

Amorphous Germanium Carbides by Radiolysis–CVD of Germane/Ethyne Systems: Preparation and Reaction Mechanisms

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Amorphous germanium carbides have been prepared by X-ray-activated chemical vapor deposition from germane/ethyne systems. Different mixtures containing the two reagents in variable molar ratios have been investigated with the aim of determining the factors which lead to the highest yields of solid products and of obtaining information on the main ionic and radical reaction paths giving the amorphous material. To this purpose, samples were irradiated consecutively four times in 0.5-h steps. Both qualitative and quantitative GC/MS analyses of the volatile products as well as the determination of the solid composition by elemental analysis were performed after each irradiation. Moreover, the ion/molecule reactions have been studied by ion trap mass spectrometry, determining the ionic reaction mechanisms and the rate constants of the most significant processes. The results indicate that two main and opposite factors affect the formation of the amorphous product: (a) both radical and ionic paths are favored by the presence of ethyne in excess with respect to germane; (b) the increase of content of ethyne in the irradiated mixtures lowers the total number of activated species. Therefore, the best yield of amorphous germanium carbides is obtained when germane and ethyne have a molar ratio between 2/1 and 1/1.

Introduction

Semiconductors are fundamental materials in current technologies with increasing importance in the future. As semiconductive properties are uncommon in elements, compounds are to be considered as alternative materials for application purposes. Moreover, in some cases it is convenient to use semiconductors in the amorphous form rather than in the crystalline one, for their low cost compared with slightly lower performances.^{1,2}

The most important amorphous semiconductor compounds are binary species of elements of group 14 of the periodic table. Today, while Si–C and Ge–Si alloys are the subject of both chemical and physical detailed studies,^{3–10} less attention is given to Ge–C alloys. In fact, their synthesis with simple methods is rather difficult, even if different techniques, such as rf sputtering, laser ablation, chemical vapor deposition, and activated reaction evaporation, have been used.^{11–18}

In our laboratory, we prepare directly solid α -GeC:H starting from mixtures of volatile germanium hydrides and small hydrocarbons activated by high-energy radiation.^{19–24} In fact, X-rays as well as γ -rays have energies in large excess with respect to chemical energies and, therefore, give similar amounts of reactive species even from molecules with very different bond energies, such as germanium hydrides and hydrocarbons.

It has been observed that the composition of the products strongly depends on the nature of the hydrocarbon mixed with germane and on their molar ratio. For GeH₄/alkane mixtures, the percentage of carbon atoms in the solid increases from methane to propane, but it never exceeds 30% even for irradiation of GeH₄/C₃H₈ with a 1:3 molar ratio.^{20,21} When irradiation of germane takes place in the presence of ethene, the

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carbon content in the solid becomes higher than that of germanium already starting from gas mixtures containing only 8% ethene.²⁴ This behavior is not surprising considering that the reactivity of ethene toward radicals is so high to be often used as a scavenger. Moreover, both mass spectrometric studies^{25,26} and investigations on intermediate species during radiolysis show that chain propagation is favored by increasing insaturation of hydrocarbons.^{23,24}

Therefore, following these results, we report in this paper the study of the reactivity of systems containing germane and ethyne in different ratios under irradiation with X-rays that should enhance the chain propagation for the increased degree of insaturation of the hydrocarbon. The formation of both volatile and solid products is investigated also under a quantitative point of view. The same mixtures are studied by ion trap mass spectrometry to determine the ion paths leading to Ge–C clusters of increasing size and to have information on the relative contribution of radical and ion species.

Finally, a description of the reaction mechanisms leading to the amorphous solid may also give a suggestion on the presence of sp^2 or sp hybridized species that would form materials with energy gap values lower than that of germanium and further decrease with increasing carbon fraction in the solid.

Experimental Section

Materials. Monogermane was prepared as described in the literature²⁷ starting from GeO_2 and KBH_4 ; ethyne was supplied by SIAD SpA at 99.99% stated purity. Both gases were purified by bulb-to-bulb distillation under vacuum and dried with sodium sulfate. The different GeH_4/C_2H_2 mixtures for irradiation had relative composition 9:1, 4:1, 2:1, 1:1, and 1:5 and were prepared in 365-mL Pyrex vessels at a total pressure of 700 Torr (1 Torr = 133 Pa) prior to the X-ray treatment. Standard vacuum techniques were used to handle reactants and gaseous products.

In the study of the ion reaction mechanisms performed by ion trap mass spectrometry, the mixtures of germane and ethyne (5:1, 1:1, and 1:5) were prepared in the cell of the ion trap by connecting the two separate flasks to the gas inlet system. In these experiments, helium was used as the buffer gas and obtained from SIAD SpA as research gas at an extra-high purity of 99.9999%.

Ion Reaction Mechanisms. All experiments were performed on a Finnigan ITMS instrument maintained at 333 K to obtain results comparable with studies of other systems.^{28,29}

