fied in terms of the symmetry species of this point group, of their respective π and σ nature as referred to the separated ethylene and SO_2 systems, and of the molecular parts (C═C or SO_2) where they are mostly localized. For the purpose of classification the substituted derivatives of **2**, **14**, and thiirane 1,1-dioxide are also treated to have C_{2v} symmetry.

(15) (a) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); (b) R. Hoffmann, A. Imamura, and T. G. Zeiss, *ibid.*, **89**, 5215 (1967).

(16) (a) U. Weidner and A. Schweig, *Angew. Chem.*, **84**, 551 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 537 (1972); (b) A. Schweig, U. Weidner, J. G. Berger, and W. Grahn, *Tetrahedron Lett.*, 557 (1973); (c) A. Schweig, U. Weidner, D. Hellwinkel, and W. Krapp, *Angew. Chem.*, **85**, 360 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 310 (1973); (d) A. Schweig, U. Weidner, R. K. Hill, and D. A. Cullison, *J. Amer. Chem. Soc.*, **95**, 5426 (1973).

(17) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N.Y., 1969.

(18) The validity of Koopmans' theorem is assumed: T. Koopmans, *Physica*, **1**, 104 (1934). The determination of MO energies throughout this work is based on the validity of this theorem.

(19) M. B. Robin, C. R. Brundle, N. B. Kuebler, G. B. Ellison, and K. B. Wiberg, *J. Chem. Phys.*, **57**, 1758 (1972).

(20) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.

(21) The He–I (584 Å) photoelectron spectra were recorded on a PS-18 spectrometer from Perkin-Elmer, Beaconsfield, England.

(22) C. Müller and A. Schweig, *Tetrahedron*, **29**, 3973 (1973).

(23) A. Schweig, U. Weidner, and G. Manuel, *Angew. Chem.*, **84**, 899 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 837 (1972).

(24) E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung, and A. de Meijere, *Helv. Chim. Acta*, **54**, 783 (1971).

(25) It is interesting to note that the previously calculated MINDO/2 values (cyclopropenone = 0.29 e^3, 2,3-di-*tert*-butylcyclopropenone = 0.24 e^3, tropone = 0.15 e, and cyclopentadienone = 0.00 e) are in full accord with the present CNDO/S results.

Chemical Effects of Fission Recoils. II. Influence of Density and Oxygen Concentration on Product Formation in Ethylene

G. G. Meisels,* J. P. Gregory, A. A. Siddiqi,
J. P. Freeman, and W. C. Richardson

Contribution from the Chemonuclear Group, Department of Chemistry, University of Houston, Houston, Texas 77004. *Received June 27, 1974*

Abstract: The radiolysis of gaseous ethylene induced by recoils from fissioning U^{235} has been investigated in the density range 9×10^{-3} to 1.1×10^{-1} g cm^{-3} in the presence of small amounts of oxygen. The effect of density on acetylene yields was in accord with stabilization of initially formed excited molecules and/or ions, and with a change from differential to total energy loss of the fission recoil. From such studies the fission recoil range in ethylene was estimated to be 0.05 g cm^{-2}. The addition of oxygen was found to suppress the yields of *n*-butane and hexene-1 albeit only partially, but caused an increase in some other product yields. Plausible mechanisms consistent with reaction rate data are suggested and compared with conventional low-pressure ethylene radiolysis results.

One of the primary goals of radiation chemistry is the elucidation of principal processes occurring during the degradation of an energetic particle in a medium. The fission of the uranium atom has been employed only sparingly as a source but is interesting because the kinetic energy release of 170 MeV attendant to the fission process is well above that associated with conventional radiolytic sources, and because much of this energy is deposited in a very small volume.

The nuclear fission process has been studied extensively from a physical and theoretical point of view because of its obvious importance in nuclear power generation.[1] It is well known that the products of U^{235} fission induced by thermal neutron capture are distributed into two groups of light and heavy nuclei and that there is a wide distribution of recoil energies associated with each mass pair. The average energy per recoil is taken to be 85 MeV.[2] A summary of the nuclear properties of U^{235} is given in Table I.

Considerably less effort has been devoted to the study of the chemical changes induced by recoiling fission fragments in well defined chemical systems. Preliminary governmental and industrial studies generally focused on the use of the kinetic energy of recoiling fission products for the production of chemicals. Investigations of this kind were pioneered in the 1950's by Harteck and Dondes.[3] Moseley and Truswell[4] employed uranium-clad foil enriched with ^{235}U as a chemonuclear fuel element in the fission recoil radiolysis of N_2O. These investigations placed primary emphasis on developing a means of measuring energy deposition and the fixation of nitrogen in N_2–O_2 mixtures. At about the same time, a substantial effort along this line was initiated at the Brookhaven National Laboratory by Steinberg, Manowitz, and their coworkers.[5] A third effort in this direction was exerted by an industrial group under Air Force sponsorship, which was directed toward the synthesis of hydrazine by irradiation of ammonia.[6] All three groups employed, at least partially, circulating gas loops wherein the chemonuclear element was placed in the reactor and reactants were passed

Table I. Properties of ^{235}U Fission[a]

Total energy released in fission	190 MeV
Kinetic energy of fission recoils	160 MeV
Light fragment energy	103 MeV
Heavy fragment energy	57 MeV
Neutron energy	5 MeV
Prompt γ energy	5 MeV
Neutron capture γ energy	10 MeV
Decay γ	5 MeV
β radiation	5 MeV
Neutrons per fission	2.47
Light fragment mass	95 amu
Heavy fragment mass	140 amu
Light fragment charge	38 e
Heavy fragment charge	54 e

[a] Compiled from ref 2 and R. D. Evans, "The Atomic Nucleus," McGraw Hill, New York, N. Y., 1955.

