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Matrix Effect. Dimerization of Silylenes at 77 K in the Matrix

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The dimerization of silylenes was studied in hydrocarbon matrix ranging in viscosity from 10^6 to 10^{12} at 77 K. The silylenes dimerized to disilenes in soft matrix at 77 K without annealing.

The matrix isolation technique has widely been used in the observation of the highly reactive molecules.[1] The first spectroscopic investigation of an organosilylene was demonstrated in 1979 and dimethylsilylene was generated in solid argon at 10 K and 3-methylpentane (3-MP) at 77 K by the photolysis of dodecamethylcyclohexasilane.[2] Subsequently, dimesitylsilylene was isolated in 3-MP matrix at 77 K.[3] The latter has been shown to dimerize to a stable tetramesityldisilene on annealing the matrix.[3] We wish to report here that silylenes can dimerize in soft matrix at even 77 K without annealing the matrix and the rate of the dimerization is highly dependent on the viscosity of the matrix.

Irradiation of 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane at 77 K in 3-MP matrix with a low pressure mercury lamp led to the formation of a band at 577 nm attributed to dimesitylsilylene. The color of the matrix bacame intense blue as reported.[3] This absorption band did not decrease at 77 K on the prolonged standing. However, the band disappeared on the careful annealing to give a new band with a maximum of 420 nm due to tetramesityldisilene. These results are completely identical with those reported by West.[3] On the other hand, the dimerization of the dimesitylsilylene took place in isopentane/3-MP matrix at 77 K without annealing. Thus, a mixture of isopentane and 3-MP containing the trisilane ($\approx 6 \times 10^{-3}$ M) was placed in a quartz cell and cooled to 77 K. Irradiation of the resulting matrix for 15 min. led to the generation of the two absorption bands due to dimesitylsilylene (573 nm) and tetramesityldisilene (420 nm).[4] When the matrix was allowed to stand in the dark at 77 K, the absorption band at 573 nm due to the dimesitylsilylene gradually diminished as a function of time with concurrent grows of an absorption band at 420 nm due to the tetramesityldisilene. The band at 420 nm grows on at the almost same rate with decrease of the band at 573 nm. This indicates that the silylene can dimerize in soft matrix at even 77 K without annealing. The dimesitylsilylene also dimerized in n-pentane/neohexane (3 : 8) matrix at 77 K. The relation

between the half life of the dimesitylsilylene and the viscosity of the matrix is given in Table 1 which shows that the dimerization of the silylene is strongly influenced by the viscosity (hardness) of the matrix. Since 3-MP is a hard matrix (viscosity: 9.4×10^{11} P at 77 K), the silylene cannot dimerize in 3-MP matrix.

Dimethylsilylene also dimerized to tetramethyldisilene in isopentane/3-MP matrix at 77 K without annealing. Thus, the band at 453 nm due to dimethylsilylene diminished in the dark at 77 K with concurrent grows of the band at 345 nm attributed to tetramethyldisilene in isopentane/3-MP (5 : 5) matrix.[5] However, the absorption band of the dimethylsilylene did not decrease in 3-MP matrix at 77 K.

Table 1. Relation between the half life of silylenes and the viscosity of the matrix at 77 K

Silylene	Matrix solvent	Half life of silylene (min)	Viscosity at 77 K η (poise)[a]
Mes_2Si:	IP/3-MP (0 : 1)[b]	-[c]	9.4×10^{11}
"	IP/3-MP (4 : 6)	-[c]	5.1×10^{9}
"	IP/3-MP (5 : 5)	-[d]	5.9×10^{8}
"	IP/3-MP (6 : 4)	290[e]	1.8×10^{8}
"	IP/3-MP (7 : 3)	75[e]	5.2×10^{7}
"	n-pentane/neohexane (3 : 8)	70[e]	4.8×10^{7}
"	IP/3-MP (8 : 2)	60[e]	1.8×10^{7}
"	IP/3-MP (9 : 1)	25[e]	3.6×10^{6}
Me_2Si:	IP/3-MP (0 : 1)	-[c]	9.4×10^{11}
"	IP/3-MP (5 : 5)	68[e]	5.9×10^{8}

a) The viscosity data were taken from Ref. 6. b) IP: Isopentane. c) The dimerization of silylenes did not take place. d) Dimesitylsilylene dimerized very slowly. e) The absorption band of the disilene grew on with respect to decrease of the band of the silylene.

References

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3) R. West, M. J. Fink, and J. Michl, Science, 214, 1343 (1981); R. West, Science, 225, 1109 (1984).
4) The small hypsochromic shift of the dimesitylsilylene from 3-MP matrix to isopentane/3-MP matrix is probably due to the solvent effects.
5) The absorption band of tetramethyldisilene is reported to be 350 nm in 3-MP. H. Vancik, G. Raabe, M. J. Michlczyk, R. West, and J. Michl, J. Am. Chem. Soc., 107, 4097 (1985).
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