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Radicals Produced by UV Irradiation of Acridan and Acridine in Glassy and Crystalline Medium at 77°K

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Choosing two groups of solvent a) methanol, ethanol, isopropanol (glassy at liquid nitrogen temperature) and b) *t*-butanol, benzene, tetrahydrofuran (crystalline at liquid nitrogen temperature), ESR studies have been made on the irradiated solutions of A] acridine (A)+acridan (AH_2) (1 : 1), B] A alone, and C] AH_2 alone at 77°K. 1) 365 mμ irradiation of A] and B] in the solvents of a) group does not cause any photochemical reaction, whereas in the solvents of b) group, the $A^* + AH_2 \rightarrow 2AH\cdot$ reaction occurs. A resultant singlet ESR line has been assigned to AH·. 2) Irradiation of A] and C] with the entire output from a superhigh pressure mercury lamp gives, for solvents of group a), the ESR spectra which can be attributed mainly to alcohol radicals ($R\dot{C}HOH$) but gives electronic absorption spectra ascribed only to AH· ; for the solvents of group b) the results were almost the same as in 1).

In a series of papers dealing with the kinetics of the photoreduction of acridine, the participation of semi-reduced acridine, AH·, appears to be fully substantiated.[1-4] In particular, there is scarcely any doubt about the assignment of a transient species observed in flash experiments as AH·[1,4] in view of spectroscopic and kinetic evidence. However, the direct evidence for its radical nature is still lacking. ESR studies, although most promising for detecting a radical species, cannot be applied to the similar systems as employed in the kinetic studies, because the lifetime of AH· is too short. Hence, various attempts have been made to catch the ESR signal of AH· at liquid nitrogen temperature. At first, three kinds of alcohol, in which appreciable photoreduction of acridine occurs at room temperature, have been used as solvents. Irradiation by 365 mμ of the solutions of acridine and acridan as well as of acridine alone, has failed to give any sign of reaction. Irradiation of the solution of acridan by the total output from a superhigh pressure mercury lamp has given a certain species light brown in color, which is rather stable at liquid nitrogen temperature. The electronic spectra of this species agree with the ones in the flash experiment[1] and yet, the ESR spectra consist of the lines mainly originating from alcohol molecules.

Secondly, a group of solvents (benzene, *t*-butanol and tetrahydrofuran) which is known to take the crystalline form at liquid nitrogen temperature has been attempted with some success. It has been found that after dissolving acridine and acridan in these solvents at room temperature and irradiation with 365 mμ at liquid nitrogen temperature, the samples become colored in light brown and give ESR signals which are practically common to three solvents and are most likely attributed to AH·. The same signals as well as the same tint of color have been obtained with the samples containing only acridan on irradiation with a total output from a mercury lamp. We believe that most of the findings

1) A. Kira, S. Kato and M. Koizumi, This Bulletin, **39**, 1221 (1966).
2) A. Kira, Y. Ikeda and M. Koizumi, *ibid.*, **39**, 1673 (1966).
3) S. Niizuma, Y. Ikeda and M. Koizumi, *ibid.*, **40**, 2249 (1967).
4) A. Kira and M. Koizumi, *ibid.*, **39**, 2486 (1967).

obtained in the present investigation, are interesting from the standpoint of the reactivity of acridine and of acridan in general and of the sensitized decomposition of alcohols, not to speak of the confirmation of ESR spectra from AH·.

Experimental

ESR Spectrometer. A Nippon-Denshi P-10 type-ESR spectrometer was used.

Light Source. Light from a superhigh prssure mercury lamp (500 W and 100 W) was used without or with filters (in the latter case mainly 365 mμ but including 334 mμ).

Sample. *Benzene, Methanol and Isopropanol.* G. R. samples from Wako Junyaku were used without further purification.

Ethanol and t-Butanol. Reagents from Wako Junyaku were submitted to distillation. Tetrahydrofuran was distilled after refluxing over sodium. The solvent was kept over sodium and potassium metals. The concentrations of acridine and acridan were usually 10^{-2}—10^{-3} M. When the mixture of acridine and acridan was used, the composition was always 1 : 1.

