

CLEAVAGE OF THE SILOXANE BOND IN POLY(DIALKYL SILOXANES)
BY ALKYL ORTHOTITANATES

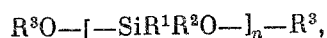
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Treatment of cyclic dialkylsiloxanes with butyl orthotitanate at high temperatures leads to cleavage of the siloxane bond and formation of monomeric and polymeric silyl organic esters [1, 2]. It has also been established [3] that the reaction is a general one which is applicable to linear and branched siloxanes of varying structures.

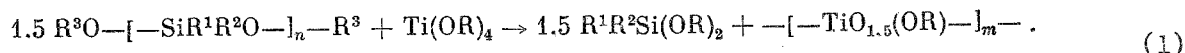
In the present paper we have investigated the reaction of linear polydialkylsiloxanes, which differ in the substituents attached to the Si atom, the nature of the end groups, and their molecular weights, with various alkyl orthotitanates, with the goal of determining the effect of the structure of the reacting substances on the cleavage reaction.

Linear polydialkylsiloxanes having the following general formula were used as the substrates in this study:



where $R^1 = R^2 = Me$; $R^1 = Me, R^2 = Ph$; $R^1 = Et, R^2 = Ph$; $R^1 = R^2 = Et, R^3 = H, SiMe_3$; the alkyl orthotitanates were of the form $Ti(OR)_4$, where $R = Et, n-Bu, i-Pr, \text{ and } t-Bu$. The characteristics and abbreviations for these compounds are given in Table 1.

The reagent ratio used corresponded to a molar ratio for the $SiOSi$ and $Ti(OR)_4$ groups of 1.5:1, i.e., the concentration of alkoxy groups in the reaction mixture was sufficient to cleave completely all of the siloxane bonds in the substrate, according to the scheme



Under reaction conditions guaranteeing removal and separation of the product alkoxy silanes, polydialkylsiloxanes readily undergo cleavage upon heating with a variety of alkyl orthotitanates, with the exception of tert-butyl orthotitanate; as can be seen from Table 1, these reactions are independent of the structure of R radicals attached to the Si atom, their molecular weight, or nature of the end groups in the substrate. The yields of alkoxy silanes were in the range 82-93%. Thus, in the reaction of dialkylsiloxanes with alkyl orthotitanates at high temperatures there does not appear to be any effect of structure of the reagents on the course of the reaction; this is in contrast to the situation with hexaalkyldisiloxanes, for which such a dependence has been demonstrated previously [3].

In the case of siloxanes containing OH end groups, the reactions occur even at $\sim 20^\circ C$, as evidenced by the appearance of signals due to the protons of the $SiOCH_2$ groups of the alkoxy silicon products at δ 3.65 ppm in the PMR spectra of mixtures of siloxanes and alkyl orthotitanates [4]. This occurs simultaneously with a reduction in the intensity of the signal for the $TiOCH_2$ group protons at δ 4.21 ppm, as the spectrum in this region takes on the appearance characteristic of polybutoxytitanoxane.

Figure 1 shows the kinetic curves for cleavage of polydialkylsiloxanes by alkyl orthotitanates at $\sim 20^\circ C$. The degree of conversion in these reactions was determined by integration of the PMR spectra, specifically, the ratio of the signal area for the $SiOCH_2$ group protons versus the total signal area for the $SiOCH_2$ and $TiOCH_2$ groups. As can be seen from Fig. 1, the rate and extent of conversion decrease in the case where sterically hindered ethyl and phenyl groups are attached to the Si atoms and where the alkyl radicals attached to the Ti atom are branched; the rate and degree of conversion also increase, however, as

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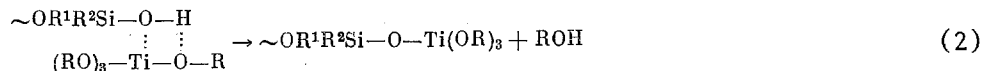
TABLE 1. Treatment of Dialkylsiloxanes with Alkyl Orthotitanates

Siloxane*	in Ti(OR) ₄	T †, °C	Alkoxysilane	
			yield, %	bp., °C (p, mm Hg)
PDMS -I	C ₄ H ₉	240	82	187 (745)
PDMS -II	C ₂ H ₅	140	92	113 (760)
PDMS -II	C ₃ H ₇	200	90	134 (750)
PDMS -II	C ₄ H ₉	260	91	187 (735)
PDMS -II	C ₄ H ₉	115	82	85 (13)
PDMS -III	C ₄ H ₉	245	87	188 (740)
PMPS	C ₄ H ₉	240	86	211 (738)
PMPS	C ₄ H ₉	140	87	102 (2)
PEPS	C ₄ H ₉	210	88	175 (10)
PDES	C ₄ H ₉	270	92	226 (742)
PMS 100	C ₄ H ₉	120	87	83 (17)

