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Spectroscopic Evidence of Jet-Cooled *o*-Chloro-α-Methylbenzyl Radical in Corona Excitation

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We report the first spectroscopic evidence of the *o*-chloro-α-methylbenzyl radical. The electronically hot but jet-cooled *o*-chloro-α-methylbenzyl radical was formed from precursor *o*-chloro-ethylbenzene seeded in a large amount of inert carrier gas helium, by employing the technique of corona excited supersonic expansion with a pinhole-type glass nozzle. The vibronic emission spectrum was recorded with a long path monochromator in the $D_1 \rightarrow D_0$ electronic transition in the visible region. By comparing the observed spectrum with that of the *o*-chlorobenzyl radical reported previously, we could easily identify the spectroscopic evidence of the jet-cooled *o*-chloro-α-methylbenzyl radical generated in the corona discharge of *o*-chloro-ethylbenzene, from which the electronic transition energy and several vibrational mode frequencies in the ground electronic state were accurately determined.

Introduction

The benzyl radical, a prototypical aromatic free radical, has been one of the interesting spectroscopic subjects, having attracted much attention from spectroscopists. Earlier results on the benzyl radical have been reported by Schuler et al.[1] and Walker and Barrow[2] in the visible region. Bindley et al.[3,4] have extended the work to methyl-substituted benzyl radicals generated by an electric discharge of xylenes.

The technique of laser-induced fluorescence has been applied by Charlton and Thrush[5] not only to obtain the laser excited vibronic spectrum but also to measure the lifetimes of the excited electronic state of halogen-substituted benzyl-type radicals. Recently, Lee et al.[6−12] observed, using corona excited supersonic expansion (CESE), the vibronic emission spectra of many benzyl-type radicals, in which a hydrogen atom was substituted by halogen atom, cyano group, and methyl group. They succeeded in generating multisubstituted fluorobenzyl radicals composed of up to 5 fluorine atoms.[13] However, experiments on chlorobenzyl radicals have been quite rare because the fluorescence quantum efficiency substantially decreases with increasing numbers of chlorine atoms.

The CESE technique, originally invented by Engelking[14,15] and further developed by Lee et al.,[16] has been recognized as a useful technique for laser-free spectroscopic observation of the emission spectra of jet-cooled transient species. Spectral simplification and stabilization of transient species associated with the expansion of an inert carrier gas cannot be obtained in any other way.[17] Of the emission sources developed for corona discharge, the one providing sufficient continuous fluorescence intensity for weak transitions is the pinhole-type glass nozzle,[14,15] which recently has been modified to improve the stability of corona discharge,[16] making it possible to observe spectra with much better S/N. Although the mechanism for generation and excitation of the corona discharge of benzyl-type radicals has not been well established, the analysis of such vibronic spectra provides spectroscopic evidence for identification of the transient species produced.

In this Article, we report the first spectroscopic evidence of the *o*-chloro-α-methylbenzyl radical, which was generated by breaking off the C−H bond at the α-position of the ethyl group. From an analysis of the spectrum, the spectroscopic data of the electronic transition and vibrational mode frequencies were accurately determined by comparison with those from an ab initio calculation as well as those of the precursor.

Experimental Section

The experiment in this work was carried out with an apparatus that has been described elsewhere.[18] Briefly, we used a proper precursor as well as conditions that are believed to play a crucial role in the optimum generation of benzyl-type radicals in a corona discharge.

Electronically hot but jet-cooled benzyl-type radicals were produced in a CESE from precursor *o*-chloro-ethylbenzene seeded in large amount of inert carrier gas helium. The precursor of reagent grade was purchased from Sigma-Aldrich and used without further purification. The concentration of the precursor in the carrier gas was adjusted by opening a bypass valve for the maximum emission intensity monitored from the strongest band and was believed to be less than 1% in the mixture at ambient temperature. The gas mixture was corona discharged by expansion through the 0.3 mm diameter of the pinhole-type glass nozzle[16] made in this laboratory according to a method described elsewhere. A sharpened long stainless steel rod, acting as an anode inside the glass nozzle cavity, was electrically connected to a high voltage dc power supply in the negative polarity, in which the axial discharging current was 5 mA at 2000 V dc potential and stabilized using a 150 kΩ current-limiting ballast resister. The expansion chamber made of Pyrex glass was evacuated by a 800 L/min mechanical rotary vacuum pump, resulting in a chamber pressure of 5.0 mbar during continuous jet expansion, with 3.0 bar of backing pressure. We maintained the backing pressure at a low level, given the tolerable pressure limitations of glass materials. The chamber

