Emission Spectra of Phenol, Anisole, and Phenetole by Controlled Electron Impact

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Upon the impact of an electron beam (100—450 eV) on PhOH, $PhOCH_3$, $PhOC_2H_5$, $PhCOCH_3$, and $(Ph)_2CO$ at low pressures, the S_1 emission of the parent molecule (not from $PhCOCH_3$ and $(Ph)_2CO$) and the photoemissions from such fragments as H, CH, CO, CO^+, and OH were observed in the 200—520 nm region. It was concluded that the S_1 emission of the parent molecule originates through both the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ (cascade) $\rightarrow S_1$ excitation processes and that the direct excitation into the lower vibronic levels of S_1 is responsible for the appearance of the vibrational structures. Most excited species including $CO^+(A)$ from PhOH were confirmed to be primarily produced; however, $CO^+(A)$ from $PhOCH_3$, $PhOC_2H_5$, and $PhCOCH_3$, and CO(b) from $PhCOCH_3$ were found to be produced competitively through one-electron and two-electron excitation processes in relation to the intensity measurements. The relative contribution of the two-electron excitation process in producing $CO^+(A)$ increased with a larger substituent, and it was larger than that for CO(b) in $PhCOCH_3$.

The spectroscopic analysis of the optical emission resulting from the collision of an electron with molecules at a low pressure provides direct information about the energy states not only of ionic products, which have been well investigated by mass spectrometry, but also of radical and neutral ones. In the previous papers,[1-7] we have reported the emission spectra of various aromatic molecules in the ultraviolet and visible regions as studied by means of the crossed electron-beam and molecular-jet method. Many aromatic molecules showed the characteristic S_1 emission of the parent molecule, and in the case of naphthalene[5] the cascading processes from S_2 and S_3 to S_1 were concluded to be mainly responsible for the S_1 emission. Photoemissions from several excited fragments were also observed; most of them were confirmed to be primarily produced in relation to their intensity measurements. The formation of $CO^+(A)$ from three isomers of dimethoxybenzenes[6] was an exceptional case, which involves a secondary reaction, and the results were interpreted in terms of the competition between the one-electron and the two-electron excitation processes. However, no studies have been carried out on the emission spectra and the mechanism of the dissociative excitation of monosubstituted benzene with an oxygen atom, except for our previous communications on anisole[1] and nitrobenzene.[4] In this paper, we will describe the emission spectra of phenol, anisole, phenetole, acetophenone, and benzophenone under a controlled electron-impact excitation (100—450 eV) and will discuss the mechanism of the S_1 emission of the parent molecule and that of the formation of the excited species.

Experimental

The apparatus and the experimental conditions were essentially identical with those described previously.[3] The electron-beam current in the collision chamber ranged between 10 and 3000 μA for electron energies from 100 to 450 eV. The pressure of the sample gases in the collision chamber, which was proportional to that in the gas reservoir, was estimated to be of the order of 10^{-3} Torr.

The photoemission in the 200—520 nm region was detected by the use of a JASCO CT-50 scanning spectrometer in the first order of a 1200 grooves/mm grating blazed at 300 nm. The spectra were recorded at a resolution of about 4 Å (FWHM). An EMI 9558QB photomultiplier and a Burr-Brown 3421K OP amplifier were used for recording the spectra. The current and pressure dependences of the emission intensities were measured with the aid of a HTV R585 photomultiplier, and the output pulses from the photomultiplier were amplified and counted by means of an NF-PC 545A photon counter. The absence of changes in the observed spectra when a suppressor electrode was put just above the electron target or when an aluminum target was replaced by a golden one reinforced the conclusion that the excitation by secondary electrons ejected from the target was negligible.

The reagents were obtained either from the Wako Pure Chemical Co. or from Kishida Chemical Ind. They were subjected to several freeze-pump-thaw cycles to remove dissolved atmospheric gases.

