Reactions of Ethyl, Propyl, and Butyl Cations with Methyl- and Ethylsilanes[1]

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Abstract: The gas-phase reactions of $C_2H_5^+$, *sec*-$C_3H_7^+$, and *t*-$C_4H_9^+$ with $(CH_3)_nSiH_{4-n}$ and of $C_2H_5^+$ with $(C_2H_5)_nSiH_{4-n}$ (n = 0, 1, 2, 3, 4) have been studied in a tandem mass-spectrometric apparatus. Reaction cross sections at 1 eV kinetic energy in the laboratory system have been determined for the reaction of $C_2H_5^+$ ions by comparison with the known cross section for hydride ion transfer from SiH_4 to CH_3^+. The predominant processes are H^- and CH_3^- (or $C_2H_5^-$) transfer from the silane to the attacking ion, with the alkyl anion transfer becoming dominant when the number of CH_3 groups in the silane is three or four. The reaction energetics show that CH_3^- and $C_2H_5^-$ transfer occurs as a process involving the simple interchange of the molecular anion between reactants.

Introduction

It has been shown[2,3] recently that CH_3^+ ions react with methylsilanes, $(CH_3)_nSiH_{4-n}$ (n = 1, 2, 3, 4), and ethylsilanes, $(C_2H_5)_nSiH_{4-n}$ (n = 1, 2, 3, 4), to form trivalent siliconium ions by two principal paths: (1) the expected transfer of a hydride ion from silicon to CH_3^+; (2) the unexpected transfer of negatively charged alkyl ions, CH_3^- and $C_2H_5^-$, from silicon to CH_3^+. Alkyl anion abstraction from alkylsilanes appears to be a process not often considered in studies of organosilicon chemistry.[4,5] However, CH_3^+ ions are extremely reactive carbonium ions and, while not particularly difficult to work with in the gas phase, are not often encountered in liquid-phase systems. In order to determine if alkyl anion transfer is a general reaction occurring between alkyl ions and alkylsilanes, and not one limited to CH_3^+ ions, we have studied the reactions of $C_2H_5^+$ with methyl- and ethylsilanes. In addition, we have identified the reactions occurring when $C_3H_7^+$ and $C_4H_9^+$ ions attack methylsilanes.

Experimental Section

1. Apparatus and Techniques. The experiments were carried out in an ion-beam, target gas apparatus that has been described previously.[2] Briefly, it consists of a modified plasma ion source (Colutron Corp.) for ion formation,[6] a Wien velocity filter[7,8] for reactant ion selection, a collision chamber for reaction of the mass-selected ions with the target molecules, and a quadrupole mass filter and electron multiplier for analysis of the ionic products. Electrostatic lenses are used to focus the ion beam into the Wien filter, to decelerate[9] the reactant ions to energies in the range of 0.5–5 eV before they enter the collision chamber, and to focus the ionic products into the quadrupole mass filter.

Absolute cross sections for the reactions of $C_2H_5^+$ ions with the various methyl- and ethylsilanes were determined at 1 eV (laboratory) by comparison with the process[10,11]

$$CH_3^+ + SiH_4 \rightarrow CH_4 + SiH_3^+ \qquad (1)$$

the cross section of which has been redetermined[2] to be σ_2(1 eV, lab) = 54 ± 2 Å^2. The apparent cross sections, determined for any given ionic product, X^+, by the relationship

$$\sigma = \frac{i(X^+)}{i(C_2H_5^+)P} \qquad (2)$$

where the i's are currents and P is the pressure, were extrapolated to the limit of zero pressure in the collision chamber in order to eliminate the influence of further collision reactions of product ions. Pressures in the collision chamber were measured with a capacitance manometer and were varied from 0.5 to 2.0 × 10^{-3} Torr. We believe that the cross sections measured at 1 eV laboratory energy of $C_2H_5^+$ are accurate to within ~15%. Reaction cross sections were not measured for the reactions of propyl and butyl ions.

The form of the dependence of relative cross section on the kinetic energy of $C_2H_5^+$ was used to classify experimentally the reactions as exothermic or endothermic.[2,3] All ion intensities were corrected for the naturally occurring isotopes of silicon and carbon, namely, ^{29}Si = 4.7%, ^{30}Si = 3.1%, and ^{13}C = 1.1%.

2. Materials. SiH_4 was purchased from the Matheson Co. while all the alkylsilanes, with the exception of $C_2H_5SiH_3$, were obtained from Peninsular Chemresearch. $C_2H_5SiH_3$ was prepared by the reduction of $C_2H_5SiCl_3$ (Peninsular Chemresearch) with $LiAlH_4$ (Alpha Inorganics). Propane, isobutane, and neopentane which were used in the ion source to produce $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ ions, respectively, were Phillips Research Grade hydrocarbons. All gases and liquids were subjected to freeze–pump–thaw cycles on a high-vacuum line prior to use.

