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Transient Species Obtained by the Flash Photolysis of Chloranil in Various Solutions

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Transient absorption spectra have been obtained by the flash photolysis of chloranil in various organic solvents. In trichlorotrifluoroethane, two T-T′ absorption systems of chloranil were obtained with well-resolved vibrational structures. In tetrahydrofuran, on the other hand, absorption spectra mostly consist of semiquinone radical formed by the hydrogen abstraction from solvent. In benzene and in acetone, the first T-T′ absorption system was much more diffuse and was accompanied by a weak, broad absorption at longer wavelength ($\lambda >$ 550 nm) which might be assigned to a charge transfer absorption from triplet chloranil as acceptor and the solvent molecule as donor. In acetone and in methanol, it has also been found that there is an equilibrium between semiquinone radical and semiquinone anion.

Porter and his co-workers obtained transient absorption spectra by the flash photolysis of quinones and assigned them to semiquinone radicals, semiquinone anions, and relatively short-lived triplet quinones (quinones in the lowest triplet state).1) Recently, Kemp and Porter2) illuminated a degassed ethanol solution of chloranil with a nitrogen laser and obtained the transient absorption spectrum of triplet chloranil with a maximum at about 500 nm. The triplet chloranil is expected to have a larger electron affinity than in

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1) N. K. Bridge and G. Porter, *Proc. Roy. Soc.* (London), **A244**, 259, 276 (1958).

2) D. R. Kemp and G. Porter, *Chem. Commun.*, **1969**, 1029.

