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Antiozonant Activity of the Silica Modified with 3*d* Metal Complexes

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Abstract—Criteria for preliminary selection of the antiozonants based on the silica modified with the complexes of 3*d* metal were proposed and the activity of the antiozonants as a dependence on the nature of the ligands (Schiff bases, Cl^-, NO_3^-) and metal ions [Cu(II), Co(II), Mn(II)] was established. We found that advantageous were complexes $MnL_2/\overline{Si}$, where L denotes a Schiff base of phenol or quinoline series, whose kinetic and specific stoichiometric energy parameters of the reaction were the largest because of the formation during the reaction of the manganese oxide form which performs the catalytic decomposition of ozone.

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Ozone and intermediates of its decomposition, like $OH^\bullet$ radicals which are strong oxidants, show a destructive effect on the polymer and rubber materials, motor oils, fuel, fat, food, etc. In order to prevent oxidation at different stages of technological processes, the antiozonants are used as stabilizers. Principally, organic compounds of different classes can be used as the antiozonants [1]. One of the drawbacks of such antiozonants is their low stoichiometric coefficient characterizing the number of moles of decomposed ozone per one mole of the substance. For example, in the case tetraethylthiuramdisulfide (tetds) it is 3.2 and is close to this value for many other stabilizers (e.g., *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine, tributylthiourea, 2,4,6-tri-*t*-butylphenol) [2]. Use of metal chelates as antiozonants significantly improves the stoichiometric ratio. Certain series of antiozonant activity in dependence on the nature of the central atom and ligands have been obtained for metallochelates of type $M(dtc)_n$ and $M(dtp)_n$ dissolved in CCl_4 [dtc is dithiocarbamate; dtp is dithiophosphate; M = Cu(II), Ni(II), Mn(II), Co(II), Zn(II), Cd(II), Pt(II), Cr(III), etc.] [2]. At the same time the greatest activity is shown by the complexes of Cu(II), and Ni(II), whose stoichiometric coefficient is 2–4 times higher as compared with tetraethylthiuramdisulfide. There is a very limited number of examples of increasing antioxidant activity of the complex compounds, including metal chelates, at the immobilization on the layered graphite and silica gel [3].

As we have shown [4–6], the immobilization in different ways of complexes of 3*d* metals on silica [$ML_2/\overline{Si}$ and MX_2/SiO_2, where M = Cu(II), Co(II), Mn(II); $L/\overline{Si}$ denotes Schiff bases L immobilized on aerosil $\overline{Si}$; X = Cl^-, NO_3^-; SiO_2 is silica gel (MSM)] offers great opportunities to vary their catalytic activity in the low-temperature reaction of decomposition of ozone, and, therefore, to focus on selection of effective antiozonants.

As a rule, for testing performance (the duration of protective action) of antiozonants labor-intensive and time-consuming experiments should be carried out, therefore for the selection of promising materials their pre-express evaluation is carried out initialy by measuring kinetic and stoichiometric parameters of the reaction that characterize the ozone decomposition in liquid phase [1, 2].

The purpose of this work is to provide the criteria for the pre-selection of antiozonants based on the silica modified with the complexes of 3*d* metal and to determine their activity depending on the nature of the ligands and metal ions.

We used Schiff bases and their complexes with Cu(II), Co(II), and Mn(II) immobilized on aerosil, as well as the acidocomplexes of these metals supported on silica gel. General formulas of the immobilized Schiff bases are shown in Schemes 1 and 2, and the nature of substituents, the names and symbols of the ligands are shown in Tables 1 and 2.