---

* Address correspondence to Department of Chemistry, University of Nebraska, Lincoln, Neb. 68508.

over it and if necessary recirculated to obtain sufficient yields for measurements. Irradiations using stationary systems (capsules) were also employed. In the early 1960's the Aerojet group joined forces with Union Carbide's Nuclear Division at Tuxedo, N. Y., but all projects were discontinued in approximately 1966. Since then, very little work along this line has been performed or reported, with the exception of the use of californium-252, a spontaneously fissioning isotope, in gas phase luminescence studies by Calo and Axtmann,[7] and as a reaction initiator in methanol solutions by Raitsimring, Tsvetkov, and Moralev.[8] Liquid phase studies have also been carried out in water[9] and cyclohexane;[10] one vapor phase study of water has been reported.[11]

These earlier studies showed clearly that fission recoils could be employed to bring about chemical change, and that product yields obtained were similar but not identical with those observed with conventional forms of high-energy radiation such as electrons or γ rays. They also demonstrated considerable difficulties in obtaining reproducible results, and showed that the use of uranium glass fiber wool as a fuel was unsatisfactory because of sintering, local intensive heating, and other structural problems. This difficulty was essentially overcome in the development by Steinberg and Tucker[12] of a platinum-clad uranium-paladium alloy, 93% enriched in ^{235}U. This fuel, which consists of a sandwich very thinly clad with an outer layer of platinum, is stable, and if necessary can be processed into self supporting and structurally rigid honeycomb devices. The fuel has been tested to 25% uranium-235 burn-up and was found to maintain structural rigidity even at burn-ups equivalent to those employed in nuclear reactors used for power generation.[13] However, the development of this fuel came at the end of the period of initial activity in this field. While the early work demonstrated experimental feasibility of such studies, little information was gained on peculiarities or characteristics for fission recoils which would explain the difference in observations between this source of radiation and conventional forms, or which would permit an assessment of the conditions within the fission recoil track and their effect on the chemistry.

Some insight can be gained by summarizing the characteristics of the fission recoil track based on gross considerations and comparison with conditions found when conventional radiation is employed. This information is summarized in Table II. It must be recognized, however, that the radical densities calculated are based on a maximum track size, defined by the ranges of the recoil and of the most energetic δ ray, so that one would really expect greater initial radical concentrations than those indicated here. As a consequence, all lifetimes of reactant species are in fact smaller than and their mean concentrations essentially larger than those given in Table II. It is apparent that the initial radical concentrations in the fission recoil track are on the order of magnitude of those employed in the high-energy intense-pulse radiolysis using Febetron accelerators with nanosecond pulsing.[14] LET in fission recoil systems is the highest of any form of radiation employed so far and is expected to favor pair-wise reactions second order in intermediates. These superficial calculations cannot address themselves to temperature in the track and other important kinetic parameters. The thermal spike model,[15] on which recoil temperature calculations are based, is not applicable when the majority of the initial interactions do not involve adiabatic heating. However, within a very short period after formation of the track, temperatures may be well above ambient, although a recent study of N_2O has not found evidence for a major temperature increase.[16]

If further insight is to be obtained into the chemical effects of fission recoils, and if any existent information available from other sources is to be applied to fission radiolysis conditions, it is apparent that detailed information on mean radical densities, mean ion concentrations, track lifetime, and effective track temperature are required. The approach we have chosen to obtain such information is the radiolysis by fission recoils of a system whose conventional radiation chemistry is relatively well understood, and where the yields and identities of major intermediates have been measured at low pressures.[17-19] Ethylene is particularly suitable for such studies, not only because it has been investigated extensively in several laboratories, but also because it provides a wide range of free radical and ion-molecule reactions whose rates and temperature dependency are well established.[20]

Experimental Section

A. Introduction. The primary irradiation capsules used in fission recoil radiolyses, experimental arrangements, and sample preparation have been described previously.[16] Briefly, samples were irradiated in the 1 MW Triga reactor (Nuclear Science Center, Texas A&M University) operated at reduced power under conditions to obtain a neutron flux of about 10^{15} neutron V/hr. Capsules (37 cm^3 volume) remained in the neutron field for 33-47 min depending on the configuration of the reactor core. The mean bulk temperature of all irradiations was 25 ± $-5°$. This does not mean that the track temperatures were ambient as discussed further below. The total absorbed dose was 3.0×10^{20} eV based on nitrous oxide dosimetry using $G(N_2) = 9.7$ molecules/100 eV.[16]

B. Sample Analysis. Chemical analysis was performed by gas chromatography on aliquots of the original and irradiated samples. The sampling loop was similar to one described previously.[21] A Perkin-Elmer Model 810 gas chromatograph was used in the analysis of C_1–C_6 hydrocarbons. The chromatograph was equipped with a flame ionization detector, and nitrogen (dry) was used as the carrier gas. Carrier and flame gases were pretreated by passing through conventional purification trains consisting of molecular sieve (Linde 5A) scrubbers for removal of water vapor and other contaminants.

For analysis of the lightest components two columns were used. A 10 ft × 0.25 in. Copper Poropak N (60-80) column was used for the analysis of methane at ambient temperature; it could be pro-

Table II. Reaction Probabilities in the Fission Recoil Track[a,b]

Gas pressure	880	590	psia
Gas density	0.128	0.0621	g/cm^3
Concentrations			
Gas	4.6×10^{-3}	2.3×10^{-3}	mol/cm^3
"Initial ions" ($W = 26.1$)	2.0×10^{-6}	2.3×10^{-7}	mol/cm^3
"Initial radicals" ($G = 8.0$)	4.0×10^{-6}	4.5×10^{-7}	mol/cm^3
Initial reaction rates			
Ion-electron ($k = 5 \times 10^{16}$)	2.0×10^{5}	2.6×10^{3}	mol/cm^3/sec
Ion-molecule ($k = 10^{15}$)	9.2×10^{6}	5.3×10^{5}	mol/cm^3/sec
Radical-radical ($k = 10^{14}$)	1.6×10^{3}	2.4×10^{1}	mol/cm^3/sec
H + ethylene ($k = 10^{13}$)	1.8×10^{5}	1.0×10^{4}	mol/cm^3/sec
Radical + ethylene ($k = 10^{7}$)	1.8×10^{-1}	1.0×10^{-2}	mol/cm^3/sec

[a] Example, ethylene. [b] Based on known range and track diameter and assuming both are inversely proportional to density.

grammed to 100° for analysis of products containing up to four carbons at decreased resolution. An activated alumina, 20% EDO-1 on Chromosorb A (60-80) column gave 100% separation of ethane. C_2-C_4 hydrocarbons were separated on a tandem dimethylsulfolane-squalane column operated at ambient temperatures. This column was constructed in two parts. The first part was a 20 ft × 0.25 in. (Copper) dimethylsulfolane (20%) on Chromosorb P column; the second part was a 10 ft × 0.25 in. (Copper) squalane (10)) on firebrick column. A 35 cm^3 min^{-1} carrier gas flow rate gave suitable separation of C_2-C_4 products. C_4-C_6 hydrocarbon analysis was carried out using an 18.5 ft × 0.25 in. (Copper) 20% UCON LB55OX on 60-80 mesh Chromosorb P column[22] operated at 60° with a flow rate of 40 cm^3 min^{-1}. Oxygenated products were measured using a Triton X on Chromosorb W column operated at 100°.

