Tertiary trisilyloxonium ion in cationic ring-opening polymerisation of a model cyclic siloxane, octamethyl-1,4-dioxatetrasilacyclohexane

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Abstract

The formation of the cyclic trisilyloxonium ion is observed by the ^{29}Si-NMR spectroscopy as a result of hydride transfer reaction between triethylsilane and Ph_3C^+ $B(C_6F_5)_4^-$ in the presence of octamethyl-1,4-dioxatetrasilacyclohexane, $^2D_2$. This ion is transformed by the reaction with another $^2D_2$ molecule into the cyclic trisilyloxonium ion at the polymer chain end. The mechanism of polymerisation of $^2D_2$ is discussed in relation with the mechanism of polymerisation of cyclic siloxanes.

1. Introduction

The mechanism of the cationic ring-opening polymerisation (ROP) of cyclosiloxanes has been studied for many years [1–8], but still some questions are not definitely answered. One of these unsolved problems is the role of tertiary cyclic trisilyloxonium ion derived from monomer as the intermediate in this process. Formation of tertiary silyloxonium ions generated from hexamethylcyclotrisiloxane, D_3, and octamethylcyclotetrasiloxane, D_4, was observed in the NMR spectroscopy at low temperatures by Olah et al. and the participation of these ions as active propagation centres in the cationic ROP of these monomers was postulated [6]. However, the main objection against this mechanistic concept is a relatively low rate of polymerisation when the initiator able to form persistent tertiary oxonium ion is used [7]. The results of sequence analysis in the polymer formed by cationic ROP of a cyclotrisiloxane with mixed siloxane units were explained by the mechanism of chain extension with reversible deactivation, in which the cyclic trisilyloxonium ion is not a persistent active propagation centre but only a transient intermediate in each act of monomer addition [8].

Additional helpful information on the mechanism of polymerisation of cyclic siloxanes may be deduced from the studies of other systems involving breaking and reformation of the siloxane bond. Some time ago we found that the kinetics of polymerisation of octamethyl-1,4-dioxatetrasilacyclohexane (permethylated tetrasila-1,4-dioxane), $^2D_2$, initiated with CF_3SO_3H could be best understood on the grounds of the analogous mechanism assuming the formation of cyclic trisilyloxonium intermediate [9–11]. The most interesting feature of this polymerisation is that the equilibration of monomer $^2D_2$ with its cyclic oligomer homologues, the nine-membered ring $^2D_3$ and the 12-membered ring $^2D_4$, is considerably faster than the equilibration of the monomer with the linear polymer [10]. The kinetics of the formation of these cyclic oligomers and linear polymer indicates that they are formed via the same intermediate, which most likely is the cyclic trisilyloxonium ion. These kinetic features of the polymerisation of $^2D_2$ make this monomer an interesting model for deeper studies on the cyclic trisilyloxonium ion question. Polymerisation of $^2D_2$ initiated by CF_3SO_3H occurs purely by opening of the siloxane bond and shows very close similarity to the cationic ROP of D_4. Being analogue of cyclic ether, $^2D_2$ may form more stable silyloxonium ion compared to permethylcyclooligosiloxanes which are analogues of cyclic acetals.

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The proposed mechanism of the cationic ROP of $^2D_2$ is based on the kinetic results. Since kinetic studies give only indirect information about the mechanism of such a complex reaction, the goal of this work is to provide a direct evidence of the assumed intermediates by spectroscopic methods. Therefore, we performed NMR studies of the system involving such an initiator which could produce the persistent trisilyloxonium ions derived from $^2D_2$.

Since the ability of the formation of the silyloxonium ion is related to the ability of siloxane oxygen to bind a cationic species we also performed theoretical studies to compare the basicity of this monomer with the basicities of D_3 and D_4.

