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Determination of the Intersystem Crossing Probabilities of Acridine in Various Alcohols[1]

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Intersystem crossing probabilities ϕ_{ST} of acridine in methanol, ethanol, and 2-propanol were determined by two newly developed methods, relative (r) and absolute (a). The results are as follows. Methanol; 0.27 (r), 0.31 (a). Ethanol; 0.29 (r), 0.33 (a). 2-Propanol; 0.43 (r), 0.45 (a). The above ϕ_{ST} values added to the quantum yield values already obtained of photoreduction occurring at T(n-π^*), *viz.*, $2\phi_R{}^T$ (radical mechanism *via* T(n-π^*), disproportionation of semiquinone being taken into account by a factor of 2) + $\phi_M{}^T$ (molecular mechanism *via* T(n-π^*)), become about the same for the three alcohols. Thus the present data are consistent with our previous data on photoreduction if the intersystem crossing is assumed to occur mainly *via* S*(π-π^*)$\rightarrow$T(n-π^*)$\rightarrow$T(π-π^*) with the same total ϕ_{ST} for the three alcohols but with T(n-π^*) participating in the reaction in different extent according to the alcohol.

An interesting problem in the photoreduction of acridine is the participation of a higher T(n-π^*) state in the reaction. The possibility was porposed for the first time by Kellmann and Dubois in the photoreduction of acridine in methanol.[2] Vander Donckt and Porter found that only a singlet excited state is involved in the case of 2-propanol.[3] Wilkinson and Dubois also reported a similar result for ethanol.[4] Our results[5] were recently reexamined and corrected to some extent; they show that 53, 33, 31, and 0% of the entire reaction occur at T(n-π^*) in methanol, ethanol, *n*-propanol, and 2-propanol respectively,[6] in agreement with the results of Kellmann, Dubois[2] and Vander Donckt and Porter,[3] but not with those of Wilkinson and Dubois.[4]

The reason for this difference between the four kinds of alcohols is still unknown; determination of the intersystem crossing probabilities ϕ_{ST} in various alcohols might be enlightening. The lowest T(π-π^*) is most likely reached *via* T(n-π^*) since intersystem crossing occurs far more efficiently between n and π states than between π and π,[7] and the level of the former is nearer to the lowest singlet excited state. The ϕ_{ST}-values experimentally obtained are expected to be in the order 2-propanol>ethanol>methanol, if the yields of T(n-π^*) (sum of the yield of T(π-π^*) and the part of T(n-π^*) consumed in reaction) are the same for all the alcohols as is plausible.

Two methods have been newly developed for determining the ϕ_{ST} value. (a) A relative method in which a quantity of fluorescence emitted during a flash is taken as a measure of light absorption, and which is an application of the emission-absorption flash technique.[8] (b) An absolute method in which the quantity of light is measured by means of a K–Fe(III) oxalate actionometer. Knowledge of the yield of triplet state is necessary for both methods.

A necessary condition for the relative method is that the substance under investigation and the reference substance have a common wavelength region for both absorption and fluorescence. Anthracene which satisfies such a condition can be used as a reference for acridine,

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[1] Photochemistry of Acridines. XX.

[2] A. Kellmann and J. T. Dubois, *J. Chem. Phys.*, **42**, 2518 (1965). A. Kellmann, *ibid.*, **63**, 936 (1966).

[3] E. Vander Donckt and G. Porter, *ibid.*, **46**, 1173 (1967).

[4] F. Wilkinson and J. T. Dubois, *ibid.*, **48**, 2651 (1968).

[5] a) M. Koizumi, Y. Ikeda, and T. Iwaoka, *ibid.*, **48**, 1869 (1968). b) M. Koizumi, Y. Ikeda, and H. Yamashita, This Bulletin, **41**, 1056 (1968).

[6] M. Hoshino and M. Koizumi, *ibid.*, **45**, 2988 (1972).

[7] S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **1966**, 207 (1966).

[8] a) K. Kikuchi, H. Kokubun, and M. Koizumi, This Bulletin, **41**, 1545 (1968); **43**, 2732 (1970). b) *ibid.*, **44**, 1527 (1971).

but the fluorescence intensity of the latter is not strong and there is some difficulty in practice. The principle of the method is as follows. The triplet yield per one flash $[\mathrm{T}]_0$ which is given by

$$[\mathrm{T}]_0 = \frac{[\mathrm{D_T}]_0(\lambda')}{\varepsilon_\mathrm{T}(\lambda')\mathrm{d}} \tag{1}$$

(where $[\mathrm{D_T}]_0(\lambda')$, optical density immediately after a flash, $\varepsilon_\mathrm{T}(\lambda')$, molar extinction coefficient at λ') is related to the quantity of light absorption by

$$[\mathrm{T}]_0 = \phi_\mathrm{ST}\int I_\mathrm{ab}\mathrm{d}t \tag{2}$$

in which the integral over the wavelength is omitted for the sake of simplicity. The time integrated fluorescence intensity is written as

$$\int I_\mathrm{F}(\lambda)\mathrm{d}t = \alpha(\lambda)\phi_\mathrm{F}\int I_\mathrm{ab}\mathrm{d}t \tag{3}$$

where ϕ_F is the fluorescence quantum yield and $\alpha(\lambda)$ is a constant depending on the setup of the apparatus and experimental conditions. From Eqs. (1), (2), and (3) we have

$$\phi_\mathrm{ST}\varepsilon_\mathrm{T}(\lambda')\mathrm{d} = \alpha(\lambda)\phi_\mathrm{F}[\mathrm{D_T}]_0(\lambda')\Big/\int I_\mathrm{F}(\lambda)\mathrm{d}t \tag{4}$$

