The intramolecular hydrogen atom transfer in the photodissociation of \( \text{o-chorotoluene} \)

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Abstract

Based on ab initio calculated results, a new mechanism is proposed that intramolecular hydrogen atom transfer may occur during the photodissociation of \( \text{o-chorotoluene} \) at 266 nm. This mechanism is different from the general suggestion, i.e. (1) \( \text{o-chorotoluene} (S_1) \rightarrow \text{o-chorotoluene} (T_1) \rightarrow \text{Cl} + \text{o-tolyl} \rightarrow \text{benzyl} + \text{Cl} \). Our suggestion is (2) \( \text{o-chorotoluene} (S_1) \rightarrow \text{o-chorotoluene} (T_1, S_0) \rightarrow \text{5-methylene-6-chloro-1,3-cyclohexadiene} (\text{MCC}) (S_0) \rightarrow \text{benzyl} + \text{Cl} \). Our results show that the energy barrier of the rearrangement from \( \text{o-tolyl} \) to \( \text{benzyl} \) in path (1) is too high to be overcome, but the intramolecular H atom transfer of \( \text{o-chorotoluene} \) in path (2) may be more reasonable. © 1998 Elsevier Science B.V.

1. Introduction

With the development of computer techniques, ab initio calculation has become a strong implement for studying chemical reaction systems and amends some mechanisms proposed by experiment. For example, in the photodissociation of gloxal at 454.5 nm, Loge and Parmenter, measured a mixture of products, including \( \text{H}_2 \) and \( \text{CO} \) [1]. They suggested that the products come from two steps, i.e. first, \( \text{H}_2\text{C}_2\text{O}_2 \rightarrow \text{H}_2\text{CO} + \text{CO} \) and second, \( \text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO} \). However, Schaefer and coworkers [2,3] were sceptical of this mechanism based on ab initio calculated results. The energy barrier of the decomposition of \( \text{H}_2\text{CO} \) is too high to allow further reaction, therefore Schaefer and coworkers suggested that the \( \text{H}_2 \) product observed by Loge and Parmenter maybe explained by the direct dissociation of \( \text{H}_2\text{C}_2\text{O}_2 \). The proposal has been proved by the experiment of Hepburn et al. [4]. This example indicates the importance of ab initio calculations in studying chemical reactions. In this Letter, an example of a new mechanism for the H atom transfer in the photodissociation of \( \text{o-chorotoluene} \) is proposed, based on ab initio calculation results.

Benzyl radicals play important roles in photochemical reactions. They may be produced not only from the dissociation of the reactant involving a benzyl group but also from those involving the tolyl group (mainly refer to \( \text{o-chorotoluene} \) [5–8]. Childress et al. [5] first reported this appearance by CIDNP measurements and found the benzyl radical...
formed by the thermal decomposition of \( \alpha,\alpha'- \)dimethylbenzoyl peroxide in the presence of hexachloroacetone. Porter and Wright [6] reported the formation of the benzyl radical by the flash photolysis of \( \alpha \)-chlorotoluene. Certainly, the traditional suggestion for the mechanism of benzyl product formation, observed by experiment, is that the \( \alpha \)-tolyl radical yielded by the primary decomposition of \( \alpha \)-chlorotoluene is rearranged to the benzyl radical [7,8]. Following this train of thought, in order to measure the rate constant of the rearrangement from \( \alpha \)-tolyl to benzyl, Ichimura and Mori [7] used a 266 nm laser to photodissociate the \( \alpha \)-chlorotoluene and detected the increasing absorption spectrum of the benzyl radicals. They regarded the rate constant of the rearrangement of \( \alpha \)-tolyl radicals as the rate constant of the increasing absorption of benzyl. Moreover, the process of the production of benzyl radical should be divided into two steps:

(1) 

\[
\begin{align*}
\text{Cl} & \quad \longrightarrow & \quad \text{Cl} + \text{Cl} \\
\text{Cl} & \quad \longrightarrow & \quad \text{Cl} \\
\end{align*}
\]

with enthalpies \( \Delta H = 85 \text{ kcal/mol} \) [20] and \( \Delta H = 23 \text{ kcal/mol} \) [19], respectively.

