Reactions of Recoiling Germanium Atoms in Germane, Digermane, and Germane–Silane Mixtures[1,2]

Peter P. Gaspar* and John J. Frost

Contribution from the Department of Chemistry, Washington University, Saint Louis, Missouri 63130. *Received August 16, 1972*

Abstract: Product studies on reactions of recoiling germanium atoms in germane, digermane, and germane–silane mixtures support a mechanism in which $^{75}GeH_2$ is an important intermediate giving rise to a next higher homolog of the substrate and also to products of unimolecular decomposition of the higher homolog. Scavenger, moderator, and pressure dependence experiments are discussed, as is the possibility that $^{75}Ge^+$ is an active intermediate. A complete mechanism is suggested for the reactions of germanium atoms recoiling in germane and germane–silane mixtures: $^{75}Ge + GeH_4 \rightleftharpoons (H^{75}GeGeH_3)^*$ (10); $^{75}Ge + SiH_4 \rightleftharpoons (H^{75}GeSiH_3)^*$ (11); $(H^{75}GeGeH_3)^* + M \rightarrow H^{75}GeGeH_3$ (19); $(H^{75}GeSiH_3)^* + M \rightarrow H^{75}GeSiH_3$ (20); $(H^{75}GeGeH_3)^* \rightarrow {}^{75}GeH_2 + GeH_2$ (21); $(H^{75}GeSiH_3)^* \rightarrow {}^{75}GeH_2 + SiH_2$ (22); $H^{75}GeGeH_3 + GeH_4 \rightarrow GeH_3{}^{75}GeH_2GeH_3$ (12); $H^{75}GeGeH_3 + SiH_4 \rightarrow SiH_3{}^{75}GeH_2GeH_2$ (13); $H^{75}GeSiH_3 + GeH_4 \rightarrow SiH_3{}^{75}GeH_2GeH_3$ (14); $H^{75}GeSiH_3 + SiH_4 \rightarrow SiH_3{}^{75}GeH_2SiH_3$ (15); $^{75}GeH_2 + GeH_4 \rightleftharpoons ({}^{75}GeH_3GeH_3)^*$ (3); $^{75}GeH_2 + SiH_4 \rightleftharpoons ({}^{75}GeH_3SiH_3)^*$ (8); $({}^{75}GeH_3GeH_3)^* + M \rightarrow {}^{75}GeH_3GeH_3$ (5); $({}^{75}GeH_3SiH_3)^* + M \rightarrow {}^{75}GeH_3SiH_3$ (23); $({}^{75}GeH_3GeH_3)^* \rightarrow {}^{75}GeH_4 + GeH_2$ (4); $({}^{75}GeH_3SiH_3)^* \rightarrow {}^{75}GeH_4 + SiH_2$ (9).

We are studying the reactions of recoiling silicon and germanium atoms in order to understand the interplay between structure and energy as factors which determine what happens in a fundamental chemical process (reactive collision between a polyvalent atom and a molecule). Since the free atoms which interest us are difficult to produce for study by other kinetic techniques, nuclear recoil has been employed for the production of germanium atoms. The nuclear recoil technique, a highly versatile method for the production of free atoms under very mild conditions, is generally useful for the study of atomic reactions only if radiation damage is minimized by the production of the smallest number of free atoms (10^8 to 10^{15}) which can be accurately detected by means of their radioactive decay. The small number of free atoms produced precludes direct rate measurements for reactive intermediates. In recoil studies, the chemically stable end products of a series of reactions initiated by a free atom provide the data used to reconstruct the reaction mechanism.[3a] Direct reaction rate measurements of germanium atoms produced in macroscopic quantities will complement these studies.[3b] To our knowledge only one other report of germanium recoil chemistry has appeared.[4]

Germanium atoms, like silicon, are of interest to us because they share the half-filled valence shell electronic structure of carbon. This ensures that a multistep reaction sequence occurs before chemically stable products are produced, a complicating factor in the elucidation of reaction mechanism.

A comparison of atoms with identical electronic structure but quite different sizes, polarizabilities, and electronegativities promises some new insight into the factors which control the reactivity of carbon as well as silicon and germanium atoms. A very naive view of these experiments would be to regard them as substituent studies on carbon atom reactions.[5] The very large *differences* between the chemistry of tetravalent carbon on the one hand and silicon and germanium on the other suggest that silicon and germanium atoms should behave very differently from carbon atoms. The higher energy of π bonds involving germanium and silicon *vs.* those of carbon removes a thermodynamic sink which might otherwise have led to similar reactions for the three atoms.

This paper reports product yield studies of the reactions of germanium atoms recoiling from the $^{76}Ge(n,2n)^{75}Ge$ nuclear transformation in gaseous reaction systems. The estimated recoil energy, 4×10^4 eV, is sufficient to rupture all bonds in the precursor molecule germane, GeH_4.[6] Calculations of charge-transfer cross-section maxima according to the resonance rule predict neutralization of initially charged germanium ions before sufficiently low kinetic energies are reached for bond-making processes to occur. The existence of a metastable state of ^{75}Ge, 0.139 MeV above the ground state, provides an unwanted but possibly important complication. The metastable state decays to the ground state by an isomeric transition of 48-sec half-life. Without empirical knowledge of the ratio of formation of the two states in the (n,2n) transformation, one can say only that the ground state is favored over the metastable excited state.[7] The metastable state, to the extent formed, should give rise to chemically reactive positive species by virtue of the low recoil energy from the isomeric transition and the high probability of internal conversion and charging by the Auger process.[8]

Our purpose in the present series of experiments has been to identify reaction products, reactive intermedi-

---

(1) This is paper II in a series; for paper I see: P. P. Gaspar, C. A. Levy, J. J. Frost, and S. A. Bock, *J. Amer. Chem. Soc.*, 91, 1573 (1969).

(2) Financial support from the United States Atomic Energy Commission is gratefully acknowledged. This is AEC Technical Report COO-1713-33.

(3) (a) P. P. Gaspar and M. J. Welch, "Nuclear Transformations in Solids," G. Harbottle and A. G. Maddock, Ed., North-Holland Publishing Co., Amsterdam, in press; (b) P. P. Gaspar, K. Y. Choo, E. Y. Y. Lam, and A. P. Wolf, *Chem. Commun.*, 1012 (1971).

(4) K. Akerman, *Monatsh. Chem.*, 102, 864 (1971).

(5) P. P. Gaspar and B. Jerosch Herold, "Carbene Chemistry," 2nd ed, W. Kirmse, Ed., Academic Press, New York, N. Y., 1971, Chapter 13, p 504.

(6) Recoil energy estimated by D. G. Sarantites, private communication.

(7) Private communication from D. G. Sarantites.

