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Mass-spectral Isotope Effects in the Metastable Transition of Benzene and Perdeuterio Benzene. Model Calculation

Ryuichi Arakawa and Yozaburo Yoshikawa*
Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560

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The abundances of $C_6H_5^+$, $C_6H_4^{+\cdot}$, $C_4X_4^{+\cdot}$, and $C_3X_3^+$ (X=H, D) fragments occurring in the metastable transition of benzene and perdeuterio benzene have been measured by means of electron-impact ionization. The isotope effects on the relative intensities were reproduced by the simple model calculation on the basis of the RRKM theory. The vibrational frequencies of the transition states for the deuteriated and the nondeuteriated were obtained by a vibrational analysis for the assumed geometries and force fields. The transition states for the $C_6H_5^+$ and $C_6H_4^{+\cdot}$ channels preferred a benzene structure while those for the $C_4H_4^{+\cdot}$ and $C_3H_3^+$ has a propargylcyclopropene structure. The calculated decay rates for the $C_6H_5^+$, $C_4H_4^{+\cdot}$, and $C_3H_3^+$ fragmentation were compared with those of the photoion photoelectron coincidence (PIPECO) results.

In the study of the metastable transitions of partly deuteriated ions, the isotope effect has been a tool in the structural assignment of both transition and reactant states. The application of the mass-spectral ion abundances of isotopically substituted molecules has been reviewed by Holmes.[1] The relative intensities of fragmentation from complex molecules have been readily explained by the statistical calculation without any serious discrepancy.[2,3] Systematic studies of the transition states have been done in the unimolecular reaction of the methyl radical and the hydrogen-atom loss from 1,3-butadiene and in that of its perdeuterio analog.[4] The model calculation of kinetic isotope effects showed the most plausible transition state for the methyl-elimination reaction to be a 2-methylcyclopropenium ion.

In the metastable transitions of benzene ions, the molecular ions lose $H^\cdot$, H_2, C_2H_2, and $C_3H_3^\cdot$ to yield fragments of $C_6H_5^+$, $C_6H_4^{+\cdot}$, $C_4H_4^{+\cdot}$, and $C_3H_3^+$ respectively. Mass spectral results on ^{13}C- and ^2H-labeled benzene have shown that there was a significant scrambling of carbon and hydrogen atoms prior to dissociation.[5] The first measurement concerning the dissociation rates for the benzene ion as a function of the internal energy was carried out by Andlauer and Ottinger using the charge-transfer reactions with ions of various ionization potentials.[6] Their results triggered arguments for the exsistence of two isolated $C_6H_6^{+\cdot}$ states, one producing $C_6H_5^+$ and $C_6H_4^{+\cdot}$, and the other giving $C_4H_4^{+\cdot}$ and $C_3H_3^+$.[7] Rosenstock *et al.*, by interpreting the photoionization mass spectrum,[8] suggested that the precursor ion for the $C_3H_3^+$ fragment was not the ground state of the benzene ion. Finally, Baer *et al.* measure the absolute fragmentation rates for internal-energy- selected $C_6H_6^{+\cdot}$ ions of several isomers, such as 2, 4- and 1, 5- hexadiyne, obtained by photoion photoelectron coincidence (PIPECO).[9] Their experimental and RRKM calculated rates indicate that benzene and these isomers rearrange to a common precursor and fragment to all product channels by competing pathways and that the existence of isolated states or noncommunicating isomeric structures is highly unlikely.

In the present communication, the mass-spectral isotope effects from metastable transitions were investigated in order to understand better the unimolecular process of benzene ions. The rates of unimolecular decomposition were calculated on the basis of the RRKM theory. The reaction paths were simulated by changing the structures of the transition state (TS) models, including a variety of reaction coordinates. The TS models were determined by changing the bond orders and the angles of the bonds involved in the reaction so as to reproduce the experimental isotope effects. The absolute rate constants of the $C_6H_5^+$, $C_4H_4^{+\cdot}$, and $C_3H_3^+$ fragments obtained from the PIPECO results[9] were helpful in constraining the assumed TS models.

Experimental

A home-built tandem mass spectrometer[10] was used to measure fragment ions. The temperature of the ion source was 150 °C. The electron-ionization energy was 30—50 eV, the electron current was 3 μA, and the ion-accelerating voltage was 1.2 kV. The pressure in the field-free region was always less than 1×10^{-6} Torr (1 Torr=133.32 N m^{-2}).

