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Reactions of Hydroperoxides with Amines and Aminoalcohols in Aqueous Solutions in the Presence and Absence of Metal Ions

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The intermolecular interactions in hydroperoxide-amine and hydroperoxide-amine-M^{2+} systems in aqueous media are examined. The formation of binary complexes between the system components is demonstrated; the amine complexes of metals $(MA)^{2+}$ show the highest activity in the decomposition of hydroperoxides. The fundamental kinetic characteristics of the decomposition reactions of hydroperoxides with amines in an aqueous medium in the presence and absence of metal ions are reduced from the data obtained and reaction mechanisms are proposed.
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I. INTRODUCTION

The study of the mechanism of the decomposition of hydroperoxides (ROOH) is of both theoretical and applied importance. They are intermediates in oxidation reactions in living organism and also in the autoxidation of low- and high-molecular weight organic substances. Hydroperoxy-compounds have found major practical applications as oxidising agents for various organic compounds and in the organic synthesis of oxygen, sulphur, phosphorus, and nitrogen compounds.

Nitrogen-containing organic compounds, particularly amines, aminoalcohols, aminoacids, etc. (present in the living organism as component parts of proteins and enzymes), form complexes with "metals of life" such as Co^{n+} (n = 2, 3), Cu^{n+} (n = 1, 2), Fe^{n+} (n = 2, 3), Mo^{n+} (n = 5, 6), Mn^{n+} (n = 2, 3, 4), Na^+, K^+, Zn^{2+}, Mg^{2+}, Ca^{2+}, etc. Some of them induce the catalytic decomposition of hydroperoxides in aqueous solutions analogous to that observed in enzyme catalysis.

The oxidation of high-molecular-weight compounds (polymers, rubbers, etc.) is an undesirable phenomenon which leads to their degradation and ageing. (Oxidation with atmospheric oxygen results in the formation on the hydrocarbon chains of the polymer of hydroperoxy-groups OOH, whose radical decomposition actually induces the degradation and hence also the ageing of polymers.) The elimination of or the prevention of the formation of the ROOH groups in macromolecules can be achieved by employing certain aminoalcohols and amine complexes as stabilisers.

This review deals with the kinetics and mechanisms of the reactions of cumenyl or t-butyl hydroperoxides with amines (A) in the presence and absence of M^{2+} ions in aqueous solutions. The studies were undertaken to elucidate the mechanism of the decomposition of hydroperoxides in aqueous media, to select amino-compounds and their complexes for reactions with specified pathways and products, and to select the necessary systems consisting of amines and M^{2+} complexes to be used as stabilisers in adhesive latexes and rubbers based on polychloroprene. In addition, the results obtained in studies on ROOH–A and ROOH–A–M^{2+} systems made it possible to explain the positive influence of Cu^{2+}, Co^{2+}, and monoethanolamine on the organisms of animals and man.

The kinetics of the formation and decomposition of ROOH in the absence and presence of variable-valence metal ions in organic solvents have been studied[1-7]. This review deals with investigations in aqueous media. All vital processes occur in water and nitrogen-containing compounds and hydroperoxides play an important role in them[8].

II. INTERMOLECULAR INTERACTIONS IN HYDROPEROXIDE–AMINE AND HYDROPEROXIDE–AMINE–M^{2+} SYSTEMS IN AQUEOUS MEDIA

The H_2O–ROOH–A–M^{2+} system is complex and several processes and reactions can occur simultaneously in it. In order to elucidate the character and mechanisms of the possible individual stages, studies were therefore made of complex formation and the binary interactions between the system components.

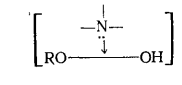
1. Complexes between ROOH and A

De La Mare et al.[9] showed in an earlier study that the interaction of hydroperoxides with amines in solution in the latter results in the formation of a hydrogen-bonded complex;



(I)

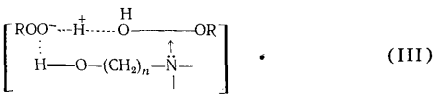
It has been shown[10,11] that the interaction of a hydroperoxide with amines in aqueous media involves conjugation between the electrons at the nitrogen atom and the oxygen bond with formation of a complex having a different structure:



(II)

The formation of complex (II) in aqueous media had been postulated earlier on the basis of kinetic data[12]. The authors of that investigation[12] also suggested that complex (III) between the ROOH dimer and an aminoalcohol molecule is

formed, in addition to complex (II), in aqueous solutions in the presence of aminoalcohols:



(III)

Subsequently this was also demonstrated by infrared spectroscopy[13].

It has been shown by NMR that complexes are formed in organic solvents (benzene, acetone, ethanol, etc.). The chemical shifts of the OOH group in t-butyl (TBHP), cumenyl (CHP), and t-pentyl hydroperoxides on formation of complexes with proton-accepting compounds (ethers and amines) have been investigated[14,15]. Depending on the concentration of, for example, triethylamine (TEA), there are three types of associated species (i.e. hydrogen-bonded complexes between TEA and TBHP) with a 1 : 1 composition; the hydroperoxide–hydroperoxide complex of the type ROOH....$\overset{H}{O}$OR predominates at low amine concentrations, while at high amine concentrations a complex resembling (II) is the dominant species. According to Yablonskii and co-workers[14,15], the O–O bond of the hydroperoxide in the complexes with amines is weakened more than in associated species with other proton acceptors and for this reason ROOH in saturated hydrocarbons (at 130–140 °C) and in water (up to 90 °C) are thermally stable[12,16], while in the presence of amines in aqueous solutions they decompose already at 30–40 °C.[12] Since the O–O bond of the hydroperoxide in complex (II) is weakened, the reaction is of first order with respect to ROOH.[12]

The formation of complexes between CHP and TEA has been investigated by proton magnetic resonance (^{1}H NMR) in aqueous solution at 34 °C.[17] It was found that the complex has the 1 : 1 composition and that the equilibrium

$$\text{ROOH} + \text{:N}- \rightleftarrows [\text{ROOH} \cdots \text{:N}-] \qquad (1)$$

exists. The complex formation constant (K_p = 0.18 litre mol^{-1} at 34 °C) was calculated graphically[18] using the equation

$$\Delta/[\text{A}]_0 + K_p\Delta = K_p\Delta_0 \qquad (2)$$

where Δ_0 is a standard quantity which represents the difference between the chemical shifts of the OOH group in the complex and in the ROOH–cyclohexane system (CHP was diluted with an inert solvent—cyclohexane), Δ is the difference between the chemical shifts of the CHP–TEA system in cyclohexane and of the CHP–cyclohexane system and is a measure of the reaction between OH and :N– alone, and $[\text{A}]_0$ is the initial amine concentration; we have $[\text{A}]_0 \gg [\text{ROOH}]$.

