Studies on Photochromic Salicylideneanilines. I. Photo-induced Electron Spin Resonance Spectra in Salicylideneaniline-Phenothiazine Complexes

MAMORU KAMIYA and YUKIO AKAHORI

Shizuoka College of Pharmacy¹⁾

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It has been found that photo-reversible electron spin resonance signals are observed on low-temperature irradiation into various powdered complexes composed of anil and phenothiazine. And on the basis of studies on the photo-stationary structure and photo-after decay rate of the spectrum, a main component of the signal has been proposed as phenothiazine cation which is produced by a charge-transfer type interaction with the photocolored quinoidlike form of anil.

Introduction

It has been noted hitherto by several workers²⁻⁶⁾ that photochromic anils usually exhibit no paramagnetism as evidenced by magnetic susceptibility and electron spin resonance measurements, and this seems to support that radical mechanism is not associated with the photochromic process of anils themselves. In spite of this, recent researches on the photochromism of anils by Ottolenghi and McClure^{7,8)} have shown the presence of photoexcitation emissions in low-temperature rigid solution which have been related to the lowest excited triplet state or to a transient intermediate formed in the intramolecular hydrogen-transfer process. If these are the cases, it may be possible to detect, in suitable experimental conditions, electron spin resonance (ESR) signals for the above metastable species or some other radicals yielded by their photoprimary reactions.

From this viewpoint, many samples of the anils doped with the reactive compounds, chiefly electron-donors which would interact with the metastable quinoidlike species of anils, have been tested for ESR measurements with low-temperature irradiation. Consequently, it has been found that among a number of the powdered complexes composed of the photochromic anil and phenothiazine several complexes yield characteristic photo-reversible ESR signals on low-temperature irradiation.

Results and discussion for detailed natures of these ESR signals will be given in the following in order to elucidate some reasonable mechanisms for the present radical-formation.

Experimental

ESR Measurements—Electron spin resonance measurements were carried out with a JES-3BS-X-type spectrometer with 100 Kc modulation, where the sample sealed in a 5 mm o.d. quartz tube could be irradiated in the spectrometer cavity. The concentration of unpaired electrons in the powdered complex was estimated from the ratio of the absorption intensity of the signal to that of a standard DPPH sample containing 4×10^{15} spins. The *g*-values were determined relative to the two-center lines of the Mn^{2+} ion in MgO with

- 1) Location: Oshika 2-2-1 Shizuoka-Shi, Shizuoka.
- 2) S.S. Bhatnagar, P.L. Kapur and M.S. Hashimi, *J. Indian Chem. Soc.*, **15**, 573 (1938).
- 3) M. Singh and T.R. Datt, *J. Indian Chem. Soc.*, **19**, 130 (1942).
- 4) S.S. Bhatnagar and P.L. Kapur, *Z. Electrochem.*, **45**, 373 (1939).
- 5) H.S. Gutowsky, R.L. Rutledge and I.M. Hunsberger, *J. Chem. Phys.*, **29**, 1183 (1958).
- 6) N. Ebara, *Nippon Kagaku Zasshi*, **82**, 941 (1961).
- 7) M. Ottolenghi and D.S. McClure, *J. Chem. Phys.*, **46**, 4620 (1967).
- 8) W.F. Richey and R.S. Becker, *J. Chem. Phys.*, **49**, 2092 (1968).

a g -value of 1.981 for the higher field line and a splitting of 87.5 gauss. According to this method a g -value of 2.0037 ± 0.0002 was obtained for the DPPH sample, in good agreement with the usual results.

Irradiation was done with a collimated light of a 500W high-pressure mercury lamp located about 70 cm apart from the quartz front-window of the cavity, and the light intensity was monitored with the change of lamp current.