Results and Discussion

1. Reactions of Ethyl Ions with Methylsilanes. The reactions of $C_2H_5^+$ with the series $(CH_3)_nSiH_{4-n}$ (n = 0, 1, 2, 3, 4) are considerably simpler than those of CH_3^+, in that hydride ion removal and methide ion (CH_3^-) removal from the silane comprise more than 97% of the total reaction for all values of n. One reason for this greater selectivity of $C_2H_5^+$ toward hydride and methide ion removal processes is that the lower ionization potential of C_2H_5 (8.38 eV)[12] as compared with CH_3 (9.84 eV)[12] eliminates simple charge transfer as an energetically feasible reaction channel. Only in the case of the reaction of $C_2H_5^+$ with $(CH_3)_4Si$ is any charge transfer observed at all and in this single case it amounts to only about 1% of the total reaction.

The major reactions (>97%) of $C_2H_5^+$ with the silane series $(CH_3)_nSiH_{4-n}$ (n = 0, 1, 2, 3, 4) are shown in Table I. All the reactions were observed to be exothermic. Also shown in Table I are the standard enthalpy changes calculated from thermochemical data,[13,14] the reaction cross sections at 1 eV reactant ion energy, and phenomenological rate constants calculated from the cross sections and the ion velocity.

In the remainder of this section we shall discuss some further details of the reactions shown in Table I.

(a) $C_2H_5^+$ + SiH_4. Only one significant product, namely, SiH_3^+, is observed when $C_2H_5^+$ ions having 1 eV of kinetic energy are injected in SiH_4 and this product must be produced by reaction 3 in Table I. This process must be a simple hydride ion transfer between reactants because there is not sufficient energy released in the process to permit further dissociation of the neutral product.

The reaction occurs with a cross section and phenomenological rate constant (cf. Table I) that are 93% of the values for Langevin-type orbiting collisions.[15]

(b) $C_2H_5^+$ + CH_3SiH_3. Only two reactions are observed when $C_2H_5^+$ ions collide with CH_3SiH_3, namely, those designated as reactions numbered 4 and 5 in Table I. These two reactions comprising H^- loss, (4), and CH_3^- loss, (5), from

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Table I. Major Reactions of Ethyl Cations with Monosilane and Methylsilanes at 1 eV (lab)

reaction no.	reaction	$\Delta H°$, kcal	σ, Å^2	$10^9 k$ cm^3/s
3	$C_2H_5^+ + SiH_4 \rightarrow SiH_3^+ + C_2H_6$	−8	51	1.3
4	$C_2H_5^+ + CH_3SiH_3 \rightarrow CH_3SiH_2^+ + C_2H_6$	−20	81	2.1
5	$C_2H_5^+ + CH_3SiH_3 \rightarrow SiH_3^+ + C_3H_8$	−1	9.3	0.24
6	$C_2H_5^+ + (CH_3)_2SiH_2 \rightarrow (CH_3)_2SiH^+ + C_2H_6$	−35	62	1.6
7	$C_2H_5^+ + (CH_3)_2SiH_2 \rightarrow CH_3SiH_2^+ + C_3H_8$	−12	50	1.3
9	$C_2H_5^+ + (CH_3)_3SiH \rightarrow (CH_3)_3Si^+ + C_2H_6$	−49	22	0.57
10	$C_2H_5^+ + (CH_3)_3SiH \rightarrow (CH_3)_2SiH^+ + C_3H_8$	−27	91	2.3
12	$C_2H_5^+ + (CH_3)_4Si \rightarrow (CH_3)_3Si^+ + C_3H_8$	−46	99	2.6

CH_3SiH_3 must be exactly as written in order to be exothermic processes as demanded by experimental observation. One thus concludes that (4) and (5) are elementary processes in which simple transfers of H^- and CH_3^- between the reactants occur. Such simple transfers of H^- ions have been observed frequently.[2,3] The occurrence of CH_3^- transfer in the thermoneutral (or resonant) isotopic reaction between $(CH_3)_2{}^{10}B^+$ and $(CH_3)_3{}^{11}B$ to produce $(CH_3)_3{}^{10}B$ and $(CH_3)_2{}^{11}B^+$ has been reported.[16] We believe the present results to be the first demonstration of the simple transfer of CH_3^- between reactants in a process involving chemical change. Our previous studies[2,3] of CH_3^+-ion attack on alkylsilanes suggested the occurrence of simple alkide ion transfer but with CH_3^+ ions the neutral products were not unambiguously defined as in the present case.