The rate constant of reaction (2) equalled the rate constant of the yield of benzyl, which was measured as \( 1.5 \times 10^8 \text{ s}^{-1} \) in the experiment of Ichimura and Mori [7].

Calculating the energy barrier of this rearrangement, we state our scepticism concerning the importance of reaction (2) in the formation of the benzyl radical. Section 3 shows that since the energy barrier of the rearrangement from tolyl to benzyl was 43 kcal/mol at the B3LYP//UHF/6-31G* level and only 22 kcal/mol of the available energy went into the internal energy of tolyl radical, it was difficult to yield the benzyl radical from the tolyl radical. Therefore, we assume that the benzyl radical observed by Ichimura and Mori [7] may come from the reactions:

(3) 

(4) 

The purpose of the present work is to theoretically explore the viability of reactions (3) and (4). Although it cannot be stated unequivocally that reaction (4) is the source of benzyl in the \( \alpha \)-chlorotoluene photodissociation, this work provides firm theoretical support for the plausibility of such a molecular rearrangement.

2. A qualitative prediction for theory

Here, we develop in considerably more detail the qualitative prediction made earlier, namely that the H atom may be transferred during the process of photodissociation of \( \alpha \)-chlorotoluene. This argument is made in the light of Fig. 1, which summarizes both probable mechanisms.

The hinge of our discussion of Fig. 1 is the energy for the rearrangement of the \( \alpha \)-chlorotoluene. In order to elucidate this question, the photochemistry of the \( \alpha \)-chlorotoluene should be studied systematically. However, it has not yet been studied in detail. Thus we cogitate it by referring to the photochemistry of some systems similar to this one, for example, the photolysis of \( \text{C}_6\text{H}_4\text{Cl} \) at 248 nm [9].

Nishi et al. [9] detected the translational energy distribution of the recoiling Cl atom, the photofragment of chlorobenzene, and found that the photolysis of \( \text{C}_6\text{H}_4\text{Cl} \) at 248 nm gave rise to a translational energy distribution which consisted of two modes, one Boltzmann and the other Gaussian. This result can lead to a conclusion that the photo-decomposition of the C–Cl bond in chlorobenzene by the 248 nm excitation takes place through two different dissociation channels with probabilities of similar magnitudes: one channel via vibrationally excited levels.

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Fig. 1. Schematic energy relationships for the decomposition of o-chlorotoluene. The relative energies in the brackets are calculated at the B3LYP/6-31G*//HF/6-31G* + ZPE(HF/6-31G*) level. (The ZPE is scaled by 0.894 for anharmonicity correction.)

of the triplet state and another channel via highly excited vibrational levels of the electronic ground state (hot molecules). The initial optically excited singlet (π*, π) state is prohibited from directly crossing over to the repulsive potential, therefore the fast intersystem crossing generates the vibrationally excited triplet state and the highly excited vibrational levels of the electronic ground state. Similarly, in the photolysis of a series of chlorobenzene [10–13], the channel via highly excited vibrational levels of the electronic ground state always exists.

Therefore, considering the system discussed in this Letter, one could logically assume that some branch of the S1 o-chlorotoluene is internally converted to the excited vibrational manifold of the S0 ground state. Moreover, since the 266 nm line of the laser is used in this system by Ichimura and Mori [7] it is entirely reasonable to assume that the experiment begins with S1 o-chlorotoluene at an energy of 107.5 kcal/mol above the S0 ground state of o-chlorotoluene. Then the radiationless transition leaves an amount of molecules with the same 107.5 kcal/mol of energy, but now in S0 internal energy. If we only consider the rearrangement at the electronic ground state, the ultimate question now becomes obvious: over what barriers may the ground-state o-chlorotoluene with 107.5 kcal/mol of internal energy pass?

