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Nucleophilic Photoreaction of Chlorobenzene in Methanol as Studied by Emission Spectroscopy

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The photoreaction of chlorobenzene in methanol has been studied by means of emission spectroscopy. Upon irradiation with UV light, chlorobenzene reacts with methanol to form anisole with a quantum yield of 0.049 at 18 °C. Contrary to the case of chlorobenzene, the photoreaction of *p*-dichlorobenzene with methanol is not observed. By combining these results with those of our recent studies on the dual phosphorescence from low-lying triplet states of halogenated benzenes, it is suggested that the photoreaction of chlorobenzene with methanol, which is a nucleophilic substitution reaction, occurs in the $^3(\pi,\sigma^*)$ state. From the temperature dependence of the quantum yield, the activation energy for the nucleophilic photoreaction is estimated to be larger by about 3—4 kcal mol^{-1} than the apparent activation energy for a combination of the nonradiative $^3(\pi,\sigma^*)\rightarrow S_0$ process and the homolytic dissociative process concerning the C–Cl bond in the $^3(\pi,\sigma^*)$ state. It is suggested that the nucleophilic photoreaction contrasts with the radical reaction leading to the dissociation of the C–Cl bond; the latter reaction occurs in the $^3(\pi,\pi^*)$ state as well as in the $^3(\pi,\sigma^*)$ state.

Halogen substitutions in benzene cause significant changes in its phosphorescence spectrum. Benzene exhibits a structured phosphorescence spectrum with a maximum near 370 nm in rigid-glass solution, while chlorobenzene (abbreviated to CB) shows a broad, structureless one with a maximum near 480 nm.[1,2] Lim and Chakrabarti assigned this phosphorescence for CB to an emission originating from a triplet excimer.[2] Recently we studied the phosphorescence emission and the dynamics in the triplet states of CB, *p*-dichlorobenzene (DCB), and *p*-dibromobenzene in 2-methylpentane in the temperature range 70 to 100 K by means of time-resolved emission spectroscopy.[1,3] From the results of these studies we concluded that CB exhibits dual phosphorescence which consists of the structureless spectrum mentioned above and a somewhat structured one with a maximum near 400 nm, and that the former spectrum is not due to the triplet excimer. The phosphorescence properties of the halogenated benzenes were explained in terms of two low-lying triplet states, $^3(\pi,\pi^*)$ and $^3(\pi,\sigma^*)$, as shown in Fig. 1.[1,3] The intersystem-crossing (ISC) quantum yields from the S_1 state to the $^3(\pi,\pi^*)$ and $^3(\pi,\sigma^*)$ states may possibly amount to 0.6 and 0.4 for CB at 77 K, respectively, while for DCB the ISC to the $^3(\pi,\pi^*)$ state predominates, to a great extent, over the ISC to the $^3(\pi,\sigma^*)$ state. The nonradiative decay rate from these triplet states is particularly large at higher temperatures (> 85 K) compared with the corresponding rate of other analogous compounds, *e.g.*, halogenated naphthalenes. Accordingly, a process peculiar to the halogenated benzenes is considered to play an important role in the relaxation from the two triplet states. We suggested that this process corresponds to homolytic dissociation of the C–Cl bond.

On the other hand, the photolysis of halogenated benzenes has been widely studied, because the halogenated compounds are often concerned with environmental pollution.[4] It is known that the photolysis of CB generates a phenyl radical,[5] which is important as an intermediate in organic radical reactions. Ichimura and Mori suggested that the photolysis of CB in the vapor phase proceeds from the triplet state.[6] Bunce *et al.* showed that a radical reaction occurs in the triplet state of CB in cyclohexane.[7] Soumillion and De Wolf found that upon irradiation benzene and anisole are formed simultaneously in a solution of CB in methanol (MeOH), and they proposed a mechanism involving the triplet excimer for this photoreaction.[8] It is thus inferred that the photoreaction of CB is related to the nonradiative process from the triplet state.