Sample Preparation—The anils studied here were synthesized from equimolar amounts of the anilines and the *ortho*-hydroxyaldehydes and purified by vacuum sublimation prior to use for the complex-formation. Recrystallization frequently does not remove the odor of starting aldehyde, whereas vacuum sublimation was usually found to be sufficient. *o*-Deutero-salicylideneaniline was prepared from 1 part of the light anil dissolved in 20 parts of D_2O and 10 parts of anhydrous dioxane dried with metal sodium. After refluxing in a sealed vessel for 15 hr, the extent of hydroxyl hydrogen exchange was found to be about 90% by mass-spectroscopic analysis. Crude phenothiazine was recrystallized from toluene, and purified by repeated vacuum sublimations until the blue-green color was completely removed. Crude phenothiazine was found sometimes to show a weak ESR signal, but it disappeared through the above purification process. The complex was formed by mixing freshly prepared anil and phenothiazine in hot chloroform or dioxane, evaporating the solution and evacuating the residual solid thoroughly. A color change to yellow-green was usually detected on the complex-formation. The evacuated complex did not show any ESR signal on keeping in dark for 2 or 3 days.

2-Hydroxybenzylideneaniline (I) mp = 51° (ligroin). Found: C, 79.04; H, 5.56; N, 7.30. Calcd. for $C_{13}H_{11}ON$: C, 79.16; H, 5.62; N, 7.10.

2-Hydroxybenzylidene-*p*-methoxyaniline (II) mp = 84° (ethanol). Found: C, 73.82; H, 5.85; N, 6.21. Calcd. for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77; N, 6.16.

2-Hydroxybenzylidene-*p*-nitroaniline (III) mp = 155° (acetone). Found: C, 64.78; H, 4.25; N, 11.55. Calcd. for $C_{13}H_{10}O_3N_2$: C, 64.46; H, 4.16; N, 11.57.

5-Bromo-2-hydroxybenzylidenaniline (IV) mp = 121° (methanol). Found: C, 56.63; H, 3.67; N, 5.07. Calcd. for $C_{13}H_{10}ONBr$: C, 56.54; H, 3.65; N, 5.07.

2,4-Dihydroxybenzylideneaniline (V) mp = 108° (benzene). Found: C, 72.93; H, 5.32; N, 6.35. Calcd. for $C_{13}H_{11}O_2N$: C, 73.22; H, 5.20; N, 6.57.

5-Nitro-2-hydroxybenzylideneaniline (VI) mp = 132° (benzene). Found: C, 64.63; H, 4.22; N, 11.51. Calcd. for $C_{13}H_{10}O_3N_2$: C, 64.46; H, 4.16; N, 11.57.

3-Nitro-2-hydroxybenzylideneaniline (VII) mp = 135° (benzene). Found: C, 64.37; H, 4.29; N, 11.38. Calcd. for $C_{13}H_{10}O_3N_2$: C, 64.46; H, 4.16; N, 11.57.

4-Methoxy-2-hydroxybenzylideneaniline (VIII) mp = 69° (methanol). Found: C, 73.91; H, 5.77; N, 6.06. Calcd. for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77; N, 6.16.

3-Methoxy-2-hydroxybenzylidene-*p*-methoxyaniline (IX) mp = $95-96^\circ$ (methanol). Found: C, 69.92; H, 5.97; N, 5.27. Calcd. for $C_{15}H_{15}O_3N$: C, 70.02; H, 5.88; N, 5.44.

3-Methoxy-2-hydroxybenzylidene-*p*-nitroaniline (X) mp = 167° (methanol + chloroform). Found: C, 61.46; H, 4.61; N, 10.01. Calcd. for $C_{14}H_{12}O_4N_2$: C, 61.76; H, 4.44; N, 10.29.

2-Hydroxynaphthylideneaniline (XI) mp = 93° (methanol). Found: C, 82.44; H, 5.26; N, 5.89. Calcd. for $C_{17}H_{13}ON$: C, 82.57; H, 5.30; N, 5.66.

Result and Discussion

Photo-effects on the ESR signals of the anil-phenothiazine powdered complexes have been examined by using the evacuated (10^{-6} Torr.) fresh samples because preliminary studies indicate that the ESR spectra are markedly lowered in intensity and broadened in line-width by the contact with small amount of oxygen gas, and this change is not almost recovered by a second evacuation. Then, it has been discovered on low-temperature irradiation that several complexes exhibiting an intense photocoloration (red-brown) show photo-reversible ESR signals which are observed with neither component alone nor non-photocoloring complexes. These results present a remarkable contrast with the data reported in reference 5 and 6 for the absence of ESR signals in irradiated anils.