Earlier [4–6] the formation of immobilized on aerosil Schiff bases and their complexes with Cu(II), Co(II) and Mn(II) was confirmed. by the diffusion reflectance and IR spectroscopy. As a rule, in the spectra of surface complexes a decrease in the frequency of stretching vibrations of azomethine C=N group by 20–40 cm^{-1} as compared with the free ligand and a high-frequency shift of the maximum of the ligand charge transfer band (π–π*) are observed. Analysis of the spectra in the region of *d*–*d* transitions taking into account the stoichiometry and data of molecular modeling showed that, depending on the nature of the ligand, two types of bischelate complexes can be formed: pseudotetrahedral in the field of the ligands L1–L5 and pseudooktahedral in the field of the ligand L6 with water molecules and chloride ions as additional ligands. Similarly, for a number of ligands of quinoline series when bidentate coordination N(azomethine)–N(quinoline) is possible (L7–L13), in the field of the ligands pseudotetraedral bischelates are formed, otherwise (L14) pseudooctahedral complexes.

The testing of the synthesized samples L/$\overline{\text{Si}}$ and ML_2/$\overline{\text{Si}}$ in the reaction of ozone decomposition was carried out at the concentration $c^{\text{init}}(\text{O}_3)$ = 200 mg m^{-3} (4.2×10^{-6} M) and the sample weight 0.2 g. Figures 1 and 2 show by the example of immobilized Schiff bases L3 and L6 and their complexes with Cu(II), Co(II), and Mn(II) the typical kinetic curves of the ozone decomposition. Note that in case of the ligands the final concentration of ozone grows relatively quickly and, depending on the nature of the ligand, reaches the initial value in 100–200 min. The kinetics of the ozone decomposition with the complexes ML_2/$\overline{\text{Si}}$ [M = Cu(II), Co(II), Mn(II)] differs considerably: the reaction duration increases, which leads to an increase in the amount of decomposed ozone ($Q_{\text{decomp.}}$), at the same time of the reaction the final concentration

Scheme 1.

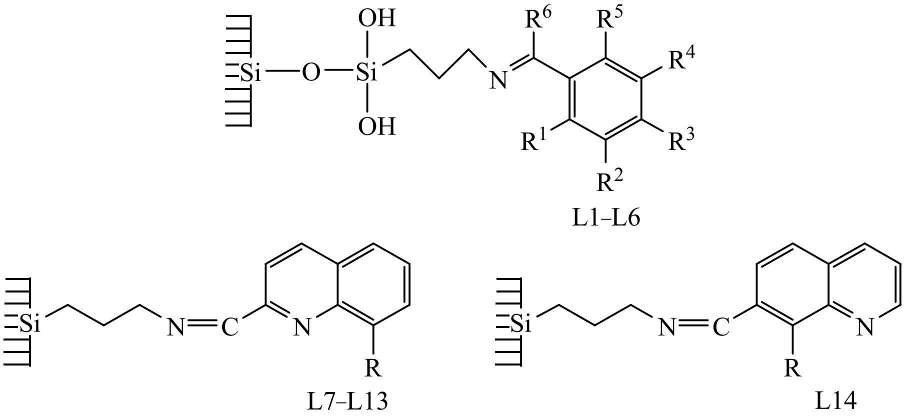


Table 1. The ligands of phenol series L/$\overline{\text{Si}}$ (L = L1–L6)

Comp. no.	Ligand	R^1	R^2	R^3	R^4	R^5	R^6
L1	Salicylaliminopropyl	OH	H	H	H	H	H
L2	5-Bromsalycylaliminopropyl	OH	H	H	H	Br	H
L3	2-Hydroxynaphthaliminopropyl	OH	H	(–C_4H_4)		H	H
L4	2-Hydroxy-3-methoxybenzaliminopropyl	OH	OCH_3	H	H	H	H
L5	2-Hydroxy-3,5-dichloroacetophenoneiminopropyl	OH	Cl	H	Cl	H	CH_3
L6	4-Hydroxy-3-methoxybenzaliminopropyl	H	OCH_3	OH	H	H	H

Table 2. The ligands of quinoline series L/$\overline{\text{Si}}$ (L = L7–L14)

