

Light-Induced Changes of the Radical Concentration and Microwave Saturation in Solutions of Coal-Tar and Petroleum

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When oxygen-containing solutions of coal-tar and crude petroleum dissolved in benzene are irradiated by visible light, their contents of free radicals exhibit a characteristic biphasic change. Measurements of the signal intensity of the ESR-absorption at different microwave power levels indicate that these changes involve an initial real increase of the radical contents due to a photo-induced reaction in which oxygen is consumed. In connection with the consumption of the dissolved paramagnetic oxygen in this reaction the spin-lattice relaxation time increases, and a signal saturation is introduced which simulates a subsequent decrease of the signal intensity, especially at high power levels.

Recently some light-induced radical reactions in solutions of coal-tar in benzene were described (Lagercrantz and Yhland¹). Through the technique of electron spin resonance (ESR) it was found that the contents of free radicals in solutions of coal-tar in benzene were considerably altered upon irradiation by visible light. The kinetic curve exhibited an increase of the radical contents immediately after turning on the light. After the curve had passed through a maximum, the concentration decreased to a value considerably below the figure shown prior to irradiation. Degassing the solution before irradiation eliminated the initial increase of the radical concentration.

At first it seemed likely that the reaction mechanism involved a formation as well as a destruction of radicals. In some preliminary experiments, however, it was observed that the appearance of the kinetic curves was largely influenced by the magnitude of the microwave power applied to the sample. The initial increase of the radical concentration at a high power level was found to be relatively small, but the subsequent decrease considerable as compared to the results obtained at a low power level. These findings indicated a saturation of the ESR-signal in connection with the irradiation.

Similar effects have been observed in other radical systems. Thus, Saraceno and Coggeshall² found that the ESR-signal of the free radicals present in petroleum oils is easily saturated. Bubbling through oxygen or dilution of the

oils with organic solvents such as benzene, produced a reduction of the saturation effect. Degassing of the samples was found to restore or increase the original saturation. When petroleum samples contained in sealed tubes were irradiated by light, it was noted that the signal saturation slowly increased. The saturation of the ESR-signal in petroleum was ascribed to a relatively long spin-lattice relaxation time which was shortened by the presence of dissolved paramagnetic oxygen. The increase of the spin-lattice relaxation time noted in the irradiation experiments was considered to be connected with consumption of oxygen in some kind of photo-chemical reaction. Any real changes of the concentration of the free radicals were not observed to be caused by light, oxygen, or organic solvents.

In view of the saturation effects, suspected to be involved in the experiments with solutions of coal-tar,¹ and the results reported by Saraceno and Coggeshall,² it could be open to question as to which extent the kinetic curves, obtained when irradiating the coal-tar solutions, reproduced real changes of the radical concentration. Some experiments with solutions of coal-tar and petroleum performed in order to elucidate this problem will now be described.

EXPERIMENTAL

The recordings were obtained by a Varian 100 kc spectrometer. The irradiation of the samples were performed *in situ* through the slots of the spectrometer cavity as previously described.¹ All runs were made at room temperature, with the solutions contained in a flat sample cell. Degassing of the samples was performed as described before.¹ Kinetic runs were obtained at constant magnetic field after adjustment to maximum response. The saturation diagrams (Figs. 1 and 2) were obtained when the instrument was operated in the High-Power arrangement by the aid of the variable attenuator fitted to the spectro-

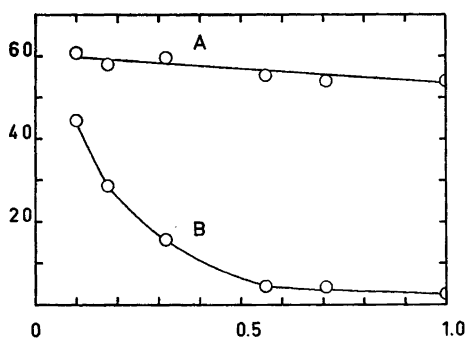


Fig. 1. Saturation diagram obtained with a non-degassed 5% solution of coal-tar in benzene. The normalized relative signal intensity is plotted as a function of the square root of the relative microwave power. Curve A shows the result obtained with a non-irradiated sample, curve B the result obtained during *in situ* irradiation by light.

