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Abstract

Full Text

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ON THE MECHANISM OF RADICAL FORMATION DURING PHOTOIRRADIATION OF TRIPHENYLAMINE ETHANOL SOLUTIONS FROZEN AT 77°K

(Presented by Academician A. N. Terenin, 23 IX 1963)

During photoirradiation of frozen methanol and ethanol solutions of luminophores (indole, carbazole, diphenylamine, triphenylamine, etc.), intensive formation of alcohol radicals is observed ($^{1-4}$).

In work (^{5}) it was shown that, upon photoirradiation at the temperature of liquid nitrogen of solutions of triphenylamine in ethyl alcohol, in the presence of silica gel, hydrogen atoms are adsorbed on the latter. From this it was concluded that radical formation proceeds through detachment of hydrogen atoms from alcohol molecules under the influence of photoexcited triphenylamine molecules.

Fig. 1. E.p.r. spectrum of a photoirradiated solution of triphenylamine in ethanol
($C = 10^{-3}$ mol/l, $T = 77$°K)

Fig. 2. E.p.r. spectrum of a photoirradiated solution of triphenylamine in ethanol CH_3CH_2OD
($C = 10^{-3}$ mol/l, $T = 77$°K) with silica gel

It is known that in alcoholic solutions luminophores containing heteroatoms form, by means of hydrogen bonds, weak complexes with alcohol molecules. The alcohol molecules themselves are also linked with one another by hydrogen bonds. Upon irradiation of ethanol solutions with a concentration of 10^{-3} mol/l of triphenylamine, the radicals $CH_3\dot{C}HOH$, $\dot{C}H_3$, and $\dot{C}HO$ were identified. The

EPR spectra of photoirradiated triphenylamine solutions in deuterated alcohols

Figure 2: EPR spectra of photoirradiated triphenylamine solutions in deuterated alcohols

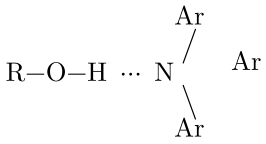
yield of $CH_3\dot{C}HOH$ radicals is proportional to the square of the intensity of the light source, which indicates a two-photon process of radical formation ($^{4-6}$). In contrast to methanol solutions, the yield of $\dot{C}HO$ radicals in ethanol solutions is small. Figure 1 shows the spectrum

E.p.r. of the photoirradiated solution of triphenylamine in ethyl alcohol, from which it is seen that the yield of $\dot{C}HO$ radicals is approximately two orders of magnitude smaller than that of $CH_3\dot{C}HOH$ radicals.

To elucidate the mechanism of radical formation, studies were carried out on solutions of triphenylamine in deuterated alcohols CD_3CH_2OH, CH_3CD_2OH, and CH_3CH_2OD. The choice of triphenylamine excludes the possibility of deuterium exchange with molecules of CH_3CH_2OD.

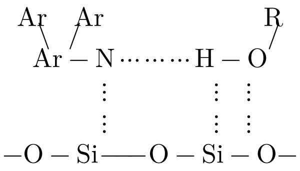
Fig. 3. E.p.r. spectra of photoirradiated solutions of triphenylamine in deuterated alcohols ($C = 10^{-3}$ mole/l).
a–CD_3CH_2OH, *b*–CH_3CD_2OH

Schematically, the ethyl alcohol + triphenylamine complex may be represented as follows:



In the presence of silica gel, the indicated complex is adsorbed on its surface as a result of interaction of the hydroxyl group, as well as of the nitrogen atom–

···of contact of the triphenylamine molecule with silicon and oxygen atoms:



Thus, if during photoirradiation of the complex the primary act in the process of radical formation is cleavage of the O – H bond, leading to the formation of the radical $CH_3CH_2\dot{O}$, then hydrogen (deuterium) atoms of this group should be adsorbed on the surface of the silica gel. The formation of the radicals

$CH_3\dot{C}HOH$, $\dot{C}H_3$, and $\dot{C}HO$ is a secondary process: the result of interaction of the radical $CH_3CH_2\dot{O}$ with neighboring alcohol molecules. Upon photoirradiation of a solution of triphenylamine in CH_3CH_2OD in the presence of silica gel, e.p.r. signals of deuterium atoms were observed. The e.p.r. spectrum of the photoirradiated frozen solution of triphenylamine with CH_3CH_2OD is shown in Fig. 2. In addition to the e.p.r. signals of deuterium atoms, e.p.r. signals of hydrogen atoms are also observed; this is the result of incomplete deuteration of the OH groups in the alcohol and partial deuterium exchange between the OD groups of the alcohol and the OH groups of water adsorbed on the surface of the silica gel, which is difficult to remove completely even by prolonged calcination at 500°C under vacuum.