2. Complex Formation Reactions between A and M^{n+}

The thermodynamically stable ammine and amine complexes of copper and cobalt have the composition $(MA_4)^{2+}$.[19] Kinetic studies have shown that the decomposition of the hydroperoxide in the presence of M^{n+} complexes of amines obeys a first-order equation with respect to the amine[20,21]. Spectroscopic measurements (infrared spectroscopy and NMR) also indicate the formation of complexes in aqueous media between amino-compounds and metal ions[19,22]. It follows from the data of Grigoryan and co-workers[21,23] that 1 : 1, 1 : 2, and 1 : 3 complexes are formed together with the complexes $(MA_4)^{2+}$ in aqueous solutions of monoethanolamine, TEA, morpholine, etc. in the presence of Cu^{2+} and Co^{2+}.

The formation of complexes between ligands and M^{2+} was demonstrated by ^{1}H NMR [24,25] on the basis of the paramagnetic shifts of the M^{2+} signals in the presence of different ligands. The NMR spectra of the coordinated ligands not only yield information about the delocalisation of spin density over the bond system of the ligand but also make it possible to determine the equilibrium (complex formation) constant, the heat of complex formation, and other parameters[26].

The concentration dependence of the ^{1}H NMR spectra of TEA (taken in excess) in the presence of Ni^{2+} in aqueous solutions has been investigated[23]. The magnitude and signs of the spin density of the protons in the TEA molecules as well as the constant for the complex formation reaction between TEA and Ni^{2+} were determined from the shifts of the signals; the complex has the 1 : 1 composition. A downfield shift of the signals of the protons in the methylene and methyl groups of TEA was observed in the test solutions, for $[\text{TEA}]_0$ = 0.05–0.35 M and $[Ni^{2+}]_0 = 5 \times 10^{-3}$ M, the shift of the methylene proton signals being greater than the shift of the methyl proton signal. At the same time the multiplet signals of these groups are broadened and distorted, which indicates the existence in the solutions of labile paramagnetic complexes[27]. The signals for the CH_2 and CH_3 group are displaced downfield, which means that positive spin density is located on the protons of these groups following the formation of complexes. The dependence of the shift of the NMR lines on the ligand concentration is described by the formula[28,29]

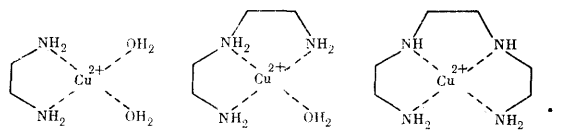
$$-\mu/\delta = 1/\alpha aK + S/\alpha a\,, \qquad (3)$$

where μ is the molar concentration of the paramagnetic substance (in this case Ni^{2+}), δ the paramagnetic shift (p.p.m.) equal to the difference between the chemical shifts in the presence and absence of paramagnetic species (Ni^{2+}), S the molar concentration of TEA with $[\text{TEA}]_0 \gg [Ni^{2+}]_0$, K the complex formation constant, a the hyperfine coupling (HFC) constant (G) at 304 K, and α = 72.8). The HFC constants for the methylene and methyl protons of TEA and the complex formation constants were determined from the graphical analysis of the linear dependence of μ/δ on $[\text{TEA}]_0$ and $a^H_{CH_2}$ = +0.02 G, $a^H_{CH_3}$ = +0.008 G, and $K = 1.32 \times 10^2$ litre mol^{-1} (34 °C) were obtained.

The mechanism of the transfer of spin density to the atomic orbitals of the TEA molecule is as follows. For chelate Ni^{2+} complexes of amines, the unpaired electron is delocalised as a result of the formation of a σ-bond. The unshared electron pair of the nitrogen atom and the d_{z^2} orbital of the Ni^{2+} ion are involved in the formation of the Ni^{2+}–TEA σ-bond. In this case the spin density at the nitrogen atom is positive.

On comparing the complex formation constants obtained for Ni^{2+} ($K = 1.32 \times 10^2$) with the constants for the analogous Co^{2+} ($K = 2.6 \times 10^4$) and Cu^{2+} ($K = 6.1 \times 10^{15}$) complexes[30,31], we may note that the Ni.TEA complex is less stable. It is noteworthy that, in contrast to the analogous Cu^{2+}, Co^{2+}, and Mn^{2+} complexes, the above complex does not exhibit catalytic activity in the CHP and TBHP decomposition reactions in an aqueous medium[21]. The presence of free orbitals in the chelate complex apparently also plays an important role under these conditions. Thus it has been found that the manifestation of a catalytic activity by chelate Cu^{2+} complexes of diamines requires that the complexes contain two coordination-unsaturated bonds. The chelate Cu^{2+} complexes in which all the orbitals are occupied are inactive in the ROOH or HOOH decomposition reactions[32]. This is evident from a

comparison of the chelate copper(II) complexes of the following diamines: ethylenediamine, diethylenediamine, and triethylenediamine; they are illustrated schematically below:



The activity in the ROOH or HOOH decomposition reactions decreases in the sequence ethylendiamine (en) ≫ diethylenediamine (dien) > triethylenediamine (trien), i.e. the complex in which the central atom is not fully blocked by the ligand proved to be the most active; complexes with tetradentate ligands show almost no catalytic activity.

3. The Formation of Complexes between ROOH and M^{n+}

The formation of an intermediate complex between the hydroperoxide and the metal ions in organic media has been established[33–36]. The formation of complexes between metal ions (Ni^{2+}, Mn^{2+}, etc.) and TBHP in CCl_4 and CH_2Cl_2 has been demonstrated by NMR.[29] The intermolecular interactions between ROOH and M^{n+} in aqueous solutions were first investigated by Markaryan et al.[37] At very high water concentrations it becomes almost impossible to demonstrate the occurrence of the interaction of ROOH with Mn^{2+}, since the signals of the hydroperoxide and water protons merge; the complex formation in the CHP–Co^{2+} system was therefore investigated at low water concentrations. The results made it possible to estimate quantitatively the degree of intermolecular interaction between the ROOH and M^{n+} in aqueous solutions. The concentration dependence of the shift of the signal due to the protons of the CHP molecule in aqueous solutions in the presence of an excess of the hydroperoxide (>97, 98, 98.5, and 99%) was investigated. The constant for the complex formation between CHP and Co^{2+} was determined by Eqn.(3) from the shift; it proved to be $K = 0.158$ litre mol^{-1} at 34 °C.