Since this relation holds both for reference (A) and sample (B), it follows that

$$\frac{\phi_\mathrm{ST}^\mathrm{B}\cdot\varepsilon_\mathrm{T}^\mathrm{B}(\lambda')}{\phi_\mathrm{ST}^\mathrm{A}\cdot\varepsilon_\mathrm{T}^\mathrm{A}(\lambda')} = \frac{(\alpha(\lambda)\phi_\mathrm{F})^\mathrm{B}}{(\alpha(\lambda)\phi_\mathrm{F})^\mathrm{A}} \times \left\{\frac{[\mathrm{D_T}]_0(\lambda')^\mathrm{B}}{\int I_\mathrm{F}^\mathrm{B}(\lambda)\mathrm{d}t}\Big/\frac{[\mathrm{D_T}]_0(\lambda')^\mathrm{A}}{\int I_\mathrm{F}^\mathrm{A}(\lambda)\mathrm{d}t}\right\} \tag{5}$$

λ was chosen so that the fluorescence intensities of the two samples could be compared accurately. It is desirable that the fluorescence intensities of the two are nearly equal, that there is no reabsorption at λ and that $\mathrm{d}I_\mathrm{F}/\mathrm{d}\lambda$ is small at λ for both compounds. If $\phi_\mathrm{ST}^\mathrm{A}$ is known, the experimental determinations of

$$\frac{\varepsilon_\mathrm{T}^\mathrm{B}(\lambda')}{\varepsilon_\mathrm{T}^\mathrm{A}(\lambda')}, \frac{(\alpha(\lambda)\phi_\mathrm{F})^\mathrm{B}}{(\alpha(\lambda)\phi_\mathrm{F})^\mathrm{A}} \text{ and } \left\{\frac{[\mathrm{D_T}]_0(\lambda')^\mathrm{B}}{\int I_\mathrm{F}^\mathrm{B}(\lambda)\mathrm{d}t}\Big/\frac{[\mathrm{D_T}]_0(\lambda')^\mathrm{A}}{\int I_\mathrm{F}^\mathrm{A}(\lambda)\mathrm{d}t}\right\}$$

are all that is required to evaluate $\phi_\mathrm{ST}^\mathrm{B}$. These are obtained respectively from energy transfer experiments, comparison of fluorescence intensities and the plots of $[\mathrm{D_T}]_0(\lambda')$ *vs.* $\int I_\mathrm{F}(\lambda)\ \mathrm{d}t$.

A direct method is suitable for a substance with weak or no fluorescence. Bowers and Porter developed a somewhat similar method to ours.[9] In order to determine the light absorbed by a sample I_ab, they used the relation

$$\frac{I_\mathrm{ab}}{I_0} = \frac{\int T_\mathrm{f}(\nu)[1-T_\mathrm{c}(\nu)]\mathrm{d}\nu}{\int T_\mathrm{f}(\nu)\mathrm{d}\nu}$$

where I_0 is the incident light and T_f and T_c are the transmission coefficients of a filter and a sample, respectively. I_ab was determined from I_0 and the magnitude of the right term obtained graphically from the transmission profiles of a filter and a sample.

Our method is more experimental in nature. As shown in Fig. 1 an argon lamp specially designed is placed about 7 cm from a sample cell. The lamp and cell are connected with a cylinder with inner wall painted black. Two cells for sample solution (A) and for actinometer solution (B) (K–Fe(III) oxalate) are placed close to each other. Three sets of measurements are necessary for determining the light quantity absorbed by a sample: a) n_A^0, the number of Fe(II) molecules produced by one flash in B-cell, is determined experimentally when the solvent is in A and the actinometer solution is in B. b) A similar quantity n_A^S is determined when the sample is charged in A and the actinometer solution in B. c) Putting the actinometer solution into A and B, similar quantities m_A in A and n_A^A in B are determined. Thus from (a) and (b), the light absorbed by a sample solution I_ab^S is given by

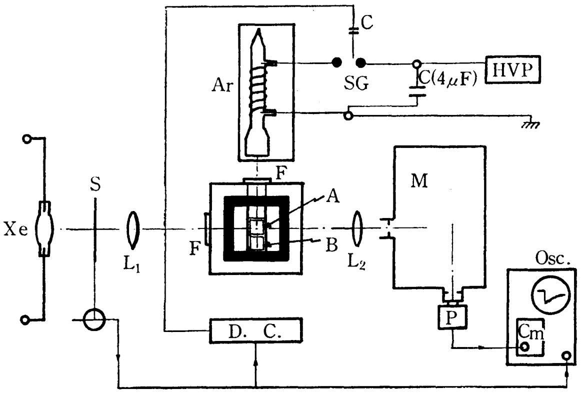

Fig. 1. Diagram of the flash apparatus.
Xe: xenon arc lamp, Ar: argon flash lamp (36 Torr). c: condenser, SG: spark gap, HVP: high voltage pulse, M: grating monochrometer, P: photomultiplier, Osc.: oscilloscope, Cm: comparator, D.C.: delay circuit, A: sample cell, B: actinometer cell, F: filter, $\mathrm{L_1,L_2}$: lens, S: shutter.

