An Experimental and Theoretical Study of Gaseous Products in the Radiolysis of Germane/Ethylene Mixtures

Paola Antoniotti,[a] Paola Benzi,[a] Mario Castiglioni,[a] and Paolo Volpe*[a]

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Gas-phase radical reactions of germane/ethylene mixtures have been investigated using theoretical calculations and radiolysis techniques. Ab initio quantum chemical calculations have been performed on reactions starting from GeH_x (x = 0–3) radicals and C_2H_4. The geometrical structure and relative stability of isomeric GeC_2H_n (n = 4–7) radicals have been investigated and restricted to the species in which a C–C bond is present, at the MP2(FROZEN) level of calculation with double-ζ quality basis sets. To better evaluate the relative stability of the investigated species, single-point calculations at the QCISD(T) level were performed with a 6-311G(3df,2p) basis set. Reaction enthalpies and heats of formation of the species have also been determined using theoretical calculations. From irradiation of GeH_4/C_2H_4 mixtures, condensed products and volatile species were obtained. Composition, amount, and characteristics of the condensed phase products are reported. The volatile compounds were identified and their amounts determined. From experimental results and theoretical calculations some hypotheses on the reaction mechanisms are presented.

Introduction

In the last few years much work has been done on the photovoltaic applications of amorphous materials, as they are less expensive and more direct in use than the crystalline ones. Amorphous alloys, such as Si−C, Si−Ge, and Ge−C, are very interesting because they can be obtained with variable compositions, and hence with tunable physical properties, by varying the nature and concentration of the reagents. Si−C and Si−Ge have been widely studied[1−9] while Ge−C has been generally neglected, even though the Davis and Mott equation[10] suggests that amorphous Ge−C can have good photovoltaic properties, depending on the Ge/C ratio.[11] This is probably due to the difficulties encountered in its preparation using simple methods, although many different synthetic paths have been exploited.[12−18] One of these methods is the radiolysis of gas mixtures of GeH_4 and hydrocarbons. The use of high-energy radiation (namely X-rays) overcomes the problem of the activation of compounds having very different bond energies (Ge−H, C−H, and C−C).

In our laboratory, studies on the decomposition of gas-phase mixtures of germane and saturated hydrocarbons using high-energy radiation have been performed. By this method, powders and thin films of materials containing Ge and C in different ratios have been obtained,[19−21] but even at high mol fraction of alkane in the reacting mixture, the C content of the solids is generally low.[22] A study of radiolysis of germane/unsaturated hydrocarbon mixtures is now in progress which has been undertaken because of the presence of the more reactive double bond which may lead to an increase in the number of carbon atoms incorporated into the solid.

[a] Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino,
C.so Massimo D'Azeglio, 48, I-10125 Torino, Italy

This paper will deal with the gas-phase reactivity of monogermane/ethylene mixtures. In order to find a relationship between the gaseous reactant molar fraction and the abundance of the corresponding atoms in the solid, it is of fundamental importance to know the gas-phase behaviour of the reacting molecules. The combination of experimental and theoretical investigations is becoming a useful approach to the study of gas-phase chemistry.[23,24] In fact, in this paper, we report results of ab initio theoretical calculations to determine the structure, relative stability, and thermochemical data of the ground state of some products of the more probable gas-phase reactions proposed as a consequence of the experimental results. These calculations can help in some qualitative speculation on the whole mechanism involved.

Radiolysis of GeH_4/C_2H_4 Mixtures

Following irradiation of germane/ethylene mixtures gaseous and solid products are obtained, the latter being deposited on the bottom of the irradiation ampoules. For the samples containing more than of 15% ethylene, small amounts of a viscous liquid phase are formed which easily dissolve some of the volatile products making sampling and analysis of the gas phase products difficult.

Besides unreacted germane and ethylene, analysis of the gas-phase products indicates the presence of variable amounts of species containing both Ge and C. Only traces of volatile hydrocarbons, formed by polymerization of ethylene and mainly containing eight C atoms, is sometimes observed. The amounts of volatile species (other than GeH_4 and C_2H_4) as a function of ethylene percentage are reported in Table 1.

From Table 1 it appears that (i) apart from in the 30% ethylene mixture, the percentage of Ge found in the gas-

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Table 1. Amounts of gaseous species formed upon irradiation of GeH_4/C_2H_4 mixtures with different compositions; note that the μmol values are affected by an error of 20%

Species	Amount of ethylene [μmol] 3%	5%	8%	15%	30%
GeC_2H_8	1.40	4.31	6.4	7.45	1.89
Ge_2H_6	5.38	3.03	2.92	$9.45\cdot10^{-1}$	n.d.[a]
GeC_4H_{12}	$2.56\cdot10^{-1}$	$2.90\cdot10^{-1}$	$8.05\cdot10^{-1}$	1.26	$9.74\cdot10^{-1}$
$Ge_2C_2H_{10}$	$3.22\cdot10^{-1}$	1.05	$8.42\cdot10^{-1}$	$2.86\cdot10^{-1}$	$6.11\cdot10^{-2}$
Ge_3H_8	$2.92\cdot10^{-1}$	$3.12\cdot10^{-1}$	$3.06\cdot10^{-2}$	n.d.[a]	n.d.[a]
GeC_6H_{16}	$9.70\cdot10^{-2}$	$6.98\cdot10^{-2}$	$4.17\cdot10^{-2}$	$8.60\cdot10^{-2}$	$1.33\cdot10^{-1}$
$Ge_2C_4H_{14}$	$1.71\cdot10^{-2}$	$9.15\cdot10^{-2}$	$6.09\cdot10^{-1}$	$8.19\cdot10^{-1}$	$3.05\cdot10^{-2}$
$Ge_3C_2H_{12}$	$2.81\cdot10^{-3}$	$1.03\cdot10^{-2}$	$1.58\cdot10^{-2}$	$3.03\cdot10^{-3}$	n.d.[a]
$Ge_2C_6H_{18}$	n.d.[a]	$1.07\cdot10^{-2}$	$3.62\cdot10^{-2}$	$1.08\cdot10^{-2}$	$3.29\cdot10^{-2}$
$Ge_3C_4H_x$	n.d.[a]	n.d.[a]	$1.25\cdot10^{-2}$	$6.31\cdot10^{-3}$	$5.14\cdot10^{-3}$
n.i.[b] (> Ge_3C_4)	$7.65\cdot10^{-2}$	n.d.[a]	$6.78\cdot10^{-1}$	$3.31\cdot10^{-2}$	$7.00\cdot10^{-2}$

[a] n.d.: not detected. – [b] n.i.: not identified.

