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3,4-Dimethylbenzyl Radical Formed in a Corona Discharge of 1,2,4-Trimethylbenzene

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A precursor, 1,2,4-trimethylbenzene, seeded in a large amount of an inert carrier gas, helium, was electrically discharged in a corona-excited supersonic expansion using a pinhole-type glass nozzle. The blue-green colored fluorescence emanating from the downstream jet was recorded with a long path monochromator to observe the vibronic emission spectrum of the benzyl-type radical formed. Analysis of the spectrum suggests that the most dominant product of the corona discharge is the 3,4-dimethylbenzyl radical formed by extracting a hydrogen atom from the methyl group at the 4-position. The electronic energies of the D_1 and D_2 states and the vibrational mode frequencies of the 3,4-dimethylbenzyl radical were accurately obtained for the first time by comparison with those from an ab initio calculation as well as those of the known vibrational mode frequencies of the precursor.

Introduction

Whereas the benzyl radical, a prototype of the aromatic radical, has attracted much attention from spectroscopists, methyl-substituted benzyl (xylyl) radicals have been less studied as large aromatic radicals.[1,2] Earlier work on the xylyl radicals in the visible region were reported by Schuler et al.[3] and by Walker and Barrow.[4] Bindley et al.[5,6] made vibronic assignments of the bands from analysis of the emission spectra of xylyl radicals produced by an electric discharge of the xylenes.

Charlton and Thrush[7] have observed the laser-induced fluorescence (LIF) spectra of methyl-substituted benzyl radicals and have measured the lifetime of the excited vibronic states. Recently, the Lee group, from analysis of the vibronic emission spectra, has extended the assignments of the vibrational modes of the xylyl radicals. The controversial assignments of the *p*-xylyl radicals have been resolved by an analysis of the band shapes of vibronic bands from high-resolution emission spectra.[8] The torsional barrier of the internal methyl group has been calculated for the xylyl radicals by Lin and Miller[9] from an analysis of laser-induced fluorescence excitation and dispersed emission spectra. Although the exact mechanism of the generation and excitation of benzyl-type radicals in a corona discharge is not known, the analysis of observed vibronic spectra provides the spectroscopic evidence for identification.

Supersonic jet expansion has been recognized as a powerful spectroscopic technique of observing molecular spectra in the gas phase.[10] The spectral simplification and transient molecular stabilization associated with the expansion of an inert carrier gas cannot be achieved in any other way. Combining supersonic jet expansion with the emission spectroscopy technique has had an enormous impact on the repertoire of spectroscopic studies of transient molecular species. Of the emission sources utilizing this combination, only the pinhole-type glass nozzle[11,12] provides enough continuous photon intensity for high-resolution studies of weak transition, which apparatus has been widely employed to observe the vibronic emission spectra of transient species.[13] The pinhole-type glass nozzle has been applied to the observation of the vibronic emission spectra of jet-cooled benzyl-type radicals in the gas phase.[14−20]

In this paper, we report the formation of the benzyl-type radical in the corona discharge of 1,2,4-trimethylbenzene and provide the spectroscopic evidence of the 3,4-dimethylbenzyl radical, for the first time, of which the $D_1 \rightarrow D_0$ electronic transition and the vibrational mode frequencies in the ground electronic state were determined by comparison with those from both an ab initio calculation and the known vibrational mode frequencies of the precursor.

Experimental Details

The corona discharge of 1,2,4-trimethylbenzene was carried out using the technique of corona excited supersonic expansion (CESE), of which the experimental apparatus is similar to those described elsewhere.[21] Briefly, it consists of a pinhole-type glass nozzle coupled with a high voltage dc discharge, a portable six-way cross-type Pyrex glass expansion chamber, and a spectrometer for observing the vibronic emission spectrum in the visible region.

Electronically excited but jet-cooled benzyl-type radicals were produced from the corona discharge of the precursor, 1,2,4-trimethylbenzene (Aldrich, reagent grade), after it was seeded in a large amount of helium. The concentration of the precursor in the carrier gas, 2 atm, which was believed to be less than 1% of the mixture, was adjusted for the maximum emission intensity monitored from the strongest band. The gas mixture was expanded through the 0.3 mm diameter pinhole-type glass nozzle made in this laboratory according to the method described previously.[22] The sharpened long tungsten rod acting as an anode was connected to the high-voltage dc power supply in the negative polarity, in which the axial discharging current was 5 mA at a 1500 V dc potential and stabilized using a 150 kΩ current-limiting ballast resister.