Despite these investigations the relationships among the type of the excited state, the nonradiative

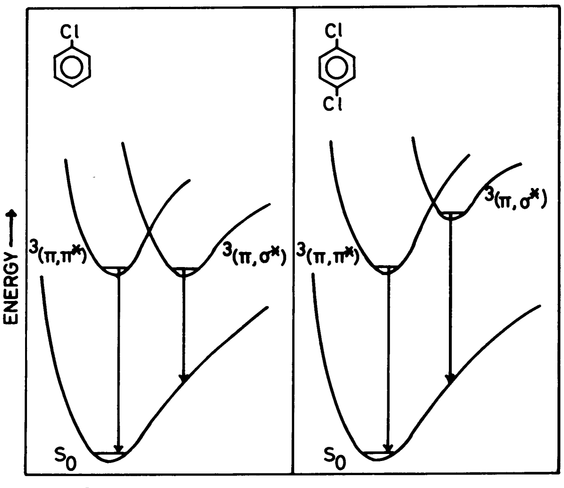


Fig. 1. Schematic sketch of potential curves of the low-lying triplet states of CB and DCB. The $^3(\pi,\sigma^*)\rightarrow S_0$ phosphorescence of DCB can be observed at temperatures higher than 85 K,[3] though it is too weak to be detected at 77 K.[1]

process, and the photoreaction have not fully been explored for halogenated benzenes, although such information is necessary for understanding the detailed mechanism of the photoreaction. Under these circumstances it would be worthwhile to examine the role of the two low-lying triplet states, $^3(\pi,\pi^*)$, and $^3(\pi,\sigma^*)$, in the photochemistry of halogenated benzenes.

From these points of view we have investigated the photoreaction of CB with MeOH by means of emission spectroscopy. One of the reaction products was found to be anisole, as shown by Soumillion and De Wolf,[8] indicating that a nucleophilic substitution reaction takes placae. The quantum yield of the nucleophilic photoreaction was determined, and the temperature dependence of the yield was examined to elucidate the reaction dynamics. The property of this reaction is compared with that of the radical photoreaction leading to the dissociation of the C–Cl bond. It is suggested that the nucleophilic reaction occurs in the $^3(\pi,\sigma^*)$ state, but that the radical reaction occurs in the $^3(\pi,\pi^*)$ state as well as in the $^3(\pi,\sigma^*)$ state. The photochemistry of DCB was also investigated for the sake of comparison.

Experimental

Materials. Chlorobenzene (CB), *p*-dichlorobenzene (DCB) (Wako Pure Chemical Co.), biacetyl, anisole, and *p*-chloroanisole (Nakarai Chemicals, Ltd.) were purified by repeated vacuum sublimation or distillation. Spectroscopic grade methanol (MeOH) and cyclohexane (Wako Pure Chemical Co.) were used without further purification. All sample solutions were degassed by the freeze-pump-thaw method prior to measurements.

Apparatus and Procedure. Unless otherwise stated, experiments were made at room temperature using a 1-cm square quartz cell. Absorption spectra were taken with a Cary 15 or a Hitachi 228A spectrophotometer. Emission and excitation spectra were measured by the photon-counting method, using a high-sensitivity emission spectrophotometer with a Hamamatsu R585 photomultiplier as detector.[9] The emission and excitation spectra were not corrected for the spectral sensitivity of the detector and the spectral intensity of the exciting light, respectively. In the photochemical experiments, unless otherwise stated, irradiation was carried out at 265 nm in the region of the $S_1 \leftarrow S_0$ transition with a bandwidth of 19 nm by the use of light from a system of a 150 W xenon arc and an *f*/4.5 monochromator.

The absolute quantum yield of the photoreaction of CB with MeOH was determined at 18 °C by means of trioxalatoferrate (III) actinometry, using a deaerated MeOH solution of 10^{-3} M (1 M=1 mol dm^{-3}) CB. Before irradiation of the solution, the intensity of fluorescence obtained by excitation at 265 nm was measured. After irradiation for 2 h, the fluorescence intensity was measured again under the same conditions as before to know the increase of the intensity resulting from the irradiation. This intensity increase was then compared with the intensity of the fluorescence from a 10^{-4} M solution of anisole in MeOH to evaluate the concentration of anisole formed by the photochemical reaction. It is to be noted here that the decrease in intensity of the fluorescence of CB need not be taken into account, because this decrease is very small compared with the intensity increase caused by anisole produced. The incident photons were counted after the method established by Hatchard and Parker.[10] These data permit determination of the quantum yield of the photoreaction. The quantum yields of photoreaction at 45, 0, −26 and −44 °C, relative to the yield at 18 °C, were also measured using three types of cryostats. By combining the results with the absolute yield at 18 °C, the absolute quantum yields were obtained for the different temperatures mentioned above.