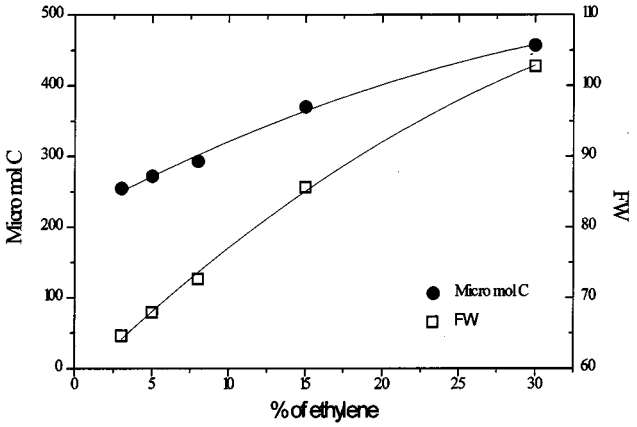

Figure 1. Absolute amounts of carbon and formula weight (FW) of the condensed-phase products vs. C_2H_4 percentage

phase products compared with Ge present in the reacting mixture is quite constant at about 0.1%, probably because of the formation of compounds of very low volatility and/or the solubility of the gases in the liquid phase; and (ii) the percentage of C found in the volatile products with respect to its starting amount is constant at about 0.6%, except for the samples at 30% ethylene, for the same reasons given above. The volatile products may be obtained from addition of GeH_x ($x = 1-3$) species with germane molecules or with ethylene or ethylene derivatives. It can be observed that with increasing amounts of ethylene in the reacting mixture, the amounts of the products containing only Ge and H decrease. In contrast, the amounts of the compounds containing both Ge and C increase, though for the latter the quantity decreases as the number of Ge atoms in the compound increases.

The low amounts of volatile products observed seems to indicate that the reactions which lead to condensed-phase products are favoured. In Table 2, amounts, composition and other characteristics of the condensed phases products obtained by irradiation of GeH_4/C_2H_4 mixtures with various ethylene percentages are reported. Ge/C and H/(Ge + C) atomic ratios observed for the condensed phase products are also reported.

Table 2 and Figure 1 show that both the absolute amount and the formula weight of the condensed-phase products increase as C_2H_4 increases. Moreover from Table 2 it can be observed that the Ge/C ratio decreases while the H/(Ge + C) ratio increases as the ethylene percentage is enhanced.

It is noteworthy that even if both volatile compounds and condensed-phase products (reported in Table 1 and 2) are considered, the decomposition of the GeH_4 is low with respect to the analogous germane/alkane mixtures.[22] In fact, the percentage of germane decomposed with respect to the germane initially present in the mixture varies from 0.5% to 2.0% when ethylene ranges from 3.0% to 30.0% corresponding to G ($-GeH_4$) values (μM/J) ranging from 1.4 to 5.2. In the GeH_4/alkane systems previously studied, the G ($-GeH_4$) values are 11.7 and 10.7 with ethane and propane, respectively, for mixtures with 25% of alkane. To explain this decomposition with respect to that observed when GeH_4 is irradiated alone, G ($-GeH_4$) = 1.26, the poor energy transfer between excited molecules of GeH_4 and hydrocarbon molecules has been invoked.[22] In fact, in such conditions the collisional quenching decreases and an excited GeH_4 molecule may therefore suffer decomposition after a few collisions. In the present study, ethylene is generally a minor component of the irradiated mixture and it is

Table 2. Characterization of the condensed-phase products obtained from irradiation of GeH_4/C_2H_4 mixtures with different compositions

	3% C_2H_4	5% C_2H_4	8% C_2H_4	15% C_2H_4	30% C_2H_4
Weight [mg]	5.0 ± 0.8	7.0 ± 1.4	10.0 ± 2.0	15.0 ± 1.2	20.0 ± 2.0
Description	brown orange dusty solid	dark orange dusty solid	orange dusty solid	range waxy solid	viscous colourless liquid
% of the original carbon[a]	5.5	5.7	5.6	5.8	5.8
% of the original germanium[b]	0.39	0.61	0.88	1.30	1.95
Empirical formula	$GeC_{0.88}H_{2.39}$	$GeC_{0.99}H_{2.74}$	$GeC_{1.13}H_{3.13}$	$GeC_{1.66}H_{4.46}$	$GeC_{2.26}H_{5.92}$
% of carbon[c]	20.6	20.9	21.4	23.3	24.6
Ge/C atomic ratio	1.14	1.01	0.88	0.60	0.44
H/(Ge + C) atomic ratio	1.27	1.37	1.47	1.67	1.81

[a] Percentage of C atoms in the condensed-phase products with respect to the C atoms present in the reacting mixture. – [b] Percentage of Ge atoms in the condensed-phase products with respect to the Ge atoms present in the reacting mixture. – [c] Percentage of carbon atoms in condensed-phase products.

generally present in too low percentage to prevent the energy transfer from excited germane molecules to germane molecules in the ground state.

As far as the condensed-phase products are concerned, it is interesting to study the hydrogen content as a function of the C_2H_4 percentage in the starting mixture, as shown in Figure 2.

