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Spectroscopic Studies on Radicals Produced from Acridine and Acridan in γ-Irradiated Rigid Solutions at −196°C

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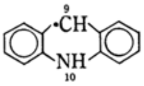
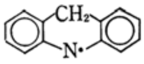
Dilute solutions of acridine in ethers and amines were frozen at −196°C to a glassy solid and were γ-irradiated. Electrons ejected by ionization are effectively scavenged by acridine to produce acridine anions which are the sole species having an electronic absorption band in the visible region. In alcohol and ester matrices the anion abstracts a proton from the matrix molecule even at −196°C and yields a semiquinone radical equivalent to the species formed by H-atom abstraction at the 9-position of acridan (dihydroacridine). Acridan in γ-irradiated butyl chloride matrix forms acridan cation which has a characteristic absorption band at 500—750 mμ. Detachment of a proton from the acridan cation produces another semiquinone radical identifiable with the species formed by H-atom abstraction at the 10-position of acridan. Both radicals have a similar yet clearly distinguishable absorption band in the visible region.

Flash photolytic studies on acridine and acridan systems have revealed that H-addition to acridine produces a C-radical (I) and that H-abstraction from acridan forms an N-radical (II).[1]



(I)



(II)

Since the spectral assignment of the N-radical in the previous work[1] was achieved by a process of elimination, it is desirable to get positive confirmation of the assignment by an independent method. Photolysis of rigid solutions at low temperatures often proves to be informative to the identification of reactive intermediates. Zanker *et al.* have shown that UV-illumination of alkylated acridans in alcoholic matrices at low temperatures yield radicals homologous to the N-radical shown above.[2]

Despite a seemingly prevailing preoccupation that γ-irradiation of organic systems leads to a chaotic mess, we have shown in a series of work[3] that γ-irradiation of rigid solutions at the liquid nitrogen temperature very frequently gives only a single species having absorption bands in the near UV through near infrared (IR) region. Applying the same radiation chemical technique we have studied acridine and acridan systems and obtained acridine anion and cation, acridan cation, the C- and N-radicals, each of which is produced exclusively from the others in a proper matrix.

Experimental

Preparations of acridine and acridan have been described in the previous paper.[1] The solvents, methyltetrahydrofuran (MTHF), diisopropyl ether, triethylamine (TEA), and *s*-butylamine were purified by vacuum distillation immediately after passing through an activated alumina column. Reagent grade *s*-butyl chloride (BuCl) and ethanol were used without further purification. Ethyl *n*-butyrate was distilled using a Vigreux column. All samples were degassed by freeze-thaw-reflux cycles, and sealed in a 1.5 mm Suprasil quartz cell which was irradiated with Co-60 γ-rays at −196°C.

A Cary 14R spectrometer and a quartz Dewar vessel with quartz windows were used for the optical measurement. Absorption spectra were obtained by plotting the difference of the absorption at the low temperature before and after irradiation.

Results

Pure MTHF forms a clear glass at −196°C which, upon γ-irradiation, yields a broad, intense absorption band with the $\lambda_{\max} \cong 1.2\ \mu$. The band has been associated with the electron trapped by the matrix.[4] When 50 mM of acridine was present in the MTHF matrix, the band due to the solvent-trapped electron was replaced by a new absorption band in the visible region (Fig. 1). The spectrum

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

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

[3] T. Shida, *J. Phys. Chem.*, **72**, 2597 (1968).

[4] P. J. Dyne and O. A. Miller, *Can. J. Chem.*, **43**, 2696 (1965).

agrees well with the reported spectrum of acridine anion which had been produced by the treatment of acridine with alkali metals.[5] Besides MTHF, glassy matrices of *s*-butylamine and diisopropyl ether, when doped with acridine, also gave a spectrum almost identical with that shown in Fig. 1.

