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The Photochemistry of the Host-Guest Complex. V. The Effect of the Sodium Ion on the Photoreaction of Benzil Derivatives with a Crown Ether Moiety

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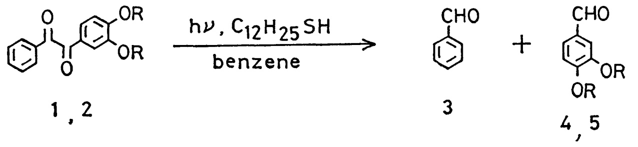
The photolysis of 4′-(2-phenyl-1,2-dioxoethyl)benzo-15-crown-5 in benzene containing 1-dodecanethiol gives benzaldehyde and 4′-formylbenzo-15-crown-5. The formation of the aldehydes was inhibited by the sodium ion, whereas the photolysis of 1-(3,4-dimethoxyphenyl)-2-phenylethanedione was not inhibited by the sodium ion. This inhibition must be due to the decrease in the formation of benzoyl radicals from the triplet excited state of the crown ether derivative. The salt effect was discussed on the basis of the spectral data.

We have been studying the effect of a guest ion on the photoreactivity of crown ether derivatives,[1)] and have shown that the formation of a host-guest complex affects the photoreaction in several aspects. In the course of our study of the photoreaction of a host-guest complex, the photoreactivity of benzil derivatives was tested in the presence of a guest cation.[2)] In this paper we wish to report the photolyses of 4′-(2-phenyl-1,2-dioxoethyl)benzo-15-crown-5 (**1**) and 1-(3,4-dimethoxyphenyl)-2-phenylethanedione (**2**) in benzene containing 1-dodecanethiol.

The excitation of benzil in hydrogen-donating solvents gives a complex mixture of products,[3)] which derives from the ketyl radical[4)] formed by hydrogen abstraction by a triplet-excited benzil.[5)] However, the excitation of benzil in benzene does not cause a remarkable reaction. This behavior of benzil must be due to the lack of ketyl-radical formation in benzene, a poor hydrogen-donating solvent. Another photochemical process of benzil is the formation of benzoyl radicals by an α-cleavage, but the benzoyl radicals preferentially recombine to regenerate the starting material. In the present study, 1-dodecanethiol was added to the reaction mixture as a scavenger of the benzoyl radicals[6)] formed by the α-cleavage of the benzil derivative.

Results and Discussion

Photoreactions of Benzil Derivatives in the Absence or Presence of the Sodium Ion. The irradiation of **1** in deoxygenated benzene–acetonitrile (6:4) containing 1-dodecanethiol gave benzaldehyde (**3**) and 4′-formylbenzo-15-crown-5 (**4**). The irradiation of **2** in the same manner gave benzaldehyde (**3**) and 3,4-dimethoxybenzaldehyde (**5**). All the products were identified by comparison with authentic aldehydes. The starting material in the reaction mixture did not change in the dark. The photolyses of **1** and **2** (2.5×10^{-2} mol dm^{-3}) are sluggish, and only *ca.* 30% of the starting materials disappeared after irradiation for 40 h (see the experimental section for details of the reaction conditions). The sluggishness of the photolyses of **1** and **2** is accounted for by the rapid recombination of benzoyl radicals in a solvent cage. It has been reported that 0.03 mol dm^{-3} of 1-dodecanethiol scavenges the cage-free benzoyl radical formed by the photolysis of 1,2-diphenylethanone.[6)] In the present study, we used enough 1-dodecanethiol (0.25 mol dm^{-3}) as the scavenger of benzoyl radicals.



1, 2   3   4, 5

1,4 : RR = $(CH_2CH_2OCH_2CH_2)_2O$
2,5 : R = CH_3

(Eq. 1)

The effect of the guest cation on the photoreactivity of the crown ether derivative (**1**) was tested by adding varying amounts of sodium perchlorate. Figure 1 shows the effects of the added sodium perchlorate on the relative quantum yield (ϕ_{rel}) of aldehyde **3** and **4**. The depressing in ϕ_{rel} can not be due to the perchlorate anion, since the addition of tetrabutylammonium perchlorate stimulated ϕ_{rel}. The photolysis of **2** in the presence of sodium perchlorate gave an entirely different result from that of the photolysis of **1**, and the addition of sodium perchlorate increased the formation of aldehyde **3** and **5** (Fig. 2). These results clearly show that the effect