The cross sections for (4) and (5) (cf. Table I) show that, as expected, $C_2H_5^+$ ions are more discriminating in their reactions with CH_3SiH_3 than are the more reactive CH_3^+ ions. Thus, the relative occurrences of abstraction of CH_3^- and H^- from the methylsilanes, $(CH_3)_nSiH_{4-n}$ (n = 1, 2, 3, 4), by CH_3^+ is almost statistical in the number of CH_3 groups and H atoms bound to silicon,[2] i.e., $\sigma(CH_3^-)/\sigma(H) \approx 1/4$. On the other hand, as may be seen in Table I, the probability for the less reactive $C_2H_5^+$ ions to abstract a CH_3^- ion rather than an H^- ion from CH_3SiH_3 is only about 1/9. This discrimination is probably due to the differences in energetic requirements of the two reactions.

(**c**) **$C_2H_5^+$ + $(CH_3)_2SiH_2$.** Two processes comprise 99% of the total reaction when $C_2H_5^+$ ions are injected into $(CH_3)_2SiH_2$ and these are H^- transfer and CH_3^- transfer, as shown by reactions 6 and 7, respectively, in Table I. It is energetically possible for the neutral products of (6) to be $C_2H_4 + H_2$ instead of C_2H_6 and, therefore, (6) may not be a simple H^- transfer. On the other hand, (7) must be the simple CH_3^- transfer, as written, in order for the reaction to be exothermic. Thus, we have here a second example of an elementary chemical reaction involving simple CH_3^- transfer between reactants.

The relative probabilities of H^- and CH_3^- abstraction are seen in Table I to be nearly statistical. This is probably a consequence of the fact that for $(CH_3)_2SiH_2$ both processes are quite exothermic and the difference in energetic requirements of the two reactions is small.

In addition to the two major processes (6) and (7), small amounts of SiH_3^+ are also observed as products from collisions of $C_2H_5^+$ with $(CH_3)_2SiH_2$. The reaction is an endothermic process having a threshold energy of 1.6 eV in the laboratory frame of reference. Reaction 8, which could occur as a unimolecular dissociation of $(CH_3)_2SiH^+$

$$C_2H_5^+ + (CH_3)_2SiH_2 \rightarrow SiH_3^+ + C_2H_6 + C_2H_4 \quad (8)$$

following H^- transfer, (6), or as a unimolecular dissociation of $(CH_3)_2SiH_3^+$ subsequent to H^+ transfer,[16] is endothermic[13,14] by 29 kcal; this predicts a threshold in the laboratory frame of reference of 1.9 eV. Given the uncertainties in the thermochemical value of $\Delta H°$ (±5 kcal) and in the experimental threshold of the reaction (±0.2 eV), we think that the data suggest strongly that (8) is responsible for the formation of SiH_3^+. We have no firm basis for a choice between the two mechanisms mentioned.

(**d**) **$C_2H_5^+$ + $(CH_3)_3SiH$.** About 98% of the total reaction observed when $C_2H_5^+$ ions react with $(CH_3)_3SiH$ are accounted for by H^- and CH_3^- loss from the neutral reactant, as shown by reactions 9 and 10, respectively, in Table I. It is possible, energetically, for the electrically neutral products of (9) to be $C_2H_4 + H_2$, so the reaction may not be the simple H^- transfer as written. Similarly, (10), as written, is sufficiently energetic for the electrically neutral products to be $C_2H_4 + CH_4$.

Inspection of the reaction cross sections in Table I reveals that the probability of removing a CH_3^- rather than an H^- from $(CH_3)_3SiH$ is ~4, i.e., a little greater than, but near, the statistical value of 3.

An endothermic process with a threshold below 1 eV results in the formation of the product ion $CH_3SiH_2^+$. The cross section at 1 eV (laboratory) is 1.8 Å^2. We suggest the reaction forming this product to be

$$C_2H_5^+ + (CH_3)_3SiH \rightarrow CH_3SiH_2^+ + C_2H_6 + C_2H_4;\ \Delta H° = +18 \text{ kcal} \quad (11)$$

which can be viewed as a unimolecular dissociation of the ionic product of hydride transfer (9) or as a unimolecular dissociation of $(CH_3)_3SiH_2^+$ following H^+ transfer.[16]

(**e**) **$C_2H_5^+$ + $(CH_3)_4Si$.** A single ionic product, namely, $(CH_3)_3Si^+$, produced by the CH_3^- abstraction shown as (12) in Table I, accounts for more than 98% of the total reaction of this reactant pair. Hydride ion abstraction from $(CH_3)_4Si$ by $C_2H_5^+$ is not observed, a fact that is consistent with our previous studies[2] of the reactions of CH_3^+ with $(CH_3)_4Si$.

