Emission Spectra of Naphthalene Derivatives by Controlled Electron Impact

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Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 1-naphthol, 1-naphthylamine, 2-chloronaphthalene, 1-bromonaphthalene, 2-bromonaphthalene, and tetralin were excited in a very low pressure by controlled electron beam of 150—400 eV. The molecules, except those with a halogen atom, revealed an intense emission band similar to fluorescence. The band was assigned to the transition from their lowest-excited singlet state to their ground state. It was concluded that the most important process of photoemission is the excitation into a higher excited state in the primary collision and the subsequent non-radiative transfer to the lowest-excited state. The molecules showed photoemission of such excited fragments as H, CH, C_2, $C_4H_2^+$, CN, NH, OH, CO, CO^+, HCl^+, and HBr^+. A two-electron process by way of an intermediate was found to be important for the formation of such fragments as CN from naphthylamine.

The electron impact method has certain advantages for the investigation of the elementary process of molecular excitation, ionization, and dissociation. A comparatively intense photoemission can be obtained in a very low pressure and the excitation energy can be controlled easily in a wide range. The discharge method was used for this purpose; however, the use of a controlled electron beam in a low pressure has made it possible to investigate the elementary process without collision participation. The emission spectra of benzene,[1] its derivatives,[1,2] and naphthalene[3] by this method have been reported and the primary process of their excitation and dissociation has been investigated.[4]

The emission spectra of naphthalene derivatives, noteworthy for a stronger fluorescence than that of benzene derivatives, will be presented in this report. The excitation process of these molecules and the effect of a substituted group on the spectrum will be discussed in reference to the results of the benzene derivatives.

Experimental

The experimental apparatus was essentially the same as the one described previously.[1] The collision chamber was made of glass and was separated into two parts by a brass plate with a hole of 4 mm at its center. The thermal electrons were accelerated and collimated in the upper part, and introduced into the collision region (the lower part) through the hole. The sample was deaerated and introduced into the collision region through a nozzle (0.1—8 mm). When necessary, the sample manipulation line could be heated for the purpose of increasing the vapor pressure of sample. The collision chamber was continuously evacuated with two oil-diffusion pumps, the sample pressure in the collision region being estimated to be 10^{-2}—10^{-3} Torr. The sample vapor revealed photoemission upon collision with the electron beam. The photoemission was observed photoelectrically by use of a Jasco CT-50 monochromator (blazed for 300 nm). The energy of the electron beam was 150—400 eV, and the electron-beam current was 10—200 μA.

The excitation spectrum of fluorescence in a solution was recorded on a Hitachi MPF-4 fluorescence spectrophotometer. The spectral response of this instrument was calibrated down to 250 nm in references to the fluorescence of rhodamine B.

The naphthalene derivatives (Tokyo Kasei Co. and Kishida Chem. Co.) and cyclohexane, the solvent for the measurement of the excitation spectrum (luminasol, Dojindo Chem. Co.), were used.

Results

A typical spectrum of 2-methylnaphthalene is shown in Fig. 1. A diffuse band in the 315—390 nm region was assigned to the transition from the lowest-excited electronic state (S_1) to the ground electronic state (S_0), since its fluorescence spectrum was located in the same region[5] and the similar spectrum was obtained for toluene.[1] Some vibrational structures appeared on the spectrum of toluene[1] and naphthalene.[3] However, the spectrum of 2-methylnaphthalene indicated no definite structures even by measurement with a 2.5 Å resolution. The hydrogen Balmer lines and the bands of CH(A-X) and CH(B-X) were observed in the spectrum. The bands of C_2 and $C_4H_2^+$ were also observed in the longer wavelength region. The spectrum of 1-methylnaphthalene was very similar to that of 2-methylnaphthalene.

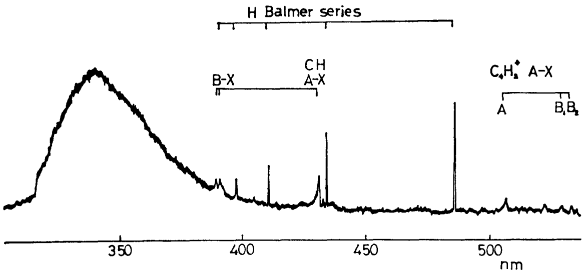

Fig. 1. Emission spectrum of 2-methylnaphthalene by controlled electron impact. Electron energy, 200 eV; electron-beam current, 30 μA.

