Cyclopropane ring opening in the reaction of methylenecyclopropane with silyl radicals stabilized on an activated Aerosil surface

V. I. Pergushov, N. Yu. Osokina, Yu. V. Razskazovskii, and M. Ya. Mel'nikov*

Department of Chemistry, M. V. Lomonosov Moscow State University,
Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: 007 (095) 932 8846. E-mail: melnikov@melnik.chem.msu.su

Alkyl type radicals stable at room temperature and incorporating a double bond not conjugated with the free valence, ≡Si—C(=CH_2)—CH_2—CH_2˙, are formed in the reaction of methylenecyclopropane with silyl radicals (≡SiO)$_3$Si˙ on an activated Aerosil surface.

Key words: methylenecyclopropane; silyl radicals; Aerosil, activated surface; ESR spectra.

The use of activated Aerosil surface for generation and stabilization of active radical intermediates of various structures opens up unique opportunities for investigation of the mechanisms of radical reactions.[1–4] The mechanisms of reactions of compounds containing strained bonds with "soft" radical reagents such as silyl radicals (≡SiO)$_3$Si˙ (≡Si˙) stabilized on an activated Aerosil surface are of interest for the chemistry of strained molecules, which is one of the rapidly progressing fields of organic chemistry.[5]

In this work, we studied the reaction of methylenecyclopropane with the silyl radicals ≡Si˙ stabilized on an activated Aerosil surface.

Figure 1 presents the ESR spectra recorded for the activated Aerosil surface before and after interaction with methylenecyclopropane. Analysis of the ESR spectrum of the reaction products indicates that it consists largely (according to our estimates, by no less than 70%) of a triplet of triplets with splittings of 2.1 and 2.5 mT and with an intensity ratio of ~1 : 2 : 1. The parameters of the observed ESR spectrum are close to those recorded previously[1] for type R—CH_2—CH_2˙ radicals stabilized on an Aerosil surface.

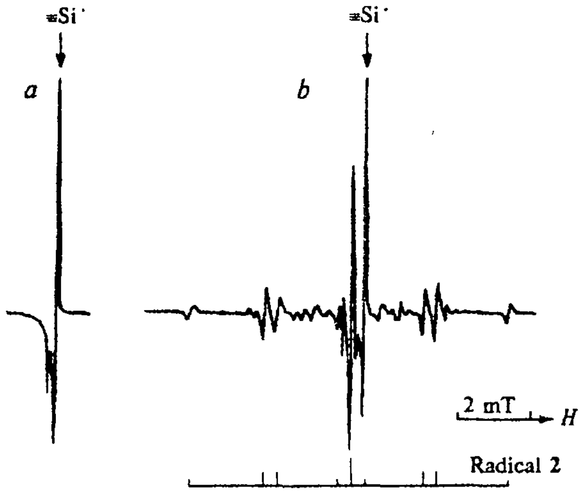
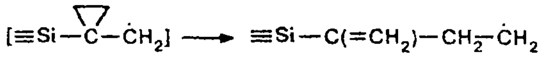


Fig. 1. ESR spectra of silyl radicals ≡Si˙ (*a*) and of the products of their interaction with methylenecyclopropane (*b*) on activated Aerosil surface at 300 K.

The reaction of silyl radicals with methylenecyclopropane involving the ring C atom attached to the exocyclic double bond, *i.e.*, the site with the maximum electron density in the molecule,* should yield mostly radicals of the cyclopropylcarbynyl type (**1**); the latter are known[6,7] to be unstable at room temperature and to rearrange into radicals of the 3-butenyl type (**2**).



1 **2**

It is these radicals **2** that we detected by ESR spectroscopy. In addition, the ESR spectrum exhibits components corresponding to paramagnetic centers other than those in radicals **2**. The strong overlap and the low intensity of the lines allow only the suggestion, based on the small values splitting, that they may belong to allyl type radicals.

Thus, our results confirm the possibility of easy homolytic cleavage of a ring bond in cyclopropane derivatives and indicate that the interaction of silyl radicals with methylenecyclopropane molecules involves mostly the C atom that bears the maximum electron density.

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* The authors are grateful to D. A. Tyurin for performing calculations of electron density distribution in the molecule of methylenecyclopropane using the MOPAC program package (Version 6.01).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 1065—1066, May, 1997.

1066-5285/97/4605-1028 $18.00

Experimental

Commercial Aerosil, with a specific surface of 100 m^2 g^{-1} after repeated activation, was used in the study. The method of thermochemical activation of Aerosil was described in detail previously.[8] The reaction of methylenecyclopropane occurring in the gas phase with $\equiv Si^{\cdot}$ radicals on the Aerosil surface (the concentration of $\equiv Si^{\cdot}$ was $\sim 3 \cdot 10^{15}$ m^{-2}) was carried out at 190 K. Since it was found that under the experimental conditions, the second methylenecyclopropane molecule reacts with the radicals formed faster than with $\equiv Si^{\cdot}$, small quantities of methylenecyclopropane (smaller than the concentration of $\equiv Si^{\cdot}$ on the Aerosil surface) were used, and complete conversion of $\equiv Si^{\cdot}$ into radical products was not attained. The ESR spectrum was recorded on a Varian E-3 radiospectrometer operating in the three-centimeter range.

The authors are grateful to T. S. Kuznetsova for help and useful discussion.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 96-03-33662).

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Received November 19, 1996

Dynamic and electrooptical properties of FH...F and FH...N hydrogen bridges

G. V. Yukhnevich, T. T. Merzlyak, and O. Yu. Tsoi*

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117071 Moscow, Russian Federation.
Fax: 007 (095) 954 1279. E-mail:gvyukhn@ionchran.msk.ru

The dynamic and electrooptical parameters of the hydrogen bridges in $(HF)_2$, FH...FCD_3, FH...NCH, and FH...$NCCH_3$ complexes were calculated by the MINDO/3 method. Relationships between these parameters have been found. These parameters for the F—H...Y bridges mainly coincide with the relationships previously established for the hydrogen O—H...Y bridges.

Key words: hydrogen fluoride, hydrogen bond; potential energy surface, force constant; dipole moment.

Intermolecular interactions in gases and liquids result in the formation of various complexes and associates. The compositions and structures of these molecular forms affect the different physicochemical properties of a substance and its reactivity. That is why the structures of molecular and ion-molecular complexes have become an object of investigation in various scientific areas. In these investigations, IR spectroscopy is often used, which requires knowledge of the dynamic and electrooptical properties of the intermolecular bonds uniting the molecules into a complex. These properties, characterized by the dynamic and electrooptical parameters of the bonds and angles, are usually determined by solving the inverse spectral problems (ISP) or by quantum-chemical calculations. The dynamic and electrooptical parameters of the different strength hydrogen bonds formed by

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 1067—1069, May, 1997.