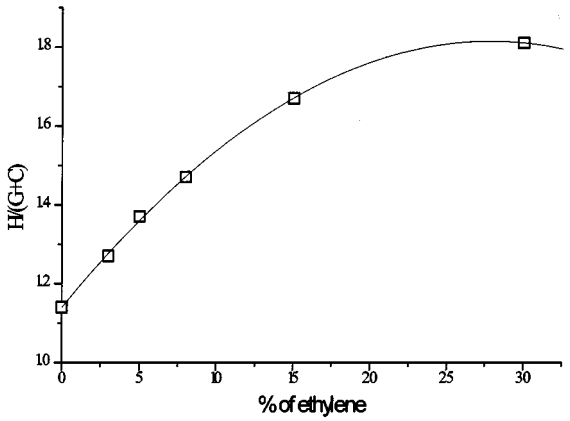

Figure 2. H/(Ge + C) atomic ratio in the condensed-phase obtained by irradiation of GeH_4/C_2H_4 mixtures with different ethylene percentages; the point on the *y* axis is an extrapolated value

Extrapolation to 0% ethylene, gives a value of H/Ge = 1.14 which is very close to the 1.29 value found in the γ radiolysis of pure GeH_4, measured using a radioisotopic technique.[25] The agreement improves considering the higher irradiation dose used in those experiments and that the extent of hydrogenation slowly increases with the dose.

During the irradiation both ionic and radical species may be involved in the formation of volatile and condensed-phase products. The ionic contribution to these processes can be investigated by mass-spectrometric experiments of both single reactants and their mixtures. The most important ions in the mass spectrum of pure ethylene are $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$ with abundances of 38, 23, and 22%, respectively, and other ions such as $C_2H_5^+$,$C_3H_n^+$ (n = 5, 7), and $C_5H_n^+$ (n = 7, 9) are also formed by ion−molecule reactions.[27] In germane the most abundant ionic species are GeH_3^+, GeH_2^+, GeH^+, and Ge^+. In addition, the formation of dimeric, trimeric, and tetrameric ions in ion−molecule reactions has been also observed.[28,29]

In a Fourier-transform mass-spectrometric study[27] of GeH_4/C_2H_4 mixtures it has been observed that reaction between $C_2H_4^+$ ions and GeH_4 molecules gives GeH_3^+ and, to a lesser extent, GeH_2^+ ions. Further reactions of GeH_3^+ ion species with GeH_4 or C_2H_4 neutrals lead to the formation of mixed species or ions containing two Ge atoms, respectively (Equations. 1, 2, and 3).

$$GeH_3^+ + GeH_4 \rightarrow Ge_2H_3^+ + 2\,H_2 \quad (1)$$
$$GeH_3^+ + GeH_4 \rightarrow Ge_2H_5^+ + H_2 \quad (2)$$
$$GeH_3^+ + C_2H_4 \rightarrow GeC_2H_5^+ + H_2 \quad (3)$$

Moreover, it is reasonable to suppose that ions obtained from the above reactions react further with GeH_4 and/or C_2H_4 leading to products with longer chains. This hypothesis is supported by the finding that in mass-spectrometric experiments performed under chemical ionization conditions on GeH_4/C_2H_4 mixtures, several ions containing one Ge and up to four C atoms were detected with relatively high abundance. Ions with two Ge and two to four C atoms were also observed.[27]

In summary, the ionic reaction mechanisms reported in a previous study,[27] using Fourier-transform and high-pressure mass-spectrometric methods, are in satisfactory agreement with the observations of this work.

In the radiolysis a great contribution to the products is, however, given by radical species. In order to evaluate the relative contribution of ions and radicals, the energy required for ionization and for the formation of a radical should be considered. The average energy absorbed for the formation of an *ion pair* (W)[26] in GeH_4 is about 22.0 eV ($8.41 \cdot 10^{-22}$ kcal)[22] and because the ionization potential (I) of GeH_4 is only 10.7 eV ($4.08 \cdot 10^{-22}$ kcal),[25,31] there is an excess energy ($W - I$) of about 11.3 eV ($4.33 \cdot 10^{-22}$ kcal) available for the formation of excited molecules and/or radicals. Considering the germylene radical (which from energetic data reported below, is the more probable primary radical) the energy required is 2.16 eV ($8.27 \cdot 10^{-23}$ kcal).[32] It follows that about four radicals can be formed in addition to each ion. It can therefore be concluded that radical reactions should give the major contribution to the product formation.

In previous experiments on GeH_4/alkane mixtures, high amounts of gaseous products were obtained and none of the product yields seemed to be affected by the addition of oxygen as a radical scavenger.[22] In contrast, in mixtures where ethylene is used instead of an alkane, a very low abundance of volatile products is formed. In particular, the amount of Ge_2H_6 is low and decreases with increasing concentration of ethylene, whereas the amount of GeC_2H_8 species increases with ethylene pressure showing that ethylene strongly competes with germane in the reactions with the GeH_x (x = 1−3) radicals and that germane−alkene reactions are mainly scavenging processes.

This hypothesis is supported by the data of Tables 1 and 2 which show that while the fraction of carbon in the products (gas and condensed phase) is about 6% of carbon in the reactant over the whole range of ethylene concentration, the fraction of germanium present in the products increases from about 0.5 to about 2% with increasing concentration of C_2H_4.

The radicals formed during the germane radiolysis are germyle, GeH_3, and germylene, GeH_2; it has been proposed that their formation occurs by decomposition of excited molecules according to the Equations 4 and 5.[33]

$$GeH_4^* \rightarrow GeH_3 + H \quad (4)$$
$$GeH_4^* \rightarrow GeH_2 + H_2 \quad (5)$$

The formation of GeH_3 and GeH_2 radicals requires an activation energy of $2.27 \cdot 10^{24}$ eV mol^{-1} (87.20 kcal mol^{-1})

and $1.30 \cdot 10^{24}$ eV mol^{-1} (49.80 kcal mol^{-1}), respectively,[32] so the reaction forming GeH_2 radicals should be energetically favoured. Moreover, it has been observed that GeH_2 further decomposes according to Equations 6 and 7, which compete with each other in the ratio 9:1[32] and suggest that the Ge and GeH species must also be considered in the products formation.

$$GeH_2 + M \rightarrow Ge + H_2 + M \quad (6)$$
$$GeH_2 + M \rightarrow GeH + H + M \quad (7)$$
M = neutral molecule

