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# Reaction of Trimethylsilylketene With HCl: Mechanistic Study

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**ABSTRACT:** Ketenes are involved in various important reactions, such as [2+2] cycloadditions or nucleophilic additions. Among them, silylketenes are particularly stable, and their reactivity reveals interesting features. Indeed, they can behave as nucleophiles or electrophiles. Recent experimental results in our laboratory showed that trimethylsilylketene **1** can react with hydrogen chloride at room temperature, leading to the cleavage of the Si—C bond of the ketene moiety and the formation of trimethylsilylchloride **4** and acetylchloride **5**. To propose a reaction profile for this unexpected result, a theoretical study was carried out at the density functional theory (DFT) level. This mechanistic study was supported by a spectroscopic analysis in a cryogenic argon matrix in order to monitor the reaction. Intermediate **2** was then identified, and we accounted for it in the postulated reaction pathways. © 2005 Wiley Periodicals, Inc. *Int J Quantum Chem* 106: 719–726, 2006

**Key words:** DFT; reaction profile; trimethylsilylketene; HCl; Si—C bond cleavage

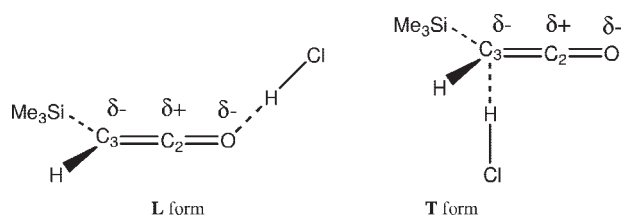
## Introduction

Reactions between ketenes and electrophilic compounds as well as ketene–hydrogen halide complexes have attracted the attention of many experimental and theoretical chemists [1, 2]. Recent investigations of these complexes, generated in the

gas or in the solid phase, show a strong interaction between the hydrogen atom of the halide and the C<sub>β</sub> carbon atom of the ketene moiety [3]. Among the ketene family, silyl ketenes, discovered 40 years ago [4], are remarkably stable as compared with other ketenes.

Indeed, trimethylsilylketene **1** has an extraordinary resistance toward dimerization and its low reactivity in hydration reactions (**1** is less reactive than *t*Bu(H)C=C=O by a factor of 400 [5]) reflects the ground-state stability of this ketene. However,

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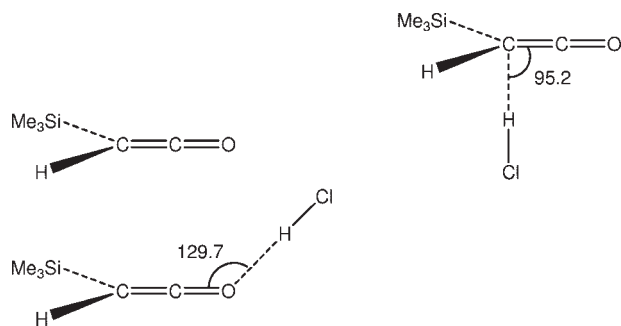


**SCHEME 1.** Arrangements of **1**:HCl complexes.

the ability of the Si atom to stabilize  $\alpha$  negative charge enhances the rates of some processes. Previous experiments at room temperature in the gas phase and in  $\text{CH}_2\text{Cl}_2$  solution showed an unexpected reaction between **1** and HCl, which induces a cleavage of the Si—C bond of the ketene moiety with the formation of trimethylsilylchloride **4** and acetylchloride **5**. Matrix isolation experiments [6], used to monitor the reaction and trap highly reactive intermediates, led to the identification of intermediate trimethylsilylacetylchloride **2**. The purpose of the present work is to propose a reaction pathway from **1**:HCl molecular van der Waals complexes through the intermediate **2** to the final products **4** and **5**.

## Computational Details

As a first step, calculations of stationary points and reaction profiles were performed at a semiempirical level with the SAM1/*d* method [7] available in the Ampac 7.0 package (Semichem, Shawnee Mission, KS). The SAM1/*d* method was selected because chlorine and silicon *d* orbitals are taken into account. All stationary points (minima and transition states) were characterized by the calculation of



**SCHEME 2.** Optimized geometries at the B3PW91/6-31++G(*d,p*) level of **1**, and **T** and **L** **1**:HCl complexes. Angles are in degrees (°).

