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SYNTHESIS AND APPLICATION OF ANTIOXIDANT PROPERTIES OF AZOMETHINES AND ITS COMPLEXES

Aysel R. Rahimova[1*], Zakir I. Ismailov[1], Teymur M. Ilyasly[1]

[1]Department of Chemistry, Baku State University, Baku, Azerbaijan

Abstract. A total three new compounds, -p-aminophenol and its metal complexes have been successfully prepared. The complexes obtained are characterized by using IR, NMR, EPR spectroscopy. It has been established that they have shown a high antioxidant properties and are inhibitors of complex action. Studies have shown that the investigated metal complexes are effective inhibitors of the oxidation of complex action: Terminated chain oxidation reaction with peroxide radicals and hydroperoxide are catalytically decomposed. Azomethine derivatives have been found to be more effective standards oxidants as the process dominantly affects the overall antioxidant behavior of.

Keywords: *azomethine, antioxidant properties, metal complexes.*

Corresponding Author: *Aysel Rahimova, Department of Chemistry, Baku State University, Z. Khalilov str., 23, AZ1148, Baku, Azerbaijan, e-mail: rahimova_aysel@mail.ru*

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1. Introduction

Schiff bases derived from an amino and carbonyl compound are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively. In azomethine derivatives, the C=N linkage is essential for biological activity. The literature survey reveals that the metal complexes and derivatives have nucleus enhanced pharmaceutical, agricultural and industrial values so, the medicines containing azomethine nucleus are now used extensively in medical, biomedical and biotechnological facililties (Abdel-Rahman *et al.*, 2013). It has been shown to posses industrial, fungicidial, insecdicidial, medicinal values. The synthetic applications of azomethine derivatives have been investigated and shown to have enough potential in the synthesis of nitrogen and sulfur containing heterocyclic compounds (Abdel-Rahman *et al.*, 2014). Some derivatives of azomethine possesantituberculoses, anticancer, antitumor, antipyretic activities. These drugs have been shown to posses a diverse range of physiological activities, plant growth, promoting activity, antitumor, antibacterial, antidiabetic values (Abu-Dief & Nassr, 2015; Abdel-Rahman *et al*., 2016). Some azomethines were also found to be active against S. aureus, E. coli, and C.albicans (Abdel-Rahman *et al.*, 2017). In the literature it is known that a numberthiocarbamides and their various derivatives are widely used in industry as a monomers, copolimers, corrosion inhibitor, herbicides and fungicides in agriculture (Abdel-Rahman *et al.*, 2018).

2. Experimental part

2.1. Benzylidene-p-aminophenol

The ligand was synthesized by the condensation of p-benzaldehyde p-aminophenol in 1:1 molar ratio using absolute alcohol as the reaction medium. The mixture was refluxed on water bath for 1 and a half an hour and then allowed to stand overnight at room temperature. The product was crystallized from the same solvent.
Melting point- 112 ^{0}C, yield-68 %.
Elemental analyses:
Found, % C-74.8, H-7.6, N-17.6, $C_{21}H_{28}N_4$.
IR spectra (ν, sm^{-1}): 1650 (C=N), 1610 (C=C), 1470, 1180 (C-N $(CH_3)_2$. NMR spectra (δ, ppm): 8.146 (C=N), 3.641-3.028 $(CH_3)_2N$, 2.050 (4H), 1.205-1.131 (CH_2).
The IR spectra of the complexes C=N zone is observed at 1650 sm^{-1}. In comparison with its position in the spectrum of the ligand (1637 sm^{-1}) it is shifted to low-frequency zone. Such a change proves presence of coordination of metal with N atom C=N bond (635-620 sm^{-1}, M=N). On the base of above-mentioned we can conclude that complexes should have such a structure: $M(L)_2X_2$, where X-anion.The following is the NMR spectrum.

