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Kinetics of Radical-Forming Homolyses in Alkenyl- and *tert*-Butylsilanes. The Stability of α- and β-Silicon-Substituted Alkyl Radicals

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From gas kinetic experiments in which α-silylalkyl and β-silylalkyl radicals were generated by pyrolytic cleavage of weak carbon–allyl or carbon–*tert*-butyl bonds, it is suggested that α-silyl and β-silyl substituents may each stabilize alkyl radicals by about 2.6 ± 1 kcal·mol^{-1}.

Introduction

In the pyrolysis of allyltrimethylsilane (I), the use of methyl chloride as a selective trap for silyl radicals enabled separate Arrhenius parameters to be measured for the two concurrent primary reactions, namely, radical-forming homolysis and retroene elimination of dimethylsilene.[1,2] The same method applied to the pyrolysis of 4-(dimethylsilyl)-1-butene (II) led to quantitative conclusions about the energy barrier for the isomerization by a 1,2-hydrogen shift of the α-silylalkyl radical formed by dissociation of the weak carbon–allyl bond in compound II:[3]

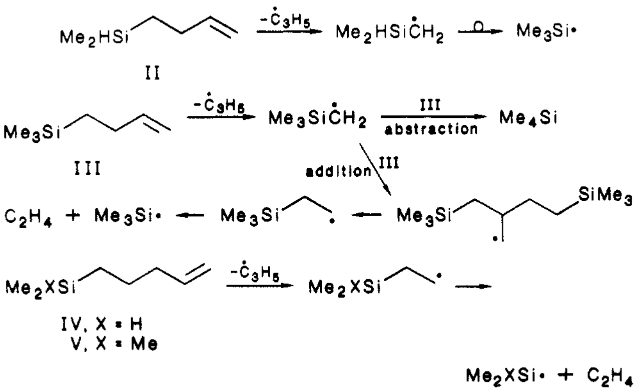
$$\cdot CH_2SiMe_2H \rightarrow Me_3Si\cdot \qquad (1)$$

We were thus encouraged to apply this fruitful method to the longstanding question of the stabilization of alkyl radicals by α- and β-silyl substituents by pyrolysis studies on compounds that would give such radicals cleanly by rupture of a weak bond. The first compounds chosen for this study were compound II, 4-(trimethylsilyl)-1-butene (III), 5-(dimethylsilyl)-1-pentene (IV), and 5-(trimethylsilyl)-1-pentene (V); these were expected to give α-silylalkyl (compounds II and III) or β-silylalkyl (compounds IV and V) radicals by dissociation of a carbon–allyl bond. Although this expectation was fulfilled, the pyrolyses were rather complex and we turned to the pyrolysis of two compounds that would give α- and β-silylalkyl radicals by rupture of a carbon–*tert*-butyl bond, 2,2-dimethyl-3-(trimethylsilyl)propane (VI) and 2,2-dimethyl-4-(trimethylsilyl)butane (VII). The hydrocarbon 2,2-dimethylbutane (VIII) was pyrolyzed as a reference compound in the latter experiments.

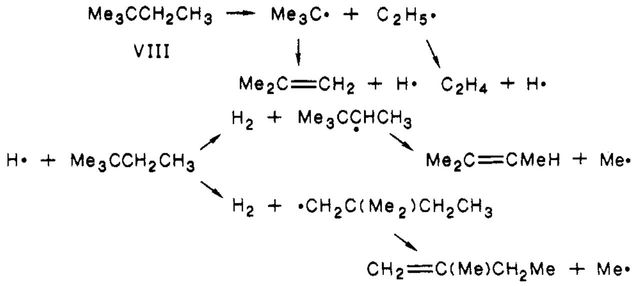
Results

1. Pyrolysis of Compounds with Carbon–Allyl Bonds. In our low-pressure pyrolysis (LPP) apparatus we separately pyrolyzed compounds II, III, IV, and V, each in the presence of a 9-fold excess of methyl chloride, measuring the kinetics of formation of Me_3SiCl in each case. The results are compared with those for I in Table I. Reasonable routes to a silyl radical, and hence to a chlorosilane in the presence of methyl chloride, are shown in Scheme I. The route for each compound, II–V, in Scheme I is rate-determined by carbon–allyl bond rupture, but the primary radical formed from III can undergo other reactions, only forming $Me_3Si\cdot$ radicals in a series of secondary reactions. The *A* factor for formation of Me_3SiCl is therefore low, making that process a very minor one (ca. 8% of total decomposition). Formation of Me_3SiCl is also a minor process (16–19%) in the pyrolysis of IV and V, as it was in the pyrolysis of I. Even in the case of II formation of Me_3SiCl only accounted for 54% of the total decomposition. For that reason and because there is some uncertainty about the allyl stabilization energy and about alkyl–allyl and silyl–allyl bond dissociation energies, we cannot draw firm conclusions about radical stabilization effects from the results in Table I. These compounds were also pyrolyzed in the SFR; the results were less suitable than those in Table I for elucidating primary processes but gave information about product composition, retroene reactions, and secondary reactions. Details of the SFR experiments are published separately.[4]

