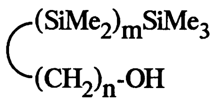
CHEMISTRY LETTERS, pp. 601-602, 1991

Mass Spectral Fragmentations of Polysilanylalkanols. The Analogies between Mass Spectrometry and Photo-Induced Electron Transfer

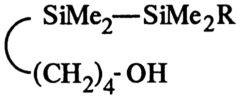
Yasuhiro NAKADAIRA, Shinju OTANI, Soichiro KYUSHIN, Mamoru OHASHI,
Hideki SAKURAI,† Yasuhito FUNADA,† Kenkichi SAKAMOTO,† and Akira SEKIGUCHI†
Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182
†Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

The mass spectra of polysilanylalkanols can be rationalized on the basis of their characteristic reactions under photo-induced electron transfer reactions.

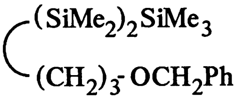
To prove intervention of the polysilanyl radical cation by a nucleophilic trap in photo-induced electron transfer (ET) reactions, polysilanylalkanols **1** - **2** have been prepared in which a hydroxyl group is introduced into the polysilanyl unit at the appropriate position. As expected, the radical cations $1^{+\cdot}$ - $2^{+\cdot}$ are readily trapped intramolecularly to give the corresponding cyclic siloxanes, for example $\mathbf{2b}^{+\cdot}$ gives **4** and **5**.¹⁾ The process of bond cleavage of the radical cation produced by ET is reasonably assumed to be similar to that of the molecular ion ($M^{+\cdot}$) generated by electron ionization, even though there are some fundamental differences in both processes.²⁾ In connection with our recent studies of the photo-induced ET reactions,¹⁾ ³⁾ we have investigated mass spectral fragmentations of **1** - **2** in some detail. Herein, we report the characteristics of mass spectroscopic behavior of **1** - **2** and the analogies with those of photo-induced ET reactions.



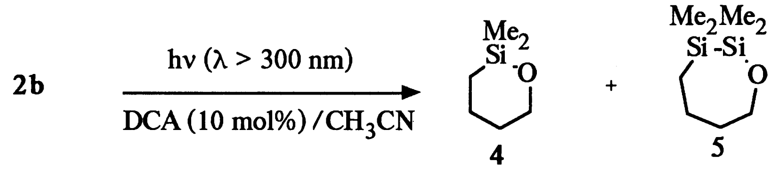
1a; m = 1, n = 3
1b; m = 2, n = 3
2a; m = 1, n = 4
2b; m = 2, n = 4



2c; R = C_6H_5
2d; R = C_6H_4(p-Me)
2e; R = C_6H_4(p-MeO)
2f; R = C_6H_4(p-CF_3)

