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The Photochemical Rearrangement of Phenyl Acetate

Haruo SHIZUKA and Toshifumi MORITA
Department of Chemistry, Gunma University, Tenjin-cho, Kiryu, Gunma

and Yuji MORI and Ikuzo TANAKA
Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

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The photochemical rearrangements of phenyl acetate and *p*-substituted phenyl acetates have been studied. The quantum yields of the rearrangements of phenyl acetate in cyclohexane were independent of the irradiation time, the concentration of phenyl acetate ($<2\times10^{-2}$ mol/*l*), the temperature (20—70°C), and the presence of piperylene (a triplet quencher) or oxygen. The quantum yields for the formations of *o*- and *p*-hydroxyl acetophenones and of phenol were 0.17, 0.15, and 0.06 respectively in cyclohexane. Comparing the quantum yields for phenyl acetate rearrangements with those for *p*-methylphenyl acetate, the quantum yields for the predissociation of the O–CO bond and the back reaction, and the recombination ratio were estimated to be 0.61, 0.23, and 0.9 respectively in cyclohexane. The relative rate constants of the back reaction and the *o*- and *p*-rearrangements were parallel to the odd π electron densities of the phenoxy radical. These results have shown that the reaction scheme of phenyl acetate in the liquid phase at 2537 Å is similar to that of acetanilide.

The photochemical reactions of phenyl esters in a solution yield products of rearrangement similar to those of the Fries reaction. Anderson and Reese[1] have reported that phenyl esters rearrange to yield *o*- and *p*-hydroxyl-aryl ketones by UV irradiation. Kobsa,[2] Finnegan and Hagen,[3] and Elad *et al.*[4] have reported similar findings on the photo-Fries-rearrangement.

In the study of the photochemical reactions of acetanilide,[5–7] it has been shown that, in the liquid phase, the photochemical rearrnagement occurs *via* the predissociation by the intersystem crossing ${}^3\sigma_0(\text{N–C})\leftarrow S_1(\pi\pi^*)$, forming anilino and acetyl radicals which recombine efficiently in a solvent cage into the original substance, *o*- and *p*- isomers. The photochemical reactions have been examined in the vapor phase and in a rigid matrix, but no photochemical rearrangement was observed in either case.[8]

The photochemical reaction of phenyl acetate has been investigated and discussed on the basis of the mechanism of the photo-Fries-rearrangement, which was established in the study of the photochemical rearrangement of acetanilide.

Experimental

The experimental procedure and solvents were similar to those previously described.[5–7] The phenyl acetate, phenol, *p*-cresol, *p*-chlorophenol, *p*-nitrophenol and *p*-hydroxyacetophenone were Tokyo Kasei Co. G. R.-grade products. The *p*-methyl, *p*-chloro, and *p*-nitrophenyl acetates were prepared by treating the corresponding *p*-substituted phenols with acetic anhydride and were purified by distillation or by recrystallization. The 2-hydroxy-5-methyl- and 2-hydroxy-5-chloroacetophenones were produced from the corresponding phenyl acetates by means of Fries reactions and were purified by repeated recrystallization.

A low-pressure mercury lamp with a Vycor glass filter was used as the 2537 Å radiation source. Actinometry was carried out in the same way as has been described in a previous paper.[5] The light intensity at 2537 Å was 9.7×10^{14} photons sec^{-1} cm^{-2}.

The flash apparatus was an ordinary one and has previously been described.[7] The fluorescence and phosphorescence were measured by Hitachi MPF-2 and Aminco Bowman Spectrophotofluorometers respectively. In these measurements, the concentrations of the solutions were so adjusted that the values of optical density were 0.600 at 2537 Å.

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[1] J. C. Anderson and C. B. Reese, *Proc. Chem. Soc. (London)*, **1960**, 217; *J. Chem. Soc.*, **1963**, 1781.

[2] H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962).

[3] R. A. Finnegan and A. W. Hagen, *Tetrahedron Letters*, **1963**, 369.

[4] D. Elad, *ibid.*, **1963**, 873; D. Elad, D. V. Rao and V. I. Stenberg, *J. Org. Chem.*, **30**, 3252(1965).