Results

A typical emission spectrum of phenol excited by an electron beam of 300 eV at 2 mA is shown in Fig. 1. The continuous features with discrete structures in the 275—340 nm region were assigned to the $S_1(^1B_1) \rightarrow S_0(^1A_1)$ transition of the parent molecule. No appreciable alteration in the shape or position of the S_1 emission was found by changing the excitation energies between 100 and 450 eV. Prakash[8] measured photographically the fluorescence spectrum of phenol at the vapor phase excited by the radiation from a condensed iron spark and analyzed the observed S_1 emission in the 275—303 nm region. He found the 0-0 band at 2751 Å; this band was very weak because of the self-absorption by the unexcited molecules. In the present spectrum, taken under a very low pressure, where such a self-absorption effect and collisional deactivation within the lifetime of the excited species are expected to be negligible, the 0-0 band appears intensively at the shortest wavelength. Although our spectrum is less resolved, several features at the shorter wavelengths can be interpreted as an overlapping of some fluorescence bands given by Prakash.

Since energetic electrons bring about not only the excitation but also the dissociation of target molecules, photoemissions from the excited fragments can be ob-

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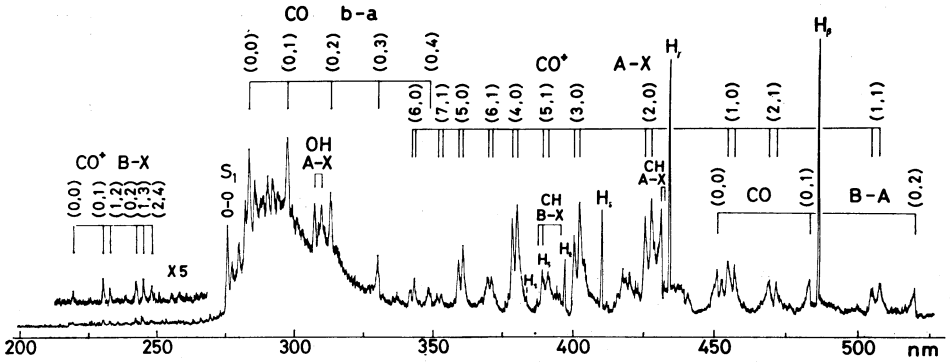

Fig. 1. Emission spectrum of phenol by controlled electron impact. Electron energy 300 eV, electron-beam current 2 mA.

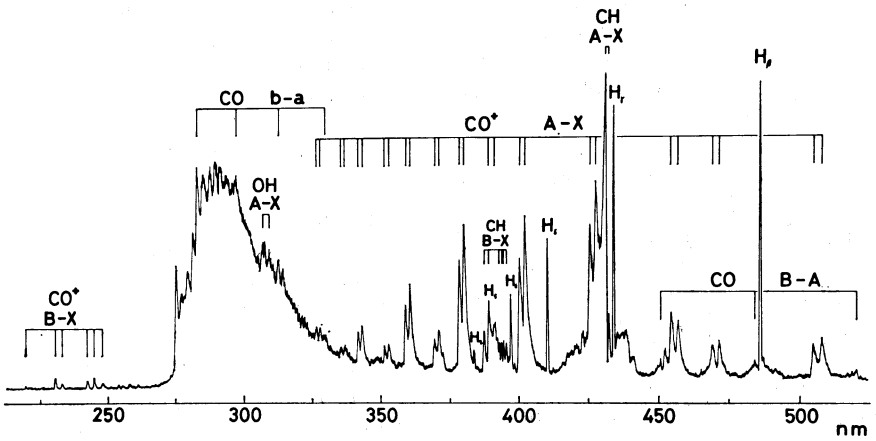

Fig. 2. Emission spectrum of anisole by controlled electron impact. Electron energy 300 eV, electron-beam current 1 mA.

