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# Kinetics of radical formation and decay in photooxidation of 4-halophenols sensitized by 4-carboxybenzophenone in aqueous solutions

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Kinetics of formation and recombination of radicals formed by quenching of the triplet state of 4-carboxybenzophenone (CB) with *para*-substituted phenol derivatives $RC_6H_4OH$ (R = OMe, H, Cl, Br, I) in aqueous solutions was studied by nanosecond laser photolysis. At pH ≥ 5.4, quenching proceeds with high rate constants ($(1—3) \cdot 10^9$ L mol$^{-1}$ s$^{-1}$) through electron transfer to form the radical anion $CB^{\bullet -}$ and radical cation $RC_6H_4OH^{\bullet +}$. The latter is transformed into the phenoxyl radical within ≤10 ns. At pH ≤ 8, the $CB^{\bullet -}$ radical anion is protonated in a phosphate buffer with the rate constant increasing from $4 \cdot 10^6$ to $15 \cdot 10^6$ s$^{-1}$ with a decrease in the pH from 8 to 5.4. The yield of radicals decreases from 100 to 13% as the atomic weight of halogen in the $RC_6H_4OH$ molecule increases due to an increase in the probability of recombination of the primary triplet radical pair in the solvent cage and partial intersystem crossing in an encounter complex ($^3$CB, $RC_6H_4OH$). The effect of heavy atom is also observed in the kinetics of volume recombination of the radicals, the magnitude of effect corresponds to the acceleration of the primary recombination of the triplet radical pair.

**Key words:** 4-carboxybenzophenone, 4-halophenol, laser photolysis, triplet states, electron transfer, radical recombination, heavy atom effect.

The mechanism of photooxidation of phenols sensitized by carbonyl compounds, in particular, aromatic ketones, is being of permanent interest for researchers for more than 40 years.[1] The primary step of the process in organic solvents is the hydrogen atom transfer from the phenol OH group to the ketone triplet state. The reaction proceeds with a high efficiency and involves both nπ*- and ππ*-triplet states of ketones. Unlike saturated hydrocarbons, hydrogen atom abstraction from a phenol molecule does not require electron deficiency on the oxygen atom of the triplet state of the carbonyl compound.[1,2] The determining role belongs to a combination of the following factors: the energy characteristics of both electron and proton transfer, the ability of reactants to form hydrogen bonds, and the electron overlap of aromatic systems of the donor and acceptor.[1—5] The mechanism of hydrogen atom transfer from the phenol molecule to triplet states of ketones is interpreted as the mutually consistent electron and proton transfer in an intermediate triplet exciplex with a hydrogen bond.[1,4,5] Unlike processes in organic media, studies of quenching of triplet states of ketones with phenols in aqueous solutions are scanty.[6—9] A principal distinctive feature of the mechanism of this reaction in water is that the process can proceed only *via* electron transfer.[8,9] The direct observation of the primary quenching products of the 4-carboxybenzophenone* (CB) triplet state with a rather strong electron donor (2,4,6-trimethylphenol) in water at pH 7 using laser photolysis technique showed[8] that the primary reaction product is the radical anion $CB^{\bullet -}$, which is further transformed into a radical $CBH^{\bullet}$ upon acid-base equilibration, rather than the ketyl radical.

The quenching of triplet states of ketones with phenols affords the corresponding radicals in high yields, which are often close to 100%.[1—9] The exception can be a system involving a heavy atom (for example, Br or I).[2,6] Reasons for a decrease in the radical yield when heavy atoms are introduced into the phenol molecule were discussed from the viewpoint of acceleration of intersystem crossing in the triplet state of ketone in an encounter complex with iodo-substituted phenol (external heavy

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* According to the IUPAC nomenclature, 4-benzoylbenzoic acid.

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atom effect)[2,6] or acceleration of recombination of a triplet radical pair (RP) formed due to quenching in the solvent cage.[6,10—14] Studies of the kinetics of geminal recombination of RPs in micellar or viscous solutions showed that the introduction of heavy atoms into radicals accelerated the process.[10—14] To reveal relative contributions of these two mechanisms in a homogeneous nonviscous medium, it seems of interest to study the effect of heavy atom on the kinetics of triplet state quenching, the escape of formed radicals from the solvent cage, and the kinetics of volume radical recombination.