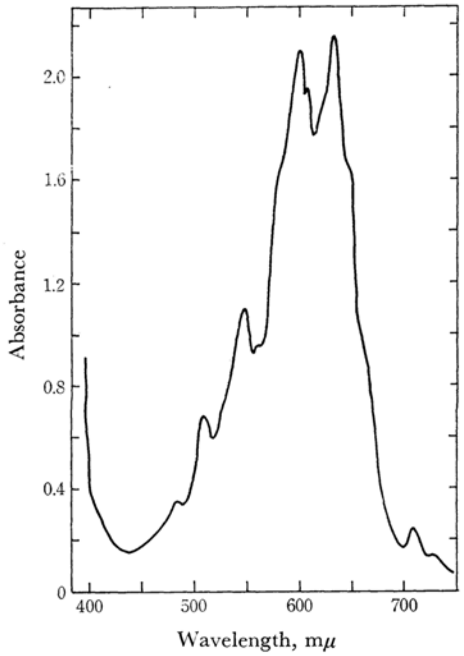

Fig. 1. Absorption spectrum of acridine anion. Acridine (50 mM) in MTHF glass γ-irradiated to the dose of 3.8×10^{19} eV/m*l*.

In contrast with ethers and amines, matrices of alcohols or esters did not yield the band of acridine anion or the band of solvent-trapped electrons; instead, a new spectrum similar to that of the C-radical in our previous paper[1] was obtained (Fig. 2). In Fig. 2 the result of acridine-ethanol system is shown. Acridine in glassy ethyl-*n*-butyrate also gave a similar spectrum.

Unlike acridine, acridan in MTHF did not affect appreciably the IR band due to the trapped electron nor did any new absorption band appear in the accessible spectral region. Apparently acridan does not scavenge electrons to form the anion. On the other hand, both acridine and acridan in BuCl matrix produced a new absorption band characteristic of the solutes (Fig. 3 and curve 1 of Fig. 4). When the irradiated acridan-BuCl solid was slightly warmed (*ca.* −170°C), the color of the sample changed from blue to purplish pink. Curve 2 of Fig. 4 demonstrates the spectrum of the pink solid measured at −196°C.

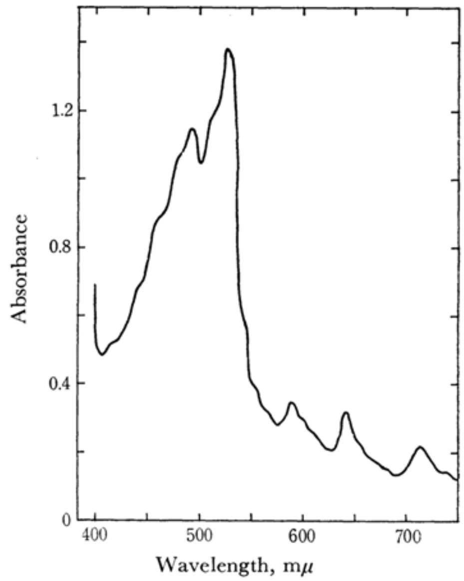

Fig. 2. Absorption spectrum of the C-radical. Acridine (50 mM) in ethanol galss γ-irradiated to the dose of 3.8×10^{19} eV/m*l*.

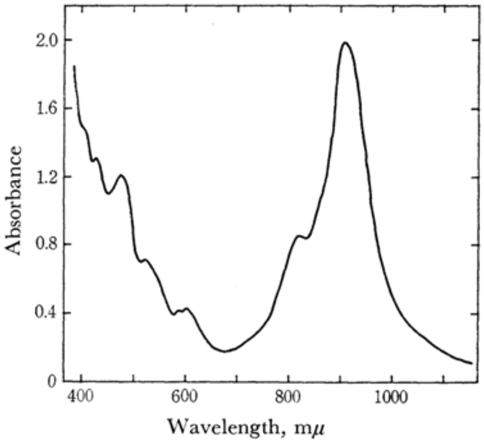

Fig. 3. Absorption spectrum of acridine cation. Acridine (50 mM) in *s*-BuCl glass γ-irradiated to the dose of 9.3×10^{19} eV/m*l*.

