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Emulsion polymerization initiated by alkylcobalt–tridentate Schiff base complexes in relation to kinetics and mechanism of their decomposition

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Summary

Former studies of decomposition of the title alkylcobalt(III)–tridentate Schiff base complexes (*RCo*) in acidic media have been extended to neutral and alkaline aqueous solutions including micellar ones. In combination, results of both the works indicate a common reaction mechanism, with homolysis of the Co–C bond preceded by substitution of extra ligand(s) with water molecules. Both protons and hydroxyl ions catalyze the latter aquation step after the conventional pattern of acid–base catalysis. Effect of surfactants on the reaction rate has been explained by electrostatic and hydrophilic/hydrophobic interactions between the cationic complexes and other components of micelles formed.

On these bases, the use of RCo, which had been formerly proved to be advanced pH-dependent initiators of emulsion polymerization in acidic to neutral media, was extended to alkaline ones. Namely, the emulsion polymerization of styrene was shown to proceed at pH 7 to 13 in the presence of surfactants of any type up to high conversions, but did so, *ceteris paribus*, much slower than in acidic media. Polystyrene with molecular mass as high as 12×10^6 was thus obtained at pH 9–10. The effect of pH on the rate of emulsion polymerization as well as on characteristics of its products was related to the corresponding rates of decomposition of RCo as well as to stability of emulsion systems and polar interactions in the adsorption layer.

Introduction

Development of advanced processes of radical polymerization allowing improvement and/or diversification of characteristics of their products remains an important trend in chemistry and technology of polymers [1, 2]. In this connection, organocobalt initiators of radical processes that have been under investigation over a quarter of century [3–5] are of particular interest. These alkylcobalt–tridentate Schiff base

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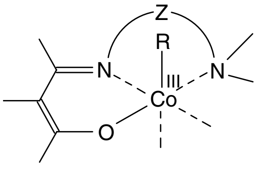
[*] Died in the year 2004.



1 (*RCo*)

complexes (**1**) were shown to effectively and controllably initiate polymerization in slightly acidic media under very mild conditions, down to negative (in the centigrade scale) temperatures [6–8].

Mechanistic studies of the decomposition of complexes **1** in acidic solutions [3, 9, 10] revealed that their homolytic splitting at the Co–C bond was preceded by replacement of extra ligand(s) occupying the 5th and 6th coordination sites with water molecules. On the other hand, it is well known that the reversible aquation of ammonia and amine complexes of cobalt(III) is not only shifted rightwards by acids, but also catalyzed by both the latter and bases [11]. Therefore one can suggest that alkylcobalt–tridentate Schiff base complexes including extra amine (diamine) ligands may initiate radical polymerization in alkaline media as well as in acidic ones. Development of highly efficient polymerization processes in alkaline emulsions would have not only certain principal value, but practical implications as well, since some important industrial high-molecular materials, *e. g.* butadiene–styrene copolymers, are prepared just in such media.

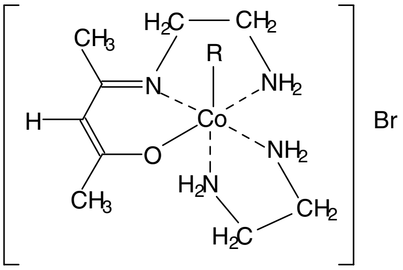
On this ground, we have undertaken an investigation of emulsion polymerization of styrene as a model monomer, using the alkylcobalt initiators in the neutral to alkaline pH range. It was supplemented with a relevant study of their decomposition.

Results of this work were preliminarily published in brief as a conference report [12].