One must note that the interaction of the individual components (ROOH and A) with water (as the medium) was also investigated by ^1H NMR. After the addition of water to CHP, the signal of the OOH group of the hydroperoxide is slowly displaced downfield as a result of the formation of the hydrogen bond between ROOH and H_2O.[37] The calculated rate constants for proton exchange and the proton lifetime in the complex [ROOH...H_2O] formed are $K = 8.5 \times 10^{-1}$ s^{-1} and $\tau = 1.2 \times 10^{-2}$ s. The formation of associated species comprising water and the TBHP dimer under ambient conditions had been demonstrated previously by infrared spectroscopy[13]. It was also established[38,39] that associated species involving the amine and water are formed in aqueous solutions of amines via both hydrophobic and hydrophilic interactions.

Thus intermolecular interactions occur in aqueous ROOH + A + M^{n+} systems with formation of binary associated species and complexes differing in their stability. Under standard conditions, these intermediate compounds are stable (some of them exhibit a catalytic activity in the ROOH decomposition reaction). Among the binary complexes indicated, the highest activity is shown in the decomposition of cumenyl and t-butyl hydroperoxides in an aqueous medium by the complexes of the amine with the metal ions $(MA)^{n+}$; this is indicated not only by the formation constants but also by kinetic data obtained in the study of the decomposition of hydroperoxides under the influence of these complexes[17,20,21].

III. KINETICS OF THE REACTIONS OF HYDROPEROXIDES WITH AMINES AND AMINOALCOHOLS IN THE ABSENCE AND PRESENCE OF M^{2+}

1. Kinetics of the Decomposition of ROOH in the Presence of the Amine and M^{2+}

The complex formation constants for the components of binary systems are listed below[30,31]:

System	CHP-TEA	CHP-Co^{2+}	TEA-Ni^{2+}	MEA-Cu^{2+}
K_p, litre mol^{-1}	1.6	0.16	132	26 000

Their comparison shows that the complex $(MA)^{2+}$ should be the most active[17,23]. For example, the ratios $K_{A+M^{2+}}/K_{A+ROOH}$ and $K_{A+M^{2+}}/K_{ROOH+M^{2+}}$ are approximately 10^2–10^6. Indeed the kinetic data obtained confirm that the hydroperoxides in the H_2O–ROOH–A–M^{2+} systems decompose mainly catalytically[20,21] as a result of the effect of the complex $(MA)^{2+}$ (although two other reactions can also occur simultaneously with the above reaction), the rate of the reaction catalysed by the complex $(MA)^{2+}$ being several times that in the absence of the complex[20,21].

The data permit the following conclusions concerning the decomposition of ROOH in the presence of amines and metal ions.

1. In the presence of monoethanolamine, pyridine, and some of its derivatives at temperatures up to 80 °C hydroperoxides hardly decompose in aqueous media[40–42]. Nor do the ROOH decompose at an appreciable rate in the presence of only the cations Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, etc.) (up to 90 °C).[12,42,44]

2. The rate of decomposition of hydroperoxides in the presence of aminoalcohols and M^{n+} for $[A]_0 = [ROOH]_0$ in aqueous solutions is expressed by the general equation[40–44]

$$w_{tot} = -\frac{d[ROOH]}{dt} = w_1 + w_2 + w_3 = k_1[A]_0[ROOH]_0 + k_2[ROOH]_0^2 + k_3[M^{2+}]^n[A]_0[ROOH]_0 , \quad (4)$$

where w_1 is the initial rate of reaction directly between ROOH and the aminoalcohol, w_2 the initial rate of decomposition of the CHP dimer catalysed by the aminoalcohol, w_3 the initial rate of the catalytic reaction catalysed by the complex $(MA)^{2+}$, and n is the order of the reaction with respect to M^{2+}, which is between zero and 1.[21] The kinetics of the reaction of ROOH with aminoalcohols have been studied in the range 40–80 °C.[12] In the presence of aminoalcohols the amount of CHP in the system decreases as a result of the occurrence of two independent simultaneous reactions, both being of second order; although the aminoalcohol is involved in one of them, it is not consumed as a reactant: ROOH is consumed to a greater extent in the reactions with aminoalcohols than the aminoalcohol[12,42].

The excess consumption of the hydroperoxide is due to the occurrence of two simultaneous reactions, one of which takes place directly between the hydroperoxide and the aminoalcohol and the other involves the decomposition of the hydroperoxide by the aminoalcohol[12]. It has been established[40] that the first reaction, whose rate is w_1, takes place between ROOH and A molecules, while the second, whose rate is w_2, is the aminoalcohol-catalysed reaction between the $ROOH^-$ and $ROOH_2^+$ species, i.e. involves the formation of the cumenyl hydroperoxide dimer. Both reactions have a non-radical mechanism[40], although one cannot rule out a

slight "radical contribution" (3–5%) to the decomposition of the hydroperoxide in the presence of amines in aqueous solutions[52], despite the fact that this hydroperoxide decomposition pathway is difficult to demonstrate by a kinetic method. The catalytic activity of aminoalcohols (except monoethanolamine) can be explained by the presence of two groups in their molecules—proton donating (the hydroxy-group) and proton accepting (the nitrogen atom), which may entail the formation of complex (III).[12,40] Indeed in the presence of amines and without an alcoholic group hydroperoxides are not decomposed catalytically and only the direct reaction between ROOH and A takes place[41,45]. Table 1 shows that an increase in the number of hydroxy-groups and their removal from the nitrogen atom in the aminoalcohol molecule as well as the presence of hydrogen atoms at the nitrogen atom in the same molecule decrease the overall rate of decomposition of the hydroperoxide[12,40]: under these conditions, the formation of the intermediate active complexes (II) and (III) is hindered.