Comp. no.	Ligand	R
L7	Quinoline-2-aliminopropyl	H
L8	8-Hydroxy quinoline-2-aliminopropyl	OH
L9	8-Fluoroquinoline-2-aliminopropyl	F
L10	8-Bromo quinoline-2-aliminopropyl	Br
L11	8-Triftoromethylquinoline-2-aliminopropyl	CF_3
L12	8-Benzyloxyquinoline-2-aliminopropyl	OCH_2Ph
L13	*tert*-Butyl 2-aliminopropylquinolin-8-aminocarboxylic acid	NHCOO*t*-Bu
L14	8-Nitroquinoline-2-aliminopropyl	NO_2

of ozone is much lower in the case of these complexes, and after prolonged ozonation on the kinetic curve a steady-state region is observed [$c^{\text{final}}(O_3)$ = const].

The preliminary assessment of the effectiveness of antiozonants we carried out on the basis of the data on the kinetic and stoichiometric parameters of the reaction of ozone decomposition (Tables 3 and 4). Detailed studies of the kinetics of decomposition of ozone by immobilized Schiff bases and their complexes with the 3*d* metals showed that after 10–30 min a deviation was observed from first order with respect to ozone, which indicates the development of secondary processes caused by the appearance of radicals from both the oxidant and the reducer. The analysis of the rate constants (k_1) of ozone decomposition listed in Tables 3 and 4 leads to the following conclusions. The immobilized Schiff bases (L/$\overline{\text{Si}}$) decompose ozone on their own, and the effect of the substituent nature on the rate constant k_1 is clearly seen

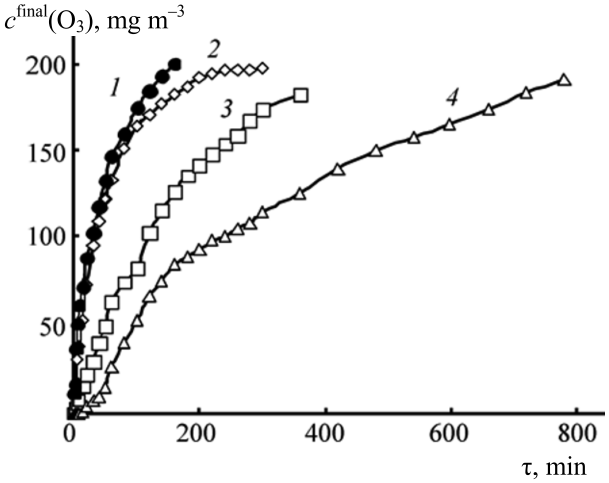
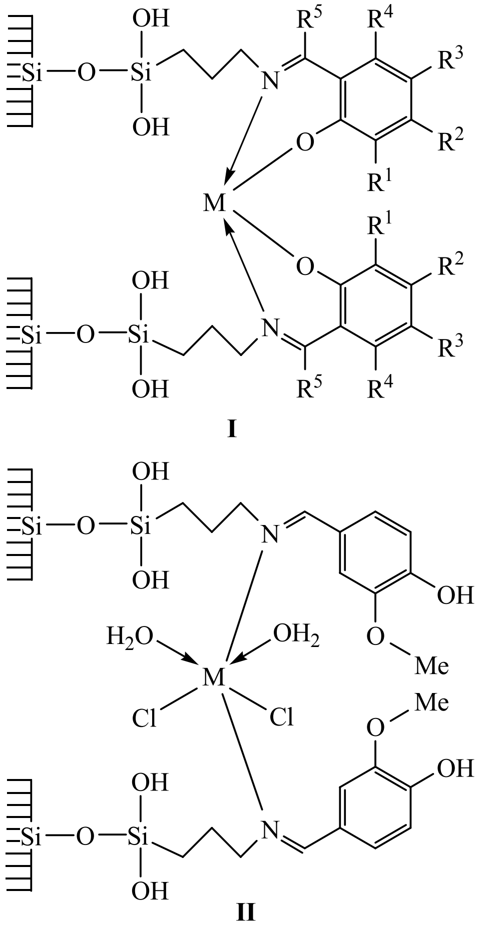