Ion trap mass spectrometry theory and methods are discussed in previous works.^{28–30} Briefly, in this kind of mass spectrometer it is possible to keep ions in stable trajectories inside the cell, operating on the intensity of radio frequency (rf) and direct current (dc) electric fields and with the assistance of an unreactive gas, called buffer gas, which is typically helium. The main advantage of the trapping instruments is the possibility of selectively isolating ion species at specific m/z values and to keep them in the cell for suitable times, during which they react with neutrals present in the trap at steady pressures. Samples were admitted to the trap via an inlet system modified to permit the simultaneous introduction of three gases (two reagents and helium buffer gas) through different lines. Pressures measured with a Bayard Alpert ionization gauge were typically $2.0\text{--}10.0 \times 10^{-7}$ Torr for germane and ethyne and about 5.0×10^{-4} Torr for helium. A calibration factor accounting for the geometry of the instrument²⁹ (distance between the gauge and the cell) and the relative sensitivity of the gauge (1.94 for GeH_4 , 1.534 for C_2H_2)³¹ were applied to calculate the real pressure in the trap. The scan modes for ion/molecule reaction experiments used to determine the overall reactivity of germane/ethyne mixtures, reaction mechanisms, and rate constants for reactions of selected ions and the corresponding calculations have been previously described in detail.^{28–30} Isolation of ions having univocal composition Ge^+ , GeH^+ , GeH_2^+ , and GeH_3^+ is difficult because of the presence of the isotopes of germanium having masses at 70, 72, 73, 74, and 76 Da; that is, if ions are selected at m/z 72, they correspond to different chemical species $^{70}GeH_2^+$ and $^{72}Ge^+$. Therefore, the species at m/z 70 ($^{70}Ge^+$), 71 ($^{70}GeH^+$), 78 ($^{76}GeH_2^+$), and 79 ($^{76}GeH_3^+$) were isolated as they are the only ones with a unique composition. Ions were formed with an electron beam at an average energy of 35 eV and 1–20 ms ionization times. For the study of reaction mechanisms or for kinetics determinations, a suitable reaction time was applied to maximize the abundance of ions to be stored prior to their isolation. Reactions with neutral molecules in the trap lasting from 50 ms for calculations of rate constants to 1 s for overall reactivity and acquisition were the successive steps.

Radiolysis. All GeH_4/C_2H_2 samples were irradiated with 250 keV X-rays; the adsorbed dose rate was about 1.0×10^4 Gy h^{-1} . During the irradiation the temperature never exceeded 323 K. The X-ray source was a CPXT-320 tube by Gilardoni SpA with a maximum output of 320 keV. Every irradiation lasted 0.5 h and was consecutively repeated four times on each sample for 2 h as the total irradiation time. After each irradiation step, a small amount of the gas phase was drawn for qualitative and quantitative analyses of volatile compounds by GC/MS. The remaining mixtures were used again in the following irradiation. The solid products were also collected at every X-ray treatment and weighted and the composition was determined via elemental (C and H) analysis.

GC/MS. A Varian 3400/Finnigan ITD gas chromatograph-mass spectrometer was used for the determination of gases, equipped with an Alltech AT-1 capillary column (poly(dimethylsiloxane), 30 m long, 0.25 mm internal diameter, and 1.0 μm film thickness). Before injection, the GC oven was cooled at about 233 K introducing liquid nitrogen; afterward, the temperature of the column was raised to room temperature and was then heated to 323 K. A split of about 15 mL/min was applied during injection; helium was used as the carrier gas at about 10 psi (1 psi = 6.89×10^3 Pa). Electron ionization was performed at 70 eV and acquisition of ions was achieved in the 15–400 u mass range. Quantitative determination of volatile compounds was obtained by correlating the areas of the gas chromatographic peaks to the total number of milli-

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Table 1. Evaluated Number of Ions, Radicals, and Molecules of GeH₄ and C₂H₂ Formed in Different Mixtures during the First 0.5 h of Irradiation

mixture	GeH ₄			C ₂ H ₂			GeH ₄ + C ₂ H ₂	
	ions	radicals	molecules	ions	radicals	molecules	ions + radicals	molecules
9/1	1.3×10^{18}	7.9×10^{18}	7.3×10^{21}	4.2×10^{16}	8.4×10^{16}	8.1×10^{20}	9.3×10^{18}	8.1×10^{21}
4/1	1.2×10^{18}	7.0×10^{18}	6.4×10^{21}	8.4×10^{16}	1.7×10^{17}	1.6×10^{21}	8.5×10^{18}	8.0×10^{21}
2/1	1.0×10^{18}	6.2×10^{18}	5.7×10^{21}	1.3×10^{17}	2.6×10^{17}	2.4×10^{21}	7.6×10^{18}	8.1×10^{21}
1/1	7.1×10^{17}	4.3×10^{18}	4.0×10^{21}	2.1×10^{17}	4.2×10^{17}	4.0×10^{21}	5.6×10^{18}	8.0×10^{21}
1/5	2.3×10^{17}	1.4×10^{18}	1.3×10^{21}	3.3×10^{17}	6.6×10^{17}	6.3×10^{21}	2.6×10^{18}	7.6×10^{21}

moles of gases, determined by measuring the pressure in the reacting vessel.

Results and Discussion

During the irradiation process, both radicals and ions are formed and the total number of these species can be estimated for the starting mixtures from the total energy absorbed by the system. Irradiation with a $1.0 \times 10^4 \text{ Gy} \cdot \text{h}^{-1}$ dose for 0.5 h corresponds to $5 \text{ J} \cdot \text{g}^{-1}$. It follows that ranging from the GeH₄/C₂H₂ 9/1 (959.11 mg) to the 1/5 (435.06 mg) mixture, the absorbed energy varies from 4.8 to 2.2 J. Moreover, these values are shared between GeH₄ and C₂H₂ on the basis of their mass, varying from 4.6 to 0.82 J for germane and from 0.18 to 1.4 J for ethyne. The energy required for the ionization and for the formation of a radical should be considered to evaluate the relative contribution of ions and radicals. Assuming for germane and ethyne 3.52×10^{-18} and $4.13 \times 10^{-18} \text{ J} \cdot \text{molecule}^{-1}$, respectively, the average energy (W) required to form an *ion pair* (i.e., the energy related to the process: $M \rightarrow M^+ + e^-$; $M = \text{GeH}_4$ or C_2H_2)³² and as the ionization potential (I) is only $1.68 \times 10^{-18} \text{ J} \cdot \text{molecule}^{-1}$ for germane³³ and $1.83 \times 10^{-18} \text{ J} \cdot \text{molecule}^{-1}$ for ethyne,³⁴ there is an excess of energy ($W - I$) for germane and ethyne of about $1.84 \times 10^{-18} \text{ J} \cdot \text{molecule}^{-1}$ and $2.30 \times 10^{-18} \text{ J} \cdot \text{molecule}^{-1}$, respectively, available for the formation of excited molecules and/or radicals.