In this work, the kinetics of quenching of the triplet state of a CB molecule with *para*-substituted phenols $RC_6H_4OH$ (R = OMe, H, Cl, Br, I) in aqueous solutions at different pH values and the kinetics of formation and decay of the accompanying radicals were studied by nanosecond laser photolysis. The direct observation showed that the quenching process proceeds in water at any pH *via* electron transfer to form the radical anion $CB^{\bullet-}$, which is protonated at pH ≤ 8 producing a ketyl radical $CBH^{\bullet}$. The quantum yields of radicals of different nature and their decay rate constants were measured. The heavy atom effect on the kinetics of volume radical recombination was found and compared with a similar effect on the quantum yield of the radicals.

## Experimental

Absorption spectra and the formation and decay kinetics of intermediates were recorded using a nanosecond laser photolysis technique.[10—14] A PRA LN 1000 nitrogen laser working in a frequency mode of 10 Hz was used as an excitation source (pulse duration 1 ns, excitation wavelength 337 nm). Kinetic curves were scanned and averaged over 16—128 laser pulses using a Biomation 6500 high-performance analog-to-digital converter (USA) attached to a personal computer based on a Pentium processor (100 MHz). Each kinetic curve contained 1024 points, the distance between which varied from 2 ns to 1 μs depending on the process duration. The data presented are the average values obtained by processing of at least ten kinetic curves under the conditions indicated. Dissolved oxygen was removed by evacuation. All measurements were carried out in a quartz cell with an optical path length of 2 mm at 20 °C.

Phenols (Aldrich) were purified by sublimation *in vacuo*. 4-Carboxybenzophenone was recrystallized from ethanol.

## Results and Discussion

**Decay kinetics of triplet state of 4-carboxybenzophenone in the phenol-free aqueous buffer and alkaline solutions.** Pulse excitation of solutions of CB (1—4 mmol $L^{-1}$) in alkaline aqueous solution ([NaOH] = 0.15 mol $L^{-1}$) or in a phosphate buffer at pH 5.4—8 (p$K_a$(CB) = 4.5 and, hence, CB exists in solution as anion at these pH) induces during a laser pulse a triplet state $^3$CB characterized by the known[15,16] absorption spectrum with a maximum at ~540 nm (Fig. 1). The decay kinetics of the $^3$CB state obeys a first-order equation with rate constants of ~$8 \cdot 10^5$ and $3 \cdot 10^5$ $s^{-1}$ in alkaline and buffer solutions, respectively. These values substantially exceed $6 \cdot 10^4$ $s^{-1}$, which value was obtained in neat water or in an aqueous solution of $NaClO_4$ (6 mol $L^{-1}$)[15,16] due to the quenching of the $^3$CB state with inorganic anions $OH^-$, $HPO_4^{2-}$, and $H_2PO_4^-$.[16,17]

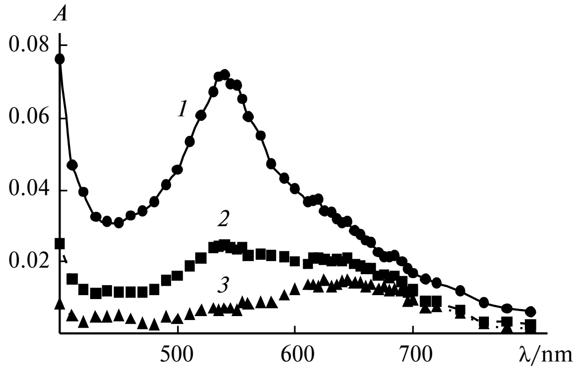


**Fig. 1.** Differential absorption spectra of intermediate products obtained by laser photolysis of deaerated aqueous alkaline ([NaOH] = 0.15 mol $L^{-1}$) solutions of CB (4 mmol $L^{-1}$) 0.2 (*1*), 2 (*2*), and 8 μs (*3*) after laser pulse.

