Homolytic scission of peroxydisulfate under conditions of free-radical phase-transfer-catalysed polymerization

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The effects of pH, ionic strength and concentration of the phase-transfer catalyst, tetrabutylammonium bromide, on the rate of decomposition of potassium peroxydisulfate under conditions of free-radical phase-transfer-catalysed (PTC) polymerization have been studied. The resulting rates of initiation and polymerization of methyl methacrylate under the same conditions, which reveal the effect of transfer of initiating species into the organic phase, are also presented. Low ionic strength of the aqueous phase and a pH value of 3–4 are the most favourable conditions to achieve the highest generation rate of free radicals in the organic phase under the conditions of PTC polymerization.

(Keywords: peroxydisulfate; phase-transfer catalysis; free-radical polymerization)

INTRODUCTION

The kinetics and mechanism of ordinary phase-transfer-catalysed (PTC) organic reactions have been investigated thoroughly[1,2], while only a few free-radical polymerization reactions are available in the literature. The extraction (phase transfer) of peroxydisulfate into the organic phase is more difficult compared with that of the ordinary nucleophilic anions used in organic synthesis. Nevertheless, the rate of free-radical PTC polymerization is similar to that of solution polymerization, because of the fast and irreversible reaction of the initiation of radical processes.

It is possible to speculate that the features of radical polymerization under the conditions of PTC are mainly determined by the initiation process. Thus an investigation of homolytic scission of potassium peroxydisulfate (PP) under the conditions of PTC polymerization is urgent and necessary.

The homolytic scission of PP is complicated, since the kinetics and mechanism of this process depend on reaction media (pH, ionic strength, type and concentration of organic additives, etc.)[3,4]. There is some disagreement in the published data on the influence of ionic strength on the rate of homolytic scission of PP. It was estimated by special studies that the ionic strength has no influence at all[5], or increases the rate of decomposition of peroxydisulfate in acidic or neutral media[6], or has no influence in neutral media but decreases the rate of heterolytic scission of PP at pH < 3 (ref. 7). In this article we have concentrated our attention on determining the effect of the factors mentioned above on the rate of decomposition of PP as well as on the resulting rates of initiation and polymerization of methyl methacrylate (MMA) under the conditions of PTC.

EXPERIMENTAL

MMA was washed successively by 5% aqueous solution of Na_2CO_3 and distilled water (until neutral reaction with respect to phenolphthalein), dried over $CaCl_2$ and distilled; b.p. 372–373 K, $n_D^{20} = 1.4150$. PP and tetrabutylammonium bromide (TBAB) were recrystallized from distilled water and from a mixture of ethyl acetate with diethyl ether (25:75), respectively. Acetonitrile (ACN) was dried over $CaCl_2$ and distilled; b.p. 353–354 K, $n_D^{20} = 1.3430$. As an inhibitor of radical processes, phenyloxyl was used without purification.

Polymerization of MMA was carried out in glass dilatometers (vol. 10–12 cm^3 and capillary radius 0.08–0.1 cm) under nitrogen atmosphere at 333 ± 0.1 K. The reaction mixture contained (if not indicated otherwise) 3.75 mol dm^{-3} MMA, 0.016 mol dm^{-3} PP, 0.032 mol dm^{-3} TBAB and water. The volume ratio of water phase to organic phase was about 1.5. Changes in ionic strength of the reaction mixture were compensated using KBr (TBAB variation), K_2SO_4 (PP variation) or KCl (pH variation). KBr was used for ionic strength variation. The contraction of MMA was observed using a cathetometer KM-8 (error $\pm 1 \times 10^{-3}$ cm). The contraction factor value for MMA (0.272) was determined by a gravimetric technique.

The rate of initiation was determined by the method of strong inhibition, i.e. using the dependence of induction period on inhibitor concentration[8].

