Reassignment of Isomeric Dimethylbenzyl Radicals Generated by Corona Discharge of 1,2,4-Trimethylbenzene

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Received August 19, 2008

Isomeric dimethylbenzyl radicals were identified by analysis of the vibronic emission spectrum recorded from the corona excited supersonic expansion through a pinhole-type glass nozzle of precursor 1,2,4-trimethylbenzene seeded in a large amount of carrier gas helium. The visible spectrum showed several vibronic bands reflecting the characteristics of the band shape of each isomer generated. An analysis based on mono-substituted methylbenzyl radicals confirmed that all three of the dimethylbenzyl isomers were formed in the corona discharge of precursor as a result of the removal of a hydrogen atom from the methyl group at the different substitution position. For the three isomeric products, the $D_1 \rightarrow D_0$ electronic transition and the vibrational mode frequencies in the ground electronic state were determined by comparing with those from both an *ab initio* calculation and the known data of the precursor.

Key Words : Dimethylbenzyl radicals, Spectroscopy, Vibronic spectrum

Introduction

Whereas the benzyl radical, a prototypical aromatic radical, has been the subject of many spectroscopic studies,[1,2] large alkyl-substituted benzyl radicals have received far less attention. Earlier works on benzyl radicals have been reported by Schuler *et al.*[3] and Walker and Barrow in the visible region.[4] Bindley *et al.*[5,6] could assign the several strong vibronic bands in the emission spectra of xylyl radicals produced in a corona discharge of xylenes. Charlton and Thrush[7] have applied the technique of laser induced fluorescence (LIF) to obtain the vibronic assignments and lifetime measurement of xylyl radicals.

Hiratsuka *et al.*[8] have calculated the energies of close-lying doublet states in benzyl and xylyl radicals, making it possible to explain vibronic coupling between two electronic states. Cossart-Magos *et al.*[2] have determined the direction of transition dipole moments upon electronic excitation, by analyzing the rotational contours of *o*-xylyl radicals. Fukushima and Obi[9] have used the LIF technique to examine the vibronic coupling between the two lowest excited electronic states of the *p*-xylyl radical. Controversial assignments of *p*-xylyl radical were satisfactorily resolved by means of band shape analysis of visible vibronic bands in high resolution emission spectra.[10] In addition, torsional analysis of the methyl rotor in xylyl radicals has been carried out by Lin and Miller.[11]

Selco and Carrick[12] have assigned many vibronic bands in the vibronic emission spectra of xylyl radicals. Lee *et al.*,[13-19] utilizing an improved corona discharge system, have observed the vibronic emission spectra of many benzyl-type radicals, in which methyl substitution, moreover, was well analyzed. They also extended the observation to multi-substituted methyl benzyl radicals such as dimethyl[17] and trimethyl[16] benzyl radicals. However, their assignment of

spectrum observed from the corona discharge of 1,2,4-trimethylbenzene[13] was not clear, because they did not explain the existence of other isomers that might be formed in the discharge.

Corona discharge has become one of the most convenient techniques for production of transient species from a precursor seeded in a large amount of carrier gas. The combination of corona discharge with supersonic expansion is for spectroscopists a useful tool for observing the emission spectra of transient molecular species, broadening the repertoire of laser-free spectroscopic study. The spectral simplification and molecular stabilization associated with the expansion of a large amount of inert carrier gas cannot be achieved in any other way. Of the emission sources utilizing that combination, the one providing enough continuous photon intensity for high resolution studies of weak transition is the pinhole-type glass nozzle[20,21] which recently was adapted for observation of the vibronic emission spectra of benzyl-type radicals.[22]

In the present study, we reassigned the vibronic emission spectra of benzyl-type radicals, dimethylbenzyl radicals observed in a corona discharge of precursor 1,2,4-trimethylbenzene, using a band shape analysis based on the characteristics of xylyl radicals. From the analysis, we identified the existence of all three isomeric dimethylbenzyl radicals and determined the spectroscopic data in the $D_1 \rightarrow D_0$ electronic transition as well as the many vibrational modes in the ground electronic state.

Experimental Details

The experiment was carried out with the same apparatus described elsewhere.[23] Briefly, corona discharge in the form of corona excited supersonic expansion (CESE) through a pinhole-type glass nozzle generates benzyl-type radicals

from a proper precursor, and the resultant vibronic emission spectra are observed with a long path monochromator in the visible region.

