velocity.[5,8] The ions of interest ($C_4F_4H_4 \cdot^+$ and $C_{12}H_{12} \cdot^+$) have large moments of inertia and thus low rotational velocities. The atomic collision partners cannot be rotationally excited. The molecules CO and N_2 have relatively small moments of inertia and might contribute on this basis. However, the strong ion–molecule potential causes the relative translational energy of the ions to become much greater than thermal and thus the translational velocity is much greater than the rotational velocity even for small molecular collision gases. For these reasons V–R transfer was not considered in the energy transfer model.

Summary

The dimerization reactions of $CF_2CH_2 \cdot^+$ in CF_2CH_2 and $C_6H_6 \cdot^+$ in C_6H_6 are found to be third order at threshold electron impact energies and thermal kinetic energies. Nonreactive collision gases are also effective in stabilizing the dimers in these two systems. These experiments confirm that the collisional deactivation mechanism of reaction 1 dominates. Absolute third-order rate constants and relative stabilization efficiencies are determined for all collision gases.

Analysis of the energy exchange between the excited dimer ion and the nonreactive collision gases using a collision duration model suggests that the excess energy removed from the dimer is in the form of low-frequency vibrational energy. The linearity of the k_i/ξ_i vs. $\mu^{1/2}$ plots, Figures 3 and 4, imply V–T exchange dominates all systems except the benzene dimer ion stabilized by the benzene neutral. In this case it appears that either V–V energy transfer or energy transfer via an exchange reaction dominates. This latter result suggests the structure of the $C_{12}H_{12} \cdot^+$ dimer may be composed of two benzene type moieties. The fact that CF_2CH_2 deactivates $C_4F_4H_4 \cdot^+$ only by V–T transfer suggests that the $C_4F_4H_4 \cdot^+$ ion has a structure unlike the parent olefin. A cyclic cyclobutane type structure is suggested.

Addition of Trimethylsilyl Radical to Ethylene. A Flash Photolysis–Electron Spin Resonance Kinetic Study[1]

Kwang Yul Choo and Peter P. Gaspar*

Contribution from the Department of Chemistry, Washington University, Saint Louis, Missouri 63130. Received September 10, 1973

Abstract: The rate of addition of trimethylsilyl radical to ethylene was measured over the temperature range $+20$ to $-74°$. At $20°$, $k = 1.7 \pm 1.0 \times 10^5 \, M^{-1} \, sec^{-1}$. An activation energy 2.5 ± 0.2 kcal/mol and frequency factor $\log A = 7.0 \pm 0.2$ were determined. It is confirmed that ethylene is an efficient scavenger for silyl radicals. This is the first direct kinetic study of an addition reaction which may be considered the prototype for the chain-carrying steps in free radical polymerization of olefins.

Addition reactions of silicon-centered radicals and olefins or acetylenes are of great synthetic importance, constituting one of the major methods for the creation of silicon–carbon bonds.[2] The detection of silyl radicals as intermediates in photochemical[3a] and nuclear recoil[3b] reaction systems by the use of olefin scavengers depends on the rapidity of the addition reaction. Very little information is available, however, on the rates of silyl radical addition reactions.[4] Recently, Strausz and coworkers have estimated the rate constant for addition of disilanyl radicals to ethylene, employing quantum yield measurements in steady-state photolysis experiments.[5]

$$SiH_3SiH_2 \cdot + CH_2=CH_2 \longrightarrow SiH_3SiH_2CH_2CH_2 \cdot$$
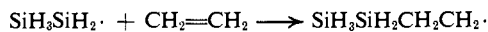
The recent detection of silyl radicals by electron spin resonance spectroscopy in the solid[6] and liquid phases[7,8] has led the way to kinetic studies of silyl radical reactions. Direct kinetic studies of self reactions (dimerization or disproportionation) of several silicon-centered radicals have been reported by Ingold and coworkers[9] and by ourselves.[10] Despite strenuous efforts over two decades, silyl radicals have not been directly detected in the gas phase.[11]

(1) This work has been carried out with financial support from the United States Atomic Energy Commission. This is AEC Technical Report No. COO-1713-41.

(2) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960.

(3) (a) H. Niki and G. J. Mains, *J. Phys. Chem.*, **68**, 304 (1964); M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **87**, 179 (1965); (b) P. P. Gaspar, S. A. Bock, and W. C. Eckelman, *ibid.*, **90**, 6914 (1968).

