Laser flash photolysis study of the phase transition effect on the kinetics of triplet-triplet annihilation of tetraphenylporphine in *n*-decanol

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The kinetics of triplet-triplet annihilation of tetraphenylporphine (TPP) in *n*-decanol was studied by nanosecond laser flash photolysis with monitoring of the transient absorption and concomitant delayed fluorescence in the temperature range from 100 to −100 °C. The freezing of the solution results in more than tenfold acceleration of the process within the same reaction mechanism. It is supposed that the phase transition is accompanied by the concentration of the TPP molecules in defect regions of the polycrystalline structure of the frozen alcohol. These domains have a homogeneous nature and are characterized by a high molecular mobility.

Key words: laser photolysis, triplet-triplet annihilation, tetraphenylporphine, *n*-decanol, phase transition.

Phase transitions from the liquid to solid state are usually accompanied by a substantial restriction of the molecular mobility and a dramatic retardation of bimolecular processes. However, in many cases where aqueous solutions of hydrophobic organic substances were frozen, acceleration rather than retardation of bimolecular reactions between dissolved organic reactants was found.[1–4] It has been assumed[5] that during ice crystal formation the molecules of dissolved organic substance can be concentrated in the space between microcrystals, which facilitates, in particular, aggregation. However, it has been reported[6] that the concentration itself is not enough for quantitative description of the influence of freezing on hydrolytic reactions. Similar effects in organic solvents are poorly studied. For example, it has been shown[7] that transition from liquid to solid *n*-decane is accompanied by the acceleration of photoisomerization due to, most likely, an increase in the free volume of the medium during phase transition. Numerous studies of the delayed fluorescence (DF) that appears during bimolecular triplet-triplet annihilation (TTA) in solids are available,[8] but the mechanism of this phenomenon remains unclear.

In this work, we studied the kinetics of TTA of tetraphenylporphine (TPP) in *n*-decanol (DC) in the temperature range from 100 to −100 °C by direct monitoring with the use of nanosecond laser photolysis, recording both the transient absorption and delayed fluorescence, and found a substantial acceleration of the process upon freezing of the solution. TTA is a well-studied bimolecular photophysical process, which in most cases is controlled by diffusion and easily performed under intense laser irradiation. The TTA kinetics can be monitored by the concentration of triplets and also by the characteristic DF because the general mechanism of TTA (Scheme 1) includes (with the spin-statistical weight 1/9) triplet-triplet energy transfer to form the excited singlet state.[8]

Scheme 1

$$
\begin{array}{llll}
\mathrm{T} + \mathrm{T} \longrightarrow {}^{1}(\mathrm{T,T}) & \longrightarrow \mathrm{S}_0 + \mathrm{S}_1 & & (k_{\mathrm{TTA}}/9) \\
\mathrm{T} + \mathrm{T} \longrightarrow {}^{3}(\mathrm{T,T}) & \longrightarrow \mathrm{S}_0 + \mathrm{T} & & (k_{\mathrm{TTA}}/3) \\
\mathrm{S}_1 \longrightarrow \mathrm{S}_0 + h\nu & & & (k_{\mathrm{fl}}) \\
\mathrm{S}_1 \longrightarrow \mathrm{T} & & & (k_{\mathrm{isc}})
\end{array}
$$

S_0 is ground singlet state,
S_1 is excited singlet state,
T is excited triplet state,
k_{fl} is radiative transition (fluorescence) rate constant,
k_{isc} is intersystem crossing rate constant.

Experimental

The transient absorption spectra and decay kinetics of intermediates were studied by a laser flash photolysis technique with a dye laser (λ = 415 nm, pulse duration 0.5 ns, energy density on the sample ≤30 mJ m^{-2}) pumped by an N_2 laser.[9] The solution under study was placed in a 1-mm cell. The exciting laser beam and light from a monitoring lamp were directed at an angle of ~90° to the plane of the cell with a divergence of 5°. Fluorescence was detected from the side of the exciting pulse at an angle of 70°. Kinetic curves were averaged by 128 laser flashes.

n-Decanol (reagent grade) was additionally purified by zone smelting and freezing to remove admixtures with a lower freezing temperature. The phase transition of purified DC from

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the liquid to polycrystalline state occurred at 7 °C. TPP was purified by recrystallization from DC. The lifetime of ^{3}TPP in a saturated (~$1 \cdot 10^{-4}$ mol L^{-1} at 20 °C) deoxygenated solution of the thus purified TPP in DC, under the conditions of weak laser pumping, was at least 0.5 ms. Air was removed from the samples by evacuation. The temperature of the samples was measured by a thermocouple.