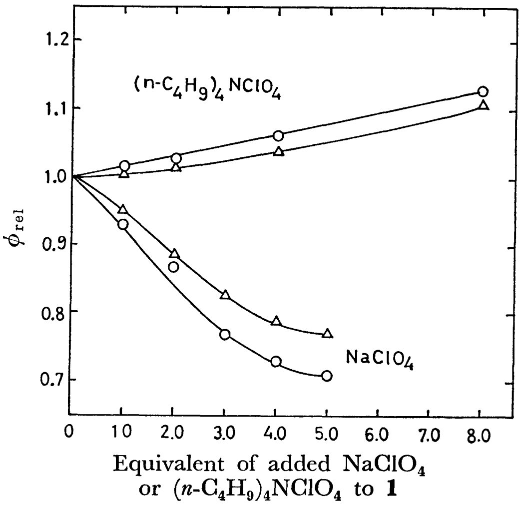


Fig. 1. Relative quantum yield of the formation of benzaldehyde (**3**) (△——△) and 4′-formylbenzo-15-crown-5 (**4**) (○——○) on the photolysis of crown ether derivative (**1**) (2.5×10^{-2} mol dm^{-3}) in the presence of $NaClO_4$ or $(C_4H_9)_4N\cdot ClO_4$.

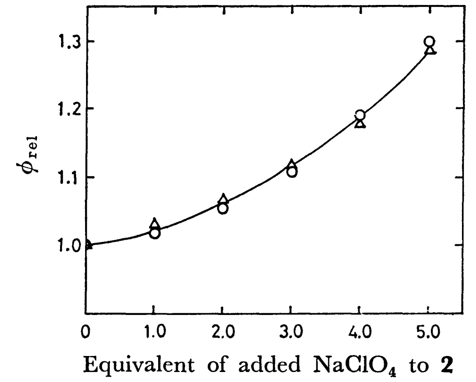


Fig. 2. Relative quantum yield of benzaldehyde (**3**) (△——△) and 3,4-dimethoxybenzaldehyde (**5**) (○——○) on the photolysis of dimethoxy compound (**2**) (2.5×10^{-2} mol dm^{-3}) in the presence of $NaClO_4$.

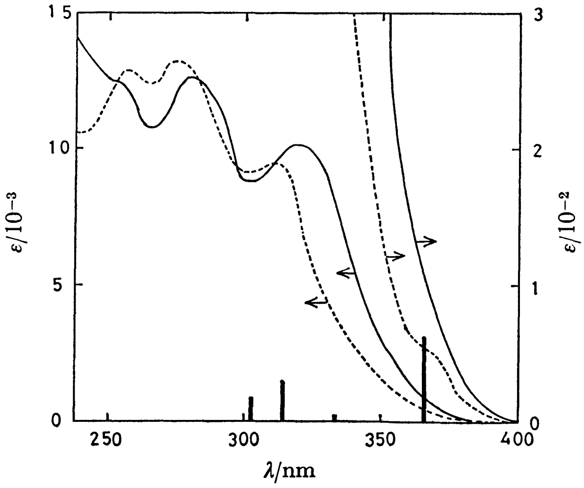
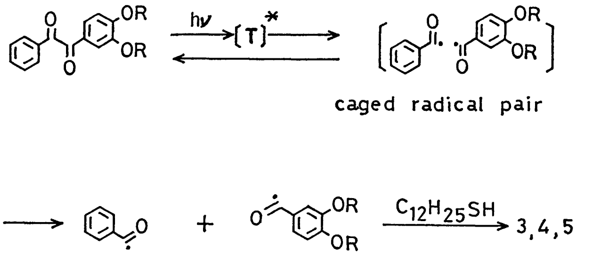


Fig. 3. UV absorption spectra of 4′-(2-phenyl-1,2-dioxoethyl)benzo-15-crown-5 (**1**) (1.00×10^{-4} mol dm^{-3} in acetonitrile) in the absence (——) and presence (……) of $NaClO_4$ (20 equivalents), and emission lines from a high pressure mercury lamp in 300—400 nm region

of the sodium salt on the photoreactivity of **1** is related to the complex formation between the sodium ion and the crown ether derivative (**1**).