(4) R. A. Jackson, *Advan. Free-Radical Chem.*, 3, 231 (1969).

(5) T. L. Pollock, H. S. Sandhu, A. Jodhan, and O. P. Strausz, *J. Amer. Chem. Soc.*, **95**, 1017 (1973).

(6) R. L. Morehaus, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1751 (1966); G. S. Jackel and W. Gordy, *Phys. Rev.*, **176**, 443 (1968).

(7) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3938 (1969).

(8) S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc. A*, 348 (1970).

(9) P. T. Frangopol and K. U. Ingold, *J. Organometal. Chem.*, **25**, C9 (1970); G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 491 (1972).

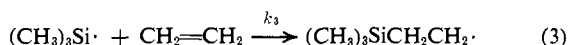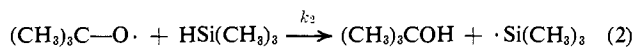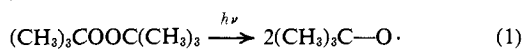(10) P. P. Gaspar, A. D. Haizlip, and K. Y. Choo, *J. Amer. Chem. Soc.*, **94**, 9032 (1972).

(11) A. E. Douglas, *Can. J. Phys.*, **33**, 801 (1955); **35**, 71 (1957); I. Dubois, G. Herzberg, and R. D. Varma, *J. Chem. Phys.*, **47**, 4262 (1967); I. Dubois and H. Leclercq, *Can. J. Phys.*, **49**, 3053 (1971).
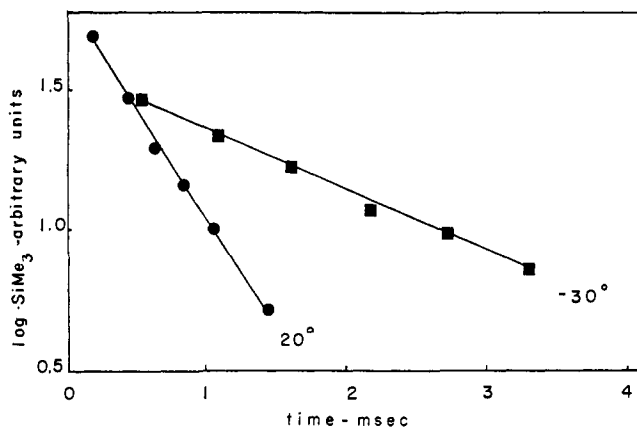
Figure 1. Typical pseudo-first-order kinetic plots for the addition of trimethylsilyl radicals to ethylene. The initial radical concentrations are *ca.* 10^{-6} M.

Figure 2. Arrhenius plot for the addition of trimethylsilyl radical to ethylene.

Kinetic studies have been carried out on the addition of various carbon-centered radicals to ethylene.[12-15] Again, product yields obtained under steady-state photolysis conditions were the primary data.

We report here the first time-resolved kinetic spectroscopic study of the addition of a group IV free radical to ethylene. The flash photolysis–electron spin resonance kinetic technique has already been described.[10] Trimethylsilyl radicals are generated within the microwave cavity of an esr spectrometer by ultraviolet irradiation of liquid phase *tert*-butyl peroxide–trimethylsilane–ethylene mixtures. The decay of the trimethylsilyl radical concentration is monitored by the decrease in the intensity of its esr signal on a millisecond time scale.

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3C-O\cdot \quad (1)$$

$$(CH_3)_3C-O\cdot + HSi(CH_3)_3 \xrightarrow{k_2} (CH_3)_3COH + \cdot Si(CH_3)_3 \quad (2)$$

$$(CH_3)_3Si\cdot + CH_2{=}CH_2 \xrightarrow{k_3} (CH_3)_3SiCH_2CH_2\cdot \quad (3)$$

This method for the generation of silyl radicals in solution was discovered by Krusic and Kochi,[7] who have also observed the β-trialkylsilylethyl radical addition products of trialkylsilyl radicals and ethylene.[16]

Experimental Section

Trimethylsilane was purchased from the Pierce Chemical Co., no purity given, and no volatile impurities were detected by gas chromatography. Ethylene, Matheson Gas Products, research grade 99.98%, was used directly from the tank. *tert*-Butyl peroxide, Matheson, Coleman and Bell, was purified by fractional distillation.[10]

The flash photolysis–electron spin resonance apparatus and the procedure for sample preparation, ultraviolet irradiations, and the recording of kinetic data have been described in detail.[10]

Kinetic measurements were made on 1:1 v/v mixtures of *tert*-butyl peroxide and trimethylsilane containing ethylene at 10^{-2} M concentration. The temperature range for the rate measurements was $+20$ to $-74°$.