Results and Discussion

The photoexcitation of TPP ($1 \cdot 10^{-4}$ mol L^{-1}) in liquid DC results in the formation of ^{3}TPP with the characteristic absorption spectrum with a maximum at ~440 nm.[10] A comparison of the maximum transient absorbance at 440 nm (0.3) measured immediately after a laser pulse under intense laser pumping to the absorbance of the initial solution at the Soret band maximum at 416 nm (3.5) shows (taking into account the known extinction coefficients) that up to 50% TPP in the reaction zone is transformed into the triplet state under the experimental conditions.[10] The decay of ^{3}TPP in the deoxygenated solution under strong laser pumping occurs with a characteristic time of 100 μs and rigidly follows the second-order law (Fig. 1). The contribution of monoexponential deactivation occurring with a characteristic time ≥0.5 ms under strong laser pumping is negligible. According to the kinetic Scheme 1,

$$-\mathrm{d}[\mathrm{T}]/\mathrm{d}t = (2/9 + 1/3)k_{\mathrm{TTA}}[\mathrm{T}]^2 - k_{\mathrm{ic}}[\mathrm{S}_1], \qquad (1)$$

$$-\mathrm{d}[\mathrm{S}_1]/\mathrm{d}t = -(1/9)k_{\mathrm{TTA}}[\mathrm{T}]^2 + [\mathrm{S}_1]/\tau_s. \qquad (2)$$

Here τ_s is the lifetime of S_1 ($\tau_s = k_{\mathrm{fl}} + k_{\mathrm{ic}}$), which is 12 ns for TPP in DC. Since τ_s is substantially shorter than the lifetime of ^{3}TPP under the experimental conditions, the steady-state approximation $\mathrm{d}[\mathrm{S}_1]/\mathrm{d}t = 0$ is acceptable. Then the effective rate constant of ^{3}TPP decay (k_{eff}) can be calculated by the formula

$$k_{\mathrm{eff}} = (5 - \varphi_{\mathrm{T}})k_{\mathrm{TTA}}/9, \qquad (3)$$

where $\varphi_{\mathrm{T}} = k_{\mathrm{ic}}\tau_s$ is the quantum yield of ^{3}TPP. The k_{eff} is $2.5 \cdot 10^8$ L mol^{-1} s^{-1} at 20 °C, which corresponds to $k_{\mathrm{TTA}} = 5.1 \cdot 10^8$ L mol^{-1} s^{-1} ($\varphi_{\mathrm{T}} = 0.6$),[10] coinciding with the rate constant of the diffusion-controlled reaction (for DC at 20 °C, viscosity (η) is 13 cP[11] and $k_{\mathrm{diff}} = 8RT/3000\eta = 5 \cdot 10^8$ L mol^{-1} s^{-1}).

TTA is accompanied by DF, whose spectrum almost coincides with that of fast fluorescence and contains two pronounced bands at 650 and 720 nm.[10] The intensity of DF ($I_{\mathrm{DF}}(t)$) is proportional to the squared concentration of ^{3}TPP (see Fig. 1), which indicates that it appears during TTA. According to Scheme 1, in the steady-state approximation the DF kinetics is described by the equation

$$I_{\mathrm{DF}}(t) = k_{\mathrm{fl}}[\mathrm{S}_1] = \varphi_{\mathrm{fl}}(1/9)k_{\mathrm{TTA}}[\mathrm{T}]^2 = \\ = I_{\mathrm{DF}}(t = 0)/(1 + k_{\mathrm{eff}}[\mathrm{T}]_0 t)^2, \qquad (4)$$

where $\varphi_{\mathrm{fl}} = k_{\mathrm{fl}}\tau_s$ is the quantum yield of TPP fluorescence, $[\mathrm{T}]_0$ is the initial concentration of ^{3}TPP, and

