Magnetic field effect on the dye formation in photoreduction of benzophenone by diphenylamine in micellar solutions

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The formation of 4-phenylaminophenyldiphenylcarbinol and related triarylmethane dye was observed upon the recombination of ketyl and diphenylamine radicals in surfactant micelles. The negative magnetic effect of the reaction studied reaches 1.8 and is caused by an increase in the escape of the radicals from the cage due to increasing lifetime of triplet radical pairs.

Key words: benzophenone, diphenylamine, triarylmethane dyes; photolysis; magnetic field; micelles.

The study of magnetic field effects on chemical processes is urgent for both the study of the reaction mechanisms[1,2] and the measurement of magnetic fields and magnetooptical registration of information. In this work, the magnetic field effect on the dye formation in the photolysis of micellar solutions of benzophenone was established, and the nature of this effect was considered.

Experimental

Benzophenone, diphenylamine, and sodium dodecyl sulfate (pure grade) were purified by twice recrystallization from ethanol. Commercial samples of agarose (Sigma), hydrochloric acid (analytically pure grade), and distilled water were used without additional purification. The preparation of layers of agarose gel and removal of air from them were carried out by the procedure described previously[3]; the thickness of the layers was ~2 mm. A solution or gel was irradiated with light at λ = 365 nm or λ > 280 nm and intensity from $5.8 \cdot 10^{15}$ to $1.8 \cdot 10^{17}$ quantum cm^{-2} s^{-1} isolated from the overall radiation of DRSh-1000 or DRK-120 lamps by glass light filters (UFS6 and SS1 or BS4) in the field of a constant magnet with magnetic induction (B) of 0.18±0.02 T or in the absence of the magnetic field (in the magnetic field of the Earth with B = 0.5 mT). The magnetic induction between the poles of the constant magnet was measured on a Sh1-8 instrument. Spectra of samples in the UV and visible regions were recorded on a Specord UV-VIS spectrophotometer.

Results and Discussion

Irradiation of micellar solutions of benzophenone in the presence of diphenylamine and small amounts of an acid (pH ≈ 3) resulted in the formation of the colored product with an absorption maximum at 502 nm. No coloring of the solution was observed upon the photolysis in the absence of the acid, but the same product as in the photolysis in the presence of HCl was detected when the acid was added to the preliminarily irradiated solution (Fig. 1).

The magnetic field decreases the rate of accumulation of the colored product (Fig. 2) and its precursor. The value of the effect measured by the ratio of the reaction rates in the absence and presence of the field is 1.8±0.1.

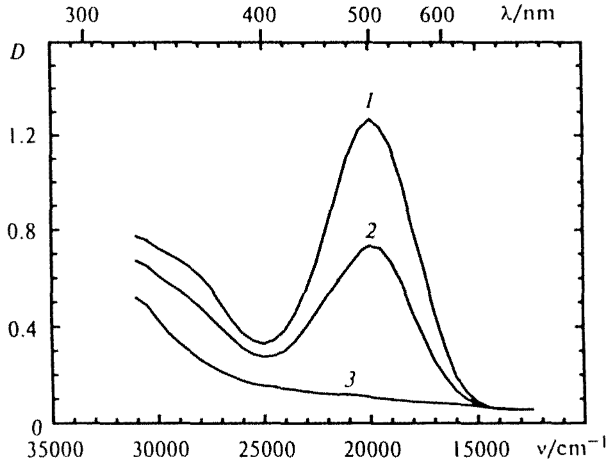

Fig. 1. Absorption spectra of the product formed after treatment with 0.1 *N* HCl of a sample of 1 % agarose gel containing benzophenone (0.01 *M*), diphenylamine (0.01 *M*), and sodium dodecyl sulfate (0.1 *M*) irradiated with light at λ > 280 nm from a DRK-120 lamp for 5 min in the absence of magnetic field (*1*) and in the applied magnetic field with B = 0.18 T (*2*) and a sample irradiated in the absence of magnetic field before treatment with HCl (*3*).

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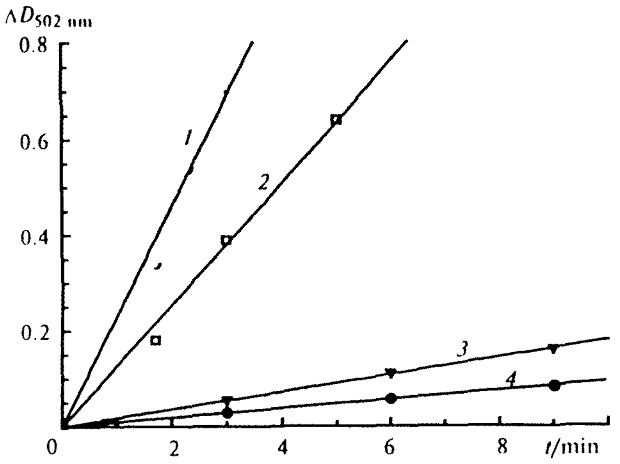
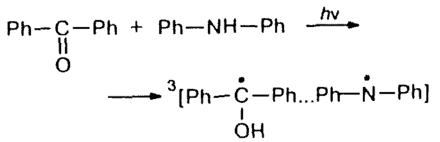
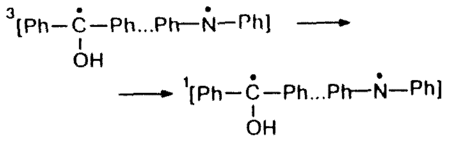


