KINETICS OF THE REACTION OF POLYPHENYLENE WITH 1,1-DIPHENYL-2-PICRYLHYDRAZYL*

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This work discusses some problems of the kinetics of the reaction of a formally valence-saturated system—polyphenylene—with the stable radical 1,1-diphenyl-2-picrylhydrazyl (DPPH), and it is a continuation of our investigations of the reactivity of polymers with a conjugated system. The common feature for all polymers with a system of conjugated bonds, the phenomenon of induced reactivity, consisting of the activating influence of paramagnetic centers of "local activation," and the possible nature of this effect have been discussed earlier [1,2]. DPPH has been used by many researchers as a radical counter in the determination of initiating rates and the study of initiation processes. However, the field of application of DPPH is limited by the fact that at present the nature of the products of the reaction between DPPH and active radicals has been established only for a few cases. In the case of polymer radicals, the reaction product may be either a direct compound of the polymer radical with DPPH or a disproportionation by stripping of hydrogen from the radical by DPPH, forming 1,1-diphenyl-2-picrylhydrazine and an unsaturated polymer molecule. In spite of the numerous complications arising in the use of DPPH, it possesses a number of advantages in comparison with other stable radicals: availability, stability to the action of the oxygen of the air in the polycrystalline state, high stability of solutions in a large number of aromatic and nonaromatic solvents. At the same time, the many shortcomings of DPPH are inherent in most of the known stable radicals, the only difference being that they have received less study.

We were guided by precisely these considerations in selecting the stable radical for evaluating the reactivity of one polymer system with conjugation on another. Under the experimental conditions and in the solvents we selected, DPPH proved stable for a time several times as long as the time of the experiment, or its concentration changed so little that this change could be neglected.

EXPERIMENTAL

We synthesized polyphenylene according to the Wurtz-Fittig reaction from paradichlorobenzene [3]. For the investigation we used the benzene-soluble fraction of polyphenylene with $M_n = 3000$ and a content of paramagnetic centers of about $10^{18}$ per gram of the substance (according to the EPR data). We described some characteristics of polyphenylene in [4]. DPPH was produced according to [5] and recrystallized from a chloroform-ether mixture. The kinetics of the reaction of polyphenylene (PP) with DPPH was studied in benzene, toluene, and dioxane. The benzene and toluene were purified in the usual way, dioxane as described in [6]. We should mention that the reaction studied is not sensitive to negligible impurities in the benzene and toluene, and the usual analytical grade solvents can be used. The reaction rate is considerably influenced by the presence of oxygen in the solvent. We conducted the experiments described below in nondegasified solvents, but the entry of oxygen during the reaction was excluded by the experimental conditions. In the case when degasification of the solvent was performed, this reservation will be made in the text. The kinetics was studied by the method of spectrophotometry (instrument SF-2M). The spectrophotometer was equipped with a thermostatic device (accuracy of temperature regulation ±0.5°). The cuvettes had a volume of about 4 cm³ and were closed with ground-glass stoppers. The variation of the DPPH concentration during the reaction was recorded according to the change in the optical density in the region of 520 μm, where DPPH has a characteristic absorption maximum.

In the region of DPPH concentrations used, in the solvents enumerated above, we observed obedience to the Beer-Lambert law. The sequence for conducting the reactions was the following: a solution of PP (about $\frac{3}{4}$ of the volume of the cuvette) was poured into both cuvettes, and equality of the PP concentrations was checked on the

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Fig. 1. Kinetic curves of the destruction of DPPH in benzene at a molar ratio PP:DPPH = 4.4:1: 1) at a temperature of 51°; 2) at 65°; 3) at 73° (reaction mixture enriched with oxygen); 4) at 73°.

Fig. 2. Dependence of the reciprocals of the DPPH concentrations on the time in the reaction with PP at a temperature of 67° and the following molar ratios PP:DPPH: 1) 4.8:1; 2) 3.9:1; 3) 2.9:1; 4) 1.9:1; 5) 1:1.

Fig. 3. Dependence of $\log k_{\text{eff}}$ of the reaction of PP with DPPH in benzene at 67° on the logarithm of the PP concentrations.

spectrophotometer; then a solution of DPPH was sprayed into one cuvette, and the solvent in an amount equal to the volume of the DPPH solution was sprayed into the second. After shaking of the cuvettes, we began to record the variation of the optical density with time. Figure 1 shows typical kinetic curves of the reaction of DPPH with PP in benzene. An analysis of these data shows that the reaction is second order with respect to DPPH. To determine the reaction order with respect to PP, we investigated the influence of the PP concentration on the reaction rate at one temperature. As can be seen from Fig. 2, in this case also the reaction is well plotted in second order with respect to DPPH. The slope of the straight line in the coordinates logarithm of the effective reaction rate constant versus logarithm of the PP concentration is equal to 1.25 (Fig. 3); consequently, we can assume a first-order reaction rate with respect to PP. The reaction is decelerated when the solution is enriched with oxygen (curve 3 in Fig. 1). This is probably due to the formation of the complex $[\text{DPPH} \cdot \text{O}_2]$, which stabilizes the DPPH solution. The formation of such a complex was considered in [7]. The stabilization of chloroform solutions of DPPH was also indicated in [8]. This also finds confirmation in our observations in a study of the kinetics of the reaction under consideration in degasified benzene. In this case an increase in the reaction rate and a decrease in the effective activation energy $E_{\text{eff}}$ are observed. $E_{\text{eff}}$ for the reaction in nondegasified benzene is equal to 11.6 kcal/mole.

The basic principles of the reaction are also preserved within a broad range of temperatures when toluene is used as the solvent (Fig. 4). $E_{\text{eff}}$ in this case is somewhat lower—10.2 kcal/mole (Fig. 5). It is possible that the observed decrease in the effective activation energy is due to the lower solubility of oxygen in toluene in comparison with benzene [9] and to the presence of the CH$_3$ group. The reaction of PP and DPPH also occurs similarly in dioxane (Fig. 6). $E_{\text{eff}} = 10.0$ kcal/mole (Fig. 7). It was of interest to investigate the kinetics of the reaction in a solvent containing no hydrogen. We could not find such a solvent for PP; hence we used polyphenylacetylene, kindly provided by M. I. Cherkashin. Polyphenylacetylene is readily soluble in carbon tetrachloride. DPPH reacts with polyphenylacetylene in carbon tetrachloride, the reaction rates in carbon tetrachloride and toluene practically not differing. $E_{\text{eff}}$ is of the same order of magnitude as for the reaction of PP with DPPH in toluene and dioxane ($E_{\text{eff}} = 9.5$ kcal/mole, Fig. 8).

An analysis of the experimental data cited in this work and the results of an investigation of the reaction by the methods of EPR, ebullioscopy, and chromatography, conducted earlier [2], give us a basis for considering the probable mechanism of the reaction of PP and other polymers with a system of conjugated bonds with DPPH. Undoubtedly, the destruction of DPPH occurs by means of a transfer of hydrogen from PP to DPPH, forming 1,1-diphenyl-2-picrylhydrazine (DPPH-H) as the basic final product. This is confirmed by the fact that the reaction under consideration proceeds both in solvents containing hydrogen (where the reaction rate is practically independent of the nature of the solvent) and in solvents not containing hydrogen (CCl$_4$). It is well known that the cleavage of the C-H bond, especially in aromatic systems, requires considerable energy expenditures. Thus, under our conditions anthracene does not react with DPPH. The transfer of hydrogen to DPPH has been observed in the dehydrogenation of 1,4-dihydronaphthalene,