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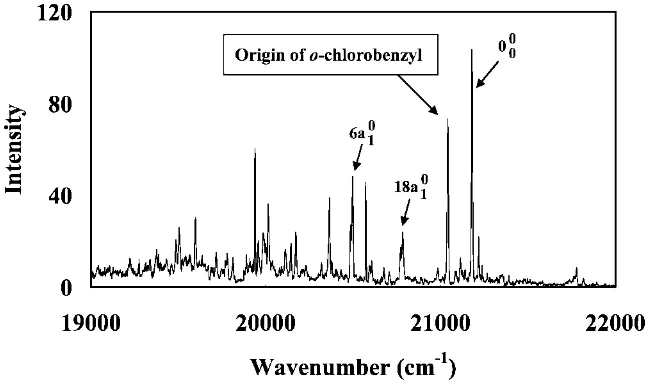

Figure 1. A portion of the visible vibronic emission spectrum observed from the jet-cooled species formed in the corona discharge of precursor, *o*-chloro-ethylbenzene, seeded in a large amount of carrier gas helium. The assignments indicated are for the *o*-chloro-α-methylbenzyl radical in the $D_1 \rightarrow D_0$ transition.

pressure, also influential in the generation of benzyl-type radicals, was controlled for the maximum total emission intensity in the visible region.

A weak blue-green colored jet was the evidence of the presence of the benzyl-type radicals in the $D_1 \rightarrow D_0$ transition. The light, emanating from the downstream jet area 5 mm from the nozzle opening, was collimated using a collecting quartz lens (d = 3.8 cm, f = 5.0 cm) placed inside the chamber and focused on the slit of the monochromator (Jobin Yvon U1000, path length = 2.0 m) 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 slit was set to 100 μm, providing an effective resolution of about 2 cm^{-1} in the visible region. The spectral region from 18 000 to 22 500 cm^{-1} was singly scanned in 2.0 cm^{-1} increments over 2 h to record the spectrum shown in Figure 1. The wavenumber of the spectrum was calibrated using the He atomic lines[19] observed in the same spectral region as the benzyl-type radicals and is believed to be accurate within ±1.0 cm^{-1}.

Results and Discussion

It has been well demonstrated that the controlled corona discharge of substituted toluenes in a large amount of inert carrier gas helium produces corresponding benzyl-type radicals in the excited vibronic states. Although the mechanism for generation and excitation of benzyl-type radicals in corona discharge has not been thoroughly established, it has been suggested that the metastable He atom[20] in the 1s2s $^3S_1$ state, about 160 000 cm^{-1} above the ground state formed in a corona discharge, transfers its excess energy to the precursor through a collisional process. The highly excited precursor then decomposes to generate corresponding benzyl-type radicals by loss of a hydrogen atom from the methyl group rather than from the benzene ring. The molecular radicals produced undergo collisional relaxation with helium atoms, in the process losing excited rovibrational energy in the excited electronic states, and producing electronically hot but vibrationally and rotationally cold benzyl-type radicals that eventually emit fluorescence in the transition corresponding to the energy difference between the two vibronic states, in which the band at the highest wavenumber represents the origin of the pure electronic transition. Thus, the spacing between the origin band and the vibronic bands in the spectrum indicates the frequency of the vibrational modes in the ground electronic state, similar to the dispersed fluorescence spectra while pumping the origin band of the electronic transition.