Fig. 2. Dependence of a change in the optical density in the range of the absorption maximum of the colored product on time of irradiation of layers of 1 % agarose gel containing benzophenone (0.01 *M*), diphenylamine (0.01 *M*), and sodium dodecyl sulfate (0.1 *M*) with light at $\lambda > 280$ nm from a DRK-120 high-pressure mercury lamp in the absence of HCl and subsequent treatment with 0.1 *N* HCl (*1,2*) and in the presence of the acid (2.4 m*M*) (*3,4*) in the applied external magnetic field with $B = 0.18$ T (*2,4*) and in the absence of magnetic field (*1,3*).

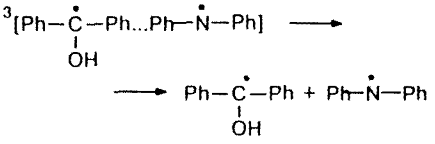
It follows from the comparison of kinetic curves *1* and *3* as well as curves *2* and *4* in Fig. 2 that the rate of accumulation of the colored product decreases considerably in the presence of HCl. Air oxygen also considerably decreases the rate of accumulation of the colored product, and the irradiation in air in the presence of the acid results in a change in its color to gray-violet related to the formation of dyes of different structures. Based on the analysis of the absorption spectra, the dependence of coloring on pH of the solution, and the available literature data on the chemistry of aminyl radicals and reactions of radical pairs, the colored product can be classified with the triarylmethane series, and its precursor can be assigned to the corresponding triarylcarbinol formed due to the geminate recombination of radical pairs in the surfactant micelles according to the scheme:



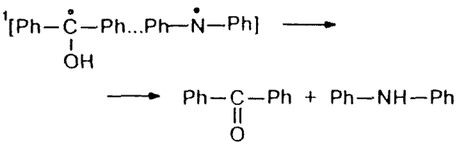
$$\mathrm{Ph}-\underset{\mathrm{O}}{\overset{}{\underset{\|}{\mathrm{C}}}}-\mathrm{Ph} + \mathrm{Ph}-\mathrm{NH}-\mathrm{Ph} \xrightarrow{h\nu} {}^3[\mathrm{Ph}-\underset{\mathrm{OH}}{\dot{\mathrm{C}}}-\mathrm{Ph}\ldots\mathrm{Ph}-\dot{\mathrm{N}}-\mathrm{Ph}] \qquad (1)$$



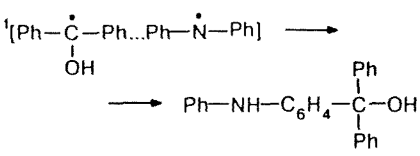
$$ {}^3[\mathrm{Ph}-\underset{\mathrm{OH}}{\dot{\mathrm{C}}}-\mathrm{Ph}\ldots\mathrm{Ph}-\dot{\mathrm{N}}-\mathrm{Ph}] \longrightarrow {}^1[\mathrm{Ph}-\underset{\mathrm{OH}}{\dot{\mathrm{C}}}-\mathrm{Ph}\ldots\mathrm{Ph}-\dot{\mathrm{N}}-\mathrm{Ph}] \qquad (2)$$



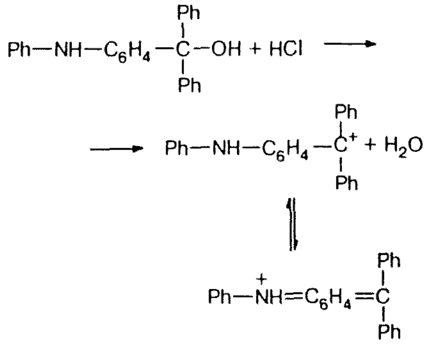
$$ {}^3[\mathrm{Ph}-\underset{\mathrm{OH}}{\dot{\mathrm{C}}}-\mathrm{Ph}\ldots\mathrm{Ph}-\dot{\mathrm{N}}-\mathrm{Ph}] \longrightarrow \mathrm{Ph}-\underset{\mathrm{OH}}{\dot{\mathrm{C}}}-\mathrm{Ph} + \mathrm{Ph}-\dot{\mathrm{N}}-\mathrm{Ph} \qquad (3)$$



