Four Radical Species Produced Photochemically in the Solid Mixture of Acridine and Acridan

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It has been established from measurement of the fusion curve that a 1 : 1 complex of acridine and acridan is formed in the solid state. The complex has an absorption band at 400—500 nm and is considered to be of C-T character although hydrogen bonding plays a role in complexing. Excitation of this complex gives rise to four radical species which display the corresponding characteristic ESR signals *a*, *b*, *c*, and *d*. The line width of *a* (α) and the line separations of *b*, *c*, *d* (β, γ, δ) are $\alpha=18.0\pm3.5$, $\beta=112\pm2$, $\gamma=137\pm5$, $\delta=212\pm6$ gauss. Studies on the dependence of the relative intensities of *a*, *b*, *c*, and *d* upon the acridine-acridan ratio and upon the length of irradiation have led to the conclusion that *a* and *b* are due to C- and N-radicals (the latter, triplet with separation of 44 gauss) and *c* and *d* are two kinds of radical pair. Detection of $\Delta M=\pm2$ transition at 1670 gauss (with 9337.4 MHz) also confirmed the above assignment of *c* and *d*. It is likely that the mutual transformation occurs only during irradiation. It is concluded that C-radical is more stable than N-radical in agreement with the result in fluid state. An interesting decay feature of signal *a* was found and was given a plausible interpretation.

The photoreduction of acridine in the fluid state has been extensively investigated and four main features in the reaction have been elucidated. 1) Photoreduction in alcohols occurs mainly at singlet excited state but a higher $T(n\text{-}\pi^*)$ can participate in the reaction to some extent in methanol and to a very little extent in ethanol.[1-3] 2) Although the lowest $T(\pi\text{-}\pi^*)$is not a reactive state in alcohol, it can be in some cases, for example in tetrahydrofuran.[7] 3) Reaction occurs in general *via* two mechanisms; *viz.*, a molecular mechanism in which no intermediate can be detected by the usual flash technique, and a radical one in which half reduced radical can be captured in a free state.[1,2,8] 4) Two types of radical are produced generally,[9,10] *i.e.*, C-radical and N-radical, with an unpaired electron on 9-C-atom and on N-atom, respectively. Only C-radical is produced in the photoreduction in alcohols,[9]while in the reaction between acridine and acridan, the former yields C-radical and the latter, N-radical. We have been continuing ESR studies on the radical anions[12] and neutral radical species[14] related to acridine and acridan. However, the information obtained on the neutral radical species is still very scanty. We have only succeeded in detecting an ESR spectrum of radical species originating from acridine or acridan in the crystalline medium of benzene, tetrahydrofuran or of t-butanol at 77°K. In these media, the ESR spectrum appeared upon irradiation of acridan (except benzene) or by excitation of acridine in the acridine-acridan mixture. During the course of this work, we found that the mixture of acridine and acridan is colored yellow at 77°K, suggesting the formation of a certain molecular complex.

The present paper deals with an extension of the above work. By irradiating at 430—600 nm, the mixture of acridine and acridan in crystalline benzene medium at 77°K, or by irradiating the mixture with no medium, obtained either by distilling off the solvent or by fusing the mixture of two components, we could detect four types of ESR signal, two of which are due to radicals in the free state, most likely C- and N-radical, and the other two kinds of radical pair. The study on the fused sample was particularly successful and it has been established that a molecular complex, perhaps of C-T type, consisting of 1 acridine and 1 acridan is formed in the solid state having an absorption band ~450 nm. The excitation in this band region produced four different radical species, the behavior of which was studied under various conditions.

Experimental

Materials. Acridine, ethanol, and tetrahydrofuran were purified as described previously.[13] Preparation and purification of acridan were carried out in the same way. Benzene of Wako Junyaku G.R. was used without further purification. *N*-methylacridan was prepared by reducing *N*-methylacridinium iodide (obtained from acridine and

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[1] M. Koizumi, Y. Ikeda, and T. Iwaoka, *J. Chem. Phys.*, **48**, 1869 (1968).

[2] M. Koizumi, Y. Ikeda, and H. Yamashita, This Bulletin, **41**, 1056 (1968).

[3] According to Kellmann and Dobois,[4] singlet excited state and $T(n-\pi^*)$ are reactive in methanol, while Vander Donkt and Porter[5] concluded that only singlet excited state is reactive in isopropanol. Wilkinson and Dubois[6] claimed that singlet excited state mainly participates in the reaction in ethanol. All these statements are essentially consistent with our data.

