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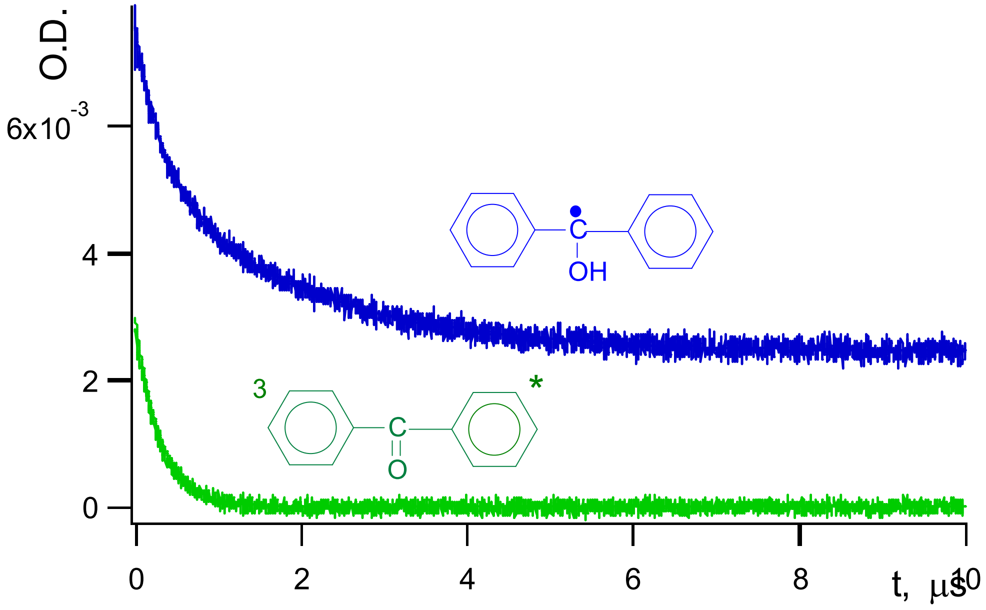
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Kinetics of Benzophenone Ketyl Free Radicals Recombination in a Polymer: Reactivity in the Polymer Cage *vs*. Reactivity in the Polymer Bulk

Peter P. Levin,[ab] Alexei F. Efremkin,[b] Igor V. Khudyakov*[cd]

The decay kinetics of intermediates produced under photolysis of benzophenone (**B**) dissolved in soft rubber poly(ethylene-*co*-butylene) films (abbreviated as **E**) was studied by ns laser flash photolysis in the temperature range of 263 – 313 K. We monitored decay kinetics of the triplet state of ^{3}**B*** and of benzophenone ketyl free radical **BH•** . The fast exponential decay of $^3B^*$ (life-time $\tau_T \approx 200$ ns) is accompanied by hydrogen atom abstraction from **E** with a formation of **BH•** and a polymer free radical **R•**. Decay of ^{3}**B*** was followed by decay of **BH•** in the polymer cage (geminate recombination) with $\tau_c \approx 1$ μs. Cage recombination in turn was followed by a decay of **BH•** in the polymer bulk ($\tau_b \approx 100$ μs). Fortunately, all three processes are separated in time. Both cage and bulk reactions were decelerated by the application of magnetic field (MF) of 0.2 T by approximately 20%. Geminate recombination was fit to the first-order kinetic law, and recombination in the solvent bulk fits well to the second-order law. Both geminate recombination and recombination in the solvent bulk are predominantly a reaction between **BH•** and **R•**. It was assumed that the reaction radius ρ_{12} and a mutual diffusion coefficient D_{12} of **BH•** and **R•** are the same for the cage and bulk recombination, respectively. This led to an estimation of $\rho_{12} = 3.3$ nm and $D_{12} = 1 \times 10^{-7}$ cm^2/s. These values are discussed. We obtained activation energy, E_{act}, equal to 6 kcal/mol and 7 kcal/mol for cage decay and for recombination in the polymer bulk, respectively. These E_{act} coincide with each other within experimental error of their determination (±0.5 kcal/mol).

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This indicates the same diffusion character in the cage and in the polymer bulk. It was demonstrated that an exponential model of cage effect sufficiently describes the obtained experimental data in rubber.