Since the original nozzle developed by Engelking was easily clogged when used with heavy organic compounds, we employed the improved pinhole-type glass nozzle, which significantly reduces clogging by allowing excitation to occur after expansion. The six-way cross-type Pyrex expansion chamber

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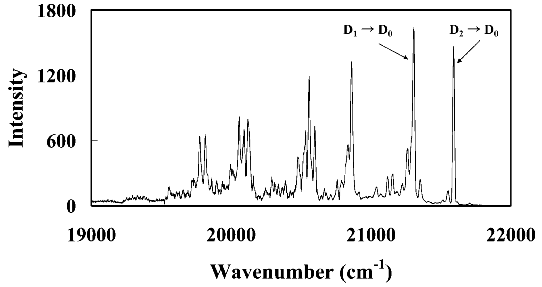

Figure 1. Portion of the visible vibronic emission spectrum of the species formed by the corona discharge of the precursor 1,2,4-trimethylbenzene with a large amount of carrier gas helium, possibly the 3,4-dimethylbenzyl radical in the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions.

was made of thick walled Pyrex tubes (Chemglass CG-138-02) of 50 mm diameter. The chamber was evacuated using a 800 L/min mechanical rotary vacuum pump, resulting in a pressure of 2.0 Torr during continuous expansion with 2.0 atm of backing pressure. A long copper cathode 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 provided the evidence for the presence in the expansion of the benzyl-type radicals of the $D_1 \rightarrow D_0$ transition. The light emanating from the downstream jet area 5 mm away from the nozzle opening was collimated by a quartz lens ($f = 5.0$ cm) placed inside the expansion chamber and focused onto the slit of the monochromator (Jobin Yvon U1000) containing 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 0.100 mm, providing a resolution of about 2 cm^{-1} in the visible region. The spectral region from 18500 to 22000 cm^{-1} was scanned at a step of 2.0 cm^{-1} over 2 h to obtain the final spectrum shown in Figure 1. The wavenumber of the spectrum, believed to be accurate within ± 1.0 cm^{-1}, was calibrated using the He atomic lines[23] observed in the same spectral region as the benzyl-type radicals.

Since the vibrational assignments of the benzyl-type radicals have not been completely confirmed, ab initio calculations on the D_0 state 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 and 248 MB RAM, and with the standard methods included in the Gaussian 98 program for the Windows package. The geometry optimization and vibrational frequency calculations were performed at the DFT level, and a 6-311G basis set was employed in all of the calculations.

3. Results and Discussion

It has been reported that a well-controlled corona discharge of substituted toluenes seeded in a large amount of carrier gas predominantly produces corresponding benzyl-type radicals in the excited vibronic state. Although the mechanism for the generation and excitation of benzyl-type radicals is not exactly known, it has been suggested that the metastable He atom produced during corona excitation transfers the excess energy to the substituted toluenes through a collisional process, generating corresponding benzyl-type radicals by extracting a hydrogen atom from the methyl group rather than the benzene ring.

In methyl-substituted benzyl radicals, the electronic interaction between the methyl group and the benzene ring is undoubtedly of the second-order compared to that between the methylene group and the benzene ring, since the molecule has a planar structure with seven delocalized π electrons, the CH_2 group contributing an electron. Thus, the electronic structure of methyl-substituted benzyl radicals should exhibit a close relationship to that of the benzyl radical: one can closely relate the two lowest lying electronic states of the methyl-substituted benzyl radicals to the parental benzyl $2^2B_2(D_2)$ and $1^2A_2(D_1)$ states.[8]

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.[24] The two excited states can be mixed by vibronic coupling,[25] and ring substitution is also expected to differently affect the energies of the excited electronic states. Most of the benzyl-type radicals have the lowest excited electronic state of 1^2A_2, except for the *p*-cyanobenzyl radical, which has that of 1^2B_2.[26,27]

Figure 1 shows a portion of the vibronic emission spectrum in the visible region of the species formed by the corona discharge of the precursor 1,2,4-trimethylbenzene, in which spectrum many of the strong bands are observed with an excellent S/N in the region of 19000−22000 cm^{-1}. The spectrum consists of two series of vibronic bands starting from the bands at 21306 and 21600 cm^{-1} (in air), which are believed to be the origin bands of the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions, respectively, followed by a series of lower-energy vibronic bands. The absence of bands with an observable intensity in the blue region of the origin, along with the efficient vibrational cooling during the supersonic jet expansion, easily confirms the origin band, as the many benzyl-type radicals in a corona discharge.