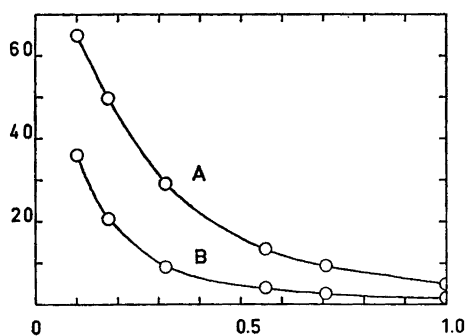


Fig. 2. Saturation diagram obtained with a degassed 5% solution of coal-tar in benzene. Curve A: non-irradiated sample, curve B during *in situ* irradiation by light.

meter. The power range with this arrangement is between zero and -20 db. The unattenuated power, feeding the cavity arm, was about 160 mW.

Experiments were also carried out when the instrument was operated with the Low-Power Bridge.³ Due to an uncompensated drift of the resonance frequency of the sample cavity, caused by a slight temperature rise during the irradiation by light, relative to the resonance frequency of the external cavity used in this set-up as a reference for the klystron stabilization, an admixture of the dispersion mode appeared which gave rise to inaccurate results, especially in the form of a base line drift. With a considerable sacrifice in power attenuation, this inconvenience was eliminated by operating the spectrometer in the Low-Power arrangement, locking the frequency stabilization to the sample cavity in a conventional manner. By this method the power range was extended to 35 db down. The power levels below 20 db were used in the kinetic experiments only, and were not incorporated in the saturation diagrams.

The relative radical concentration, used in the saturation diagrams, were obtained from the derivative recordings with the aid of the moment method.⁴

Saturation measurements

In order to study the saturation effects, suspected to be involved in the irradiation of the tar solutions, direct measurements of the spin-lattice relaxation time T_1 would be profitable. With the available spectrometer equipment, T_1 can be obtained with the continuous wave (cw) method by recording the absorption at a high saturating microwave power and at a relatively low level.^{5,6} In order to obtain the value of T_1 it is necessary to know the microwave power at the sample and the spin-spin relaxation time T_2 . An absolutely accurate determination of T_1 , however, seems to be difficult to obtain by the cw method. Thus, Saraceno and Coggeshall² preferred to give relative values only of T_1 in their study of the saturation behaviour of petroleum oils. No attempts were made in the present study to evaluate T_1 explicitly. The saturation behaviour of the systems concerned is shown in a diagram (Figs. 1 and 2) where the normalized signal intensity, *i.e.* the ratio of the signal intensity to the square root of the relative microwave power applied to the sample, is plotted as a function of the square root of the relative power. In this diagram a relatively non-saturating spin system (T_1 short) will exhibit a straight line, almost parallel with the x axis. With the introduction of an increasing amount of saturation, the curve will exhibit an increasing slope, due to the diminished signal intensity at high power.