1. Introduction

Diffusion and reactivity of small molecules in polymers is of considerable practical and theoretical importance, see e.g., refs 1-5. It was demonstrated that free volume of a polymer V_f essentially affects the diffusion rate of individual low MW molecules (radicals).[1,2] Low and high MW free radicals are formed during photodegradation of polymers. Polymers may have additives (residual photoinitiator, antioxidant, etc.) It is well-known that free radicals are formed as radical pairs (RPs) under photolysis. They form geminate (G-) pairs. A part of photogenerated pairs react within G-pair. The rest of free radicals separate and can recombine in the polymer bulk as free (F-) pairs. Self-termination of radicals is the only path of their decay assuming no reactions with dioxygen and additives. Polymer is a viscous media and most of the radical reactions in a polymer are diffusion-controlled. One should expect that rates of bimolecular reactions of free radicals will be determined not by individual diffusion coefficient of a radical D_1, cm^2/s but by a sum of diffusion coefficients of two radicals, $D_{12} = D_1 + D_2$. The chemical reaction takes place when one radical reaches the reaction radius of the other radical, $\rho_{12}=\rho_1+\rho_2$, where $\rho_{1(2)}$ is the van der Waals radius of a radical.[2,6-9]

In this paper we addressed the following questions: *What kinetic law the recombination of low MW and high MW radicals follow? Is diffusional movement of closely positions radicals in a polymer (G-pair) is characterized by the same* D_{12} *as mutual diffusion of spatially separated radicals (F-pairs)? Is there a difference in reactivity of G- and F-pairs of the same radicals in the same polymer matrix at the same temperature?*

To answer these questions we studied the effect of the polymer matrix on fast reactions of benzophenone (**B**) ketyl free radical **BH•** in the polymer cage (G-pairs) and in the polymer bulk

(F-pairs). Our approach is described elsewhere.[10-12] Polymers obviously decrease diffusivity of low MW species (molecules, free radicals) similar to a decrease of diffusion rates by viscous liquids.[2-6, 10-14] In the present work we continued our research, and studied temperature effect on kinetics of recombination of G- and of F-pairs. As a polymer media, we selected soft rubbery polymer. Application of an external magnetic field (MF) effects the rates of radicals in viscous media.[8,12,14] The study of recombination of radicals in G- and in F-pairs as well as the study of magnetic field effects (MFE) shed light on reactivity and diffusivity of low MW radicals in polymers. The photochemistry of **B** including its photochemistry in constrained media and relevant MFEs have been studied for decades, see e.g. refs 7,15. Thus, **B** can serve as a convenient probe of a polymer.

Specifically, the present study is devoted to the temperature effect on **BH•** recombination in G- and F-pairs in soft rubber poly(ethylene-*co*-butylene) (**E**) in order to get the activation energies of both processes. The goal was to study differences or similarities between reactions in the G- and F-pairs of the same radicals in a polymer.

2. Experimental

2.1.Materials

Briefly, **B** and solvents were obtained from Sigma-Aldrich and used as received. Characteristics of **E** from Dow are described in elsewhere.[12-16] Films were cast form solutions of **B** and a polymer **E** in chloroform on a cellophane support. The thickness of the prepared solid films was 100 μm and a concentration of **B** of 0.1 M. For more details on films preparation see ref. 12.

2.2.Devices

We used a ns laser photolysis apparatus described in details [10-12]. We used a PRA LN 1000 N_2 laser (with pulse duration of 1 ns and emission wavelength of 337 nm), operating at ≤ 10 Hz. The data presented in this paper are average values obtained by processing *at least ten kinetic curves* under the same selected conditions. All kinetic measurements were made in thermostated fused silica cell in the temperature range of 263 to 313 K. A polymer film with **B** was placed in the cell. The air was removed from the samples by prolonged evacuation. In experiments with magnetic field (MF) application, the cell was placed between the poles of a permanent magnet (magnetic flux density $B = 0.2$ T) at room temperature.

The laser flash irradiated area was only 1 mm x 2 mm. After each experiment the cell of 1 cm size was slightly moved up or down to enable irradiation of a fresh portion of the film.