2. Results and discussions

The cationic ROP of permethyl-1,4-dioxatetrasilacyclohexane, $^2D_2$, shows close similarity to the cationic ROP of permethylcyclotetrasiloxane, D_4, which is the most common monomer for ROP of siloxanes. Rings of both these monomers are almost strainless [13,14] and their ability to form polymer results from unusual flexibility of their chains leading to positive entropy of the ring-chain transformation [11,12]. Although the ROP of $^2D_2$ initiated by CF_3SO_3H is faster than that of D_4, rates and activation parameters of these reactions exhibit similar dependences on the initial water concentration in the polymerisation system [9]. The higher reactivity of $^2D_2$ could be well explained by a higher basicity of this monomer and consequently easier formation of the tertiary silyloxonium ion intermediate. We verified the assumption of higher basicity of $^2D_2$ by quantum mechanical ab initio calculations of proton affinity and basicity of hydrogen substituted analogues of $^2D_2$ and D_4. Some other hydrogen substituted oligosiloxanes were also subjects of these calculations for comparison. The results, which fully confirm our assumption, are presented in Table 1.
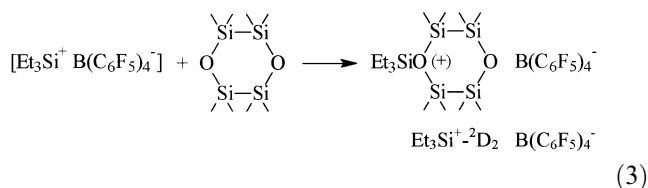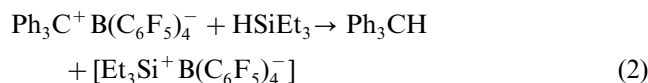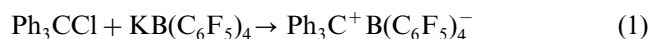
Table 1
Calculated proton affinity, i.e., negative enthalpy (PA), and basicity, i.e., negative Gibbs free energy (ΔG) of the protonation reaction, both in the gas phase

Siloxane	B3LYP/6-311+G(2d,p)//B3LYP/6-31G*	
	PA/kcal mol^{-1}	ΔG/kcal mol^{-1}
$H_3SiOSiH_3$	182.3	174.2
$(H_2SiO)_2$	189.0	182.6
$(H_2SiO)_3$	182.4	178.3
$(H_2SiO)_4$	185.7	177.6
$(H_2SiH_2SiO)_2$ ($^2D_2^H$)	190.6	183.6

The proton affinity and the basicity of $^2D_2$ are significantly higher than those for all other siloxanes, including very reactive cyclotrisiloxane. Although the calculation results concern isolated molecules in vacuum or in the gas phase, it is reasonable to assume that the interactions of siloxanes having similar structures with a solvent should not affect much the basicity order, at least in weakly interacting solvents [15].

The reason for a higher basicity of $^2D_2$ compared to D_4 is a different orbital interaction pattern involving the lone electron pair of oxygen, due to the difference in the structures of their ring skeletons. Contribution from hyperconjugation effect n(O)→σ*(SiO) in polysiloxanes significantly reduces the electron density on oxygen. This effect is less important in the case of polyoxymultisilylenes [14], because the n(O)→σ*(SiSi) interaction is much weaker. Thus, $^2D_2$ is expected to be more basic and to form the cyclic trisilyloxonium ion in cationic polymerisation systems easier than D_4. Therefore, direct observation of these cations derived from $^2D_2$ should be possible in a system similar to that in which the corresponding cations derived from D_4 and D_3 were observed.

The reaction between a triphenylmethylium (trityl) salt and a hydrosilane leads to the hydride transfer from the silane to the carbenium ion. If a fully ionized trityl salt is used, the rate of the reaction in dichloromethane solution is independent of the structure of counter-ion, which means that at least a transient formation of a complex of tricoordinate silicon cation with solvent occurs [16]. Lambert et al. [17] showed that if a stable counter-ion of very low nucleophilicity is used, the complex of silylenium ion with solvent is a persistent species. Tetrakis(pentafluorophenyl)borate was successfully explored for this purpose [18] and this system was later used by Olah et al. [6] for generation of trisilyloxonium ions derived from D_4 and D_3 which were observed by the NMR spectroscopy at very low temperatures ($-70\,^\circ C$). Following this concept and performing the hydride transfer from a hydrosilane to the trityl ion in the presence of $^2D_2$ should lead to the immediate formation of cyclic trisilyloxonium ion derived from $^2D_2$ according to Eq. (2) and Eq. (3).