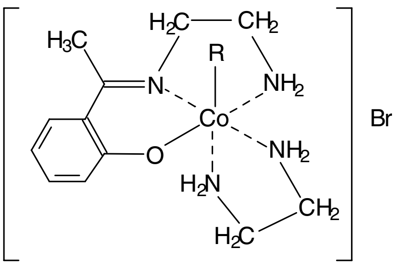
Experimental

Materials

Alkylcobalt complexes of the **1A** and **1B** series (alkyl[2-[(2-aminoethyl)imino]pent-3-ene-4-olato]- and -[2-[1-[(2-aminoethyl)imino]ethyl]phenolato](1,2-ethanediamine)-cobalt(III) bromides) were prepared and characterized as described earlier [13–16]. Commercial styrene (Russia) was liberated from the stabilizing hydroquinone admixture by washing with a 10% aqueous solution of NaOH (reagent of *Reakhim*, Russia, *pro analysis* grade). Then it was washed with water until its reaction turned neutral, dried with anhydrous calcium chloride, twice recondensed under vacuum and characterized as follows: b. p. 145°C, d_4^{20} 0.909 g/cm^3, n_D^{20} 1.5462. Oxyethylated *n*-cetyl alcohol including, in the mean, 20 $-(CH_2)_2O-$ links per a molecule was prepared by interaction of *n*-$C_{16}H_{34}OH$ (reagent of *Aldrich*, *99%* grade) with



[RCo(acacen)(en)]Br (**1A**)



[RCo(7-Me-salen)(en)]Br (**1B**)

a stoichiometric amount of ethylene oxide (commercial product, Russia) in the presence of NaOH catalyst (0.5 weight % with respect to $C_{16}H_{34}OH$) at 135–145°C for 9 h in a pressure vessel under anaerobic conditions. The product (*C-20*) was washed with water many times, dried at 50°C under vacuum and characterized with specific conductivity (as a measure of washing off the alkali) which lay in the range of $1.1 \cdot \times 10^{-5}$–$1.3 \cdot \times 10^{-5}$ $Ohm^{-1}mm^{-1}$, critical micelle concentration (CMC)–$5.13 \cdot \times 10^{-4}$ M, and surface tension on the boundary of its aqueous solution at CMC with air–40 mN/m. Other chemicals, namely sodium pentadecylsulfate (*E-30*, of *Merck*, *Reagent* grade), *n*-cetylpyridinium chloride monohydrate (*CPC*; of *Aldrich*, *98%* grade) myristyltrimethylammonium bromide (of *Aldrich*, *99%* grade), dextran (of *Sigma,* fraction of molecular mass 35,000–45,000), *β*-cyclodextrin (of *Sigma*), *N-tert*-butyl-*α*-phenylnitrone (*PBN*, of *Aldrich*, *98%* grade), *trolox* (of *Aldrich*, *97%* grade) and conventional components of phosphate buffers, *viz*. KH_2PO_4 and $Na_2HPO_4 \cdot \times 2H_2O$ (of *Reanal* (Hungary), of *pro analysis* grade) were used as received.

Instruments, Techniques and Procedures

To monitor decomposition of organocobalt complexes, both spectrophotomety and oxymetry (Clarke electrode) techniques were applied. Namely, uv–vis scanning spectrometer *Uvikon 922* of *Kontron Instruments* (France), and pO_2-meter *MO-128* of *Mettler Toledo* (Switzerland) connected to a computer terminal *via* a plugged-in digital–analog converter were used.

Volatile hydrocarbon products of decomposition of the complexes were analyzed on a gas chromatograph *Chrom-5* of *Laboratorni Pristroje* (former Czechoslovakia) using a column with *Chromosorb Q* packing and a flame ionization detector.

Polymerization processes were performed under anaerobic conditions, temperature control and permanent stirring, and monitored with dilatometric technique. A typical experiment was carried out as follows. A calibrated dilatometric vessel provided with a magnetic stirrer was first charged with an initiator (12 μmol), and then connected to a vacuum apparatus including reservoir flasks pre-charged with styrene (4.53 g, 44 mmol), and a water solution (10 mL) of a standard 0.15 M phosphate buffer providing an appropriate pH, as well as of a surfactant (0.40 g). Both styrene and the water solution were degassed by two freeze/pump cycles and allowed to pour out into the dilatometric (reaction) vessel. Then the vessel was disconnected from the vacuum apparatus and closed under argon flow, and thermostated within 0.1°C. Polymerization was launched by turning on the stirrer.

Mean molecular masses of polymers were determined *via* measurements of intrinsic viscosities of solutions in toluene at 25°C.

Results and Discussion

Kinetics and Mechanism of Decomposition[1]

Behavior of several complexes of the [RCo(acacen)(en)]Br (**1A**) and [RCo(7-Me-salen)(en)]Br (**1B**) series (R = Et, *i*-Pr, *n*-Bu, *i*-Bu, C-hex[2]) was

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[1] Results of this study are presented here in brief, as far as they are directly related to the use of the complexes in question as initiators. In full, this work will be submitted to a periodical specializing in chemical kinetics such as the *Inorganic Reaction Mechanisms* journal.

