ESR Detection of the Isotopic-site-preference in the Jahn–Teller Distorted Benzene Cation Radicals Produced in MCM-41, Silica Gel, and Halocarbons

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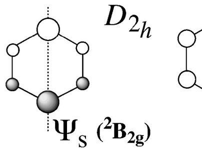
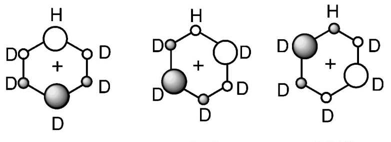
Isotopic-site-preference was detected in partially-deuterated benzene cation radicals, which were distorted by the Jahn–Teller effect to the D_{2h} symmetry. In all cases, C–H bonds tend to occupy the positions with higher spin densities in the distorted cation.

Static Jahn–Teller (J–T) distortion of the cation radicals, which were derived from the molecules with degenerated highest occupied molecular orbitals (HOMO), has been a prosperous research theme since the first ESR detection of the J–T distorted ethane cation radical in the SF_6 matrix.[1] Many researches on the cation radicals of basic molecules, including benzene, followed.[2] The D/H isotope effect on the J–T distortion has been an interesting research theme.[3–7] In the case of partially deuterated methane and other alkane cations, a strict site-selection was found for the C–H bonds in the distorted forms.[3–5] That is, the C–H bond predominantly occupies the position where a higher unpaired electron density appears. It is well known that the site selectivity is explained by the total zero point vibrational energy (ZPVE) of the cation radical, and the extent of selectivity is calculated by the Boltsmann's equation.[8,9] Now, whether the isotope effect can be observed for the distorted benzene cation is an interesting problem, because the role of C–H or C–D bond is small in the vibrational mode of the benzene skeleton.[7,10]



Static J–T distortion of benzene cation radical was observed by ESR at 4.2 K in frozen halocarbon matrices ($CFCl_3$ and $CF_2ClCFCl_2$),[10] on silica gel, zeolites,[11] and mesoporous silica (MCM-41).[12] It has been deduced that the ground state is $^2B_{2g}$ of D_{2h} symmetry (Ψ_S) and the molecular shape is a compressed hexagon (see inset) in all these matrices. The purpose of the present work is to clarify whether the isotope substitution affects the static distortion, and also whether the site-selection occurs in the distorted forms as in the ethane cation.

Partially deuterated benzenes, benzene-1,4-d_2 ($C_6D_2H_4$), benzene-1,2,4,5-d_4 ($C_6D_4H_2$), and benzene-d_5 (C_6D_5H), were purchased from Osaka Sanso Co. (Japan), $CFCl_3$ and CF_3CCl_3 from Aldrich Chemicals Co. (USA), and silica gel from Wako Pure Chemicals (Japan). MCM-41, a mesoporous silica, was synthesized following the literatures from tetraethoxysilane (TEOS) by using cetyltrimethylammonium bromide (CTAB) for the template.[12,13]



(I) **(II)** **(II')**

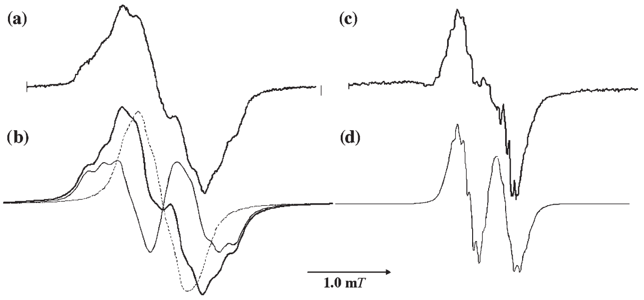


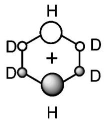
Figure 1. ESR spectra of $C_6HD_5^+$ generated in MCM-41 by X-ray irradiation at 4.2 K and observed at 4.2 K (a), and at 77 K (c). (b) is the simulation for the site-isomer I and II (traced with thin lines) and the sum of them with the ratio of 1.1 to 1.0 (thick line). (d) is the simulation for (c) assuming $A(\mathrm{H}) = [-0.30, -0.505, -0.490]$ m*T*, $A(\mathrm{D}) = A(\mathrm{H}) \times \mu_{\mathrm{D}}/\mu_{\mathrm{H}}$, and $g = [2.0029, 2.0029, 2.0023]$.

