Waugh, Ed., Academic Press, New York, N.Y., 1973.
(9) M. T. Jones, T. C. Kuechler, and S. Mertz, *J. Magn. Resonance*, **10**, 149 (1973).
(10) (a) The *g* values were measured on a Varian E-9 ESR spectrometer using the dual cavity technique.[10b] (b) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance: Elementary Theory and Practical Applications", Mcgraw-Hill, New York, N.Y., 1972, p 464. (c) The *p*-benzosemiquinone-*tert*-butyl alcohol system was used as a *g* value standard.[6,7]
(11) (a) It has been previously observed that salts of this type are dissociated in HMPA; see P. Bruno, M. D. Monica, and E. Righetti, *J. Phys. Chem.*, **77**, 1258 (1973). (b) The ion association constant for KI was found to be about 4 in HMPA.[12]
(12) G. R. Stevenson and A. E. Alegría, unpublished results.
(13) N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961).
(14) T. Yonezawa, T. Kawamura, M. Ushio, and Y. Nakao, *Bull. Chem. Soc. Jpn.*, **43**, 1022 (1970).

Department of Chemistry
University of Puerto Rico
Rio Piedras, Puerto Rico 00931
Gerald R. Stevenson*
Antonio E. Alegría

Received November 11, 1974

Absence of an Energy Dependence for $CH_2(^1A_1)$ Reaction with the C-H and Si-H Bonds of Dimethylsilane

Publication costs assisted by the Petroleum Research Fund

Sir: The insertion of singlet methylene radicals into Si-H bonds is one of the fastest $CH_2(^1A_1)$ reactions.[1] For various substituted alkylsilanes $CH_2(^1A_1)$ radicals formed by diazomethane photolyses at 3660 and 4358 Å insert 7-9 times faster into Si-H bonds than C-H bonds.[1,2] Though various hypotheses have been suggested, the origin of this reactivity difference has not been identified.[2]

In this work we have investigated the effect of excess methylene vibrational energy and temperature on the relative reactivity of $CH_2(^1A_1)$ radicals with dimethylsilane

$$^1CH_2 + CH_3SiH_2CH_3 \rightarrow (CH_3)_3SiH\ [\mathrm{TMS}] \qquad (1)$$

$$\rightarrow C_2H_5SiH_2CH_3\ [\mathrm{MES}] \qquad (2)$$

For many bimolecular reactions, excess vibrational energy has a significant effect on reaction cross sections and the resulting product distributions.[3] In addition, if there is an Arrhenius activation energy difference for singlet methylene insertion into Si-H and C-H bonds, it should be detectable by relative rate measurements at different temperatures.

There is a continuing controversy concerning the electronic energy difference between $CH_2(^1A_1)$ and $CH_2(^3B_1)$, which is the ground state.[4-8] The major point of dispute involves the interpretation of different chemical activation rate measurements.[7,8] It has been suggested that these differences could be reconciled if there was a threshold for singlet methylene insertion reactions.[9] Some discrepancies may also arise if there are different excitation functions for $CH_2(^1A_1)$ reactions with various types of bonds, so that some molecules select the more energetic methylenes while others react with thermalized methylene radicals. Since Si-H bonds are more highly reactive than C-H bonds, these suggestions can be partially tested by studying the effect of excess $CH_2(^1A_1)$ vibrational energy and temperature on Si-H and C-H relative insertion reactivities.

TABLE I: Experimental Trimethylsilane: Methylethylsilane Ratios for the Singlet Methylene ($^1A_1$)-Dimethylsilane Reaction

Singlet methylene precursor	Temp, °C	CF_4:DMS	TMS:MES[a]
CH_2N_2—3660 Å	24		2.30 ± 0.13
CH_2N_2—4358 Å	0		2.24 ± 0.03
CH_2N_2—4358 Å	24		2.34 ± 0.01
CH_2N_2—4358 Å	90		2.40 ± 0.08
CH_2N_2—4358 Å	24	5.4	2.30
CH_2N_2—4358 Å	24	17.0	2.28
CH_2CO—3340 Å	0		2.17 ± 0.08
CH_2CO—3340 Å	24		2.25 ± 0.02
CH_2CO—3340 Å	100		2.16 ± 0.12

[a] For experiments where no error is given only one measurement was made.