[2] Here and below, *C-hex* designates cyclohexyl.

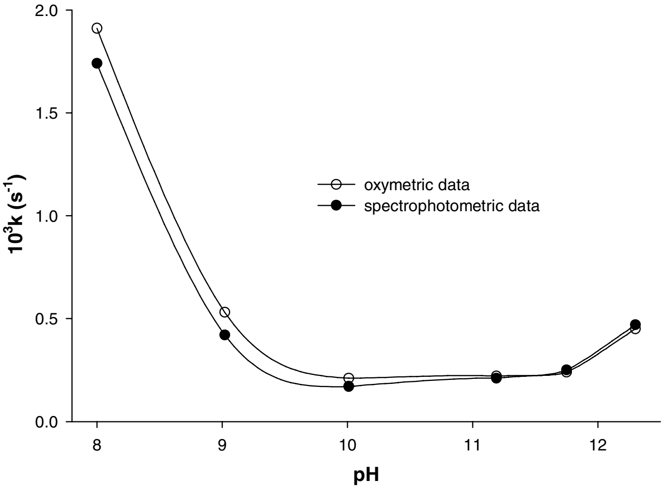

Figure 1. Decomposition of [*i*-PrCo(acacen)(en)]Br in neutral to alkaline solutions in the air at 25°C: pH profile of the apparent 1st-order rate constant

investigated in aqueous buffer solutions with I = 0.15 M at pH 3–14 and 15–60°C both in the absence and presence of surfactants. Spectrophotometric measurements (carried out both under aerobic and anaerobic conditions) allowed monitoring conversion of colored organocobalt species while oxymetric ones (carried out, naturally, in the air) were used to detect fast consumption of dioxygen by transient primary products of the homolysis of Co–C bonds, namely alkyl free radicals $R^\bullet$ and low-spin paramagnetic Co(II) complexes.[*]

The set of kinetic data thus obtained was formally treated in terms of the 1st-order rate equation. Experimental points proved to deviate from its mean linear anamorphoses no more than by 15%. The apparent 1st-order rate constants obtained from spectrophotometric measurements at various wavelengths nearly coincided, which indicated practical reliability of these calculations. A close agreement between "spectrophotometric" and "oxymetric" sets of kinetic data exemplified with Figure 1, as well as presence of isobestic points at series of spectra recorded in the course of the decompositions implies that no intermediates are accumulated in these cases. Hence it follows that if these reactions comprise several consecutive steps, the last of them is rate-determining, just as in acidic solutions [3].

Apparent rate constants of the decomposition in the extended pH range were found to depend on pH in an extremal manner, which indicated that its mechanism is, in general case, more complicated than that established [3, 9, 10] for acidic media.

Last but not least, this kinetic study did confirm our suggestion that decomposition of the complexes in question is accelerated not only by acid, but also by alkali, which is clearly evidenced by upturned bell-shaped pH profiles of reaction rate thus obtained (Figure 1). On the other hand, it is characteristic that these curves are definitely

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[*] In the kinetic measurements carried out under aerobic (a) or anaerobic (b) conditions, respectively, the *trolox* antioxidant (a) or PBN (b) was usually added in excess, in order to suppress chain propagation reactions involving alkylcobalt complexes, which might have been caused otherwise [3] by the resulting alkylperoxy (a) or alkyl (b) free radicals.

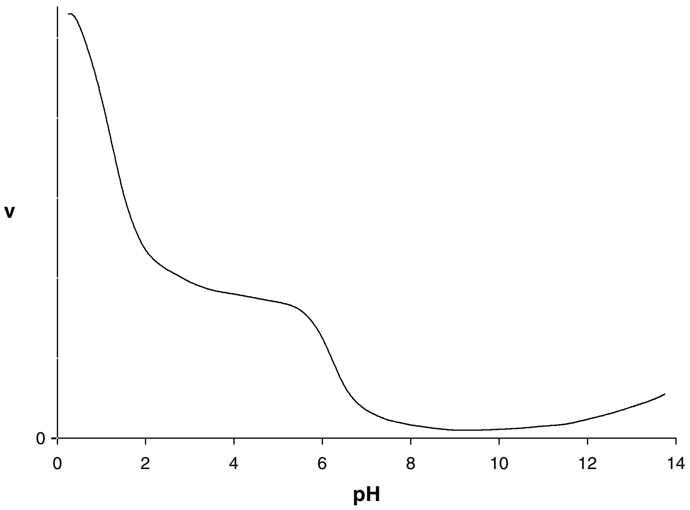


Figure 2. Kinetic pattern of decomposition of alkylcobalt complexes with tridentate Schiff bases: typical pH profile of reaction rate

asymmetric: their "acidic" branches are much sharper than the "alkaline" ones and that positions of their minima are notably shifted towards alkaline pH values.

