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Journal of Organometallic Chemistry 691 (2006) 4843–4849
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Electronic structures of permethyloligosilane radical cations at the ground and low-lying excited states

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Received 12 June 2006; received in revised form 1 August 2006; accepted 2 August 2006
Available online 15 August 2006

Abstract

The electronic structures at the ground and low-lying excited states of permethyloligosilane radical cations, $Si_n(CH_3)_{2n+2}^+$ ($n = 4$–7), have been investigated using DFT and ab initio calculations. The calculations showed that positive charge (hole) is delocalized along the Si–Si main chain at the ground and first excited states. On the other hand, the hole is transferred to the methyl side-chain at the second and higher excited states. From these results, it was concluded that hole can move along the Si–Si main chain at thermal conditions. Also, it was predicted that intermolecular hole hopping takes place by photo-irradiation to the permethyloligosilane radical cation. The mechanism of hole transfer was discussed on the basis of the results.

Keywords: Radical cation; Oligosilane; Hole transport; Excited state; Ab initio CIS; DFT

1. Introduction

Polysilanes have been extensively investigated because of their potential utility as hole and electron transport materials in organic multilayer light emitting diodes (LEDs), one-dimensional semi-conductors, photo-resist materials, and high-density optical data storage materials [1–10]. These characteristic features are originated from high hole mobility of 10^{-4} cm^2 V^{-1} s^{-1} and a low-lying excited state of polysilanes at doped state, which correlates strongly with the electron and hole conductivities as an organic semi-conductor. Hence, determination of the electronic structures of ionic states at both ground and excited states is an important theme in development of new materials of silane systems.

Charge transport in charge-injected polysilanes has been investigated extensively using time-of-flight [11,12] and time resolved microwave conductivity techniques [13–17]. The experiments indicate that thermal activation and field-assistance enhance hole mobility in polysilanes. The mobility of hole is as high as 10^{-4} cm^2 V^{-1} s^{-1}, while that of excess electron is a few order of magnitude lower. To elucidate mechanism of hole and excess electron transfers in polysilanes, several experiments have been carried out. Seki et al. measured [16] the transient absorption spectra of radical cations of a variety of substituted polysilanes by means of pulse radiolysis. It was suggested that phenyl rings bonded to the Si–Si skeleton are important in hole transport process between polymer chains. If the side chain is alkyl groups, hole mobility is significantly slower than in phenyl group. This is considered that spin densities on the phenyl group is larger than that of alkyl group. However, detailed mechanism for hole transport is still not clearly understood.

In the present, ab initio and density functional theory (DFT) calculations were applied to the oligosilane radical cation with methyl group in the side-chain to elucidate the mechanism of hole transport in oligosilane radical cation. In particular, we focus our attention on the hole transport processes at the low-lying excited states.

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0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.08.008

It is known that spin density on the side-chain of radical ions of polysilane correlates strongly to charge transport and conductivity. If the spin density exists on the side chain, the hole hopping between polymer chains is possible via the side chain. On the other hand, if the spin density is localized only in the Si main chain, the hole transfer takes place along the intramolecular Si main chain. For example, the electron conductivity in radical anion of poly(methylphenylsilane) is significantly smaller than that of radical cation [18]. Electron spin resonance (ESR) and optical absorption spectra show that the spin density in the side-chain is close to zero in the radical anion, whereas that in the radical cation is larger than that of radical anion. The difference of charge conductivity is originated from the difference of spin densities in the side-chain. In the present study, we focus our attention on the difference of spin densities at the ground and excited states, and discuss the mechanism of hole conductivity in radical cation of permethyloligosilane.

2. Method of calculations

Almost all calculations were carried out at the DFT(B3LYP)/3-21G(d) level of theory. A linear oligosilane with methyl groups in side chain, permethyloligosilane ($Si_n(CH_3)_{2n+2}$) ($n = 4$–7), was examined as model of polysilane. For comparison, electronic states of phenylmethyloligosilanes were investigated.

First, the initial geometry of neutral oligosilane was made by MM2 calculation. Using the optimized geometry of the MM2 calculation, Next, direct molecular orbital–molecular dynamics (MO–MD) calculation was carried out for oligosilane to obtain the stable structure. The dynamics calculation was performed at semi-empirical PM3 level of theory. Using the geometries obtained by the MO–MD calculations, the structures of the oligosilane radical cations were fully optimized at the DFT(B3LYP)/3-21G(d) level of theory. Details of direct MO–MD calculations are described in recent our paper [19].

