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"Elimination of Ethylene from Metastable Isomeric Silylenium Ions in the Gas Phase: Experiment and Theory" IN FINAL FORM

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Supporting Information

Details of the statistical phase space calculations used for modeling the experimental kinetic energy release distributions are provided here.

The experimental KERDs were modeled with statistical phase space theory.¹⁻⁴ The vibrational frequencies and geometric mean rotational constants for $\text{Si}(\text{CH}_3)_3^+$, $\text{HSi}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$, $\text{HSi}(\text{CH}_3)_2^+$, $\text{H}_2\text{Si}(\text{C}_2\text{H}_5)^+$ and the tight transition states **TS1**, **TS2** and $\text{H}_2\text{Si}(\text{CH}_3)(\text{CH}_2^+)$ were obtained from *ab initio* calculations. The vibrational frequencies and rotational constants for the orbiting transition states (OTS) were taken as the values for the separated products. The parameters for $\text{H}_2\text{Si}(\text{CH}_3)^+$, SiH_3^+ and $(\text{CH}_3)\text{Si}(\text{CH}_2)^+$ were obtained by *ab initio* calculations and the parameters for C_2H_4 and H_2 were taken from the literature.⁵ The parameters used are listed in Tables 1 and 2. In order to check the sensitivity of the modeling to the parameters obtained from *ab initio* techniques, the three lowest frequencies and rotational constants were varied by $\pm 25\%$. The calculated KERD was not affected to a significant extent by this variation.

The models used to fit the data were based on the potential energy surface calculated by *ab initio* methods. For dissociation of $\text{HSi}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ to $\text{H}_2\text{Si}(\text{CH}_3)^+$ and C_2H_4 , the model included the reactant ion, the product species, the orbiting transition state in the exit channel, and the primary carbenium ion **TS2** as an equilibration channel. The effect of **TS3** and **TS4** on the dissociation was checked by a separate calculation which included reactants, OTS, and either **TS3** or **TS4**. For the dissociation of $\text{Si}(\text{CH}_3)_3^+$, both isomerization pathways were considered. Thus, the model included both **TS1** and **TS2**, the precursor ion $\text{Si}(\text{CH}_3)_3^+$, and the product OTS. The model used for the reactions of the SiC_2H_7^+ ions is given in Figure 4.

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For the calculation of the KERDs, the fraction of molecules with internal energy E , and angular momentum J , that dissociate through channel i with translational energy E_t is given by eq. 1.

$$P_i(E, J) = \frac{F_i^{orb}(E, J; E_t)}{F_i^{orb}(E, J)} \quad (1)$$

The overall probability of forming products in channel i with translational energy E_t is evaluated using eq. 2:

$$P_i(E_t) = \frac{\int \int P(E) dE P(J) dJ P_{diss}(E, J) f_i(E, J) P_i(E, J; E_t)}{\int \int P(E) dE P(J) dJ P_{diss}(E, J) f_i(E, J)} \quad (2)$$

in which $P(E)$ and $P(J)$ are the internal energy and total angular momentum distributions respectively, $P_{diss}(E, J)$ is the probability of dissociation in the second field-free region (eq. 3), $f_i(E, J)$ is the branching fraction (eq. 4) and $P_i(E, J; E_t)$ is given in eq. 1.

$$P_{diss}(E, J) = \exp[-k_i(E, J)t_1] - \exp[-k_i(E, J)t_2] \quad (3)$$

$$f_i(E, J) = \frac{k_i(E, J)}{\sum_i k_i(E, J)} \quad (4)$$

In eq. 3 t_1 and t_2 are the transit times for an ion to reach the entrance and exit respectively of the second field-free region. For reaction coordinates that include a tight transition state prior to dissociation, the effect of the transition state may be incorporated into the calculation using eq. 5.

$$P_i(E_t) = \frac{\int \int P(E) dE P(J) dJ P_{diss}(E, J) f_i(E, J) N^\ddagger(E, J) P_i(E, J; E_t)}{\int \int P(E) dE P(J) dJ P_{diss}(E, J) f_i(E, J) N^\ddagger(E, J)} \quad (5)$$

where $N^\ddagger(E, J)$ is the sum of available states above the tight transition state at energy E and total angular momentum J .

In order to model the KERDs, it is necessary to integrate over the energy and angular momentum distribution of the reactant ion. Because the reactant ions were formed by dissociative ionization, the energy distribution of the reactant ions is unknown. To test for sensitivity of the calculated KERD to assumed forms of $P(E, J)$, three different energy

distributions were used in the modeling. The first is a square distribution in which it was assumed that the probability was a constant over the energy range being studied (eq. 6).

$$P(E) = \text{constant} \quad (6)$$

The second function used was a decreasing linear function (eq. 7). A number of different slopes m were used in the calculations.

$$P(E) = 1.00 - mE \quad (7)$$

The third function that was used was a Boltzmann distribution (eq. 8), with $T = 425$ K.

$$P(E) = \exp(-E/kT) \quad (8)$$

In all three cases, the expressions for $P(E)$ are further modified by the inclusion of the experimental time window, as revealed in the dissociation probability (eq. 3). The calculated KERDs were found not to vary to a significant extent with the different functions used. This is most likely a consequence of the restrictions imposed by eq. 3. The angular momentum distribution used in the calculations is a Boltzmann distribution at a temperature of 425K, the source temperature used for these experiments.