The fluorescence decay (or the lifetime) was measured on a laser spectrophotomeric system reported previously,[11] using the time-correlated single photon counting method. The frequency of a pulsed dye laser (Molectron DL14) pumped by a nitrogen laser (Molectron UV22) was doubled by KDP crystal. The generated UV pulses, which were used for exciting the sample, have a duration of ≈3 ns. The emission was detected by a Hamamatsu R106 photomultiplier.

Results and Discussion

Photoreaction of CB with MeOH. In Fig. 2(a) the solid curves 1 and 2 represent the fluorescence and fluorescence-excitation spectra of 10^{-3} M CB in MeOH, and the broken curves 1′ and 2′ those of 10^{-3} M

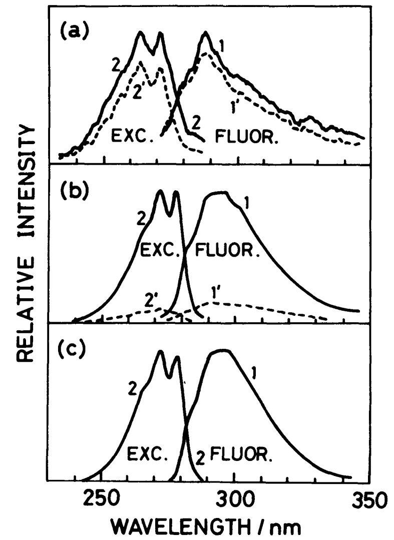
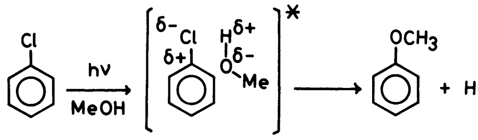


Fig. 2. (a) Fluorescence and fluorescence-excitation spectra of 10^{-3} M CB in MeOH (——) and 10^{-3} M CB in MeOH containing 10^{-2} M biacetyl (- - -). The fluorescence spectra (1 and 1′) were obtained by excitation at 265 nm and the excitation spectra (2 and 2′) by monitoring the emission at 300 nm. The spectra for the two sample solutions were recorded under the same conditions. (b) Same as (a) except that the two sample solutions were irradiated for 10 h. (c) Fluorescence spectrum (1) and fluorescence-excitation spectrum (2) of 10^{-4} M anisole in MeOH.

CB in MeOH containing 10^{-2} M biacetyl. Since the spectra for the two solutions were recorded under the same conditions, it is obvious that the fluorescence of CB is not quenched efficiently by biacetyl. This observation is consistent with the report that the lifetime of the S_1 state of CB is very short (80—800 ps).[12,13] On the other hand, from the latter solution containing biacetyl, strong sensitized biacetyl phosphorescence was observed, indicating that low-lying triplet states of CB are populated to a great extent.

Upon irradiation of the MeOH solution of CB alone, the fluorescence intensity increases with irradiation time, and the fluorescence spectrum undergoes a drastic change. In Fig. 2(b) the solid curves 1 and 2 represent the fluorescence and its excitation spectra for the MeOH solution of CB taken after irradiation for 10 h. These spectra are significantly different in shape and position from spectra 1 and 2 of Fig. 2(a), and are considered to originate from a photoproduct. In fact spectra 1 and 2 of Fig. 2(b) are very similar to the corresponding spectra of anisole in MeOH shown in Fig. 2(c). The fluorescence lifetime of the photoproduct (9.4 ns) also is similar to that of anisole in MeOH (9.8 ns). From these results, it is concluded that CB reacts with MeOH to form anisole upon irradiation. This photoreaction may be assumed to proceed in the excited state *via* a nucleophilic attack by MeOH on the carbon adjacent to the chlorine atom, followed by heterolysis of the C–Cl bond:



It has been found that photoreactions of alkyl halides in MeOH proceed through similar processes and generate methoxyalkanes.[14] A similar photosolvolysis was also reported for benzyl chloride in *t*-butyl alcohol.[15]