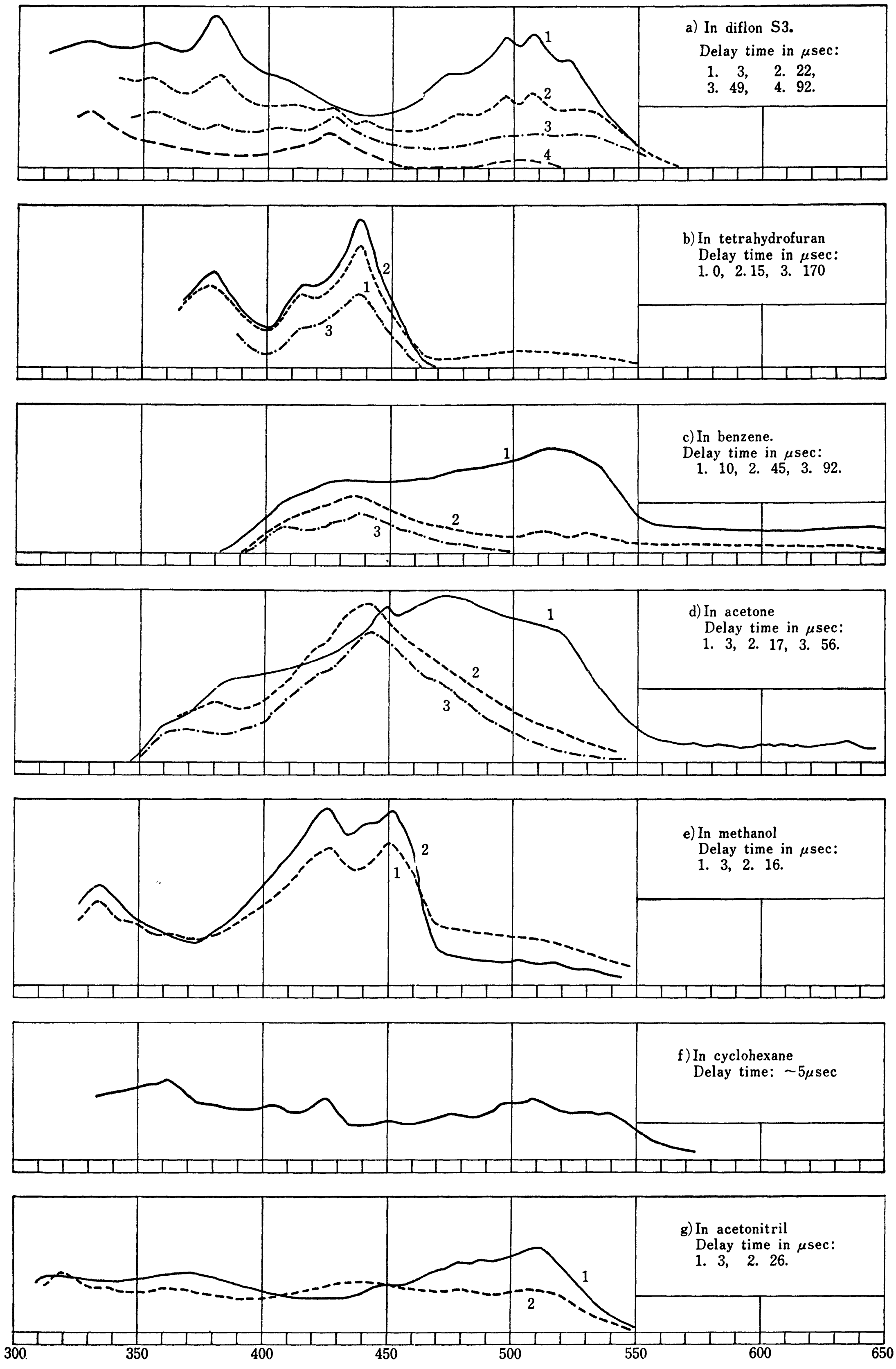


Fig. 1. Absorption spectra of transient species obtained by the flash photolysis of chloranil in various solvents.

the ground state, and might have specific interactions with solvents having electron-donating properties. We have carried out detailed investigations on the T-T′ spectra of chloranil using various solvents in order to obtain evidence on any such donor-acceptor interactions, and also on the chemical properties of semiquinones formed photo-chemically.

Experimental

Materials. Chloranil was purified by recrystallization from benzene, passing through a calcium carbonate column, and further recrystallization from benzene. Trichlorotrifluoroethane (Diflon S3), a commercial product from Daikin Kogyo Co., Ltd. and which may be a mixture of isomers, was shaken with sulfuric acid, neutralized, dried with calcium chloride and distilled with a Widmer column. Acetone was refluxed with potassium permanganate for half a day, dried with calcium sulfate and distilled. Tetrahydrofuran was refluxed overnight with potassium hydroxide, distilled, refluxed with sodium wire again and then distilled. Benzene was shaken with sulfuric acid, neutralized, dried with calcium chloride, refluxed with sodium wire and then distilled with a Widmer column. Methanol was refluxed overnight on sodium wire and then distilled. Acetonitrile was purified by passing through an alumina column, refluxed with calcium hydride and then distilled.

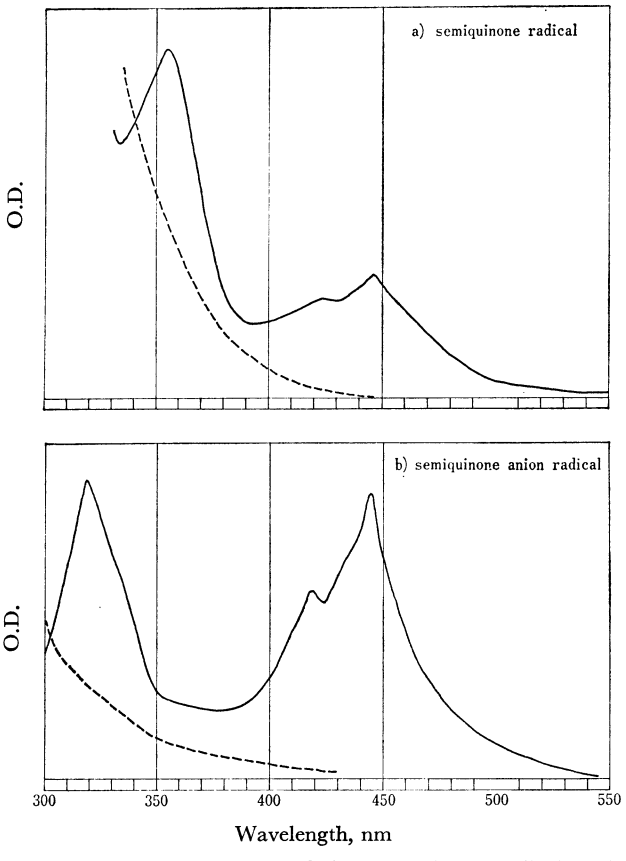


Fig. 2. Absorption spectra of the semiquinone radical and semiquinone anion chemically produced from chloranil.

a) ------ Absorption of chloranil in α-methyltetrahydrofuran at 77°K.
—— The same, after irradiation with a high pressure mercury lamp.