Therefore, it can be proposed that the germane radicals react with ethylene molecules leading to mixed species according to Equations (8) to (15). In these reactions ethylene addition or addition followed by elimination of hydrogen molecules or atoms occurs.

$$Ge + C_2H_4 \rightarrow GeC_2H_4 \quad (8)$$
$$GeH + C_2H_4 \rightarrow GeC_2H_5 \quad (9)$$
$$GeH_2 + C_2H_4 \rightarrow GeC_2H_4 + H_2 \quad (10)$$
$$GeH_2 + C_2H_4 \rightarrow GeC_2H_5 + H \quad (11)$$
$$GeH_2 + C_2H_4 \rightarrow GeC_2H_6 \quad (12)$$
$$GeH_3 + C_2H_4 \rightarrow GeC_2H_5 + H_2 \quad (13)$$
$$GeH_3 + C_2H_4 \rightarrow GeC_2H_6 + H \quad (14)$$
$$GeH_3 + C_2H_4 \rightarrow GeC_2H_7 \quad (15)$$

Because the long-chain products derive from the light ones, the same mechanisms for beginning a chain may be invoked to explain the formation of both volatile species and condensed-phase products. In fact, the species obtained from the above reactions may further react (by analogous mechanisms) with germane or ethylene with chain propagation leading to condensed-phase products, but the chain can be stopped by reaction with hydrogen radicals leading to the observed volatile species.

Considering the hydrogenation extent of the condensed-phase products, two hypotheses on the product formation can be proposed: (i) the main radicals which contribute to the Ge−C mixed compounds are the ones poor in hydrogen (Ge and GeH) and (ii) if germyle and germylene are the reactants, then in the reactions H (or H_2) is released. Some evidence supports the first hypothesis; in fact Figure 2 shows that the extent of condensed-phase hydrogenation increases with the carbon content. It is possible to think that the hydrogen enters in the chain mainly bonded to carbon atoms. This is because when an ethylene molecule leads upon a radical addition reaction it incorporates four hydrogen atoms, i.e. two hydrogen atoms for each carbon atom. To reach the empirical formula reported in Table 2 any germanium atom must lead, on average, to less then two hydrogen atoms. Moreover, even if from the above energetic considerations the germylene is the more probable primary radical, it must undergo an extensive decomposition leading to Ge and GeH. Thus, even Ge and GeH radicals have an important function in chain propagation leading to condensed-phase products which should, as a result, be poor in hydrogen.

Theoretical Study of the GeC_2H_n ($n = 4-7$) Species

In order to determine the most probable reaction pathways leading to the formation of the condensed-phase products, ab initio theoretical calculations on the products obtained from the previous reactions have been performed. Since in the radiolysis of ethylene the products maintaining the C−C bond predominate,[34] only the GeC_2H_n ($n = 4-7$) species in which such a bond is present were considered.

The enthalpies[35] of reactions leading to the most stable isomer have been calculated at the QCISD(T)/6-311G(3df,2p) level of theory and are reported in Table 3. Formation enthalpies $\Delta H°_f$ for the most stable GeC_2H_n ($n = 4-7$) species considered in this paper have also been computed and are reported in Table 4. They have been obtained by the method proposed by Pople et al.[36] The method was used with the following modifications: (i) The QCISD(T)/6-311G(3df,2p) energies (reported in Table 5) have been directly used throughout in order to evaluate the energy difference relevant to the isogyric reaction; (ii) instead of the ZPE correction to the energy, the full thermal correction at the MP2/BS level of theory has been applied (as outlined in ref.[35]).

Table 3. Enthalpies of reactions leading to the most stable products [kcal mol^{-1}]

Equation	Reaction	$\Delta H°$
(8)	$Ge + C_2H_4 \rightarrow GeC_2H_4$	−31.5
(10)	$GeH_2 + C_2H_4 \rightarrow GeC_2H_4 + H_2$	−3.0
(9)	$GeH + C_2H_4 \rightarrow GeC_2H_5$	−19.4
(11)	$GeH_2 + C_2H_4 \rightarrow GeC_2H_5 + H$	49.0
(13)	$GeH_3 + C_2H_4 \rightarrow GeC_2H_5 + H_2$	5.8
(12)	$GeH_2 + C_2H_4 \rightarrow GeC_2H_6$	−35.2
(14)	$GeH_3 + C_2H_4 \rightarrow GeC_2H_6 + H$	23.6
(15)	$GeH_3 + C_2H_4 \rightarrow GeC_2H_7$	−25.2

Table 4. Heats of formation for the most stable GeC_2H_n ($n = 4-7$) species [kcal mol^{-1}]

	Species	$\Delta H°_f$
3a	GeC_2H_4	74.0
4a	GeC_2H_5	76.2
5a	GeC_2H_6	42.1
6a	GeC_2H_7	45.4

GeC_2H_4

The investigation of the potential-energy surface of singlet and triplet GeC_2H_4 radicals suggested the existence of three distinct species. The geometrical parameters are shown in Figure 3 and the total and relative energies are reported in Table 5. The structure **3a**, a singlet species with C_S symmetry, obtained from the reaction of the Ge radical with the ethylene molecule (reaction 8), is the global minimum on the potential-energy surface. This structure contains a Ge atom bridging the two carbon atoms. The exo-

thermicity of the reaction (-31.5 kcal mol^{-1}) suggests that the formation of these radicals are rather probable. The structure **3b,** also with C_S symmetry, is a triplet state, less stable than structure **3a** by 17.6 kcal mol^{-1} at the QCI level of theory. Once again, the results of the calculations suggest that reaction is rather probable. The structure **3c** can probably be obtained from the reaction of the GeH_2 radical with the ethylene molecule with a subsequent elimination of a hydrogen molecule. Structure **3c** is a cyclic species calculated to lie 38.4 kcal mol^{-1} above **3a** at the highest level of calculation. Results for the enthalpy calculations for the **3c** formation reaction show that more than 35.4 kcal mol^{-1} are necessary to overcome the barrier for dissociation of a H_2 molecule.