The spectrum revealed no appreciable alteration with a change in the electron energy (150—400 eV). The intensity of the bands of the parent molecule, $H(H_\beta)$, and CH(A-X) was proportional to the electron-beam current at 200 eV excitation. This indicates that the excitation of the parent molecule and the dissociative excitation of H and CH proceed through one-electron primary processes.

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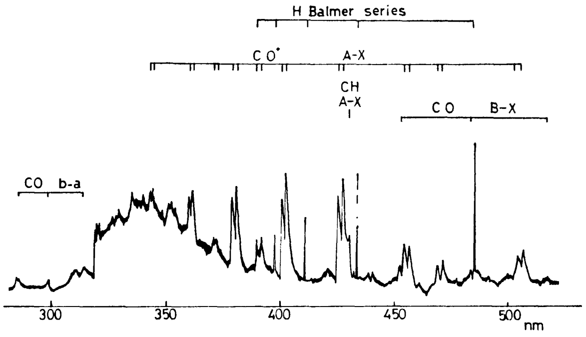

Fig. 2. Emission spectrum of 1-naphthol by controlled electron impact. Electron energy, 200 eV; electron-beam current, 80 μA.

A typical emission spectrum of 1-naphthol is shown in Fig. 2. The band of the S_1-S_0 transition of the parent molecule was diffuse, its peak being located at *ca.* 340 nm. The hydrogen Balmer lines, and the bands of CH(A-X), CO^+(A-X), CO(b-a), and CO(B-A) were also observed. The intensity of the emission of the parent molecule, H, and CH was proportional to the electron-beam current, indicating that these excited species are produced in one-electron primary processes. The intensity of the band of CO^+, however, was found to be proportional to about 1.5 powers of the electron-beam current; its formation should involve some secondary process.

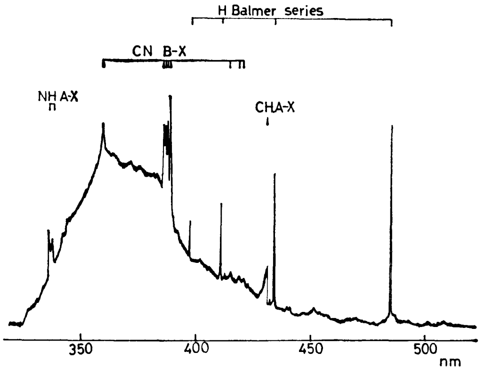

Fig. 3. Emission spectrum of 1-naphthylamine by controlled electron impact. Electron energy, 200 eV; electron-beam current, 20 μA.

A typical emission spectrum of 1-naphthylamine is shown in Fig. 3. The band of the S_1-S_0 transition of the parent molecule was diffuse, its peak being located at *ca.* 370 nm. The bands of NH(A-X), and CN(B-X) were observed in addition to those of H and CH. The intensity relationship of these bands excited at 200 eV is shown in Fig. 4. The intensity of the bands of the parent molecule, H, and CH was proportional to the electron-beam current as in the case of other molecules. However, that of CN was proportional to *ca.* 1.2 powers of the electron-beam current.

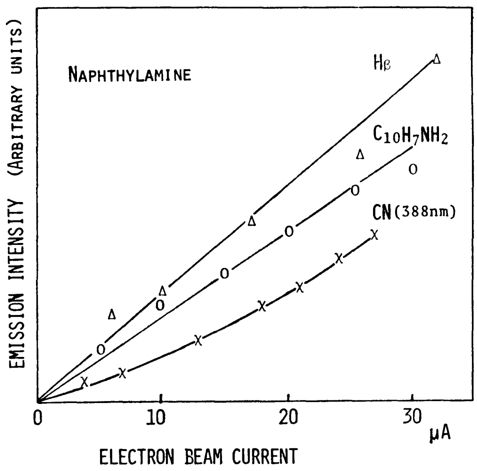

Fig. 4. Dependence of emission intensities on the electron-beam current. Electron energy, 200 eV.

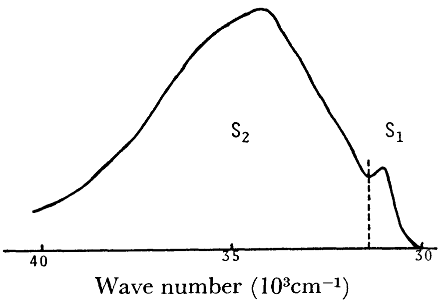

Fig. 5. Excitation spectrum of fluorescence of 1-naphthol in a cyclohexane solution. The spectral response of the spectrophotometer was corrected.

