

Evidence of Molecular Rearrangement in Benzyl-type Radicals

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Searching for new molecular radicals which are believed to play an important role as reaction intermediates in aromatic chain reactions, we have applied the technique of corona excited supersonic expansion employing a pinhole-type glass nozzle to obtain the vibronic spectrum from the corona discharge of precursor 3,5-difluorotoluene with a large amount of inert carrier gas helium. An analysis of the observed spectrum revealed that many vibronic bands are from other isomeric difluorobenzyl radicals generated in the jet by migration of the fluorine atom or methylene group to the adjacent position in the 3,5-difluorobenzyl radical. A possible mechanism was proposed for the formation of other isomers by using a bridged cyclic intermediate structure.

Key Words: Molecular rearrangement, Spectroscopy, Difluorobenzyl radical

Introduction

The benzyl radical, the prototype aromatic molecular radical, is one of the most important intermediates in aromatic chemistry and the subject of numerous spectroscopic studies.¹⁻³ With the knowledge based on the electronic structure of the benzyl radical, the effect of substitution on the electronic energy of benzyl-type radicals has been extensively examined to understand the substitution effect.

Bindley *et al.*⁴ have initiated the study on fluorine substituted benzyl radicals by producing fluorobenzyl radicals from corresponding fluorotoluenes, in which the contribution of fluorine has been identified for all three isomers of fluorobenzyl radicals from analysis of the vibronic emission spectra. The laser-induced fluorescence (LIF) spectra⁵ of fluorobenzyl radicals have been recorded by monitoring the fluorescence from the decomposition products of precursors.

Over the past decade, we reported the vibronic emission spectra of fluorine-substituted benzyl-type radicals, from which the electronic energy and vibrational mode frequencies of mono-,⁶ bi-,⁷⁻⁹ and penta¹⁰-substituted radicals were determined. Although fluorine-substituted benzyl radicals have been recognized as suitable candidates for spectroscopic studies due to their strong fluorescence, the observation of multi fluorine-substituted benzyl radicals has been greatly limited by the difficulty in getting suitable precursors.

There are a total of 6 isomers of difluorobenzyl radicals: 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-difluorobenzyl radicals. Of these, the 2,6-isomer⁶ was the first to be successfully identified through vibronic emission spectrum, in which many of the observed vibronic bands were clearly assigned. Since then, all of the other isomers except for 3,5-difluorobenzyl radical have been examined sequentially in this laboratory.

In this paper, we present the unexpected observation of other isomeric difluorobenzyl radicals from the corona discharge of precursor 3,5-difluorotoluene in the technique of corona excited supersonic expansion using a pinhole-type glass nozzle. A possible mechanism is proposed for the isomerization to other isomers in the gas phase.

Experimental Section

The experiment was carried out in a corona excited supersonic expansion (CESE) using a pinhole-type glass nozzle that has been described in detail.¹¹ The vibronic emission spectra from the corona discharge of the precursor were recorded with a long path monochromator.

The vapor of precursor 3,5-difluorotoluene (Aldrich, reagent grade) at room temperature was mixed with 2.0 atm of He gas, in which the concentration of precursor in the gas mixture was controlled for the maximum emission intensity monitored from the strongest band in the spectrum. A pinhole-type glass nozzle (D = 12.7 mm) with very small orifice (D = 0.3 mm) in the center was used to produce supersonic jet expansion as well as corona excitation using a DC discharge of 3 mA at 1.5 kV that was adjusted for the brightest emission intensity as well as the least production of small fragments such as C₂ and CH radicals.

The blue-green colored emission in the jet, the evidence of the presence of benzyl-type radicals in the D₁ → D₀ electronic transition, was collected from the area below the nozzle throat and focused on to the slit of the monochromator (Jobin Yvon U1000) equipped with a cooled photomultiplier tube (PMT, Hamamatsu R649). The vibronic emission spectra were recorded by scanning from 18000 to 22500 cm⁻¹ at steps of 2.0 cm⁻¹ with a slit width of 0.2 mm over 1 hr. The wavenumber of the spectrometer was calibrated by the He atomic lines¹² recorded with the spectra and believed to be accurate within ±1.0 cm⁻¹.

