CHEMISTRY LETTERS, pp. 59-64, 1972. Published by the Chemical Society of Japan

ON THE STABLE RADICAL CATION PRODUCED DURING THE PHOTOREDUCTION OF 9,9'-BIACRIDYL IN ETHANOL AND ITS ESR SPECTRUM

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ESR spectrum due to 9,9'-biacriden radical cation ($BAH_2^{+}\cdot$) was detected and its hfs was analysed. $BAH_2^{+}\cdot$ exists in the degassed acidic ethanol solution of 9,9'-biacridyl (BA) and biacriden (BAH_2) and is also produced by the photoreduction of BA in the acidic ethanol. All the findings support the following equilibrium. $BAH^{+} + BAH_2 + H^{+} \rightleftarrows 2BAH_2^{+}\cdot$.

In a previous paper$^{1)}$ we have reported that the photoproduct obtained when 9-Cl-acridine in ethanol is irradiated by 365 nm, exhibits an ESR spectrum. The spectrum consists of 17 lines with about 1.7 gauss separations at over modulation, each of which splits further to five or six lines at suitable modulation (Fig. 1). The signal is stable for more than several hours in dark.

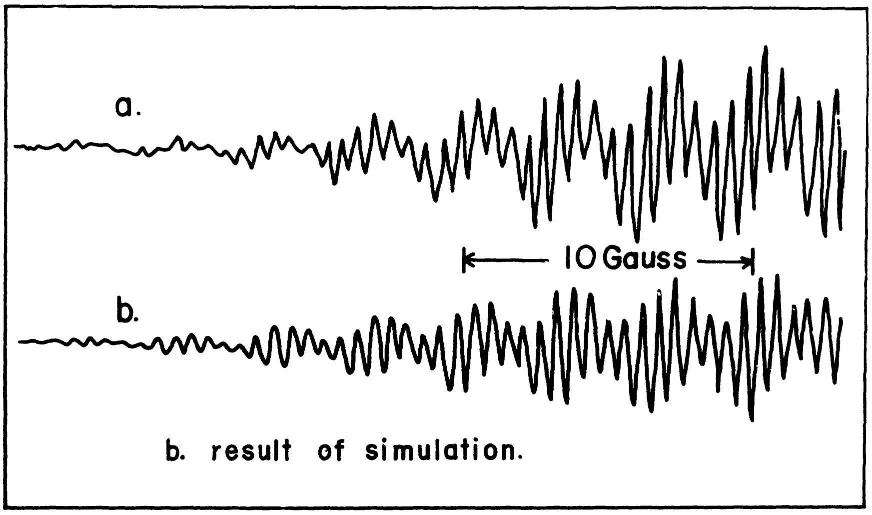
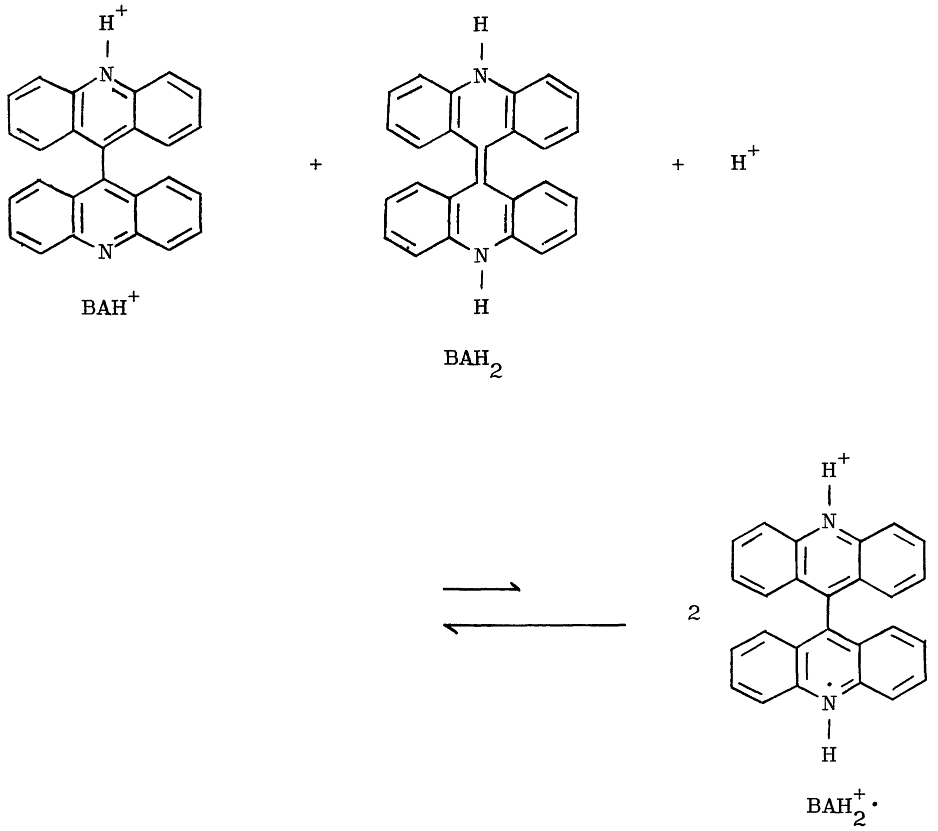