Discussion of the Salt-effect Based on the Spectroscopic Data. The ultraviolet absorption of **1** changes upon the addition of sodium perchlorate due to the formation of a host-guest complex (Fig. 3). The absorption of **2** is essentially the same as that of **1**, but it does not change upon the addition of sodium perchlorate. The formation constant ($K=2.8\times10^3$ mol^{-1} dm^3 in acetonitrile) of the complex between **1** and the sodium ion can be obtained by the analysis of the spectral change by means of the Benesi-Hildebrand equation (Eq. 2),[7] in which **Abs** denotes the absorbance (solution thickness: 1.0 cm) of the mixture of **1** and the sodium ion, while $\Delta\varepsilon$ denotes the difference in the molar absorptivity of **1** and the complex. From Eq. 2 we calculated $\Delta\varepsilon(=674)$ at 366 nm, at which a high-pressure Hg lamp has a strong emission line. The $\Delta\varepsilon$ thus obtained and the molar absorptivity of **1** at 366 nm ($\varepsilon=962$) gave the molar absorptivity of the host-guest complex at 366 nm ($\varepsilon=268$). We photolyzed a 2.5×10^{-2} mol dm^{-3} solution of the crown ether derivative (**1**) in the presence of varying amounts of sodium perchlorate (0.0—1.25×10^{-1} mol dm^{-3}). The absorbance of the reaction solution at 366 nm is calculated to be **Abs**(366)=6.7 (path length: 1.0 cm) when the crown ether derivative (**1**) exists entirely as the complex. This analysis shows that the **Abs** (366 nm) of the reaction mixture must be larger than 5.7, even at a solution thickness of 1.0 mm, and that a 366-nm light is almost completely absorbed by the reaction mixture contained in a Pyrex tube 1 cm in diameter. The reaction mixtures containing varying amounts of the sodium salt, therefore, must absorb the same number of photons under the present conditions. Other emission lines (304, 313, and 334 nm) from the Pyrex-filtered lamp should be completely absorbed by the reaction mixture, since it has large absorption coefficients at these wave lengths (see Fig. 3) and since the number of the excited molecule is essentially not affected by the existence of the sodium ion.

$$\frac{[\mathbf{1}]\cdot[\mathrm{Na}^+]}{\mathbf{Abs}}=\frac{[\mathrm{Na}^+]}{\Delta\varepsilon}+\frac{1}{\Delta\varepsilon\cdot K} \tag{2}$$



(Eq. 3)

1-Dodecanethiol is an efficient scavenger of a cage-free benzoyl radical,[6] and the decrease in ϕ_{rel} upon the complex formation with the sodium ion must be due to the retardation of benzoyl-radical formation from the crown ether derivative (**1**).

The phosphorescence from **1** in glassy EPA (1.02×10^{-4} mol dm^{-3}) shows a spectrum with a diffused vibrational structure, presumably from the $^3(n\pi^*)$ or $^3(\pi\pi^*)$ of a considerable mixing with $^3(n\pi^*)$, and the emission neither shifts nor changes its shape on the addition of sodium perchlorate. The intensity of the phosphorescence from **1**, however, diminishes by *ca.* 15% upon the addition of sodium perchlorate (7.05×10^{-4} mol dm^{-3}). The dimethoxy analog (**2**) shows essentially the same phosphorescence spectrum as that of the crown ether derivative (**1**), but the spectrum is not affected by the addition of sodium perchlorate or tetrabutylammonium perchlorate. The lifetime of the emissive state of **1** was determined to be $\tau=54$ ms, and it was not affected by the sodium salt. Since the lifetime of the triplet state of **1** is insensitive to the sodium ion, the decreases in the ϕ_{rel} of the reaction and the phosphorescence intensity can not be attributed to the additional decay process of the triplet state, but must be attributable to the decrease in the quantum yield of the triplet state upon the complex formation. Decreases in the rate of intersystem crossing are attributable to several factors: (i) an electronic-field perturbation by the added electrolyte, (ii) an external heavy-atom effect, and (iii) the energy gap between the S_1 and T_1 states (ΔE_{ST}). The first two factors can not be important in the present case, however, since another intersystem crossing, $T_1 \rightarrow S_0$, is not affected, as is evidenced by the insensitivity of the lifetime of the phosphorescence to the sodium salt. The energy level of the triplet state (T_1) of **1** does not change upon the complex formation, as is evidenced by the wavelength of the phosphorescence, whereas the complexation of **1** with the sodium ion raises the energy level of the singlet excited state (S_1) of **1**, as is evidenced by the absorption spectrum in acetonitrile; λ_{max}: 319 nm (without Na^+) and λ_{max}: 310 nm (with Na^+). This increase in ΔE_{ST} is one of the most probable factors in retarding the intersystem crossing ($S_1 \rightarrow T_1$) and, hence, the formation of a benzoyl-radical pair from the T_1 state.

It is still uncertain why the relative reactivities of **1** and **2** increase upon the addition of the ammonium perchlorate. Since the addition of sodium perchlorate to the reaction system of **2** (see Fig. 2) increases its photoreactivity, these effects must, however, be related to the perchlorate anion. We must await further studies about other aspects for the solution to this problem.

