Reactions of dimethylzinc on Aerosil

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It has been established by IR spectroscopy, mass spectrometry, and quantum-chemical calculations that dimethylzinc reacts with Aerosil to form complexes with strained siloxane bonds on the SiO_2 surface; subsequent reactions of these complexes with free hydroxyl groups afford Si—O—Zn—Me and Si—Me surface structures. Alternative ways of formation of the above-mentioned structures are discussed.

Key words: dimethylzinc, aerosil, surface structures, thermolysis.

Silicon dioxide is known as a promising filler for composites, a carrier for supported catalysts, and a support in microelectronic and optical devices. In this connection, it is of interest to study reactions of organometallic compounds on the SiO_2 surface. Previously, reactions of a series of alkyl derivatives of Groups II and III elements (Zn, Cd, B, and Al) with Aerosil were studied by IR spectroscopy and mass spectrometry.[1—5] An analysis of the results allows the statement that the major direction of the reaction, regardless of pretreatment of the oxide, is the reaction of organometallic compounds with the hydroxyl groups of the surface, which results in formation of organometallic fragments. Strained siloxane bonds (Si—O—Si)*, which are formed on thermal dehydroxylation of SiO_2, are other reaction centers of the aerosil surface. Reactions of the above-mentioned organometallic compounds with these reaction centers on the surface afford Si—C bonds stable to hydrolysis. However, in the above-mentioned works, activation parameters of the mentioned reactions were not discussed, and the reaction kinetics was not analyzed. It was proposed that the reactions under discussion proceed in one stage; the mechanism of these reactions was not considered in detail, and possible alternative ways of reactions of organometallic compounds with different active centers of the Aerosil surface, in particular, with surface defects of the Si—O$^{\cdot}$ (Si—O$^-$) and Si=O types, were not discussed.

The aim of this work is to study reactions of dimethylzinc with different active centers of the SiO_2 surface by IR spectroscopy, mass spectrometry, and the use of quantum chemical methods.

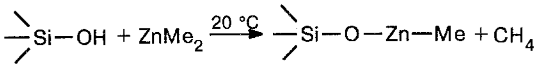
Experimental

Aerosil (Degussa) (S_{sp} = 175 m^2 g^{-1}), which was pressed into pellets (12 mg cm^{-2}), was used as the adsorbent. Before carrying out reactions with $ZnMe_2$, the Aerosil was pretreated for 3 h at 600 °C *in vacuo* ($1.3 \cdot 10^{-3}$ Pa) for removing physically adsorbed water and partial dehydroxylating. Adsorption of dimethylzinc was performed for 30 min at 20 °C in a special-purpose spectroscopic cell.[6] IR spectra were recorded on a UR-20 spectrophotometer; mass spectra were obtained on an MI-1305 mass spectrometer. Synthesis and purification of $ZnMe_2$ were carried out according to known procedures.[7] Samples were analyzed for Zn^{2+} ions using the reaction with aqueous solutions of $CuSO_4$ and ammonium tetrarhodanomercuriate.[8]

Results and Discussion

In the IR spectrum of calcined (600 °C) Aerosil, an intense sharp absorption band of free hydroxyl groups is observed at 3750 cm^{-1} (Fig. 1, spectrum *1*). After gaseous dimethylzinc was introduced in the cell (p = 6÷9 Torr, T = 20 °C), surface hydroxyl groups enter into the reaction with organometallic compounds. An absorption band at 3750 cm^{-1} disappears, and a broad low intensity absorption band with a maximum at 3680 cm^{-1} appears (intermolecular hydrogen bonds). In addition, absorption bands in the region 3000—2800 and 1430 cm^{-1} (ν(C—H) and δ(C—H), respectively) appear in the spectrum (see Fig. 1, spectrum *2*). According to data of mass spectrometric analysis, 95.7 mol.% of methane and 2.4 mol.% of ethane are evolved into the gas phase.

