ab initio STUDY OF PHOTOCHEMICAL DECOMPOSITION MECHANISM OF TRIPHENYLSULFONIUM SALTS FOR KrF EXCIMER LASER EXPOSURE

NORIHITO OHMORI, YOSHIKAZU NAKAZONO, EIICHI ARAKI,
MASAYUKI HATA, TADATSUGU HOSHINO and MINORU TSUDA
*Laboratory of Physical Chemistry, Faculty of Pharmaceutical Sciences,
Chiba University, Chiba 263, JAPAN*

1. Introduction

Triphenylsulfonium salt is one of the most important photoinitiators in industry as photoacid generator (PAG) in the process of KrF excimer laser lithography [1, 2]. For this reason, many research papers have been published on the photochemical acid generation mechanism from this compound [2–6].

It was found theoretically there are two ways of photochemical acid generation from triphenylsulfonium salts; i.e., one is the process *via* photochemical isomerization [5, 6] and the other *via* photochemical decomposition [5]. In experimental research, only the decomposition mechanism was considered [1, 2, 4], where the photochemical reaction product in the initial step is a phenyl radical [4] or a phenyl cation [2].

In this paper, *ab initio* molecular orbital-CI calculation was performed in order to elucidate the decomposition mechanism and the reaction product was identified in each of the excited states.

2. Method of Calculation

The same methods were used as described in another paper in this issue [7].

3. Results and Discussions

3.1. Photochemical Decomposition Mechanism of Triphenylsulfonium

The potential energy changes in the excited singlet states S_1 – S_{15} were calculated by S-CI method with 3-21G* basis set following the decomposition process (1) and shown in Fig. 1, where the

Fig. 1. Potential energy changes following the S-C separation in the reaction (1) along the lowest and shortest potential energy path of Ph_3S^+ in the ground singlet state S_0 . S-CI calculation using 3-21G* basis set.

potential energy changes in the ground singlet state S_0 is the lowest energy path along the S-C distance separation in the reaction (1). The potential energy increases monotonously following the decomposition process (1) in the ground state S_0 . In the lower-lying excited singlet state $\text{S}_1 \sim \text{S}_{15}$, the potential energies increase at the initial stage of the S-C distance separation except the 7th and 10th excited states (S_7 and S_{10}). The lowest excited singlet state S_1 is favorable for the decomposition after the S-C separation becomes longer than 2.0 Å. Tentatively assumed that this curve S_1 is the lowest potential energy path, the activation energy is 3.57 kcal/mol which is the detailed calculation results in the initial stage of the reaction (1). The 254 nm KrF excimer laser light excites triphenylsulfonium Ph_3S^+ to its 4th and 5th excited state (S_4 and S_5). Since S_4 and S_5 have monotonously increasing potential energy curves along the S-C separation, the internal conversion from S_4 or S_5 to S_1 must be assumed to occur after the S-C separation becomes longer than 2.0 Å. Tentatively provided that the curve S_4 shows the lowest potential energy change, the activation energy is 9.02 kcal/mol for the decomposition process (1) which takes place from the S_4 via the internal conversion to S_1 .

The potential energy elevator in each of the excited singlet states at the initial stage of the S-C separation (1) is the characteristic of aromatic sulfonium Ar_3S^+ . Because of this characteristic, the isomerized products may be produced in high yield in the photochemical reaction of triphenylsulfonium salt in experiments [2]. As shown in Fig. 2 for SH_3^+ as well as in another paper for $(\text{CH}_3)_3\text{S}^+$ [7], the potential energies of these sulfoniums in the lower-lying excited singlet

Fig. 2. Potential energy changes following the decomposition of SH_3^+ along the lowest and shortest potential energy path of the ground singlet state S_0 . SDTQ-CI calculation using 6-31G** basis set with 4s and 4p Rydberg orbitals.

state decrease monotonously

for the S-C separation and the photochemical decompositions of these sulfoniums are expected to occur spontaneously.