Together with a few examples of the actual photo-ESR signals (Figure 1a), Figure 1b illustrates typical time-dependent changes of the photo-induced ESR signals for the salicylideneaniline (SA)-phenothiazine (PH) complex which were recorded by setting the magnitude of sweeping magnetic field at a peak of the first derivative curve of the single resonance line. As can be known from this, the ESR signals gradually grow on irradiation followed by the photocoloration of the complex and reach a photo-stationary intensity, but they decay rather quickly when the irradiation is removed.

Fig. 1a

- 1) the photo-induced ESR signal in SA-PH system at 173°K
- 2) the photo-induced ESR signal in SA-PH system at 123°K
- 3) the photo-induced ESR signal in 5-bromo-2-hydroxybenzylideneaniline-PH system at 173°K
- 4) the photo-induced ESR signal in 2-hydroxynaphthylideneaniline-PH system at 173°K

Fig. 1b. Time-Dependent Changes of the Photo-induced ESR Signal In SA-PH System at 173°K

Several basic properties of these photo-induced ESR signals have been derived from detailed studies on the SA-PH complex; Although remarkable lowering of the photo-effect upon the ESR signal was found for the aged or air-exposed samples, repeated cycles of light-on and light-off reproduced a similar photo-ESR signal if every irradiation time was limited within five minutes or so, but an irreversible color change into red-brown was concurrently observed to a much extent during the process. The photo-stationary intensity of the ESR signal varied linearly with the irradiation power though the intensity was clearly saturated for an excessive light intensity. Also, the photo-stationary ESR intensity was found to rise with increased SA content to reach a maximum at 1~2:1 molar ratio of SA:PH. Unless otherwise stated, the compositions of the other complexes investigated herein were fixed to 1:1 molar ratio. As one of the large temperature effects, it was found that the signal came into observation only below $-40\sim-50^\circ$ and after that grew on lowering temperature until it decayed again below $-160\sim-170^\circ$. This feature seems to be in parallel with the result obtained by Cohen, *et al.*⁹⁾ that the photochromism of anils occurs only between lower and upper temperature limits. Investigations on the film samples gave an interesting result that the sample prepared by vacuum sublimations in the order of SA and PH onto the inner wall of a sample tube yielded the photosignal, but a much less signal was observed on the sample prepared by an inverse order of sublimation which would protect the SA layer from irradiation.

These results indicate that the photocolored species of the anils growing on irradiation are closely related to the photo-ESR signals. Namely, it is likely that some paramagnetic species yielded from the metastable photocolored anil and phenothiazine is responsible for this signal. It is of interest to note that the samples containing anils with nitro-substituted salicylidene group exhibited a remarkably decreased photo-ESR signal in spite of the appearance of the photocoloration.

Detailed studies of the natures of the photosignals will be given on the basis of the interpretations of the g -value, line-width, hyperfine structure of the signals, and the kinetics of the signal decay after photoirradiation. A series of the pertinent data are given in Table 1. Most of the spectra are of only a single resonance line above low temperature limits in spite of the presence of a few asymmetric signals suggesting overlap of multiple components. It seems to be hard to determine whether the radical responsible for the photo-ESR signal is formed from either of two components of the complex or from both of them.

TABLE I. Results of the Photo-induced ESR Signals at 153°K

Anil component	Relative spin concentration ^{a)}	g -Value	Δ Hmsl (gauss)	First-order rate constant for photo-after decay ($\times 10^2 \text{ sec}^{-1}$)
I	1.0	2.0052	10.2	5.8
II	0.8	2.0045	9.4	4.6
III	0.8	2.0047	8.0	3.5
IV	1.4	2.0057	14.5 (A)	5.2
V	0.5	2.0060	10.8	4.0
VI	0.2	2.0044	12.4 (A)	—
VII	0.1	2.0062	15.4 (A)	—
VIII	1.2	2.0039	8.7	4.5
IX	0.4	2.0054	9.5	5.0
X	0.7	2.0065	10.5	4.7
XI	0.5	2.0058	4.2	3.0

a) spin concentration of [I] = 2×10^{15} spin/g
A = asymmetric line shape

9) M.D. Cohen, G.M.J. Schmidt and S. Flavian, *J. Chem. Soc.*, 1964, 2041.