Results

A) Glassy Medium. After having established that 365 mμ irradiation of the solution of acridine or of the solution of acridan and acridine in ethanol, methanol and isopropanol, did not cause any reaction, the samples were irradiated with the total output from a mercury lamp without filters. Since the results obtained are essentially the same as those in the solutions of acridan alone, both of them will be described here at the same place. It was checked that the irradiation of the solvents alone gives no appreciable signals under the similar conditions.

Methanol. A typical example for the deaerated solution is shown in Fig. 1. The radicals produced are quite stable at this temperature, the shape of the signal showing no change 1.5 hr after irradiation. In the presence of oxygen, the central three lines become somewhat unsymmetric. Three central lines (triplet) and the other two lines outside (doublet) are assigned to two different species, because the dependence on irradiation time of these two groups are different. Table 1 gives the relative height of the peak neighboring a central one and of the outermost peak, in reference to the height of the central peak. Figure 2 and 3 give respectively the build-up curves of the doublet and of the triplet. S-shape character for the former indicates that the doublet

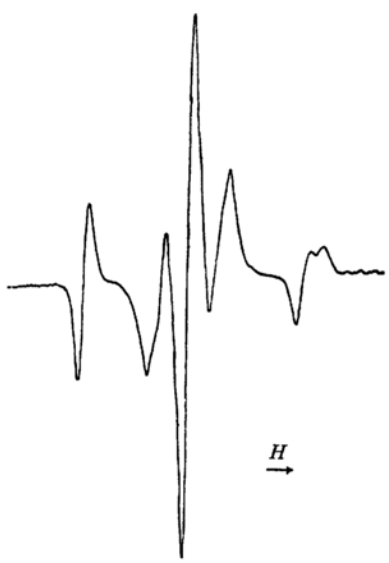

Fig. 1. ESR spectrum obtained by irradiating deaerated methanol solution of acridan for 25 min.

Table 1. Relative heights of the peaks as a function of irradiation time

Exp. No.	Time of irradiation min	Relative height of the peak: Neighbouring the central one	Relative height of the peak: Lying outermost
1	2	0.27	0.11
	14	0.27	0.22
	17	0.24	0.29
	25	0.26	0.33
2	25	0.24	0.36
	46.5	0.26	0.58
3	40	0.27	0.51
	50	0.28	0.38
	60	0.27	0.36

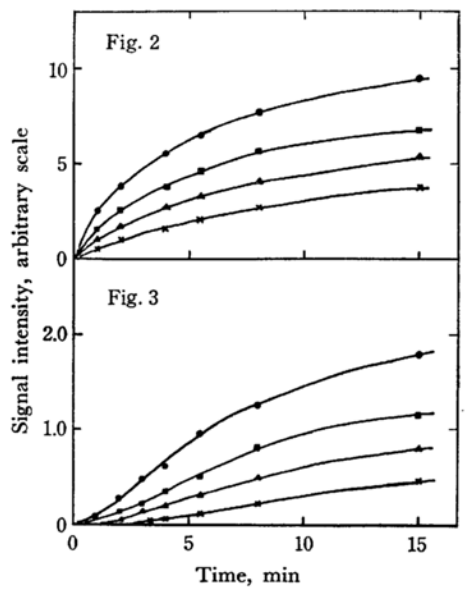

Fig. 2, 3. The build-up curves of the triplet (Fig. 2) and of the doublet (Fig. 3).
●: Irradiation without neutral filter (100% transmittance)
■: Irradiation with 61% neutral filter
▲: Irradiation with 46% neutral filter
×: Irradiation with 32% neutral filter

