retarding effect of the double bond in the monotosylates (VIII/VII) is seen to be about 3.5; the retarding effect of the second tosylate group in the saturated systems (VIII/VI) is about 350,000. The unsaturated ditosylate under scrutiny (III) reacts more rapidly than the saturated ditosylate (III/VI = 500) and somewhat more slowly than the unsaturated monotosylate (VII/III = 200), *i.e.*, the double bond in III is rate accelerating and the second tosylate group is much less rate retarding than in VI. The composite rate acceleration for III is thus at least 1700 (500 × 3.5 or 350,000/200). These observations are those expected for nearly concerted loss of both tosylate groups to form a cyclobutenium-stabilized dicarbonium ion. The stepwise mechanism, in which the molecule passes through a monocarbonium ion (V), an acetoxy tosylate, and another monocarbonium ion, can also furnish a rationale of the data.[8]

Table I. Kinetic Parameters for Solvolysis in Buffered Acetic Acid at 75°

Comp	Rate, sec^{-1}	ΔH^{*}, kcal/mol	ΔS^{*}, eu
III	8.6×10^{-6}	27.6	−3
VI[a]	1.7×10^{-8}	31.4	−4
VII	1.7×10^{-3}	21.2	−11
VIII	5.9×10^{-3}	22.2	−5

[a] Because this compound solvolyzes so slowly, the rate at 75° had to be extrapolated from measurements at higher temperatures with the aid of the Arrhenius equation.

If the two tosylate groups ionize almost simultaneously to form a dicarbonium ion, the first-order rate should be constant throughout time. The unsaturated ditosylate III solvolyzes with a constant rate or with a slight upward drift in rate, as has been noted previously.[5] If the reaction were stepwise, the situation would be much more complicated,[9] because the intermediate acetoxy tosylate might be expected to react at a different rate from the ditosylate. The solvolysis rate of the saturated ditosylate VI, and of other similar systems,[5] was observed to decrease significantly. These contrasting observations for III and VI are consistent with (but do not require) a dicarbonium ion mechanism in the first case and a stepwise reaction in the second.

The products of the reaction appear to be two isomeric bicyclo[2.2.1]heptenyl diacetates and two tricyclo[2.2.1.$0^{2,6}$]heptyl diacetates. The product distribution was invariant after one, two, three, four, or five half-lives. Analysis of the reaction mixture after one half-life revealed only product diacetates and starting-material ditosylate, but no acetoxy tosylates.

The kinetic behavior of III and the product studies are consistent either with a dicarbonium ion intermediate (IV) or with an acetoxy tosylate that reacts at least as rapidly as III. The rate of III relative to VI–VIII is most easily explained in terms of the dicarbonium ion pathway, although a rationale can also be constructed from the two-step mechanism.[8] We hope to obtain further evidence concerning the mechanism from deuterium labeling in the products and from secondary deuterium isotope effects. We are also examining other similar systems for this effect.[10]

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(8) Explanation of the rate data in terms of the stepwise mechanism would have to argue that homoallylic participation in III is better able to separate the positive charge from the remaining tosylate group than can σ participation in VI.

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, pp 166–169.

(10) An excited-state effect that we interpret as analogous to the interaction in intermediate IV has been reported by J. J. Bloomfield and R. E. Moser, *J. Am. Chem. Soc.*, **90**, 5625 (1968).

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Germanium Atoms.
Reactions with Germane and Silane[1]

Sir:

Recent interest in the chemistry of silicon atoms[2] prompts us to report observations on the reactions of recoiling germanium atoms. Striking similarity between germanium and silicon atoms has been found in analogous reaction systems.

Germanium atoms were produced from gaseous germane by recoil from the nuclear transformation ^{76}Ge(n,2n)^{75}Ge. Reaction mixtures at 2.2 atm were irradiated with a fast-neutron flux of *ca.* 10^8 neutrons/(cm^2 sec), as described previously for silicon experiments.[3] In addition to ^{75}Ge (half-life, 82 min), very low activities of other radioactive germanium and gallium isotopes were produced, since germane of natural abundance was irradiated. None of the other activities interferes with the analysis of ^{75}Ge. The cross section for formation of ^{75}Ge increases rapidly from the threshold energy of 9.35 MeV to 1.82 barns for 14.5-MeV neutrons.[4] That free, neutral germanium atoms are indeed produced under these conditions is indicated by the calculated recoil energy, 4×10^4 eV, sufficient to rupture all bonds in the precursor molecule, and also by calculations of charge-transfer cross-section maxima according to the resonance rule.[5]

Irradiation of pure germane with fast neutrons produced germane and digermane as the sole volatile radioactive products detected by standard radio-vapor-chromatographic methods.[3] Radioactive products were compared with authentic materials on three different columns and the identity of the radio-nuclide verified by decay analysis and γ-ray spectroscopy on individually trapped, separated products. The product ratio $\mathrm{H_3{}^{75}GeGeH_3} : \mathrm{{}^{75}GeH_4} = 5.0 \pm 0.8$ is identical within experimental error with the product ratio $\mathrm{H_3{}^{31}SiSiH_3} : \mathrm{{}^{31}SiH_4} = 4.8 \pm 0.9$ ob-

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(1) AEC Standard Technical Report No. COO-1713-8.

(2) See P. P. Gaspar, S. A. Bock, and C. A. Levy, *Chem. Commun.*, 1317 (1968), for recent references.