$$Ph_3CCl + KB(C_6F_5)_4 \rightarrow Ph_3C^+ B(C_6F_5)_4^- \qquad (1)$$

$$Ph_3C^+ B(C_6F_5)_4^- + HSiEt_3 \rightarrow Ph_3CH$$
$$+ [Et_3Si^+ B(C_6F_5)_4^-] \qquad (2)$$

$$(3)$$

The best tool to observe trisilyloxonium ions is ^{29}Si-NMR [6]. The Eq. (2) was performed in the presence of $^2D_2$ in dichloromethane solution at −45 °C, which was almost the monomer solubility limit. The ^{29}Si-NMR spectrum, taken shortly after the reaction mixture was prepared, is shown in Fig. 1A. Then the temperature was raised and the spectra at −30 °C (Fig. 1B) and at 0 °C (Fig. 1C) were registered. In the presence of $^2D_2$ the formation of the trisilyloxonium ion should immediately follow the hydride transfer. The rate of the generation of this ion is, however, limited by the rate of hydride transfer which at −45 °C occurs relatively slowly.

Assignment of the signals on the spectra was not straightforward. Chemical shifts for the trisilyloxonium ion formed by Eq. (3) may be predicted on the basis of theoretical calculations. We applied two methods of NMR calculations: GIAO [19] and IGLO [20]. The obtained values of the ^{29}Si isotropic chemical shifts for the trisilyloxonium ion produced in reaction 3 and for Et$_3$SiH and $^2D_2$ are listed in Table 2.

One should be aware of the limitation of the theoretical methods for evaluation of NMR parameters. Results of NMR calculations are very sensitive to

Table 2
Experimental and calculated ^{29}Si-NMR chemical shifts in ppm relative to TMS for model compounds

	GIAO	IGLO	Exp.
Et$_3$SiH (A)	−10.6		
Et$_3$SiH (B)	0.2	−0.4	0.2 [21]
$^2D_2$	1.7	7.3	3.9 [10]
	50.0(1c), 51.1(1b)	70.5(1c), 67.6(1b)	56.4(1c) [a]
$^2D_2$–SiEt$_3^{(+)}$	53.4(1b), 6.4(1a)	63.4(1b), 17.1(1a)	48.8(1b) [a]
	7.4(1a)	17.8(1a)	9.6(1a) [a]

For assignment of signals in Et$_3$Si$^+$–$^2D_2$ see Fig. 1.
[a] At −45 °C.