**TABLE I**  
Relative stability and structural parameters of **1**:HCl complexes.

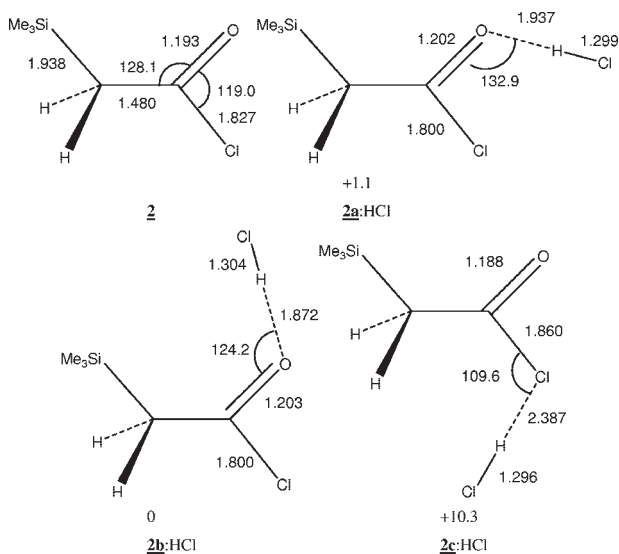
	<b>1</b>	<b>1</b> :HCl ( <b>L</b> form)	<b>1</b> :HCl ( <b>T</b> form)
Relative energy <sup>a,b</sup>	0.0	−10.6	−9.8
$d(\text{C}=\text{C})^a$	1.312	1.306	1.320
$d(\text{C}=\text{O})^a$	1.170	1.178	1.167
$d(\text{C}-\text{Si})^a$	1.880	1.889	1.901
$d(\text{C}\cdots\text{H})^a$	—	—	2.065
$d(\text{O}\cdots\text{H})^a$	—	2.018	—
$d(\text{H}\cdots\text{Cl})^a$	—	1.293	1.316
$\theta(\text{CCO})^a$	177.7	177.5	176.6
Charge at O <sup>c</sup>	−0.40	−0.36	−0.36
Charge at C <sub>2</sub> <sup>c</sup>	0.67	0.64	0.63
Charge at C <sub>3</sub> <sup>c</sup>	−0.94	−0.90	−0.74

<sup>a</sup> Relative energies are in  $\text{kJ} \cdot \text{mol}^{-1}$ , interatomic distances in Ångstroms and angles in degrees.

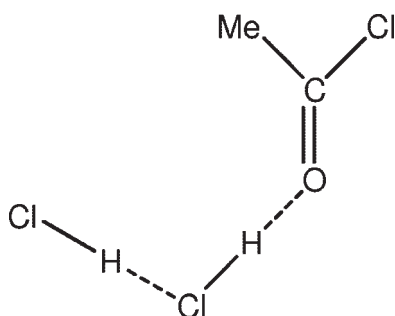
<sup>b</sup> BSSE-corrected energies accounting for the monomer geometry relaxation [11].

<sup>c</sup> Charges calculated with the CHelpG method [13].

the normal modes of the optimized structures. Reaction profiles were determined by a calculation with the CHAIN algorithm [8] and checked by the intrinsic reaction coordinate method (IRC).



**SCHEME 3.** Optimized geometries at the B3PW91/6-31++G(*d,p*) level for **2** and three arrangements of the **2**:HCl complex. Relative energies are given in  $\text{kJ} \cdot \text{mol}^{-1}$ . Interatomic distances are given in Ångstroms (Å) and angles in degrees (°).



**SCHEME 4.** Arrangement of the **5**:(HCl)<sub>2</sub> complex identified by comparison of calculated and experimental vibrational frequencies.