RESULTS

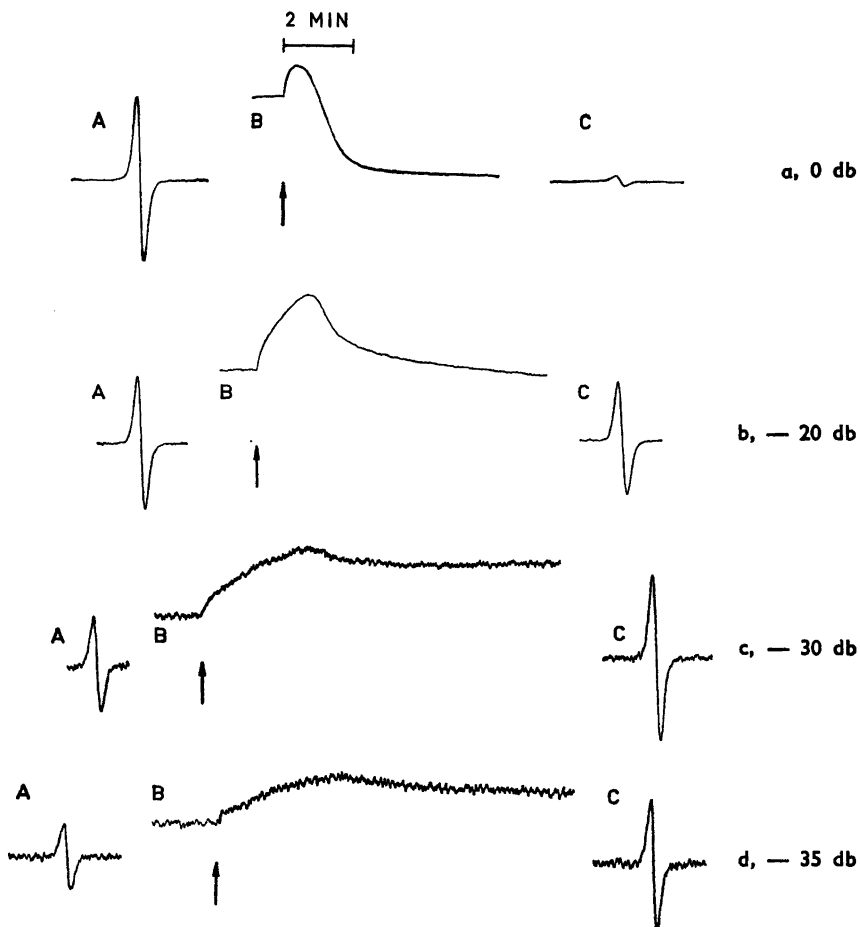
A. Coal-tar. Saturation measurements. Fig. 1 shows the saturation diagram obtained for a non-degassed 5 % coal-tar solution in benzene (*Pyroloem lithantracis*, *Pharmacopoea Svecica*, Ed. XI). The unirradiated solution gives rise to a curve, A, with only a small deviation from a straight line parallel to the x axis, and the saturation is consequently low. Curve B shows the results obtained with the same sample during *in situ* irradiation by light. A considerable amount of saturation is introduced, and the normalized signal intensity at 0 db (1.0 in the figure) is reduced by a factor of about 20 as compared with the unirradiated sample.

Fig. 2 shows the diagram obtained with a degassed coal-tar solution. The curves obtained for both the unirradiated and the light-irradiated sample exhibited a considerable amount of saturation.

B. Coal-tar. Kinetic curves. In the figures shown the curves labelled A give the ESR-spectra in the dark before any irradiation. Those labelled B give the kinetic curves in which the first derivative of the ESR-absorption is recorded as a function of time. The arrows shown in these curves indicate the turning-on

of the light. The curves labelled *C* represent the ESR-spectra in light after recording the kinetic curves.

Irradiation of a non-degassed 5 % coal-tar solution in benzene at a high microwave power (0 db) produced a biphasic curve (Fig. 3a) of the type previously described,¹ exhibiting an initial increase of the signal amplitude followed by a decrease to a value below that recorded in the dark prior to any irradiation. When the experiment was repeated at lower power levels (Fig. 3b, -20 db; Fig. 3c, -30 db; Fig. 3d, -35 db) it was found that the initial increase of the signal amplitude was enhanced, and that the subsequent decrease obtained at high power, had been almost completely eliminated. In another experiment the light was turned off at the maximum point of the signal increase (Fig. 3e). It was found that the signal amplitude attained persisted unchanged in the dark for an indefinite period. No saturation could be detected when the reaction was stopped at this point.



