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Occlusion of Organosilanes by Urea[1]

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The presence of a silicon atom in a hydrocarbon chain does not prevent occlusion by urea. The occlusion compounds of three monoalkylsilanes and four dialkylsilanes formed, decomposed, and can be purified and separated in the same manner as the corresponding hydrocarbons.

Introduction

Urea occlusion compounds variously referred to as urea-inclusion compounds, urea complexes, urea adducts and channel complexes can be made with a variety of organic molecules bearing various functional groups.[2] Briefly, urea, the host molecule, forms a hexagonal prism into which a guest molecule having the requisite length and cross-sectional diameter can fit.[2] The cross-sectional diameter of the guest molecule cannot exceed 6 Å. This figure was determined by measuring the maximum cross-sectional diameters of those molecules already reported to form urea occlusion compounds. Among the hydrocarbons, retained only by van der Waals forces, *n*-hexane is the smallest member which can form an occlusion compound. On the other hand, *n*-butyric acid and acetone are the shortest acid and ketone, respectively, which will form an occlusion compound. In all cases the guest molecule must assume a planar zigzag conformation in order to have the necessary cross-sectional diameter. In any homologous series the stability of the occlusion compounds increases with the chain length of the molecule.[3]

Urea occlusion compounds have been most extensively used in the petroleum, oil and fat fields. This study was undertaken to determine the feasibility and applicability of preparing urea channel complexes of alkylsilanes.

Discussion

In order to determine whether or not alkylsilanes would form urea channel complexes, the necessary mono- and dialkylsilanes[4] were prepared. The maximum cross-sectional diameter determined from Stuart–Briegleb models was 5.1 Å., for both monoalkyl and dialkylsilanes[4] as compared to 4.6 Å., for a linear hydrocarbon chain. Both measurements were made after the molecular models were oriented in the planar zigzag conformation. The minimum and maximum inside channel cross-sectional measurements of the hexagonal urea prism are approximately 5.3 and 6.0 Å., respectively.[5]

Hence, for a mono- or dialkylsilane approaching a planar zigzag conformation, the cross-sectional diameter should permit the formation of a urea occlusion compound.

Experimental

Sources of Silanes.—The starting chlorosilanes were a product of Peninsular Chemresearch, Inc., of Gainesville, Fla., and were purified by distillation before use.

Diamyl- and dibutylsilane[6] were kindly supplied by Professor John S. Peake.

Trinonylsilane, dodecyl-tri-decylsilane and dodecyltri-*n*-propylsilane were kindly supplied by Dr. Christ Tamborski.

Dioctylsilane.—From the distillation of commercial dioctyldichlorosilane[7] there was obtained a fraction, b.p. 160° at 1.5 mm., $n^{21}\text{D}$ 1.4542. This fraction (40.70 g., 0.125 mole) was added under nitrogen with stirring to a 100-ml. ether suspension of 6.2 g. (0.163 mole) of lithium aluminum hydride at a rate that kept the ether boiling gently. After the addition was complete, the ether was boiled off and the remaining silane was decanted from the solid residue and distilled. There was obtained 22.5 g. (70.4%), b.p. 160–164° at 6 mm., $n^{25}\text{D}$ 1.4441, of a clear colorless acrid smelling liquid.

The other silanes were similarly prepared. The low boiling amylsilane and hexylsilane were isolated by distilling through a 10″ Vigreux column at atmospheric pressure.

A summary of the physical properties and data obtained on the prepared silanes are listed in Table I. The spectral data are listed in Table II.

A band of marked intensity for the monoalkylsilanes occurred at about 925 cm.$^{-1}$. For the dialkylsilanes, this band occurred at about 943 cm.$^{-1}$. These bands may be attributed to the deformation vibrations of the SiH_3– group and –SiH_2– group, respectively.[6] The Si–H stretching occurred at 2300 cm.$^{-1}$ for the monoalkylsilane and at 2125 cm.$^{-1}$ for the dialkylsilanes. The dialkylsilanes also showed a strong band at 862 to 826 cm.$^{-1}$ associated with silicon–carbon stretching and a rocking[6] mode of the –SiH_2– group which is completely lacking in the monoalkylsilanes. Monoamylsilane was an exception with an Si–H stretching at 2150 cm.$^{-1}$.