$$\frac{I_\mathrm{ab}^\mathrm{S}}{I_0^\mathrm{i}} = \frac{n_\mathrm{A}^0-n_\mathrm{A}^\mathrm{S}}{n_\mathrm{A}^0} \tag{6}$$

where $I_0{}^\mathrm{i}$ is the light intensity close to the inner front side of cell A. Similarly from (a) and (c) we have

$$\frac{I_\mathrm{ab}^\mathrm{A}}{I_0^\mathrm{i}} = \frac{n_\mathrm{A}^0-n_\mathrm{A}^\mathrm{A}}{n_\mathrm{A}^0} \tag{7}$$

and

$$\frac{m_\mathrm{A}}{\phi_\mathrm{Fe(II)}} = I_\mathrm{ab}^\mathrm{A}\ (\phi_\mathrm{Fe(II)},\ \text{quantum yield of actinometer}) \tag{8}$$

Hence

$$I_0^\mathrm{i} = \frac{n_\mathrm{A}^0}{n_\mathrm{A}^0-n_\mathrm{A}^\mathrm{A}} \times \frac{m_\mathrm{A}}{\phi_\mathrm{Fe(II)}} \tag{9}$$

From Eqs. (6) and (9) we obtain

$$I_\mathrm{ab}^\mathrm{S} = \frac{n_\mathrm{A}^0-n_\mathrm{A}^\mathrm{S}}{n_\mathrm{A}^0-n_\mathrm{A}^\mathrm{A}} \times \frac{m_\mathrm{A}}{\phi_\mathrm{Fe(II)}} \tag{10}$$

The method requires strict constancy in the energy output of the lamp.

Experimental

Substances. Specially purified anthracene was supplied by Prof. S. Kato, Tokyo University. Acridine was purified by the standard method. Proflavine sulfate ($\mathrm{C_{13}H_{11}N_3}\cdot$

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[9] P. G. Bowers and G. Porter, *Proc. Roy. Soc. Ser A*, **296**, 435 (1967). G. Porter and P. G. Bowers, *ibid., Ser .A*, **299**, 348 (1967).

$H_2SO_4 \cdot H_2O$, Tokyo Kasei) was treated with 10N NH_3 aqueous solution and was recrystallized three times from ethanol. Purity of a free base thus obtained was checked by elementary analysis and absorption spectrum. *o*-Phenanthroline (Wako Junyaku) was used without further purification. K-ferrioxalate ($K_3Fe(C_2O_4)_3 \cdot 3H_2O$) was prepared by mixing 300 ml aqueous solution of 1.5 M K-oxalate and 100 ml aqueous solution of 1.5 M $FeCl_3$. A crude sample was purified by recrystallization three times.

Apparatus. An ordinary flash apparatus was used. For the relative method, a xenon arc lamp was used for monitoring the absorption spectra of intermediates. A direct generator was used as a source in most experiments, but was replaced by a lead accumulator when the concentrations of intermediates were very low. The sample cell made of quartz and cylindrical in shape has a 10 cm light path. For the direct method, an argon (36 Torr) flash lamp (Fig. 1) was used. Its time characteristic is shown in Fig. 2 and transmissions of the filters in Fig. 3. All the measurements were made at room temperature.

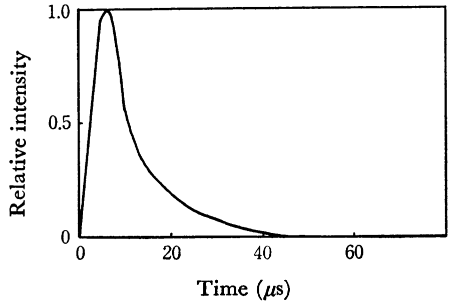

Fig. 2. Time character of the argon lamp.

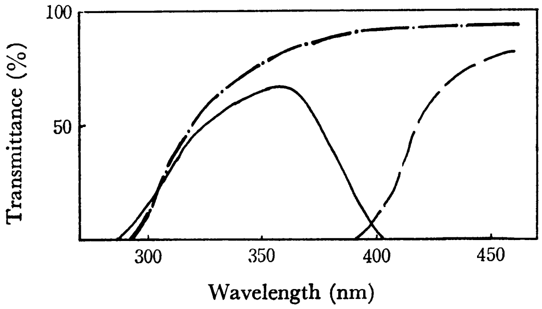

Fig. 3. Character of the filters employed.
—— UVD-2, — —VY-43, —·— alkali glass.

Results

Relative Method. The test was carried out with 9-methyl and 9-phenylanthracene as a sample and anthracene as a reference. The ϕ_{ST} values obtained for ethanol solutions are listed in Table 1 together with the values given in literature. Though the results are found to be satisfactory, the experiments carried out with acridine whose fluorescence is very weak were difficult in contrast to those with great fluorescence intensity. A UVD-2 filter was used for the excitation of anthracene and acridine and VY-43 for the excitation of proflavine.

a) *Determination of the Quantity.*

$$\frac{[D_T]_0^B(\lambda_B')\Big/\int I_F^B(\lambda)dt}{[D_T]_0^A(\lambda_A')\Big/\int I_F^A(\lambda)dt}$$

The plots of $[D_T]_0$ *vs.* $\int I_F\, dt$ for anthracene and acridine in methanol, when both quantities were measured at various flash intensities, are shown in Fig. 4. The $[D_T]_0(\lambda')/\int I_F(\lambda)\, dt$ value was evaluated from the slope of the plot. λ was selected in such a way that the ratio of fluorescence intensities I_{An}/I_{Ac} is the smallest. This is also a necessary condition for the accurate determination of $\alpha(\lambda)\phi_F$.

