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Emission Spectra of Aromatic Halides by Controlled Electron Impact

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Fluorobenzene, chlorobenzene, and bromobenzene were excited at a very low pressure in the vapor phase by a controlled electron beam of 60—300 V. Their emission spectra were then measured and compared with those excited by the photon. Fluorobenzene showed a characteristic photoemission of the parent molecule in the 260—320 nm region. The band was assigned to the transition from the lowest excited state to the ground state, and its shape did not vary appreciably with the energy of the electron beam. Though the spectrum had some features of "resonance fluorescence," the vibrational structure of the band was not identical with that of any of the spectra obtained by photon impact between 4.7—4.9 eV. This seems to indicate that the molecule gave different spectra according to the excitation energy. However, the excitation by 60 V electrons and that by 300 V electrons did not produce any remarkable difference in the spectra under the resolution of the spectrometer used. Other aromatic halides failed to show any characteristic band of the parent molecules; instead, they showed weak lines due to Cl^+ or Br^+ and pronounced bands due to HCl^+ or HBr^+. This result was ascribed to the spin-orbit coupling effect and the predissociation of the excited parent molecules.

Photochemical investigations of the excited states of aromatic molecules have been carried out by various authors. The effects of pressures and exciting wavelengths on the fluorescence spectra and their lifetimes have given information on the relaxation processes. However, few studies have been carried out at very low vapor pressures, and ultraviolet radiation has been used for the excitation in most of the previous studies.

Electric-discharge methods of various sorts have been effective sources of molecular excitation. The complicated character of the discharge, however, disturbs the detailed studies of the mechanism of fragmentation and excitation. The crossed electron and molecular beam method was proposed to overcome the difficulties and the emission spectra of the OH radical upon electron impact were studied.[1] Since then various di- and tri-atomic molecules have been studied by this method. This method has recently been developed for the investigation of large molecules,[2] and the emission spectra of some aromatic molecules have been reported.[3] In this controlled electron impact method, the photoemission of excited species is obtained at a very low pressure where the effect of molecular collisions is greatly reduced. The energy of electrons can be controlled from the outside. Thus, the method has proved to be of great use in studying the excited states and the emission spectra of various molecules.

The ionization and the fragmentation of molecules by electron impact have also been studied by mass spectroscopy. The information thus obtained, however, has been restricted to the ionized species, and little is known on the excited species in the ionization chamber. Thus, spectroscopic studies of the excited species by electron impact in a high vacuum would be of use.

The fluorescence of fluorobenzene in the vapor phase has been measured by Bass and Sponer[4] and by Nakamura.[5] Both the fluorescence spectra and the quantum yield have been measured at various wavelengths of excited radiation, and the mechanism of energy relaxation has been discussed.[5] If the molecules are raised to a certain vibrational level of an upper electronic state on the absorption of monochromatic light, and if the gas pressures are sufficiently low so that practically no collisions occur during the lifetime of the excited molecules, the light emission of these molecules will show a resonance fluorescence and the shape of fluorobenzene band will vary according to wavelengths of the radiation used for excitation. However, the energy values in his study were confined between 253—266 nm.[5] In the electron excitation method, the impact energy can be varied easily over a wider range, though the experimental

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[1] T. Horie, T. Nagura and M. Otsuka, *J. Phys. Soc. Jap.*, **11**, 1157 (1956).

[2] T. Ogawa, I. Fujita, M. Hatada, and K. Hirota, This Bulletin, **44**, 659 (1971); I. Fujita, M. Hatada, T. Ogawa, and K. Hirota, *ibid.*, **44**, 1751 (1971).

[3] T. Ogawa, M. Tsuji, M. Toyoda, and N. Ishibashi, *Chem. Lett.*, **1972**, 233.

[4] A. M. Bass and H. Sponer, *J. Opt. Soc. Amer.*, **40**, 389 (1950).

[5] K. Nakamura, *J. Chem. Phys.*, **53**, 998 (1970).

difficulties prevented us from using an excitation energy of less than 60 V. Chloro- and bromobenzenes are known not to show any fluorescence; this is attributable to a heavy halogen atom inducing spin-orbit relaxation.[4]

In the present study, the emission spectra of fluoro-, chloro-, and bromobenzenes under electron impact excitation will be reported. The relations of the spectra under electron impact excitation with those under photon irradiation excitation will also be discussed.