Products were identified by comparison with known retention times and/or by trapping with subsequent mass spectrometric identification. Chromatographic response was checked using calibrated C_2-C_6 mixtures with each set of analyses.

C. Materials. Ethylene gas was used directly from a Phillips 99.8 mol % minimum purity cylinder. Chromatographic analysis showed no impurities above 0.2% and ethane as the major contaminant (~0.15%). Scavenger gases used were Matheson Gas Products ultra high purity oxygen. Calibration gas mixtures were made up from Phillips research grade hydrocarbons as received. Acetylene was purified before using as a calibrant. The gases and their stated purities used in the flame ionization chromatograph were Linde cylinder compressed air (oxygen 17-22%, nitrogen 78-84%), nitrogen (dry, 99.99%), and hydrogen (99.5%).

D. Data Analysis. The product yields of interest here are only those brought about by fission recoils. However, fast neutrons and background γ rays from the reactor also cause chemical change. The extent of n,γ damage was assessed by simultaneous irradiation of cells containing no fuel, but a section of platinum foil equal in weight to the fuel foil in the other cells. The n,γ yields from these cells were subtracted from yields obtained in fueled cells assuming that the contributions to product formation from this source were equal in the presence and absence of fuel. All yields were further normalized to a uniform total dose. Slight fission recoil dose variations were caused by unequal fuel masses among the cells.[16] Thus the yield (N, molecules) of a particular product (P) was calculated from the following equation

$$N_{FR}^{\;P} = (N_{cell}^{\;P} - N_{n,\gamma}^{\;P})c \qquad (I)$$

where N_{FR} is the fission recoil yield of product P, N_{cell} is the total yield in a fueled cell, $N_{n,\gamma}$ is the yield of products resulting from the pile n,γ radiation, and c is a dose normalization factor resulting from fuel uneveness. In the present work c varied between 1.0 and 1.2. The extent of the n,γ correction may be expressed in terms of the ratio $N_{n,\gamma}^{P}/N_{FR}^{P}$, and depends on the particular product, pressure, foil mass, and foil condition; it never exceeded unity.

About 15% of the total fission energy appears in forms other than the kinetic energy of the fragment atoms (prompt γ, β decay, see Table I). No corrections were applied for these minor contributions.

Results

The results are presented in separate sections summarizing effects of pressure and of oxygen. Where possible yields from fission recoil radiolyses are expressed as G, molecules/100 eV, based on nitrous oxide dosimetry ($G(N_2)$ = 9.7 molecules/100 eV) which had yielded[16] a factor 3.0×10^{20} eV per 10^{15} neutron for a fuel mass of 0.0640 g.[23] Oxygen was an essential additive in all ethylene irradiations to reduce polymerization; polymer formation occurred and was visible during periodic inspections of the cells and fuel foils.

A. Pressure. Initial runs were made to identify products in the fission recoil radiolysis of C_2H_4-O_2 (0.5%) mixtures and ascertain the effect of density on product yields over a wide pressure regime (2-60 atm). Products identified were acetylene, methane, ethane, cyclopropane, propane, propylene, *n*-butane, isobutane, isobutene, 1-butene, *cis*- and *trans*-butene-2, allene, methylacetylene, cyclobutane, 1,3-butadiene, isopentane, pentene-1 and -2, vinylacetylene, 3-methylpentane, *n*-hexane, and hexene-1 and -2. Analyses were not carried out for hydrocarbon products above C_6 and for hydrogen, a product whose detection required modification of the experimental arrangement described above. Preliminary results[23b] from C_2H_4-NO irradiations where G_{H_2} was specifically sought indicated an increase of G_{H_2} with pressure. The variations of selected representative product yields in moles are shown in Figures 1-3. Dramatic changes may be noted in the acetylene and methane yields at lower densities. Reliable dosimetry was not then available, but the conversion factor given above may be employed as a guide to G values.

B. Oxygen. The complete product analysis for fission recoil radiolysis of C_2H_4-O_2 mixtures is given in Table III for irradiations at 300, 370, 450, 590, and 700 psia total pressure and various concentrations of oxygen. The maximum O_2 content was dictated by the upper limits for nonexplosive C_2H_4-O_2 mixtures.[24a] There are minor discrepancies between the sets of data, but they do show a pronounced effect of oxygen. The yields of hexene-1 and *n*-butane decrease with increasing O_2 concentration (Figures 4 and 5), while those of vinylacetylene and hexene-2 are enhanced. G(*n*-butane) decreases by a factor of 2 for a threefold in-

Table III. Product Yields in the ^{235}U Fission Recoil Radiolysis of Ethylene-Oxygen Mixtures

		G, molecule/100[c]											
Pressure[a]	% O_2[b]	C_2H_2	C_3H_4	C_4H_{10}	*i*-C_4H_8 and C_4H_8-1	*cis*- and *trans*- C_4H_8	C_4H_4	c-C_4H_8	*i*-C_4H_8 and C_4H_8-1	C_5H_{10}-1	3-Methylpentane	C_6H_{12}-1	C_6H_{12}-2
300	0.47	2.3	0.11	0.13	0.10	0.036	0.054	0.037	Nd	0.0023	Nd	0.0073	0.53
300	0.75	2.2	0.18	0.14	0.16	0.064	0.052	0.041	Nd	—	Nd	0.0055	0.63
300	1.0	2.8	0.16	0.12	0.13	0.059	0.055	0.040	Nd	—	—	—	0.67
370	0.2	2.5	0.13	0.54	0.23	0.094	0.094	Nd	—	0.033	0.055	0.039	0.097
370	0.4	2.1	0.12	0.28	0.12	0.064	0.15	Nd	0.0057	0.016	0.030	0.0065	0.24
370	0.6	3.0	0.15	0.19	0.19	0.105	0.19	Nd	0.013	0.034	0.037	0.0088	0.39
450	0.2	3.6	Nd	0.80	Nd	Nd	0.050	0.031	0.0044	0.027	0.035	0.023	0.19
450	0.4	4.1	Nd	0.34	Nd	Nd	0.065	0.027	0.0050	0.015	0.025	0.0071	0.36
450	0.6	3.4	Nd	0.31	Nd	Nd	0.070	0.030	0.0044	0.015	0.028	0.0096	0.42
590	0.2	2.2	Nd	0.74	Nd	Nd	0.033	0.031	0.0039	0.031	0.028	0.035	0.042
590	0.4	2.7	Nd	0.89	Nd	Nd	0.072	0.045	0.0057	0.040	0.049	0.022	0.21
590	0.6	2.5	Nd	0.74	Nd	Nd	0.074	0.049	0.0059	0.028	0.041	0.014	0.46
700	0.1	3.2	0.18	1.1	0.45	0.055	0.042	0.044	0.0061	0.063	0.11	0.060	0.063
700	0.3	4.1	0.26	0.78	0.40	0.070	0.077	0.031	0.0031	0.049	0.11	—	0.63
700	0.47	2.1	0.18	0.49	0.24	0.055	0.053	0.037	0.0061	0.032	0.069	0.018	0.59