It is well known that bands occur in the region of 1100 to 1000 cm.$^{-1}$ for Si–O.[8] In tetradecylmethoxysilane a broad band at 1080 cm.$^{-1}$ is attributed to the Si–O function.

Urea Occlusion Compounds.[9]—All urea occlusion compounds were prepared by mixing a solution of urea in methanol (0.15 g. of urea/cc. of methanol) with the compound to be tested and shaking for 2–3 minutes or until crystals formed. A blank was run by adding the compound to be tested to methanol. If cooling was required, a second blank of the urea methanol solution was used to indicate at what temperature urea comes out of solution. The crystals were filtered on a büchner funnel and washed with a small quantity of ethanol. Lastly, the crystals were dried 17 hours at room temperature and 1 mm. over anhydrous calcium sulfate.

Properties of Occlusion Compounds.—All of the occlusion compounds were white crystalline solids with the melting point of urea. A summary of the X-ray data is listed in Table III.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Southeastern Regional Meeting of the American Chemical Society in Durham, N. C., November 16, 1957.

[2] R. F. Marschner, *Chem. Eng. News*, **33**, 494 (1955).

[3] R. W. Schiessler and D. D. Neiswender, Jr., *J. Org. Chem.*, **22**, 697 (1957).

[4] *Alkyl* as used in this paper will refer only to the normal-primary variety unless otherwise specified.

[5] W. Schlenk, Jr., *Svensk Kem. Tidskr.*, **67**, 450 (1955).

[6] H. E. Opitz, J. S. Peake and W. H. Nebergall, THIS JOURNAL, **78**, 292 (1956).

[7] A product of Peninsular Chemresearch, Inc., of Gainesville, Fla.

[8] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 124 (1949).

[9] All urea occlusion compounds give a positive Beilstein test whether or not halogen is present in the guest member. It should be noted that urea alone gives a positive Beilstein test, *vide* R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 60.

TABLE I

SILANES PREPARED

Silane	B.p. °C.	B.p. Mm.	$n^t{}_D$	t, °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Silicon, % Calcd.	Silicon, % Found	Yield, %
Amyl	75–77	737	1.3995	26	..	..	..	..	27.5	27.3	4.2
Hexyl	...	...	....	..	..	..	..	..	24.2	23.0	19
Dodecyl	71–80	6.7	1.4380	25	71.9	72.2	14.1	14.3	14.0	13.8	48
Tetradecyl	156–164	7	1.4440	28	..	..	..	..	12.3	12.0	34
Dioctyl	160–164	6	1.4441	25	74.9	75.3	14.2	14.0	10.9	10.9	70
Didecyl	...	...	1.4449[a]	25	..	..	..	..	9.0	8.1	25
Tetradecylmethoxy	...	...	1.4410	25	..	..	..	..	10.9	10.9	2.0

[a] d^{25}_4 0.8000; *M*D found 104, calcd. 105.

TABLE II

SUMMARY OF INFRARED DATA[a]

Compound	Wave numbers, cm.$^{-1}$ 4260–4200	2910–2890	2160–2140	2130–2125	1460–1456	1380	1165–1125	1080–1075	943–920
$C_5H_{11}SiH_3$	W	S	S		S	S	W		
$C_{12}H_{25}SiH_3$		S	S		M				S
$C_{14}H_{29}SiH_3$	W	S	S		S			M	S
$C_{14}H_{29}SiH_2(OCH_3)$	W	S	S		S			M	S
$(C_{10}H_{21})_2SiH_2$	W	S		S	S	W	W		
$(C_8H_{17})_2SiH_2$		S		S	M				M

[a] W, weak; M, medium; S, strong.

TABLE III

INTENSITIES[a] OF INTERPLANAR SPACINGS OF OCCLUSION COMPOUNDS, Å.