[5] H. Shizuka and I. Tanaka, This Bulletin, **41**, 2343 (1968).

[6] H. Shizuka, *ibid.*, **42**, 52 (1969).

[7] H. Shizuka, *ibid.*, **42**, 57 (1969).

[8] H. Shizuka and I. Tanaka, *ibid.*, **42**, 909 (1969).

Results and Discussion

Electronic Structures of Phenyl Acetate. Table 1 shows the near UV absorption band of para-substituted phenyl acetates, which are related to the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzene at 255 mμ and which resemble the absorption bands in the corresponding phenols (See Table 2, Figs. 2 (a), 3(a), and 4).

TABLE 1. NEAR UV ABSORPTION BANDS OF *p*-X-SUBSTITUTED PHENYL ACETATES

Substance X	λ_{max} mμ	ε_{max}
H	259	290
CH_3	266	540
Cl	269	500

Baba and Suzuki have shown that acetylation causes a blue shift and a decrease in intensity for the Band I ($^1B_2 \leftarrow {}^1A_1$) of aniline, while for Band II ($^1A_1 \leftarrow {}^1A_1$) it causes a red shift and an increase in intensity.[9] For the longest wavelength band ($^1B_2 \leftarrow {}^1A_1$) of phenol, the acetylation also causes a blue shift and a decrease in intensity. It is believed that the acetylation to the electron-donating atom (oxygen atom) surpresses the electron migration from the oxygen atom to the phenyl group, and that the electron migration to the carbonyl group results in a shift of the n–π^* band in phenyl acetate to a shorter wavelength (blue shift), as in the case of acetanilide.[6] Therefore, the n–π^* level in phenyl acetate may lie above the lowest singlet excited state, $S_1(\pi\pi^*)$; this possibility is supported by the observation of the fluorescence (Fig. 1(a)). That is, it is reasonable to assume that the fluorescence is the emission from $S_1(\pi\pi^*)$ to S_0 because of its red shift in a polar solvent. On the other

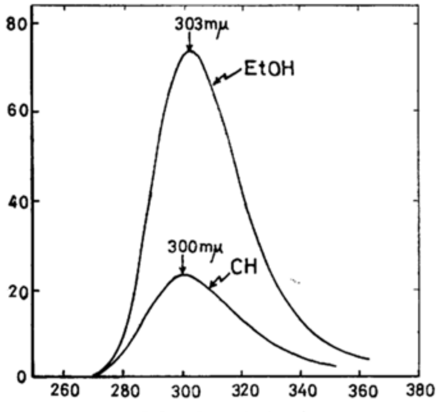

Fig. 1(a). Fluorescence spectra of phenyl acetate by the excitation at 2537 Å at room temperature.

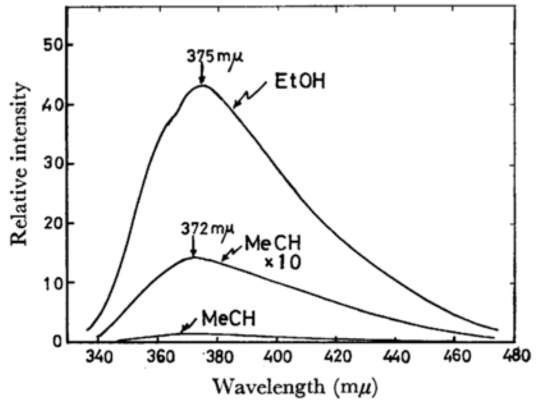

Fig. 1(b). Phosphorescence spectra of phenyl acetate by the excitation at 2537 Å at 77°K.

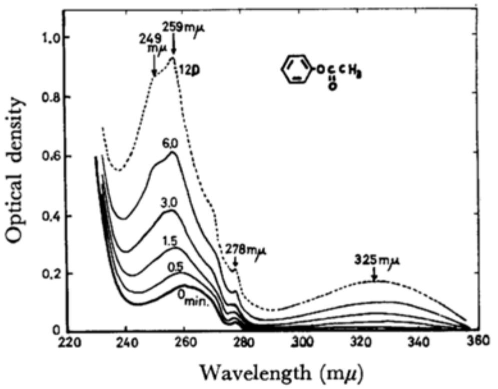

Fig. 2(a). Spectral change of cyclohexane solution of phenyl acetate with lapse of time at 2537 Å. Numbers refer to time at measurement in minutes.

