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The Behavior of Radical Anion of Acridine as Revealed from ESR Studies

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Nature of acridine anions produced by the addition of alkali metals to the tetrahydrofuran solutions of acridine has been studied by means of ESR and VU spectra. In excess of acridine (A), a green species G is produced. This has been identified as A^-Na^+ (or A^-K^+ *etc.*). A^-Na^+ gives under suitable conditions, ESR spectra with hfs consisting more than fifty lines. This species reverts to acridine upon addition of a small quantity of water or ethanol. With the fall of temperature, the intensity of ESR spectra of G decreases remarkably and accompanied with it, UV spectra of G also decline with no change of the spectral shape. $\log I$ *vs.* $1/T$ plots where I is either the intensity of UV absorption or of the ESR signal are satisfactorily linear; this has been interpreted to be due to a large equilibrium constant of the process, $2A^-Na^+ \rightleftarrows (Na^+A^-)_2$ in which $(Na^+A^-)_2$ is a colorless diamagnetic substance. This interpretation has led to the value of enthalpy of dissociation of $(Na^+A^-)_2$ as *ca.* 14 kcal. When sodium is in excess, a diamagnetic violet species is produced. This has been assigned as $Na^+A^{2-}Na^+$. The chemical processes pertaining to A^-Na^+ and $Na^+A^{2-}Na^+$ can be summarized as follows:

$$\begin{tikzcd}
A \arrow[r, shift left, "Na"] & A^-Na^+ \arrow[l, shift left, "O_2"] \arrow[r, shift left, "Na"] \arrow[d, shift left] & Na^+A^{2-}Na^+ \arrow[l, shift left, "O_2"] \\
 & (A^-Na^+)_2 \arrow[u, shift left] \arrow[ul, "O_2 \text{ or } H_2O \text{ or } C_2H_5OH"] &
\end{tikzcd}$$

In a series of papers on the photoreduction of acridine reported by one of the present authors (M. K.) and his collaborators, it was established that semiquinone or half-reduced radical of acridine is formed in the irradiated alcoholic solution.¹⁾ In connection with these studies, it is interesting to study the chemical nature of the various forms of half-reduced acridine such as neutral radical and radical anion by means of an ESR technique in addition to UV measurement.

This paper reports the behavior of radical anion which is produced by treating acridine with alkali metals in tetrahydrofuran (THF). Hitherto, there seems to be no papers on the ESR spectra which were decisively attributed to acridine radical anion, although some reports were made on other *N*-heterocyclics.²,³⁾ Carrington⁴⁾ said, by the

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1) A. Kira, S. Kato and M. Koizumi, This Bulletin, **39**, 1221 (1966).

2) R. L. Ward, *J. Am. Chem. Soc.*, **83**, 3623 (1961).

3) R. Pointean, J. Favede and P. Delhaes, *J. Chim. Phys.*, **61**, 1129 (1964).

4) A. Carrington and J. D. Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

analogy with pyridine which upon contact with sodium in DME (dimethoxyethane) or THF, yields dipyridyl anion, that acridine radical anion, being also unstable, might convert to a dimeric form. Kuwata *et al.*5) found that acridine, upon contact with metallic sodium in THF, gives a diamagnetic substance red in color, and the solution, when heated, turns blue and gives broad ESR spectra consisting of a single line with $\Delta H_{\mathrm{msl}}=13\mathrm{G}$ and $g=2.003$. They suggested that this is due to a radical anion of acridine. Russel *et al.*6) reported in a paper dealing with some radical anions existing in a 1 : 1 solution of some unsaturated and its dihydro compounds in $(CH_3O)_2SO$ containing *t*-Bt-OK), that electron transfer occurs between acridine and acridan. No remark was made, however, on the ESR spectra.

In the present paper, we would like to report the following findings; 1) Radical anion of acridine, A^- gives under suitable conditions, ESR spectra with hfs consisting more than fifty lines. 2) A^- transforms to dianion A^{2-} when the quantity of sodium is in excess. 3) The intensity of ESR decreases remarkably at lower temperatures; this suggests the existence of a dimerization (or polymerization) equilibrium of the type $2A^-Na^+ \rightleftarrows (A^-Na^+)_2$.