Based on the obtained experimental data, it may be concluded that after introducing $ZnMe_2$, replacement of hydrogen atoms of free silanol groups occurs according to the following general scheme:


(1)

Although we did not make a precise estimation of activation parameters of this reaction based on kinetic

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1912—1916, October, 1995.

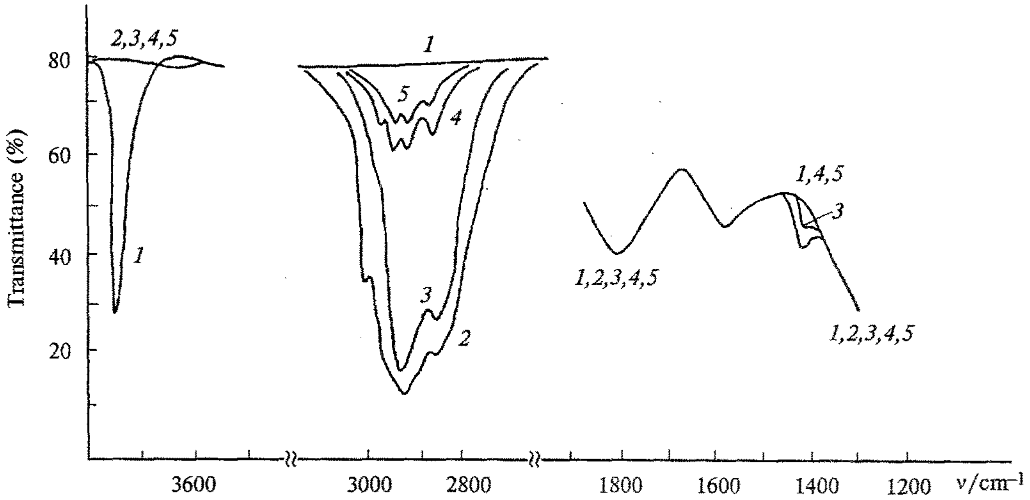


Fig. 1. IR spectra of Aerosil evacuated *in vacuo* at 600 °C (*1*), then treated with dimethylzinc at 20 °C (*2*), and evacuated *in vacuo* for 30 min at 200 °C (*3*), 400 °C (*4*), and 600 °C (*5*).

experiments, rapid changes in the IR spectrum, which were observed after introducing $ZnMe_2$, allow the conclusion that this reaction (1) proceeds virtually without activation. This suggests the formation of a stable intermediate complex at the initial stage through the lone electron pair of the oxygen atom of the Si—OH group and unoccupied p orbitals of the Zn atom followed by the replacement of the methyl group. We performed quantum-chemical study of the reaction of $ZnMe_2$ with silanol groups by semiempirical PM3,[9] AM1,[10,11] and MNDO[12,13] methods in the cluster approximation with full optimization of geometry of the $ZnMe_2$ molecule. The surface hydroxyl group was modeled by the $Si_4O_6(OH)_4$ cluster (**1**) (Fig. 2). This cluster corresponds to the unit cell of SiO_2 not exactly; the Si—O—Si angles are 120° (in β-cristobalite, these angles are ~140°).[14] However, for purposes of this work, this cluster is sufficiently representative because the real structure of the surface of amorphous silica also differs from the that of an ideal crystal. The geometry of the reacting OH group was optimized; the remaining part of the cluster was fixed.

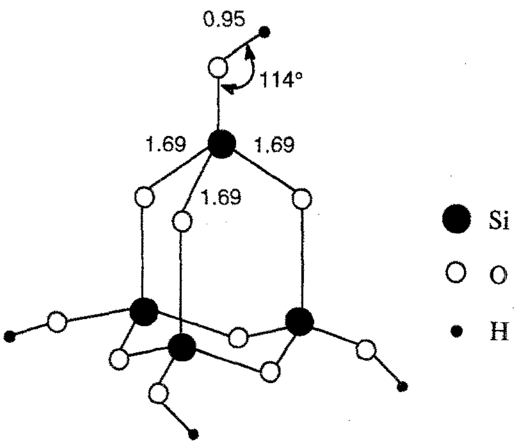


Fig. 2. Geometry of the cluster that was used for modeling the surface Si—OH group.

