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Mechanism of Photochemical Reaction from Benzyl Chloride to Toluene in Solution

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Synopsis. The photochemical reaction from benzyl chloride to toluene has been investigated in rigid glasses and fluid solutions. The experimental results indicate that toluene formation from benzyl chloride in 2-methylpentane proceeds via hot benzyl radicals or higher triplet states that are isoenegitic to the vibrationless level of the S_1 state of BzCl and proceeds negligibly from stable benzyl radicals.

Benzyl chloride (BzCl) is photochemically very active and its photochemistry has been widely studied.[1-4] Although it is known that upon irradiation with UV light, BzCl in alkane solvents yields a variety of photochemical products, several problems for the reaction mechanism remain unsettled, especially concerning intermediates in the excited state leading to photoproducts. This note is concerned with the mechanism of the photochemical reaction from BzCl to toluene, which was believed to proceed via benzyl radicals (Bz radicals) as a reaction intermediate.[1-4]

On the other hand, it is difficult to observe any emission of the fluorescence and phosphorescence of BzCl in the usual organic solvents at any temperature.[1,5-7] This suggests that the lifetime of the S_1 state of BzCl in solution is very short (less than 10^{-12} s; cf. Results and Discussion) and that the T_1 state is poorly populated because the intersystem crossing rate from the S_1 state to an excited triplet state is unlikely to be as fast as 10^{12} s^{-1}. Accordingly, the photochemistry of BzCl in solution is considered to proceed exclusively from the S_1 state and/or from the higher triplet states. This consideration corresponds to the results by Cristol and Bindel, who indicated that the photoreaction of BzCl in *t*-butyl alcohol occurs via a short-lived upper state, S_1, or a higher triplet state.[2]

In this study, we attempt to elucidate the photochemical processes concerning the formation of toluene from BzCl as a prototype of the homolytic photochemical reaction and to reveal the energy-relaxation processes in the excited states of BzCl as a series of studies on those of halogenated benzenes.[7-11]

Experimental

Benzyl chloride (Wako Chemical Co.) was purified by repeated vaccum distillations. 2-Methylpentane (Tokyo Kasei Co.) was purified after the method described in a previous paper.[8] Absorption and emission spectra were measured, respectively, with a Hitachi 228 spectrophotometer and a high-sensitivity fluorescence and phosphorescence spectrophotometer by means of the photon-counting technique using a Hamamatsu R585 photomultiplier. Unless otherwise stated, the photochemical experiments were made at 77 K using 1-cm square quartz cell and irradiation was carried out at 265 nm with a bandwidth of 10 nm by the use of light from a 150-W xenon arc passed through a monochromator.

Upon irradiation of BzCl in 2-methylpentane (2-MP) at 77 K, the contents of Bz radicals and toluene produced are quantitatively obtained by monitoring the fluorescence of Bz radicals and the phosphorescence of toluene. In measurements of the fluorescence of Bz radicals and of the phosphorescence of toluene, the excitations were carried out at an absorption band of 318 nm for Bz radicals and at a band of 254 nm for toluene (with a bandwidth of 2 nm). The concentrations of BzCl in 2-MP examined were in the range 10^{-4}—10^{-5} M.

Results and Discussion

Upon irradiation with a UV light shorter than 270 nm, BzCl in 2-MP at 77 K reacts to form Bz radicals and toluene. Bz radicals show a structured fluorescence spectrum commencing at 465 nm and has a very strong absorption band at 318 nm. Therefore, the formation of Bz radicals can be quantitatively observed by monitoring the fluorescence spectrum excited at 318 nm. Toluene produced can also be detected by monitoring the phosphorescence of toluene by means of time-resolved spectroscopy.[8,9] The fluorescence from toluene can not be used as a quantitative measure of toluene because of the very low concentration of toluene produced and because of interference from the Raman scattering light due to solvents. It should be noted here that the fluorescence of BzCl could not be detected within our experimental accuracies (the quantum yield is less than 10^{-5}).

Also, no phosphorescence from BzCl could be observed. Fresh BzCl in 2-MP at 77 K did not show any emission with a lifetime longer than 10^{-3} s (the quantum yield is less than 10^{-5}). Although no fresh BzCl showed a structured emission spectrum starting at 390 nm with a lifetime of 3—5 ms, which is similar to the phosphorescence spectrum reported in Ref. 5, it was found from the excitation spectrum of the

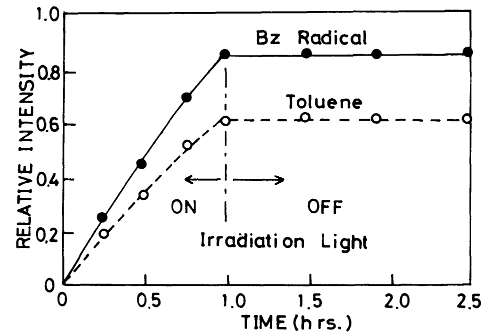

Fig. 1. Plots of the fluorescence intensities of Bz radicals (-●—●-) and the phosphorescence intensities of toluene (-○- -○-) as a function of the time with and without irradiation light of 265 nm of BzCl in 2-MP at 77 K.

emission that the emission is due to an impurity: maybe benzaldehyde. The emission with a lifetime of 2 s (produced by irradiation) can be attributed to toluene on the basis of the phosphorescence and its excitation spectra.