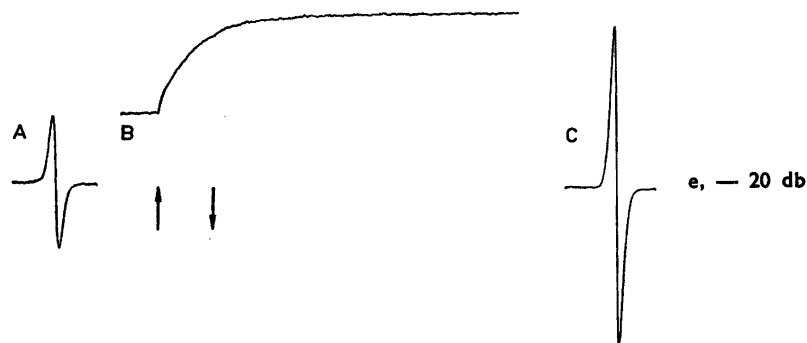


Fig. 3. Kinetic curves (see the text for explanations) obtained upon irradiation of a non-degassed 5% solution of coal-tar in benzene at different microwave powers. Fig. 3 e shows the result obtained at -20 db when the light was turned off as indicated by the arrow directed downwards.]

The analogous experiments carried out with a degassed solution are shown in Fig. 4. The kinetic curves recorded exhibit only a rapidly appearing decrease

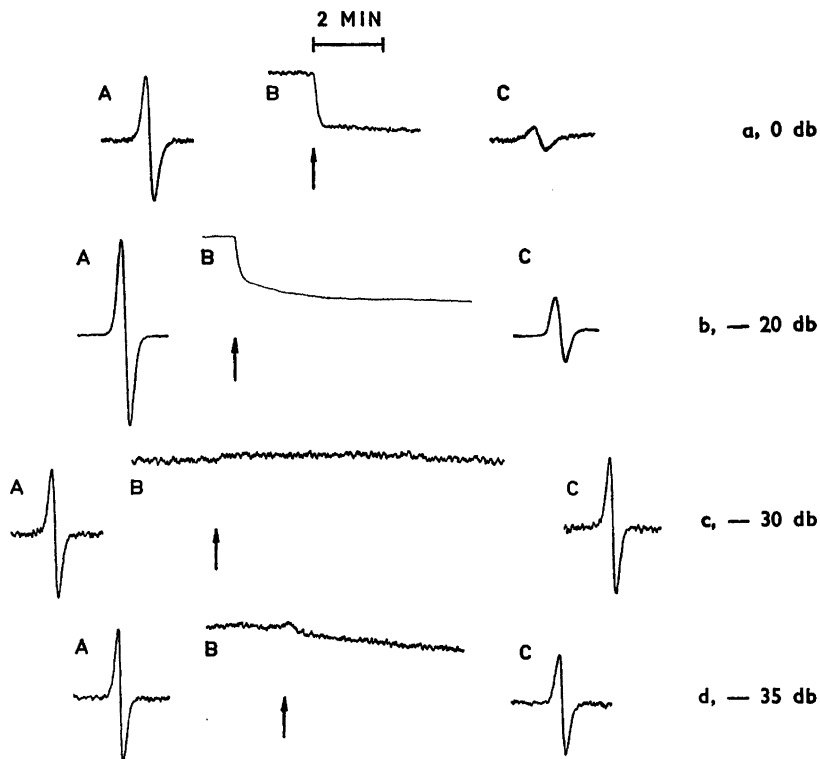


Fig. 4. Kinetic curves obtained upon irradiation of a degassed 5% solution of coal-tar in benzene at different microwave powers.

of the signal amplitude upon irradiation. It is seen that this decrease is much more pronounced at high power (Fig. 4a, 0 db) than at a low power level (Fig. 4b, -20 db; Fig. 4c, -30 db; Fig. 4d, -35 db).