After $^3$CB disappeared, the absorption of longer-lived intermediates is observed: $CB^{\bullet-}$ (p$K_a$ = 8.2) and radicals $CBH^{\bullet}$ (in buffer solutions), whose absorption spectra have maxima at 650 and 570 nm, respectively[15,16] (see Fig. 1). The quantum yields of the $CB^{\bullet-}$ and $CBH^{\bullet}$ radicals estimated from the 100% yield of the $^3$CB state and molar absorption coefficients (ε = $6.25 \cdot 10^3$, $7.7 \cdot 10^3$, and $5.2 \cdot 10^3$ L $mol^{-1}$ $cm^{-1}$ for $^3$CB, $CB^{\bullet-}$, and $CBH^{\bullet}$ at λ = 540, 650, and 570 nm, respectively[15,16]) are 0.15 and 0.22, respectively. These values are much higher than those ≤0.08 observed in neat water or in the presence of $NaClO_4$ (6 mol $L^{-1}$).[15,16] The interaction of $^3$CB with inorganic anions $OH^-$, $HPO_4^{2-}$, and $H_2PO_4^-$ is accompanied by the formation of the corresponding radicals with a minor quantum yield.[16,17] The decay kinetics of the $CB^{\bullet-}$ and $CBH^{\bullet}$ radicals obeys a second-order law with the rate constants $k_r = 1.1 \cdot 10^7$ and $1.2 \cdot 10^9$ L $mol^{-1}$ $s^{-1}$ in alkaline and buffer solutions, respectively (obtained from the experimental values $k_r/\varepsilon l$, where $l$ is the optical path length).

No noticeable changes in the decay kinetics and quantum yields of intermediates are observed on going from $H_2O$ to $D_2O$. The isotope effects in reactions of electron or hydrogen atom transfer from inorganic anions to $^3$CB and recombination of radicals $CB^{\bullet-}$ and $CBH^{\bullet}$ are not higher than 1.1.

The decay of $^3$CB, $CB^{\bullet-}$, and $CBH^{\bullet}$ is accelerated on going from deaerated to air-saturated solutions. The corresponding bimolecular rate constants of reactions of these intermediate species with molecular oxygen in an aque-

**Table 1.** Rate constants of quenching of the triplet state of 4-carboxybenzophenone with phenols 4-$RC_6H_4OH$ ($k_q$), decay of 4-carboxybenzophenone radical anions in buffer solutions ($k_-$), and radical recombination ($k_R$), quantum yields of the $CB^{\bullet -}$ ($\varphi_{CB^{\bullet -}}$) and $CBH^{\bullet}$ ($\varphi_{CBH^{\bullet}}$) radicals, and probabilities of recombination of primary and secondary triplet radical pairs ($W_1$ and $W_2$, respectively)*

| R | pH | $k_q \cdot 10^{-9}$ /L mol$^{-1}$ s$^{-1}$ | $\varphi_{CB^{\bullet -}}$ | $\varphi_{CBH^{\bullet}}$ | $k_- \cdot 10^{-6}$ /s$^{-1}$ | $k_R \cdot 10^{-9}$ /L mol$^{-1}$ s$^{-1}$ | $W_1$ | $W_2$ |
|---|---|---|---|---|---|---|---|---|
| | | | % | | | | | |
| H | 5.4 | 2.1 | 75 | 92 | 15 | 2.8 | — | — |
| H | 5.9 | 2.0 | 98 | 110 | 15 | 2.2 | — | — |
| H | 7.2 | 1.1 | 100 | 98 | 9.7 | 1.9 | — | — |
| H | 7.2** | 1.1 | 85 | 92 | 4.7 | 1.7 | — | — |
| H | 8.0 | 1.1 | 78 | 110 | 4.2 | 1.9 | — | — |
| OMe | 7.2 | 2.0 | 81 | 97 | 10 | 1.8 | — | — |
| Cl | 7.2 | 1.8 | 73 | 90 | 9.7 | 2.1 | 0.0 | 0.0 |
| Br | 7.2 | 2.2 | 41 | 48 | 10 | 2.9 | 0.4±0.2 | 0.1±0.1 |
| I | 7.2 | 3.2 | 18 | 17 | 11 | 5.8 | 0.7±0.1 | 0.6±0.2 |
| H | 13 | 2.4 | 110 | — | — | 1.8 | — | — |
| OMe | 13 | 2.3 | 110 | — | — | 2.0 | — | — |
| Cl | 13 | 2.4 | 110 | — | — | 1.8 | 0.0 | 0.0 |
| Br | 13 | 2.6 | 55 | — | — | 2.9 | 0.5±0.2 | 0.2±0.1 |
| I | 13 | 2.7 | 13 | — | — | 6.5 | 0.9±0.1 | 0.9±0.2 |

* The relative errors of determination of the rate constants and quantum yields are ±10%. The errors of calculation of $W_1$ and $W_2$ were estimated from the errors of determination of the rate constants and quantum yields.