geometry. For example, two stable conformations found for Et$_3$SiH (Fig. 2), differing in energy by ca. 2.5 kcal mol^{-1}, show ^{29}Si-NMR chemical shifts different by more than 10 ppm (Table 2). Chemical shift calculations are usually carried out for the structures of the lowest energy. The real chemical shift in solution, however, reflects averaging between rapidly inter-converted conformations. It is also affected by the interactions of the solute with a medium, which can be particularly strong
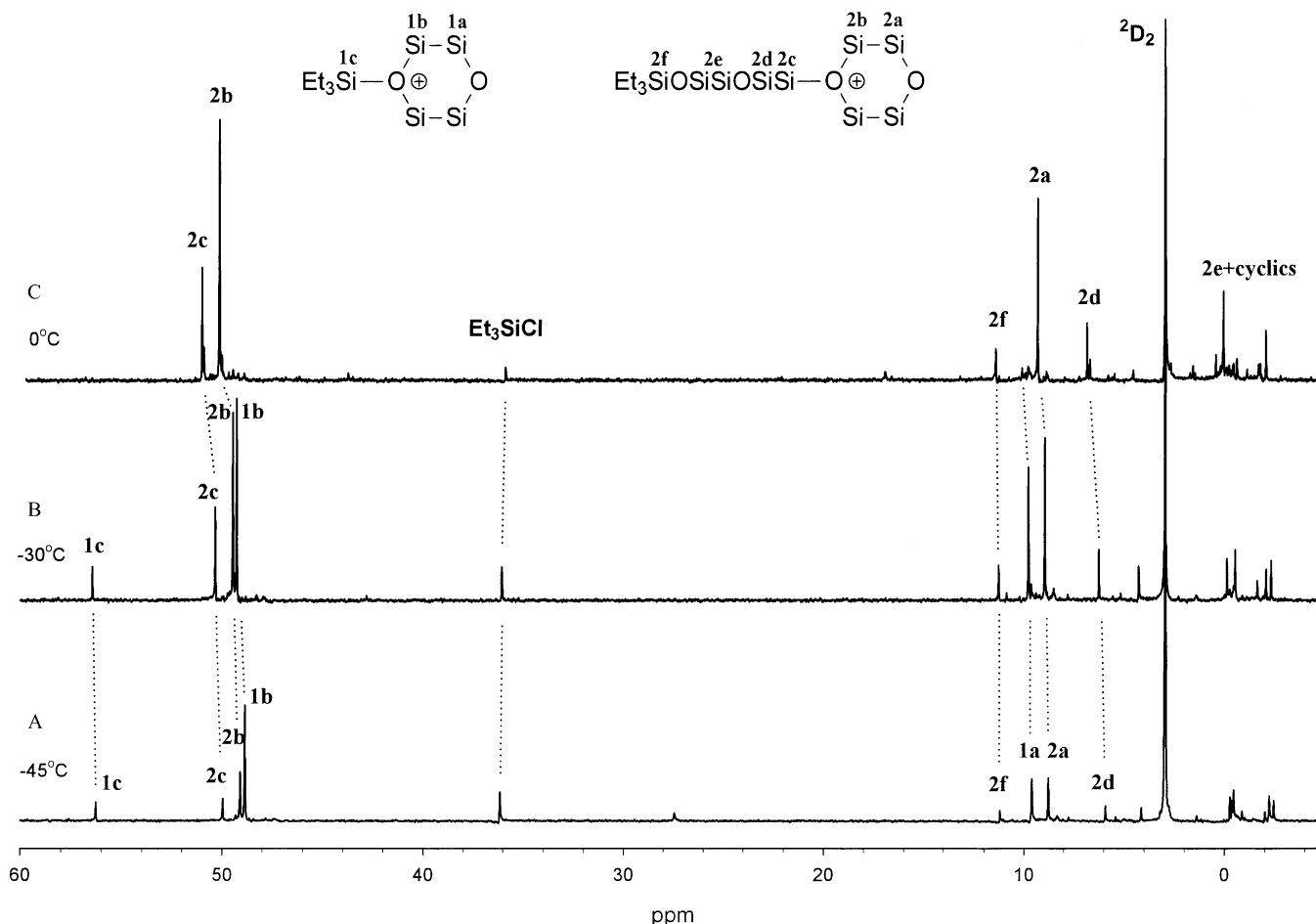