C. Petroleum. Saturation measurements. The experiments were performed with a petroleum preparation used for industrial heating ("eldningsolja 3"). In addition to the single line of free radicals, the ESR-spectrum of the undiluted oil exhibited the multiple-line structure of vanadium ions which is a characteristic feature of many crude petroleum fractions.⁷

A non-degassed 5 % solution of petroleum in benzene exhibited very little saturation. During irradiation, a considerable degree of signal saturation was introduced. The appearance of the saturation diagram was similar to that of the coal-tar solution. Also, the degassed petroleum samples exhibited a saturation similar to that obtained in respect of the coal-tar solutions. The results obtained with the petroleum samples appear to be qualitatively consistent with those reported by Saraceno and Coggeshall.²

D. Petroleum. Kinetic curves. Irradiation of a non-degassed 5 % solution of petroleum in benzene at a high microwave power (Fig. 5a, 0 db) exhibited

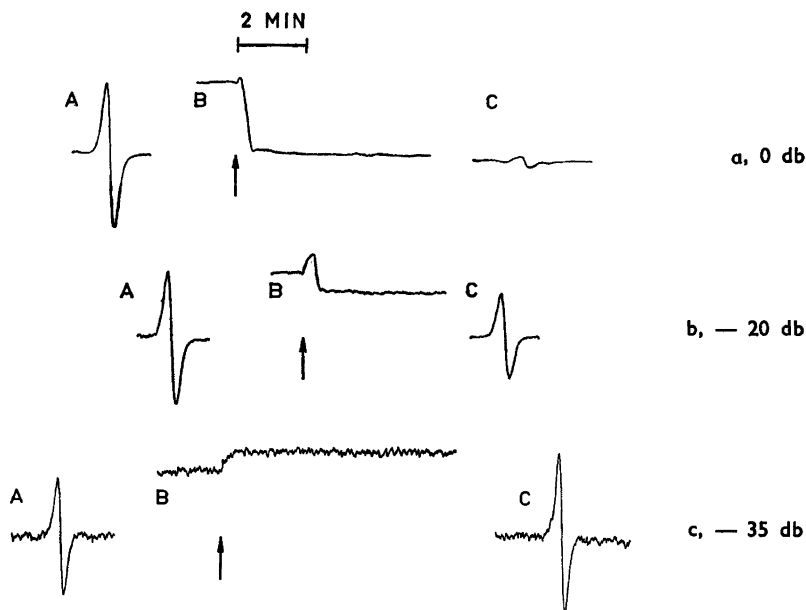


Fig. 5. Kinetic curves obtained upon irradiation of a non-degassed 5 % solution of petroleum in benzene at different microwave powers.

only a rapidly appearing decrease of the signal amplitude, except for a small initial increase of very short duration. When the experiment was performed at lower power (Fig. 5b, -20 db), this initial increase of the signal amplitude was more distinct. At still lower levels the initial increase dominates, and at

—35 db (Fig. 5 c) no trace of a secondary decrease of the signal could be observed.

Upon irradiation the kinetic curves obtained with degassed petroleum solutions in benzene exhibit only a rapidly appearing decrease of the signal amplitude (Fig. 6). The curves are similar to those recorded in the analogous experi-