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

molecules	origin band	shift[d]
benzyl[b]	22 002	0
o-chlorobenzyl[c]	21 040	962
m-chlorobenzyl[c]	21 194	808
p-chlorobenzyl[c]	21 645	357
2,6-dichlorobenzyl	20 153	1849
o-chloro-α-methylbenzyl	21 180	822

[a] Measured in vacuum (cm^{-1}). [b] Reference 23. [c] References 7, 24, and 25. [d] With respect to the origin band of benzyl radical (22 002 cm^{-1}).

In substituted benzyl-type radicals, the electronic interaction between the substituents and the benzene ring is undoubtedly of the second-order[21] as compared to 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 methylene group contributes an additional π electron. Thus, the electronic structure of substituted benzyl-type radicals should be similar to that of the benzyl radical, and indeed one might be able to closely relate the two lowest-lying electronic states of such benzyl-type radicals to the parent benzyl radical of the $2^2B_2(D_2)$ 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, in which transitions the two excited states can be mixed by vibronic coupling,[22] and in which ring substitution is expected to differently affect the energies of the excited states. Rapid relaxation from the D_2 to the D_1 state through vibronic coupling transfers most of the population to the D_1 state, thereby rendering observable only the transitions from the D_1 to D_0 state.

Figure 1 shows a portion of the visible vibronic emission spectrum observed from the benzyl-type radical species formed in the corona discharge of *o*-chloro-ethylbenzene with a large amount of inert carrier gas helium. The origin band of the most of benzyl-type radicals in the $D_1 \rightarrow D_0$ electronic transition was observed in the region of 20 000−22 000 cm^{-1}, as shown in Table 1. The benzyl radical[23] exhibits the origin band with a weak intensity at 22 002 cm^{-1}. With substitutions into the benzene ring, the location of the origin bands shifts to the red region. The origin bands of *o*-, *m*-, and *p*-chlorobenzyl radicals[7,24,25] were observed at 21 040, 21 194, and 21 645 cm^{-1}, a shift of 962, 808, and 357 cm^{-1} from the benzyl radical, respectively. The 2,6-dichlorobenzyl, the only dichlorobenzyl radical that has been observed, is reported to have the origin band at 20 153 cm^{-1}.[26]

For species formed in the corona discharge of *o*-chloro-ethylbenzene, we postulate that two different products can be generated from the precursor, as shown in Figure 2. The cleavage of the C−CH$_3$ and C−H bonds at the α-position of the ethyl group generates the *o*-chlorobenzyl and *o*-chloro-α-methylbenzyl radicals, respectively. In this case, the breaking off the C−CH$_3$ bond is the preferential pathway with regard to the mean bond dissociation energy of C−C (344 kJ/mol) and C−H (415 kJ/mol). However, the two hydrogen atoms at the α-position have higher statistical weights than the one CH$_3$ group in the reaction process. Thus, we tried to identify the products by comparing the observed spectrum with the vibronic emission spectra of the *o*-chlorobenzyl radical in CESE reported previously.[7]

The origin band of the *o*-chlorobenzyl radical in the $D_1 \rightarrow D_0$ electronic transition was observed in this work with strong

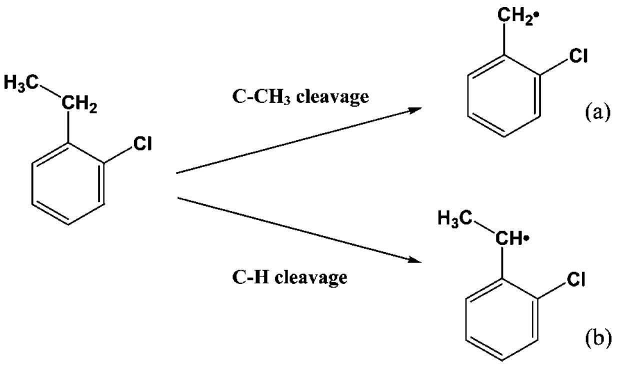

Figure 2. Production of the (a) *o*-chlorobenzyl and (b) *o*-chloro-α-methylbenzyl radicals from precursor, *o*-chloro-ethylbenzene, by corona discharge. The cleavage of C−CH$_3$ and C−H bonds at the α-position of ethyl group generates the *o*-chlorobenzyl and *o*-chloro-α-methylbenzyl radicals, respectively.