[4] A. Kellmann and J. T. Dubois, *J. Chem. Phys.*, **42**, 2518 (1965).

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

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

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

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

[9] A. Kira and M. Koizumi, This Bulletin, **42**, 625 (1969).

[10] V. Zanker and his collaborators observed the formation of C- and N-radicals in the photooxidation of acridan derivatives and some other reactions.[11,12]

[11] V. Zanker, E. Erhardt, and H. H. Mantsch, *Z. Phys. Chem. N. F.*, **58**, 1 (1968).

[12] V. Zanker and E. Erhardt, *Ber. Bunsenges. Phys. Chem.*, **72**, 267 (1968).

[13] S. Niizuma and M. Koizumi, This Bulletin, **41**, 795 (1968).

[14] S. Niizuma and M. Koizumi, *ibid.*, **41**, 1090 (1968).

methyliodide) by $NaBH_4$. It was recrystallized from ethanol. mp 94.5—95.5°C.

Apparatus and Procedures. As a light source for UV irradiation, an Ushio USH-500 mercury lamp or a Toshiba SHL-100 UV was used and for the visible light irradiation, a tungsten lamp of Kondo 1 kW or 500 W was used. The filters used for visible light, $CuSO_4$ aq. solution—Toshiba VY-43 (or VY-45 or VY-48), for the UV irradiation, Hoya crystal U-2—Toshiba L-1A—water, 1 cm. The former transmits 430 (or 450 or 480) ~600 nm while the latter only 365 nm. In the case of irradiation at shorter wavelengths, the light from a mercury lamp was passed through 1 cm layer of water. Samples were prepared as follows. Removal of the solvent from benzene or tetrahydrofuran solution of acridine and acridan, was performed in a sample tube for ESR by distillation *in vacuo*. The fused sample was prepared by keeping a ESR capillary cell containing a mixture of acridine and acridan in an electric furnace, after having been evacuated and sealed, at temperatures higher than melting point by 5—15°C for 1—5 min. It was then cooled rapidly with water. A JEOL P-10-type ESR spectrometer (X-band 100 Kc modulation) was used for the measurement of $\Delta M=\pm 1$ transition, and a Hitachi Model 771-ESR spectrometer for that of $\Delta M=\pm 2$.[15] Electronic spectra were taken with a Hitachi EPS-3T spectrophotometer.

Results and Assignment of Radical Species

Experiment Using a Sample in a Benzene Medium. A solution of acridine and acridan in benzene colored yellow when frozen. Upon irradiation by 365 nm at 77°K, it turned brown and gave an ESR spectrum. The signal intensity grew rapidly in a few minutes irradiation and then the increase became much more gradual. Figures 1a and b give two examples of ESR signals for acridine: acridan=1 : 2 and 1 : 5, respectively. All the spectra are characterized by four peaks (or shoulders) *a*, *b*, *c*, *d* as shown in the figure. The line width of *a* (ΔH_{msl}) and the line separations of *b*, *c*, and *d* are denoted by α, β, γ, and δ, respectively. Although the relative intensities *a*, *b*, *c*, and *d* varied according to experimental conditions (for instance, *b* which exists as a shoulder in this figure becomes a peak in some other cases), the values of α, β, γ, and δ remained almost the same. The mean values determined from a number of experiments are

$$\left.\begin{aligned}\alpha &= 18.0 \pm 3.5 \text{ gauss}\\ \beta &= 106 \pm 2 \text{ gauss}\\ \gamma &= 135 \pm 2 \text{ gauss}\\ \delta &= 226 \pm 9 \text{ gauss}\end{aligned}\right\} \tag{1}$$

The g-value of peak *a* was 2.004. As a general tendency, peak *a* becomes stronger with the increase in the mole ratio of acridine to acridan, $[A]/[AH_2]$. An over-all survey of the results leads us to the conclusion that these four peaks (or shoulders) are ascribed to different radical species.