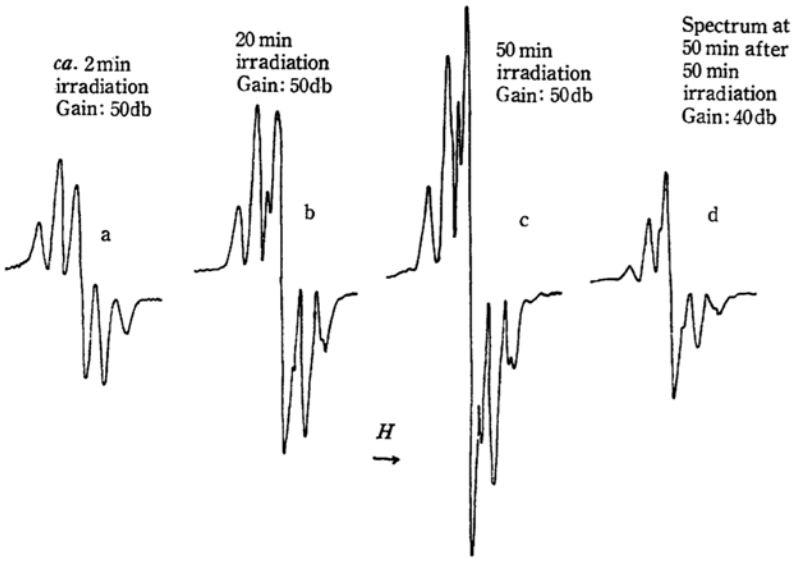

Fig. 4. ESR spectra obtained by irradiating acridan and acridine in deaerated ethanol.
a: *ca.* 2 min irradiation Gain: 50 db
b: 20 min irradiation Gain: 50 db
c: 50 min irradiation Gain: 50 db
d: Spectrum at 50 min after 50 min irradiation Gain: 40 db.

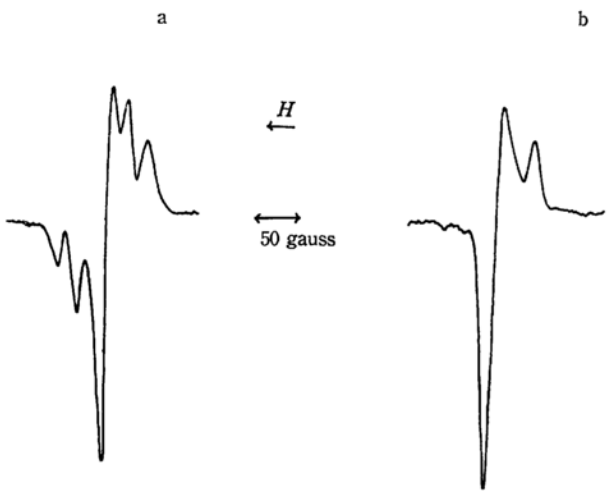

Fig. 5. ESR spectrum obtained by irradiating aerated ethanol solution of acridan.
a: When irradiated for a short time
b: When kept in the dark for 30 min after irradiation.

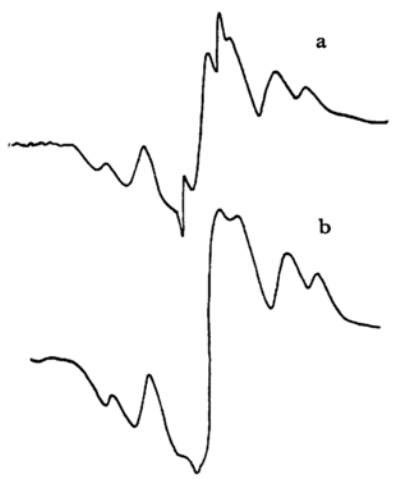

Fig. 6. ESR spectrum obtained from deaerated isopropanol solution of acridan.
a: When irradiated for a short time
b: When kept in the dark for four days after irradiation.

is produced not primarily but in the secondary reaction. Comparing the present results with the ones reported in the literature,[5-7] the triplet and the doublet may be assigned to methanol radical, $\cdot CH_2OH$ and formyl radical $H\dot{C}O$, respectively. The signal intensity of triplet is proportional to the light intensity, as is clear from Fig. 2. Therefore the main reaction is a one-photon process.

