Ab initio Study of the Insertions of CH_2 and SiH_2 into H_2

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Summary While the insertion of CH_2 into H_2 proceeds with no energy barrier, the SiH_2 insertion has to overcome a 36 kJ mol^{-1} barrier, calculated by SCF + MP2 methods.

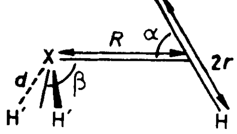

FIGURE 1. Approach of XH_2 to H_2 (X = C or Si); H′ are the SiH_2 hydrogens.

THE insertion of singlet CH_2 into H_2 to form methane has been the subject of two recent *ab initio* papers.[1,2] With correlation effects included, both papers conclude that the insertion proceeds with no energy barrier. This is consistent with experimental evidence[3] that little or no activation barrier exists for the methylene insertion. In contrast, based on the co-pyrolysis of disilane with H_2, John and Purnell[4] predict a 23 kJ mol^{-1} activation energy for the insertion of SiH_2 into H_2. In view of this striking difference between the two reactions, an *ab initio* study of the two insertions has been carried out in this laboratory.

For CH_4, the C_s reaction path (Figure 1), suggested by previous workers,[1,2] was used. The dependent parameters, d, r, α, β (the angle between R and the H′–X–H′ plane), and H′–X–H′ were optimized for each value of R, using the 3-21G basis set [5,6] and a numerical gradient technique.[7] While the SCF calculations give rise to a small insertion barrier, single-point calculations along the 3-21G path, but with a 6-31G^* basis set[8,9] augmented by second-order perturbation corrections[10] (6-31G^* + MP2//3-21G) predict the insertion to occur with no energy barrier, in agreement with previous calculations.

Even though the choice of R as reaction co-ordinate leads to a down-hill path for the CH_2 insertion, the sharp changes in geometry and energy at intermediate values of R† suggest that variation of R may not correspond to a minimum energy path. Indeed, following the same procedure for X = Si, it becomes clear that R is not a proper choice for the reaction co-ordinate. For values of R between 1·5 and 2·0 Å, two minima may be found: one corresponds to $2r \approx r_e$ (H_2) and the other to much larger values of r. This behaviour is found at both the SCF and SCF + MP2 levels of approximation. To determine the 3-21G SCF transition state, a grid of points was mapped using R and r as independent parameters and by optimizing the remaining four parameters. By this procedure, a point was detected for which the quadratic force-constant matrix has only one negative eigenvalue. From this point the transition state was easily found using the procedure suggested by Hilderbrandt.[11] At the saddle point, the parameters are R 0·1524 nm, $2r$ 0·1103 nm, d 0·1484 nm, α 82·02, H′–X–H′ 112·51, and β 108·83° and the 6-31G* parameters are very similar. A schematic diagram of the normal mode which corresponds to the reaction co-ordinate at the saddle point is shown in Figure 2. The reaction co-ordinate contains strongly coupled motions of R and r, but has very little contribution from the internal SiH_2 structure.

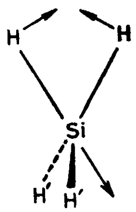

FIGURE 2. Schematic representation of the SiH_4 reaction co-ordinate at the saddle point; H′ are the SiH_2 hydrogens.

The calculated barrier to SiH_2 insertion is predictably too high at the SCF level; 110·9 and 78·2 kJ mol^{-1} for 3-21G and 6-31G*, respectively. When MP2 corrections are added to the 6-31G* results, the predicted barrier drops to 36·0 kJ mol^{-1}, in reasonable agreement with the experimental estimate of 23·0 kJ mol^{-1}.

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† The same result has been reported in ref. 2.

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