2. Reactions of Ethyl Ions with Ethylsilanes. The reactions of $C_2H_5^+$ with the series $(C_2H_5)_nSiH_{4-n}$ are very similar to those of $C_2H_5^+$ with the methylsilanes and only in the cases of the higher members of the ethylsilane series are significantly greater complexities observed. The major reactions undergone by this reactant pair along with estimated standard enthalpy changes, reaction cross sections, and phenomenological rate constants are shown in Table II. All the reactions shown were observed to be exothermic.

(**a**) **$C_2H_5^+$ + $C_2H_5SiH_3$.** The elementary processes of H^- transfer and $C_2H_5^-$ transfer, shown as reactions 13 and 14 in Table II, comprise more than 98% of the total reaction of this system. The magnitudes of the standard enthalpy changes indicate that the reactions must be exactly as written. Therefore, (13) and (14) represent simple transfers of H^- and $C_2H_5^-$ between the reactants $C_2H_5^+$ and $C_2H_5SiH_3$. The simple transfer between reactants of a large complex species such as $C_2H_5^-$ is quite remarkable and to our knowledge has not been reported previously. In an earlier paper[3] we reported that CH_3^+ reacted with ethylsilanes to remove $C_2H_5^-$ from the silane but the energetic possibility of dissociation of any C_3H_8 formed in the process precluded a proof of simple $C_2H_5^-$ transfer.

(**b**) **$C_2H_5^+$ + $(C_2H_5)_2SiH_2$.** The two major products (~93% of the total) observed in this system are $(C_2H_5)_2SiH^+$ and $C_2H_5SiH_2^+$ as shown in reactions 15 and 16 of Table II. In this

Table II. Major Reactions of Ethyl Cations with Ethylsilanes at 1 eV (lab)

reaction no.	reaction	$\Delta H°$, kcal	σ, Å^2	10^9k, cm^3/s
13	$C_2H_5^+ + C_2H_5SiH_3 \rightarrow C_2H_5SiH_2^+ + C_2H_6$	−16[a,b]	102	2.6
14	$C_2H_5^+ + C_2H_5SiH_3 \rightarrow SiH_3^+ + C_4H_{10}$	−2[a]	6.5	0.17
15	$C_2H_5^+ + (C_2H_5)_2SiH_2 \rightarrow (C_2H_5)_2SiH^+ + C_2H_6$	−44[b]	47	1.2
16	$C_2H_5^+ + (C_2H_5)_2SiH_2 \rightarrow C_2H_5SiH_2^+ + C_4H_{10}$	−18[b]	59	1.5
17	$C_2H_5^+ + (C_2H_5)_3SiH \rightarrow (C_2H_5)_3Si^+ + C_2H_6$	−52	16	0.41
18	$C_2H_5^+ + (C_2H_5)_3SiH \rightarrow (C_2H_5)_2SiH^+ + C_4H_{10}$	−38[b]	62	1.6
19	$C_2H_5^+ + (C_2H_5)_4Si \rightarrow (C_2H_5)_3Si^+ + C_4H_{10}$	−45	58	1.5
20	$C_2H_5^+ + (C_2H_5)_4Si \rightarrow (C_2H_5)_2SiH^+ + C_4H_{10} + C_2H_4$	−9[b]	23	0.59

[a] Estimated using the average CH_2 increment to $\Delta H_f°$ of neutral silane molecules of −3 kcal/mol.[13] [b] Estimated using the average CH_2 increment to $\Delta H_f°$ of ions derived from silanes of −8 kcal/mol.[13]

Table III. Major Reactions of Propyl and Butyl Ions with Methylsilanes at 1 eV (lab)

reaction no.	reaction	$\Delta H°$, kcal	rel probability
21	$(CH_3)_2CH^+ + CH_3SiH_3 \rightarrow CH_3SiH_2^+ + C_3H_8$	+2	38
22	$(CH_3)_2CH^+ + (CH_3)_2SiH_2 \rightarrow (CH_3)_2SiH^+ + C_3H_8$	−13	58
23	$(CH_3)_2CH^+ + (CH_3)_2SiH_2 \rightarrow CH_3SiH_2^+ + i\text{-}C_4H_{10}$	+9	3
24	$(CH_3)_2CH^+ + (CH_3)_3SiH \rightarrow (CH_3)_3Si^+ + C_3H_8$	−27	36
25	$(CH_3)_2CH^+ + (CH_3)_3SiH \rightarrow (CH_3)_2SiH^+ + i\text{-}C_4H_{10}$	−7	10
26	$(CH_3)_2CH^+ + (CH_3)_4Si \rightarrow (CH_3)_3Si^+ + i\text{-}C_4H_{10}$	−21	100
27	$(CH_3)_3C^+ + CH_3SiH_3 \rightarrow CH_3SiH_2^+ + i\text{-}C_4H_{10}$	+21	1
28	$(CH_3)_3C^+ + (CH_3)_2SiH_2 \rightarrow (CH_3)_2SiH^+ + i\text{-}C_4H_{10}$	+6	4
29	$(CH_3)_3C^+ + (CH_3)_3SiH \rightarrow (CH_3)_3Si^+ + i\text{-}C_4H_{10}$	−8	3
30	$(CH_3)_3C^+ + (CH_3)_3SiH \rightarrow (CH_3)_2SiH^+ + \text{neo-}C_5H_{12}$	+9	0.3
31	$(CH_3)_3C^+ + (CH_3)_4Si \rightarrow (CH_3)_3Si^+ + \text{neo-}C_5H_{12}$	−5	1