Experimental

A Nippon-Denshi P-10 type ESR spectrometer was used; its characteristics are X-band, 100 kc field modulation and H_{011} mode of cavity. The constancy of temperature was maintained within ±2°C by streaming through a cavity either nitrogen gas (from the liquid nitrogen) for low temperatures or hot air for high temperatures.

Materials. First grade tetrahydrofuran (THF) from Wakojunyaku was refluxed with sodium for several hours, distilled and then stored *in vacuo*. Na-K-alloy was added to the stock solvent to remove a trace of water. Sodium and potassium were made free from surface contamination by dropping fused metals down through a capillary *in vacuo*. Lithium was not specially purified. Acridine was purified by a usual method.

UV Spectra of the Solution in Contact with Alkali Metals. Several mg of acridine dissolved in 2 m*l* of degassed THF was brought into contact with *ca.* 0.2—0.4 g sodium through a breakable seal. The solution gradually turned green in several to ten and several minutes and finally became violet after a long time. The two species will be designated as G and V. Essentially similar results were obtained with both potassium and lithium. The absorption spectra are shown in Figs. 1 and 2. Table 1 gives the comparison of the

Table 1. Peak positions of the absorption spectra for G and V species (at room temp)

	G	V
Reduction by K	599, 626 mμ	545, 580 mμ
Reduction by Na	590, 619	545, 570

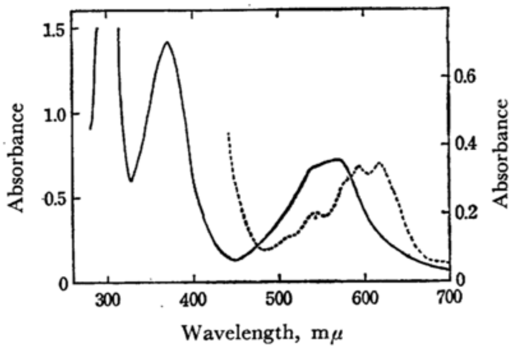

Fig. 1. Absorption spectra of G and V species (see text) (in contact with metallic sodium).
Dotted line, G species (right ordinate)
Solid line, V species (left ordinate)

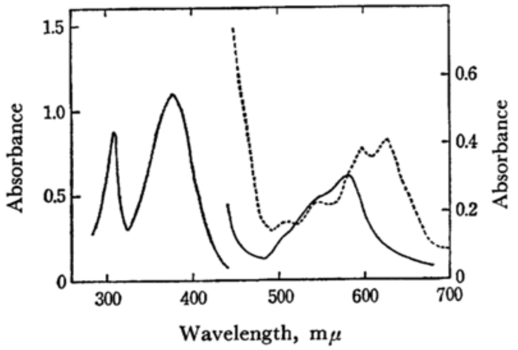

Fig. 2. Absorption spectra of G and V species (see text) (in contact with metallic potassium).
Dotted line, G species (right ordinate)
Solid line, V species (left ordinate)

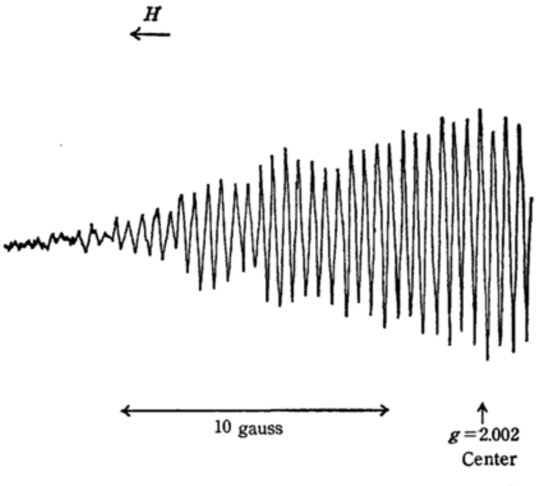

Fig. 3. ESR spectrum of acridine anion radical from acridine with metallic sodium.

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5) K. Kuwata, T. Ogawa and K. Hirota, This Bulletin, **34**, 291 (1961).

