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Fig. 1. Change in the EPR spectrum during the reaction in benzene at 70°: a —spectrum at the initial concentration of DPPH; b —after addition of PF solution; c —45 min after the start of the reaction; d —after oxidation of the final reaction products (recorded under instrumental conditions different from a, b, c)

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Abstract

Full Text

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On the Induced Reactivity of Certain Compounds with a Conjugated System in Reaction with 1,1-Diphenyl-2-picrylhydrazyl

(Presented by Academician N. N. Semenov on 7 VIII 1963)

It was reported earlier that there is a new kinetic effect consisting in the activating influence of paramagnetic polymer fractions on the reactivity of polymeric and monomeric substances with a system of π–π conjugation (1−3). In considering the probable mechanism of this effect, one of us put forward the hypothesis that it is due to the influence of the local electromagnetic fields of polymeric ion-radicals formed in the course of synthesis or during subsequent heat treatment of compounds with a conjugated system (4). In the present communication we set forth data on the interaction in solution of 1,1-diphenyl-2-picrylhydrazyl (DPPH) with polymeric compounds (polyphenylene (PF), polyazophenylene, polymetallopyridylacetylene, polyphenylacetylene, heat-treated anthracene) and monomeric (anthracene) compounds with a conjugated system (4). The polymers studied possessed paramagnetism in the solid state and in solutions. The EPR signal, consisting of a narrow singlet, corresponds to a concentration of paramagnetic centers of 10^{17}–10^{18} per 1 g of substance. According to EPR data, the anthracene that we used did not contain paramagnetic particles.

Fig. 1. Change in the EPR spectrum during the reaction in benzene at 70°: *a* —spectrum at the initial concentration of DPPH; *b* —after addition of PF solution;

Fig. 2

Figure 2: Fig. 2

c —45 min after the start of the reaction; *d* —after oxidation of the final reaction products (recorded under instrumental conditions different from *a*, *b*, *c*).

The kinetics of interaction with the above-indicated substances was studied by the EPR method and by spectrophotometry. EPR spectra were recorded on an EPR-2 radiospectrometer ([5]), equipped with a thermostating device that allowed the temperature of the sample in the spectrometer resonator to be regulated with an accuracy of ±1°C. The electronic absorption spectrum of DPPH has a characteristic maximum at 520 mμ, and therefore spectrophotometry is a convenient method for studying the kinetics. We used an SF-2M spectrophotometer with a thermostating device (temperature regulation accuracy ±0.5°C). Measurements were carried out in cylindrical cuvettes with a total volume of ~ 4 cm^3, hermetically sealed by ground-

formed samples. To determine the change in the number of particles during the reaction, ebullioscopic measurements were carried out jointly with V. V. Tartaryntsev. The ebullioscopic temperature difference was measured with an accuracy of up to 10^{-4} using a thermopile of 16 copper-constantan thermocouples and a DC amplifier F-116/1. The solvents used were benzene, toluene, dioxane, and carbon tetrachloride.

Fig. 2. Curves for the disappearance of DPPH according to EPR data.
1 —temperature 54° (in air); 2 —at the same temperature (solution deoxygenated); 3 —at 65° (solution deoxygenated)

DPPH was obtained according to (6) and purified by recrystallization from a chloroform-ether mixture. It is well known that DPPH in solutions gives a nuclear hyperfine EPR structure consisting of five components. Under the chosen experimental conditions, DPPH solutions proved sufficiently stable, even for exposures several times exceeding the duration of the experiments. When polyphenylene was added to a DPPH solution (in a more than molar ratio), intense disappearance of DPPH was observed. The rate of disappearance can be judged from the decrease with time in the amplitude of one of the components of the hyperfine structure. At the end of the reaction the hyperfine structure disappears, and a singlet remains with an intensity approximately equal to the intensity of the EPR signal of the added polymer (Fig. 1, a, b, c). This indicates that the DPPH radical does not interact with the paramagnetic centers of the polymer. To clarify the influence of these centers on the reactivity of polyconjugated systems in reactions with radicals, we carried out a comparative study (under identical conditions and concentrations) of the interaction of DPPH with anthracene and with anthracene into which a polymer fraction had been introduced, obtained by fractionation of heat-treated anthracene (7). It was found that in the absence of the paramagnetic fraction no disappearance of

Fig. 3

Figure 3: Fig. 3

DPPH is observed. Figure 2 presents the curves for the disappearance of DPPH upon interaction with PP in benzene, according to EPR data. The rate of disappearance increases with increasing temperature and depends on the presence of atmospheric oxygen. In the case of a deoxygenated solution the reaction rate increases. The reaction is second order with respect to DPPH (Fig. 3) and first order with respect to PP. The effective activation energy is $E_{\text{eff}} = 11.6$ kcal/mol. In Fig. 3 the dashed straight line denotes the linear anamorphosis for an experiment in which the benzene solution of PP was specially enriched with oxygen before DPPH was added. The reaction rate decreased markedly. DPPH interacts analogously with PP in toluene and dioxane. To clarify the chemistry of the reaction under consideration, the reaction products were subjected to oxidation with lead dioxide (solvent—ben-