Fig.1. ESR spectrum of the photoproduct obtained when 9-Cl-acridine in ethanol is irradiated by 365nm.

In this communication, we will report firstly that A) this spectrum is due to 9,9'-biacriden radical cation ($BAH_2^{+}\cdot$) and secondly, that B) this radical cation is most likely in equilibrium with 9,9'-biacriden (BAH_2) and 9,9'-biacridyl (BA) according to the following equation.



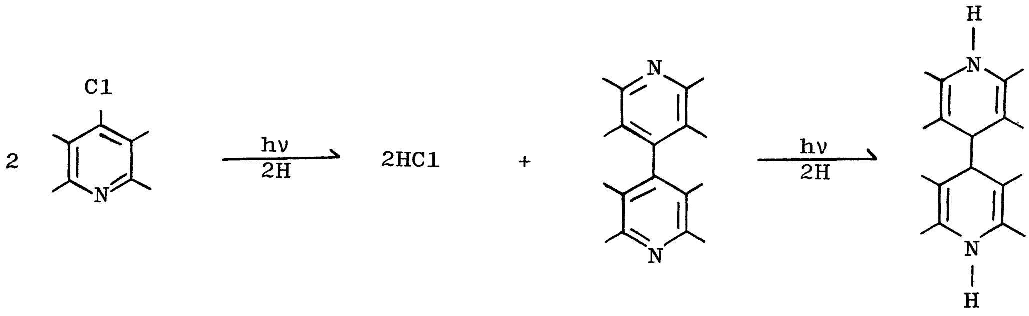
BAH^+ BAH_2 $BAH_2^{+\cdot}$

(I)

Thirdly, C) the result of simulation will be compared with the theoretical calculation

A) As mentioned in the previous paper, BA in ethanol does not exhibit ESR upon irradiation although UV spectrum clearly demonstrates the production of BAH_2. However, the addition of acid to the solution gave rise to an essentially similar ESR spectrum as given in Fig. 1. This strongly suggests the formation of radical cation by an electro transfer from BAH_2 to BAH^+ according to reaction (I).

Since 9-Cl-acridine (Cl-A) in ethanol undergoes the following photochemical reaction as established in the previous paper,



it is evident that the medium has become acidic in the first step of reaction, so that the radical cation can exist.

To establish reaction (I) more conclusively, the acidic ethanol solution of 10^{-3}M of BA was added to the ethanol solution of BAH_2 (through a breakable seal). As expected, a similar ESR spectrum could be detected, although UV spectrum of BAH_2 was not affected appreciably. When we used phenazine instead of BA, we obtained the ESR signal of dihydrophenazine cation. But no radical species was produced by acridine. It is concluded therefore, that electron transfer can occur between BAH_2 and an electron acceptor with suitable electron affinity. It is understandable that $BAH_2^{+}\cdot$ is stabilized to some extent, because its two resonance structures are equivalent.