Semiempirical stationary points were the starting points of the density functional theory (DFT) calculations, which were performed with the Gaussian 98 package [9]. All calculations were carried out at the B3PW91/6-31++G(*d,p*) level, and all stationary points were characterized by a calculation of the vibrational frequencies derived from the analytical second derivatives of the total energy of the optimized structures. Starting from the transition state (TS) structures, reaction profiles were determined by IRC calculations. The zero-point energy (ZPE) was added to energy values with vibrational frequencies scaled by 0.9772, as recommended by Scott and Radom [10]. The stabilization energy of the complexes involving **1** and **2** was corrected for the basis set superposition error (BSSE) through the "7-point" formula, taking into account monomer geometry relaxation [11]. For systems involving more than two subsystems in

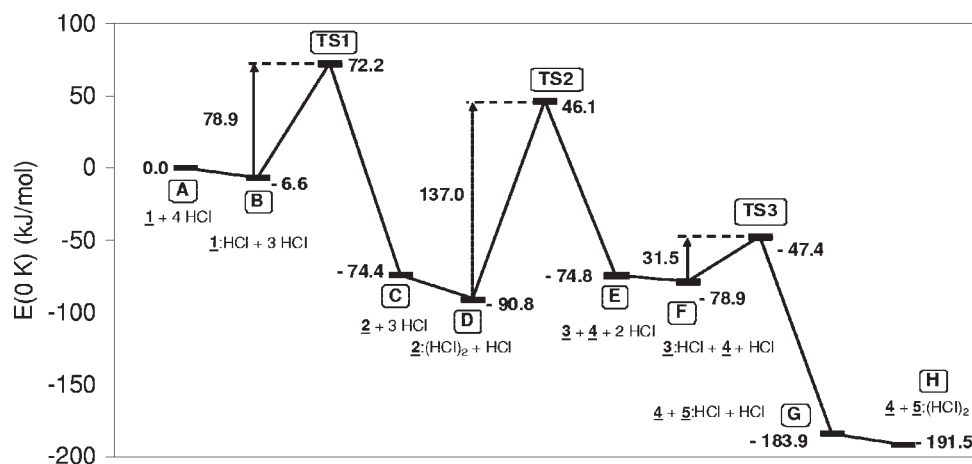
reaction profiles, the electronic energy of the whole system was calculated by a single point with molecules spaced 5 Å apart from each other. Only the DFT calculations are reported in the next section.

## Results and Discussion

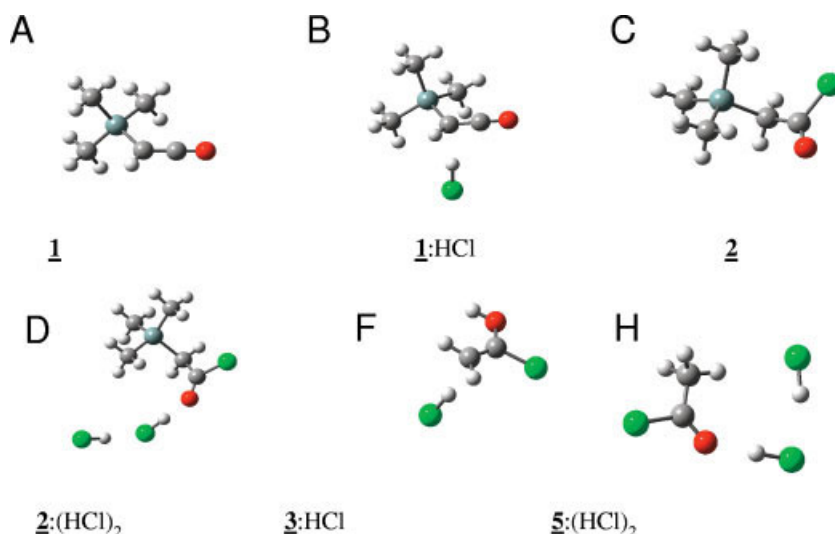
### GEOMETRY OF TRIMETHYLSILYLKETENE **1** AND **1**:HCl COMPLEXES

According to the partial charges and resonance structures of ketenes [1, 5, 12], there are two possible geometric arrangements of the trimethylsilylketene **1**:HCl complex (Scheme 1): the **L** form, which involves a hydrogen bond between HCl and the oxygen atom of the ketene, and the **T** form, in which the HCl molecule interacts with the terminal carbon atom of the ketene.