Figure 2 shows the effect of irradiation time upon the intensity ratio (evaluated from the peak to peak height of the differential curve) of *a* and *c* for a sample for which $[A]/[AH_2]=1$.[16] A remarkable change in

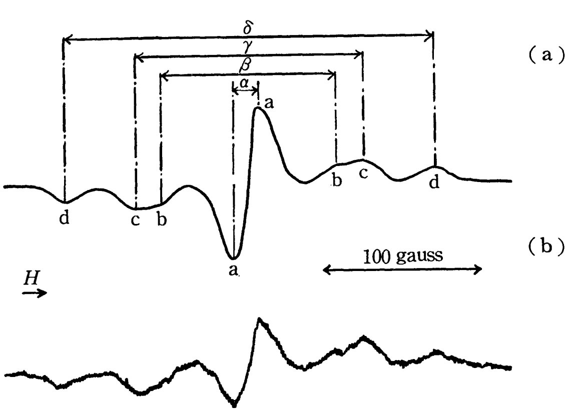

Fig. 1. ESR signals of the mixtures of acridine and acridan in benzene media.
(a) acridine : acridan=1 : 2
(b) acridine : acridan=1 : 5

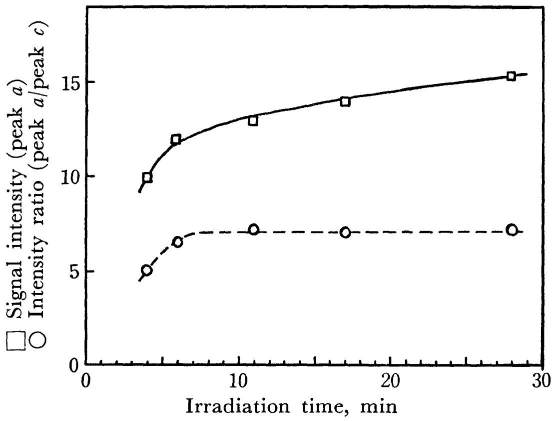

Fig. 2. Effect of irradiation time upon intensity ratio of *a* to *c*. ($[A]/[AH_2]=1$).

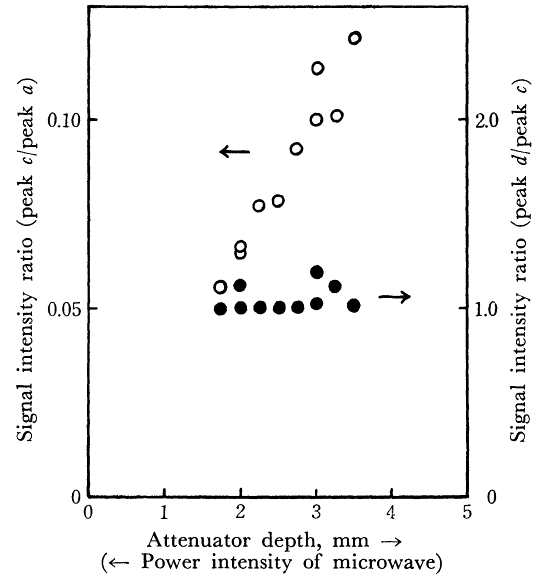

Fig. 3. Effect of microwave intensity upon intensity ratio of *c* to *a* and that of *d* to *c*.

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[15] Thanks are due to Dr. Y. Ikegami and Dr. M. Iwaizumi of Chem. Res. Inst. of Non-Aqueous Solution for use of their instrument.

[16] It is thought that *b* contributes to the intensity of *c* to some extent.

this ratio during the first seven minutes clearly indicates that *a* and *c* are different species. Figure 3 shows the effect of microwave intensity upon the intensity ratio of *c* and *a* and that of *c* and *d* for the sample, $[A]/[AH_2]=1/2$. It is evident that the former changes remarkably while the latter remains almost constant. This again shows that *a* and *c* are different species.

Although at 77°K the signals are quite stable and the intensity scarcely decreases after being kept for a night in the dark, they decay more rapidly with rising temperature. The temperature effecton the signal shape and the decay rate was examined from −27 to −158°C using the sample for which $[A]/[AH_2]=1$. Since the signal intensities are so weak at higher temperatures that the peaks other than *a* are almost comparable with the noise, the decay could be measured only at peak *a*. It is remarkable that all the decays in the whole temperature region could be analysed as a sum of two first order terms. As an example a decay at −57°C is shown Fig. 4. Furthermore, moderately good Arrhenius plots were obtained for the two rate constants k_S (short lived species) and k_L (long lived species) as shown in Fig. 5. The activation energies obtained are for the former 3.3 and for the latter 3.9 kcal/mol. The values of k_S and k_L at various temperatures are listed in Table 1. It should be noted that the point at 114°K deviates a great deal from the linear plot. Since the second order transition point of benzene exists at 110°K[17] the above anomaly can be ascribed to the different state of benzene medium, if the error in temperature measurement is taken into account. The ratios of the quantity of short lived and long lived species immediately after the interruption of irradiation, which were evaluated by extrapolating the linear part in the later stage (decay of a long lived species), to the time origin, are plotted against the temperature in Fig. 6. There is a clear tendency for a relative yield of short lived species to increase with the rise of temperature. The temperature effect strongly suggests that there are two independent species (or states) with different stability and that the four radical species do not mutually transform thermally. If this were to occur such a simple behavior as obtained would not be expected.

