Decomposition kinetics of free radical initiators in micellar solutions

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The kinetic parameters of thermal decomposition of initiators, azo-bis-isobutyronitrile (AIBN) and dicyclohexyl peroxydicarbonate (PC), have been measured in aqueous micellar solutions of sodium dodecylsulfate (SDS), cetyltrimethylammonium bromide (CTAB), and egg lecithin. The inhibitor technique and acceptors of free radicals have been used to estimate the efficiency of the initiation during AIBN decomposition. The rate constant of PC decomposition in a SDS micellar solution is the same as in *n*-decane. CTAB and lecithin accelerate the rate of PC decomposition. Mechanisms of surfactant effect on the PC decomposition are discussed.

Key words: initiator decomposition, azo-bis-isobutyronitrile, dicyclohexyl peroxydicarbonate, sodium dodecylsulfate, cetyltrimethylammonium bromide, lecithin, micelles, inhibitor technique.

The rate of free radical initiation is an important characteristic of radical chain processes. Initiators with known decomposition rate constants (k_d) and coefficients of radical escape from a solvent cage ($2e$) are usually used in quantitative studies. Azo compounds and peroxides for which k_d and $2e$ are measured are widely used in homogeneous solutions as initiators.[1—3] In these systems, the nature of the solvent mainly affects the radical escape from the cage, which decreases, as a rule, as the viscosity of the solvent increases.[4]

As many authors mention, the rate of free radical initiation is the least studied value for microheterogeneous solutions, which makes it difficult to obtain quantitative information about radical processes in these media.[5] In the present work, kinetic regularities of the decomposition of radical reaction initiators are studied in micellar solutions of surfactants of different nature. Widely used oil-soluble initiators of radical reactions, azo-bis-isobutyronitrile and decyclohexyl peroxydicarbonate, are studied.

Experimental

Azo-bis-isobutyronitrile (AIBN) was purified by recrystallization from ethanol, dicyclohexyl peroxydicarbonate (PC) was reprecipitated from acetone to a methanol—water (5 : 1) mixture.

***N,N*-di-β-naphthyl-*p*-phenylenediamine** (NPDA) and *N,N*-diphenyl-*p*-phenylenediamine (PPDA) were purified by reprecipitation from acetone to hexane; 4-(*spiro*-tetrahydrofuryl-2')-2-*spiro*-cyclohexyl-1,2,3,4-tetrahydroquinoline-1-oxyl (NR) was synthesized from the corresponding amine according to the previously published procedure.[6] 3,5,7,3',4'-Pentahydroxyflavone (quercetin, Q) (Chemapol) was used without additional purification.

Sodium dodecyl sulfate (SDS) was twice recrystallized from ethanol; cetyltrimethylammonium bromide (CTAB) (Serva) and egg lecithin (Serva) were used without additional purification.

Chlorobenzene, *n*-decane, DMSO, and acetonitrile (AN) were purified according to standard procedures.

Thermal decomposition of AIBN was performed in aqueous micellar solutions of SDS or CTAB (60 °C), PC was decomposed in an aqueous micellar solution of SDS (45—75 °C) and in a *n*-decane solution of egg lecithin (60 °C). An ultrasonic disperser was used for initiator solubilization in aqueous solutions of surfactants. Inhibitors were introduced to the reaction mixture by addition of a small amount of their DMSO or AN solutions with known concentrations to the micellar solution of an initiator.

The concentration of PC was measured by colorimetry,[7] concentrations of AIBN, inhibitors, and products of their transformation were measured by spectrophotometry. All concentrations are given in moles per liter of the overall solution volume.