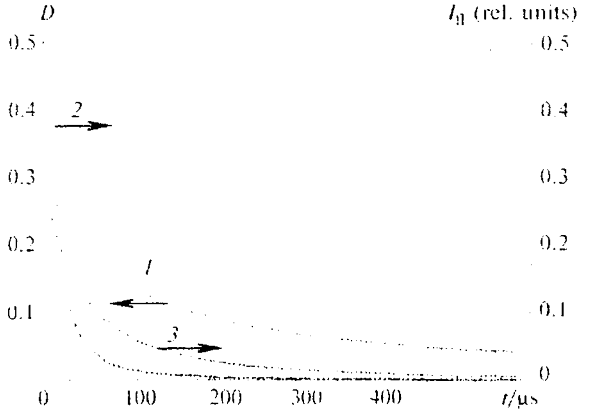

Fig. 1. Kinetic curves of the disappearance of the transient absorption at 440 nm in an *n*-decanol solution of TPP ($1 \cdot 10^{-4}$ mol L^{-1}) at 20 °C (*1*) and delayed fluorescence decay at 720 nm at −20 (*2*) and 20 °C (*3*). The lines are the result of fitting to the second-order equation and formula (4), respectively.

$I_{\mathrm{DF}}(t = 0) = \varphi_{\mathrm{fl}}(1/9)k_{\mathrm{TTA}}[\mathrm{T}]_0^2$ is the initial DF intensity. The use of Eq. (4) for the approximation of the experimental kinetic curves of DF gives the $k_{\mathrm{eff}}[\mathrm{T}]_0$ values, which almost coincide with similar values obtained by the corresponding approximation of the kinetic curves of ^{3}TPP decay.

An important quantitative characteristic of DF is the ratio $Y_{\mathrm{DF}}/Y_{\mathrm{PF}}$, where Y_{DF} and Y_{PF} are the integral amounts of photons (the surface areas under the corresponding kinetic curves) emitted during delayed and prompt fluorescence (PF), respectively. The measured values of $Y_{\mathrm{DF}}/Y_{\mathrm{PF}}$ reach 15%, which almost coincides with that expected in the framework of the kinetic Scheme 1 ($Y_{\mathrm{DF}}/Y_{\mathrm{PF}} = \varphi_{\mathrm{T}}/(5 - \varphi_{\mathrm{T}}) = 0.14$). Such a good correlation between the experimental and calculated parameters indicates that TTA in DC solutions of TPP is in complete agreement with the kinetic model.

An increase in the temperature of a DC solution of TPP is accompanied by acceleration of TTA and DF and, correspondingly, $I_{\mathrm{DF}}(t = 0)$ increases. The temperature plot of k_{eff} in the 8—100 °C range is described by the Arrhenius law with an activation energy of 7.3 kcal mol^{-1} (Fig. 2), which is close to that of the viscous flow of DC (6.3 kcal mol^{-1})[11] and also indicates that TTA is controlled by diffusion. The yield of the triplet state of TPP and τ_s, Y_{PF}, and $Y_{\mathrm{DF}}/Y_{\mathrm{PF}}$ are almost independent of the temperature of the solution.

A decrease in the temperature of the solution to 5 °C results in the freezing of DC and formation of a light-scattering layered polycrystalline structure. The parameters of prompt fluorescence τ_s and Y_{PF} measured by the diffuse reflectance mode almost coincide (only a slight increase in Y_{PF} of at most 20% is observed) with those for the liquid solution and, as in the liquid solution, they are almost temperature-independent down to −100 °C. Thus, we may conclude that the photophysical parameters of TPP remain unchanged on going from the liquid