case, as with that of $(CH_3)_2SiH_2$, sufficient energy is released in (15) to permit the neutral products to be $C_2H_4 + H_2$. Therefore, (15) may not be a simple H^- transfer as indicated in Table II. On the other hand, there is no ambiguity about the $C_2H_5^-$ transfer process in (16). In order for the formation of $C_2H_5SiH_2^+$ from these reactants to be exothermic, the reaction must be exactly as written; i.e., this reaction is another example of a simple transfer of $C_2H_5^-$.

(c) **$C_2H_5^+$ + $(C_2H_5)_3SiH$.** The ions $(C_2H_5)_3Si^+$ and $(C_2H_5)_2SiH^+$ account for about 81% of the total ionic products of this reactant pair and the reactions forming these major projects are shown as simple H^- and $C_2H_5^-$ transfers, respectively, in reactions 17 and 18 of Table II. The enthalpy changes in this case are such that further dissociation of both sets of neutral products can occur. Thus (17) and (18) may not be simple transfers, as written, but may involve more dissociated neutral products.

In addition to the major reactions shown in Table II, small amounts of products are observed at masses 59, 73, 86, and 116 amu. The product ion at 116 amu is $(C_2H_5)_3SiH^+$ formed by exothermic[12,13] charge transfer from the 1-2% of $^{13}C^{12}CH_4^+$ in the reactant beam. The reactions responsible for the other products have not been identified.

(d) **$C_2H_5^+$ + $(C_2H_5)_4Si$.** The major product of this reaction pair at 1 eV is $(C_2H_5)_3Si^+$ formed in the $C_2H_5^-$ abstraction process as shown by reaction 19 in Table II. However, a much greater variety of reactions occurs in this system than in the other silanes investigated, so that (19) comprises only 58% of the total reaction. As in the case of the $C_2H_5^+$-$(C_2H_5)_3SiH$ system, (19) may not be a simple $C_2H_5^-$ transfer between reactants because sufficient energy is released to permit further dissociation of the neutral product.

The next most probable reaction in this system is one which produces an ion of 87 amu, the most likely structure of which is $(C_2H_5)_2SiH^+$. The reaction forming it is most likely that shown as (20) in Table II. This reaction can be pictured as a $C_2H_5^-$ transfer followed by unimolecular dissociation of the product ion or as a proton transfer[16] followed by unimolecular dissociation of $(C_2H_5)_4SiH^+$.

A slight amount of hydride transfer amounting to about 0.6% of the total reaction is observed in this system and a product ion at 43 amu, which is most likely $C_3H_7^+$, is also found. In addition, endothermic reactions of small cross sections to produce $C_2H_5SiH_2^+$, $CH_3SiH_2^+$, and SiH_3^+ are observed. Other than the hydride transfer, none of these reactions has been identified.

3. Reactions of Propyl and Butyl Ions with Methylsilanes. Product ion distributions have been determined for the reactions of $C_3H_7^+$ and $C_4H_9^+$ ions, having 1 eV of kinetic energy, with the series $(CH_3)_nSiH_{4-n}$ and the reactions identified are shown in Table III. Absolute reaction cross sections were not determined in these systems but the relative probabilities of occurrence of the various reactions in the two systems are shown in Table III, along with the standard enthalpy changes calculated from thermochemical data.[12,13] The total cross sections for reaction of $C_3H_7^+$ with the silanes seem to be comparable to those for reactions of $C_2H_5^+$; however, the total cross sections of the reactions of $C_4H_9^+$ appear to be lower by one to two orders of magnitude.

Propyl ions were obtained by the decomposition of isobutane in the plasma ion source. It is, of course, possible that the reactant ions of 43 amu so produced are $(CH_3)_2CH^+$ or $CH_3CH_2CH_2^+$ or a mixture of both. We believe, however, that the propyl ion beam was mostly $(CH_3)_2CH^+$ because of the striking difference in product distribution produced as compared with that found for the reaction of $C_2H_5^+$ ions with $(CH_3)_nSiH_{4-n}$. Thus, on energetic grounds, we expect the reactions of $CH_3CH_2CH_2^+$ to be quite similar to those of $C_2H_5^+$ but those of $(CH_3)_2CH^+$ to be markedly different.

