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Theoretical Studies of the Insertions of Germylene into Methane

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Abstract: The reaction mechanism for the insertion of germylenes into the C-H bond of methane has been investigated using the B3LYP/6-311G* level of theory. It is found that the more electropositive and/or stronger π-accepting the substituents on the germylenes are, the smaller the insertion barrier and the more exothermic the reaction. Our theoretical findings agree well with the available experiments.

Germylenes, the germanium analogues of carbenes, have been extensively studied over the last two decades.[1] Most of these compounds are unstable under normal conditions and thus have been used as reactive intermediates.[2] Intuitively, germylenes behave as heavy carbene analogues. Accordingly, they undergo concerted addition of 1,3-dienes via a thermal [2+4] cheletropic mechanism.[3] Besides, several insertion reactions into σ bonds have been described.[1,2] However, no detailed mechanistic studies of insertion into a carbon-hydrogen bond have been performed so far.

The purpose of the present work is therefore to investigate the influence of different substituted groups upon the energetics of the intermediates as well as the transition states. We have thus undertaken a systematic investigation of the insertion reactions of substituted germylenes XYGe: into the C-H bond of methane, where GeXY = GeH_2, $Ge{=}CH_2$, GeHLi, $GeLi_2$, $GeH(CH_3)$, $Ge(CH_3)_2$, GeHF, GeF_2, GeHCl, $GeCl_2$, GeHBr, and $GeBr_2$. See eq (1). In the present study, four stationary points on the potential energy surfaces will be considered: germylene plus free methane, the germylene-methane complex, the transition state, and the insertion product.

$$XYGe: + H\text{–}CH_3 \rightarrow XYGe{:}\bullet CH_4 \rightarrow TS \rightarrow Ge(X)(Y)(H)(CH_3) \qquad (1)$$

The geometries and energetics of the stationary points on the potential energy surface of eq (1) have been calculated with density functional theory (i.e., the B3LYP method)[4] in conjunction with the 6-311G* basis set.[5] All the stationary points have been positively identified as equilibrium structures (the number of imaginary frequency (NIMAG=0) or transition states (NIMAG=1)). The relative energies of the germylene insertion reactions are summarized in Table 1. The major conclusions that can be drawn from Table 1 are as follows.

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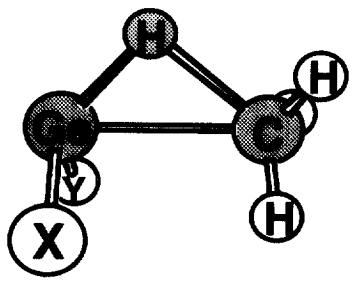
Table 1.

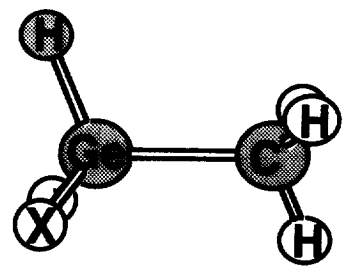
Relative Energies (kcal/mol) for Singlet and Triplet XTGe: Species and for the Process XTGe: + H–CH_3 → Precursor Complex → Transition State → Product.[a]

System	ΔE_{st} [b]	Reactants	ΔE_{cpx} [c]	$\Delta E^{\ddagger}$ [d]	ΔH [e]
GeH_2	+27.3	0	-0.936	+33.2	-28.0
$Ge{=}CH_2$	+59.0	0	-0.0487	+58.0	-5.25
GeHLi	-4.70	0	-0.453	+24.6	-28.6
$GeLi_2$	-5.95	0	+0.374	+29.3	-17.9
$GeHCH_3$	+28.6	0	-0.191	+35.8	-26.8
$Ge(CH_3)_2$	+30.7	0	-0.0157	+39.1	-25.1
GeHF	+46.4	0	-0.982	+48.6	-17.1
GeF_2	+83.9	0	-1.40	+77.7	+0.350
GeHCl	+42.2	0	-0.233	+48.1	-15.6
$GeCl_2$	+63.7	0	-0.0926	+70.0	-0.0812
GeHBr	+40.4	0	-0.171	+48.2	-14.5
$GeBr_2$	+56.8	0	+0.0247	+68.3	+1.28

(a) At the B3LYP/6-311G* level. (b) A positive value indicates a singlet ground state. (c) The stabilization energy of the precursor complex, relative to its corresponding reactants. (d) The activation energy of the transition state, relative to its corresponding reactants. (e) The reaction enthalpy of the product, relative to its corresponding reactants.