6) G. A. Russel, E. G. Janzen and E. T. Strom, *J. Am. Chem. Soc.*, **84**, 4155 (1962).

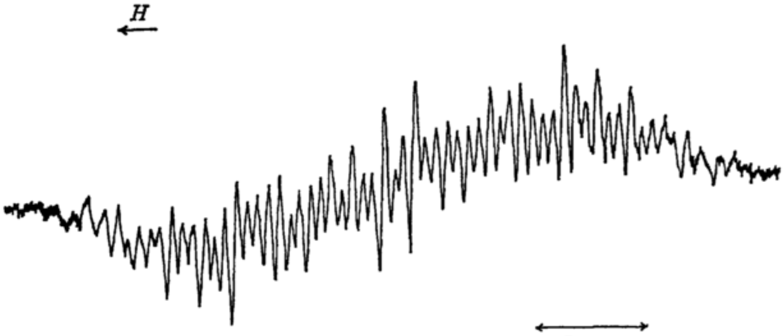

Fig. 4. ESR spectrum of acridine anion radical from acridine with metallic potassium.

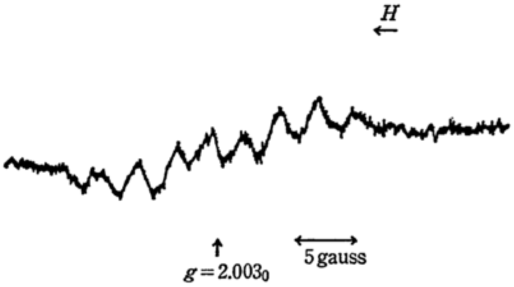

Fig. 5. ESR spectrum of acridine anion radical from acridine with metallic lithium.

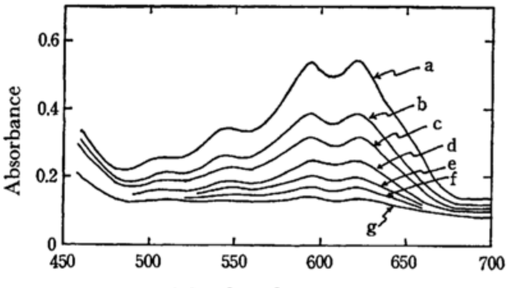

Fig. 6. Temperature change in absorption spectra of G species (produced from acridine with metallic sodium).

a : 20°C
b : 4°C
c : −3°C
d : −11°C
e : −24°C
f : −32°C
g : −47°C

peak positions of G and V for the longest wavelength absorption in the case of sodium and potassium.

It was established that as long as unreacted acridine exists, only G is produced and that the production of V occurs as soon as acridine disappears.

Behavior of Green Species. Species G displays ESR spectra which are shown in Figs. 3—5. Upon addition of a very small quantity of water or ethanol, it transformed entirely to acridan; this was confirmed by UV spectra. G is photochemically stable; any slight change does not occur by 5890 Å illumination. The influence of temperature change on the intensity of ESR (produced by the addition of sodium) was investigated. It increases with the rise of temperature from −42 to ∼77°C; at −63°C the signal was scarcely detected. Hfs in the ESR spectra at 77°C is essentially the same as the ones at ordinary temperatures except for fine details. This implies that one radical species is responsible to ESR spectra. At extremely low temperatures, the solution becomes colorless and is accompanied with the appearance of a white precipitate. This precipitate is redissolved by the introduction of air or by warming the solution. Figure 6 shows the temperature change of UV spectra.

As seen from the figure, the intensity at −47°C decreases nearly ten times as that at 20°C without any change in the spectral shape. Thus the intensity change in the absorption spectra runs parallel with that in the ESR signal. The determination of ε for G was performed by measuring the ESR signal and UV spectra at the same temperature and by using the radical concentration evaluated from the former. The value obtained is ε (at 620 mμ)$=6900\pm500$ $\text{M}^{-1}\text{cm}^{-1}$.