A big question arose when we examined the photochemical reaction products in each of the ground and excited states. At 3.6 Å of the S-C distance in Fig. 1, phenyl cation and diphenylsulfide ($\text{Ph}^+ + \text{Ph}_2\text{S}$) is produced in the ground singlet state, but phenyl radical and diphenylsulfide cation radical ($\text{Ph}^\bullet + \text{Ph}_2\text{S}^+\bullet$) is generated from the lowest singlet state S_1 as well as in the lowest triplet state T_1 . The products from $S_2 \sim S_{15}$ at this S-C distance were indicated in Fig.1 for each of the excited singlet states. However, when the decomposition reaction (1) has been completed, ($\text{Ph}^\bullet + \text{Ph}_2\text{S}^+\bullet$) has lower potential energy than ($\text{Ph}^+ + \text{Ph}_2\text{S}$); i.e., ($\text{Ph}^\bullet + \text{Ph}_2\text{S}^+\bullet$) is generated from the ground singlet state S_0 and the lowest triplet state T_1 , but ($\text{Ph}^+ + \text{Ph}_2\text{S}$) is produced from the lowest excited singlet state S_1 . What is the origin of this exchange of the final products between the different electronic states occurred during the decomposition process of triphenylsulfonium? For making this mystery clear, more precise CI calculations are required.

3.2. Photochemical Decomposition Mechanism of SH_3^+ - A Precise Research

Because of the difficulty in the exact determination of the excited states of a molecule which contains a large number of electrons by *ab initio* CI calculation, SH_3^+ was chosen as a model compound for precise research. The lowest potential energy change for the decomposition reaction $\text{SH}_3^+ \rightarrow (\text{SH}_2 + \text{H}^+)$ was determined in the ground singlet state S_0 . The vertical excitation

energies from the ground state to the lower-lying excited states were calculated for the determination of the potential energy changes following the photochemical decomposition process through the excited singlet states $S_1 \sim S_9$ (Fig. 2). The lowest potential energy change in the lowest triplet state T_1 is also shown in Fig. 2 although the structure change is different from that in the singlet state S_0 . The precise energy levels in the singlet states were calculated by SDTQ-CI method. The photochemical decomposition products from the lowest excited singlet state S_1 are SH_2 and a proton whereas those from the ground state S_0 as well as the lowest triplet state T_1 are $SH_2^{+\bullet}$ and a hydrogen atom because of a strong configuration interaction among the ground state S_0 and many of excited singlet states S_n . As shown in Fig. 2, SH_2 and a proton are initially generated from the ground singlet state S_0 at the S-H distance of 2.0 Å. On the other hand, $SH_2^{+\bullet}$ and a hydrogen atom are produced from the lowest excited singlet state S_1 . The mixing of electronic states of $S_0 \sim S_n$, however, occurs strongly at the longer distance of the S-H bond than 2.0 Å, and finally $SH_2^{+\bullet}$ and a hydrogen atom are produced from the excited singlet state S_1 , but $SH_2^{+\bullet}$ and a hydrogen atom are generated from the ground singlet state S_0 , respectively. This situation is exactly the same as observed in the case of triphenylsulfonium Ph_3S^+ . The strong interaction among the ground and excited singlet states is the origin of the exchange of the final product. This phenomenon was observed also in the case of trimethylsulfonium [7]. One should note that the final products were already generated at the S-H distance of 3.6 Å (Fig. 2). In the lowest triplet state T_1 , $SH_2^{+\bullet}$ and a hydrogen atom are produced simply along the potential energy change. When the separation of S-H bond is completed, the sum of the potential energies of $SH_2^{+\bullet}$ and H is lower than that of SH_2 and H^+ (Fig. 2).

References

1. H. Ito and C. G. Willson, *Polym. Eng. Sci.*, **23** (1983) 1012.
2. J. L. Dektar and N. P. Hacker, *J. Am. Chem. Soc.*, **112** (1990) 6004.
3. T. Ueno, H. Shiraishi, S. Uchino, T. Sakamizu and T. Hattori, *J. Photopolym. Sci. Technol.*, **7** (1994) 397.
4. S. P. Pappas, *J. Iwaging Technol.*, **11** (1985) 146.
5. S. Oikawa, N. Fujii, M. Hata and M. Tsuda, *J. Photopolym. Sci. Technol.*, **7** (1994) 483.
6. N. Ohmori, Y. Nakazono, A. Tsujino, M. Hata, S. Oikawa and M. Tsuda, *J. Photopolym. Sci. Technol.*, **8** (1995) 653.
7. Y. Nakazono, E. Araki, N. Ohmori, M. Hata, S. Oikawa and M. Tsuda, *J. Photopolym. Sci. Technol.*, **9** (1996) 693.