On this ground and taking into account our former studies [3] carried out in acidic media, a typical overall dependence of the decomposition rate on pH can be qualitatively presented with Figure 2.

While the rates of decomposition in strongly enough alkaline solutions increase along with rising pH under both aerobic and anaerobic conditions, those measured under argon are substantially higher than the corresponding values in the air (Figure 3) or in the presence of spin traps. This result suggests, by analogy to that obtained with such

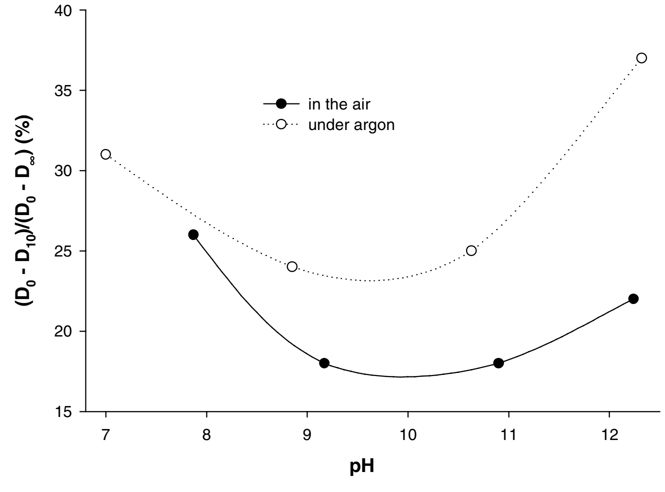


Figure 3. Decomposition of [*i*-PrCo(acacen)(en)]Br in neutral to alkaline solutions at 40°C: pH profiles of relative decrements of optical densities at $\lambda = 306$ nm for the first ten minutes

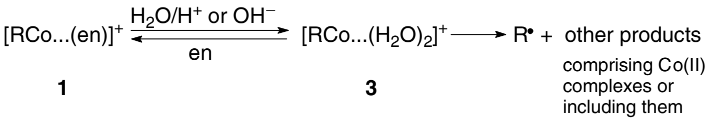
Table 1. Relative yields of hydrocarbon products from decomposition of [EtCo(acacen)(en)]Br (RCo) in aqueous solutions of NaOH adjusted to I = 1 M with $NaClO_4$ at 60°C under anaerobic conditions

$[RCo]_0$ (M)	[NaOH] (M)	Relative yields of hydrocarbon products, $C_2H_4 : C_2H_6 : n\text{-}C_4H_{10}$ (moles per mole)
5.9×10^{-4}	0.05	1 : 3.4 : 2.5
5.9×10^{-3}	The same	1 : 4.4 : 0.75
5.9×10^{-4}	1	1 : 3.3 : 1.3
5.9×10^{-3}	The same	1 : 5.1 : 0.35

complexes in acidic solutions [3, 9, 10], that (*i*) homolytic splitting of the metal–carbon bond proceeds here in effect irreversibly, and (*ii*) in the absence of appropriate acceptors of free radicals, it may initiate radical chain decomposition of the starting complex. The latter conclusion is grounded on predominance of the RH alkane over the related alkene (R_{-H}) in products, as well as on the effects of concentrations of alkali (*via* the decomposition rate) and the starting complex on the RH : R_{-H} ratio, as exemplified by Table 1. The effect of alkali concentration also suggests that alkyl free radical here abstracts a hydrogen atom from the amide form of the alkylcobalt complex (**2**) rather than from the initial amine one (**1**):

$$\underset{\mathbf{1}}{[RCo(H_2N...)...]^+} + OH^- \rightleftharpoons \underset{\mathbf{2}}{[RCo(HN...)...]} + H_2O \qquad (1)$$