3. Results and discussion

3.1.Triplet state decay

Photoexcitation of **B** with ns UV-light pulses leads to the formation of triplet state ^{3}**B***, cf. Figure 1-1. We have demonstrated elsewhere[10-14] that photoexcitation of **B** in

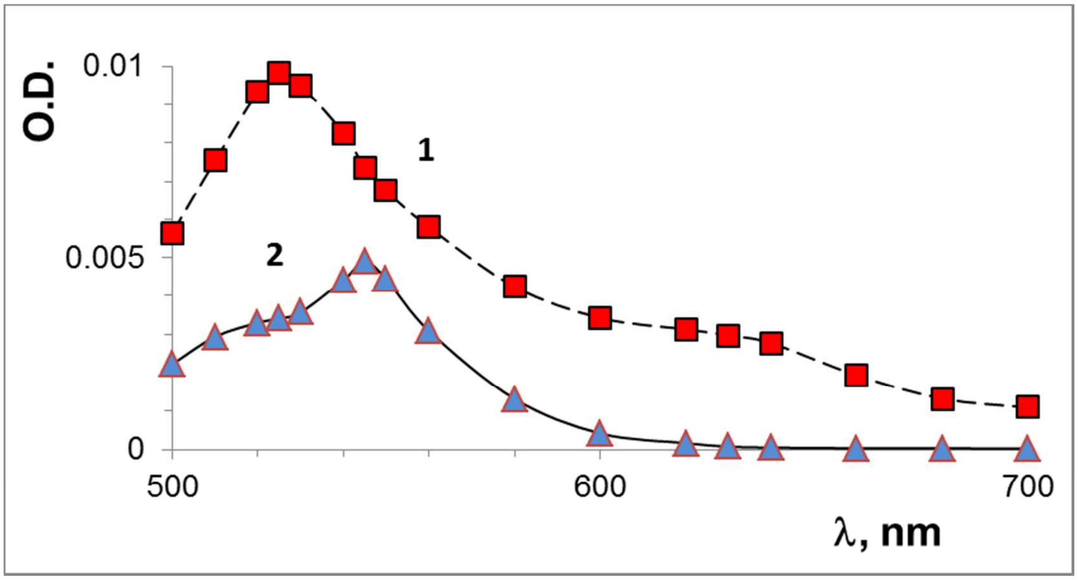
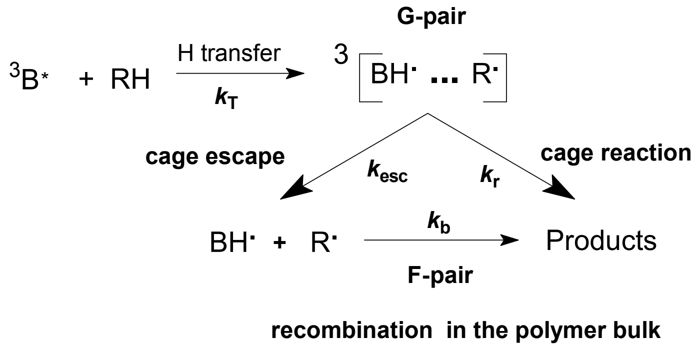


Fig. 1. Absorption spectra of transients in **E** film obtained at room temperature under laser flash photolysis of **B** in **E** with a delay after laser flash of: (1) 20 ns; (2) 0.5 ms. O.D. refers to optical density in this and subsequent Figures.

viscous media allows observation of *three processes*: decay kinetics of ^{3}**B*** which is accompanied by hydrogen abstraction from polymer, decay of the polymer cage consisting of **BH•** and a polymer radical **R•**, cf. Scheme 1 below:



Scheme 1

Recombination in the polymer bulk occurs via F-pairs: ^{1,3}[**BH•**…**R•**].

The observed characteristic ^{3}**B*** spectrum in the **E** film is similar to the well-known absorption spectrum of ^{3}**B*** in liquid hydrocarbon solvents: it has λ_{max} = 525 nm and a shoulder at 600-700 nm.[17-19] The decay kinetics of ^{3}**B*** were measured in the spectral area $\lambda > 600$ nm, where absorption by other transients is negligible,[17] cf. Figure 1. The decay kinetics of ^{3}**B*** in **E** film (Figure 2-1) fits

