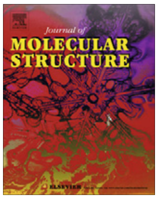
Journal of Molecular Structure 1020 (2012) 1–5

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



Mechanism of the intramolecular hydrogen transfer reaction at ground and excited state of tert-butyl radical: An ESR and DFT study

Tomoya Takada [a], Hiroshi Kawabata [b], Hiroto Tachikawa [c,*]

[a] Department of Material Chemistry, Asahikawa National College of Technology, Syunkodai, Asahikawa 071-8142, Japan
[b] Venture Business Laboratory, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan
[c] Division of Materials Chemistry, Graduate School of Engineering, Hokkaido University, Kita-ku, Sapporo 060-8628, Japan

ARTICLE INFO

Article history:
Received 21 October 2011
Received in revised form 3 April 2012
Accepted 3 April 2012
Available online 10 April 2012

Keywords:
ESR
DFT
Radical
Hydrogen transfer
Photoreaction

ABSTRACT

Hydrogen transfer reactions at the ground and excited states of tert-butyl radical to form iso-butyl radical have been investigated by means of ab initio calculation and electron spin resonance (ESR) spectroscopy. It was found that tert-butyl radical irradiated with 254 nm ultraviolet light converts quite efficiently to iso-butyl radical. Also, it was suggested that this conversion occurs as an intramolecular hydrogen transfer from a methyl group of tert-butyl radical to a radical site (central carbon atom). The theoretical calculations showed that barrier height of hydrogen transfer at the excited state is significantly lower than that of ground state. The mechanism of internal hydrogen atom conversion from tert-butyl to iso-butyl radicals was discussed.

1. Introduction

The proton and hydrogen atom transfers between molecules are the most fundamental processes in chemistry and in biochemistry [1–3]. It is known that the proton transfer is caused by Coulomb interaction, and the proton can transfer easily to anion at both ground and excited states. Theoretical calculations of proton transfer process shows that activation barrier exists for both ground and excited states, but the barrier height at the excited state is remarkably lower than that of the ground state. This is due to the fact that the magnitude of charge separation becomes bigger at the excited state. This charge separation induced by the electronic excitation is expressed by the reaction,

$$\text{A—H}^{\delta+}\text{---B}^{\delta-}(\text{ground state}) \xrightarrow{h\nu} \text{A—H}^{+}\text{---B}^{-}(\text{excited state})$$

where H^+, A–H and B mean a proton, proton donor and acceptor molecules, respectively. The B molecule interacts with the proton via a hydrogen bond (denoted by a dashed line). Therefore, a long-range proton transfer is possible at the excited state. Thus, the proton transfer reaction at the excited state is well-known in several reaction systems [4–6].

Hydrogen atom transfer reactions at the excited state are also investigated by several groups [7–9]. For example, it is known that excited ketones, azoalkanes and organic radicals can abstract a hydrogen atom from hydrogen donor molecules. Iwasaki and Toriyama observed for the first time that the photo-induced hydrogen atom transfer reaction in tert-butyl radical [10,11]. From electron spin resonance (ESR) measurement, it was found that tert-butyl radical (denoted hereafter by **tert-Bu**) is efficiently converted to iso-butyl radical (denoted by **iso-Bu**) by UV-irradiation at 77 K. This reaction takes place as an intramolecular hydrogen transfer reaction,

$$\text{tert-butyl radical (I)} \xrightarrow{h\nu} \text{iso-butyl radical (II)}$$

Also, it was found that the reverse reaction (II → I) occurs by day-time scale without UV-irradiation [10,11]. From the experiment using deuterium substitution of hydrogen atoms of tert-Bu, they pointed out that the tunneling effect is important in proceeding of the hydrogen transfer at the excited state.

More recently, Takada et al. (one of the authors in the present paper) have observed the hydrogen atom transfer at the excited states in normal alkyl radicals [12–15]. They found that the deuterium substitution causes significant lowering of the reaction rate. However, the reaction mechanism is still unclear.

In the present study, the intramolecular hydrogen atom transfer reaction in tert-Bu at the ground and excited states are investigated by means of ESR spectroscopy and density functional theory (DFT) methods in order to shed light on the reaction mechanism on the H-atom transfer at the excited states. The potential energy curves (PECs) for both ground and excited states are calculated by time-dependent (TD) DFT calculations. The model of the

---

* Corresponding author. Fax: +81 11706 7897.
E-mail address: hiroto@eng.hokudai.ac.jp (H. Tachikawa).

http://dx.doi.org/10.1016/j.molstruc.2012.04.005

hydrogen transfer at the excited states is proposed on the basis of theoretical results.

2. Methods

2.1. ESR measurement

Chemicals used were tert-butyl chloride, perdeuterated methanol, and perdeuterated 2-propanol. Tert-butyl chloride was supplied by Tokyo Kasei, while perdeuterated methanol and perdeuterated 2-propanol were supplied by Aldrich. Tert-butyl chloride was added to the mixture of 95 vol.% of perdeuterated methanol and 5 vol.% of perdeuterated 2-propanol to make the solution containing 2 vol.% tert-butyl chloride. The mixed sample was frozen at 77 K and irradiated with γ-ray with a dose of about 10 kGy using ^{60}Co. The sample was then irradiated with 254 nm ultraviolet light at 77 K using a low-pressure mercury lamp. It has been reported that tert-Bu shows the 3p Rydberg absorption around the wavelength of 254 nm [16]. EPR spectra of the sample were recorded using an X-band EPR spectrometer (JEOL JES-TE200).