Singlet methylene insertion was studied by photolyzing ketene or diazomethane with added oxygen. Oxygen is an effective scavenger for the $CH_2(^3B_1)$ radicals.[1,2] Ketene, diazomethane, and dimethylsilane were prepared by conventional techniques.[1,2,7] The diazomethane 4358-Å photolyses were performed using a Hanovia 673 A medium-pressure mercury arc lamp with Corning colored glass filters, No. 5850 and 3389. For the rest of the photolyses a 200-W Osram high-pressure mercury arc lamp was used. Corning colored glass filter No. 5840 was used to isolate the 3130-, 3340-, and 3660-Å lines for the ketene photolyses and Corning colored glass filters No. 5860 and 7380 were used for 3660-Å photolyses of diazomethane. The reaction mixtures were photolyzed in Pyrex vessels. A normal mixture consisted of dimethylsilane-ketene or diazomethane-oxygen in a ratio of 10:1:1. Total pressures were always greater than 50 Torr so the trimethylsilane and dimethylsilane, eq 1 and 2, were collisionally stabilized.[10] Tetrafluoromethane was added to some mixtures as a moderator. Trimethylsilane (TMS) and methylethylsilane (MES) were measured by glpc.

The experimental results are listed in Table I. Though the filter used in the ketene photolyses transmitted the 3130-, 3340-, and 3660-Å mercury lines, most of the photolysis occurred at 3340 Å. The combination of the filter and Pyrex vessel removed most of the 3130-Å line and as a result of the small extinction coefficient[11] and photodissociation quantum yields[12] for CH_2CO at 3660 Å only a small fraction of the singlet methylenes were formed by 3660-Å photolyses. However, even if the 3660- and 3130-Å lines were not completely removed, it would have only a minor effect on our experiments since the average energies of singlet methylenes formed at 3660 and 3130 Å are only ~1 kcal/mol lower and higher, respectively, than those formed by 3340-Å photolyses.[8,13]

The key in comparing the results using diazomethane and ketene is the difference in the vibrational energy content of the singlet methylenes. The average vibrational energy of the singlet methylenes formed by diazomethane photolysis at 3660 Å is ~13 kcal/mol higher than that of those formed by CH_2CO photolysis at 3340 Å.[7,14] By photolyzing CH_2N_2 at 4358 Å and using CF_4 as a moderator to deactivate vibrationally the singlet methylene radicals,

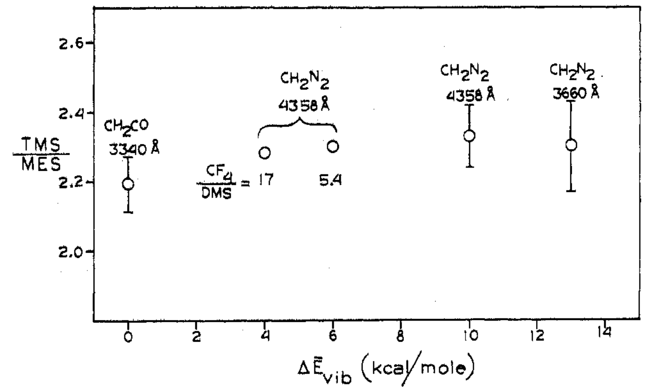

Figure 1. Plot of TMS:MES ratios vs. relative average singlet methylene vibrational energy ($\Delta\bar{E}_{vib}$). Only one measurement was made for points without error bars.

their average energy may be varied between the above extremes.[7] The TMS:MES ratios, as a function of relative singlet methylene average vibrational energy, are shown in Figure 1.

The results displayed in Figure 1 show the relative reactivities of the Si–H and C–H bonds of dimethylsilane do not change within experimental error as the average vibrational energy of $CH_2(^1A_1)$ is varied by 13 kcal/mol. This means the ratio in the excitation functions for Si–H and C–H insertion does not change with this alteration in the singlet methylene vibrational energy. Therefore, there is no discrimination on the part of C–H and Si–H bonds toward singlet methylenes with different vibrational energies. However, these results do not rule out the possibility that there are identical changes in the excitation functions as the $CH_2(^1A_1)$ vibrational energy is varied. It should be pointed out that these results do not pertain to the role dimethylsilane vibrational energy may play in the insertion dynamics.

