

Photo-Induced Free Radical Reactions in the Solutions of Some Tars and Humic Acids

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When irradiated by visible light, the free radical content in the solutions of some tars and humic acids exhibited considerable changes. The light-induced radical reactions involved both the apparent destruction of radicals previously present in the dark (coal-tar) and the formation of new radicals. In the solutions of coal-tar and humic acids the light-induced changes of the radical concentration are more or less irreversible. The solutions of wood-tar, chimney-soot and tobacco smoke condensate exhibited both an irreversible and a reversible formation of radicals.

The reaction mechanism is discussed in terms of a photo-induced charge-transfer between donor substances and coloured acceptor substances. It is suggested that the dark pigments of the materials investigated behave as acceptors.

By the technique of electron spin resonance (ESR) it has been found that several of the products formed by pyrolysis of a variety of organic materials may contain free radicals. Thus, carbon blacks were found to contain a very high number of unpaired electrons^{1,2}. These radicals have been extensively studied during the last years, and have been found to be very stable. Condensates of tobacco smoke collected at low temperature were shown by Ingram *et al.*³ to contain short-lived radicals which disappeared on heating to room temperature. Besides these radicals, the smoke condensates and the tobacco tars contained stable radicals which could partly be dissolved in organic solvents. Such stable radicals, soluble in organic solvents, are present in coal and wood tars of various origins. With exception of the carbon blacks, very little seems to be known about the nature of all these radicals.

When irradiated by visible light, it has been found that the radical content of solutions of tars varies in a characteristic manner. This report describes the results obtained with the tars together with some analogous experiments performed with solutions of humic acids.

EXPERIMENTAL

The ESR-measurements were performed by a Varian 100 kc spectrometer. All runs were made at ambient room temperature with the solutions contained in a flat sample cell. The samples were irradiated *in situ* through the slots of the spectrometer cavity. The light source was a mercury lamp (Osram HBO-200) equipped with suitable UV cut off filters (50 % transmission at 408 m μ , 10 % at 387 m μ). The light source was mounted in an "Universal-Mikroskopierlampe" (Wild, Switzerland) at a distance of 40 cm from the cavity. Degassing was performed when the sample was contained in a small tube fitted to the sample cell, by freezing, evacuating and melting. Before the final melting the volume over the solution was filled with nitrogen of atmospheric pressure. Kinetic runs were performed at constant magnetic field adjusted to maximum response. The radical concentrations were estimated by comparison with a freshly prepared solution of diphenylpicrylhydrazyl in benzene.

RESULTS

I. *Coal-tar. (a)*. When prepared and kept in the dark, a 5 % (w/v) solution of coal-tar (*Pyroleum lithantracis, Pharmacopoea Svecica, Ed. XI*) in benzene was found to contain about 5×10^{17} spins per ml.