In the **L** form, the HCl fragment interacts with a lone pair of the oxygen atom and the C=O bond is lengthened by 0.011 Å. In the **T** form, the HCl molecule is in the plane of the  $\pi_{C=C}$  bond and the C<sub>2</sub>=C<sub>3</sub> bond is lengthened by 0.008 Å. Since, according to our DFT calculations (Scheme 2, Table I), the **L** form is more stable than the **T** form by less than 1 kJ · mol<sup>-1</sup>, we assumed that both forms are present in the argon matrix. Previous MP2 calculations [1(c)] on the parent H<sub>2</sub>C<sub>2</sub>O:HCl complex indicated a preference for the **T** form (−11.5 kJ · mol<sup>-1</sup> compared with the **L** form). Such a preference was attributed to the high nucleophilicity of C<sub>3</sub>. In the case of compound **1**, the electropositive Si atom leads to a large negative partial charge on carbon C<sub>3</sub>, enhancing its nucleophilicity, but the sterically



**FIGURE 1.** Reaction profile I.



**FIGURE 2.** Optimized structures of the main minima of reaction profile I.

crowded trimethylsilyl moiety may destabilize the T form due to steric hindrance.

#### GEOMETRY OF TRIMETHYLSILYLACETYLCHLORIDE **2** AND **2:(HCl)<sub>n</sub>** COMPLEXES ( $n = 1, 2$ )

Three geometries of the trimethylsilylacetylchloride **2:HCl** complex (Scheme 3), where the HCl molecule is complexed to the carbonyl oxygen atom or the chlorine atom, were investigated. If we con-

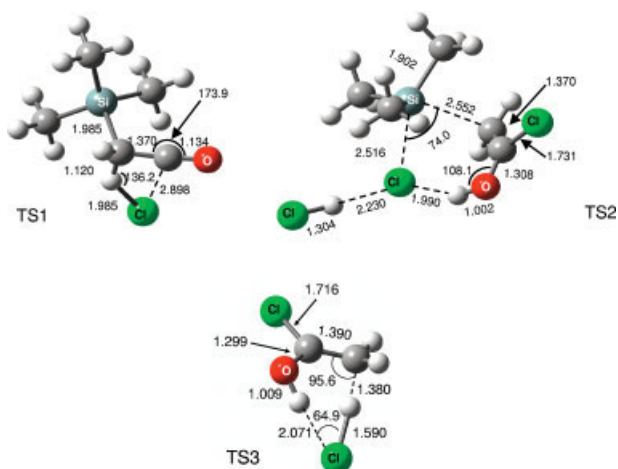
sider  $\text{H} \cdots \text{Cl}$  and  $\text{O} \cdots \text{H}$  bond lengths, **2a:HCl** and **2b:HCl** structures are the most strongly bonded complexes. This was confirmed by the relative energies (Scheme 3). The **2c:HCl** structure showed a weak interaction between the HCl molecule and the chlorine atom of **2**. In the following determination of reaction profiles, only the geometry of **2b:HCl** was considered (the BSSE-corrected stabilization energy of the **2b:HCl** was  $16.1 \text{ kJ} \cdot \text{mol}^{-1}$ ). Starting from **2b:HCl**, a second HCl molecule was added (**2:(HCl)<sub>2</sub>**) in order to form a hydrogen bond with the first HCl molecule, and the geometry of the whole complex was optimized. The stabilization energy of **2:(HCl)<sub>2</sub>** was  $16.4 \text{ kJ} \cdot \text{mol}^{-1}$ .

#### FINAL PRODUCTS

The structure and vibrational frequencies of acetylchloride **5:(HCl)<sub>n</sub>** complexes ( $n = 1, 2$ ) were calculated. Experimental (cryogenic argon matrix) and calculated vibrational frequencies were compared, in order to assign the experimental spectral features [6]. According to this study, the bands are attributed to a  $1:n$  complex (where  $n > 2$ ) and a  $1:2$  complex, respectively (Scheme 4). Moreover, trimethylsilylchloride **4** does not form any complex with HCl.

#### REACTION PROFILES

Starting from both L and T **1:HCl** complexes, we investigated various reaction mechanisms leading,



**FIGURE 3.** Structure of the transition states of reaction profile I. Interatomic distances are given in Ångströms (Å) and angles in degrees (°).