Contrary to the data of Ref. 15, in which the reactions of gaseous $ZnCl_2$ with silica gel were studied and the conclusion was drawn that the molecule of zinc chloride is coordinated to two Si—OH groups of the surface, quantum-chemical calculations, which we have performed, provide evidence that coordination of $ZnMe_2$ by the OH oxygen atom is thermodynamically unfavorable. When the $ZnMe_2$ molecule approaches the OH group, the total energy of the system calculated by the AM1 and MNDO methods increases monotonically. Calculations by the PM3 method are indicative of the presence of a local minimum, which corresponds to a metastable complex. The O—Zn bond length is 2.46 Å; the enthalpy of formation of this complex from $ZnMe_2$ and $Si_4O_6(OH)_4$ is 24 kJ mol^{-1}. Calculations of potential curves of the reaction of $ZnMe_2$ with a double cluster **1** ($ZnMe_2$ is tetrahedrally coordinated by two OH groups; analogous data see in Ref. 15) lead to the same result: calculations by the PM3 method are indicative of the formations of a metastable complex with ΔH_{compl} = 32 kJ mol^{-1}; the AM1 and MNDO methods provide evidence of the repulsion between the molecules of organometallic compounds and Si—OH groups. Therefore, approach of the $ZnMe_2$ molecule to the Si—OH group requires expenditure of energy of 20—35 kJ mol^{-1}; taking into account the additional potential barrier, which is overcome upon cleavage of O—H and Zn—C bonds, reaction (1) should have an activation energy no lower than 40—60 kJ mol^{-1}. This is in contradiction with the observed experimental data, and, therefore, the actual pathway of reaction (1) should be different.

An alternative way is coordination of ZnMe$_2$ to other surface-active SiO$_2$ centers, in particular, to strained siloxane bridges (Si—O—Si)*. In addition, we considered the possibility of coordination of ZnMe$_2$ to surface defects of the Si—O$^{\cdot}$ (Si—O$^-$) type, which occur as a result of homolytic or heterolytic cleavage of the strained (Si—O—Si)* bond (see Ref. 16). Double cluster **1** (Fig. 3, *a*), with the Si—O bond length in the (Si—O—Si)* fragment equal to 1.78 Å, was used as the model of these active centers, which corresponds to the present view of the structure of strained bridges.[16] Quantum-chemical calculations performed by the PM3 method demonstrated that coordination to the siloxane bridge bond is rather favorable: the enthalpy of formation of the complex from free components is −29 kJ mol^{-1}. The geometry of the formed complex is shown in Fig. 3, *b*. The >O...Zn< coordination bond has a substantial order (0.514) and is determined by donation of oxygen electron density to the unoccupied p orbital of the zinc atom. The Zn—C bonds are substantially elongated (by 0.06 Å) compared to those in the uncoordinated molecule; these bonds are activated (loosened). According to the results of calculations by the PM3 method, the energy of cleavage of the bridge siloxane bond is 41 kJ mol^{-1}. Therefore, coordination of the ZnMe$_2$ molecule to the bridging oxygen atom may readily cause cleavage of the bond to form a defect of the Si—O type. The charge on the oxygen atom is −0.510, and, therefore, the Si—O group is in a state intermediate between the Si—O$^{\cdot}$ and Si—O$^-$ terminal structures.