The relaxation process from the D_2 to the D_1 state in many benzyl-type radicals is known to be efficient, since the energy separation between the two electronic states is comparable to those of vibrational mode frequencies. Weak and slow relaxation process has been detected in the *p*-chlorobenzyl radical,[27] where the separation of 95.2 cm^{-1} between the two excited electronic states is too small to induce vibronic coupling. The transition from the second excited electronic state has not been observed in the benzyl radical, in which the energy difference between the two electronic states is calculated to be about 800 cm^{-1}. We believe that the relaxation efficiency is closely related to the vibronic coupling that describes the energy exchange between the vibrationless D_2 state and the excited vibrational state belonging to the D_1 state. Thus, the relaxation from the D_2 state to the D_1 state is limited due to the less vibronic coupling, producing two series of vibronic structures in the spectrum as shown in Figure 2.

The vibronic structure of the red region of the origin band reflects the vibrational structure belonging to the ground electronic state, since the emission spectrum observed using a pinhole-type nozzle is similar to the dispersed fluorescence spectrum obtained by exciting the origin band of the electronic transition, as has already been proven in several benzyl-type radicals. Thus, the spacing of the vibronic bands from the origin band represents the vibrational mode frequencies in the ground electronic state because the emission spectrum observed with the CESE scheme in Figure 2 is similar to the single vibrational level (SVL) dispersed fluorescence spectrum observed by pumping the origin band of the electronic transition.

Although it has been reported that the diradical[28] can be generated from mesitylene in the matrix isolation by extracting a hydrogen atom from each of the two methyl groups rather than from the benzene ring, no one has ever reported the

TABLE 1: Comparison of the Observation with the Calculation on Each Isomer[a]

mode	observation[b]	calculation[c]		
		3,4-dimethyl	2,4-dimethyl	2,5-dimethyl
origin ($D_1 - D_0$)	21306(0)	21 185	21 045	20 828
origin ($D_2 - D_0$)	21600(0)			
6b	20862(−444)	445	441	445
12	20558(−748)	748	784	752
18a	20124(−1182)	1197	1188	1186
7a	20056(−1250)	1277	1241	1286

[a] In units of wavenumber (cm^{-1}) measured in air. [b] The numbers in parentheses are the spacing from the each origin band. [c] The origin was calculated by the substitution effect and the vibrational mode frequencies were obtained with DFT/6−311g without scaling factor.

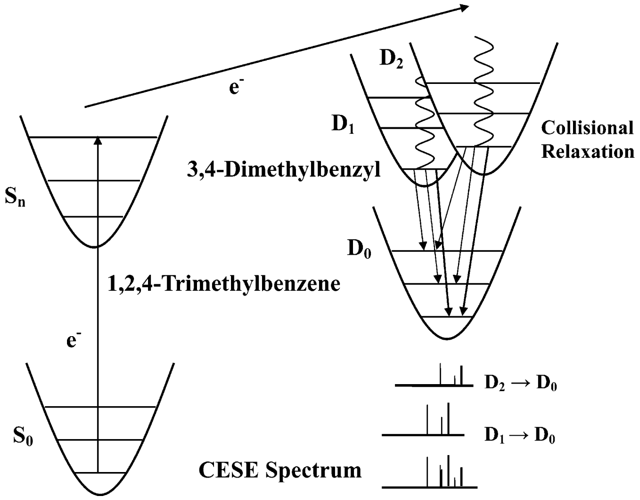

Figure 2. Scheme of the CESE spectroscopy for observing vibronic emission spectrum of benzyl-type radicals from the corona discharge of the precursor seeded in a large amount of carrier gas helium using a pinhole-type glass nozzle. The $D_1 \rightarrow D_0$ and the $D_2 \rightarrow D_0$ transitions show comparable intensity due to the inefficient vibronic relaxation from the D_2 to the D_1 states.

observation of diradicals in the gas phase, owing to their extremely short lifetime and the low concentration in the medium.

Thus, from the corona discharge of the precursor, it is possible that three isomers such as the 2,4-dimethyl-, 2,5-dimethyl-, and 3,4-dimethylbenzyl radicals could be generated by extracting a hydrogen atom from different positions within the methyl group. Because those three isomers have comparable electronic energies, they cannot be easily distinguished from each other through any experimental method except for electronic spectrum, as reported for xylyl radicals. For example, the origin band of the $D_1 \rightarrow D_0$ electronic transition of the xylyl radicals was observed at 21346, 21486, and 21700 cm^{-1} for the *o*-, *m*-, and *p*-isomers, respectively.[1] The observation of origin band in vibronic emission spectra seems to be very powerful technique for the analysis of the isomers.