Fig. 1. Changes of $c^{\text{final}}(O_3)$ in time during the decomposition of ozone by the Schiff base immobilized on Aerosil A-300 and the Schiff base complexes $M(L3)_2/\overline{\text{Si}}$: (*1*) L3, (*2*) $Cu(L3)_2$, (*3*) $Co(L3)_2$, (*4*) $Mn(L3)_2$ [$c^{\text{init}}(O_3)$ 200 mg m^{-3}, 4.2×10^{-6} M].

Scheme 2.



I

II

in the case of ligands L1, L2, L4–L6. The rate constant for the decomposition of ozone decreases with increasing electron-acceptor properties of the substituents in the series L4 ~ L6 > L1 > L2 > L5.

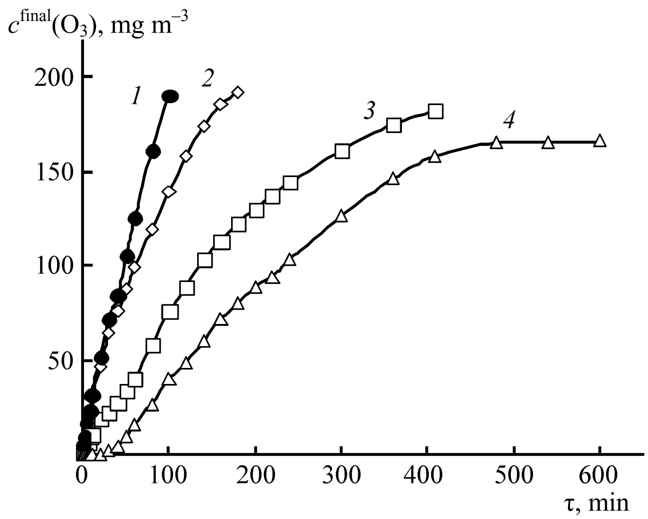


Fig. 2. Changes of $c^{\text{final}}(O_3)$ in time during the decomposition of ozone by the Schiff base immobilized on Aerosil A-300 and the Schiff base complexes $M(L6)_2/\overline{Si}$: (*1*) L6, (*2*) $Cu(L6)_2$, (*3*) $Co(L6)_2$, (*4*) $Mn(L6)_2$ [$c^{\text{init}}(O_3)$ 200 mg m^{-3}, 4.2×10^{-6} M].

A more complicated dependence of k_1 on the nature and position of substituents is observed for the ligands of the quinoline series L7–L13. Obviously, the distant location of substituents from the reaction center, which is the azomethine C=N group [1, 8], as well as the possibility of the nitrogen atom of the heterocycle and the substituents themselves (OH, Br, OCH_2Ph, and NHCOOBu-*t*) to be involved in the reaction with ozone complicates the dependence of the rate constant on the nature of the substituent. Moreover, despite the fact that in L14 the electron-acceptor substituent NO_2 is closer to the azomethine group, the expected reduction of the rate constant as is in the case of L5 was not observed. The sample showed high activity at the beginning of the experiment and therefore, due to very low final constant concentration of ozone [$c^{\text{final}}(O_3) <$ 1.0 mg m^{-3}] it was impossible to calculate the constant k_1. Guided by the values of k_1, it is possible to arrange the immobilized Schiff bases according to their reactivity in series: L14 > L12 > L13 > L10 ~ L8 ~ L9 > L11 ~ L7. The analysis of the values of the constants k_1 for the studied $L/\overline{Si}$ samples shows that the greatest difference, about 6 times, is observed only for

Table 3. Kinetic and stoichiometric parameters of the reaction of ozone with Schiff bases immobilized on aerosil