** In $D_2O$ solution.

ous solution are about $1 \cdot 10^9$ L mol$^{-1}$ s$^{-1}$, which values were estimated from the $O_2$ concentration in air-saturated water ($2.8 \cdot 10^{-4}$ mol L$^{-1}$).

**Quenching of the 4-carboxybenzophenone triplet state with phenols in aqueous buffer solutions at pH ≤ 8.** A successive increase in the $RC_6H_4OH$ concentration in buffer solutions is accompanied by an increase in the rate constant of $^3$CB decay and the yield of comparatively long-lived radicals $CBH^{\bullet}$ (only exception is 4-iodophenol). The corresponding quenching rate constants ($k_q$) and quantum yields of $CBH^{\bullet}$ radicals ($\varphi_{CBH^{\bullet}}$) are given in Table 1. However, at rather high concentrations of a quenching agent, when the lifetime of the $^3$CB state becomes <100 ns, relatively short-lived radicals $CB^{\bullet -}$ are formed first in parallel with the disappearance of $^3$CB (Fig. 2). The quantum yield of $CB^{\bullet -}$ formation ($\varphi_{CB^{\bullet -}}$) almost coincides with $\varphi_{CBH^{\bullet}}$ (see Table 1). The $CBH^{\bullet}$ radicals are formed in parallel to the disappearance of $CB^{\bullet -}$ due to acid-base equilibration.

The kinetics of $CB^{\bullet -}$ decay and $CBH^{\bullet}$ formation obeys the first-order equation with rate constants $k_-$ (see Table 1), whose values depend rather weakly on pH and exceed similar values in a buffer-free water by several orders of magnitude ($7 \cdot 10^5$, $8 \cdot 10^4$, and $2 \cdot 10^4$ s$^{-1}$ at pH 5, 6, and 7, respectively).[18] It is most likely that $CB^{\bullet -}$ is protonated in a buffer solution mainly due to the interaction with anions $H_2PO_4^-$ and $HPO_4^{2-}$ rather than with water molecules and cations $H_3O^+$, as it occurs in a buffer-free water.[18] The reaction of $CB^{\bullet -}$ with $H_2PO_4^-$ and $HPO_4^{2-}$ is characterized by a considerable isotope effect: transition from solutions in $H_2O$ to $D_2O$ in which the corresponding anions are completely deuterated is accompanied by a 2.1-fold decrease in $k_-$ (see Table 1). The resulting value of the kinetic isotope effect corresponds to the primary isotope effect and indicates that the proton transfer is the rate-determining step of protonation.[19]

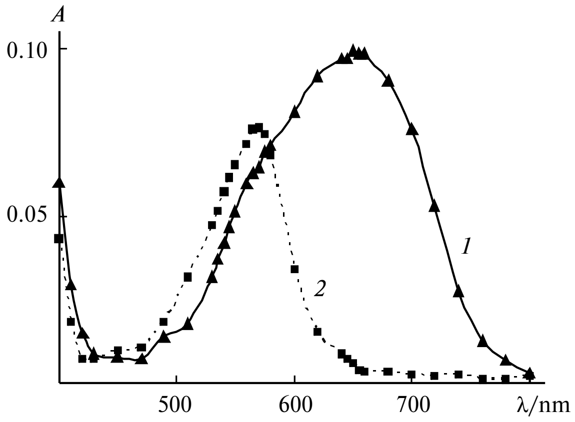


**Fig. 2.** Differential absorption spectra of intermediate products obtained by laser photolysis of deaerated aqueous buffer solutions of CB (pH 7.2, 4 mmol L$^{-1}$) in the presence of phenol (0.1 mol L$^{-1}$) 0.02 (*1*) and 1 μs (*2*) after laser pulse.