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

position	intensity	spacing[b]	assignments[c,d]
21 238	vw	−58	α (2)
21 217	m		He atomic line
21 180	vs	0	origin (2)
21 114	w	66	α (2)
21 040	vs	0	origin (1)
20 986	w	194	$9b^0_1$ (2)
20 784	m	396	$18a^0_1$ (2)
20 772	m	408	$7a^0_1$ (2)
20 706	vw	66	α (2)
20 674	w	366	$9b^0_1$(1)
20 606	w	574	$6b^0_1$ (2)
20 592	w	448	$7a^0_1$ (1)
20 570	s		H atomic line
20 498	s	682	$6a^0_1$ (2)
20 484	m	556	$6b^0_1$ (1)
20 432	vw	66	α (2)
20 380	w	800	12^0_1 (2)
20 362	s	678	$6a^0_1$ (1)
20 320	w	860	$17a^0_1$ (2)
20 174	m	1006	$18b^0_1$ (2)
20 146	m	1034	$\delta_{as}{}^{-}CH_3$
20 114	m	1066	1^0_1 (2)
20 014	m	1026	1^0_1 (1)
19 986	w	1054	$18a^0_1$ (1)
19 958	w	1222	13^0_1 (2)
19 940	w		He atomic line
19 814	w	1366	$6a^0_2$ (2)
19 780	w	1260	14^0_1 (1)
19 774	vw	1406	$18a^0_1 18b^0_1$ (2)
19 718	w	1462	$\delta_{as}{}^{+}CH_3$
19 638	vw	1542	$18a^0_1$ (2)
19 598	m	1582	$18b^0_1$ (2)
19 506	m	1674	
19 488	m	1692	$6a^0_1 18b^0_1$ (2)

[a] Measured in vacuum (cm^{-1}). [b] Spacing from the origin bands at 21 040 and 21 180 cm^{-1} for the *o*-chlorobenzyl and *o*-chloro-α-methylbenzyl radicals, respectively. [c] Greek letter indicates the sequence bands associated with the strong vibronic band. [d] The numbers 1 and 2 indicate the *o*-chloro-α-methylbenzyl and the *o*-chlorobenzyl radicals, respectively.

intensity at 21 040 cm^{-1}, exactly the same position reported previously.[7] Also, many vibronic bands belonging to the *o*-chlorobenzyl radical were found at the same wavenumber, listed in Table 2. The vibronic bands at 20 484 and 20 362 cm^{-1} are the $6b^0_1$ and $6a^0_1$ bands of the *o*-chlorobenzyl radical, respectively, which are the vibrational modes of C−C−C angle deformation. The splitting between modes 6a and 6b, degenerate in benzene at 606 cm^{-1}, increases with the increasing mass of the substituents.[27] The separation is 59 cm^{-1} for *o*-fluorobenzyl[6] only, 122 cm^{-1} for *o*-chlorobenzyl. 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. After subtracting the bands belonging to the *o*-chlorobenzyl radical from the spectra observed, we found a series of vibronic bands similar to those reported for most benzyl-type radicals.