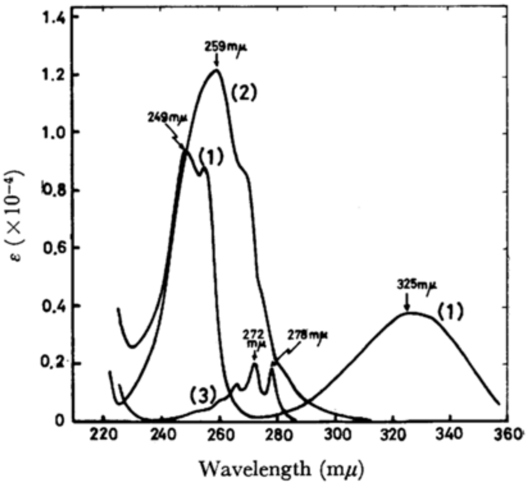

Fig. 2(b). UV absorption spectra of *o*-hydroxyacetophenone (1), *p*-hydroxyacetophenone (2), and phenol (3).

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9) H. Baba and S. Suzuki, *J. Chem. Phys.*, **32**, 1706 (1960).

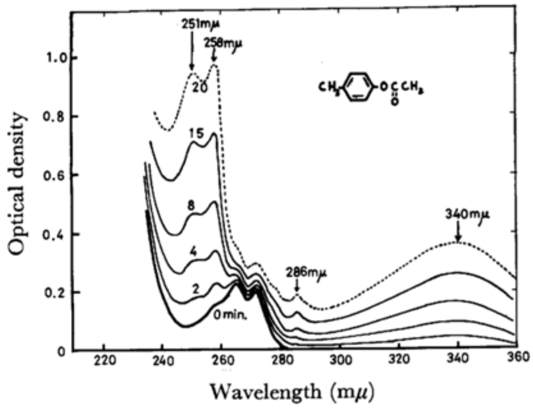


Fig. 3(a). Spectral change of cyclohexane solution of *p*-methylphenyl acetate at 2537 Å.

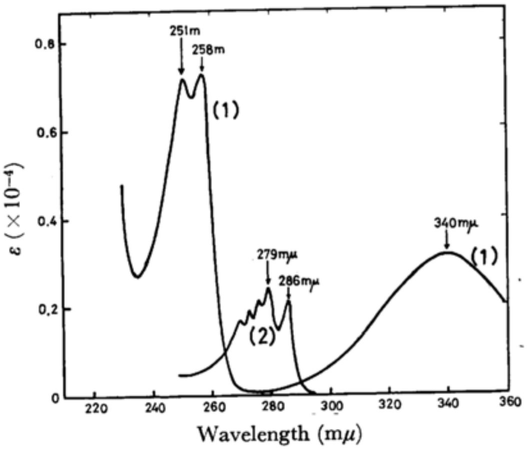


Fig. 3(b). UV absorption spectra of 2-hydroxy-5-methylacetophenone (1) and *p*-cresol (2).

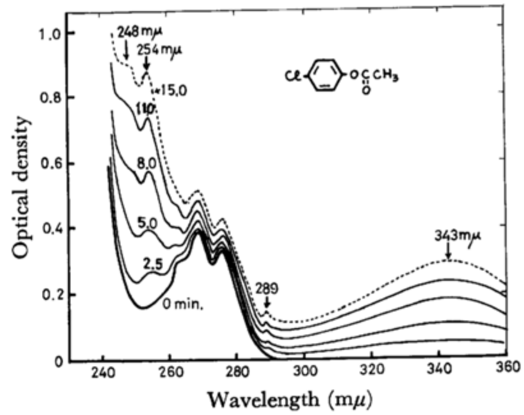


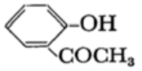
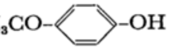
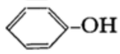
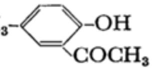
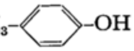
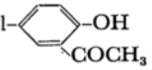
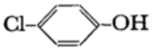
Fig. 4. Spectral change of cyclohexane solution of *p*-chlorophenyl acetate at 2537 Å.

hand, the phosphorescence which is shown in Fig. 1(b) can be assigned to the emission from the triplet state $T_1(\pi\pi^*)$ to S_0, since the phosphorescence has a long lifetime (several seconds) at 77°K.