**TABLE II**  
Energy data from DFT calculations at the B3PW91/6-31++G(d,p) level.\*

Structure	Electronic energy (a.u.)	ZPE correction (a.u.)	Relative energy (kJ · mol <sup>-1</sup> )
<b>A</b>	-2404.164879	0.158547	0
<b>B</b>	-2404.169487	0.160638	-6.6
<b>B'</b>	-2404.170084	0.160242	-9.2
<b>B''</b>	-2404.174048	0.161885	-15.3
<b>TS1</b>	-2404.140784	0.161957	72.2
<b>TS1'</b>	-2404.110161	0.160144	147.9
<b>TS1''</b>	-2404.135983	0.161901	84.7
<b>C</b>	-2404.200709	0.166067	-74.4
<b>C'</b>	-2404.000690	0.165433	14.8
<b>C''</b>	-2404.169113	0.166763	10.5
<b>D</b>	-2404.212197	0.171282	-90.8
<b>D''</b>	-2404.173399	0.168632	4.1
<b>TS2</b>	-2404.162080	0.173306	46.1
<b>TS2''</b>	-2404.162911	0.161051	29.2
<b>E</b>	-2404.209263	0.171357	-82.9
<b>E''</b>	-2404.213443	0.170004	-8
<b>F</b>	-2404.212310	0.173184	-86.1
<b>TS3</b>	-2404.199336	0.171800	-55.7
<b>G</b>	-2404.248234	0.171878	-183.9
<b>H</b>	-2404.252795	0.173558	-191.5

\* B', C', and TS1' refer to reaction profile II; B'', TS1'', C'', D'', TS2'', and E'' refer to reaction profile III.

through intermediate **2**, to the final products **4** and **5**:(HCl)<sub>2</sub>.

#### REACTION PROFILE STARTING FROM THE T FORM **1**:HCl COMPLEX

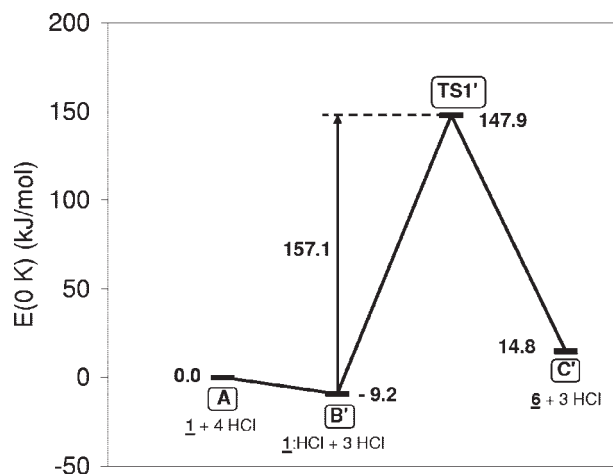
We propose a reaction profile involving three steps and three main complexes. Since experimental vibrational spectra show that the final product **5** forms a van der Waals complex with at least two HCl molecules, four HCl molecules were involved in calculations throughout the whole process. This is in agreement with the experimental conditions in which the relative **1**/HCl ratio is between 1/2 and 1/10. After the complexation between a HCl molecule and the C<sub>3</sub> of **1**, the intermediate structure **2** was obtained through the asynchronous concerted addition of HCl to the C<sub>2</sub>=C<sub>3</sub> double bond with an activation energy of 78.9 kJ · mol<sup>-1</sup> (Figs. 1–3, Table II). This first activation energy was consistent with the experimental observation of the addition from 20 K. The formation of a complex between the

oxygen atom of **2** and two HCl molecules stabilized the system by 16.4 kJ · mol<sup>-1</sup> (Fig. 1, Table II). The **2**:(HCl)<sub>2</sub> complex evolved by a dissociative process to give enol chloride **3** (cleavage of the Si—C bond), trimethylsilylchloride **4** (formation of a new Si—Cl bond) and two HCl molecules. In the transition state of this step, the Si atom is pyramidal and displays partial Si—C (2.55 Å) and Si—Cl (2.52 Å) bonds involving its vacant *d* orbital and, the *p* orbital of C<sub>3</sub> and the lone pair of the Cl atom respectively (Fig. 3). As a consequence, the silicon atom shift occurs with retention of configuration, in agreement with previous studies of the 1,3-silyl shift [2(b), 13]. **TS2** is lower in energy than **TS1** and favored because a pseudo-six-membered ring is formed in the TS structure. In this profile, both HCl molecules were involved in **TS2**, but a similar activation energy was obtained (137.7 kJ · mol<sup>-1</sup>) with only one HCl molecule, showing no assistance in the mechanism from the second HCl molecule. Enol chloride **3** may also form a complex (**3**:HCl) with another HCl molecule.

