The Role of the Triplet State in Insertion Reactions of Silylenes

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Summary The allowed or forbidden nature of silylene insertion reactions is considered on symmetry grounds together with the consequent energy requirement for such reactions

IN recent work[1] we have constructed a theoretical method for calculating internally consistent heats of formation and bond dissociation energies for di-, tri- and tetra-substituted silicon species.

In the Figure the calculated ΔH_f° values (for SiH_x) are plotted *vs.* x. Of particular significance is the fact that a smooth curve pertains to $x = 0,1,3,4$ whereas ΔH_f° for the singlet species SiH_2 is some 50 kJ mol^{-1} more stable than predicted by the smooth curve.

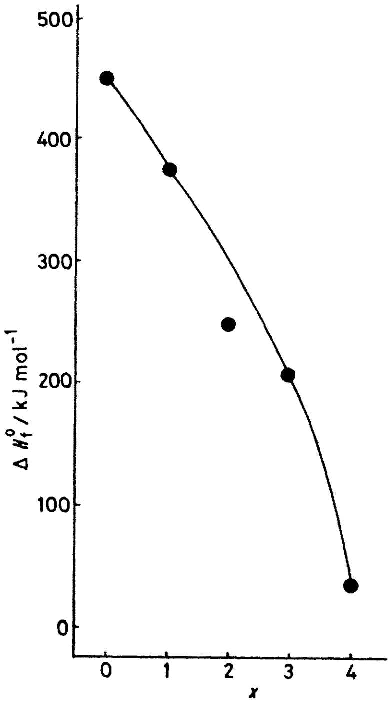

FIGURE. Plot of heats of formation of SiH_x *vs.* x.

The $^1A_1$ ground and the first excited $^3B_1$ states of SiH_2 have been estimated by different authors[2,3] to differ by $\leqslant 59$ and 42 kJ mol^{-1}. Thus, we opine that the difference of *ca.* 50 kJ mol^{-1} between the calculated point and that estimated from the smooth curve at $x = 2$ corresponds to the $^1A_1-{}^3B_1$ separation for SiH_2.

By an exactly analogous argument we found the singlet–triplet separations to be *ca.* 100 kJ mol^{-1} for $SiMe_2$ and *ca.* 115 kJ mol^{-1} for $SiCl_2$.

These conclusions have an important bearing on the interpretation of current kinetic work in silylene chemistry. Thus, Davidson and Mathews,[4] from decomposition studies on Si_2Me_5H, estimate $\Delta H_f^{\circ}(SiMe_2)$ *ca.* 68 kJ mol^{-1}, whereas Strausz and Neudorfl's[5] decomposition studies of Me_2SiH_2, yield ΔH_f° $(SiMe_2)$ *ca.* 176 kJ mol^{-1}. These experimentally estimated values differ by *ca.* 108 kJ mol^{-1}, close to our calculated triplet–singlet separation for $SiMe_2$ *ca.* 100 kJ mol^{-1}. We believe this experimental difference is due to the energy consequence of the symmetry allowed or forbidden nature of the two reactions.

In this communication we advance the basis for a general symmetry theory of silylene insertions (the reverse of silane decomposition), to account for the observed allowed and forbidden nature of such reactions.

For simplicity we first consider the reaction $SiH_2 + H_2 \rightarrow SiH_4$, which requires electrons to be transferred from the donor SiH_2 species into the antibonding molecular orbital of H_2. The latter is antisymmetric with respect to rotation about the reaction co-ordinate; however, our SCF calculation shows the highest donor bonding level of SiH_2 is symmetric to this operation. Hence reaction of $^1A_1$ SiH_2 with H_2 is symmetry-forbidden.

The lowest antibonding orbital of SiH_2 is substantially the non-bonding p_π orbital localised on Si which is occupied in the $^3B_1$ state; this matches in symmetry the antibonding H_2 orbital. Hence we suggest that the singlet–triplet excitation energy of SiH_2, at least, must be supplied as activation energy for the reaction to take place.

Conversely, for the decomposition of silane into SiH_2 and H_2, the activation energy must overcome the enthalpy of reaction plus the triplet excitation energy of SiH_2 in the immediate dissociation products.

Our calculations show that for both $SiMe_2$ and $SiCl_2$ the symmetry properties of both the highest bonding and lowest antibonding molecular orbitals are similar to those for SiH_2. Hence insertion of $SiMe_2$ and $SiCl_2$ into H_2 will again be limited by symmetry and require excitation to the $^3B_1$ state.

The same effect should obtain for all symmetrical subtrates in which the lowest-lying antibonding orbital is antisymmetric across the central bond. Thus insertion of SiX_2 into Si_2H_6 and Si_2Me_6 will be forbidden, the lowest unoccupied orbital between the two silicon atoms being strongly antibonding.

Allowed silylene insertions will proceed without excitation energy when the antibonding orbital relating to the bond into which the insertion occurs is symmetric with respect to the reaction co-ordinate.

Thus, in the process, $SiH_2 + SiH_4 \rightarrow Si_2H_6$, where the reaction is occurring along a path of C_{2v} symmetry, one orbital of the first degenerate set of antibonding molecular orbitals of SiH_4 corresponds to the highest bonding orbital of SiH_2, and the reaction is symmetry-allowed. Direct calculation of the reaction co-ordinate[6] shows that the reaction proceeds without activation energy.

The symmetry considerations above allow an explanation for the apparent discrepancy for the values of ΔH_f° $(SiMe_2)$ determined from the decomposition of Me_2SiH_2 and Si_2Me_5H.

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