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Photochemistry of Acetanilide. I. Quantum Yields of the Rearrangement and Benzene Photosensitized Reaction

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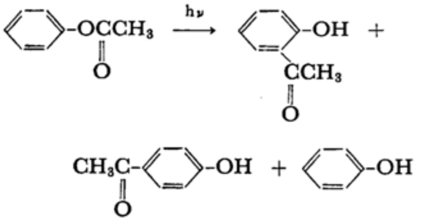
The photochemical rearrangement of acetanilide under 2537 Å irradiation has been studied by spectrophotometry. The quantum yield of the rearrangement in cyclohexane solution was independent of the irradiation time, concentration of acetanilide, presence of oxygen and light intensity. It was found that electronic energy transfer from the electronically excited benzene to acetanilide occurred in the mixed solution, and the transfer mechanism was explained by singlet-singlet nonradiative energy transfer. It was observed that the energy transfer rate constant was about 22 times greater than that predicted by diffusion theory (the transfer rate constant, $k_3=1.45\times10^{11}\ l\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$). From these studies, it is proposed that the rearrangement of acetanilide is an introamolecular reaction and does not occur from the triplet state but from the lowest singlet excited state.

It is known that organic carbonyl compounds give rise photochemically to many interesting reactions; abstraction, rearrangement, addition, dimerization and decomposition.

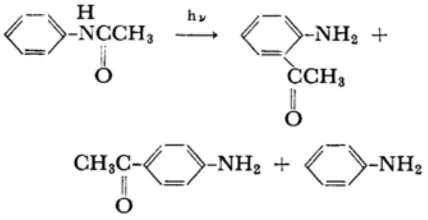
The photochemical reactions of phenyl esters in solution yield products of rearrangement similar to those of the Fries reaction. Hence, this rearrangment is termed the photo-Fries-rearrangement.

Anderson and Reese2) reproted that phenyl esters rearrange to yield *ortho*-hydroxyl aryl ketones as well as *para* isomers by irradiation with UV light, as indicated by Eq. (1).



(1)

Kobsa3) and Finnegan *et al.*4) reported similar findings. Elad and coworkers reported the photochemical reaction of anilide, another carbonyl derivative.5)



(2)

Kobsa suggested a mechanism for the photo-Fries-reaction involving homolysis of the phenyl ester into a free-radical pair, held together in a solvent cage, with subsequent rearrangement.3) However, little mechanistic work on the photo-Fries-rearrangement has been reported.

On the other hand, a molecular-orbital calculation has been carried out to determine the π-electronic structure of acetanilide.6) The subject of electronic energy transfer between unlike molecules in solution through a resonance interaction has received considerable interest.7-15) The study of electronic energy transfer is very useful for investigating the role of excited states in photochemical

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2) J. C. Anderson and C. B. Reese, a) *Proc. Chem. Soc. (London)*, **1960**, 217; b) *J. Chem. Soc.*, **1963**, 1781.

3) H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962).

4) R. A. Finnegan and A. W. Hagen, *Tetrahedron Letters*, **1963**, 365.

5) a) D. Elad, *ibid.*, **1963**, 873; b) D. Elad, D. V. Rao and V. I. Stenberg, *J. Org. Chem.*, **30**, 3252 (1965).

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

7) Th. Förster, *Ann. Physik*, **2**, 55 (1948).

8) Th. Förster, *Discussions Faraday Soc.*, **27**, 7 (1959).

9) Th. Förster, a) *Z. Elektrochem.*, **53**, 93 (1949); b) *Z. Naturforschung*, **4**, 321 (1949); c) *Trans. Faraday Soc.*, **51**, 774 (1955).

10) W. F. Watson and R. Livingston, *J. Chem. Phys.*, **18**, 802 (1950).

11) E. J. Bowen and B. Brocklehurst, *Trans. Faraday Soc.*, **49**, 1131 (1953).

12) E. J. Bowen and R. Livingston, *J. Am. Chem. Soc.*, **76**, 6300 (1954).

13) W. R. Ware, *ibid.*, **83**, 4374 (1961).

