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Emission Spectra of Dimethoxybenzenes by Controlled Electron Impact

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The emission spectra of *o*-, *m*-, and *p*-dimethoxybenzenes under controlled electron impact excitation (200 eV) were measured in the 220—450 nm region at very low pressures. The photoemissions of the excited parent species and such fragment species as H, CH, CO, and CO$^+$ were observed and assigned. The relative intensities of the photoemissions of the parent species were compared with those of the fluorescence spectra (photoexcitation) in an *n*-hexane solution. The excited parent species, H, and CH were concluded to be produced in one-electron processes; however, the CO$^+$ species were assumed to be produced in both one- and two-electron processes, and the relative contributions are evaluated. It was concluded that the rate of the predissociation of *o*-dimethoxybenzene was faster than those of the other two isomers, and the observed characteristics of *o*-dimethoxybenzene had something to do with this faster rate.

Research on molecular excited states has recently been carried out by many investigators, mostly by the photoexcitation method. Among various methods for excitation, the controlled electron impact method has two advantages; (1) the photoemission of excited species can be obtained at very low pressures, where the effect of molecular collision is greatly reduced, and (2) the energy of incident electrons can be controlled externally and continuously from the X-ray energy region (1000 eV) down to the ultraviolet energy region (several eV). Thus, the investigation of emission spectra by this method will be fruitful for the study of the mechanism of the excitation and fragmentation of various molecules.

The emission spectra of various aliphatic[1—3] and aromatic[4—10] molecules produced by this method have been reported, and the mechanism of excitation has been discussed in relation to the intensity measurements. However, no kinetic treatment on the species which may not be produced primarily has ever been carried out. In the present report, the emission spectra of *o*-, *m*-, and *p*-dimethoxybenzenes will be described and the mechanism of their excitation and fragmentation, including species produced secondarily, will be discussed.

Experimental

The electron-impact apparatus is essentially identical with that described in a previous paper.[8] The sample vapor was crossed so as to collide with an electron beam *in vacuo* and the photoemission was observed photoelectrically with a Jarrel-Ash JE 25 monochromator. The slit width used was 100 μ, corresponding to a bandpass of 3.3 Å. The intensity was measured by the peak height of the band at each specified wavelength, where there was negligible overlap with other features.

The dimethoxybenzenes used were obtained from Wako Pure Chemical Ind. They were degassed *in vacuo* a few times just before use.

The relative intensities of the fluorescence were measured with a Hitachi 204 fluorescence spectrophotometer. The solvent, *n*-hexane, was of a non-fluorescent grade (Luminasol) of the Dojindo Co.

Results

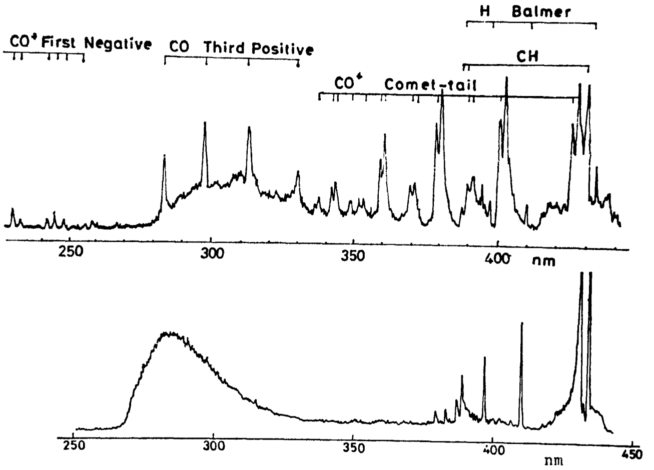

Fig. 1. Emission spectra by controlled electron impact.
Top; *o*-dimethoxybenzene, electron energy 200 eV, electron-beam current 0.7 mA.
Bottom; *o*-xylene, electron energy 300 eV, electron-beam current 1 mA.