Antiozonant	Substituent	σ Constant [7]	$c_L\times10^4$, mol g^{-1}	$k_1\times10^3$, s^{-1}	$Q_{\text{exp}}\times10^5$, mol O_3	$Q^*\times10^5$, mol O_3	n_L
$L1/\overline{Si}$	–	0	7.0	3.8	11.1	55.5	0.8
$L2/\overline{Si}$	Br	0.232	7.0	2.8	10.6	53.0	0.8
$L3/\overline{Si}$	C_4H_4	–	7.0	3.2	17.0	85.0	1.2
$L4/\overline{Si}$	CH_3O	–0.268 (*p*) 0.115 (*m*)	7.2	6.2	25.4	127.0	1.8
$L5/\overline{Si}$	Cl	0.227 (*p*) 0.373 (*m*)	5.0	1.3	13.2	66.0	1.3
$L6/\overline{Si}$	CH_3O	–0.268 (*p*) 0.115 (*m*)	7.0	5.6	19.6	98.0	1.4
$L7/\overline{Si}$	–	0	4.9	3.8	33.7	168.5	3.4
$L8/\overline{Si}$	OH	–0.370	4.7	4.6	10.5	65.6	1.4
$L9/\overline{Si}$	F	0.062	4.6	4.2	24.1	120.5	2.6
$L10/\overline{Si}$	Br	0.232	3.4	5.0	31.1	155.5	4.6
$L11/\overline{Si}$	CF_3	0.540	4.6	3.8	26.2	154.6	3.4
$L12/\overline{Si}$	OCH_2Ph	–0.420	3.2	8.3	23.4	146.3	4.7
$L13/\overline{Si}$	NHCOO*t*-Bu	–	3.3	6.5	15.1	75.5	2.3
$L14/\overline{Si}$	NO_2	0.778	5.1	–	27.4	137.0	2.7

Table 4. Kinetic and stoichiometric parameters of the reaction of ozone with silica-supported Cu(II), Co(II), and Mn(II) complexes

Antiozonant	Content of Me(II)×10^4 mol g^{-1}	k_1×10^3, s^{-1}	Q_{exp}×10^5, mol O_3	Specific stoichiometric parameters		
				Q^*×10^5, mol O_3	n_L	n_M
			$ML_2/\overline{Si}$			
$Cu(L1)_2$	1.00	3.0	11.3	56.5	0.8	3.8
$Cu(L2)_2$	1.80	3.3	8.5	42.5	0.6	2.3
$Cu(L3)_2$	1.25	5.9	22.9	114.5	1.6	9.0
$Cu(L4)_2$	1.67	3.9	24.1	120.5	1.7	7.5
$Cu(L5)_2$	2.00	1.1	9.2	46.0	1.2	3.0
$Cu(L6)_2$	1.68	4.0	25.0	125.0	1.8	7.5
$Cu(L7)_2$	2.00	2.6	15.7	78.5	1.6	4.0
$Cu(L8)_2$	2.92	–	19.7	98.5	2.1	3.4
$Cu(L9)_2$	1.60	–	18.2	91.0	1.7	5.7
$Cu(L10)_2$	2.00	4.2	13.3	66.5	1.9	3.3
$Cu(L11)_2$	2.00	3.6	21.4	107.0	1.8	5.4
$Cu(L12)_2$	2.00	–	23.0	115.0	3.0	5.8
$Cu(L13)_2$	2.00	8.3	13.4	67.0	1.8	3.4
$Cu(L14)_2$	2.00	–	23.8	119.0	2.3	6.0
$Co(L1)_2$	1.44	3.3	25.5	127.5	1.8	8.9
$Co(L2)_2$	1.43	3.3	25.9	129.5	1.9	9.0
$Co(L3)_2$	1.50	4.2	52.6	263.0	3.8	17.5
$Co(L4)_2$	1.55	4.2	28.1	140.5	2.0	9.0
$Co(L5)_2$	1.86	10.8	30.4	152.0	4.0	11.0
$Co(L6)_2$	1.50	7.0	78.0	390.0	5.6	26.0
$Co(L7)_2$	1.83	6.8	30.9	154.5	3.1	8.4
$Co(L9)_2$	1.63	6.2	29.4	147.0	2.9	9.0
$Co(L10)_2$	1.73	1.6	28.1	140.5	2.8	8.1
$Co(L11)_2$	1.73	5.8	26.0	130.0	2.6	7.5
$Co(L12)_2$	1.73	–	37.5	187.5	3.8	10.8
$Co(L14)_2$	1.67	9.2	32.7	163.5	3.3	9.8
$Mn(L1)_2$	0.6 0	3.8	42.1	210.5	3.0	38.3
$Mn(L2)_2$	0.80	3.4	6.4	32.0	0.5	4.0
$Mn(L3)_2$	0.17	–	127.0	635.0	9.1	374.1
$Mn(L4)_2$	0.80	6.0	101.0	505.0	7.0	63.1
$Mn(L4)_2$	2.21	7.0	130.0	650.0	9.0	29.4
$Mn(L4)_2$	3.18	8.5	137.0	685.0	9.5	21.5
$Mn(L5)_2$	1.60	2.8	35.3	176.5	4.7	15.0
$Mn(L6)_2$	0.70	5.1	93.7	468.5	6.7	66.8
$Mn(L6)_2$	2.40	–	103.5	517.5	7.4	21.5
			MX_2/SiO_2[a]			
$Cu(NO_3)_2$	1.80	0.5	13.0	1.3	–	0.05
$CuCl_2$	1.20	–	72.0	7.2	–	0.5