Here, bearing in mind that in various organic molecular solid energy storage of irradiated light is often achieved in a form of intermolecular electron-and/or hole-transfer and their trapping which result in formation of transient ion radicals as evidenced by photo-induced ESR signal, it may be assumed, as one of the possibilities, that the paramagnetic species is produced by an electron-transfer between the photocolored quinoidlike anil and phenothiazine. It is known that phenothiazine acts as good electron-donor¹⁰⁾ and many amine-quinone complexes show paramagnetism due to charge-transfer mechanism. Now, if such a strongly coupled donor(D)-acceptor (A) complex as gives splitting into a diamagnetic singlet and paramagnetic triplet is actually formed on irradiation, it is probable that the g -values of the single resonance lines may lie close to the average of the g -values of the D^+ and A^- ions because of strong electron-exchange interaction between the two species with different g -values, as reported by Kinoshita,¹¹⁾ and that the temperature-dependence of the photo-stationary intensity obey either of the following equations depending on the magnitude of singlet-triplet separation (δ)¹²⁾: $1/T[3+\exp(\delta/kT)]$ ($E_T > E_S$) and $1/T[3+\exp(-\delta/kT)]$ ($E_T < E_S$).

The observed g -values of all the single resonance lines locate in a range of 2.004–2.006, whereas the g -values as high as 2.007–2.009¹³⁾ and 2.005–2.006^{12–14)} have been observed for some salts of *o*-quinone and for phenothiazine cations in conc. H_2SO_4 , respectively. Thus, it is found that the observed g -values tend to be rather close to but slightly lower than the averaged g -value. This may suggest that the interaction as above mentioned should not be neglected at all at a low temperature of 153°K. Furthermore, studies on temperature-dependence of the signal intensity were performed in detail for the SA-PH complex at a sufficiently low microwave power so as to avoid saturation effects since quite complicated results were found in published data for other amine-quinone type charge-transfer complexes.^{12,15)} Figure 2 shows a plot of the reciprocal of the ESR signal intensity against the absolute temperature, and this indicates that the Curie-law holds rather well at 110–150°K. The absence of a Weiss field associated with spin-spin interactions seems to be actually reflected in the appearance of a resolved structure at 120°K. The present results on the g -values indicating that spin-spin interaction should not be neglected at all is plausible since it was obtained on the basis of the g -values measured at 153°K, where the plot begins to deviate from the Curie-law linearity. Above 160–170°K a marked decrease of the signal intensity was observed in comparison with that expected when the Curie-law curve was extrapolated. In such case a plot of the logarithm of the observed intensity to the extrapolated one against $1/T$ also yielded a linear line of the Arrhenius-type with $E \simeq 2.0$ kcal. This means the validity of an endothermic process removing the unpaired electrons, such as radical recombination.

Thus, we consider tentatively that the single resonance lines observed at 110–150°K are primarily due to either of the D^+ or A^- ion radicals with weak interactions. In this case it is likely that the signals are due to the donor ion radical, phenothiazine cation, because of a considerable similarity between the g -values. However, the absence of the signal for the counter anion radical is somewhat unaccountable. This would be explained by the following assumptions; The unpaired electrons in the acceptor radicals may exchange so rapidly among the various acceptor molecules which were considered by Le Fevre¹⁶⁾ to have strong mutual interactions in solid state. Otherwise, this may be due to a short relaxation time of

- 10) D.R. Kearns and M. Calvin, *J. Phys. Chem.*, **34**, 2026 (1961); J.E. Lyons and J.C. Mackie, *Nature*, **197**, 589 (1963).
- 11) M. Kinoshita, *Bull. Chem. Soc. Japan*, **36**, 307 (1963).
- 12) D. Bijl, H. Kainer and A.C. Rose-Innes, *J. Chem. Phys.*, **33**, 765 (1959).
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- 14) L.D. Tuck and D.W. Schieser, *J. Phys. Chem.*, **66**, 937 (1962).
- 15) H. Kainer, D. Bijl and A.C. Rose-Innes, *Naturwiss.*, **13**, 303 (1954).
- 16) R.J.W. Le Fevre, *J. Chem. Soc.*, **1939**, 1457.

