

Photo-Induced Electron Spin Resonance in Solutions of Some Electron-Donor-Acceptor Complexes

CARL LAGERCRANTZ and
MARGARETA YHLAND

Department of Medical Physics, University
of Göteborg, Sweden

The charge transfer in molecular complexes composed of an electron donor and an acceptor part (EDA-complexes) will sometimes introduce an unpairing of the electrons involved which gives a detectable electron spin resonance (ESR). Considering complexes in which both the donor and the acceptor parts are organic molecules an ESR-signal has mostly been found in solid state samples. In solutions, however, rather few complexes of this type have been reported to exhibit an ESR-signal^{1,2}. (For a recent review on EDA-complexes see Briegleb³). We now wish to report that

an ESR-signal can be induced in solutions of some organic EDA-complexes when irradiated by light.

Experimental. The electron acceptor was dissolved in an electron donor solvent which had been distilled immediately before use. The solutions to be studied were degassed twice by freezing, evacuating and melting within the sample tube. Before the final melting the volume over the solution was filled with nitrogen of atmospheric pressure. The samples were irradiated *in situ* through the irradiation slots in the cavity wall of a 100 kc Varian spectrometer equipped with the variable temperature accessory. The light source was mounted in an "Universal-Mikroskopierlampe" (Wild, Switzerland) at a distance of 40 cm from the cavity. Two different light-source-filter combinations were used: (A) A high pressure mercury lamp (Osram HBO-200) together with an UV cut off filter (50 % transmission at 408 m μ , 10 % at 387 m μ). Most of the experiments were performed with this source. (B) A high pressure xenon lamp (Osram XBO-150) together with a band pass filter (Wild UG1) with a maximum transmission about 360 m μ . Transmission data

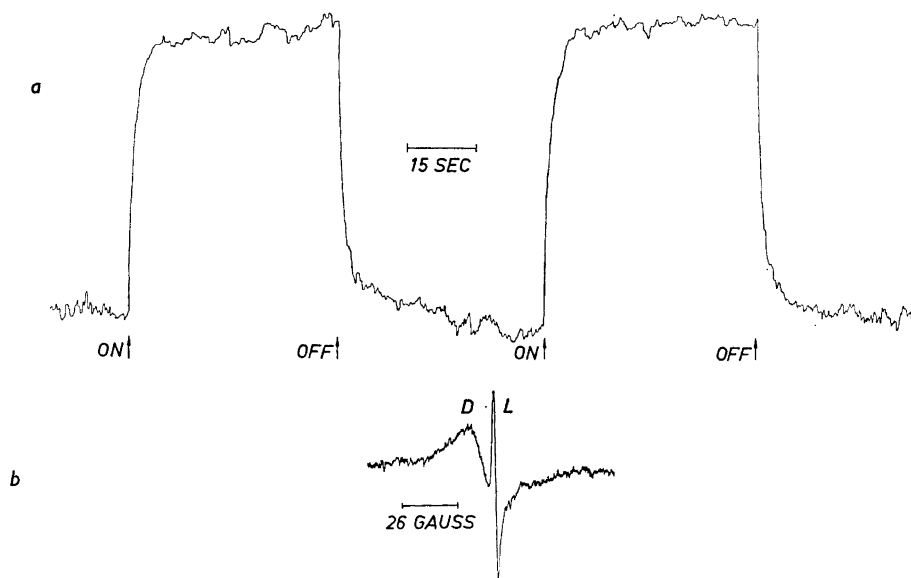


Fig. 1. Photo-induced paramagnetism in a 0.05 M solution of *p*-chloranil in tetrahydrofuran. Light-source-filter: (A).

a. Kinetic curve at -26°C . The relative spin concentration is recorded as a function of time. Constant magnetic field adjusted to maximum response.

b. ESR-spectrum at $+20^{\circ}\text{C}$. The first derivative of the absorption is recorded as a function of the magnetic field.

of filters, solvents and solutions were obtained by a Cary model 14 spectrophotometer.

In none of the experiments an ESR-signal could be detected prior to irradiation when the solutions had been prepared and kept in the dark. No ESR-signals could be detected when only the solvents were irradiated.

The kinetic experiments in which the reactions were relatively fast (Fig. 1 a), were performed with a time constant of the detector circuit of 0.3 sec and with a recorder of 0.25 sec response.

Results. Solutions of the electron acceptor *p*-chloranil in electron donor solvents as tetrahydrofuran, *p*-dioxane, xylene, mesitylene and *o*-chlorophenol exhibit a photo-induced ESR-signal. When the light is turned on there is a rapid increase of the signal from zero to a maximum steady state value (Fig. 1 a). When compared with a solution of diphenylpicrylhydrazyl (DPPH) in benzene, it was found that about 0.1 % of the acceptor molecules were transformed to paramagnetic centres. There is also a rapid decay of the signal to zero when the exciting light is turned off. The decay to half-value in a 0.05 M solution of chloranil in tetrahydrofuran was about 1 sec. No dependence on the temperature could be observed in a range of about 50° between -23°C and $+27^{\circ}\text{C}$. The reac-

tion could be recycled an infinite number of times with a rather good reproducibility. The ESR-spectra of the chloranil systems recorded during light excitation exhibited a single narrow line (L in Fig. 1 b) with a *g*-value close to that of DPPH. After irradiation of a solution of chloranil in tetrahydrofuran for about one hour (source (A)), a new line (D in Fig. 1 b) appeared which was broader than the original one. This new line did not disappear when the light was turned off. Degassing of the sample had no influence. When chloranil was dissolved in *p*-dioxane no such secondary line could be detected.