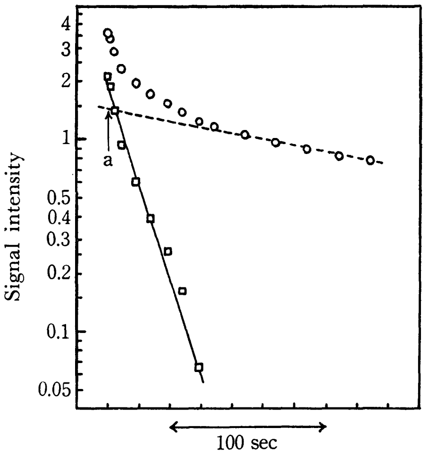

Fig. 4. Decay of signal intensity measured at peak *a*.

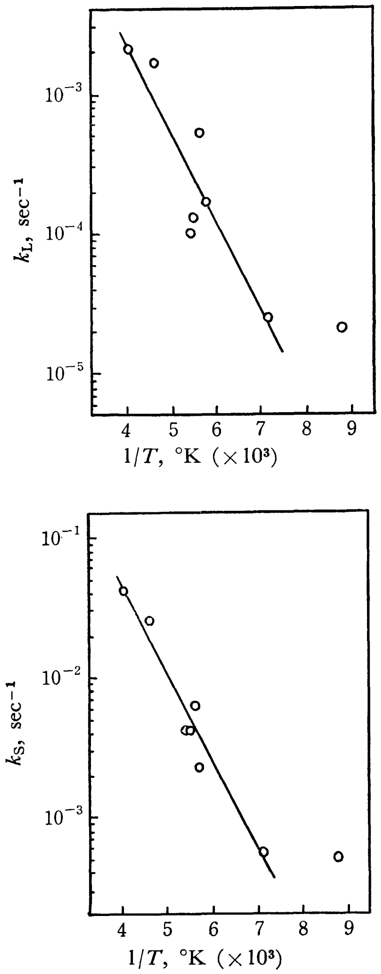

Fig. 5. Arrhenius plots for the decay constants of long lived (k_L) and short lived species (k_S).

TABLE 1. DECAY CONSTANTS OF SHORT-LIVED (k_S) AND LONG-LIVED SPECIES (k_L) AT VARIOUS TEMPERATURES

Temp., °C	Irrad. time	k_S (sec^{-1})	k_L (sec^{-1})
−158—−160	12 min 4 sec	5×10^{-4}	$2.2_2 \times 10^{-5}$
−131—−134	24 min 40 sec	5.5×10^{-4}	$2.5_0 \times 10^{-5}$
−95— −97	26 min 20 sec	$2.2_4 \times 10^{-3}$	$1.6_7 \times 10^{-4}$
−95	ten several min	6.17×10^{-3}	$5.2_4 \times 10^{-4}$
−89— −92	5 min 35 sec	4.21×10^{-3}	1.02×10^{-4}
−85— −89	15 min 11 sec	4.16×10^{-3}	1.29×10^{-4}
−57	several min	2.50×10^{-2}	1.67×10^{-3}
−27	several min	4.17×10^{-2}	$2.1_7 \times 10^{-3}$

The results obtained for the solid mixture of acridine and acridan prepared by evaporating the solvent (benzene or tetrahydrofuran) were essentially the same as above. The sample was deep yellow at room temperature, suggesting again the strong interaction between the two components. The ESR signals obtained upon 365 nm irradiation at 77°K showed similar spectral feature and spectral change during irradiation.

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[17] N. N. Semenov, "XVIIIth International Congress of Pure and Applied Chemistry. Special Lectures," Butterworths, London (1962), p. 353.