Fig. 1. ^{29}Si-NMR spectra of the reaction system of Et$_3$Si$^+$ B(C$_6$F$_5$)$_4^-$ with $^2D_2$ taken at (A) −45 °C; (B) −30 °C and (C) 0 °C.
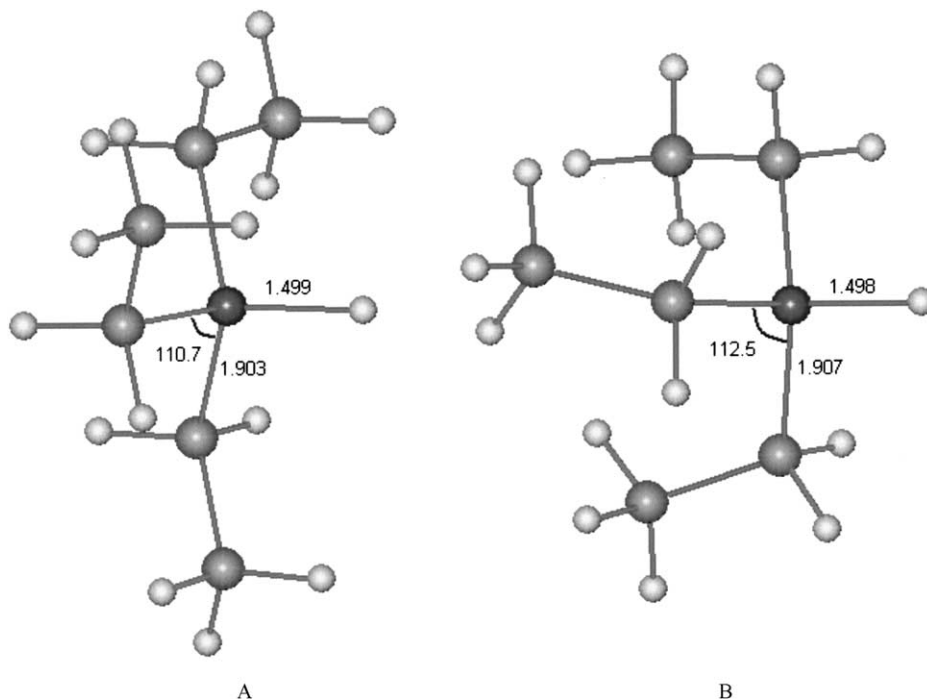
Fig. 2. B3LYP/6-31G* optimised geometries of Et_3SiH. Given are Si–H, Si–C bond distances in Å and CSiC bond angle in (°). Conformation A is by 2.5 kcal mol^{-1} more stable than conformation B.

for ionic species. Theoretical estimation of these effects is very difficult and time consuming. Despite these limitations, theoretical NMR calculations have been often used to support the NMR assignment in the case of short-living, reactive intermediates. For example, they helped to identify silyloxonium ions formed from cyclosiloxanes in ^{29}Si-NMR spectra [6].

Unfortunately, because of the large size and complex structure of the silyloxonium ion $Et_3Si^+ - {}^2D_2$, we were not able to perform full conformational analysis. Such analysis was made for Et_3SiH and for the hydrogen-substituted analogue of the monomer, ${}^2D_2^H$. The optimised structure of the latter served as the starting point to find the lowest energy structure of its methylated analogue, ${}^2D_2$. The ring of ${}^2D_2$ has a twisted geometry, very similar to that found for ${}^2D_2^H$. The starting geometry of $Et_3Si^+ - {}^2D_2$ was constructed by substituting the optimised structure of ${}^2D_2$ to the optimised structure of Et_3SiH in place of hydrogen atom directly bound to silicon. Further optimisation was performed on so constructed structure of silyloxonium ion. Optimised conformation of trisilyloxonium ion $Et_3Si^+ - {}^2D_2$ is shown in Fig. 3. The calculated ^{29}Si chemical shifts are shown in Table 2. Since calculations were performed for fixed geometry, all silicon atoms in the molecule have different chemical shieldings. As already mentioned, the calculations were made for isolated structures, while oxonium ions in solution are strongly solvated, which affects their conformations and the magnetic environ-

ment. There are also differences between the results of the two computational methods, due to different approximations assumed.