Silane	7.13–7.19[b]	7.08–7.10	4.11–4.15	4.00	3.85–3.87	3.56–3.62	3.39–3.41	3.05	2.70
Dodecyl	0.5	..	1.0	..	0.1	0.9	0.1	..	0.1
Tetradecyl	.3	..	1.0	..	.1	.8	0.2	..	0.1
Dibutyl	.1	..	0.2	1.0	.1	.3	..	0.3	..
Diamyl	.5	..	1.0	0.4	.2	.7	0.3	..	..
Dioctyl	.2	0.2	1.0	..	.1	.8	.2	..	..
Didecyl	.2	0.3	1.0	..	.1	.8	.2	..	..
(Urea)				(1.0)		(0.4)		(0.5)	

[a] Relative intensities; 1.0 the strongest. [b] CuKα radiation.

Decomposition of Urea Occlusion Compounds.—The crystalline urea complex of the organosilane was decomposed by shaking with excess water in a separatory funnel. When all the crystals were decomposed, a small quantity of ether was added to dissolve the silane. The ether layer is repeatedly washed with distilled water to remove all the urea. Both the decomposition of the urea complex and the subsequent washes of the ether solution were done so as to minimize the contact time of the organosilane with water.

The washed ether solution of the silane was dried over anhydrous granular sodium sulfate and concentrated.[10] If necessary, the residue was distilled. The isolated material was stored in a glass stoppered bottle under nitrogen.

Separation of Tetradecylsilane from Tetradecylchlorosilane.—A mixture of lithium aluminum hydride (2.2 g., 0.0580 mole) and purified tetrahydrofuran[11] (50 cc.) was treated dropwise with stirring with impure *n*-tetradecyltrichlorosilane[7] (19.34 g., 0.0583 mole) over a period of two hours. The reaction mixture was heated for all but the first seven minutes of addition, and was refluxed and stirred for three hours after addition was complete. The tetrahydrofuran was removed at atmospheric pressure and the residual liquid was decanted and distilled. A 4.48-g. fraction (33.6%) was obtained, b.p. 156–164° at 7 mm., $n^{27.8}{}_D$ 1.4440.

Anal. Found: Si, 10.82; Cl, 9.54.

This material (2.47 g.) was shaken with a solution of urea (4.5 g.) in 30 ml. of methanol. The crystals, which formed in less than a minute, were collected, washed with ether (10 ml.) and decomposed by shaking with distilled water. The organic material was then taken up in ether, washed several times with distilled water, dried, and concentrated. The residue, 0.30 g., had a negative Beilstein test, $n^{26}{}_D$ 1.4412.

Anal. Calcd. for $SiC_{14}H_{32}$: Si, 12.29. Found: Si, 12.02.

When the mother liquor and the ether washings from the first crystal crop were combined, a second crop of crystals separated. The crystals were filtered off, washed with 10 ml. of ether, and decomposed as before yielding 0.30 g. (2.0%) of material which gave a negative Beilstein test, $n^{25}{}_D$ 1.4410.

Anal. Calcd. for $SiC_{15}H_{34}O$: Si, 10.87. Found: Si, 10.94.

The remaining mother liquor and washings were dissolved in ether and washed thoroughly with distilled water. The ethereal solution was dried and evaporated leaving 0.75 g. of residue, $n^{25}{}_D$ 1.4500, believed to contain tetradecyldimethoxysilane.

Anal. Calcd. for $SiC_{16}H_{36}O_2$: Si, 9.74. Found: Si, 10.28.

Conclusions

From the experimental results we can conclude that the silicon atom *per se* in the backbone of a linear hydrocarbon chain does not prevent the formation of a urea occlusion compound. However, the data indicate that a silicon atom in the hydrocarbon chain has a destabilizing influence. Hexane is the shortest hydrocarbon molecule that will form a urea complex whereas neither amylsilane nor hexylsilane forms a urea complex.

The greater stabilizing influence of the longer over the shorter alkyl chains is illustrated by the X-ray data. Since these data were taken two weeks after the various urea complexes were prepared, the less stable occlusion compounds partly dissociated. Consequently, the X-ray data indicate that the dibutylsilane urea complex is mixed with a considerable amount of urea which resulted

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[10] J. Radell and P. D. Hunt, *Chemist-Analyst*, **46**, 73 (1957).