Reaction Products. Figures 2(a), 3(a), and (4) show, respectively, the spectral changes of cyclohexane solutions of phenyl acetate, *p*-methylphenyl acetate, and *p*-chlorophenyl acetate during photolysis at 2537 Å.

The spectral change in phenyl acetate upon the irradiation at 2537 Å (Fig. 2(a)) indicates that the reaction products are *o*-hydroxyacetophenone, *p*-hydroxyacetophenone, and phenol, the absorption spectra of all of which have been measured (Fig. 2(b)). The spectral change in *p*-methylphenyl acetate indicates that not a *p*-rearrangement but an *o*-rearrangement product is obtained, plus *p*-cresol, as is shown in Fig. 3(a); Fig. 3(b) shows the absorption spectrum of each of the reaction products. The photochemical reaction of *p*-chlorophenyl acetate is similar to that of *p*-methylphenyl acetate (Fig. 4). Scarcely no spectral change was observed in an ethanol solution of *p*-nitrophenyl acetate. The substituted nitro group has an intramolecular quenching action.[7,10,11] The quantum yields for the formation of these photochemical products were measured spectrophotometrically. The molar extinction coefficients of the photochemical products are summarized in Table 2.

TABLE 2. MOLAR EXTINCTION COEFFICIENTS[a)]

Substance	λ mμ	ε(×10⁻⁴)
 -OH COCH$_3$	249 325	0.927 0.374
CH$_3$CO-  -OH	259	1.22
 -OH	272 278	0.199 0.189
CH$_3$-  -OH COCH$_3$	258 340	0.731 0.308
CH$_3$-  -OH	286	0.211
Cl-  -OH COCH$_3$	254 343	0.429 0.235
Cl-  -OH	289	0.178

a) In a cyclohexane solution.

Effect of Irradiation Time, Concentration, Oxygen, Temperature, Solvent, and Triplet Quencher on Quantum Yields. The quantum yields were measured under various conditions; the results are shown in Fig. 5 and in Table 3. The quantum yields for the product formations from phenyl acetate in cyclohexane at 2537 Å did not

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10) I. Tanaka, Y. Mori, *et al.*, presented at the Symposium on Electronic State, Osaka, Oct., 1966.

11) H. Kokubun and M. Kobayashi, presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

TABLE 3. QUANTUM YIELDS FOR THE PRODUCT FORMATIONS OF *p*-X-SUBSTITUTED PHENYL ACETATES AT 2537 Å

X	Solvent	Quantum yield (Φ) Φ_o	Φ_p	Φ_{OH}
H	Cyclohexane (aerated)	0.17	0.15	0.06
	Cyclohexane (degassed)	0.17	0.15	0.06
	Ethanol (aerated)	0.14	0.13	*
	Ethanol (degassed)	0.14	0.13	*
	Water (aerated)	0.09	0.08	*
CH_3	Cyclohexane (aerated)	0.23	0	0.07
	Ethanol (aerated)	0.20	0	*
Cl	Cyclohexnae (aerated)	0.26	0	0.08
	Ethanol (aerated)	0.22	0	*

Φ_o, Φ_p, and Φ_{OH} are the quantum yields for the formation of *o*- and *p*-rearrangements and *p*-X-phenol respectively.