Typical emission spectra of *o*-xylene and *o*-dimethoxybenzene in the region of 250—450 nm under electron impact excitation are shown in Fig. 1, where the impact voltage is 300 V and the electron-beam current is 1 mA for *o*-xylene and 200 V and 0.7 mA for *o*-dimethoxybenzene. The characteristic band in the 280—340 nm region of the latter, which overlapped with several sharp bands, was assigned to the electronic transition from the lowest excited singlet state to the ground state of the parent molecule, as in the case of the emission spectra of *o*-xylene,[6] methoxybenzene,[5] and other aromatic molecules,[7—9] since the location of the band was identical to the fluorescence spectra in the n-hexane solution. Many sharp bands in these spectra were assigned to the fragment species. The lines at 434, 410, and 397 nm in both spectra were assigned to the hydrogen Balmer series, and the bands at 431 and 389 nm, to CH ($A^2\Delta$—$X^2\Pi$) and CH ($B^2\Sigma^-$—$X^2\Pi$) respectively. The other bands in the spectrum of *o*-dimethoxybenzene were assigned to the bands of CO and of CO$^+$, as in the case of methoxybenzene;[5] the bands in the 230—260 nm region, to the first negative system of CO$^+$ ($B^2\Sigma^+$—$X^2\Sigma^+$), the sharp bands in the 280—330 nm region, to the third positive system of CO ($b^3\Sigma^+$—$a^3\Pi$), and the doublet bands above 336 nm, to the comet-tail

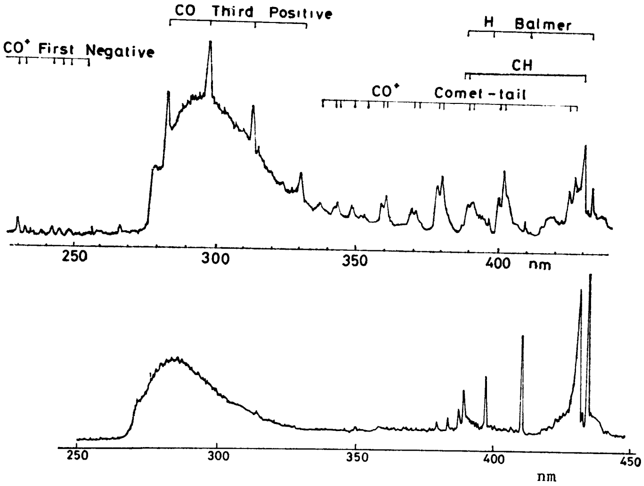

Fig. 2. Emission spectra by controlled electron impact.
Top; *m*-dimethoxybenzene, electron energy 200 eV, electron-beam current 1 mA.
Bottom; *m*-xylene, electron energy 300 eV, electron-beam current 0.5 mA.

system of CO^+ ($\mathrm{A}^2\pi\Pi-\mathrm{X}^2\Sigma^+$).

Typical emission spectra of *m*-xylene and *m*-dimethoxybenzene under controlled electron impact excitation are shown in Fig. 2. The band of the A—X transition of *m*-dimethoxybenzene was shifted to wavelengths shorter by several nanometers from that of *o*-dimethoxybenzene, and it is more intense than the latter. Those of *p*-xylene and *p*-dimethoxybenzene are shown in Fig. 3. The band of the A—X transition of *p*-dimethoxybenzene is shifted to wavelengths longer by about 15 nm from that of *o*-dimethoxybenzene, and it is the most intense among the three isomers.

The intensities of the photoemissions of these molecules were determined for various amounts of incident electrons. The dependence of the emission intensities of the parent molecules of *o*-, *m*-, and *p*-dimethoxybenzenes, and those of H and CH from *m*-dimethoxybenzene, on the electron-beam current are shown in Fig. 4. In all cases, the relative intensity is proportional to the electron-beam current, and an identical relation was obtained for H and CH from the other isomers. The dependence of the emission intensity on the gas pressure was difficult to determine accurately because of the low vapor pressure of dimethoxybenzenes; however, the intensity of the band of *m*-dimethoxybenzene seemed to be proportional to the pressure.

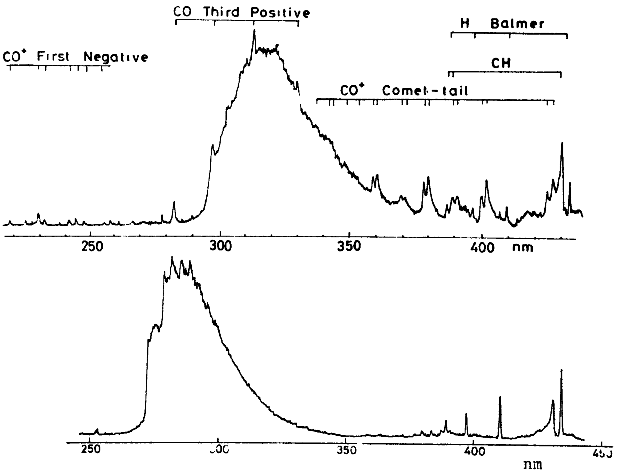

Fig. 3. Emission spectra by controlled electron impact.
Top; *p*-dimethoxybenzene, electron energy 200 eV, electron-beam current 1 mA.
Bottom; *p*-xylene, electron energy 200 eV, electron-beam current 1 mA,