Fragment ions from metastable transitions occurring in the field-free region between two magnets were detected and their intensities integrated by mean of a multiscan system. For the measurement of the mass spectra, about one hundred scans over several hours were needed to accumulate 10^6 counts for molecular ions. The sample of benzene-d_6 (99% atom D; MERCK) was a commercially available one.

Results and Discussion

The peak-intensity ratios, P_X, of fragment ions for the metastable transitions of $C_6X_6^{+\cdot}$ (X=H,D) are summarized in Table 1. The error given shows the

TABLE 1. RELATIVA PEAK INTENSITIES OF THE FRAGMENT IONS FOR THE METASTABLE TRANSITION OF $C_6X_6^{+\cdot}$ (X=H,D)

X	E/eV	$C_6X_5^+$	$C_6X_4^{+\cdot}$	$C_4X_4^{+\cdot}$	$C_3X_3^+$
P_H	50	100	16±2	3.8±0.1	1.1±0.1
	40	100	18	4.2	1.2
	30	100	19	4.5	1.1
P_D	50	100	20±1	10±0.3	2.4±0.1
	40	100	20	11	2.5
	30	100	25	12	3.8

standard deviation after several runs. It is considered impossible to include the systematic error. There was no pressure effect on the measured peak ratios of the parent and metastable product ions. The main process is the hydrogen-atom elimination. The peak ratios did not change above the electron energy of 30 eV. The internal energy distribution, $P(E)$, of the molecular ions formed by electron impact is almost constant in this energy region of ionizing electrons.

The peak intensity of an i-th fragment ion in the mass spectra which does not undergo further decomposition is given by:

$$I_i = c\int_0^\infty P(E)k_i(E)T(E)/\sum k_j(E)\mathrm{d}E.$$

Here, c is a constant, E is the internal excitation energy of the molecular ion, $k_i(E)$ is the rate constant for decay into the i-th fragment, and $T(E)$ is the time factor, $T(E)=\exp(-t_1\sum k_j(E))-\exp(-t_2\sum k_j(E))$, where t_1 and t_2 are the entrance and exit times of the molecular ion in the field free region relative to the time of ion formation($t_1=3.6$ and $t_2=8.5$ μs for $C_6H_6^{+\cdot}$).

The specific rate constant for unimolecular decomposition is given by

$$k(E) = L^*(I^*_{\mathrm{ABC}}/I_{\mathrm{ABC}})^{1/2}\sum P(E^*)/(hN(E_0+E^*)),$$

where h is Planck's constant, E_0 is the activation energy, $\sum P(E^*)$ is the total number of vibrational-rotational states of the activated complex at energy E^*, $N(E_0+E^*)$ is the level density of the reactant molecule at energy $E=E_0+E^*$, the I^* and I values are the products of the principal moments of inertia for the activated complex and reactant, and L^* is a statistical factor. An algorithm of Stein and Rabinovitch[11] was used for directly computing harmonic oscillator eigenstate sums and densities.

The internal energy of molecular ions consists of the internal thermal energy plus the energy transferred into the ion by the ionization process. Several methods of approximating the expression of $P(E)$ have been examined and these shortcomings analyzed.[12] In the present calculation, the energy-transfer probability was estimated by folding the photoionization cross-section[13] into the HeI photoelectron spectrum[14] under the optical approximation proposed by Miesels *et al.*[12]

The activation energies for the unimolecular decomposition of the benzene ion resulting in the loss of $H^{\cdot}$, C_2H_2, and $C_3H_3^{\cdot}$ are 3.60, 4.22, and 4.37 eV respectively, while the ionization energy of benzene is 9.24 eV.[9] That of the H_2 loss was estimated to be 3.86 eV.[15] The activation energies of the deuteriated species are estimated from applying the zero-point energy correction to the values for the nondeuteriated molecules. These corrections were all less than 0.05 eV.