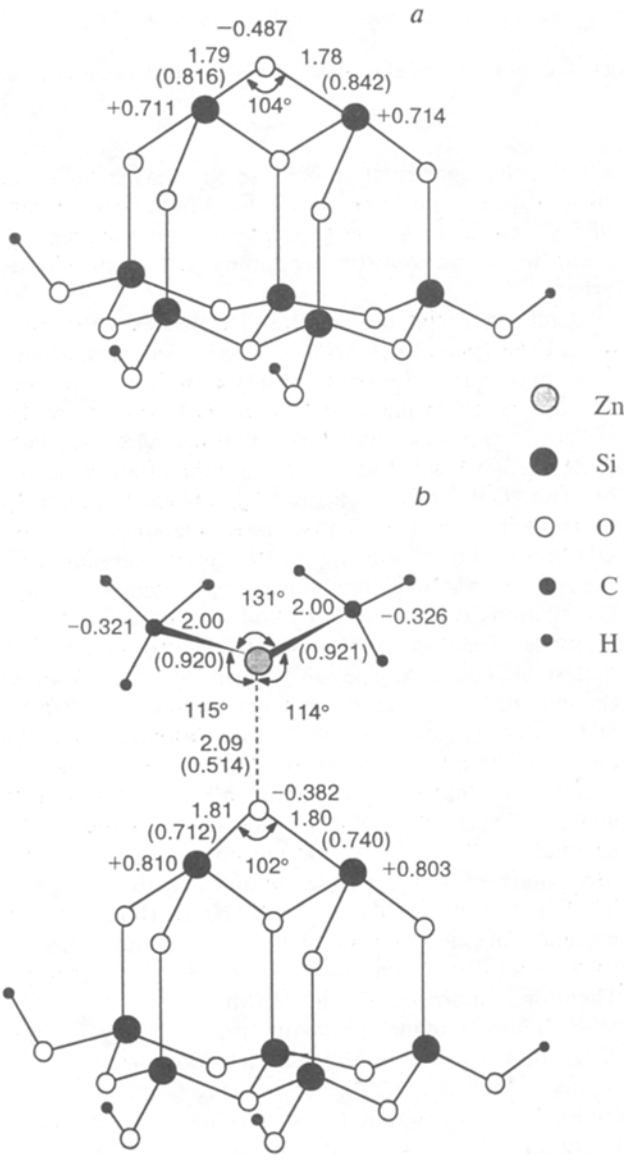


Fig. 3. Calculated geometric parameters, atomic charges, and bond orders (in parentheses) of the cluster that models the (Si—O—Si)* group (*a*) and the ZnMe$_2$ molecule coordinated to (Si—O—Si)* (*b*).

Coordination of organometallic compounds on the defect of the latter type with the formation of the Si—O$^{\cdot}$...ZnMe$_2$ complex is even more favorable. The enthalpy of the coordination reaction is −60 kJ mol^{-1}; the O—Zn bond length in the complex is 1.97 Å; the bond order is 0.647. The Zn—C bonds are lengthened to 2.01 Å. The presence of OH groups in proximity to this complex can result in formation of hydrogen bonds, the corresponding absorption bands of which are observed in the IR spectrum.

Coordination of the ZnMe$_2$ molecule by one of the above-mentioned ways results in both thermodynamic stabilization of the system and substantial activation of Zn—C bonds; when the Si—OH group is present in proximity to a coordinated molecule, this coordination leads also to a substantial decrease in the activation barrier of reaction (1). Therefore, based on quantum-chemical calculations, it may be concluded that the reaction of ZnMe$_2$ with surface silanol groups is more complex than it was represented in Scheme (1). We believe that at the initial stage, coordination of organometallic compounds occurs with the participation of strained siloxane bonds, part of which are broken in the process. Defects of the Si—O$^{\cdot -}$ type (or Si—O$^{\cdot}$...ZnMe$_2$ complexes) form hydrogen bonds with neighboring OH groups. Coordinated molecules of organometallic compounds subsequently react with the nearest OH groups. A low activation energy of this reaction is determined by thermodynamic stabilization of complexes and loosening of Zn—C bonds in these complexes. After hydrolysis of the sample modified with ZnMe$_2$ groups, absorption bands at 2920, 2900, and 1430 cm^{-1} of methyl C—H stretching vibrations are retained in the IR spectrum (Fig. 4, spectrum *3*), and the absorption band (ν(O—H)) at 3750 cm^{-1} appears on subsequent thermolysis (see spectrum *4*). Reactions of ZnMe$_2$ with Aerosil and with surface siloxane bridges according to Scheme (2) are a plausible explanation for this experimental fact; in this case, Si—Me structures, which are not subjected to hydrolysis, are formed.