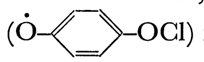
b) ------ Absorption of chloranil in degassed tetrahydrofuran.
—— The same, after contact with sodium-potassium alloy.

Methods. Concentrations of the solutions of chloranil used in the experiment were mostly in the range 1—3× 10^{-4}M. Solutions were bubbled with highly purified nitrogen gas so as to purge dissolved oxygen, and then poured in a cylindrical silica cell 1.5 cm in diameter and 20 cm in length. The apparatus used for the flash spectroscopic measurements is mostly the same as that described in an earlier paper.[3]

Results

The transient spectra obtained by the flash photolysis of chloranil in various solvents are shown in Fig. 1, a)—g). For the sake of comparison, the spectrum of semiquinone radical obtained by the photolysis of chloranil in an α-methyltetrahydrofuran matrix at 77°K is shown in Fig. 2 a), and that of the semiquinone anion obtained by the reduction of chloranil in tetrahydrofuran with sodium-potassium alloy in Fig. 2 b).

The spectra obtained in trichlorotrifluoroethane (Diflon S3) is shown in Fig. 1 a). The solvent was used for the purpose of obtaining pure T-T′ absorption spectrum of chloranil, for it was expected to be inert to excited chloranil, especially with the hydrogen-abstraction reaction. There is a band system at around 500 nm with four apparent vibrational sub-bands at 522, 507, 497, and 473 nm, and a second eminent one with a principal maximum at 379 nm. Both these two systems may be assigned to the T-T′ transitions of chloranil, since they could not be detected in the solution saturated with oxygen. The general characteristics of the first 500 nm system coincide also with those of the T-T′ spectrum reported by Kemp and Porter in an ethanol solution, though the resolution in their spectrum is a little poorer than ours. They did not measure the T-T′ spectrum in the region below 450 nm, while our results give the second system lying below 400 nm. We have also determined the life time of the triplet state (decay of these bands) to be *ca.* 30 μsec.

Besides these T-T′ absorptions, a minor transient band centered at 425 nm was obtained which persists for a longer time than the triplet state. The spectrum is like that of the semiquinone radical mentioned later, and is tentatively assigned to a radical () formed by the abstraction of chlorine atom from the solvent.

The spectra obtained in tetrahydrofuran is shown in Fig. 1 b). The main feature at around 430 nm is quite like that of the first band-system of the semiquinone radical (Fig. 2 a)), though the former is shifted to the blue by about 10 nm. The semiquinone anion radical has a similar band system at the same region. However, the semiquinone radical has a band at 357 nm, while semiquinone anion lacks it. The presence of a band at around 375 nm in the spectra of Fig. 1 b) seems to indicate that the semiquinone radical is the main product formed by flash photolysis. This is also in harmony with the fact that the α-hydrogen of tetrahydrofuran is easily abstracted.[4]

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[3] N. Yamamoto, Y. Nakato, and H. Tsubomura, This Bulletin, **39**, 2603 (1966).

The weak absorption appearing in the 500 nm region is ascribable to the T-T′ absorption. The absorption decays in a few microseconds, indicating a rapid hydrogen abstraction in the triplet state. It was also found that the semiquinone radical was formed even in an aerated tetrahydrofuran solution (containing oxygen). This indicates that the hydrogen abstraction occurs at least partly at the singlet excited state of chloranil. In aerated ethanol, no semiquinone radical was formed.