[a] Corresponding densities are 9.24×10^{-4}, 1.24×10^{-3}, 1.57×10^{-3}, 2.28×10^{-3}, 2.84×10^{-3} mol cm^{-3}, respectively. [b] Mole per cent. [c] Special designations are Nd for products not determined and — for 0.0 yields.

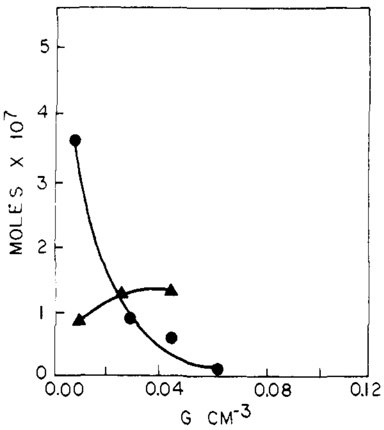

Figure 1. Product yields *vs.* ethylene density in the C_2H_4-O_2 (0.5 mol %) ^{235}U fission recoil system for ethane (●) and methane (▲) at a total absorbed dose of 3.0×10^{20} eV.

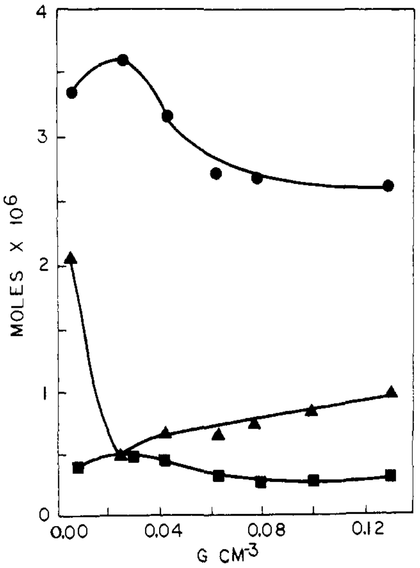

Figure 2. Product yields *vs.* density in the C_2H_4-O_2 (0.5 mol %) ^{235}U fission recoil system for acetylene (●), the 2-butenes (■), and isobutene, butene-1, and *n*-butane taken together (▲) at a total absorbed dose of 3.0×10^{20} eV. The latter curve predominantly reflects the variation of the *n*-butane yield.

crease in O_2. In contrast, G(*n*-butane) = 2.1 in the conventional radiolysis of 100 Torr C_2H_4;[18a] *n*-butane is not formed in detectable quantities in the conventional scavenged radiolysis or in the pile n,γ irradiations of C_2H_4-O_2 mixtures. The yields of *n*-hexane are not reported in Table III because most were too small to measure accurately. They are 0.06 at 0.2% O_2 at 370 psia, 0.03 at 0.2% O_2 at 450 psia, and 0.05 and 0.01_2 at 0.2 and 0.4% O_2 at 590 psia.

Oxygen has little or no effect on the yields of other products. In a few cases analyses were performed for oxygen-containing species. The major identified products were acetaldehyde, acetone, formaldehyde, and ethanol (Table IV).

Table IV. Yield of Oxidation Products in Fission Radiolysis of Ethylene in the Presence of Oxygen at Total Pressures of 450 and 590 psia

Density, g/cm^3	0.044	0.044	0.044	0.064	0.064
Per cent oxygen	0.2	0.4	0.6	0.2	0.3
Product	Yield, molecules/100 eV				
Acetaldehyde	0.30	0.29	0.47	0.60	0.58
Acetone	0.85	1.5	2.1	0.49	1.6
Formaldehyde	0.14	0.20	0.10		0.18
Ethanol	0.051	0.001	0.019	0.023	0.013

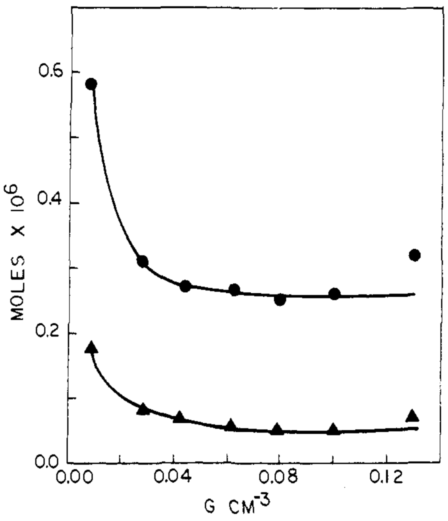

Figure 3. Product yields *vs.* density in the C_2H_4-O_2 (0.5 mol %) ^{235}U fission recoil system for propane and propene (●) and cyclopropane (▲), at a total absorbed dose of 3×10^{20} eV.

Discussion

Free radical and excited state reactions are examined in this paper. The importance of various processes can be estimated by examining results from conventional radiolytic systems and extrapolating to the high pressure high LET conditions of the present system. Information gained from conventional radiolytic systems has shown the importance of excited ethylene molecules in the primary decomposition and significant yields of products resulting from intermediates that were scavenged by oxygen.

Elucidation of ^{235}U fission recoil radiolysis of pure ethylene is difficult as a result of the requirement that oxygen be present to inhibit polymerization during the cooling off period. Certain product variations with experimental conditions may be the result of the simultaneous actions of collisional stabilization and free radical scavenging.