(8) G. Friedlander, J. W. Kennedy, and J. M. Miller, "Nuclear and Radiochemistry," 2nd ed, Wiley, New York, N. Y., 1964, pp 255–261.

ates, and modes of reaction, thereby elucidating the operative reaction mechanism. This has been accomplished as in previous hot-atom studies by determining the effects on product yields of changes in the reaction conditions, *i.e.*, variation in the composition and pressure of the gaseous reaction mixtures.

In addition to pure germane and digermane, we have examined the two-component reaction system germane–silane. Silane possesses the advantage of being a reactive substrate *without* producing detectable volatile radioactive products through fast neutron induced nuclear reactions.

Experimental Section

Materials. Germane (99.9% minimum) and silane (semiconductor grade) from Matheson Gas Products were used without purification. No impurities were detected by gas chromatography, infrared spectroscopy, and mass spectroscopy. Neon (cp 99.99%) and nitric oxide (cp 99.0%) were obtained from Air Products and Chemicals Inc. and were used without purification. Methane and ethylene (both research grade 99.98%) were obtained from Phillips Petroleum Co. and used without purification. Industrial grade oxygen was used without purification. Digermane,[9,10] silylgermane,[11] trigermane,[9,10] Ge_2SiH_8,[9,12,13] $GeSi_2H_8$,[9,12,13] and normal- and isotetragermane[9,10] were synthesized by circulating germane and germane–silane mixtures through a silent electric discharge as described below. These compounds were identified by mass spectrometric analysis of purified compounds trapped from the effluent of a gas chromatograph.

The apparatus consisted of a discharge tube immersed in an ice-water mixture, a cold trap immersed in an acetone–Dry Ice bath, a 1-l. expansion bulb, and a peristaltic tubing pump all connected in series. This circulating system was connected to a conventional vacuum line for the addition of reactants and the removal of products. The initial reaction mixtures consisting of pure germane or 1:1 germane–silane mixtures at 200–300 Torr were circulated through the 8000-V silent discharge for *ca.* 1 hr at 400 ml/min. After removal of the remaining gaseous substances at the end of the reaction period, the contents of the −78° trap were transferred to the vacuum line for vapor chromatographic analysis using chromatographic conditions described below.

Reaction Mixtures. Reaction mixtures were prepared on a conventional high-vacuum line previously described.[14] Reaction mixtures were prepared by freezing condensible gases into 6 or 14 mm i.d. × 9 cm quartz ampoules followed by any noncondensible components. The ampoules were sealed with a natural gas–oxygen flame.

Fast Neutron Irradiations. Sets of ampoules irradiated together were rotated on a spindle to ensure equal integrated neutron fluxes for all ampoules. The ampoules were protected from thermal neutrons by a thin cadmium shield. No detectable ^{31}Si activity is produced from a 3000-Torr sample of pure silane in a 6-mm ampoule, indicating that the thermal neutron flux is less than 10^6 neutrons/cm^2/sec at the reaction mixtures. Irradiations of duration 45 to 60 min were employed. Fast neutrons were produced by a 20 μA current of 13 MeV deuterons in the Washington University cyclotron impinging on a beryllium target. The $^9Be(d,n)^{10}B$ nuclear transformation produced a flux of *ca.* 10^8 neutrons/cm^2/sec at the reaction mixtures.

Analysis of Reaction Mixtures. The radio-gas chromatographic procedures employed to detect radioactive products and to determine their yields have been described previously.[15] The apparatus in the configuration employed in the present experiments has also been described recently.[14]

Chromatographic columns are 0.25-in. o.d. aluminum tubing, 20 ft long. All product yields were determined, and authentic samples separated, on a stationary phase consisting of 20 g of SF96 silicone oil per 100 g of 40–50 mesh diatomaceous earth solid support (Anakrom ABS, acid and base washed and silanized).

Radioactive reaction products were identified by comparison of retention times with those of authentic GeH_4, Ge_2H_6, $GeSiH_6$, Ge_3H_8, Ge_2SiH_8, $GeSi_2H_8$, n-Ge_4H_{10}, or i-Ge_4H_{10}, injected serially and simultaneously. The amounts of authentic samples of higher molecular weight than Ge_2H_6 used as carriers for quantitative yield studies were kept minimal in order to avoid quenching the windowless flow counter.[14] Germane, digermane, and germylsilane were identified by comparison of reaction products with authentic samples on two additional columns: diethyl phthalate plus silicone oil on diatomaceous earth operated at room temperature with 60 ml/min He carrier gas flow rate, and a Porapak Q (50–80 mesh) column operated at variable temperature increasing from 30 to 110° over 35 min with the carrier gas flow rate also 60 ml/min.

Radioactive decay analyses were carried out on separated products GeH_4, $GeSiH_6$, and Ge_2H_6 trapped from the radio chromatographic effluent. The samples were trapped on powdered charcoal in thin-walled polyethylene tubing which was heat sealed. The tubes were mounted below gas-filled proportional counters and the decay curves determined by taking periodic readings of the decay rate. Germane and silylgermane gave straight line plots of log decay rate *vs.* time whose slope gave a half-life of 87 ± 3 min, in satisfactory agreement with the literature value of 82 min.[16] Digermane gave a decay plot with two components, >97% of the activity with the proper half-life for ^{75}Ge, 87 ± 7 min, the other 3% consisting of a 15 ± 1 hr activity, presumably ^{72}Ga (literature $t_{1/2}$ = 14.1 hr)[16] due to $^{72}Ge(n,p)^{72}Ga$. The gallium may be incorporated in $^{72}GaGeH_6$ unresolved chromatographically from Ge_2H_6. Since germanium of natural isotopic abundance was used as the precursor to ^{75}Ge, several other nuclear reactions might have been expected to give detectable radioactivity, *e.g.*, $^{70}Ge(n,p)^{70}Ga$ ($t_{1/2}$ = 21 min)[16] and $^{73}Ge(n,p)^{73}Ga$ ($t_{1/2}$ = 4.8 hr),[16] but these nuclides were not detected.

Quantitative analyses of reaction mixtures were carried out with the catherometer (hot-wire) detector, chromatographic column, breaker, and connecting lines at 80° and the counter at 100°. The helium carrier gas flow was 80 ml/min. Propane counter gas (Matheson instrument grade 99.5% passed through a pyrogallol deoxygenating tower and several drying towers) flow was 100 ml/min. The counter performance has been discussed previously.[14]

Absolute yield measurements were carried out by trapping separated radioactive products on glass wool in Pyrex ampoules after they had left the flow counter, breaking the ampoules under scintillator fluid in closed counter vials, and measuring the radioactivity in a liquid scintillation counter. The activity of individual products was compared with the total activity induced in a reaction mixture, measured by breaking a complete reaction ampoule in a counting vial. An error analysis has been published.[15]

Dose. The total dose in these experiments was less than 10^{-3} eV/molecule as determined by acetylene dosimetry.[17]

Results

Product yields have been determined from the fast neutron irradiation of the following gaseous reaction mixtures: (a) pure germane, (b) germane–silane, (c) germane–neon, (d) germane–scavengers, and (e) pure digermane.