Behavior of Violet Species. The following observations were made on the samples treated with sodium. ESR signals decrease as G transforms to V and no signal is observed in the solution containing only species V. V is stable both thermally (from room temperature up to +70°C) and photochemically. The introduction of air causes the change V→ G→acridine to occur. From the change of UV spectra observed when the air is introduced to the solution containing only V species, it is concluded that V transforms to acridine at one to one ratio. This enables one to evaluate ε_{570} of V as 4600 ± 300 $\text{M}^{-1}\text{cm}^{-1}$. The temperature effect on the absorption spectra is shown in Fig. 7. For the sample treated with potassium, such temperature effect is given as the change with time, after the solution which had been kept in the dry ice bath was put out of the bath. The complicated change in both cases suggest that more than two species or two states may exist in thermal equilibrium. The present result is somewhat similar to the one reported by Smid⁷⁾ for fluorene radical anion.

Finally, it may be worthwhile to add that the temperature effect on the absorption spectra of the solution

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7) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).

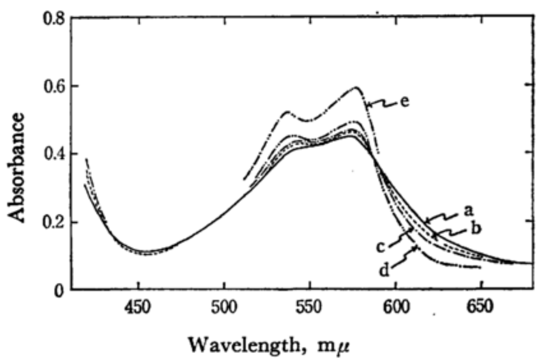


Fig. 7a. Temperature change in absorption spectra of V species (produced from acridine with metallic sodium).
a : 26°C d : −70°C
b : −9°C e : −108°C
c : −33°C

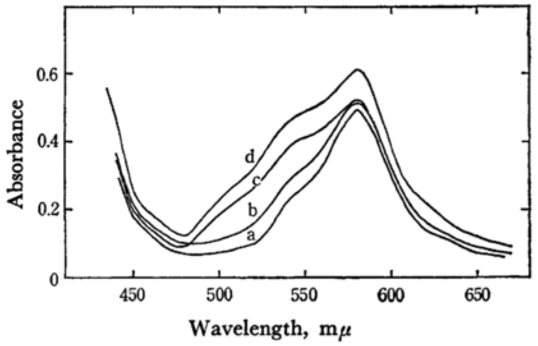


Fig. 7b. Change of the absorption spectra of V species (produced from acridine with metallic potassium) with time, after the solution was put out of the dry ice bath;
a : *ca.* 0—2 min
b : *ca.* 2—4 min
c : *ca.* 4—6 min
d : *ca.* 20 min after

containing both V and G, appears to be mere superposition of that on the solution containing only V or G alone.

Discussion

By the analogy with the general behavior of aromatic compounds in contact with alkali metals, there is scarcely any doubt that G species is a radical anion A^- (or A^-Na^+) produced by the electron transfer from alkali metals to acridine. The finding that the admittance of air transforms G into acridine is thought to negate the formation of diacridyl anion, which is expected to yield diacridan. It is most reasonable to identify V species as dianion A^{2-}, since V species is diamagnetic and is produced only in the existence of excess alkali metals. It is interesting to compare the above behavior with that of pyridine. According to Ward,[2] pyridine, when treated with alkali metals in DMF solutions, changes to a reddish violet substance in a short time but after a long time, becomes a yellow substance, the former being paramagnetic and the latter diamagnetic. In this case, however, the paramagnetic species was identified as dipyridyl anion on the basis of hfs of its ESR spectra. Thus one can say that acridine radical