Scheme I



Scheme II



2. Pyrolysis of Compounds with Carbon–*tert*-Butyl Bonds. To overcome the above-noted ambiguities in the

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† The University, Leicester.
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(1) Davidson, I. M. T.; Wood, I. T. *J. Organomet. Chem.* **1980**, *187*, C65.

(2) Barton, T. J.; Burns, S. A.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Wood, I. T. *J. Am. Chem. Soc.* **1984**, *106*, 6367.

(3) Barton, T. J.; Revis, A.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Hughes, K. J.; Gordon, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 4022.

(4) Davidson, I. M. T.; Hughes, K. J.; Ijadi-Maghsoodi, S. *Organometallics*, in press.

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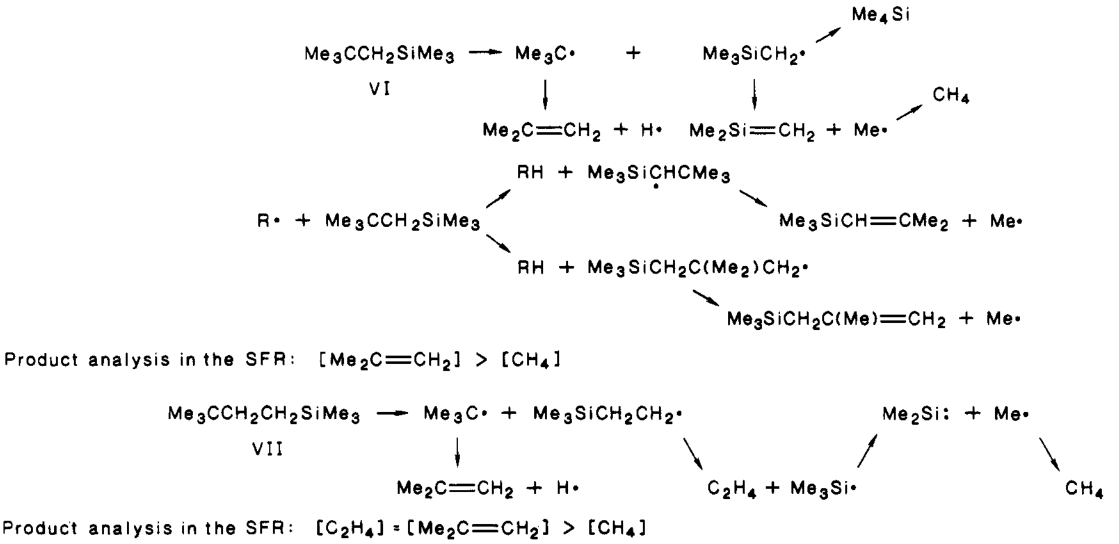
Scheme III



Product analysis in the SFR: $[Me_2C{=}CH_2] > [CH_4]$

Product analysis in the SFR: $[C_2H_4] \approx [Me_2C{=}CH_2] > [CH_4]$

Table I. Kinetic Results by LPP (R = Allyl)

compd	formatn of Me_3SiCl log A	formatn of Me_3SiCl E/kcal·mol^{-1}	total decompositn log A	total decompositn E/kcal·mol^{-1}	temp/°C
HMe_2SiCH_2R (II)	15.5 ± 0.4	68.4 ± 2	12.8 ± 0.2	56.9 ± 1	532–593
Me_3SiCH_2R (III)	14.6 ± 0.4	68.6 ± 2	12.1 ± 0.2	54.7 ± 2	567–630
$HMe_2SiCH_2CH_2R$ (IV)	15.4 ± 0.4	67.6 ± 2[a]	11.5 ± 0.2	49.7 ± 1	500–575
$Me_3SiCH_2CH_2R$ (V)	15.3 ± 0.5	67.4 ± 2	11.8 ± 0.2	50.7 ± 1	510–579
[cf. Me_3SiR (I)	15.6 ± 0.5	73.0 ± 2	12.9 ± 0.1	59.5 ± 0.5	590–670]

[a] Product was HMe_2SiCl, not Me_3SiCl.

