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Chemical dynamics of radical pairs formed by benzophenone photoreduction in solid polymers

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Strong reducing agents, such as phenols and amines, decrease substantially the quantum yield of aromatic ketone consumption in solid polymers. A significant quenching of ketone phosphorescence and an increase in the yield of radical pairs are unambiguous evidence for the efficient primary intermolecular transfer of H atoms under these conditions. The effect in question is related to a sharp change in the ratio of recombination and disproportionation rates of geminate radical pairs in solid polymers in comparison with solutions and micellar systems. The main reason for the phenomenon is the low molecular mobility, which provides no sufficiently fast reorganization of reacting species and their environment needed for the formation of radical pair recombination products.

Key words: radical pairs, recombination, disproportionation, ketones, phenols, amines, photoreduction, polymers.

Radical pairs are among key intermediate species of many photochemical processes. Although they are evidently significant from the scientific and practical points of view, only several works on the evolution of radical pairs in solid polymers are known.[1—5] Meanwhile, just these systems can demonstrate unusual effects related to rather long lifetime of radical pairs and enable its controlling by physical and chemical methods. Radical pairs formed by the photoreduction of aromatic ketones with phenols and amines are used, as a rule, as the main objects of studies. This is primarily due to an almost quantitative yield of radical pairs in these systems.[1—5] In addition, it is convenient to use absorption spectra for monitoring transformations of each component of a radical pair. An extensive material on the evolution of radical pairs of the same or close nature in solutions and micellar systems is also important.[6—8] In the works on studying radical pairs in polymers, the main attention was given to specific features of the kinetics of their consumption[1—3,5] and spin dynamics.[4,5] The purpose of this study is to reveal the main routes of chemical processes involving radical pairs formed by the photoreduction of ketones with phenols and amines in solid polymers.

Experimental

Commercial poly(vinyl chloride) (PVC, trade mark M 64) was purified by precipitation with ethanol from a solution in 1,2-dichloroethane. Unstabilized commercial poly(methyl methacrylate) (PMMA) with the molecular weight 160 000 was used as received. Benzophenone (reagent grade), 2,4,6-trimethylphenol (Fluka), and diphenylamine (analytical grade) were recrystallized from ethanol.

Films with a thickness of 20—100 μm were prepared by the slow evaporation of the solvent from a PVC solution in 1,2-dichloroethane deposited on a glass polished surface. Necessary additives of benzophenone (2—6 wt.%) and 2,4,6-trimethylphenol or diphenylamine (up to 15 wt.%) were introduced into a polymer solution prior to film preparation.

Steady-state photolysis was carried out on a DRSh-1000 high-pressure mercury lamp (λ = 365 nm) using the BS6 and UFS6 light filters. The photoreduction of benzophenone that occurs in PVC with a quantum yield of 0.16 was used as a chemical actinometer.[9]

The kinetics of benzophenone consumption was detected by a decrease in the absorbance at 1690 cm^{-1} in the IR spectrum. The accumulation of recombination products of radical pairs formed in the presence of phenol was monitored by a change in the absorbance in the UV region (λ = 340 nm; the quinoid structure characteristic of light-absorbing intermediates is designated as LAT).[10,11]

Phosphorescence spectra were recorded on a spectrofluorimeter consisting of a radiation source (DKsSh-150 xenon lamp), excitation (SPM-2) and emission (MC-80) monochromators, and a recording system (FEU-128 and a K-20 recorder).

The UV-vis absorption spectra were recorded on a Specord UV-Vis spectrophotometer. The IR absorption spectra were measured on a Specord IR-75 spectrophotometer.