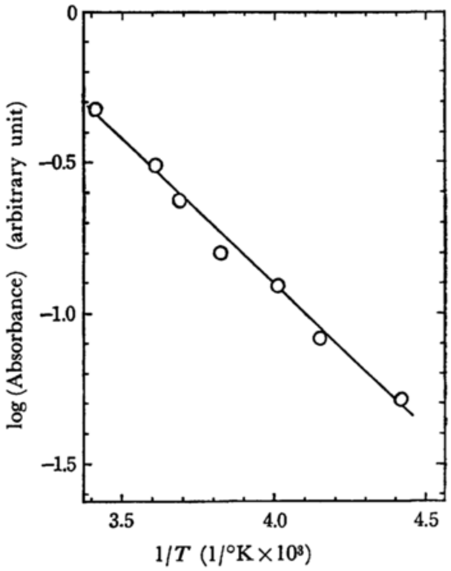


Fig. 8a. log (Absorbance) *vs.* $1/T$ plot of G species. Absorbance, at 619 mμ (ε_{max})

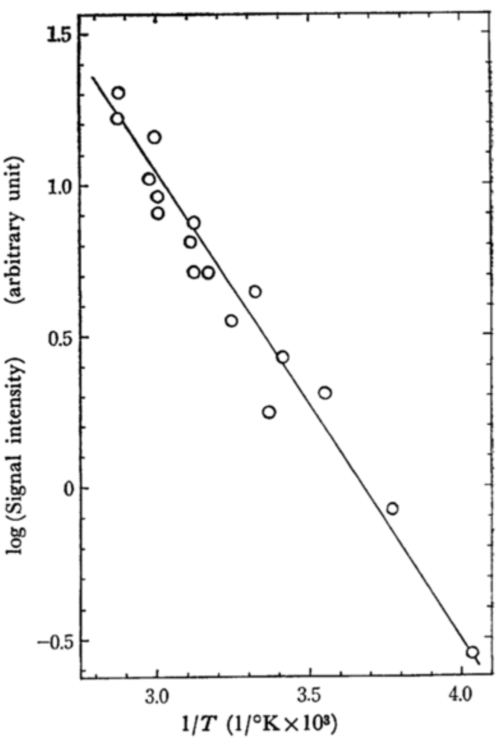


Fig. 8b. log (Signal intensity of ESR) *vs.* $1/T$ plot of G species.

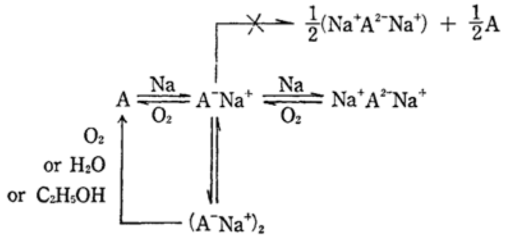
anion is more stable than pyridine radical anion.

The effect of temperature on the intensity of both ESR spectra and of the visible absorption spectra, clearly indicates that the paramagentic G species is in thermal equilibrium with another diamagnetic species (having no absorption spectra in the visible region), the formation of the former being favored by the rise of temperature. It is most plausible to attribute this equilibrium to the following process

$$2A^-Ma^+ \rightleftarrows (A^-Na^+)_2 \qquad (1)$$

or to an association of higher degree. A white precipitate obtained at lower temperatures may be $(A^-Na^+)_2$ or the higher associate. This is consistent with the finding that it is redissolved upon the introduction of air. Figure 8 gives a logarithmic plot of the intensity in the absorption spectra and in the ESR signal (Curie law is taken into consideration) against the reciprocal temperature. The linear relationship holds for the both plots although the slopes are somewhat different. This suggests that the equilibrium constant of (1) is quite large; if this is assumed, the heat of dissociation for the (1) process is estimated to be ~14 and ~9 kcal respectively from ESR and UV data. Perhaps the former value is more reliable.

In conclusion, the chemical processes related with the acridine radical anion in the THF solution (containing sodium, for instance) may be summarized as follows:



A species represented as $(A^-Na^+)_2$ may alternatively be a higher associate or a mixture of various associates.

Analysis of the HFS is not yet thoroughly successful. Judging from the entire width, the McConnell's *Q*-value seems to be much larger than 23 gauss. It appears that the unpaired spin densities evaluated on the basis of a simple LCAO method assuming $\alpha_N=\alpha_C+\chi\beta_{CC}$, $\beta_{CN}=\beta_{CC}$, $\chi=0.8$ or 0.6 or 0.4, cannot give a satisfactory interpretation. The exact analysis is now being attempted, which will be published in near future.