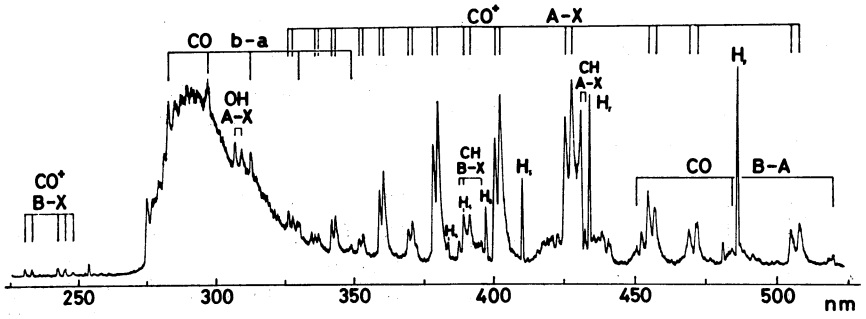

Fig. 3. Emission spectrum of phenetole by controlled electron impact. Electron energy 300 eV, electron-beam current 1 mA.

served. The Balmer series of the hydrogen atom ($H_{\beta-\eta}$) and the two systems of CH, the 4300 Å system ($A^2\Delta$-$X^2\Pi$) and the 3900 Å system ($B^2\Sigma^-$-$X^2\Pi$), were identified in the 384—486 nm region. The features around 306 nm and the bands at 283, 298, 313, and 331 nm, superimposed upon the intense S_1 emission of the parent molecule, were assigned to the 3064 Å system of OH ($A^2\Sigma^+$-$X^2\Pi$) and the third positive system of CO ($b^3\Sigma^+$-$a^3\Pi$). The bands at 451, 484, and 520 nm were assigned to the Ångström system of CO ($B^1\Sigma^+$-$A^1\Pi$). The numerous other bands were ascribed to the comet tail system ($A^2\Pi$-$X^2\Sigma^+$) and the first negative system ($B^2\Sigma^+$-$X^2\Sigma^+$) of CO^+.

Figures 2 and 3 show the emission spectra of anisole and phenetole excited by an electron beam of 300 eV at 1 mA. The S_1 emission of the parent molecule, the shape and position of which were independent of the excitation energy (100—450 eV), can be observed at the identical wavelength region in the case of phenol, and the 0-0 band is found at 275 nm in both spectra. Their vibrational structures are very similar to those of phenol, although the fraction of the unresolved continuum becomes larger with an enlargement of the substituent. Several features of anisole at the shorter wavelengths can be interpreted as an overlapping of some fluorescence bands measured and assigned by Prakash and Singh in the vapor phase.[9] The S_1 emission of phenol, anisole, and phenetole are more diffuse than the spectrum of benzene,[3] while they are sharper than the spectrum of naphthalene.[5] Photoemissions from

the same atomic and diatomic fragments can be identified in both spectra.

The striking optical features of benzene monoderivatives with a carbonyl group are the appearance of strong phosphorescence instead of fluorescence in the solution and in the low-temperature matrix.[10] In the electron-impact excitation of acetophenone and benzophenone at low pressures, no photoemission from the excited parent molecule could be observed, just as in the case of the optical excitation; all the observed bands were attributed to the photoemissions from the excited fragment species: H, CH, CO, and CO^+. Both spectra were similar to the emission spectrum of nitrobenzene,[4] except for the absence of the band systems of NO and CN.

The current and pressure dependences of the photoemission intensities of the parent molecule and the fragment species were measured in order to elucidate the reaction mechanism. Figure 4 shows such intensity measurements on anisole. The band intensities of the parent molecule, H, and CH are proportional both to the electron-beam current and to the gas pressure, just as in the cases of other aromatic molecules.[2-7] However, the band intensity of CO^+(A) varies non-linearly with the electron-beam current, although it is proportional to the gas pressure. The pressure dependence of the intensity of CO^+(A) from CO[11] and CH_3OH[7] has been found to be linear at a low pressure, and a similar linear relationship has been presumed on $PhNO_2$[4] and $Ph(OCH_3)_2$.[6] The present observation of the linearity in anisole indicates the validity of the previous assumption.