Results and Discussion

It is known that the rate of AIBN decomposition in various hydrocarbons obeys the first-order kinetic law and is virtually independent of their nature:[1—3]

$$-d[AIBN]/dt = k_d[AIBN]. \quad (1)$$

The thermal decomposition of AIBN in an 0.34 *M* aqueous micellar solution of SDS is also described by Eq. (1). The value $k_d = 1 \cdot 10^{-5}$ s^{-1} (60 °C) was ob-

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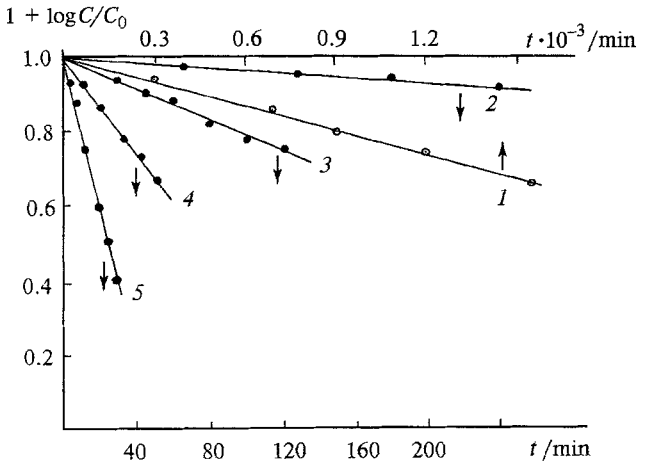

Fig. 1. Semilogarithmic anamorphoses of kinetic curves of AIBN (*1*) and PC (*2—5*) decomposition in a 0.34 mol L^{-1} aqueous solution of SDS; $[AIBN]_0 = 10^{-2}$ mol L^{-1}, 60 °C; $[PC]_0 = 5 \cdot 10^{-3}$ mol L^{-1}: 45 °C (*2*); 60 °C (*3*); 70 °C (*4*); and 75 °C (*5*).

tained from the semilogarithmic anamorphoses of the kinetic curves (Fig. 1, curve *1*).

The inhibitor technique is used for measurements of the rate of free radical formation (w_i) and for calculations of the coefficient of the radical escape from the cage ($2e$):[1—3]

$$w_i = f\mathrm{d}[\mathrm{InH}]/\mathrm{d}t = 2ek_\mathrm{d}[I] \text{ and } 2e = w_i/k_\mathrm{d}[I], \qquad (2)$$

where f is the stoichiometric coefficient of the chain termination by the inhibitor (InH), and I is the initiator.

The consumption rates of inhibitors of different nature were measured to determine $2e$ during AIBN decomposition in microheterogeneous systems. Compounds with different solubility in water and organic solvents were used.

N,N'-diphenyl-*p*-phenylenediamine (PPDA) is a standard inhibitor used for measurements of the initiation rate in homogeneous solutions (the stoichiometric coefficient $f = 2$, see Refs. 8, 9). It is quantitatively transformed to the corresponding colored quinone diimine (QDI) in reactions with peroxy radicals and peroxides, which makes it possible to easily measure the rate of its accumulation. PPDA is almost insoluble in water.

The aromatic nitroxyl radical (NR) is a convenient free radical scavenger with $f = 1$ (see Ref. 10). It transforms to quinone-nitron (X) in the reaction with peroxy radicals. The absorption bands of NR and X are separated in optical spectra, therefore, the consumption of NR (λ_{max} = 289 nm) and accumulation of X (λ_{max} = 371 nm) can be simultaneously recorded by spectrophotometry.[10] NR reacts with alkyl radicals to form the corresponding hydroxylamine ethers, which do not absorb in the visible spectral region.[10] Nitroxyl is difficultly soluble in water ($[NR]_{max} = 8 \cdot 10^{-5}$ mol L^{-1} in water and $5.6 \cdot 10^{-2}$ mol L^{-1} in *n*-decane, 20 °C), therefore, it is likely to be mainly in micelles in a micellar solution.

Table 1. Initiation efficiency of AIBN decomposition in various media

Medium	[AIBN][a]	[InH]	[InH][a]	W^b_{InH}	f	$2e$
Aqueous	0.5	Q	2.0	1.61	2	0.68
SDS	0.5		3.0	1.90		0.78
0.34 mol L^{-1}	1.0		0.75	2.54		0.50
	1.0		1.45	2.94		0.58
	1.0		1.45	2.62		0.52
	1.0		2.0	2.68		0.54
	1.0		2.84	2.60		0.52
	0.5	PPDA	0.02	1.83		0.74
	0.25		0.02	0.77		0.62
	0.5	NR	1.0	1.75		0.35
	0.5		2.0	1.8		0.36
	1.0		0.5	3.7		0.37
Aqueous	0.13	Q	0.75	0.38	2	0.58
CTAB	0.13	PPDA	0.02	0.31	2	0.48
0.01 mol L^{-1}	0.10		0.03			0.48
	0.13	NR	0.7	0.48	1	0.37
Chloro-		Q			2	1.2
benzene		NR			1	1.2
n-decane		NPDA			2	0.9