Solutions of the electron acceptors *s*-trinitrobenzene, picrylchloride and *m*-dinitrobenzene in donor solvents as tetrahydrofuran, *p*-dioxane, dimethoxyethane, benzaldehyde, xylene and mesitylene exhibit a photo-induced ESR-signal different from that found for chloranil. There is a less rapid response to light (Fig. 2 a). The decay rates are lower than those obtained with chloranil and show a definite temperature dependence. Thus, the time for a decay to half-value was about 1 min at $+20^{\circ}\text{C}$ in contrast to about 3 min at -10°C for a 0.1 M solution of *s*-trinitrobenzene in tetrahydrofuran. In most of the systems investigated there was a complete decay of the

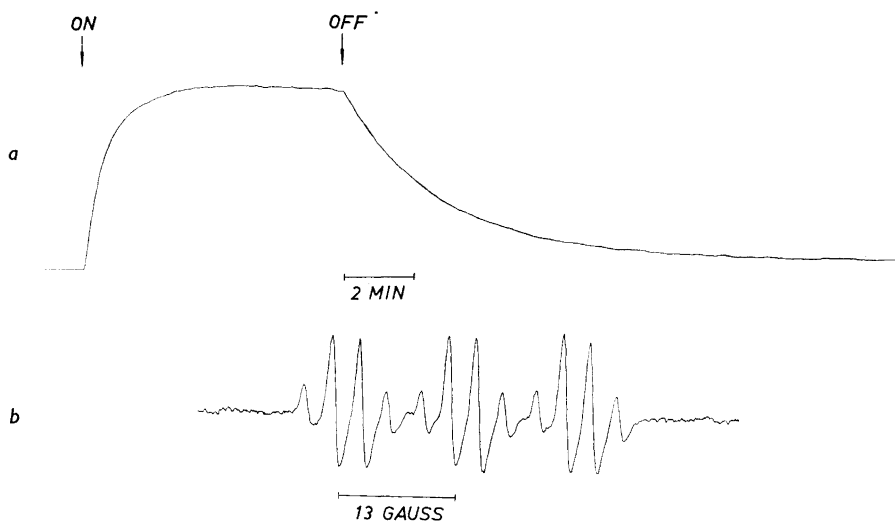


Fig. 2. Photo-induced paramagnetism in a 0.1 M solution of *s*-trinitrobenzene in tetrahydrofuran. Light-source-filter: (A).

- a. Kinetic curve at $+11^{\circ}\text{C}$.
b. ESR-spectrum at $+20^{\circ}\text{C}$.

ESR-signal. Some systems, however, exhibited an ESR-signal detectable even after that the irradiated samples had been kept in the dark overnight. The maximum spin concentration indicated that about 0.1 % of the acceptor molecules had been transformed to paramagnetic centres.

The ESR-spectra recorded during light excitation exhibit a hyperfine structure which can be more or less definitely correlated with a free radical derived from the acceptor part of the EDA-complexes. Fig. 2b shows the light-induced ESR-spectrum of *s*-trinitrobenzene dissolved in tetrahydrofuran. Due to the high symmetry of the molecule the three nitrogen nuclei produce a common splitting into three main lines separated by 13 gauss. Each of these lines is split into a quartet of equally spaced lines (3.0 gauss) by the three hydrogen atoms with the intensity ratio of 1:3:3:1. The appearance of this spectrum did not change even after irradiation for several hours. When dissolved in dimethoxyethane, however, a further splitting of the spectrum initially identical with that obtained in tetrahydrofuran was observed after prolonged irradiation.

The spectral distribution of the energy from light source (A) is well outside the absorption of tetrahydrofuran without any solute, and involves only a rather weak absorption in the solutions here investigated, whereas source (B) emits radiation in a region of relatively high absorption as concerns both the solvent and the solutions. Comparing the results obtained for the systems tetrahydrofuran — chloranil and tetrahydrofuran — *s*-trinitrobenzene by use of (A) and (B) respectively, however, no qualitative differences could be detected.

Discussion. It is believed that a charge transfer which unpairs the electrons involved is produced by the absorption of radiant energy. The subsequent reactions of the paramagnetic complex, a triplet state or, more probable, a biradical may take different paths. The excited chloranil complexes seem to return to the initial state without any dissociation into radical ions as judged from the relatively rapid decay rates and their apparent independence of the temperature. On the other hand the photo-activated complexes involving the nitro substituted derivatives of benzene are dissociated into radical ions as evidenced by their temperature dependent decay rates. The hyperfine structure of the *s*-trinitrobenzene spectrum is consistent with the formation of negative free radical ions by

a transfer of one electron without any transfer of hydrogen atoms. In other systems the radical ions formed evidently partake in secondary reactions.

Evidence for positive radical ions derived from the donor part of the EDA-complexes seems to be lacking. A hypothetical explanation may involve a very short life time of these radicals.

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Enrichment of Light Isotopes of Sulphur, Carbon and Oxygen Using an Anion Exchanger

KARL ERIK HOLMBERG

Division of Chemistry, Section for Nuclear Chemistry, AB Atomenergi, Studsvik, Tystberga, Sweden

It is known that upon displacement of hydrogensulphite ions from an anion exchanger by a strong acid there is an enrichment of heavy sulphur isotopes at the boundary formed¹. Similarly it is to be expected that upon absorption of sulphur dioxide from a solution on an anion exchanger column in the acetate ion form there will be an enrichment of the light sulphur isotope at the boundary formed. Several experiments have confirmed this. In the following only one is described.

In the experiment the 7 columns used were of 12 mm inner diameter and about 140 cm length, filled with Dowex 2-x10, 100–200 mesh, acetate ion form. They were connected in series by narrow glass tubes (2 mm inner diameter). On the columns there were absorbed a number of samples of SO₂, pre-enriched in ³²S by ion exchange, until there had formed a band of 255 cm length, visible by its yellow color.