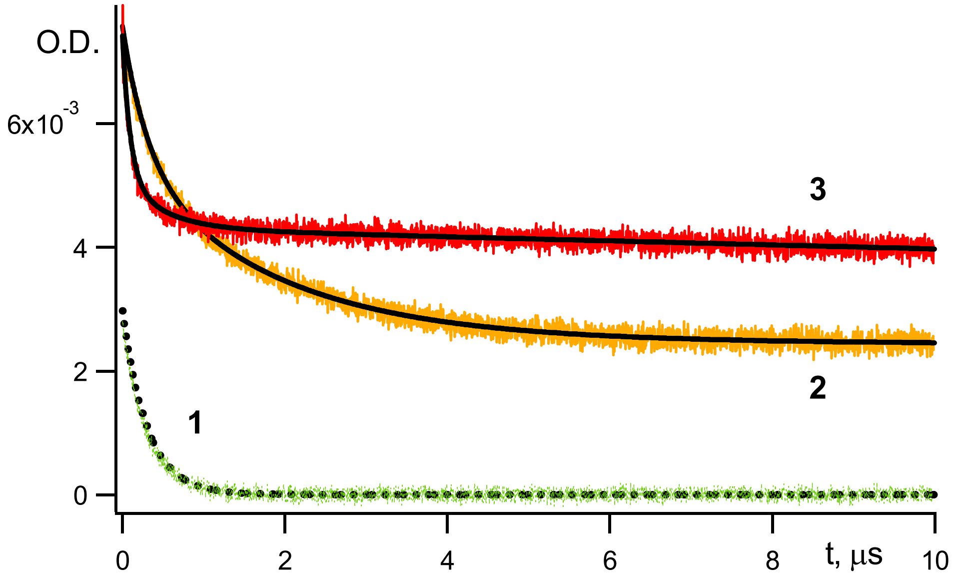


Fig. 2. Kinetics of $^{3}\mathbf{B}^{*}$ measured at λ 630 nm at 263 K obtained under laser flash photolysis of **B** in **E** film (1); decay kinetics of $^{3}\mathbf{B}^{*}$ and **BH•** measured at λ 545 nm at 263 (2) and at 313 K (3) in the same film. Solid black lines are the computer fit of experimental curves to formulas described in the text and in the Scheme 1.

well into single exponent with life-time $\tau_T \leq 300$ ns at all used temperatures. The rate constant of $^{3}\mathbf{B}^{*}$ decay k_T *and* activation energy of this process E_{actT} are presented in the Table 1 below.

We conclude that $^{3}\mathbf{B}^{*}$ behaves in **E** as it would in a liquid. Relatively short $^{3}\mathbf{B}^{*}$ life-time in **E** testifies to the high reactivity of C-H bonds in **E**, which contains tertiary C-H bonds with low bond dissociation energy.

3.2.Ketyl radical decay in the cage

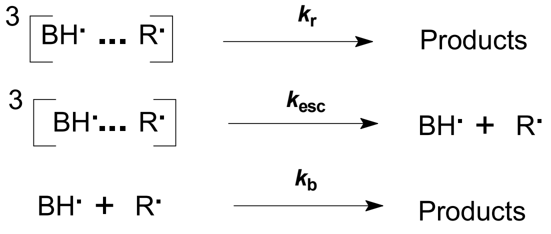
Reactions of **BH•** are presented in the Scheme 1. We imply by "recombination" here and below any bimolecular reaction between these two radicals. It should be assumed that **R•**, a radical centered on the polymer chain, is practically immobile compared with mobility of low MW species, and **BH•** escapes the cage. According to a simple exponential model of the cage of a G-pair, decay consists of two processes: recombination inside the cage (k_r, s^{-1}) and dissociation of the cage with k_{esc}, s^{-1}. cf. Scheme 1.[20,21] Radicals in the polymer bulk recombine with k_b, M^{-1}·s^{-1}, cf. Scheme 1.

Such approach that G-pair decay in two concurrent first-order processes corresponds to the exponential model of cage effect in liquid, see, e.g. refs 20,21. **BH•** and **R•**, which escaped recombination in a cage (G-pair), become "independent of each other" radicals. They recombine as F-pairs, cf. Scheme 1 above.

The ketyl radical **BH•** with its characteristic absorption maximum $\lambda_{max} = 545$ nm is observed at ~0.5μs after the laser flash, cf. Figure 1.[12, 17-19] Therefore, $^{3}\mathbf{B}^{*}$ and **BH•** can be differentiated in **E** not only by their absorption spectra (cf. above) and by the fact that the **BH•** decays much slower than ^{3}**B*** (Figures 1,2). C-centered aliphatic **R•** of a polymer matrix absorbs in the UV-region and was not observed in our experiments. The decay of **BH•** was monitored at λ_{max} = 545 nm. Comparison of the initial absorption ^{3}**B*** at λ 525 nm with that of **BH•** at λ 545 nm at 0.5 μs after laser pulse (cf. Figure 1-1, -2) demonstrate that practically all ^{3}**B*** yields **BH•.** This comparison is based on the literature data of extinction coefficients of these transients in benzene: ε_{530} = 7220 and ε_{545} = 4600 $M^{-1}\cdot cm^{-1}$ of ^{3}**B*** and **BH•**, respectively.[17-19] Thus, practically all ^{3}**B*** decays by hydrogen abstraction (Scheme 1).