Ethanol. Figure 4 gives one example of the variation of the ESR spectra with the time of irradiation. Broadly speaking, the spectra consist of five lines which are due to $CH_3\dot{C}HOH$. The continued irradiation causes a slight but obvious change; an

5) Sr. P. J. Sullivan and W. S. Koski, *J. Am. Chem. Soc.*, **85**, 384 (1963).
6) V. E. Kholmogorov, E. V. Baranov and A. H. Terenin, *Dokl. Akad. Nauk. SSSR*, **149**, 142 (1963).
7) F. J. Adrian, E. L. Cochran and V. A. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962).

additional line appears and becomes gradually larger in between the central and the next line. The height of the peaks at the initial stage is 1 : 2 : 4 : 2 : 1. ESR spectra labeled by d are the ones when c was kept in the dark for 50 min. It is seen that the two lines existing in the later stage have almost disappeared. In spite of this structural change, the integrated intensity remains the same within ±5%. At this stage, the height of the peaks is approximately in the ratio 1 : 3 : 5 : 3 : 1. It has been established that the signal intensity is proportional to the light intensity. A signal obtained in the aerated sample is unsymmetrical from the initial stage of irradiation (Fig. 5a); when it is kept in the dark for 30 min, it turns into a peroxide-like signal (Fig. 5b). The formation of peroxide is reasonable, but it is not certain whether the spectra are due to peroxide radical or $C_2H_5O\cdot$.[8,9] It is remarkable that 4 min irradiation of the deaerated solution dissolving 1×10^{-3} M of acridan produces $\sim2\times10^{-3}$ M of radical (at the stage of about half saturation).

Isopropanol. In the absence of oxygen, the signal at the initial stage of irradiation consists of septet attributable to $(CH_3)_2\dot{C}OH$[5,6] and small additional bands which decay very gradually in the dark. Figure 6 gives one example. The integrated intensity decreases about several percent in 1.5 hr.

Electronic Spectra for Alcoholic Solutions. In the ESR spectra the signals to be ascribed to AH· are lacking or very insignificant, but all the solutions, after having been irradiated, become light brown and show blue emission with a long duration suggesting the existence of AH·. Preliminary measurement of the absorption spectra has been attempted. Since the results are essentially the same for three alcohols, they will be described all together. Absorption spectra of the ethanol solution of acridine and acridan (both in 2.5×10^{-4}M) before irradiation are shown in Fig. 7. The spectra in methanol and isopropanol are quite similar. A large and broad peak around 280 mμ belongs to acridan. Other peaks are due to acridine. Figures 8 and 9 are the absorption spectra of the above solution after 30 min irradiation with the total output from a superhigh pressure mercury lamp at liquid nitrogen temperature. It is seen that the acridan absorption near 280 mμ has completely disappeared. A very sharp band near 280 mμ and the new bands appearing at 520—522 mμ and around 485 mμ agree with the bands which were assigned to AH· in the flash studies.[1,4] A remarkable change in the spectral shape in the region from 345—365 mμ indicates that AH· has an appreciable absorption in this region. It is worth while to add that a small peak near 570 mμ was lacking in the previous flash experiment where the solution of acridine in ethanol was used. Since the above changes are essentially

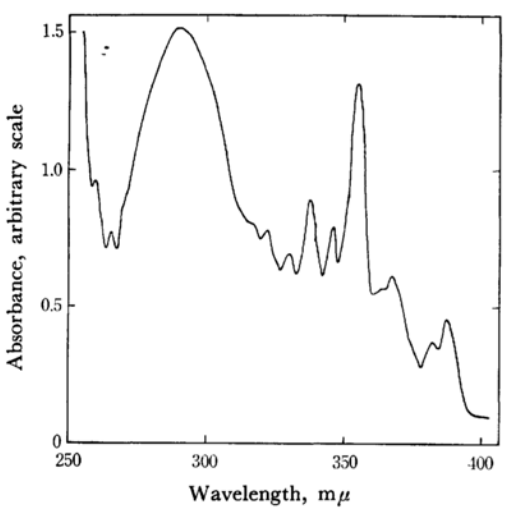

Fig. 7. UV absorption spectrum of deaerated acridine and acridan (both 0.25×10^{-3}mol/l) in ethanol at 77°K, before irradiation. It has no absorption in the visible region.

