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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	2947	3072	2261	3016
	2942	2934	3024	2261	2961
	2886	2826	3014	2197	2929
	2884	2841	2966	912	2915
	2826	2811	2920	912	2837
	2825	2234	2172	813	1381
	2209	2199	2161	3106	1365
	1382	1454	1397	3026	1332
	1379	1446	1394	2989	1263
	1373	1396	1388	1623	923
	1369	1361	1282	1444	832
	1290	1242	1071	1342	799
	1282	1203	880	1023	760
	915	1014	863	3103	616
	865	947	843	1236	569
	829	939	801	949	258
	745	914	680	943	92
	628	726	607	826	89
	616	647	575		4403
	597	547	519		
	449	486	342		
	210	223	178		
	41	194	136		
	24	61			
$B, \text{cm}^{-1} \text{ }^b$	0.289	0.288	0.271	4.18	0.382
				1.59	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	$\text{H}_2\text{Si}(\text{CH}_3)^+ + \text{C}_2\text{H}_4$
ν, cm^{-1} ^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, cm^{-1} ^b	0.150	0.151	0.164	0.154	0.745
$\alpha, \text{\AA}^3$ ^c					1.588
σ^d	6	1	1	1	4.25
$\Delta\Delta E, \text{eV}$ ^e	0.0	0.82	3.06	2.88	2.86
			(2.25)	(2.50)	
μ, amu ^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.