



Radicals generated from 2-chloro-5-fluorotoluene by corona discharge



Eun Hye Yi, Young Wook Yoon, Sang Kuk Lee*

Department of Chemistry and The Chemistry Institute of Functional Materials, Pusan National University, Pusan 609-735, Republic of Korea

ARTICLE INFO

Article history:

Received 17 February 2014

In final form 7 May 2014

Available online 17 May 2014

ABSTRACT

The generation of molecular radicals in corona discharge was investigated spectroscopically by varying the experimental conditions applied to a substituted toluene precursor. Vibronic emission spectra were observed from the corona discharge of 2-chloro-5-fluorotoluene seeded in a large amount of carrier gas helium. From an analysis of emission spectra observed, it was confirmed that bond dissociation energy plays a key role in radical formation. The possible pathway for the formation of benzyl-type radicals is proposed to explain the observation.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Transient molecules have long been a topic of great interest in chemistry because they play an important role as reaction intermediates, created in one step and quickly consumed in a subsequent step of chain reaction. For those interested in the fundamental issues of chemical reaction, the characteristics and structure of radicals serve to define the nature of chemical reactivity [1].

Most transient molecules are generated from stable precursors when sufficient energy is applied to break chemical bonds [2]. However, it is difficult to isolate transient molecules in sufficient concentrations for spectroscopic study due to their short lifetime and high reactivity. Engelking et al. [3,4] invented a simple device to generate jet-cooled molecular radicals using an electric discharge. Although the original pinhole-type glass nozzle has been employed to generate carbon-free diatomic radicals such as OH radical for spectroscopic purposes, it could not be extended to large aromatic compounds because sticky soot deposits block the nozzle throat and reduce stability of the corona discharge.

The benzyl radical [5] is the prototypic aromatic free radical that is believed to be a key intermediate in aromatic chain reactions and has been the subject of numerous spectroscopic works. On the other hand, ring-substituted benzyl-type radicals have received less attention due to the difficulties associated with the production of radicals from precursors and possible intramolecular rearrangements at the excited electronic states [6].

The generation of benzyl-type radicals from substituted toluenes by corona discharge is complicated due to the dissociations of

substituents which compete with methyl C–H bonds in this respect. For example, the corona discharge of 2,6-dichlorotoluene forms 2-chlorobenzyl and 2,6-dichlorobenzyl radicals, the proportions of which strongly depend on the strength of the electric discharge [7].

On the other hand, it has been reported [6] that the 3,5-difluorobenzyl radical undergoes intramolecular rearrangement in a corona discharge to produce more stable isomers. Recently, relations between bond dissociations and substitution positions were examined by observing the fluorescence from difluorobenzyl radicals [8] generated by corona discharge of 1,2,3-trifluorotoluene. Although the prediction of the possible benzyl-type radicals produced from precursors is useful for analysis of the observed spectrum, the concept underlying the bond dissociation process has not been well established for substituted toluenes.

In this study, we report the vibronic emission spectra observed from the corona discharge of 2-chloro-5-fluorotoluene at different voltages. From comparing the observed emission intensities of each species produced, we identified factors responsible for the formation of benzyl-type radicals. In addition, we propose a possible pathway for the generation of benzyl-type radicals which can explain the results of the spectroscopic observation.

2. Experimental

A technique of corona excited supersonic jet expansion (CESE) was used to generate vibronically excited but jet-cooled molecular radicals from the precursor, 2-chloro-5-fluorotoluene using a home-made pinhole-type glass nozzle, which is similar to that originally invented by Engelking [4] except that the nozzle has a round base to reduce soot deposition in the nozzle throat. Visible vibronic emission spectra were recorded using a long-path double monochromator.

* Corresponding author. Fax: +82 51 516 7421.

E-mail address: sklee@pusan.ac.kr (S.K. Lee).

Commercially available 2-chloro-5-fluorotoluene (Aldrich, reagent grade) was employed without further purification and vaporized at room temperature inside a Pyrex vaporizing vessel containing helium carrier gas at 2 bar. The precursor was subjected to corona discharge and supersonic jet expansion through a modified glass nozzle of throat diameter 0.3 mm. The concentration of precursor in helium was adjusted for the maximum total visible intensity and calculated to be less than 1% in terms of vapor pressure.

A pointed stainless steel rod was used as the anode and was connected to the negative terminal of a high voltage DC power supply. The discharging current was held at 3 mA by varying voltage, and the system was stabilized using a 150 k Ω current-limiting ballast resistor. The Pyrex expansion chamber was evacuated using a mechanical vacuum pump, to maintain a chamber pressure of about 3.0 mbar for continuous jet expansion.

During discharge, a weak green colored jet indicated the presence of the benzyl-type radicals. Fluorescence from the downstream jet region at 5 mm below the nozzle throat was collected through a quartz lens ($F = 50$ mm and $D = 38$ mm) positioned inside the expansion chamber and focused onto the slit of a monochromator (Jobin Yvon U1000) equipped with a cooled photomultiplier tube (Hamamatsu PMT, R649) and a photon counting system. The vibronic emission spectra of benzyl-type radicals were obtained by scanning from 19000 to 22000 cm^{-1} in increments of 2.0 cm^{-1} using a slit width of 0.1 mm over 1 h. The wavenumber of the spectrum was calibrated using the He and H atomic transition lines [9] recorded in the same spectral region and believed to be accurate to ± 1.0 cm^{-1} .