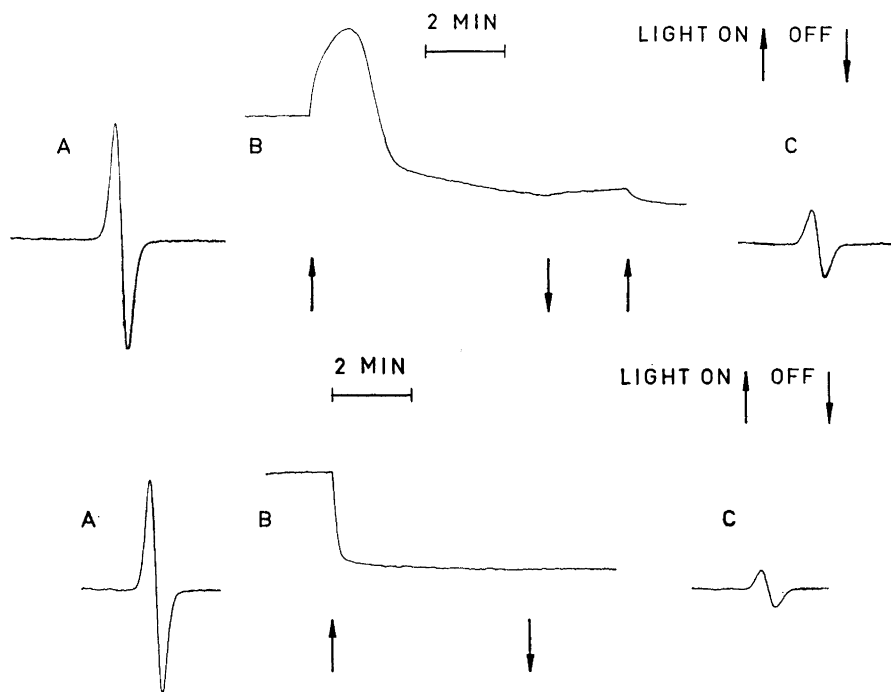


Fig. 1. ESR-recordings of the free radicals in a solution of coal-tar (5 %) in benzene. The runs were performed with equal spectrometer sensitivity.

- A. ESR-spectrum before irradiation. The positive (or negative) deflection is a measure of the relative concentration of radicals.
 B. Kinetic curve. The relative concentration of radicals is recorded as a function of time.
 C. ESR-spectrum in the dark after irradiation.

Fig. 1 a. (above) No degassing.

Fig. 1 b. (below) Degassed.

(b) The radical concentration of this solution was reduced by a factor of ten when *p*-toluenethiol was added to make the concentration 0.1 %. When left standing in an open vessel or shaken, the radical concentration of this solution increased rapidly to almost the original level.

(c) When irradiated by visible light, the radical concentration of a non-degassed solution (5 % in benzene (a)) began to increase immediately (Fig. 1 a). After one minute the concentration passed through a maximum value. It then decreased to a constant level which was considerably lower than that recorded before the irradiation. The maximum increase during irradiation amounted to about 80 % of the concentration present before the irradiation. Only a very small regeneration of the radical concentration was observed when the light was switched off.

(d) Degassing of the solution prior to irradiation completely eliminated the initial increase of the radical concentration observed in the non-degassed

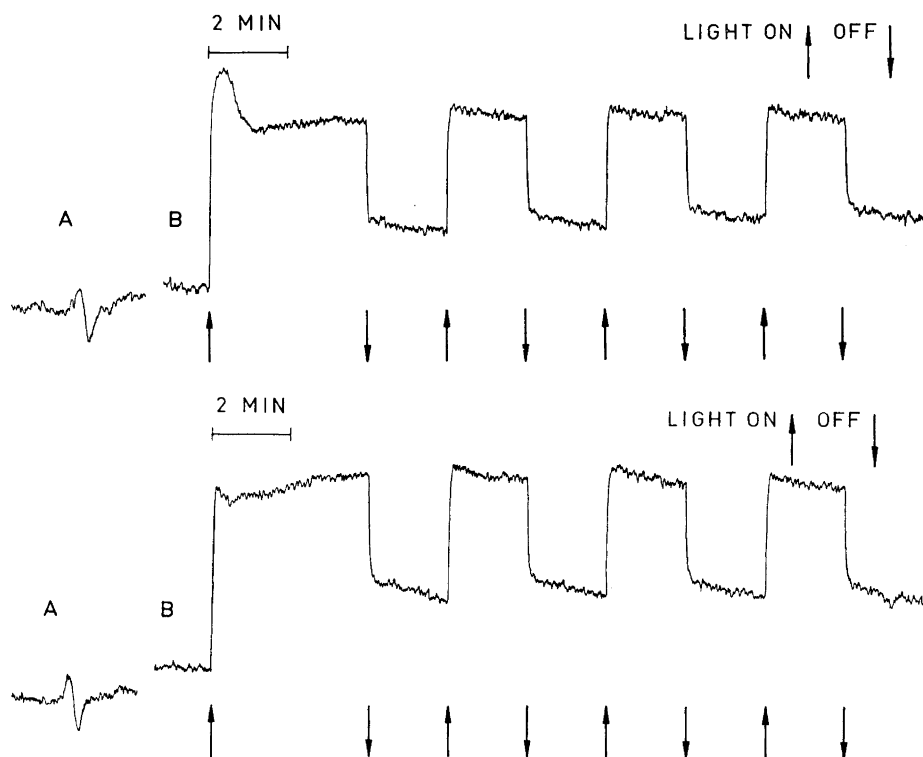


Fig. 2. ESR-recordings of the free radicals in a solution of wood-tar in benzene (1:1 v/v). The runs were performed with equal spectrometer sensitivity.