It is to be seen in Table III that hydride transfer from CH_3SiH_3 to $C_3H_7^+$, (21), occurs but CH_3^- transfer, which would be endothermic for ground-state reactants by 22 kcal/mol, is not observed. Both hydride transfer, (22), and CH_3^- transfer, (23), from $(CH_3)_2SiH_2$ to $(CH_3)_2CH^+$ take place, although H^- transfer is much more probable. Both types of transfer occur with $(CH_3)_3SiH$, i.e., (24) and (25), but again the relative probabilities favor H^- transfer and are far removed from the statistical distributions. We note that in the cases of

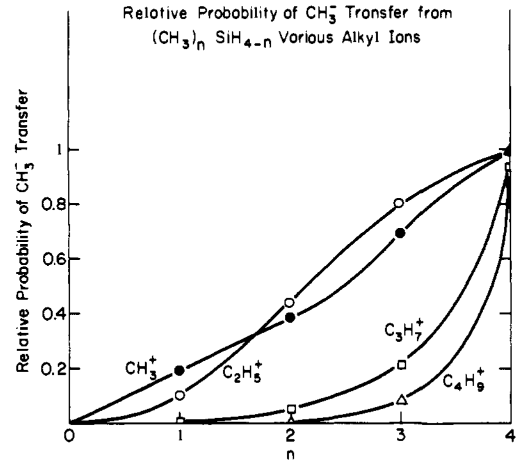

Figure 1. Relative probability of CH_3^- transfer in the reaction of alkyl ions with $(CH_3)_nSiH_{4-n}$ as a function of n: ●, CH_3^+; ○, $C_2H_5^+$; □, $C_3H_7^+$; △, $C_4H_9^+$.

$(CH_3)_2SiH_2$ and $(CH_3)_3SiH$ the energetics strongly indicate that simple transfer of CH_3^- between reactants is taking place. The only significant reaction of $C_3H_7^+$ with $(CH_3)_4Si$ is removal of CH_3^- as shown by (26). In this latter reaction dissociation of C_4H_{10} to C_3H_6 + CH_4 is energetically feasible so that (26) may not be simple CH_3^- transfer.

The relative probabilities for CH_3^- transfer rather than H^- transfer in the reactions of various alkyl ions with the silane series $(CH_3)_nSiH_{4-n}$ (n = 0-4) are shown in Figure 1. Here it is to be seen graphically how different are the reactions of $C_3H_7^+$ from those of $C_2H_5^+$ and the even less discriminating CH_3^+. Thus in terms of the predominant reactions of H^- and CH_3^- transfer, the CH_3^+ reactant behaves almost statistically. Energetic limitations restrict somewhat the CH_3^- transfer to $C_2H_5^+$ for CH_3SiH_3 (n = 1); however, the statistical distribution is approached for the higher members of the series. Energetic restrictions on the CH_3^- transfer from the lower members of the series (n = 1, 2, 3) are evident with $C_3H_7^+$ and even more pronounced with $C_4H_9^+$ reactant ions.

The intensities of product ions from the reaction of $C_4H_9^+$ ions with the silane series $(CH_3)_nSiH_{4-n}$ were one to two orders of magnitude lower than observed for the reaction of $C_3H_7^+$ ions, even though the intensities of the reactant ions were comparable. This, in itself, is evidence that the major fraction of the $C_4H_9^+$ beam (obtained from ionization and dissociation of neopentane in the ion source) is comprised of $(CH_3)_3C^+$ ions, since n-$C_4H_9^+$ and $(CH_3)_2CHCH_2^+$ would be expected to behave similarly to $C_2H_5^+$ and $CH_3CH_2^+CHCH_3$ would most likely react similarly to $(CH_3)_2CH^+$. This conclusion is in agreement with a recent report[17] that the electron impact ionization of neopentane produces $(CH_3)_3C^+$.

Although the extent of reaction was small, the major processes observed along with their relative probabilities and calculated enthalpy changes[12,13] are shown in Table III. Three of the reactions of $C_4H_9^+$ in Table III are endothermic for ground-state reactants and undoubtedly this is the reason for such small probabilities of reaction. It is likely that the ionic reactant in (27), a strongly endothermic reaction, is an isomeric and more reactive $C_4H_9^+$ ion. The small extent of reaction indicates the low abundance of such species in the $C_4H_9^+$ beam. A similar reason could explain the occurrence of the endothermic processes (28) and (30) at 1 eV (lab) but in these cases an internal energy of only a few tenths of an eV could also be responsible. The relative probabilities of CH_3^- transfer rather than H^- transfer to $C_4H_9^+$ from $(CH_3)_4SiH_{4-n}$ are also shown in Figure 1 and here it is to be seen graphically how the nature of the reactions of $C_4H_9^+$ differ from those of the other alkyl ions.