The photoemission intensities of the parent molecule, H, and CH produced from phenol, phenetole, and acetophenone, and that of OH from phenol were also proportional to the electron-beam current. However, their pressure dependence could not be measured in the present study because of the low vapor pressures of these compounds. Figure 5 shows the dependence

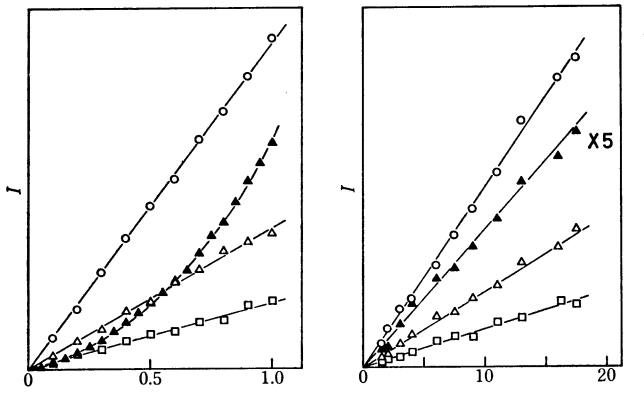

Fig. 4. Dependence of band intensities (I, arbitrary units) from anisole on the electron-beam current (mA) and on the pressure in the gas reservoir (mmHg). Electron energy 300 eV, electron-beam current in the measurement of the pressure dependence 50 μA.
○: $PhOCH_3$(285 nm), △: CH(431 nm), □: H_δ, ▲: CO^+(402 nm).

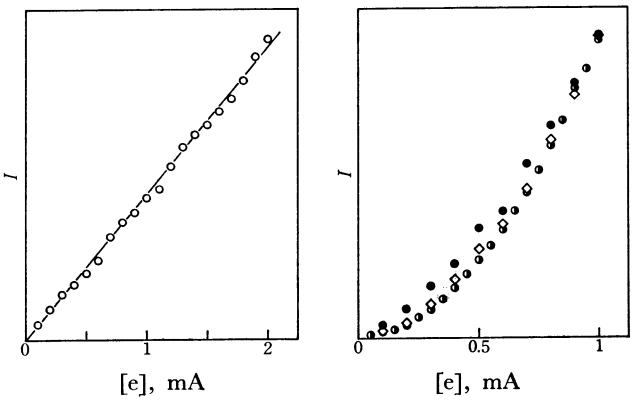

Fig. 5. Dependence of photoemission intensities (I, arbitrary unit) on the electron-beam current [e]. Electron energy 300 eV.
Left; ○: CO^+(A) from phenol (402 nm).
Right; ●: CO(b) from acetophenone (298 nm), ◇: CO^+(A) from acetophenone (402 nm), ◑: CO^+(A) from phenetole (380 nm).

of the photoemission intensity of CO^+(A) from phenol and phenetole, and that of CO(b) and CO^+(A) from acetophenone, where the intensities in the right figure are normalized at the value of 1 mA. A significant deviation from the linearity is observed in the intensity of CO^+(A) from phenetole, and that of CO(b) and CO^+(A) from acetophenone, while a linear relationship is established in the intensity of CO^+(A) from phenol.

The non-linearity of the photoemission intensity (I) may be interpreted by considering the quadratic term with respect to the electron-beam current [e]:

$$I = K_1[e] + K_2[e]^2, \quad (1)$$

where K_1 and K_2 are constant. It is convenient to divide this equation by the electron-beam current and to plot $I/[e]$ as a function of [e]:

$$I/[e] = K_1 + K_2[e]. \quad (2)$$

The current dependence of the emission intensities of CO^+(A) and CO(b) described in this form is given in Figs. 6 and 7. The reasonable fit to a straight line in all cases indicates the validity of this equation. The measurement of the intensity of CO(b) from the other