The photoreaction in the MeOH solution of CB is quenched by biacetyl. In Fig. 2(b) the broken curves 1′ and 2′ represent the fluorescence and its excitation spectra of 10^{-3} M CB in MeOH containing 10^{-2} M biacetyl after being irradiated in the same way as the MeOH solution of CB alone. These spectra were recorded under the same conditions as those for the solution without biacetyl, *i.e.*, spectra 1 and 2 of Fig. 2(b). Figure 3 shows the increase of the fluorescence intensity with irradiation time. The open and solid circles refer to the solutions of CB in MeOH in the absence and presence of biacetyl, respectively. It is seen that the efficiency of the photoreaction becomes very low when biacetyl is added to the solution. Since the photoreaction is quenched efficiently by biacetyl in contrast to the case of the fluorescence, this reaction is considered to occur mainly in the low-lying triplet state, $^3(\pi, \pi^*)$ and/or $^3(\pi, \sigma^*)$. Tissot *et al.* also showed that the photohydrolysis of chlorobenzene in aqueous solution involves a triplet state.[16]

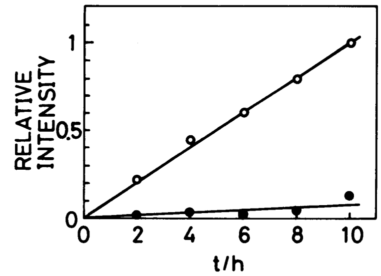


Fig. 3. Increase of the fluorescence intensity with irradiation time for 10^{-3} M CB in MeOH (○) and 10^{-3} M CB in MeOH containing 10^{-2} M biacetyl (●). The intensity was measured by excitation at 265 nm and by monitoring the emission at its intensity maximum.

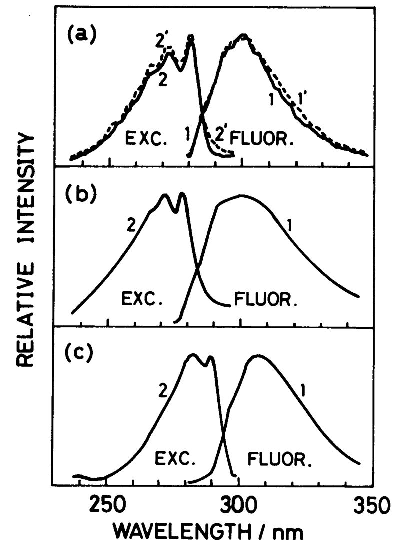


Fig. 4. (a) Fluorescence and fluorescence-excitation spectra of 10^{-3} M DCB in MeOH (——) and those of the same solution after irradiation for 10 h (- - -). The fluorescence spectra (1 and 1′) were obtained at 273 nm and the excitation spectra (2 and 2′) by monitoring the emission at 310 nm. The spectra before and after irradiation were recorded under the same conditions. (b) Fluorescence (1) and fluorescence-excitation (2) spectra of 10^{-3} M DCB in MeOH after irradiation for 3 min with intense light from a 250 W high-pressure Hg lamp. (c) Fluorescence (1) and fluorescence-excitation (2) spectra of 10^{-4} M *p*-chloroanisole in MeOH.

Contrary to the case of CB, the nucleophilic photoreaction was not observed for DCB. In Fig. 4(a) the solid curves 1 and 2 show the fluorescence and its excitation spectra of 10^{-3} M DCB in MeOH, and the broken curves 1′ and 2′ the spectra of the same solution after being irradiated under the same experimental conditions as the solution of CB in MeOH. The solid and broken curves were recorded under the same conditions. If the nucleophilic reaction of DCB occurred in MeOH, the fluorescence and its excitation spectra of DCB should be changed to those of *p*-chloroanisole shown in Fig. 4(c). Actually the spectra of DCB remain essentially unchanged upon irradiation, as is seen in Fig. 4(a). It was found, however, that on irradiating DCB with intense light from a 250 W high-pressure Hg lamp (without being dispersed by a monochromator), the spectra were changed ultimately to those of anisole, as shown in Fig. 4(b). Moreover, during the course of the above irradiation there was no indication that *p*-chloroanisole was formed. These experimental results for DCB can be explained as follows. In the first stage of the photochemical reaction, the homolysis of DCB takes place in MeOH to form CB, as shown by Mansour *et al.*,17) and then the CB molecule is changed to anisole by the photochemical nucleophilic reaction as described before. It is thus concluded that in the low-lying triplet states of DCB the nucleophilic reaction does not occur at all or proceeds only slowly.