All kinetic measurements were carried out by ultraviolet irradiation of liquid reaction mixtures degassed and sealed in Suprasil quartz tubes thermostated within the microwave cavity of a Varian E-3 electron spin resonance spectrometer. The photolysis light source was a 150 W xenon flash lamp (Eimac R150-2) controlled by
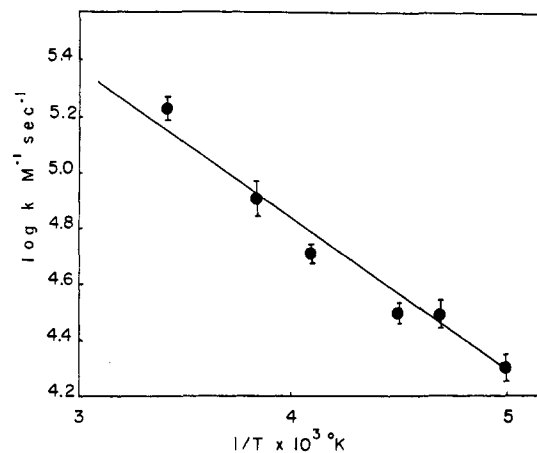
a variable on–off time pulse generator. Kinetic measurements were made by averaging and storing for many cycles the esr signal intensity as a function of time during the several millisecond light-on, light-off cycles.

Since the addition of trimethylsilyl radicals to ethylene is quite rapid, a low ethylene concentration was required for the half-life of the addition reaction to be sufficiently *long* (>0.1 msec) to be measured under the instrumental conditions employed. However, if the ethylene concentration is too low, pseudo-first-order conditions no longer prevail, and second-order decay of trimethylsilyl radicals due to recombination can compete with the addition to ethylene.

It was found that at ethylene concentrations of *ca.* 10^{-2} mol/l., the decay of trimethylsilyl radical is kinetically first order for more than 3 min total irradiation time, permitting the collection of sufficient repetitive scans, each of several millisecond duration, for the measurement of a rate constant. After prolonged irradiation (>20 min) the decay of the trimethylsilyl radical concentration was found to be a second-order process, indicating the depletion of ethylene. Therefore, kinetic measurements were made as brief as possible, total irradiation times kept below 30 sec, and fresh samples frequently employed to prevent changes in ethylene concentration during reaction. As an additional precaution vapor-chromatographic analyses were carried out before and after irradiation (of separate identically made reaction mixtures) and the ethylene concentration was found to remain constant within experimental error, $\pm 10\%$.

The coupling constants observed in the esr spectra of the trimethylsilyl ($a_{CH_3} = 6.2 \pm 0.2$) and β-trimethylsilylethyl ($a_{\alpha H} = 21.0$, $a_{\beta H} = 17.6$ G at $-80°$) radicals agree with the values reported in the literature.[7,17] The growth of the β-trimethylsilylethyl radical esr signal was observed to correspond to the decay of the trimethylsilyl radical signal, although no quantitative kinetic measurements were carried out on the appearance of the β-trimethylsilylethyl radical.

The first-order decay of the trimethylsilyl radical concentration was analyzed according to the kinetic scheme, reactions 1 to 3, given above.

$$\frac{-d[\cdot Si(CH_3)_3]}{dt} = k_3[\cdot SiCH_3)_3][CH_2{=}CH_2]$$

$$= k_{obsd}[\cdot Si(CH_3)_3]$$

Upon integration $\ln [\cdot Si(CH_3)_3] = \ln [\cdot Si(CH_3)_3]_0 - k_{obsd}t$. The slope of a plot of $\ln [\cdot Si(CH_3)_3]$ *vs.* t is $-k_{obsd}$. Two such plots are illustrated in Figure 1. The activation energy and frequency factor were obtained from the Arrhenius plot, Figure 2. Numerical values of the rate constant at various temperatures are given in Table I. The Arrhenius parameters for the addition of trimethylsilyl radical to ethylene are compared with those taken from the literature for alkyl radical addition in Table II.

Discussion

The addition of trimethylsilyl radical to ethylene is much more rapid than the addition of the simple alkyl

(12) L. Endrenyi and D. J. Le Roy, *J. Phys. Chem.*, **71**, 1334 (1967).