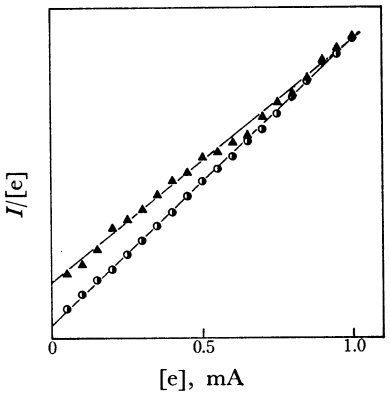

Fig. 6. Dependence of $I/[e]$ (arbitrary unit) on [e].
▲: CO^+(A) from anisole, ◑: CO^+(A) from phenetole.

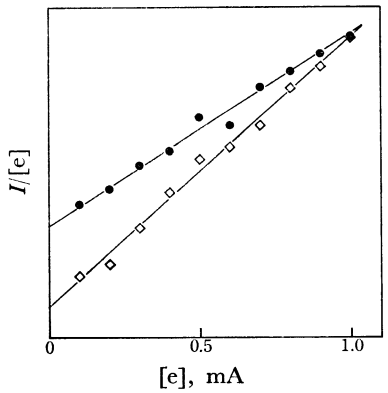

Fig. 7. Dependence of $I/[e]$ (arbitrary unit) on [e]. ●: CO(b) from acetophenone, ◇: CO^+(A) from acetophenone.

compounds was difficult because of the weak intensity and the band overlapping with the intense S_1 emission of the parent molecule.

Discussion

The Emission of the Parent Molecule. There is a significant difference in the excitation into the neutral states between the photon and the electron. The former pumps molecules resonantly into one or a few specific vibronic levels; on the other hand, the latter excites them simultaneously into all the vibronic levels below the electron energy. Therefore, phenol, anisole, and phenetole are expected to be primarily excited into any of the S_1, S_2, and higher singlet states under the impact of fast electrons. However, photoemission can be observed almost exclusively from the S_1 state; this indicates that the radiationless transition occurs with a high efficiency at higher excited singlet states under a very low pressure.

The probability of excitation by fast electrons into an upper state, s, with an energy, E_s, is known to be proportional to $M_s^2=f_sR/E_s$ in the case of an optically allowed transition according to the Bethe theory,[12-14] where f stands for the optical oscillator strength, which can be obtained from the energy-loss (absorption) spectrum, and where R is the Rydberg constant. The efficiency of the radiative transition from an excited state is given by the fluorescence quantum yield Φ, which can be measured in an optical excitation. Hence, the relative contribution of the S_1 emission from the various primary excitation processes can be estimated by the product, $\Phi_s(S_1)M_s^2$. Although the energy-loss spectra of phenol, anisole, and phenetole have not been reported, it is justifiable to use the oscillator strengths obtained by the ultraviolet absorption spectra, because the oscillator strengths obtained through the two methods agreed well with each other.[15] Kimura and Nagakura[16] measured the f values of these molecules in the vapor phase and found them to be 0.020—0.028 for $S_0\rightarrow S_1$ (E_1=4.59 eV), 0.132—0.188 for $S_0\rightarrow S_2$ (E_2=5.75—5.82 eV), and 0.529—0.636 for $S_0\rightarrow S_3$ (E_3=6.60—6.70 eV). These values show that the $S_0\rightarrow S_2$ and $S_0\rightarrow S_3$ excitation is 5—6 and 13—22 times stronger than the $S_0\rightarrow S_1$ excitation. The quantum yield of the S_1 emission as a function of the excitation energy has, to our knowledge, been measured only on phenol in dilute solutions in the 280—200 nm region;[17] the quantum yield in a nonpolar solvent is almost constant within the first absorption band ($\Phi_1(S_1)=7.5\times10^{-2}$) and within the second one ($\Phi_2(S_1)=3.0\times10^{-2}$). The non-zero value of the quantum yield in the S_2 region shows the existence of some contribution of the S_1 emission, followed by a fast internal conversion from S_2 to S_1. Assuming that the value of the quantum yield in a dilute solution can be carried over to that in the low-pressure vapor, the relative contribution of the S_1 emission from the two excited states is obtained as follows: $\Phi_1(S_1)M_1^2$: $\Phi_2(S_1)M_2^2$ = 1.0 : 2.1. This result indicates that the contribution of the S_1 emission through the $S_0\rightarrow S_2$ excitation, followed by the fast internal conversion from S_2 to S_1, is larger than that through the direct $S_0\rightarrow S_1$ excitation. The routes of the S_1 emission of anisole and phenetole are probably similar to that of phenol.