Results and Discussion

Irradiation of PVC films containing benzophenone results in the fast consumption of ketone (Fig. 1, *a*). In

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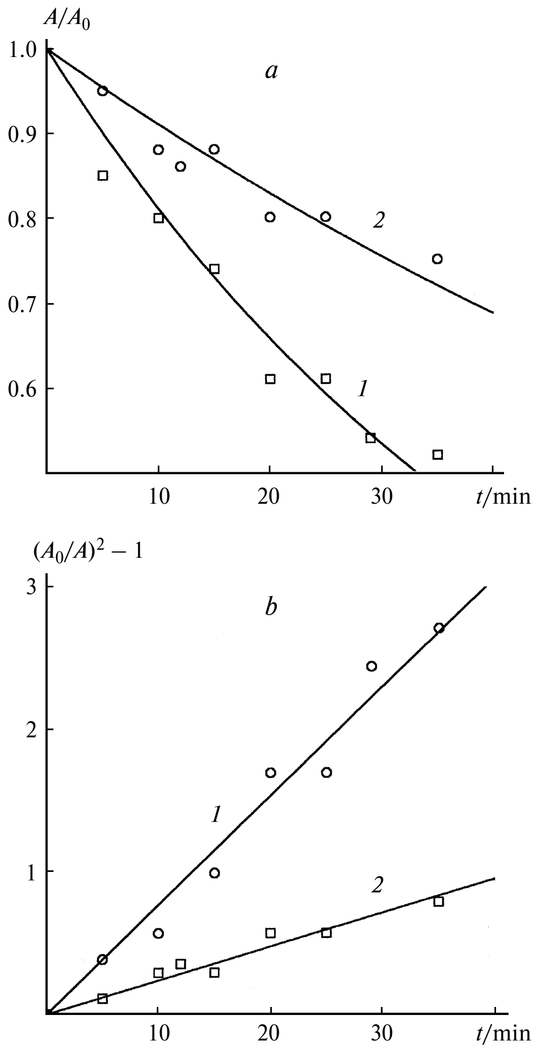

Fig. 1. Kinetic curves of benzophenone consumption (*a*) and their linear anamorphoses according to Eq. (I) at $n = 2$ (*b*): irradiation of PVC films with a thickness of 40 μm containing 2 wt.% benzophenone *in vacuo* at λ = 365 nm in the absence of other additives (*1*) and in the presence of 15 wt.% 2,4,6-trimethylphenol (*2*).

the presence of phenol or amine, benzophenone transformation slows down substantially (see Fig. 1, *a*, curve *2*). The kinetic curves of the process do not correspond to regularities of simple chemical reactions but are described rather well by an extrapolating function

$$C(t)/C_0 = (1 + nWt)^{-1/n}, \qquad \text{(I)}$$

where $W = \partial C(t)/\partial t|_{t=0} = \int kf(k)\mathrm{d}k = k_{\mathrm{av}}$ is the relative initial rate of the process or the rate constant averaged over the initial distribution, n is the parameter characterizing the width of the reactivity distribution of species, and $C(t)$ and C_0 are the reactant concentrations at the moment t and in the beginning of the process (at the moment $t = 0$). It should be emphasized that similar kinetic regularities have been observed previously[3] for the kinetics of radical pair consumption in solid polymers. The data presented in Fig. 1, *b* show that the initial rate of benzophenone phototransformation decreases more than threefold upon phenol addition.

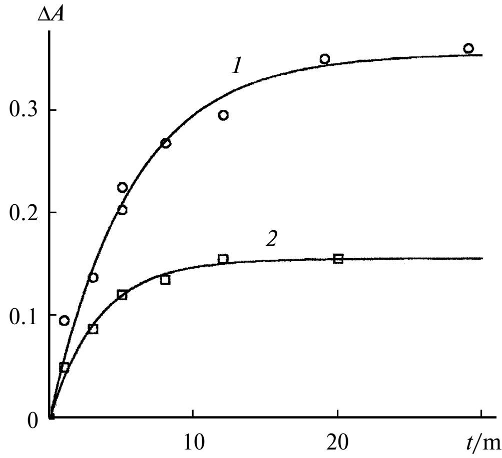

Fig. 2. Kinetic curves of accumulation of the recombination products of radical pairs formed upon benzophenone photolysis (λ = 340 nm) in the absence of other additives (*1*) and in the presence of 2,4,6-trimethylphenol (*2*) (for the irradiation conditions and additive concentrations, see Fig. 1).

In the presence of phenol, the initial rate of formation and steady-state concentration of the quinoid recombination product of a radical pair with an absorption maximum at 340 nm also decrease (Fig. 2).

