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Abstract

Full Text

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On the Role of the Triplet State of Aromatic Amines in the Photoreaction of Alcohol Dehydrogenation at 77°K

In a previous communication (^{1}), preliminary results were described of an investigation, by the method of electron paramagnetic resonance (EPR), of the photodehydrogenation of alcohols by aromatic amines at 77°K under ultraviolet irradiation. It was suggested that the photoreaction proceeds with participation of the triplet (phosphorescent) state of the amines and that its high efficiency is due to the formation of amine-alcohol associates, probably linked by a hydrogen bond. Experiments carried out to clarify the mechanism of the reaction of photodehydrogenation of alcohols by amines at 77°K are described below.

Measurements were performed on an RE-1301 EPR radiospectrograph. Samples of amine solutions in alcohols were placed in thin-walled quartz ampoules 4 mm in diameter, permitting vacuum treatment of the solution. Control experiments carried out with evacuated samples and with untreated samples showed no substantial differences in the course of the reaction. A mercury lamp DRSh-250 with various standard light filters was used as the light source; these filters served to isolate spectral regions corresponding to the long-wavelength portions of the amine absorption bands (experiments showed that light with wavelength $\lambda < 313$ mμ destroys alcohol radicals*). For example, in the case of triphenylamine and diphenylamine, the filters UFS-4 and UFS-2, respectively, were used.

Fig. 1. EPR spectrum of the radicals CH_2OH and C_6H_7, obtained upon illumination of a solution of triphenylamine in methanol (10^{-3} M) in a mixture with benzene (10^{-2} M) at 77°K.

It was observed that, when a sample was thawed, a gas bubble was released

Fig. 2. EPR spectrum of the radicals $\dot{C}H_2OH$ and $\dot{H}$ obtained upon illumination of a solution of triphenylamine in methanol in the presence of silica gel at 77°K

Figure 2: Fig. 2. EPR spectrum of the radicals $\dot{C}H_2OH$ and $\dot{H}$ obtained upon illumination of a solution of triphenylamine in methanol in the presence of silica gel at 77°K

from the portion of the solution that had been exposed to light. To determine the possible intermediate appearance of hydrogen in the photoreaction under study, the following experiment was carried out. In the previous communication (^{1}), the inhibiting effect of adding naphthalene on the efficiency of alcohol dehydrogenation by amines was shown; this was explained by selective transfer of energy from the triplet level of the amine to the triplet level of naphthalene (^{3}). Indeed, this inhibitory effect on the photoreaction is absent if, instead of naphthalene, benzene is added to the methanolic solution of triphenylamine at a concentration up to 10^{-2} M. However, after such a sample is illuminated at 77°K, the EPR spectrum, along with the intense components of the alcohol radical, reveals relatively weak hyperfine-structure lines of the radical $\dot{C}_6H_7$ (^{4}) with an intensity ratio of $1 : 2 : 2 : 1$ (Fig. 1). The central group of lines of the radical C_6H_7 does not appear in the spectrum obtained because of the high intensity of the EPR lines.

of the radical $\dot{C}H_2OH$. Evidently, the radical $\dot{C}_6H_7$ arose as a result of addition to benzene of an H atom abstracted from methanol.

To trap H atoms abstracted from the alcohol molecule, the method of stabilizing hydrogen atoms on solid surfaces at 77°K was then used (^{5}-^{7}). Excess silica gel, degassed in air at 500°C, was added to an ampoule with a solution of triphenylamine in methanol (10^{-3} M).

Fig. 2. EPR spectrum of the radicals $\dot{C}H_2OH$ and $\dot{H}$ obtained upon illumination of a solution of triphenylamine in methanol in the presence of silica gel at 77°K

The solution was degassed under vacuum (10^{-4} mm Hg) with repeated freezing-thawing. The EPR spectrum obtained as a result of illumination of this sample (Fig. 2) consists of two groups of lines: a central group, belonging to the radical $\dot{C}H_2OH$, and a peripheral one (a doublet with a splitting between components of 510 oersteds), belonging to atomic hydrogen. The EPR lines of atomic hydrogen stabilized on silica gel at 77°K are symmetric singlets, saturating as the microwave power is increased. In a control experiment, silica gel with triphenylamine adsorbed from a methanol solution, but with remo-

washed out with alcohol in vacuum after irradiation gave no E.P.R. spectra of al-

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* The results of this study are being published.

Fig. 3

Figure 3: Fig. 3

cohol radicals or H atoms. The same experiments were carried out with ethanol. Evidently, the H atoms split off from the alcohol molecules are transferred to the surface of the silica gel, where they become fixed.