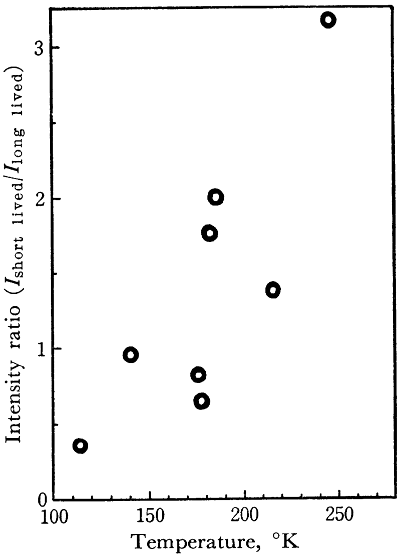

Fig. 6. Ratio of the quantity of short lived and long lived species plotted against temperature.

Experiments Using the Solid Sample prepared by Fusing the Mixture of Acridine and Acridan. The ESR signals obtained in this sample had better S/N ratios than the preceeding ones and the spectral feature could be studied more satisfactorily.

First, the electronic spectrum of the sample was taken by the following procedure. A mixture of acridine and acridan 1 : 1 in ratio was placed between two cover glasses (for melting point determination), and was fused on a hot plate. The liquefied deep yellow mixture spread as a thin film and remained almost transparent after being solidified. The spectrum obtained is shown in Fig. 7. An acridine film prepared similarly as above is shown by a broken line and the two cover glasses by a dotted line. An absorption band is clearly observed in the region 400—500 nm.

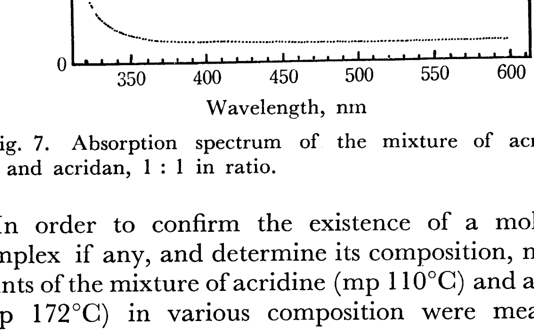

Fig. 7. Absorption spectrum of the mixture of acridine and acridan, 1 : 1 in ratio.

In order to confirm the existence of a molecular complex if any, and determine its composition, melting points of the mixture of acridine (mp 110°C) and acridan (mp 172°C) in various composition were measured. The phase diagram obtained is given in Fig. 8. It is seen that a clear peak exists at a mole fraction of ~0.52 corresponding to 1 : 1 complex. It appears that another peak exists near 0.25 which suggests the formation of 3 : 1 complex.

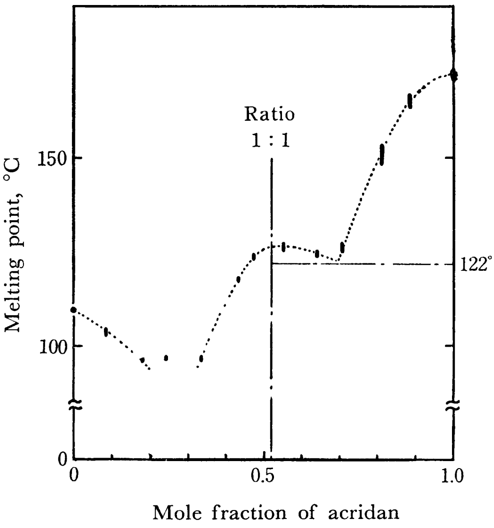

Fig. 8. Fusion curve for the mixture of acridine and acridan.

The ESR signals obtained upon irradiation were found to change considerably in their spectral shape according to the composition, and the assignment of the four species could be made on the basis of these spectral changes. In spite of the change in shape, the values of parameters β, γ, and δ were almost the same as those obtained for the sample in a benzene medium.

$$\left.\begin{aligned}\beta &= 112 \pm 2 \text{ gauss}\\ \gamma &= 137 \pm 5 \text{ gauss}\\ \delta &= 212 \pm 6 \text{ gauss}\end{aligned}\right\} \quad (2)$$

Figure 9 shows a typical example of the spectral change depending on the composition. Mixing ratio $[A]/[AH_2]$ is written on the left, and the exciting light and irradiation time on the right side. Similar signals were obtained by 365 nm- and 480—600 nm-irradiations. From a number of experiments, we could conclude as follows. 1) The relative intensity of peak *a* compared with other peaks increases with $[A]/[AH_2]$. 2) It increases with the length of irradiation time. 3) The intensity ratio of peak *d* to *c* is scarcely affected by the irradiation time and depends largely on the composition. As a general tendency, it increases with $[A]/[AH_2]$. 4) Generally the sum of *c* and *d* is relatively large in the low $[A]/[AH_2]$ region and becomes quite small in the high region. Hence in the former case, peak *b* tends to be hidden in peak *c*, while in the latter case it becomes difficult to be observed. 5) The resolution of peak *a* becomes worse whenever peak *b* is prominent.