The spectrum of irradiated acridan in TEA matrix resembles that of the sample in curve 2 of Fig. 4. The intensity of the spectrum was markedly enhanced by the addition of a small amount of alkyl chloride, the band shape being unaltered. Curve 1 of Fig. 5 shows the spectrum in the presence of 0.1M BuCl. The curve changed to curve 4 when the sample was cautiously warmed to about −170°C. The latter spectrum is practically the same as the spectrum shown in Fig. 2. Curves 2 and 3 of Fig. 5 which are the components of curve 1 will be explained later in the discussion.

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

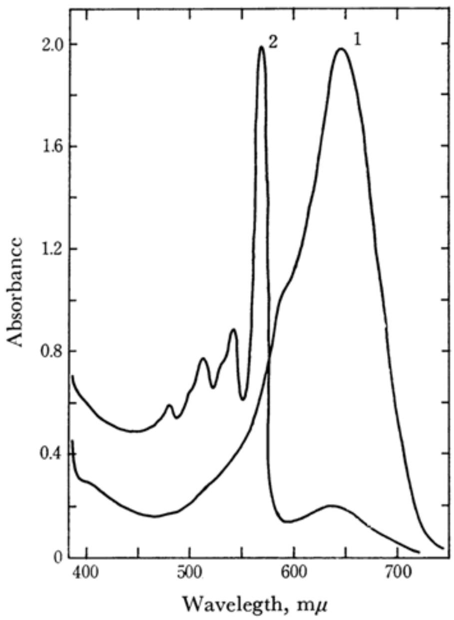

Fig. 4. Absorption spectra of acridan cation (curve 1) and the N-radical (curve 2).
Curve 1: acridan (25 mM) in *s*-BuCl glass γ-irradiated to the dose of 2.9×10^{19} eV/m*l*.
Curve 2: preceding sample after warming to *ca.* −170°C (the spectrum was recorded at −196°C).

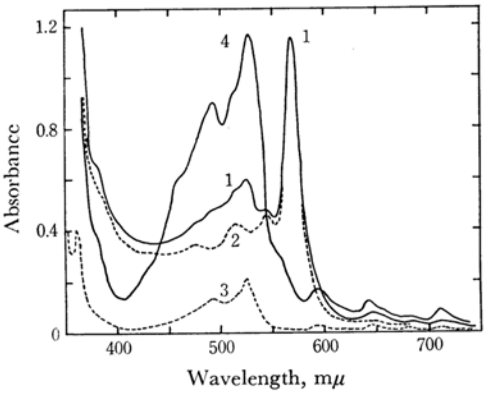

Fig. 5. Absorption spectra of the C- and N-radicals. Curve 1; acridan (50 mM) plus *s*-BuCl (100 mM) in TEA glass γ-irradiated to the dose of 9.3×10^{19} eV/m*l*. Curve 1 is divisible into two components, curves 2 and 3 where curve 2 matches with the spectrum of the N-radical shown in Fig. 4 and curve 3 is comparable with the spectrum of the C-radical in Fig. 2. Curve 4; preceding sample giving curve 1 after warming to *ca.* −170°C (the spectrum was recorded at −196°C).

Discussion

Electronic Absorption Spectra. In the low temperature rigid solution, events ensuing from ionization of the matrix molecule which is the major component of the system are "frozen" so that observation can be made at leisure. Electrons and positive holes are stabilized as intermediate products of reactions with solutes or matrix molecules. The metastable species thus formed often have strong absorption in the UV through near IR region. A proper choice of matrix enables us to produce a single species which is solely responsible for the absorption in the visible and near IR regions. Criteria for the choice have been expounded in previous papers.[3,6] A brief summary would be conducive to the following discussion; mass spectroscopic studies indicate that the parent ion of ethers, amines, alcohols and esters performs an efficient proton transfer reaction,

$$RH^+ + RH \rightarrow R\cdot + RH_2^+ \qquad (1)$$

Therefore when these substances are used as an isolating matrix for a small amount of solutes, ionization induced in the matrix molecule should result in reaction (1) while the detached electron migrates in the matrix to produce a solute anion. A typical example of this type of matrix is MTHF. Since the products of reaction (1) for MTHF do not absorb in the visible region, any absorption in the spectral region should be attributed to products of the reaction of electron with solute. Appearance of a new band in the acridine-MTHF system identifiable with acridine anion (Fig. 1) is thus accounted for in terms of electron attachment to the solute acridine.