Relative values of $\int I_F(\lambda)\, dt$ were obtained by taking a photograph of oscillogram, tracing it on section paper and measuring the area under the curve. A

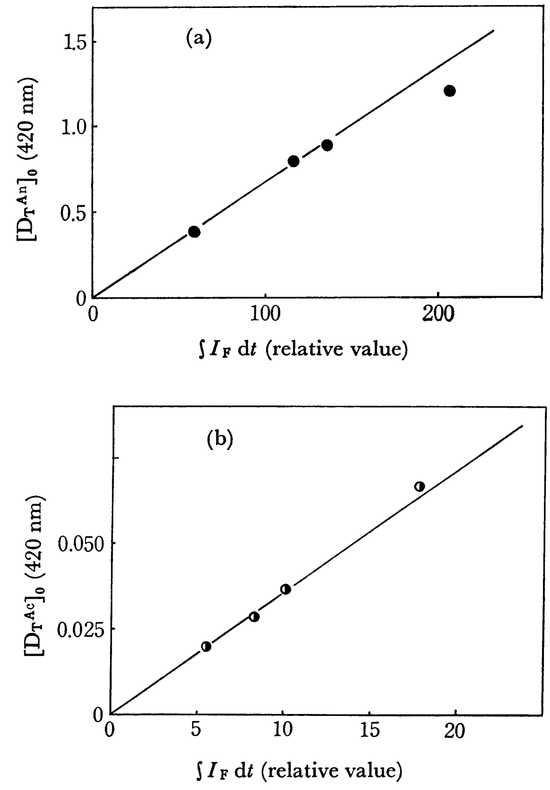

Fig. 4. Plots of $[D_T]_0$ *vs.* $\int I_F dt$ for anthracene (1.6×10^{-5} M) (a) and acridine (8.0×10^{-6} M) (b) in methanol. Absissas; relative values depending upon the experimental conditions, which are set exactly the same for (a) and (b).

Table 1. ϕ_{ST}-Values for ethanol solutions

	ϕ_F	ϕ_{ST}
Anthracene (reference)	0.30[a,b]	0.70[a,b]
9-Methylanthracene	0.35 (0.33[a])	0.67 (0.67[a])
9-Phenylanthracene	0.51 (0.49[a], 0.45[c])	0.50 (0.47[a], 0.51[c])

a) C. A. Parker, "Photoluminescence of Solutions", Elsevier Publishing Co., Amsterdam (1968).
b) C. A. Parker and T. A. Joyce, *Chem. Commun.*, **1966**, 234.
c) A. R. Harrocks, T. Medinger and F. Wilkinson, *Photochem. Photobiol.*, **6**, 21 (1967).

TABLE 2. ϕ_{ST}-VALUES AND NECESSARY DATA FOR THEIR EVALUATION

Solvent	$\dfrac{[D_T^{Ac}]_0\,(420)/\int I_F\,dt}{[D_T^{An}]_0\,(420)/\int I_F\,dt}$	$\dfrac{\alpha^{Ac}(\lambda)\,\phi_F^{Ac}}{\alpha^{An}(\lambda)\,\phi_F^{An}}$	$\dfrac{\varepsilon_T^{Ac}\,(420)}{\varepsilon_T^{Pr}\,(550)}$	$\dfrac{\varepsilon_T^{An}\,(420)}{\varepsilon_T^{Ac}\,(420)}$	ϕ_{ST}
Methanol	0.532	0.087 (λ=413 nm)	0.74_8	8.7_3	0.27
Ethanol[a)]	0.628	0.092 (λ=413 nm)	0.77_7	7.2_6	0.29
2-Propanol	0.932	0.078 (λ=413 nm)	0.67_9	8.3_9	0.43

a) T-T absorption was measured at 421 nm.

correction was made for the scattered light in the case of acridine. The results are given in Table 2.

b) *Determination of* $(\alpha(\lambda)\phi_F)^B/(\alpha(\lambda)\phi_F)^A$. Solutions were degassed to eliminate the quenching action of oxygen. By adjusting the concentration, excitation was performed at a wavelength at which the absorbance is the same for anthracene and acridine. The fluorescence intensity ratio itself then affords the required quantity. Reabsorption was negligible at the wavelength employed. The results are given in Table 2.

c) *Determination of* $\varepsilon_T^B(\lambda')/\varepsilon_T^A(\lambda')$. An energy transfer method was used to determine the ratio of extinction coefficient. Proflavine was used as an energy donor. This substance has the lowest T-level at 17100 cm^{-1} which is far below the suspected T(n-π^*) level of acridine and significantly higher than the lowest T(π-π^*) of acridine (15840 cm^{-1}) and anthracene.[10] By using a VY-43 filter, proflavine alone can be excited. At moderate concentrations of acridine and anthracene, complete T-energy transfer occurs from donor to acceptor; $[D_T]_0$ of acceptor should then be proportional to $\int I_F\,dt$ of proflavine. The former was measured at 420 nm and the latter at 494 nm. 420 nm is a peak position of T-T absorption of anthracene. The peak of acridine T-T absorption is located at 440 nm but there is an appreciable absorption of proflavine at this wavelength. The plots for anthracene and acridine in methanol are given in Fig. 5. Equally satisfactory plots were obtained also for ethanol and 2-propanol. It was confirmed that the plot of $[D_T]_0$ *vs.* $\int I_F dt$ for the solution containing proflavine alone gives a satisfactory straight line. The results are summarized in Table 2. The ϕ_{ST} values were obtained from the three sets of data.