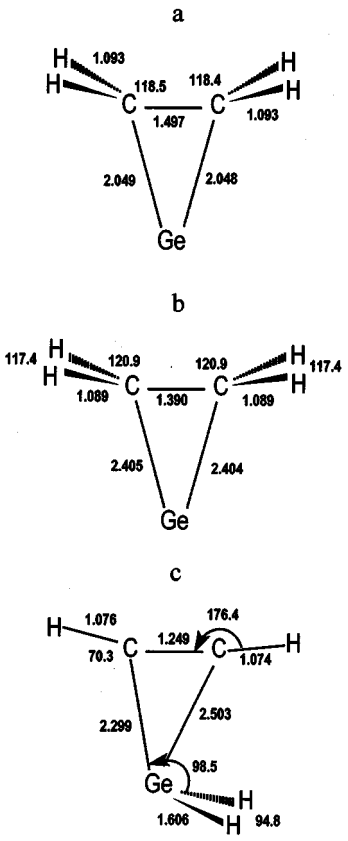

Figure 3. MP2/BS geometrical parameters of the GeC_2H_4 isomers with bond lengths [Å] and bond angles [°]

GeC_2H_5

Six different critical points have been located on the GeC_2H_5 potential-energy surface corresponding to a minimum or first-order saddle point. The optimized geometries and the total and relative energies of GeC_2H_5 isomers are reported in Figure 4 and Table 5.

The allyl-like structure **4c** with C_S symmetry, obtained most easily from Equation (11) (endothermic by 49.0 kcal mol^{-1}), was found to be a first-order saddle point corresponding to a transition structure for the rotation of the germylene group around the Ge−C bond. The activation energy of the rotation process was computed as 3.3 kcal mol^{-1} at the QCI level of calculation. This is not in agreement with that found for $GeC_2H_5^+$ ions where the allyl-like planar structure corresponds to the most stable absolute minimum.[37] The other two structures **4a** and **4b**, which can be obtained from Equation (11), have been characterized as minima on the potential-energy surface. The **4a** species, with C_1 symmetry, the most stable at the MP2 level of theory, becomes less stable by 1 kcal mol^{-1} at the QCI level with respect to **4b** which has C_S symmetry. Although these isomers are stable, the calculated enthalpy change for Equation (11) is very high (49.0 kcal mol^{-1}) and it follows that formation of these radicals from the reaction considered becomes more difficult than from Equations (9) or (13).

Only one 1-propenyl-like species, corresponding to a minimum, has been located on the potential-energy surface, indicated as **4f**. This product, derived probably from Equation (13) (endothermic by 5.8 kcal mol^{-1} compared to species **4a**), was found to be the less stable isomer at all levels of calculation. In fact, it is 27.2 kcal mol^{-1} less stable than **4b** at the QCI level. Moreover, in order to obtain this product it is probably necessary to overcome a barrier for dissociation of a H_2 molecule.

The 2-propenyl-like species **4e** has been located and characterized as a minimum on the potential-energy surface of GeC_2H_5 radicals, as a product of Equation (13). In this case too, in addition to the reaction endothermicity, the energy of this species was found to be rather high (22.5 kcal mol^{-1} with respect to the species **4a**). This is probably due to the contamination of the spin state (see Table 5).

The only thermally allowed reaction according to Equation (9) (-19.4 kcal mol^{-1}), which follows from the junction of a GeH radical and an ethylene molecule, gives rise to the species **4d**. Although this product was found to be less stable by 21.2 kcal mol^{-1} with respect to structure **4a**, the reaction remains feasible.

GeC_2H_6

Five critical points have been located on the potential-energy surface of the singlet GeC_2H_6 species. The geometrical parameters are shown in Figure 5 and the absolute and relative energies are collected in Table 5.

The staggered and eclipsed (C_s symmetry) conformations of vinylgermane have been located on the potential-energy surface. They are indicated as **5b** and **5c**, respectively. The former corresponds to a minimum and the latter corresponds to a first-order saddle point for rotation of GeH_3 around the Ge−C bond. The energy difference between **5b** and **5c** is computed to be as large as 1.2 kcal mol^{-1} at the QCI level of calculation. Moreover, the staggered conformation of vinylgermane results to be more stable than **5a** by 4.3 kcal mol^{-1} at the QCI level of theory and the global minimun on the GeC_2H_6 potential-energy surface. The species **5b** can probably be obtained from Equation (14) (but this process is endothermic) following a hydrogen atom dissociation, or from equation (12) (exothermic by 35.2 kcal

Table 5. Total and relative energies [Hartree and kcal mol^{-1}] of the investigated GeC_2H_n ($n = 4-7$) radicals

Species (NIMAG[a])	UMP2 (FROZEN)/BS[b]	ΔE	$<S^2>$[c]	QCISD(T)/6-311G(3df, 2p)	ΔE	ZPE[d]
3a (0)	2151.666487	0.0	0.0	−2153.832970	0.0	32.6
3b (0)	−2151.644778	13.6	2.0226	−2153.804955	17.6	33.4
3c (0)	−2151.597615	43.2	0.0	−2153.771804	38.4	26.0
4a (0)	−2152.221537	0.0	0.7528	−2154.415308	1.0	35.7
4b (0)	−2152.218953	1.6	0.8276	−2154.416910	0.0	36.3
4c (1)	−2152.207728	8.7	0.9267	−2154.410043	4.3	35.1
4d (0)	−2152.196235	15.9	0.7662	−2154.383159	21.2	35.5
4e (0)	−2152.166337	34.6	0.9272	−2154.380980	22.5	32.8
4f (0)	−2152.162187	37.2	0.9153	−2154.373585	27.2	32.6
5a (0)	−2152.850449	0.0	0.0	−2155.048495	0.0	44.8
5b (0)	−2152.840411	6.3	0.0	−2155.055417	−4.3	40.6
5c (1)	−2152.838854	7.3	0.0	−2155.053513	−3.1	40.4
5d (0)	−2152.833696	10.5	0.0	−2155.039476	5.7	42.8
5e (0)	−2152.825597	15.6	0.0	−2155.031992	10.4	42.7
5f (0)	−2152.816532	21.3	2.0044	−2155.009337	24.6	45.3
5g (0)	−2152.777011	46.1	2.0196	−2154.980569	42.6	41.1
5h (1)	−2152.771834	49.3	2.0161	−2154.975185	46.0	40.5
5i (0)	−2152.735584	72.1	2.0157	−2154.952319	60.3	37.8
6a (0)	−2153.431692	0.0	0.7528	−2155.646408	0.0	50.3
6b (0)	−2153.394454	23.4	0.7653	−2155.619322	17.0	46.5
6c (0)	−2153.392628	24.5	0.7653	−2155.620345	16.4	46.7
6d (1)	−2153.389900	26.2	0.7636	−2155.614387	20.1	46.7