Considering the enthalpies^{34,35} of the reactions leading to the radicals formed in higher abundance from the two reactants,



it is possible to calculate that about six radicals are formed from germane and two radicals from ethyne for each ion and to evaluate the number of ions and radicals obtained after absorption of the energy amount corresponding to 0.5 h of irradiation in all the systems studied here (Table 1).³²

Formation of GeH₃ radicals from germane is also possible and requires about $5.56 \times 10^{-19} \text{ J} \cdot \text{molecule}^{-1}$, thus lowering the number of Ge containing active

species that, in any case, are higher than those containing carbon atoms. Moreover, GeH₄ produces a germyn radical by elimination of a hydrogen radical, which in turn, may react with neutral molecules to give new radicals, and again, the energetics balance is in favor of Ge:H species. Therefore, it is evident that when the ethyne content is increased in the mixtures irradiated by a constant dose, the number of activated species decreases for two reasons: (i) the lower energy absorbed by C₂H₂ as compared with GeH₄; (ii) the higher energy required by C₂H₂ with respect to GeH₄ to form ions and radicals. In successive reactions in the vessel, the decomposed species can lead to both gas and solid products.

Ion Reaction Mechanisms. The ion reaction mechanisms were investigated by ion trap mass spectrometry in three different kinds of experiments. At first, the formation of mixed ions containing germanium and carbon atoms was considered as a function of the composition of the reacting mixture. To this purpose, three germane/ethyne mixtures were examined at the same total pressure of about 1.2×10^{-6} Torr, but with different relative amounts of the two reagent gases. In these experiments, all ions formed during the ionization (primary ions) were kept in the cell together with the neutral molecules for increasing reaction times up to 2 s. In a second step, the 1:1 mixture was used to determine the ion reaction mechanisms starting from primary ions of both reagents by isolation of selected ions and reaction delay up to 500 ms. Finally, in a third kind of experiment, the rate constants of the most interesting processes were measured by isolating ion species for reaction times of 50 ms by 0.2 ms steps.

Figure 1a shows the mass spectrum recorded in the 1:1 GeH₄/C₂H₂ mixture after 1 s of reaction where many different ion families are present. Each multiplet is formed by the superimposition of signals of ions containing different germanium isotopes and different amounts of hydrogen atoms. Therefore, the formula reported indicates the ion family in terms of Ge and C content, but it is impossible to define also the number of hydrogen atoms with good reliability. Some of them (GeH_{*n*}⁺, Ge₂H_{*n*}⁺, Ge₃H_{*n*}⁺, and Ge₄H_{*n*}⁺) do not contain carbon atoms and are formed in self-condensation processes of germane ions; some others are mixed ions (GeCH_{*n*}⁺, GeC₂H_{*n*}⁺, GeC₃H_{*n*}⁺, Ge₂C₂H_{*n*}⁺, Ge₃C₂H_{*n*}⁺), precursors of amorphous germanium carbides. For the same germane/ethyne mixture, the variations of ion percentage intensities of the main ion families with reaction time are reported in Figure 1b. The ethyne primary ions (C₂H_{*n*}⁺) and their direct self-condensation products (C₄H_{*n*}⁺) disappear in a very short time and no other hydrocarbon ions display significant abundances up to 2 s of reaction. To the contrary, the abundance of the GeH_{*n*}⁺ primary ions decreases slowly and their

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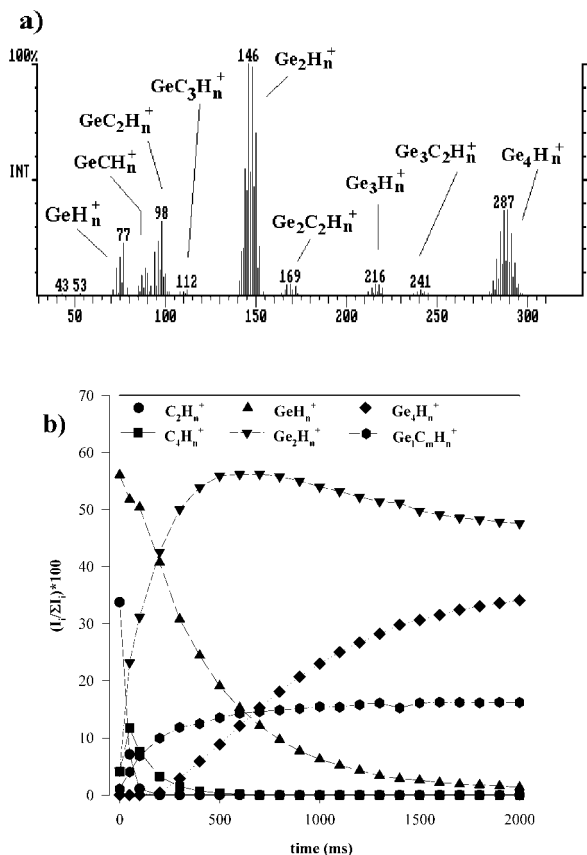


Figure 1. Mass spectrum recorded at 1 s of reaction for the 1:1 germane/ethyne mixture (a) and variation of the ion percentage intensities with reaction time of the main ion families of the same mixture (b).

