

INFLUENCE OF MAGNETIC FIELD ON THE RATE OF PHOTOOXIDATION OF AROMATIC HYDROCARBONS

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The influence of weak magnetic fields on the rate of interaction of paramagnetic particles or excitons was first revealed by the change of the photoconductivity [1] and fluorescence intensity [2 - 4] of anthracene and tetracene to which a constant magnetic field was applied. This phenomenon is connected with the change of the probability of a transition with spin conservation of a system of two interacting particles (e.g., an electron and a hole [5], two triplet excitons [6], a triplet exciton and a hole [7]) in the final state. The transition probabilities are determined by the mixing of the eigenfunctions of the pair of interacting paramagnetic particles, which depends on the magnetic field.

We have observed for the first time the influence of a magnetic field on the rate of the interaction of oxygen with an excited aromatic hydrocarbon (tetracene), i.e., the influence of a magnetic field on the rate of a photochemical reaction.

The investigation was carried out on tetracene layers deposited on quartz substrates by vacuum sublimation. We measured in vacuum the surface conductivity excited in the layer by the light in the singlet-singlet absorption band of the tetracene. When oxygen was admitted into the chamber with the sample, the photoconductivity increased. Admission of other gases (nitrogen, helium, argon) caused no change of the photocurrent. An increase of the photoconductivity in the presence of oxygen on the surface was observed earlier [8 - 11]. It is usually attributed to the appearance of oxidation products resulting from the interaction between the oxygen and the excited molecules of the aromatic hydrocarbon and serving as exciton dissociation centers. Under such conditions the increment of the photocurrent i accompanying the interaction of the oxygen with the optically excited sample is a measure of the amount of the products of this interaction. Figure 1 shows the dependence of the photocurrent on the time in the presence of oxygen. Shutting off the light during the process of slow increase of the photoconductivity caused a rapid ($\tau \approx 1$ sec) decrease and increase of the current (Section BC on the curve of Fig. 1). This shows that the photocurrent is a practically inertialess measure of the amount of tetracene oxidation products.

Figure 2a shows the variation of the photocurrent following application of a field $H = 2000$ Oe on the sample in vacuum; Fig. 2b shows the result of the application of the same field on a sample in oxygen

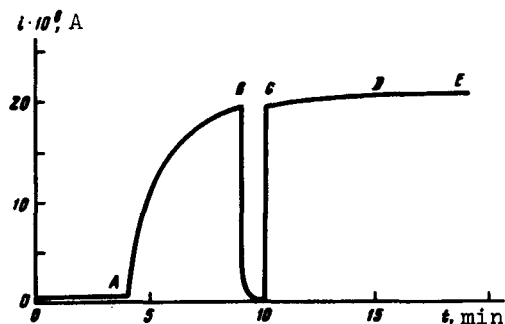


Fig. 1. Dependence of the photocurrent in tetracene on the time. Oxygen is admitted at the point A, pressure 160 mm Hg, light intensity 10^{13} quanta/cm²sec, $T = 22^\circ C$, sample thickness $\sim 1 \mu$, distance between electrodes 2 mm, electrode length 25 mm each, sample voltage 100 V. In section BC the light is turned off.

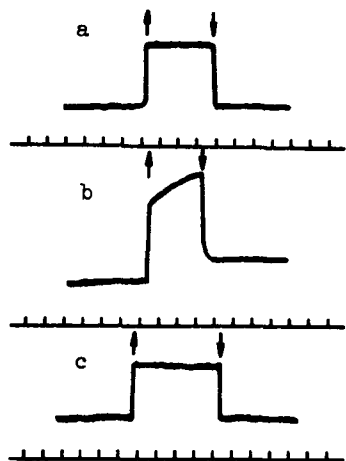


Fig. 2

Fig. 2. Time variation of photocurrent when the magnetic field is turned on. The arrows \uparrow and \downarrow show the instants of turning the magnetic field on and off: a - magnetic field $H = 2000$ Oe, sample in vacuum; b - $H = 2000$ Oe, sample in oxygen (160 mm Hg); c - $H = 400$ Oe, sample in oxygen. One abscissa division equals 1 min. The maximum change of the photocurrent is $\Delta i/i \approx 3\%$.