The replacement of the hydrogen atom in the alcoholic group by the methyl group deprives the amine of catalytic activity in the CHP decomposition reaction. It is thereby confirmed that the catalytic action of the aminoalcohol in the process under consideration involves the migration of the proton in the intermediate active complex (III).[12,41]

The presence of two idential proton-accepting centres (for example, in hydrazine $H_2\ddot{N}-\ddot{N}H_2$) does not lead to the catalytic decomposition of ROOH; the presence of pyridine or triethylamine together with ethanolamine in equimolar proportions or separately does not induce the catalytic decomposition of CHP.[12,41] The catalytic decomposition of the hydroperoxide requires the joint presence in the same molecule of two opposed active centres[12,40,41].

At 30° and 35 °C and for $[CHP]_0 = [TEA]_0$, the consumption of the aminoalcohol is not observed, whereas more than 10% of the initial amount of the hydroperoxide is consumed. i.e. only the catalytic decomposition of ROOH takes place[12]. In addition it has been shown kinetically that a little less than 10% of the consumption of the hydroperoxide is due to its decomposition purely via the catalytic pathway (the overall ratio of the consumptions of ROOH and A is 1.12 : 1). A similar equimolar amount of oxygen evolved was determined in the overall ROOH decomposition reaction in the presence of triethanolamine under the same conditions[12,40].

Table 1 presents kinetic data for the reaction of CHP with amines in an aqueous medium at 80 °C [k_1 and k_2 are the rate constants for the first and second reactions catalysed by the aminoalcohol (litre mol^{-1} min^{-1}); $k = k_1 + k_2$; for amines without alcoholic groups, $k_2 = 0$]. For comparison, Table 1 also lists the activation energies E (kcal mol^{-1}) and pre-exponential factors A (litre mol^{-1} min^{-1}) for the first and second reactions.

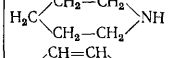
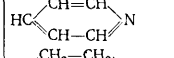
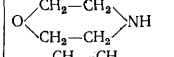
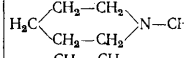
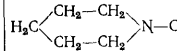
Thus, in the presence of only aminoalcohols such as diethanolamine, triethanolamine, diethylaminoethanol, diethylaminopentanol, diethylbutanolamine, diethyl-2,3-dimethylaminopropanol, β-piperidinylethanolamine, etc. (except monoethanolamine), the rate of reaction is expressed by the following equation[21,40]:

$$w_{tot} = w_1 + w_2 = k_1[A]_0[ROOH]_0 + k_2[ROOH]_0^2 \qquad (5)$$

if $[A]_0 = [ROOH]_0$. If has been shown[40] that w_1 and w_2 are comparable in magnitude; for example, $w_1/w_2 = k_1/k_2 = 1.67$ for the reaction of CHP with triethanolamine at 80 °C.

It has been established by ^1H NMR [14,15,17] that at high amine concentrations a complex of type (II) predominates and there is therefore virtually no catalytic decomposition

Table 1. Kinetic parameters of the reactions of CHP with amines (in water at 80 °C).

No.	Amine	Formula	k, litre mol^{-1} min^{-1}	k_1, litre mol^{-1} min^{-1}	k_2, litre mol^{-1} min^{-1}	E_1, kcal mol^{-1}	E_2, kcal mol^{-1}	$10^{-8}A_1$, litre mol^{-1} min^{-1}	$10^{-8}A_2$, litre mol^{-1} min^{-1}
1	Monoethanolamine	$H_2N-CH_2-CH_2-OH$	0	0	0	—	—	—	—
2	Diethanolamine	$HN-(CH_2-CH_2-OH)_2$	0.124	0.040	0.084	20.6	17.7	2880	28.5
3	Triethanolamine	$N-(CH_2-CH_2-OH)_3$	0.165	0.100	0.065	13.7	19.7	0.0484	167
4	Diethylaminoethanol	$(C_2H_5)_2-N-CH_2-CH_2-OH$	0.584	0.480	0.104	17.8	17.8	537	155
5	Diethylaminopentanol	$(C_2H_5)_2-N-(CH_2)_5-OH$	0.720	0.658	0.062	*	—	—	
6	Diethylaminobutanol	$(C_2H_5)_2-N-(CH_2)_4-OH$	0.570	0.468	0.102	*	—	—	—
7	Dimethylaminoethanol	$(CH_3)_2-N-CH_2-CH_2-OH$	0.479	0.380	0.099	*	—	—	—
8	Diethylisobutanolamine	$(C_2H_5)_2-N-CH_2-CH(OH)-CH_2-CH_3$	0.592	0.500	0.092	*	—	—	—
9	Diethyl-2,3,-diethyl-aminopropanol	$(C_2H_5)_2-N-CH_2-CH(CH_3)-CH(OH)-CH_3$	0.303	0.230	0.078	*	—	—	—
10	Triethylamine	$N-(C_2H_5)_3$	0.171	0.171	0	14.7	—	5.4	—
11	Diethylamine	$HN-(C_2H_5)_2$	0.192	0.192	0	17.5	—	87.1	—
12	Piperidine		0.280	0.280	0	16.0	—	22.4	—
13	Pyridine		0	0	0	—	—	—	—
14	Morpholine		0.052	0.052	0	16.0	—	4.37	—
15	β-Piperidinylethanolamine		0.287**	0.204**	0.083**	17.2	13.7	194	0.426
16	Methyl β-piperidinyl-ethyl ether		0.338	0.338	0	16.5	—	44.8	—

*Values not determined.
**At 70 °C.

of the hydroperoxide under the influence of the aminoalcohol when $[A]_0 \gg [ROOH]_0$. For example, $w_1/w_2 = 15$ for the reaction of CHP with triethanolamine, i.e. the rate of the catalysed reaction may be neglected compared with w_1.[40] We therefore obtain from Eqn.(5)

$$w_{tot} = k_1[A]_0[ROOH]_0 . \quad (6)$$

In the presence of amines without alcoholic groups [triethylamine, diethylamine, morpholine, piperidine, methyl β-piperidinylethyl ether, octylmorpholine, hydrazine, etc. [except pyridine and its derivatives)] the rate of consumption of ROOH (in the absence of M^{2+}) is expressed by an equation[40,41,45] analogous to Eqn.(6):

$$w_{tot} = w_1 = k_1[A]_0[ROOH]_0 . \quad (7)$$

In the presence of M^{2+} for equal initial reactant concentrations, i.e. with $[A]_0 = [ROOH]_0$ it is necessary to use Eqn.(4) instead of Eqn.(5) whereupon the following expression is obtained:

$$w_{tot} = w_1 + w_3 = k_1[A]_0[ROOH]_0 + k_3[M^{2+}]^n[A]_0[ROOH]_0 . \quad (8)$$

The same expression is obtained from Eqn.(4) when $[A]_0 \gg [ROOH]_0$; as above, one can assume in this case that $w_2 \to 0$, since

$$w_2 \ll w_1 \text{ and } w_2 \ll w_3 .$$

When $[A]_0 \gg [ROOH]_0$ and in the case of monoethanolamine or pyridine for any amine concentration, only one reaction catalysed by the complex $(MA)^{2+}$ takes place, its rate being expressed by the equation

$$w_{tot} = w_3 = k_3[M^{2+}]^n[A]_0[ROOH]_0 = k_{cat}[ROOH]_0 , \quad (9)$$

where $k_3[M^{2+}]^n[A]_0 = k_{cat}$ (k_{cat} is a constant for given concentrations of M^{2+} and A).