Pure Germane. The simplest system in which to study the reactions of recoiling germanium atoms is pure germane, and it is the system most pertinent to a comparison of recoil germanium chemistry with recoil silicon chemistry. Product yields from pure germane were determined over a wide pressure range to assess the importance of internal energy deposition and unimolecular dissociation in the reaction sequences leading to observed products. Figures 1 and 2 show the results of these experiments.

---

(9) S. D. Gokhale, J. E. Drake, and W. L. Jolly, *J. Inorg. Nucl. Chem.*, 27, 1911 (1965).

(10) W. L. Jolly and A. D. Norman, *Prep. Inorg. React.*, 6, 1 (1968).

(11) E. J. Spanier and A. G. MacDiarmid, *Inorg. Chem.*, 2, 215 (1963).

(12) P. L. Timms, C. C. Simpson, and C. S. G. Phillips, *J. Chem. Soc.*, 1467 (1964).

(13) T. D. Andrews and C. S. G. Phillips, *J. Chem. Soc. A*, 46 (1966).

(14) P. P. Gaspar, P. Markusch, J. D. Holten, III, and J. J. Frost, *J. Phys. Chem.*, 76, 1352 (1972).

(15) P. P. Gaspar, S. A. Bock, and W. C. Eckelman, *J. Amer. Chem. Soc.*, 90, 6914 (1968).

(16) C. M. Lederer, J. M. Hollander, and I. Perlman, "Table of Isotopes," 6th ed, Wiley, New York, N. Y., 1967.

(17) L. M. Dorfman and F. J. Shipko, *J. Amer. Chem. Soc.*, 77, 4723 (1955).

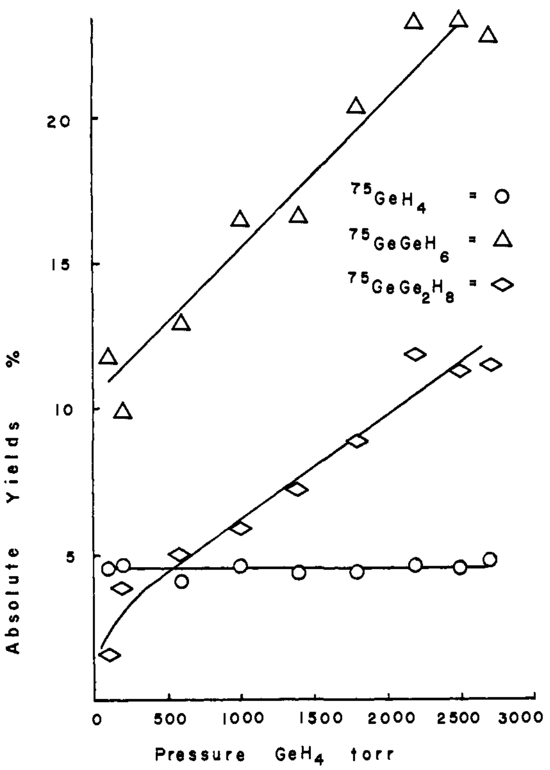

Figure 1. Variation of absolute product yields from pure germane as a function of pressure.

Below 3000 Torr, germane, digermane, and trigermane are the only volatile radioactive products detected from the fast neutron irradiation of pure germane.[18] The tetragermane detected at pressures greater than 3000 Torr may be due to a *ca.* 0.1% digermane impurity. Trigermane and tetragermane were not reported in the preliminary communication.[1]

The marked dependence of product yields, both absolute and relative, on total pressure reflects both unimolecular processes and recoil loss. If corrections for recoil loss were applied, the absolute yield of germane would appear to rise at low pressures. Approximate recoil loss is zero at 1000 Torr, 10% at 500 Torr, and 35% at 200 Torr.

The total yield of volatile products decreases with decreasing pressure even in the pressure region where recoil loss is negligible. The sum of observed product yields is considerably less than 100% at all pressures studied, indicating the formation of undetected products of low volatility.

The increase in relative yield of germane with decreasing pressure and the decrease in the relative yield of trigermane indicate that unimolecular dissociation contributes to the formation of germane and to the destruction of trigermane or its precursor.

Germane–Silane. The high reactivity of silane toward recoiling silicon species[14] suggested its use as a substrate for recoiling germanium atoms. The structures of the reaction products from germane–silane mixtures and the variations in their yields as a function of substrate concentrations suggest that insertion reactions of germanium atoms and divalent germanium species (germylenes) are the predominant paths to product formation.

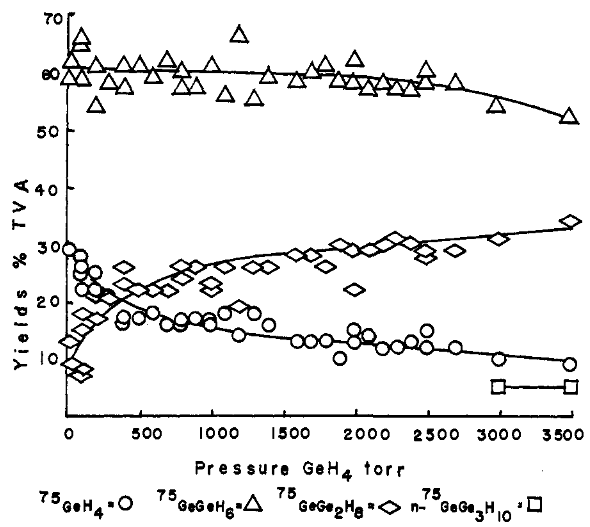

Figure 2. Variation of relative product yields (as per cent of total volatile activity) from pure germane as a function of pressure.

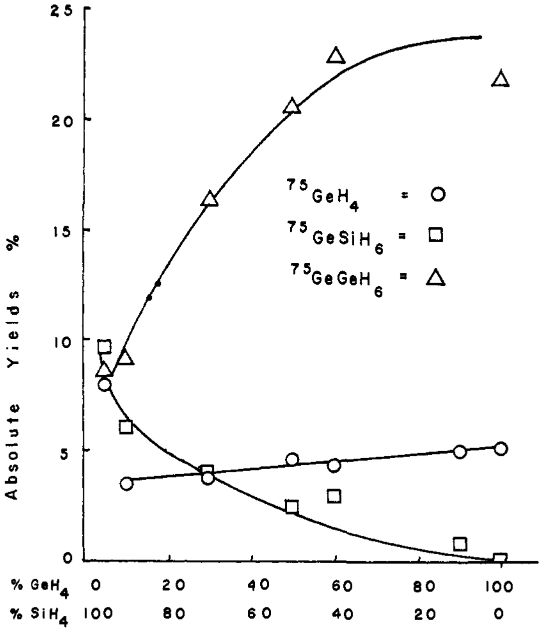

Figure 3. Variation of absolute yields of lower molecular weight products from germane–silane mixtures as a function of composition at constant total pressure (2000 Torr).