Table II. Kinetic Results by LPP (R = *tert*-Butyl)

compd	log A	E/kcal·mol^{-1}	temp/°C
Me_3SiCH_2R (VI)	16.2 ± 0.1	73.9 ± 1	600–653
$Me_3SiCH_2CH_2R$ (VII)	16.1 ± 0.2	73.9 ± 1	606–668
CH_3CH_2R (VIII)	16.1 ± 0.1	76.5 ± 1	650–712

pyrolysis of II–V, we turned to the pyrolysis of the *tert*-butyl compounds, 2,2-dimethyl-3-(trimethylsilyl)propane (VI) and 2,2-dimethyl-4-(trimethylsilyl)butane (VII), with 2,2-dimethylbutane (VIII) as reference compound. The only primary reaction of VI–VIII would be homolysis of the *tert*-butyl–carbon bond, with no concurrent retroene reactions.

Compounds VI–VIII were each pyrolyzed by LPP with partial pressures of reactant between 0.005 and 0.04 torr. Pyrolyses with emphasis on product analysis were also carried out in a stirred-flow apparatus (SFR), with reactant partial pressures of 0.08–0.8 torr in ca. 1000 torr of N_2. Kinetic results for the decomposition of these compounds are in Table II.

Experimental Section

Compounds II–VII were synthesized by methods fully described elsewhere.[5] Compound VIII was obtained commercially (Aldrich).

Gas kinetic experiments were carried out on the improved LPP and SFR apparatus, also fully described elsewhere.[6]

Discussion

Although the experiments on the allylic compounds II–V were complicated by the problems described in the Results, it is noteworthy that there is excellent agreement between the homolysis activation energies for compounds II and III (68.5 ± 2 kcal·mol^{-1}) and between the corresponding activation energies for compounds IV and V (67.5 ± 2 kcal·mol^{-1}). If the former activation energy measures the α-silyl radical stabilization effect and the latter the β-silyl effect, then these effects only differ by ca. 1 kcal·mol^{-1}. Comparison with the results for I, taking into account likely differences between silyl–allyl and alkyl–allyl bond energies,[7] indicates that both effects may be 3–4 kcal·mol^{-1}.

The early stages of the pyrolysis of VIII would be as shown in Scheme II, followed by similar abstraction reactions by Me· radicals to propagate a chain forming CH_4 and C_5H_{10}. All of these products were detected in the SFR, but $[Me_2C{=}CH_2] = [C_2H_4] > [CH_4]$; i.e., the chain did not develop. As the kinetic data in Table II were obtained by LPP at *lower* pressures of VIII, the Arrhenius parameters should relate to the initial dissociation of the *tert*-butyl–ethyl bond. Similar arguments should apply to VI and VII, as shown in Scheme III. Kinetic data were unaffected by LPP experiments with added methyl chloride or hydrogen chloride, strengthening our belief that the pyrolyses of VI–VIII were nonchain under LPP conditions. Kinetic results in the SFR at 1000 torr indicated that the results in Table II were little affected by unimolecular fall-off; insofar as they were, the effect would be greatest for VIII. The activation energy differences in Table II should therefore be a reasonable measure of the relative strengths of the bonds broken, especially as the A factors in Table II are essentially constant; we conclude that both α- and β-silyl substituents appear to stabilize alkyl radicals equally by (76.5–73.9) kcal·mol^{-1}, i.e., 2.6 ± 1 kcal·mol^{-1}.

Kinetic experiments by Walsh and co-workers led to an estimate of 3 ± 1 kcal·mol^{-1} for the β-silyl stabilization energy,[8] but only 0.4 ± 1 kcal·mol^{-1} for the α-stabilization.[9]

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(5) Revis, A. Ph.D. Thesis, Iowa State University, 1984.

(6) Davidson, I. M. T.; Dean, C. E. *Organometallics*, in press. Davidson, I. M. T.; Hughes, K. J.; Ijadi-Maghsoodi, S. *Organometallics*, in press.

(7) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(8) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207.

