

Preliminary communication

Kinetic study on thermal *syn*–*anti* isomerization of
dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane¹

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Abstract

When heated at 493 K, *syn*-dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane (*syn*-1) isomerizes to *anti*-dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane (*anti*-1); isomerization of *anti*-1 to *syn*-1 does not occur at 493 K. Thermodynamic parameters were determined for the one-way isomerization of *syn*-1 to *anti*-1: $E_a = 42.3 \text{ kcal mol}^{-1}$, $\log A = 15.1 \text{ s}^{-1}$, $\Delta H^\ddagger = 41.4 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 7.6 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1}$ and $\Delta G_{493\text{K}}^\ddagger = 37.6 \text{ kcal mol}^{-1}$. The activation energy is considerably larger than that for the analogous thermal isomerization of *syn*-tricyclo[4.2.0.0^{2,5}]octane (*syn*-2) to *anti*-tricyclo[4.2.0.0^{2,5}]octane (*anti*-2), indicating that the bond dissociation energy of the bridgehead Si–Si bond of *syn*-1 is larger than that of the bridgehead C–C bond of *syn*-2.

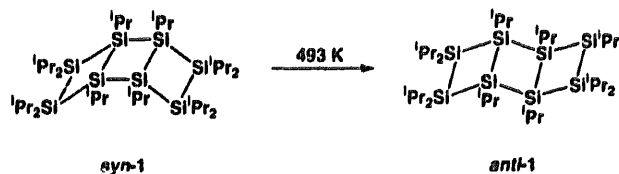
Keywords: Silicon; Ladder polysilane; Thermolysis; *syn*–*anti* Isomerization; Kinetics

1. Introduction

Since the first ladder polysilane, decaisopropylbicyclo[2.2.0]hexasilane, was reported in 1987, the structures, electronic properties and reactions of ladder polysilanes have been investigated by our group [1]. The ladder polysilanes were prepared via the co-condensation of 1,2-dichloro-1,1,2,2-tetraisopropylidisilane and 1,1,2,2-tetrachloro-1,2-diisopropylidisilane with lithium, and we found that the reaction afforded both *anti*-dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane (*anti*-1) and *syn*-dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane (*syn*-1) [2]. X-ray crystallographic studies showed that: *syn*-1 has a more strained structure than *anti*-1; the Si–Si bond lengths in *syn*-1 (2.369(4)–2.436(4) Å, average 2.402 Å) are longer than those in *anti*-1 (2.346(3)–2.405(4) Å, average 2.388 Å) [2]. This prompted us to examine the thermal stability of these isomers. We report below the results of a study on the thermal isomerization of *syn*-1 to *anti*-1, and discuss the thermodynamic parameters for the isomerization.

2. Results and discussion

When a solution of *syn*-1 in decahydronaphthalene was heated at 493 K, *syn*-1 isomerized to *anti*-1 quantitatively. When *anti*-1 in decahydronaphthalene was likewise heated at 493 K, no isomerization of *anti*-1 to *syn*-1 was observed, and *anti*-1 was recovered. It is noteworthy that the thermolysis of *syn*-tricyclo[4.2.0.0^{2,5}]octane (*syn*-2) was reported to give 1,5-cyclooctadienes, *anti*-tricyclo[4.2.0.0^{2,5}]octane (*anti*-2) and 1,2-divinylcyclobutanes in 51%, 41% and 8% respectively [3]. The results indicate that there is a significant difference in the thermolysis pathway for *syn*-1 and *syn*-2.



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It is interesting to compare thermodynamic parameters for the isomerization process from *syn*-1 to *anti*-1

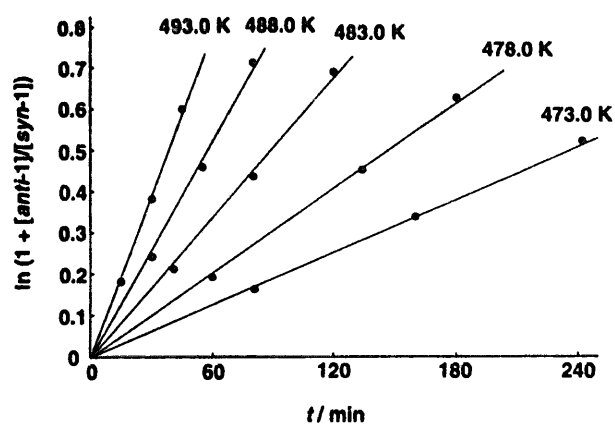


Fig. 1. Plot of $\ln(1 + [\text{anti-1}]/[\text{syn-1}])$ vs. t for thermal isomerization of *syn-1* to *anti-1*.

with those reported for the isomerization of *syn-2* to *anti-2* [3]. To allow such a comparison, a kinetic study was carried out. The thermal isomerization of *syn-1* to *anti-1* shows a first-order dependence on the concentration of *syn-1* in accord with Eq. (1).

$$\ln(1 + [\text{anti-1}]/[\text{syn-1}]) = kt \quad (1)$$

Fig. 1 shows the plot of $\ln(1 + [\text{anti-1}]/[\text{syn-1}])$ vs. t . Each plot shows good linearity with a correlation coefficient of 0.999. The rate constants are listed in Table 1. In Fig. 2 are shown plots of $\ln k$ vs. T^{-1}

($r = -0.9996$) and $\ln k/T$ vs. T^{-1} ($r = -0.9996$); from these, the thermodynamic parameters were determined by use of the following equations, where R , k and h are the gas constant, the Boltzmann constant and the Planck constant respectively. These parameters are listed in Table 1.