[a] Number of imaginary frequencies. — [b] For the specification of the basis set BS, see the Computational Details section. — [c] Eigenvalues of spin operator at the UHF/BS level of theory. — [d] Zero-point energies [kcal mol^{-1}] at the UMP2 (FROZEN)/BS level of theory.

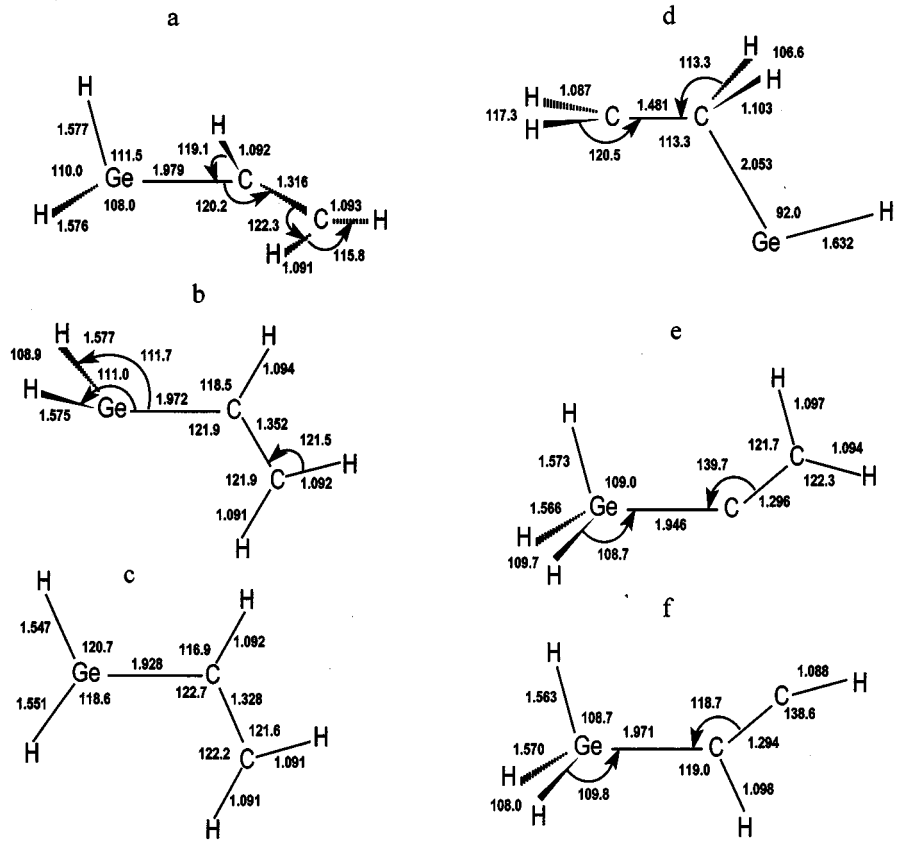

Figure 4. MP2/BS geometrical parameters of the GeC_2H_5 isomers with bond lengths [Å] and bond angles [°]

mol^{-1}) through a hydrogen-atom migration. The ethylgermylene **5a**, the most stable at the MP2 level of theory, becomes less stable at the QCI level. This product cannot be obtained directly from the exothermic reaction according to Equation (12), but through a rearrangement of the structure after this reaction or a rearrangement and a loss of a

hydrogen atom after the reaction according to Equation (14). The 2-methyl-1-germaethylene **5e** was found to be 14.7 kcal mol^{-1} above the most stable species **5b**. This structure, which can be derived from the more feasible process according to Equation (12), requires a transposition of a hydrogen atom. The germacyclopropane **5d** can only be obtained directly from the thermally favoured formation reaction of GeC_2H_6. Although the energy of the germacyclopropane was found to be higher by 10.0 kcal mol^{-1} with respect to that of **5a**, the reaction remains thermally allowed.

The investigation of the potential-energy surface of the triplet GeC_2H_6 species provides four other structures that are shown also in Figure 5 (**5f** to **5i**). The total and relative energies are collected in Table 5. The products obtained directly from the process according to Equation (12) correspond to the species **5g** and **5h**, the former being a minimum on the potential-energy surface, the latter a first-order saddle point for rotation of a methylene group around the C−C bond. The activation energy of the rotation process was calculated to be 3.4 kcal mol^{-1}. The energy of the minimum **5g** was found to be 42.6 kcal mol^{-1} higher than that of the most stable GeC_2H_6 species **5a**.

The other two species **5f** and **5i** can be obtained from the exothermic reaction according to Equation (12) only through rearrangements of the molecular structure that require overcoming energy barriers. Moreover, if the energy of the **5f** species was found to be only 24.6 kcal mol^{-1} higher than that of **5a**, the **5i** species is 60.3 kcal mol^{-1} higher in energy. The energy required for these reactions is very high which therefore are the least feasible.

GeC_2H_7

Four different critical points have been located on the potential-energy surface of the GeC_2H_7 radical obtained from Equation (15). The main geometrical parameters are shown in Figure 6, absolute and relatives energies are collected in Table 5.

Two different 1-propyl-like structures can be conceived, i.e. $CH_3CH_2GeH_2$ and $GeH_3CH_2CH_2$.