Transformation of Eqn.(8) yields

$$w_{tot} = k_{non\text{-}cat}[ROOH]_0 + k_{cat}[ROOH]_0 = (k_{non\text{-}cat} + k_{cat})[ROOH]_0 = k_{eff}[ROOH]_0 , \quad (10)$$

where $k_{non\text{-}cat} = k_1[A]_0$. The constant k_{eff} is determined from Eqn.(10).

Table 2. Temperature variation of the rate constants for the decomposition of CHP and TBHP in the presence of the monoethanolamine–Cu^{2+} complex.

t, °C	$10^2 k_{CHP}$, min^{-1}	$10^2 k_{TBHP}$, min^{-1}
60	0.35	0.06
65	0.80	0.12
70	1.34	0.23
75	2.73	0.54
80	4.95	0.90

Note. The initial concentrations of monoethanolamine and ROOH were 0.05 M: $[CuSO_4]_0 = 10^{-3}$ M.

The rate constants for the decomposition of the hydroperoxide by the amine complex $(MA)^{2+}$ are calculated in this way. Next, taking into account the fact that $k_{non\text{-}cat}$ is known[40], k_{cat} is determined:

$$k_{cat} = k_{eff} - k_{non\text{-}cat} . \quad (11)$$

For monoethanolamine or pyridine, k_{cat} is determined from Eqn.(9). One must note that, in contrast to the direct interaction of ROOH with the aminoalcohol and the decomposition of the hydroperoxide dimer by the aminoalcohol[40,41], the catalytic ROOH decomposition reactions under the influence of the complex $(MA)^{2+}$ have a radical-chain mechanism, although the chains are very short[21]. In certain cases the radical character of the reaction is hardly noticed, as in the decomposition of CHP and TBHP in the presence of the 1 : 1 Co^{2+} or Cu^{2+} complex of monoethanolamine.

It is noteworthy that the rate of decomposition of CHP in the presence of the 1 : 1 Cu^{2+}–monoethanolamine complex exceeds severalfold the rate of decomposition of TBHP (Table 2).

Comparison of the temperature variations of the rates of decomposition of the above hydroperoxides readily shows that the rate of decomposition of CHP increases appreciably in the presence of the phenyl group in the hydroperoxide molecule (being a weaker electron donor than the methyl group, the phenyl group diminishes the electron density in the O–O bond and thereby facilitates the decomposition of the CHP compared with TBHP). The mechanism of the catalytic decomposition is apparently independent of the type of hydroperoxide, since the activation energies are almost identical:

$$k_{CHP}\,(\text{min}^{-1}) = 8.13 \cdot 10^{17} \cdot \exp[(31\,000 \pm 500)/RT] \cdot$$
$$k_{TBHP}\,(\text{min}^{-1}) = 1.62 \cdot 10^{17} \cdot \exp[(31\,500 \pm 500)/RT] \cdot \quad (12)$$

Like metal ions, amines are catalysts of the decomposition of ROOH in aqueous solutions; it has been shown by the kinetic and chromatographic methods[21] that, in the course of the decomposition of ROOH, the amine is not consumed and after the complete decomposition of ROOH the amount of amine remains unchanged.

The rate of consumption of the hydroperoxide in the presence of Cu^{2+} is higher than in the presence of Co^{2+} or Mn^{2+}, which can be explained by the stability of the amine complexes whose criterion is the oxidation potential of the metal; there is a correlation between the normal oxidation potential of the cation and the rate of decomposition of the hydroperoxide: the rate of decomposition of ROOH increases in parallel with the increase of the normal oxidation potentials of M^{2+}.[21]

One must note that there are also other factors which influence the stability of metal ion complexes (the presence of unfilled orbitals in the complex, the charge and size of the ion, the nature or basicity of the ligand, and others[32]).

2. The Amine Complexes of Metal Ions as Models of Enzymes in the Decomposition Reactions of Cumenyl and t-Butyl Hydroperoxides in an Aqueous Medium

The hypothesis of the formation of an intermediate active complex of the type $[ROOH...(MA)^{2+}]$ has been used to account for the kinetics of the homogeneous catalytic reactions of cumenyl and t-butyl hydroperoxides in the presence of an amine and M^{2+} in an aqueous medium[42].

As mentioned above, in the presence of amines or aminoalcohols and M^{2+} ions, the decomposition of the hydroperoxide catalysed by the M^{2+} complexes of the aminoalcohol may be accompanied by the simultaneous occurrence of other reactions. The complex catalyst (E), consisting of M^{2+} and A, can be regarded as the simplest analogue of an enzyme inducing the decomposition of hydroperoxides[42].

It is known[19] that the thermodynamically stable ammine or amine complexes of copper or cobalt have the composition $(MA_4)^{2+}$. Studies have shown[21] that the decomposition of ROOH obeys a first-order kinetic equation with respect to A, indicating that the amine complex of the bivalent metal involved in the chemical reaction has the composition $(MA)^{2+}$.

The formation of the given intermediate complex between the amine complex (E) and the hydroperoxide can be represented by the equation

$$E + n\text{ROOH} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [E \cdots n\text{ROOH}] \quad . \qquad (13)$$

Reaction (13) is reversible and, since $k_{-1} \gg k_1$, the equilibrium is established faster than the decomposition of the intermediate active complex[17,46]. All amines and aminoalcohols have the capacity to form such complexes in aqueous solutions[17,42], but MEA in the presence of Cu^{2+} or Co^{2+} constitutes a purely model system, because in the joint presence of the above reactants the catalytic process is not accompanied by other simultaneous reactions.