Only very fast unimolecular dissociations should be possible at the increased densities employed here. The bimolecular collision frequency can be used to set lower limits in the unit efficiency assumption. The collision frequency in ethylene at ambient temperature (σ = 4.066 Å)[24b] is 2.6×10^{11} sec^{-1} at 370 psia and increases to 8.8×10^{11} sec^{-1} at 800 psia, limiting molecular fragmentation to processes with lifetimes $<10^{-12}$ sec, *i.e.*, processes involving species with high internal energies.

Hydrogen atoms produced in primary processes generally disappear by addition to ethylene (reaction 1) since the addition to ethylene is fast ($k_1 = 1.61 \times 10^{12}$ cm^3 molecule^{-1} sec^{-1}).[25] At the densities in the present work the H-atom lifetime with respect to reaction 1 is 1-8 $\times 10^{-10}$ sec. The resulting ethyl radicals disappear by combination and/or scavenging. Radical combination is not normally competitive with scavenging under the usual steady state conditions. Reaction 2 occurs nearly with unit collision efficiency

$$H + C_2H_4 \longrightarrow C_2H_5 \qquad (1)$$

$$C_2H_5 + O_2 \longrightarrow C_2H_5O_2 \longrightarrow \text{products} \qquad (2)$$

($k_2 = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}),[26] and at the oxygen concentrations in the present study the lifetime of ethyl radical with respect to scavenging is about $\sim 10^{-9}$ sec. This establishes an internal standard for estimating radical concentrations based on radical-radical reactions with known rate constants which are expected to compete in the high

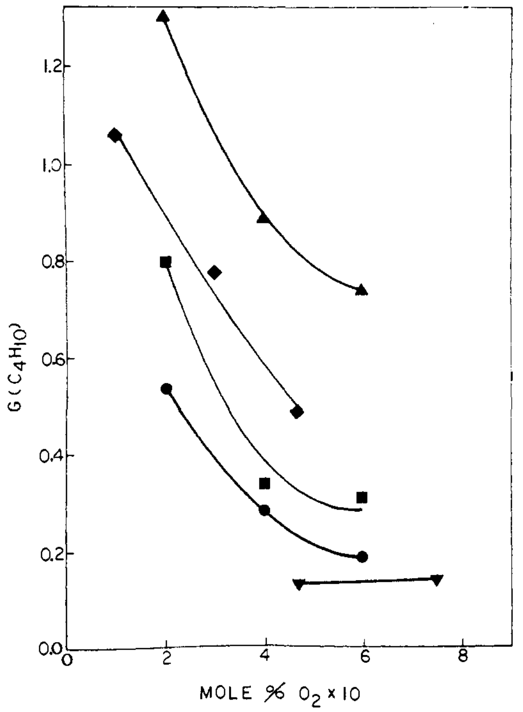

Figure 4. Variation of the radiation chemical yield of *n*-butane with mol % O_2 additive in the ^{235}U-C_2H_4-O_2 system. Data are plotted for the following pressures (densities): 590 psia (2.28 mol cm^{-3}) (▲); 700 psia (2.84×10^{-3} mol cm^{-3}) (◆); 450 psia (1.57×10^{-3} mol cm^{-3}) (■); 370 psia (1.24×10^{-3} mol cm^{-3}) (●); 300 psia (9.24×10^{-4} mol cm^{-3}) (▼).

dose rate and/or high LET conditions typical of fission recoil radiolysis.

A. Effect of Pressure on Product Yields. Four factors may be responsible for the variation of product yields with pressure: the variation of the fission fragment range with density, collisional deactivation of excited neutral and ionic intermediates, the variation of relative conversion with density at a constant integrated neutron flux, and the competition between radical combination and radical reaction with oxygen. The importance of collisional suppression of molecular fragmentation has already been well documented in the ethane radiolysis system.[27]

The variation in the yield of acetylene with density most clearly demonstrates the effect of pressure. This product arises largely from neutral dissociation processes, and its yield should reflect mainly changes in fission recoil energy deposition and the quenching of first-order fragmentation steps. Excited ethylene dissociates as follows:

$$C_2H_4^* \longrightarrow C_2H_2 + H_2 \tag{3}$$

$$C_2H_4^* \longrightarrow (C_2H_3 \text{ or } C_2H_3^*) + H \tag{4}$$

$$C_2H_3^* \longrightarrow C_2H_2 + H \tag{5}$$

A reduction in the yield of acetylene may be the result of a competitive deactivation step involving any of the intermediates asterisked in eq 3, 4, and 5. Competition with step 5 should lead to an increase in vinyl radicals and the resultant products 1-butene and 1-hexene. Such an increase was indeed observed qualitatively.

At low densities, below ~0.027 g cm^{-3}, the yield of acetylene drops off rapidly. This may be ascribed to the onset of fission recoil energy loss to the walls. As the density decreases, the range of the recoil begins to exceed the mean distance between the fuel foil and the cell walls. While there exists a distribution of distances because of the geometry of the cells, our data suggest that the emergent fission recoil loses all its energy in the gas phase and none into the cell wall above approximately 0.03 g cm^{-3}. We conclude that the upper limit of the range of the fission fragment in ethylene is about 0.05 g cm^{-2} since the minimum distance of travel for a fission fragment in this cell is about 1.5 cm. This is reasonable in comparison with the range of 0.023 g cm^{-2} of 100 MeV^{89} Sr ions in water.[28]

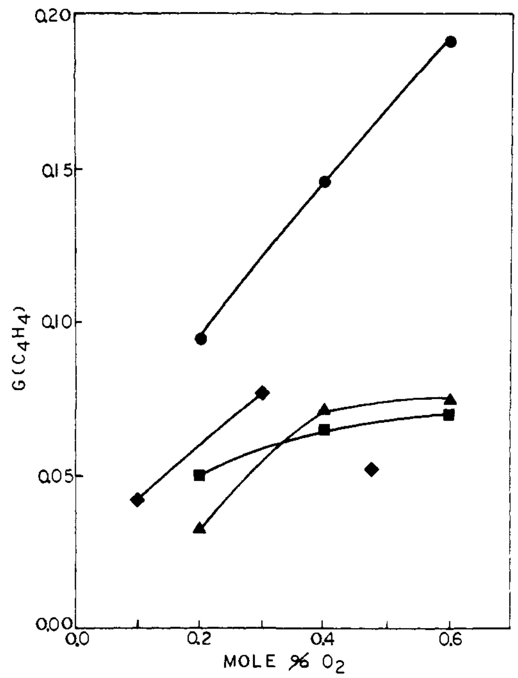

Figure 5. Variation of the radiation chemical yield of vinylacetylene with mol % O_2 additive in the ^{235}U-C_2H_4-O_2 system at a total absorbed dose of 3.0×10^{20} eV. Curves are plotted for data at 370 psia (1.24×10^{-3} mol cm^{-3}) (●), 590 psia (2.28 mol cm^{-3}) (▲), 450 psia (1.57×10^{-3} mol cm^{-3}) (■), and 700 psia (2.84×10^{-3} mol cm^{-3}) (◆).