Our data ([1]) on the quenching of the photoreaction of alcohol dehydrogenation by amines and Smaller' s data ([2]) on the photosensitization by benzophenone of a similar reaction in the indole—methanol system at 77° K indicate the participation of the triplet state of amines in this reaction. Taking into account the long lifetime of amines in the triplet state ($\tau = 0.7 \div 7.6$ sec. ([8])), it is possible to compare, from the E.P.R. spectra, the amount of alcohol radicals formed over a definite interval of continuous illumination, for example over 5 sec.*, and over the same illumination time, but with alternation of the exposure period (1 sec.) with a dark period (2 sec.), i.e., over 15 sec. of intermittent illumination. An experiment,* carried out on an ethanolic solution of diphenylamine ($10^{-2}M$), showed that the concentration of the alcohol radicals formed was independent of the mode of exposure; i.e., it showed that alcohol radicals arise only during illumination, while in the dark period their formation ceases, although there is a sufficiently high concentration of phosphorescing triplet molecules. It follows from this that the main triplet (phosphorescent) state of the amine does not directly participate in the reaction of alcohol dehydrogenation.

Fig. 3. Increase in the concentration of $CH_3\dot{C}HOH$ radicals arising upon illumination of solutions of triphenylamine in ethanol at 77° K for concentrations: 1—$5 \cdot 10^{-3}$; 2—10^{-3}; 3—$5 \cdot 10^{-4}$; 4—10^{-4} M

It may be assumed that the splitting off of an H atom from an alcohol molecule requires absorption by the amine molecule of two photons: one to transfer the amine into the triplet (phosphorescent) state, and a second to excite it to a higher triplet level. In that case the rate of increase in the concentration of alcohol radicals (in the absence of light saturation of the amine triplet excitation ([9])) should depend on the intensity of the light incident on the sample according to a quadratic law ([10]). To test this assumption, the amount of alcohol radicals formed during the same illumination time of a methanolic solution of diphenylamine ($5 \cdot 10^{-4}M$) was measured as a function of light intensity.** For this purpose, wire screens with calibrated transmission were used, placed between the source and the sample.*** When the light intensity was increased by a factor of 2, the increase in the concentration of the alcohol radicals formed, measured from the ratio of the intensities of the middle components of the superhyperfine structure of the E.P.R. spectrum of the $\dot{C}H_2OH$ radical, occurred by a factor of $3.6 \div 3.8$, i.e., almost by a factor of 4. Thus, the agreement with the quadratic law, independently also observed in work ([11]), is satisfactory.

* The time corresponding to the linear portion of the time dependence of the accumulation of alcohol radicals in the course of the photoreaction under study.

** The maximum illumination of the sample, at which no light saturation of the amine triplet excitation yet occurs, was determined in advance from the dependence of the phosphorescence intensity on the intensity of the exciting light ($\lambda = 313$ mμ).

*** The illumination time, determined experimentally so as to attain a signal-to-noise ratio of ~ 2 when illuminating the sample through a screen with 50% transmission, was 1 min.

An attempt was made to detect the effect of triplet–triplet excitation of diphenylamine on the formation of alcohol radicals. For this purpose, the concentrations of ethyl alcohol radicals formed under two conditions of intermittent illumination of samples of a solution of diphenylamine in ethanol were compared. In one experiment the irradiation periods (1 sec) alternated with dark periods (2 sec). In the second, the dark period was replaced by a period of illumination with visible light from the same source, isolated by means of a BS-7 light filter. The illumination cycle consisted of fivefold illumination and darkening (or illumination with visible light) and lasted 15 sec. In both experiments the amounts of ethyl alcohol radicals formed proved to be identical. This result indicates that the energy of a visible-light quantum with wavelength greater than 400 mμ, absorbed by an amine molecule in the phosphorescent state, is insufficient for carrying out the photoreaction of alcohol dehydrogenation.

It is possible that the photoreaction requires ionization of the amine molecule in the triplet state, and reaction of the positive amine ion with an alcohol molecule with subsequent transfer of hydrogen to the acceptors present (benzene, silica gel).

Figure 3 gives the results of measurements of the increase in concentration of alcohol radicals in samples of solutions of triphenylamine in ethanol at 77° K as a function of the amine concentration and illumination time. The samples were illuminated directly in the resonator of the spectrograph. The concentration of $CH_3\dot{C}HOH$ radicals was estimated by comparison with the EPR signal of calibrated solutions of diphenylpicrylhydrazyl (DPPH) in benzene. It is seen from Fig. 3 that the amount of $CH_3\dot{C}HOH$ radicals formed is commensurate with the number of triphenylamine molecules. Deviations toward a decrease occur only in concentrated solutions, apparently because of complete absorption of the exciting light in the illuminated layer of the sample. The stability of the alcohol radicals formed at 77° K after cessation of illumination indicates the absence of their mutual recombination, the absence of chemical interaction of the alcohol radicals with the abstracted hydrogen, and also with amine molecules.

Experiments to elucidate the mechanism of the photoreaction are continuing.

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