Decomposition of PP was investigated in three different media: i.e. in water; in 1.3% aqueous solution of the free-radical acceptor, methacrylonitrile (MAN); and in the water phase of the two-phase polymerization system of MMA described above. The concentration of PP under the conditions of decomposition was determined by a spectrophotometric method as proposed earlier[9]. The dilute solution of PP (3 cm^3) was mixed with

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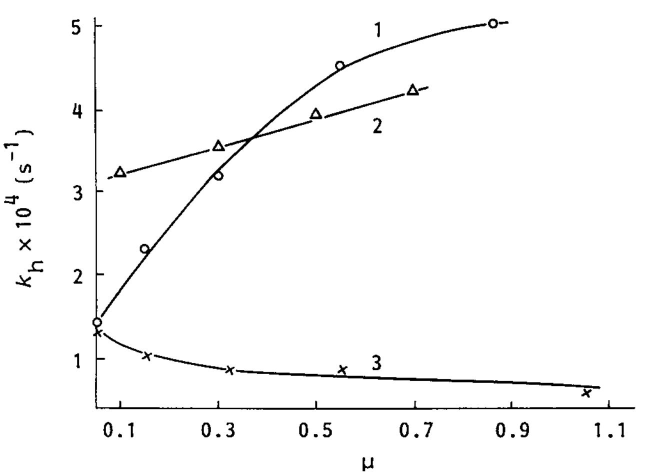

Figure 1 Dependence of the rate coefficient of homolytic scission of PP on ionic strength in aqueous solution of MAN (1) and MMA (2) and in water (3)

1 cm^3 of aqueous 6 M solution of KI, and the resulting solution was buffered to pH 6.86. The optical density of iodine produced was measured by a spectrophotometer SF-26 (USSR); the molar absorption coefficient determined experimentally at wavelength $\lambda = 355$ nm was $\varepsilon = 269$ dm^3 mol^{-1} m^{-1}.

The rate coefficient of homolytic decomposition of PP was calculated from the slope of the linear dependence of ln [PP] on time. The conductivity of TBAB solutions was measured by a conductometer using platinized platinum electrodes[10].

RESULTS AND DISCUSSION

The dependence of the rate coefficient k_h of homolytic scission of PP on ionic strength is different in various media (*Figure 1*). In homogeneous aqueous solution of the free-radical acceptor MAN and in the aqueous phase of the PTC polymerization mixture of MMA, the rate coefficient of homolytic scission of PP increases when the ionic strength becomes higher (*Figure 1*, curves 1 and 2). Such a dependence can be explained in terms of induced decomposition of PP.

Organic substances present in the solution may be oxidized by PP radicals, resulting in a new kind of radical, and the latter can promote further decomposition of PP[7,11]. Monomers or other free-radical acceptors inhibit the reaction of induced decomposition.

According to these considerations, induced decomposition must be suppressed in the presence of MMA or MAN, resulting in nearly the same rate of decomposition of PP as in water. On the other hand, radical acceptors can be oxidized if their concentration is low[12]. The fraction of PP decomposed by the chain (induced) mechanism and, subsequently, the rate coefficient of the decomposition reaction are higher if the concentration of monomers or other free-radical acceptors is lower. Current experiments support this point of view. Indeed, the corresponding values of k_h in curves 1 and 2 (*Figure 1*) are higher than those in curve 3 because the rate of induced decomposition is always higher than the radical generation rate. Also it is known that induced decomposition of PP does not proceed in water[7]. Values of k_h increase with ionic strength in the aqueous phase of the PTC system, but the rate of initiation and the overall rate of polymerization of MMA under the same conditions decrease (*Figure 2*). We suppose that the concentration of the monomer MMA under the conditions of PTC polymerization in the aqueous phase is not enough to suppress the induced decomposition of PP.

Induced decomposition of PP in the presence of TBAB may be expressed as follows:

$$S_2O_8^{2-} \xrightarrow{k_0} 2SO_4^{\bullet -}$$

$$SO_4^{\bullet -} + Q \xrightarrow{k_1} Q^{\bullet} + HSO_4^-$$

$$Q^{\bullet} + S_2O_8^{2-} \xrightarrow{k_2} SO_4^{\bullet -} + \text{products}$$

where Q and Q$^\bullet$ are TBAB and its radical.