Solute anions produced in alcoholic matrices often undergo further change by a proton addition,[7]

$$S^- + ROH \rightarrow \cdot SH + RO^- \qquad (2)$$

Acridine as the solute would yield a semiquinone radical by reaction (2). Since the band appearing in acridine-ethanol system (Fig. 2) resembles closely that of the C-radical proposed in a previous paper,[1] we regard that reaction (2) holds good for this system also. Since the electron in the acridine anion would most plausibly be populated at the nitrogen atom,[8] the alcoholic proton must have been bridged to the nitrogen of the anion before it is incorporated into the acridine ring. Thus the C-radical and not the N-radical should be favorably formed. Besides alcohols, glass-forming esters, when used as a matrix for acridine, gave the C-radical. For this system reaction (3) will take over reaction (2) to give the same radical,

$$S^- + RCH_2COOR \rightarrow \cdot SH + RCHCOOR^- \qquad (3)$$

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[6] T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 4372 (1966).

[7] T. Shida and W. H. Hamill, *J. Am. Chem. Soc.*, **88**, 3689 (1966).

[8] A quantitative study on the electronic state of acridine anion is currently being carried out by us.

The formation of the carbanion is assumed in numerous organic reactions.

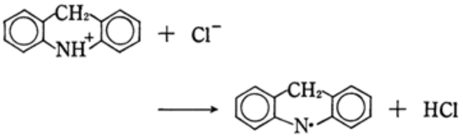
In contrast with the matrices so far discussed, the matrix of alkyl halides provides cationic species of solute molecules.[3] This is because the electron ejected from matrix molecules is scavenged by another matrix molecule and cannot reach a solute molecule in the distance. Meanwhile the positive hole in the matrix is found to migrate quickly to the solute molecule.[3] Processes in the butyl chloride matrix will be summarized as follows,

$$\mathrm{BuCl} \xrightarrow{\gamma} (\mathrm{BuCl^+})_{\mathrm{mobile}} + \mathrm{e^-} \tag{4}$$

$$\mathrm{e^-} + \mathrm{BuCl} \rightarrow \mathrm{Bu}\cdot + \mathrm{Cl^-} \tag{5}$$

$$(\mathrm{BuCl^+})_{\mathrm{mobile}} + \mathrm{S} \rightarrow \mathrm{BuCl} + \mathrm{S^+} \tag{6}$$

Decisive evidence for reaction (5) has been obtained by ESR studies.[9] In the absence of solute S migrating holes are eventually trapped by the matrix itself giving rise to the band of the trapped hole at about 400—600 mμ.[6] The band was eliminated when acridine or acridan was present in the chloride matrix and the new bands shown in Figs. 3 and 4 appeared which is accomodated to the above scheme with the assignment of the newly appearing bands to the respective solute cations. It is noted that the spectrum of acridan cation is very much like the spectrum of diphenylamine cation,[10] and is also comparable with the spectrum of alkylated acridan cations studied by Zanker *et al.*[2] Spectral change from curve 1 to 2 in Fig. 4 is explained as follows; upon softening the sample the chloride ion produced by reaction (5) will diffuse to the acridan cation in which the positive charge would be mainly localized at the nitrogen atom. Abstraction of the proton attached to the nitrogen by chloride ion will produce the N-radical,

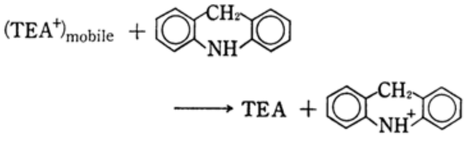

(7)

Similarity of curve 2 with both the spectra of N-radicals of alkylated acridans[2] and the spectrum of N-radical in our previous paper[1] gives credence to the previous assignment.