14) J. B. Birks and K. N. Kuchela, *Proc. Phys. Soc. (London)*, **77**, 1083 (1961).

15) D. W. Ellis and B. S. Solomon, *J. Chem. Phys.*, **46**, 3497 (1967).

reactions. It is very interesting to elucidate the correlation between the photochemical reaction and the electronically excited state for acetanilide through photosensitization by benzene in the liquid phase. The photosensitizations by benzene have been studied in the gas phase.[16-19]

This paper reports measurements of quantum yields under various conditions and the mechanism of electronic energy transfer from the excited benzene to acetanilide, in order to make clear the mechanism of the photo-Fries-rearrangement.

Experimental

Materials. Acetanilide was a Tokyo Kasei Co. G. R. grade product and was purified by repeated recrystallization from water. *o*-Amino acetophenone, *p*-amino acetophenone and piperylene were Tokyo Kasei Co. G. R. grade products. Benzene was a Kokusan Chemical Works Ltd. G. R. grade product and was purified by vapor-phase chromatography. Cyclohexane was a Nichiri Co. reagent grade product and was purified by passage through silicagel and by distillation.

Light Source. A low pressure mercury resonance lamp containing neon was used as the 2537 Å radiation source with a Vycor glass filter.

Light Intensity Measurement. Actinometry was carried out in a reaction cell (quartz) using a ferric oxalate actinometer solution. The light intensity at 2537 Å was determined by the difference in light intensities with and without the benzene solution filter which cut off the wavelengths below 2700 Å. In the case of benzene photosensitization, a reaction cell of 1 cm length was used and the light intensity (I_0) at 2537 Å was 9.7×10^{14} photons·sec^{-1}·cm^{-2}.

Analysis. The amounts of *o*-amino acetophenone and *p*-amino acetophenone produced by the photochemical reaction were determined spectrophotometrically. Ultraviolet absorption spectra at room temperature were taken with Hitachi 139 and Hitachi EPS 2 spectrophotometers.

Results and Discussion

Reaction Products. The spectrum of the solution of acetanilide changed markedly upon irradiation with 2537 Å light as shown in Fig. 1. Absorption Band II (240 mμ) of acetanilide decreased and new bands with maxima at 225, 287 and 355 mμ appeared as the irradiation time increased, with two isosbestic points at 233 and 255 mμ. The reaction products corresponded to *o*-amino acetophenone (absorption peaks 225 and 355 mμ) and *p*-amino acetophenone (absorption peaks 224 and 287 mμ) as shown in Table 1.

Therefore, quantum yields of *o*-amino acetophenone, *p*-amino acetophenone and the disappearance of acetanilide were measured spectrophotometrically. The samll amount of aniline which was produced from the primary process of the photochemical reaction for acetanilide[5] could not be directly determined by means of the