If the radical generation rate is $V_0 = 2k_h[S_2O_8^{2-}]$, the rate of induced decomposition of PP, according to the theory of long kinetic chains[13], may be proportional to:

$[S_2O_8^{2-}]^{1/2}$[TBAB]	if bimolecular chain termination occurs exclusively through Q$^\bullet$
$[S_2O_8^{2-}]^{3/2}$	if bimolecular chain termination occurs exclusively through $SO_4^{\bullet -}$
$[S_2O_8^{2-}]$[TBAB]$^{1/2}$	if bimolecular cross-chain termination occurs

The experimentally observed value of the reaction order of homolytic scission of PP with respect to $S_2O_8^{2-}$ was found to be 1.48 ± 0.13. The high value of the reaction order means that the induced decomposition of PP has a remarkable effect on the rate of reaction. One can see also that termination occurs mainly through $SO_4^{\bullet -}$ or macroradicals derived therefrom.

According to the general theory of the transition state, the electric charge and its distribution for the anion $S_2O_8^{2-}$ in the ground and activated states must be similar because redistribution of electric charge under homolytic reactions is insignificant[13]. This means that the rate of homolytic scission of PP must be independent of ionic strength. The experimental data, however, do not confirm this hypothesis. The observed k_h value decreases with ionic strength if the aqueous solution does not contain organic substances (*Figure 1*, curve 3). This dependence can be explained in terms of the Debye–Hückel theory.

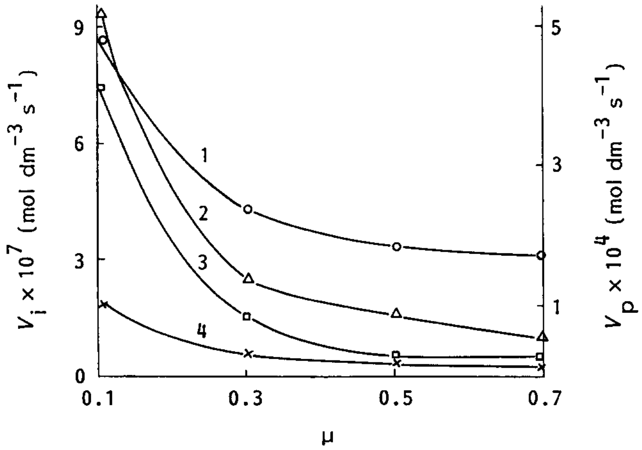

Figure 2 Dependence of the rates of polymerization (1, 4) and initiation (2, 3) on the ionic strength of aqueous phase in PTC polymerization of MMA. Initiator PP + TBAB (1, 2) and PP (3, 4), $T = 333$ K