Experimental

The sample vapor from a nozzle was crossed so as to collide with an electron beam in a chamber, as is shown schematically in Fig. 1. The details of the apparatus were described elsewhere.[6] The cell was made of glass; it was 4.5 cm in diameter and 40 cm in length. The electron beam (b) from a tungsten filament (a) was accelerated by grids (not shown in the figure) and was introduced into the chamber through a slit. The sample (c) was jetted through a nozzle 0.1—1.0 mm in diameter and was excited by electrons. The chamber was evacuated (e) continuously to a high vacuum; a penning gauge attached to the chamber indicated a pressure of the order $10^{-4}\sim10^{-5}$ mmHg during electron impact. The actual pressure in the impact region was expected to be higher than the above value and smaller than 10^{-2} mmHg. The photoemission (d) was observed through a quartz window.

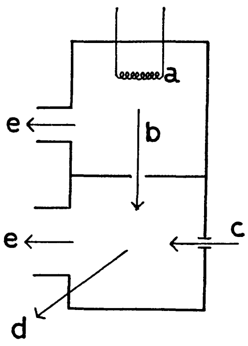

Fig. 1. Schematic diagram of the collision chamber. a; tungsten filament, b; electron beam, c; sample vapor, d; photoemission, e; to vacuum pump.

The spectra were obtained with a Jarrell-Ash JE 25 monochromator, which was equipped with two 1200 grooves/mm gratings blazed for 300 and 600 nm; it had a 100 μm slit and a reciprocal dispersion of about 33 Å/mm. The photometric measurements were carried out with an EMI 9558QB photomultiplier and a Burr-Brown 3421J OP amplifier. The mass spectrum was taken with a Hitachi RML-6E mass spectrometer. Fluorobenzene (Kishida, guaranteed grade), chlorobenzene (Kishida, guaranteed grade) and bromobenzene (Tokyo Kasei, guaranteed grade) were frozen and degassed in a high vacuum just before use.

Results and Discussion

A typical emission spectrum of fluorobenzene under electron-impact excitation is shown in Fig. 2. The band in the 260—320 nm region is similar to that of toluene,[3] which is identical to fluorobenzene in symmetry and which may, therefore, be expected to have similar vibronic interaction. The fluorine atom causes little change in the position of the absorption band around 260 nm, which is a typical band of aromatic molecules. The vibrational structure of the emission spectrum of fluorobenzene upon electron impact is similar to the fluorescence spectra in the vapor phase,[5] but not identical to any of them. Aromatic hydrocarbons such as benzene, toluene, xylenes and cumene show the band in a similar region in the electron-impact emission spectra[7] and in the fluorescence spectra,[8] as does fluorobenzene. Consequently, the observed band was assigned to the transition from the lowest excited singlet state to the ground state as in the cases of other hydrocarbons.[3,7] The other features in the spectrum in Fig. 2 were assigned to the hydrogen Balmer series and to the CH radical.

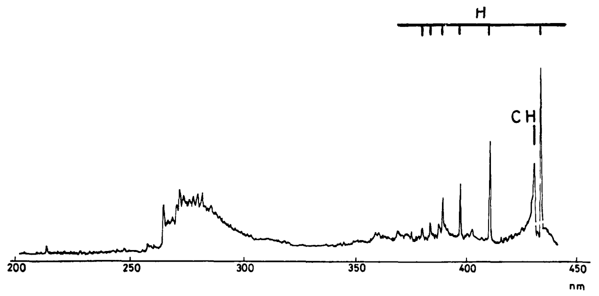

Fig. 2. Emission spectrum of fluorobenzene by electron impact. Impact voltage 200 V, electron beam current 1 mA.

The intensities of the photoemission of fluorobenzene were determined for various amounts of incident electrons and for various gas pressures. The intensities of the emissions from H and CH were found to

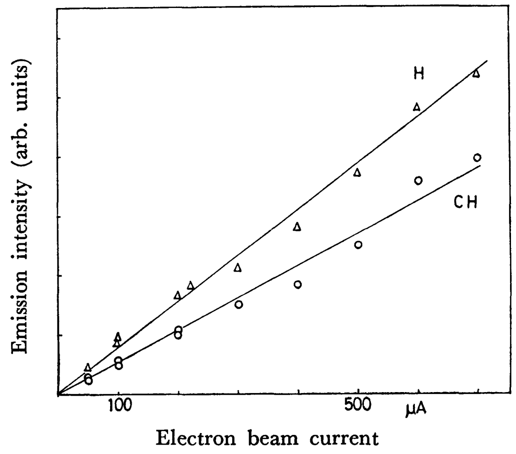

Fig. 3. Relationship between the emission intensity and the electron beam current. Hydrogen Balmer series (△) and CH radical (○). For the sake of clarity, 16 data for each species were omitted from the figure below 100 μA, all of which lay on the same straight line. Impact voltage 200 V.

