# ELECTRON SPIN RESONANCE DETECTION OF OSCILLATING PEROXY RADICAL CONCENTRATION IN THE CUMENE–ANTHRAQUINONE SYSTEM

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## Summary

Kinetic electron spin resonance spectroscopy has been applied in order to follow the variation in peroxy radical concentration in the cumene–anthraquinone system in the presence of oxygen and during UV irradiation. A periodic variation in concentration was observed, which can be caused either by hydrodynamic convections or by diffusion-controlled photochemical oscillations. For the latter case, a model was suggested in which the anthraquinone regeneration, controlled by the local oxygen concentration, can serve as a feedback mechanism, and the oscillations can be maintained by concentration gradients between the irradiated and the dark zones and by the different diffusion rates of oxygen and anthraquinone.

## 1. Introduction

Recently a few papers have appeared that account for the periodic or aperiodic instabilities in the light emission or absorption of one of the components in various photochemical systems [1 - 7]. It was originally claimed that the oscillation behaviour is a consequence of the combined effects of diffusion and photochemical processes. Although photochemical oscillations can exist in principle, as pointed out by Nitzan and Ross [8], most recent investigations clarify the actual reasons for the reported oscillations: they are created by time-dependent hydrodynamic convections caused either by gas evolution [7] or by temperature gradients in the sample [9, 10]. In other words, none of the reported systems can be considered as a realization of a true photochemical oscillator. A common feature of the previous experiments is that both the stimulation of processes and the detection of variations were carried out by optical means. Since free-radical reactions always take place in photochemical systems, electron spin resonance (ESR) spectroscopy, being a sensitive tool for detecting free radicals, seemed to be a promising method for the study of kinetic instabilities in photochemical systems. The ESR technique has also been found useful in

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studying oscillations of the $Mn^{2+}$ ion concentration in the classical Belousov–Zhabotinskii reactions [11].

In this paper we report our kinetic ESR investigations of the peroxy radical concentration in the cumene–anthraquinone system in the presence of oxygen and in the course of UV irradiation. This work has led to the discovery of a periodically changing radical concentration. We raise the question as to whether a photochemical oscillation can occur in this case and offer a qualitative scheme, as a working hypothesis, in order to explain the observed periodicity in the kinetics.

## 2. Experimental details

The UV irradiation was carried out by a high pressure mercury lamp *in situ* of the cavity of an ESR spectrometer (JEOL-JES-FE-3X) working in the X band with 100 kHz field modulation. The temperature was varied in the range −70 to −85 °C. Portions of cumene solvent containing $10^{-2}$ - $10^{-3}$ M anthraquinone were inserted in quartz sample tubes of inner diameter 3 mm up to a height of 4 cm.

Both air-saturated solvents (about $10^{-4}$ M dissolved oxygen) and solvents with reduced oxygen content (about $10^{-5}$ M) were investigated. Closed sample tubes were used to minimize external oxygen uptake in the course of irradiation. The irradiation reached the sample tubes within a zone of 5 - 25 mm. At the 330 nm absorption band of anthraquinone [12], where the cumene has no absorption, the penetration depth of non-filtered light is no more than a few tenths of a millimetre at the applied concentration range, *i.e.* an irradiated and a dark zone should be distinguished, where the volume of the irradiated zone is much smaller.

## 3. Results

In the photochemical system under study, two types of ESR signal can be detected at low temperature. One of the signals was observed only at low oxygen concentration and decayed within a few minutes at −80 °C during irradiation. On the basis of the $g$ value ($g = 2.0037$) and the hyperfine pattern of four equivalent protons ($a_H = 0.3$ mT) this signal can be assigned to the semianthraquinone radical ($QH^{\bullet}$) [13]. $QH^{\bullet}$ can be formed by hydrogen abstraction from cumene (RH) by the triplet state anthraquinone ($Q^T$) [14] according to the reactions

$$Q + h\nu \longrightarrow Q^* \xrightarrow{\text{intersystem crossing}} Q^T \qquad (1)$$

and

$$Q^T + RH \longrightarrow QH^{\bullet} + R^{\bullet} \qquad (2)$$

The alkyl radicals formed in reaction (2) cannot be detected under the applied experimental conditions owing to their fast termination processes

$$2R^{\bullet} \longrightarrow \text{products} \qquad (3)$$

Interestingly, in tri-isopropylbenzene at —50 °C, where the very high viscosity effectively blocks translational diffusion while the rotational diffusion is still fast, the signal of tertiary alkyl radicals can be detected at $g = 2.0027$ with hyperfine couplings of $a_{6H} = 1.632$ mT and $a_{3H} = 0.5$ mT.