The measured $k_q$ values are only insignificantly (by 2—6 times) lower than the diffusion limit ($k_d = 8RT/3\eta = 6.5 \cdot 10^9$ L mol$^{-1}$ s$^{-1}$, where $\eta$ is the viscosity of water) and quenching rate constants of the triplet state of unsubstituted benzophenone with phenol and 4-methoxyphenol in a phosphate buffer at pH 8 in the presence of 0.5—2 vol.% methanol or with 4-methoxyphenol in water—acetonitrile mixtures ((4—5) $\cdot$ $10^9$ L mol$^{-1}$ s$^{-1}$).**[2,6,9]** The reduction potential of $^3$CB is even somewhat higher than that of the triplet state of unsubstituted benzophenone (1.83 and 1.69 eV *vs.* normal hydrogen electrode, respectively).**[9,16]** The abstraction of an electron from 4-methoxyphenol by these triplets (oxidation potential 1.23 eV *vs.* normal hydrogen electrode) is strongly exothermic and should be diffusionally controlled.**[9]** It can be assumed that the lowered $k_q$ value for $^3$CB compared to that of unsubstituted benzophenone is caused by differences in the diffusion coefficients due to the presence of the carboxyl group in $^3$CB.

The $k_q$ value depends on the composition of a buffer solution, increasing twofold when pH decreases from 8.0 to 5.4 (see Table 1). The isotope effect is virtually absent, which is characteristic of both electron transfer and diffusionally controlled reactions.**[1]** At the same time, when the electron-releasing ability of phenol decreases (on going from 4-methoxyphenol to unsubstituted phenol and further to 4-chlorophenol), $k_q$ first decreases, as expected for electron transfer reactions, but then increases, which can indicate a certain role of prototropic interactions.**[1,3,20]** This substituent effect is more pronounced than that for unsubstituted benzophenone in a phosphate buffer in the presence of 0.5—2 vol.% methanol but is much weaker than in water—acetonitrile mixtures (50 vol.%).**[6,9]**

The $k_q$ value increases substantially with an increase in the atomic weight of a halogen atom in the $RC_6H_4OH$ molecule (see Table 1, going from 4-chloro- to 4-bromo- and 4-iodophenol). This indicates the appearance of a new channel of $^3$CB quenching. In addition to electron transfer, intersystem crossing is accelerated (external heavy atom effect) in an encounter complex of $^3$CB with $RC_6H_4OH$ containing a heavy atom. A comparison of $k_q$ for 4-chloro- and 4-iodophenols shows that the expected rate constant for quenching with 4-iodophenol due to the heavy atom is ~1 $\cdot$ $10^9$ L mol$^{-1}$ s$^{-1}$. The estimated value is much higher than the value expected for the quenching of the benzophenone triplet state with iodo-substituted toluenes**[21]** or with the same phenols in benzene**[2]** and water containing 50 vol.% acetonitrile.**[6]**

Phenoxyl radicals $RC_6H_4O^\bullet$ are formed simultaneously with the decay of $^3$CB and formation of radicals $CB^{\bullet-}$. The spectra of $RC_6H_4O^\bullet$ contain bands at $\lambda$ = 400, 415, 420, 430, and 480 nm, which are characteristic of the unsubstituted phenoxyl radical and its analogs with R = OMe, Cl, Br, and I in the *para*-position, respectively.**[6]** A comparison of the initial absorbances of $RC_6H_4O^\bullet$ and $CB^{\bullet-}$, taking into account their molar absorption coefficients, shows that these radicals are formed in equimolar amounts.**[6]** It is reasonable to assume that the primary product of electron transfer from $RC_6H_4OH$ to $^3$CB is a phenol radical cation $RC_6H_4OH^{\bullet+}$ (p$K_a$($RC_6H_4O^\bullet$) $\le -1$), which is deprotonated within $\le$10 ns (the expected time is 2 ps).**[22,23]**

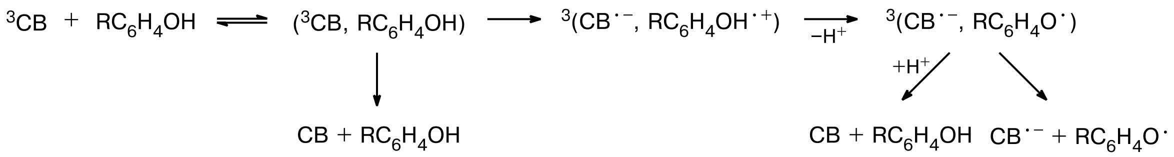
The quantum yield of radicals in buffer solutions and other media for the systems containing no heavy atoms is close to 100% (see Table 1).**[1,2,6]** The introduction of a heavy atom into a phenol molecule is accompanied by a decrease in the yield of radicals, and the heavy atom effect substantially exceeds the value expected on the basis of the external heavy atom effect on the quenching constant of $^3$CB. This discrepancy is caused by the external heavy atom effect and also by the internal heavy atom effect in the triple RP in a solvent cage. The latter appears as the acceleration of its geminal recombination in the presence of heavy atoms in radicals.**[6,10—14]** The values for probability of this recombination ($W_1$) calculated from the yields of radicals in systems with halogen-substituted phenols taking into account the external heavy atom effect