The equilibrium constant is given by

$$K = \frac{k_1}{k_{-1}} = \frac{[E \cdots n\text{ROOH}]}{[\text{ROOH}]^n [E]} \quad . \qquad (14)$$

If $[E]_0$ is the initial overall concentration of the bound and free catalyst, then the following relation is valid:

$$[E] = [E]_0 = [E \cdots n\text{ROOH}] \quad . \qquad (15)$$

On substituting Eqn.(15) in Eqn.(14), we obtain

$$K = \frac{[E \cdots n\text{ROOH}]}{[\text{ROOH}]^n ([E]_0 - [E \cdots n\text{ROOH}])} \quad ,$$

whence the concentration of the intermediate complex is given by the expression

$$[E \cdots n\text{ROOH}] = \frac{K [\text{ROOH}]^n [E]_0}{1 + K [\text{ROOH}]^n} \quad . \qquad (16)$$

The final reaction products are obtained as a result of the decomposition of this complex[21,46]:

$$[E \cdots n\text{ROOH}] \xrightarrow{k_{\text{decomp}}} (MA)^{2+} + \text{final products.} \qquad (17)$$

If the overall rate of decomposition of the initial hydroperoxide or the rate of formation of the reaction products are determined by the rate of reaction (17), one can write

$$w = d[\text{ROOH}]/dt = k_{\text{decomp}} [E \cdots n\text{ROOH}] . \qquad (18)$$

From Eqns.(16) and (18), we obtain an expression for w:

$$w = \frac{k_{\text{decomp}} K [\text{ROOH}]^n [E]_0}{1 + K [\text{ROOH}]^n} \quad . \qquad (19)$$

The initial concentration of the complex catalyst $[E]_0$ cannot be greater than the concentration of the metal ions (Cu^{2+}, Co^{2+}, Mn^{2+}, etc.). Consequently $[E]_0$ in Eqn.(19) can be expressed in terms of the initial concentration of the metal ion bearing in mind that the stability constants of the complexes $(MA)^{2+}$ are much greater than unity[17,30,31]. An equation of the Michaelis–Menten type is then obtained in the following form:

$$w = \frac{k_{\text{decomp}} K [\text{ROOH}]^n [M^{2+}]_0}{(1 + K [\text{ROOH}]^n)} \quad . \qquad (20)$$

After rearranging Eqn.(20) and taking into account the fact that, according to kinetic data[42] the order of the reaction with respect to the hydroperoxide is $n = 1$, we obtain

$$\frac{1}{w} = \frac{1}{k_{\text{decomp}} [M^{2+}]_0} + \frac{1}{k_{\text{decomp}} K [\text{ROOH}] [M^{2+}]_0} \quad . \qquad (21)$$

Eqn.(21) was used for the graphical evaluation of K and k_{decomp} (Table 3) from plots of $1/w$ against $1/[\text{ROOH}]$ (Lineweaver and Burk[47]) for the intermediate active complexes in the reactions of CHP with the Cu^{2+} or Co^{2+} complexes of monethanolamine, diethanolamine, triethanolamine, TEA, morpholine, etc.[42]

It has been shown that there are correlations between k_{decomp} and K_{form}—the formation constant of the complexes $(MA)^{2+}$ between A and M^{2+}, and also between the stability constant K_{st} and $\lg k_{\text{decomp}}$. The results demonstrate the validity of the selected model of the process for the test systems. Thus the M^{2+} complexes of amines and aminoalcohols $(MA)^{2+}$ in aqueous solutions behave as simple analogues of enzymes of the catalase type in the CHP and TBHP decomposition reactions. One must point out that these complex catalysts (particularly the complexes of monoethanolamine and pyridine) are also not consumed in the reactions and, behaving as models of enzymes, induce the continuous decomposition of ROOH.[42]

Table 3. The constants K and k_{decomp} for intermediate complexes of the type [E...ROOH] in the reactions of CHP with $(MA)^{2+}$.

	A	K, litre mol^{-1}	k_{decomp}, min^{-1}
TEA	(60°)	5.4	3.7
Morpholine	(80°)	3.5	58.8
Morpholine*	(80°)	6.0	6.7
Monoethanolamine	(78°)	3.7	18.2
Diethanolamine	(80°)	4.7	62.5
Triethanolamine	(60°)	2.5	66.7
Triethanolamine*	(80°)	2.2	4.0

*M = Co; in the remaining cases M = Cu.

3. The Effect of Monoethanolamine and Its Bivalent Copper and Cobalt Complexes on the Living Organism

It is known that the oxidation of organic substances (proteins, fats, carbohydrates, alcohols, etc.) in the living organism is regulated by various enzymes. The final stable products (H_2O, CO_2, N_2, etc.) of such oxidation are obtained mainly as a result of the decomposition of the intermediate nitrogen-containing and hydroperoxy-compounds. Enzymes containing in many instances the ions of "metals of life" (Cu^{2+}, Co^{2+}, Mn^{2+}, etc.) control the mechanism and rate of decomposition of these hydroperoxides by virtue of the specificity of their action[32].

Numerous investigations have shown[6,56] that, apart from certain biometals (for example, Cu^{2+} and Co^{2+}), monoethanolamine plays a definite biochemical role in the living organism. It has been established that the introduction of the above substances in microamounts separately or jointly into the living organism (both healthy and diseased) enhances its biochemical activity. For example, the growth and development of birds, calves, and plants are accelerated and a number of human diseases are cured (sugar diabetes, diseases of the liver, kidneys, heart etc.). The experimental data obtained indicate an appreciable intensification of the metabolism of substances, particularly when monoethanolamine is introduced together with Cu^{2+}. Monoethanolamine is also an active stimulant enhancing the egg laying capacity in chickens, etc.[8]

The use of monoethanolamine in the treatment of the chronic renal failure in man has a positive influence on functional parameters of the operation of kidneys such as diuresis, the secretion of urine, etc. Monoethanolamine is non-toxic in small doses and, on being introduced into the organism, sharply enhances its protective responses. Monethanolamine is capable of inhibiting the development of

cardiac hypertrophy without influencing the contracting function of the heart at the same time. It has been shown that the aminoalcohol does not stimulate the absorption of O_2 when glutamate is used as the respiratory substrate[8].

One should note that hitherto there has been no explanation in the literature of the wide variety of the positive effects of monoethanolamine (colamine) and its Cu^{2+} and Co^{2+} complexes on living organisms.