Absolute Method. The test was carried out with

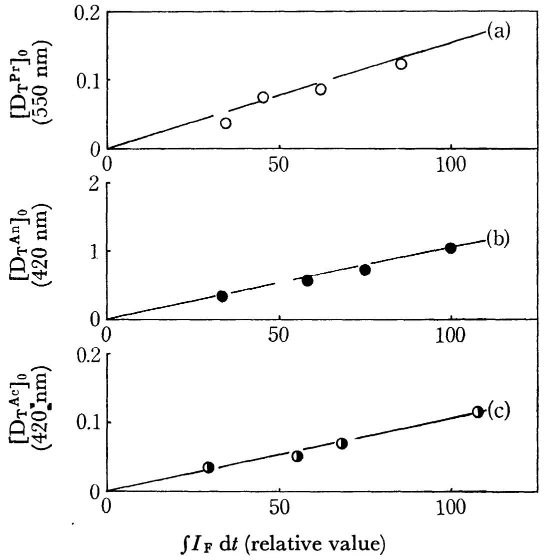

Fig. 5. (a) Plots of $[D_T]_0$ (550 nm) *vs.* $\int I_F dt$ for proflavine in methanol.
(b), (c) Similar plots for (b) anthracene $[D_T^{An}]_0$, (c) acridine $[D_T^{Ac}]_0$ added respectively to the solution of (a) as a T-energy acceptor.

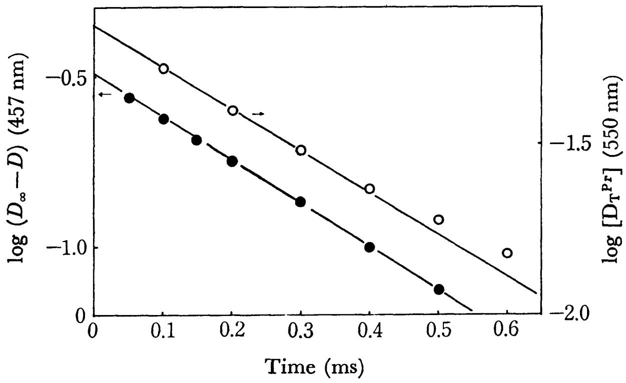

Fig. 6. Decay of triplet (○) and recovery of the ground state (●) for proflavine (1.0×10^{-6} M) in methanol.

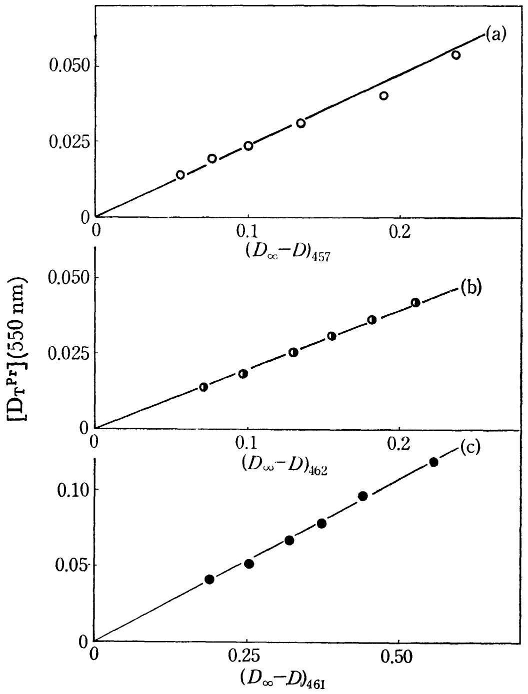

Fig. 7. Relation between $[D_T^{Pr}]$ and $(D_\infty - D)$ values at the same points after flashing.
a) methanol [proflavine] = 1.0×10^{-6} M
b) ethanol [proflavine] = 1.0×10^{-6} M
c) 2-propanol [proflavine] = 1.7×10^{-6} M.

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[10] C. A. Parker, C. G. Hatchard, and T. A. Joyce, *Nature*, **205**, 1282 (1965).

TABLE 3. MOLAR EXTINCTION COEFFICIENTS OF T-T ABSORPTION OF PROFLAVINE, ANTHRACENE, AND ACRIDINE

Solvent	ε_S^{Pr} (λ)	ε_T^{Pr} (550)	ε_T^{An} (λ)	ε_T^{Ac} (λ)
Methanol	5.08×10^4 (457)	1.11×10^4	6.57×10^4 (420)	8.23×10^3 (420)
			1.92×10^4 (398)	1.86×10^5 (440)
Ethanol	5.44×10^4 (462)	1.1×10^4 [8b)]	4.89×10^4 (420)	8.91×10^3 (424)
			5.20×10^4 (421)	1.85×10^4 (440)
2-Propanol	4.55×10^4 (461)	0.98×10^4	5.68×10^4 (420)	6.67×10^3 (420)
				1.51×10^4 (440)