(13) F. W. Lampe and F. H. Field, *Can. J. Chem.*, **37**, 995 (1959).

(14) J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **55**, 572 (1959).

(15) J. M. Tedder and J. C. Walton, *Trans. Faraday Soc.*, **62**, 1859 (1966).

(16) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 6161 (1969).

(17) T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972).

Table I. Addition Reaction to Trimethylsilyl Radical to Ethylene

Temp, deg C	$k,^a$ 10^4 M^{-1} sec^{-1}	$E_a,^a$ kcal	log $A,^a$ M^{-1} sec^{-1}
20	17 ± 1.0		
-15	7.3 ± 0.3		
-30	5.7 ± 0.1		
-50	3.5 ± 0.1		
-60	3.4 ± 0.2		
-74	2.0 ± 0.1	2.5 ± 0.2	7.0 ± 0.2

^{a} Errors are the standard deviations of the slopes from which the rate constants and E_a are derived and of the intercept which is log A.

Table II. Arrhenius Parameters for the Addition Reactions of Group IV Radicals

Radical	Substrate	E_a, kcal	log A, M^{-1} sec^{-1}	Ref
$\cdot Si(CH_3)_3$	Ethylene	2.5 ± 0.2^a	7.0 ± 0.2^a	This work
$\cdot CH_3$		6.8	8.1	b
$\cdot C_2H_5$		5.5	7.4	c
$\cdot n\text{-}C_3H_7$		5.1, 6.5	7.4, 7.9	b, d
$\cdot CCl_3$		3.2	5.6	e

^{a} Standard deviations of the k vs. $1/T$ plot. ^{b} Reference 12. ^{c} Reference 13. ^{d} Reference 14. ^{e} Reference 15.

radicals methyl, ethyl, n-propyl, and trichloromethyl. Comparison of the Arrhenius parameters, given in Table II, indicates that the activation energy for trimethylsilyl radical addition is considerably lower than that for methyl, ethyl, and n-propyl radicals. The frequency factor for trimethylsilyl radical addition is lower than the value for methyl but similar to that for ethyl and n-propyl. Thus, it is the low-activation energy for trimethylsilyl radical addition which enhances its rate of addition.

Strausz and coworkers also found that the addition of disilanyl radicals to ethylene is several orders of magnitude more rapid than the addition of methyl radical.[5] These workers attributed the lowering of the energy barrier for silyl radical addition to the greater physical size of the 3p orbital of silicon, greater polarizibility and the availablity of d orbitals on the silicon atom, and the tetrahedral configuration of silyl vs. the planar configuration of alkyl radicals. We suggest that product stability may be the dominant factor favoring silyl radical addition. The stabilization of a carbon-centered free radical by a β-silicon substituent has been shown to be significant;[16,17] the interaction between the radical center and the β-silicon substituent has been estimated to be as great as 5 kcal/mol.[18]

The results reported here indicate clearly that ethylene is an efficient scavenger for trimethylsilyl radicals under the usual steady illumination photochemical reaction conditions. At the usual concentrations of ethylene used as a radical scavenger (mole fraction of ethylene ≥ 0.01), addition of trimethylsilyl radicals is much faster, for low concentrations of silyl radicals (mole fraction $\leq 10^{-6}$), than is dimerization of trimethylsilyl radicals and other competing abstraction and displacement reactions.[19] Preliminary experiments showed that the addition of unsubstituted silyl radical $\cdot SiH_3$ to ethylene is even more rapid than the addition of trimethylsilyl radical. The rapidity of the addition reaction and the relative broadness of the individual lines in the esr signal for SiH_3 made it impractical to obtain quantitative data for its addition rate. It is safe to say, however, that ethylene is an effective scavenger for SiH_3 in most silane reaction systems.

Since this work represents the most direct kinetic study to date of a group IV free radical addition to an olefin, its greatest significance may be to point to the feasibility of direct kinetic spectroscopic investigation of such important free radical reactions as the chain-carrying steps in free radical polymerization.

(18) T. Kawamura and J. K. Kochi, *J. Organometal. Chem.*, 30, C8 (1971).

(19) M. A. Ring, M. J. Puentes, and H. E. O'Neal, *J. Amer. Chem. Soc.*, 92, 4845 (1970); J. H. Purnell and R. Walsh, *Proc. Roy. Soc., Ser. A*, 293, 543 (1966).