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![Fig. 1. E.p.r. spectra](image)

1963

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Abstract

Full Text

PHYSICAL CHEMISTRY

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STUDY BY THE E.P.R. METHOD OF THE SENSITIZATION OF THE PHOTOREACTION OF ALCOHOL DEHYDRATION AT 77°K

Ingram and co-workers ([1–3]) showed by the e.p.r. method that, during the photolysis of dissolved H_2O_2 (at 77°K), the OH radicals that arise react with molecules of the solvent (alcohols), forming secondary radicals: $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, $(CH_3)_2\dot{C}OH$, etc. This indicates the presence of a dehydration reaction of alcohols by a strong oxidizing agent—the OH radical. Recently a report appeared ([4]) on an e.p.r. study of the photolysis of methanol proceeding at 77°K under prolonged irradiation with u.v. light ($\lambda = 254$ m), with formation of the radicals $\dot{C}H_2OH$, $\dot{C}H_3$, and $\dot{C}HO$. In studying by the e.p.r. method the photoreaction of electron detachment from aromatic amines ([5]) in an alcohol-ether mixed (2 : 1) solvent at 77°K, which proceeds only under the action of $\lambda\lambda < 313$ m *, we unexpectedly discovered the abundant appearance of alcohol radicals under the action of longer-wavelength u.v. radiation ($\lambda\lambda \geq 334$ m). Subsequently a detailed investigation of this phenomenon was carried out on solutions of aniline, diphenylamine, triphenylamine, carbazole, fluorene, and naphthalene in methanol, ethanol, isopropanol, *n*-butanol, and isobutanol at 77 and 90°K. Concentrations of $10^{-3} \div 10^{-1}$ mole/liter were used. The alcohols were subjected to preliminary distillation in air. The measurements were carried out on an RE1301 apparatus. Samples of the solutions were placed in thin-walled quartz ampoules 4 mm in diameter and 10 mm long, fitted with a tap for evacuation to 10^{-4} mm Hg. Illumination of the samples was performed both in the resonator itself and outside it, with a high-pressure mercury lamp SVDSh-250, whose light was focused by a quartz condenser (diameter 50 mm, focal length 50 mm) onto the lower part of the ampoule containing the solution. The ampoule was at the same time immersed in liquid nitrogen or in liquid oxygen poured into a special Dewar vessel. In separate experiments a (1 : 2) light-power monochromator with a diffraction grating was used for illumination. Removal of dissolved oxygen from the solutions was carried out by repeated thawing and freezing of the solutions under evacuation.

Fig. 1. E.p.r. spectra illuminated with the total light of SVDSh-250: 1—methanol, 2—ethanol, and 3—isopropanol at 77°K (A—lines of alcohol radicals; B—lines of the radical $\dot{C}H_3$; C—lines of the radical $H\dot{C}O$). The lower curves show the change in the spectra upon standing of the evacuated samples in the dark at 90°K.

As a result of one hour of irradiation of pure solvents at 77°K with the total light of SVDSh-250, insignificant concentrations of free radicals appeared, with an e.p.r. spectrum characteristic of each solvent (Fig. 1). The structure of the spectra shows the presence of radi-

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* The next article is devoted to the results of this investigation, carried out in 1960.

radicals $\dot{C}H_3$, $\dot{C}H_2OH$, and $C\dot{H}O$ in methanol, $\dot{C}H_3$, $CH_3\dot{C}HOH$ in ethanol, and $(CH_3)_2\dot{C}OH$ in isopropanol. [2] Irradiation of the solvents at 77°K for 5 min does not lead to the appearance of detectable E.P.R. signals. Free radicals also do not arise upon prolonged (1-1.5 h) illumination of the solvents through the combined light filters UFS-4 and BS-6, which transmit the region from 330 to 380 mμ (attenuation of the light flux by 90% at the boundaries of the transmission region). It should be noted that in the region $\lambda \leq 248$ mμ lie the long-wavelength declines of the absorption bands of the solvents investigated. Apparently, under illumination with the full light of the lamp, the energy of the absorbed UV quantum with $\lambda \leq 248$ mμ is sufficient for photolysis of the alcohol molecules to occur, with the appearance of active free radicals capable of producing secondary free alcohol radicals at 77°K. [4]