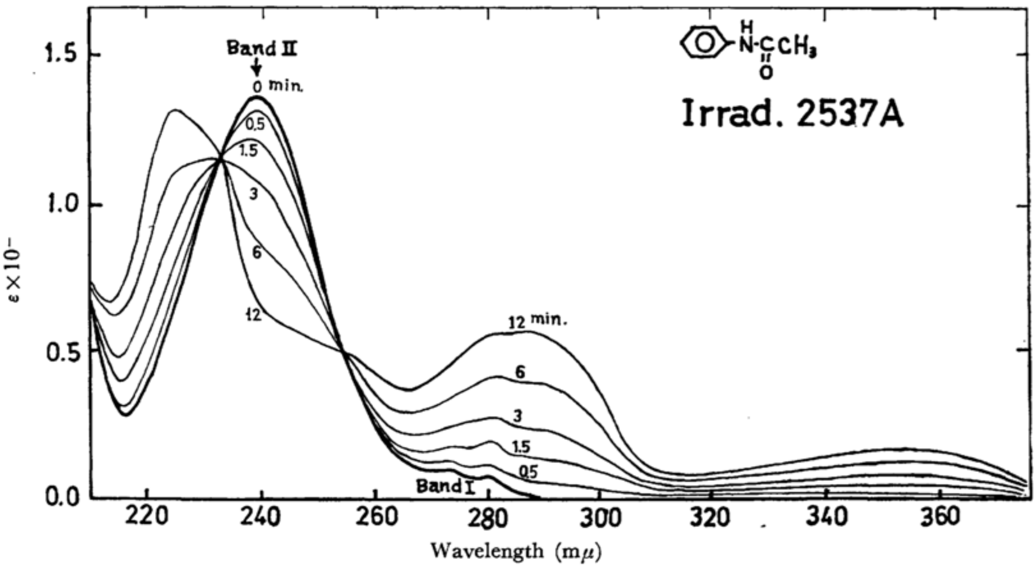

Fig. 1. Spectral change of acetanilide in cyclohexane solution with lapse of time at room temperature by irradiation with 2537 Å light. Numbers refer to time at measurement in minutes.

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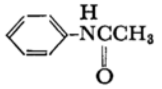
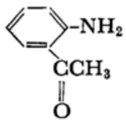
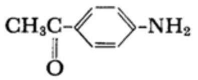
16) H. Ishikawa and W. A. Noyes, *ibid.*, **37**, 583 (1962).

17) R. B. Cundall, F. J. Fletcher and D. G. Milne, a) *Trans. Faraday Soc.*, **60**, 1146 (1964); b) *J. Chem. Phys.*, **39**, 3536 (1963).

18) S. Sato, K. Kikuchi and M. Tanaka, *J. Chem. Phys.*, **39**, 239 (1963).

19) a) E. K. C. Lee and N. W. Lee, *J. Phys. Chem.*, **71**, 1167 (1967); b) E. K. C. Lee, *ibid.*, **71**, 2804 (1967).

TABLE 1. MOLAR DECADIC EXTINCTION COEFFICIENTS[a)]

Substance	λ mμ	$\varepsilon \times 10^{-4}$
	240 274	1.36 0.093
	225 355	2.84 0.53
	224 287	1.12 2.00

a) In cyclohexane solution

spectrophotometric method, because of the overlapping acetanilide, *o*-amino acetophenone and *p*-amino acetophenone spectra.

Effect of Irradiation Time, Concentration, Oxygen, and Light Intensity on Quantum Yields. Quantum yields were obtained under various conditions (Fig. 2). The quantum yields of the rearrangement in cyclohexane did not change with variation in irradiation time, concentration of acetanilide and light intensity (Fig. 2 a, b and d). The effect of oxygen dissolved in the solution on the quantum yield was probably absent because there was no difference in quantum yields between an aerated solution and one deaerated by flushing with nitrogen at room temperature (Fig. 2c) The quantum yields of *o*-amino acetophenone and *p*-amino acetophenone in cyclohexane solution at 20°C were 0.07 and 0.06, respectively. The quantum yield of the disappearance of acetanilide was about 0.15. The addition of piperylene as a triplet quencher ($E_T \sim 2.48$ eV)[20)] did not affect the quantum yield of this isomerization in a concentration range 10^{-4} to 10^{-2} mol/*l* (Fig. 2e).