If oxygen is also present, a singlet signal appears at $g = 2.015$ during UV irradiation in the cumene–anthraquinone system. This signal can be assigned to $RO_2^{\bullet}$ peroxy radicals [15] formed by the oxidation of alkyl radicals:

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \qquad (4)$$

The peroxy radicals at —75 °C proved to be sufficiently persistent for the study of the kinetics of their formation and decay. In these kinetic ESR experiments, the magnetic field was fixed at a value [16] at which the $g = 2.015$ signal is at a maximum and the amplitude was measured during UV irradiation.

The observed kinetics of peroxy radical formation and decay depend critically on the flux of irradiation, which is changed by the slit of the

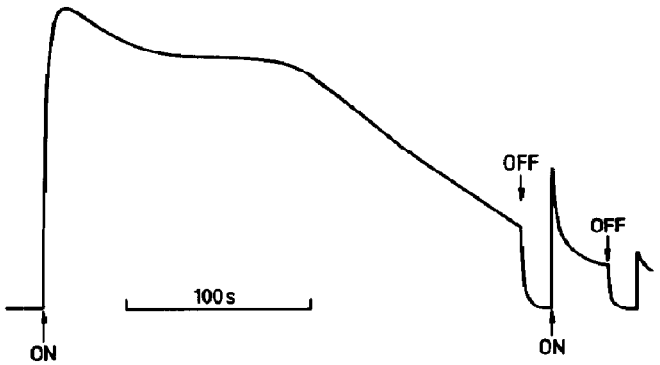


Fig. 1. Kinetic ESR spectra of the $g = 2.015$ peroxy free-radical signal in air-saturated cumene containing $8 \times 10^{-3}$ M anthraquinone recorded at —83 °C. The arrows indicate the switch-on and switch-off time of the irradiation.

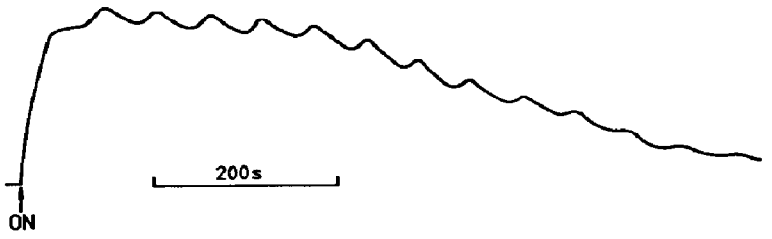


Fig. 2. Kinetic ESR spectra of the $g = 2.015$ peroxy free-radical signal in cumene containing about $10^{-5}$ M dissolved oxygen and $4 \times 10^{-3}$ M anthraquinone recorded at —75 °C. The arrow indicates the time when the irradiation was started.

irradiation window and the relative concentrations of anthraquinone and oxygen. For a high anthraquinone concentration, the fast build-up is followed by a fast decay without oscillation (see Fig. 1). There is a shoulder on the decay region, which is probably not caused by the variation in the peroxy radical concentration but by the line-narrowing effect of a smaller oxygen concentration, *i.e.* at a higher oxygen concentration the peroxy signal is somewhat broader, resulting in a smaller amplitude. This effect can be partially compensated by using a modulation amplitude higher than the line width. In the course of irradiation, the observed decay rate of the peroxy concentration was found to increase with the increase in anthraquinone concentration and with the decrease in temperature. Consequently, the decay of the peroxy concentration is caused by the depletion of oxygen in the irradiated zone, which cannot be balanced by diffusion from the dark zone. If the irradiation is switched off until the diffusion regenerates the oxygen concentration (see Fig. 1), a signal overshoot can be seen when irradiation is resumed. However, there is a remarkable difference between the diffusion rate of oxygen and that of anthraquinone. It can be seen visually that the discolouration caused by the photoproduct of anthraquinone [12] is limited to the area where the incident light reached the solvent.