$$W_1 = 1 - k_q\varphi_{CBH^\bullet}/k_q{}^0\varphi^0{}_{CBH^\bullet},$$

where $k_q{}^0$ and $\varphi^0{}_{CBH^\bullet}$ are the quenching rate constant and yield of radicals $CBH^\bullet$ for $^3$CB quenching by 4-chlorophenol, respectively, are presented in Table 1. It was assumed that $W_1$ = 0 in the case of 4-chlorophenol, because the radical yields in this system almost coincide with similar values in systems without heavy atoms (see Table 1).

Thus, the process of $^3$CB quenching by phenols in buffer aqueous solutions can be presented by Scheme 1, where ($^3$CB, $RC_6H_4OH$) is the encounter complex, and ($CB^{\bullet-}$, $RC_6H_4OH^{\bullet+}$) and ($CB^{\bullet-}$, $RC_6H_4O^\bullet$) are the corresponding radical pairs in the solvent cage. The characteristic time for dissociation of the encounter complex

**Scheme 1**



CB is 4-carboxybenzophenone

of molecules of two reactants in water (estimated in the framework of the theory of diffusion-controlled reactions as $\pi\eta\sigma^3/2k_BT$ = 200 ps, where $\sigma$ = 0.7 nm is the sum of the van der Waals radii of the reactants, and $k_B$ is the Boltzmann constant) is by two orders of magnitude longer than the deprotonation time of $RC_6H_4OH^{\bullet+}$. The recombination can be assumed to occur in the relatively long-lived RP ($CB^{\bullet-}$, $RC_6H_4O^{\bullet}$). The heavy atom effect increases substantially with an increase in the solvent viscosity, for instance, on going to micellar or viscous solutions.[6,10–14,24]

The exchange interaction between the RP radicals in the solvent cage, where they are close to each other (contact RPs), can be rather high. Therefore, intersystem transitions in contact RPs occur, as in triplet molecules, due to the corresponding spin-orbital interaction in an RP, which can be considered as a quasi-molecule. The two main mechanisms of recombination of triplet contact RPs are discussed in literature: transition to the RP singlet state followed by recombination or transition directly to recombination products bypassing the RP singlet state.[14,25–27] If RPs recombine *via* electron transfer, then an advantage of the second mechanism is suggested (so-called intersystem electron transfer), which is explained by the selection rule on symmetry.[25–27] The ($CB^{\bullet-}$, $RC_6H_4O^{\bullet}$) pair recombines, most likely, *via* intersystem electron transfer followed by $RC_6H_4O^-$ anion protonation.

**Quenching of the triplet state of 4-carboxybenzophenone with phenolate anions in aqueous alkaline solutions.** The $k_q$ values obtained for the quenching of $^3$CB with the phenolate anions $RC_6H_4O^-$ in alkaline aqueous solutions depend rather weakly on the structure of these anions (see Table 1). Phenolate anions are much stronger electron donors than the starting phenols (difference in oxidation potentials is ≥0.7 V).[9] This accelerates the electron transfer in the encounter complex between the reactants on going from neutral to alkaline solutions and decreases the relative contribution of the reaction channel due to the external heavy atom effect.

The quenching of $^3$CB with phenolate anions in alkaline aqueous solutions in systems containing no heavy atoms produces radicals $CB^{\bullet-}$ and $RC_6H_4O^{\bullet}$ in ~100% yield (see Table 1). As expected, the heavy atom effect on the yield of radicals in alkaline and buffer solutions coincides within the experimental error, because this effect is observed in the same RPs $^3$($CB^{\bullet-}$, $RC_6H_4O^{\bullet}$).