In agreement with the partial charges and the lowest unoccupied molecular orbital (LUMO) coefficients, the HCl molecule is bound to C<sub>3</sub>. The last step then requires a small amount of energy (30.4 kJ · mol<sup>-1</sup>) to give the final products **4** and **5**:HCl. The last step is again particularly favored because of a pseudo-six-membered ring in **TS3** structure (Fig. 3).

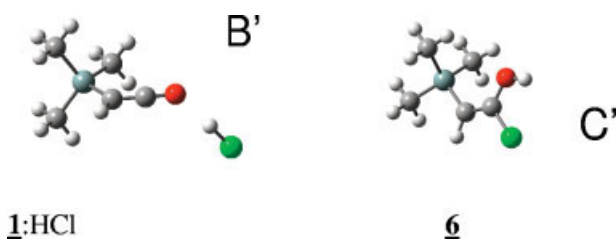
Alternative routes for this reaction were also investigated.

First, if we consider a direct addition of the HCl molecule of **2**:HCl and the following cleavage of the



**FIGURE 4.** Reaction profile II.



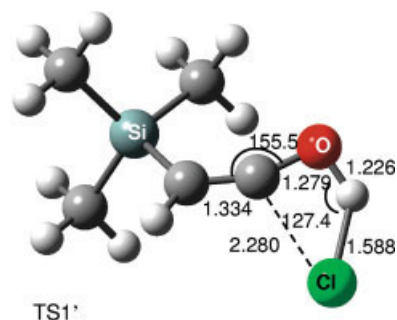


**FIGURE 5.** Minima for the first step of reaction profile II.

Si—C bond to give  $\text{SiMe}_3\text{Cl}$  **4** and  $\text{MeCOCl}$  **5** directly, the activation energy is  $212.4 \text{ kJ} \cdot \text{mol}^{-1}$  (electronic energy). Such a reaction profile is not in agreement with experimental observations because (i) the activation energy of this second step is too high to explain the detection of  $\text{SiMe}_3\text{Cl}$  and  $\text{MeCOCl}$  from 20 K; and (ii) the intermediate trimethylacetylchloride **2** should have been detected before the final products.

In a second hypothesis, if we postulate a last step involving an intramolecular keto-enolic conversion starting from **3**, the activation energy of such a step is again too large to be consistent with experimental observations: the electronic activation energy is  $211.2 \text{ kJ} \cdot \text{mol}^{-1}$  compared with  $31.5 \text{ kJ} \cdot \text{mol}^{-1}$  (Fig. 1).

The whole reaction profile I is thus consistent with experimental data. As soon as enough energy is provided to the system to reach the first TS structure (TS1), all the following stationary points being lower in energy, the whole reaction mecha-

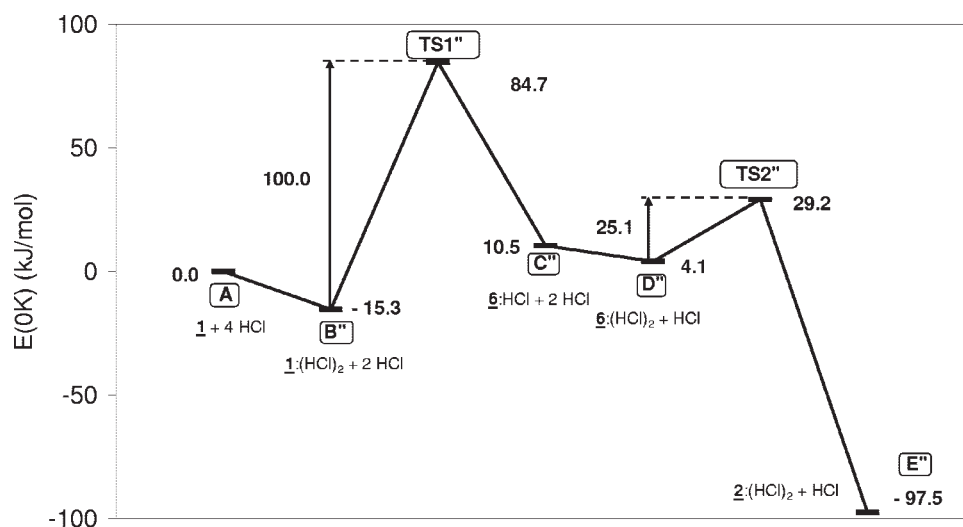


**FIGURE 6.** Structure of the first transition state of reaction profile II. Interatomic distances are given in Ångströms (Å) and angles in degrees (°).