We assigned the strongest band at 21 180 cm^{-1} in this spectrum to the origin band of the *o*-chloro-α-methylbenzyl radical in the $D_1 \rightarrow D_0$ transition. The large shift of the origin band from the benzyl radical could be expected, the *o*-isomer showing the largest shift among the three isomers. In the vibronic emission spectra of benzyl-type radicals observed in the CESE system, the origin band always shows the strongest intensity at the highest wavenumber, due to the efficient vibrational cooling in the D_1 state and the large Franck−Condon factor in electronic transition. The weak band at 20 986 cm^{-1}, a shift of 194 cm^{-1} from the origin band, was assigned to mode 9b of C−Cl in-plane bending vibration because the mode should have the lowest frequency among the in-plane vibrational modes. The calculation gives 203 cm^{-1} for this mode. The frequency of mode 9b decreases rapidly with heavy substitution, although this mode is degenerate at 1178 cm^{-1} in benzene with mode 9a. The medium intensity bands at 20 784 and 20 174 cm^{-1}, a shift of 396 and 1006 cm^{-1}, were assigned to modes 18a and 18b of C−Cl in-plane bending vibration, respectively, due to the coincidence with the calculation (400 and 997 cm^{-1}). Also, precursor shows a good agreement with the observation for these modes. One of the distinct modes in substituted benzyl-type radicals, mode 7a of C−Cl stretching vibration, was assigned to the band at 20 772 cm^{-1} with medium intensity, a shift of 408 cm^{-1}. The *o*-chlorobenzyl radical shows a similar frequency for this mode. The weak band at 20 606 cm^{-1} and strong band at 20 498 cm^{-1}, a shift of 574 and 682 cm^{-1} from the origin band, respectively, were assigned to modes 6b and 6a of C−C−C angle deformation, degenerate in benzene at 606 cm^{-1}. The splitting between modes 6a and 6b is 108 cm^{-1}, which is similar to 121 cm^{-1} of the *o*-chlorobenzyl.[7] Mode 1 of ring breathing vibration was assigned to the medium intensity band at 20 114 cm^{-1}, a shift of 1066 cm^{-1}, because the frequency of this mode should be less sensitive to substitution.[27] The *o*-chlorobenzyl radical and *o*-chloro-ethylbenzene show this mode at 1026 and 1061 cm^{-1} from the origin band, respectively.

The weak band at 20 380 cm^{-1} was assigned to mode 12 of radial skeletal vibration with weak intensity, a shift of 800 cm^{-1} from the origin band, because the calculation gives the only wavenumber of a′ symmetry within ±100 cm^{-1}. Also, precursor exhibits a good agreement with the observation. Mode 17a of C−H out-of-plane vibration was assigned to the weak band at 20 320 cm^{-1}, a shift of 860 cm^{-1} from the origin band, because the calculation and the precursor show an excellent agreement with the observation. The weak band at 19 958 cm^{-1}, a shift of 1222 cm^{-1} from the origin band, was assigned to mode 13 of C−Cl stretching vibration based upon the calculation. Fairly large shift from the precursor to the radical reflects the electron density of carbon. The degenerate mode 8 of the C−C stretching vibration is split by substitution into modes 8a and 8b. In the *p*-isomer, the frequency of mode 8a is higher than that of mode 8b, whereas the case is reversed in the *o*- and *m*-isomers. Thus, the bands at 19 638 and 19 598 cm^{-1}, a shift of 1542 and 1582 cm^{-1} from the origin band, were assigned to modes 8a and 8b, respectively. The calculation gives similar results for these modes, which belong to the highest wavenumber except for the C−H stretching vibrations of 3000 cm^{-1}.

Of asymmetric bending vibrations of CH_3 group, the rocking mode of this group can be distinguished by $\delta_{as}{}^{-}CH_3$ and $\delta_{as}{}^{+}CH_3$. In this case, $\delta_{as}{}^{-}CH_3$ mode at about 1030 cm^{-1} is generally strong, but the band due to $\delta_{as}{}^{+}CH_3$ mode at about 1180 cm^{-1} is often very weak due to the steric hindrance of the chlorine atom. The same case was observed in this work to the theoretical consideration. The bands at 20 146 and 19 718 cm^{-1}, a shift of 1034 and 1462 cm^{-1}, were assigned to modes $\delta_{as}{}^{-}CH_3$ and $\delta_{as}{}^{+}CH_3$, respectively. The calculation shows good agreements with the observation for these modes. In this spectrum, the band at 19 506 cm^{-1}, a shift of 1674 cm^{-1} from the origin band, was not assigned, although it shows relatively strong intensity and broadband shape in this spectrum. Besides the bands belonging to benzyl-type radicals, we observed a few He and H atomic lines,[19] which were used for calibration of wavenumber of spectrum in this work. The atomic lines can be easily distinguished by their line shape. One particularly interesting line is a H atomic line at 20 572 cm^{-1} generated by C−H bond cleavage of precursor.