[a] 10^2/mol L^{-1}. [b] 10^{-8}/mol^{-1} L s^{-1}

3,5,7,3',4'-Pentahydroxyflavone (quercetin, Q) has a characteristic absorption band in the visible spectral region; it is difficultly soluble in water, however, its solubility in water is higher than in paraffin hydrocarbons. Therefore, one can assume that in micellar solutions it is mainly localized in an aqueous phase or at the interface. The stoichiometric coefficient f for Q depends on the ratio of w_i to [Q], the nature of the medium, and the pH. In the concentration range of Q and AIBN in chlorobenzene used in the present work (Table 1),

$$f = 2ek_\mathrm{d}\,[\mathrm{AIBN}]/(\mathrm{d}[\mathrm{InH}]/\mathrm{d}t) = 2,$$

where $e = 0.6$ in aromatic solvents.[11,12]

The results of the measurements of the rate of inhibitor consumption and calculations of the efficiency of the initiation $2e$ during AIBN decomposition are presented in Table 1. It is seen that the values of $2e$ are almost the same for cationic CTAB and anionic SDS, *i.e.*, the charge of the micelle does not considerably affect the rate of AIBN decomposition and the radical escape. However, the values of $2e$ somewhat differ for various inhibitors, which can result from lower reproducibility as compared with homogeneous solutions. The values obtained are close to the value $2e = 0.6$ for the decomposition of di-*tert*-butylhyponitrite in SDS micelles,[13] but they are higher than the estimates of the initiation efficiency by AIBN and other azo compounds in the processes of emulsion polymerization of styrene ($2e$ = 0.04)[14] and oxidation of egg lecithin in bilayered aqueous dispersions ($2e = 0.18$).[9] However, they are somewhat lower than $2e = 0.98$ for decomposition of water-soluble 2,2-azo-bis(2-amidinopropane)dihydrochloride in a micellar solution of SDS (see Ref. 15) and $2e = 0.9$

for AIBN decomposition in *n*-decane at 60 °C, which was measured from the accumulation of quinone diimine (see Table 1). This may be caused by relatively high microviscosity of the organic core of the micelle as compared with that of *n*-decane.

Unlike azo compounds, the decomposition rate of peroxide initiators to a greater extent depends on the nature of the medium.[16] The kinetic regularities of the thermal decomposition of dicyclohexyl peroxydicarbonate was previously studied in detail in various solvents.[17] It is established that the chain induced decomposition of PC occurs in the majority of solvents (*S*).

$$\mathrm{PC} \rightarrow 2r\mathrm{O}^{\bullet}, \qquad (k_d)$$
$$r\mathrm{O}^{\bullet} + S \rightarrow \mathrm{S}^{\bullet} + r\mathrm{OH},$$
$$\mathrm{PC} + S^{\bullet}, r\mathrm{O}^{\bullet} \rightarrow r\mathrm{O}^{\bullet} + \text{Products}, \qquad (k_p)$$
$$S^{\bullet} + S^{\bullet} \rightarrow \text{Products}, \qquad (k_t)$$
$$S^{\bullet} + r\mathrm{O}^{\bullet} \rightarrow \text{Products},$$
$$r\mathrm{O}^{\bullet} + r\mathrm{O}^{\bullet} \rightarrow \text{Products}$$

This appears in an increase of the effective decomposition rate constant k_{eff} as the initial concentration of peroxide increases, according to Eqs. 3 and 4:

$$-\mathrm{d[PC]}/\mathrm{d}t = k_{eff}[\mathrm{PC}], \qquad (3)$$

$$k_{eff} = k_d + a[\mathrm{PC}]^{0.5}, \qquad (4)$$

where k_d is the rate constant of the homolytic cleavage of the peroxide bond and $a = (k_p/k_t^{0.5})(2ek_d)^{0.5}$ is the parameter of the induced chain decomposition, which takes into account the participation of the solvent in the induced PC decomposition.