Experimental

Synthesis of 4′-(2-Phenyl-1,2-dioxoethyl)benzo-15-crown-5 (1). A mixture of benzo-15-crown-5 (2.68 g, 1.0×10^{-2} mol) and phenylacetic acid (2.04 g, 1.5×10^{-2} mol) in 10 cm^3 of polyphosphoric acid was stirred for 5 h at 70 °C. After cooling, the mixture was poured into ice water (*ca.* 15 cm^3); the new solution was stirred for 1 h to hydrolyze polyphosphoric acid, and the resulting aqueous mixture was extracted by chloroform (20 $cm^3 \times 3$). The evaporation of the extract after successive washing by water and a saturated solution of sodium hydrogencarbonate and drying over magnesium sulfate gave a pale yellow solid. The chromatography of the crude product on an alumina column ($1.0(\phi) \times 20$ cm) (chloroform, 70 cm^3), followed by recrystallization from methanol, gave 4′-(2-phenyl-1-oxoethyl)benzo-15-crown-5; 1.62 g (42%). Mp 73.5—74.5 °C; IR(CCl_4): 1660, 1590, 1510, 1425, 1262, and 1130 cm^{-1}; NMR($CDCl_3$): δ 7.50—7.35 (2H, m), 7.14 (5H, m), 6.63 (1H, d, J=8 Hz), 4.02 (2H, s), 3.99 (4H, m), 3.75 (4H, m), and 3.57 (18H, diff. s).

A mixture of 4′-(2-phenyl-1-oxoethyl)benzo-15-crown-5 (1.0 g, 2.6×10^{-3} mol), selenium dioxide (0.35 g, 3.2×10^{-3} mol), dioxane (20 cm^3), and water (10 cm^3) was refluxed for 15 h, after which the solvent were removed *in vacuo*. Benzene (20 cm^3) was then added to the residue, and the mixture was evaporated twice to remove the residual dioxane and water. The solid residue was dissolved in chloroform (20 cm^3) and filtered to remove the solid selenium. The filtrate was condensed *in vacuo* after drying over magnesium sulfate to give a pale yellow product. The purification of the product by passing it through a column of alumina ($1.0(\phi) \times 10$ cm, and chloroform 70 cm^3) and subsequent recrystallization from methanol gave 4′-(2-phenyl-1,2-dioxoethyl)benzo-15-crown-5 (**1**); 0.78 g, (75%). Mp 110—112 °C; Found: C, 65.85; H, 5.97%. Calcd for $C_{22}H_{24}O_7$: C, 65.99; H, 6.04%. $\lambda_{max}^{CH_3CN}$: (ε) 252 (1.26×10^4), 282 (1.26×10^4), and 318 nm (1.01×10^4); IR($CHCl_3$): 1665, 1595, 1510, 1438, 1280, and 1135 cm^{-1}; NMR($CDCl_3$): δ 7.95(2H, m), 7.52(5H, m), 6.72(1H, d, J=8 Hz), 4.15 (4H, m), 3.75(4H, m), and 3.66(8H, diff. s).

Synthesis of 1-(3,4-Dimethoxyphenyl)-2-phenylethanedione (2). 1-(3,4-Dimethoxyphenyl)-2-phenylethanone was prepared from 1,2-dimethoxybenzene (13.8 g, 1.0×10^{-1} mol) and phenylacetic acid (17.0 g, 1.25×10^{-1} mol) in polyphosphoric acid (100 cm^3) by the procedure used for the preparation of 4′-(2-phenyl-1-oxoethyl)benzo-15-crown-5. The crude product was purified by distillation under reduced pressure (230 °C/0.15 mmHg(20.0 Pa)); subsequent recrystallization from methanol gave 20.0 g (78%) of the product. Mp 79—80 °C; IR(CCl_4): 1675, 1590, 1520, 1420, 1152, and 1012 cm^{-1}; NMR($CDCl_3$): δ 7.46(1H, dd, J=8 and 2 Hz), 7.42 (1H, s), 7.18(5H, m), 6.68(1H, d, J=8 Hz), 4.05(2H, s), and 3.77(6H, s).