[11] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Inc., Boston, Mass., 1955, p. 292.

from dissociation of the complex. The X-ray data of the diamylsilane complex show considerably less urea. On the other hand, the X-ray data of the urea complexes of dioctylsilane, didecylsilane, dodecylsilane and tetradecylsilane showed no signs of dissociation as evidenced by the presence of interplanar spacings characteristic of urea.

The presence of the silicon atom in the linear hydrocarbon chain does not appear to interrupt the planar zigzag arrangement of the molecule required for complex formation.

A summary of classes, cross-sectional diameters and complex-forming ability of alkylsilanes is listed in Table IV.

TABLE IV

CROSS-SECTIONAL DIAMETER IN ÅNGSTRÖMS OF PLANAR ZIGZAG CONFORMATION

	Max.	Min.
$RSiH_3$[a,d]	5.1	4.3
$RSiH_2R$[a]	5.1	4.3
$RSiHCl_2$[b]	6.6	5.4
$RSiCl_3$[b]	6.6	5.7
$RSiHClR$[b]	6.6	5.4
$RSiCl_2R$[b]	6.7	5.4
$RSiH_2OCH_3$[a]	5.1	4.3
$RSiH(OCH_3)_2$[b]	8.5	4.3
$RSiH(OCH_3)R$[b]	8.5	4.3
$RSiH_2Cl$[c]	5.3	4.3

[a] Form urea occlusion compounds. [b] Do not form urea occlusion compounds. [c] Would be expected to form a urea occlusion compound in a non-solvolyzing medium. In our work the Cl was hydrolyzed by methanol to methoxyl and isolated by the formation of a urea complex. [d] Rs sufficiently long normal primary alkyl group.

In separating tetradecylsilane from a mixture of the chlorosilanes remaining after reduction of tetradecyltrichlorosilane with lithium aluminum hydride, a weight-ratio of urea to silane of 1.8 was used. The occlusion compound of tetradecylsilane formed preferentially, and was filtered from the methanol solvent. Upon addition of ether to the filtrate, the occlusion compound of tetradecylmethoxysilane separated. Since tetradecylchlorosilane has the necessary dimensions for complex formation, isolation of the occlusion compound of the methoxysilane only suggests that methanolysis is considerably more rapid than complex formation. The analyses of the material isolated from the mother liquor indicated a mixture of tetradecylmethoxysilane and tetradecyldimethoxysilane.

The presence of an alkoxy[12] group on silicon does not prevent occlusion compound formation. Contrariwise, the alkyldimethoxysilane in the planar zigzag conformation has a maximum cross-sectional diameter of *ca.* 8.5 Å. and does not form an occlusion compound. Urea complex formation thus constitutes a general procedure for separation of alkylmonoalkoxysilanes from alkyldialkoxysilanes.

A number of general applications become apparent. Linear silanes (mono- and dialkylsilanes) may be separated from tri- and tetraalkylsilanes or from highly branched mono- and dialkylsilanes. Furthermore, alkylsilanes which form occlusion compounds may be stored as solid complexes thus providing a means of protecting the reactive silicon hydride which tends to be decomposed slowly by the alkali present in glass in which the material is sealed.[13]

The X-ray powder diffraction diagrams of the urea occlusion compounds of organosilanes are similar to those of all other urea occlusion compounds and different from that of urea[14] alone. Although the X-ray technique is valuable in determining whether or not the occlusion compound has formed, it cannot be used to distinguish one occlusion compound from another. All urea occlusion compounds of the organosilanes had the melting point of urea, although a transition point described by Swern, *et al.*,[15] was observed.

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[12] Alkoxy is used to designate a derivative of a primary normal alcohol only.

[13] E. Rochow, private communication.

[14] A. E. Smith, *Acta Cryst.*, **5**, 224 (1952).

[15] H. B. Knight, L. P. Witnauer, L. P. Coleman, J. E. Noble and D. Swern, *Anal. Chem.*, **24**, 1331 (1952).