Table 4. (Contd.)

Antiozonant	Content of Me(II)×10^4 mol g^{-1}	$k_1 \times 10^3$, s^{-1}	$Q_{exp} \times 10^5$, mol O_3	Specific stoichiometric parameters		
				$Q^* \times 10^5$, mol O_3	n_L	n_M
			MX_2/SiO_2[a]			
$Co(NO_3)_2$	1.00	1.6	290.0	29.0	–	3.0
$CoCl_2$	1.00	7.0	306.0	30.6	–	3.0
$MnCl_2$	1.00	–	165.0	16.5	–	1.7

[a] Sample weght 10.0 g.

the ligand L5 and L12; in other cases the difference is no more than 2 times.

The formation of surface complexes with Schiff bases by Cu(II), Co(II) and Mn(II) has little effect on the values of the constants k_1 (Table 4). However, it is noteworthy that in contrast to the event of free ligands, the number of cases increased where it is impossible to determine the k_1 constant in the initial part of the kinetic curve: $Cu(L)_2/\overline{Si}$ (L = L8, L9, L12, L14), $Co(L12)_2/\overline{Si}$, $Mn(L)_2/\overline{Si}$ (L = L3, L6). The attempt to increase the content of complexes, for example, $Mn(L4)_2$, on the aerosil surface (the content of manganese(II) increased from 0.80×10^{-4} to 3.18×10^{-4} mol g^{-1}) led only to 1.5-fold increase in the rate constant. The nature of substituents has different effects on the reactivity of the $M(L)_2/\overline{Si}$ complexes with respect to ozone. Like in the case of the free ligand L1, L2, L4–L6, in the case of the complexes $Cu(L)_2/\overline{Si}$ and $Mn(L)_2/\overline{Si}$ the ozone decomposition rate constant decreases with increasing electron-acceptor properties of substituents, while in the case of cobalt(II) complexes higher activity, on the contrary, show the complexes with acceptor substituents, $Co(L5)_2/\overline{Si}$ and $Co(L14)_2/\overline{Si}$. These features of the Co(II) complexes with Schiff bases appear in the other reactions like oxidation of phenols [9].

The absence on the whole of significant changes in the values of rate constants k_1 is due, in our opinion, to the fact that in the initial step in the reaction with ozone the reaction center of the immobilized ligands $L/\overline{Si}$ and complexes $M(L)_2/\overline{Si}$, except for some cases with $Co(L)_2/\overline{Si}$, is the same: the azomethine group. It is known [1] that benzene ring weakly interacts with ozone.