Three further products from germane–silane mixtures, $^{75}GeGe_2H_8$, $^{75}GeGeSiH_8$, and $^{75}GeSi_2H_8$, have been identified in addition to $^{75}GeH_4$, $^{75}GeGeH_6$, and $^{75}GeSiH_6$ reported in the preliminary communication. Figures 3 and 4 show the variation of the absolute product yields as a function of the composition of the reaction mixtures at constant total pressures, 2000 Torr.

The increase in digermane yield and decrease in germylsilane yield with increasing germane concentration points to a competition between germane and silane for a single intermediate. The monotonic increase in trigermane yield, and decrease in $^{75}GeSi_2H_8$ yield, with increasing germane concentration, while the yield of $^{75}GeGeSiH_8$ passes through a maximum, is consistent with consecutive reactions in which intermediates are partitioned between germane and silane.

Germane–Neon. The effect of added neon was investigated in two series of experiments. In the first, at varying total pressures, the product yields from a constant partial pressure of germane were determined

---

[18] If one ignores the trace (<3%) of (presumably) $^{72}GaGeH_6$ discussed above.

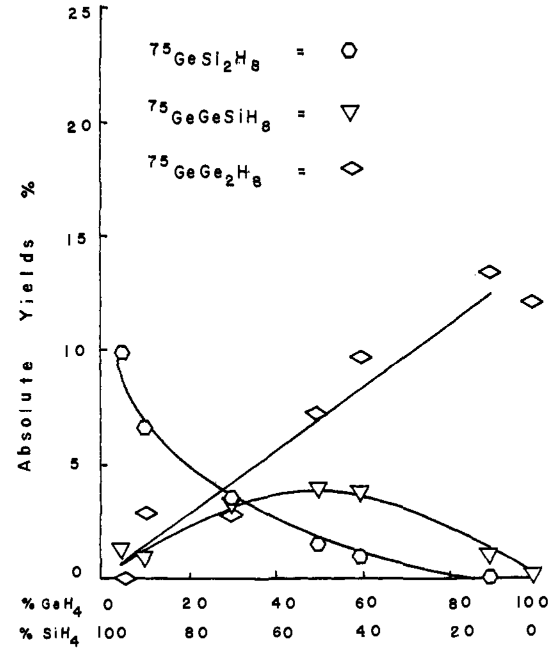

Figure 4. Variation of absolute yields of higher molecular weight products from germane–silane mixtures as a function of composition at constant total pressure (2000 Torr).

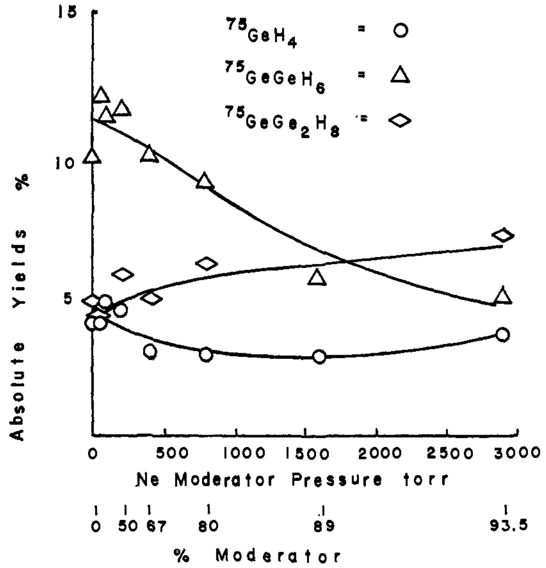

Figure 5. Variation of absolute product yields from germane–neon mixtures containing a constant partial pressure of germane (200 Torr) as a function of the partial pressure of neon.

as a function of the amount of added neon. As the amount of neon present increases, the ratio of nonreactive collisions of germanium atoms, in which kinetic energy is lost, to reactive collisions, in the "hot-atom" energy region, increases. Along with this increase in kinetic energy moderation, the effectiveness of collisional deactivation of vibrationally excited product molecules also increases, thus reducing the extent of unimolecular decomposition. The results of this experiment are shown in Figure 5. The sizable decrease in digermane yield at high moderator pressures indicates that a true hot-atom reaction may be required for its formation.

In a second series of experiments the germane–neon ratio was varied at constant total pressure, 2000 Torr. The reaction medium thus becomes *less* effective at removing vibrational excitation as the mole fraction of neon increases, although the ratio of moderating to reactive collisions increases. The results are shown in Figure 6. At high moderator concentrations (above 80%) the digermane yield decreases and the trigermane and germane yields increase, suggesting that the recoiling germanium atoms undergo reactions before their kinetic energy is equilibrated with the reaction mixture. However, there is a larger effect at low moderator concentration (0–20%), the trigermane and digermane yields decreasing, germane remaining constant. This indicates that vibrational excitation of intermediates and products is at least as important as kinetic excitation of the recoiling atoms.

Germane–Scavengers. To ascertain the importance of free radical intermediates in the recoiling germanium atom reactions, the effect on product yields from pure germane of the presence of small amounts (5%) of nitric oxide, ethylene, and oxygen was determined. These substances are known to be efficient trapping reagents for free radicals of diverse types. Ethylene is known to react efficiently with silyl radicals,[19,20] and nitric oxide is believed also to trap silyl radicals.[21] For comparison, added methane and silane were also examined as "scavengers." The results are given in Table I. In the presence of nitric oxide, the total product yield decreased *ca.* 25%. Decreases noted in the presence of ethylene and oxygen were 35 and 50%, respectively. Variations in individual product yields are discussed below. Silane and methane, as expected, do *not* cause decreases in product yields.

Digermane. The reaction products from germanium atoms recoiling in digermane can shed light on the identity of the reactive intermediates. Trigermane would be expected from insertion by germylene, while digermane and trigermane could result from a radical mechanism.

Product yields from fast neutron irradiation of *digermane* at low pressures are given in Table II. Trigermane is the major product. These low pressures were chosen to avoid quenching the counter. Considerable recoil loss and unimolecular decomposition must be expected to occur at these low pressures. For comparison, the product yields from pure germane at comparable pressures are given.

Discussion

Comparison of Germanium and Silicon Recoil Reaction Systems. The most vivid impression of the results presented is that the reactions of germanium atoms recoiling in germane give products analogous to those obtained from silicon atoms recoiling in silane-rich phosphine–silane mixtures. Germane, digermane, and trigermane are obtained in the germanium case, while silane, disilane, and trisilane are the major volatile products in the silicon system. Digermane and disilane are the most abundant products formed in the respective systems and the digermane–germane ratio at 1000

---

(19) Rapid addition of silyl radicals to ethylene ($\cdot SiH_3 + CH_2{=}CH_2 \rightarrow SiH_3CH_2CH_2\cdot$) has been observed directly by electron spin resonance spectroscopy (K. Y. Choo and P. P. Gaspar, unpublished work).