The emission spectra of 2-chloronaphthalene and 1- and 2-bromonaphthalene were similar to those of chloro- and bromo-benzene,[2] respectively. In both cases, no features identifiable as the S_1-S_0 transition of the parent molecule could be observed, partly because the intense bands of HCl^+(A-X) or HBr^+(A-X) were located in the interesting region. The emission spectrum of tetralin revealed a band in the 270—315 nm region, which could be assigned to the S_1-S_0 transition of the parent molecule, since the location and band shape were similar to those of xylene.[1]

A typical excitation spectrum of fluorescence at 338 nm of 1-naphthol is shown in Fig. 5. Its absorption maxima were reported to be at 31300 and 34100 cm^{-1} for the S_1-S_0 and S_2-S_0 transitions, respectively.[6] The band was divided into two parts in the valley at 31400 cm^{-1} and the relative intensity was determined by the band area. Identical measurements were also carried out for naphthalene and 2-methylnaphthalene and the results are shown as ϕf in Table 1.

TABLE 1. RELATIVE CONTRIBUTION OF THE TWO EXCITATION PROCESS

		ϕf	$\phi f/E$
Naphthalene	S_1	1	1
	S_2	45	40
2-Methyl-naphthalene	S_1	1	1
	S_2	34	30
1-Naphthol	S_1	1	1
	S_2	22	20

Discussion

The Spectrum. The results of emission spectra observed in the present study are summarized in Table 2. The bands are classified according to their intensity relation to the electron-beam current.

TABLE 2. EMISSION SPECTRA OF NAPHTHALENE DERIVATIVES BY CONTROLLED ELECTRON IMPACT

Compound	S_1-S_0[a)]	H	CH	$C_4H_2^+$	Others[b)]
Naphthalene	○	○	○	○	
1-Methylnaphthalene	○	○	○	▽	
2-Methylnaphthalene	○	○	○	▽	
1-Naphthylamine	○	○	▽	▽	CN ●, NH ▽
1-Naphthol	○	○	▽		CO^+●, CO▽
2-Chloronaphthalene	×	▽	▽	▽	HCl^+ ▽
1-Bromonaphthalene	×	▽	▽	▽	HBr^+ ▽
2-Bromonaphthalene	×	▽	▽	▽	HBr^+ ▽
Tetralin	○	○	○	▽	

○: Band observed; intensity proportional to the electron-beam current. ●: Band observed; intensity not proportional to the electron-beam current. ▽: Band observed; intensity not measured. × : No band observed. a) Band of the parent molecule from the lowest excited state (S_1) to the ground state (S_0). b) Bands of excited fragment species.

The bands of the S_1-S_0 transition of the naphthalene derivatives are broad, lacking remarkable structures in contrast to their fluorescence spectra in cyclohexane.[5)] Although the resonance fluorescence of naphthalene (0.05 Torr) is sharp and has many structures, it becomes broad and diffuse upon irradiation into the second excited state (S_2).[7)] Thus, the band shape of the emission spectra by electron impact is similar to that of the resonance fluorescence obtained by the S_2 excitation. This is due to the fact that the excitation into higher excited states (such as S_2) is important in the electron-beam excitation.

The location and intensity of the S_1-S_0 transition of parent molecule depend on the kind of substituted group. The bands of the methyl and hydroxyl derivatives shift a little to the longer wavelength region as compared with that of naphthalene; the band of the amino derivative shifts considerably in the same direction. Although some fluorescence band was observed for the halogen derivatives in the cyclohexane solution, its quantum efficiency was small,[5)] and no emission could be identified as their S_1-S_0 transition under electron-impact excitation. Heavy halogen atoms, such as Cl or Br, attached to an aromatic molecule are known to accelerate the rate of intersystem crossing and reduce the quantum efficiency. Furthermore, the C–X bond is susceptible to the bond scission and this can also contribute to the reduction of the emission intensity.

Excitation Process. Most fluorescent molecules, in a vapor phase or in a solution, emit fluorescence radiation mostly from the S_1 state, even when they are excited into a higher state. This is also the case with the emission spectra by controlled electron impact. Since an electron can excite a molecule into various excited states below the electron energy, it is significant to determine which excited state is actually contributing the observed photoemission.

The probability of the excitation of a molecule from the S_0 state to the S_i state is proportional to f_i/E_i, where f_i and E_i denote the oscillator strength and the transition energy of the i-th transition, respectively.[9)] The probability of photoemission from the S_i state after the non-radiative transfer from the initially prepared state (S_i) to the S_1 state is represented by the fluorescence quantum yield (ϕ_i). Thus, the intensity of photoemission (I_i), which involves the S_i state in the primary process, is[3)]

$$I_i = a\phi_i f_i/E_i, \tag{1}$$

where a is a proportionality constant.