Electronically hot but jet-cooled benzyl-type radicals were produced from the corona discharge of precursor 1,2,4-trimethylbenzene (Aldrich, reagent grade) with a large amount of inert carrier gas helium. The concentration of precursor in the carrier gas was adjusted for the maximum emission intensity as monitored from the strongest band, and was believed to be less than 1% in the mixture. The gas mixture was corona discharged through the 0.3 mm diameter of the pinhole-type glass nozzle described previously.[22] A sharpened long stainless steel rod acting as an anode was connected to a high voltage dc power supply in the negative polarity, in which the axial discharging current was 5 mA at a 1.5 kV dc potential, and stabilized using a 150 kΩ current-limiting ballast resister.

The six-way cross-type expansion chamber made of thick-walled Pyrex tubes of 50 mm diameter was evacuated by a 800 L/min mechanical rotary vacuum pump, resulting in a pressure range of 5.0 mbar during continuous expansion, with 3.0 bar of backing pressure that was limited by the tolerable pressure limitations of glass materials. A cathode in the form of a long copper rod was positioned parallel to the jet direction under the expansion chamber to avoid arc noise reaching the spectrometer.

A weak blue-green-colored jet was the evidence for the presence of the benzyl-type radicals of the $D_1 \rightarrow D_0$ transition in the expansion. The light emanating from the downstream jet area 5 mm from the nozzle opening was collimated by a collecting quartz lens (f = 5.0 cm) placed inside the chamber and focused to the slit of the monochromator (Jobin Yvon U1000) equipped with two 1800 lines/mm gratings, and detected with a cooled photomultiplier tube (Hamamatsu R649) and a photon counting system. During the scans, the slits were set to 100 μm, providing an effective resolution of about 2 cm^{-1} in the visible region. The spectral region from 18000 to 22500 cm^{-1} was singly scanned in 2.0 cm^{-1} increment over 2 hrs to obtain the spectrum shown in Figure 1. The wavenumber of the spectrum was calibrated using the He atomic lines[24] observed in the same

Figure 1. Vibronic emission spectrum observed from precursor 1,2,4-trimethylbenzene with a large amount of inert carrier gas helium in CESE.

spectral region as the benzyl-type radicals, and is believed to be accurate within ± 1.0 cm^{-1}.

Since the vibrational modes of benzyl-type radicals have not been completely assigned, *ab initio* calculations of the ground electronic state (D_0) of isomeric dimethylbenzyl radicals were carried out to assist the assignment of the vibronic structure of the spectrum. The calculations were performed with a personal computer equipped with an Intel Pentium IV CPU 2.80 GHz processor with 2.0GB RAM, according to the standard methods included in the Gaussian03 program. The geometry optimization and vibrational frequency calculations were performed at the DFT level, and the 6-311G** basis set was employed in all of the calculations.

Results and Discussion

It has been demonstrated that a well-controlled corona discharge of substituted toluenes seeded in a large amount of carrier gas produces corresponding benzyl-type radicals in the excited vibronic state. Although the mechanism for the generation and excitation in corona discharge of benzyl-type radicals has yet to be established, it has been suggested that the metastable He atom in the 1s2s $^3S_1$ state, about 160,000 cm^{-1} above the ground state produced by corona excitation,[25] transfers the excess energy to the substituted toluenes through a collisional process, producing corresponding benzyl-type radicals by removing a hydrogen atom from the methyl group rather than the benzene ring.

Although it has been known that the diradical[26] can be produced in the matrix isolation from mesitylene by extracting a hydrogen atom from each of the two methyl groups rather than from the benzene ring, no one has ever succeeded the observation of diradicals in the gas phase, owing to their extremely short lifetime and the low concentration in the medium.

In methyl substituted benzyl-type radicals, the electronic interaction between the methyl group and the benzene ring is undoubtedly of the second-order compared with that between the methylene group and the benzene ring, because the molecule has a planar structure with 7 delocalized π electrons, to which structure the CH$_2$ group contributes an electron. Thus, the electronic structure of methyl substituted benzyl radicals should exhibit a close relationship to that of the benzyl radical, and indeed one might be able to closely relate the two lowest lying excited electronic states of the methyl substituted benzyl radicals to the parental benzyl $2^2B_2(D_2)$ and $1^2A_2(D_1)$ states. The weak visible emission from benzyl-type radicals is believed to arise from transitions to the $1^2B_2(D_0)$ ground state from the close-lying D_2 and D_1 excited electronic states. These two excited states can be mixed by vibronic coupling, and ring substitution would be expected to affect the energies of the two excited electronic states differently.