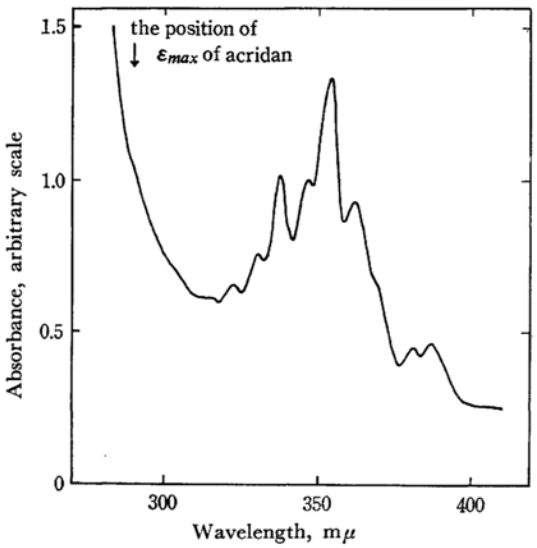

Fig. 8. UV absorption spectrum of deaerated acridine and acridan (both 0.25×10^{-3}mol/l) in ethanol at 77°K after 30 min irradiation.

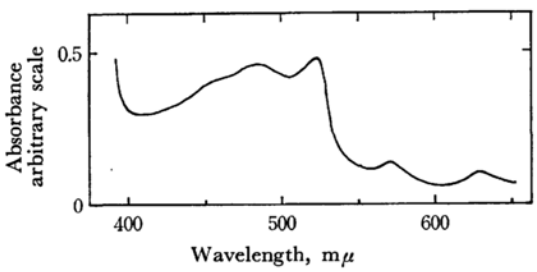

Fig. 9. Visible absorption spectrum of deaerated acridine and acridan (both 0.25×10^{-3}mol/l) in ethanol at 77°K after 30 min irradiation.

8) J. E. Bennett and A. Thomas, *Proc. Roy. Soc.*, **280**, 123 (1964).
9) Sr. P. J. Sullivan and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 159 (1964).

common to methanol and isopropanol solutions, they are all interpreted to be concerned with acridan. Various radicals originating from alcohols which have been amply confirmed by ESR spectra, give no appreciable absorption from 250 to 600 mμ. When the irradiated solution was warmed up to room temperature and cooled again to 77°K, it gave essentially the same spectra as the ones of the non-irradiated solutions. This implies that acridine does not participate in the eventual reaction and that most of the half-reduced acridine in a fluid state, reconverts to either acridan or diacridan (The latter has the absorption spectra not differing so much from those of acridan.). It was checked that the 365 mμ irradiation of the above samples and the solutions of acridine alone for more than an hour, does not give any change in the absorption spectra.

B) Crystalline Medium. Benzene, *t*-butanol and THF are the solvents which have crystalline state at liquid nitrogen temperature. When the samples containing acridine and acridan in 1 : 1, were irradiated by 365 mμ at 77°K, they were colored in light brown and gave a prominent single ESR line. ΔH_{msl} values were 16.7, 17.5 and 22 for benzene *t*-butanol and THF, respectively. There is scarcely any doubt that these signals arise from the interaction of excited acridine and acridan, although there is some possibility of the participation of solvent molecules, because weak side bands depend upon the solvent used. Irradiation by a total emission from a mercury lamp gave essentially the same result. This may be due partly to the high intensity of 365 mμ of a light source. Of course it was checked that no signal was detected in the cases of solvents alone.

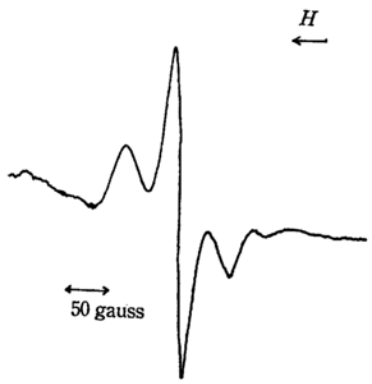

Fig. 10. ESR signal obtained by irradiating deaerated acridan and acridine in butanol at 77°K with 365 mμ of superhigh pressure mercury lamp.