B) In the photoreduction of BA, it is very likely that half-reduced radical BAH· is primarily produced. In the medium with such an acidity wherein 9,9'-biacridyl exists partially as BAH^+, the radical species produced by H-abstraction from ethanol will exist entirely as a protonated species $BAH_2^{+}\cdot$. From analogy to the acridinium ion,[2)] this species is expected to react with alcohol less easily than neutral BAH·, and the present result demonstrates that it is really stable. Therefore the only reaction that follows will be the disproportionation of $BAH_2^{+}\cdot$ (reaction (I)).

If one assumes that this disproportionation occurs so quickly that the equilibrium (I) holds approximately during the reaction, then the following relation exists at any time,

$$K = [BAH_2^{+}\cdot]^2 \,/\, [BAH^+]\,[BAH_2]\,[H^+] \qquad (1)$$

Denoting the initial concentration of BAH^+ a, and the concentrations of BAH_2, and $BAH_2^{+}\cdot$ at time t respectively as x and y, we rewrite (1) into (2).

$$K' = y^2 \,/\, (a - x - y)x \qquad (2)$$

Simple calculation shows that y becomes maximum when a-y-x=x, ie., when the concentrations of BAH_2 and BAH^+ become equal, and at this time point y is given as

$$y = x\sqrt{K'} \qquad (3)$$

If the rate of disproportionation is slow, the maximum ESR intensity may be realized at a smaller concentration of BAH_2.

To examine whether the above situations hold or not and with the hope to get the information on the possible equilibrium, we studied the time dependence of ESR signal intensity and of the UV peak height of BAH_2 at 420 nm upon irradiation. Figures 2a) b) show respectively the results in ethanol and in benzyl alcohol.

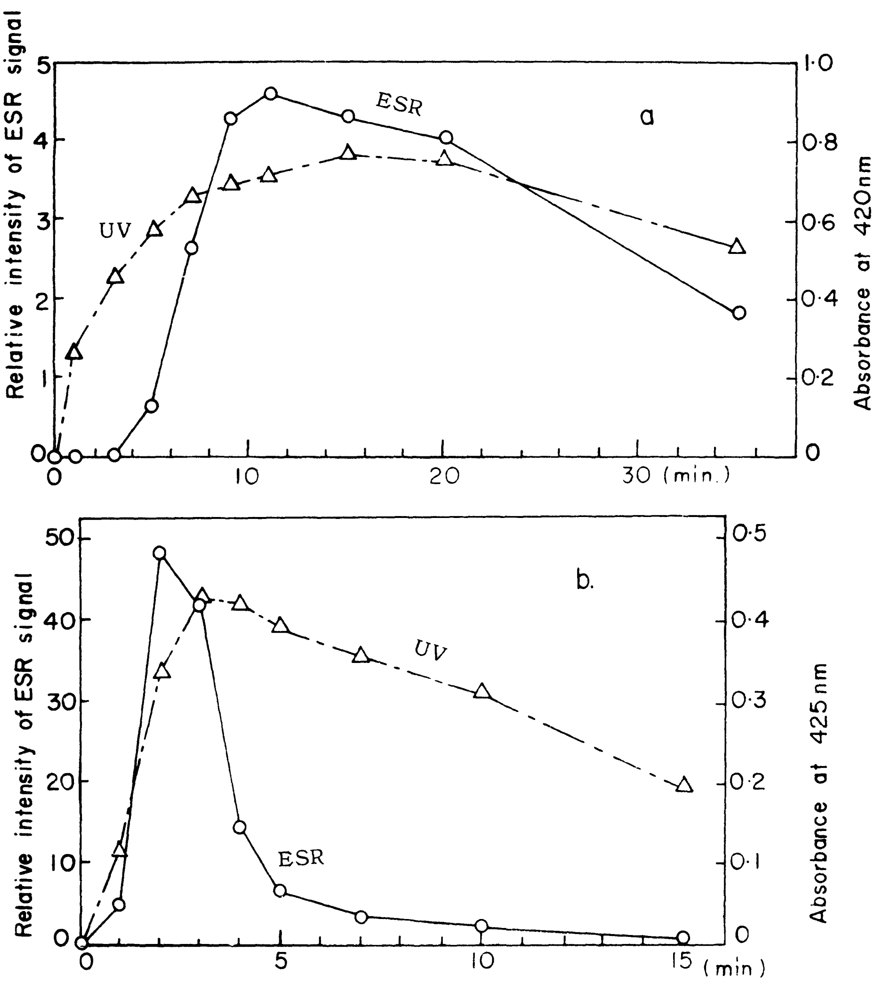


Fig. 2. Time dependence of ESR signal intensity and of the UV peak height of BAH_2

a) Cl·A (2 x 10^{-3}M) in ethanol

b) BA in acidic benzyl alcohol.