From the investigations of the resonance fluorescence of aromatic molecules, the S_1 emission has been established to become increasingly diffuse as the molecules are excited into the higher vibronic levels.[18] For instance, no vibrational fine structure could be observed when toluene was excited into the higher vibronic levels at 1189 cm^{-1} above the 0-0 level of the $S_0\rightarrow S_1$ transition.[19] The present S_1 emissions of phenol, anisole, and phenetole exhibit some vibrational structures on a broad continuum, and it is reasonable to consider that the vibrational structure and the continuum come from different origins; the direct excitation into the lower vibrational levels of the S_1 state is responsible for the vibrational structure and the excitation into the higher levels for the continuum photoemission. The density of the vibrational levels increases with a larger substituent; therefore, the fraction of the broad continuum increases in the order of phenol, anisole, and phenetole.

It has been found that the predominant process of the S_1 emission of benzene[20-22] contrasts with that of naphthalene.[5,23] The former emission exhibits a sharp vibrational structure[3] and arises mostly from the lower vibrational levels of the S_1 state. The latter emission is very broad, shifts to the red in comparison with the resonance fluorescence obtained at low excitation energies, and occurs mostly from the highly excited vibrational levels of the S_1 state populated through rapid internal conversion from the primarily excited S_2 and S_3 states. In the present study, it was concluded that the S_1 emission of phenol originates through both the $S_0\rightarrow S_1$ and $S_0\rightarrow S_2$ (cascade)$\rightarrow S_1$ excitation processes; probably this is the case for anisole and phenetole also.

The S_1 emission could not be observed from acetophenone and benzophenone. In these carbonyl compounds, the lowest excited singlet state is of the n,π^* type, and a rapid intersystem crossing to the triplet state occurs. The quantum yields of the intersystem crossing in these molecules have been reported to be unity in benzene at room temperature.[24]

The Kinetic Study of the Reaction. In the crossed electron-beam and molecular-jet method, most emitting excited species produced from aromatic molecules have been confirmed to be primary products in terms of the

current and pressure dependences of the emission intensity.[2-7] In the present study, the intensities of the parent molecule, H, and CH from phenol, anisole, phenetole, and acetophenone have been found to be proportional to the electron-beam current. Their intensities from anisole were also found to be proportional to the gas pressure, and similar linear relationships can be expected to hold for the other molecules, because their pressures in the reaction chamber were still lower than that in the case of anisole. Therefore, it can be concluded that the formation of excited parent molecule, H, and CH from such compounds proceeds through a primary collision of an electron with a molecule.

It has been found that the current dependence of the band intensity of $CO^+(A)$ from small molecules, such as CO[6] and CH_3OH,[7] differs from that from larger aromatic molecules, such as $PhNO_2$[4] and $Ph(OCH_3)_2$;[6] the former was linearly proportional, while the latter was non-linear. The linear relationship of the band intensities of $CO^+(A)$ and OH from phenol shows that these fragments are also primary products. However, since the intensities of $CO^+(A)$ from anisole, phenetole, and acetophenone, and CO(b) from acetophenone are represented by Eq. 1, a secondary collision with another electron participates in the formation of such excited fragments.