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[6] T. Ogawa, M. Toyoda, M. Tsuji, and N. Ishibashi, *Technology Repts. Kyushu Univ.*, **45**, 427 (1972).

[7] T. Ogawa, M. Tsuji, M. Toyoda, and N. Ishibashi, *Chem. Lett.*, **1972**, 1157; This Bulletin, submitted.

[8] I. B. Berlman "Handbook of Fluorescence Spectra of Aromatic Molecules," 2nd ed., Academic Press, N. Y. (1971).

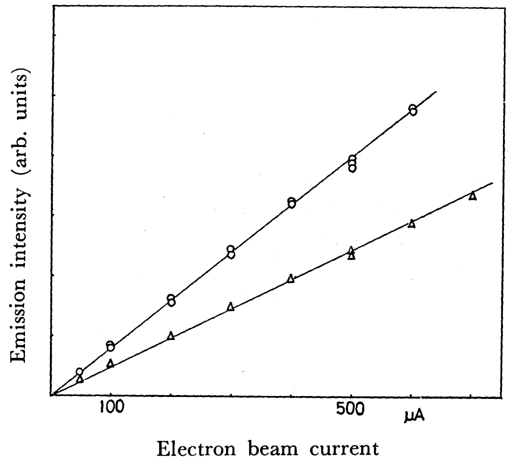

Fig. 4. Relationship between the emission intensity and the electron beam current. Intensities at 265 nm (△) and at 272 and 278 nm (○). For the sake of clarity, 12 data for each species were omitted from the figure below 100 μA, all of which lay on the same straight line. Impact voltage 200 V.

be proportional to the electron-beam current, as is shown in Fig. 3. This result is in agreement with that in the case of methane;[2] it shows that the fragmentation and the excitation of these species consist of a one-electron process. The relationship between the electron-beam current and the emission intensities of three peaks of the excited parent molecules in the 260—320 nm region is shown in Fig. 4. The excitation of a π electron of fluorobenzene was also concluded to be a one-electron process like the excitations of H and CH. The intensities of photoemissions of all species mentioned above were found to be proportional to the pressure in the gas reservoir, as is shown in Fig. 5. The pressure in the gas reservoir was estimated to be proportional to the pressure in the region of collisions by the use of a penning gauge attached to the impact chamber. Thus, inter-molecular quenching processes by collision seem to be unimportant. These results seem to indicate that the excitation and the fragmentation take place through one-electron processes, such as;

$$X \xrightarrow{e} X^* \qquad (1)$$

$$X \xrightarrow{e} X^{**} \left\{ \begin{array}{l} \xrightarrow{\text{fast}} X^* \\ \xrightarrow{\text{fast}} H,\ CH^* \cdots \end{array} \right. \qquad (2)$$

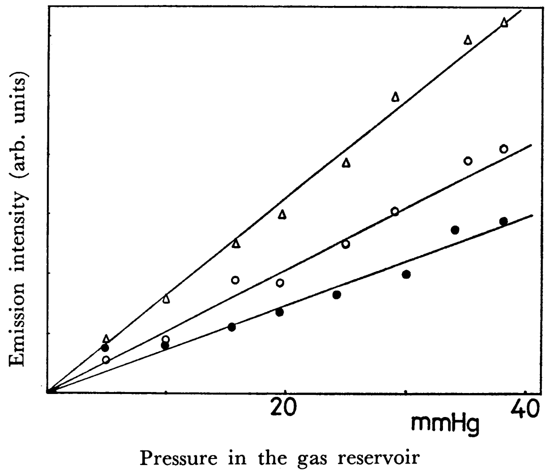

Fig. 5. Relationship between the emission intensity and the gas pressure in the gas reservior. Hydrogen Balmer series (△), CH radical (○) and the parent band at 264 nm (●). Impact voltage 200 V, electron beam current 50 μA.