Results and Discussion

A well-controlled corona discharge of substituted toluene with a large amount of inert carrier gas produces corresponding jet-cooled benzyl-type radicals¹³ in the excited vibronic state. Although the mechanism for the generation and excitation of benzyl-type radicals in corona discharge has not been exactly established, it has been suggested that when using He as a carrier gas, the metastable He atom in the 1s2s ³S₁ state initially excited by the corona discharge transfers its excess energy to the precursor through a collisional process.¹⁴ The highly excited

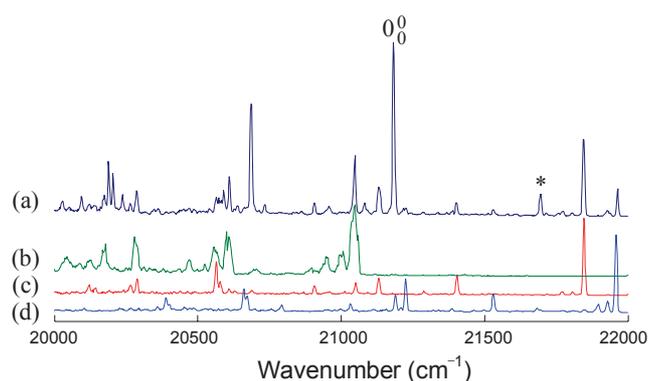


Figure 1. Comparison of the vibronic emission spectra of difluorobenzyl radicals. The spectra (a), (b), (c), and (d) were obtained from the corona discharge of precursors 3,5-, 2,5-, 2,4-, and 3,4-difluorotoluenes, respectively. Many bands in the spectrum (a) coincide with those of the strong vibronic bands of the other isomers, suggesting the evidence of isomerization. The origin band of the *m*-fluorobenzyl radical in the $D_1 \rightarrow D_0$ transition is indicated by an asterisk in the spectrum (a).

precursor then decomposes to produce corresponding benzyl-type radicals by losing a hydrogen atom from the vulnerable methyl group rather than from the benzene ring.¹⁵ The molecular radicals thus generated undergo collisional relaxation with He atoms and, in this process, remove rotational and vibrational energy in the excited electronic state, eventually producing electronically hot but rovibrationally cold species.

Figure 1 shows the comparison of the vibronic emission spectra observed in CESE using a pinhole-type glass nozzle. The spectra (a), (b), (c), and (d) were recorded from the corona discharge of precursors 3,5-, 2,5-, 2,4-, and 3,4-difluorotoluenes, respectively, with a large amount of inert carrier gas He under almost the same experimental condition. Most of the bands were observed with very good S/N ratio in the spectral region of 20000 - 22000 cm^{-1} . Table 1 lists the position of the origin band of mono- and di-fluorobenzyl radicals, in which the substitution in the benzene ring shifts to red region compared to the parental benzyl radical at 22002 cm^{-1} .

The vibronic emission spectra of benzyl-type radicals observed in CESE typically exhibit the strongest band at the highest wavenumber, as evident in the spectra (b), (c), and (d), since the fluorescence almost always occurs from the lowest excited state of the molecules. However, the pattern of spectrum (a) is slightly different from those of typical benzyl-type radicals by showing the strongest band at 21182 cm^{-1} and other strong bands to the blue region.