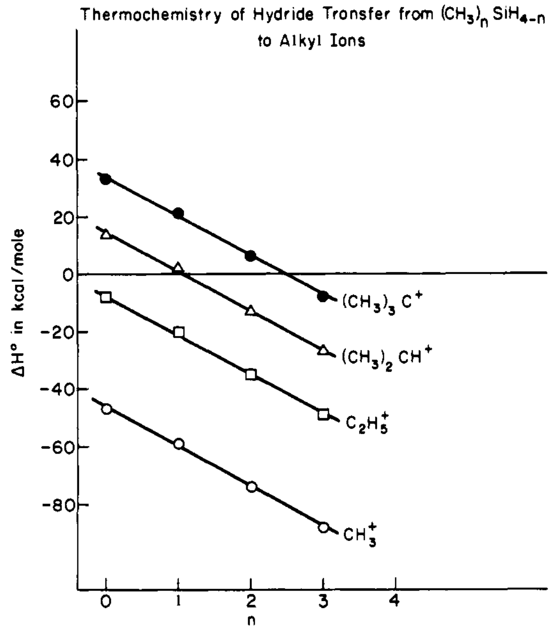

Figure 2. Thermochemistry of hydride transfer from $(CH_3)_nSiH_{4-n}$ to alkyl cations.

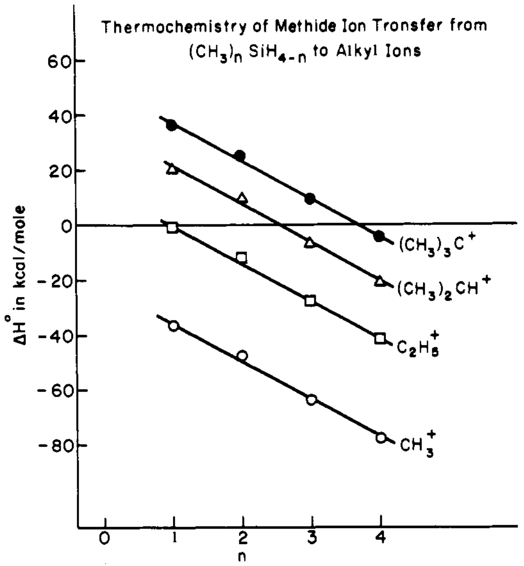

Figure 3. Thermochemistry of CH_3^- transfer from $(CH_3)_nSiH_{4-n}$ to alkyl cations.

4. Thermochemistry of the Reactions of Alkyl Ions with Methylsilanes. It has been shown that the predominant reactions of alkyl ions with the methylsilanes are hydride transfer and CH_3^- transfer from the silane to the attacking ion. Our classification ofthe various reactions as exothermic or endothermic on the basis of the dependence of cross section on kinetic energy agrees, in general, with the standard enthalpy changes for ground-state reactants calculated from thermochemical data. The few cases in which such agreement was not obtained can be rationalized on the basis of the existence of up to 0.2-0.3 eV of internal excitation in the reactant ion and/or of the presence of more reactive isomers in the ion beam. The thermochemistry of the H^- and CH_3^- transfer from methylsilanes,[13,14] which is confirmed by our experimental results, is summarized graphically in Figures 2 and 3.

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References and Notes

(1) U.S. Department of Energy Document No. EY-76-S-02-3416-11.
(2) G. W. Goodloe, E. R. Austin, and F. W. Lampe, *J. Am. Chem. Soc.*, **101**, 3472 (1979).
(3) G. W. Goodloe and F. W. Lampe, *J. Am. Chem. Soc.*, **101**, 5649 (1979).
(4) D. H. O'Brien and T. J. Hairston, *Organomet. Chem. Rev., Sect. A*, **7**, 95 (1971).
(5) R. J. P. Corrier and M. Henner, *J. Organomet. Chem.*, **74**, 1 (1974).
(6) M. Menzinger and L. Wåhlin, *Rev. Sci. Instrum.*, **40**, 102 (1969).
(7) W. Wien, *Ann. Phys. (Leipzig)*, **65**, 440 (1898).
(8) L. Wåhlin, *Nucl. Instrum. Methods*, **38**, 133 (1965).
(9) M. Menzinger and R. Wolfgang, *J. Chem. Phys.*, **50**, 2991 (1969).
(10) G. W. Stewart, J. M. S. Henis, and P. P. Gaspar, *J. Chem. Phys.*, **57**, 1990 (1972).
(11) T. M. H. Cheng, T. Y. Yu, and F. W. Lampe, *J. Phys. Chem.*, **77**, 2587 (1973).
(12) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).
(13) P. Potzinger, A. Ritter, and J. R. Krause, *Z. Naturforsch. A*, **30**, 347 (1975).
(14) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969).
(15) E. W. McDaniel, V. Cermak, A. Dalgarno, E. E. Ferguson, and L. Friedman, "Ion-Molecule Reactions", Wiley-Interscience, New York, 1970, p 13 ff.
(16) M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 1433 (1976).
(17) D. M. Shold and P. Ausloos, *J. Am. Chem. Soc.*, **100**, 7915 (1978).