The vibronic relaxation process has been discussed for methyl substituted benzyl radicals. The emission intensity of the transition from the D_2 to the D_0 state is inversely
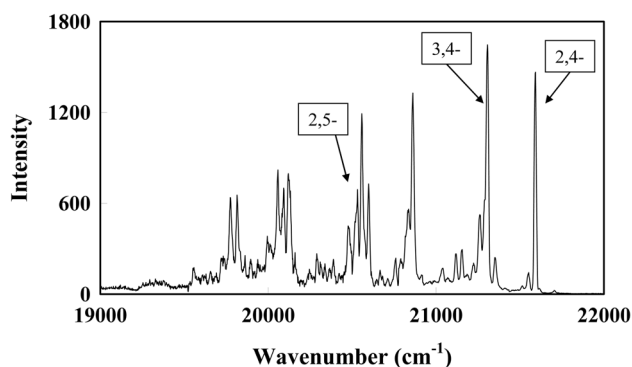
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Bull. Korean Chem. Soc. **2008**, Vol. 29, No. 12   2343

Table 1. Origin Bands in the $D_1 \rightarrow D_0$ Transition of Benzyl-type Radicals[a]

| molecules	origin band (cm^{-1})	shift (cm^{-1})[d]
benzyl[b]	22002	0
o-methylbenzyl[c]	21346	656
m-methylbenzyl[c]	21486	516
p-methylbenzyl[c]	21700	302
α-methylbenzyl[e]	21778	224
2,6-dimethylbenzyl[c]	20616	1386

[a]Measured in vacuum (cm^{-1}). [b]Reference 1. [c]Reference 12. [d]With respect to the origin band of benzyl radical (22002 cm^{-1}). [e]Reference 31.

proportional to the collisional relaxation rate that is related to the density of vibrational states in the excited electronic states. The fairly strong observation of *p*-chlorobenzyl[27] in the $D_2 \rightarrow D_0$ transition is attributed to the small energy difference of 95 cm^{-1} between the two excited electronic states. However, the large separation[28] of approximately 800 cm^{-1} between the D_2 and D_1 states in the benzyl radical includes many vibrational levels, which increase the rate of collisional relaxation to the D_1 state, resulting in almost negligible emission intensity in the $D_2 \rightarrow D_0$ transition.

Figure 1 shows a portion of the vibronic emission spectrum of the benzyl-type radicals formed by the corona discharge of precursor 1,2,4-trimethylbenzene, in which spectrum many of the strong bands are observable with a very good S/N in the region of 19000-22000 cm^{-1}. The origin bands of the benzyl-type radicals were observed in the region of 20000-22000 cm^{-1}, as listed in Table 1. Whereas the benzyl radical exhibits the origin band at 22002 cm^{-1}, the methyl substituted benzyl radicals show red-shifted origin bands, with substitutions into the benzene ring. The *o*-, *m*-, and *p*-xylyl radicals show the origin bands at 21345, 21485, and 21700 cm^{-1}, shifted by 657, 517, and 302 cm^{-1} from the benzyl radical, respectively.[12] The origin band in the $D_1 \rightarrow D_0$ electronic transition of 2,6-dimethylbenzyl radical[14] has been reported to be located in this region as well.

Since the emission spectrum observed with a pinhole-type glass nozzle in the CESE system is similar to the laser excited dispersed fluorescence spectrum obtained by pumping the origin of the electronic transition, the spacing of the vibronic bands from the origin band represents the vibrational mode frequencies in the ground electronic state, as already proved, for many benzyl-type radicals. Thus, in the present study, the other vibronic bands were assigned with reference to these origin bands, by comparison with those of the *ab initio* calculation as well as in the known data of the precursor.

In the corona discharge of precursor 1,2,4-trimethylbenzene, it is possible to generate three isomeric radicals, 2,4-, 2,5-, and 3,4-dimethylbenzyl radicals, by removing a hydrogen atom from the methyl group at the different substitution position, as shown in Figure 2. Because the contribution of the methyl group to the electronic energy of the radical is negligible compared with that of the methylene group, which donates a π electron to form delocalized π
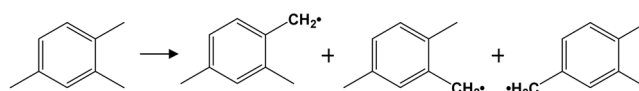

Figure 2. Formation of three isomeric dimethylbenzyl radicals by removal of hydrogen atom from methyl group at the different substitution position in precursor 1,2,4-trimethylbenzene.

bonding, one expect that predicting the electronic energy and stability of isomers may not be possible in the vibronic spectrum. The most trustworthy way is to analyze a high resolution spectrum exhibiting a rotational structure, as in the routine process of spectroscopic analysis of molecules.