Overall, the above kinetic data, in combination with the earlier ones for acidic media [3], agree with a common mechanism of the decomposition (Scheme 1) comprising two consecutive steps.* The first of them consist in a reversible aquation catalyzed by both H^+ and OH^- ions, which is typical of cobalt(III) complexes with ammonia and amines [11]. It results in substitution of the chelating ethylenediamine ligand with water molecules. Therefore both acid and alkali accelerate decomposition of complexes **1A**, **1B**. The second step, which is practically irreversible [3], corresponds to the homolysis proper.



$$\underset{\mathbf{1}}{[RCo...(en)]^+} \underset{en}{\overset{H_2O/H^+ \text{ or } OH^-}{\rightleftharpoons}} \underset{\mathbf{3}}{[RCo...(H_2O)_2]^+} \longrightarrow R^\bullet + \text{other products comprising Co(II) complexes or including them} \qquad (2)$$

Scheme 1. Simplified mechanism of decomposition of alkylcobalt–tridentate Schiff base complexes in aqueous media

In particular, this mechanism accounts for the above-mentioned asymmetry of pH profiles of the decomposition rates, as well as for the observed positions of minima of these curves at moderately basic pH values (*cf.* Figure 1). Namely, the action of acid is

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[*] This scheme does not encompass (*i*) the further acceleration of the decomposition occurring in strongly acidic media (*cf.* Figure 2), which is caused, in the long run, by protonation of the diaqua-complex **3** at the enolate oxygen atom of the tridentate “Schiff” ligand [3], and (*ii*) radical-chain propagation processes developing in the absence of appropriate external acceptors of alkyl free radicals such as (di)oxygen (see above), spin traps or vinylic monomers [3, 9, 10].

more effective than that of alkali, since the former not only catalyze the reversible aquation step, but also shifts its equilibrium rightwards by fixation of its amine product, in this particular case ethylenediamine, as a salt of the latter.

Thus, the organocobalt complexes in question well may be efficient initiators of radical reactions in alkaline media just as they were proved [5, 8] in acidic to neutral ones.

To qualitatively pre-estimate the influence of nature of surfactants, first of all, of their charge, on the initiation step of emulsion polymerization, we tried to model it by studying decomposition of the complexes in relevant micellar solutions. The resulting general pattern shown in Figure 4 can be summarized as follows.

1. Non-ionic surfactants increase stability of the complexes over the whole pH range. Evidently, this is due to decreasing effective concentration of both the water reagent and ionic catalysts (H^+ and OH^-) in hydrophobic micellar cavities.
2. In the cases of ionic surfactants, sign of their effect on stability of the complexes is determined by the electrostatic interaction between a charged micelle and the ionic catalyst, H^+ or OH^-, operating in a given pH region. Evidently, their attraction or repulsion, respectively, enhances or reduces decomposition.
3. Quantitatively, the micellar effect also depends on the type of surfactant, decreasing along the series anion-active > non-ionic > cation-active one. Thus, it is evidently related to the electrostatic interaction between cationic complexes **1** and a given micelle, and ultimately to their affinity.

Obviously, this pattern agrees with the common knowledge about the influence of micellar structures on heterolytic reactions [17] such as the 1st (aquation) step of the decomposition while their role in the homolysis proper, if any, seems less important.

