product is fairly stabile.

If the ability of a monomer to form adducts with β-cyclodextrin is measured by the yield of the reaction, the following order is established: dimethyldichlorosilane > mixture of dimethyldichlorosilane and diphenyldichlorosilane > methylphenyldichlorosilane > diphenyldichlorosilane. Methyltrichlorosilane and silica tetrachloride probably do not fulfill the second condition, because they are very reactive monomers [13] and give hydrolysis and condensation a chance to occur before the process of inclusion can occur.

EXPERIMENTAL

Materials

β-Cyclodextrin from Corn Products Company was crystallized from water; $\alpha_D^{25} = +162°$ (H_2O). The NMR spectrum of β-cyclodextrin was in agreement with literature data [5].

Dimethyldichlorosilane (DMDCS), methyltrichlorosilane (MTCS), diphenyldichlorosilane (DFDCS), methylphenyldichlorosilane (MFDCS), triphenylchlorosilane (TFCS), dimethyldimethoxysilane, dimethyldiacetoxysilane, diethoxydichlorosilane, and silicon tetrachloride were freshly distilled or crystallized.

Analytically pure or freshly distilled solvents were used.

Equipment

IR spectra were obtained on a Specord 71 IR spectrometer. NMR spectra were obtained on a JNM-MH-100 NMR spectrometer. Mass spectrography was with an LKB-9000 instrument (Sweden). The x-ray radiography was carried out with a 50 JM diffractometer (Soviet Union).

Action of DMDCS on β-Cyclodextrin Solution

β-Cyclodextrin (8 g) was dissolved in 400 ml of water and DMDCS (4 g) added during mixing. After 2 hr of reaction a precipitate was separated on the Schott funnel and was successively rinsed with water, acetone, ethyl acetate, acetone, and water. The sediment was air-dried and then dried in a desiccator over P_2O_5 . The yield of the reaction was 68.9% by weight. The IR spectrum is the same as for β-CD, showing in addition bands at 1270, 910, 810, and 780 cm^{-1}. NMR (DMSO-d_6) showed δ = 0.08 (64 H, $-CH_3$); 4.53 (s, 32 H, O_6H); 4.85 (s, 31 H, C_1H), and 5.76 (s, 64 H, $O_2H + O_3H$). The mass spectrum showed peaks with m/e (and I/I_{max}) = 43 (48%), 55 (24%), 60 (55%), 73 (25%), 77 (27%), 85 (15%), 90 (19%), 103 (13%), 113 (31%), 126 (17%), 133 (24%), 144 (17%), 151 (17%), 163 (2%), 191 (11%), 193 (9%), 207 (100%), 223 (3%), 249 (2%), 251 (3%), 263 (3%), 281 (59%), 355 (6%).

Determination of the Influence of the Amount of DMDCS on the Content of the Inclusion Compound

The amount of organosilicon monomer was increased, that is 1.5 g of monomer was used instead of 0.5 g per 50 ml of the 2% aqueous solution of β-cyclodextrin. The other conditions of the reaction remained unchanged. The product was separated as described above; 1.74 g of the compound was obtained (57.8% by weight). NMR (DMSO-d_6) showed δ = 0.08 (s, 30 H, CH_3-), 4.53 (s, 16 H, O_6H), 4.85 (s, 15 H, C_1H), and 5.76 (s, 32 H, $O_2H + O_3H$). A 2.0-g portion of β-cyclodextrin was dissolved in 100 ml of water and 1.0 g of monomer was added. Then after 0.5 hr of reaction, 1.0 g of monomer was added again, and another 1.0 g after another hour. The reaction was carried on for another 2 hr. The product was separated in the usual way. The yield of the reaction was 62.1% by weight. NMR (DMSO-d_6) showed δ = 0.08 (s, 10 H, CH_3-), 4.53 (s, 6 H, O_6H), 4.85 (s, 6 H, C_1H), and 5.76 (s, 12 H, $O_2H + O_3H$).

Determination of Stability of β-CD·MSO Inclusion Compound

The dried crude precipitate of the β-CD·MSO compound was extracted with ethyl acetate in a Soxhlet apparatus, anhydrous conditions being maintained. A 1.1 g portion of precipitate was extracted with 20 ml of solvent over a period of 25 hr and at the boiling temperature of ethyl acetate (77°C). The precipitate was dried and weighed, yielding 1.1 g. The NMR of the sediment (DMSO-d_6) showed δ = 0.08 (s, 20 H, CH_3-), 4.53 (s, 10 H, O_6H), 4.85 (s, 10 H, C_1H), and 5.76

(s, 19 H, $O_2H + O_3H$). β-CD•MSO compound (5 g) was added to 250 ml of boiling water and kept at a boil for 10 min. When the solution was cooled to room temperature, no precipitate was observed. Signs of oil could be seen on the walls of the vessel. The solution was evaporated to dryness and was rinsed in the known way. The IR spectrum of the oil showed bands at 1270, 910, 810, and 780 cm^{-1}. NMR of the precipitate (DMSO-d_6) showed $\delta = 4.53$ (s, 19 H, O_6H), 4.85 (s, 19 H, C_1H), and 5.76 (40 H, $O_2H + O_3H$).