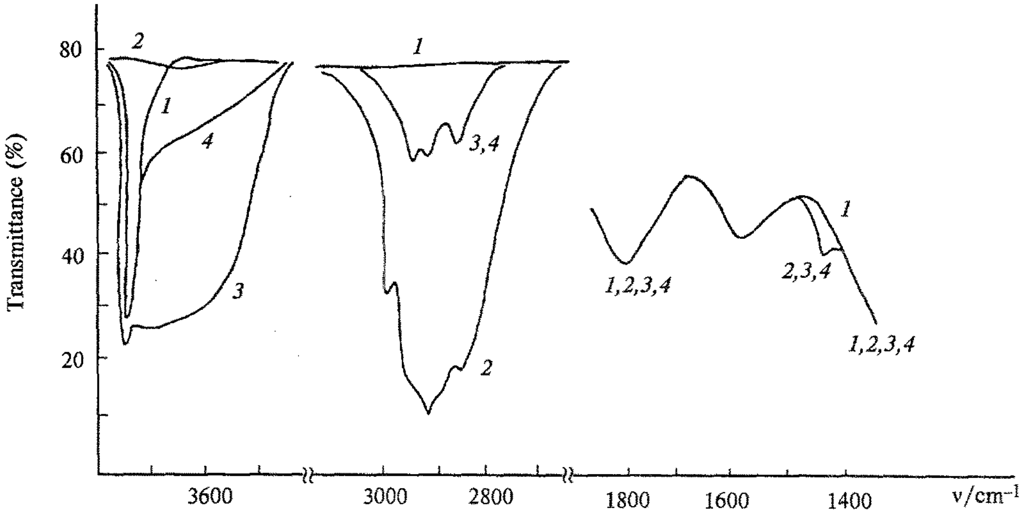
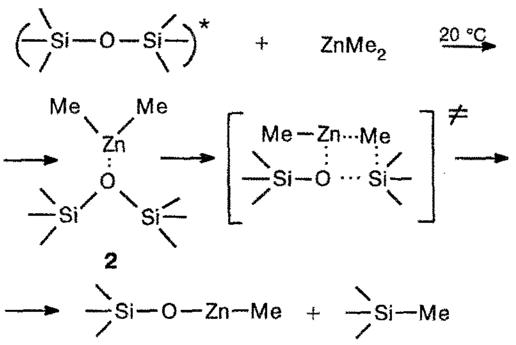
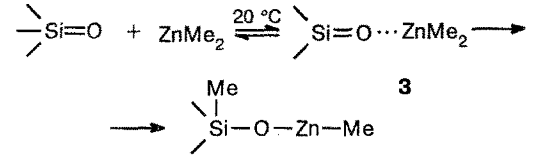


Fig. 4. IR spectra of Aerosil evacuated *in vacuo* at 600 °C (*1*), then modified with dimethylzinc at 20 °C (*2*), treated with aqueous vapor at 20 °C (*3*), and evacuated *in vacuo* for 30 min at 300 °C (*4*).



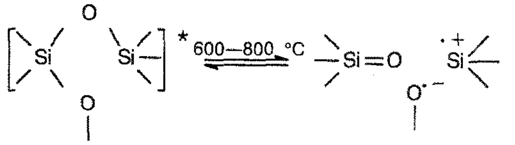
(2)

The reaction of $ZnMe_2$ with Si=O, silanone centers, the existence of which was proposed previously,[16,17] may be an alternative way of formation of surface Si—C bonds:



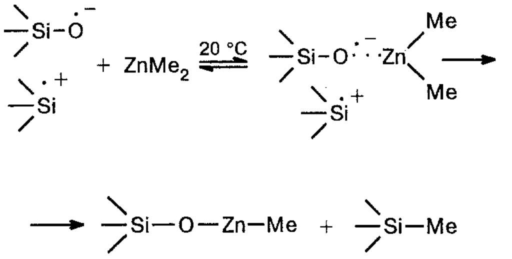
(3)