A. ESR-spectrum before irradiation.

B. Kinetic curve. The relative concentration of radicals is recorded as a function of time.

Fig. 2 a. (above) No degassing.

Fig. 2 b. (below) Degassed.

solution (Fig. 1 b). The decay of the radicals, however, was present just as in the non-degassed solution.

(e) The faintly brown coloured aqueous layer separated subsequent to extraction of a benzene solution of coal-tar by an alkaline water solution was found to contain only a rather low concentration of free radicals. When irradiated by visible light, a considerable increase of the radical concentration was induced.

II. *Wood-tar.* (a) A solution of *Pyroleum oxycedri* (*Pharmacopoea Svecica*, Ed. XI), the tar obtained from the wood of *Juniperus oxycedrus* L., in benzene (1:1 v/v) contained about 5×10^{15} spins per ml.

(b) When a non-degassed sample of this solution was irradiated by visible light, a very rapid increase of the radical concentration was observed (Fig. 2 a). The increase amounted to about eight times the value observed in the dark. After about 20 sec the initially induced radical concentration decreased to a constant level which amounted to about five times the value observed in the dark. When the light was switched off the concentration dropped rapidly to a value corresponding to about three times the initial value in the dark prior to any irradiation. The turning on of the light a second time introduced a rapid

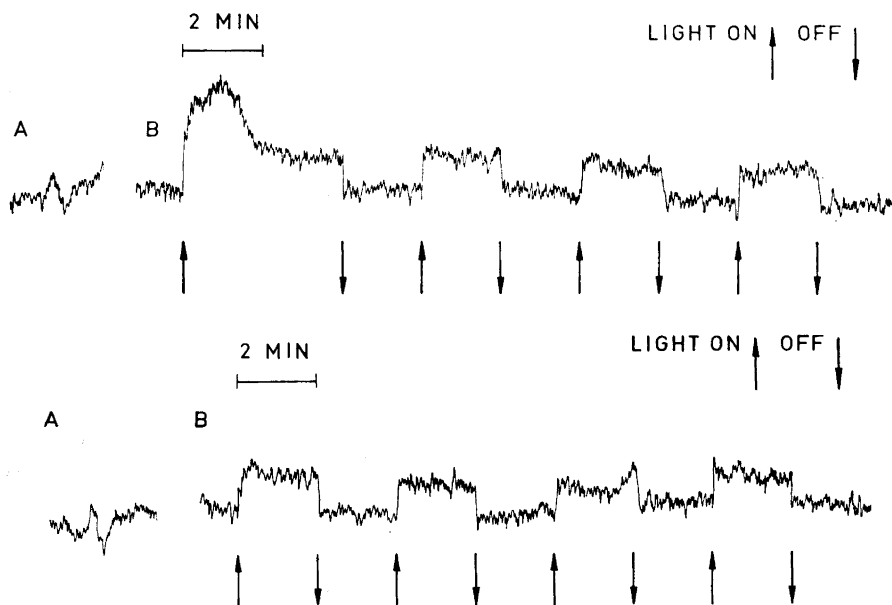


Fig. 3. ESR-recordings of the free radicals in an ethanol extraction of a tobacco smoke condensate. Ascorbic acid was added to make the concentration 1%. The runs were performed with equal spectrometer sensitivity.

A. ESR-spectrum before irradiation.

B. Kinetic curve. The relative concentration of the radicals is recorded as a function of time.

Fig. 3 a. (above) No degassing.

Fig. 3 b. (below) Degassed.

increase to the level observed at the end of the first period of irradiation. It was found that the process could be recycled an indefinite number of times.

(c) When the same experiment was repeated with a degassed sample, an almost identical result was obtained except for the hump observed in the beginning of the first period of irradiation. This hump could not be seen in the curve obtained with the degassed sample (Fig. 2 b).

III. *Tobacco smoke condensate*. The smoke from 50 cigarettes burned under standard conditions was collected in a trap chilled by a mixture of carbon dioxide and acetone. The condensate (1.8 g) was first extracted with 100 ml benzene and then with 50 ml ethanol*.

(a) No radicals could be detected in the benzene solution neither in the dark nor when the sample was irradiated by light.

(b) When kept in darkness no radicals could be detected in the ethanol solution. In this solution which was far more darkish brown than the benzene solution (a), a small amount of free radicals was induced by irradiation. As soon as the light was switched off the radicals disappeared.