Crystallization of the β-CD•MSO Inclusion Compound

A 7.0-g portion of compound was added to 350 ml of water and heated to the boiling point. The precipitate obtained after cooling was filtered off, rinsed, dried in air, and then in a desiccator over P_2O_5. The yield calculated for pure β-CD was 18.3% by weight.

NMR (DMSO-d_6) showed $\delta = 0.08$ (s, 21 H, CH_3), 4.53 (s, 10 H, O_6H), 4.85 (s, 11 H, HC_1), and 5.76 (s, 20 H, $O_2H + O_3H$).

Recrystallization did not give positive results despite cooling with ice.

Attempts to React of DMDCS with Linear Dextrins

The reaction of DMDCS with linear dextrins was carried out in the same way as with β-cyclodextrin. No precipitate was observed to form during the reaction or during the next few days. Drops of oil were visible on the surface of the mixture. The solution was neutralized with sodium carbonate and filtered through a wet filter. Then the water was evaporated and the precipitate was rinsed and dried. The IR spectrum is the same as that of linear dextrin.

Action of Methylsiloxane Oligomers (MSO) on β-CD

A 2% aqueous solution of β-CD was treated with silicon oil, previously obtained in the hydrolytic polycondensation of DMDCS and shaken for 1 hr. No precipitate was observed. After separation and evaporation of water the precipitate was rinsed in the usual way. NMR of the precipitate (DMSO-d_6) showed $\delta = 4.53$ (s, 15 H, O_6H), 1.85 (s, 15 H, C_1H), 5.76 (s, 30 H, $O_2H + O_3H$).

Action of DMDCS and DFDCS Mixture on β-CD

A 7.0-g portion of β-CD was dissolved in 350 ml of water. During vigorous mixing 3.5 g of 10% DFDCS solution in DMDCS was added.

After 2 hr the product was separated in the usual way; 4.47 g of white crystalline precipitate was obtained. The yield of the reaction was 63.0% by weight. NMR (DMSO-d_6) showed δ = 0.08 (, 14 H, CH_3), 4.47 (s, 10 H, O_6H), 4.83 (s, 10 H, C_1H), 5.76 (s, 19 H, $O_2H + O_3H$). 7.02, 7.60 [t, 3H, C_6H_5 + HO–Si–$(C_6H_5)_2$].

The synthesis of inclusion compounds of β-CD with other mixtures was conducted in a similar way. The weight ratio of monomers to β-CD was maintained, only the composition of the monomer mixture changed and was as follows: for product (a), 30% DFDCS and 70% DMDCS; for product (b), 50% DFDCS and 50% DMDCS; for product (c), 70% DFDCS and 30% DMDCS. The yield of the individual syntheses was 56.1%, 24.5%, 22.5%.

NMR spectra of all products were similar as shown in Table 1. Table 1 does not show less characteristic peaks of β-CD at δ = 3.30–3.64.

The mass spectra for product (a) above showed m/e (and I/I_{max}) = 28 (68%), 44 (46%), 60 (6%), 66 (98%), 78 (35%), 84 (98%), 96 (18%), 133 (19%), 139 (91%), 154 (40%), 188 (12%), 207 (100%), 216 (43%), 222 (5%), 281 (13%), 296 (3%), 355 (2%). The mass spectrum for product (b) showed m/e (I/I_{max}) = 28 (82%), 44 (48%), 55 (22%), 78 (74%), 84 (20%), 133 (37%), 139 (70%), 151 (38%), 188 (14%), 207 (100%), 216 (30%), 222 (10%), 224 (7%), 281 (20%), 355 (1%).

Attempts to Obtain Inclusion Compounds in the Reaction between β-CD and Siloxane Oligomer

Silicon oil was added to a 2% aqueous solution of β-CD. The oil had been obtained from hydrolytic condensation of DMDCS and DFDCS monomer mixture, used in the proportions 30% DFDCS and 70% DMDCS and also 50% DFDCS and 50% DMDCS. During the 2 hr of reaction and vigorous mixing no precipitate was formed. After the separation of the oil and the evaporation of water the dry residue was examined by NMR. The NMR (DMSO-d_6) showed δ = 4.53 (s, 12 H, O_6H), 4.85 (s, 12 H, C_1H), 5.76 (s, 24 H, $O_2H + O_3H$).

Action of DFDCS on β-CD

A 4-g portion of β-CD was dissolved in 200 ml of water and 2 g DFDCS added. After 2 hr reaction, the product was separated in the usual way and 0.25 g of precipitate was obtained. The yield of the reaction was 6.2% by weight. NMR (DMSO-d_6) showed δ = 4.50 (s, 17 H, C_6H), 4.85 (s 18 H, C_1H), 5.82 (s, 36 H, $O_2H + O_3H$) 7.20, 7.68 [t, 14 H, $(C_6H_5)_2$ Si–].

