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Interaction of organodialkoxysilanolates with carbon dioxide

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Abstract: A series of organo(alkoxy)disiloxanes was obtained by the reaction of carbon dioxide with sodium alkoxy(organo)silanolates under high pressure as well as by bubbling CO_2 through the reaction mixture. It has been suggested that the reaction involves intermediate formation of carbonate derivative of sodium alkoxy(organo)silanolates.

Introduction: The reactions of compounds containing a SiO-M bond (where M is either an s-block or a d-block metal) are undoubtedly one of the most fascinating branches of organosilicon chemistry. The usage of various silanolates allowed to obtain stereospecific functional macrocycles [1-8] and polyfunctional olygomers [9]. A major contribution to the development of this area was marked by Rebrov salts [10]. Based on these compounds organometallic dendrimers, hyperbranched organosilicon polymers were obtained for the first time and siloxane molecular brushes were synthesized [11-15].

However, the synthetic potential of these compounds is not well developed. For example, the insertion reaction of CO_2 molecules into the SiO-M bond has not been studied so far. Meanwhile, the carbonate derivatives of sodium alkoxy(organo)silanolates are promising reagents that can broaden the range of silanolates synthetic applications in the synthesis of organoelement compounds.

High reactivity of silanolate groups may cause siloxane bond cleavage during basic interaction with chlorosilane groups, which requires the reaction to be carried out at a low temperature. On the other hand, interaction between known carbonate derivatives of silanolates with chlorosilanes is not accompanied with such complications, i.e. occurs more selectively. It should be noted that sodium organo(alkoxy)silanolate carbonate derivatives and their properties are not described in literature.

The goal of this investigation is to study the reaction between sodium alkoxy(organo)silanolates and carbon dioxide and to analyze the synthetic versatility of the products formed.

Results and discussion

At first, the reactions of sodium diethoxy(methyl)silanolate with liquid carbon dioxide were carried out in an autoclave-type reactor at room temperature.

After the decompression of CO_2 a white heterogeneous mixture was formed. The mixture was then separated into two fractions: a soluble and a non-soluble in organic solvents. The soluble fraction was extracted with diethyl ether and separated from the precipitate. The solid part was identified as sodium carbonate. After the solvent was evaporated, the residue was analyzed by means of various analytical techniques.

Within the time limits studied (from several minutes to several hours), the reaction product composition showed no dependence on the reagent contact time. The organosoluble fraction contained the identified ethoxy(organo)silane olygomers. Diorgano(tetraethoxy)disiloxane 4 was shown to be the major component of those olygomers. A possible pathway of its formation is shown in Scheme 1:



Scheme 1. Suggested mechanism of sodium diethoxy(organo)silanolate reaction with carbon dioxide.

Apparently, the intermediate carbonate derivative **2** further reacts with remaining sodium alkoxy(organo)silanolate molecules 1 quite easily. Based on the data provided by the papers [14-18], one could suggest that the first stage is the CO_2 molecule insertion into the SiO-Na bond of molecule **1**, which is a good

leaving group (pKa – 10.3, ethylate group pKa – 16). At the same time, the salt 1 (in excess) is a strong nucleophile that reacts with the compound 2. As a result, a symmetrical disiloxane 4 and sodium carbonate 3 are formed.

It was impossible to isolate compound 2 in a pure form. However, at a lower solution of temperature, as the dilute the salt 1 (sodium diethoxy(phenyl)silanolate) in tetrahydrofurane was added dropwise to dry ice a product was formed. After the reaction mixture was warmed to room temperature, the IR spectrum has been made. The IR spectrum of this product was significantly different from the spectrum of the reaction mixture obtained in the autoclave at room temperature (Fig. 1 (1)). The absorption band at 1626 cm-1 (Fig. 1 (2)) corresponds to the stretching vibration of the -Si-OCOONa bond. The presence of this band confirms that the reaction mixture contained the carbonate derivative 2. Apparently, most of initial sodium diethoxy(phenyl)silanolate was transformed into its carbonate derivative, due to the large excess of CO_2 and low temperature. Otherwise, after the reaction mixture was warmed, symmetrical disiloxane was to be formed as described in Scheme 1 in no more than 5 minutes.



Figure 1. IR spectrum of 1 – the reaction mixture after synthesis in autoclave, 2 – after reaction with dry ice.

The further treatment of the reaction mixture with chlorotrimethylsilane at room temperature resulted in the formation of a non-symmetrical disiloxane **6** which could be described by Scheme 2:



Scheme 2. Formation of non-symmetrical disiloxane

As shown by the Scheme 2, the intermediate salt 2 acts as a nucleophile and thus reacts with chlorosilane to form the carbonate 5. The compound 5 was not detected in the reaction product mixture, presumably due to its low stability. Instead of it, the product of its decarboxylation was obtained, i.e. nonsymmetrical disiloxane 6. This result is in good correlation with the data from [16]. The GC analysis of the reaction mixture revealed the presence of both the trimethylsililation non-symmetrical product of 6 and symmetrical diphenyl(tetraethoxy)disiloxane 4. The symmetrical disiloxane probably had formed according to Scheme 1, before the initial diethoxy(phenyl)silanolate 1 had time to go to the Scheme 2. This explains the presence of the sodium carbonate absorption band in the IR spectrum (Fig. 1 (2)).