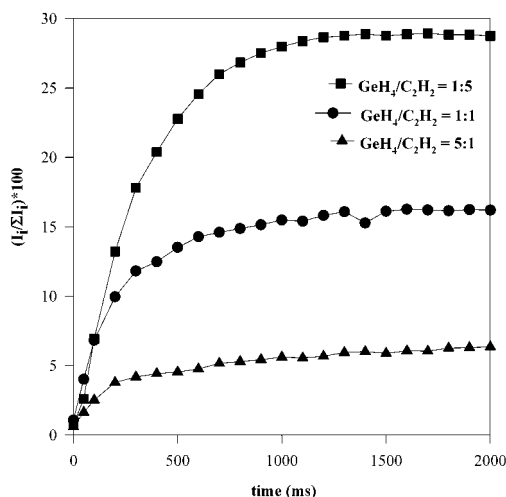
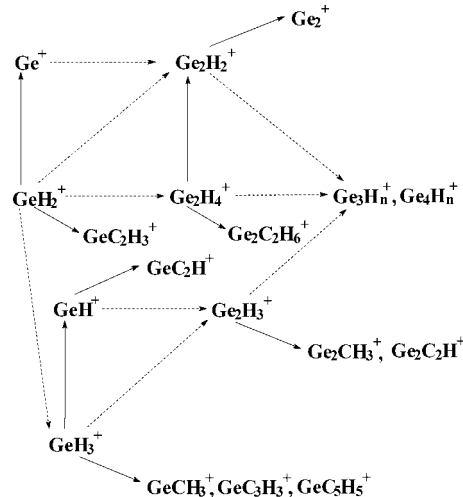


Figure 2. Variation of the sum of the ion percentage intensities of mixed ions as a function of reaction time for each of the 1/5, 1/1, and 5/1 germane/ethyne mixtures.

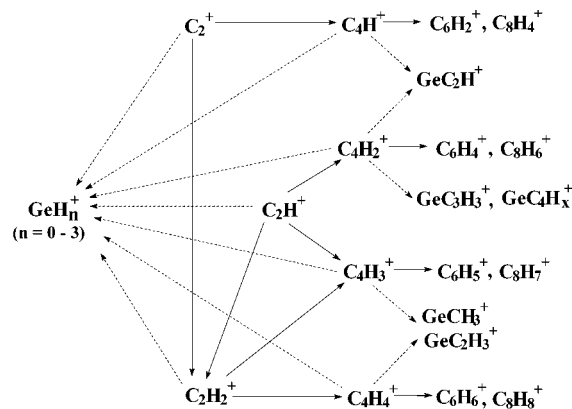
products Ge_2H_n^+ and Ge_4H_n^+ are very abundant in the time range considered here. The sum of the ion percentage intensities of all mixed ions present in the mixture ($\text{Ge}_l\text{C}_m\text{H}_n^+$; $l = 1, m = 1-3$; $l = 2, m = 2$; $l = 3, m = 2$) increases rather rapidly up to 500 ms of reaction (about 12%) and very slowly at a longer reaction time ($\approx 16\%$).

In Figure 2 the variations of the sum of the ion percentage intensities of mixed ions for three germane/ethyne mixtures at the approximate ratios 1:5 [$p(\text{GeH}_4) = 2.0 \times 10^{-7}$ Torr, $p(\text{C}_2\text{H}_2) = 11.0 \times 10^{-7}$ Torr], 1:1

Scheme 1. Ion/Molecule Reactions Starting from Primary Ions of Germane with Ethyne (Normal Arrows) and Germane (Dashed Arrows)



Scheme 2. Ion/Molecule Reactions Starting from Primary Ions of Ethyne with Ethyne (Normal Arrows) and Germane (Dashed Arrows)



[$p(\text{GeH}_4) = 6.5 \times 10^{-7}$ Torr, $p(\text{C}_2\text{H}_2) = 6.1 \times 10^{-7}$ Torr], and 5:1 [$p(\text{GeH}_4) = 10.1 \times 10^{-7}$ Torr, $p(\text{C}_2\text{H}_2) = 2.0 \times 10^{-7}$ Torr] respectively, are reported as a function of reaction time. All three systems show a similar trend: an initial sharp increase of the Ge–C containing ions is followed by constant values up to 2 s. Moreover, it is evident that excess of ethyne yields the highest amount of mixed ions, which is almost twice that in the 1:1 mixture and 4 times that in the presence of germane in excess. Such behavior is unusual with respect to all previous silane or germane/hydrocarbon mixtures^{28,29,36,37} in which the formation of mixed ions was always unfavored by excess of the hydrocarbon species.

The results of the second set of experiments are summarized in Schemes 1 and 2, which report the ion mechanisms starting from primary ions of germane and ethyne, respectively. These schemes have been obtained by isolation of each primary ion of both reagents (GeH_n^+ , $n = 0-3$, for germane; C_2H_n^+ , $n = 0-2$, for ethyne) and successive isolation of their products until the low sensitivity of ion species prevented the obtainment of

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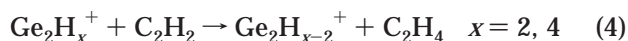
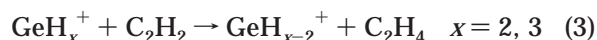
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Table 2. Rate Constants for Reactions of GeH^+ with Ethyne and of C_2H_n^+ ($n = 0-2$) and C_4H_n^+ ($n = 2-4$) Ions with Germane^a