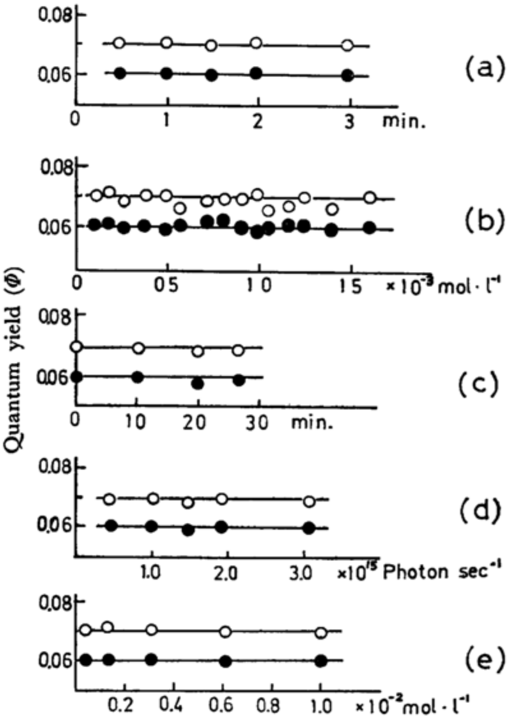


Fig. 2. Dependence of quantum yield in cyclohexane solution.
(a) On irradiation time at 20°C with initial concentration of 9.48×10^{-4} mol/*l*
(b) On concentration at 20°C
(c) On deaeration by flushing with nitrogen at room temperature
(d) On light intensity at 20°C
(e) On addition of piperylene
○…Φ of *o*-amino acetophenone
●…Φ of *p*-amino acetophenone

From these results, it is assumed that acetanilide does not react from the triplet state $T_1(\pi-\pi^*)$. The photochemical rearrangement of acetanilide may be an intramolecular reaction in dilute solutions ($<\sim 10^{-3}$ mol/*l*) as suggested for phenyl acetate by Anderson and Reese.[2)] However, it has been reported that an intermolecular reaction occurred in the rearrangement of acetanilide.[5a)] It is though that the intermolecular reaction occurs at high concentrations.

Energy Transfer from the Electronically Excited Benzene to Acetanilide. The photosensitization has been studied quantitatively in a cyclohexane solution at room temperature through a determination of the relative rate R/R_0 of product formation, varying the concentrations of benzene and acetanilide, where R and R_0 are the reaction rates with and without benzene in acetanilide solution, respectively. The reaction rates of the

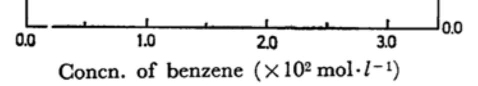


Fig. 3. Plot of R/R_0 against the concentration of benzene. Acetanilide concentration is 5.22×10^{-5} mol/*l* in cyclohexane. Dotted line denotes plot of I_A/I_{A0} against the concentration of benzene.
○…*o*-amino acetophenone} open air
●…*p*-amino acetophenone}
⦶…*o*-amino acetophenone} N_2 saturated
◐…*p*-amino acetophenone}

[20)] a) P. E. Eaton, W. S. Hurt, *J. Am. Chem. Soc.*, **88**, 5038 (1966); b) E. Y. Y. Lam, D. Valentine and G. S. Hammond, *ibid.*, **89**, 3482 (1967).

product formations (*o*-amino acetophenone and *p*-amino acetophenone) were measured spectrophotometrically. Figure 3 shows the dependences of the relative rates R/R_0 on the concentration of benzene in aerated or deaerated cyclohexane solutions. An effect of dissolved oxygen ($\sim 10^{-3}$ mol/l) was not observed within the experimental error as shown in Fig. 3. An increase in the rate of rearrangement could not be detected even in a carefully degassed solution. This could be explained by the fact that the maximum rate of the quenching reaction by dissolved oxygen of 10^{-3} mol/l was about one tenth of the overall deactivation rate of the excited singlet benzene ($^1B_{2u}$), considering it to be diffusion controlled, as is discussed later. Figure 4 shows the dependence of the relative rate R/R_0 on the concentration of acetanilide. The energy transfer efficiency γ from the excited benzene to acetanilide was calculated from the following equation;

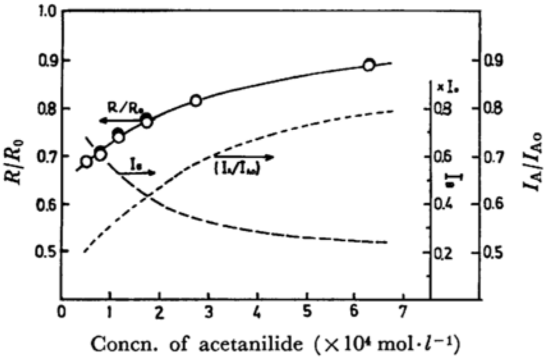


Fig. 4. Plot of R/R_0 against the concentration of acetanilide. Benzene concentration is 5.4×10^{-3} mol/l in cyclohexane. Dotted line denotes plot of I_A/I_{A0} and broken line denotes plot of I_B against the concentration of benzene, respectively.