Both the bisected and the eclipsed conformations of $GeH_3CH_2CH_2$, henceforth indicated as **6d** and **6b**, have been located in the C_S symmetry on the potential-energy surface. The bisected conformation (Figure 6d) has been characterized as a first-order saddle point for rotation of the methylene group around the C−C bond, the activation energy of this process being computed as 3.1 kcal mol^{-1} at the QCI level of calculation. The eclipsed conformation **6b** was found to be a minimum on the potential-energy surface with an energy 17.0 kcal mol^{-1} higher with respect to the most stable $CH_3CH_2GeH_2$ radical **6a** in the C_1 symmetry. Since the reaction enthalpy corresponds to −25.2 kcal mol^{-1} this process is thermochemically feasible. However, species **6a**, the global minimum on the potential-energy surface of the GeC_2H_7 radical, cannot be obtained directly from Equation (15) but only through a rearrangement of an H atom from a Ge to a C atom.

Only one 2-propyl-like structure can be conceived for the GeH_3CHCH_3 radicals. The structure obtained is reported in Figure 6c; the energy was found 16.4 kcal mol^{-1} higher than that of **6a**. In this case, the structure cannot be obtained directly from Equation (15) but a migration of an H atom over a C−C bond is necessary.

Comparing these results with those for the $GeC_2H_7^+$ ions[38] the 1-propyl-like species appears to be the most stable structure, which is in agreement with the available data concerning the $GeC_2H_7^+$ ions. However, there is a difference between the ions and radicals as, in the latter case, a cyclic structure has not been obtained.

Conclusions

The results of the mass-spectrometric study outlined above, together with the composition of the condensed-phases products and the low yield of volatile species observed in the radiolysis of GeH_4/C_2H_4 mixtures seem to suggest a propensity for ethylene to react with both neutral or ionic GeH_x species. The above findings appear to solve the problems regarding the poor content of carbon of the solid obtained from GeH_4/alkane mixtures.

The theoretical calculations indicate that, among the considered reactions, the most probable are those which take place without atomic or molecular hydrogen dissociation. Moreover, among the reactions whose products are obtained by addition of the two reagent species, the processes without molecular rearrangements are favoured. In particular, for the species GeC_2H_4 and GeC_2H_5 the **3a**, **3b**, and **4d** isomers, from Equations (8) and (9), can be easily obtained. With regard to the GeC_2H_6 species, the structure **5d** is the most probable isomer which originates from Equation (12), but it is a closed-shell structure without free electrons. The most probable GeC_2H_7 radical obtained from reaction 15 is the **6b** isomer.

As reported above, the more abundant radical species derived from GeH_4 radiolysis seem to be Ge and GeH and so the most abundant primary mixed compounds are the GeC_2H_4 isomers **3a** and **3b**obtained from Equation (8) and the GeC_2H_5 isomer **4d** from Equation (9). These mixed products are probably the species which result from reactions with germane radicals and/or with ethylene molecules, leading to formation of condensed-phase products and also to volatile compounds with longer chains. This is consistent with the low hydrogen content of the products in the condensed phase and it is in agreement with the trend of the H/(Ge + C) ratio as a function of ethylene percentage, reported in Figure 2. It seems to indicate that the hydrogen atoms present in the chain are those of ethylene which remain bonded to carbon atoms.

Experimental Section

Radiolysis: Monogermane was prepared according to the literature[39] and purified by bulb-to-bulb distillation. Ethylene was high-purity SIAD (Società Italiana Acetilene e Derivati) gas and was

