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MASS SPECTROSCOPY OF ORGANOSILICON COMPOUNDS. FRAGMENTATION PATTERNS OF LINEAR ORGANOPOLYSILANES

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SUMMARY

Mass-spectral fragmentation patterns of some lower homologues of linear polysilanes are discussed. Two main types of fragmentation were observed. type A fragmentation involves elimination of a trimethylsilyl group from a molecular ion followed by a successive loss of a dimethylsilylene unit, while type B fragmentation involves elimination of a neutral fragment through a four-membered transition state to give a "disilene" radical cation.

INTRODUCTION

The mass spectra of various types of organosilicon compounds have been reported recently, and novel intramolecular migrations of silyl groups appear in the fragmentation processes[1-5]. However no investigations on the mass spectroscopic properties of organopolysilanes have been reported to date except for some disilane derivatives[6,7]. In contrast to the carbon analogues, some remarkable features have been reported recently for organopolysilanes on thermolysis[8] and photolysis[9-12]. In connection with the studies, it seemed desirable to elucidate the mass-spectroscopic behavior of some lower homologues of organopolysilanes, and this paper describes the general fragmentation patterns of linear polysilanes.

RESULTS AND DISCUSSION

Fragmentation processes for a linear polysilane can be classified into two types. Type A fragmentation involves elimination of a trimethylsilyl group from a molecular ion followed by a successive loss of a dimethylsilylene unit, as shown in Scheme 1. In the case of a straight chain hydrocarbon, this type of fragmentation process apparently constitutes a main fragmentation path and makes its mass spectrum a useful tool for structural determination. Type B fragmentation involves the elimination of a neutral fragment through a four-membered transition state as depicted in Scheme 2 In contrast to type A process, this second fragmentation pattern is unique to linear organopolysilanes.

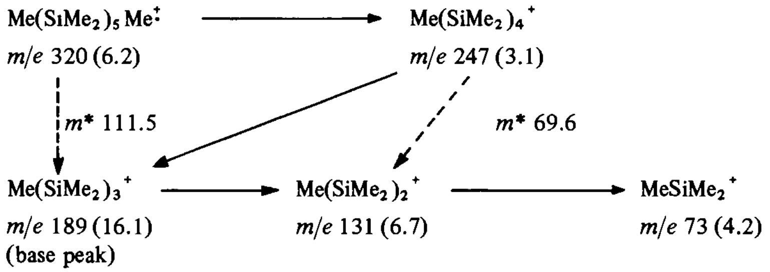
A relationship between mass spectroscopic properties and photochemical

SCHEME 1

TYPE A FRAGMENTATION

$$Me(SiMe_2)_nMe^{\ddagger} \longrightarrow Me(SiMe_2)_{n-1}^{+} \longrightarrow Me(SiMe_2)_{n-2}^{+}$$

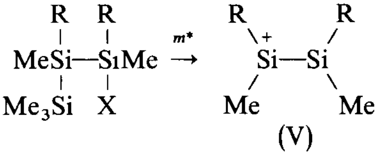
Example



SCHEME 2

TYPE B FRAGMENTATION

Figures in parenthesis are the Σ_{40} values of the corresponding peaks



(I) $R = Me, X = Me$	(Va) m/e 116 (13.1)
(II) $R = Me, X = SiMe_3$	(Vb) m/e 116 (8.7)
(III) $R = Me, X = Si_2Me_5$	(Vc) m/e 116 (8.7)
(IV) $R = -(CH_2)_2, X = Me$	(Vd) m/e 142 (3.3)

reactions has been suggested in recent years[13-15]. Irradiation of an organopolysilane with ultraviolet light has been shown to evolve a silylene[9-12], but no significant peaks corresponding to this type of photochemical process were detected. Therefore, direct loss of a dimethylsilylene unit from a molecular ion of a polysilane does not occur, at least as a main path.

Type A fragmentation

The fragments produced by the type A path are apparently very abundant, and constitute major peaks in mass spectra of linear polysilanes, as illustrated by Fig. 1. These processes are confirmed by the presence of some appropriate metastable peaks. Although the mechanisms of these fragmentation steps can be expected to be quite similar to one another, the corresponding metastable transitions are not always observed in all cases For example, even in what is formally the same process as the fragmentation of the pentamethyldisilanyl to the trimethylsilyl cation, with octamethyltrisilane (I), decamethyltetrasilane (II) and dodecamethylpentasilane (III), the corresponding metastable peak is not detected in the case of (I). This may be attributed to either different energy distribution in the fragments or different ion structures. In contrast, for the step from the heptamethyltrisilanyl to the pentamethyldisilanyl cation, the corresponding metastable peak is observed in both (II) and (III). In addition to the fragmentation path A, elimination of a pentamethyldisilanyl group from a molecular ion (shown by a dotted line in Scheme 1) is indicated by the presence of an appropriate metastable peak. This process gives the peak at (M–131) which can also arise from the path A, involving the elimination of a trimethylsilyl unit (M–73) followed by the ejection of a dimethylsilylene unit (M–73–58). These peaks then constitute the base peaks in the mass spectra of (III) and (II) measured at 25 eV. This suggests that the loss of the disilanyl unit may be rather important in the fragmentation process of a linear permethylated organopolysilane. This may be rationalized on the basis of the fact that a radical or a radical cation derived from a disilane is more stabilized than that from a monosilane[16]

