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Studies on the Electronic Spectra of the Semiquinones of Anthracene and Its Related Heterocycles. I

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Electronic absorption spectra of two types of half reduced acridine, *i. e.*, C-radical (unpaired electron on 9-C-atom) and N-radical (unpaired electron on N-atom), of half-reduced anthracene and of xanthene deprived of one hydrogen atom, are measured in several rigid solvents at 77°K. It has been established that these radicals can be produced conveniently by irradiating the rigid solutions of the reduced forms, by a medium high pressure mercury lamp. It has been found that the absorption spectra of these radical species are generally classified into three groups, a) ~ 250 nm (4.9 eV), b) ~ 350 nm (3.5 eV) and c) visible (2.3—2.8 eV). Peculiar features for each radical species are; i) anthracene radical has no visible absorption, ii) acridine N-radical has no absorption at ~ 250 nm, and iii) acridine C-radical has a prominent sharp peak at 281 nm. Flash photolytic and ESR studies have also been performed on the radical species produced upon irradiation of dihydroanthracene and xanthene; the results obtained have substantiated the assignment of the intermediates observed in rigid solvents.

Our group has long been engaged in the studies of the primary processes of the photoreduction of some typical dyes and also of acridine.¹⁻⁵⁾ Further studies on the photoreduction in relation to acridine are now being extended to phenazine and anthracene. Under such circumstances, it is highly desirable to measure the accurate electronic absorption spectra of the semiquinones of anthracene and its related heterocycles and also to investigate theoretically their electronic structures. Such studies are considered also to be important as the basic information of dye photochemistry, since the foregoing types of compound are the skeletons of various dyes.

From such a view point, accurate measurement of the absorption spectra of semiquinones of

anthracene, acridine and xanthene were made in rigid solvents, and the open shell SCF calculation including CI was attempted to discuss the electronic structures of these semiquinones. The present paper is mainly concerned with the experimental results, deferring the theoretical ones to the next paper.

It has been found that these types of semiquinone can be produced most conveniently by the photochemical dehydrogenation of the reduced forms (acridan, dihydroanthracene, xanthene). Since they have no absorption below 300 nm and since they were almost completely converted to semiquinones by irradiation, reliable measurement could be performed throughout the region from 230 to 1000 nm.

It has been established that the absorption spectra of these semiquinones are well correlated with each other as is expected from the resemblance of the absorption spectra of the oxidized form (except xanthene) apart from minor differences. ESR and flash experiments have also been performed to confirm the assignment of the intermediate species in question.

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.*, **40**, 2486 (1976).

5) M. Koizumi, H. Yamashita and Y. Ikeda, *ibid.*, **41**, 1056 (1968); *J. Chem. Phys.*, **48**, 1869 (1968).

Experimental

Materials. 9,10-Dihydroanthracene and xanthene of G. R. grade were purified by repeated recrystallization from ethanol. Acridan was synthesized by reducing acridine with sodium amalgam.

Solvents used for Low Temperature Spectroscopy. Ethanol (99.5 vol%) of G. R. grade was used without any treatment, while the one of E. P. grade was purified by distillation. Isopentane and ethyl ether were dried over sodium and then distilled. Methylcyclohexane was treated with fuming sulfuric acid several times, washed with alkaline aqueous solution and then with water, shaken with alkaline KMnO_4 solution, rewashed with water, desiccated over CaCl_2 and silica gel and finally distilled with a fractionating column. All the solvents purified were checked by UV spectra. No absorption was observed above 210 nm for isopentane and above 220 nm for methylcyclohexane.

Solvents used for ESR Measurements. Poly-trifluoroethylene (Daiflon) was used without any purification. Tetrahydrofuran of First Grade from Wako-junyakku was refluxed with sodium for several hours, and then distilled.

Degassing of the samples was performed by at least five cycles of freeze-pump-thaw or by distillation method, both on a vacuum line.

Apparatus and Procedure. *Low Temperature Spectroscopy.* After having tried various types of apparatus, the final and most satisfactory one which is shown in Fig. 1, was manufactured.