Several similar relationships have been pointed out, and the excited species which show non-linear relationships have been classified in the following two groups:[6] (a) fragments which are produced through the scission of two skeletal bonds—*e.g.*, CN(anilines[4]) and CO^+ (dimethoxybenzenes[6]) and (b) a new chemical bond is created on its formation—*e.g.*, HCl^+(chlorobenzene[7]) and HBr^+(bromobenzene[7]). The formation of CO^+ (A) from anisole and phenetole can be classified in Group (a). It should be noticed that aromatic molecules with a large substituent containing an oxygen atom give fragments abundantly produced in the non-linear process.

For the interpretation of the empirical Eq. 1, the following reaction scheme is assumed:

$$\mathrm{M} + \mathrm{e} \xrightarrow{k_1} \mathrm{CO}^{+}{}^{*}$$
$$\mathrm{M} + \mathrm{e} \xrightarrow{k_2} \mathrm{X}$$
$$\mathrm{X} + \mathrm{e} \xrightarrow{k_3} \mathrm{CO}^{+}{}^{*}$$
$$\mathrm{X} + \mathrm{e} \xrightarrow{k_4} \mathrm{Y}$$
$$\mathrm{X} \xrightarrow{k_5} \mathrm{Z}$$
$$\mathrm{CO}^{+}{}^{*} \xrightarrow{k_6} \mathrm{CO}^{+}(\mathrm{X}) + h\nu,$$

where M and CO^+* denote a target molecule and the $A^2\Pi$ state of CO^+. X, which stands for some unidentified neutral or ionic intermediates, disappears upon another collision with an electron, producing CO^+* or other products (Y). It is also removed from the reaction zone mainly by the evacuation process, where the removed species are represented as Z.[25] The radiative lifetime of CO^+*, reported as 2.1—3.8 μs,[26] is short enough to emit radiation within the observation region. A similar reaction scheme is applicable to the formation of CO(b) from acetophenone. The observed emission intensity is proportional to $k_6[CO^+*]$:

$$I = ak_6[CO^+*], \tag{3}$$

where a is a proportionality constant. The rates of the formation of CO^+* and X are represented as follows:

$$d[CO^+*]/dt = k_1[M][e] + k_3[X][e] - k_6[CO^+*], \tag{4}$$

$$d[X]/dt = k_2[M][e] - k_3[X][e] - k_4[X][e] - k_5[X]. \tag{5}$$

Since the photoemission was observed in a flowing system at the stationary state, the steady-state conditions hold; therefore, the following equations can be derived:

$$[X] = k_2[M][e]/\{(k_3+k_4)[e]+k_5\}, \tag{6}$$

$$I = ak_1[M][e] + ak_2k_3[M][e]^2/\{(k_3+k_4)[e]+k_5\}. \tag{7}$$

If $(k_3+k_4)[e] \ll k_5$, an equation identical with the one obtained empirically, Eq. 1, is derived by substituting $ak_1[M]/k_5=K_1$ and $ak_2k_3[M]/k_5=K_2$. Therefore, we can conclude that $CO^+(A)$ and CO(b) are produced competitively through one-electron and two-electron excitation processes where most of the X is removed by the evacuation process. The relative contribution of the two-electron excitation process to the one-electron excitation process, K_2/K_1, was evaluated, by means of the slope and the intercept of the straight line, as 1.0: 2.0 : 5.2 : 0.39 for $CO^+(A)$ from anisole, acetophenone, and phenetole, and for CO(b) from acetophenone, respectively. The relative contribution of the two-electron excitation process in the formation of $CO^+(A)$ from dimethoxybenzenes has been attributed to the difference in the intra-molecular interaction of two adjacent groups.[6] In the present study, an increase in the mass of the substituent, taking phenol as a limiting case, enhances the relative rate (K_2/K_1) of the two-electron excitation process. In the competitive formation of $CO^+(A)$ and CO(b) from acetophenone, the relative rate of the two-electron excitation process for producing $CO^+(A)$ is about 5 times faster than that for producing CO(b).

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