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Kinematics of Hydride Transfer Reactions in Methylsilane¹

by

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MASTER

Abstract

Kinematics of hydride transfer reactions in methylsilane have been investigated by isotopic distribution measurements and kinetic energy analysis of product ions in a tandem mass spectrometer. Reactions are observed to proceed predominately via a direct stripping type process, yielding an $\text{CH}_3\text{SiD}_2^+$ or $\text{CH}_3\text{SiH}_2^+$ ion with very little kinetic energy, and by a complex formation mechanism that is particularly prominent at low collision energies. The process is interpreted as making a transition from complex in nature at low energies to direct at high collision energies.

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INTRODUCTION

In a preceding paper² we have presented data and rate constants for a large number of ion-molecule reactions in methylsilane. The bimolecular reactions occurring in this system are dominated by those involving the net transfer of small particles, H^- , H_2^- , H . It has been shown³ that these type reactions, which are also dominant in various other silane systems, for the most part occur via direct stripping type mechanisms. For example, at the lowest collision energies studied, the reaction

was shown to proceed predominately through both direct H^- and H atom transfer mechanisms, while about 20% of the observed product could be attributed to the formation of a long-lived complex.

This paper examines similar reactions in methylsilane in order to further characterize the nature of these reactions and to observe the effects of an addition of an alkyl group to the silane system.

EXPERIMENTAL

The tandem mass spectrometer used in this study has been described previously,^{3,4} The experimental procedure consists of injecting mass selected ions with kinetic energies variable down to ~ 1 eV into a collision chamber containing the neutral target gas. Products scattered into the forward direction are collected, energy analyzed in a retarding-field energy analyzer, mass analyzed and detected. Performance of the energy analyzer has been described previously.³

Methylsilane (CH_3SiH_3) gas, obtained from the P.C.R. Co., was fractionated on the vacuum line and checked mass spectrometrically for satisfactory purity. Methylsilane- d_3 (CH_3SiD_3) was synthesized by reduction of CH_3SiCl_3 with LiAlD_4 in di-n-butylether solution.⁵ It was purified in the same manner as CH_3SiH_3 .

RESULTS & DISCUSSION

In previous work in this laboratory³ we interpreted the kinematics of H and H^- transfer reactions in monosilane in terms of two models. In the spectator stripping model,⁶ in which the transfer of a particle takes place with little or no redistribution of energy among the reactants, the "spectator" particle is left with essentially the same energy it possessed before reaction. Then for a reaction involving transfer of a neutral particle from the target to the projectile ion we can predict the kinetic energy of the product ion, namely:

$$E_3(s) = \frac{m_1}{m_3} E_1 \quad (2)$$

where m_1 , E_1 are the mass and energy of the projectile, m_3 , $E_3(s)$ are the mass and energy of the product predicted by the stripping model.² The complex formation model^(6,7) refers to the formation of a persistent intermediate complex in which there occurs complete randomization of the internal energy of the complex, followed by a statistical unimolecular decomposition to products. In this situation the kinetic energy of the product ions is predicted to be:

$$E_3(c) = \frac{m_3 m_1}{(m_1 + m_2)^2} E_1 \quad (3)$$

where m_1 , E_1 are mass and energy of projectile ion, m_2 is the mass

of the target, and m_3 , E_3 (c) are the mass and kinetic energy of the product ion predicted by the complex model.

Table I lists the major reactions observed in methylsilane that can be described as net transfers of one or more hydrogenic particles. In the remainder of this paper we discuss for each reactant ion the kinematics of the reactions shown.

(a) $\text{CH}_3\text{SiH}_2^+$ (m/e 45). As indicated previously² we believe the most probable structure of the m/e 45 ion formed by electron-impact on CH_3SiH_3 to be as written. When $\text{CH}_3\text{SiH}_2^+$ is injected into CH_3SiD_3 products of reaction (4) are observed at m/e 46 (CH_3SiHD^+) and m/e 47 ($\text{CH}_3\text{SiD}_2^+$). We rule out $\text{CH}_3\text{SiH}_3^+$ as contributing to m/e 46 since it is not observed when $\text{CH}_3\text{SiH}_2^+$ reacts with CH_3SiH_3 .² A typical product mass spectrum at collision energies of 0.94 eV, center-of-mass, is shown in Fig. 1a. The fact that virtually no product is observable at m/e 48 indicates that hydrogens bound to the carbon atoms are not participating in the reaction. Formation of a complex followed by dissociation with complete scrambling of H and D atoms bound to the silicones only would yield products indicated by reaction 10a - 10c, in the ratio a:b:c = 1:6:3. As is evident from Fig. 1a, $\text{CH}_3\text{SiD}_2^+$ is present in much

greater abundance than would be the case for a randomized complex mechanism. As in the analogous reaction in monosilane³ we conclude that this ion arises predominately via a direct D⁻ transfer from the

target to the projectile indicated by reaction (11). The kinetic energy distribution of product ions at m/e 47, shown in Fig. 2

for two different collision energies, confirms this conclusion.