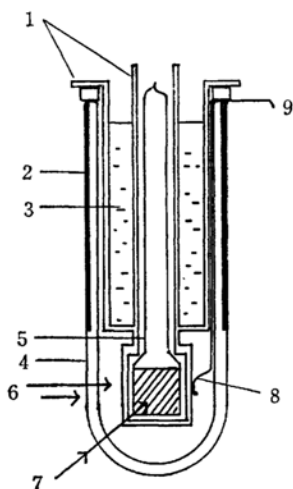


Fig. 1. (1) cell-holder of copper, (2) plated with silver, (3) liquid nitrogen, (4) quartz Dewar vessel, (5) quartz cell, (6) analysing beam, (7) exciting beam, (8) copper-constantan thermopile, (9) to microampere-meter

A quartz cell (5) settled in a copper cell-holder (1) was cooled slowly by pouring liquid nitrogen into the cell-holder. The apparatus was mechanically stable. A constant and sufficient low temperature of 77°K was attained in about ten minutes. There was no fear of the depression of the meniscus below the center of the cell, which would have interfered with an accurate measurement. After being kept at 77°K for more than

twenty minutes, the sample was irradiated by a medium pressure mercury lamp (Toshiba Chokoatsu SHLUV, with a cover glass removed) with no filter.

All the absorption spectra were measured by a Hitachi EPS-3 spectrophotometer. Temperature was measured by a copper-constantan thermopile (8), the tip of which was fixed on the cell-holder (1) near the quartz cell.

The solvents used were

1) isopentane and methylcyclohexane mixture (1 : 1 — 1 : 4)

2) EPA (5 : 5 : 2 — 5 : 2 : 3)

3) ethanol. When not evacuated, a little water (6 vol%) was sometimes added; this procedure was very efficient for preventing cracking of rigid matrix. This was unnecessary for the evacuated ethanol solution.

Flash Apparatus. Same one as has been described in previous papers.^{1,4)}

ESR Spectra. A Nippon Denshi (Japan Electron Optics) P-10-type ESR spectrometer (X-band) with 100 kc field modulation, was used. As solvents, benzene, tertiary butanol, tetrahydrofuran and Daiflon were used; good ESR signals were obtained in the last two solvents. The reason for not having used the usual rigid solvents is that they often give rise to some free radicals of their own origin and complicate the ESR signals;⁶⁾ all the foregoing solvents have no easily detachable hydrogen atoms. Although the solutions when cooled to a low temperature of 77°K, assume the polycrystalline state, it was expected from the previous work,⁶⁾ that they would give the ESR spectra originating from only the solute species. 500 W medium pressure mercury lamp was used as a light source. The light was passed through a water layer 1 cm thick and focused on the quartz cell by means of a lens.

Results and Discussion

Anthracene Semiquinone. When the solutions of dihydroanthracene 1.0×10^{-4} M in rigid solvents were illuminated by a mercury lamp at 77°K, they always colored slightly yellow. At

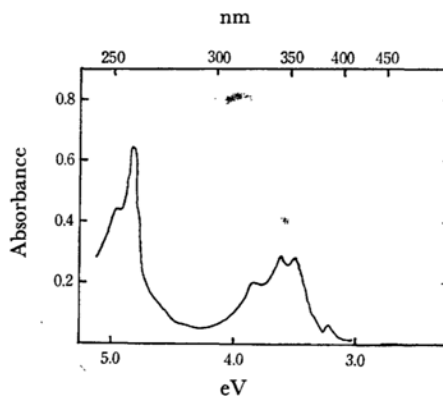


Fig. 2. The electronic spectrum of anthracene semiquinone obtained by irradiating MP (9 : 3) solution of 9,10-dihydroanthracene, 1.0×10^{-4} M at 77°K.

