Stabilization of a germanium–oxygen double bond: a theoretical study

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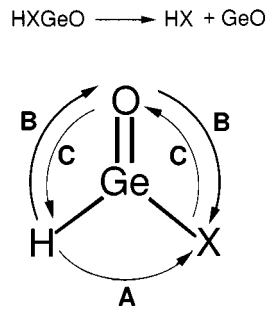
Both B3LYP and CCSD(T) computational results suggest that fluorine substitution can dramatically stabilize $F_2Ge{=}O$, with respect to FGe–OF, both from a kinetic and from a thermodynamic viewpoint.

It is generally acknowledged that intermediates with germanium doubly bonded to other elements (such as oxygen, sulfur, nitrogen *etc.*) are very unstable.[1,2] Indeed, most of our experimental knowledge of multiply bonded germanium still comes from matrix isolation studies. Therefore, the study of compounds having multiple bonds to germanium has been one of the major challenges in main group chemistry.[3,4] For instance, the first evidence for compounds containing the Ge=O moiety was reported in 1971.[5] Since then several schemes for the synthesis of germanones have been devised. Nevertheless, up to now only indirect evidence was available to suggest their transient existence.[6–9] Moreover, according to our previous study,[10] three reaction pathways for the unimolecular decomposition of HXGe=O to HX and GeO exist. These are shown in Scheme 1. The theoretical findings suggest that the most favorable dissociation path is predicted to be the 1,2-H shift route, while the 1,2-X shift path has the highest energy requirement and therefore is the least energetically favorable path. It is these intriguing theoretical results that have inspired this study. If the 1,2-X shift is the most unfavorable mechanism for the unimolecular dissociation of HXGe=O, would it be possible to extend this to synthesize and isolate compounds containing the Ge=O double bond at room temperature? What interests us particularly is to explore the possibility of designing molecular systems where $X_2Ge{=}O$ is more stable than the isomeric XGe–OX, and where relatively large barriers separate the two isomers.



Path A:1,1-HX elimination
Path B:1,2-H shift (the most favorable)
Path C:1,2-X shift (the most unfavorable)
(X = H, F, Cl and Br)

Scheme 1

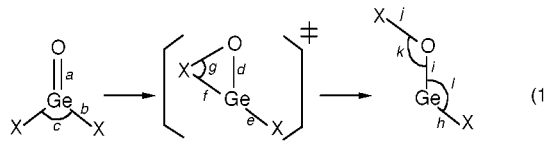
In view of the interest in isolating compounds containing a Ge=O double bond, we consider the possibility of stabilizing this moiety with various substituents. Here, we report a theoretical study concerning the effect of various substituents X (X = H, F, Cl, Br and Me) on the relative stability of $X_2Ge{=}O$ and XGe–OX isomers as well as on the transition states connecting them. See eqn. (1) in Table 1.

The geometries and energies of stationary points on the potential energy surface of eqn. (1) have been calculated using the non-localized density functional theory (DFT) in conjunction with the 6-311G* basis set, which is denoted as B3LYP/6-311G*.[11] All the stationary points have been positively identified as equilibrium structures [the number of imaginary frequency (NIMAG = 0) or transition states (NIMAG = 1)]. For better energetics, single-point calculations with B3LYP/6-311G* geometries were carried out at a higher level of theory which used coupled cluster single and double excitations including perturbative triple substitutions,[12] *i.e.* CCSD(T)/6-311++G**//B3LYP/6-311G* [hereafter designated CCSD(T)]. Unless otherwise noted, relative energies given in the text are those determined at CCSD(T) and include vibrational zero-point energy (ΔZPE) corrections determined at B3LYP/6-311G*.[13]

Some interesting points arising from the above calculations are as follows:

(1) Selected geometrical parameters of $X_2Ge{=}O$, XGe–OX, and the transition state for the reaction $X_2Ge{=}O \rightarrow$ XGe–OX [*i.e.* eqn. (1)] are listed in Table 1. It is apparent from Table 1 that halogen substitution (*i.e.* F, Cl and Br) strengthens the Ge=O double bond. In contrast, such substitutions seem to weaken the Ge–O single bond. On the other hand, methyl substitution appears to lengthen both Ge=O and Ge–O bonds slightly.

Table 1 Geometrical parameters of structures for eqn. (1) at the B3LYP/6-311G* level of theory (distances in Å, angles in degrees).



(1)

X	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*
H	1.644	1.546	112.8	1.722	1.590	1.589	64.73	1.606	1.808	0.9642	112.8	92.63
Me	1.650	1.964	113.3	1.736	2.019	2.230	46.69	2.006	1.813	1.418	122.7	93.77
F	1.630	1.726	101.8	1.794	1.766	1.961	58.68	1.769	1.860	1.448	103.4	90.11
Cl	1.634	2.142	106.4	1.739	2.218	2.371	43.74	2.213	1.846	1.738	113.8	92.76
Br	1.638	2.300	108.4	1.727	2.386	2.506	41.01	2.373	1.836	1.875	114.9	93.43