In the experiments where the anthraquinone concentration is smaller or the slit of the irradiation window is thinner, the build-up period of peroxy radicals is followed by a slow decay modulated with equidistant oscillations (see Fig. 2). Then oxygen regeneration by diffusion from the dark zone into the irradiated zone can maintain a concentration at which the oxidation rate of alkyl radicals in reaction (4) is fast with respect to the termination processes of reaction (3). In this case the slow signal decay can be caused either by the consumption of the overall amount of oxygen in the sample or by the local depletion of anthraquinone in the irradiated zone.

## 4. Discussion

In the light of previous work, which provides ample evidence that all reported oscillational phenomena in the photochemical systems are related to hydrodynamic convections [7, 9, 10], great care should be taken before any system is claimed to be a true photochemical oscillator. It has been pointed out by previous authors [1 - 7] that the periodicity is poorly reproducible and quite often aperiodic variations in the emitted light intensity can be observed. The phenomena were also found to be highly sensitive to the stirring of the sample. In our experiments we obtained quite good reproducibility, and although the amplitude of oscillation differed from experiment to experiment, the periodicity and the regularity of the oscillation profile were stable. Also, by hitting or turning away the sample tube we did not observe any breakdown of oscillations. We studied the oscillatory behaviour in a rather narrow temperature range (between —75 and —85 °C) since the lifetime of the peroxy radical was long enough only at low temperatures [16].

The time of periodicity varied between 40 and 60 s, and was found to decrease slightly with increasing temperature and with the reduction in the illuminated area. The above-mentioned characteristics seem to indicate a non-convectional origin of the oscillation in the cumene–anthraquinone system. The role of convection, however, cannot be excluded with certainty in our experiments, since in the heat-isolated Dewar vessel of the temperature control unit the incident light may cause a slight local warming-up and the special geometry of the sample tube and the high solvent viscosity at low temperature might stabilize the convectional oscillations.

Below, we outline a qualitative model in order to show that, at least in principle, the photochemical processes and the diffusion due to concentration gradients within the sample can produce an oscillatory variation in the peroxy concentration. Any mechanistic scheme describing oscillation should include a feedback mechanism. In our system this can be the anthraquinone regeneration in the presence of oxygen:

$$QH^{\bullet} + O_2 \longrightarrow Q + HO_2^{\bullet} \qquad (5)$$

The regeneration is complete if the oxygen concentration is large [14]. If the oxygen concentration is less than a critical value, the concurrent reactions

$$2QH^{\bullet} \longrightarrow Q + QH_2 \qquad (6)$$

and

$$QH^{\bullet} + RH \longrightarrow R^{\bullet} + QH_2 \qquad (7)$$

can prevent the complete regeneration of anthraquinone, since the reaction of dihydroxyanthracene ($QH_2$) is also controlled by the oxygen concentration:

$$QH_2 + O_2 \longrightarrow QH^{\bullet} + HO_2^{\bullet} \qquad (8)$$

The different lifetimes and diffusion rates of radicals $R^{\bullet}$, $RO_2^{\bullet}$, $HO_2^{\bullet}$ and $QH^{\bullet}$ are the source of concentration gradients between the irradiated and the dark zones. In the experiments where the rates of oxygen consumption and diffusion are comparable, the fast reactions (4) and (5) consuming oxygen take place mainly in the irradiated region of the solvent and thus no alkyl and semiquinone radicals can diffuse out of the irradiated zone. However, the self-termination processes of peroxy radicals [16, 17] are rather slow:

$$2RO_2^{\bullet} \longrightarrow O_2 + \text{products} \qquad (9)$$

and

$$2HO_2^{\bullet} \longrightarrow O_2 + H_2O_2 \qquad (10)$$

This means that a large portion of the peroxy radicals can diffuse into the dark region of much larger volume and regenerate the oxygen there.