(20) D. G. White and E. G. Rochow, *J. Amer. Chem. Soc.*, **76**, 3897 (1954).

(21) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Ganning, *J. Amer. Chem. Soc.*, **87**, 179 (1965).

Table I. Yields of Volatile Radioactive Products from Pure Germane and Germane–Scavenger Mixtures[a–c]

	Product yields							Product ratios	
	$^{75}GeH_4$		$^{75}GeGeH_6$		$^{75}GeGe_2H_8$				
Sample, Torr	Abs, counts	Rel, % TVA	Abs, counts	Rel, % TVA	Abs, counts	Rel, % TVA	TVA Abs, counts	^{75}Ge-GeH$_6$/^{75}GeH$_4$	^{75}Ge-Ge$_2$H$_8$/^{75}GeH$_4$
2000 GeH$_4$	3660	12	17,021	56	9,953	33	30,534	4.65	2.72
2000 GeH$_4$	2850	13	12,862	57	6,830	30	22,542	4.51	2.40
100 NO	2904	13	13,076	57	7,082	31	23,062	4.50	2.44
2000 GeH$_4$	2411	15	9,482	60	4,026	25	15,919	3.93	1.67
100 C$_2$H$_4$	3119	13	14,762	63	5,403	23	23,284	4.73	1.73
2000 GeH$_4$ 100 O$_2$	2469	14	10,715	60	4,574	26	17,758	4.34	1.85
2000 GeH$_4$ 100 CH$_4$	4347	13	18,552	55	10,937	32	33,836	4.27	2.52
2000 GeH$_4$	4098	13	17,403	56	9,739	31	31,240	4.25	2.38
100 SiH$_4$	4371	13	19,462	56	11,120	32	34,953	4.45	2.54

[a] All samples irradiated simultaneously at equal flux. TVA = total volatile activity. [b] Number of counts extrapolated to end of irradiation for each sample. [c] Probable errors are ±10% for all data in this table.

Table II. Yields of Volatile Radioactive Products from Pure Digermane and Germane at Low Pressures[a]

	Product yields								
	$^{75}GeH_4$		$^{75}GeGeH_6$		$^{75}GeGe_2H_8$		n-$^{75}GeGe_3H_{10}$		
Pressure, Torr	Abs, arbitrary units	Rel, % TVA	Abs, arbitrary units	Rel, % TVA	Abs, arbitrary units	Rel, % TVA	Abs, arbitrary units	Rel, % TVA	TVA[c] Abs, arbitrary units
5 Ge$_2$H$_6$	130	34	74	19	179	47	*b*	*b*	384
10 Ge$_2$H$_6$	87	21	53	12	284	67	*b*	*b*	424
25 Ge$_2$H$_6$	102	19	57	10	335	61	58	11	552
50 Ge$_2$H$_6$	92	13	98	13	424	60	92	13	705
12.5 GeH$_4$	160	29	322	59	68	13	*b*	*b*	550
25 GeH$_4$	176	28	388	62	56	9	*b*	*b*	622
62.5 GeH$_4$	204	26	470	60	112	14	*b*	*b*	788
75 GeH$_4$	208	26	468	59	118	15	*b*	*b*	792
87.5 GeH$_4$	212	24	520	58	168	19	*b*	*b*	904
100 GeH$_4$	208	22	570	60	168	18	*b*	*b*	946

[a] All GeH$_4$ samples irradiated simultaneously at equal neutron flux. Ge$_2$H$_6$ samples irradiated similarly as a set. Ampoules employed in these experiments were 14-mm i.d. Probable errors are ±20% for all entries in this table. [b] Product not detected even with authentic carrier. [c] Recoil loss >50% in all samples. Absolute yields *ca.* 5 to 15%. TVA = total volatile activity.

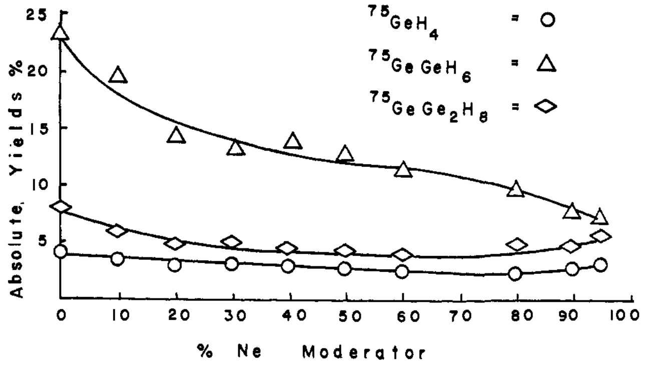

Figure 6. Variation of absolute product yields from germane–neon mixtures at constant total pressure (2000 Torr) as a function of the mole fraction of neon.

Torr (3.5 ± 0.4:1) is similar to the disilane–silane ratio (5.6 ± 0.8:1).[14] The dependence of yields on pressure is more pronounced in germane than in phosphine–silane mixtures, possibly reflecting differences in vibrational energy deposition or in thermal stability of products. Trigermane is a more important product in germane, accounting for 30% of the volatile products and 20% absolute yield at 3000 Torr, compared with 10% relative and 8% absolute yield for trisilane in a 2000 Torr 1:1 phosphine–silane mixture. The sum of the volatile product absolute yields in germane is only 40% at 3000 Torr and 25% at 1000 Torr compared with 80% at 2000 Torr and 66% at 1000 Torr in 1:1 phosphine–silane mixtures.

Product-Forming Reactions in Pure Germane. We propose a mechanistic analogy between the reactions of recoiling germanium and silicon atoms. Just as $^{31}SiH_2$ and $^{31}SiH_3$ were regarded as the intermediates most likely to give rise to the products $^{31}SiH_4$ and $^{31}SiSiH_6$ from phosphine–silane mixtures,[14] so we believe that $^{75}GeH_2$ or $^{75}GeH_3$ are the two intermediates most likely to give rise to $^{75}GeH_4$ and $^{75}GeGeH_6$ in germane.