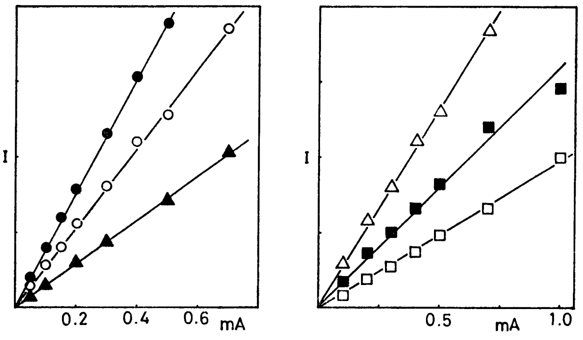

Fig. 4. Dependence of photoemission intensity (I, arbitrary units) on the electron-beam current (mA).
Left; Emission of dimethoxybenzenes at 200 eV.
▲ *ortho*(303 nm), ○ *meta*(294 nm), ● *para*(316 nm).
Right; Emission of fragment species from *m*-dimethoxybenzene at 200 eV.
△ parent (294 nm), ■ H(410 nm), □ CH(431 nm).

Contrary to these results, the dependence of the emission intensities of the comet-tail bands of CO^+ from dimethoxybenzenes on the electron-beam current failed to show any proportionality. The results are shown in Fig. 5, together with that of CO^+ from CO. A considerable deviation from the linear relationship was observed for CO^+ ($\mathrm{A}^2\Pi$) from *m*-dimethoxybenzene, as in the case of CO^+ ($\mathrm{A}^2\Pi$) from nitrobenzene;9) however, the emission of CO^+ ($\mathrm{A}^2\Pi$) from CO showed a linear relationship as in the case of CO^+ ($\mathrm{A}^2\Pi$) from methanol.2) Quantitative measurements were difficult for $\mathrm{CO}^+(\mathrm{B}^2\Sigma^+)$ and for CO

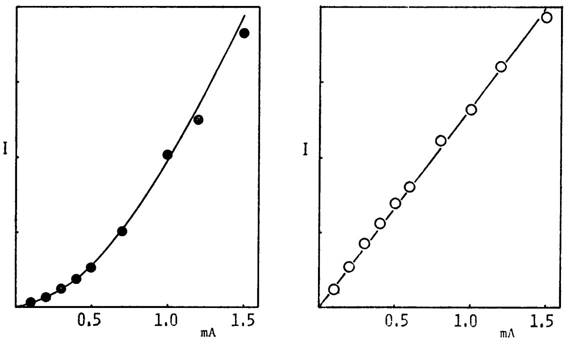

Fig. 5. Dependence of photoemission intensity (*I*, arbitrary units) on the electron-beam current (mA). 200 eV impact.
Left; CO^+ ($\mathrm{A}^2\Pi$) from *m*-dimethoxybenzene (402 nm).
Right; CO^+ ($\mathrm{A}^2\Pi$) from CO (402 nm).

($b^3\Sigma^+$) because of the weak intensity and the band overlap.

Discussion

The three isomers of dimethoxybenzenes give equally the emission spectra of the parent species and of such fragment species as H, CH, CO, and CO^+. While the spectrum of *p*-xylene shows some distinct vibrational structures, no clear structures are observed in the spectra of dimethoxybenzenes. Since the symmetry of the molecule is approximately D_{2h} for *p*-xylene, but lower for *p*-dimethoxybenzene because of the oxygen atoms in the methoxy groups, the spectrum of the latter becomes more diffuse as a result of the increase in the vibrational levels, which interact with the electronic level.

The relative intensities of the A—X transitions of three dimethoxybenzenes to those of the bands of CO^+ differ from each other, as are shown in Figs. 1, 2, and 3; *o*-dimethoxybenzene gives the weakest intensity for the bands of the parent species and the strongest intensity for those of CO^+, while *p*-dimethoxybenzene gives the opposite.