* denotes that the quantum yield for the formation of *p*-X-phenol could not be observed spectrophotometrically because of the overlapping of the absorption spectra.

change with the variation in the irradiation time and the concentration of phenyl acetate ($<2\times10^{-2}$ mol/*l*), as is shown in Figs. 5(a) and (b). Dissolved oxygen had no effect on the quantum yields, as is shown in Table 3. The addition of piperylene as a triplet quencher (E_T=2.48 eV)5,12,13) did not affect the quantum yields of this isomerization in concentration from 10^{-4} up to 10^{-2} mol/*l*, as is shown in Fig. 5(d). There was scarcely no effect of the temperature (20—70°C) on the quantum yields of phenyl acetate photoisomerization (Fig. 5(c)), though a small temperature effect has been observed in the case of acetanilide.7) This difference may be due to the fact that the intersystem crossing, ${}^3\sigma_0(O\leftarrow CO)\leftarrow S_1(\pi\pi^*)$, in phenyl acetate is quite rapid in comparison with that in acetanilide. The very small effect of the temperature on the quantum yields for phenyl acetate rearrangements is due to the high quantum yield for the predissociation of phenyl acetate, as will be described later. Of course, the effect of the temperature on the quantum yield at low temperatures (*e. g.*, at the temperature of liquid nitrogen) may be expected because of the increasing stiffness of the solvent cage at low temperatures, as has been described in a previous paper.8)

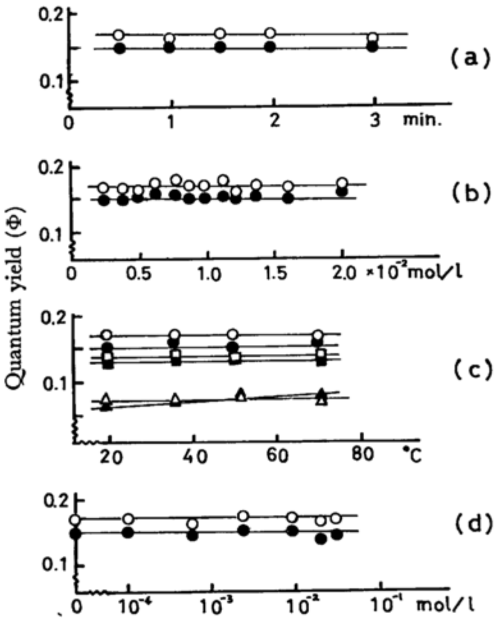

Fig. 5. Dependence of quantum yeild.

(a) on irradiation time at 20°C with initial concentration of 8.5×10^{-3} mol/*l*.
(b) on concentration at 20°C
(c) on temperature
(d) on addition of piperylene

Φ of *o*-hydroxyacetophenone;
○ in cyclohexane, □ in EtOH, △ in water
Φ of *p*-hydroxyacetophenone;
● in cyclohexane, ■ in EtOH, ▲ in water

The quantum yields decreased in polar solvents, as is shown in Table 3. However, the variation in the rearrangement quantum yields on solvents were smaller than that of acetanilide.6) This may be due to the fact that phenyl acetate has no hydrogen atom to form a hydrogen-bond with a proton acceptor.

The features of the lowest excited singlet state and of the photochemical reaction of phenyl acetate are very close to those of acetanilide.5–7) Its reaction mechanism involves the predissociation to phenoxy and acetyl radicals and subsequent recombination reactions between the pair radicals in a solvent cage.

Estimations of Back Reaction and Predissociation Quantum Yields. The recombination reaction between pair radicals consists of a back reaction and of *o*- and *p*-rearrangements in a solvent cage. These reactions have been shown in the photochemical rearrangement of acetanilide.7) The quantum yield for the back reaction (Φ_B) and the predissociation (Φ_{dis}) were estimated by the method described in a previous paper.7)

In the first approximation, the photochemical primary process in *p*-methylphenyl acetate is the same as that in phenyl acetate, because the UV absorption spectrum of *p*-methylphenyl acetate is similar to that of phenyl acetate. Therefore, Eq. (1) is given on the basis of the same assumption as was presented in a previous paper;7)

$$\Phi^{H}_{dis} \approx \Phi^{CH_3}_{dis} \tag{1}$$

Blocked by a methyl group at the *p*-position of the phenoxyl radical, *p*-rearrangement can not occur.

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12) P. E. Eaton and W. S. Hurt, *J. Am. Chem. Soc.*, **88**, 5038 (1966).