TABLE 4. ϕ_{ST}-VALUES OF ACRIDINE IN METHANOL, ETHANOL AND 2-PROPANOL OBTAINED BY THE ABSOLUTE METHOD

D_{356}	$[\mathrm{Fe(II)}]_1$ (M)	$[\mathrm{T}]_0$ (M)	$\frac{n_A^0-n_A^A}{n_A^0-n_A^S}$	$\frac{n_A^0-n_A^S}{n_A^0}$	$\frac{m_A}{n_A^0}$	ϕ_{ST}
Methanol						
1.10_8	5.68×10^{-7}	2.20×10^{-7}	1.48	0.676	0.987	0.33_0
1.11_0	8.18×10^{-7}	3.06×10^{-7}	1.50	0.667	1.15	0.32_3
0.54_1	1.05×10^{-6}	2.18×10^{-7}	2.30	0.424	1.19	0.27_4
0.26_6	9.68×10^{-7}	1.30×10^{-7}	4.00	0.250	1.17	0.30_8
						Mean 0.31 ± 0.02
Ethanol						
0.21_3	8.85×10^{-7}	1.06×10^{-7}	4.86	0.206	1.19	0.33_4
0.19_1	8.68×10^{-7}	1.18×10^{-7}	4.29	0.233	1.14	0.33_6
0.19_4	8.71×10^{-7}	1.17×10^{-7}	4.34	0.230	1.15	0.33_4
						Mean 0.33 ± 0.02
2-Propanol						
1.22_1	8.84×10^{-7}	4.77×10^{-7}	1.61	0.621	1.37	0.49_7
0.59_3	1.09×10^{-6}	3.44×10^{-7}	2.18	0.598	1.19	0.41_4
0.66_9	1.06×10^{-6}	4.13×10^{-7}	1.98	0.505	1.20	0.44_6
0.26_2	8.65×10^{-7}	2.05×10^{-7}	3.10	0.322	1.19	0.42_2
						Mean 0.45 ± 0.04

anthracene in 2-propanol. The ϕ_{ST} value obtained was 0.7_6 which agrees fairly well with that in literature.

Determination of $[T]_0$: The optical density and molar extinction coefficient for T-T absorption are required for knowing the triplet concentration. Since $\varepsilon_T^{An}/\varepsilon_T^{Pr}$ and $\varepsilon_T^{Ac}/\varepsilon_T^{Pr}$ are known we need to determine the value of ε_T^{Pr}. Decay of T-T absorption and recovery of the ground state absorption were measured with very dilute solutions of proflavine (1×10^{-6} or 1.17×10^{-6} M). Proflavine has a tendency of dimerization which is especially large in 2-propanol. Hence higher concentrations are undesirable. As shown in Fig. 6, the log $[D_T^{Pr}]$ *vs. t* plot for the former and the log $(D_\infty-D)$ *vs. t* plot for the latter, both methanol solutions, give straight lines with the same slopes. (D_∞ is the optical density when the ground state is recovered completely.) Similar results were obtained for ethanol and 2-propanol solutions.

The $[D_T^{Pr}]$-values are plotted against the $(D_\infty-D)$ values of the corresponding time points in Fig. 7; both values were taken from the results in Fig. 6 and the similar ones. Figure 7 indicates that the ground state proflavine recovers in one to one correspondence as the triplet state decays. ε_T^{Pr} and then ε_T^{Ac} and ε_T^{An} were determined from the slopes and are listed in Table 3.

The yield of triplet state was obtained by extrapolating the decay curve of T-T absorption to the time point of 25 μsec after flashing. The time point was selected taking the time character of the flash lamp (Fig. 2) and the decay rate of the triplet acridine into consideration. n_T, the number of triplet molecules produced, was calculated from the equation

$$n_T = [T]_0 \times \frac{V_1 N}{1000} \tag{11}$$

where V_1 is the irradiated volume and N is Avogadro's number.

Measurement of the Absorbed Light: Because of low power of the flash, flashing was repeated 30—60 times, for a K-Fe(III) oxalate actinometer to be applicable. The method of measurement was modified to some extent, particularly with respect to coloration. The pH was adjusted to 3.5. Reflection on the cell windows and light scattering were taken into consideration. A correction formula proposed for the case of parallel light was applied,[11] but the correction factors were almost within experimental error.

The quantity of light absorption can be determined by Eq. (10). It is desirable to keep the value of $(n_A^0-n_A^S)/n_A^0$ in the range 0.15—0.20 in order to secure uniform formation of the triplet state. This was not possible experimentally, but the results were satisfactory. It was confirmed that the absorption spectrum of the solution subjected to flashing 30—60 times changed little, indicating that scarcely any reaction occurred.

Optical density of Fe(II)-orthophenanthroline chelate complex at 510 nm D_{510} was measured after being

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[11] R. E. Hunt and J. L. Hill, *J. Chem. Phys.*, **15**, 111 (1947). M. J. Dignam and D. J. LeRoy, *ibid.*, **26**, 964 (1957). M. A. Davies and P. P. Manning, *J. Amer. Chem. Soc.*, **79**, 5148 (1957).

subjected to flashing 30—60 times. m_A was then evaluated by the following equations.

$$m_A = [\text{Fe(II)}]_1 \times \frac{V_2 N}{1000} \qquad (12)$$

$$[\text{Fe(II)}]_1 = \frac{D_{510}}{\varepsilon_{510}\cdot d} \times \frac{1}{P}$$

where ε_{510} is the molar extinction coefficient of chelate complex, d the light path (1 cm), V_2 a volume of the solution of chelate complex and P the number of flashes.

