BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 298—299(1972)

Rotational Isomerism in Ethylmethylsilane

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(Received July 27, 1971)

Although many experimental data have been accumulated concerning rotational isomerism, a number of molecules have not yet been studied. In this note, we will deal with the vibrational spectra of ethylmethylsilane in relation to the rotational isomerism.

Experimental

The samples of ethylmethylsilane and its deuterated species ($CH_3CH_2SiD_2CH_3$) were prepared as follows. Methyltrichlorosilane was treated by an ethyl Grignard reagent, and the product ($CH_3CH_2SiCl_2CH_3$) was reduced with $LiAlH_4$ or $LiAlD_4$ respectively.[1]

The infrared spectra in the region from 4000 to 200 cm^{-1} were recorded with Perkin-Elmer instruments (model 621 and 521) and Hitachi instruments (EPI-L and FIS-3). For the measurements in the crystalline state, the vapor of the sample was directly condensed on CsI plate in a cell cooled with liquid nitrogen in a vacuum and was then annealed several times in order to keep the sample from being in the supercooled liquid state. The method was also extended to measurements in the liquid state at about 19°C, since the boiling point of the sample is rather low for measurements using the usual technique.

Results and Discussion

According to the reported vibrational assignments for similar molecules, such as dimethylsilane[2] and ethylsilane,[3] CCSi deformation, SiH_2 rocking, twisting, wagging, Si–C symmetric, and asymmetric stretching modes would be expected in the regions around 300, 467(389), 591 (472), 643(558), 659(636), and 728(700) cm^{-1} respectively, where the frequencies in parentheses indicate the expected frequencies for the deuterated species.

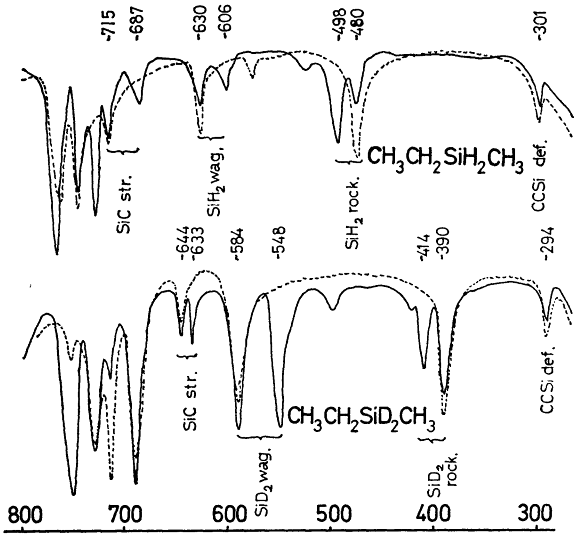

Fig. 1. The infrared spectra of ethylmethylsilane and its deuterated species; —— in the liquid state (19°C), ······ in the crystalline state.

As is shown in Fig. 1, in the region from 700 to 300 cm^{-1}, too many spectra exist there to be an unique molecular form, and some of the spectra vanish in the crystalline state. These facts provide us with evidence of the existence of rotational isomers in the liquid state. The assignments of the observed spectra can easily be found for this region; some are shown in Fig. 1.

The SiH_2 wagging mode and one of the Si–C stretching modes for the parent species are found at frequencies slightly different from those for dimethylsilane. However, this can be understood if these modes originally have nearly equal frequencies and are strongly coupled in ethylmethylsilane, while the corresponding modes in dimethylsilane are separated because of the symmetry of the molecule.

In the gaseous state, the resolution of the spectra becomes worse because of the broad envelopes of the unresolved rotational fine structures.

However, for the deuterated species, the SiD_2 rocking mode is seen as doublets like those in the liquid state; this is considered to be definite evidence of the existence of the rotational isomers in the gaseous state.

As for the parent species, careful measurements with a higher resolution give weak Q branches of the bands at 479 and 498 cm^{-1} over the broad band envelope; these correspond to the bands assigned to the SiH_2 rocking modes in the liquid state. Therefore, the isomers also exist in the parent species. The molecular forms of the isomers would be the *trans* and the *gauche* forms, as in the case of 1,2-dihalogenoethane.

One of the present authors (M.H.) has actually found the *trans* form in the gaseous state by microwave spectroscopy,[4] but he could not find the other form, since the observed microwave spectra were too weak for him to make definite assignments of the transitions for the *gauche* form at the temperature of dry ice.

As usual experimental techniques, such as solvent-effect measurements of the vibrational spectra, seem to be invalid for the determination of the molecular forms of ethylmethylsilane, normal vibration calculations for the skeletal vibrations were attempted regarding ethylmethylsilane as a four-body problem and using a set of force constants which had been obtained from the observed skeletal vibration frequencies of methylsilane,

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1) F. S. Kipping, *Proc. Chem. Soc.*, **20**, 15 (1904), W. Dilthey, *Ber.*, **37**, 319 (1904), and A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1199 (1947).

2) D. F. Ball, P. L. Goggin, D. C. McKean, and L. W. Woodward, *Spectrochim. Acta*, **16**, 1358 (1960).

3) K. M. Mackay and R. Watt, *ibid.*, **23A**, 2761 (1967).

4) M. Hayashi and C. Matsumura, to be published.

ethylsilane, and dimethylsilane.

However, the observed skeletal frequencies of ethylmethylsilane could not be reasonably reproduced by this over-simplified treatment. Therefore, at present, we cannot conclude whether or not one of the isomers is in the *gauche* form and which isomer persists in the crystalline state.

The authors wish to express their thanks to Professor Tatsuo Miyazawa of Osaka University and to the staff of his research group for allowing us to use their instruments and for their technical assistance.