In the framework of the spectator stripping model, the product ion is the spectator to the reaction. It receives therefore very little momentum from the projectile, and thus should have a very low (thermal) kinetic energy and, moreover, this kinetic energy should be independent of collision energy. This is seen to be the case in Fig. 2. The point marked "c" indicates the most probable energy expected from the complex model, calculated from equation (3). (As noted previously³ the peak in the product energy distribution at $\sim 0.5 - 1.0$ eV is probably an instrumental artifact due to poor collection efficiency of low energy ions. We believe the actual maximum should be closer to, or at, zero energy).

From the relative intensities of m/e 46 and 47 one may estimate the contributions from complex and direct processes to the total product ion production. At the lowest energies measured, ~ 0.5 eV center-of-mass, about 60% of the total product may be accounted for by the complex process resulting in scrambling of H and D atoms. This contribution from the complex process decreases rapidly with increasing collision energy such that at 2.0 eV collision energy, the complex accounts for only 20% of the total product production, the remainder occurring via the direct D⁻ transfer. This transition from complex to direct processes as collision energy increases has been observed quite frequently³,

and is due to the inability of the complex to accommodate the internal energy it acquires at increased collision energies.

(b) CH_3SiH^+ (m/e 44). The major reaction of this ion was reported to be that involving the net transfer of either H^- or H from target to projectile as shown by reaction 5 in Table I. This particular reaction is of great interest because of the variety of possible mechanisms leading to the same product ion. The equivalent reaction in monosilane, indicated by reaction (1) was reported to proceed via direct H atom and H^- transfer, as well as through a complex. The various isotopic products expected for these mechanisms when CH_3SiD_3 is used as target, and when it is assumed that the methyl hydrogens are not involved, are illustrated in reaction (12), viz.

The product in (12a) would be expected from a D-atom transfer process, while that of (12b) is formed via D^- transfer. A complex mechanism statistically, would yield both species in the ratio $a:b = 1:1$. Fig. 1b shows a typical product mass spectrum at 1.4 eV, center of mass. As evident from the figure both isotopic species are present in nearly equal amounts. The ratio of $a:b$ remains fairly constant as a function of collision energy up to about 5 eV with the $\text{CH}_3\text{SiD}_2^+$ product becoming dominant at energies higher than 5 eV center of mass. Product energy distributions for these ions are shown in Figs. 3 and 4. It can be seen that the $\text{CH}_3\text{SiD}_2^+$ ion displays energy distributions characteristic of a direct D^- transfer reaction. At the lowest energies, the product energy

resolution is insufficient to indicate a direct or complex distinction, but clearly at higher energies the reaction is direct, leaving the product with very little energy and specifically with less energy than predicted for a complex mechanism.

The product energies of the CH_3SiHD^+ appear quite different. At low collision energy the product energy band is nearly centered on the "C" point, and at higher collision energies, the band becomes very broad and centered on a energy about 1.5 volts above the "C" point. The broadening of the band is an indication of a great deal of energy partitioning among the reactant partners, and the position of the band indicates a mechanism much closer to that of complex formation than to direct D atom transfer. The analogous reaction³ in monosilane was shown to proceed through a direct D atom transfer that approached the spectator stripping model prediction, i.e. "S" point, at higher collision energies. Clearly, this appears not to be the case in methylsilane. Although the center of the product energy band lies at greater energy than predicted by the complex model, it is far from the stripping prediction. At energies greater than the 4.5 eV collision energy shown in Fig. 4 the intensity of CH_3SiHD^+ drops off sharply, further indicating that a direct D atom transfer is not a very likely reaction in this system.

Additional evidence for the existence of a randomized complex is the appearance of the ion at m/e 45, shown in Fig. 1b. This ion most probably represents the dissociation of a complex back to reactants that follows scrambling of the H and D atoms in the complex as illustrated by reaction (13), viz.

The cross-section for formation of this ion drops off much more rapidly with increasing collision energy than the products of reaction (12), consistent with previous observations^{3,8,9} of transition from complex to direct mechanisms with increasing collision energy.