Nevertheless, the observed positions of signals on the spectra of the reaction mixture correspond reasonably well to those obtained from theoretical calculations. Four peaks appear in the region about 50 ppm predicted for the resonance of the trisilyloxonium species. This is reasonable to assume that those which tend to disappear on rising the temperature belong to the $Et_3Si^+ - {}^2D_2$ species and the two others, which increase with temperature correspond to the product of its reaction with monomer, according to Eq. (4). Thus, the signal at the lowest field, at 56.3 ppm, is assigned to exocyclic ethyl-substituted silicon in $Et_3Si^+ - {}^2D_2$, while the stronger peak at 48.9 ppm is assigned to the endocyclic silicon atoms in the oxonium centre. Two other signals at 49.2 and 50.0 ppm (-45 °C) represent silicon atoms at the oxonium centre in the chain end in the product of Eq. (4). After rising the temperature to -30 °C all these four signals are preserved, although the proportions change. The signals attributed to the product of Eq. (4) become relatively stronger. Two other endocyclic silicon atoms neighbouring to the oxonium silicons show resonance at 9.6 and 8.8 ppm for $Et_3Si^+ - {}^2D_2$ and $\sim SiSi^+ - {}^2D_2$ species respectively. At 0 °C, signals of the primary $Et_3Si^+ - {}^2D_2$ species almost disappeared, while these corresponding to trisilyloxonium ion-ended chain remain.
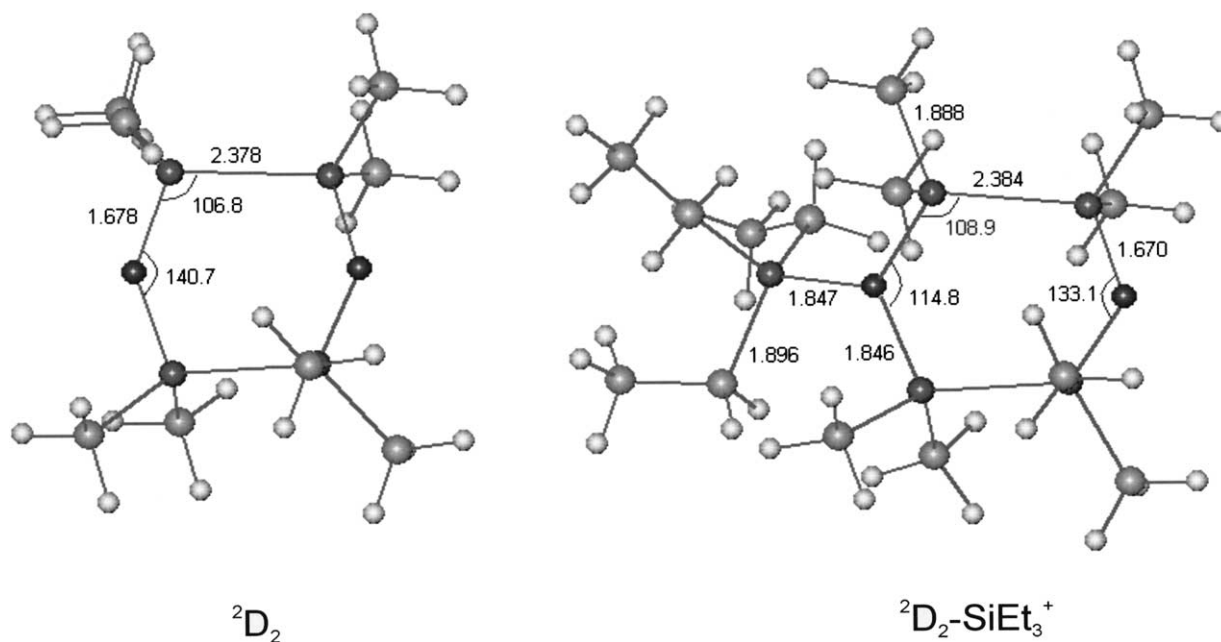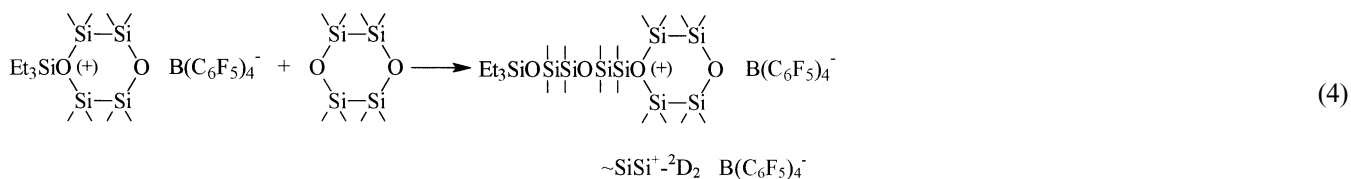
Fig. 3. B3LYP/6-31G* optimised structures of octamethyl-1,4-dioxatetrasilacyclohexane, $^2D_2$, and trisiloxonium ion $Et_3Si^+ - {}^2D_2$. Bond distances are in Å and bond angles are in (°).