The spectra obtained from the flash photolysis of benzene solutions in the range $\lambda > 320$ nm are shown in Fig. 1 c). At the delay time of 10 μsec, a broad spectrum was obtained with the principal peak at 516 nm, which is assigned to the first T-T′ system. It decays quickly, and another system ascribable to the semiquinone radical appears at a longer delay time. It is generally believed difficult to abstract a hydrogen atom from benzene. However, our present results have revealed that a hydrogen abstraction can occur from benzene.[5] It is to be noted that the T-T′ spectrum in the case of benzene solution is much more broad and structureless than that in Diflon S3. There is also a broad, weak absorption beyond 550 nm, which decays at nearly the same rate as the triplet state. Transient spectra obtained for a number of solutions containing both benzene and Diflon S3 (Fig. 3) show that the absorption intensity in the 550 to 650 nm region, relative to that of the first T-T′ system, increases obviously with the increase in the benzene content. This seems to indicate strongly that a new absorption system is found which arises from the interaction of benzene and triplet chloranil.

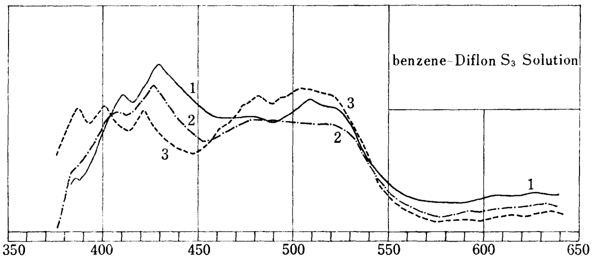
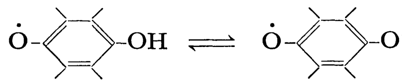


Fig. 3. Absorption spectra of transient species obtained by the flash photolysis of chloranil in a mixture of trichlorotrifluoroethane (Diflon S3) and benzene, at a delay time of 15 μsec. The volume ratio, Diflon S3/benzene for each curve, is given below:
1) 3/7 2) 7/3 3) 9/1

The transient spectra obtained for the acetone solutions is shown in Fig. 1 d). In this case, the flash excitation was carried out in the region $\lambda > 330$ nm by use of a combination filter system composed of a glass plate and an aqueous solution of sodium nitrate. Absorption in the region 450—550 nm appearing at the delay time of 3 μsec fades out mostly at 17 μsec and a new system appears at about 440 nm. The former (450—550 nm) may be assigned to the T-T′ spectrum of chloranil from its wavelength and decay time, while the latter does not exactly fit into the spectrum of either semiquinone radical or semiquinone anion but can be explained by assuming that the two species are mixed, indicating that the semiquinone radical formed in the first place by the flash undergoes ionic dissociation and is in the following acid-base equilibrium in acetone.



The situation is quite similar to the photolysis product of hydroquinone in neutral or acid solutions.[6] In the acetone solution, a broad absorption is also found beyond 550 nm, which may most probably be interpreted as an absorption arising from the interaction between triplet chloranil and acetone similar to the case of benzene solutions.

In methanol, the transient spectra (Fig. 1e)) can be interpreted as an assembly of the T-T′ absorption and the absorption by semiquinone radical and semiquinone anion. The bands at 426 and 451 nm decay in the first order kinetics with different decay constants.

The transient spectra obtained in cyclohexane showed bands ascribable to the T-T′ and the semiquinone radical absorption (Fig. 1 f)). Those in acetonitrile show the T-T′ absorption and the absorption mostly ascribable to the semiquinone radical (Fig. 1 g)).

The peak wavelengths of the transient spectra obtained in various solvents and their assignments are summarized in Table 1.

TABLE 1. THE PEAK WAVELENGTHS OF TRANSIENT ABSORPTION SPECTRA OBTAINED BY THE FLASH PHOTOLYSIS OF CHLORANIL IN VARIOUS SOLVENTS IN nm

Transient Species	Triplet Chloranil	Semiquinone Radical	Semiquinone Anion
Diflon S3	522, 507, 497, 473; 410, 379	425	
Cyclohexane	539, 507, 495, 474	425, 403	
Benzene	516	436, 408	
THF	~500	437, 415, 377	
Acetone	520, 503; 471	(441, 420, 365)[a]	
Methanol	~500	426	451
Acetonitril	510, 487, 479; 372	(440, 319)[a]	

a) Strongly overlapped.