The acetylene yield reported here may be compared with yields observed in the low density conventional radiolysis of ethylene, where it is formed at 100 Torr with a yield of 3.1 molecules/100 eV.[18a] Experimental measurements in the gas phase are not available at high density so far, and comparison is possible only with studies performed in the liquid phase[29] at reduced temperatures where a yield of 1.8 molecules/100 eV was reported. The liquid density is 0.8 g cm^{-3} and the current data can be extrapolated smoothly to that density. It is of interest to note that a Stern-Volmer plot of the acetylene yield in the conventional manner does not yield a straight line. Such behavior is expected in radiolytic systems where the decomposing species have a wide range of internal energies. In addition, several dissociation processes each with a different pressure dependency may take place concurrently. It should also be noted that it is conceivable that ionic processes may contribute to some extent to the formation of acetylene. This step has never been established clearly, and should not make a major contribution at pressures much in excess of 1 atm.

The yield of *n*-butane appears to decrease sharply as the pressure increases, to rise again slowly after ~0.02 g cm^{-3}. This observation is in part an artifact because it results from the increasing relative conversion with decreasing pressure. For a constant integrated neutron flux, fractional conversion increases as the density is decreased. At the lowest pressures employed, the total number of radicals produced, based on $G(R) = 6$ radicals/100 eV, is approximately twice the initial concentration of oxygen. In subsequent runs, where kinetic information was derived, the conversion was, therefore, reduced and a slightly higher oxygen concentration was employed to reduce the change in oxygen concentration during radiolysis.

The yields of ethane showed similar behavior for the same reason. Moreover, as the density increases the small correction for the original ethane impurity in ethylene becomes so large that radiolytic ethane formation becomes small in comparison to the amount initially present, making it difficult to obtain meaningful data.

Methane, a product thought to be the result of ionic processes,[18f,30] was produced in small yields only (Figure 1), and increased slightly with pressure; this may be a result of increased experimental uncertainty because of the original impurities as discussed above. Methane formation in Febetron irradiation of ethylene has been reported[31] to be high, $G = 0.5$ molecules/100 eV at 1 atm, and decreases to 0.25 at 10 atm. The fission recoil results are consistent with a further reduction in the methane yield ($G < 0.1$) at pressures above 20 atm.

B. Effect of Oxygen on Product Yields. The radiolysis of ethylene with electrons[18a] and γ-rays[19c] at subatmospheric pressures leads to molecular products such as acetylene, and to products whose production can be totally inhibited by small amounts of oxygen. The sequence begins with the generation of hydrogen atoms in the primary process, followed by addition to ethylene with stabilization of the ethyl radical. Radical combination (6) and disproportionation (7)

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \tag{6}$$

$$C_2H_5 + C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \tag{7}$$

account for ethane and *n*-butane. From the present data (Figures 1 and 2) the disproportionation-combination rate constant ratio is 0.12 at 0.03 g cm^{-3} in agreement with the literature value[26] of 0.14. This ratio decreases toward higher pressures but there is increasing uncertainty in the ethane yield.

While the rate constants for reactions 7 and 8 are large, $k_7 = 3.57 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1},[26] these are not normally competitive with oxygen scavenging in reaction 2. Since the range of all particles should vary as the cube of reciprocal density, radical-radical and radical-scavenger reactions are competitive at higher densities. In addition the high dose rate and/or high LET of fission recoils favors radical-radical reactions. Indeed it is observed that *n*-butane is not scavenged at the lowest densities and the yield increases with density at the same oxygen concentration. In order to be competitive with (2) the ethyl radical lifetime with respect to (6) and (7) must be within an order of magnitude as that with respect to (2). Assuming a quasi steady state requires that the initial ethyl radical concentration be 10^{18}–10^{19} molecules cm^{-3} at the highest density. Quantitative evaluation of the dependence of G(*n*-butane) on oxygen concentration and density provides information on the fission recoil track size and radical concentrations and will be presented elsewhere.

Further radical addition and recombination yield higher alkanes

$$C_2H_5 + C_2H_4 \longrightarrow C_4H_9 \tag{8}$$

$$C_4H_9 + C_2H_5 \longrightarrow C_6H_{14} \tag{9}$$

particularly *n*-hexane. Disproportionation products from this series give ethane, *n*-butane, ethylene, and butene-1. *n*-Hexane was observed only at the lower oxygen concentrations (~0.2–0.4 mol %) and is totally suppressed at higher concentrations. The analysis for butene-1 was complicated by the presence of isobutene, but no major trend was noted. The important step in the formation of *n*-hexane is ethyl radical addition to ethylene, a process with an appreciable activation energy, $E_a = 6.9$ kcal mol^{-1}, and a small preexponential factor, $\log A = 7.7$ (l. mol^{-1} sec^{-1}).[26] At 300°K this process is very slow, $k = 4.8 \times 10^{-19}$ cm^3 molecule^{-1} sec^{-1}. The fact that *n*-hexane is observed at all in the presence of oxygen may indicate that the track temperature is substantially above ambient.

The participation of the vinyl radical in the mechanism for ethylene decomposition is indicated by the formation of 1-hexane and substantiated by the variation of the 1-hexene product yield with added oxygen. A plausible sequence for 1-hexene formation is generation of C_2H_3 by (5) followed by

$$C_2H_3 + C_2H_4 \longrightarrow C_4H_7 \tag{10}$$

$$C_4H_7 + C_2H_5 \longrightarrow C_6H_{12} \tag{11}$$

where C_4H_7 is the 1-butenyl radical. The rate constant for vinyl radical addition to ethylene (reaction 10) has not been reported but it is expected to be large.