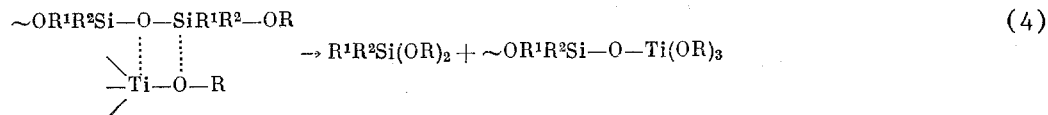
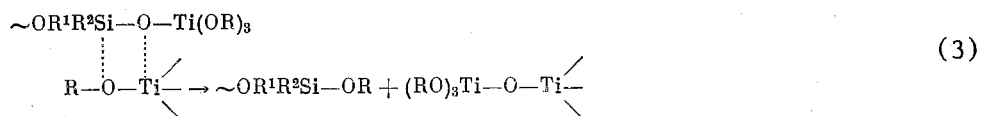
*PDMS-I, PDMS-II, and PDMS-III are polydimethylsiloxanes having molecular weights of 2900, 7200, and 12,800, respectively; PMPS is polymethylphenylsiloxane, M 2700; PEPS is polyethylphenylsiloxane, M 2100; PDES is polydiethylsiloxane M 2140; and PMS-100 is polydimethylsiloxane with trimethylsilyl end groups, M 4150.

†Bath temperature corresponding to onset of distillation of the dialkylalkoxysilane.

the molecular weight of the siloxane is decreased, i.e., as the concentration of OH groups increases. Siloxanes containing trimethylsilyl end groups are not cleaved under these reaction conditions. These data indicate that the presence of OH end groups determines the reactivity of the siloxane with respect to cleavage. Apparently, a "silanol condensation" occurs in the first stage of the reaction:



This type of reaction occurs very readily [5] and the resulting titanoxides are easily converted in the presence of excess Ti-O-C bonds in the reaction mixture to titanoxane compounds and alkoxysiloxanes, which then undergo further cleavage to give monomeric dialkoxysilanes.



The formation of titanoxides according to this scheme was substantiated by the appearance of absorption bands due to Ti-O-Si bonds at 935 cm⁻¹ in the IR spectra of reaction mixtures. In this way, therefore, the reaction begins with the OH end groups, and is followed by cleavage of the siloxanes containing end alkoxy- or Ti(OR)₃-groups, as the Si-O-Si bonds in the chain of the polysiloxane are not broken. The formation of complexes in the polysiloxane-alkyl orthotitanate systems has also been verified by light scattering [6], which indicated that complexes are also formed in the case of siloxane containing triethylsilyl end groups. These complexes might involve Si and O atoms in the chain of the polysiloxane, since heating is required for their rearrangement. If the heating is carried out to low degrees of conversion, then the reactions continue at ~20°C, which supports the reaction scheme outlined above. Heating results in cleavage of Si-O-Si bonds within the siloxane chain, and gives siloxanes containing titanoxido or alkoxy end groups, which are then reactive to cleavage at ~20°C. The reaction scheme shown above is also supported by the observa-

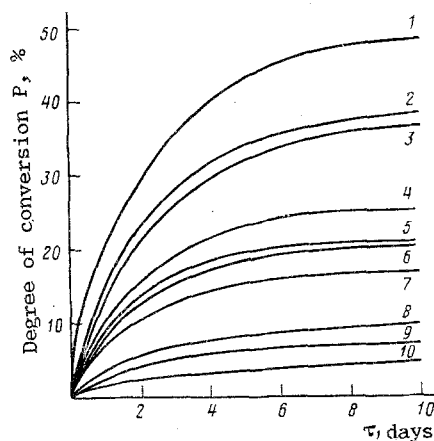
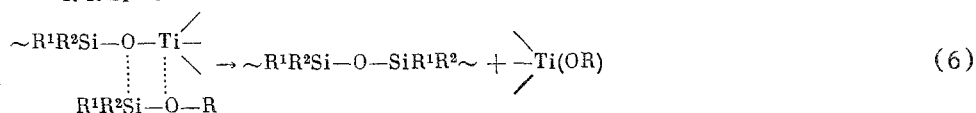
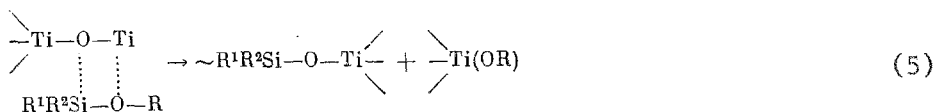