Transition State
1



Insertion Product
2

The transition structures for the insertion of germylene into methane are very similar to each other. Our DFT results show that the primary similarity among these transition structures is the three-center pattern involving germanium, carbon and hydrogen atoms, as shown in **1**. Moreover, our model calculations show that all the insertion products Ge(X)(Y)(H)(CH_3) adopt a staggered enthane-like structure as depicted in **2**. A comparison of the aforementioned twelve transition states reveals several interesting trends. From Table 1, it is readily seen that fluorine substitution has a large effect on the insertion barrier which, at B3LYP/6-311G*, are (kcal/mol) 33.2, 48.6, and 77.7 for GeH_2, GeHF, and GeF_2, respectively. Moreover, the more electronegative substituents lead to larger activation barriers. For instance, the B3LYP calculations indicate that the insertion barrier decreases in the order: GeF_2 (77.7 kcal/mol) > $GeCl_2$ (70.0 kcal/mol) > $GeBr_2$ (68.3 kcal/mol). On the other hand, it is observed that electropositive substituents on the germylene can increase the reaction rate of insertion. For example, the insertion barrier decreases in the order: $Ge(CH_3)_2$ (39.1 kcal/mol) > $GeH(CH_3)$ (35.8 kcal/mol) > GeH_2 (33.2 kcal/mol) > $GeLi_2$ (29.3 kcal/mol) > GeHLi (24.6 kcal/mol). It is worth noting that, as seen in Table 1, the activation barriers for methyl and dimethyl germylene insertion into methane are 35.8 and 39.1 kcal/mol, respectively, but those for germylidene and halogen-substituted germylene insertion are in the range 48.1 – 77.7 kcal/mol. Thus, these theoretical results indicate that the magnitude of the activation barriers for methane insertion that we have examined so far depends more strongly on electronic factors than on steric interactions.[6]

Furthermore, a plot of the activation energy ($\Delta E^{\ddagger}$) versus the reaction enthalpy (ΔH) shows that for all the compounds examined $\Delta E^{\ddagger}$ varies linearly with ΔH. That is, a linear correlation between $\Delta E^{\ddagger}$ and ΔH obtained at the B3LYP/6-311G* level of theory is $\Delta H = 0.6235\Delta E^{\ddagger} - 44.96$, as shown in Figure 1. Accordingly, our theoretical results are consistent with the prediction that the activation barrier should be correlated with the exothermicity of germylene insertion.[7]

In summary, this work represents an attempt to use the density functional theory to investigate the potential energy surface for the insertion of germylenes into C–H bonds. From our model calculations, it is apparent that germylene insertions occur in a concerted, synchronous manner with large barriers (24.6 – 77.7 kcal/mol). Thus, our theoretical findings are consistent with the experimental evidence, i.e., it is generally agreed that C–H bonds are significantly stable toward germylenes.[2] The driving force for this may be traced to $\Delta E_{\sigma\sigma^*}$ (= $E_{triplet} - E_{singlet}$ for CH_4) and steric effects.[6] Nevertheless, on the basis of the results of the present study, we are confident in predicting that for the substituted germylenes XYGe:, the more electropositive the substituents, the lower the activation barrier and the larger the exothermicity of its insertion into saturated C–H bonds.

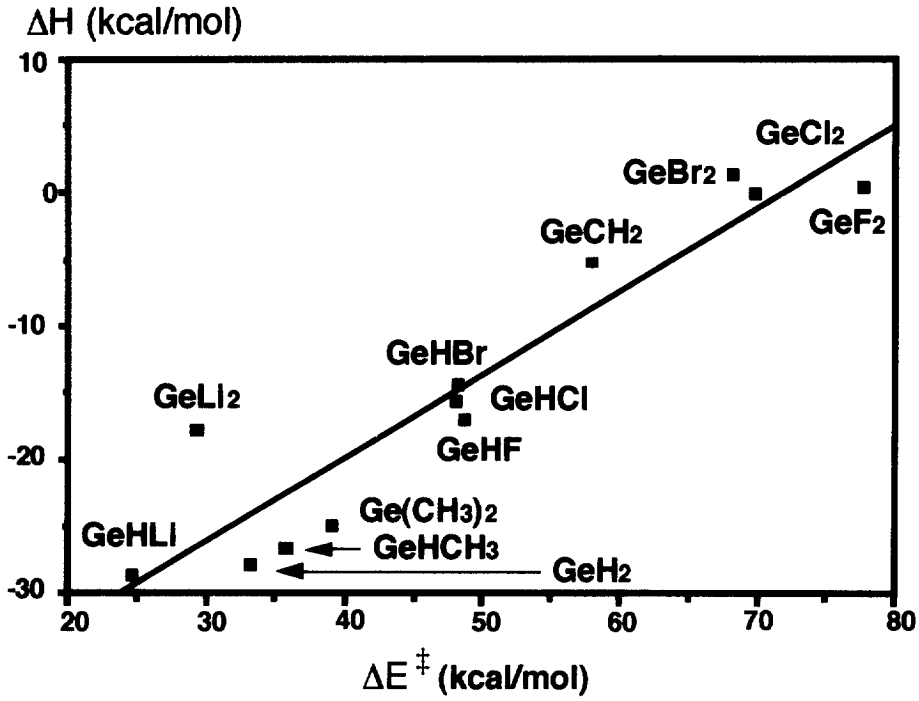


Figure 1: The activation energy ($\Delta E^{\ddagger}$) vs. the reaction enthalpy (ΔH) for the insertion of XYGe: into H–CH3. The linear regression equation is $\Delta H = 0.6235\Delta E^{\ddagger} - 44.96$ and with a correlation coefficient R = 0.879.

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