The extent to which each of the $^3(\pi,\pi^*)$ and $^3(\pi,\sigma^*)$ states is involved in the nucleophilic photoreaction depends evidently upon the degree of populating the triplet state concerned. According to our recent study, the ISC quantum yield from the S_1 state to the $^3(\pi,\sigma^*)$ state may possibly amount to 0.4 for CB, but it is essentially zero for DCB in 2-methylpentane at 77 K; that is, the $^3(\pi,\sigma^*)$ state of DCB is populated from S_1 to a far smaller degree than the same state of CB. In either compound, the mutual conversion between the two low-lying triplet states $^3(\pi,\pi^*)$ and $^3(\pi,\sigma^*)$ is negligible at 77 K.3) In DCB the $^3(\pi,\pi^*)$ state is considered to be significantly lower in energy than the $^3(\pi,\sigma^*)$ state (Fig. 1).1,3) Accordingly, even if the conversion mentioned above occurs rapidly at high temperature, the $^3(\pi,\sigma^*)$ state of DCB will be popuuated *via* $^3(\pi,\pi^*)$ only to a slight degree. It seems reasonable, therefore, to assume that the overall degree of populating the $^3(\pi,\sigma^*)$ state of DCB is much less than that of CB even under the present experimental conditions. This difference in population degree of the $^3(\pi,\sigma^*)$ state between CB and DCB may be the main factor responsible for the difference in reactivity between the two compounds. Thus, the most probable mechanism of the nucleophilic photoreaction of CB with MeOH is that the reaction proceeds from the $^3(\pi,\sigma^*)$ state. Our recent *ab initio* study on the low-lying triplet states of CB also has suggested that the $^3(\pi,\sigma^*)$ state is more favorable to the nucleophilic photoreaction than the $^3(\pi,\pi^*)$ state.18)

From the phosphorescence and its excitation spectra of the irradiated sample solution of CB in MeOH, which were measured at 77 K after irradiation at room temperature, we noticed formation of benzene in addition to anisole. As mentioned previously, Soumillion and De Wolf also found that benzene and anisole are formed simultaneously upon irradiation of a solution of CB in MeOH, and they proposed a new mechanism which involves formation of a pair of radical ions *via* the triplet excimer.8) Their argument is based on the suggestion by Lim and Chakrabarti2) that the phosphorescence from CB in EPA at 77 K is due to the triplet excimer. However, we demonstrated that the phosphorescence is not attributable to the triplet excimer, but that it can be explained in terms of the two low-lying triplet states.1) It is unlikely, therefore, that the photoreaction proceeds *via* the triplet excimer. This is consistent with the results obtained by Bunce *et al.*7)

Reaction Quantum Yield and Its Temperature Dependence. The quantum yield of the nucleophilic photoreaction (Φ_{react}) of CB at 18 °C was determined to be 0.049 by means of actinometry. The temperature dependence of Φ_{react} of CB is shown in Fig. 5. The value of Φ_{react} decreases as the temperature is lowerd. The results were analysed under the view that the reaction proceeds from the $^3(\pi,\sigma^*)$ state.

Since the ISC in CB seems to dominate over the other deactivation processes from the S_1 state, the total ISC quantum yield is assumed to be unity. The ISC is considered to take place to both the $^3(\pi,\pi^*)$ and the (π,σ^*) states. At room temperature, the rates of the radiative decays from the two triplet states can safely be regarded as much less than those of the nonradiative decays, so that the radiative decays will be neglected in the following discussion. The rate constants for the nonradiative decay processes and the nucleophilic photoreaction are assumed to change with temperature and to be expressible in the forms of the Arrhenius equation. In order to understand the experimental results, two simple and extreme cases will be discussed. In Case 1, the mutual conversion between the $^3(\pi,\pi^*)$ and $^3(\pi,\sigma^*)$ states is regarded as much slower than the other nonradiative processes from these two triplet states. In Case 2, we assume that just the reverse is the case, namely, that a