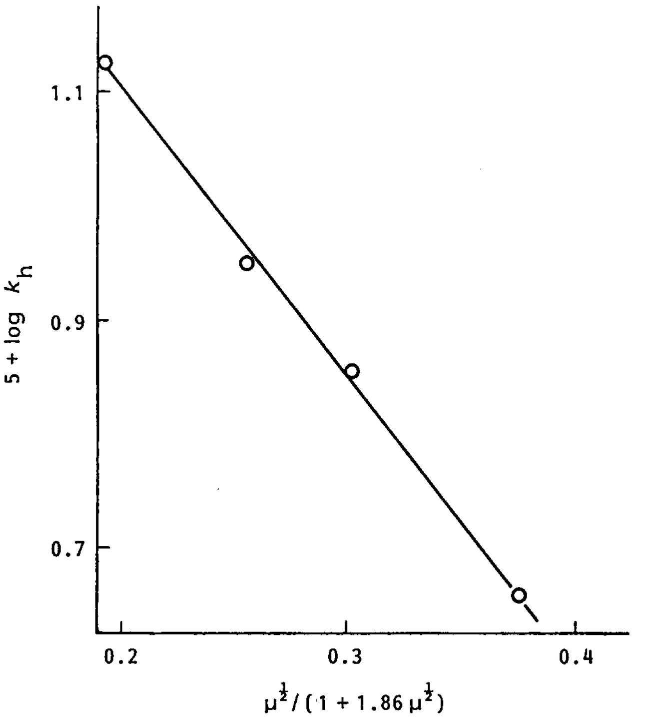

Figure 3 Dependence of the rate coefficient of homolytic scission of PP in water on ionic strength in the coordinates of the modified Debye–Hückel equation

The activity coefficient γ of strong electrolytes at very high concentrations can be expressed by the equation[13]:

$$\lg\gamma = -Qz^2\mu^{1/2}/(1+\alpha\mu^{1/2}) \qquad (1)$$

where

$$Q = -1.82\times10^6(\varepsilon T)^{-3/2}$$

z is the ionic charge, ε is the dielectric constant of the solvent, and α is an empirical coefficient.

For an aqueous solution ($\varepsilon=66.5$) of PP ($z=-2$) at 333 K, equation (1) may be transformed to:

$$\lg k = \lg k_0 - 2.21\mu^{1/2}/(1+\alpha\mu^{1/2}) \qquad (2)$$

assuming the decomposition rate of PP to be:

$$V_h = 2k_0\gamma[S_2O_8^{2-}]$$

where k and k_0 are PP decomposition rate coefficients in the presence and absence of ionic strength.

The experimental data fit equation (2) when $\alpha=1.86$ (*Figure 3*). The non-zero value of α shows that the radius of $S_2O_8^{2-}$ is relatively large and the PP anion cannot be accepted as a point charge, i.e. it is impossible to apply the general Debye–Hückel theory for dilute solutions to the solutions under investigation.

An analysis of equation (2) in conjunction with the data of *Figure 1* leads to the statement that the rate coefficient of homolytic scission of PP observed experimentally depends on ionic strength owing to the secondary effect of the latter, i.e. the ionic strength changes the activity coefficient of peroxydisulfate. The fraction of PP decomposed by the induced mechanism increases with ionic strength if the monomer concentration in the aqueous solution is low (i.e. under conditions of PTC polymerization of MMA).

It is known[14,15] that TBAB is an effective phase-transfer agent in radical polymerization of lipophilic monomers using water-soluble peroxydisulfates as initiators. The rate of heterophase polymerization initiated by PP–TBAB is increased by 10 or more times as compared to that initiated by PP. Moreover, TBAB increases the rate of homogeneous polymerization of hydrophilic monomers, e.g. methacrylic acid[15].

The dependence of the rate coefficient of homolytic scission of PP on [TBAB] falls on a straight line, if the concentration of the latter is comparable to that of PP (*Figure 4*). The interaction of PP and TBAB may be expressed by the scheme:

$$\begin{array}{ccccc} S_2O_8^{2-}+2Q^+ & \overset{K_1}{\rightleftharpoons} & [Q^+S_2O_8^{2-}]^- + Q^+ & \overset{K_2}{\rightleftharpoons} & (Q^+)_2S_2O_8^{2-} \\ \downarrow k_0 & & \downarrow k_1 & & \downarrow k_2 \end{array} \qquad (3)$$

According to this scheme the rate of decomposition of PP is:

$$-\mathrm{d}[S_2O_8^{2-}]/\mathrm{d}t = k_0[S_2O_8^{2-}]+k_1[Q^+S_2O_8^{2-}] + k_2[(Q^+)_2S_2O_8^{2-}]$$

or

$$-\mathrm{d}[S_2O_8^{2-}]/\mathrm{d}t = [S_2O_8^{2-}]\{k_0+k_1K_1[Q^+] + k_2K_1K_2[Q^+]^2\} \qquad (4)$$

An analysis of equation (4) reveals that the linear dependence of k_h on [TBAB] is possible only if $k_2K_1K_2[Q^+]^2\approx0$. It is evident also from the slope of the curves that neither k_0 nor k_1 can be neglected at the concentrations $[Q^+]$ under investigation. In media of the mixed solvents ACN:H_2O = 50:50 the term k_1K_1 is a little higher than that in water (*Figure 4*). This is not unexpected because of suppressed dissociation of $[Q^+S_2O_8^{2-}]^-$ in mixed water–organic solutions.