In sharp contrast to the behavior of pure solvents, irradiation of alcoholic solutions of aromatic amines—aniline, diphenylamine, triphenylamine—as well as carbazole, by the same source through the combined light filters UFS-4 and BS-6 leads to the appearance, within a few seconds after the start of illumination, of appreciable concentrations ($\sim 10^{-4}$-10^{-3} mole/liter) of alcohol radicals. From the E.P.R. spectra obtained (Fig. 2) it is seen that the alcohol radicals arose as a result of the detachment of an H atom in the α-position from the alcohol molecule. Consequently, under these conditions a reaction of photodehydrogenation of alcohols by the amines dissolved in them, and also by carbazole, takes place. Irradiation of solutions of triphenylamine and carbazole in alcohols at 77°K with the 334 mμ line of an SVDSh-250 lamp through a monochromator with a diffraction grating led to the appearance of the corresponding alcohol radicals. The same phenomenon was observed both in a degassed solution and with dissolved air. The radicals are not stable, since their spectra change in the dark when the temperature of the solution is raised above 77°K. In the case where the solutions had first been thoroughly degassed by 10-fold freezing and thawing under vacuum conditions (10^{-4} mm Hg), raising the temperature of the solution above 77°K leads to the disappearance of the alcohol radicals without the appearance of detectable concentrations of other free radicals. If,

Fig. 2. E.P.R. spectra

Figure 2: Fig. 2. E.P.R. spectra

however, the temperature of nondegassed solutions previously illuminated at 77°K is raised, then already at 90°K disappearance of the alcohol radicals and the appearance of peroxide radicals are observed (Fig. 2), which disappear upon further raising the temperature of the solution.

Fig. 2. E.P.R. spectra of alcoholic solutions irradiated with filtered light ($\lambda\lambda$ = 330-380 mμ) of an SVDSh-250 lamp at 77°K: **1** —triphenylamine in methanol ($5 \cdot 10^{-3}$ mole/liter); **2** —carbazole in ethanol (10^{-2} mole/liter); **3** — diphenylamine in isopropanol (10^{-2} mole/liter); **4** —aniline in *n*-butanol (10^{-2} mole/liter); **5** —change in the spectrum of the ethanol radical upon thawing of a previously irradiated, nondegassed solution of carbazole in ethanol (10^{-2} mole/liter) from 77 to 90°K (see [2]).

Obviously, in the present case there is a reaction of interaction of the alcohol radicals with dissolved oxygen, with formation of peroxide radicals according to the scheme

$$\dot{C}H_2OH + O_2 \rightarrow \begin{array}{c} CH_2OH \\ | \\ O \\ | \\ O\cdot \end{array}, \qquad CH_3\dot{C}HOH + O_2 \rightarrow \begin{array}{c} H_3CHOH \\ | \\ O \\ | \\ O\cdot \end{array}$$

The long-wavelength edges of the first absorption bands of the compounds studied lie in the transmission region of the light filters used (see Table 1).

It may be assumed that the photodehydrogenation reaction of alcohols by these compounds is associated with excitation of the singlet level of the amine or carbazole molecule, which, as is known, has an anomalous lifetime and subsequently undergoes transition to the phosphorescent triplet state.

Table 1

Position of the long-wavelength edge (λ, mμ) of absorption ($\log \varepsilon = 1 \div 3$) of the compounds studied

Substance	λ_{edge}	λ_{max}	Solvent	Source
Aniline	320 ($\log \varepsilon = 1$)	293	Ethanol (−70°C)	[10]
Diphenylamine	320 ($\log \varepsilon = 3$)	290	Ethanol (−70°C)	[10]
Triphenylamine	360 ($\log \varepsilon = 3$)	300	Ethanol (20°C)	[12]

Substance	λ_{edge}	λ_{max}	Solvent	Source
Carbazole	250 ($\log \varepsilon = 2$)	280	Hexane (20°C)	([13])
Fluorene	220 ($\log \varepsilon = 2$)	260	Hexane (20°C)	([13])
Naphthalene	315 ($\log \varepsilon = 1$)	270	Mixture of ethanol + methanol (90°K)	([14])