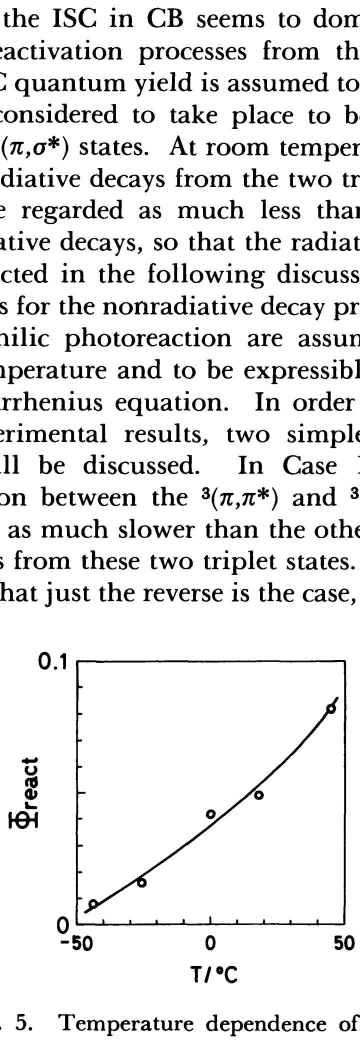


Fig. 5. Temperature dependence of Φ_{react}.

dynamic equilibrium is attained between the two triplet states.

In Case 1, we can show that the following relation holds between Φ_{react} and temperature:

$$\frac{\Phi_{\mathrm{ISC}}^{\pi\sigma}}{\Phi_{\mathrm{react}}} - 1 \propto \exp\left(\frac{E_{\mathrm{r}}-E_{\sigma}}{RT}\right), \tag{1}$$

where $\Phi_{\mathrm{ISC}}^{\pi\sigma}$ denotes the quantum yield of the ISC to the $^3(\pi,\sigma^*)$ state; E_{r} is the activation energy of the pseudo first order nucleophilic photoreaction from the $^3(\pi,\sigma^*)$ state, and E_{σ} represents the apparent activation energy associated with the total rate constant, k_{σ}, for a combination of the nonradiative $^3(\pi,\sigma^*)\rightarrow S_0$ process and the homolytic dissociative process concerning the C–Cl bond in the $^3(\pi,\sigma^*)$ state.

In Case 2, on some assumptions, the relation between Φ_{react} and temperature is given by

$$\frac{1}{\Phi_{\mathrm{react}}} - 1 \propto \exp\left(\frac{E_{\mathrm{r}}-E_{\sigma}}{RT}\right). \tag{2}$$

The assumptions which have to be introduced are described in the following.

Previously, we suggested that the homolytic dissociative process of the C–Cl bond is dominant in the decay from the two low-lying triplet states of halogenated benzenes in 2-methylpentane above 85 K.[1,3] It is not unreasonable, therefore, to assume that the rate of the homolytic dissociative process of the C–Cl bond is much greater than those of the other nonradiative processes in CB under our experimental conditions. Furthermore, the dissociation of the C–Cl bond of CB is much more likely to occur in the $^3(\pi,\sigma^*)$ state than in the $^3(\pi,\pi^*)$ state, because the C–Cl bond length in the $^3(\pi,\sigma^*)$ state is considered to be significantly longer than that in the $^3(\pi,\pi^*)$ state.[1,3,18] It is thus assumed that k_{σ} is far greater than the total rate constant for a combination of the nonradiative $^3(\pi,\pi^*)\rightarrow S_0$ process and the homolytic dissociative process concerning the C–Cl bond in the $^3(\pi,\pi^*)$ state. It is further assumed that for CB the ratio of the rate constant for the $^3(\pi,\sigma^*)\rightarrow{}^3(\pi,\pi^*)$ conversion process to the rate constant for the reverse process is not much larger than unity.