reaction			k_{exp}	Σk_{exp}	k_{L}^b	efficiency ^c	ΔF_{298}^d
$\text{C}_2^+ + \text{GeH}_4$	→	$\text{Ge}^+ + \text{C}_2\text{H}_4$	3.6				-215
	→	$\text{GeH}^+ + \text{C}_2\text{H}_3$	1.4				-185
	→	$\text{GeH}_2^+ + \text{C}_2\text{H}_2$	0.74				-173
	→	$\text{GeH}_3^+ + \text{C}_2\text{H}$	1.4	7.1	12.19	0.58	-127
$\text{C}_2\text{H}^+ + \text{GeH}_4$	→	$\text{Ge}^+ + \text{C}_2\text{H}_5$	2.8				-127
	→	$\text{GeH}^+ + \text{C}_2\text{H}_4$	1.6	4.4	12.00	0.37	-162
$\text{C}_2\text{H}_2^+ + \text{GeH}_4$	→	$\text{Ge}^+ + \text{C}_2\text{H}_6$	1.9				-87
	→	$\text{GeH}^+ + \text{C}_2\text{H}_5$	0.78				-59
	→	$\text{GeH}_2^+ + \text{C}_2\text{H}_4$	1.3				-54
	→	$\text{GeH}_3^+ + \text{C}_2\text{H}_3$	1.9	5.9	11.83	0.50	-38
$\text{C}_4\text{H}_2^+ + \text{GeH}_4$	→	$\text{GeC}_2\text{H}^+ + \text{C}_2\text{H}_5$	1.8				
	→	$\text{GeC}_3\text{H}_3^+ + \text{CH}_3$	1.2	3.0	9.477	0.32	
	→	$\text{GeCH}_3^+ + \text{C}_3\text{H}_4$	0.64				-42
$\text{C}_4\text{H}_3^+ + \text{GeH}_4$	→	$\text{GeC}_2\text{H}_3^+ + \text{C}_2\text{H}_4$	0.96	1.6	9.420	0.17	
	→	$\text{GeCH}_3^+ + \text{C}_3\text{H}_5$	0.41				-45
$\text{C}_4\text{H}_4^+ + \text{GeH}_4$	→	$\text{GeC}_2\text{H}_3^+ + \text{C}_2\text{H}_5$	0.51	0.92	9.365	0.098	
	→	$\text{GeC}_2\text{H}^+ + \text{H}_2$	0.14	0.14	9.736	0.014	

^a Rate constants are expressed as $10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$; uncertainty is within 20%. ^b Collisional rate constants have been calculated according to the Langevin theory, taking polarizability of germane ($4.966 \times 10^{-24} \text{ cm}^3$) from ref 39 and that of ethyne ($3.33 \times 10^{-24} \text{ cm}^3$) from ref 40. ^c Efficiency has been calculated as the ratio $k_{\text{exp}}/k_{\text{collisional}}$. ^d Reaction enthalpies, expressed in $\text{kcal} \cdot \text{mol}^{-1}$, have been calculated taking thermochemical data from refs 30 and 35.

reproducible results. The normal arrows indicate reactions with ethyne and the dashed arrows with neutral germane. Species after commas are the only products of the preceding ions reacting with the same neutral species indicated by the arrow. In Scheme 1, formation of heavy ion species proceeds through secondary ions of germane reacting with ethyne ($\text{Ge}_2\text{C}_2\text{H}_n^+$) or from GeH_3^+ and C_2H_2 in consecutive reaction steps to GeC_3H_5^+ as the last product identified. In some cases, reactions between germanium-containing ions and ethyne do not give condensation products of increasing size, but transfer a hydrogen molecule to C_2H_2 , yielding ethene as a neutral product:



Ethyne ions display similar behavior (Scheme 2) as only reactions of its secondary ions (C_4H_n^+ , $n = 1-4$) with germane form mixed ion species up to GeC_4H_x^+ . C_2H_n^+ ($n = 0-2$) ion species do react with GeH_4 , but only in charge exchange processes to give the whole family of primary ions of germane, GeH_n^+ ($n = 0-3$). These results are in agreement with the observation on the best yield of mixed ions in the presence of ethyne in excess. In fact, a large fraction of C_2H_2 molecules and hydrocarbon ions seems to be consumed in processes such as hydrogenation or charge exchange, which are useless to the formation of large ion species containing both germanium and carbon atoms. Only the remaining fraction of its total amount gives mixed condensation products.

The determination of the rate constants of these processes (Table 2) gives a more detailed description of this phenomenon. The collisional rate constants calculated according to Langevin theory,³⁸ the reaction efficiencies (ratio between experimental and collisional rate constants), and the reaction enthalpies are also shown in this table. Rate constants of self-condensation

processes of primary ions of germane, GeH_n^+ ($n = 0-3$), are not reported as they have published.⁴¹ Reactions of hydrocarbon ions with germane show good efficiencies in charge exchange processes, but give low yields of products containing both germanium and carbon atoms. Among germanium primary ions, only GeH^+ reacts with ethyne with a measurable rate constant; however, the reaction efficiency is lower than that in the previous processes involving ions of ethyne and molecules of germane. Since the Ge_2H_3^+ and Ge_2H_4^+ secondary ions of germane could not be isolated separately in the rate constant experiments, it was impossible to determine their reaction rate constants.

Reaction enthalpies have been calculated taking the most thermodynamically stable among the possible ion or molecule isomers.^{30,38} Formation of the GeH_n^+ ions by charge exchange is always an exothermic process for the high ionization energies of the C_2H_n ($n = 0-2$) species.³⁸ Among mixed ions, only the heat of formation of GeCH_3^+ is known³⁰ and the reaction enthalpies of processes starting from C_4H_3^+ and C_4H_4^+ resulted in negative values.

Kinetic results confirm the previous hypothesis as (i) the most efficient reactions consume C_2H_2 to produce primary ions of germane, (ii) primary ions of germane react further very slowly, and (iii) mixed ion species that can in principle propagate the clusterization process are formed with low efficiencies of reactions from secondary ions of ethyne. Therefore, as far as the ion mechanism is concerned, reactions producing Ge-C-containing species require the presence of ethyne in large excess for (i) the very low efficiency of processes of germanium ions with C_2H_2 , (ii) the use of two C_2H_2 molecules to form species (C_4H_n^+) able to give mixed ions, and (iii) the existence of competitive dehydrogenation processes useless to our purposes.