Because the energies of **TS1** and **TS2** were found to be very sensitive to the level of theory used, these parameters were varied over a range of about 1 eV in the modeling, as described in the text. The overall thermochemistry for the dissociation of $\text{Si}(\text{CH}_3)_3^+$ to $\text{H}_2\text{Si}(\text{CH}_3)^+$ and C_2H_4 was taken from the literature and adjusted to 0 K.⁶ For dissociation of $\text{HSi}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$, the overall thermochemistry is not known, but was estimated from the known thermochemistry for the $\text{Si}(\text{CH}_3)_3^+$ reaction and the relative energies of $\text{Si}(\text{CH}_3)_3^+$ and $\text{HSi}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$ determined by *ab initio* techniques.

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Table 1. Parameters Used in Statistical Phase Space Modeling for SiC_2H_7^+ .

	$\text{HSi}(\text{CH}_3)_2^+$	$\text{H}_2\text{SiC}_2\text{H}_5^+$	$\text{H}_2\text{Si}(\text{CH}_3)\text{CH}_2^+$ transition state	$\text{H}_3\text{Si}^+ +$ C_2H_4	$\text{CH}_3\text{SiCH}_2^+$ $+ \text{H}_2$
$\nu, \text{cm}^{-1} \text{ }^a$	2944 2942 2886 2884 2826 2825 2209 1382 1379 1373 1369 1290 1282 915 865 829 745 628 616 597 449 210 41 24	2947 2934 2826 2841 2811 2234 2199 1454 1446 1396 1361 1242 1203 1014 947 939 914 726 647 547 486 223 194 61	3072 3024 3014 2966 2920 2172 2161 1397 1394 1388 1282 1071 880 863 843 801 680 607 575 519 342 178 136	2261 2261 2197 912 912 813 3106 3026 2989 1623 1444 1342 1023 3103 1236 949 943 826	3016 2961 2929 2915 2837 1381 1365 1332 1263 923 832 799 760 616 569 258 92 89 4403
$B, \text{cm}^{-1} \text{ }^b$	0.289	0.288	0.271	4.18 1.59	0.382 60.8
$\alpha, \text{\AA}^3 \text{ }^c$				4.25	0.804
$\sigma \text{ }^d$	2	1	1	24	2
$\Delta\Delta E, \text{eV} \text{ }^e$	0.0	0.91	2.65	3.05	3.05
$\mu, \text{amu} \text{ }^f$				14.7	1.93

^a Vibrational frequencies, determined as described in the text. ^b Geometric mean rotational constants. ^c Polarizability of neutral products. ^d Rotational symmetry number. ^e Energy relative to $\text{HSi}(\text{CH}_3)_2^+$. ^f Reduced mass.

Table 2. Parameters Used in Statistical Phase Space Modeling for SiC_3H_9^+ .

	$\text{Si}(\text{CH}_3)_3^+$	$\text{HSi}(\text{CH}_3)(\text{C}_2\text{H}_5)^+$	TS1	TS2	$\text{H}_2\text{Si}(\text{CH}_3)^+ + \text{C}_2\text{H}_4$
$\nu, \text{cm}^{-1} \text{ }^a$	2940	2946	3058	3050	2941
	2939 (2)	2943	3045	3001 (2)	2896
	2888 (3)	2929	2961	2977 (2)	2814
	2830	2885	2956	2949	2242
	2828 (2)	2863	2932	2891	2207
	1387	2840	2916	2890	1377
	1382 (3)	2826	2845	2219	1365
	1378 (2)	2811	1916	1409	1285
	1294	2202	1904	1402	943
	1286	1456	1470	1397	870
	878 (2)	1448	1413	1393	827
	829	1395	1401	1389	675
	708 (2)	1380	1395	1269 (2)	531
	706	1376	1298	1044	490
	649 (2)	1365	1204	881	24
	552	12868	1193	872	3106
	212	1244	1115	865	3026
	201 (2)	1206	1087	787	2989
	59	1016	1069	693	1623
	32 (2)	940	1056	683	1444
		923	831	629	1342
		896	825	596	1023
		764	796	590	3103
		757	685	522	1236
		645	664	239	949
		571	625	210	943
		561	478	176	826
		435	469	148	
		329	305	136	
		201	194		
		135	186		
		56	15		
		41			
$B, \text{cm}^{-1} \text{ }^b$	0.150	0.151	0.164	0.154	0.745
$\alpha, \text{\AA}^3 \text{ }^c$					1.588
$\sigma \text{ }^d$					4.25
$\sigma \text{ }^d$	6	1	1	1	8
$\Delta\Delta E, \text{eV} \text{ }^e$	0.0	0.82	3.06	2.88	2.86
			(2.25)	(2.50)	
$\mu, \text{amu} \text{ }^f$					17.26

^a Vibrational frequencies, determined as described in the text. Degeneracies shown in parentheses. ^b Geometric mean rotational constants. ^c Polarizability of neutral products.

^d Rotational symmetry number. ^e Energy relative to $\text{HSi}(\text{CH}_3)_2^+$. ^f Reduced mass.