From Eqs. (10), (11), and (12), ϕ_{ST} can be evaluated by

$$\phi_{ST} = \frac{n_T}{I_{ab}} = \frac{[T]_0}{[\text{Fe(II)}]_1} \times \frac{n_A^0 - n_A^A}{n_A^0 - n_A^S} \times \frac{V_1}{V_2}\phi_{\text{Fe(II)}} \qquad (13)$$

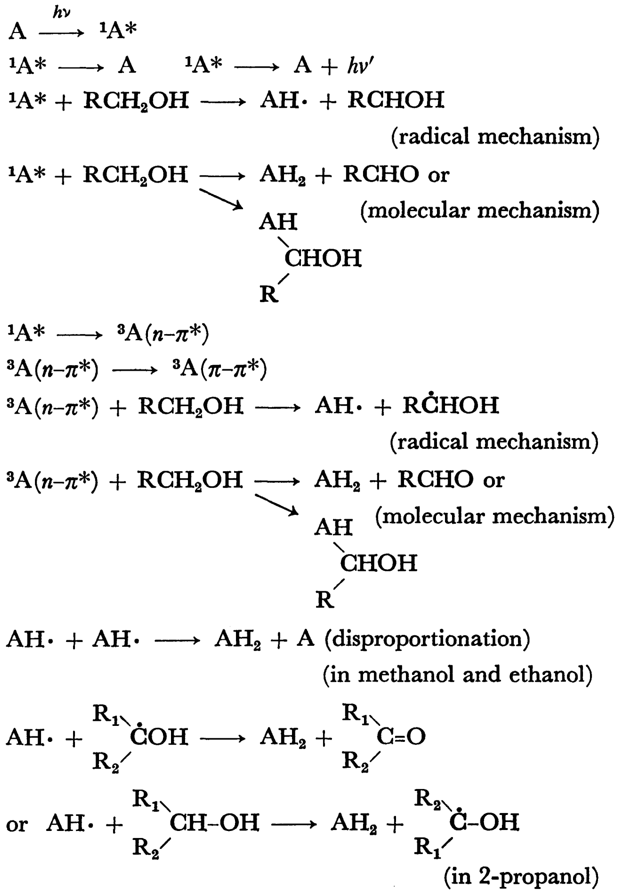
The value of 1.15 was used as $\phi_{\text{Fe(II)}}$.[12]

The ϕ_{ST}-values of acridine are listed in Table 4 together with other related quantities. Constancy of the energy output was checked by observing the T-T absorption repeatedly in the course of experiment. This was confirmed by the constancy of $m_A/n_A{}^0$ for succeeding experiments. No systematic concentration dependence is observed. Experimental error can not be estimated accurately but might be less than ±10%.

Discussion

The ϕ_{ST}-values of acridine obtained by the two methods are listed in Table 5 together with the quantum yields of photoreduction *via* various paths[6] and with other related data. We see that the values obtained by the relative method are systematically a little smaller than those by the absolute method. It is remarkable that the ϕ_{ST}-value in 2-propanol is significantly larger than that in methanol and in ethanol; this is common to the results by the two methods.

It seems reasonable to correlate the large value in 2-propanol with the fact that T(n-π*) participates in the photoreduction to some extent in ethanol and methanol but not in 2-propanol. ϕ_M^S, ϕ_R^S, ϕ_M^T, and ϕ_R^T in the table are the quantum yields of photoreduction *via* four paths. Subscripts M and R stand for molecular and radical mechanisms, respectively, and superscripts S and T for singlet excited and T(n-π*) states, respectively. The general scheme of the photoreduction of acridine in alcohols presented by us is as follows.[5,6]



$$\begin{array}{l}
\text{A} \xrightarrow{h\nu} {}^1\text{A}^* \\
{}^1\text{A}^* \longrightarrow \text{A} \qquad {}^1\text{A}^* \longrightarrow \text{A} + h\nu' \\
{}^1\text{A}^* + \text{RCH}_2\text{OH} \longrightarrow \text{AH}\cdot + \text{RCHOH} \quad \text{(radical mechanism)} \\
{}^1\text{A}^* + \text{RCH}_2\text{OH} \longrightarrow \text{AH}_2 + \text{RCHO or } \text{AH}\diagdown\text{CHOH}\diagup\text{R} \quad \text{(molecular mechanism)} \\
{}^1\text{A}^* \longrightarrow {}^3\text{A}(n\text{-}\pi^*) \\
{}^3\text{A}(n\text{-}\pi^*) \longrightarrow {}^3\text{A}(\pi\text{-}\pi^*) \\
{}^3\text{A}(n\text{-}\pi^*) + \text{RCH}_2\text{OH} \longrightarrow \text{AH}\cdot + \text{R}\dot{\text{C}}\text{HOH} \quad \text{(radical mechanism)} \\
{}^3\text{A}(n\text{-}\pi^*) + \text{RCH}_2\text{OH} \longrightarrow \text{AH}_2 + \text{RCHO or } \text{AH}\diagdown\text{CHOH}\diagup\text{R} \quad \text{(molecular mechanism)} \\
\text{AH}\cdot + \text{AH}\cdot \longrightarrow \text{AH}_2 + \text{A (disproportionation)} \\
\qquad \text{(in methanol and ethanol)} \\
\text{AH}\cdot + {}^{\text{R}_1}_{\text{R}_2}\!\!>\!\dot{\text{C}}\text{OH} \longrightarrow \text{AH}_2 + {}^{\text{R}_1}_{\text{R}_2}\!\!>\!\text{C=O} \\
\text{or AH}\cdot + {}^{\text{R}_1}_{\text{R}_2}\!\!>\!\text{CH-OH} \longrightarrow \text{AH}_2 + {}^{\text{R}_2}_{\text{R}_1}\!\!>\!\dot{\text{C}}\text{-OH} \\
\qquad \text{(in 2-propanol)}
\end{array}$$

