Organometallics **1984**, *3*, 324–325

Communications

Germaethene. Barrier Heights for the 1,2-Hydrogen Shift and the Reaction with Water

Shigeru Nagase* and Takako Kudo

Department of Chemistry, Faculty of Education
Yokohama National University, Yokohama 240, Japan

Received August 4, 1983

Summary: To extend knowledge of the germanium–carbon double bond, the title reactions of singlet germaethene were investigated with ab initio calculations. It is found that germaethene resembles silaethene closely in stability and reactivity, though germanium is more reluctant to form doubly bonded compounds than silicon.

In view of recent dramatic developments in silaethene chemistry,[1] analogous extensive studies of germanium–carbon doubly bonded compounds, germaethenes, should soon be forthcoming and open up new areas. Evidence consistent with the transient existence was accumulated in the last few years.[2] However, most of the experimental evidence is only indirect. In addition, very little is known about the mechanistic aspects of the reactions of the important intermediates.

Theory should provide helpful information in this regard, and two reports of calculations on germaethene and its 1,2-hydrogen-shifted isomers have already appeared.[3,4] Although much more stable than germylmethylene,[3] germaethene was predicted to be 23[3]–15[4] kcal/mol less stable in a thermodynamic sense than methylgermylene. However, none of the reports dealt with the nature of the transition state or the energy barrier separating the doubly bonded from the more stable divalent species, still less with the reactivity toward trapping reagents. In an attempt to characterize the stability and reactivity of germaethene, we report here ab initio calculations of the 1,2-hydrogen shift as well as the reaction with water and compare these with data on silaethene at comparable levels of theory.

All calculations for closed-shell singlets were carried out with the double-ζ (DZ) and DZ+d basis sets.[5] Geometries were fully optimized at the Hartree–Fock (HF) level with the analytical gradient technique, using the DZ basis. Electron correlation was incorporated at the DZ-optimized geometries through third-order Møller-Plesset perturbation (MP3) theory.[6]

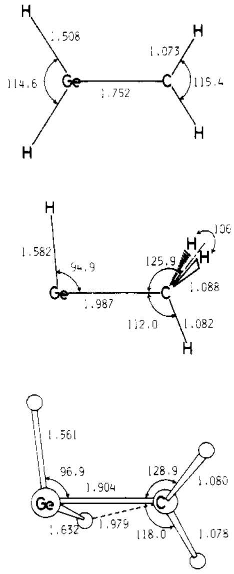

Figure 1. Optimized geometries for germaethene, methylgermylene, and the transition state connecting them in angstroms and degrees, obtained at the HF/DZ level.

The 1,2-Hydrogen Shift. The optimized geometries of germaethene, methylgermylene, and the transition state connecting them are shown in Figure 1.[7] Germaethene is again calculated to be considerably less stable than methylgermylene by 24.8 (HF/DZ), 24.2 (HF/DZ+d), and 17.6 (MP3/DZ+d) kcal/mol. This is in contrast with the relative stability of silaethene and its isomer methylsilylene, since these silicon isomers are calculated to be nearly degenerate in energy.[8] The large energy difference favoring $\ddot{\mathrm{H}}\mathrm{Ge{-}CH_3}$ over $\mathrm{H_2Ge{=}CH_2}$ indicates that germanium is more reluctant to form doubly bonded compounds than silicon.

The transition state in Figure 1 is "early" only in a sense that the shifting hydrogen is still bound to Ge with a small increase in bond length (0.124 Å). In several of the remaining geometrical parameters, however, the transition state resembles methylgermylene and is "late". Reflecting the "late" transition state, the energy barrier for the isomerization of germaethene to methylgermylene is calculated to be 38.1 (HF/DZ) and 36.2 (HF/DZ+d) kcal/mol. Even at the MP3/DZ+d level, the barrier is as large as 37.5 kcal/mol, suggesting that germaethene itself is kinetically, sufficiently stable to isomerization. It is of interest to note that the calculated barriers are only a few kilocalories per mole smaller than that of ca. 41 kcal/mol

---

[1] For comprehensive reviews, see: (a) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529–577. (b) Coleman, B.; Jones, M. *Rev. Chem. Intermed.* 1981, *4*, 297–367. (c) Schaefer, H. F. *Acc. Chem. Res.* **1982**, *15*, 283–290.