Complex **3** is thermodynamically favorable. The enthalpy of formation of this complex calculated by the PM3 method ($\Delta_f H = -80$ kJ mol^{-1}) may be sufficient to activate one or several Zn—C bonds. This is evidenced by an increase in these bond lengths in the complex (1.96 Å) compared to those in the free $ZnMe_2$ molecule (1.94 Å). Although formation of complex **3** is energetically more favorable compared to complex **2**, no definite conclusion was drawn in this work about a predominant contribution of reactions (2) or (3), because surface concentrations of particular defects associated with the energy and the means of their formation must be taken into account. Different points of view on the ways of formation of >Si=O defects are available. Some researchers believe[16] that these defects are formed upon high-temperature destruction of geminal hydroxyl groups ($Si(OH)_2$) and that the concentration of these defects is insignificant; other authors[17] found silanone groups upon mechanical activation of silicon dioxide and believed that these groups are formed by a homolytic mechanism from ordinary Si—O—Si bonds. We follow a different point of view. It can be proposed that on high-temperature treatment of Aerosil (600—800 °C), partial destruction of the silicon—oxygen framework (homolytic or, less probably, heterolytic depolymerization) with simultaneous formation of the silanone structure occurs according to Scheme (4):



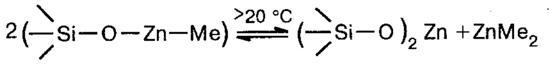
(4)

On interaction with molecules of organometallic compounds, the reaction with Si=O groups occurs (see Scheme (3)) as well as the restoration of the silicon—oxygen framework when new fragments are built in cavities of the surface. Therefore, it is possible that in parallel with the reaction with the participation of free hydroxyl and siloxane bonds, other highly reactive defects of partially destructurized SiO_2 are involved in the reaction of $ZnMe_2$ with Aerosil:



(5)

We studied thermal stability of surface structures, which were formed on reaction with Aerosil, in the temperature range from the room temperature to 600 °C. According to the data of mass spectrometry, predominantly methane (87.9 mol.%) and a small amount of ethane (1.3 mol.%) are evolved into the gas phase on thermolysis, as in the case of chemisorption at room temperature, As the temperature increases, intensities of absorption bands in the region 3000—2800 cm^{-1} (ν(C—H)) and at 1430 cm^{-1} (δ(C—H)) gradually decrease and the absorption band at 3750 cm^{-1} (ν(O—H)) is not virtually restored (see Fig. 1, spectra *3—5*). We believe that when a sample is gradually heated, complexes, which are formed on reaction of $ZnMe_2$ with surface-active centers and which do not react with OH groups at 20 °C, either decompose to evolve $ZnMe_2$ into the gas phase or enter into the reaction of elimination of methane according to Scheme (1). Furthermore, at temperatures 200 °C and higher, surface zincsiloxane groups are symmetrized to evolve $ZnMe_2$ into the gas phase:



(6)

The presence of Zn-containing components on the surface and in the gas phase was confirmed analytically from formation of the colored complex Zn^{2+} salt with solutions of copper sulfate and ammonium tetrarhodanomercuriate. The presence of a small amount of ethane in the gas phase is attributable to dimerization of methyl radicals in the coordination sphere of zinc.

Therefore, based on the obtained experimental data and quantum-chemical calculations, it may be concluded that $ZnMe_2$ reacts with Aerosil to form surface Si—O—Zn—Me and Si—Me fragments. Formation of these structures cannot proceed in one stage and involve a series of successive reactions with the participation of different intermediate complexes, the most probable of which are complexes of $ZnMe_2$ with strained and broken siloxane bonds and silanone groups. This type of coordination results in activation of the molecule of an organometallic compound and promotion of subsequent reactions at the surface.

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Received December 15, 1994;
in revised form March 13, 1995