**Kinetics of bimolecular recombination of radicals formed by quenching of the triplet state of 4-carboxybenzophenone with phenols and phenolate anions.** The kinetics of $CB^{\bullet-}$ or $CBH^{\bullet}$ decay in alkaline or buffer aqueous solutions obeys a second-order law with rate constants $k_R$ (see Table 1), whose values exceed $k_r$, *i.e.*, the recombination rate constants of the same radicals formed by the reaction of $^3$CB with inorganic anions under the same experimental conditions but in the absence of phenols in solutions. The time dependence of the concentration of the $RC_6H_4O^{\bullet}$ radicals is also described by a hyperbolic function (Fig. 3). In this case, the corresponding rate constants exceed, as a rule, $k_R$ but no more than by 30%. The main channel of radical decay is, most likely, the recombination of $CB^{\bullet-}$ or $CBH^{\bullet}$ with $RC_6H_4O^{\bullet}$ in alkaline or buffer solutions, respectively.

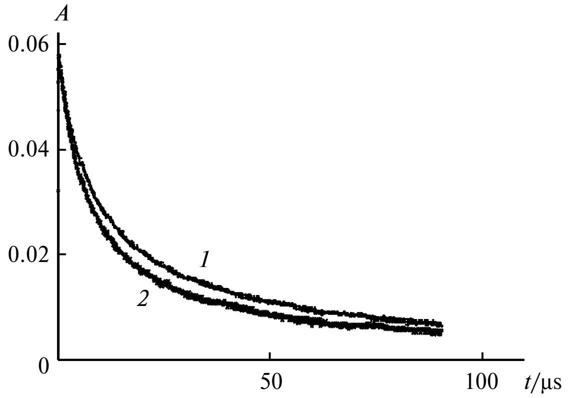


**Fig. 3.** Decay kinetics of intermediate products absorbing at λ = 415 (*1*) and 570 nm (*2*) during laser photolysis of deaerated aqueous solutions of CB (pH 7.2, 3 mmol $L^{-1}$) in the presence of 4-methoxyphenol (0.02 mol $L^{-1}$). The curves obtained by approximation using the second-order equation are superimposed on the experimental curves.

In systems without heavy atoms, the $k_R$ values depend weakly on the nature of substituents in $RC_6H_4O^{\bullet}$ and are close to $k_d/4$ (see Table 1), *i.e.*, the reaction is diffusion-controlled taking into account the statistical factor, because only the radicals that form singlet RPs upon collision recombine.[10–14] The kinetic isotope effect for OH group deuteration in $CBH^{\bullet}$ is insignificant. As for the quenching reaction, the radical recombination rate constant in buffer solutions increases insignificantly with a decrease in pH.

The introduction of heavy atoms as substituents into the $RC_6H_4O^{\bullet}$ radicals is accompanied by a substantial increase in the recombination rate constant (see Table 1). When the system contains heavy atoms, a new reaction channel appears: recombination of radicals that form a triplet RP upon collision and, therefore,

$$k_R = k_d(1 + 3W_2)/4,$$

where $W_2$ is the probability of recombination of triplet RPs formed due to random collisions of radicals. The $W_2$ values calculated from the difference in the $k_R$ values in the systems with halogen-substituted $RC_6H_4OH$ under assumption that $W_2 = 0$ for 4-chlorophenol are presented in Table 1.

The $W_2$ values coincide with experimental error with the $W_1$ values. The heavy atom effects on the recombination of the primary and secondary RPs are close in value even when the primary RP is ($CB^{\bullet-}$, $RC_6H_4O^{\bullet}$) and the secondary RP is ($CBH^{\bullet}$, $RC_6H_4O^{\bullet}$). This can indicate, most likely, that electron transfer is the rate-determining step in both cases. It is of interest to compare the heavy atom effects on the recombination of the primary and secondary RPs, because the spin-orbital interactions have a pronounced anisotropic character and depend substantially on the mutual orientation of radicals in the RP.[25] Coincidence of these effects indicates the recombination of thermodynamically "relaxed" primary RPs that do not differ from the secondary RPs.

Thus, the distinctive feature of phenol photooxidation sensitized by carbonyl compounds in water is that the primary event is electron transfer to the triplet state of a photosensitizer. In this case, prototropic interactions between reactants that play a certain role in organic media are insignificant in water. A decrease in the reaction energy due to the solvation of the reactants with water molecules, in particular, due to prototropic interactions with water, allows, most likely, the "classical" outer-sphere electron transfer to occur, which requires no specific orientation of the reactants in the encounter complex. The heavy atom effect is observed on the rate constant of triplet state quenching with phenols, quantum yield of radicals, and recombination rate constant. The study of various heavy atom effects for a combination of forward and backward reactions occurring during sensitized photooxidation provides helpful information on the mechanism and dynamics of processes involving excited states and radicals.

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