Methyl-Substituted Allyl Cations. A Comparison of Experimental Stability, Rotational Barrier, and Solvolysis Data with ab Initio Calculations

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Abstract: Three sources of quantitative data for methyl-substituted allyl cations are available experimentally: Gas phase heats of formation, rotational barriers in solution, and rates of solvolysis. NMR chemical shifts also provide an index of charge distribution. This paper draws all these lines together in comparison with results of STO-3G ab initio molecular orbital calculations performed on planar and perpendicular methyl-substituted allyl cations. Sequential substitution of the terminal positions by one, two, three, and four methyl groups stabilizes allyl cations electronically by 17, 15, 13, and 11 kcal/mol, respectively; a methyl group on the central carbon has a much smaller stabilizing effect (~5 kcal/mol). The steric strain for the first *endo*-methyl group was determined to be 3 kcal/mol, whereas a second *endo*-methyl experiences a somewhat greater strain of 5 kcal/mol. Allyl solvolysis rates correlate well with gas phase allyl cation stability data, but there is a reduction in magnitude due to solvation. The calculated rotational barriers also are 4–12 kcal/mol higher than the activation free enthalpies determined in superacid solution; the difference provides further evidence for differential solvation effects—the more highly delocalized planar forms are solvated to a lesser extent than their rotational transition states. The rotational barrier of the parent allyl cation is predicted to be 34 kcal/mol in the gas phase but to decrease to 23.7 ± 2 kcal/mol in superacid solution.

Allyl cations, the prototype π delocalized carbenium ions, have been studied experimentally for many decades.[1] The solvolysis studies, which first proved the existence of allyl cations as short-lived reactive intermediates, preceded generation and direct observation of stable allyl cations in superacid media.[1] In recent years, many thermodynamic data on allyl cations in the gas phase have become available, particularly by means of ion cyclotron resonance measurements.[2]

Previous theoretical studies have concentrated on the parent allyl cation.[3-8] With few exceptions,[9a] methyl-substituted allyl cations have only been investigated by semiempirical methods[10,11] or by ab initio calculations without geometry optimization.[12] Since these calculations give considerable deviations with experimentally determined energy differences, we undertook a comprehensive ab initio MO study of methyl-substituted allyl cations with geometry optimization in order to assess and to augment the experimental data.

Methods

All ab initio MO calculations on planar and perpendicular allyl cations were performed by utilizing the STO-3G minimal basis set[13] and the Gaussian 70 series of programs.[14] For the planar allyl cations, the heavy atom framework was fully optimized, until the total energy was constant to better than 10^{-5} au, bond lengths to 0.001 Å, and angles to 0.1 degrees; standard bond lengths and angles were used for the CH bonds (Table I). The energy values thus obtained were only slightly higher than those of completely optimized structures, e.g., **1** (ΔE = 0.5 kcal/mol), **4** (ΔE = 0.7 kcal/mol), and **6** (ΔE = 1.0 kcal/mol).[15] The fully optimized structures are included in Table I.

The geometries of the perpendicular allyl cations were based on the completely optimized structure of the parent system.[7] This geometry proved to be satisfactory also for substituted cations, since complete optimization of perpendicular **5** and **8** (rotation of CH_2 group) resulted in energies only 0.5 and 1.8 kcal/mol, respectively, below those given in Table IV.

Since the errors introduced by our less than complete optimization appear to be small and more or less constant, they tend to cancel in many of the energy comparisons. In section A2, it will be shown that the relative energies of allyl cations, thus calculated, coincide with experimental gas phase data, which justifies the approximations employed.

Results and Discussion

A. Planar Allyl Cations. 1. Geometry. Heavy-Atom Framework. The results of STO-3G calculations on the planar allyl cations are summarized in Table I. All allyl cations were assumed to have planar heavy-atom ground states. This was justified on the basis of the planar preference of a member of the set more prone to twisting: An energy increase was calculated when the 3,3-dimethylallyl cation (**8**), which has a relatively low rotational barrier (see below), was twisted by only 15° around the C-2–C-3 bond. In contrast, INDO predicted

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