Since the benzyl-type radicals belong to molecules having rotational constants of the order of 0.1 cm^{-1}, it is not possible to observe the rotationally resolved spectrum in the visible electronic transition. Rather, the analysis of the rotational contour is the convenient technique for the assignment of the transition. The controversial assignments of the *p*-xylyl radical have been clearly resolved by means of band shape analysis of the vibronic bands in the high resolution emission spectra.[10]

In the vibronic emission spectrum of the xylyl radicals, each isomer shows the characteristic band shape for the origin band, as shown in Figure 3, due to the torsional effect and differences in rotational constants. The band shape of each isomer was observed from the xylyl radicals formed by the corona discharge of corresponding precursor xylenes. Thus, we attempted to compare the band shapes of dimethylbenzyl radicals with those of two isomeric xylyl radicals, because each methyl group contributes to the band shape independently. The band shape of the 2,6-dimethylbenzyl radical, with two methyl groups at the *o*-position, has been well reproduced by combining the two band shapes of the *o*-xylyl radical.[14]

The strong band at 21592 cm^{-1}, which has been reported previously[13] to the origin band of the 3,4-dimethylbenzyl radical in the $D_2 \rightarrow D_0$ transition, was reassigned to the origin band of the 2,4-dimethylbenzyl radical in the present study, because the rapid collisional relaxation to the D_1 state cannot gain any appreciable intensity from the D_2 state, as already proved in the case of the benzyl radical, and with reference to the band shape. The band shape of one strong peak is a typical characteristic of *p*-substitution, so we could reproduce this band shape by combining those of *o*- and *p*-substitutions, as shown in Figure 4. With assignment of the
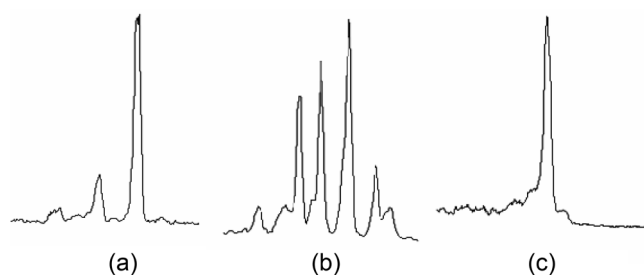

Figure 3. Characteristic band shapes of origin bands of (a) *o*-, (b) *m*-, and (c) *p*-xylyl radicals in visible vibronic emission spectra.
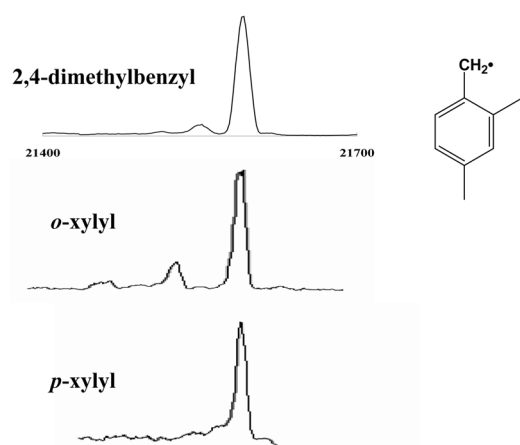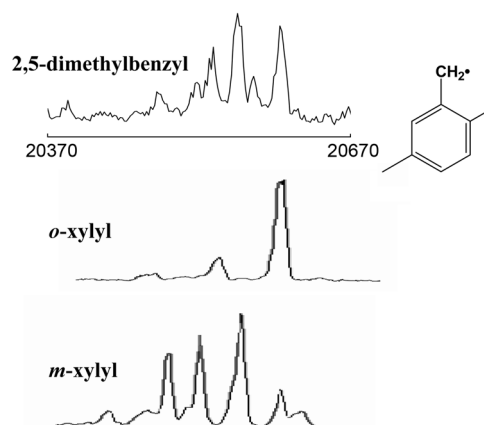
Figure 4. Comparison of band shape of origin band of 2,4-dimethylbenzyl radical with those of *o*- and *p*-xylyl radicals.

origin band of the 2,4-dimethylbenzyl radical, a few vibrational modes were identified by comparison with those from an *ab initio* calculation and from the known data of the precursor.[29] Mode 6b of C-C-C ring deformation, of medium intensity, was assigned to the band at 21156 cm^{-1}, which is degenerate with mode 6a in benzene at 606 cm^{-1}. The splitting between these two modes increases with increasing mass of the substituents. With splitting, mode 6a has a higher wavenumber than mode 6b for the *o*- and *m*-isomers, but the trend is reversed for the *p*-isomer. In the molecules of the C$_s$ point group, the intensity of mode 6b is very strong, whereas that of mode 6a is negligible. Mode 1 of ring breathing vibration was assigned to the strong band at 20862 cm^{-1}, a shift of 730 cm^{-1} from the origin band. The vibrational frequency of mode 1 is less sensitive to the substitution, which can be verified in 2,6-dimethylbenzyl radicals because the frequency of this mode should be less sensitive to substitution.