Relatively short progression involving vibrational mode 6a was observed at 19 814 cm^{-1} with observable intensity. Also, the vibrational modes with strong intensity listed in Table 1 are active in combination bands. A low frequency sequence band was regularly observed with very weak intensity in the vicinity of a few strong vibronic bands at intervals of approximately 66 cm^{-1} from the vibronic band, as listed in Table 2. A problem remains in explaining the origin of low frequency sequence bands. Cossart-Magos and Cossart[28] have observed several weak bands near the origin band of *p*-fluorobenzyl radical and assigned them as combination bands coupled with the origin band. Fukushima and Obi[29] have also identified weak bands in the vicinity of the strong bands and attributed them as belonging to the van der Waals molecules. However, it seems unlikely in this work that the bands could be attributed to dimers or van der Waals molecules because the same bands were observed with another carrier gas Ar, albeit with much weaker intensity. A possible explanation of these low frequency sequence bands might be attributed to the sequence bands associated with the most intensive bands in the spectrum because the intensity of the sequence bands is proportional to that of the strong vibronic bands. However, it may not be possible at this moment to attempt the assignments of the bands due to the insufficient vibrational mode frequencies at the excited electronic state.

It has been generally accepted that the DFT calculation using the Gaussian 03 program with the cc-pvdz basis set can predict the vibrational mode frequencies within ±10% of the experimental values, in most cases. In the present study, from the calculation for the *o*-chloro-α-methylbenzyl radical, a total of 45 vibrational mode frequencies were obtained, of which 30 and 15 modes belonged to the a′ and a″ symmetries of in-plane and out-of-plane vibrations in the C_s point group, respectively. The calculated values were unscaled and correlated with the observed values, as in the case of *o*-chlorobenzyl radical. Table 3 lists the observed and calculated vibrational mode frequencies of the *o*-chloro-α-methylbenzyl radical as well as those of *o*-chloro-ethylbenzene with the symmetry of vibrational modes.

TABLE 3: Vibrational Frequencies (cm^{-1}) of the *o*-Chloro-α-Methylbenzyl Radical

mode[a]	this work[b] (D_0)	ab initio[c] B3LYP/ cc-pvdz (D_0)	precursor[d] (S_0)	symmetry (C_s)
origin	21 180			
1	1066	1061	1061	a′
6a	682	684	674	a′
6b	574	577	522	a′
7a	408	478	440	a′
8a	1542	1569	1566	a′
8b	1582	1600	1591	a′
9b	194	202	265	a′
12	800	798	778	a′
13	1222	1241	1197	a′
17a	860	859	856	a″
18a	396	400	369	a′
18b	1006	997	1024	a′
$\delta_{as}{}^{+}CH_3$	1462	1458	1441	a′
$\delta_{as}{}^{-}CH_3$	1034	1035	1044	a′

[a] Reference 30. [b] Measured in vacuum (cm^{-1}). [c] Not scaled. [d] Reference 27.

The strong observation of the *o*-chloro-α-methylbenzyl radical in the spectrum indicates that the formation of this radical in corona discharge from precursor is a favorable pathway despite the large mean bond dissociation energy of C−H at the α-position of ethyl group. Also, it was found that the intensity ratio of the *o*-chloro-α-methylbenzyl to the *o*-chlorobenzyl did not change much by variation of the experimental conditions such as discharging current and voltage.

Conclusion

We identified spectroscopically the formation of the *o*-chloro-α-methylbenzyl radical and the *o*-chlorobenzyl radical by an analysis of the vibronic emission spectrum observed from the species generated by corona discharge of precursor *o*-chloroethylbenzene seeded in a large amount of inert carrier gas helium. By comparing the observed spectrum with those of ab initio calculations and of the known data of precursor, the energy in the $D_1 \rightarrow D_0$ electronic transition and the vibrational mode frequencies of the *o*-chloro-α-methylbenzyl radical in the ground electronic state were accurately determined for the first time.

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