13) E. Y. Y. Lam, D. Valentine and G. S. Hammond, *ibid.*, **89**, 3482 (1967).

Thus, the values of quantum yields for the back reaction (Φ_B), the *o*-rearrangement (Φ_o), and the *p*-methylphenol formation increase.

$$\varDelta\Phi_o = \Phi_o^{\mathrm{CH_3}} - \Phi_o^{\mathrm{H}} = 0.06 \tag{2}$$

$$\varDelta\Phi_B = \Phi_\Sigma^{\mathrm{H}} - \Phi_\Sigma^{\mathrm{CH_3}} = 0.08 \tag{3}$$

$$\varDelta\Phi_{\mathrm{OH}} = \Phi_{\mathrm{OH}}^{\mathrm{CH_3}} - \Phi_{\mathrm{OH}}^{\mathrm{H}} = 0.01 \tag{4}$$

where:

$$\Phi_\Sigma^{\mathrm{H}} = \Phi_o^{\mathrm{H}} + \Phi_p^{\mathrm{H}} + \Phi_{\mathrm{OH}}^{\mathrm{H}},\ \Phi_\Sigma^{\mathrm{CH_3}} = \Phi_o^{\mathrm{CH_3}} + \Phi_p^{\mathrm{CH_3}} + \Phi_{\mathrm{OH}}^{\mathrm{CH_3}}$$

The ratio of Φ_B to 1/2 Φ_o is given approximately by:

$$\frac{\Phi_B}{\frac{1}{2}\Phi_o} \approx \frac{\varDelta\Phi_B}{\frac{1}{2}\varDelta\Phi_o} = 2.7 \tag{5}$$

Therefore, the values of Φ_B and Φ_{dis} may be evaluated as follows:

$$\left.\begin{aligned} \Phi_B^{\mathrm{H}} &= \frac{1}{2}\Phi_o^{\mathrm{H}} \times 2.7 \approx 0.23 \\ \Phi_{dis}^{\mathrm{H}} &= \Phi_B^{\mathrm{H}} + \Phi_\Sigma^{\mathrm{H}} \approx 0.61 \end{aligned}\right\} \tag{6}$$

and:

$$\left.\begin{aligned} \Phi_B^{\mathrm{CH_3}} &= \frac{1}{2}\Phi_o^{\mathrm{CH_3}} \times 2.7 \approx 0.31 \\ \Phi_{dis}^{\mathrm{CH_3}} &= \Phi_B^{\mathrm{CH_3}} + \Phi_\Sigma^{\mathrm{CH_3}} \approx 0.61 \end{aligned}\right\} \tag{7}$$

Also, the values of Φ_B^{Cl} and Φ_{dis}^{Cl} are estimated to be 0.35 and 0.69 respectively. The quantum yields for the back reaction and the predissociation are summarized in Table 4.

TABLE 4. QUANTUM YIELDS FOR THE BACK REACTION (Φ_B) AND THE PREDISSOCIATION (Φ_{dis}) OF *p*-X-SUBSTITUTED PHENYL ACETATE AT 2537 Å

Substance X	Quantum yield (Φ) Φ_Σ	Φ_B	Φ_{dis}
H	0.38	0.23	0.61
$\mathrm{CH_3}$	0.30	0.31	0.61
Cl	0.34	0.35	0.69

The quantum yield for the predissociation of phenyl acetate is quite large in comparison with that of acetanilide (~0.25).⁷⁾ This means that the intersystem crossing probability for the predissociation of phenyl acetate is larger than that of acetanilide.