The formation of the N-radical was also noticed in another system. As mentioned before alkyl amines (primary and secondary) are subject to reaction (1) and are therefore used as a matrix to obtain solute anions. In tertiary amines such as TEA, however, it was found that the positive hole can migrate to some extent apparently because of the lack of protonation reaction (1).[11] Since acridan is expected to have a lower ionization potential than that of TEA,[12,13] acridan in TEA might produce acridan cation by accepting the migrating positive hole. Contrary to expectation, the spectrum obtained is very similar to that of the N-radical (curve 1 of Fig. 5). The enhancement of the signal by the addition of electron scavenger (100 mM of BuCl) suggests that the precursor of the N-radical is cationic. For the result the following scheme is proposed,

$$\mathrm{TEA} \xrightarrow{\gamma} (\mathrm{TEA^+})_{\mathrm{mobile}} + \mathrm{e^-} \tag{8}$$

$$\mathrm{e^-} + \mathrm{BuCl} \longrightarrow \mathrm{Bu}\cdot + \mathrm{Cl^-} \tag{9}$$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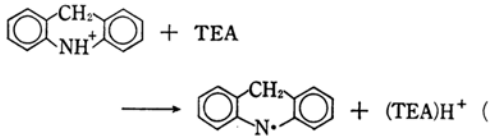
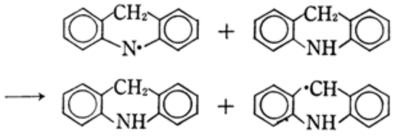

(11)

That is, although the acridan cation is once formed by reactions (8) and (10), the proton of the cation will be transferred to TEA on account of the high basicity of the amine. The spectral change from curve 1 to 4 in Fig. 5 indicates the transformation of the N-radical to the C-radical in the soft medium. In such a relaxed matrix the N-radical will be able to diffuse. On encountering an acridan molecule the radical may induce the following substitution reaction,


(12)

Careful comparison of curve 1 of Fig. 5 with the spectrum of the N-radical (curve 2 of Fig. 4) and of the C-radical (Fig. 2) shows that the curve in Fig. 5 comprises a small contribution of the C-

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[9] D. W. Skelly, R. G. Hayes and W. H. Hamill, *J. Chem. Phys.*, **43**, 2795 (1965).

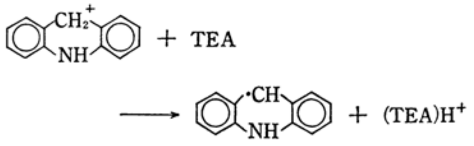
[10] T. Shida and W. H. Hamill, *ibid.*, **44**, 2369 (1966).

[11] T. Shida and W. H. Hamill, *J. Phys. Chem.*, **72**, 723 (1968).

[12] K. Watanabe, T. Nakayama and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962).

[13] A. Terenin and F. Vilessov, "Advances in Photochemistry," Vol. 2, Interscience Publishers, N. Y. (1964), p. 406.

radical. The broken curves in Fig. 5 illustrate that curve 1 is divisible into the two components. At present it is not known whether the concomitant C-radical is formed by reaction (13) which competes with reaction (11),


(13)

or it is subsequently formed from the N-radical by reaction (12) as a result of possible local softening of the matrix upon the formation of N-radical. The notation for acridan cation in reaction (13) implies that a fraction of positive charge may reside in the carbon atom at the 9-position.

Although conformational data are not available for the acridan molecule, most probably it has a bent form. The extraordinarily sharp peaks and well-structured spectrum of the N-radical suggest that the radical is planar or near-planar[14] and the equilibrium nuclear distances of the radical do not appreciably change upon the electronic excitation corresponding to the visible band.[14,15]

The authors wish to thank Professor Masao Koizumi for his pertinent comment on the mechanism of radical transformation (*cf.* reaction (12) in the text) and for reading the manuscript.

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[14] H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, N. Y. (1967), p. 339.

[15] L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., N. Y. (1966), p. 351.