It follows from a number of studies[40–45,52–54] that, in aqueous solutions at temperatures starting from 30–40 °C, CHP and TBHP decompose at a moderate rate in the presence of amines and aminoalcohols. However, in the presence of monoethanolamine or M^{2+} alone[21,42,44] at temperatures up to 90 °C hydroperoxides hardly decompose, while in the joint presence of the above substances with $M^{2+} = Cu^{2+}$, Co^{2+}, Mn^{2+}, etc. CHP and TBHP are decomposed catalytically mainly via a non-radical mechanism. As already mentioned, the M^{2+} complexes of monoethanolamine of the type $(MA)^{2+}$ are "non-consumable" catalysts in the decomposition of ROOH under conditions where hydroperoxides are continuously added to the reaction system, i.e. the effect of the complexes $(MA)^{2+}$ can be identified with enzyme catalysis (naturally in a model form).

On the basis of the data obtained, we shall attempt to explain the role of monoethanolamine and its Cu^{2+} and Co^{2+} complexes in the living organism. The accumulation of hydroperoxides (or peroxides) in the living organism is an undesirable phenomenon, since their decomposition via a radical mechanism results in the formation of extremely active free radicals, which can decompose cells and can induce chemical changes in enzymes, proteins, etc.[57] Hydroperoxides thereby initiate definite biochemical modifying processes, which lead to functional damage in the organism.

To prevent such action of hydroperoxides, one must stimulate their decomposition, preferably in a continuous manner and via a non-radical mechanism[57]. This role is apparently played by monoethanolamine and its Cu^{2+} and Co^{2+} complexes, which catalyse the non-radical decomposition of hydroperoxides. "Biometals", in particular Cu^{2+} and Co^{2+}, are present in microamounts in the living organism and, when monoethanolamine is introduced (providing the amount of colamine in the organism is small), the above scattered ions are "collected" by monoethanolamine in the form of complexes.

Thus it is extremely likely that monoethanolamine, jointly with certain variable-valence metal cations (including Cu^{2+} and Co^{2+}), regulates the required level of hydroperoxides in the organism.

IV. THE MECHANISM OF THE REACTIONS OF HYDROPEROXIDES WITH AMINES AND AMINOALCOHOLS IN THE PRESENCE AND ABSENCE OF M^{2+}

In order to elucidate the mechanism of the reactions of ROOH and A and of ROOH, A, and M^{2+} in aqueous media, the final stable reaction products were identified, in addition to studies of the intermolecular interactions between the components of the reacting systems (determination of the compositions of the intermediate complexes) and the study of the kinetics.

Amines and aminoalcohols exhibit interesting properties in reactions with hydroperoxides (in the absence and presence of M^{n+}): (a) they react with hydroperoxides in both aqueous[40–42] and organic solvents with a high dielectric constant, for example, in amides[40–42,48,49]; (b) they are effective complex-forming agents (ligands) for metal cations, for example, Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, etc. The complexes $(MA)^{2+}$ induce the decomposition of hydroperoxides in an aqueous phase via a mechanism which sometimes resembles homogeneous enzyme catalysis[20,21,42,44]; (c) the products of the reactions of amines with hydroperoxides are in many instances of practical interest[40–42]; (d) certain aminoalcohols and their chelate complexes with bivalent copper, cobalt, etc. ions are stabilisers and hardening agents respectively for polychloroprene and butadiene-acrylonitrile (with an epoxy-resin) adhesives [50,51].

The nature of the products of reactions of ROOH, A, and M^{2+} depends on the nature of the amines and hydroperoxides, on the presence of M^{2+}, and also on the solvent[21,40–42,52]. In aqueous media the oxidation of amines by hydroperoxides (in the absence of M^{2+}) leads to the formation of an aminoaldehyde in 89.3% yield (in the case of CHP) [12] and the amine oxide (in the case of TBHP).[52] It has been shown by infrared spectroscopy and elemental analysis that the corresponding alcohols are then obtained from the hydroperoxides—phenylisopropyl alcohol (yield 97.6%) and t-butyl alcohol[21,23,54].

The simultaneous catalytic decomposition of the CHP dimer by the aminoalcohol (diethanolamine, triethanolamine, etc. except monoethanolamine) in aqueous media results in the formation of phenylisopropyl alcohol and oxygen in 9.6% yield[40,54].

As mentioned above, in the presence of variable-valence metal cations (Cu^{2+}, Co^{2+}, Mn^{2+}, etc.) the reactions between ROOH and amines are accompanied also by the catalytic decomposition of ROOH by the amine complexes $(MA)^{2+}$.[21,42,44] The latter reaction predominates—its rate is several times greater than the rates of the other two reactions. Identification of the final stable products of the reaction of ROOH, A, and M^{2+} in water by infrared spectroscopy, ^1H NMR, chromatography, polarography, volumetric measurements, and elemental analysis showed that the final products are phenylisopropyl alcohol (for CHP) or t-butyl alcohol (for TBHP) and oxygen (the yield of all the products was 99.6%).[54] In the presence of diethanolamine, triethanolamine, and other aminoalcohols involving the simultaneous occurrence of the above reactions (direct interaction between CHP and A and the decomposition of the cumenyl hydroperoxides dimer catalysed by the aminoalcohol molecule)[40], an aminoaldehyde is obtained apart from the corresponding alcohol and oxygen. The aminoaldehyde was determined polarographically by elemental analysis and by other methods[54]. In the presence of monoethanolamine and pyridine only one reaction catalysed by the metal–amine complex takes place and for this reason the aminoaldehyde was not detected among the products of the reactions of these amines. However, the polarograms obtained for the reaction between ROOH and an aminoalcohol in the absence and presence of M^{2+} show that the aldehyde is formed only via the first, direct reaction between ROOH and the aminoalcohol. These data agree with the earlier kinetic results[40–42].

On the basis of the data presented, we put forward mechanisms for the reactions investigated which are presented below [the charges of the species shown in the various schemes (RO_2^-, RO_3^-, etc.) reflect the tendency towards a redistribution of electron density].

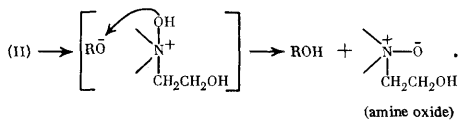
1. The First Reaction—Direct Interaction between ROOH and Aminoalcohols (except Monoethanolamine)

As an example, we shall consider the reaction of CHP with triethanolamine. As stated at the beginning of the review, the first step in the reactions of hydroperoxides with amines in water involves the formation of complex (II):

$$\mathrm{ROOH} + :\!\underset{|}{\overset{|}{\mathrm{N}}}\!- \rightleftarrows (\mathrm{II}) \quad (22)$$

The mechanism of the decomposition of complex (II) to the products depends on the nature of R for given amine and solvent.