(c) After ascorbic acid had been added to the ethanol solution to make the concentration 1 %, the yield of free radicals was increased upon irradiation by light (Fig. 3 a). When the light was turned off, the radical concentration dropped rapidly almost to zero. The process could be recycled an indefinite number of times. In a non-degassed solution there was a hump in the kinetic curve, most likely analogous to that observed in respect of *Pyrooleum oxycedri* (Fig. 2 a). The initial hump in the curve could not be detected after degassing (Fig. 3 b).

IV. *Chimney-soot*. The material consisted of the soot, collected when cleaning the chimney of an oil-heating plant of a medium sized house. Extraction of this material with a mixture of ethanol and acetone (1:1 v/v) produced a deeply brownish-red solution.

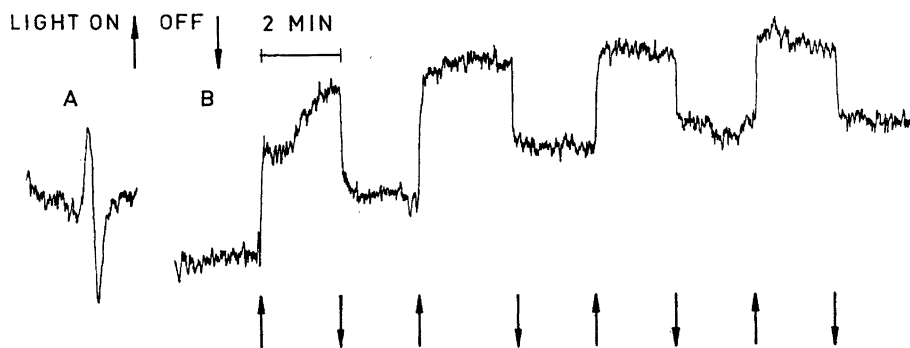


Fig. 4. ESR-recordings of the free radicals in an extraction of chimney-soot by a mixture of ethanol-acetone (1:1 v/v). The solution was saturated with ascorbic acid. The runs were performed with equal spectrometer sensitivity. No degassing.

A. ESR-spectrum before irradiation.

B. Kinetic curve. The relative concentration of radicals is recorded as a function of time.

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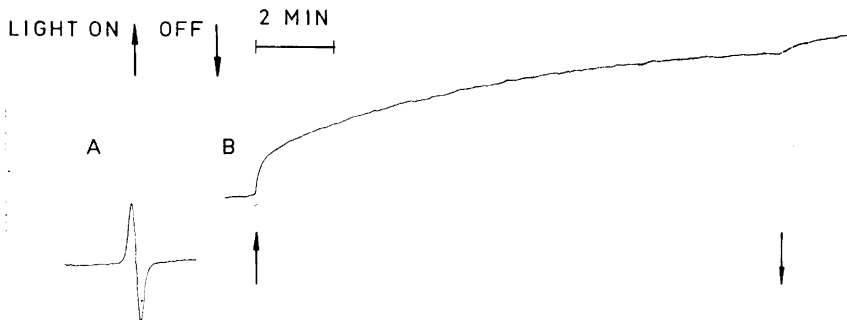


Fig. 5. ESR-recordings of the free radicals in a 5 % solution of humic acids in 0.1 N NaOH. The runs were performed with equal spectrometer sensitivity.

A. ESR-spectrum before irradiation.

B. Kinetic curve. The relative radical concentration is recorded as a function of time.

(a) No radicals could be detected in this solution neither in darkness nor when irradiated by light.

(b) After the coloured solution had been saturated with ascorbic acid, a small amount of free radicals was present in the dark (Fig. 4 a).

(c) Irradiation by light induced a rapid increase of the radical concentration of the solution containing ascorbic acid. When the light was turned off the radical concentration decreased rapidly to a level considerably higher than that observed before irradiation (Fig. 4). The process could be recycled, and the kinetic behaviour was similar to that observed with *Pyroleum oxycedri* (Fig. 2) and to that containing a solution of tobacco smoke condensate to which ascorbic acid had been added (Fig. 3).

V. *Humic acids.* (a) A 5 % solution of humic acids (preparation obtained from Light and Co.) in 0.1 N NaOH contained about 2×10^{17} spins per ml.