where X stands for fluorobenzene, where ** indicates highly-excited states, and where * indicates the lower electronically-excited state from which the photoemission was observed. The relative importance of the two processes (1) and (2) could not be determined in the present study. X** would be a kind of superexcited state[9] which has excitation energy in excess of the first ionization energy. These superexcited states are considered to play an important role in the radiation chemistry[9] and in the fragmentation in mass spectrometry.[10]

The behavior of the first excited singlet state of fluorobenzene in the vapor phase was studied by Nakamura[5] by exciting the molecule with monochromatic light between 253 and 266 nm. The emission spectra varied in shape according to the wavelengths of incident radiation. The fluorescence spectra excited at longer wavelengths (*e.g.* 263 and 266 nm) were confined at wavelengths longer than the (0, 0) band (264 nm) and had the pronounced vibrational structure. The fluorescence spectra excited at shorter wavelengths (*e.g.* 253 and 258 nm), however, were broad and showed some emission at wavelengths shorter than the (0, 0) band. It was concluded that some resonance emission occurred at the shorter wavelengths of incident radiation.[5]

The present spectrum observed by the electron-impact excitation has some features at wavelengths shorter than the (0, 0) band; they probably arise from transitions which start at vibrational levels higher than those in statistical equilibrium with the surroundings. A comparison of the present emission spectra with those obtained by Nakamura reveals that the present spectra are close to those excited at the shorter wavelengths. However, the present spectrum, shown in Fig. 2, has a pronounced peak at 265 nm, whereas his spectrum, excited at 253 nm, has only a small peak at 265 nm; thus, the details of the vibrational structure of the present spectrum does not coincide with those of any of the fluorescence spectra. In the present study, the variation in the impact voltage between 60—200 V did not induce any appreciable change in the appearance of the spectrum under the present experimental resolution. It may be concluded that the molecule received enough excess energy and showed the resonance emission even when it was excited with electrons of 60 V, and that a similar resonance emission was observed for the excitation by electrons of higher energies.

A typical emission spectrum of chlorobenzene by electron impact and that of bromobenzene are shown

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[9] R. L. Platzman, *Radiation Res.*, **17**, 419 (1962).

[10] K. Hirota, *Nippon Kagaku Zasshi*, **89**, 327 (1968); **91**, 585 (1970).

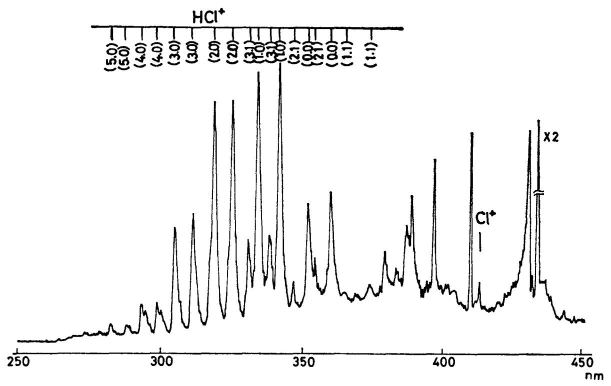

Fig. 6. Emission spectrum of chlorobenzene by electron impact. Impact voltage 300 V, electron beam current 300 μA.

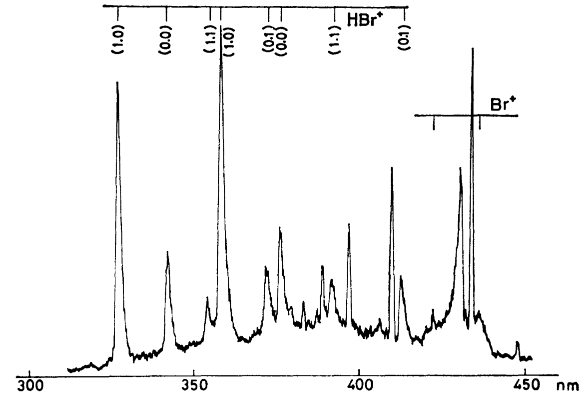

Fig. 7. Emission spectrum of bromobenzene by electron impact. Impact voltage 200 V, electron beam current 500 μA.

in Figs. 6 and 7 respectively. No appreciable bands of parent molecules could be detected in the spectra. Instead, they show strong bands of HCl^+ or HBr^+ and weak lines of Cl^+ or Br^+. Heavy atoms generally tend to reduce the fluorescence quantum yield through an spin-orbit coupling effect.[8] That is, the rate for intersystem crossing becomes large and competes effectively with the rate for fluorescence. Thus, the radiationless transition from the lowest excited singlet state to the triplet state should have a much higher probability when heavy substituents are involved. Bass and Sponer[4] tried to measure the fluorescence of fluoro- and chlorobenzenes in the vapor phase and observed no emission from the latter. The present finding that both chloro- and bromobenzenes did not show any remarkable photoemission under electron-impact excitation is consistent with the previous findings.