All the solutions studied exhibited intense phosphorescence upon irradiation at 77°K. The excited singlet state may possess dehydrogenating ability, for example in quinones ([6]). However, for aromatic amines, which tend rather toward oxidation with loss of an electron or an H atom ([5]), dehydrogenating ability with respect to alcohols is unusual. In order to determine the participation in the dehydrogenation reaction of the phosphorescent state of the dissolved compounds, the following experiments were carried out on selective deactivation of the triplet state. As was shown by Ermolaev and one of the authors ([7]), the triplet state of molecules is effectively deactivated by radiationless transfer of its energy to molecules with a suitable height of the triplet level. For such transfer to occur it is necessary ([8]) that the triplet level of the energy-acceptor molecule be lower than the triplet level of the donor molecule. Energy transfer through triplet levels is more conveniently observed in the case when the excited fluorescent level of the donor lies below the fluorescent level of the acceptor. This makes it possible to excite the donor without directly exciting the acceptor. The following pairs ([9]) satisfy these requirements, for example; in them the first member is the donor: triphenylamine ($24.50 \cdot 10^3$ cm^{-1})—naphthalene ($21.25 \cdot 10^3$ cm^{-1}), carbazole ($24.48 \cdot 10^3$ cm^{-1})—naphthalene ($21.25 \cdot 10^3$ cm^{-1}). The height of the triplet level, expressed in cm^{-1}, is given in parentheses. A comparison was made of the intensities of the signals of alcoholic radicals obtained during 4 min irradiation of alcoholic solutions of triphenylamine and carbazole with naphthalene and without it.

Table 2

Effect of selective deactivation of the triplet state on the "yield" of alcoholic radicals*

Solution	Without naphthalene, mol/l	With naphthalene, mol/l
Triphenylamine in methanol	$1.8 \cdot 10^{-3}$	$2 \cdot 10^{-4}$
Carbazole in ethanol	$5 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$

* The concentration of free radicals was estimated by comparison with a standard DPPH solution using the graphical method of double integration of the EPR spectra.

The following solutions were investigated: triphenylamine ($5 \cdot 10^{-3}$ mol/l) in methanol, carbazole (10^{-2} mol/l) in ethanol. The naphthalene solution added to the solution created in it a concentration of $2 \cdot 10^{-1}$ mol/l. Control experiments on irradiation of naphthalene solutions ($2 \cdot 10^{-1}$ mol/l) in methanol and ethanol at 77°K with the light of an SVDSh-250 lamp through combined UFS-4 and BS-6 light filters showed that under these conditions naphthalene is not directly excited. In contrast to a solution of naphthalene alone, the presence of triphenylamine or carbazole in the solution caused, under this illumination, a very intense

green phosphorescence of naphthalene, in agreement with experiments on sensitized phosphorescence (7-9). Illumination through a UFS-3 light filter of a solution of naphthalene alone at 77°K showed that alcohol radicals, in amounts sufficient for detection, do not arise under these conditions*, despite the presence of intense green phosphorescence. Meanwhile, illumination with filtered light (through combined UFS-4 and BS-6 filters) of solutions in which, in addition to naphthalene, triphenylamine or carbazole was present led, for the same exposure time (4 min), to the appearance of intense EPR signals of alcohol radicals, but, in terms of quantity, approximately 5 times smaller than in the case of solutions of triphenylamine or carbazole alone (Fig. 3).

This result (Table 2), proving the selective inhibiting effect of the naphthalene additive**, is evidence in favor of the fact that dehydrogenation of alcohols is carried out by molecules of aromatic amines and carbazole in the triplet state. The efficiency of the reaction apparently increases because amines form associates with alcohols (10). Confirmation of this conclusion is provided by an experiment with irradiation of alcoholic solutions of the hydrocarbon analogue of carbazole—fluorene—at 77°K, in which no alcohol radicals were detected. Indeed, in contrast to compounds containing in their structure a nitrogen atom with unshared electrons, included in the groups $-NH_2$, $=NH$, and $-N<$, which make possible the formation of a hydrogen bond with the hydroxyl of the alcohol, fluorene possesses an acidic H in the $C-H$ bond. Recently a paper by Smaller (11) appeared, in which an EPR study is reported of the photoreaction of indole in the triplet state with methanol upon uptake of energy from the triplet state of benzophenone in a methanolic solution at 77°K. Further parallel measurements of the quenching of amine luminescence and inhibition of the alcohol dehydrogenation reaction by them should clarify the relative role of the singlet and triplet states in this reaction.

Fig. 3. Effect of quenching of the triplet state of triphenylamine (1) and carbazole (2) by naphthalene on the "yield" of alcohol radicals upon illumination with filtered light ($\lambda\lambda = 330 \div 380\,\mathrm{m}\mu$) for 4 min of alcoholic solutions of these compounds at 77°K.

The authors express their gratitude to V. L. Ermolaev for valuable advice and assistance in the work.

Received
11 XII 1962

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* Upon prolonged illumination of alcoholic solutions of naphthalene at 77°K, insignificant concentrations of alcohol radicals appear, approximately 100 times smaller than in the case of amine solutions.

** Benzene added to the solution does not decrease the "yield" of alcohol radicals.

Note: Figure translations are in progress. See original paper for figures.

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