In Fig. 1 the fluorescence intensities of Bz radicals and the phosphorescence intensities of toluene are plotted as a function of the time with and without irradiation of BzCl in 2-MP at 77 K with a light of 265 nm. The concentrations of Bz radicals and toluene increase with the irradiation time and show no change for at least 3 h after irradiation. This is consistent with the observation that stable Bz radicals ("stable" means Bz radicals are in the vibrationless level in the ground state) in rigid glass solutions at 77 K react negligibly with solvents.1)

Figure 2 shows the formation rates of Bz radicals and toluene against the intensities of the irradiation light, indicating that each of the rates is linear to the light intensities under experimental conditions; that is, the photoreaction from BzCl to toluene as well as to Bz radicals is a one-photon process.

Now we are in a position to consider the mechanism regarding the photoreaction from BzCl to toluene. On the basis of the experimental results described above, we can give three mechanisms as candidates of a plausible path for the toluene formation from BzCl: (1) a reaction of toluene$\leftarrow$stable Bz radical involves an appropriate orientation between the Bz radical and solvent molecules concerned and is accompanied by considerable amounts of the activation energy; (2) stable Bz radicals react with alkyl radicals produced by the reaction between the solvent and the chlorine atom (comes photochemically from BzCl) to form toluene with a negligible amount of the activation energy; and (3) toluene arises from a hot Bz radical or a higher triplet state isoenergitic to the vibrationless level of the S_1 state of BzCl and arises negligibly from stable Bz radicals. Mechanisms (1) and (2) involve the concentrations of stable Bz radicals, while (3) does not.

In order to decide which mechanism is acceptable, it is desirable to examine the oxygen effect on the photochemical reaction in question in a fluid solution. The lifetime of Bz radicals is found to be considerably long in a degassed alkane solvent and decreases with an increase in the concentration of oxygen.1) Accordingly, if the photochemical reaction in the fluid solution was influenced by aeration, mechanism (3) would be excluded from a possible mechanism. On the contrary, if the aeration effect on the reaction in the fluid solution is negligible, the contributions from (1) and (2) are less for the photochemistry in interest, and (3) is favorable.

BzCl in 2-MP at room temperature was irradiated for 3 h under deaerated and aerated conditions; then, the phosphorescence of toluene produced was quantitatively observed at 77 K. For both samples, deaerated and aerated solutions, the contents of the toluene produced by irradiation were almost equal to each other within our experimental accuracies. That is, the effect of oxygen on the reaction could not be clearly observed. The experimental results also showed that the toluene formation under fluid conditions was not in an order of magnitude appreciably different from those in rigid glass at 77 K. These facts indicate that the reaction of interest had no appreciable amounts of activation energy and involved no relatively long-lived species as intermediates (such as stable Bz radicals and the T_1 state of BzCl). In addition, the fact that the rate of the toluene formation is linear against the intensity of the irradiation light (as described before), excludes mechanism (2) from a possible path for the photoreaction.

Thus, the experimental results described above lead us to the conclusion that the photochemical reaction from BzCl to toluene proceeds via a very short-lived Bz radical (hot Bz radical) as the reaction intermediate and does not via stable Bz radicals and the T_1 state of BzCl. That is, hot Bz radicals produced from the S_1 state or the isoenergitic higher triplet state transform into toluene during the very short lifetime. These reaction processes seem to correspond to the mechanism of the heterolytic photoreaction of BzCl in *t*-butyl alcohol which is considered to occur via the short-lived S_1 state or a higher triplet state.2)

Figure 3 schematically shows the photochemical mechanism proposed. For BzCl in 2-MP, the lifetime of the S_1 state can be estimated to be shorter than one picosecond from the fluorescence quantum yield ($\leqslant 10^{-5}$) and radiative lifetime ($\approx 10^{-7}$ s estimated from the oscillator strength of S_0—S_1 absorption). This indicates that the S_1 state deactivates dominantly

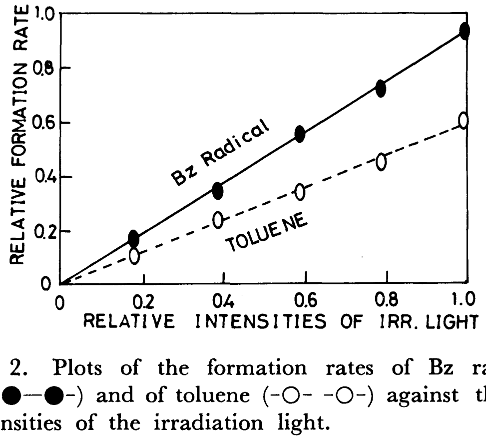

Fig. 2. Plots of the formation rates of Bz radicals (-●—●-) and of toluene (-○- -○-) against the intensities of the irradiation light.

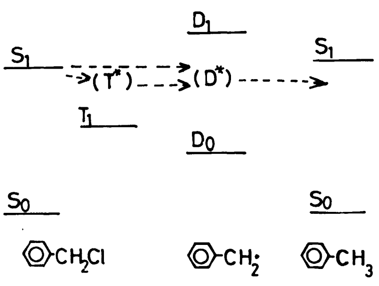

Fig. 3. Possible mechanism for photochemical reaction from BzCl to toluene in alkane solvent. The reaction proceeds along arrows in competition with vibrational relaxations.

to the radical formation directly or to higher triplet states. Although we could not decide whether the hot Bz radicals were formed directly from the S_1 state or via a higher triplet state, hot Bz radicals are actually regarded as being produced almost directly from the S_1 state.[12]

Finally, we shall show the results of a photochemical reaction for benzyl bromide (BzBr). BzBr also shows no fluorescence and phosphorescence under any condition and gives almost no Bz radicals. However, toluene is considerably produced from BzBr in 2-MP at 77 K upon irradiation with UV light. This seems to give some evidence that the photochemical process of toluene formation proceeds along the mechanism shown in Fig. 3.

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