(c) SiH_3^+ (m/e 31). The hydride transfer reaction of SiH_3^+ with CH_3SiH_3 , reaction (6) appears to be very similar to other direct H^- transfer reactions observed. The $\text{CH}_3\text{SiH}_2^+$ is formed with very little kinetic energy which, furthermore, is independent of collision energy.

(d) SiH_2^+ (m/e 30). The interpretation that these reactions undergo a transition from complex to direct mechanism as the collision energy increases is clearly born out by the kinetic energy distribution of the product ion of reaction (7), shown in Fig. 5. The reaction of SiH_2^+ with methylsilane was studied in detail only with CH_3SiH_3 as the target molecule. In this case the products of both direct and complex mechanisms will appear at the same mass. The breadth of this product ion kinetic energy band is a clear indication of the energy transfer processes taking place. At 1.93 eV center-of-mass collision energy, the product energy band is quite broad and centered on the energy prediction of the complex model. As one increases the collision energy, however, the band becomes increasingly narrow and moves closer to zero while the "C" point moves to higher energies. The broadness of the band at low energies is due to partitioning of the available energy of the system among internal and translational degrees of freedom during the lifetime of the complex. As one increases the collision energy, the reaction becomes more direct in character and little of the available energy of the system is redistributed and

deposited into translation of the product ion, or "spectator". The available energy of the system remains largely in translation of the neutral product.

The apparent inability of the methylsilane system to undergo H atom transfer reactions, as opposed to the case in monosilane³, is also evident in the failure to observe a D-atom transfer reaction between SiH_2^+ and CH_3SiD_3 . Although the energetics are favorable (from the most recent data¹⁰ we calculate the H atom transfer to be exothermic by at least 5 kcal) only very small amounts of this product have been observed, and only at collision energies above about 2.5 eV, center-of-mass.

(e) Si^+ : Reactions (8) and (9) in Table 1 were observed to occur in methylsilane with quite large cross-section despite their endothermicity. This was attributed to the presence of a high percentage of electronically excited Si^+ ions in the reactant beam. Reaction (8) is of particular interest as it involves the net transfer of more than one atom. Although transfer reactions involving more than one hydridic particles are not uncommon in hydrocarbons¹¹ and silanes⁴, because of the considerable rearrangement involved in the transfer of three atoms or, alternatively, the transfer of a methyl group, it would appear less likely to proceed through the direct stripping type mechanism evident in hydridic transfer reactions involving transfer of only one atom. However, our measurements of the kinetic energies of CH_3Si^+ product of reaction (8) appear identical to the observations of reaction (7) indicating that the silicon atom in the CH_3Si^+ product is the one originally contained in the neutral molecule, and the reaction proceeds via the transfer of an H_3^- species which approaches a direct stripping

type mechanism at high collision energies. Reaction (9) is also observed to proceed predominantly via the direct H^- transfer mechanism.

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Reprint Review

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Table I. Hydride Transfer Reactions in Methylsilane

Reaction No.	Reaction	ΔH° (kcal/mole)
4	$\text{CH}_3\text{SiH}_2^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{SiH}_2^+ + \text{CH}_3\text{SiH}_3$	0
5	$\text{CH}_3\text{SiH}^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{SiH}_2^+ + \text{CH}_3\text{SiH}_2$	-1
6	$\text{SiH}_3^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{SiH}_2^+ + \text{SiH}_4$	-11
7	$\text{SiH}_2^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{SiH}_2^+ + \text{SiH}_3$	-11
8	$\text{Si}^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{Si}^+ + \text{SiH}_3$	+30
9	$\text{Si}^+ + \text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3\text{SiH}_2^+ + \text{SiH}$	+10

Figure Captions

- Fig. 1. Isotopic distributions of products using CH_3SiD_3 as target gas.
- (a) Reaction (4), collision energy = 0.94 eV, center of mass.
 - (b) Reaction (5), collision energy = 1.4 eV, center of mass.
- Fig. 2. Product kinetic energy distributions of $\text{CH}_3\text{SiD}_2^+$ from reaction (4).
- Fig. 3. Product kinetic energy distributions of $\text{CH}_3\text{SiD}_2^+$ from reaction (5).
- Fig. 4. Product kinetic energy distributions of CH_3SiHD^+ from reaction (5).
- Fig. 5. Product kinetic energy distributions of $\text{CH}_3\text{SiH}_2^+$ from reaction (7).

Fig. 1

Fig. 2

Fig 3

Fig. 4

Fig. 5