6) S. Niizuma and M. Koizumi, This Bulletin, **41**, 1090 (1968).

this temperature, the color remained unaltered for more than an hour when the light was off. Figure 2 gives the absorption spectrum in MP (9:3). Prominent peaks are seen around 250 and 340 nm regions. When the sample was warmed to room temperature, the major part of these bands disappeared and the absorption spectra of the resulting solution clearly showed that a small quantity of anthracene was produced. Hence it is most likely to attribute the above absorption bands to anthracene semiquinone, which is produced during the dehydrogenation reaction of 9,10-dihydroanthracene. It is, however, worthy noticing that the spectral shape of 340 nm region resembles closely that of anthracene, apart from a slight blue shift and the non-existence of 380 nm peak of anthracene. As to the assignment, therefore, the authors at first conceived of the possibility of the detachment of two hydrogen atoms in one act, yielding a certain anthracene-like intermediate such as distorted anthracene stabilized in rigid solvents. But such a view has proved to be ruled out; the assertion that the spectrum in question is really to be ascribed to semiquinone, has been substantiated from the following flash photolytic and ESR investigations.

Figure 3 gives the transient absorption spectrum obtained when the solution of dihydroanthracene 5×10^{-4} M, in ethanol was illuminated by the flash. The absorption in the region around 425 nm is most likely to be ascribed to the triplet state, while the one in the region 305–360 nm, to semiquinone, because the former decays as the superposition of the first and second order processes with a half life of 60 μ sec and the latter, on the other hand, decays in second order with a much longer life of 370 μ sec. Evidently the absorption around 305–360 nm corresponds to the one in rigid solvents. No transient absorption spectrum was detected in the aerated solution. The finding that the absorption in question decays as of second

order and with a large half-value period can never be reconciled with the view of the distorted anthracene.

Table 1 gives the solvent effect on the absorption spectrum.

TABLE 1. SOLVENT EFFECTS ON THE WAVE NUMBERS OF THE ABSORPTION MAXIMA OF ANTHRACENE SEMIQUINONE

Solvent			
MP	30860	29760	28410
Ethanol ^{a)}	31150	29330	28410
Ethanol ^{b)}	31550	29500	28740

a) contains a little water (6 vol%)

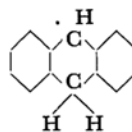
b) obtained from the flash photolysis

ESR studies were performed by using the solution of dihydroanthracene 5×10^{-2} M in Daiflon and tetrahydrofuran. When irradiated by a mercury lamp at 77°K, the sample colored yellow and gave good ESR signals. Some parameters of the signals are listed in Table 2.

TABLE 2. PARAMETERS OF ESR SIGNALS OF ANTHRACENE SEMIQUINONE

Solvent	<i>g</i> -Value	ΔH_{msl} (gauss)
Daiflon	2.0029	20.4
Tetrahydrofuran	2.0028	32.5

Somewhat larger value of ΔH_{msl} for tetrahydrofuran will be discussed later. From the *g*-value and the value of ΔH_{msl} there is scarcely any doubt that the signal is due to a π -radical, which in the present case is most likely to have the following structure.



Although the media for the spectral and ESR studies are different, it is reasonable to consider, from the similar coloration, that the same reaction is occurring in the two cases.

One more point to be worthy noticing in respect to the feature of UV spectrum is that anthracene semiquinone has no absorption in the visible region, in sharp contradistinction to other semiquinones investigated in the present investigation.

Acridine Semiquinone. When solutions of acridan in rigid solvents were irradiated by mercury lamp at 77°K, the solution always colored brown. The color remained for more than an hour after the light was off, but it disappeared upon warming the sample to room temperature. Two examples of the absorption spectrum are shown in Fig. 4, a and b. The bands in three wavelength regions

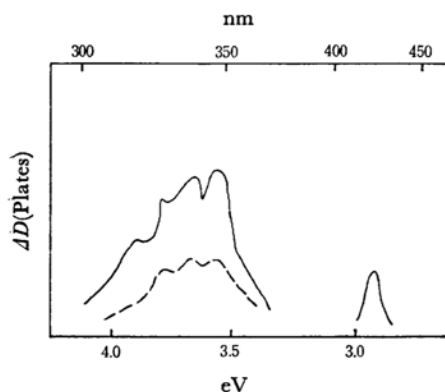


Fig. 3. The transient absorption spectra from the ethanol solution of 9,10-dihydroanthracene, degassed and 5.0×10^{-4} M at room temperature. — 93 μ sec, ---- 360 μ sec