○···*o*-amino acetophenone } open air
●···*p*-amino acetophenone }

$$\gamma = \frac{I_\Sigma - I_A}{I_B} \tag{3}$$

where

$$I_\Sigma = \frac{R}{R_0} I_{A0} \tag{4}$$

and I_{A0} is the light intensity absorbed by acetanilide in the absence of benzene, which was determined experimentally, I_A and I_B are the light intensities absorbed by acetanilide and by benzene in the mixed solution, respectively, which have been calculated using Beer's law. Figure 5(a) or 6(a) shows the transfer efficiency γ as a function of the concentration of benzene (donor) or of acetanilide (acceptor), respectively. It seems that the excited state of benzene for this energy transfer should be the lowest singlet excited state ($^1B_{2u}$) since the effect of dissolved oxygen on the photosensitization was absent as shown in Fig. 5(a). If the energy transfer had occurred from the triplet state of benzene ($^3B_{1u}$), the reaction rate of an aerated solution would be small in comparison with that in a deaerated solution.

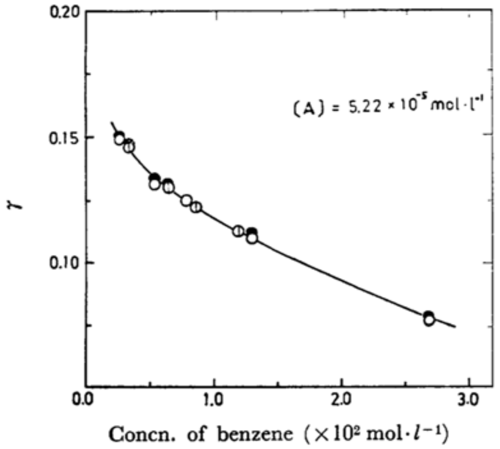


Fig. 5(a). The dependence of the transfer efficiency γ on the concentration of benzene.

○···*o*-amino acetophenone } open air
●···*p*-amino acetophenone }
⦶···*o*-amino acetophenone } N_2 saturated
◐···*p*-amino acetophenone }

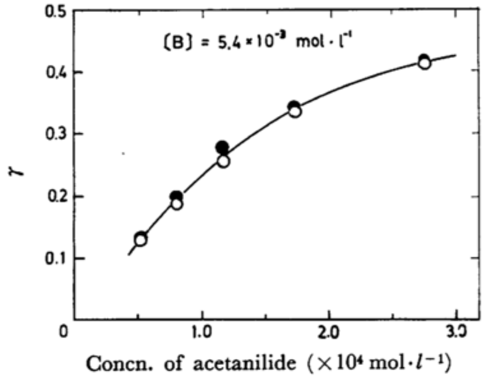


Fig. 6(a). The dependence of the transfer efficiency γ on the concentration of acetanilide.

○···*o*-amino acetophenone } open air
●···*p*-amino| acetophenone }

The characteristics of the lower excited state of benzene and acetanilide are summarized in Table 2. If energy considerations are kept in mind, the following reactions may occur when benzene molecules absorb radiation at 2537 Å in the mixed solution;

$$\begin{tikzcd}
B^* \arrow[r, "k_3", "(+A)"'] \arrow[d, shift left, "k_1"'] \arrow[d, shift left=4, "k_2", "(+B)"'] & A^* \arrow[r, "\Phi"] & \text{Reaction product} \\
B \arrow[u, shift left=2, "h\nu"] & & k_1 = k_B{}^c + k_B{}^s + k_B{}^f
\end{tikzcd}$$

$$B \xrightarrow{h\nu} B^* \tag{5}$$

TABLE 2. ENERGIES, OSCILLATOR STRENGTHS AND WAVE FUNCTIONS FOR LOWER EXCITED STATES OF BENZENE AND ACETANILIDE

	Symmetry	Observed excitation energy, eV	Observed oscillator strength	Wave function	Band assignment
Benzene[a]	$^1B_{2u}(D_{6h})$	4.88	0.0014	$1/2(V_{24}-V_{35})$	I
Acetanilide[b]	$^1B_2(C_{2v})$	4.53_2	0.01	$0.481V_{24}$ $-0.875V_{35}$	I
	$^1A_1(C_{2v})$	5.18_3	0.28	V_{34}	II

a) See Ref. 21.
b) See Ref. 6.