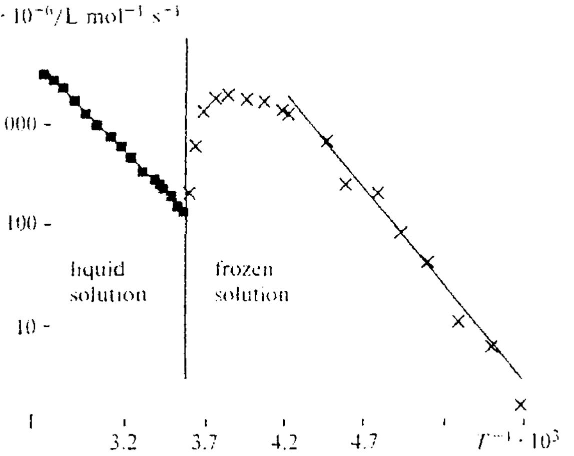

Fig. 2. Temperature plot of the effective rate constant of TTA of a solution of tetraphenylporphine ($1 \cdot 10^{-4}$ mol L^{-1}) in *n*-decanol in the Arrhenius coordinates.

DC solution to the frozen solution. This also affirms that the total amount of ^{3}TPP in the reaction zone does not significantly change, and TTA delay should be expected due to the restrictions of the molecular mobility in crystals as compared to liquid. Note that $Y_{\rm DF}/Y_{\rm PF}$ remains virtually unchanged upon DC freezing and, as in liquid DC, is independent of the temperature of the frozen solution, indicating an unchanged mechanism of TTA.

At the same time, DC freezing results in the sharp acceleration of the DF decay and the corresponding increase in $I_{\rm DF}(t = 0)$. Moreover, the further decrease in the temperature to −20 °C is accompanied by further acceleration of the DF decay and the corresponding increase in $I_{\rm DF}(t = 0)$. Figure 2 presents the temperature plot of $k_{\rm eff}$ in the range from +5 to −100 °C obtained by approximation of the kinetic curves of DF from formula (4) using the value of $[{\rm T}]_0$ in the liquid solution, which was corrected to the corresponding change in $Y_{\rm PF}$. Equation (4) describes the DF kinetics in the frozen solution as effectively as that in the liquid solution. The $k_{\rm eff}$ value at −20 °C exceeds more than tenfold the corresponding value measured at 10 °C. At temperatures below −40 °C, the temperature function of $k_{\rm eff}$ takes the Arrhenius form with an activation energy of 8.8 kcal mol^{-1} (see Fig. 2), which only slightly exceeds the value in the liquid solution. The direction and rate of the temperature change and the freezing velocity have no noticeable effect on both the qualitative and quantitative parameters of the temperature plot. The $k_{\rm eff}$ values obtained by gradual decrease in the temperature of the system coincide with those measured at fast freezing to the specified temperature in liquid nitrogen and on heating the system precooled to the temperature of liquid nitrogen.

Thus, we found an unusual change in the regime of the bimolecular diffusion-controlled process involving organic molecules in organic alcohol during its freezing. The reaction rate increases by approximately an order of magnitude on going from the liquid to solid state. By analogy to aqueous solutions, we can assume that the effect is based on the concentration of the reactant molecules on freezing.[1–6] Solvent crystallization can be accompanied by the "extrusion" of the molecules of the dissolved substance from the nucleating crystal and their localization in defects at the interface of microcrystals. However, the kinetics of the bimolecular process in a frozen solution is solely homogeneous. Frozen DC did not exhibit kinetic polydispersity, which usually appears for bimolecular processes, in particular, TTA, in solid and heterogeneous media and is due to the nonuniform spatial distribution of the reactants and molecular environment.[8] Moreover, the found value of the effect (the tenfold acceleration of the reaction) assumes very high local concentrations of the reactant, at which porphyrin molecules are usually strongly aggregated, which is pronounced in the spectral and fluorescence parameters. The fluorescence parameters (spectrum, lifetime, and quantum yield) of the porphyrin in frozen and liquid DC are the same. The experimental data indicate the very high mobility of the porphyrin molecules in the regions of their localization in frozen DC and the homogeneous nature of these regions. It can be assumed that the porphyrin molecules "slide" over the microcrystal surface, using the available free volume.

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