Cage effect φ is defined as a fraction of **BH•** decayed in the fast cage reaction. φ were calculated by computer simulation decay reactions (Figure 2). Upon completion of cage decay kinetic curve reaches *quasi* plateau, Figure 2. The usually modest signal-to-noise ratio observed during the study of cage kinetics justifies in a sense exponential model.

We summarize observations of **BH•** decay (Figure 2 and Figure 5 below) at λ=545 nm. We started to analyze **BH•** decay at t_o= 300÷500 ns (depending upon temperature) after a laser flash. At t_o ^{3}**B*** has decayed**,** and **BH•** is the only light absorbing at λ=545 nm transient. The following reactions involving **BH•** proceed:



Scheme 2

Scheme 2 is a part of Scheme 1, cf. above. k_b-Values is known, cf. Table 1 and Section 3.3 below. Computer simulation of experimental data presented in Figure 2 wih two fitting parameters k_{esc} and k_r (each in s^{-1}, Scheme 2) allowed getting these two constants (Table 1).

Further, geminate recombination lasts till t= 2÷10 µs (Figure 2). Recombination in the solvent bulk lasts 1-2 ms, cf. Figure 5 below. Thus, one can analyze separately the first part of a curve as a first-order "fast" reaction, and the second part of the curve analyze as a second-order "slow" reaction. The obtained results coincide within their determination error (Table 1) with the results of computer simulation.

φ at 293 K in the absence and in the presence of MF is presented in the Table 1. Variation of temperature results in significant change in φ and in the k_{esc} , cf. Figures 2,3, Table 1.

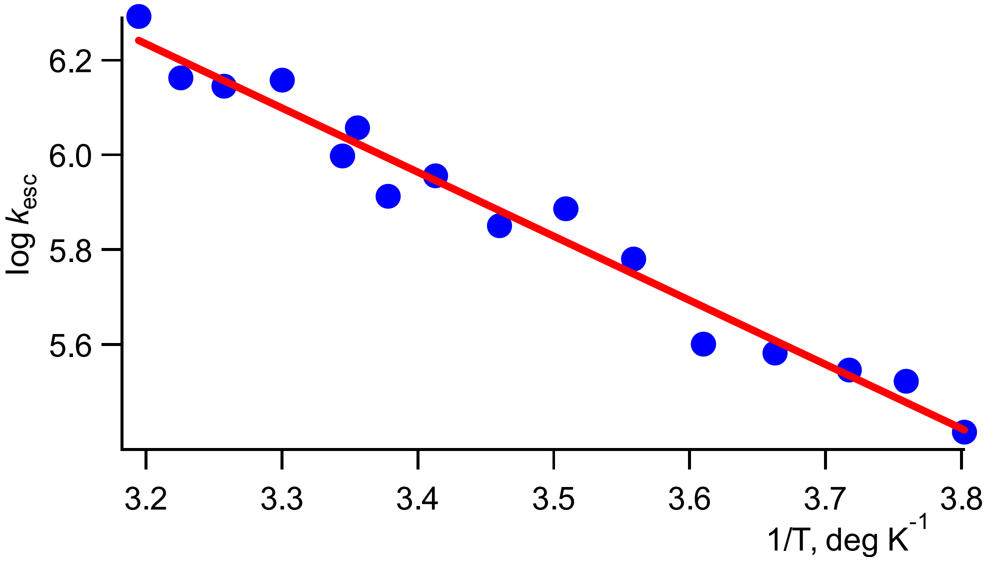


Fig. 3. Dependence of k_{esc} vs temperature in Arrhenius coordinates.