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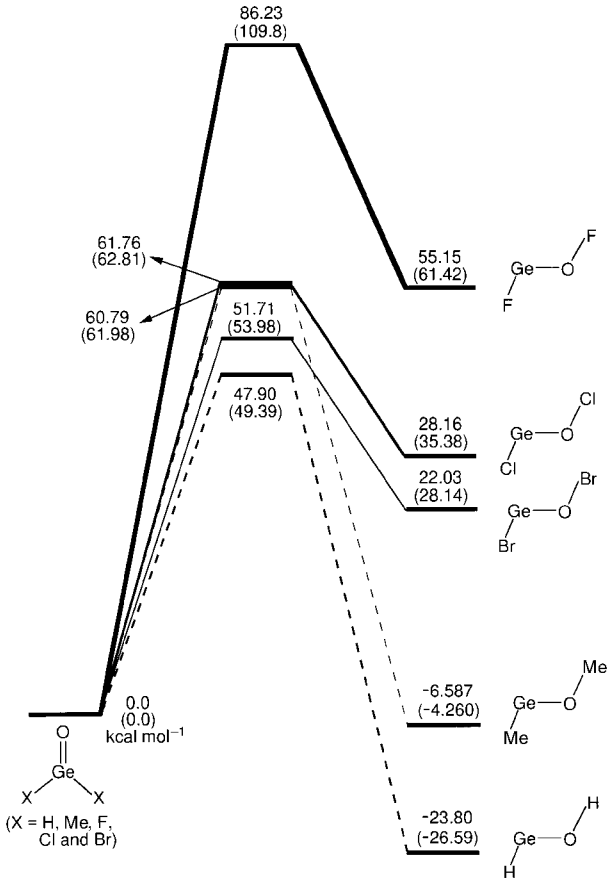

Scheme 2

(2) Scheme 2 shows the effects of various substitutions on the relative stabilities of $X_2Ge{=}O$ and XGe–OX at the B3LYP and CCSD(T) (in parentheses) levels of theory. It is worth noting that the relative stabilities of the doubly bonded and the *trans*-bent (singly bonded) species are dramatically reversed when hydrogens are replaced by electronegative substituents (such as F, Cl and Br). It is apparent from Scheme 2 that the energies of the XGe–OX molecules are much higher than those of the corresponding $X_2Ge{=}O$ by 61, 35 and 28 kcal mol^{-1} for X = F, Cl and Br, respectively. By contrast, the energies of HGe–OH and MeGe–OMe are below the energies of $H_2Ge{=}O$ and $Me_2Ge{=}O$ by 27 and 4.3 kcal mol^{-1}, respectively. Thus, the effect of dihalogen substitution is of special interest since it strongly stabilizes $X_2Ge{=}O$ relative to XGe–OX. In particular, our CCSD(T) results indicate that the endothermicity of eqn. (1) increases in the order X = Br (28 kcal mol^{-1}) < X = Cl (35 kcal mol^{-1}) < X = F (61 kcal mol^{-1}). It is therefore predicted that the more electronegative the halogen, the more stable the germanone ($X_2Ge{=}O$).

(3) The thermodynamic stability of $X_2Ge{=}O$ relative to XGe–OX may be understood in terms of the Ge–X *vs.* O–X bond energies.[14] That is to say, from eqn. (1) it is clear that a strong Ge–X bond and the weak O–X bond can overturn the large intrinsic preference of XGe–OX over $X_2Ge{=}O$.[15] Another surprising piece of evidence is that halogen substitution causes a shortening of the Ge=O double bond, as mentioned earlier. Therefore, it appears that halogen substitution strengthens the Ge=O double bond, particularly in the case of fluorine, assuming that bond energy–bond length relationships are valid. Furthermore, halogen substitution not only stabilizes the formal Ge=O double-bonded structure relative to XGe–OX, but it also raises the barrier to the $X_2Ge{=}O \rightarrow$ XGe–OX isomerizations, thus increasing the kinetic stability of the germanone molecules. For instance, as demonstrated in Scheme 2, the barrier for the isomerization of $X_2Ge{=}O$ to XGe–OX decreases in the order: X = F (110 kcal mol^{-1}) > X = Cl (63 kcal mol^{-1}) ≈ X = Me (62 kcal mol^{-1}) > X = Br (54 kcal mol^{-1}) > X = H (50 kcal mol^{-1}). In brief, fluorine is a particularly appealing possibility because of the strength of the Ge–F bonds.

(4) It should be pointed out that methyl substitution in eqn. (1) is predicted to be nearly thermoneutral, with an exothermicity of only 4.3 kcal mol^{-1}. Additionally, the barrier height for 1,2-CH_3 shift of $Me_2Ge{=}O$ is sizeable (63 kcal mol^{-1}), indicating that both $Me_2Ge{=}O$ and MeGe–OMe will have kinetic stability for such a migration reaction. This larger barrier ensures that, both isomers will be relatively stable kinetically if they were produced. Bulky substituents are generally expected to destabilize $X_2Ge{=}O$ relative to XGe–OX, owing to the steric effects.

In summary, the present work predicts that germanone $X_2Ge{=}O$ itself lies at the minimum of the potential energy surface and can be strongly stabilized in both a kinetic and a thermodynamic sense with a proper choice of substituents. For instance, the theoretical findings suggest that Ge=O double bonds can be synthesized as part of a stable compound by taking advantage of kinetic stabilization using bulky substituents as steric protection groups. Besides this, on the basis of the present theoretical results, we confidently predict that $F_2Ge{=}O$ should be very stable from both a thermodynamic and a kinetic viewpoint and should be easily observed experimentally.

We eagerly await experimental results to confirm our predictions.

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