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Table 3. Composition of the Gas Mixtures after Irradiations of the GeH₄/C₂H₂ Systems

mixture, time	gases (μmol) ^a					
	GeH ₄	C ₂ H ₂	GeC ₂ H ₄	GeC ₂ H ₆	Ge ₂ C ₂ H ₆	Ge ₂ C ₂ H ₈
9/1	12062	1340				
9/1, 0.5 h	11763	862	48.46	2.40	80.40	329.13
9/1, 1.0 h	10680	777	25.14	4.11	54.41	171.71
9/1, 1.5 h	10089	297	7.55	5.84	106.37	555.55
9/1, 2.0 h	10252		15.30	10.57	142.15	711.98
4/1	10722	2680				
4/1, 0.5 h	9792	1922	50.52		92.18	463.77
4/1, 1.0 h	8984	1338	55.76		124.68	688.49
4/1, 1.5 h	9125	1070	41.92	10.21	129.24	647.58
4/1, 2.0 h	8191	1108	20.09	10.59	83.46	357.22
2/1	9513	4077				
2/1, 0.5 h	9189	3356	108.79	8.93	104.65	454.77
2/1, 1.0 h	8490	2181	72.07	14.62	114.92	527.13
2/1, 1.5 h	7433	893	15.92	15.90	90.62	425.45
2/1, 2.0 h	7050	848	5.50	16.68	89.20	361.16
1/1	6548	6548				
1/1, 0.5 h	5858	6041	221.41		50.29	266.48
1/1, 1.0 h	5037	5193	61.66		73.30	482.78
1/1, 1.5 h	4702	4602				142.28
1/1, 2.0 h	3984	3914				229.49
1/5	2135	10426				
1/5, 0.5 h	2055	9775				
011/5, 1.0 h	1988	9418				
1/5, 1.5 h	1822	8914	60.78			4.67
1/5, 2.0 h	1663	8049	137.36		2.84	17.62

^a Determinations are affected by an error within 15%.

Free Radical Reactions (and Polymerization).

From irradiation of GeH₄/C₂H₂ mixtures, gaseous and solid products are obtained, the latter being deposited on the bottom of the irradiation vessel. It has been observed in previous works that from activation of germane all the GeH_{*n*} (*n* = 0–3) cations and radicals^{23,26} are obtained, whereas C₂H₂⁺, C₂H⁺ ions (relative abundance 100:21), and C₂H radical are the most abundant active species from ethyne.³²

Table 1 shows that, for each ion, about six radicals are formed from germane and two radicals from ethyne, thus indicating that radical reactions should give major contribution to the products formation.

Table 3 reports the quantities of the most abundant gas species present in the reaction vessel after each irradiation step determined by GC/MS analyses. In the GeH₄/C₂H₂ 9/1 mixture, Ge₂H₆ is present in traces and appreciable amounts of C₄H₄, C₆H₆, and GeC₄H₆ also have been detected in the mixture containing ethyne in excess. All the values are the average of at least three analyses performed injecting different volumes of gas and have been corrected taking into account the amounts of gases removed from the reaction vessel for every series of GC/MS determination. A check on the total amounts of products, both gases and solids, with respect to the conservation of the starting mass in milligrams, indicates an experimental error that never exceeds 15%.

Table 4 reports the Ge/C ratio in the gas mixtures before each irradiation together with some features of the corresponding solid phase. It always consists of a powder whose color varies from yellow to white with increasing carbon content. The aim of this table is to relate the actual amounts of gases with the composition of the solid products and, therefore, they have not been corrected as in Table 3.

Table 4. Composition of the Gas Mixtures Irradiated and of the Solid Products Obtained after Irradiations of GeH₄/C₂H₂ Mixtures

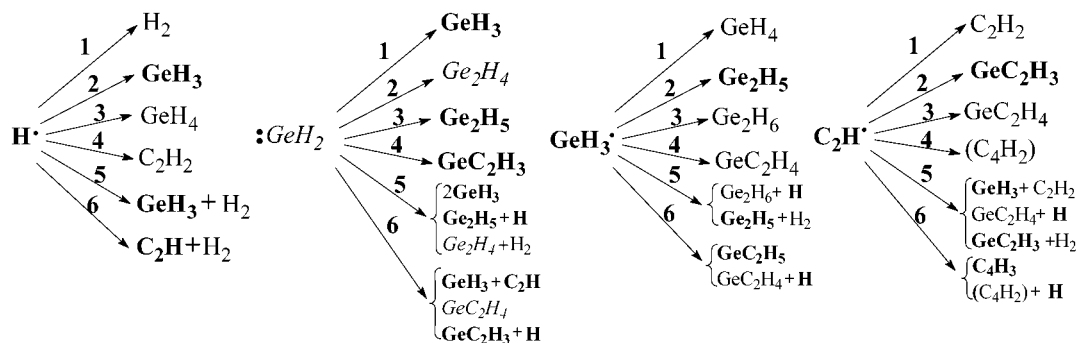
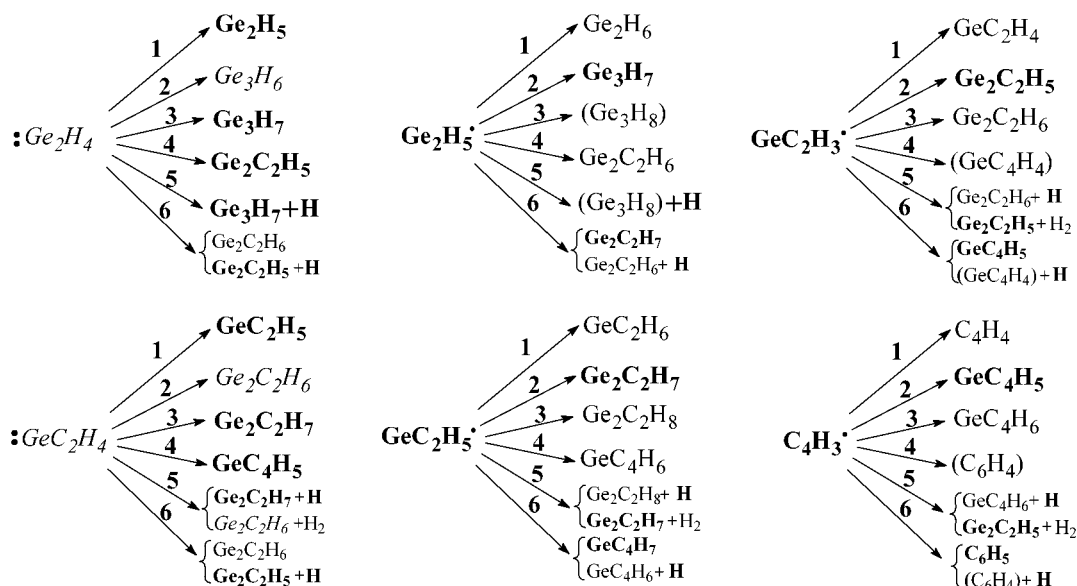
mixture, time	conditions of the irradiated gas mixture		solid products			
	Ge/C (total) ^a	mg	composition	Ge/C	mg	%
9/1, 0.5 h	4.50	959.11	GeC _{1.65} H _{4.68}	0.61	10.6	1.10
9/1, 1.0 h	3.83	924.33	GeC _{2.23} H _{5.22}	0.45	14.9	1.61
9/1, 1.5 h	5.40	883.76	GeC _{3.13} H _{5.38}	0.32	6.8	0.77
9/1, 2.0 h	5.88	829.76	GeC _{3.55} H _{5.73}	0.28	2.1	0.25
4/1, 0.5 h	2.22	891.32	GeC _{1.90} H _{5.12}	0.53	28.8	3.23
4/1, 1.0 h	2.16	842.36	GeC _{2.84} H _{4.72}	0.35	22.9	2.72
4/1, 1.5 h	2.42	767.14	GeC _{3.30} H _{6.69}	0.30	24.7	3.22
4/1, 2.0 h	2.82	719.09	GeC _{4.15} H _{6.81}	0.24	2.4	0.33
2/1, 0.5 h	1.16	835.06	GeC _{3.27} H _{5.84}	0.31	37.5	4.49
2/1, 1.0 h	1.29	769.17	GeC _{3.74} H _{5.89}	0.27	66.1	8.59
2/1, 1.5 h	1.70	692.97	GeC _{5.29} H _{6.32}	0.20	63.0	9.09
2/1, 2.0 h	2.95	588.40	GeC _{5.88} H _{7.06}	0.17	4.0	0.68
1/1, 0.5 h	0.50	672.20	GeC _{2.00} H _{4.82}	0.50	23.2	3.45
1/1, 1.0 h	0.50	622.59	GeC _{2.13} H _{5.72}	0.47	51.0	8.19
1/1, 1.5 h	0.50	553.29	GeC _{2.38} H _{5.91}	0.42	46.6	8.42
1/1, 2.0 h	0.51	485.03	GeC _{2.49} H _{6.83}	0.40	38.7	7.98
1/5, 0.5 h	0.10	435.06	none			
1/5, 1.0 h	0.10	410.09	none			
1/5, 1.5 h	0.10	395.11	none			
1/5, 2.0 h	0.10	389.35	none			