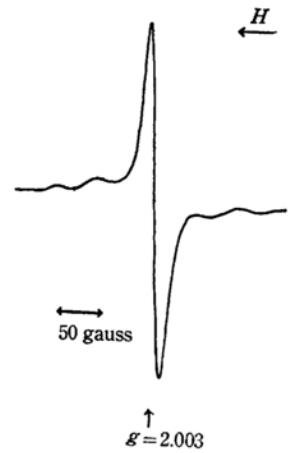

Fig. 11. ESR signal obtained by irradiating deaerated acridan and acridine in benzene at 77°K with 365 mμ of mercury lamp.

TABLE 2

Solute		Medium	Irradiation from Hg lamp: 365 mμ	Irradiation from Hg lamp: Total output
A) Acridine and acridan	a	Methanol	×✳	◎◎ (doublet & triplet)
	a	Ethanol	×	◎◎ (quintet)
	a	Isopropanol	×	○ (septet)
	b	*t*-Butanol	○ (singlet)	○ (singlet)
	b	Benzene	◎◎ (singlet)	○ (singlet)
	b	THF	◎◎ (singlet)	◎◎ (singlet)
B) Acridine	a	Ethanol	×	×
	a	Isopropanol	×	
	b	Tetrahydrofuran	×	
	b	Benzene	×	×
C) Acridan	a	Methanol		◎◎ (doublet & triplet)
	a	Ethanol		◎◎ (quintet)
	a	Isopropanol		◎◎ (septet)
	b	*t*-Butanol		◎◎ (singlet)
	b	Benzene		×✳
	b	THF		○ (singlet)

○ Signal in the deareated condition
× No signal in the deaerated condition
◎ Signal in the aerated condition
✳ No signal in the aerated condition

When THF and *t*-butanol containing acridan alone were irradiated by a mercury lamp without filters, they gave the similar signal as the above systems. In a very sharp contrast to *t*-butanol and THF, acridan solution of benzene did not give any ESR spectra.

t-Butanol. Figure 10 gives the ESR spectra obtained by irradiating with 365 mμ the deaerated solution of acridine and acridan. In the aerated system, the relative height of the central peak was somewhat low.

Benzene. As Fig. 11 shows, ESR spectra have four weak side bands in addition to a main line with $\Delta H_{msl}=16.7$ and $g=2.003$. The decay of the main line was measured at -95, -57 and -27°C. It increases with the rise of temperature, but the signal can be observed even near 0°C.

Tetrahydrofuran. Figure 12 gives the ESR spectra obtained by irradiating (without filters) the system of acridine and acridan in THF. In addition to a main single line, a broad absorption and a doublet 508 gauss apart, which is due to hydrogen atom, are apparently observed. Table 2 gives a brief summary of the present ESR studies.

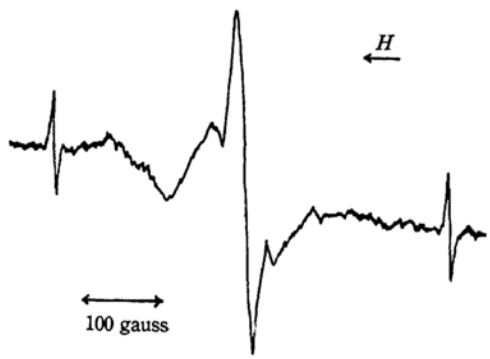

Fig. 12. ESR signal obtained by irradiating aerated acridine and acridan in tetrahydrofuran at 77°K with 365 mμ of mercury lamp.

It is to be noted that the results in glassy media and crystalline media are quite distinctive.