The rate of decomposition of PP increases when the values of pH become lower (*Figure 4*). It is possible that in acidic media the second-order reaction of heterolytic scission of PP catalysed by H^+ takes place[16], as detected by isotopic method earlier[17]:

$$^-OS(O)_2OO \vdots S(O)_2O^- + H\overset{*}{O} \vdots H$$

$$\rightarrow {}^-OS(O)_2OO^- + H^+ + H\overset{*}{O}S(O)_2O^-$$

$$H \vdots \overset{*}{O}H + {}^-OS(O)_2 \vdots OO^- + H^+$$

$$\rightarrow H_2O_2 + H\overset{*}{O}S(O)_2O^-$$

where $\overset{*}{O}$ is ^{18}O.

The activation energy of the reaction catalysed by H^+ is lower than that of homolytic scission[5,16]. Thus the overall rate of PP decomposition at low values of pH may be expressed:

$$-\mathrm{d}[S_2O_8^{2-}]/\mathrm{d}t = k_h[S_2O_8^{2-}] + k_{ht}[H^+][S_2O_8^{2-}]$$

where k_{ht} is the rate coefficient of heterolytic decomposition of PP.

If the fraction of PP decomposed by the heterolytic mechanism is significant, the radical generation rate (and, subsequently, the rate of initiation) must be lower at low values of pH. The dependences of V_i and V_p on pH for polymerization of MMA, however, show evident maxima at pH ≈ 3 (*Figure 5*). Thus it is clear that the shape of the curves must mainly be determined not by the dependence of the rate of PP decomposition on pH, but by the rate

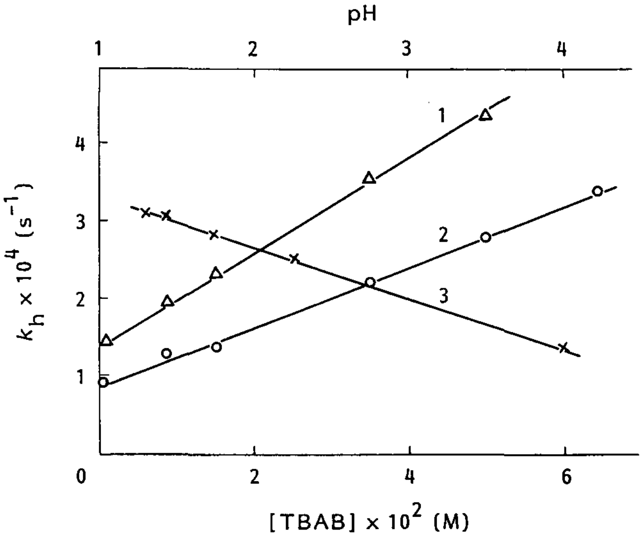

Figure 4 Dependence of the rate coefficient of homolytic scission of PP on concentration of TBAB (1, 2) and on pH (3) in aqueous solutions of MAN (2, 3) and in MAN solution in mixed solvent ACN:H_2O = 50:50 (1). [MAN] = 0.2 M, T = 323 K (1) and 333 K (2, 3)

