A THEORETICAL STUDY OF THE UNIMOLECULAR DECOMPOSITION OF DIFLUOROCHLOROMETHANE

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Nonempirical quantum-chemical calculations have been performed in the 4-31G basis on the equilibrium geometry and vibrational frequencies of difluorochloromethane, as well as on the transition state in the decomposition $\text{CHF}_2\text{Cl} \rightarrow \text{CF}_2 + \text{HCl}$. The potential-energy surface has been constructed and a simplified 1D dynamic model has been formulated for the reaction, which is based on dividing the degrees of freedom into active (dynamic) and adiabatic ones. Measurements on the reaction kinetics have been analyzed from calculations on the rate constant from the RRKM theory and within the framework of the 1D model.

Considerable interest attaches to theoretical study of the unimolecular decomposition of excited difluorochloromethane

$$\text{CHF}_2\text{Cl}^* \rightarrow \text{CF}_2 + \text{HCl}$$

(1)

because extensive measurements have been made on it. The activation energy is quite low ($E_0 = 230$ kJ/mole), so it is convenient for multiphoton IR dissociation [1, 2]. Particularly, measurements have recorded the energy distributions of the products, which cannot be explained completely on the basis of the Rice–Ramsberger–Kassel–Marcus (RRKM) unimolecular decomposition theory [3, 4]. From our viewpoint, particular interest attaches to the decomposition caused by chemical activation [5], since the rate constant in (1) can be estimated. Vibrationally excited CHF$_2$Cl$^*$ molecules are formed from

$$\text{CHFCl} + \text{CF}_3\text{OF} \rightarrow \text{CHF}_2\text{Cl}^* + \text{CF}_3\text{O},$$

(2)

whose heat $\Delta H \approx -318$ kJ/mole exceeds the threshold in (1). The rate constants for the decomposition as measured and as derived from the RRKM theory diverge by 1.5-2 orders of magnitude, so it has been suggested [5] that the decomposition of these activated molecules is non-statistical.

This discrepancy can arise from two factors. Firstly, the structure of the transition state (TS) in (1) is unknown, so there is an arbitrary element in choosing the parameters for the RRKM calculation. Secondly, the energy is incompletely distributed over all the degrees of freedom, i.e., the decomposition is nonstatistical, so one can distinguish active degrees of freedom, where the energy redistribution determines the decomposition, and nonactive ones (adiabatic). One assumes one can neglect energy exchanges between the active and inactive degrees during the decomposition.

Theoretical study of the mechanism in (1) requires one to construct the potential surface and perform dynamic calculations to derive the rate constant and details of the energy redistribution during decomposition. No exact solution can be obtained at present. An approach is proposed here, which has two parts. In the first, a nonempirical quantum-chemical calculation is performed on the molecule and the TS in (1) is examined, while the vibrational frequencies are calculated in the equilibrium geometry together with the TS geometry. The data are used to construct the potential-energy surface (PES). The PES is used in a simplified model for (1) (a 1D model), in which the dynamic subsystem includes only two degrees of freedom (in the product valley, one of them corresponds to vibration of the HCl molecule and the other to the translational motion of it with respect to the CF$_2$). The second part involves calculating the rate constant from the RRKM theory, where one uses quantum-chemical data on the TS structure and analyzes the decomposition dynamics from the 1D model.
**Fig. 1.** Forms of the normal vibrations $\nu_4$ and $\nu_6$ of the CHF$_2$Cl molecule; the crosses denote the positions of the H and Cl atoms in the TS in (I).

**TABLE 1.** Measured [6] and Calculated (in parentheses) Geometrical Parameters at Stationary Points on the Potential Surface in Å

<table>
<thead>
<tr>
<th>Bond length</th>
<th>CHF$_2$Cl</th>
<th>TS</th>
<th>CF$_3$+HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$(C--H)</td>
<td>1.096 (1.066)</td>
<td>(1.245)</td>
<td></td>
</tr>
<tr>
<td>$R$(C--Cl)</td>
<td>1.747 (1.836)</td>
<td>(2.675)</td>
<td></td>
</tr>
<tr>
<td>$R$(H--Cl)</td>
<td>2.468 (1.641)</td>
<td>1.275</td>
<td></td>
</tr>
<tr>
<td>$R$(C--F)</td>
<td>1.350 (1.355)</td>
<td>(1.236)</td>
<td>1.300</td>
</tr>
</tbody>
</table>

*Estimated value.

**TABLE 2.** Measured [6] and Calculated (in parentheses) Vibrational Frequencies (cm$^{-1}$) for the CHF$_2$Cl Molecule, TS, and Reaction Products in (I)

<table>
<thead>
<tr>
<th>Vibration</th>
<th>CHF$_2$Cl</th>
<th>TS</th>
<th>CF$_3$+HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha'$</td>
<td>$\nu_1$</td>
<td>3024 (3436)</td>
<td>(1712)</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>1312 (1431)</td>
<td>(174)</td>
<td></td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>1178 (1181)</td>
<td>(1247)</td>
<td></td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>809 (789)</td>
<td>(833)</td>
<td></td>
</tr>
<tr>
<td>$\nu_7$</td>
<td>585 (585)</td>
<td>(674)</td>
<td></td>
</tr>
<tr>
<td>$\nu_8$</td>
<td>422 (400)</td>
<td>(1056)</td>
<td></td>
</tr>
<tr>
<td>$\nu_9$</td>
<td>1347 (1508)</td>
<td>(1203)</td>
<td></td>
</tr>
<tr>
<td>$\nu_{10}$</td>
<td>365 (361)</td>
<td>(130)</td>
<td></td>
</tr>
</tbody>
</table>

There are two modes $\nu_4$ and $\nu_6$ of CHF$_2$Cl of the main interest for (I) (Fig. 1); $\nu_4$ is close in form to vibration of the HCl product and evidently goes over to it as a result of the reaction, while $\nu_6$ corresponds to H and Cl coming together while simultaneously receding from CF$_2$; it corresponds to displacement along the reaction path, and can lead to dissociation if the energy is sufficient. By displacing H and Cl in accordance with $\nu_6$ (Fig. 1), one gets the approximate position of the TS, which can then be refined by minimizing the gradient norm. The vibrational calculation on this configuration (Table 1 and Fig. 1) showed that there is one vibration with imaginary frequency (Table 2), which confirms that the structure represents the transition state.

The TS parameters show that the hydrogen atom moves towards the chlorine atom on the initial part of the path, while at the same time the C--Cl bond lengthens. The difference in C--H bond lengths in the equilibrium configuration and in the TS is fairly small (Table 1), being less than 0.2 Å, whereas the displacement of the hydrogen atom from the equilibrium position is about 1.4 Å. The H--Cl bond length in the TS is considerably more than the equilibrium value in HCl, i.e., this bond is formed after the barrier has been overcome.

The geometrical parameters and frequencies for the molecule and TS in (I) are sufficient to give the rate constant from the RRKM theory, but it is necessary to construct the complete PES to consider the reaction dynamics, where the natural reaction coordinates (NRC) are the most convenient, in which the PES for an N-atom system near the reaction path is represented as a harmonic valley in a space of 3N - 6 variables [7, 8]:

$$ V(s, q_1 \ldots q_{3N-7}) = V(s) + \frac{1}{2} \sum_{k=1}^{3N-7} \omega_k^2(s) q_k^2 $$