The presence of vinylacetylene and hexene-2 whose yields are enhanced with added oxygen is not unexpected. The formation of vinylacetylene is not affected by the scavenging of free radicals by oxygen and has been postulated to be formed by ion-molecule reactions. Mass spectrometric studies support that the $C_4H_5^+$ (butynyl ion),[20a] the probable precursor of vinylacetylene, is formed by ion-molecule reactions of acetylene ion

$$C_2H_2^+ + C_2H_4 \longrightarrow (C_4H_6^+)^* \tag{12}$$

$$(C_4H_6^+)^* \longrightarrow C_4H_5^+ + H \tag{13}$$

Reaction 13 is not expected to compete with stabilization at high pressures, but even if it were present through another mechanism, it must undergo proton transfer to form vinylacetylene.

$$A + C_4H_5^+ \longrightarrow C_4H_4 + AH^+ \tag{14}$$

Oxygen does not have a proton affinity suitable for such a mechanism. However, the oxygenated products observed in the present study have high proton affinities [C_2H_5OH, 193 kcal mol^{-1}][32] and may be produced in sufficient amounts ($\Sigma G \approx 2.0$) to be effective. Recent evidence from γ-radiolysis studies[19e,33] has clearly shown that oxygenated hydrocarbons with large proton affinities such as ethanol, diethyl ether, and dimethyl ether are very efficient proton acceptors. This may be particularly important in the fission recoil track where accumulation of oxygenated products occurs and where local concentrations are much higher than expected from considerations based on bulk composition. Such an effect has also been observed in ethylene-trace O_2 γ-radiolysis at lower pressures.[19d]

The variation in the 2-hexene yield with oxygen is profound. A series of ion-molecule reactions suggested by mass spectrometric studies beginning with the vinyl ion gives the hexyl ion

$$C_2H_3^+ + C_2H_4 \longrightarrow (C_4H_7^+)^* \tag{15}$$

$$(C_4H_7^+)^* \longrightarrow C_2H_5^+ + C_2H_2 \tag{16}$$

$$C_2H_5^+ + C_2H_4 \longrightarrow C_4H_9^+ \tag{17}$$

$$C_4H_9^+ + C_2H_4 \longrightarrow C_6H_{13}^+ \tag{18}$$

followed by proton transfer

$$C_{16}H_{13}^+ + C_2H_4 \longrightarrow C_6H_{12} + AH^+ \tag{19}$$

is a possible mechanism for enhancement of the 2-hexene product yield in the presence of accumulating oxygenated products. However, step 16 should not be important at high pressure.

Conclusion

The mechanism of ethylene radiolysis by fission recoils has been found to be in general consistent with that elucidated at lower pressures in conventional radiolysis when allowance is made for the increased density and the inhomogeneous energy deposition. The former results primarily in the suppression of the fragmentation of activated intermediates. The latter leads to localized free radical concentrations along the entire track too high to be scavenged by up to 0.75 mol % oxygen.

Acknowledgment. This investigation was supported in part by the U. S. Atomic Energy Commission under Contract AT-(40-1)-3606. This assistance and the cooperation and help by the staff of the Nuclear Science Center at Texas A & M University are gratefully appreciated.

References and Notes

(1) B. G. Harvery, *Annu. Rev. Nucl. Sci.*, **10**, 235 (1960).
(2) A. Mozumder, *Advan. Radiat. Chem.*, **1**, 1 (1969).
(3) (a) F. Morse, P. Harteck, and S. Dondes, *Radiat. Res.*, **29**, 317 (1966); (b) P. Harteck and S. Dondes, *Saf. Ser., Int. At. Energy Ag.*, **9** (1960); (c) *Z. Elektrochem.*, **64**, 983 (1960); (d) *J. Chem. Phys.*, **27**, 546 (1957); (e) *Nucleonics*, **15**, 94 (1957).
(4) F. Moseley and A. E. Truswell, AERE-R-3078, 1960.
(5) B. Manowitz and M. Steinberg, BNL 804, 1963.
(6) (a) E. R. White, *Int. J. Appl. Radiat. Isotop.*, **16**, 419 (1965); (b) D. A. Landsman and C. M. Noble, AERE-M-921, 1961.
(7) (a) J. M. Calo, R. C. Axtmann, and R. G. Persing, *Rev. Sci. Instrum.*, **41**, 1639 (1970); (b) J. M. Calo, *Nucl. Sci. Eng.* **42**, 424 (1970); R. Axtmann and J. Sears, *J. Chem. Phys.*, **44**, 3279 (1966).
(8) (a) A. M. Raitsimring, Yu. D. Tsvetkov, and V. M. Moralev, *Int. J. Radiat. Phys. Chem.*, **5**, 249 (1973); (b) L. A. Bulanov, E. V. Starodubtseva, and E. A. Borisov, *Khim. Vys. Energ.*, **6**, 476 (1972).
(9) J. W. Boyle, C. J. Hochandel, T. J. Sworski, J. A. Ghormey, and W. F. Kieffer, *Proc. Int. Conf. Peaceful Uses At. Energy*, **1**, 576 (1955).
(10) A. W. Boyd and H. W. J. Conner, *Can. J. Chem.*, **42**, 1418 (1964).
(11) A. W. Boyd and O. A. Miller, *Can. J. Chem.*, **46**, 3773 (1968).
(12) M. Steinberg, W. Tucker, and G. Farber, BNL 10998-R, 1967.
(13) M. Steinberg, BNL 804, 1963.
(14) (a) C. Willis, A. W. Boyd, and D. A. Armstrong, *Can. J. Chem.*, **47**, 3783 (1969); (b) R. E. Rebbert, S. G. Lias, and P. Ausloos, *J. Res. Nat. Bur. Stand., Sect. A*, **77**, 249 (1973).
(15) F. Seitz and J. S. Koehler, "Solid State Physics," Vol. II, F. Seitz and D. Turnbull, Ed., Academic Press, New York, N. Y., 1956, p 35.
(16) G. G. Meisels, J. P. Freeman, and J. P. Gregory, *J. Phys. Chem.*, submitted for publication.
(17) (a) M. C. Sauer and L. M. Dorfman, *J. Phys. Chem.*, **66**, 322 (1962); (b) *J. Chem. Phys.*, **35**, 497 (1961).
(18) (a) G. G. Meisels, *J. Amer. Chem. Soc.*, **87**, 950 (1965); (b) *Trans. Amer. Nucl. Soc.*, 7, 308 (1964); (c) *J. Chem. Phys.*, **42**, 2328 (1965); (d) *ibid.*, **42**, 3237 (1965); (e) G. G. Meisels and T. J. Sworski, *J. Phys. Chem.*, **69**, 815 (1965); (f) *ibid.*, **69**, 2867 (1965).
(19) (a) J. Gawlowski and J. Niedzielski, *Int. J. Radiat. Phys. Chem.*, **5**, 419 (1973); (b) J. Niedzielski and J. Gawlowski, *ibid.*, **5**, 239 (1973); (c) *Nukleonika*, **15**, 531 (1970); (d) *Radiochem. Radioanal. Lett.*, **2**, 291 (1969); (e) *Nukleonika*, **16**, 143 (1971).
(20) (a) G. G. Meisels, *Advan. Chem. Ser.*, **58**, 243 (1966); (b) G. G. Meisels, "Organic Gases" in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968.
(21) W. H. Wahl and G. G. Meisels, *Rev. Sci. Instrum.*, **36**, 508 (1965).
(22) J. Gawlowski, J. Niedzielski, and A. Bierzynski, *Chem. Anal. (Warsaw)*, **15**, 721 (1970).
(23) (a) There exists a slight difference in dose between the N_2O and the C_2H_4 experiments due to fuel foil differences. In the radiolysis of N_2O the primary irradiation capsules utilized larger foil. The ethylene radiolysis utilized smaller fuel foil and consequently the dose is smaller. (b) W. C. Richardson and G. G. Meisels, to be published.
(24) (a) J. A. Miller, "Combustion" in "Ethylene and Its Industrial Derivatives," J. A. Miller, Ed., Benn Limited, London, 1969; (b) K. Goldman, *ibid.*, "The Physical Properties of Ethylene."
(25) J. V. Michael, D. T. Osborne, and G. N. Suess, *J. Chem. Phys.*, **68**, 2800 (1971).
(26) For recent compilations of pertinent kinetic data see the following comprehensive articles: (a) J. A. Kerr, "Rate Processes in the Gas Phase," in "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973; (b) M. Gibian and R. C. Corley, *Chem. Rev.*, **73**, 441 (1973), and references therein.
(27) (a) P. T. Holland and J. A. Stone, *Can. J. Chem.*, **52**, 348 (1974); (b) H. H. Carmichael, R. Gordon, Jr., and P. Ausloos, *J. Chem. Phys.*, **42**, 343 (1965); (c) C. M. Wodetzki, P. A. McCusker, and D. B. Peterson, *J. Phys. Chem.*, **69**, 1056 (1965).
(28) L. C. Northcliffe and R. F. Schilling, *Nucl. Data, Sect. A*, 7, 233 (1970).
(29) R. A. Holroyd and R. W. Fessenden, *J. Phys. Chem.*, **67**, 2743 (1963).
(30) T. O. Tiernan and J. H. Futrell, *J. Phys. Chem.*, **72**, 3080 (1968).
(31) C. Willis, O. A. Miller, A. E. Rothwell, and A. W. Boyd, *Advan. Chem. Ser.*, **No. 81**, 539 (1968).
(32) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969).
(33) P. G. Clay and A. A. Siddiqi, *Chem. Commun.*, 1271 (1969).