Fig. 4. E.p.r. spectrum of a photoirradiated solution of triphenylamine in isopentane containing 0.4% ethanol ($C = 10^{-3}$ mol/l).

Upon photoirradiation of solutions of triphenylamine in CH_3CD_2OH and CD_3CH_2OH, no e.p.r. signals of deuterium atoms were detected; spectra of hydrogen atoms and of the radicals $CH_3\dot{C}DOH$, $CD_3\dot{C}HOH$, $\dot{C}H_3$, and $\dot{C}D_3$ were observed. For illustration, Fig. 3 gives recordings of the e.p.r. spectra of photoirradiated solutions of triphenylamine in CD_3CH_2OH and CH_3CD_2OH. From the data obtained it follows that the primary act in the process of radical formation is associated with abstraction of a hydrogen atom from the OH group forming a hydrogen bond with the nitrogen atom of triphenylamine.

The yield of hydrogen atoms is strictly correlated with the yield of $CH_3\dot{C}HOH$ radicals and, at low light intensities, is proportional to the square of the intensity.

Additional confirmation of the conclusion drawn is provided by studies carried out with solutions of triphenylamine in mixtures of ethyl alcohol + isopentane. In photoirradiated solutions of triphenylamine in isopentane, a weak single e.p.r. line was detected; its appearance is apparently associated with the presence in isopentane of impurity compounds containing hydroxyl or carbonyl groups. When ethyl alcohol is added to the isopentane solution of triphenylamine, a singlet e.p.r. signal is observed (Fig. 4), the intensity of which increases with increasing concentration of ethyl alcohol. When the concentration of ethyl alcohol is changed from 0.5% to 0.8%, the e.p.r. spectrum changes abruptly: intense signals from the radical $CH_3\dot{C}HOH$ appear, as well as weak signals from $\dot{C}H_3$ and $\dot{C}HO$. Such a sharp change in the appearance of the spectrum can be explained by the fact that, upon reaching a concentr-

···concentrations of 0.5-0.8% ethanol in isopentane, chains of alcohol molecules are formed, linked by hydrogen bonds to one another and to the radical $CH_3CH_2\dot{O}$, as shown in the scheme.

$$\text{Energy levels: } S^*,\ T^*,\ T; \quad h\nu_1,\ h\nu_2;$$

$$(\mathrm{Ar})_3\mathrm{N}\cdots \mathrm{H{-}O{-}R} \longrightarrow (\mathrm{Ar})_3\mathrm{N}^+\cdots \mathrm{H{-}O}\cdots \mathrm{H}\cdots \longrightarrow (\mathrm{Ar})_3\mathrm{NH}^+ + \dot{\mathrm{O}}\text{-radical products,}$$

$$\text{secondary processes} \quad \mathrm{H{-}O{-}\dot{C}H{-}CH_3} \text{ and others.}$$

In conclusion, we note that the investigation carried out indicates the important role of the hydrogen bond in the processes of deactivation of excited molecules leading to the formation of radicals, as was reported earlier in work (7).

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CITED LITERATURE

1. B. Smaller, *Nature*, **195**, No. 4841, 593 (1962).
2. V. E. Kholmogorov, E. V. Baranov, A. N. Terenin, DAN, **149**, No. 1, 142 (1963).
3. A. K. Piskunov, R. N. Nurmukhametov, D. N. Shigorin, V. I. Muromtsev, G. A. Ozerova, *Izv. AN SSSR*, ser. **27**, No. 5, 634 (1963).
4. Yu. I. Kozlov, V. I. Muromtsev, A. K. Piskunov, D. N. Shigorin, G. A. Ozerova, N. V. Verein, *ZhFKh*, **37**, No. 12 (1963).
5. V. E. Kholmogorov, E. V. Baranov, A. N. Terenin, DAN, **152**, No. 6 (1963).
6. Kh. S. Bagdasaryan, V. I. Muromtsev, Z. A. Sinitsyna, DAN, **152**, No. 2 (1963).
7. D. N. Shigorin, N. A. Shcheglova, A. K. Piskunov, G. A. Ozerova, N. S. Dokunikhin, DAN, **150**, No. 4, 862 (1963).

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