Although the origin band of the 2,6-dimethylbenzyl radical has previously been reported[14] at 21164 cm^{-1} in the vibronic emission spectrum, the band shapes suggest that the bands at 20616 and 21164 cm^{-1} could be assigned as the origin bands of the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions, respectively, because the same vibrational structure in the ground electronic state as in the *p*-chlorobenzyl radical transition has been discovered.[27]

The origin band of the $D_1 \rightarrow D_0$ transitions of the 2,6-dimethylbenzyl radical, at 20616 cm^{-1}, and shifted 1386 cm^{-1} from the benzyl radical, agrees well with the calculation given by the substitution effect that suggests that the shift of the origin band of multisubstituted benzyl-type radicals can be easily estimated from those of monosubstituted benzyl radicals. The substitution effect has been well applied to the 2,6-dimethylbenzyl,[14] 2,6-difluorobenzyl,[29] and 2,6-dichlorobenzyl[20] radicals.

TABLE 2: List of the Vibronic Bands Observed and Their Assignments

position[a]	intensity	spacing from the origin[b]	assignments[c]
21 600	vs	0	origin of $D_2 - D_0$
21 306	vs	0	origin of $D_1 - D_0$
21 156	m	444(2)	$6b_1^0$(2)
20 862	vs	444(1)	$6b_1^0$(1)
20 852	m	748(2)	12_1^0(2)
20 600	s	706(1)	1_1^0(1)
20 558	vs	748(1)	12_1^0(1)
20 420	m	1180(2)	$18a_1^0$(2)
20 390	w	1210(2)	13_1^0(2)
20 124	s	1182(1)	$18a_1^0$(1)
20 094	s	1212(1)	13_1^0(1)
20 056	s	1250(1)	$7a_1^0$(1)
19 814	m	1492(1)	$19b_1^0$(1)
19 776	m	1530(1)	$8a_1^0$(1)

[a] Measured in air (cm^{-1}). [b] The numbers 1 and 2 in parentheses indicate the spacing from the origin band of the $D_1 \rightarrow D_0$ and the $D_2 \rightarrow D_0$ transitions, respectively. [c] The numbers 1 and 2 in parentheses indicate the bands belonging to the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions, respectively.

Table 1 lists the calculated origin band of each of three possible isomers to be generated from the precursor, together with the observation of the origin of the benzyl-type radical formed from 1,2,4-trimethylbenzene. Of the three isomers, the 3,4-dimethylbenzyl radical shows very good agreement with the observation. With two methyl substitutions at the *m*- and *p*-positions, the origin band can be calculated by simply adding the two shifts given by the *m*- and *p*-xylyl radicals, $517 + 302 = 819$ cm^{-1}. Another strong band at 21600 cm^{-1} can be assigned as the origin band of the $D_2 \rightarrow D_0$ transition because of the observation of the same vibrational structure in the ground electronic state as well as the different band shapes shown in Figure 3, since the D_2 state has a different symmetry from the D_1 state. The observation of the $D_2 \rightarrow D_0$ transition can be attributed to the inefficient vibronic coupling process from the D_2 state resulting from the small energy difference between the two excited electronic states.[30]

The observed vibronic bands were assigned with the help of those from an ab initio calculation as well as the known vibrational frequencies of the 1,2,4-trimethylbenzene,[31] because the vibrational structure of benzyl-type molecules is subject to the isodynamic approximation that indicates a correspondence between vibrational mode frequencies and between the transition intensities of molecules with similar structures. The bands observed in this study, along with their assignments, are listed in Table 2.

The well-resolved strong band at −444 cm^{-1} from the origin band was assigned to mode 6b of C−C−C angle deformation vibration, which is degenerate with mode 6a at 606 cm^{-1} in benzene. The splitting between modes 6a and 6b increases with

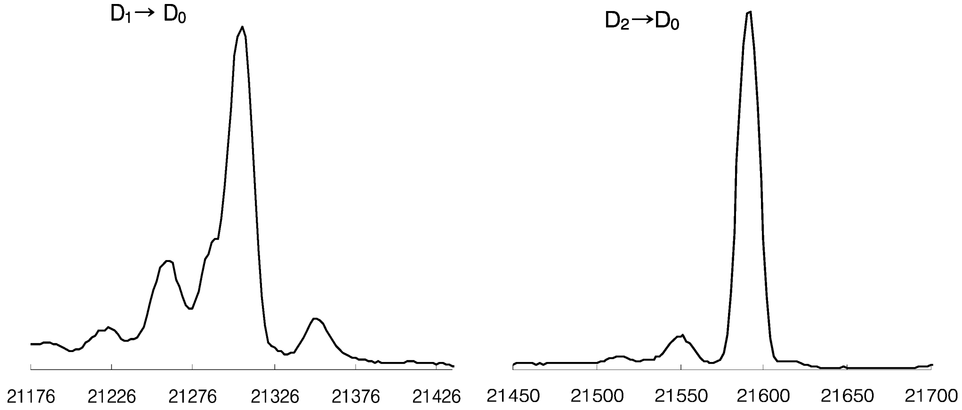

Figure 3. Band shapes of the origin band of the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions.