At rather high concentrations of phenol used in experiments, whose results are presented in Figs 1 and 2, almost all radical pairs formed by the photoreduction of ketone consist of the ketyl and phenoxyl radicals. In particular, this is indicated by the data obtained by laser pulse photolysis, according to which the kinetic curves of consumption of ketyl and phenoxyl radicals are completely identical.[3] An additional argument is presented by the quenching of benzophenone phosphorescence in the PVC films by phenols. These data confirm the almost complete (by at least 90%) deactivation of triplet states at high phenol concentrations (15 wt.%). The efficient quenching of the triplet states of benzophenone by phenol accompanied by the formation of radical pairs is also observed in PMMA, which indicates a rather general character of the phenomenon.

Similar results were observed for benzophenone consumption in the presence of diphenylamine (Fig. 3). The inhibition of benzophenone transformation with an increase in the amine concentration correlates with the quenching of ketone phosphorescence (see Fig. 3, curve *2*).

The phenomenon of inhibition of ketone transformation upon the introduction of an additional reagent, which seems paradoxical from the first sight, can be explained by a substantial change in the ratio of the main channels

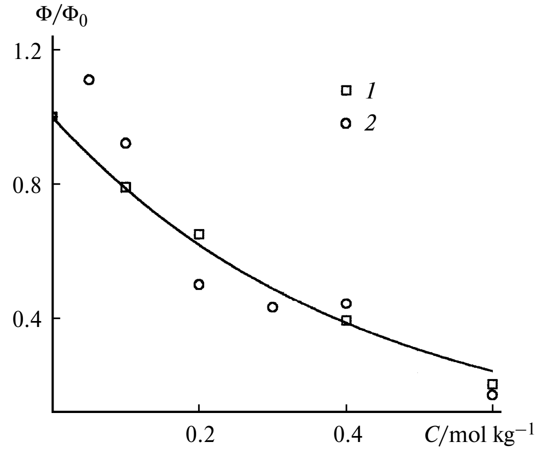

Fig. 3. Relative quantum yield (Φ/Φ_0) of benzophenone consumption (*1*) and phosphorescence (*2*) as a function of the diphenylamine concentration in PVC films (initial benzophenone concentration 1.8 wt.%, excitation wavelength 365 nm).

of chemical transformation of radical pairs: recombination resulting in the irreversible consumption of ketone and disproportionation inducing its regeneration. In the general form, the scheme of processes that occur during ketone photoexcitation in the polymer in the presence of phenol (or amine) can be presented as follows:

$$\mathrm{PhC(=O)Ph} + h\nu \rightarrow {}^1\mathrm{PhC(=O)Ph} \rightarrow {}^3\mathrm{PhC(=O)Ph}, \tag{1}$$

$${}^3\mathrm{PhC(=O)Ph} + \mathrm{PH} \rightarrow {}^3[\mathrm{PhC^{\bullet}(OH)Ph...P^{\bullet}}], \tag{2}$$

$${}^3\mathrm{PhC(=O)Ph} + \mathrm{PhOH} \rightarrow {}^3[\mathrm{PhC^{\bullet}(OH)Ph...PhO^{\bullet}}], \tag{3a}$$

$${}^3\mathrm{PhC(=O)Ph} + \mathrm{PhNHPh} \rightarrow \\ \rightarrow {}^3[\mathrm{PhC^{\bullet}(OH)Ph...PhN^{\bullet}Ph}], \tag{3b}$$

$${}^3[\mathrm{PhC^{\bullet}(OH)Ph...P^{\bullet}}] \rightarrow {}^1[\mathrm{PhC^{\bullet}(OH)Ph...P^{\bullet}}], \tag{4}$$

$${}^3[\mathrm{PhC^{\bullet}(OH)Ph...PhO^{\bullet}}] \rightarrow {}^1[\mathrm{PhC^{\bullet}(OH)Ph...PhO^{\bullet}}], \tag{5a}$$

$${}^3[\mathrm{PhC^{\bullet}(OH)Ph...PhN^{\bullet}Ph}] \rightarrow \\ \rightarrow {}^1[\mathrm{PhC^{\bullet}(OH)Ph...PhN^{\bullet}Ph}], \tag{5b}$$