Thus, interaction of sodium alkoxy(organo)silanolate with CO_2 leads to a new route of siloxane bond formation. It will supplement a number of already

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existing methods from classic hetero- and homofunctional condensation of organosilicon monomers [21–25] to various reactions with Lewis acids [26–30].

At the same time when the reaction is carried out with a large excess of CO_2 and low temperature, the carbonate derivative **2** of alkoxy(organo)silanolate was obtained. Further reaction of the carbonate derivative of alkoxy(organo)silanolate with chlorotrimethylsilane leads to the formation of a non-symmetrical disiloxane **6**. This may be an alternative to a cross-coupling reaction of Si-ONa and Si-Cl functional groups that occurs without the involvement of CO_2 [10,31–33]. This method will help to avoid side reactions of the strong nucleophilic Si-ONa if a substrate contains siloxane bond.

To sum up, the reaction of various sodium alkoxy(organo)silanolates with carbon dioxide under high pressure according to Scheme 1 yielded a series of sodium alkoxy(organo)silanolates (Table 1).

As evidenced by the presence of more high-molecular products in the reaction mixture, compound 2 might undergo decomposition through a different pathway, e.g. by ethoxy group elimination.

Besides the previously mentioned process at a high pressure, an alternative one bubbling of consists in simple CO_2 through the sodium diethoxy(organo)silanolate solution trialkoxy(organo)silane. in Wherein trialkoxy(organo)silane remains after the synthesis of the initial sodium silanolate [9]. Therefore, the synthesis of the silanolate itself and its subsequent reaction with CO₂ occurs "in one pot" (in situ), which makes the overall process much simpler. Contrary to the first design, the process is carried out at 0 °C for 60 min. The GC analysis of the reaction mixture demonstrated that the yield of ethoxy(diorgano)disiloxanes is higher in the second case (Table 1). The GPC data are in the agreement with those of GC and confirm that there are no highmolecular products in the reaction mixture.



Figure 2. GPC curves of reaction product mixture from reaction of sodium diethoxy(methyl)silanolate with CO_2 in autoclave and after bubbling of CO_2 .

Product	reaction design	reaction temperature, °C	reaction time, min	yield, %
(PhSi(OEt) ₂) ₂ O	autoclave	25	5	94
	bubbling	0	60	95
(VinSi(OEt) ₂) ₂ O	autoclave	25	5	74
	bubbling	0	60	85
(MeSi(OEt) ₂) ₂ O	autoclave	25	5	53
	bubbling	0	60	70
$(Me_2Si(OEt))_2O$	autoclave	25	5	75
	bubbling	0	60	61

Table 1. Experimental results of reaction between sodium alkoxy(organo)silanolates and CO_2

Comparing the symmetrical ethoxy(organo)disiloxane yields (Table 1), one can conclude that electronegative substituents at the silicon atom increase the reactivity of the intermediate alkoxy(organo)sodium carbonate salts. As a result, they react efficiently with the starting sodium alkoxy(organo)silanolates. The overall process therefore becomes a convenient preparative method for the synthesis of symmetrical ethoxy(organo)disiloxanes.

Conclusion

In this work it was established that interaction of ethoxy(organo)silanolates with carbon dioxide leads to a new route of siloxane bond formation. Insertion of CO_2 into the Si-ONa bond leads a significant to change in ethoxy(organo)silanolates reactivity. Since in the reaction mixture both intitial silanolate and its carbonate derivative that is formed during the reaction are present, symmetric ethoxy(organo)disiloxane is a predominant product of the reaction. Therefore, the reactivity of sodium ethoxy(organo)silanolates has been found to be higher compared to that of the previously known non-functionalized analogues.

After the interaction of diethoxy(phenyl)silanolate with large excess of CO2 and low temperature, intermediate carbonate derivative of at an alkoxy(organo)silanolate was detected by IR spectroscopy. Further reaction of the carbonate derivative of alkoxy(organo)silanolate leads to the formation of an non-symmetrical disiloxane. Two routes of ethoxy(organo)silanolates reaction with carbon dioxide were described in the work: reaction in an autoclave and reaction with CO_2 bubbling through the reaction mixture. The second route obtain ethoxy(organo)disiloxanes allows to directly from one the organosiloxane with ethoxy(organo)silanolates forming "in one pot" in situ. Conditions for the preparative synthesis of symmetrical ethoxy(organo)disiloxanes with 53-95% yields have been determined.

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