It is worth mentioning that the chemical shifts of the trisilyloxonium ions are temperature sensitive. With the temperature increase from −45 to 0 °C they move downfield about 1 ppm. This may be due to a change in solvation and in conformational equilibrium of these species.

(4)

Thus, the spectra show that the original trisilyloxonium ion formed by Eq. (2) is transformed by Eq. (4) into the cyclic trisilyloxonium ion at the polymer chain end. This ion is therefore likely to be the active propagation centre, or one of the possible propagation centres, in the cationic ROP of $^2D_2$.

It may be concluded that $^2D_2$, due to its higher basicity and nucleophilicity, forms much more stable oxonium ion than permethylcyclosiloxanes. Thus, it is a good model for the study of the role of cyclic trisilyloxonium ions in the cationic polymerisation of cyclic siloxanes.

3. Experimental part

3.1. Monomer

Octamethyl-1,4-dioxatetrasilacyclohexane ($^2D_2$) was synthesised by hydrolytic condensation of 1,2-dichloro-tetramethyldisilane [22]. It was purified by recrystallisation from ethanol and sublimation.

3.2. Solvents

Dichloromethane (Fluka) was shaken with conc. H_2SO_4, then washed with water and Na_2CO_3, dried with $CaCl_2$ and distilled from CaH_2. It was stored in dark in a glass ampoule with Rotaflo stopcock over CaH_2. *n*-Hexane was distilled from CaH_2. Dichloromethane-2D (Dr Glaser AG) was stored over calcium hydride and distilled from it in vacuum line before use.

3.3. Reagents

Triphenylmethylium chloride (Aldrich, 98%) was crystallised from dry hexane. Potassium tetrakis(pentafluorophenyl)borate, $K^+B(C_6F_5)_4^-$, was obtained from Drs D. Cardinaud and C. Priou (Rhodia Silicones). It was dried by keeping at 60 °C under high vacuum for 24 h.

Triphenylmethylium tetrakis(pentafluorophenyl)borate, $Ph_3C^+B(C_6F_5)_4^-$, was prepared from triphenylmethyl chloride and $K^+B(C_6F_5)_4^-$ according to [23].

Et_3SiH (Fluka, pure grade, >97%) was dried over CaH_2, distilled under vacuum to an ampoule with Rotaflo stopcock and stored under argon.

3.4. NMR studies

Trityl salt (80 mg, 0.083 mmol) and 0.5 mmol of $^2D_2$ was dissolved in 0.5 ml of CD_2Cl_2 in a 5 mm NMR tube sealed with rubber septum. The tube was cooled to −70 °C under the flow of argon and 0.035 mmol of triethylsilane was added with a microsyringe to start the reaction. The ^{29}Si-NMR spectra were made at the lowest possible temperature, −45 °C. Below this temperature the sample solidified. NMR spectra were recorded with Bruker DRX 500 spectrometer using INEPT technique assuming $^2J_{SiH}$ of 7.5 Hz.

3.5. Theoretical methods

Geometries of model compounds ($^2D_2^H$, $^2D_2^H-H^{(+)}$, $^2D_2$, $^2D_2-SiEt_3^{(+)}$, Et_3SiH) were calculated at the B3LYP/6-31G* level. Stationary points were confirmed by vibrational analysis. Final electronic energies were calculated at B3LYP/6-311+G(2d,p). Vibrational energies at 298 K were scaled by 0.98. Calculations were performed for the gas phase conditions, using the GAUSSIAN 98 package [24].

NMR calculations were performed for B3LYP/6-31G* geometries with two methods: GIAO-HF/6-311+G(2d,p) [19] and IGLO II [20]. IGLO II was applied using the A2 auxiliary basis set and PW91 functional, as implemented in DEMON ver. 1.0 program [25].

Acknowledgements

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