3. Theoretical approach

All ab initio results presented in this Letter have been carried out with the Gaussian 94w program [14]. The equilibrium geometries and the transition state geometries characterized by one and only one imaginary frequency, are optimized at the HF/6-31G* level without symmetry constraints. Then the energies are refined by using BLYP and B3LYP calculations, two functionals used in density functional theory (DFT). DFT is described in detail elsewhere [15–17]. While calculating the energies of radicals, the spin contamination of the refined energies at the B3LYP level have been controlled, i.e. \( \langle S^2 \rangle \) is less than 0.79. The energies at B3LYP levels should be reasonable for our discussion.

4. Results and discussions

4.1. The geometries and vibrational frequencies

Fig. 2 shows that the geometries of o-chlorotoluene, the transition state (TS) from o-chlorotoluene to o-5-methylene-6-chloro-1,3-cyclohexadiene (MCC), MCC, o-tolyl, the TS from o-tolyl to benzyl and benzyl labeled as structures 1, 2, 3, 4, 5 and 6, respectively. The calculated energy of the benzyl radical, structure 6, is 24.7 kcal/mol lower than that of the o-tolyl radical, structure 4. The π orbital on methylene is stabilized by the conjugation with the aromatic ring, so that the benzyl radical has a more stable geometry than o-tolyl radical.

A saddle point was found at the UHF/6-31G* level, structure (5), which located on the path for the H atom transferring from the methyl to the aromatic ring, with the refined energy at the B3LYP/6-31G* level. The energy barrier was 43 kcal/mol high beyond the o-tolyl radical with the corrected zero-point energy (ZPC). Investigating the geometry of the transition, we showed that at the saddle point, the
The geometries optimized at the HF/6-31G* level. Geometries (1), (2) and (3) are o-chlorotoluene, the transition state and the intermediate MCC, respectively; geometries (4), (6) and (5) are the o-tolyl, the benzyl and the transition state between them, respectively. Distances are in Å.

The structures of various C,H,Cl isomers are also shown in Fig. 2. As has been shown recently, the HF/6-31G* approximation gives geometries for o-chlorotoluene in reasonable agreement with higher level MP2/6-31G* calculations and the calculated rotational barriers at the HF level are in good agreement with the experimental value [18]. We expect that the geometric parameters of the C,H,Cl structures obtained at the HF/6-31G* level have semiquantitative accuracy, enough to discuss the dynamics of the rearrangement of o-chlorotoluene.

In structure (1) of Fig. 2, the C–C, C–C and C–C bond lengths are 1.383 Å, similar to the C–C bond lengths of benzene. The C–C and C–H bond lengths have bond lengths ~1.5 Å, due to the ‘electron donating’ effect of the methyl group.

The intermediate 5-methylene-6-chloro-1,3-cyclohexadiene (MCC) in reaction (3), structure (3), is predicted in Fig. 2. In the MCC geometry, the C1 atom which connects the chlorine atom and the H1 atom transferred from C6 is sp3 hybridized, thus the C1–C2 and C2–C3 bonds have typical C–C single bond lengths of 1.5 Å.

The transition state is qualitatively analyzed by its geometry. The C1–C1 and C1–C2 bond lengths are approximately equal to the mean value of the C–C aromatic bond and the C–C single bond. The H1 atom connects with both C1 and C2 atoms. The C1–H1 and C1–H1 distances all approximately equal to 1.5 Å, ~0.5 Å longer than a normal C–H bond. It is shown that the TS lies in the middle point on the reaction coordinate linking the reactant with the intermediate. The C1–C1 and C1–C2 bond lengths are longer than the reactant, evolving into C–C single bonds in the intermediate MCC. From the structure (1) to (3), the C–Cl bond lengths increase in se-
Table 1
The energetics (kcal/mol) of reactions (1)–(4)