The excitation energies were calculated by means of time-dependent (TD)-DFT and singly excited configuration interaction (SE-CI) calculations. Six excited states were solved in these calculations. All hybrid DFT and ab initio calculations were carried out using GAUSSIAN03 program package [20]. Note that the similar levels of theory give reasonable features for several molecular device systems [21–23].

3. Results

3.1. Structures of oligosilanes ($n = 4$–7)

The geometrical structures of neutral and radical cation of oligosilane ($n = 4$–7) are fully optimized by means of the PM3 method. Using the optimized structures, direct MO–MD calculation is carried out to elucidate the effects of rotation of methyl group on the structure. Since previous experiments for the oligosilane radical cation have been performed mainly at 77 K, we chose 100 K for simulation temperature of oligosilane. As an example, snapshots of radical cation of oligosilane with $n = 7$ are illustrated in Fig. 1. At time zero, the oligosilane has a regular all-transoid structure. By thermal activation, methyl groups are freely rotated, but change of Si–Si skeleton is not large. After 4.0 ps, the structure of oligosilane is deformed, but the all-transoid structure is not changed. The distance between head and tail silicon atom of $n = 7$ is plotted as a function of time in Fig. 2A. At time zero, the distance is 11.34 Å. This distance vibrates in the range 11.10–11.85 Å during the simulation, indicating that the all-transoid structure is kept at 100 K. Temperature of the system is monitored as Fig. 2B. Mean temperature is 100 K.

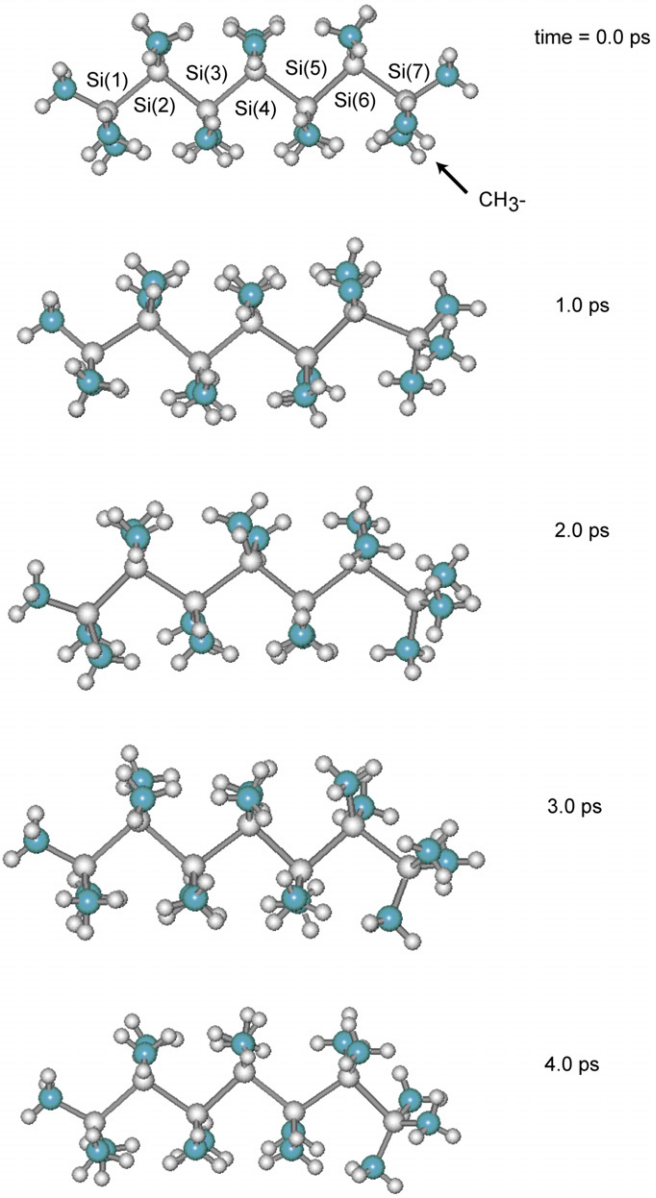

Fig. 1. Snapshots of structures of $Si_n(CH_3)_{2n+2}$ ($n = 7$) calculated using direct MO–MD method (PM3 level). Simulation temperature is 100 K.