According to the exponential model, cage effect value φ is:[20,21]

$$\varphi = k_r/(k_r + k_{esc}) \qquad (1)$$

The application of MF leads to decrease of φ and of k_r up to almost three times (Table 1). The observed deceleration of cage recombination under application of moderate MF is usually observed due to hyperfine coupling mechanism (HFC) of MFE on triplet PR.[7-9,12,14] HFC in radicals of a pair mixes S-T states of RP. Application of a moderate MF makes T_+ and T_- - states of RP unavailable for mixing. That way exit of triplet RP in a solvent bulk increases or a decrease of φ is observed. [7-9,12,14] Comparative analysis of MFE on the cage recombination and recombination of non-correlated radicals was done elsewhere.[12]

Table 1

Rate constants of transients decay and a number of other parameters in Earth's magnetic field and in the external MF at 293 K, cf. the text

Parameter	$B \approx 0$	$B = 0.2$ T
$k_T \times 10^{-6}$, s^{-1} [a]	6.9	6.9
$k_{esc} \times 10^{-6}$, s^{-1} [b]	0.89	0.89
$k_r \times 10^{-6}$, s^{-1} [b]	0.31	0.11
φ [c]	0.26	0.10
$k_b \times 10^{-7}$, $M^{-1}.s^{-1}$ [a]	11	8.9
E_{actT}, kcal/mol [d]	3.8	
E_{esc}, kcal/mol [d]	5.5	-
E_r, kcal/mol [d]	0	-
E_b, kcal/mol [d]	7.0	-
E_{NO}, kcal/mol [d]	6.0	-
$D_{12} \times 10^8$, cm^2/s [e]	1	-
ρ, nm [e]	3.3	-

Determination error: ^{a} – 15%, ^{b} – 20%; ^{c} – 10%; ^{d} – ±0.5 kcal/mol;
^{e} Calculated

The fact that activation energies $E_{\mathrm{esc},}$ E_{b} (cf. below) and E_{NO} (Table 1) coincide with each other within their determination error is an indication that diffusion at short distances (G-pairs), long distances (F-pairs) and rotation of a probe in polymer have the same activation mechanism.

3.3.Decay of BH• in the polymer bulk

BH$^{\bullet}$, which escaped the cage, decays relatively slow in the polymer bulk (Schemes 1,2; Figure 4):