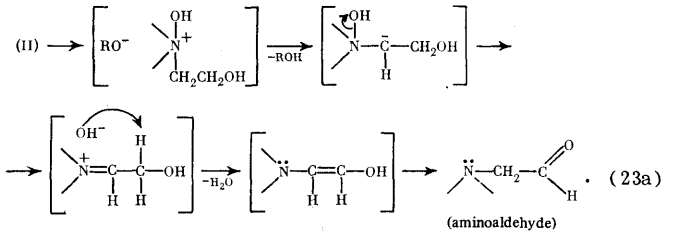
(a) R = $(CH_3)_3C$. The t-butyl group is electron repelling:



(23)

CH_3

(b) R = $C_6H_5-C-CH_3$. By virtue of the presence of the phenyl substituent, the phenylisopropyl group has distinct electron repelling properties and the mechanism can be represented in this instance in the following manner:



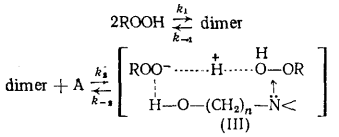
(23a)

2. Second Reaction—Decomposition of the Hydroperoxide Dimer Catalysed by the Aminoalcohol (except Monoethanolamine)

The rate of this reaction is described by an equation of type (4):[40]

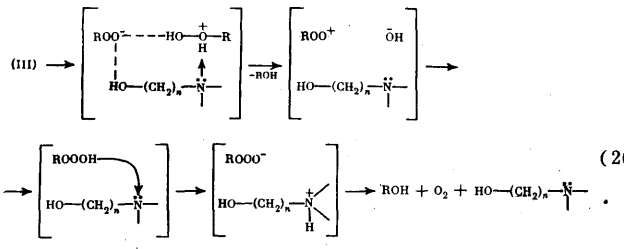
$$w_2 = k_{cat}[ROOH]^2, \qquad (24)$$

where $k_{cat} = k_2[A]$. The involvement of the cumenyl hydroperoxide dimer in the catalytic decomposition of CHP by the aminoalcohol has been established on the basis of this equation and kinetic data[12,40-42]:



(25)

It has been established[55] that alkali catalyses the decomposition of CHP in aqueous solution, the rate of decomposition being a maximum for $[ROOH]/[ROO^-] = 1$. In the intermediate complex (III) this ratio in fact obtains; the ROO^- group is an electron donor, while the O–O bond is an electron acceptor. Taking this into account, the following transformations within the complex, leading to the formation of the final stable products, have been postulated:



(26)

3. Third Reaction—Decomposition of Hydroperoxides Catalysed by the M^{2+}–Amine Complex

According to the present author[42], the cationic complex $(MA)^{2+}$ is catalytically active in the ROOH–A–M^{2+} reaction system. It is known[19] that amine complexes having the composition $[MA_n]^{2+}$, where $n = 4$ or 6, are thermodynamically active. In particular, when $M^{2+} = Cu^{2+}$, Co^{2+}, etc., $n = 4$ and the complex has the structure $[MA_4]^{2+}$.

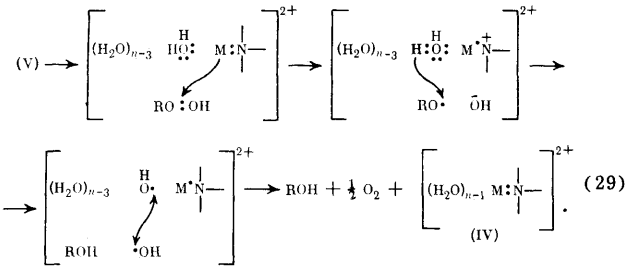
The following equilibria obtain in aqueous solutions[19]:

$$[MA_n]^{2+} \xrightleftharpoons{H_2O} [H_2OMA_{n-1}]^{2+} \xrightleftharpoons{H_2O} \cdots \xrightleftharpoons{H_2O} \underset{(IV)}{[(H_2O)_{n-1}MA]^{2+}}. \qquad (27)$$

However, the aquo-complex (IV) is catalytically active[21]. The reaction of complex (IV) with CHP and TBHP can be represented as follows:

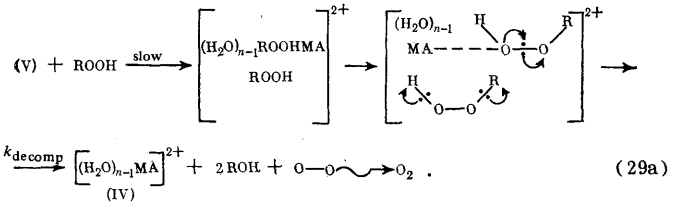
$$[(H_2O)_{n-1}MA]^{2+} + ROOH \xrightleftharpoons{fast} H_2O + \underset{(V)}{\left[(H_2O)_{n-3}H_2OMA\begin{matrix}\\ ROOH\end{matrix}\right]^{2+}}. \qquad (28)$$

The transfer of one or two electrons from the aminoalcohol molecule to the hydroperoxide actually occurs in complex (V) via the catalyst cation:



(29)

The mechanism of the formation of the final products (the corresponding alcohols and oxygen) can be represented by another scheme[32] if it is assumed that the rate-limiting stage is the interaction of complex (V) with ROOH:



(29a)

Eqn.(9) shows that the order of the reaction with respect to M^{2+} is unity[44]. However, in many cases the order of the decomposition reaction of hydroperoxides catalysed by the complex $(MA)^{2+}$ is less than unity with respect to M^{2+}.[21] This can be explained by the equilibrium

$$(IV) + [MA]^{2+} \rightleftarrows \underset{(VI)}{[(H_2O)_{n-2}MA]^{2+}} + [(H_2OMA_{n-1}]^{2+}. \qquad (30)$$

According to a study by the present author[42], when $n \geq 2$, the complexes, including complex (VI), are inactive in the decomposition of hydroperoxides in an aqueous medium. Thus only complex (IV) is a catalytically active amine complex in the decomposition of ROOH in aqueous media.

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† $[(H_2O)MA]^{2+}$? (Ed.of Translation).

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