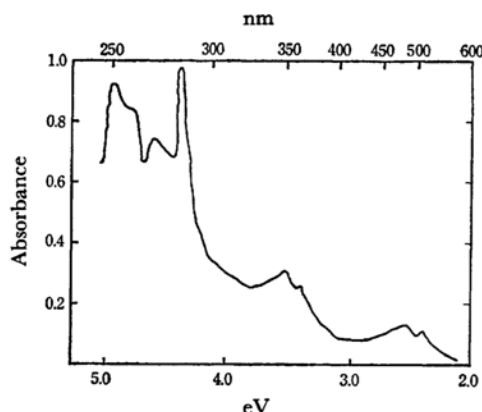


Fig. 4a. The electronic spectrum of acridine semiquinone obtained by irradiating aerated EPA (4:4:2) solution of acridan, 3.6×10^{-5} M at 77°K.

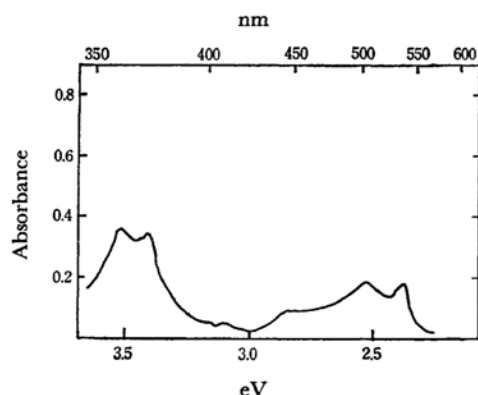


Fig. 4b. The electronic spectrum of acridine-C semiquinone obtained by irradiation of the degassed MP (4:1) solution of acridan, 3×10^{-4} M at 77°K.

are distinguished, the prominent peaks being (253, 281 nm^{*1}) (365 nm) (480, 520 nm). In the flash experiment¹³ using ethanol solution of acridine, the region around 365 nm had escaped the observation because of the superposition of the acridine absorption. The peaks at 281, 480 and 522 nm mentioned above, agree fairly well with the ones published before as well as with the ones obtained by the photolysis of diacridan.⁶² Hence the above spectrum is safely assigned to a C-radical (see Fig. 6). The values of molar absorbance evaluated under the assumption that the entire acridan is converted to semiquinone, are given in Table 3.

Besides the aforementioned peaks, a broad absorption extending from 500 to 700 nm was observed in EPA and in ethanol. This may be due to solvated electrons but there is no definite evidence at present.

*1 According to theory, the appearance of this only in this case, is peculiar.

TABLE 3. ESTIMATED MOLAR ABSORBANCE OF ACRIDINE C-RADICAL

Solvent	365 nm	488 nm	523 nm
MP	0.9×10^4	4.0×10^3	3.5×10^3
EPA (4:4:2)	0.8×10^4	2.2×10^3	1.8×10^3
EPA (5:2:3)	1.0×10^4	1.7×10^3	1.8×10^3
Ethanol ^{a)}	1.1×10^4	2.6×10^3	3.0×10^3
Ethanol ^{b)}	$3 \pm 1 \times 10^4$		1.0×10^4

a) contains a little water (6 vol%)

b) by Kira¹³

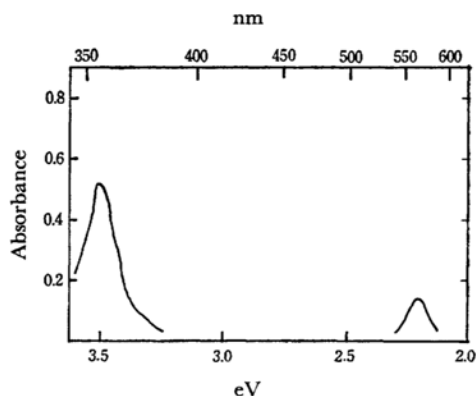


Fig. 5. The electronic spectrum of acridine-N semiquinone obtained by irradiating the aerated ethanol solution of acridan, 1.0×10^{-4} M at 77°K. This ethanol solution included a little water (6%).