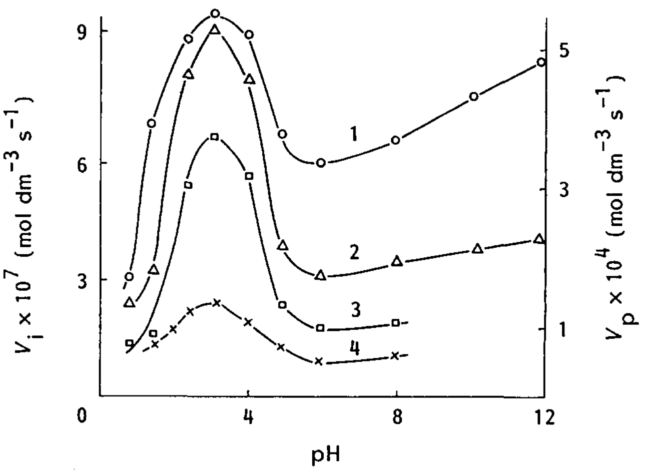

Figure 5 Dependence of the rates of polymerization (1, 4) and initiation (2, 3) on pH of aqueous phase in PTC polymerization of MMA. Initiators PP+TBAB (1, 2) and PP (3, 4), T = 333 K

of phase transfer of initiating species (i.e. by the dependence of tetraalkylammonium persulfate extraction coefficient on pH).

It is known that the values of extraction coefficient of anions are directly related to their lipophilicity, which is proportional to anion radius and inversely proportional to anion charge[1,2]. One can expect that $Q^+HS_2O_8^-$ has a higher extraction coefficient value as compared to that of $(Q^+)_2S_2O_8^{2-}$. The order of the initiation reaction for polymerization of MMA with respect to $[Q^+]$ is 0.99 ± 0.13. One can expect that under conditions of polymerization the main initiating species transferred into the organic phase is $Q^+HS_2O_8^-$, and therefore the radical generation rate in the organic phase increases when the pH of the aqueous phase decreases.

Decomposition of PP by heterolytic mechanism becomes prevailing at a pH of the aqueous phase lower than 3 and that is why the rate of initiation suddenly drops under such conditions. The relatively high values of V_i and V_p in alkaline media (*Figure 5*) are probably related to effective generation of free radicals by a redox system that could be formed between PP and tributylamine, i.e. the product of partial decomposition of TBAB by Hofman's reaction at $\mathrm{pH} > 7$.

It is observed that a dimerization or some other aggregation of tetraethyl- and tetrapropylammonium salts (bromides) takes place in dilute solutions, and micellization occurs if the concentration of salts is high (above 4 M and 1.4 M, respectively)[18]. The micellization concentration of TBAB was found[19] to be 0.039 M, but still discussions are open on whether such aggregates could be accepted as micelles or not[20]. The micellization concentration of TBAB detected by us was 0.028 M. It means that TBAB forms some aggregates in aqueous solutions of PP but they have no influence on the decomposition rate of PP, nor on rates of initiation and polymerization of MMA.

CONCLUSIONS

The rate coefficient of homolytic scission of PP increases monotonically when pH decreases, but the decomposition of PP by heterolytic mechanism not leading to free radicals becomes prevailing at pH of the aqueous phase lower than 3. Extreme dependence of the rates of initiation and polymerization of MMA on pH is determined mainly by peculiarities of phase transfer of initiating species, i.e. by dependence of tetraalkylammonium peroxydisulfate extraction coefficient on pH.

The rate coefficient of homolytic scission of PP decreases with increasing ionic strength due to PP activity coefficient being decreased. The induced decomposition of PP is remarkable under the conditions of PTC polymerization, and the fraction of PP decomposed by induced mechanism increases with ionic strength.

The role of TBAB in free-radical polymerization of vinyl monomers is complex: it facilitates decomposition of PP and acts as phase-transfer agent of initiating species.

TBAB forms some aggregates in aqueous solutions of PP but the latter have no influence on the decomposition rate of PP, nor on rates of initiation and polymerization under the conditions of PTC polymerization of MMA.

The most favourable conditions to achieve the highest radical generation rate in the organic phase under the conditions of PTC polymerization are low ionic strength of the aqueous phase and pH value being at 3–4.

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