Walsh's method and ours are both indirect, each with assumptions that are reasonable but not infallible. Consequently, while the agreement over β-stabilization is pleasing, the extent of α-stabilization remains an open question. From ESR studies on $\cdot CH_2SiMe_3$ radicals generated by hydrogen abstraction, Krusic and Kochi[10] concluded that these radicals might be more stable than their alkyl counterpart. Although their explanation for the nature of that stabilization has been challenged,[11] it remains an experimental fact that radicals could be generated from Me_4Si but not from Me_4C under the same conditions. Similar enhanced reactivity in analogous circumstances was observed by Sakurai and co-workers.[12] Likewise, Wilt and co-workers found that α-halosilanes were more reactive than haloalkanes in free radical reduction by organotin hydrides; stabilization of the transition state for halogen abstraction by a polar effect was the preferred explanation,[13] but α-silyl radical stabilization could have been a contributory factor. Ingold and his co-authors[14] found enhanced reactivity toward hydrogen abstraction at both the α- and β-carbons of Et_4Si; they considered the β-stabilization effect to be greater than the α-effect, but comparisons are complicated by uncertainty over the allowance that should be made for steric hindrance when Et_4Si was compared with hydrocarbon prototypes. Walsh[15] has suggested that some of the "α-stabilization" we observed with compound VI may simply result from release of gauche interactions, but these are believed[16] to be small in organosilanes because bonds to silicon are long. We undertook some measurements with Chemgraf[17] that were consistent with that. We found in these measurements that the difference in energy between gauche and trans conformations in *n*-propyltrimethylsilane was 4 times smaller than that in VIII. As the gauche interaction in the latter is 0.8 kcal,[18] the two gauche interactions in VI would total only 0.4 kcal.

Clearly, both the α- and β-silyl stabilization effects are small and elusive, but our results indicate that they may be closer in magnitude to each other than has been supposed hitherto.

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[9] Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2908.

[10] Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 6161.

[11] Lyons, A. R.; Neilson, G. W.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 807.

[12] Sakurai, H.; Hosomi, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 568.

[13] Wilt, J. W.; Belmonte, F. G.; Zieske, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 5665.

[14] Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 208.

[15] Walsh, R., personal communication.

[16] O'Neal, H. E.; Ring, M. A. *J. Organomet. Chem.* **1981**, *213*, 419.

[17] Chemgraf, created by E. K. Davies, Chemical Crystallography Laboratory, Oxford University, developed and distributed by Chemical Design Ltd., Oxford.

[18] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

Kinetics of Pyrolysis of Some Alkenylsilanes

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Kinetic measurements and product analyses are described for the pyrolysis of four alkenylsilanes: 4-dimethylsilyl-1-butene (I), 4-(trimethylsilyl)-1-butene (II), 5-(dimethylsilyl)-1-pentene (III), and 5-(trimethylsilyl)-1-pentene (IV). Retroene reactions and secondary radical reactions leading to the observed products are discussed.

Introduction

Our gas-kinetic studies of the pyrolysis of allyltrimethylsilane[1,2] have shown that there are two concurrent primary reactions, homolysis of the silicon–allyl bond to form radicals and retroene elimination of dimethylsilene, and that one of the major products, trimethylvinylsilane, is formed by a secondary radical addition reaction rather than by the unimolecular sequences previously suggested.[3,4] The two concurrent primary reactions were distinguished from each other by pyrolysis with excess methyl chloride, which acted as a selective trap for trimethylsilyl radicals, thus enabling Arrhenius parameters for the homolysis to be deduced from the kinetics of formation of trimethylchlorosilane.

We have subsequently applied the same methods to four higher alkenylsilanes: 4-(dimethylsilyl)-1-butene (I), 4-(trimethylsilyl)-1-butene (II), 5-(dimethylsilyl)-1-pentene (III), and 5-(trimethylsilyl)-1-pentene (IV). Trapping with methyl chloride enabled some conclusions to be drawn about the effect of α- and β-silyl substitution on the stability of the alkyl radicals formed by homolysis of the allyl–carbon bonds in I–IV.[5] In the case of I, it was also possible to investigate quantitatively the radical isomerization reaction (1).[6] As in the pyrolysis of allyltrimethylsilane, these radical-forming primary homolyses

$$^{\bullet}CH_2SiMe_2H \rightarrow Me_3Si^{\bullet} \qquad (1)$$

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[1] Davidson, I. M. T.; Wood, I. T. *J. Organomet. Chem.* **1980**, *187*, C65.

[2] Barton, T. J.; Burns, S. A.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Wood, I. T. *J. Am. Chem. Soc.* **1984**, *106*, 6367.

[3] Sakurai, H.; Hosomi, A.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1970**, 767.

[4] Neider, S. M.; Chambers, G. R.; Jones, M., Jr. *Tetrahedron Lett.* **1979**, *40*, 3793.

[5] Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Revis, A.; Paul, G. C. *Organometallics*, second of three papers in this issue.

[6] Barton, T. J.; Revis, A.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Hughes, K. J.; Gordon, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 4022.