The solvent nature influences both parameters of Eq. (4), *i.e.*, on k_d determined by extrapolation of the dependence of k_{eff} on $[\mathrm{PC}]_0^{0.5}$ to $[\mathrm{PC}]_0 \rightarrow 0$, and on a calculated from the slope. These parameters have the least values for PC decomposition in paraffin hydrocarbons, and they are the greatest in aromatic solvents and acetonitrile.[17] The induced decomposition is not observed in alkylbenzenes and in all of the solvents in the presence of oxygen, evidently, due to the lower activity of alkylaromatic and peroxyl radicals in the acts of chain propagation.

PC is practically insoluble in water but it is solubilized in micellar solutions of SDS (specific solubilization $S_m = 0.23$). PC decomposition in SDS micelles is described by a first-order equation (see Fig. 1). The value of k_d obeys the Arrhenius equation at 45—75 °C:

$$k_d = 10^{15.44}\exp(-124300/RT),$$

which coincides with the expression for the rate constant of the monomolecular PC decomposition in *n*-decane.[17]

It is difficult to use the inhibitor technique for determination of the initiation efficiency for PC decomposition in homogeneous solutions because of its high reactivity. PC directly reacts with polyphenols, amines, and aminophenols, and it quantitatively oxidizes NPDA

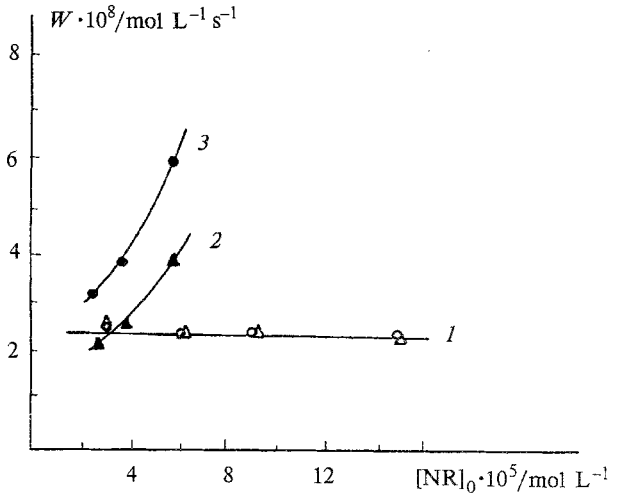

Fig. 2. Dependences of the rates of NR consumption (*1,3*) and X accumulation (*1,2*) on the initial NR concentration in PC decomposition in *n*-decane (*1*) and an 0.34 mol L^{-1} aqueous solution of SDS (*2, 3*). $[\mathrm{PC}]_0 = 2 \cdot 10^{-4}$ mol L^{-1}, 60 °C.

to the corresponding diimine in a stoichiometric ratio of 1 : 1. This reaction is used for colorimetric determination of small amounts of PC and benzoyl peroxide.[7]

Nitroxyl radicals accelerate PC decomposition in homogeneous solutions *via* two directions. The catalytic decomposition in aromatic solvents (benzene and chlorobenzene) with participation of cyclohexyl and cyclohexadienyl radicals formed from the solvent and the direct interaction (induced decomposition) are possible.[18] However, these reactions can be neglected at sufficiently low concentrations ([NR] < $1.5 \cdot 10^{-4}$ mol L^{-1})[17] and NR can be used for measurement of the rate of radical formation from PC. The coefficients $2e$ of the radical escape from the solvent cage during PC decomposition are 1.45 (60 °C) in ethylbenzene,[19] 1.35 (50 °C) in *m*-xylene,[19] 1.5 (60 °C) in chlorobenzene,[20] and 1.5 (60 °C) in *n*-decane.[17] The rates of NR consumption and X accumulation are the same and comprise $W_{NR} = W_X = 1.5k_d[\mathrm{PC}]$[17] for PC decomposition in *n*-decane at [NR] < $1.5 \cdot 10^{-4}$ mol L^{-1} (Fig. 2, curve *1*). In an aqueous micellar solution of SDS (curves *2* and *3*) $W_{NR} > W_X$ and both rates increase as the initial NR concentration increases. It is likely that the condition [NR] < $1.5 \cdot 10^{-4}$ mol L^{-1} is not fulfilled in micellar solutions due to concentrating of reagents, their direct interaction is sharply accelerated and, hence, it becomes impossible to use NR for measurement of $2e$ by the inhibitor technique.