1-(3,4-Dimethoxyphenyl)-2-phenyl-1-ethanone (12.88 g, 5.0×10^{-2} mol) was oxidized by selenium dioxide (7.0 g, 6.3×10^{-2} mol) in dioxane (70 cm^3) and water (30 cm^3) by means of the procedure used for the preparation of 4′-(2-phenyl-1,2-dioxoethyl)benzo-15-crown-5 (**1**). The product was purified by recrystallization from methanol to give 12.0 g (89%) of 1-(3,4-dimethoxyphenyl)-2-phenylethanedione (**2**). Mp 111—113 °C; Found: C, 71.42; H, 5.09%. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22%. $\lambda_{max}^{CH_3CN}$: (ε) 253(1.28×10^4), 281(1.26×10^4), and 319 nm(1.04×10^4); IR (CCl_4): 1663, 1585, 1512, 1252, and 862 cm^{-1}; NMR (CCl_4): δ 7.90(2H, m), 7.60—7.20(5H, m), 6.75(1H, d, J=8 Hz), and 3.83(6H, s).

Photoreaction of 4′-(2-Phenyl-1,2-dioxoethyl)benzo-15-crown-5 (1) in the Presence of 1-Dodecanethiol. To a solution of **1** (100 mg, 2.5×10^{-4} mol) and 1-dodecanethiol (505 mg, 2.5×10^{-3} mol) in 10 cm^3 of a mixed solvent of benzene–acetonitrile (6:4) were added varying amounts of sodium perchlorate (0.0—1.25×10^{-3} mol). The solutions, placed in Pyrex tubes, were dipped in an ultrasonic bath and bubbled with nitrogen from a syringe needle for 10 min. The solutions were then irradiated externally for 40 h with a 450-w high-pressure Hg lamp mounted in a rotary irradiation apparatus (Rikosha RH-400), the distance between the lamp and the reaction tube being *ca.* 5 cm. The reaction mixtures were condensed to *ca.* 3 cm^3, a 4-cm^3 portion of chloroform was added, and the solutions were dried over magnesium sulfate. After the removal of the drying agent and the precipitated sodium perchlorate, the solutions were condensed to *ca.* 0.5 cm^3, and a weighed amount of tetrachloroethane was added as an internal reference for the determination of the relative yields of aldehydes, benzaldehyde, and 4′-formylbenzo-15-crown-5. The results are shown in Fig. 1. Under these conditions about 35% of the starting diketone was photolyzed to give 4′-formylbenzo-15-crown-5 (**4**). The chromatography of the reaction mixture from the photolysis without sodium perchlorate on a column of silica-gel ($1.0(\phi) \times 10$ cm) removed 1-dodecanethiol as a hexane eluate and gave the product mixture as a methanol. 4′-Formylbenzo-15-crown-5 (**4**) was separated from the product mixture by preparative TLC on a silica-gel plate using a mixed solvent of chloroform–methanol (50:7); it was identical with an authentic sample prepared by a previously reported procedure.[8)]

Photolysis of 1-(3,4-Dimethoxyphenyl)-2-phenylethanedione (2) in the Presence of 1-Dodecanethiol. 1-(3,4-Dimethoxyphenyl)-2-phenylethanedione (**2**) was photolyzed in the manner used for the photolysis of the crown ether derivative (**1**). The product aldehydes, benzaldehyde, and 3,4-dimethoxybenzaldehyde (**5**), were found to be identical with authentic samples in terms of GLC results (PEG-20M on Chromosorb W, N_2, 200 °C) and their NMR spectra. Fig. 2 shows the effect of the added sodium perchlorate on the photoreactivity of **2**.

Photolysis of 4′-(2-Phenyl-1,2-dioxoethyl)benzo-15-crown-5 (1) in the Presence of Tetrabutylammonium Perchlorate. A mixture of the crown ether derivative (**1**) (2.5×10^{-2} mol dm^{-3}) and 1-dodecanethiol (2.5×10^{-1} mol dm^{-3}) was photolyzed in the presence of tetrabutylammonium perchlorate (0—8 equivalents) in the same manner as was used for the photolysis in the presence of sodium perchlorate. The results are shown in Fig. 1.

Phosphorescence from 4′-(2-Phenyl-1,2-dioxoethyl)benzo-15-crown-5 (1) and 1-(3,4-Dimethoxyphenyl)-2-phenylethanedione (2). The phosphorescence spectra were measured by means of a Hitachi EPA-4 spectrometer at 77 K in EPA (ether–isopentane–ethanol, 5:5:1). **1** and **2** show phosphorescence spectra similar in wave length (440—600 nm ($\lambda_{\max}^{\text{emiss}}$: 498 nm)) and in intensity. The addition of sodium perchlorate or tetrabutylammonium perchlorate (7 equivalents) to the dimethoxy analog (**2**) did not affect the spectrum. In contrast, the addition of sodium perchlorate to **1** (7 equivalents) gave a spectrum similar in wave length, but decreased the intensity by *ca.* 15%.

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