$$B^* \xrightarrow{k_B{}^c} B_T \tag{6}$$

$$B^* \xrightarrow{k_B{}^s} B \tag{7}$$

$$B^* \xrightarrow{k_B{}^f} B + h\nu' \tag{8}$$

$$B^* + B \xrightarrow{k_2} 2B \tag{9}$$

$$B^* + A \xrightarrow{k_3} B + A^* \tag{10}$$

where B and A are the ground states of benzene and acetanilide, respectively, B* is the excited singlet state of benzene ($^1B_{2u}$), B_T the lowest triplet state of benzene ($^3B_{1u}$), A* the lowest singlet excited state of acetanilide ($^1B_2$) and Φ the quantum yield of the product. Then, using a steady-state treatment, the following equations are obtained.

$$[B^*] = \frac{I_B}{k_1 + k_2[B] + k_3[A]} \tag{11}$$

$$\gamma = \frac{k_3[B^*][A]}{I_B} = \frac{k_3[A]}{k_1 + k_2[B] + k_3[A]} \tag{12}$$

The transfer efficiency γ decreased as the concentration of benzene increased (Fig. 5(a) and Eq. (12)), due to self-quenching (Eq. (9)). On the other hand, γ increased when the concentration of the acceptor (acetanilide) increased, as shown in Fig. 6(a) and Eq. (12).

Equation (13) is derived from Eq. (12),

$$\frac{1}{\gamma} = \frac{k_1 + k_2[B]}{k_3[A]} + 1 \tag{13}$$

Figure 5(b) shows that the results corresponding to Eq. (13) are well represented by a linear plot of $1/\gamma$ *vs.* [B], where $[A]=5.22\times 10^{-5}$ mol/l. From the slope and intercept of the plot shown in Fig. 5(b), k_2 and k_3 can be obtained.

$$\frac{k_2}{k_3[A]} = 2.3\times 10^2\ l/\text{mol}$$

$$\frac{k_1}{k_3[A]} + 1 = 6.1$$

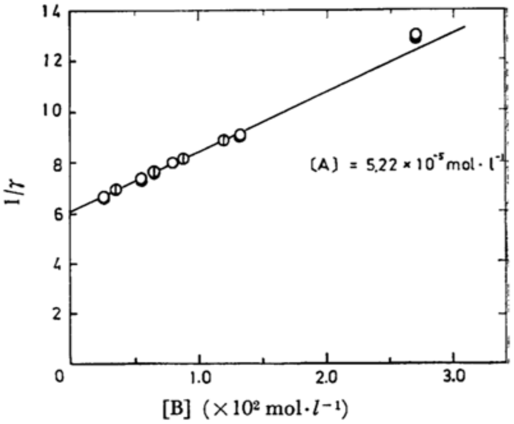


Fig. 5(b). Plot of $1/\gamma$ against the concentration of benzene.

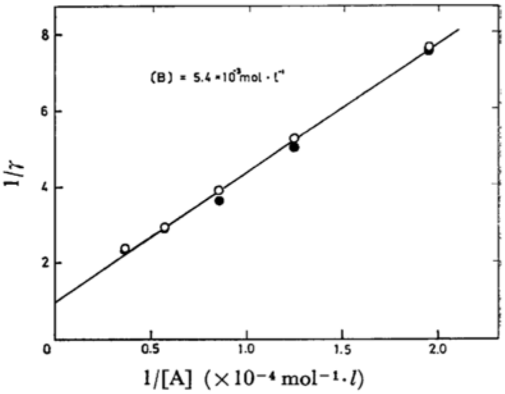


Fig. 6(b). Plot of $1/\gamma$ against the reciprocal of acetanilide concentration.