Fig. 2. A Plot of the Reciprocal of the ESR Signal Intensity against the Absolute Temperature

I = Photostationary signal intensity

Fig. 3. Examples of First-Order Plots for the Dark Decay of the Photo-induced ESR Signal (153°K)

I : signal intensity
 ○: plot for D-substituted [I]

the unpaired electrons captured by the photocolored anils which are found to undergo rapid conformational change between the *cis* and *trans* forms in the course of photofading reaction.

The observed fact that no correlation exists between the photostationary spin concentration and the nature of ring-substituents of the anils appears not to be parallel with the present mechanism for electron-transfer, but this is not necessarily unreasonable if the yield of the photo-induced radicals is much limited by the concentration of the photocolored product of the anils of which yield is also found by Cohen, *et al.*⁹ to be almost independent on the ring-substituents.

An important fact regarding the behaviour of the photo-induced radicals is that their decay rates after photoirradiation usually follow, as is illustrated in Figure 3, unimolecular kinetics below 173~183°K with a rate constant of $3\sim5\times10^{-2}\text{ sec}^{-1}$, and that these are accelerated on lowering temperature with an activation energy of $-2\sim-3\text{ kcal}$. At the upper limit of temperature the decay rate was not fitted with unimolecular kinetics.

In addition, the rate study using *o*-deuteriosalicylideneaniline did not give an observable isotope effect on the decay rate at 123~173°K, though a small isotope effect has been observed by Cohen, *et al.*⁹ in the dark fading reaction of anils. These facts may suggest that the back-toward migration of carriers, electron and/or hole, is the rate-determining step for the radical decay after photoirradiation since it has been evidenced by Leblanc, *et al.*¹⁷ that carrier mobilities in organic solids increase on lowering temperature.

When irradiation was continued for 2~3 hr at 153~173°K, many of the photoactive complexes gave similar spectra of three lines with splitting of 9.5~10 gauss, as is shown in Figure 4(a). These signals were found to be almost photo-irreversible excepting that the central peak gradually decays to such an extent that the final intensity was close to those of the other two lines.

On further irradiation, the shape of the absorption curve frequently changed so remarkably as to suggest the formation of some different radical species, as is shown in Figure 4(b).

17) O.H. Leblanc, *J. Chem. Phys.*, **33**, 626 (1960); D.R. Kearns and M. Calvin, *J. Chem. Phys.*, **34**, 2026 (1961).

Fig. 4. Photo-irreversible Changes of the ESR Signal in SA-PH System

- a) the photo-irreversible signal after 2 hr irradiation at 173°K
- b) the photo-irreversible signal after 3 hr irradiation at 173°K
- c) the signal obtained from a degassed DME solution of the (b) powdered complex

When these samples were dissolved into thoroughly degassed dimethoxyethane or dimethylformamide solution, spectra of five resolved lines with splitting of about 10 gauss (Figure 4(c)) were detected. If the irreversible signal-changes are due to some secondary reactions of the initial radicals or due to the trapped stabilization of them during a prolonged irradiation, the three-line signal may be related to the interaction of unpaired electron with the one nitrogen nucleus in trapped phenothiazine cation, but the five-line spectrum observed in solutions is quite unexpected. As one of the probable explanations for this, we assume that a bimolecular phenothiazine radical ion in which the hole is equally localized on the two nitrogen nuclei is formed by interactions between accumulated phenothiazine cations in solid or by their dimerization in dissolved solvents.

Further studies on the present photo-reversible ESR signals are now in progress by using low-temperature rigid solutions.