The vibrational frequencies of the deuteriated and the non-deuteriated molecules for the reactant and the TS are obtained by a vibrational analysis for the assumed geometries and force fields.[16] The reactant and the TS models for the competing reactions are represented by the same internal coordinates. The relative rate constants yielding the relative intensities are thought to be independent of the influence of the approximate frequencies resulting from the approximate simple valence force field(diagonal force constant matrix), but one thought to be related to the TS structures. For the TS model, the reacting bond length r modified from the empirical length r_0 is described along the reaction coordinate and adjusted on the basis of Pauling's expression; $r=r_0-0.3\ln(n)$ where n is the bond order. The geometry of each model was most conveniently specified in terms of the bond orders and bond angles. The bond lengths of benzene are summarized in Table 2. The stretching force constants F_r° of the initial state for the reacting bond are modified for the TS model according to $F_r=nF_r^\circ$. The angle bending force constants are also given by $F_a=g(\theta)n_in_jF_a^\circ$, where n_i and n_j are the bond orders in the bending mode and F_a° is the initial bending force constant. The value of $g(\theta)$ refers to the hybridization factor, $g(\theta)=1.39+1.17\cos(\theta)$, where θ is the bond angle. Torsional and out-of-plane bending force constants are retained at the values of the reactant force constants for all the modes. The force constants employed in the frequency calculation are shown in Table 2. In the reaction coordinate, the decomposition frequency is imaginary when the curvature is negative at the barrier. For the reaction proceeding through a simple bond cleavage in the TS model, the force constant for the stretching mode of the reacting bond will be negative.

The reactant configuration of the $C_6X_6^{+\cdot}$ ion formed from benzene by ionization is taken to be identical with that of the neutral molecule. The TS models

TABLE 2. BOND LENGTHS AND FORCE CONSTANTS TO BE EMPLOYED IN THE FREQUENCY CALCULATION

Type of bond	r_0/Å	F_r/mdyn $Å^{-1}$ a)
sp^3C-sp^2C	1.5075	5.0
sp^2C-sp^2C	1.46	5.8
sp C−sp C	1.37	8.0
sp^3C-H	1.094	5.0
sp^2C-H	1.083	5.2
Type of angle		F_a/mdyn Å rad^{-2} b)
HCH		0.55
HCC		0.65
CCC		1.0
Out-of plane		0.2
Torsion		0.072

a) Stretching force constants are given for bonds with an order of unity. b) Bending force constants correspond to angles of 109.47°, subtended by bonds with an order of unity.

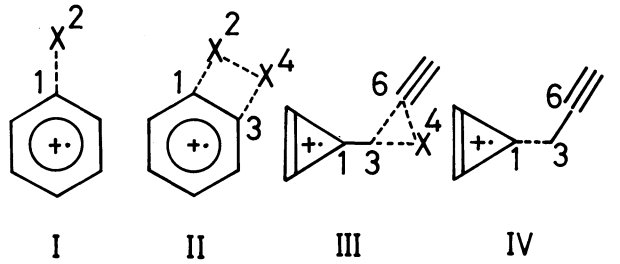

Fig. 1. Assumed geometries of the $C_6X_6^{+\cdot}$ ion for TS models of $X^{\cdot}$(I), X_2(II), C_2X_2(III), and $C_3X_3^{\cdot}$(IV) loss(X=H, D).

TABLE 3. CALCULATED ISOTOPE EFFECT ON PEAK INTENSITIES ASSUMING VARIOUS TS MODELS

Models	Parameters	Fragment	Peak intensities	
			P_H	P_D
I	$n_{12}=0.1$[a] $F_S=-2.0$[b]	$C_6X_5^+$	100(100)[d]	100(100)
II	$n_{12}=0.1$ $n_{34}=0.5$ $F_S=-2.0$	$C_6X_4^{+\cdot}$	15(16)	20(20)
III	$n_{36}=0.2$ $n_{46}=1.0$ $F_S=-2.0$ $N_{rot}=3$[c]	$C_4X_4^{+\cdot}$	4.1(3.8)	7.1(10)
IV	$n_{13}=0.2$ $F_S=-2.0$ $N_{rot}=3$	$C_3X_3^+$	1.2(1.1)	2.6(2.4)

a) n_{ij} is the bond order of the i and j-th atoms: in Fig. 1. b) F_S means the force constant for the corresponding stretching mode of the reacting bond. c) Number of internal free rotations. d) Values in parentheses are experimental.