$${}^1[\mathrm{PhC^{\bullet}(OH)Ph...P^{\bullet}}] \rightarrow \mathrm{PhC(OH)C_6H_4(P)H\ (LAT)} \\ \mathrm{(or\ PhC(P)(OH)Ph)}, \tag{6}$$

$${}^1[\mathrm{PhC^{\bullet}(OH)Ph...P^{\bullet}}] \rightarrow \mathrm{PhC(=O)Ph} + \mathrm{PH}, \tag{7}$$

$${}^1[\mathrm{PhC^{\bullet}(OH)Ph...PhO^{\bullet}}] \rightarrow \\ \rightarrow \mathrm{PhC(OH)C_6H_4(PhO)H\ (LAT)} \\ \mathrm{(or\ PhC(PhO)(OH)Ph)}, \tag{8a}$$

$${}^1[\mathrm{PhC^{\bullet}(OH)Ph...PhN^{\bullet}Ph}] \rightarrow \mathrm{PhNHC_6H_4C(OH)Ph_2} \\ \mathrm{(or\ PhC(NPh_2)(OH)Ph)}, \tag{8b}$$

$${}^1[\mathrm{PhC^{\bullet}(OH)Ph...PhO^{\bullet}}] \rightarrow \mathrm{PhC(=O)Ph} + \mathrm{PhOH}, \tag{9a}$$

$${}^1[\mathrm{PhC^{\bullet}(OH)Ph...PhN^{\bullet}Ph}] \rightarrow \\ \rightarrow \mathrm{PhC(=O)Ph} + \mathrm{PhNHPh}, \tag{9b}$$

where PhC(=O)Ph, PhOH, or PhNHPh are the molecules of benzophenone, 2,4,6-trimethylphenol, or diphenylamine, respectively; PH is the polymer; the left upper indices "1" and "3" indicate the singlet excited or triplet state of the molecule or the radical pair ([PhC$^{\bullet}$(OH)Ph...P$^{\bullet}$], [PhC$^{\bullet}$(OH)Ph...PhO$^{\bullet}$], or [PhC$^{\bullet}$(OH)Ph...PhN$^{\bullet}$Ph]) formed by the interaction of benzophenone with the polymer, phenol, or amine; letters "a" and "b" in the numbers of equations concern the processes involving phenol or amine, respectively.

Reactions (1), (3a), (5a), (8a), and (9a) predominate at rather high phenol concentrations. The above data show that the disproportionation of radical pairs *via* reaction (9a) is the main channel for their conversion, and the corresponding apparent rate constant exceeds the rate constant of recombination (8a) by at least an order of magnitude. The same estimates for radical pairs consisting of the ketyl and aminyl radicals indicate that the disproportionation reaction similar to reaction (9) prevails in the case of the reaction of benzophenone with diphenylamine. In this system, one of the recombination products (triarylcarbinol) is easily detected as the corresponding triarylmethane dye.[4] Therefore, the ratio between this channel and disproportionation can be estimated more exactly. Since the quantum yield of dye formation at an amine concentration of 0.6 mol kg^{-1} is only ~0.0027, the initial rate of radical pair recombination followed by the formation of this product is almost 300-fold lower than the disproportionation rate with initial reactant regeneration. Note that in micellar solutions, unlike solid polymers, recombination for the same radical pairs with the quantum yield $\geq$0.5 is predominant.[12]

Thus, in solid polymers, the ratio of the main channels of radical pair transformation changes sharply, and radical disproportionation with the regeneration of the starting reactants becomes predominant. This is caused by a low molecular mobility that strongly hinders the rearrangement of species, which is necessary for the formation of radical recombination products. The intermolecular H atom transfer from a phenol (or amine) molecule and the backward H atom transfer from the ketyl to phenoxyl (or aminyl) radical represent, in fact, the nonradiative deactivation of the electron excitation energy. Naturally, this process is not so efficient as the intramolecular H atom transfer from the phenoxyl to carbonyl group (and backward) in molecules of 2-hydroxybenzophenone derivatives. Therefore, this system cannot act as photostabilizing. However, its efficiency is quite sufficient to suppress almost completely the photoinitiating activity of ketone in processes of controlled destruction and modification of polymers.

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