$$\ln k = -E_a/RT + \ln A \quad (2)$$

$$\ln k/T = -\Delta H^\ddagger/RT + \Delta S^\ddagger/R + \ln k/h \quad (3)$$

$$\Delta G^\ddagger = RT(\ln kT/h - \ln k) \quad (4)$$

In the thermal isomerization of *syn-1* to *anti-1*, a relatively high temperature (473–493 K) is necessary because of the large activation energy (42.3 kcal mol⁻¹). Since the heat of formation of *syn-1* calculated by the MM2 method is larger than that of *anti-1* by 13.4 kcal mol⁻¹, the activation energy for the isomerization of *anti-1* to *syn-1* is estimated to be greater than 55 kcal mol⁻¹, so that isomerization of *anti-1* to *syn-1* cannot take place at 493 K. In contrast, it has been reported that the activation energy for thermal isomerization of *syn-2* to *anti-2* is relatively low (31.4 kcal mol⁻¹), and that isomerization occurs at lower temperatures (390–419 K) [3]. At present, the mechanism of the thermal isomerization of *syn-1* to *anti-1* is not clear. However, if it is assumed to proceed via a biradical intermediate, as reported for the isomerization

Table 1
Thermodynamic parameters for thermal isomerization of *syn-1* to *anti-1*

T (K)	k (s ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)	E_a (kcal mol ⁻¹)	$\log A$ (s ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (kcal mol ⁻¹ K ⁻¹)
493	$(2.17 \pm 0.09) \times 10^{-4}$	37.63 ± 0.04	42.3 ± 0.4	15.1 ± 0.2	41.4 ± 0.4	$(7.6 \pm 0.8) \times 10^{-1}$
488	$(1.44 \pm 0.06) \times 10^{-4}$	37.63 ± 0.04				
483	$(9.32 \pm 0.38) \times 10^{-5}$	37.66 ± 0.04				
478	$(5.68 \pm 0.18) \times 10^{-5}$	37.73 ± 0.03				
473	$(3.53 \pm 0.09) \times 10^{-5}$	37.77 ± 0.02				

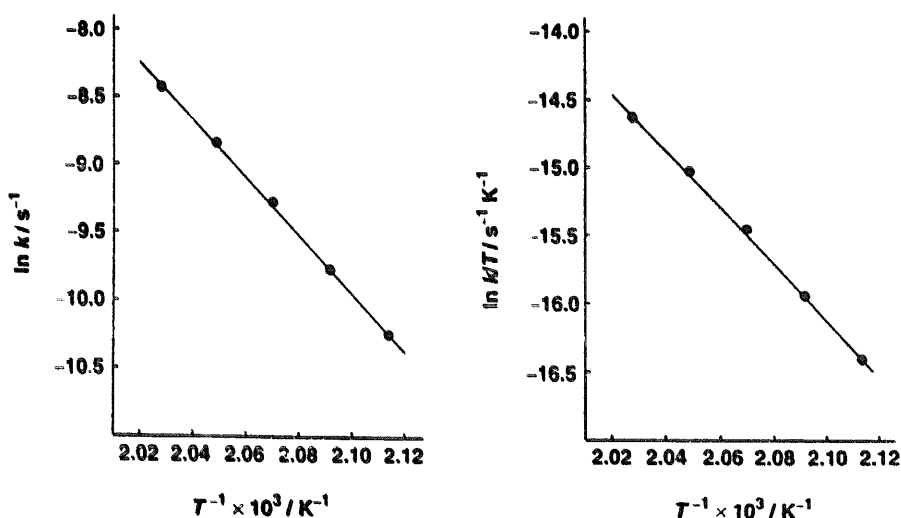


Fig. 2. Plots of $\ln k$ vs. T^{-1} (left) and $\ln k/T$ vs. T^{-1} (right) for thermal isomerization of *syn-1* to *anti-1*.

of *syn-2* [3], the activation energy approximately corresponds to the bond dissociation energy. Although the bond dissociation energy of the bridgehead Si–Si bond of *syn-1* is much smaller than those of common Si–Si bonds (ca. 70–80 kcal mol⁻¹) [4] because of ring strain, it is significantly larger than that of the bridgehead C–C bond of *syn-2*. The larger bond dissociation energy of the bridgehead Si–Si bond of *syn-1* may be attributed in part to the reduced ring strain in ladder polysilanes compared with that in ladderaranes [5]. The log *A* value for the thermal isomerization of *syn-1* to *anti-1* (15.1 s⁻¹) is slightly larger than that for the thermal isomerization of *syn-2* to *anti-2* (13.4 s⁻¹). The activation entropy (7.6 × 10⁻³ kcal mol⁻¹ K⁻¹) is very low, in accord with the fact that the thermal isomerization is a unimolecular reaction.

3. Experimental

syn-Dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane (*syn-1*) was prepared as previously described [2]. Decahydronaphthalene was treated with concentrated sulfuric acid, washed successively with aqueous sodium hydrogen carbonate and aqueous sodium chloride, dried over calcium chloride and distilled from sodium wire. Thermal reactions were carried out in a silicone oil bath (Toray Dow-Corning Silicone, SRX310), the temperature of which was controlled to within ±0.1 K, using a Riko MSR-15D magnetic stirrer. HPLC analyses were performed with an ODS column (Chemco, chemcosorb 5-ODS-H, 4.6 × 250 mm) using methanol–THF (7:3) as an eluent.

3.1. Kinetic measurement of thermal isomerization of *syn-1* to *anti-1*

A solution of *syn-1* in decahydronaphthalene (0.07 M) was degassed by freeze–pump–thaw cycles and the glass tube containing the solution was sealed and placed in a silicone oil bath at 473–493 K. After an appropriate

time, the tube was opened, and the concentration ratio of *anti-1* to *syn-1* was determined by HPLC.

Acknowledgements

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