Figure 1 shows the ESR spectra of the cation radical of benzene-d_5 (<0.2 wt %) generated by X-ray irradiation at 4.2 K in MCM-41 matrix and measured at 4.2 K (a) or at 77 K (c). The spectrum changed reversibly (a $\rightleftarrows$ c) with the observing temperature. The assignments of these spectra a) and c) to the benzene-d_5 cation ($C_6HD_5^+$) distorted to D_{2h} with the electronic state of $^2B_{2g}$ and that in pseudo rotation, respectively, are made without ambiguity from the results for the benzene-h_6 cation.[12] Spectrum b) is the simulation for a) by superposing the spectra of the two types of $^2B_{2g}$ cations, (I: $D(C_6D_4)H^+$) and (II: $D(C_6D_3H)D^+$), with the relative amount of 0.5:0.5. (Here, the protons and deuterons written outside the parenthesis are bonded to the carbons on which the unpaired electron density is higher compared with those on other carbons (see inset)). The ESR parameters were employed from those reported for $C_6H_6^+$ in $CFCl_3$.[10] Since the population ratio between the radicals I and II + II′ expected from the simple statistics is 1:2, a D/H site-preference is clearly indicated in the observed result; i.e., the isomer I is energetically lower than II and II′.

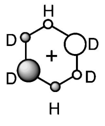
As mentioned above, the spectrum changes from (a) to (c) at 77 K by the "pseudo-rotation": i.e., rapid jumping among the three forms, I, II, and II′. Figure 1d is a simulation spectrum made with this model. In this calculation, however, the orthorhombic hyperfine tensor for H was needed, indicating that the molecular motion is restricted even along the axis normal to molecular plane. By raising the observing temperature above 90 K, molecular migration on the surface takes place to form dimer cation before giving a well resolved isotropic hyperfine structure.

Similar results were obtained for the frozen solutions of benzene-d_5 in CF_3CCl_3 or $CFCl_3$. In these systems, however, the spectra of the cations generated by radiolysis at 4.2 K changed irreversibly by raising the sample temperature once at 77 K. We call this spectral change “the annealing effect,” since the total radical concentration was kept almost unchanged during these processes. This annealing effect was ascribed to the change of the ratio between the two components (I:II). In other word, a part of II was converted into I by annealing. The ratios of the two isomers estimated by spectral simulation are listed in Table 1.

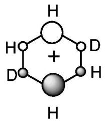
We interpreted the annealing effect as follows: the cation radicals generated at 4.2 K distort spontaneously to D_{2h} to the direction determined by the surrounding molecules. The cation cannot relax to the form with the most stable isotopic disposition at that temperature, if the interaction between the matrix and the cation radical is strong and its formation process, hole transfer from the matrix, is a low energy one. Since $CFCl_3$ and CF_3CCl_3 matrices trap the cation radical at the bottom of the deep potential well made by their large dipole moments,[14] the onset temperature of pseudo-rotation for the benzene cation is high; eg. 90 K for $CFCl_3$.[10] On the other hand, in the matrix of MCM-41 or silica gel the pseudo-rotation starts at around 20 K,[11,12] indicating that the interaction between the solute and the matrix is weak. This weak interaction lets the cation radicals relax to the most stable isotopic disposition during the irradiation at 4.2 K. So, the population ratio in MCM-41 at 4.2 K, which did not change by annealing, can be used to estimate the energy difference between the isotopic-site isomers. Thus, the difference between the ZPVE’s of I and II could estimated to be around 24 J/mol.