GeH$_3$ mechanism

$$^{75}GeH_3 + GeH_4 \longrightarrow {}^{75}GeH_4 + GeH_3 \tag{1}$$

$$^{75}GeH_3 + GeH_3 \longrightarrow {}^{75}GeH_3GeH_3 \tag{2}$$

GeH$_2$ mechanism

$$^{75}GeH_2 + GeH_4 \rightleftharpoons [{}^{75}GeH_3GeH_3]^* \tag{3}$$

$$[{}^{75}GeH_3GeH_3]^* \longrightarrow {}^{75}GeH_4 + GeH_2 \tag{4}$$

$$[{}^{75}GeH_3GeH_3]^* + M \longrightarrow {}^{75}GeH_3GeH_3 \tag{5}$$

The scavenger experiments indicate that the GeH$_2$ mechanism is the dominant reaction pathway. Ethylene, known to react very rapidly with *silyl* radicals in the liquid phase,[19] and believed to react efficiently in the gas phase,[20] leads to only a 35 ± 15% decrease in total product yields without changing the digermane–germane product ratio. Nitric oxide, also believed to be an efficient scavenger for silyl radicals,[14,21] gives only

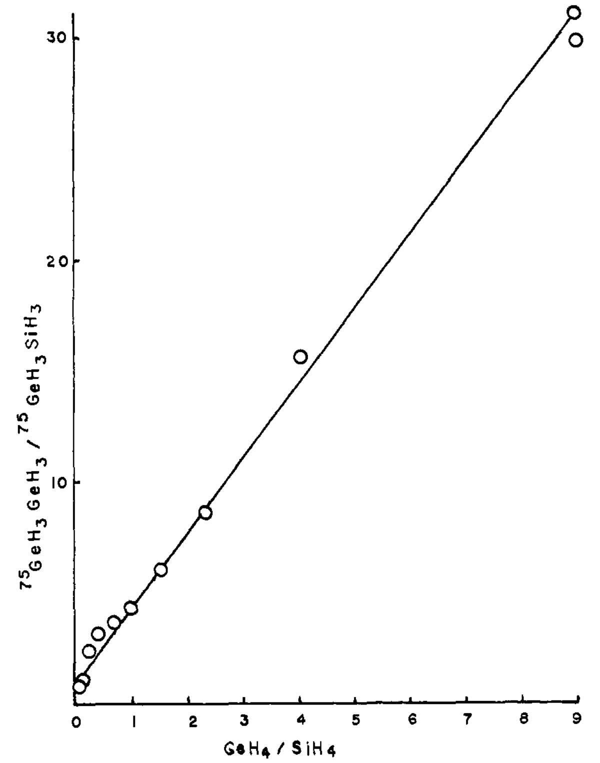

Figure 7. Variation of the digermane to silylgermane product yield ratio from germane–silane mixtures at constant total pressure (2000 Torr) as a function of the substrate ratio.

a 25 ± 5% reduction in total yields. Even oxygen, a classical radical scavenger, leads to only a 50% reduction in product yields.

Let us state clearly that very little is known about the reaction of GeH_3 radicals. Germyl radical reactions are being studied in this laboratory,[22] and we believe that GeH_3 and SiH_3 will be found to react similarly. In systems in which silyl radicals seem to be produced from silane, 5% scavenger is sufficient to entirely suppress reactions attributed to silyl radicals.[21] Therefore, we believe that the moderate scavenger effects observed in germane exclude germyl radicals from a major role in product-forming reactions. However, since the reactivity of neither GeH_3 nor GeH_2 toward these scavengers is known, the moderate decreases in product yields observed may be due to the trapping of GeH_2 or to a contribution from GeH_3.

Since the scavengers did *not* affect the digermane–germane product ratio even while reducing yields up to 50%, it may be inferred that a common precursor is being scavenged, *or* that a single intermediate is responsible for both products. The latter proposition will be argued below. The relative amount of trigermane was reduced *more* than germane and digermane, indicating that a *different* precursor is responsible for the formation of trigermane. This too will be argued below.

The GeH_2 mechanism is also favored by the finding of trigermane as the major volatile radioactive product from germanium atoms recoiling in digermane. The GeH_3 mechanism requires that trigermane be formed by coupling of $^{75}GeH_3$ with nonradioactive $\cdot GeH_2GeH_3$ formed from digermane by radiation damage. This is unlikely at the low doses employed. Radiolysis of digermane would be expected to produce $\cdot GeH_3$ in addition to $\cdot GeH_2GeH_3$, although the relative amounts are not known. Thus the large trigermane : digermane product ratio also speaks against a dominant radical mechanism.

Germane–Silane Mixtures. The six radioactive products observed from the fast neutron irradiation of gaseous germane–silane mixtures may be considered in two groups. The first, consisting of $^{75}GeH_4$, $^{75}GeGeH_6$, and $^{75}GeSiH_6$, are products which we believe arise from the reactions of $^{75}GeH_2$. The scavenger experiments discussed above indicate that in pure germane $^{75}GeH_4$ and $^{75}GeGeH_6$ are derived from a common intermediate, which is unlikely to be $^{75}GeH_3$. The formation of $^{75}GeGeH_6$ and $^{75}GeGeH_8$ as the major products from germane and digermane, respectively, point to $^{75}GeH_2$ as the immediate precursor of both products.

The formation of silylgermane as well as digermane is compatible with a $^{75}GeH_2$ intermediate.

$$^{75}GeH_2 + GeH_4 \longrightarrow {}^{75}GeH_3GeH_3 \qquad (6)$$

$$^{75}GeH_2 + SiH_4 \longrightarrow {}^{75}GeH_3SiH_3 \qquad (7)$$

The variation of product yields with substrate ratio lends support to a mechanism in which digermane and silylgermane are formed in a competition by germane and silane for a single intermediate. Figure 1 shows that the silylgermane yield decreases and the digermane yield increases with increasing germane mole fraction. There is also excellent quantitative agreement with this mechanism. Figure 7 shows the product ratio $^{75}GeH_3GeH_3 : {}^{75}GeH_3SiH_3$ plotted as a function of the $GeH_4 : SiH_4$ ratio. The function is satisfactorily linear, and the slope 3.5 ± 0.3 gives the relative reactivity of GeH_4 and SiH_4 toward the common intermediate, believed to be $^{75}GeH_2$.

The linear dependence of the $^{75}GeH_3GeH_3 : {}^{75}GeH_3SiH_3$ product ratio on the substrate ratio is compatible with *either* a single intermediate giving rise to these products *or* a *set* of intermediates formed in constant ratio. It is unlikely, however, that if several intermediates were involved, they would be formed in constant ratio over the entire range of compositions studied. Another possibility, equally unlikely, is that several intermediates are involved, all reacting to give the *same* product ratio.

We believe that radioactive germane is produced by unimolecule decomposistion of vibrationally excited intermediates and products. A major source of radioactive germane seems to be the decomposition of vibrationally excited digermane and silylgermane.

$$^{75}GeH_2 + GeH_4 \rightleftharpoons [{}^{75}GeH_3GeH_3]^* \qquad (3)$$

$$^{75}GeH_2 + SiH_4 \rightleftharpoons [{}^{75}GeH_3SiH_3]^* \qquad (8)$$

$$[{}^{75}GeH_3GeH_3]^* \longrightarrow {}^{75}GeH_4 + GeH_2 \qquad (4)$$

$$[{}^{75}GeH_3SiH_3]^* \longrightarrow {}^{75}GeH_4 + SiH_2 \qquad (9)$$

This scheme accounts for the very small increase in the yield of germane over the entire range of germane–silane mixtures. That the yield does not remain constant may reflect a dependence of the rates of vibrational deactivation on the identity of M. The energy deposited in the two products may also differ as well as the activation energy for unimolecular decomposition.