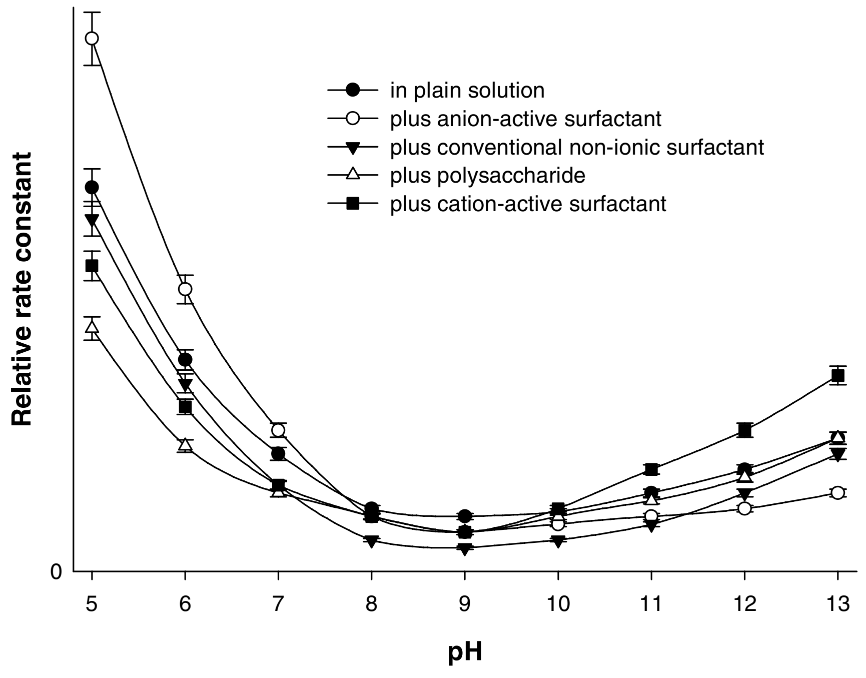

Figure 4. Effects of surfactants on decomposition of alkylcobalt chelates with tridentate Schiff bases: typical pH profiles of rate constants

Polymerization

That of styrene was studied over a wide pH range, using initiators of the [RCo(acacen)(en)]Br series and emulsifiers of various types: anion-active, neutral and cation-active ones. Results are summarized in Table 2 and partially illustrated with Figures 5, 6. They reveal that emulsion polymerization of a vinylic monomer using organocobalt initiators in question proceeds in alkaline media principally as well as in acidic ones [5, 8]. Thus, in combination with the previous studies carried out in acidic media, the present work shows that application of the alkylcobalt initiators allows high (> 90%) conversions to be achieved in a wide pH range even at ambient temperature and low (~ 0.03 molar %) concentrations of the initiators.

Nevertheless, rates of the polymerizations in alkaline media are, *ceteris paribus*, by far lower than in acidic ones, which wholly agrees with the above kinetic data on decomposition of the complexes in solutions. Therefore in the former case, to run emulsion polymerizations at an appropriate speed at ambient temperature, the *sec*-alkylcobalt initiators, *e .g.* those with R = *i*-Pr or C-hex, which are more reactive than the corresponding complexes with primary alkyl ligands [3], should be used.

Table 2. Emulsion polymerization of styrene in the presence of [C-hexCo(acacen)(en)]Br: effect of pH on the course and results of the process (20°C, starting ratio of aqueous phase to monomer 2:1 (v/v); $[RCo]_0$ = 0.028 molar (*i. e.* 0.10 weight) %; [Emulsifier] = 4 weight %)

pH	Stationary rate, %/min	Conversion, %	Characteristics of the product	
			[η], dl/g	MM × 10^{-6}
Sodium pentadecylsulfonate (E-30) as emulsifier				
4.8	7.3	56	5.0	3.0
5.5	6.2	61	5.5	3.5
7.0	3.9	73	5.5	3.5
8.0	3.6	91	5.7	3.6
9.0	1.2	90	8.8	6.8
10.0	0.7	93	12.2	11.0
12.0	0.8	92	10.3	8.6
12.9	0.9	92	10.1	8.3
Cetylpyridinium chloride (CPC) as emulsifier				
4.8	5.8	56	5.3	3.3
5.5	5.6	56	3.8	2.0
7.0	4.3	63	3.8	2.0
8.0	3.6	71	3.1	1.5
9.0	2.1	90	13.5	12.6
10.0	1.8	93	12.6	11.5
12.0	1.4	92	12.4	11.2
Oxyethylated cetyl alcohol (C-20) as emulsifier				
4.8	4.7	92	4.3	2.4
5.8	3.7	95	4.8	2.8
7.0	3.0	95	4.2	2.3
8.0	2.2	95	4.9	2.9
9.0	0.4	[*]	12.8	11.7
10.0	0.4	[*]	10.5	8.7
12.0	0.4	[*]	7.6	5.5

[*] In these cases of relatively slow polymerization, monitoring of the process was cut short of its termination.