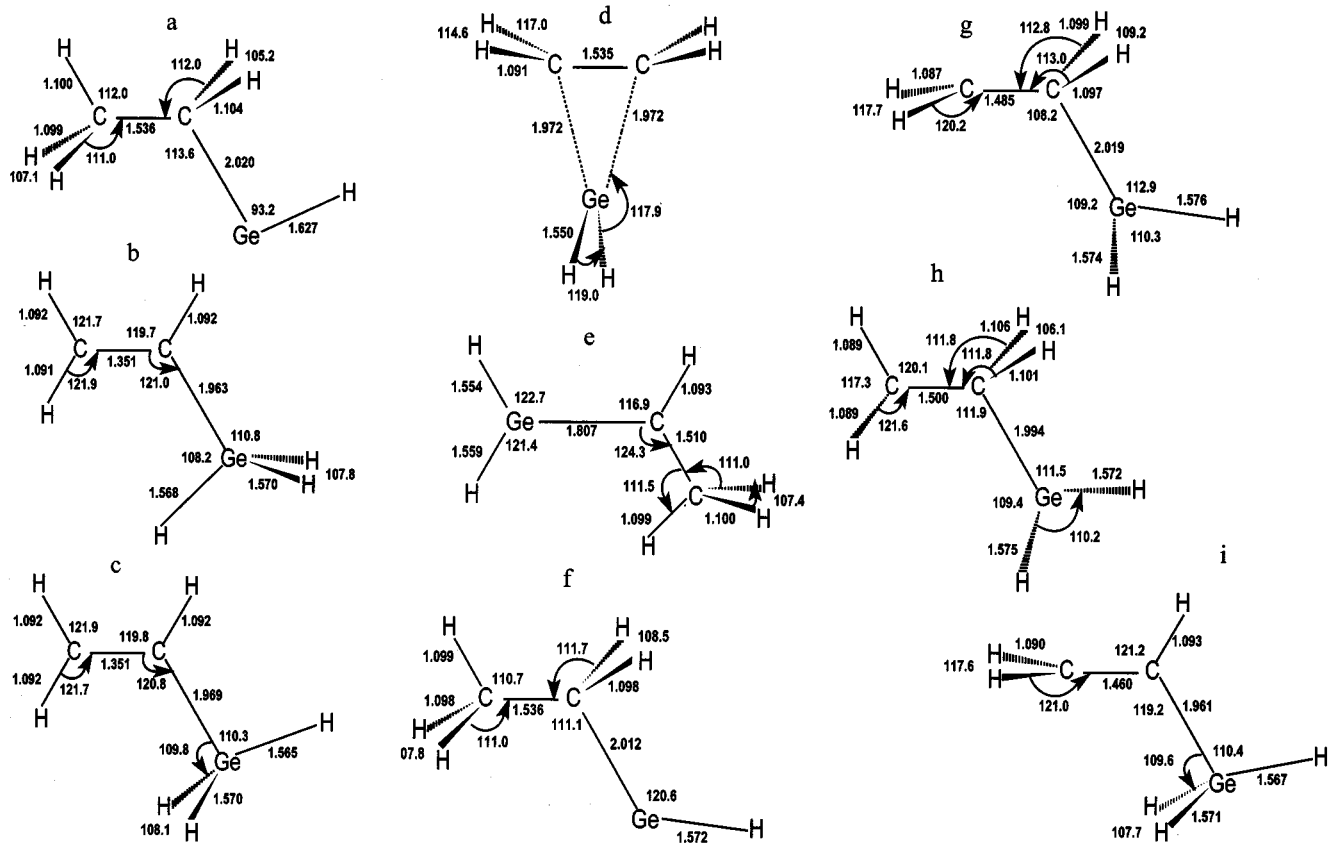

Figure 5. MP2/BS geometrical parameters of the GeC_2H_6 isomers with bond lengths [Å] and bond angles [°]

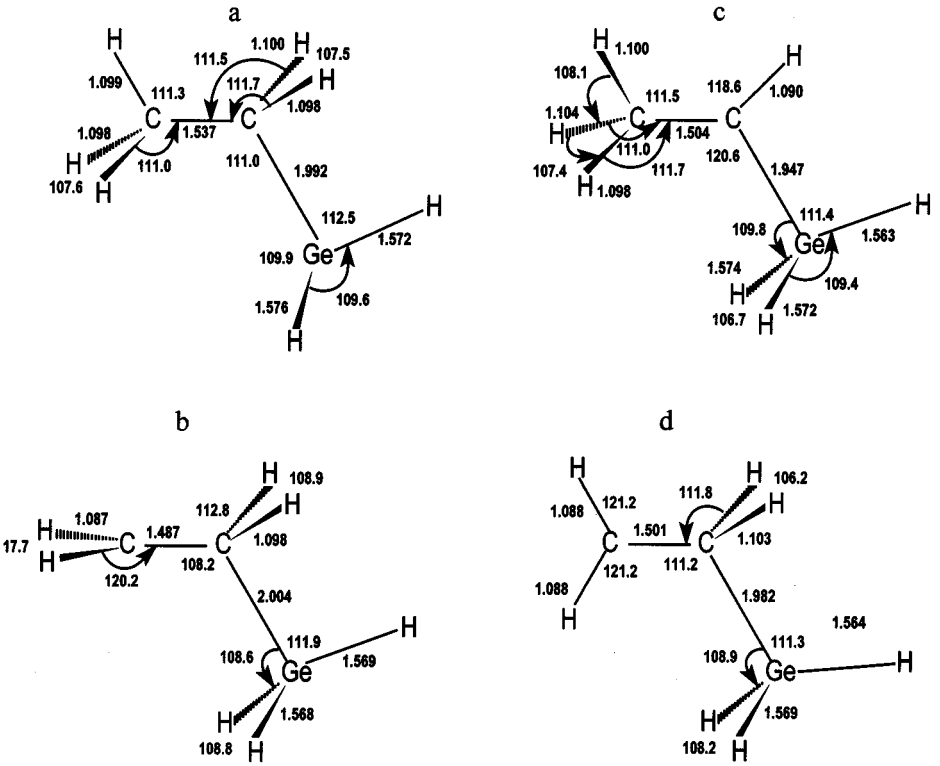

Figure 6. MP2/BS geometrical parameters of the GeC_2H_7 isomers with bond lengths [Å] and bond angles [°]

used without purification. Samples of GeH_4/C_2H_4 mixtures of different compositions were irradiated with 250-keV X-rays in 365-ml Pyrex vessels at a total pressure of 700 Torr. Standard vacuum techniques were used to handle both reactants and gaseous products. The X-ray source was a CPXT-320 tube (GILARDONI) with a maximum output of 320-keV X-ray. The dose absorbed by each sample was evaluated to be $5.0 \cdot 10^4$ Gy at a rate of $1.0 \cdot 10^4$ Gy h^{-1}. During the irradiation the temperature did not exceed 320 K. The gaseous product analysis was performed by gas chromatography and mass spectrometry using a VARIAN 3400/Finnigan ITD instrument equipped with Alltech AT-1 chromatographic column (polydimethylsiloxane, length 30 m, i.d. 0.25 mm, film thickness 1.0 μm). The temperature ranged from 243 to 523 K at 10 K/min. A 10 psi He carrier front column was used. Ionisation in the ion trap was achieved by electron impact at 70eV and acquisition of ions was obtained in the 20−650 unit mass range. Quantitative determination of volatile compounds was effected by calibrating the gas chromatograph with GeH_4. The values reported are the averages of at least four experiments.

Computational Details: Ab initio quantum-mechanical calculations were performed using an IBM RISC/6000 and a DIGITAL α STATION version of Gaussian 94 set of programs.[40] The geometries of investigated species were optimized by gradient-based techniques[41] at the unrestricted Möller−Plesset level of theory[42] truncated at the second order and with the frozen-core approximation (UMP2/FROZEN). The basis set (BS) used was obtained as follows. For the germanium atoms, starting with Huzinaga (4333/433/4) basis,[43] the last s and p atomic orbitals were decontracted to the double-ζ level to give (43321/4321/4); in addition, a set of polarization functions[43] was added with exponent α = 0.246. For the carbon atom, starting with the Huzinaga (43/4/1) basis, the last s and p atomic orbitals were decontracted to the double-ζ level to give (421/31/1). For the hydrogen atom, the 6-31G basis set was employed.[44] The critical points were characterized as minima at this level through diagonalization of analytically calculated Hessian matrices (vibrational frequencies calculation). The UMP2/(FROZEN)/BS geometries were employed to recompute the relative energies by quadratic configuration-interaction calculations at the QCISD(T) level[45] with the more extended basis set 6-311G (3df,2p).[46a−46d] Zero-point vibrational energies were computed at the UMP2(FROZEN)/BS level.[47]

Acknowledgments

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