The presence of a threshold difference for $CH_2(^1A_1)$ insertion into the Si–H and C–H of dimethylsilane can be investigated by varying the temperature. If the difference in reactivities of the Si–H and C–H bonds at 24° is solely an activation energy difference, the TMS:MES ratio for CH_2CO 3340-Å photolysis should be 2.7 and 1.5 at 0 and 100°, respectively. However, within experimental error, we find for both CH_2CO 3340-Å and CH_2N_2 4358-Å photolyses the TMS:MES ratio is independent of temperature, and if there is an activation energy difference, it is very small. Lack of an activation energy difference for singlet methylene insertion into these two different types of bonds suggests that the threshold for insertion may be small. Support for this hypothesis is found by using the rate constant of 1.9×10^{-12} cm^3 molecule^{-1} sec^{-1} for the $CH_2(^1A_1) + CH_4 \rightarrow C_2H_6$ reaction[15] and the measurement of 7.1 for the ratio of the $CH_2(^1A_1)$ reaction with dimethylsilane relative to that with methane[16] to determine the rate constant for total $CH_2(^1A_1)$ reaction with dimethylsilane equal to 1.3×10^{-11} cm^3 molecule^{-1} sec^{-1}. This rate constant is only ~50 times smaller than the collision frequency,[17] which is consistent with a maximum activation energy at 25° of 2.3 kcal/mol for singlet methylene reaction with dimethylsilane. In addition, extended Hückel[18] and MINDO/2[19] calculations have predicted that the activation energy for $CH_2(^1A_1)$ insertion into the C–H bonds of CH_4 is small.

Recent quantum mechanical calculations[18,19] suggest that $CH_2(^1A_1)$ reaction with CH_4 is a concerted reaction, with the methylene attacking along a C–H axis. It would be interesting to see if such a model without an activation energy difference for Si–H and C–H insertion can predict the experimental ratios of relative Si–H and C–H insertion in alkylsilanes and the independence of the reactivity ratios with varying amounts of $CH_2(^1A_1)$ vibrational energy.

Acknowledgments. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corp. W.L.H. wishes to thank Wayne State University for a Summer Research Fellowship.

References and Notes

(1) C. J. Mazac and J. W. Simons, *J. Am. Chem. Soc.*, **90**, 2484 (1968).
(2) W. L. Hase, W. G. Brieland, and J. W. Simons, *J. Phys. Chem.*, **73**, 4401 (1969).
(3) J. C. Polanyi and W. H. Wong, *J. Chem. Phys.*, **51**, 1439 (1969).
(4) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **13**, 30 (1972).
(5) C. F. Bender, H. F. Schaefer, D. R. Franceschetti, and L. C. Allen, *J. Am. Chem. Soc.*, **94**, 6888 (1972).
(6) M. J. S. Dewar, R. C. Haddon, and P. K. Weiner, *J. Am. Chem. Soc.*, **96**, 253 (1974).
(7) W. L. Hase, R. J. Phillips, and J. W. Simons, *Chem. Phys. Lett.*, **12**, 161 (1971); R. J. Phillips, M.S. Thesis, New Mexico State University, Las Cruces, N.M.
(8) M. G. Topor and R. W. Carr, Jr., *J. Chem. Phys.*, **58**, 757 (1973).
(9) K. C. Kim and D. W. Setser, *J. Phys. Chem.*, **77**, 2021 (1973).
(10) W. L. Hase, W. G. Brelland, P. W. McGrath, and J. W. Simons, *J. Phys. Chem.*, **76**, 459 (1972).
(11) J. W. Rabalais, J. M. McDonald, V. Scherr, and S. P. McGlynn, *Chem. Rev.*, **71**, 73 (1971).
(12) P. G. Bowers, *J. Chem. Soc. A*, 466 (1967).
(13) G. B. Kistiakowsky and B. B. Saunders, *J. Phys. Chem.*, **77**, 427 (1973).
(14) J. W. Simons and G. W. Taylor, *J. Phys. Chem.*, **73**, 1274 (1969); G. W. Taylor and J. W. Simons, *ibid.*, **74**, 464 (1970).
(15) W. Braun, A. M. Bass, and M. Pilling, *J. Chem. Phys.*, **52**, 5131 (1970).
(16) W. L. Hase and J. W. Simons, *J. Chem. Phys.*, **54**, 1277 (1971).
(17) The collision frequency was calculated using the following diameters: CH_2, 3.8 Å, $(CH_3)_2SiH_2$, 6.6 Å.
(18) R. C. Dobson, D. M. Hayes, and R. Hoffman, *J. Am. Chem. Soc.*, **93**, 6188 (1971).
(19) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Am. Chem. Soc.*, **94**, 9095 (1972).

Department of Chemistry
Wayne State University
Detroit, Michigan 48202

Patrick M. Kelley
William L. Hase*

Department of Chemistry
New Mexico State University
Las Cruces, New Mexico 88001

John W. Simons

Received November 22, 1974