Although the values of ϕ_i, f_i, and E_i measured in a vapor phase should be used to estimate I_i, no such spectroscopic parameters of naphthalene derivatives seem to have been reported. The fluorescence quantum yield of naphthalene was reported to be 0.23 in a cyclohexane solution[5)] and 0.4—0.8 in vapor;[8)] its f value did not show a large variation in proceeding from vapor to solution.[10)] The results indicate that the difference of the optical parameters in vapor and in a solution is not significant and the spectroscopic parameters in a cyclohexane solution may be carried over for a semi-quantitative estimation of the excitation process by use of Eq. 1.

The relative intensity of the excitation spectrum of fluorescence can be set to the relative value of $\phi_i f_i$ in this approximation. The results of $\phi_2 f_2$ relative to $\phi_1 f_1$ are shown in Table 1. The spectrum is similar to the absorption spectrum. This indicates that the quantum yield varies little in this region and the present estimation should be taken as a semi-quantitative one.

There are two excitation processes: The direct excitation process, in which the molecule is excited primarily into the S_1 state and radiates from this state directly, and the indirect excitation process, in which the molecule is excited in the S_2 state primarily, relaxes to the S_1 state non-radiatively and then emits radiation from the S_1 state. As shown in Table 1, the indirect excitation process is more important. Since naphthalene and its derivatives have large f_2 and f_3 and the rate of non-radiative transition to the S_1 state is relatively large, the indirect process gives a larger contribution to the photoemission than the direct process.[3)] This is partly due to a larger conjugate system and a smaller difference of the energies between the S_1 state and the S_2 and S_3 states than that of benzene derivatives.[11)]

The band of the S_1-S_0 transition of the parent molecules is more diffuse and structureless than that of fluorescence in a solution and shifts to the longer wavelength region. This has much to do with the excitation process. In a solution large intermolecular interaction induces a fast non-radiative transfer of the initially prepared excited state to the ground vibrational level of the S_1 state and the transition from this level reveals some vibrational structures. However, when the collisional deactivation within the lifetime of the radiative excited state is negligible, the initially prepared highly excited state transfers intramolecularly to the higher vibrational levels of the S_1 state and then the molecule emits radiation. Since high vibrational levels are involved and the naphthalene derivatives have more complicated vibrational levels than the benzene derivatives, the emission band becomes diffuse and structureless and shifts to the red as compared with that in a solution. This is consistent with the fact that the resonance fluorescence becomes broad and structureless with increase in excitation energy.⁷⁾

Dissociative Excitation. The emission spectra excited by controlled electron impact have many bands of excited fragment species as summarized in Table 2. The intensity of bands of H and CH is proportional to the electron-beam current. It can be concluded that these species are produced in one-electron primary processes as in the case of benzene derivatives.⁴⁾ The sum of the dissociation energy and the excitation energy in the formation of H* and CH* is larger than the ionization energy of the parent molecules. This may indicate that the formation of H* and CH* proceeds by way of a superexcited state.¹²⁾

The emission intensities of CO^+ from 1-naphthol and of CN* from 1-naphthylamine are not proportional to the electron-beam current as indicated in Fig. 4 and Table 2. The formation of CN* from aniline also exhibits a non-linear relationship,²⁾ but not that of CO^+ from phenol.¹¹⁾

The excited fragment species, the intensity of which was not proportional to the electron-beam current, often have two or more heavy atoms (C, N, O, *etc.*) and are also produced by breaking two or more skeletal bonds of the parent molecule.¹³⁾ The formation of such species was elucidated by the scheme in which two dissociative excitation processes contribute to an appreciable extent:¹¹,¹³⁾

$$C_{10}H_7NH_2 + e \longrightarrow CN^* \quad \text{(one-electron process)}$$
$$\left.\begin{array}{r} \searrow M \\ M + e \longrightarrow CN^* \end{array}\right\} \text{(two-electron process)}$$

where M stands for an unidentified intermediate species. Although the collision probability of a radiative species is negligible, any fragment species in the metastable or ground electronic states may be affected by collision. The relative importance of these two processses are dependent on the reactivity of the species concerned. In the formation of such species as H* and CH*, the two-electron process is of negligible importance in the region studied.

In brief, the emission spectra of naphthalene derivatives agree qualitatively with those of benzene derivatives; however, there are some quantitative differences.

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