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

(4) E. B. Paul and R. L. Clarke, *Can. J. Phys.*, **31**, 267 (1953).

(5) (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 & Co., Ltd., London, 1964, p 420; (c) but for examples of large charge-transfer cross sections at velocities low compared to maxima predicted by the resonance rule, see G. K. Lavrovskaya, M. I. Markin, and V. L. Tal'roze, *Kinetics Catalysis* (USSR), **2**, 21 (1961).

Table I.[a] Yields of ^{75}Ge-Labeled Products from Reactions of ^{75}Ge Atoms

Expt	Substrate	$^{75}GeH_4$[b]	$H_3{}^{75}GeGeH_3$[b]	$H_3{}^{75}GeSiH_3$[b]	$H_3{}^{75}GeGeH_3$ / $^{75}GeH_4$	$H_3{}^{75}GeGeH_3$ / $H_3{}^{75}GeSiH_3$
A	GeH_4	3900 ± 600	17,300 ± 2,800	. . .	4.5 ± 1.0	. . .
A	1:1 GeH_4–SiH_4	1500 ± 200	7,600 ± 1,200	1900 ± 300	5.2 ± 1.2	4.0 ± 0.9
B	GeH_4	2200 ± 400	8,300 ± 1,300	. . .	3.8 ± 0.9	. . .
B	GeH_4 + 10% NO	3800 ± 600	5,400 ± 900	. . .	1.4 ± 0.3	. . .

[a] All samples at total pressure 2.2 ± 0.1 atm and, within an experiment, irradiated simultaneously at equal neutron flux. [b] Yields given as counts above background extrapolated to a common time for each experiment to correct for decay.

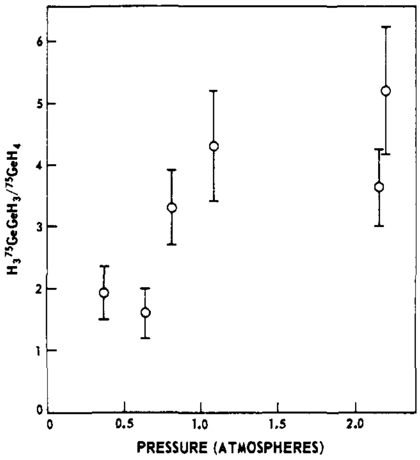

Figure 1. Variation of product ratio from pure germane with total pressure.

tained from the irradiation at equal pressure (2.2 atm) of silane-rich phosphine–silane mixtures with fast neutrons.[3] These product ratios appear to be near to the high-pressure limits for both systems. The absolute yield of volatile products from the germanium system, 20 ± 10%, is lower than that obtainable in the silicon system (> 80%). The product ratio from germane shows a marked pressure dependence (Figure 1) not observed in the silicon experiments.

Fast-neutron irradiation of a 1:1 germane–silane mixture (Table I) produced $H_3{}^{75}GeSiH_3$ as well as $^{75}GeH_4$ and $H_3{}^{75}GeGeH_3$. The presence of silane in the reaction mixture seems not to change (within experimental error, *ca.* 20%) the total yield of volatile radioactive products per unit of precursor, nor the ratio of radioactive digermane to germane. This suggests that a recoiling germanium species (or set of species formed in constant ratio) can react with silane giving silylgermane as well as reacting with germane. The greater affinity for germane over silane is consistent with the relative strengths of Ge–H and Si–H bonds for a variety of possible reaction mechanisms operative in these experiments. The total dose in all experiments was less than 10^{-2} eV per molecule. Radiation damage was very slight, as indicated by the formation of less than 0.1% digermane by radiolysis of germane.[6]

The nature of the active intermediates which intervene in the reaction sequence between free germanium atoms and the stable products observed remains to be determined. In a scavenger experiment (Table I) the yield ratio of $H_3{}^{75}GeGeH_3$ to $^{75}GeH_4$ decreased upon the addition of 10% nitric oxide to germane prior to neutron irradiation. Assignment of structures to the intermediates cannot be made unambiguously at this time because of the paucity of information about the ground-state thermal chemistry of simple germanium radicals. A plausible but not unique set of product-determining steps involves the germylene radical, $:{}^{75}GeH_2$.

$$:{}^{75}GeH_2 + GeH_4 \rightarrow H_3{}^{75}GeGeH_3$$
$$:{}^{75}GeH_2 + GeH_4 \rightarrow {}^{75}GeH_4$$
$$:{}^{75}GeH_2 + SiH_4 \rightarrow H_3{}^{75}GeSiH_3$$

Germylene has been proposed as the species responsible for the formation of mixed silicon–germanium hydrides in the copyrolysis of silane and germane.[7]

Further studies of germanium atom chemistry are underway.

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[6] The exact amount of digermane formed by radiolysis of germane is difficult to determine due to the presence of *ca.* 0.1% digermane as an impurity (useful as an internal carrier) in the germane subjected to neutron irradiation.

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

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Structural Characterization of a New Type of Tetranuclear Metal Cluster System: $Pt_4\{P(C_6H_5)(CH_3)_2\}_4(CO)_5$[1]

Sir:

As part of a systematic study to determine the structures and nature of bonding for the different polymeric platinum phosphine carbonyl complexes recently synthesized by Booth, Chatt, and Chini[2] from the reactions of Na_2PtCl_4 with tertiary phosphines, carbon monoxide, hydrazine,

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[2] G. Booth, J. Chatt, and P. Chini, *Chem. Commun.*, 639 (1965).