Table 1. Relative emission intensities of the parent species from xylenes and dimethoxybenzenes

isomers		*o*-	*m*-	*p*-
Xylene	photo-excitation FM[a]	1.3	1.0	1.7
	photo-excitation B[b]	1.1	1.0	2.4
	electron impact[c]	1.2	1.0	2.6
Dimethoxybenzene	photo-excitation[d]	1.4	1.0	2.8
	electron impact[c]	0.4	1.0	3.2

a) P. M. Froehlich and H. A. Morrison, *J. Phys. Chem.*, **76**, 3566 (1972). b) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules" 2nd Ed. Academic Press. New York (1971). c) Measured at 200 V and 0.1 mA. d) Measured in *n*-hexane solution (7×10^{-6} mol/l).

The relative emission intensities of the parent species from the three isomers of xylenes and of dimethoxybenzenes are shown in Table 1, both for the cases of electron impact excitation (the energy of the electrons was 300 eV; however, the energy which the molecules receive is expected to be around 5—30 eV) and for those of photoexcitation (5.59 eV) in an n-hexane solution. In the case of xylenes, *p*-xylene has a stronger emission band than do *o*- and *m*-xylenes for both methods of excitation. It is noteworthy that there is no notable difference between the results of electron impact excitation and that of photoexcitation, even though the energies in the former method are considerably higher. However, in the case of dimethoxybenzenes, though the relative intensity under photoexcitation is similar to the case of xylenes, the intensity of the photoemission from *o*-dimethoxybenzene by electron impact is remarkably weaker than that of other isomers.

The weak intensity of the band of *o*-dimethoxybenzene under electron impact excitation is probably related to the faster predissociation of the parent molecule from highly excited states. The observation of a more intense photoemission of the fragments from *o*-dimethoxybenzene seems to support this conclusion. Since the sum of the bond-scission energy, the ionization energy (14 eV),[11] and the excitation energy (2.5 eV) of CO^+ ($A^2\Pi$) is larger than the ionization potential of dimethoxybenzenes (7—8 eV),[11] the processes of the production and excitation of CO^+ ($A^2\Pi$) probably involve superexcited species.[12] Identical conclusion can be drawn for H and CH on the basis of similar considerations.[7–9]

The intensities of the photoemission of the parent species, H, and CH were found to be proportional to the electron-beam current, as are shown in Fig. 4. Thus, the mechanism of the production of these excited species was concluded to be one-electron processes for all isomers. However, some secondary process should be involved in the production of CO^+ ($A^2\Pi$) from dimethoxybenzenes, since the linear relation was not established, as is shown in Fig. 5. Ajello did not observe the comet-tail bands of CO^+ in the dissociative excitation of CO_2 by electron impact.[13] In the present study, however, distinct comet-tail bands were observed, and so the mechanism of CO^+ ($A^2\Pi$) production from dimethoxybenzene should be different from that from CO_2.

In the emission spectra by controlled electron impact, the band intensities of photoemission of most of the species have been found to be proportional to the electron-beam current. Two kinds of exceptions have been found; (1) species which have at least two heavy (non-hydrogen) atoms and which are produced through the scission of at least two skeletal bonds (*e.g.*, CN from aniline[9]), (2) species which have to form a new chemical bond on formation (*e.g.*, HCl^+ from chlorobenzene[7]). CO^+ ($A^2\Pi$) from dimethoxybenzene seems to belong to the first group of exceptions; its kinetic behavior was examined in the present study.

Since the emission of CO^+ ($A^2\Pi$) from CO shows a linear relationship (Fig. 5), the non-linear relationship of the photoemission of CO^+ from dimethoxybenzenes is essential to the mechanism of its production from dimethoxybenzenes. This intensity dependence of CO^+ on the electron-beam current can be interpreted by use of the following reaction scheme:

$$\mathrm{M} + \mathrm{e} \xrightarrow{k_1} \mathrm{CO}^{+*} + 2\mathrm{e} \tag{1}$$

$$\mathrm{M} + \mathrm{e} \xrightarrow{k_2} \mathrm{X} + \mathrm{e} \tag{2}$$

$$\mathrm{X} + \mathrm{e} \xrightarrow{k_3} \mathrm{CO}^{+*} + 2\mathrm{e} \tag{3}$$

$$\mathrm{CO}^{+*} \xrightarrow{k_4} \mathrm{CO}^{+} + h\nu \tag{4}$$

where M, e, and X stand for dimethoxybenzene, an electron, and some intermediate species respectively. X may be neutral or ionic; however, X is not such a species as CO_2, as has been mentioned before.