(b) The radical concentration of this solution was increased by a factor of about two when cysteine was added to make the concentration 0.1 %.

(c) When a solution of humic acids (a) was irradiated by visible light, the radical concentration slowly increased and attained a rather constant level after about 5 min. The photo-induced increase of the radical concentration amounted to about three times the value observed in the dark. When the light was turned off there was no change of the radical content during the time of observation (Fig. 5).

(d) Degassing of the solution did not appreciably change the appearance of the kinetic curve.

VI. No resolved hyperfine structure could be observed in any of the experiments.

DISCUSSION

The products studied in this instance have certain features in common. They are derived from plant material, they are dark-coloured and soluble in a variety of solvents, and some of them contain free radicals before irradiation. When irradiated by visible light there is a considerable change of their radical

content. The light-induced radical reactions seem to involve both the destruction of radicals (coal-tar), and the formation of new ones. In the solutions of coal-tar and humic acids the light-induced changes of the radical concentration are more or less irreversible. The solutions of wood-tar, tobacco smoke condensate and chimney-soot exhibit both an irreversible and a reversible formation of radicals. In some of the radical systems studied the radical concentration could also be changed by addition of reducing substances.

Due to the complex nature of the systems studied and the general lack of information about their radical systems, any conclusions drawn from the experiments described must be rather uncertain. It is believed, however, that a considerable part of the soluble radicals in the materials is connected with the dark pigments. Also, it is believed that the photo-induced radical reactions involve these pigments. Radiant energy is most likely absorbed by the pigments in these reactions which eventually lead to the formation and disappearance of radicals. Photo-induced charge-transfers between charge-donors and coloured charge-acceptors leading to the formation of free radicals have been reported⁴⁻⁸. A large number of substances have been found to behave as donors in these reactions, especially those which are unsaturated or contain active hydrogens such as levopimaric acid and ascorbic acid. It is possible that the light-induced radical reactions of the tars and the humic acids depend on a similar mechanism in which the pigments would be considered as acceptors. At present no information is available about the nature of the donors in these hypothetical charge-transfers but it seems not impossible that such substances may exist in tars and humic acids. The theory of a light-induced charge-transfer, involving a coloured acceptor, seems to be supported by the experiments described in III (c) and IV (b) in which no radicals, or very few only, could be observed until a sufficient supply of a donor substance had been obtained by the addition of ascorbic acid.

The transient increase of the radical concentration observed in a non-degassed solution of coal-tar, and the small initial hump on the kinetic curves obtained with wood-tar, and with tobacco smoke condensate with added ascorbic acid, are certainly due to the presence of molecular oxygen since these effects disappeared when the solutions had been degassed. The decrease of the radical concentration to a level below that recorded before irradiation which was observed for coal-tar solutions (Fig. 1a and 1b) may be only an apparent one. It is possible that the decrease is due to an altered spin relaxation of a nature similar to that described by Saraceno and Coggeshall⁹ for petroleum oils but experimental evidences to support such an explanation is lacking so far.

It is possible that one and the same system might contain more than one radical species. The presence of both irreversibly and reversibly light-induced radicals in the solution of *Pyrooleum oxycedri* supports this suggestion. Since the spectra recorded do not exhibit any resolved hyperfine structure no direct information is available about the structure of the radicals.

Rex¹⁰ has recently found that lignin and humic acids contain stable free radicals which were considered to be semi-quinone polymers derived from lignin. It is possible that the radicals assumed to be connected with the tar pigments have a similar structure. The suggested connexion between the photo-reactions in the tars, the humic acids and semi-quinone polymers is in part

supported by the fact that the content of free radicals of an alkaline solution of *p*-benzoquinone which had turned dark when left standing, exhibited a rather substantial increase when irradiated by visible light.

However, substances with acceptor properties other than those mentioned above may be present in the materials considered. It may be pointed out that porphyrin substances, probably derived from chlorophyll, have been found in a variety of fossil materials, such as petroleum and coal¹¹. Porphyrin derivatives have proved to be effective acceptors in photo-induced reactions leading to detectable free radicals⁸. From the discussion given it is evident that further progress in this field must involve a fractionation of the materials by chemical methods.

Finally, a relationship may possibly exist between the photodynamic action of tars observed when applied to the human skin and the free radical reactions described in this case.

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