In order to identify the origin of vibronic bands observed to the blue of the strongest band, we compared the spectra of 2,4-, 2,5-, and 3,4-difluorobenzyl radicals with that from 3,5-difluorotoluene by assuming isomerization to other isomers. Evidently, many bands were coincident with those of the other isomers, including that from *m*-fluorobenzyl radical. The *m*-fluorobenzyl radical was believed to be produced by replacing through intramolecular reaction one of the fluorine atoms at the *m*-position with a hydrogen atom of methyl group of the benzene ring.¹⁶ The 2,4-isomer was generated by transferring a methylene group to the adjacent position in the either direction while the 2,5-

Table 1. Origin bands of fluorine-substituted benzyl radicals of the $D_1 \rightarrow D_0$ transition^a

molecules	origin band	shift ^d
benzyl ^b	22002	0
<i>o</i> -fluorobenzyl ^c	21924	78
<i>m</i> -fluorobenzyl ^c	21691	311
<i>p</i> -fluorobenzyl ^c	21527	475
2,3-difluorobenzyl ^e	21338	664
2,4-difluorobenzyl ^e	21846	156
2,5-difluorobenzyl ^e	21048	954
2,6-difluorobenzyl ^e	21774	228
3,4-difluorobenzyl ^e	21962	40
3,5-difluorobenzyl ^f	21182	820

^aMeasured in vacuum (cm^{-1}). ^bReference 1. ^cReference 17. ^dWith respect to the origin band of the benzyl radical (22002 cm^{-1}). ^eReferences 7,8,18-20. ^fThis work.

and 3,4-isomers were obtained by moving one of the fluorine atoms to the *o*- and *p*-positions from the *m*-position of the benzene ring, respectively, in the either direction. In the spectrum (a), the fairly strong observation of the origin band of the 2,4-isomer suggests that bridging of a methylene group with two carbons of the benzene ring is thermodynamically a more favorable process than that of the fluorine atom, resulting in 7 membered ring. Tropylium cation is an exceptionally stable 7 membered carbonium ion because of stabilization by resonance to a very high degree.

For a theoretical understanding of the isomerization process of 3,5-difluorobenzyl radical in a corona discharge, we performed the calculation on the stability of the difluorobenzyl radicals at the DFT level with a 6-311g* basis set using a Gaussian03 program, from which the 3,5-difluorobenzyl radical showed the least stability among the isomers. The stability of difluorobenzyl radical is measured by bond dissociation energy (BDE) given by Brocks *et al.*²¹ The equation can be expressed in the following equation.

$$\text{BDE}(\text{C-H}) = 1.93 a(\text{H}_\alpha) + 57.8 \quad (1)$$

where $a(\text{H}_\alpha)$ represents the hyperfine coupling constant of hydrogen atom bonding at alpha position. Since the stability of radical is inversely proportional to the magnitude of hyperfine coupling constant, radical shows higher stability with decreasing magnitude of the constant. Also, another method for estimating stability of radicals has been developed by Dust and Arnold²² in which radical constant $\sigma_\alpha(\text{X})$ can be expressed by

$$\sigma_\alpha(\text{X}) = 1 - a(\text{H}_\alpha(\text{X}))/a(\text{H}_\alpha(\text{H})) \quad (2)$$

where $a(\text{H}_\alpha(\text{X}))$ and $a(\text{H}_\alpha(\text{H}))$ represent the hyperfine coupling constant of hydrogen atom at α -position of substituted and unsubstituted benzyl radicals, respectively. According to the equation above, the radical constant of unsubstituted benzyl radical is zero. The hyperfine coupling constant depends on the symmetry of molecules, the kind of substituents, and position of substitution. Table 2 shows the comparison of calculated results

Table 2. Comparison of calculated results representing stability of difluorobenzyl radicals

DFT/ 6-311+G(d,p) ^a	HFCC1 ^b	HFCC2 ^c	HFCC (ave.) ^d	Const. (ave.) ^e	BDE ^f
Benzyl	16.02875	16.02875	16.02875	0.00000	88.73549
2,3-difluoro-	16.00023	16.26662	16.13343	-0.00653	88.93751
2,4-difluoro-	15.97880	16.26023	16.11952	-0.00566	88.91066
2,5-difluoro-	15.87676	16.12229	15.99953	0.00182	88.67908
2,6-difluoro-	16.06264	16.06274	16.06269	-0.00212	88.80099
3,4-difluoro-	16.02434	16.05499	16.03967	-0.00068	88.75655
3,5-difluoro-	16.19491	16.19614	16.19553	-0.01040	89.05736