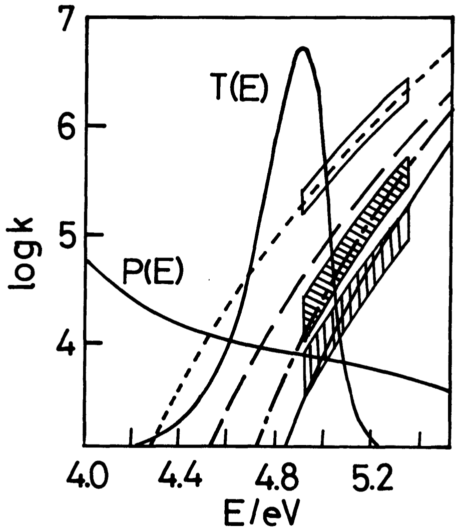

Fig. 2. Relationship among $P(E)$, $T(E)$ and decay rates for unimolecular decomposition of the $C_6H_6^{+\cdot}$ ion. Values of $P(E)$ and $T(E)$ are plotted on a linear scale versus the internal energy E. The decay curves show rate constants of $H^\cdot$(----), H_2(——), C_2H_2 (—·—), and $C_3H_3^\cdot$(——) loss. Wide lines are absolute rates obtained from PIPECO results of Baer *et al.* without the rate of H_2 loss.[9]

proceeding to the $C_6X_5^+$, $C_6X_4^{+\cdot}$, $C_4X_4^{+\cdot}$, and $C_3X_3^+$ products were assumed to be structures I—IV, they are shown in Fig. 1. The models of TS(I) and TS(II) are of a benzene molecule, and the others of a propargyl-1-cycloprop-2-ene structure similar to that chosen by Baer *et al.* The dissociations giving $C_6X_5^+$ and $C_3X_3^+$ are described as a simple-bond cleavage reactions of C_1–X_2 and C_1–C_3 as is shown in the TS(I) and TS(IV) models. In TS(II) and TS(III) models, a hydrogen-atom transition should occur. The relative motions of the migrating hydrogen atom and the loosing bond are defined by using an appropriate combination of interaction force constants(off-diagonal elements in F-matrix) for the coupling of the stretching modes of the reacting bonds. It requires a constant total bonding for the migrating atom, satisfying $n_{34}+n_{24}=1$ and $n_{34}+n_{46}=1$ for TS(II) and TS(III), respectively. For the sake of simplicity, however, the simple bond cleavage for the stretching modes of C_1–X_2, TS(II) and C_3–C_6, TS(III) are employed as the reaction coordinates. The interaction force constants were not considered. Structural parameters used here are shown in Table 3. The stretching force constants for the reacting bond are fixed at $F_S=-2.0$; the torsional modes of vibration are reduced to free internal rotations.

The calculated isotope effects on the peak intensities are shown in Table 3. The results agree well with the experimental isotope effects. The rate curves and P_X varied with the bond-order parameters, but the P_H/P_D ratio did not change greatly within the limit of the given TS model. The application of a linear structure such as a 1,5-hexadiyne ion to the $C_4H_4^{+\cdot}$ and $C_3H_3^+$ TS models gave insufficient results on isotope effects. The rate constants decaying to $C_6H_5^+$, $C_4H_4^{+\cdot}$, and $C_3H_3^+$ are compared with the results of Baer *et al.* in Fig. 2. Their rates were determined from the total decay rates and the branching ratios if the dissociation channels were in competition. The rate for the H_2 loss channel has not been presented. The vibrational frequencies for the TS(III) and TS(IV) models, obtained from the vibrational analysis, are not very different from those of Baer *et al.* used in the RRKM calculations for the $C_4H_4^{+\cdot}$ and $C_3H_3^+$ channels. The values of the peak intensities are derived from rate curves lying in a metastable window $T(E)$, 4.4—5.2 eV. There is always uncertainty on the $P(E)$ function followed by electron-impact ionization. The relative values of the $P(E)$ function, defined within narrow limits, are necessary to calculate the isotope effects. Therefore, it is improbable that the $P(E)$ curve estimated above causes a large error in the isotope effects. An increase of a few percent in the relative intensities, P_H and P_D can be calculated if the $P(E)$ function is constant. The intensity of $C_6X_5^+$ fragment is relatively reduced because of the smaller values of the $P(E)$ function in the lower-energy region of the window $T(E)$. Such a variation in $P(E)$ does not influence the isotope effects to any large extent. The decay rate for the $D^\cdot$ loss is slower by one order of magnitude than that for the $H^\cdot$ loss. The metastable window for the C_6D_6 dissociation shifts to a higher energy, 4.7—5.8 eV.

The mass spectral isotope effects support the conclusion that the dissociation of the benzene ion proceeds competitively to all products. The reactant model equivalent to the common precusor from the C_6H_6 isomers is of a benzene molecule, and the TS models are the product-like structures. The measured peak intensities can not directly reflect the absolute rate, but rather the relative TS density yielding the relative rate constant. This analysis requires the absolute decay rates in order to fix the TS model.

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