The recombination ratios (β) are obtained from Eq. (8):

$$\left.\begin{aligned} \beta_{\mathrm{H}} &= \frac{\Phi_o^{\mathrm{H}} + \Phi_p^{\mathrm{H}} + \Phi_B^{\mathrm{H}}}{\Phi_{dis}^{\mathrm{H}}} = 0.90 \\ \beta_{\mathrm{CH_3}} &= \frac{\Phi_o^{\mathrm{CH_3}} + \Phi_B^{\mathrm{CH_3}}}{\Phi_{dis}^{\mathrm{CH_3}}} = 0.89 \\ \beta_{\mathrm{Cl}} &= \frac{\Phi_o^{\mathrm{Cl}} + \Phi_B^{\mathrm{Cl}}}{\Phi_{dis}^{\mathrm{Cl}}} = 0.88 \end{aligned}\right\} \tag{8}$$

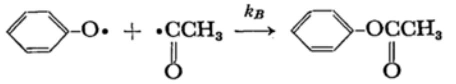
These high recombination ratios ($\beta = \sim 0.9$) indicate that the recombination reactions between phenoxy and acetyl radicals occur efficiently in a solvent cage, as do those in the photochemical rearrangement of acetanilide.⁷⁾

No intermediate absorption was observed by means of the flash technique. The absorptions of the products appeared immediately after the flash.

From these results, the photochemical secondary processes of phenyl acetate can be given as follows:

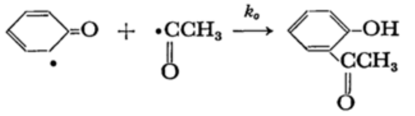
1) Recombination reaction (Main reaction)

a) Back reaction



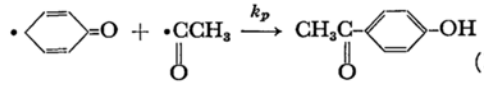
(9)

b) *o*-rearrangement



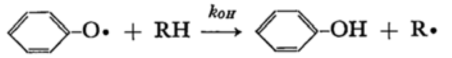
(10)

c) *p*-rearrangement



(11)

2) Hydrogen atom abstraction reaction



(12)

where k_B, k_o, and k_p are the rate constants of the back reaction, the *o*-rearrangement, and the *p*-rearrangement respectively, and where RH is a solvent molecule.

The rate constants (k_B, k_o, and k_p) for the recombination reactions between the pair radicals in a solvent cage will be proportional to the odd π electron distributions (δ) of the phenoxy radical which were obtained by Müller *et al.*¹⁴⁾ (Fig. 6).

Fig. 6. Odd π electron distributions of the phenoxy radical.

$$k_B : k_o : k_p = \Phi_B : \frac{1}{2}\Phi_o : \Phi_p \tag{13}$$

$$= 1 : 0.37 : 0.65$$

$$\delta_7 : \delta_2 : \delta_4 = 1 : 0.35 : 0.69 \tag{14}$$

$$k_B : k_o : k_p \approx \delta_7 : \delta_2 : \delta_4 \tag{15}$$

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14) E. Müller, A. Rieker and K. Scheffer, *Liebigs Ann.*, **645**, 92 (1961).

From these results, it can be said that the photochemical reaction of phenyl acetate can be explained by a mechanism similar to that for acetanilide presented in previous papers.[5-7]

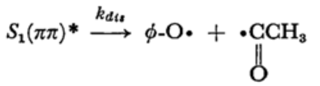
In conclusion, the reaction scheme of phenyl acetate at 2537 Å in the liquid phase is as follows:

$$S_0 + h\nu \longrightarrow S_1(\pi\pi^*)(^1B_2) \qquad (16)$$

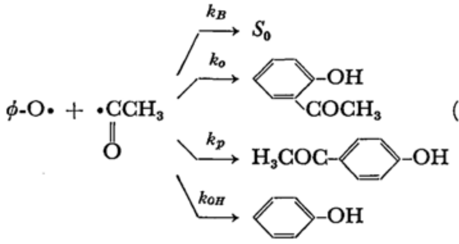
$$S_1(\pi\pi^*) \xrightarrow{k_s} S_0 \qquad (17)$$

$$S_1(\pi\pi^*) \xrightarrow{k_F} S_0 + h\nu' \qquad (18)$$

$$S_1(\pi\pi^*) \xrightarrow{k_c} T_1(\pi\pi^*) \qquad (19)$$



$$S_1(\pi\pi)^* \xrightarrow{k_{dis}} \phi\text{-O}\cdot + \cdot\underset{\underset{\displaystyle O}{\|}}{C}CH_3 \qquad (20)$$



(21)