Discussion

From the results, a considerable influence of solvents can be seen on the first T-T′ system in various solvents, especially in such electron-donating solvents as benzene and acetone. In these solvents, the first T-T′ system is much more diffuse than others. It is of particular interest that there are broad absorptions in the range $\lambda >$ 550 nm, which seem to be charge transfer bands with the solvent molecule as donor and triplet chloranil as

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[4] It is suggested that the discrepancy between the peak wavelength of the first band system in Fig. 2 a) and that in Fig. 1 b) may be attributed to differences in solvent and temperature.

[5] Rubin *et al.* reported a hydrogen abstraction reaction from benzene by excited phenanthraquinone. M. B. Rubin and Z. Neuwirth-Weiss, *Chem. Commun.*, **1968**, 1607.

[6] K. Kimura, K. Yoshinaga, and H. Tsubomura, *J. Phys. Chem.*, **71**, 4485 (1967).

acceptor. Quite independently, Briegleb and Schuster recently reported a few cases of absorption spectra of triplet pyromellitic dianhydride at 77°K showing similar bands and assigned them to charge transfer absorption from solvent to triplet pyromellitic dianhydride.[7]

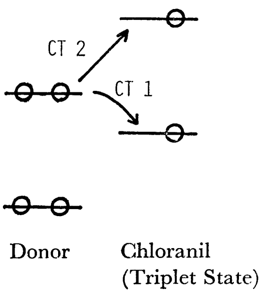

Fig. 4. Diagram indicating charge transfer between donor and triplet chloranil.

It is a delicate problem to determined whether the lowest triplet state of chloranil is (n-π^*) or (π-π^*). Shcheglova *et al.* found an emission spectrum from chloranil in a hexane (9 vol)-toluene (1 vol) solution and concluded that it arises from the lowest triplet (π-π^*) state at 17200 cm^{-1} above the ground state,[8] where π and π^* are the highest filled and lowest vacant π-MO, respectively. Thus, a charge transfer can occur from the highest filled MO of the donor (solvent) to the π-MO of chloranil, leading to a charge transfer band at very long wavelength regions (CT 1 in Fig. 4). The transition energy for a charge transfer absorption can be given approximately by the equation

$$h\nu_{\text{CT}} = I_{\text{D}} - E_{\text{A}} - e^2/r_{\text{DA}} + \Delta, \qquad (1)$$

where I_{D} and E_{A} are the ionization energy of donor and the electron affinity of acceptor, r_{DA} is the distance between donor and acceptor, and Δ is a term collecting all other minor contributions. For an ordinary benzene-chloranil complex, the charge transfer band has $\lambda_{\text{max}}=$ 335 nm, which corresponds to $h\nu_{\text{CT}}$ of 3.7 eV.[9] The electron affinity of chloranil in the lowest triplet state can be given by

$$E_{\text{A}}{}^{\text{T}} = E_{\text{A}} + W_{\text{T}} - W_{\text{G}}$$

where W_{T} and W_{G} are the energies of the triplet and ground state, respectively. Using the value derived by Shcheglova (17200 cm^{-1}=2.1 eV), we obtain for the complex between benzene and triplet chloranil

$$h\nu'_{\text{CT}} = I_{\text{D}} - E_{\text{A}} - (W_{\text{T}} - W_{\text{G}}) - e^2/r_{\text{DA}} + \Delta, \qquad (2)$$

If it is assumed that r_{DA} and Δ are the same for both complexes, then from (1) and (2), we obtain

$$h\nu'_{\text{CT}} = 1.6\ \text{eV} \equiv 780\ \text{nm}.$$

This value seems to be in harmony with our experimental result, especially when one takes account of the resonance splitting between the upper and lower states which seems to be somewhat larger than the splitting for the ordinary chloranil-benzene complex. But further investigations seem to be necessary for the elucidation of the nature of the lowest triplet state of chloranil, and the weak, long-wavelength absorption found in the present work.

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[7] G. Briegleb and H. Schuster, *Angew. Chem. (Intern. Ed.)*, **9**, 369 (1970).

[8] N. A. Shcheglova, D. N. Shigorin, G. G. Yakobson, and L. Sh. Tushishuili, *Zh. Fiz. Khim.*, **43**(**8**), 1984 (1969).

[9] G. Briegleb and J. Czekalla, *Z. Physik. Chem. N. F.*, **24**, 37 (1960); *Z. Elektrochem.*, **58**, 249 (1954).