Equation 2 (Case 2) is the same as Eq. 1 (Case 1), except that $\Phi_{\mathrm{ISC}}^{\pi\sigma}$ is replaced by unity. We attemped to estimate $E_{\mathrm{r}}-E_{\sigma}$ from the slopes of the plots of log $[(X/\Phi_{\mathrm{react}})-1]$ *vs.* $1/T$ with X varying between 0.1 and 1. The plots of $\log[(X/\Phi_{\mathrm{react}})-1]$ *vs.* $1/T$ give nearly straight lines for X between 0.2 and 1, but the plot for X=0.1 somewhat deviates from a straight line. Accordingly, we estimated $E_{\mathrm{r}}-E_{\sigma}$ only for $0.2 \leqq X \leqq 1$. From the slopes of the straight lines, the values of $E_{\mathrm{r}}-E_{\sigma}$ of CB were determined to be (3.9±1.0) and (3.0±0.7) kcal mol^{-1} (1 kcal mol^{-1}= 4.184 kJ mol^{-1}) for X=0.2 and 1, respectively, using the least squares method. $E_{\mathrm{r}}-E_{\sigma}$ decreases as X increases, but for $0.2 \leqq X \leqq 1$, $E_{\mathrm{r}}-E_{\sigma}$ does not depend largely on X. In other words, the two extreme cases, Case 1 and Case 2, lead to similar results for $E_{\mathrm{r}}-E_{\sigma}$. It may thus be said that E_{r} is larger than E_{σ} by about 3—4 kcal mol^{-1} in the actual CB molecule.

Comparison between Nucleophilic and Radical Reactions. As described previously benzene as well as anisole is formed by irradiation of CB in MeOH, indicating that the radical photoreaction occurs, besides the nucleophilic one, in the sample solution. We now compare the property of the nucleophilic photoreaction of CB with that of the radical one. Bunce *et al.* showed that the radical reaction occurs in the triplet state of CB in cyclohexane.[7] Examining the photolysis of CB in cyclohexane by a method similar to the one described before, we also concluded that upon irradiation CB in cyclohexane is converted into benzene *via* the low-lying triplet states. In order to know the detailed mechanism of this radical photoreaction, we studied the photolysis of DCB in cyclohexane also.

The fluorescence and its excitation spectra of DCB in cyclohexane are shown in Fig. 6(a). As in the case of CB in MeOH, the fluorescence is not quenched efficiently by biacetyl. Upon irradiation with the intense light from the 250 W high-pressure Hg lamp mentioned previously, the spectra changed drastically. A peak to be assigned to CB was observed at 265 nm in the excitation spectrum, together with peaks of DCB and benzene (Fig. 6(b)). On further irradiation, the fluorescence and its excitation spectra

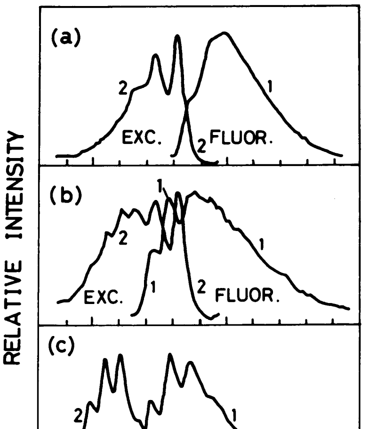


Fig. 6. (a) Fluorescence (1) and fluorescence-excitation (2) spectra of 10^{-3} M DCB in cyclohexane in a 7 mm o.d. cylindrical quartz cell. The fluorescence spectrum was obtained by excitation at 255 nm and the excitation spectrum by monitoring the emission at 310 nm. (b) Same as (a) except that the sample solution was irradiated for 10 min with intense light from a 250 W high-pressure Hg lamp. (c) Same as (b) except that the irradiation time was lengthened to 30 min.

changed finally to those of benzene alone, as may be seen from Fig. 6(c). These results indicate that the radical reaction, including the dechlorination of DCB, takes place upon irradiation. Since this photoreaction is quenched by biacetyl, it is considered to occur in the low-lying triplet states as in the case of the nucleophilic and radical photoreactions of CB. On the other hand, as has already been pointed out, the population degree of the $^3(\pi,\sigma^*)$ state of DCB is considered to be quite small. It is, therefore, reasonable to presume that the radical plotoreaction of DCB takes place in the $^3(\pi,\pi^*)$ state. The radical reaction of CB, therefore, may be supposed to occur in the $^3(\pi,\pi^*)$ state also.

From the foregoing discussion one may suppose that (1) the nucleophilic photoreaction of CB takes place in the $^3(\pi,\sigma^*)$ state, and (2) the radical photoreaction of CB leading to the dissociation of the C–Cl bond may occur both in the $^3(\pi,\pi^*)$ state and in the $^3(\pi,\sigma^*)$ state.

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