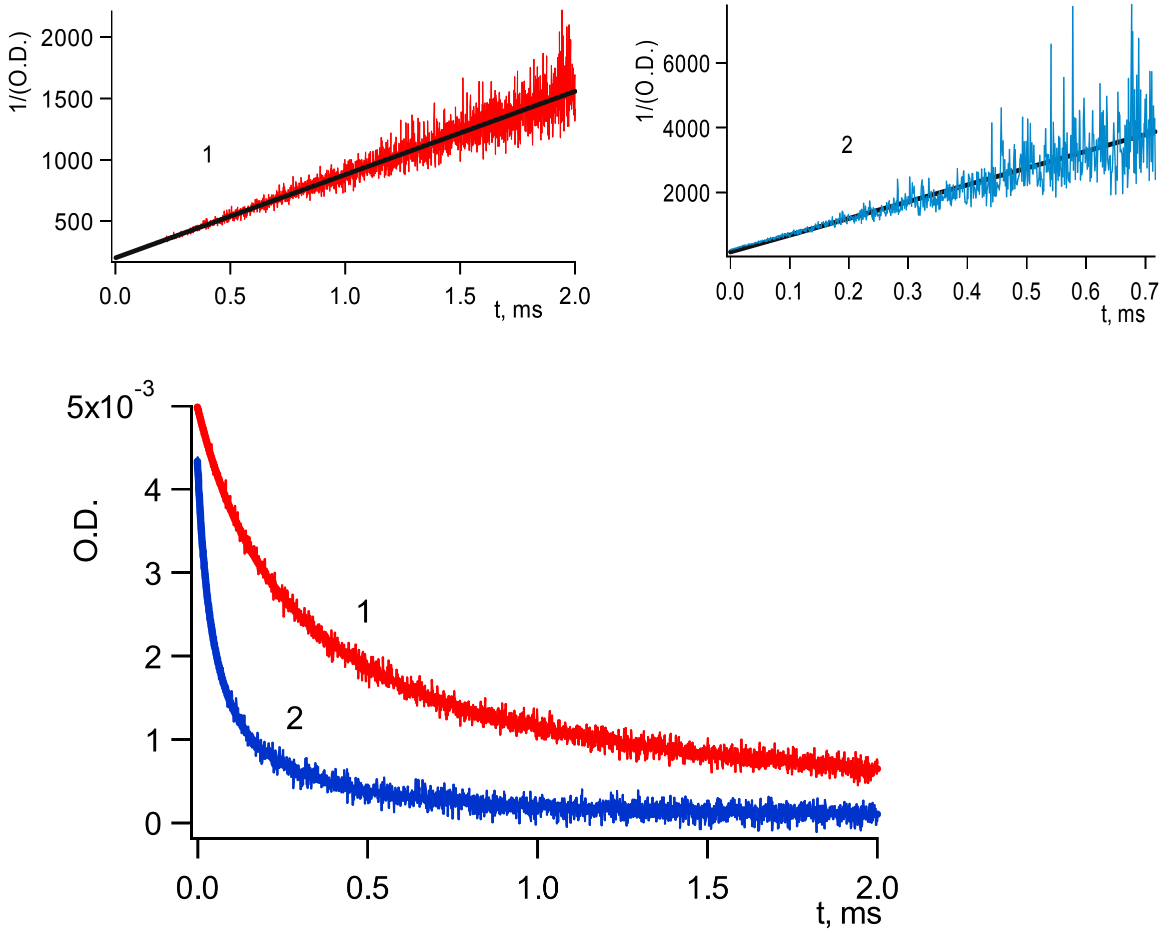


Fig. 4. Decay kinetics of **BH•** measured at λ 545 nm at times ≥ 10 μs obtained under laser flash photolysis of **B** in **E** films at 313 (1) and at 263 K (2). The top of the Figure: A fit of curves into the second-order kinetic law.

Decay kinetics fits well into the second-order kinetic law, cf. Figure 4. Table 1 presents the corresponding E_b obtained from a dependence of k_b vs T (Figure 5).

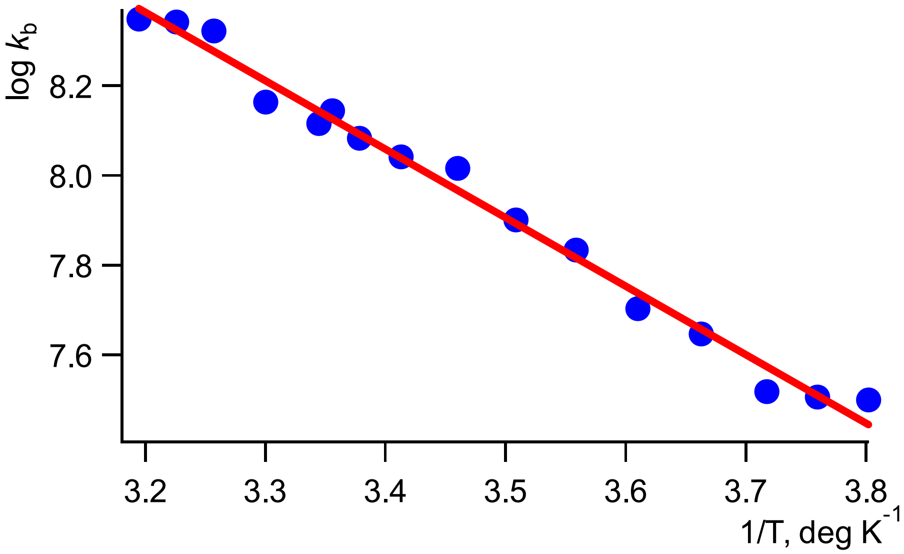


Fig. 5. Dependence of k_b vs. temperature in Arrhenius coordinates.

Retardation of both recombination in G- and F-pairs (Table 1) hints that these two processes are similar. In fact, we obtain below reactive radius ρ_{12} and a mutual diffusion coefficient D_{12} assuming that both geminate recombination and recombination in the solvent bulk are described by the same ρ_{12} and D_{12}.

3.4.Analysis of decay kinetics of G- and F-pairs in the polymer

Characteristic time of existence of molecules (radicals) as a pair or a lifetime of cage is presented by $\tau_c \sim \rho_{12}^2/D_{12}$, where ρ_{12} is a reaction radius, D_{12} is a mutual diffusion coefficient.[6,9] As an approximation we will consider RP dissociation as the first order process with

$$k_{esc} = D_{12}/\rho_{12}^2,\ s^{-1} \qquad (2)$$

Quite similar formula was suggested by Eigen:[22]

$$k_{esc} = 3D_{12}/\rho_{12}\,, \tag{3}$$

but we will use eq. 2 for our rough estimation.