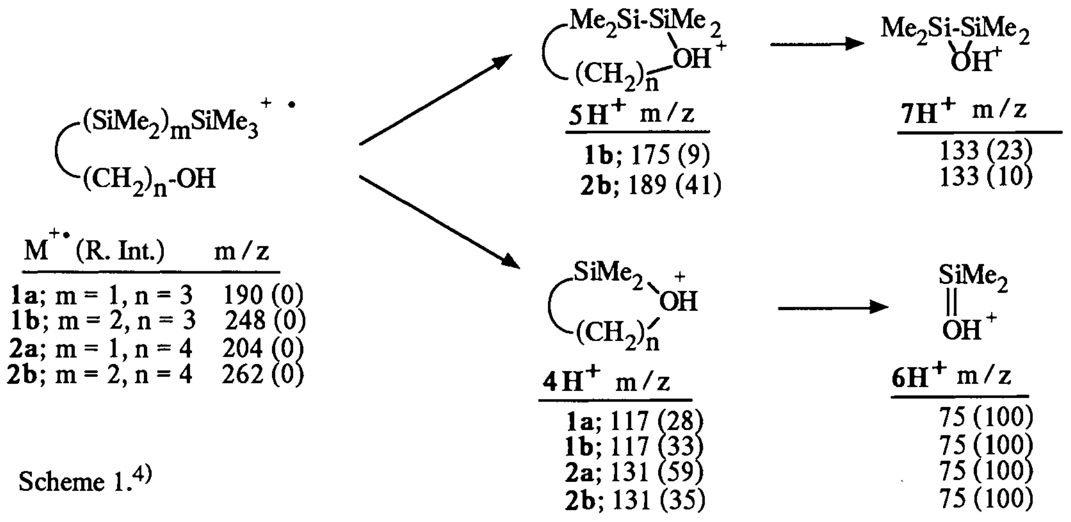


3



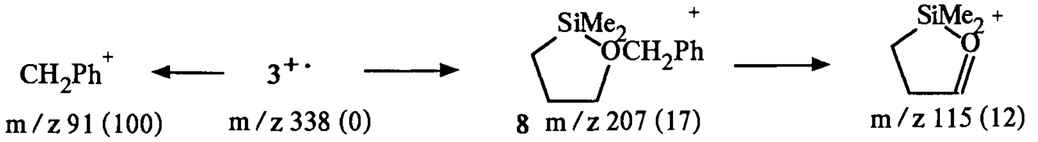
4 **5**

As summarized in Scheme 1, the mass spectra of **1** - **2** show no $M^{+\cdot}$ but rather simple fragment ions. In contrast, a linear permethylpolysilane shows moderate intensity of the peak due to $M^{+\cdot}$, which eliminates a trimethylsilyl group followed by a successive loss of a dimethylsilylene unit.⁵⁾ Thus, incorporation of the hydroxyl group alters the principal fragmentation path of the polysilanyl chain completely. The most prominent feature is the presence of the peaks at m/z 117 and 131 assignable to those due to $\mathbf{4H}^{+}$. These ions decay further to give the peak at m/z 75 due to $\mathbf{6H}^{+}$ in common. In cases of trisilanes **1b** and **2b**, there are two possible positions to be attacked by the hydroxyl group, and



Scheme 1.[4)]

in addition to $4H^+$, the peak corresponding to $5H^+$ is also observed which gives rise to the peak at m/z 133 due to $7H^+$ in a similar way. The presence of both fragmentation processes, namely, $4H^+$ to $6H^+$, and $5H^+$ to $7H^+$ are indicated by linked scannings (both B^2/E and B/E constant spectra).[6)] These fragmentations are readily interpreted on the basis of their chemical behaviors on the photo-induced ET. Thus, the cationic polysilanyl chain of **1a** and **2a** should be trapped intramolecularly by the hydroxyl group quite efficiently to give $4H^+$. The MS spectra of **2c** - **f** are very alike to those of **1a** and **2a** excepting the presence of peaks due to the corresponding phenyldimethylsilyl cation. In addition to the absence of the $M^{+\cdot}$ peak, there present $4H^+$ ion and $6H^+$ base ion peaks. Interestingly, 4-trisilanylpropylbenzylether (**3**) shows a fragmentation pattern and in this case, the fragment **8** at m/z 207 is assignable to an ion produced from the nucleophilic attack of the cationic trisilanyl chain by the oxygen of the benzyl ether.[7)]



The work was supported in part by Grants-in-Aid for Scientific Research on Priority Area Research Nos. 01648508 and 02230211, and for Scientific Research No. 02640387 from the Ministry of Education, Science and Culture.

References

1) Y. Funada, A. Sekiguchi, Y. Nakadaira, and H. Sakurai, Symposium on Photochemistry, Japan, IIA 303 (1988); Y. Nakadaira, A. Sekiguchi, Y. Funada, and H. Sakurai, submitted to publication.
2) M.Ohashi, S. Akiyama, and S. Yamada, Nippon Kagaku Kaishi, **1989**, 1386.
3) Y. Nakadaira, N. Komatsu, and H. Sakurai, Chem. Lett., **1985**, 1781; S. Kyushin, Y. Ehara, Y.Nakadaira, and M. Ohashi, J. Chem. Soc., Chem. Commun., **1989**, 279.
4) The mass spectra were measured at 15 eV on a Hitachi M-80B mass spectrometer. The ionization of 1 and 2 should take place at the Si-Si bond, and not at the oxygen atom of the hydroxyl group. (IP: $SiMe_3SiMe_3$, 8.69 eV[a]; iPrOH, 10.37 eV[b]: [a] H. Boch and W. Ensslin, Angew. Chem., **83**, 435 (1971); [b] J. W. Robinson, "Handbook of Spectroscopy", CRC press, Bocaraton, Fla., (1974), Vol. 1, p. 257.
5) Y. Nakadaira, Y. Kobayashi, and H. Sakurai, J. Organomet. Chem., **63**, 79 (1973).
6) Some other fragmentation paths are suggested from linked scannings and will be discussed elesewhere.
7) Irradiation of 3 in CH_3CN containing a catalytic amount of 9,10-dicyanoanthracene (DCA) resulted in formation of complex mixtures.

(Received December 25, 1990)