[2] Satge, J. *Adv. Organomet. Chem.* **1982**, *21*, 241–287 and references cited therein.

[3] Kudo, T.; Nagase, S. *Chem. Phys. Lett.* **1981**, *84*, 375–379.

[4] Trinquier, G.; Barthelat, J.-C.; Satge, J. *J. Am. Chem. Soc.* **1982**, *104*, 5931–5936.

[5] (a) In the DZ basis, the 6-31G basis[5b] was used except (7s)(5p)(3d) contraction of Dunning's (13s)(9p)(5d) Gaussian primitive set for Ge.[5c] In the polarized DZ+d basis, the Ge basis was augmented by a set of d functions (exponent 0.25) while the 6-31G* basis[5b] was used for other atoms. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654–3665. (c) Olbrich, G. *Chem. Phys. Lett.* **1980**, *73*, 110–113.

[6] Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1976**, *10*, 1–19. The MP3 calculations were carried out with all orbitals included except the corelike orbitals (1s, 2s, 2p, 3s, 3p, and 3d for Ge and 1s for C and O in character).

[7] Note that the geometrical parameters for germaethene and methylgermylene in Figure 1 differ little from our previous values[3] obtained with a less flexible DZ basis.

[8] (a) Gordon, M. S. *Chem. Phys. Lett.* **1978**, *54*, 9–13. Gordon, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 4352–4357. (b) Goddard, J. D.; Yoshioka, Y.; Schaefer, H. F. *Ibid.* **1980**, *102*, 7644–7650. Yoshioka, Y.; Schaefer, H. F. *Ibid. 1981*, *103*, 7366–7367. (c) Trinquier, G.; Malrieu, J.-P. *Ibid.* **1981**, *103*, 6313–6319. (d) Köhler, H. J.; Lischka, H. *Ibid.* **1982**, *104*, 5884–5889.

0276-7333/84/2303-0324$01.50/0

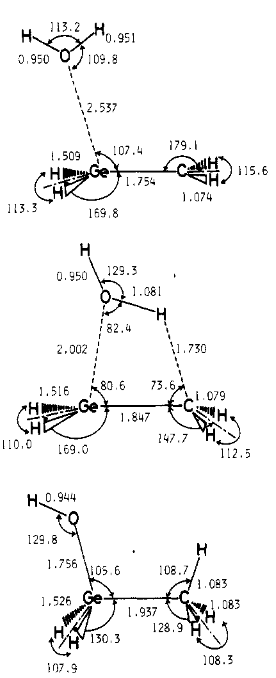

Figure 2. Optimized geometries of an intermediate complex (top), the product (bottom), and the transition state (middle) connecting them in the reaction of germaethene with water, obtained at the HF/DZ level.

calculated for the isomerization of silaethene.[8b]

The Reaction with Water. The optimized geometries of an intermediate complex, the product, and the transition state connecting them are shown in Figure 2. The reaction with water initiates with the formation of a weak complex (1.5 kcal/mol at the HF/DZ+d level and 2.6 kcal/mol at the MP3/DZ level) in a fairly early stage, in which one of the lone pairs of water is oriented for maximum interaction with the π^* orbital of germaethene localized strongly around Ge. The complex is transformed via a four-center-like transition state to the product, $H_2(OH)Ge\text{-}CH_3$. A Mulliken population analysis reveals that the attack of water is first nucleophilic and becomes electrophilic as the reaction reaches the transition state. The reaction with water is calculated to be 68.1 (HF/DZ+d) and 61.7 (MP3/DZ) kcal/mol exothermic. Reflecting the large exothermicity, the transition state rather resembles the complex in structure and is "early", as shown in Figure 2. The calculated values for the overall barrier are 15.1 (HF/DZ+d) and 7.4 (MP3/DZ) kcal/mol. These values are essentially comparable to those of 12.0 (HF/DZ+d) and 8.9 (MP3/DZ) kcal/mol for the silaethene reaction with water,[9] suggesting that germaethene is kinetically as stable as silaethene.