$$k_2 = 4.51 \times 10\ \ k_1\ l/\text{mol} \tag{14}$$

$$k_3 = 3.76 \times 10^3\ k_1\ l/\text{mol} \tag{15}$$

Figure 6(b) shows that the results corresponding to Eq. (13) give also good linearity of $1/\gamma$ *vs.* 1/[A], where $[B]=5.4\times 10^{-3}$ mol/l. The slope of the plot in Fig. 6(b)

$$\frac{k_1 + k_2[B]}{k_3} = 3.35 \times 10^{-4}\ \text{mol}/l \tag{16}$$

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21) H. B. Klevens and J. R. Platt, Tech. Rept., Laboratory of Molecular Structure and Spectra, University of Chicago, Part 1, p. 145 (1953—1954).

From Eqs. (14) and (15), Eq. (17) is derived

$$\frac{k_1+k_2[\mathrm{B}]}{k_3}=\frac{k_1+4.51\times 10k_1\times 5.4\times 10^{-3}}{3.76\times 10^3\times k_1}$$
$$=3.32\times 10^{-4}\ \mathrm{mol}/l \qquad (17)$$

These two values of the slope which are derived in different ways are in good agreement.

From the work of Ivanova *et al.*,[22] the lifetime of the benzene singlet excited state ($^1\mathrm{B}_{2u}$) in the absence of acetanilide is given by

$$\tau_{\mathrm{B}}=\frac{1}{k_1}=2.6\times 10^{-8}\ \mathrm{sec}$$
$$k_1=3.85\times 10^7\ \mathrm{sec}^{-1} \qquad (18)$$

Therefore, the self-quenching rate constant k_2 and the energy transfer rate constant k_3 are calculated from Eqs. (14) and (15), respectively.

$$k_2=1.74\times 10^9\ l\cdot\mathrm{mol}^{-1}\,\mathrm{sec}^{-1} \qquad (14')$$
$$k_3=1.45\times 10^{11}\ l\cdot\mathrm{mol}^{-1}\,\mathrm{sec}^{-1} \qquad (15')$$

It is interesting to note that the value of k_3 in this experiment is close to the 1.4—$2.5\times 10^{11}\ l\cdot\mathrm{mol}^{-1}\cdot\mathrm{sec}^{-1}$ obtained by Bowen and Livingston[12] for the mixture of anthracene derivatives and perylene (or rubrene) at room temperature in various solvents.

The rate constant of a diffusion-controlled bimolecular reaction is represented approximately by the modified Debye equation.[23,24]

$$k_{\mathrm{D}}=\frac{8\boldsymbol{RT}}{3000\eta} \qquad (19)$$

where k_{D} is in units of $l\mathrm{mol}^{-1}\mathrm{sec}^{-1}$ when η, the viscosity of the solvent, is in units of poise.

The value of k_{D} corresponding to cyclohexane at 20°C is $6.6\times 10^9\ l\cdot\mathrm{mol}^{-1}\cdot\mathrm{sec}^{-1}$.[25] The empirical value of the rate constant k_2 corresponding to the self-quenching of benzene might not exceed the value of k_{D}. In contrast to this, the energy transfer rate constant k_3 is about 22 times greater than the value of k_{D}.

The possibility that complex formation between benzene and acetanilide is responsible for this energy transfer was shown to be unlikely by the fact that the spectral intensities and the positions of the mixed solution were identical with those of the separate solutions as shown in Fig. 7.

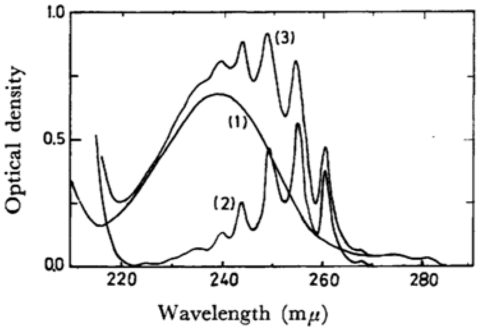

Fig. 7. Absorption curves of CH soln's of acetanilide, benzene and their mixture.
(1) Acetanilide $5.0\times 10^{-5}\ \mathrm{mol}\cdot l^{-1}$
(2) Benzene $2.6\times 10^{-3}\ \mathrm{mol}\cdot l^{-1}$
(3) Acetanilide $5.0\times 10^{-5}\ \mathrm{mol}\cdot l^{-1}$, benzene $2.6\times 10^{-3}\ \mathrm{mol}\cdot l^{-1}$