Thus, while selecting antiozonants and predicting their protecting properties it is insufficient to be guided by the data on the kinetic constants only, in contrast to the usual practice when the reactivity of organic compounds, like phenols, toward ozone differ by several orders of magnitude [1].

Tables 3 and 4 summarize the results of the analysis of the stoichiometric parameters of this reaction (Q_{exp}, n_L, n_M). Since the reaction of ozone with organic compounds are multipath ones [10–12], the stoichiometric ratio usually is not connected with the stoichiometry of a particular reaction, and the high value of this parameter shows that this reaction includes several stages. Obviously, in the case of fixing a potential antiozonant on a carrier it is necessary to consider not only the molar ratio of reagents (L, M), but also the weight of the sample used for obtaining the kinetic and stoichiometric parameters of the reaction of ozone decomposition. In this regard, alongside the traditionally used stoichiometric coefficients n_L and n_M for describing the reactions of ozone in the liquid phase, we introduce an additional parameter Q^*_{exp}, which, in fact, gives information about the performance of antiozonants and therefore allows an adequate comparison of the obtained results.

Analysis of the data (Tables 3 and 4) obtained with accounting for the stoichiometric parameters leads to the following conclusions. For the immobilized Schiff bases which content varied from 3.2×10^{-4} to 7.2×10^{-4} mol g^{-1}, the values of the coefficient n_L for the same value of rate constant k_1 can be substantially different, e.g., for L1, L7, L11. The coefficient n_L becomes close to the known (~3.2) [2] only with the ligands L7, L10, L11, and L12, and to these ligands the highest values of Q_{exp} and Q^*_{exp} correspond. For the complexes $M(L)_2/\overline{Si}$ the stoichiometric parameters of the ozone decomposition depend on the nature of the metal. The coefficient n_L increases compared with free ligand in the case of the complexes $CuL_2/\overline{Si}$ (L = L3, L6, L8), $CoL_2/\overline{Si}$ (L = L1–L6, L14), and $MnL_2/\overline{Si}$ (L = L1, L3–L6). For other systems this parameter either remains unchanged or even is reduced. The latter is typical for the Cu(II) and Co(II) complex with the Schiff bases of quinoline series. On the whole the comparison of the stoichiometric parameters of ozone decomposition resulted in the following sequence of the $ML_2/\overline{Si}$ complexes: Mn(II) > Co(II) > Cu(II). The $MnL_2/\overline{Si}$ complexes, except for L = L2 and L5, are characterized by the highest productivity, which may be due to the formation on the aerosil surface in the reaction course of the oxide form of manganese providing the catalytic decomposition of the ozone.

For comparison, in Table 4 the data are listed on the rate constants k_1 of the ozone decomposition on the MH_2/SiO_2 complexes ($X = Cl^-$, NO_3^-) which give the following sequence of activity of these complexes: $MnCl_2 > CoCl_2 > Co(NO_3)_2 > CuCl_2 > Cu(NO_3)_2$ (for $MnCl_2/\overline{Si}O_2$ the constant k_1 at the initial stage of the reaction cannot be determined). Note that the value of constant k_1 of the complex $CoCl_2/SiO_2$ is comparable with those obtained for $CoL_2/\overline{Si}$ (L = L6, L7, L9). The absolute value of the experimental amount of ozone that reacted with complexes $MX_2/\overline{Si}O_2$ is higher than for complexes with Schiff bases. However, such results were achieved with the mass of samples 10 g, which reduces the index $Q^*_{\exp}$, making it many times smaller than for the complexes $ML_2/\overline{Si}$.