nisms takes place and the final products are detected. When HCl molecules desorb due to annealing, the reaction is stopped at the **2**:HCl complex because of a lack of HCl molecules, and the  $\text{5}:(\text{HCl})_n$  complexes are not formed.

#### REACTION PROFILES STARTING FROM THE L FORM **1**:HCl COMPLEX

As experimental IR bands might be attributed to the T form or L form of **1**:HCl, we considered an alternative route starting from the L form (reaction profile II, Table II, Figs. 4–6). With a first addition of HCl on the  $\text{C}_2=\text{O}$  double bond, silylenolchloride **6** is obtained. The activation energy for this first step is  $157.1 \text{ kJ} \cdot \text{mol}^{-1}$ , i.e., two times higher than for addition to the  $\text{C}_2=\text{C}_3$  double bond starting

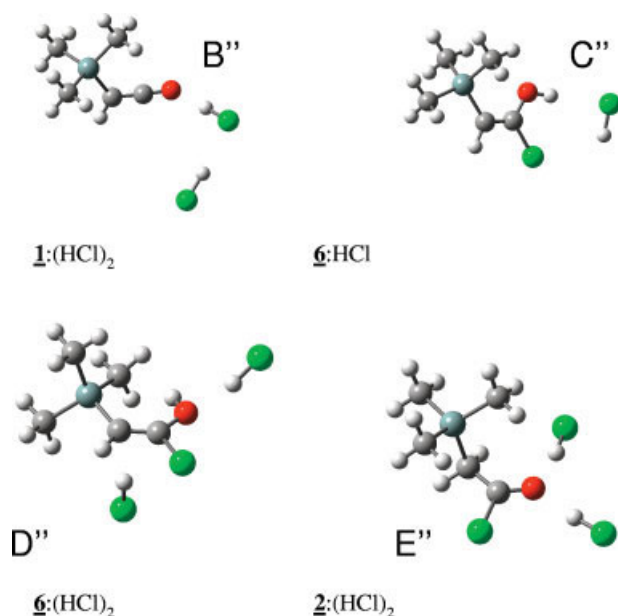


**FIGURE 7.** First steps of reaction profile III.

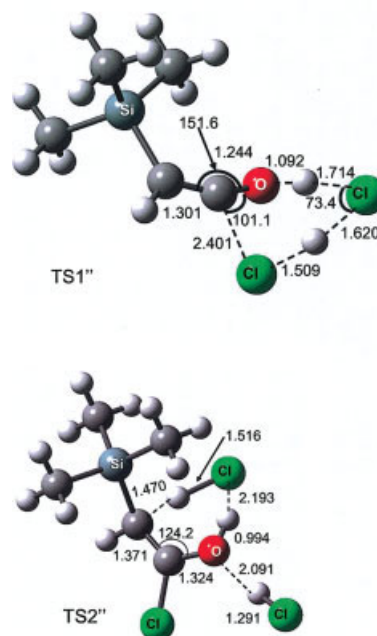
from the **T** form (profile **I**), and the reaction is endothermic. Consequently, this mechanism was not considered further. Nevertheless, to reduce the tension in **TS1'**, a second reaction profile starting from the **L** form of **1**:HCl and involving a second HCl molecule was investigated (reaction profile **III**, Table II, Figs. 7–9). The transition state **TS1''** resulting from this approach and involving a pseudo six-membered ring is only 12 kJ · mol<sup>-1</sup> higher in energy than **TS1**. The first step is slightly endothermic, but the second step leading to compound **2**:(HCl)<sub>2</sub> only requires 25.1 kJ · mol<sup>-1</sup> and is highly exothermic. Hence, it may be a competitive pathway.