---

[22] K. Y. Choo and P. P. Gaspar, unpublished work.

The importance of unimolecular decomposition as a source of $^{75}GeH_4$ is indicated by the increasing relative yield of germane with decreasing total pressure in pure germane shown in Figure 2. The absolute yield increases insignificantly as indicated by Figure 1. Therefore, radioactive germane appears also to be formed by another route, possibly the decomposition of an intermediate formed in such a highly excited state that dissociation is virtually certain at the pressures employed.

The decrease in total yield of volatile products from pure germane with decreasing pressure indicates that products higher in molecular weight than tetragermane are being formed and await detection. Their identity is being investigated in hope that further light will be shed on their mode of formation.

The three higher products from germane–silane mixtures, $^{75}GeGe_2H_8$, $^{75}GeGeSiH_8$, and $^{75}GeSi_2H_8$, form a group which is clearly *not* due to the reactions of $^{75}GeH_2$. Scavenger experiments in germane have indicated that a different intermediate is the precursor of trigermane than that responsible for radioactive germane and digermane.

Qualitatively the yield *vs.* substrate ratio data indicate that the three higher products result from a competition between germane and silane for a common intermediate. The trigermane yield increases and the $^{75}GeSi_2H_8$ yield decreases with increasing germane mole fraction. A mechanism involving successive insertions by germanium atoms accounts for the trends observed.

$$^{75}Ge + GeH_4 \longrightarrow H^{75}GeGeH_3 \tag{10}$$

$$^{75}Ge + SiH_4 \longrightarrow H^{75}GeSiH_3 \tag{11}$$

$$H^{75}GeGeH_3 + GeH_4 \longrightarrow GeH_3{}^{75}GeH_2GeH_3 \tag{12}$$

$$H^{75}GeGeH_3 + SiH_4 \longrightarrow SiH_3{}^{75}GeH_2GeH_3 \tag{13}$$

$$H^{75}GeSiH_3 + GeH_4 \longrightarrow SiH_3{}^{75}GeH_2GeH_3 \tag{14}$$

$$H^{75}GeSiH_3 + SiH_4 \longrightarrow SiH_3{}^{75}GeH_2SiH_3 \tag{15}$$

At both stages of insertion there is competition between silane and germane for the germanium atom and the divalent germanium species, respectively. Therefore, the ratio of $^{75}GeGeH_8$, requiring two molecules of germane, to $^{75}GeSi_2H_8$, requiring two molecules of silane, should vary with the *square* of the germane–silane ratio.[23] Figure 8 indicates, albeit with considerable scatter, such a linear relationship.

According to the mechanistic scheme of eq 10–15, the formation of $^{75}GeGeSiH_8$ requires the reaction of a germanium atom with *both* a silane and germane molecule. Therefore, the yield should pass through a *maximum* since the yield should be proportional to the product of the concentrations of germane and silane.[23] Figure 4 indicates that the yield of $^{75}GeGeSiH_8$ does pass through a maximum.

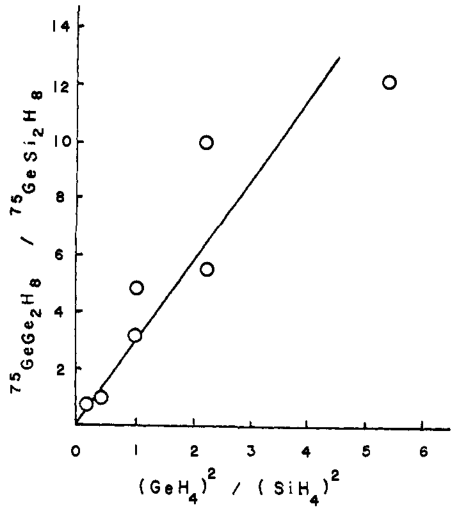

Figure 8. Variation of the $^{75}GeGe_2H_8$ to $^{75}GeSi_2H_8$ product yield ratio from germane–silane mixtures at constant total pressure (2000 Torr) as a function of the substrate ratio.

While the common precursor of the three higher molecular weight products from germane–silane mixtures may indeed be the neutral germanium atom, as suggested above, we do not consider this to be conclusively established. Recent work on ion–molecule reactions in silane indicates that Si^+ ions are capable of initiating a reaction sequence which can give rise to trisilane.[24]

$$Si^+ + SiH_4 \longrightarrow Si_2H_4{}^+ \tag{16}$$

$$Si_2H_4{}^+ + SiH_4 \longrightarrow Si_3H_8{}^+ \tag{17}$$

$$Si_3H_8{}^+ + e^- \longrightarrow Si_3H_8 \tag{18}$$

A similar sequence commencing with $^{75}Ge^+$ could give rise to the higher products in germane and germane–silane mixtures. While the adiabatic principle[25] suggests that the cross section for neutralization of initially formed $^{75}Ge^+$ will occur at high energy (*ca.* 10^4 eV), some ions may escape neutralization, or subsequent collisional reionization at lower energies could occur.[26] Once formed at nearly thermal energies, the low ionization potential of Ge^+ would prevent neutralization (IP(Ge) = 7.89 V, IP(GeH_4) = 10.7 V, IP(SiH_4) = 11.8 V),[27] and would favor ion–molecule reactions. Further work is required to establish the relative importance of ^{75}Ge and $^{75}Ge^+$ as primary reactants in recoil germanium chemistry.

The position of the radioactive germanium atom in the higher molecular weight products has not yet been established by degradation, and indeed the exact sequence of atoms in $^{75}GeGeSiH_8$ and $^{75}GeSi_2H_8$ has *not* been determined. These important data are required for the confirmation of the predictions of the proposed mechanism.

Moderator Experiments. The moderator experiments, despite considerable scatter in the data, show

---

[23] It may readily be deduced from eq 10–15, employing the steady state approximation for the intermediates $H^{75}GeGeH_3$ and $H^{75}GeSiH_3$, that

$$\frac{d[GeH_3{}^{75}GeH_2GeH_3]}{d[SiH_3{}^{75}GeH_2SiH_3]} = \frac{k_{10}k_{12}}{k_{11}k_{15}}\frac{k_{14}[GeH_4] + k_{15}[SiH_4]}{k_{12}[GeH_4] + k_{13}[SiH_4]}\frac{[GeH_4]^2}{[SiH_4]^2} \simeq k'\frac{[GeH_4]^2}{[SiH_4]^2}$$

and

$$\frac{1}{[^{75}Ge]}\frac{d[SiH_3{}^{75}GeH_2GeH_3]}{dt} = \left(\frac{k_{10}k_{13}}{k_{12}[GeH_4] + k_{13}[SiH_4]} + \frac{k_{11}k_{14}}{k_{14}[GeH_4] + k_{15}[SiH_4]}\right)[GeH_4][SiH_4] \simeq k'[GeH_4][SiH_4]$$

[24] J. M. S. Henis, G. W. Stewart, M. K. Tripodi, and P. P. Gaspar, *J. Chem. Phys.*, 57, 389 (1972).