^a GeH₄, C₂H₂ and all the gaseous products are considered.

Experiments have also been performed on germane and ethyne separately. GeH₄ gives di- and trigermane in the gas phase and an amorphous cross-linked polymer, which is a black powder, as described previously.⁴² To the contrary, no solid product is formed from ethyne and only C₄H₄ and C₆H₆ gas products are observed, in agreement with studies where the solid obtained is probably due to the much higher irradiation dose.⁴¹ It follows that the powders collected after irradiation of the GeH₄/C₂H₂ mixtures are not simple coprecipitation of hydrogenated C–C or Ge–Ge polymer chains, but contain Ge–C bonds.

Considering the composition of the gas mixture after each irradiation step (Table 3), it is evident that the amounts of reactants decrease, and it is worth noting that ethyne is consumed to a larger extent than germane in the first three mixtures. The trend of the amounts of gas products formed at every irradiation is quite irregular, probably because during the irradiation the composition of the gas mixtures changes, affecting the amount of energy adsorbed and, as a consequence, the nature and number of activated species in an unknown and unpredictable way. Generally, four gaseous products are present in the irradiated systems and they all contain both germanium (one or two atoms) and carbon (two atoms). GeC₂H₆ has low abundance and is the first product to disappear with increasing content of ethyne. The amounts of Ge₂C₂H₆ and Ge₂C₂H₈ follow the same trend, and when both of them are present, Ge₂C₂H₈ is 4–5 times more abundant than Ge₂C₂H₆. Actually, Ge₂C₂H₈ usually has the highest yield, except for the 1/5 mixture where C₄H₄ is the most abundant species. All these gas products still contain unsaturated bonds, which are likely to remain on the carbon atoms,

(42) Belluati, R.; Castiglioni, M.; Volpe, P.; Gennaro, M. C. *Polyhedron* **1987**, *6*, 441.

Scheme 3. Reactions of Primary Radicals with Themselves (Processes (1)–(4)), GeH₄ (5), and C₂H₂ (6)**Scheme 4. Reactions of Secondary Radicals with Primary Radicals (Processes (1)–(4)), GeH₄ (5), and C₂H₂ (6)**

thus indicating the presence of sp² and/or sp hybridized species.

Schemes 3 and 4 have been prepared to find the radical/radical or radical/molecule reaction mechanisms leading to the products observed experimentally. All the possible reactions of primary radicals, formed during irradiation of the GeH₄/C₂H₂ mixtures, with themselves, GeH₄, or C₂H₂ molecules are reported in Scheme 3. Similarly, reactions of secondary radicals, formed as described in Scheme 3, with primary radicals and neutral species are shown in Scheme 4. Bold and italic characters indicate radical and diradical species, respectively, whereas molecules are in regular font and molecular products never observed experimentally are written in parentheses. It is evident that only reactions between GeH₃ and C₂H radicals give in one step the formation of a stable molecule containing both Ge and C (GeC₂H₄) (Scheme 3), detected in the gas phase. In all other cases, the formed species, containing Ge–C, is again a radical, which is able to react further and to propagate the chain (Scheme 4). As observed for the volatile products, many of these intermediates of reactions show unsaturations that indicate the presence of

sp² and sp hybridations; these can reasonably be maintained in the chain propagation and in the final solid products.