## Conclusion

It is shown that trimethylsilylketene **1** reacts at room and low temperature with hydrogen chloride (HCl) through a cleavage of the Si—C bond. Reaction products **4** and **5** and the intermediate **2** were obtained in an argon matrix and identified by their infrared spectra (experimental results are reported elsewhere). As two complexes between **1** and a hydrogen chloride molecule may be formed, two reaction profiles were proposed, starting from both complexes. Both reaction profiles are exothermic, and the first step of each pathway requires similar



**FIGURE 8.** Minima of reaction profile **III**.



**FIGURE 9.** Structures of transition states **TS1''** and **TS2''** of reaction profile **III**. Interatomic distances are given in Ångströms (Å) and angles in degrees (°).

activation energies in agreement with the experimental temperature.

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## References

- (a) Tidwell, T. T.; Ketenes, John Wiley & Sons: New York, 1995; (b) Brown, R. S.; Christl, M.; Lough, A. J.; Ma, J.; Peters, E.-M.; Peters, K.; Samtleben, F.; Slebocka Tilk, H.; Sung, K.; Tidwell, T. T. *J Org Chem* 1998, 63, 6000; (c) Sumathi, R.; Chandra, A. K. *Chem Phys Lett* 1997, 271, 287; (d) Skancke, P. N. *J Phys Chem* 1992, 96, 8065; (e) Gong, L.; McAllister, M. A.; Tidwell, T. T. *J Am Chem Soc* 1991, 113, 6021.
- (a) Pommier, A.; Kocienski, P.; Pons, J.-M. *Perkin Trans 1* 1998, 2105; (b) Oblin, M.; Fotiadu, F.; Rajzmann, M.; Pons, J.-M. *J Chem Soc, Perkin Trans 2* 1997, 1621; (c) Muchall, H. M.; Werstiuk, N. H.; Ma, J.; Tidwell, T. T.; Sung, S. *Can*



- J Chem 1997, 75, 1851; (d) Allen, A. D.; Tidwell, T. T. *Tetrahedron Lett* 1991, 32, 847.
3. Piétri, N.; Chiavassa, T.; Allouche, A.; Aycard, J.-P. *J Phys Chem A* 1997, 101, 1093.
  4. (a) Loebach, J. L.; Danheiser, R. L. In *Encyclopedia of Reagents in Organic Synthesis*; Paquette, L. A., Eds.; John Wiley & Sons: New York, 1995; p 5266; (b) Shchukovskaya, L. L.; Pal'chik, R. I.; Lazarev, A. N. *Dokl Akad Nauk SSSR* 1965, 164, 357 (*Chem Abstr* 1965, 63, 18138g).
  5. Allen, A. D.; Tidwell, T. T. *Tetrahedron Lett* 1991, 32, 847.
  6. Pietri, N.; Gaudel-Siri, A.; Couturier-Tamburelli, I.; Pons, J.-M.; Aycard, J.-P. *J Phys Chem A* 2005, 109, 2120.
  7. Dewar, M. J. S.; Jie, C.; Yu, J. *Tetrahedron* 1993, 49, 5003.
  8. Liotard, D. A. *Int J Quantum Chem* 1992, 44, 723.
  9. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Vreven, T.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J. W.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian* 98, Revision A.11.4; Gaussian: Pittsburgh, PA, 2002.
  10. Scott, A. P.; Radom, L. *J Phys Chem* 1996, 100, 16502.
  11. (a) Boys, S. F.; Bernardi, F. *Mol Phys* 1970, 19, 553; (b) Lendvay, G.; Mayer, I. *Chem Phys Lett* 1998, 297, 365.
  12. Gong, L.; McAllister, M. A.; Tidwell, T. T. *J Am Chem Soc* 1991, 113, 6021.
  13. (a) Yamabe, T.; Nakamura, K.; Shiota, Y.; Yoshizawa, K.; Kawauchi, S.; Ishikawa, M. *J Am Chem Soc* 1997, 119, 807; (b) Ohshita, J.; Niwa, H.; Ishikawa, M.; Yamabe, T.; Yoshii, T.; Nakamura, K. *J Am Chem Soc* 1996, 118, 6853; (c) Antonietti, P.; Canepa, C.; Tonachini, G. *J Org Chem* 1994, 59, 3952; (d) Takahashi, M.; Kira, M. *J Am Chem Soc* 1997, 119, 1948.