Compared with the value of 68 (HF/4-31G) kcal/mol for the reaction of ethene,[10] the overall barriers for germaethene and silaethene are much smaller. One may consider that the high reactivity of germaethene and silaethene is simply due to their strongly polarized double bonds, as often pointed out.[1a,b] However, an overall barrier for the $H_2Si{=}SiH_2 + H_2O$ reaction is calculated to be as small as 3.2 (HF/DZ+d) kcal/mol.[11] At this point, it is noteworthy that HOMO levels rise in the order $H_2C{=}CH_2 \ll H_2Si{=}CH_2 \leq H_2Ge{=}CH_2 < H_2Si{=}SiH_2$ while LUMO levels drop in the same way along the series.[12] This means that in Klopman's terminology[13] the reactivity of π-bonded group 4B compounds is significantly "frontier controlled", as well as "charge controlled". This finding would be useful for the design of a kinetically more stable germaethene.

Hydrogenation Energy. Finally, an attempt was made to evaluate and compare the energies released upon addition of H_2 to germaethene and silaethene. The hydrogenation energies calculated at the HF/DZ+d level are 65.6 ($H_2Ge{=}CH_2$) and 67.9 ($H_2Si{=}CH_2$) kcal/mol, while those at the MP3/DZ level are 48.7 ($H_2Ge{=}CH_2$) and 49.0 ($H_2Si{=}CH_2$) kcal/mol.[14] Obviously, these results indicate that germaethene is as stable as silaethene in a thermodynamic sense.

The present work predicts that germaethene resembles silaethene closely in stability and reactivity except the relative stability of the doubly bonded and divalent forms. It is hoped that successful schemes for the synthesis of germaethene are soon devised. We are currently studying the reactivity toward self-dimerization.

Acknowledgment. All calculations were carried out at the Computer Center of the Institute for Molecular Science, using an IMS version of the GAUSSIAN80 series of programs[15].

Registry No. $H_2Ge{=}CH_2$, 60188-36-5; $H\ddot{G}e\text{-}CH_3$, 78800-76-7; $H_2(OH)Ge\text{-}CH_3$, 88181-62-8; H_2O, 7732-18-5.

---

[9] Hanamura, M.; Nagase, S.; Morokuma, K., to be submitted for publication.

[10] Koizumi, M.; Yamashita, K.; Yamabe, T.; Fukui, K. Abstract of a Symposium on Molecular Structures held in Kyoto, Japan, 1981, pp 768–769.

[11] The subject will be discussed in detail in a future publication by Nagase and Kudo.

[12] Nagase, S.; Kudo, T. *J. Mol. Struct.* **1983**, *103*, 35–44 (a special issue of THEOCHEM in honor of Prof. Fukui and his Nobel prize awarded in chemistry).

[13] Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223–237. Klopman, G. "Chemical Reactivity and Reaction Paths"; Wiley: New York, 1974; pp 55–165.

[14] The optimized geometries and energies for $H_3Ge\text{-}CH_3$ and $H_3Si\text{-}CH_3$ are available from the authors on request.

[15] Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seegar, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* 1981, *10*, 406.

Self-Catalysis in Arene Exchange Reactions of (Arene)tricarbonylchromium Complexes

T. G. Traylor* and Kevin Stewart

Department of Chemistry, D-006
University of California, San Diego
La Jolla, California 92093

Received September 27, 1983

Summary: The replacement of *p*-xylene from its tricarbonylchromium complex by benzene is catalyzed by (hexamethylbenzene)tricarbonylchromium without the replacement of hexamethylbenzene. This and other observations suggest that the bound carbonyl group acts as a nucleophilic catalyst in arene exchange.

The tricarbonylchromium complexes of substituted benzenes were observed to exchange with ^{14}C-labeled arene at 140–180 °C by Strohmeier and co-workers.[1]

$$ArCr(CO)_3 + Ar^* \xrightarrow{k_{obsd}} Ar^*Cr(CO)_3 + Ar \tag{1}$$

---

[1] (a) Strohmeier, W.; Mittnacht, H. *Z. Phys. Chem.* **1961**, *29*, 339–346. (b) Strohmeier, W.; Muller, R. *Ibid.* **1964**, *40*, 85–95. (c) Strohmeier, W.; Staricco, E. H. *Ibid.* **1963**, *38*, 315–325.