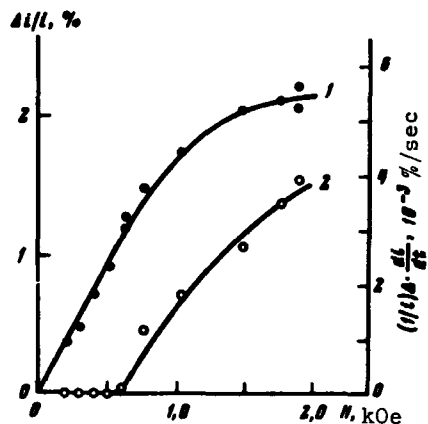


Fig. 3

Fig. 3. Dependence of the relative change of the photocurrent ($\Delta i/i$, curve 1) and of the rate of photooxidation of tetracene ($i^{-1}\Delta(di/dt)$, curve 2), on the magnetic field.

in which the photocurrent increases with time (section DE, Fig. 1); Fig. 2c shows the action exerted on a sample situated under the same conditions in oxygen and at a magnetic field $H = 400$ Oe. We see that in all cases the photocurrent variation due to the magnetic field includes a rapidly growing component, which was observed earlier [1] and discussed in [5, 12]. In addition, however, it follows from the data of Fig. 2b that in oxygen the magnetic field causes an increase in the growth rate of the photocurrent. The two effects, namely the rapid change of the photocurrent Δi and the increment in the growth rate of the photocurrent $\Delta(di/dt)$, produced by the magnetic field, have different dependences on the intensity of this field, as shown in Fig. 3. In fields $H < 400$ Oe the influence of the magnetic field on the rate of increase of the photocurrent is practically nil (Fig. 2c). The unique form of the dependence of $\Delta(di/dt)$ on H leads to the conclusion that the observed action of the magnetic field on the rate of the photooxidation is not a consequence of the known variation of the concentration of the singlet and triplet excitons: for the latter effect, which is connected with the splitting of the singlet exciton into two triplet excitons, the field dependence reverses sign at $H = 500$ Oe [13]. The quantity $i_{lim}^{-1}\Delta(di/dt)$ depends on the time after the start of the photooxidation, decreasing to a value $\sim 10^{-3}$ %/sec by the time the photocurrent assumes the stationary value $i = i_{lim}$.

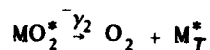
The observed influence of the magnetic field on the rate of accumulation of exciton dissociation centers in the presence of oxygen demonstrates that paramagnetic particles, namely the oxygen molecule and apparently the tetracene molecule in the triplet state M_T^* , take part in their formation. If the product of the interaction of these particles is in the singlet state and the reaction rate is determined by the conservation of the spin, then we can write, following Merrifield [6], for the rate constant of the process



and expressions of the type

$$\gamma_1 = \frac{1}{9} k_1 \sum_i \frac{k_s |S_i|^2}{k_{-1} + k_s |S_i|^2},$$

where $|S_i|^2$ is the amplitude of the singlet component of the spin function of the pair $\text{O}_2 + \text{M}_T^*$ in the i -th state, k_s is the frequency of the transition to the singlet product at $|S_i|^2 = 1$, k_{-1} is the frequency of the "back scattering" in the interacting particles, and k_1 is the rate constant of the collision of O_2 with M_T^* . A magnetic field that is weak in comparison with the zero field of the molecule O_2 causes the appearance of a singlet component in a larger number of spin states than in the absence of an external field, and consequently increases the γ_1 . The maximum increase of γ_1 , needed to explain the observed effects, reaches 20 - 40%. It is possible that the singlet product formed directly upon interaction of M_T^* with O_2 is singlet oxygen and the tetra-cene molecule in the ground state, the reaction between which yields MO_2^* . The photochemical reaction (1) is partly reversible. This possibly explains the weakening of the influence of the magnetic field on the rate of accumulation of MO_2 with increasing time, since the rate of constant of the inverse decay reaction



depends on the magnetic field in the same manner as γ_1 .

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EXPERIMENTAL VERIFICATION OF SCALE LAW IN THE CRITICAL REGION OF CYCLOPENTANE

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According to the hypothesis that the thermodynamic functions are homogeneous [1], the scale equation of state near the liquid-vapor critical point is given by [2]