Figure 5 gives the absorption spectrum of the intermediate produced by the irradiation of the aerated ethanol solution of acridan at 77°K. This spectrum is quite different from the ones shown in Fig. 4. At the time when the above results were obtained, it was a puzzling matter how to interpret these differences, because Kira and Koizumi's work⁷⁾ was not yet commenced at that time. Now that strong evidence has been given for the formation of C-radical and N-radical according to the experimental conditions, the absorption spectrum given in Fig. 5 can safely be

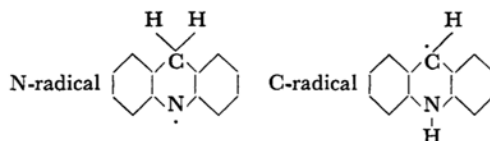


Fig. 6.

ascribed to N-radical from the agreement of the peak positions. Although there seems to be no doubt as to the assignment, a problem still remains why the N-radical is formed in the aerated ethanol solution whereas only the C-radical is formed in the

7) A. Kira, and M. Koizumi, to be published.

TABLE 4. SOLVENT EFFECTS ON THE WAVE NUMBERS OF THE ABSORPTION MAXIMA OF ACRIDINE C-RADICAL

Solvent									
MP	39525	38610	36630	35580	28409	27400		20490	19120
EPA (4:4:2)	39525	38760	36630	35580	28410	25700	25700	20490	19160
Ethanol ^{a)}	39525	38760	36760	35580	28320	27470	25700	20400	19190
Ethanol ^{b)}								20615	19230

a) Contains a little water (6 vol%)

b) Flash photolysis data by Kira¹⁾

TABLE 5. SOLVENT EFFECTS ON THE WAVE NUMBERS OF ABSORPTION MAXIMA OF XANTHENE SEMIQUINONE

Solvent									
MP	31150	30030	28990	26600	25380	23810	22220	20830	17240
Ethanol	30960	30030	29150	27030	25560	24153	22420	20830	17240
Ethanol ^{a)}			29410						

a) From the flash data

aerated EPA solution as well as in the degassed MP solution. The problem awaits further studies, together with the ESR studies which are now in progress. Table 4 gives the solvent effect on the absorption spectrum of C-radical.

From the absence of the solvent effect, all the absorption may safely be attributed to the π - π^* transition.

Xanthene Semiquinone. When the xanthene solutions in ethanol or MP were irradiated, the solutions became yellow in color. As shown in Fig. 7, the absorption spectrum displays peaks at 255 nm (with a shoulder near 270 nm), 340 nm, 580 nm and a broad absorption band extending from 370 to 400 nm. When the sample was warmed up to room temperature, the shoulder at 270 nm and the last broad band still remained to exist while the other bands disappeared completely. This implies that along with a radical

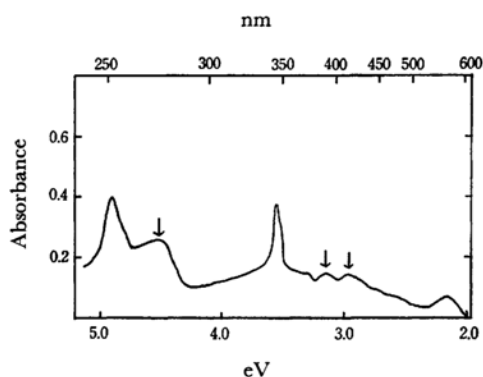


Fig. 7. The electronic spectrum of xanthene semiquinone obtained by the irradiation of the degassed ethanol solution, 1.2×10^{-4} M at 77°K. This spectrum includes the absorption of the photoproduct (\downarrow), which is not separated from semiquinone.

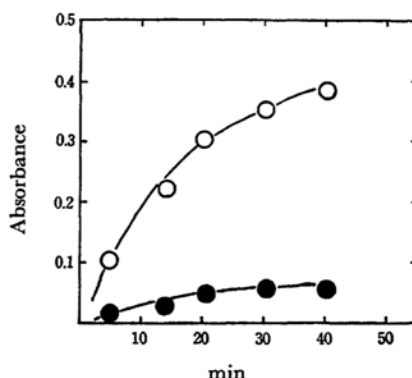


Fig. 8. A build-up of xanthene semiquinone (\circ 343 nm) and that of photoproducts (\bullet 390 nm). 8×10^{-5} M ethanol solution of xanthene.

species, some stable compound was produced simultaneously. Judging from the build-up curves shown in Fig. 8, the formation of the radical species and the stable compound in question, appears to proceed as two independent reactions. It is to be noted that the absorption bands at 252 and 270 nm were interfered with the bands of the original compound. Further, it is likely that most of xanthene semiquinone reconverts to xanthene by regaining a hydrogen atom when the solvent is melted, because the amount of xanthene was found to be almost the same as that before irradiation. The solvent effects are given in Table 5.