It is to be noted that the half-reduced radical produced by radical mechanism undergoes disproportionation in methanol and ethanol while in 2-propanol, it is entirely transformed into acridan-type compound.[6,13] The entire quantum yields for the production of T(n-π*) in methanol and ethanol are then given as the sum $\phi_{ST}+2\phi_R^T+\phi_M^T$. The values are the same for three alcohols within experimental error when one uses the ϕ_{ST} values by the absolute method. It is thus reasonable to consider that the entire quantum yield of the production of T(n-π*) is about the same for the three alcohols. Thus one can say that the ϕ_{ST} values we obtained and the quantum yields of photoreduction already published are correlated with each other in a consistent way. ϕ_{total} is a fraction of singlet excited state which disappears by reaction, fluorescence and intersystem crossing; the calculation was made in a similar way to the above. Thus $1-\phi_{\text{total}}$ is a fraction of eventural

TABLE 5. QUANTUM YIELDS OF VARIOUS PROCESSES OCCURING IN THE EXCITED ACRIDINE

Solvent	ϕ_M^S	ϕ_R^S	ϕ_M^T	ϕ_R^T	ϕ_F	ϕ_{ST}	$\phi_{ST}+2\phi_R^T+\phi_M^T$	ϕ_{total}
Methanol	0.027	0.032	0.006	0.063	0.046	r. 0.27	0.42	0.54
						a. 0.31	0.44	0.59
Ethanol	0.043	0.043	0	0.043	0.032	r. 0.29	0.38	0.54
						a. 0.33	0.42	0.58
2-Propanol	0.030	0.058	0	0	0.028	r. 0.43	0.43	0.55
						a. 0.45	0.45	0.57

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[12] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, (1966), p. 784.

[13] Y. Miyashita, S. Niizuma, H. Kokubun, and M. Koizumi, This Bulletin, **43**, 3435 (1970).

internal conversion.

Some remarks should be added on the nature of the reactive singlet excited state. Zanker and Prell[14] proposed that S*(n-π*) instead of S*(π-π*) is a reactive state for the photoreduction of 9-methylacridine in deaerated ethanol solution. According to their results, the quantum yields for the formation of T(π-π*) (ϕ_{ST}) and for the photoreduction (ϕ(R)) have about the same temperature dependence with an activation energy of about 800 cal/mol. They concluded that S*(n-π*) is located above S*(π-π*) by this amount, both reaction and intersystem crossing occurring mainly at S*(n-π*). Whitten and Lee also concluded[15] that S*(n-π*) is a reactive state for the photoreduction of acridine by isopropyl alcohol, toluene, and *p*-methylanisole in some inert solvents. Assuming that reaction occurs only at singlet excited state, they investigated the dependence of ϕ(R) and of the fluorescence of acridine ϕ(F) on the concentration of reducing agents; they found that in most cases fluorescence intensity is scarcely affected by the occurrence of photochemical reaction. We feel, however, that some of their fluorescence intensity data are consistent with the occurrence of quenching on account of the reaction. They inferred that S*(n-π*) is below S*(π-π*) in all the cases irrespective of solvent polarity, and S*(π-π*) attained immediately after the light absorption goes down more or less irreversibly to S*(n-π*) where reaction and intersystem crossing occur in competition. Conclusions on the relative positions of π-π* and n-π* reached by the two groups differ and further studies are necessary to decide which is correct. If the intersystem crossing were to occur only *via* S*(n-π*)$\rightarrow$T(π-π*), as they both concluded, reaction at T(n-π*) state would never occur. Our present results, which are consistent with our previous data of the reaction quantum yields, strongly suggest that the intersystem crossing occurs to a significant extent *via* S*(π-π*)$\rightarrow$T(n-π*)$\rightarrow$T(π-π*) in addition perhaps to the above path. But since the level difference between S*(n-π*) and S*(π-π*) is of the order of kT according to Zanker and Prell (although it appears that their values are not so reliable because of the composite nature of ϕ(R) and ϕ_{ST}), it seems more reasonable to consider that both S*(n-π*) and S*(π-π*) are mixed with each other to some extent by vibronic interaction. If this is the case, S*(π-π*) may also participate in the reaction. The temperature dependence of ϕ_{ST} as well as of ϕ(R) would then become more complicated in nature and can not be treated simply by means of the Arrhenius plot. The relative positions would be inverted according to the polarity of solvent, contrary to Whitten and Lee's conclusion.

Although both the nature of the reactive singlet excited state and the process of intersystem crossing require further studies, there is scarcely any doubt that the intersystem crossing occurs for the most part *via* S*(π-π*)$\rightarrow$T(n-π*)$\rightarrow$T(π-π*).

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[14] V. Zanker and G. Prell, *Ber. Bunsenges. Phys. Chem.*, **73**, 791 (1969).

[15] D. G. Whitten and Y. J. Lee, *J. Amer. Chem. Soc.*, **93**, 961 (1971).