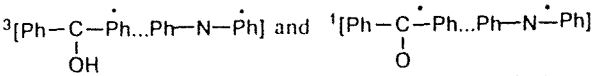
$$ {}^1[\mathrm{Ph}-\underset{\mathrm{OH}}{\dot{\mathrm{C}}}-\mathrm{Ph}\ldots\mathrm{Ph}-\dot{\mathrm{N}}-\mathrm{Ph}] \longrightarrow \mathrm{Ph}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{Ph} + \mathrm{Ph}-\mathrm{NH}-\mathrm{Ph} \qquad (4)$$



$$ {}^1[\mathrm{Ph}-\underset{\mathrm{OH}}{\dot{\mathrm{C}}}-\mathrm{Ph}\ldots\mathrm{Ph}-\dot{\mathrm{N}}-\mathrm{Ph}] \longrightarrow \mathrm{Ph}-\mathrm{NH}-\mathrm{C_6H_4}-\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{C}}}-\mathrm{OH} \qquad (5)$$



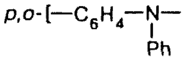
$$\mathrm{Ph}-\mathrm{NH}-\mathrm{C_6H_4}-\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{C}}}-\mathrm{OH} + \mathrm{HCl} \longrightarrow \mathrm{Ph}-\mathrm{NH}-\mathrm{C_6H_4}-\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{C}^+}} + \mathrm{H_2O} \rightleftharpoons \mathrm{Ph}-\overset{+}{\mathrm{N}}\mathrm{H}{=}\mathrm{C_6H_4}{=}\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{C}}} \qquad (6)$$



$$ {}^3[\mathrm{Ph}-\underset{\mathrm{OH}}{\dot{\mathrm{C}}}-\mathrm{Ph}\ldots\mathrm{Ph}-\dot{\mathrm{N}}-\mathrm{Ph}] \text{ and } {}^1[\mathrm{Ph}-\underset{\mathrm{O}}{\dot{\mathrm{C}}}-\mathrm{Ph}\ldots\mathrm{Ph}-\dot{\mathrm{N}}-\mathrm{Ph}]$$

are radical pairs in triplet and singlet states, respectively.

The following facts favor this scheme: the absorption spectrum of the colored product ($\lambda_{\max} = 502$ nm) is similar to that of 4-*N,N*-dimethylaminophenyldiphenylcarbonium ion ($\lambda_{\max} = 480$ nm in dichloroethane, the hypsochromic shift in a low-polar solvent[4]). The p*K* value of the dye is 3.6, *i.e.*, it occupies an intermediate position in the series of triarylcarbonium ions and is close to p*K* = 3.88 for the closest analog, 4-*N,N*-dimethylaminophenyldiphenylcarbonium ion.[5] Recombination reactions involving nonsubstituted aminyl radicals occur predominantly at *p*- and *o*-positions; in particular, the main products of the photochemical or thermal transformation of tetraphenylhydrazine in inert solvents are *p*- and *o*-semidines[6] of the general formula



$$p,o\text{-}[-\mathrm{C_6H_4}-\underset{\mathrm{Ph}}{\mathrm{N}}-]_n$$

The external magnetic field decreases considerably the decay rate of triplet radical pairs formed in the reaction of benzophenone with diphenylamine in the sodium dodecyl sulfate micelles.[7] The colored product was not formed when diphenylamine was substituted for 4,4′-di-*tert*-butyldiphenylamine, because the reaction at the *p*-position becomes impossible. A decrease in pH resulted in a decrease in the yield of the dye (or its precursor) due to the protonation of the aminyl radicals and the formation of the $Ph_2NH^{\cdot +}$ radical cations. Thus, coloring in the system studied is caused by the formation of the triarylmethane dye from the corresponding triarylcarbinol, which, in turn, is the product of the recombination of the radical pairs formed due to the elimination of the H atom from the amine by benzophenone. The substantial difference of the quantum yield of triarylcarbinol from unity (the quantum yield is equal to 0.5 even in the absence of HCl) is likely related to the high probability of disproportionation of the radical pair resulting in the regeneration of the initial substances (reaction (4)). The magnetic effect in this reaction is caused by a decrease in the decay rate of the triplet radical pairs in the magnetic field, and its value corresponds to a decrease in the probability of the recombination of the radical pair in a micelle. The decrease in the yield of triarylcarbinol (and, hence, dye) in the magnetic field occurs due to an enhancement of the relative role of decay of the radical pairs by diffusional escape of the radicals from the cage (process (3)). The system studied is of interest as a demonstration of the effect of weak magnetic fields on chemical reactions, because the result of this effect is observed directly. The system holds some promise for the development of methods for the optical registration of magnetic fields.

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