From 3), there is no doubt that *c* and *d* are due to different species and the spectral shape of *c* and *d* have been made quite clear from (a)—(c) in Fig. 9. If separately drawn, they are certainly of types C and D in Fig. 10. From the line shapes and large line separations, there is scarcely any doubt that they are due to $\Delta M = \pm 1$ transitions of certain radical pairs. If so, the signal due to transition $\Delta M = \pm 2$ should exist at the magnetic field of about half strength. In fact,

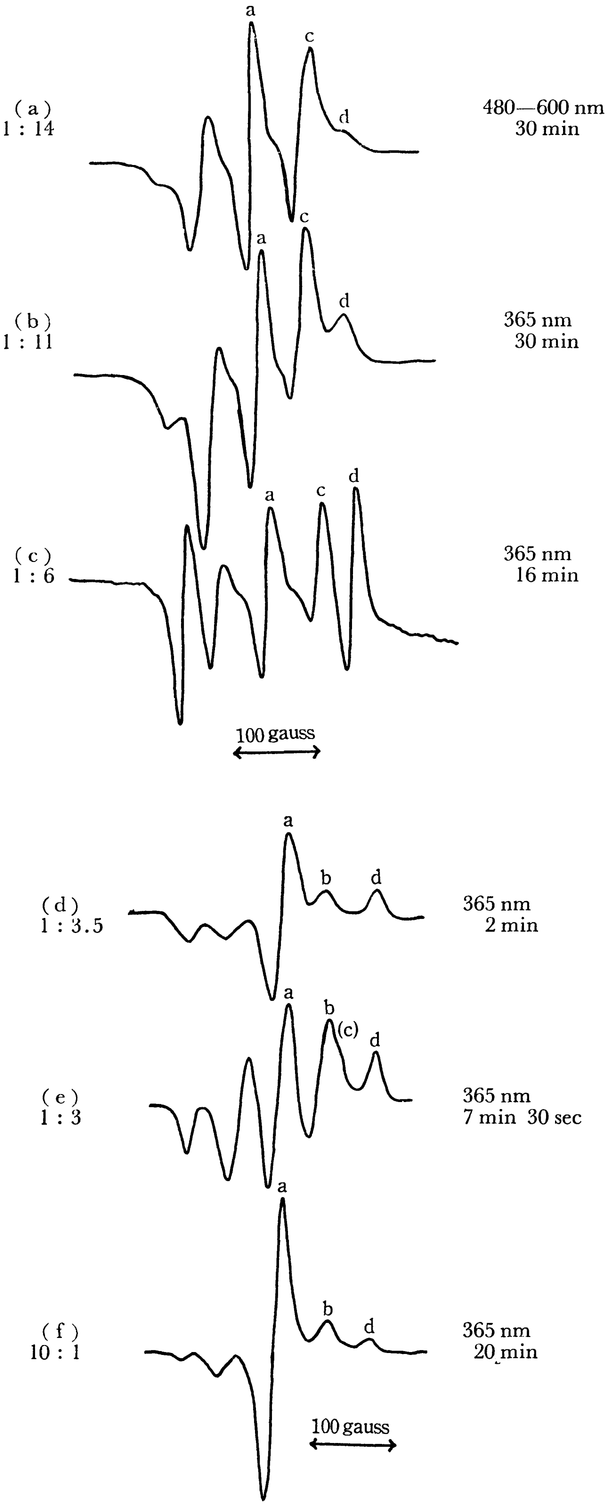

Fig. 9. Some examples of ESR spectrum.

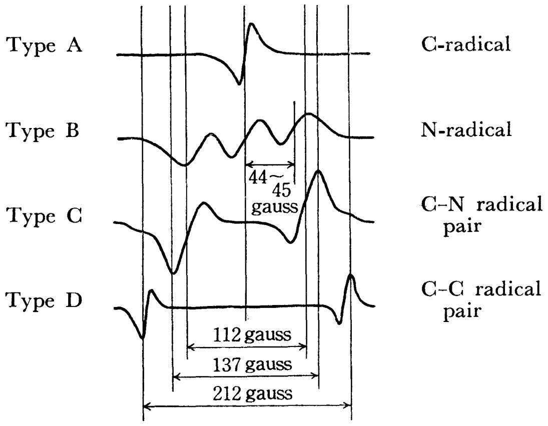

Fig. 10. ESR signal for each radical species.