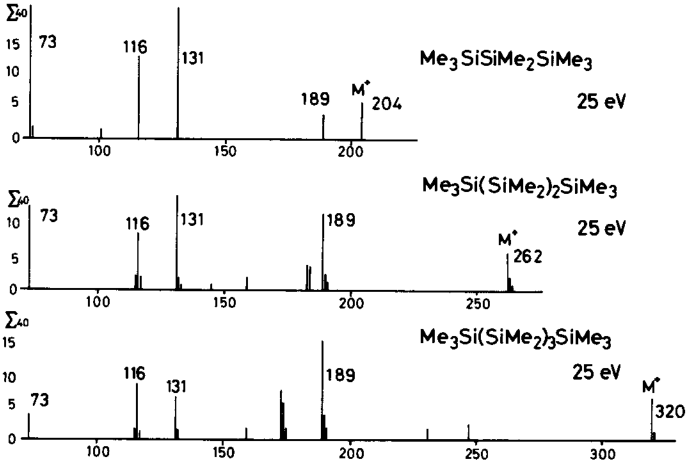


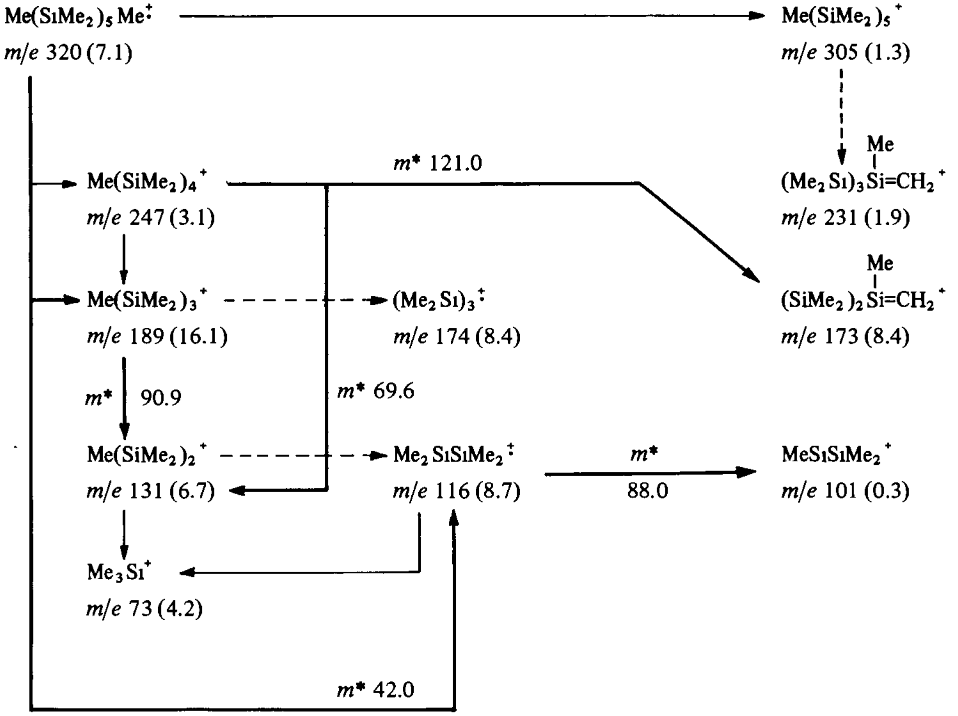
Fig 1 Mass spectra of octamethyltrisilane, decamethyltetrasilane and dodecamethylpentasilane

Type B fragmentation

The occurrence of formally four-center fragmentation processes (Type B) is supported by the presence of the appropriate metastable peaks, as shown in Scheme 2 The fragments (Va–d) formally correspond to radical cations of compounds having a Si–Si double bond. The rather high abundance of these fragments suggest that these degradation processes are important in the mass spectra of linear polysilanes. Their considerable stabilities in a mass spectrometer, in contrast to their properties in the ground state[17], are interesting.

Finally the fragmentation pattern of mass spectrum of dodecamethylpentasilane (III) is shown in Scheme 3, which may be taken as typical of the mass spectra of homologous series of linear organopolysilanes. Related work on cyclic polysilanes and carbopolysilanes will be described in a forthcoming paper.

SCHEME 3



EXPERIMENTAL

Organopolysilanes (I), (II) and (III) were prepared by methods described in the literature[18]. A new compound (IV) was prepared during the course of photochemical investigations[12]. Details will be published elsewhere.

Mass spectra were taken by Mr. T. Sato with a Hitachi RMU-60 mass spectrometer.

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