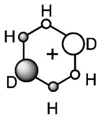
(III)



(IV)



(V)



(VI)

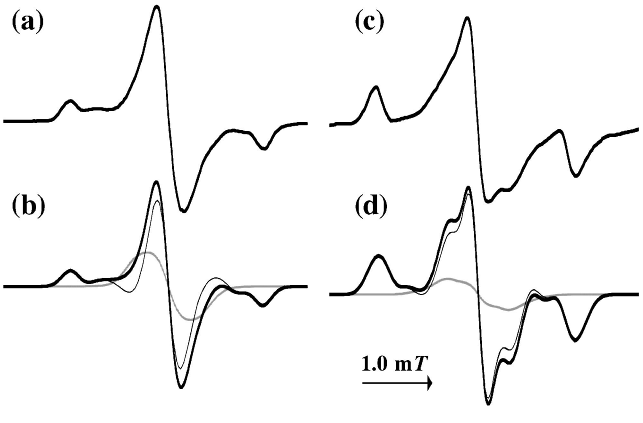


Figure 2. ESR spectra of benzene-1,2,4,5-$d_4{}^+$ (a) and benzene-1,4-$d_2{}^+$ (c) generated by X-ray irradiation of the mother molecules at 4.2 K in CF_3CCl_3 and observed at 4.2 K after annealed at 77 K. (b) and (d) are the reconstructed spectra for (a) and (c), by adding the simulated spectra for (III) and (IV) with the ratio of 2.5:1 and (V) and (VI) with the ratio of 8:1, respectively. The superposed thin lines indicate the components with the corresponding intensities.

Figure 2a shows the ESR spectrum of benzene-1,2,4,5-d_4 cation observed at 4.2 K in CF_3CCl_3, after annealing at 77 K. The spectrum has two wing peaks separated by 2.5 mT, which are characteristic to the J–T distorted benzene-h_6 cation.[10–12] This is an evidence that the cation of $^2B_{2g}$, $H(C_6D_4)H^+$ (III), is formed from benzene-d_4 as one of the main component. The lower heights of these wing peaks compared with that for benzene-$h_6{}^+$ indicates that the alternative form, $D(C_6D_2H_2)D^+$ (IV), which gives only an unresolved singlet ESR is also trapped. With the aid of spectral simulation, it was found that about 50% of IV is converted into III once the sample was warmed up to 77 K after 4.2 K irradiation. Essentially the same result was obtained in the $CFCl_3$ matrix. In silica-gel, relative heights of the wing peaks are almost the same with those in halocarbon matrices after annealing. However, no annealing effect was observed. All these results indicate that the ground state of benzene-1,2,4,5-d_4 cation is $^2B_{2g}$ and the form III with C–H bond on the primary C_2-axis is more stable than IV. The annealing effect is interpreted in the same way as in the benzene-d_5 system. For benzene-1,4-d_2 cation, the spectra for $H(C_6D_2H_2)H^+$ (V) and $D(C_6H_4)D^+$ (VI) were superposed again as shown in Figures 2c and 2d. In the halocarbon matrices, populations of V and VI right after X-ray irradiation at 4.2 K are not so much deviated from the ratio of 2:1. The former, V, increased by annealing at 77 K and the ratio approached to 7–8:1. On silica-gel the ratio between the forms V to VI was close to 5 to 1 throughout. All these results are added in Table 1.

Table 1. Relative yield of isotopic-site isomers for the partially deuterated benzene cations generated by radiolysis at 4.2 K and observed at 4.2 K after annealed at 77 K

Matrices	Benzene-d_5 $[D(C_6D_4)H^+]$ $[D(C_6D_3H)D^+]$	Benzene-1,2,4,5-d_4 $[H(C_6D_4)H^+]$ $[D(C_6D_2H_2)D^+]$	Benzene-1,4-d_2 $[H(C_6D_2H_2)H^+]$ $[D(C_6H_4)D^+]$
(statistical)	0.5	0.5	2.0
MCM-41 or silica-gel*	1.0	ca. 2*	ca. 5*
CF_3CCl_3	1.8	2.5	7 ~ 8
$CFCl_3$	1.9	2 ~ 3	5

In summary, two possible isotopic site isomers in the $^2B_{2g}$ state exist in all the systems: benzene-$d_5{}^+$, benzene-1,2,4,5-$d_4{}^+$, and benzene-1,4-$d_2{}^+$, and isotopic-site preference between those was detected obviously. These results are summarized as follows: 1) In the preferred isotopic-site isomer, higher unpaired spin density appears on the carbons bonded to H. This means that D atoms preferentially occupies the stronger C–H(D) bonds. 2) The selectivity among the isotopic distribution in the distorted cation is not so strict as that reported for the cations of methane, ethane etc., where the only one form is detected. The small isotope effect indicates that the energy difference between the isotopic-site isomers is small.

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