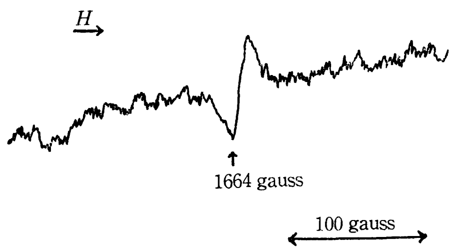

Fig. 11. ESR signal of radical pair due to $\Delta M=\pm 2$ transition.

we could succeed in detecting a signal at 1670 gauss (with 9337.4 MHz) as shown in Fig. 11. The sample composition was acridine : acridan = 1 : 5.4. The irradiation was performed for 50 min with no filter, using a 1 kW superhigh pressure mercury lamp. The signals at higher magnetic field in this sample, consisted of peaks *a*, *b*, and *d*. Peak *c* was observable only in a certain period of irradiation. For the measurement of $\Delta M=\pm 2$ transition, the sensitivity was raised 22 times that for the $\Delta M=\pm 1$ measurement. In spite of the above success, it is not certain whether this signal corresponds to type C or D. However, if the two species were to be captured at the same time, they would appear at about the same position and could not be discriminated.

c- and *d*-species now having been identified as radical pairs, unpaired electron distances for *c*- and *d*-species were evaluated by the usual method[18] as 6.0 and 5.1 Å, respectively, from the zero field splitting constant $D=$ 137 and 212 gauss (assuming $E=0$).

a- and *b*-species were assigned as follows. From 5), it can be judged that peak *b* has its component in peak *a*. That the decay for the sample in a benzene medium consists of two first order terms also supports the superposition of the two species. Hence the spectral shape of A and B can be drawn as shown in Fig. 1 . Type A with g=2.004 and $\Delta H_{\mathrm{msl}}=18$ gauss always appears under various conditions. Type B is a triplet with a separation of 44 gauss and is easily observed in the high $[\mathrm{A}]/[\mathrm{AH}_2]$ region. There is scarcely any doubt that *a* and *b* are due to C- and N-radical, respectively, the existence of which has already been fully established in the previous works.[9,11,19] The value of coupling constant 44 gauss is reasonable for ^{14}N taking anisotropy into account.[20]

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[18] Y. Kurita, H. Ohigashi, and M. Kashiwagi, *Bussei*, **9**, 87 (1968).

[19] T. Shida and A. Kira, This Bulletin, **42**, 1197 (1967).

[20] Isotropic and anisotropic hyperfine coupling constants of N-radical in *t*-butyl chloride are (private communication from Dr. T. Shida) $A_{iso}=34.6$ $A_{aniso}=6.80$ gauss.

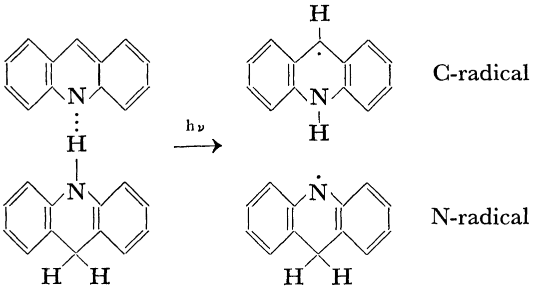
Discussion

Now that the ESR signals of the solid mixture of acridine and acridan have been successfully analysed and the four radical species, N-radical, C-radical and two kinds of radical pair have been identified, the problems to be considered are 1) the primary step for the formation of these species and 2) the nature and behavior of these radical species. They may be answered to some extent on the ground of the present results.

It is most likely that the molecules of acridine and acridan in a solid state interact in such a way that a molecular complex is formed by hydrogen bonding and that the formation of radical species is intimately connected with it. The formation of 1 : 1 complex in a solid state has been fully established by the L-S phase diagram of acridine and acridan in addition to a new band observed in the region 400—500 nm. That the hydrogen bond plays a role in this complex formation, is supported by the following facts. The formation of a similar 1 : 1 complex takes place between 9,9-dimethylacridan having N-H hydrogen and acridine (or 9-methylacridine),[21] whereas according to our experiment, *N*-methylacridine is not colored when it is fused with acridine, and furthermore, a mixture of various compositions (deaerated) never gives the ESR signal upon irradiation at 365 nm at 77°K. Thus it is reasonable to say that the hydrogen bond of N···H-N type is involved in the complex formation.