The rate of the appearance of X will be:

$$\frac{\mathrm{d(X)}}{\mathrm{d}t} = k_2(\mathrm{M})(\mathrm{e}) - k_3(\mathrm{X})(\mathrm{e}) \tag{5}$$

The second term is assumed to be small and is neglected, since the concentration of X is smaller than that of M by a few orders of magnitude and since k_3 is not expected to be larger than k_2 by such a magnitude. Then, most of the X produced is removed in the process of evacuation, and the concentration of X is proportional to (M) (e):

$$(\mathrm{X}) = k_2'(\mathrm{M})(\mathrm{e}) \tag{6}$$

CO^{+*} is produced in Processes (1) and (3) and disappears in the Process (4).

$$\frac{\mathrm{d}(\mathrm{CO}^{+*})}{\mathrm{d}t} = k_1(\mathrm{M})(\mathrm{e}) + k_3(\mathrm{X})(\mathrm{e}) - k_4(\mathrm{CO}^{+*}) \tag{7}$$

The radiative lifetime of CO^{+*} was measured as 2.1—2.9 μs,[14] considerably smaller than the inverval in which the X species remains in the collision region. Thus, the concentration of CO^{+*} can be set as stationary and Equation (7) is equal to 0.

Then,

$$(\mathrm{CO}^{+*}) = \frac{k_1(\mathrm{M})(\mathrm{e})}{k_4} + \frac{k_3(\mathrm{X})(\mathrm{e})}{k_4} = \frac{k_1(\mathrm{M})(\mathrm{e})}{k_4} + \frac{k_2'k_3(\mathrm{M})(\mathrm{e})^2}{k_4} \tag{8}$$

The intensity (I) of the photoemission of CO^+ ($A^2\Pi$) is proportional to its concentration:

$$I = ak_4(\mathrm{CO}^{+*}) \tag{9}$$

where a is a constant. From Eqs. (8) and (9) we obtain:

$$I/\mathrm{e} = ak_1(\mathrm{M})(1+(k_2'k_3/k_1)(\mathrm{e})) \tag{10}$$

The dependence of I/e on e for the bands of CO^+ ($A^2\Pi$) from *m*-dimethoxybenzene is plotted in Fig. 6. The data reasonably fit a straight line, and so it can be presumed that two-electron dissociative excitation processes, such as (2) and (3), are involved in the production of CO^+ ($A^2\Pi$). From the slopes of the lines, the ratios of CO^+ ($A^2\Pi$) production in the two-electron excitation process to that in the one-electron excitation process, $k_2'k_3/k_1$, are determined to be 1, 5, and 4 for *o*-, *m*-, and *p*-dimethoxybenzenes respectively. Thus, the one-electron process is the most important for *o*-dimethoxybenzene, which has the weakest parent band and the strongest CO^+ bands.

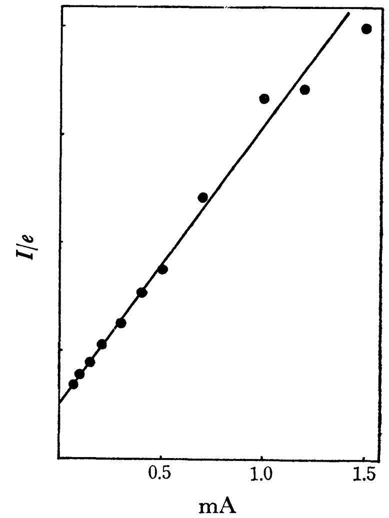

Fig. 6. Dependence of I/e (arbitrary units) on e (mA) for *m*-dimethoxybenzene at 200 eV.

It may be concluded that the intra-molecular interaction of two adjacent methoxy groups makes the molecule unstable in the highly excited states and that the rate of Process (1) (predissociation) for *o*-dimethoxybenzene becomes much faster than those of other isomers. This faster rate of Process (1) in *o*-dimethoxybenzene is concluded to be responsible for the smaller $k_2'k_3/k_1$ ratio; this interaction and the resulting instability of highly excited states probably have something to do with the weaker intensity of the photoemission of the parent species (Table 1). The evaluation of the contribution of the highly excited states on the photoemission by the cascading process in such large molecules has scarcely been studied; a recent investigation of naphthalene has, however, shown the importance of cascading processes.[10]

Although the investigation of CO^+ ($B^2\Sigma^+$) and CO ($b^3\Sigma^+$) as described here will be useful in clarifying the mechanism of the fragmentation of dimethoxybenzene, the research will be left for future study, because of the difficulties involved in the intensity measurements of these species.

The results presented above indicate the usefulness of the controlled electron impact method for the study of the excited states and their reactions.

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