The critical transfer distance R_0 is given by[7,8]

$$R_0{}^6=\frac{9000\ln 10\ \chi^2\ \varphi_s{}^0}{128\pi^6 n^4\ \boldsymbol{N}}\int_0^\infty f_s(\bar{\nu})\,\varepsilon_{\mathrm{A}}(\bar{\nu})\frac{d\bar{\nu}}{\bar{\nu}^4} \qquad (20)$$

where $\bar{\nu}$ is the wave number, $\varepsilon_{\mathrm{A}}(\bar{\nu})$ the molar extinction coefficient of the acceptor, $f_s(\bar{\nu})$ the spectral distribution of fluorescence of the sensitizer (measured in quanta and normalized to unity on a wave number scale), $\boldsymbol{N}$ Avogadro's number,

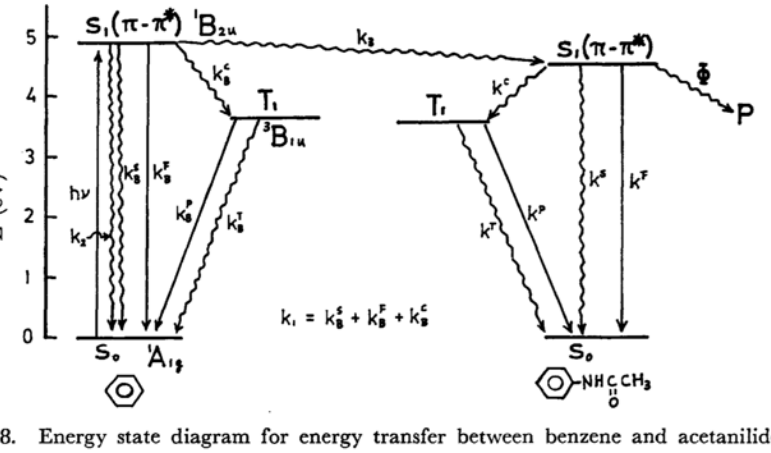

Fig. 8. Energy state diagram for energy transfer between benzene and acetanilide.

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[22] T. V. Ivanova, P. I. Kudryashov and B. Ya. Sveshnikov, *Doklad. Akad. Nauk. SSSR*, **138**, 572 (1961).

[23] P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

[24] E. J. Bowen, *Trans. Faraday Soc.*, **50**, 97 (1954).

[25] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, New York (1966), p. 627.

χ^2 an orientation factor equal to 2/3, n the index of refraction of the solvent and $\varphi_s{}^0$ the fluorescence efficiency of the sensitizer for $[A]=0$. The integral was evaluated graphically (6.72×10^{-14}). $\varphi_s{}^0$ was obtained from the work of Ivanova *et al.*22) (0.1). Then,

$$R_0 \approx 26\,\text{Å}$$

Though the ${}^1B_{2u}\leftarrow{}^1A_{1g}$ transition in benzene is a symmetry forbidden transition, the Förster equation (20) might be applied to this energy transfer because the overlap integral (6.72×10^{-14}) is not so small.

Considering the magnitude of the energy transfer rate constant k_3, it is thought that the transfer from the electronically excited benzene to acetanilide is singlet-singlet nonradiative energy transfer; a resonance transfer for a weak interaction.

Figure 8 shows the energy level diagram for the energy transfer between benzene and acetanilide

$$B^*({}^1B_{2u}) + A({}^1A_1) \xrightarrow{k_3} B({}^1A_{1g}) + A^*({}^1B_2) \tag{21}$$

In conclusion, it is said that acetanilide does not react from the triplet state, but *via* the lowest singlet excited state formed by the benzene-photosensitized reaction.

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