Kinetics of the Thermal Decomposition of Methyldisilane and Trisilane

A. J. Vanderwielen, M. A. Ring,* and H. E. O'Neal

Contribution from the Department of Chemistry, San Diego State University, San Diego, California 92115. Received July 26, 1974

Abstract: The kinetics of the gas-phase thermal decomposition of methyldisilane and trisilane in the temperature ranges 539.6–569.6°K and 529.6–560.5°K, respectively, are reported. Rate constants for the homogeneous, unimolecular initial decomposition reactions as shown are ($\theta = 2.3RT$): $CH_3Si_2H_5 \rightarrow SiH_2 + CH_3SiH_3$ ($\log k(\mathrm{sec}^{-1}) = (15.28 \pm 0.15) - (50.75 \pm 0.36)/\theta$); $CH_3Si_2H_5 \rightarrow CH_3SiH + SiH_4$ ($\log k(\mathrm{sec}^{-1}) = (14.14 \pm 0.14) - (49.89 \pm 0.35)/\theta$); $Si_3H_8 \rightarrow SiH_2 + Si_2H_6$ ($\log k(\mathrm{sec}^{-1}) = (15.69 \pm 0.18) - (52.99 \pm 0.43)/\theta$); $Si_3H_8 \rightarrow SiH_3SiH + SiH_4$ ($\log k(\mathrm{sec}^{-1}) = (14.68 \pm 0.23) - (49.24 \pm 0.55)/\theta$). It is argued that the relatively low activation energies observed support 1,2-H migration *via* hydrogen-atom bridged transition states, and that the relatively high A factors observed indicate that these transition states are quite "loose." Other derived thermodynamic and kinetic data are reported, including a value for the heat of formation of methyldisilane, $\Delta H_f°(CH_3Si_2H_5) = 12.6$ kcal/mol; heats of formation of the product silylenes, $\Delta H_f°(SiH_2) = 58.6 \pm 3.5$ kcal/mol; $\Delta H_f°(CH_3SiH) = 50.9 \pm 3.5$ kcal; $\Delta H_f°(SiH_3SiH) = 64.5 \pm 3.5$ kcal/mol; and A factors for these silylene insertion reactions (*i.e.*, the reverse of the decomposition reactions studied). Silylene insertions into (Si–C) and (C–H) bonds were not observed. Insertions into (Si–Si) bonds are argued to be inconsistent with the present data.

Initiation reactions in the thermal decompositions of saturated hydrocarbons are with no exceptions (C–C) or (C–H) bond fission reactions. Similarly, an (Si–H) bond rupture appears to be the initial step in the silane (SiH_4) thermal decomposition.[1] However, Si_2H_6,[2-4] $CH_3Si_2H_5$,[5] 1,2-$(CH_3)_2Si_2H_4$,[5] $(CH_3)_5Si_2H$,[6] and Si_3H_8[2,7] decompose *via* 1,2-hydrogen shift reactions to form silanes and silylenes,[2-7] (*cf.* reaction 1) where R represents H, SiH_3, or CH_3. This

$$R_3SiSiHR_2 \longrightarrow R_3SiH + SiR_2 \qquad (1)$$