<table>
<thead>
<tr>
<th>Reaction (1)</th>
<th>Reaction (2)</th>
<th>Reaction (3)</th>
<th>Reaction (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH₀</td>
<td>ΔH₁</td>
<td>Eₜ</td>
<td>ΔH₀</td>
</tr>
<tr>
<td>HF/6-31G⁺</td>
<td>52.7</td>
<td>24.2</td>
<td>58.2</td>
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<tr>
<td>BLYP/6-31G⁺</td>
<td>87.2</td>
<td>23.1</td>
<td>39.8</td>
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<tr>
<td>B3LYP/6-31G⁺</td>
<td>88.6</td>
<td>23.0</td>
<td>43.1</td>
</tr>
<tr>
<td>B3LYP/6-31G + G**</td>
<td>86.6</td>
<td>23.6</td>
<td>42.0</td>
</tr>
<tr>
<td>experiments</td>
<td>85b</td>
<td>23c</td>
<td></td>
</tr>
</tbody>
</table>

*Eₜ* indicates the energy barrier. *Ref. [20]. Ref. [19].

 relevance, because the isolated pair electron of the Cl atom joining the conjugation with the π bond on the aromatic ring of the o-chlorotoluene, whereas this conjugation is destroyed in the structure (3).

4.2. The decomposition of the o-chlorotoluene

The enthalpies and energy barriers of reactions (1)–(4) are listed in Table 1. The enthalpy of reaction (1) is 85 kcal/mol in experiment and 86.6 kcal/mol in our calculation; the enthalpy of reaction (2) is 23 kcal/mol in experiment and 23.6 kcal/mol in our calculation. Clearly, the calculated enthalpies of reactions (1) and (2) are in good agreement with the experimental results.

Obviously, for each computational level used, the energy barrier of this rearrangement from o-chlorotoluene is ~100 kcal/mol, which is lower than the energy of the laser, i.e. the o-chlorotoluene can be rearranged to MCC during the photodissociation processes. However, reaction (2) has an energy barrier of ~42 kcal/mol in our calculation. It is shown that the tolyl radical, which has 22 kcal/mol of available energy, released from reaction (1) cannot overcome the energy barrier (in the absence of collisions), to be allowed to react further.

The dissociation of o-chlorotoluene to tolyl and Cl atom is another important channel in the photodissociation, and it may be a direct dissociation process without energy barrier. The competition between reactions (1) and (3) may exist in the photodissociation at the same time.

As a summary, the photodynamics of o-chlorotoluene are described as follows:

\[
\text{C}_7\text{H}_7\text{Cl} + h\nu \rightarrow \text{C}_7\text{H}_5\text{Cl}(S_h) \rightarrow \text{C}_7\text{H}_5\text{Cl}(T_1),
\]

or

\[
\rightarrow \text{C}_7\text{H}_5\text{Cl}(S_0).
\]

Then the T₁ and S₀ states of o-chlorotoluene are dissociated to tolyl and Cl atom, or may be they rearrange to the intermediate MCC and then dissociate to benzyl and Cl atom.

\[
\text{C}_7\text{H}_5\text{Cl}(T_1, S_h) \rightarrow \text{tolyl} + \text{Cl} \\
\text{or} \rightarrow \text{MCC}(S_0) \rightarrow \text{benzyl} + \text{Cl}.
\]

It should be emphasized that the rearrangement mentioned above may occur on the T₁ state of the o-chlorotoluene.

In Ichimura and Mori’s explanation of their experiment [7], they only considered the photolysis channel via the T₁ state of o-chlorotoluene and did not consider the channel via the S₀ state. However, the photodecomposition of o-chlorotoluene via the highly vibrationally excited S₀ state cannot be neglected, since its branch ratio is 0.64 in the photodecomposition of chlorobenzene, which is similar to this system [9].

4.3. The experimental design

Which mechanism the formation of the benzyl radical follows should be examined by detecting the translational energy distribution of the chlorine atom. If reactions (3) and (4) exist in the dissociation of o-chlorotoluene, 44 kcal/mol of surplus energy will be distributed into the internal energy of benzyl and the translational energy of Cl atom. Otherwise, only about total 22 kcal/mol of surplus energy is distributed. Therefore, there must be difference between the translational energy distribution of the Cl atom from the two different mechanisms.
Acknowledgements

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References