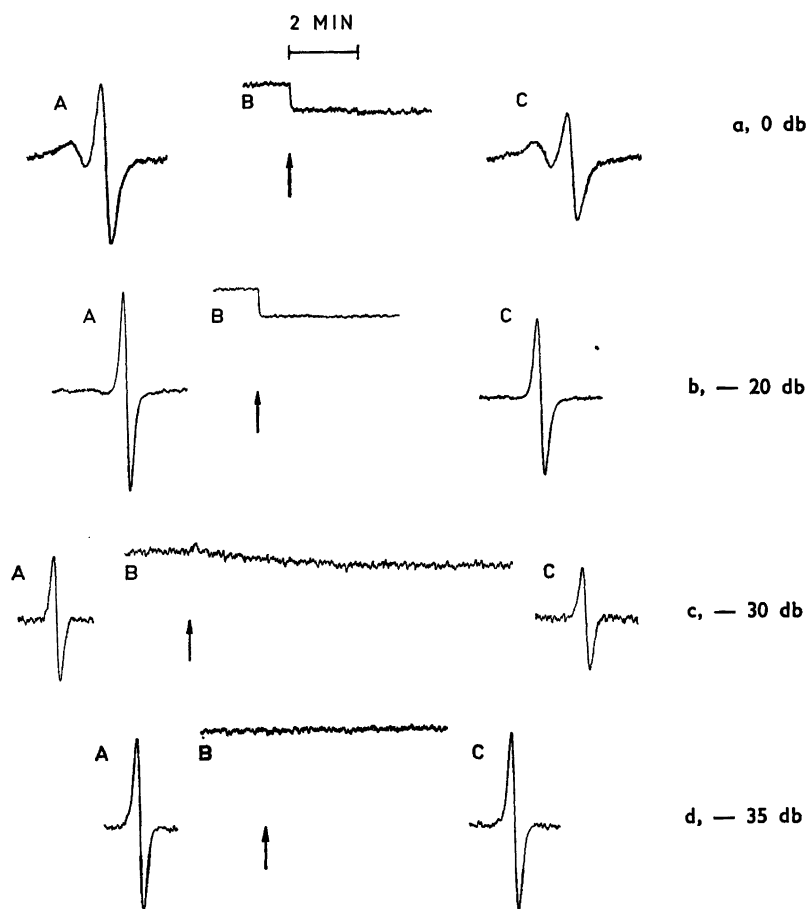


Fig. 6. Kinetic curves obtained upon irradiation of a degassed 5% solution of petroleum in benzene at different microwave powers.

ments with coal-tar. On applying a diminishing power rate, the signal decrease becomes smaller, and at —35 db, the signal level is almost unchanged upon irradiation (Fig. 6 d).

DISCUSSION

It is evident from the experiments performed that the free radical systems present in coal-tar and petroleum solutions have several features in common. Both exhibit a considerable microwave power saturation when irradiated by visible light, and on depletion of oxygen by degassing.

As evidenced from the kinetic curves obtained at low power levels, no real decrease of the radical concentration seems to be produced upon irradiation in neither coal-tar, nor petroleum solutions.

Contrary to the apparent decrease of the signal amplitude, the initial increase observed in the experiments with both coal-tar and petroleum appears to be a genuine phenomenon, and to represent a photo-induced enhancement of the contents of free radicals. The increase of the radical contents seems to be independent of the power applied to the samples, but the effect is more or less masked by the subsequent apparent decrease of the signal, especially at high power levels. From the experiments performed with degassed solutions, it is evident that the initial signal increase is dependent on the presence of dissolved oxygen. The following reaction mechanism is suggested. When the oxygen containing solutions are irradiated, a photo-induced reaction takes place in which oxygen is consumed and new free radicals are formed. As soon as the bulk of the oxygen has disappeared, this reaction ceases, and the maximum increase of the radical contents has been attained. Simultaneously with the decreasing concentration of dissolved paramagnetic oxygen, the spin-lattice relaxation time increases and the system exhibits an apparent decrease of the signal intensity, especially at high power levels.

In the degassed systems, the initial signal increase is absent. This is wholly consistent with the suggested mechanism. A system completely depleted of oxygen by degassing should not exhibit any changes at all upon irradiation even at a high power level. The kinetic curves obtained with the degassed solutions however, (Figs. 4 and 6) exhibited a considerable apparent decrease of the signal intensity upon irradiation at high power. It is believed that the last findings are due to incomplete removal of dissolved oxygen. Upon irradiation, the residual amount of oxygen is consumed in the photo-induced reaction resulting in a further prolongation of the spin-lattice relaxation time, but without a measurable increase of the radical contents.

The increase of the signal intensity upon irradiation described above seems to have escaped notice by Saraceno and Coggeshall² in their study of petroleum oils. A possible explanation of this discrepancy may be due to the fact that Saraceno and Coggeshall appear to have performed their irradiation experiments outside the spectrometer cavity without any continuous recording of the ESR-signal.

Very little seems to be known about the soluble free radicals of coal-tar and petroleum. By ultracentrifugation it has been shown that the radical contents of crude petroleum are connected with colloidal particles.^{7,8} As regards the photo-induced reaction in which oxygen is consumed and new radicals are formed, it has been suggested that the reaction in some way involves the dark pigments present in coal-tar.¹

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