Since reactions (9) and (10) can restore only half of the oxygen consumed by reactions (4) and (5), the irradiation will continually decrease the overall amount of oxygen in the sample, but the oxygen consumption

is limited to the irradiated zone. In Fig. 3 the local concentration of oxygen and anthraquinone is shown in the irradiated zone. Point A shows the time when the oxygen concentration decreases below the critical value in the irradiated zone. The concomitant conversion of anthraquinone into $QH_2$ by reactions (4), (5) and (6) will impair the efficiency of alkyl radical generation by reactions (1) and (2), and thus the rate of peroxy radical generation will also be reduced. While the anthraquinone concentration is decreasing in the irradiated zone, it is regenerated in the dark region, where $QH_2$ can diffuse to and produce Q by reaction (8), since the oxygen concentration there is large. However, because of the slow diffusion of anthraquinone, this process can contribute only slightly to the concentration gradient between the irradiated and the dark zones. This stage of the process (AB and A′B′ in Fig. 3) can be characterized as a period of increasing concentration gradients.

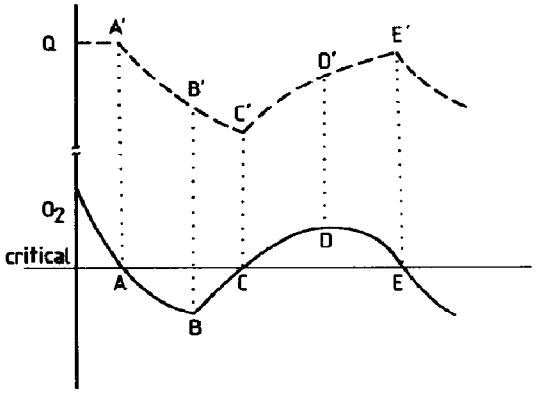


Fig. 3. Schematic representation of oscillating oxygen (——) and anthraquinone (— — —) concentration as a function of time in the irradiated zone of the sample.

This stage will be terminated because (i) increasing concentration gradients accelerate diffusion, (ii) a decreasing anthraquinone concentration in the irradiated zone reduces gradually the rate of oxygen consumption there and the rate of oxygen regeneration in the dark region. To a smaller extent, the same holds for the variation in anthraquinone concentration.

The reason why this stage does not end in a stationary state is that the balance between opposite diffusional processes is achieved sooner for the oxygen than for the anthraquinone, and hence their rates of diffusion are markedly different. This means that when the oxygen concentration reaches its minimum (point B), the anthraquinone concentration continues to decrease further (interval B′C′) and will result in slower oxygen consumption in the irradiated zone than the diffusional transport due to the concentration gradient, *i.e.* the local oxygen concentration will temporarily increase (BC). When the increasing oxygen concentration reaches the critical value (point C), the anthraquinone regeneration by reaction (5) becomes fast again and the second stage of oscillation, where the peroxy radical concentration is increasing, will start (point C′). This is the stage of oscillation where the

concentration gradients are decreasing. As the increase in anthraquinone concentration enhances the oxygen consumption, its increase stops at the time D. The increase in anthraquinone concentration and oxygen consumption, however, still goes on, and leads to the decrease in oxygen concentration until it reaches the critical value again at point E. Then the first stage of oscillation, where the peroxy concentration is decreasing, starts again.

In the above model an irradiated and a dark zone are distinguished but their borderline is not fixed since the transparency of the solvents is affected by the change in anthraquinone concentration. This effect should also be considered in a more quantitative approach.

## 5. Conclusions

In this paper we have demonstrated the oscillation of the peroxy radical concentration in the cumene–anthraquinone system in the presence of oxygen, where alkyl radicals were generated photochemically. As far as we know, it is the first case where a periodic variation in the peroxy radical concentration has been detected experimentally and also the first example of a photochemical system where oscillation has been discovered by ESR spectroscopy. The origin of the reported oscillation, however, is not yet clarified with certainty: it may be either a consequence of hydrodynamic convection or a photochemically driven oscillation combined with diffusion which is controlled by the periodic variation in the concentration gradient. As a working hypothesis, a qualitative photochemical model was suggested, which can account for the observed oscillatory behaviour. Additional work is necessary in order to prove whether the oscillations which we discovered can be considered as an example of a true photochemical oscillator.

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