Fig. 3. Linear anamorphoses of kinetic reaction curves (according to spectrophotometric data). Molar ratio PP : DPPH = 4.4 : 1.
1 —at temperature 51°; 2 —at 65°; 3 —at 73°; 4 —at 73° (reaction mixture enriched with oxygen)

sol.). In this case, restoration of the hyperfine structure of the EPR spectrum characteristic of DPPH (Fig. 1d) was observed, as well as the appearance of a maximum in the electronic absorption spectrum at 520 mμ. Thus it was established that the bleaching of DPPH is associated with hydrogen transfer and the formation of 1,1-diphenyl-2-picrylhydrazine (DPPH-H). However, some substituted DPPH compounds can give similar EPR spectra (8). By thin-layer chromatography on alumina it was possible to confirm the presence of DPPH-H in the reaction products. In addition, a product was detected with an R_f value considerably smaller than that of DPPH-H. Ebullioscopic measurements showed that, in the course of the interaction of DPPH with PP in benzene, the total number of particles in the system does not change. This may indicate that PP does not add to DPPH, but it does not yet permit one to assert that it is the hydrogen donor. In order to determine whether hydrogen transfer to DPPH from the solvent occurs, we carried out a series of experiments on the interaction of polyphenylacetylene with DPPH in carbon tetrachloride solution. As can be seen from Fig. 4, the reaction rate in this solvent and in toluene is practically the same. Consequently, the substance transferring hydrogen is the polymer with a conjugated system. This is also supported by the fact that the reaction rate depends on the nature of the polymer. Taking into account the constancy of the EPR spectra of the polyconjugated substances participating in the reaction, it may be assumed that hydrogen transfer is effected not by the paramagnetic centers, but by the diamagnetic molecules associated with them in a strong π-complex and constituting the main mass of the substance (4). On the basis of the data set forth above, the following reaction scheme appears probable. Upon dissolution, DPPH is solvated with the formation of a nonstoichiometric molecular complex with the solvent (^{9}-^{11}). With the introduction of PP, partial or complete recomplexation occurs and a π-complex of the type [DPPH(PP) solv.] is formed, since there is no doubt that PP has a lower ionization potential than any of the solvents used. Such recomplexation in DPPH solutions has recently been shown experimentally (^{10}). The paramagnetic centers of "local activation" located in PP activate the S—T transition of the diamagnetic macromolecules of PP, thereby making possible hydrogen transfer to the acceptor (DPPH):

Fig. 4. Kinetic curves of the reaction of polyphenylacetylene with DPPH in carbon tetrachloride: *a*—at 46°, *b*—at 56°, *v*—at 67°, *g*—at 76°, *d*—corresponding points for the reaction in toluene.

$$\overset{\text{HH}}{\langle\ \rangle} + \text{DPPH} \longrightarrow \cdot\langle\ \rangle{-}\text{DPPH}{-}\text{H}.$$

The active polyphenylene radical that has formed abstracts hydrogen or another atom X (for example, a halogen) from the solvating π-complex of the solvent (RX), and the radical $R\cdot$ formed in this process reacts with a second DPPH molecule:

$$\cdot\langle\ \rangle + RX \longrightarrow \langle\ _{X}\rangle + R\cdot,$$

$$R\cdot + \text{DPPH} \longrightarrow R - \text{DPPH} - \text{H}.$$

It is also not excluded that, along with this, a process of recombination of the radicals R • takes place. In general form the reaction under investigation may be described by the following kinetic scheme:

$$\text{PF} + \text{DFPG}\cdot\text{RX} \underset{k_2}{\overset{k_1}{\rightleftarrows}} [\text{PF}\cdot\text{DFPG}\cdot\text{RX}],$$

$$[\text{PF}\cdot\text{DFPG}\cdot\text{RX}] + \text{DFPG} \xrightarrow{k_3} \text{PF} - \text{X} + \text{DFPG} - \text{H} + \text{R} - \text{DFPG} - \text{H}.$$

Taking into account the presence in the reaction of an excess of PF and the obvious condition that $k_3 \ll k_2$, the proposed scheme is in good agreement with the equation for the reaction rate obtained from the experimental data:

$$W_p = K_{\text{eff}}[\text{PF}][\text{DFPG}]^2,$$

where K_{eff} is the effective reaction-rate constant. This scheme also explains the relatively low effective activation energies, the acceleration of the reaction with increasing concentration of the polymer with a conjugated system, the presence of two principal low-molecular-weight end products, etc.

Analysis of the data obtained makes it possible to assert that the reactivity of polymers with a system of conjugated bonds, induced by paramagnetic centers, opens up possibilities for the creation of new methods of organic and polymer chemistry.

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