In addition to the spin-orbit coupling effect mentioned above, the predissociation of the carbon-halogen bond may have some effect on the disappearance of the photoemission of the parent species. The mass spectra of fluoro- and chlorobenzenes were taken in order to determine the relative probability of the cleavage of the carbon-halogen bond of the two molecules. The electron-accelerating voltage used was 80 V. In both cases, the peak of the parent cation was the strongest peak. The sum of the intensity of the phenyl cation peak and that of the halogen cation peak, which are peaks of the fragments produced by the cleavage of the carbon-halogen bond, was measured in relation to that of the parent peak. The relative intensities were 0.02 for fluorobenzene and 0.68 for chlorobenzene. Thus, it can be concluded that the carbon-chlorine bond is much weaker and more scissile by electron impact and that the predissociation of the excited chlorobenzene probably plays an important role. This is consistent with the bond energy of the carbon-halogen bond. Furthermore, this conclusion is supported by the presence of the emissions of HCl^+ and Cl^+ and by the absence of the emissions of F^+ and HF^+, as will be discussed below.

In the spectra of chloro- and bromobenzenes, pronounced doublet bands were observed in the 280—400 nm region, as is shown in Figs. 6 and 7 respectively. These bands were assigned to the HCl^+ $^2\Sigma$—$^2\Pi$ transition and the HBr^+ $^2\Sigma$—$^2\Pi$ transition respectively.[2,11–13] The bands are split by the coupling of rotation and electronic motions in the ground Π state. The vibrational assignment of the HCl^+ band was carried out by means of the following formula;[12]

$$v = \begin{Bmatrix} 28446 \\ 27788 \end{Bmatrix} + 1561p - 30.3p^2 - 2573n \qquad (\mathrm{cm}^{-1})$$

where p is the vibrational quantum number of the upper electronic state and n that of the ground state. The order of intensities of transitions among various vibrational levels is $(1, 0) > (2, 0) > (3, 0) \doteqdot (0, 0)$ for HCl^+ and $(1, 0) > (0, 0)$ for HBr^+. No emission from HBr^+ above $p=1$ was observed clearly, probably because of predissociation.[14] On the other hand, the (0, 0) band was the strongest one in the study of the electric discharge.[11] Haugh measured the emission of HCl^+ in the collision of He^+ with HCl and found that the (0, 0) and (0, 1) transitions were by far stronger than any other transition.[15] The vibrational populations of the excited state of HCl^+ were also studied in the collision of $He^*(2^3S_1)$ with HCl, and the vibrational ground state of the upper electronic state of HCl^+ was found to be markedly populated.[16] Although the large difference in the internuclear lengths of the ground state (1.32 Å) and of the excited state (1.52 Å)[17] favors the present result as the calculated Franck-Condon factors[16] show, it is noteworthy that the relative intensity of the vibrational component of $HCl^+(^2\Sigma)$ varies with the method of excitation. Lines of Cl^+ and Br^+ were

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[11] R. W. B. Pearse and A. G. Gaydon "The Identification of Molecular Spectra," Chapman and Hall, London (1965).

[12] B. A. Brice and F. A. Jenkins, *Nature*, **123**, 944 (1929).

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[16] W. C. Richardson, D. W. Setser, D. L. Albritton, and A. L. Schmeltckopf, *Chem. Phys. Lett.*, **12**, 349 (1971).

[17] G. Herzberg, "Spectra of Diatomic Molecules" D. Van. Nostrand, Princeton, N. J. (1950), p. 534,

also observed in the 400—600 nm region, as is shown in part in Figs. 6 and 7. Neither HF^+ nor F^+ was observed in the spectrum of fluorobenzene. This is probably because the carbon-fluorine bond is stable against electron impact.

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