TABLE 3: Vibrational Mode Frequencies of 3,4-Dimethylbenzyl Radical[a]

mode[b]	this work (D_0)	ab initio[c] DFT/6−311g (D_0)	precursor 1,2,4-trimethylbenzene[d] (S_0)	symmetry (C_s)
origin	21600(2)[e]			
origin	21306(1)[e]			
6b	444	445	438	a′
1	706	720	717	a″
12	748	748	746	a′
18a	1182	1197	1155	a′
13	1212	1242	1212	a′
7a	1250	1277	1246	a′
19b	1492	1522	1507	a′
8a	1530	1563	1581	a′

[a] Measured in air (cm^{-1}). [b] Reference 34. [c] Multiplied by a scaling factor of 0.98. [d] Reference 31. [e] The numbers 1 and 2 in parentheses indicate the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions, respectively.

the increasing size of the substituents. For the *p*-isomer, mode 6b has a higher frequency than mode 6a, but the trend is reversed for the *o*- and *m*-isomers. For 1,2,4-trimethylbenzene, mode 6a is at a higher wavenumber and shows a strong intensity compared to mode 6b, whereas the benzyl radical has observable 6a and 6b modes of strong intensity at 524 and 615 cm^{-1}, respectively. This observation is in good agreement with the calculation (445 cm^{-1}).

The strong band at −748 cm^{-1} from the origin was assigned to mode 12 of radial skeletal vibration, similar to ring breathing of mode 1, and this coincides with the calculation (748 cm^{-1}). This mode, strongly observed in most benzyl-type radicals, shows similar frequencies in the benzyl, *p*-xylyl, and 2,6-dimethylbenzyl radicals. The strong band at −1182 cm^{-1} was tentatively assigned to mode 18a of $C-CH_2$ stretching vibration, which mode is also important in many substituted benzyl radicals. The calculation shows good agreement with the observation. Finally, the strong band at −1250 cm^{-1} was assigned to mode 7a of $C-CH_3$ stretching vibration due to the coincidences with that of the precursor (1212 cm^{-1}) and the calculation (1277 cm^{-1}). In this mode, the precursor shows a very strong intensity in the Raman spectrum. Table 3 lists the observed and calculated vibrational mode frequencies of the 3,4-dimethylbenzyl radical as well as those of 1,2,4-trimethylbenzene with symmetrical vibrational modes.

In this work, we have assigned most of the vibronic bands observed using both an ab initio calculations and the known vibrational data of 3,4-dimethylbenzyl radical within good accuracy, ruling out the possibility of generating more than one isomer in a corona discharge of the precursor. It seems that the generation of 3,4-dimethylbenzyl radical is kinetically favorable process because all isomers have very comparable thermodynamic stability in the calculation.

In this experiment, we regularly observed several low-frequency sequence bands in the vicinity of strong vibronic bands. Cossart-Magos and Cossart[32] have also observed several weak bands near the origin band of the *p*-fluorobenzyl radical in the $D_1 \rightarrow D_0$ transition, and assigned them as combination bands coupled with the origin band. Fukushima and Obi have observed several bands in the vicinity of the strong bands, and identified them as belonging to the van der Waals molecules.[33] However, in the present study, it seems unlikely that these bands could be attributed to dimers or van der Waals molecules, since the same bands were also observed with Ar carrier gas, which yields a much poorer spectral *S*/*N*. Thus, we strongly believe that the origin of the sequence bands belongs to the combination bands associated with the excited vibrational state in the upper electronic state as well as the torsional motion of the methyl group. However, at this moment, it may not be possible to assign them because of a limited signal-to-noise ratio and insufficient data in the excited electronic state.

In summary, 1,2,4-trimethylbenzene was electrically discharged with a large amount of carrier gas, helium, in a corona-excited supersonic expansion using a pinhole-type glass nozzle, from which expansion the visible vibronic emission spectra of both the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions were recorded. From a comparison with the calculation given by the substitution effect, it was found that the main product is the 3,4-dimethylbenzyl radical, of which, for the first time, an accurate electronic transition and several vibrational mode frequencies were obtained in the ground electronic state.

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