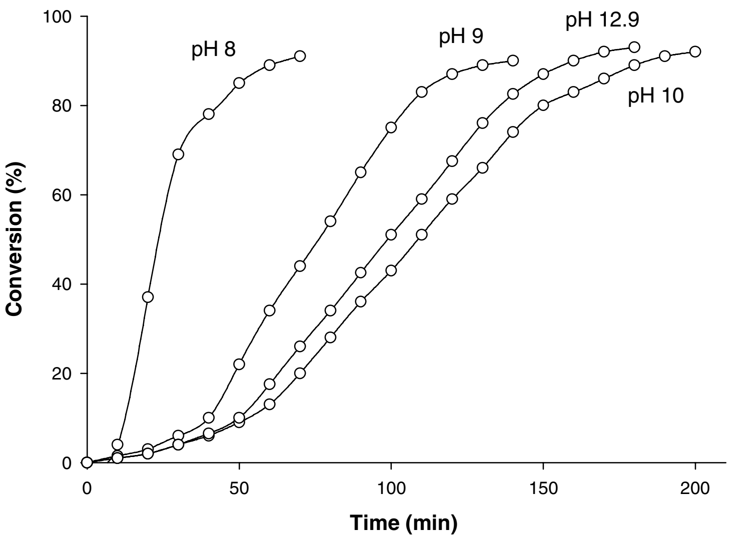

Figure 5. Kinetics of emulsion polymerization of styrene initiated by [C-hexCo(acacen)(en)]Br at 20°C and various pH, using E-30 as emulsifier; other conditions are given in the title of Table 2

On the other hand, in the latter case high conversions could not be obtained using the *sec*-alkylcobalt initiators at the same temperatures in acidic to neutral media, which is evidently due to very fast decomposition of the complexes in question under these conditions. Obviously, it should result with exhaustion of such initiators in a too short time.

Finally, the effect of pH in its neutral to alkaline range on the polymerization rates should be considered. In the cases of emulsions stabilized by C-20 or CPC, the rate does not change or even decreases along with rising pH respectively. With the latter cation-active surfactant, the well-known supramolecular effect of destabilization of emulsions by alkali apparently operates, predominating over the kinetic factor displayed in solution. As to the polymerizing system with the non-ionic C-20 emulsifier, the latter factor is probably just equilibrated by changing polar interactions in the adsorption layer. On the other hand, in the case of an anion-active surfactant, sodium pentadecylsulfonate, pH profiles of the corresponding polymerization rates and those of decomposition of the complexes in relevant solutions are qualitatively similar. This trend exemplified with Figure 7 is evidently due to a strong affinity of the cationic initiator to the anion-active surfactant and the destabilizing effect of the latter on the former in alkaline media, which was discussed above.

It is noteworthy that the processes in alkaline media readily allow production of polymers with extra high molecular masses. In our opinion, this feature is mainly due to reducing number of initiating radicals in emulsion, which is caused by relatively low rates of the decomposition. Furthermore, if molecular masses increase up to very high values, arising high-polymer film should hinder diffusion of primary radicals from water phase into a polymer–monomer particle so that chain termination would proceed mostly through interaction of two polymer radicals. Obviously, this phenomenon should reinforce the former trend.

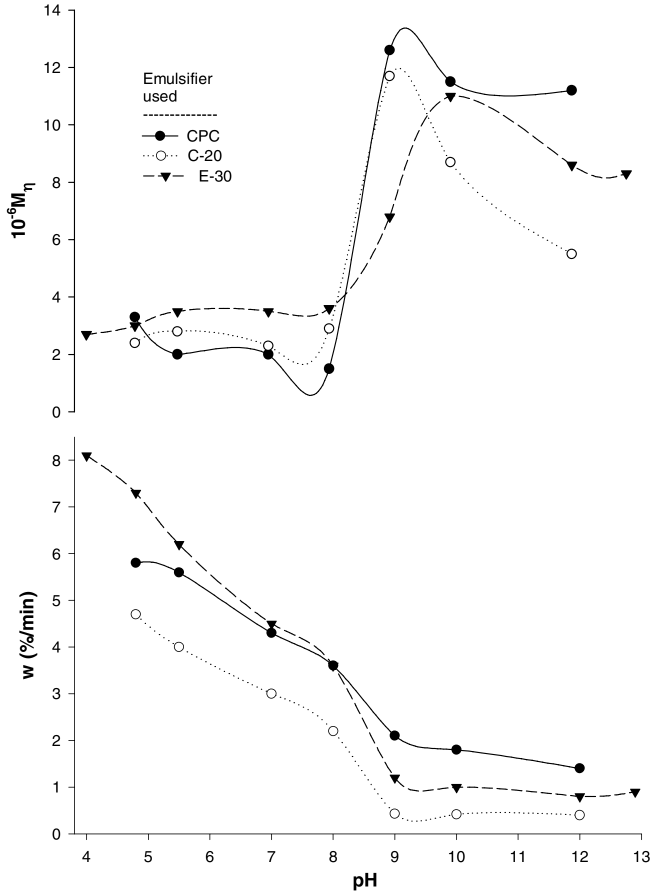

Figure 6. Emulsion polymerization of styrene in the presence of [C-hexCo(acacen)(en)]Br, using various types of emulsifiers: pH profiles of stationary polymerization rate (the lower plot) and mean molecular mass of polystyrene product (the upper plot).
Conditions of the process are given in the title of Table 2