Discussion

It is well-known that acridine is photoreduced in various kinds of H-containing solvents in the fluid state. The reactive states of acridine, according to Kellmann *et al.*,[10] Porter *et al.*[11] as well as to our group,[12] are mainly singlet excited state and partly n-π^* triplet state, the lifetimes of which are respectively $\sim 10^{-10}$ and $\sim 10^{-8}$sec. Furthermore, we have established that part of the reaction goes *via* molecular mechanism without forming semiquinone,[1,12] and that acridine and acridan react photochemically (by 365 mμ) forming diacridan in benzene, the reactive state in this case being the lowest π-π^* triplet of acridine.[3,4]

In view of these results it is somewhat remarkable that no photochemical reaction (by 365 mμ) occurs at all in B) a) group at liquid nitrogen temperature. The reason may be that for the reaction to occur, reorientation of solvent molecules surrounding an excited acridine molecule is necessary and that at liquid nitrogen temperature such reorientation is impossible during the lifetime of the excited states. In the case of acridine and acridan, A) a) group, the two solute molecules are separated by solvent molecules so far apart that no reaction can occur. In crystalline medium on the other hand, acridine and acridan molecules (A) b) group) deposited from the medium, may be close to one another and in such a relative orientation to allow the reaction $A^*+AH_2\rightarrow 2AH$ to occur. It is very natural that benzene and *t*-butanol with no easily detachable hydrogen, do not easily react with AH·. Thus the main ESR spectra are due to AH· (singlet).

Turning to the cases of irradiation without filters, the formation of AH· in alcohols, as verified by the electronic spectra, is due to the $AH_2\rightarrow AH\cdot+H\cdot$ reaction. The produced hydrogen atom is expected to react with alcohol molecules, for instance according to $H\cdot+C_2H_5OH\rightarrow H_2+CH_3\dot{C}HOH\cdot$. AH· is thought to be quite stable even photochemically, because the intensity of the electronic spectra, after reaching the saturation value, does not decrease by the continued irradiation. Thus the results from the electronic spectra implies that at liquid nitrogen temperature, AH· does not react thermally nor photochemically with any other radicals originating from alcohol or with alcohol molecules themselves. This leads to the expectation that in ESR the singlet line due to AH· should superpose on the signals of the radicals originating from alcohol molecules. It is difficult, however, to verify this unambiguously from the present data. There is also another problem, as to the quantity of radicals produced. If the production of all the radicals are initiated by such reactions, $AH_2\rightarrow AH\cdot+H\cdot$, $H\cdot+C_2H_5OH\rightarrow CH_3\dot{C}HOH+H_2$, the finding that the quantity of the total radicals exceeds that of the original acridan even at a stage of half saturation, is difficult to understand. It seems necessary to consider that the formation of more than two radicals from one radical is occurring in secondary processes. Reactions such as $\dot{C}H_2OH \xrightarrow{h\nu} CH_2O+H\cdot\rightarrow\dot{C}HO+H\cdot+H\cdot$ which Sullivan *et al.*[13] suggested in the case of methanol, might be occuring. In the case of crystalline medium

10) A. Kellmann and J. T. Dubois, *J. Chem. Phys.*, **42**, 2518 (1965); A. Kellmann and J. T. Dubois, *J. Chimie Physique*, **63**, 936 (1966).
11) E. Van der Donckt and G. Porter, *J. Chem. Phys.*, **46**, 1173 (1967).
12) M. Koizumi, Y. Ikeda and H. Yamashita, This Bulletin, **41**, 1056 (1968).
13) P. J. Sullivan and W. S. Koski, *J. Am. Chem. Soc.*, **84**, 1 (1962).

containing only acridan Reaction, $AH_2 \rightarrow AH\cdot + H\cdot$ occurs in *t*-butanol and tetrahydrofuran just as in the case of alcohols but the reaction of atomic hydrogen with solvent molecules is not so significant as with alcohol molecules. Detection of a signal of atomic hydrogen in tetrahydrofuran also supports this conclusion. The absence of the reaction in benzene may be due to easy occurrence of the back reaction.

As to the radical species produced in the alcoholic solutions of acridan, there is no doubt that most of them are of the RC(OH)R′ type. There appears to be many problems about the secondary reactions that follow, which however, are out of the scope of the present aim. Our greatest concern is how the existent AH· radicals are affecting the observed ESR spectra. But the exact and quantitative answer to this problem also awaits further studies.