[25] (a) H. S. Massey and E. H. Burhop, "Electronic and Ionic Impact Phenomena," Clarendon Press, Oxford, 1952, p 441; (b) J. B. Hasted, "Physics of Atomic Collisions, "Butterworth and Co., London, 1964, p 420.

[26] R. H. Hammond, J. M. S. Henis, E. F. Greene, and J. Ross, *J. Chem. Phys.*, 55, 3506 (1971), and earlier references cited therein.

[27] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," revised ed, Academic Press, New York, N. Y., 1970.

a decrease in the yield of the major product, digermane, in the variable pressure experiments above 80% moderator. In the constant pressure moderator experiments the digermane yield decreases slightly above 50% moderator but decreases nearly 50% between 0 and 20% moderator. Trigermane behaves similarly to digermane in the constant pressure experiments, up to 80% moderator, and then *increases*. In the variable pressure moderator experiments trigermane yield increases over the entire range. The only conclusion to be drawn at present from the moderator experiments is that there seems to be an effect of high moderator concentration suggestive of a true hot-atom reaction. The effect of *small* amounts of moderator indicates the importance of vibrational excitation in these reactions.

Acknowledgments. Valuable discussions with Dr. Alfred P. Wolf and Professor Michael J. Welch are much appreciated. These experiments were begun by Dr. S. Allan Bock and Dr. Carl A. Levy. Dr. Gerald A. Stewart and Mr. J. Dewey Holton, III, carried out the absolute yield determinations.

An Electron Spin Resonance Study of Some Arsanyl Radicals[1]

E. Furimsky, J. A. Howard,* and J. R. Morton

Contribution from the Division of Chemistry, National Research Council Canada, Ottawa, Ontario, Canada. *Received February 12, 1973*

Abstract: Arsanyl radicals of the structure $Ph_3\dot{A}sOB$ and $Ph_2\dot{A}s(OR)OB$ (where B = *tert*-butyl and R = methyl, ethyl, or *tert*-butyl) have been detected by esr spectroscopy during photolysis of di-*tert*-butyl peroxide in the presence of triphenylarsine or the appropriate alkoxydiphenylarsine (Ph_2AsOR). Replacement of the apical phenyl group in $Ph_3\dot{A}sOB$ by a more electrophilic alkoxy group increases the arsenic hyperfine interaction from 1876 to approximately 2200 MHz. On the other hand, replacing one or both of the *tert*-butoxy groups in $Ph\dot{A}s(OB)_2$ by a more electronegative alkoxy group (OMe or OEt) produces a small decrease in t_{As}. The radicals $Ph_3\dot{A}sOB$ and $Ph_2\dot{A}s(OR)OB$ decompose principally by α scission to give a phenyl radical and a trivalent arsenic compound. At low temperatures (<0°) the rate constants for decomposition of $Ph_3\dot{A}sOB$ (k_3) and $Ph_2\dot{A}s(OB)_2$ (k_5) are given by the Arrhenius equations: $\log (k_3/\text{sec}^{-1}) = (10 \pm 1.0) - (8 \pm 1)/\theta$ and $\log (k_5/\text{sec}^{-1}) = (13 \pm 1.0) - (13 \pm 2)/\theta$, where $\theta = 2.303RT$ kcal mol^{-1}. At these temperatures $Ph_2\dot{A}s(OB)_2$ is therefore considerably more stable than $Ph_3\dot{A}sOB$. The stability of arsanyl radicals of the structure $Ph_2\dot{A}s(OR)OB$ depends on the nature of R, with the stability increasing in the order $Ph_2\dot{A}s(OMe)OB < Ph_2\dot{A}s(OEt)OB < Ph_2\dot{A}s(OB)_2$.

The reaction of organic and organometallic compounds with alkoxy radicals has proved very successful for generating free radicals in the liquid phase for electron spin resonance spectroscopic and kinetic studies.[2] Generally the radicals that have been detected were produced either by hydrogen-atom abstraction or displacement from the substrate. However, in a few cases, *e.g.*, with primary, secondary, and tertiary phosphines,[3] trialkyl phosphites,[2c,4] tertiary arsines,[5] SF_4[6a] OSF_2,[6b] and SO_2,[6b,6c] the intermediate alkoxy-adduct radicals have been detected.

In this paper we report a more complete spectroscopic and kinetic study of the four coordinate arsenic radicals[7] formed by reaction of *tert*-butoxy radicals with triphenylarsine and some alkoxydiphenylarsines.

Results

Triphenylarsine. In a preliminary communication[5b] we reported the detection, by esr spectroscopy, of the arsanyl radical $Ph_3\dot{A}sOB$ produced by photolysis of di-*tert*-butyl peroxide (BOOB) and triphenylarsine (*ca.* 0.02 *M*) in either isopentane or dichlorodifluoromethane.

$$BOOB \xrightarrow{h\nu} 2BO\cdot \tag{1}$$

$$BO\cdot + Ph_3As \longrightarrow Ph_3\dot{A}sOB \tag{2}$$

This radical was found to have an arsenic hyperfine interaction of 1876 ± 5 MHz and a *g* factor of 2.0140 ± 0.0005. A second arsanyl radical, with t_{As} = 2225 MHz and *g* = 2.0060, has since been detected in this system. This radical accumulated more slowly than $Ph_3\dot{A}sOB$ and we believe it to be the secondary radical $Ph_2\dot{A}s(OB)_2$ formed by reaction of *tert*-butoxy radicals

---

[1] Issued as NRCC No. 13453.

[2] (a) J. K. Kochi and P. J. Krusic, *Chem. Soc. Spec. Publ.*, **No. 24**, 147 (1970); (b) J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7040 (1972), and preceding papers; (c) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993 (1972), and earlier papers by these authors; (d) D. Griller, *J. Magn. Resonance*, **6**, 402 (1972).

[3] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6033 (1972).

[4] G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 8784 (1972).

[5] (a) A. G. Davies, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **38**, C8 (1972); (b) E. Furimsky, J. A. Howard, and J. R. Morton, *J. Amer. Chem. Soc.*, **94**, 5932 (1972).

[6] (a) J. R. Morton and K. F. Preston, *Chem. Phys. Lett.*, **18**, 98 (1973); (b) J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 2657 (1973); (c) T. Kawamura, P. J. Krusic, and J. K. Kochi, *Tetrahedron Lett.*, 4075 (1972).

[7] Four coordinate arsenic radicals have previously been called *arsanyls*[5b] and *arsenanyls*.[5a] A more correct terminology would perhaps be *arsoranyls*.[8] However, for the present we prefer to use the shorter *arsanyl*.

[8] J. P. Casey and K. Mislow, *J. Chem. Soc. D*, 1410 (1970).