Quercetin in a micellar solution also accelerates PC decomposition (the addition of quercetin [Q] = $5 \cdot 10^{-4}$ mol L^{-1} increases the decomposition rate by more than twice).

High reactivity of PC also appears in its interaction with CTAB and egg lecithin. It is found for PC solubilization in aqueous solutions of these surfactants that the PC concentration sharply decreases in the process of

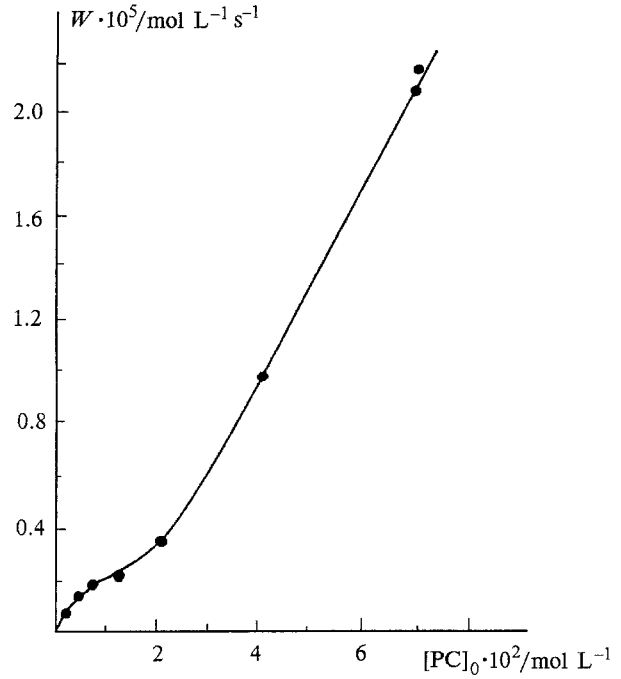

Fig. 3. Dependence of the initial rate of PC consumption on its initial concentration in the decomposition in the presence of a 2 % solution of egg lecithin; *n*-decane, 60 °C.

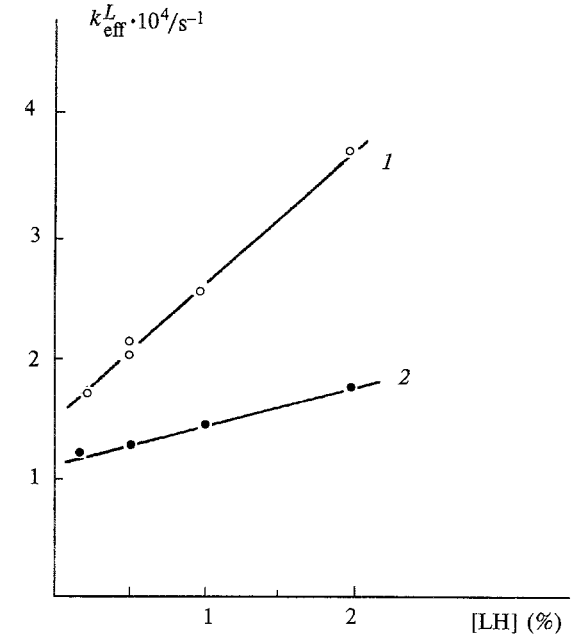

Fig. 4. Dependence of the effective rate constant of PC decomposition $k^L_{eff} = W_{0,PC}/[PC]_0$ on the initial concentration of lecithin. $[PC]_0$, mol L^{-1} = 10^{-3} (*1*); $1.2 \cdot 10^{-2}$ (*2*), *n*-decane, 60 °C. W_0 is the initial rate.

dissolvation. We have found that Br^- is oxidized to Br_2 by peroxide in the case of CTAB. The interaction between PC and lecithin is a complicated process, whose kinetic regularities were studied in a *n*-decane solution with known parameters of the thermal decomposition of PC.[17] The dependences of the consumption rate of PC (W_{PC}) on the concentration of each of the reagents elucidated several peculiarities of the lecithin (LH) action.