Reaction products in these schemes show that the reactions involving a germylene radical (GeH₂) favor chain propagation as they lead to products which are still radicals (both mono- or diradicals) and can react further. To the contrary, the germyl radical (GeH₃) is likely to be involved in the formation of the observed gas products, which can be obtained in one or two reaction steps by fast radical recombinations, the germyl being the starting and/or the terminating species.

The experimental results indicate that reactions giving species containing both germanium and carbon atoms are by far predominant with respect to self-condensation processes. This is in agreement with irradiation of ethyne alone, giving only small amounts of C₄H₄ and C₆H₆, whereas germane alone gives both solid products and gas species containing two or three germanium atoms (never observed in the present study). Therefore, when germane is irradiated in the presence of C₂H₂, it reacts preferentially with ethyne, yielding Ge–C:H species.

From these considerations, the most probable starting reactions of the polymerization process are



where the products may react further, leading to chain propagation.

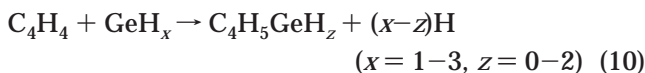
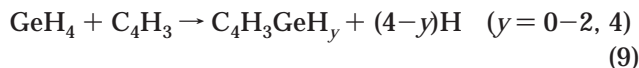
Considering that germane is present in excess with respect to ethyne in the first three mixtures (9/1, 3/1, and 2/1), reactions of species formed in processes (5) and (6) with GeH_4 molecules should be more probable than those with C_2H_2 , leading to a solid polymer with a carbon content lower than that determined experimentally (Table 4). This observation can be explained on the basis of the similarity of the radical and ion mechanisms. In fact, mass spectrometric experiments showed formation of C_4H_m^+ ($m = 1-4$) ions prior to reactions with germane to give Ge-C-containing ions. In the same way, process (7) is suggested:



The radical product C_4H_3 can be stabilized by recombination with a hydrogen radical to form C_4H_4 .



These two species, C_4H_3 and C_4H_4 , can react as C_2H and C_2H_2 in reactions (5) and (6), respectively, giving



or enter in the chain during the radical reaction propagation.

This hypothesis is also in agreement with the presence of C_4H_4 in the gas phase of the irradiated 1/5 mixture. When the $\text{GeH}_4/\text{C}_2\text{H}_2$ ratio decreases, the yield of reaction (7) increases and that of reaction (8) decreases with respect to reaction (9) because of the lower GeH_4 content. Moreover, the decreased amount of GeH_x radicals, reagents of process (10), lowers the extent to which this reaction occurs.

Results of Table 4 show that the carbon content and the amount of solid products obtained from different mixtures irradiated for the same times increase with decreasing $\text{GeH}_4/\text{C}_2\text{H}_2$ ratio of the starting system up to the 2/1 mixture. Both of them decrease in the 1/1 mixture and only traces of solid are obtained in the 5/1 system.

Some considerations are necessary to explain such behavior. At first, as already stated, germane radicals are always predominant with respect to those of ethyne (100 times higher in the 9/1 mixture and are still 10 times higher in the 1/1 systems, Table 1) and can be considered the main precursors of the polymeric chains,

whereas the contribution of the ethyne radicals is negligible at least up to the 1/1 mixture. Second, the higher ethyne percentage in the starting mixture increases the probability of reactions of ethyne (both molecules and activated species) with germane radicals, but the absolute number of these radicals decreases. It is evident that, up to the 2/1 mixture, the decrease of the GeH_x radicals is balanced by the increase of the probability of reaction with ethyne, but becomes a determining factor in the 1/1 system (Table 4).

In the $\text{GeH}_4/\text{C}_2\text{H}_2$ 1/5 mixture the number of germane radicals decrease by about 3.5 times with respect to the 1/1 system and is in agreement with the presence of only traces of solid product.

In contrast with the trend observed comparing products obtained from different mixtures after the same times of irradiation, results of Table 4 show that the carbon content of the solids formed in the same mixture at different irradiation times increases even if the ethyne percentage in the mixture decreases. It must be considered that the gas products, overall containing carbon in excess with respect to germanium, undergo radiolysis too and are involved in the formation of the solid material. Moreover, their contribution becomes more important as the amount of precursors, and especially of C_2H_2 , decreases.

Conclusion

Irradiation of the $\text{GeH}_4/\text{C}_2\text{H}_2$ mixtures leads to satisfactory results as far as the formation of an amorphous solid product is concerned. In fact, the amount of solid obtained in this system is almost 10 times more abundant than that in $\text{GeH}_4/\text{alkane}$ ²⁰ or $\text{GeH}_4/\text{ethene}$ ²³ mixtures considering the most favored conditions. Moreover, the composition is easily tunable to fit the requirements of any possible application and lower costs can be expected for the easy recovery of the solid material without any separation or purification step. From the considerations of the reaction mechanisms, the following can be concluded: (a) the most important mechanism seems to involve activated species of germanium and ethyne molecules, thus increasing the yield of both gaseous and solid products going from the $\text{GeH}_4/\text{C}_2\text{H}_2$ 9/1 mixture to the 2/1 and 1/1 ones; (b) the increase of ethyne in the mixture favors the formation of Ge-C-containing species in processes involving both ions and radicals, in agreement with the Ge/C ratio in the solid, that is generally lower than 0.5; (c) however, it must be considered that increased content of ethyne in the mixture gives a lower number of total activated species and especially of activated species of germane, in agreement with the disappearance of products in the 1/5 $\text{GeH}_4/\text{C}_2\text{H}_2$ mixture; (d) therefore, the best system should meet these two requirements and have a germane/ethyne ratio close to 2/1 and 1/1.

Moreover, both volatile products and radical intermediates leading to the solids exhibit unsaturated bonds which suggest the presence of sp^2 and/or sp hybridized species in the final amorphous products.

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