Fig. 1. Kinetic curves for the reactions of PDMS-I and ethyl (1) and isopropyl orthotitanate (3), n-butyl orthotitanate with PDMS-I (2), PDMS-II (4), PMPS (5), PDMS-III (6), and PDMS-I in benzene (7), and with PDMS-I in benzene containing 1.3 mole/liter pyridine (8), PEPS (9), and PDES (10) as additives.

tion that the siloxane cleavage reaction is suppressed in the presence of pyridine, which forms complexes with alkyl orthotitanates [7].

The degree of conversion increases significantly as the alkoxy silane which is formed during the course of the reaction is removed from the reaction mixture. This indicates that the reaction is reversible, i.e., the feasibility of cleavage of Ti-O-Si and Ti-O-Ti bonds by the action of alkoxy silane products.



This was also supported by the observed decrease in the signal due to the SiOCH₂ group protons, and the observed increase in the signal due to TiOCH₂ group protons, in the PMR spectra of a mixture of polybutoxytitanoxane with dimethylbutoxysilane, and also by the identification of hexamethyldisiloxane (by GLC) among the volatile products of the reaction of polybutoxytitanoxane with trimethylbutoxysilane. In addition, if a mixture of siloxane with alkyl orthotitanate is heated to the equilibrium state, and then the equilibrium is shifted back to the right by removal of significant amounts of dialkoxy silane by distillation, then the reaction mixture once again reaches its near equilibrium state when the dialkoxy silane is restored to the reaction mixture by heating at the same temperature.

EXPERIMENTAL

Polydialkylsiloxanes with hydroxyl end groups were prepared by hydrolysis of the corresponding dialkyl(alkylaryl)dichlorosilanes according to [8-10]. Liquid PMS-100 and PMS-400 samples which had been subjected to preliminary evacuation were used as polysiloxanes containing trimethylsiloxy end groups. The molecular weights of the siloxanes were measured by ITEK using a Hitachi-Perkin-Elmer-115 apparatus. The data are summarized in Table 1.

Ethyl- and butyl orthotitanates, chemically pure grade, were purified by twofold distillation *in vacuo*, whereas isopropyl- and tert-butyl orthotitanates were obtained according to [11]. Polybutoxytitanoxane was synthesized by hydrolysis of butyl orthotitanate in butanol [12], and dimethyldibutoxysilane and trimethylbutoxysilane were prepared in an analogous manner [13]. Physical chemical constants of all compounds agreed with literature data.

IR spectra were recorded on a Specord IR-75 spectrophotometer using 1% solutions in CCl₄. PMR spectra were obtained for 10% solutions in CCl₄ using a Tesla BS-567A spectrometer (100 MHz) relative to TMS. GLC analyses were carried out on a Tsvet-4 chromatograph with a catharometer detector, a stainless steel 2 m × 3 mm column filled with 20% SKTPT-100 on N-AW-HMDS chromatone, 0.250-0.315 mm, and He as the carrier gas.

Reactions of siloxanes with alkyl orthotitanates with simultaneous removal of alkoxy silane by distillation were carried out either at ~20°C and 1·10⁻² mm vacuum, or by heating with a gradual temperature rise up to the onset of alkoxy silane distillation, and then up to 300°C.

The reaction of polybutoxytitanoxane with dimethyldibutoxysilane was conducted at a 1:1 molar ratio (100°C, 3 h), and samples were removed every 30 min to record PMR spectra; the corresponding reaction with trimethylbutoxysilane was carried out by heating the reagents at a 1:1 ratio and analyzing the products in the distillate by GLC.

CONCLUSIONS

Linear polydialkylsiloxanes undergo cleavage upon heating with alkyl orthotitanates containing primary and secondary alkyl radicals, and the reactions are independent of the structure of radicals attached to the Si atoms, molecular weight, and the nature of the end groups. The factor which seems to determine the reactivity of polydialkylsiloxanes with respect to cleavage at room temperature is the presence of OH end groups. The rate and degree of conversion in these reactions is decreased by increasing steric hindrance at the Si or Ti atoms.

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