2.2. Theoretical calculations

The structures of tert-Bu, iso-Bu, and transition state of reaction at ground and excited states were fully optimized at the B3LYP/6-311++G(d,p) level of theory. Note that recent theoretical studies showed that B3LYP calculation gives a reasonable energetics for the radical conversion reaction [17] and several open-shell systems [18–22]. The harmonic vibrational frequency analysis for the optimized structures was also done at the same level. The potential energy curves along the reaction pathway between tert-Bu and iso-Bu at the ground and first, second, third, fourth, fifth, and sixth doublet excited states were calculated by ab initio and time-dependent density functional theory (TD-DFT) calculations at the 6-311++G(d,p) level of theory. The potential energy curves were calculated along the intrinsic reaction coordinate (IRC) from tert-Bu to iso-Bu. All calculations were carried out using Gaussian 03 program package [23].

3. Results

3.1. ESR observation of photo-conversion of tert-Bu to iso-Bu radicals

ESR measurements of the tert-Bu and the product after UV-irradiation have been done to distinctly confirm if the photo-conversion of tert-Bu to iso-Bu occurs by intramolecular hydrogen atom transfer. Fig. 1 shows ESR spectra of γ-irradiated perdeuterated methanol glass containing 2 vol.% of tert-butyl chloride. Fig. 1 (upper) shows the spectra obtained after γ-irradiation, while Fig. 1 (lower) shows the spectra obtained after successive 254 nm UV-irradiation (30 min). Fig. 1 (upper) is the typical spectrum consisting of 10 lines generated by equivalent nine hydrogen atoms of tert-butyl radical. The hyperfine coupling constant was measured to be 2.3 mT. This result indicates that tert-Bu is formed by C–Cl bond cleavage caused by dissociative electron capture:

$$\text{tert-BuCl} + e^{-} \rightarrow [\text{tert-BuCl}]^{-} \rightarrow \text{tert-Bu} + Cl^{-}$$

After UV-irradiation, the spectrum changed to 4 – line spectrum generated by two hydrogen atoms of α-CH_2 group and one hydrogen atom of β-CH group. The hyperfine coupling constants were measured to be 2.30 mT (α-CH_2 group) and 4.40 mT (β-CH group). This spectrum shift strongly indicates that tert-Bu converts efficiently to iso-Bu by the UV-irradiation. Under the experimental condition employed in this study, only intramolecular hydrogen atom transfer is possible; tert-Bu is fully isolated in the matrix, so intermolecular hydrogen transfer does not occur.

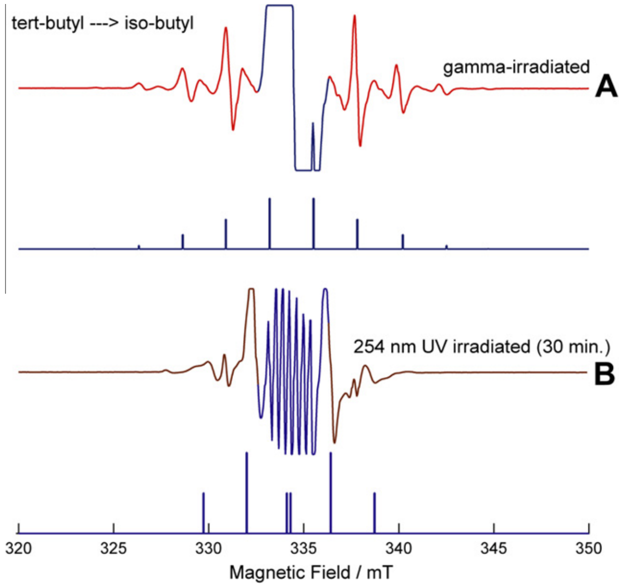


Fig. 1. ESR spectra of γ-irradiated 77 K perdeuterated methanol glass containing 2 vol.% of tert-butyl chloride: before UV-irradiation (upper); after 254 nm UV-irradiation (lower).

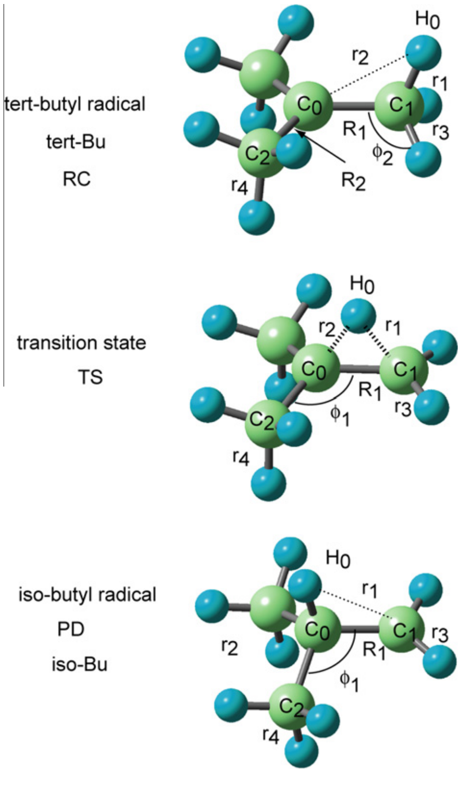


Fig. 2. Optimized structures of tert-Bu, iso-Bu, and the transition state (TS) calculated at the B3LYP/6-311++G(d,p) level.

3.2. Structures and energetics of tert-Bu, iso-Bu, and the transition state

The structures of tert-Bu, iso-Bu, and the transition state between tert-Bu and iso-Bu were fully optimized at the B3LYP/6-311++G(d,p) level of theory. The structures and geometrical parameters are given in Fig. 2 and Table 1, respectively. The optimized structures show that the carbon atoms of tert-Bu (C_0) and iso-Bu (C_1) have planar structure due to sp^2 hybrid orbital in the