TABLE 1. NMR Spectra of Products of β-CD with Monomers

	Quantitative Ratio of Protons					Monomeric (mole)	
	$O_2H + O_3H$	C_1H	C_6H	$-CH_3$	$-C_6H_5$	$CH_3-\underset{\underset{O}{\vert}}{Si}-CH_3$	$C_6H_5-\underset{\underset{O}{\vert}}{Si}-C_6H_5$
100% DMDCS	2	1	1	2.00	-	2.30	-
90% DMDCS + 10% DFDCS	2	1	1	1.40	0.3	1.70	0.22
70% DMDCS + 30% DFDCS	2	1	1	0.73	0.68	1.00	0.50
50% DMDCS + 50% DFDCS	2	1	1	0.67	0.78	0.80	0.54
30% DMDCS + 70% DFDCS	2	1	1	0.50	0.63	0.60	0.45
100% DFDCS	2	1	1	-	0.82	-	0.57
100% MFDCS	2	1	1	0.34	0.64	a	

[a] $CH_3-SiO-C_5H_6$, 0.9 mole.

Action of MFDCS on β-CD

The synthesis of β-CD and MFDCS was conducted in the same way. The yield of the reaction was 16.26% by weight. NMR (DMSO-d_6) showed $\delta = 0.18 + 0.27$ (d, 3 H, CH_3–), 4.50 (s, 8 H, O_6H), 4.85 (s, 8 H, C_1H), 5.76 (s, 16 H, $O_2H + O_3H$), 6.69 (s, 1 H, HO–Si), 7.39, 7.56 [d, 5 H, $(H_5C_6)_2$–Si–].

The mass spectrum showed the following peaks and their intensity ratios: m/e (I/I_{max}) = 32 (55%), 44 (33%), 77 (24%), 91 (12%), 121 (12%), 139 (100%), 154 (35%), 197 (77%), 213 (5%), 257 (14%), 291 (76%), 315 (3%), 394 (2%), 409 (1%).

Determination of the Stability of β-CD (MSO + FSO) Products

Compounds obtained in individual syntheses were recrystallized, and 2% solutions of these compounds were heated to the boil. β-CD dissolved completely. Drops of oil were observed on the walls of the vessel. The remaining products were partially soluble. After cooling of solutions precipitates in the form of fine white powders were obtained. Alternately, the products were placed in boiling water and boiled. In the case of β-CD•FSO, the precipitate dissolved immediately, whereas the other solids dissolved only after 1 hr. The experiments were repeated after adding ethyl acetate (1 ml/3 ml of aqueous solution). The oil phase was separated from the aqueous phase and after evaporating of the volatile material the residue was studied. The acetate layer contained pure silicone oil (NMR, IR); the aqueous layer contained pure β-CD (NMR, IR).

Inclusion Compounds of β-CD with Other Organosilicon Monomers

Methyltrichlorosilane (MTCS). A 3.0 g portion of β-CD was dissolved in 150 ml of water and 0.5 g of CH_3SiCl_3 added with vigorous mixing. A white precipitate formed immediately. It was filtered and rinsed in the usual way. The precipitate obtained did not melt, and it was partially soluble in boiling water. β-CD was recovered from the filtrate almost quantitatively by precipitation with fluorobenzene.

In the NMR spectrum of the product signals characteristic of β-CD are absent.

Triphenylchlorosilane (TFCS). A 1.5 g portion of TFCS dissolved in ethyl acetate was added to 150 ml of 2% solution of β-CD in water. The reaction was carried on for 2 hr, then the reaction product was purified. It was observed that after every elution with the rinse liquid the amount of sediment on the filter greatly decreases. Minute quantities of sediment remained on the filter.

Other Monomers. The reactions with diethoxydichlorosilane, dimethyldimethoxysilane, dimethyldiacetoxysilane, and silicon tetrachloride monomers were carried out in the same way.

No β-CD was observed in the obtained products.

CONCLUSIONS

From the results of these investigations the following conclusions can be drawn.

1. The hydrolysis of dimethyldichlorosilane, diphenyldichlorosilane, and methylphenyldichlorosilane as well as of the mixture of dimethyldichlorosilane and of diphenyldichlorosilane in the presence of β-cyclodextrin leads to the formation of compounds of β-cyclodextrin and siloxane oligomers.
2. Bonds in the products of reaction between β-cyclodextrin molecules and methylsiloxane oligomers are of nonchemical type.
3. The topological structure of compounds of β-cyclodextrin and siloxane oligomers appears to be probable.
4. The formation of a compound of β-cyclodextrin and siloxane oligomers is preceded by the formation of an inclusion compound with the chlorosilicon monomers.
5. In the presence of β-cyclodextrin, contrary to what occurs usually, the influence of methyl and phenyl substituents on the ability of chlorosilanes to form siloxane compounds with cyclic structure can be observed. Methyl cyclosiloxanes are more easily formed than phenyl cyclosiloxanes.
6. The yield of compounds of β-cyclodextrin with siloxanes depends on the type of monomer. The yield for dimethyldichlorosilane is 69%, for diphenyldichlorosilane it is 6.2%, and for the mixture of the monomers the mean between these.

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