Good ESR signals were obtained when 5×10^{-2} M of xanthene in tetrahydrofuran or Daiflon was irradiated. The sample became yellow upon irradiation. The ESR spectrum in the case of tetrahydrofuran medium, as shown in Fig. 9, is somewhat asymmetric and broad, similarly as in the case of anthracene semiquinone in the same medium.

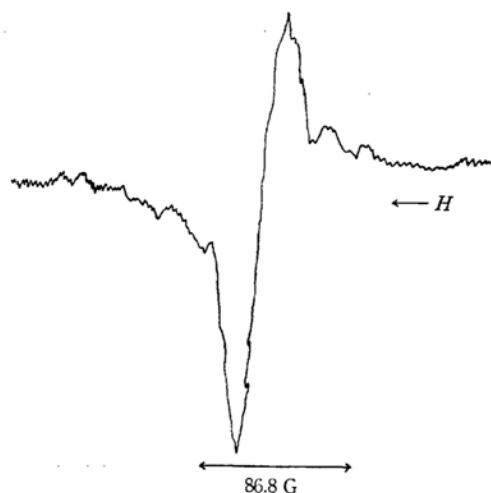


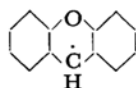
Fig. 9. ESR spectra obtained by the irradiation of tetrahydrofuran solution of xanthene, 5×10^{-2} M.

This is perhaps due to the coexistence of the tetrahydrofuran radical, which was produced through a secondary reaction between xanthene semiquinone and tetrahydrofuran molecules.⁸⁾ ESR parameters are given in Table 6.

TABLE 6. ESR PARAMETERS OF XANTHENE SEMIQUINONE

Solvent	<i>g</i> -Value	ΔH_{msl} (gauss)
Diflon	2.0043	16.2
Tetrahydrofuran	2.0046	26.0

From the *g*-value and the value of ΔH_{msl} , there is no doubt that the radical is a π -radical with the following structure:



8) S. Niizuma and M. Koizumi, to be published. T. Maruyama *et al.*, the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, 1966.

In the flash experiments, two transient absorptions were observed around 340 nm and 420 nm of which the latter was attributed to the triplet state, because of its short decay rate. That no absorption was detected in the vicinity of 580 nm, may be due to a very small absorbance of 580 nm as is evident from Fig. 7. The absorption around 340 nm evidently corresponds to the one in rigid solvents and is ascribed to xanthene semiquinone.

Comprehensive Discussion

The present investigation has established that the absorption spectra of semiquinones in question, are classified into three groups, ~ 250 nm (4.9 eV), ~ 350 nm (3.5 eV) and visible (2.3–2.8 eV).

According to an open shell SCF-CI calculation (Longuet-Higgins-and-Pople-type) the details of which will be reported in the next paper, one obtains the similar classification except for some shifts (toward shorter wavelength), *i. e.*, ~ 1 eV, ~ 0.6 eV and ~ 0.5 eV respectively for 4.9 eV group, 3.5 eV group and for a visible group. This correspondence between theory and experiment is considered to be an additional evidence for the assignment of the intermediates as semiquinones. As to the peculiarities of the spectrum of each semiquinone, the most significant findings are;

a) Acridine C-radical has a prominent sharp peak at 281 nm.

b) For acridine N-radical, the band around 250 nm is very weak.

c) Anthracene semiquinone has no visible absorption.

As to these three characteristics, reasonable interpretations will be given in the theoretical part. Finally, it will be added that the difference in reactivity toward oxygen, between acridine C- and N-radicals, may be attributed to the energy difference of the half occupied molecular orbitals of the two species. This will also be discussed in the next paper.