Further, recombination in the solvent bulk is expected to be diffusion-controlled, and the experimental rate constant k_b should be equal to a value predicted by the well-known von Smoluchowski formula:[6,8]

$$k_b = k_{diff} = p_o 4\pi\rho_{12}D_{12}\, N_A/1000,\ M^{-1}.s^{-1} \tag{4}$$

N_A in the formula (4) is Avogadro constant; $D_{12}/cm^2/s$; reaction radius ρ_{12}/cm, p_o is spin-statistical factor in the Earths' MF.[6,8] Then:[12]

$$p_o = 0.25 + 0.75 \text{ x } 0.26 = 0.45 \tag{7}$$

where $\varphi_o = 0.26$ (Table 1). Experimental values of k_{esc} and k_b were taken from the Table 1. Eqns (2) and (4) with two unknown parameters allow getting these parameters, cf. Table 1. The obtained ρ_{12} would be too large for recombination of two low MW radicals; however we deal with recombination of **BH•** with *macroradical* **R•** . D_{12} is two orders or magnitude lower than D for low MW molecules in non-viscous liquids and such values of $D_1 \sim 10^{-7}$-10^{-8} cm^2/s were obtained in similar rubbers.[3] Estimation of the rotational correlation time of a stable nitroxyl (TEMPO) in **E** at 293 K from ESR spectra of TEMPO in **E** leads to rotational correlation time $\tau_{rot} = 1.6$ ns.[23] 1.6 ns correspond to τ_{rot} of TEMPO in the liquid with dynamic viscosity of $\eta \sim 10^3$ cP.[24] A typical value of D_1 for multiatomic low MW species at such η is $D \sim 10^{-7}$-10^{-8} cm^2/s. The calculated value of D_{12} for the present system at room temperature is of the same order of magnitude. Table 1 presents E_{NO}, which is activation energy of TEMPO rotation in **E**.

D_{12} and ρ_{12} were estimated under an assumption that the same D_{12} and ρ_{12} are the same for G- and F-pairs, cf. above. Estimated D_{12} is apparently D_1(**BH**$^\bullet$) because **R•**, which has reactive –CH•– group, is located on a polymer chain of low mobility. A possible estimation of van der Waals radius of ρ_1(**BH**$^\bullet$) is 0.4 nm[8] meaning that the ρ_2(**R•**) = ρ_{12}- ρ_1(**BH**$^\bullet$) = 2.9 nm. Relatively large ρ_2(**R•**) should be expected because **R•** is not simply a small individual radical fragment –CH•–. Adjacent CH_2 groups contribute into large effective ρ_2(**R•**).

4. Conclusions

Our previous work was devoted to G- and F-pair recombination of the same radicals in the same liquid - viscous solvent.[14] We had to assume that mutual diffusion coefficient of radicals D_{12} in the G-pair is essentially lower than that in the F-pair, cf. discussion.[8,14] Further, the exponential model of a cage effect *in liquid is, strictly speaking, wrong*.[25] However, the exponential model is often used as an approximation.[20,21] Cage recombination measured with high signal to noise ratio and reaching high conversions (high φ) allows one to notice deviation from exponential decay.[14,21] However, we observed that an *exponential model works well for the studied rubber and may work for other polymers*. Activation energies of radical recombination $E_r \approx 0$ (Table 1) are known in the fast termination.[6] In addition, it is quite possible that temperature independent intersystem crossing of triplet RP into singlet RP is the limiting stage of the process.[14] Activation energies of chemical reactions are close to each other (Table 1). That observation testifies to the fact that cage dissociation, recombination of F-pairs is determined by the viscous drag of polymer and has the same activation mechanism. In a sense, **E** performs as a viscous liquid with $\eta \sim 10^3$ cP.[14] Moreover, the studied system is simpler in terms of kinetic analysis than a studied elsewhere **B** in liquid.[14,21] We made an assumption that D_{12} and ρ_{12} are the same for G- and F-pairs. After that, using eqns (2,4) we were able to get these two values (Table 1).

Observation of *significant MFE on fast radical reactions in polymer* (Table 1) is of obvious interest. Application of moderate MF effecting such reactions in polymers should find an application in polymer stabilization.

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