These two figures appear to satisfy the above deduction at least qualitatively, because the ESR intensity maximum appears while the UV peak height is still increasing. Although the quantitative discussion cannot be made especially because of the decline of the UV peak height in the later stage (perhaps due to the occurrence of a different kind of reaction), it is apparent that at the time point of the maximum ESR intensity, the concentration of BAH_2 is more than half of the maximum BAH_2 concentration. Such a situation is never explained on the basis of any reasonable models including the one mentioned above. Hence it seems reasonable to suppose, taking account of the gradual decrease of $[BAH_2]$ in the later stage, that the concentration of BAH_2 at the time-point in question is approximately equal to one half of the initial concentration BA. This implies that the concentration of $BAH_2^{+}\cdot$ is very small as compared to that of BAH^{+} and of BAH_2.

The finding already described that the addition of acidic ethanol solution of BA to the solution of BAH_2 dces not affect appreciably the UV absorption spectrum of the latter in spite of the appearance of ESR spectrum of $BAH_2^{+}\cdot$, is consistent with this conclusion. Furthermore, the agreement of the absorption spectrum of the photoproduct for the irradiated BA solution (neutral) and for 9-Cl-acridine solution (acidic because of the photochemical production of HCl) and accordingly the lack of the UV absorption attributable to $BAH_2^{+}\cdot$ species are also consistent with the above conclusion.

In addition, eq. (3) demonstrates that $[BAH_2^{+}\cdot]$ is proportional to $[BAH_2]$. In fact the ESR signal could not be detected at 10^{-4}M of BAH_2.

As a summary we can say that although $BAH_2^{+}\cdot$ is stable because of its resonance structure, the equilibrium position most likely, leans much toward the left side of equation (I).

C) Numbering C-atoms as shown in the figure, the simulation of the ESR spectrum was attempted. The best coupling constants obtained are given in Table 1. In the same table the coupling constants obtained from the spin density (calculated by McLachlan and simple Hückel) and the Q-value (see below), are also listed.

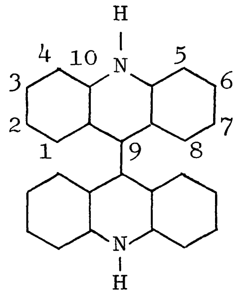


Table 1. Comparison between the experimental and theoretical (by McLachlan) coupling constants (gauss).

	obs.	cal.(21.5°)	cal.(0°)
2N	3.196	3.13	3.26 (2.81)
2H(N-H)	3.486	3.44	3.60 (3.09)
4H(1,8,1',8')	1.743	0.95	0.99 (0.92)
4H(3,6,3',6')	0.291	0.72	0.81 (0.80)
4H(4,5,4',5')	0.291	0.64	0.51 (0.65)
4H(2,7,2',7')	—	0.43	0.36 (0.54)

The data in ( ) are the ones calculated by Hückel LCAO.

The following parameters were used to calculate the spin density.

$$\text{for Hückel} \quad \begin{cases} \alpha_N = \alpha_C + \beta_{CC} \\ \beta_{CN} = \beta_{CC} \\ \alpha_C' = \alpha_C + 0.1\beta_{CC} \end{cases}$$

$$\text{for McLachlan} \quad \lambda = 1.00$$

For the evaluation of coupling constants the following relations were used.

for H McConnell's relation $a_H = Q\rho_C$ (Q = 28 gauss)3)

for N $a_N = Q_N\rho_N + \sum_i Q_i'\rho_i$ (Q_N = 20 gauss, Q_C' = 7 gauss)4)

for H(N-H) $a_{H(N-H)} = 1.1\, a_N$5)

The calculation was made for two values of the angle between the planes of two halves of a molecule. Although the agreement is not very good, there is no other reason to doubt the present assignment of radical species as $BAH_2^{+}\cdot$.

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(Received October 20, 1971)