Obviously, the choice of potential antiozonants based on the metal chelates fixed on aerosil is expedient to carry out by comparison with the most active, according to [2], antiozonants $Cu(dtc)_2$, for which the stoichiometric coefficient $n_M = 13$. According to Table 4, for all the complexes $CuL_2/\overline{Si}$, as well as $CoL_2/\overline{Si}$ (L = L1, L2, L4, L5, L7–L14) and $Mn(L2)_2/\overline{Si}$, $n_M < 13$, for the other complexes $n_M > 13$. Obviously, the preference should be given to the complexes with manganese(II), for which the largest is not only the parameter n_M, but also the specific experimental amount of ozone $Q^*_{\exp}$, which is due to the formation in the reaction course of the oxide form of manganese, performing the catalytic decomposition of ozone.

Thus, it is shown that for the express pre-assessment of antiozonant activity of complexes Cu(II), Co(II) and Mn(II) with different ligands (Schiff base, Cl^-, NO_3^-) immobilized on silica (Aerosil, silica gel), along with the traditionally used kinetic (k_1) and stoichiometric (n_L, n_M) coefficients it is appropriate to use an additional parameter $Q^*_{\exp}$ describing specific experimental amount of ozone per one gram of the antiozonant. This in fact enables us to correctly compare the antiozonants on different carriers and to select those with the highest performance.

EXPERIMENTAL

The synthetic procedure for producing γ-aminopropylaerosil with Schiff bases immobilized on it ($L/\overline{Si}$) (Tables 1 and 2) and complexes $ML_2/\overline{Si}$ (M = Cu(II), Co(II), Mn(II)) has been described in detail in [4, 5]. We synthesized and studied 14 samples of $L/\overline{Si}$ and 35 samples of $ML_2/\overline{Si}$. For comparison of the antiozonant efficiency, 5 samples $MX_2/\overline{Si}O_2$ were prepared [M = Cu(II), Co(II), Mn(II); $X = NO_3^-$, Cl^-] [4] by impregnation of silica gel with aqueous solutions of the salts.

Tests of samples with respect to antiozonant activity was carried out in thermostated at 20±0.5°C flow gas installation with a fixed bed reactor with the sample. The ozone–air mixture was prepared using the ozone generator model IG-1SH by the action of a silent electric discharge on the air oxygen. The ozone–air mixture flow was controlled using a rheometer. The initial [$c^{\text{init}}(O_3)$] and final [$c^{\text{final}}(O_3)$] ozone concentrations in the range of measured concentrations 10–400 mg m^{-3} were analyzed using an optical analyzer Cyclone-Reverse (OPTEK, St. Petersburg) with a detection limit 1.0 mg m^{-3} . Relative humidity of the ozone–air mixture was kept constant, $\varphi = 63\pm2\%$. The experiments were carried out at a constant volume flow of the ozone–oxygen mixture, $\omega = 1.66\times10^{-2}$ l s^{-1}). By blank experiments we showed that ozone is not decomposed on the walls of the glass reactor and other sites of installation under given conditions. Despite this, before the experiment the system was heated and evacuated several times.

The research results were presented in the coordinates $c^{\text{final}}(O_3)$–τ, where τ is the reaction time. Rate constant (k_1) was determined using a first-order equation, taking into account the data on changes in ozone concentrations within 10–30 min after the reaction start:

$$k_1 = \frac{1}{\tau}\ln\frac{c^{\text{init}}(O_3)}{c^{\text{final}}(O_3)}.$$

The calculation of experimental quantities of ozone ($Q_{\exp}$, mol O_3) was performed taking into account the experimental function Δc–τ. This quantity was used in the calculation of the following stoichiometric ratios: $n_L = Q_{\exp}/Q_L$, the ratio of the experimental amount of ozone per 1 mole of immobilized ligand, $n_M = Q_{\exp}/Q_M$, the ratio of the experimental amount of ozone per

1 mole of metal ion in the complexes; $Q^*_{\exp} = Q_{\exp}/m_a$, the specific experimental amount of ozone per 1 g of the antiozonant.

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