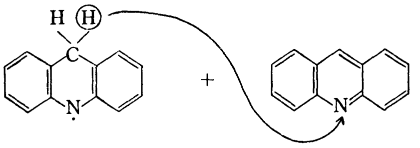
It is well known, however, that in a fluid state acridine and acridan show no sign of such hydrogen bonding. For instance, the electronic spectrum of a mixture of acridine and acridan is a mere superposition of the spectrum of two separated components.[22] In addition, it has been established from the fluorescence quenching experiment that acridan does not form a hydrogen bond with triethylamine which is a most powerful H-acceptor. In view of these facts, the hydrogen bond between acridine and acridan in a solid state must be very weak. Furthermore, the appearance of a new band at 400—500 nm strongly suggests the C-T character of the complex.

The formation of radical species was achieved only by irradiation, but the fact that the light of 480—600 nm is as equally effective as 365 nm implies that excitation of the complex leads to the radical formation in question. Thus we have schematically



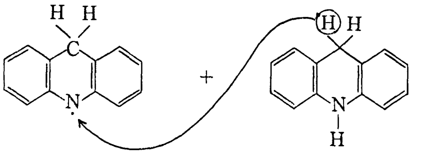
The radical species primarily produced are considered to be a radical pair consisting of C-radical and N-radical and also the equimolar separated C- and N-radicals. During the course of irradiation, however, mutual transformation occurs, and this is the reason why the spectral shape varies according to the experimental conditions.

For the nature and behavior of radical species, we have to be content with a speculative discussion in present stage. Generally the formation of radical pair is considered to depend on the diffusibility of the produced radicals, which in turn is determined by the magnitude of kinetic energy associated with the radicals and also by the rigidity of the medium. In the present case, however, we are tempted to consider the problem in terms of C- and N-radical. Assuming that the mutual transformation occurs only during irradiation, the increase in the yield of C-radical (*a*-species) and also the increase in the ratio of C-radical (*a*-species) to *c*-species both with the increase in irradiation time (finding 2) and Fig. 2) indicates that C-radical is produced efficiently from other species photochemically. The finding 1) that the yield of C-radical increases with the higher $[A]/[AH_2]$ may then be interpreted to be due to the fact that the reaction



→ C-radical + acridine (3)

occurs photochemically not but the reaction



→ C-radical + acridan (4)

This is reasonable from the thermodynamic stability of acridine and acridan.

Finding 4) (the yield of N-radical (*b*-species) is small when $[A]/[AH_2]$ is very small) can be interpreted that under such a condition it is difficult for process (3) to occur, and N-radical chiefly exists as a radical pair. This will be supported again from another point of view. The above statements are consistent with Zanker's view as well as ours, *i.e.*, C-radical is more stable than N-radical in the fluid state[7] or in the rigid solvents.[11]

It is most remarkable that the decay of *a* species is reproduced by the superposition of the two first order processes. Since the disappearance of radical occurs only by recombination or disproportionation process, the first order decay may require that radicals exist in pairs and in such neighborhood to each other that mutual attraction favors their encounter but not close enough for the ESR signal of the radical pairs to become observable. As such radical pairs lying apart, the following two are conceivable, *i.e.*, C-C radical pair (apart) and C-N radical pair (apart) (N-N radical pair does not exist appreciably since N-radical cannot exist in excess). If such a hypothesis be admitted,

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[21] W. L. Semon and D. C. Craig, *J. Amer. Chem. Soc.*, **58**, 1278 (1936); D. C. Craig, *ibid.*, **60**, 1458 (1938).

[22] S. Niizuma, Y. Ikeda, and M. Koizumi, This Bulletin, **40**, 2249 (1967).

then a short-lived species may be assigned as C-C radical pair (apart) and long-lived species as C-N radical pair (apart). The higher yield of a short-lived species at higher temperatures is consistent with this assignment, because the N-radical→C-radical process may more easily occur at higher temperatures.

Finally the radical pairs *c* and *d* may be assigned as follows. From the finding that *d* increases with the larger $[A]/[AH_2]$ as compared with *c*, *d*-species may be assigned as C-C radical pair and in consequence *c*-species as C-N radical pair. Finding 4) (*c*-species mainly exists in very low $[A]/[AH_2]$ and the non-appearance of N-radical in this region, *cf.* *a*, *b*, and *c* in Fig. 9) can be understood by the above assignment, because it is difficult for reaction (3) to occur under such a condition.