The dependence of W_{PC} on $[PC]_0$ at the constant initial concentration of lecithin is a complex curve with a variable slope and an inflection point (Fig. 3). The dependence of W_{PC} on $[LH]_0$ (Fig. 4) is close to linear, however, the specific rate $W_{PC}/[PC]_0$ at $[PC]_0 < 10^{-2}$ mol L^{-1} increases more sharply with the increase in the lecithin concentration than at greater values of $[PC]_0$.

It is convenient to analyze the effect of [PC] on the rate of its consumption in the coordinates k_{eff} *vs.* $[PC]_0^{0.5}$ (Fig. 5) in accordance with Eq. (4), which characterizes the induced decomposition of PC. For PC decomposition in *n*-decane with the addition of a 2 % lecithin solution, the dependence of $k_{eff} = W_{0,PC}/[PC]_0$ on $[PC]_0^{0.5}$ is described by a V-shaped curve with a minimum at [PC] $\approx 1.2 \cdot 10^{-2}$ mol L^{-1} (see Fig. 4). The right part of this curve can be approximated by a straight line

$$k^i_{eff} = k_d + a' [PC]_0^{0.5}, \quad (5)$$

and the left part can be approximated by a hyperbola

$$k^a_{eff} = A/[PC]_0, \quad (6)$$

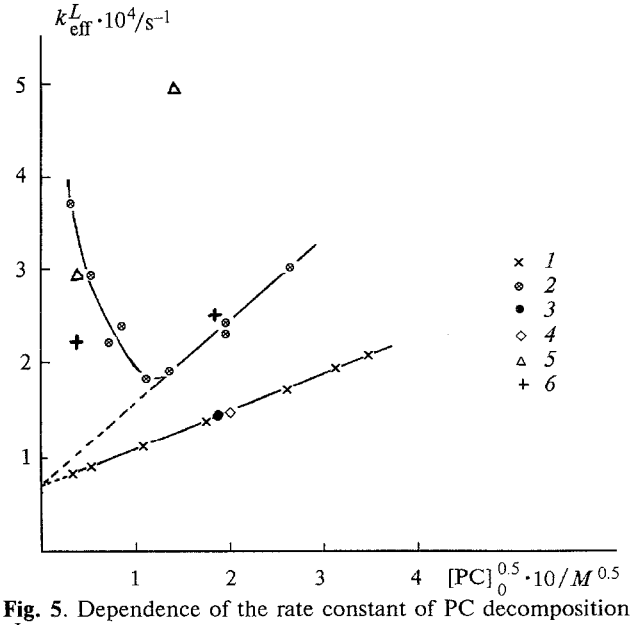

Fig. 5. Dependence of the rate constant of PC decomposition $k^L_{eff} = W_{0,PC}/[PC]_0$ on its initial concentration without additives (*1*) and in the presence of a 2 % solution of egg lecithin (*2*), soybean lecithin (*3*), acetylcholine (*4*), cephalin (*5*), and water + 2 % solution of egg lecithin in the molar ratio of 20 : 1 (*6*); *n*-decane, 60 °C.

which, as a whole, results in the equation

$$k^L_{eff} = k^i_{eff} + k^a_{eff} = k_d + a'[PC]_0^{0.5} + A/[PC]_0, \quad (7)$$

where $a' = 8.7 \cdot 10^{-4}$ (mol L^{-1})$^{-0.5}$ s^{-1} and $A = 5 \cdot 10^{-7}$ mol L^{-1} s^{-1} are empirical parameters.