Conclusions

In combination with our former related studies carried out in acidic solutions, this work has established a common mainstream mechanism of decomposition of alkylcobalt(III)–tridentate Schiff base complexes (RCo) in a rather wide pH range, from moderately acidic media to strongly alkaline ones. It includes an aquation pre-equilibrium resulting in the substitution of (a di)amine ligand(s) with water molecules and a subsequent homolytic splitting of the Co–C bond which is rate-determining and essentially irreversible. Both protons and hydroxyl ions catalyze the aquation step after the conventional pattern of acid–base catalysis, while the impact of protons on the overall decomposition rate is much stronger, since they, moreover, shift the equilibrium to the right. Effect of surfactants on the reaction rate can be explained by electrostatic and hydrophilic/hydrophobic interactions between the cationic complexes and other components of micelles formed. Evidently, it operates at the heterolytic pre-equilibrium stage.

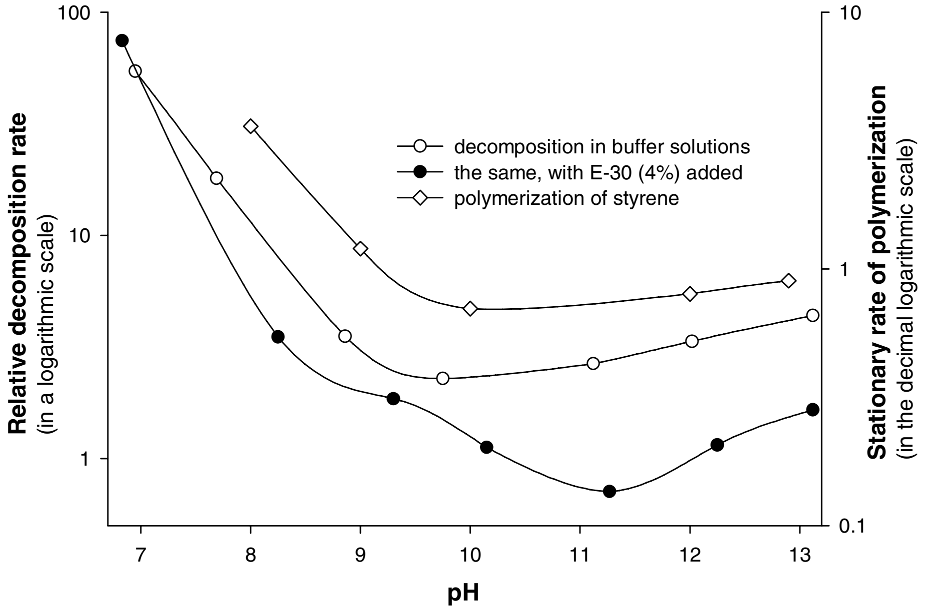

Figure 7. Confrontation of pH profile of stationary rate of emulsion polymerization of styrene (E-30 (4 weight %) as emulsifier; other conditions are given in Table 2) initiated by [C-hexCo(acacen)(en)]Br with those of its relative decomposition rates in aqueous solutions at 25°C either in the presence or absence of the same surfactant

On these bases, the use of RCo, which had been formerly proved advanced pH-dependent initiators of emulsion polymerization in acidic to neutral media, was extended to alkaline ones. Namely, the emulsion polymerization of styrene was shown to proceed at pH 7 to 13 in the presence of surfactants of any type up to high conversions, but did so, *ceteris paribus*, much slower than in acidic media. Polystyrene with molecular mass as high as 12×10^6 was thus obtained at pH 9–10. The effect of pH on the rate of emulsion polymerization as well as on characteristics of its products was related to the corresponding rates of decomposition of RCo as well as to stability of emulsion systems and polar interactions in the adsorption layer.

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