^aMethod employed in this calculation. ^bHyperfine coupling constant of hydrogen of small steric hindrance. ^cHyperfine coupling constant of hydrogen of large steric hindrance. ^dAverage of two hyperfine coupling constants. ^eRadical constant calculated from equation (2). ^fBond dissociation energy (kcal/mol) of C-H bond calculated from equation (1).

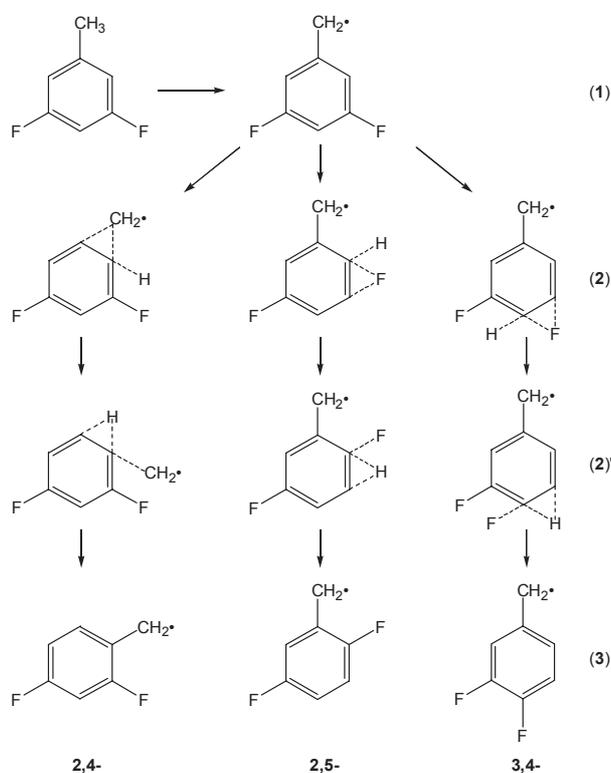


Figure 2. A possible mechanism for isomerization of the 3,5-difluorobenzyl radical to more stable isomers. Exchange of the CH₂ group with a hydrogen atom at the adjacent position generates (a) 2,4-difluorobenzyl radical while exchanging the F atom with a hydrogen atom at the adjacent position produces (b) 2,5- or (c) 3,4-difluorobenzyl radicals.

for difluorobenzyl radical isomers, in which 3,5-isomer exhibits the least stability among isomers.

Thus, we strongly believed that the 3,5-difluorobenzyl radical

generated from precursor in a corona discharge may undergo isomerization in the next step to more stable isomers by switching substituents to adjacent positions.

Figure 2 proposes a possible mechanism for the formation of other isomers by using a bridged cyclic intermediate structure. The 3,5-difluorobenzyl radical (1) is initially formed by losing a hydrogen atom from a loose C-H bonding of the methyl group in electronic excitation. In the next step, the substituent, either a fluorine atom or methylene group, may transfer to an adjacent position *via* a bridged intermediate structure (2) which partially loses aromaticity to a higher energy state, after which a hydrogen atom then moves to the previous position of the substituent to retain the aromaticity of benzyl-type radicals (3). In this process, the hydrogen atom and the substituent exchange position to produce other isomers.

In summary, we observed the evidence for the isomerization of the 3,5-difluorobenzyl radical in a jet generated from the corona discharge of 3,5-difluorotoluene seeded in a large amount of inert carrier gas helium through vibronic emission spectra. A possible mechanism is proposed for the isomerization by using a transient bridged cyclic intermediate.

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