The first term k^i_{eff} in Eq. (7) is analogous in form to k_{eff} for the induced PC decomposition in *n*-decane, therefore, it is natural to assume that k^i_{eff} characterizes the induced PC decomposition in the presence of lecithin and with its participation, which predominates at sufficiently high LH concentrations and high concentrations of PC.

$$rO^{\cdot}, S^{\cdot} + LH \rightarrow L^{\cdot} + rOH, SH$$

$$PC + L^{\cdot} \rightarrow rO^{\cdot} + \text{Products} \qquad (k^L_p)$$

$$L^{\cdot} + L^{\cdot} \rightarrow \text{Products} \qquad (k^L_t)$$

A molecule of egg lecithin contains active C—H bonds of unsaturated acidic residues, whose interaction with $rO^{\cdot}$ or $S^{\cdot}$ radicals results in the displacement by $L^{\cdot}$ radicals, which further participate in the induced PC decomposition. The higher value of the a' parameter compared to that of a' in *n*-decane seems to be caused by a lower value of k_t^L of $L^{\cdot}$ radicals than k_t of decyl radicals (10^8 (mol $L^{-1})^{-1}$ s^{-1}).[1]

In the concentration range [PC] < 10^{-3} mol L^{-1} the fraction of the induced decomposition is small in the overall rate of peroxide consumption, however, it is seen from Figs. 4 and 5 that it is precisely low concentrations of peroxide at which a considerable acceleration of lecithin appears and decreases as $[PC]_0$ increases. The hyperbolic dependence of k_{eff} (Eq. 6) can reflect the consumption of PC in reactions with microadditives (A), whose rate is limited by the amount of this additive ($A \sim [A \cdots PC] \sim [A]$). A check of the influence of different components and variations of phospholipids (see Fig. 5) showed the following: a) the same amount (2 %) of soybean lecithin containing, unlike egg lecithin, saturated acidic residues does not affect the rate of PC decomposition; b) acetylcholine also does not affect PC decomposition; c) cephalin (C), phosphatidyl ethanolamine, accelerates PC decomposition to a greater extent than egg lecithin, but acceleration is observed in the whole range of peroxide concentrations: $W_{PC} \sim [C][PC]$ at [PC] = 10^{-2}—10^{-3} mol L^{-1}. It is evident that the acceleration is related to the existence of an amino group in C, which very easily reacts with PC; and d) small additives of water (0.5 mol L^{-1}) virtually have no effect on the rate of PC decomposition in the presence of lecithin in the range of high PC concentrations (induced decomposition) and decrease the rate and k_{eff} in the range of low concentrations of peroxide.

The latter result allows us to assume that PC consumption with A rate occurs on aggregates of lecithin of the type of inverse micelles, which are formed in organic solvents.[21] It is likely that PC forms {A···PC} complexes with aggregates of lecithin in which the cleavage of the peroxide bond is easier, *i.e.*, aggregates act as a peculiar kind of microheterogeneous catalyst of peroxide decomposition. Average hydrodynamic sizes of particles, which are formed in a 2 % lecithin solution in *n*-decane with different water content, were estimated by the quasi-elastic light scattering technique. In freshly distilled *n*-decane sizes of aggregates are less than the lower measurement limit (D < 50 Å). A lecithin solution in *n*-decane with the addition of microamounts of water (molar ratio water : lecithin = 20 : 1) is a microemulsion containing particles with D ~ 600 Å. It is evident that additives of water result in confluence of aggregates and a decrease in their total number and effective surface area and, as a consequence, the rate of PC consumption also decreases.

It follows from the results obtained that lecithin can be easily involved in radical reactions. This results in a change in composition of radicals and, hence, in the rate of the chain process, as a whole. It is very interesting that lecithin can localize water dissolved in organic solvents and form inverse micelles and microemulsions. These aggregates comprise particles with qualitatively new, in particular with respect to peroxides, properties as compared with isolated lecithin molecules.

Thus, the results obtained show that initiator decomposition in microheterogeneous media is a more complicated process than that in homogeneous solutions. It is difficult to use the inhibitor technique for measurement of the rate of radical formation, however, the use of inhibitors of various nature makes it possible to estimate the maximum rate of free radical formation, which is a useful parameter for analysis of regularities of chain reactions. Surfactants, whose concentration is sufficiently high in microheterogeneous systems, can participate in exchange reactions with free radicals and can be involved in the chain process.

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