3. Results and discussion

It has been reported [10] that a well-controlled corona discharge of toluenes seeded in a large amount of carrier gas helium produces benzyl radical in their excited vibronic states. Although the mechanism responsible for the generation and excitation of benzyl radical in a corona discharge has not been established, it can be suggested that metastable He atoms ($1s2s\ ^3S_1$), about 19.82 eV above the ground state [11], formed by corona discharge transfer excess energy to precursor by collisional process, and that this results in the dissociation of a methyl C–H bond to produce the benzyl radical. Accordingly, it would be expected that benzyl-type radicals would be similarly produced from substituted toluenes. [12]

The visible emissions of benzyl-type radicals are believed to be due to transitions from the close-lying D_2 and D_1 excited states to the D_0 ground state. However, the $D_2 \rightarrow D_0$ transition is not always detected due to efficient population relaxation from D_2 to D_1 , as these two states are connected through vibronic coupling [13]. During supersonic jet expansion, molecules experience collisional vibrational relaxation from the excited vibrational states to the vibrationless D_1 state [14]. Thus, the observed vibronic emission spectra show the origin band of the $D_1 \rightarrow D_0$ transition at highest frequency, and followed by a series of vibronic bands to the red of this origin band, that is, spectra are similar to laser excited dispersed fluorescence spectrum obtained by pumping the origin band of the electronic transition [5]. Furthermore, when the molecular structure is little changed by electronic transition, the emission spectrum shows the strongest origin band and shorter spectral progression as shown in Table 1.

From the corona discharge of 2-chloro-5-fluorotoluene, the formation of three possible benzyl-type radicals, 2-chloro-5-fluorobenzyl [1], 3-fluorobenzyl [2], and 2-chlorobenzyl [3] radicals would be expected, as shown in Figure 1. The 2-chloro-5-fluorobenzyl radical is formed by the dissociation of a methyl C–H bond of the precursor, whereas the 3-fluorobenzyl

Table 1
Comparison of the origin bands in the $D_1 \rightarrow D_0$ transition of benzyl-type radicals.^a

Molecules	Origin band	Shift ^b
Benzyl ^c	22002	0
2-Chlorobenzyl ^d	21040	78
3-Fluorobenzyl ^e	21691	808
2-Chloro-5-fluorobenzyl ^f	20258	1744

^a Measured in vacuum (cm^{-1}).

^b Red-shift from the origin band of benzyl radical (22002 cm^{-1}).

^c Ref. [10].

^d Ref. [22].

^e Ref. [23].

^f Unpublished data.

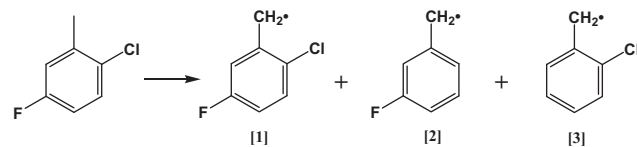


Figure 1. Formation of three possible benzyl-type radicals from 2-chloro-5-fluorotoluene by corona discharge, 2-chloro-5-fluorobenzyl [1], 3-fluorobenzyl [2], and 2-chlorobenzyl [3] radicals.

and 2-chlorobenzyl radicals are obtained, respectively, by replacing the Cl atom at 2-position and the F atom at 5-position by a H atom, along with the dissociation of a methyl C–H bond. The mechanism of methyl C–H bond dissociation has been well discussed for *o*-xylene, in which laser excitation from the S_0 to S_1 states increases vibrational amplitude and eventually causes the C–H bond dissociation to produce the *o*-xylyl radical [15].

Figure 2(a) shows a portion of the visible vibronic emission spectrum observed from the corona discharge of 2-chloro-5-fluorotoluene at a discharge voltage of 1.5 kV, and most vibronic bands in the region 19000–20300 cm^{-1} . The strongest band at 20258 cm^{-1} represents the origin band of the $D_1 \rightarrow D_0$ transition of 2-chloro-5-fluorobenzyl radical [16], and this is followed by a series of vibronic bands to lower wavenumbers. The large red-shift (1744 cm^{-1}) of the origin band as compared with the parental benzyl radical at 22002 cm^{-1} [10] is attributed to the substituent effect of Cl at the 2-position and of F at the 5-position, which both extends the space available for π electron delocalization by conjugation to the halogen p orbitals [17]. Accordingly, this red-shift is strongly dependent on the positions, the natures, and the numbers of substituents [18,19].

Discharge at 1.5 kV generates the 2-chloro-5-fluorobenzyl radical only because the collisional excitation by metastable helium preferentially dissociated the weakest bond, that is, a methyl C–H bond (bond dissociation energy = 356 kJ/mol). At 1.6 kV, the spectrum exhibited evidence of C_2 and 3-fluorobenzyl radical generation shown in Figure 2(b). Weak complicated features in the spectral region 21100–21350 cm^{-1} were due to the swan system of C_2 species formed from the precursor [20]. In fact, increasing discharge voltage causes rapid production of small fragments such as C_2 and CH with in CESE system. Further increases in discharging voltage over the threshold resulted in the formation of C_2 only, due to disruption of the benzene ring.

Since the bond dissociation energies [21] of benzylic C–H, phenylic C–Cl, and C–F bonds of 2-chloro-5-fluorotoluene are, respectively, 356, 398, and 519 kJ/mol, the replacement of the strong C–F bond by the C–H bond is thermodynamically unfavorable, which prevents the production of the 2-chlorobenzyl radical in a corona discharge. We were unable to detect any spectral evidence of the 2-chlorobenzyl radical [22], which has been reported to have an origin band at 21040 cm^{-1} and exhibit an excellent S/N for the $D_1 \rightarrow D_0$ transition.

Download English Version:

<https://daneshyari.com/en/article/5380789>

Download Persian Version:

<https://daneshyari.com/article/5380789>

[Daneshyari.com](https://daneshyari.com)