The strongest band at 21306 cm^{-1} was assigned to the origin band in the D$_1$ → D$_0$ transition of the 3,4-dimethylbenzyl radical, as reported previously. This band shows a somewhat complicated band shape, with several weak side
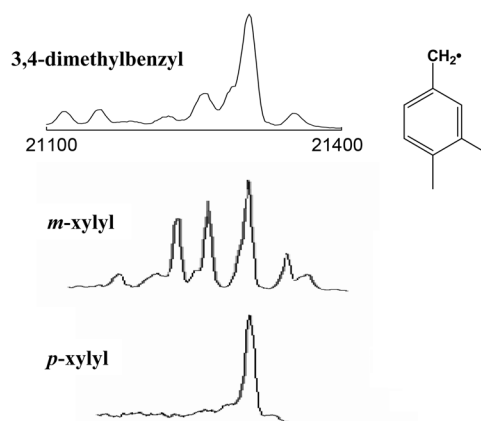
Figure 5. Comparison of band shape of origin band of 3,4-dimethylbenzyl radical with those of *m*- and *p*-xylyl radicals.

Figure 6. Comparison of band shape of origin band of 2,5-dimethylbenzyl radical with those of *o*- and *m*-xylyl radicals.

peaks around one strong peak, which is similar to the shapes of the bands obtained by combining the band shapes of the *m*- and *p*-xylyl radicals, as shown in Figure 5. A side-peak pattern is a typical band shape of the *m*-xylyl radical. The vibronic bands belonging to this isomer were identified by comparison with those of the 2,4-dimethylbenzyl radical,

Table 2. Vibrational Mode Frequencies (cm^{-1}) of Dimethylbenzyl Radicals[a]

position	mode[b]	spacing[c] (D$_0$)	*ab initio*[d] DFT/6-311G** (D$_0$)	precursor 1,2,4-trimethylbenzene[e] (S$_0$)	symmetry (C$_S$)
			2,4-dimethylbenzyl		
21600	origin	0			
21162	6b	438	441	445	a'
20848	1	752	784	752	a'
			3,4-dimethylbenzyl		
21306	origin	0			
20862	6b	444	445	445	a'
20558	1	748	748	752	a'
			2,5-dimethylbenzyl		
20558	origin	0			
20120	6b	438	445	445	a'
19814	1	744	752	752	a'

[a]Measured in vacuum (cm^{-1}). [b]Reference 30. [c]This work. [d]Not scaled. [e]Reference 29.

because the isomers should show similar intensities and vibrational mode frequencies. Medium intensity mode 6b and strong intensity mode 1 were assigned to the bands at 20840 cm^{-1} and 20558 cm^{-1}, respectively.

Finally, the band at 20600 cm^{-1}, of very complicated band shape, was assigned to the origin band of the 2,5-dimethyl-benzyl radical in the $D_1 \rightarrow D_0$ transition. The complicated several side peaks were from the *m*-xylyl radical, which could be combined with those of the *o*-xylyl radical to produce those shown in Figure 6. The same band shape was repeated at 20122 cm^{-1}, and assigned to mode 6b. Also, weak intensity mode 1 was tentatively assigned to the band at 19818 cm^{-1}. The band intensity in vibronic emission spectra generally decreases with distance from the origin band in benzyl-type radicals, owing to the fact that the Franck-Condon factor becomes smaller as energy differences grow larger.

The comparable emission intensity in the spectrum observed for the origin band indicates that the population of each isomer was almost equal in the excited electronic state, suggesting that the dissociation of the precursor from dimethylbenzyl radicals is a parallel reaction of almost equal activation energy.

In summary, precursor 1,2,4-trimethylbenzene was electrically discharged with a large amount of inert carrier gas helium in a CESE using a pinhole-type glass nozzle, from which the visible vibronic emission spectrum in the $D_1 \rightarrow D_0$ transition of the benzyl-type radicals were recorded. From an analysis based on the band shapes of the xylyl radicals, we identified three isomeric dimethylbenzyl radicals formed in the corona discharge of the precursor. The origin bands and other vibronic bands belonging to the three isomers were clearly identified by comparison with those from an *ab initio* calculation as well as those from the known data of the precursor.

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