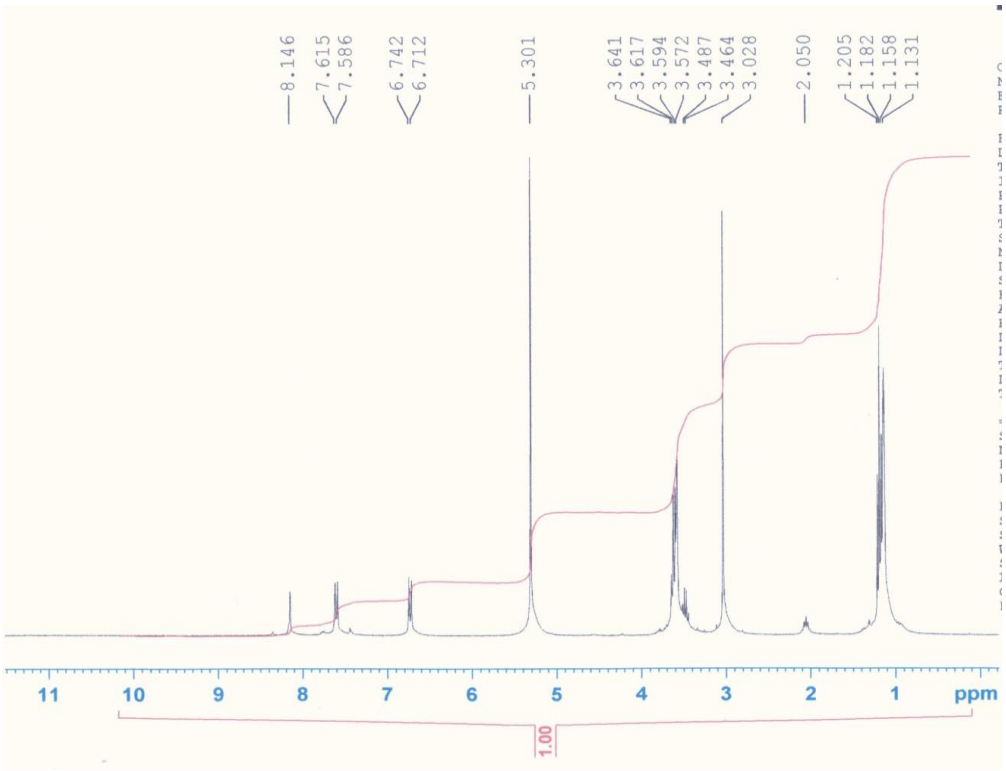

Figure 1. NMR spectrum

In the spectrum of NMR the group of azomethine in 8.146, $(CH_3)_2N$ 3.641-3.028
4 H-2.050, CH_2 1.205-1.131 ppm observed.

2.2. The complex of Cu(II)

They were prepared by reacting ethanolic solution of the ligand with ethanolic solution of metal acetate in 1:2 molar ratio. The precipitated solid coloured complexes were filtered, washed with ethanol, dried in oven. Melting point-155 ^{0}C, yield- 62 %. Found, %: C 62.50, H 3.40, N 13.53. Calculated, % C 62.37, H 3.0, N 13.73.

2.3. The complexes of Ni (II)

They were prepared by reacting ethanolic solution of metal acetate in 1:2 molar ratio. The settled down solid coloured complexes were filtered, washed with ethanol, dried in oven. Melting point- 148 ^{0}C, yield-60 % . Found, % C 62.70, H 3.90, N 12.93. Calculated, %: C 62.20, H 3.2, N 13.67.

2.4. Antioxidant properties

Antioxidant effect of synthesized metal complexes studied in model reactions. As a model reaction initated by α-α^1-azobisizobutylnitrole (AİBN) used oxidation reaction in a solution of chlorobenzene at 60^{0}C. Inhibitory properties of the compounds studied the kinetics of the reaction with radicalscumylperoxde and cumylperoxidecumyl. Chlorobenzene, cumyl and cumylhydroperoxide was purified by the standart procedure.

Reaction with radicalscumylperoxide studied initiates (AIBN) cumyl oxidation in the presence of these compounds. Initiator was injected at a concentration of 2x10^{-2}mol/l inhibitor concentration was 5x10^{-5}mol/l. Reaction cumylhydroperoxide with metal complexes was performed in a glass reactor thermostated at chlorobenzene solution while bubbling nitrogen. Samples periodically analyzed for cumylhidroperoxideiodometric. On the spending of ROOH measured reaction rate of interaction with hydroperoxides metal complexes. As can be seen from Figure1, with the study initiated by AIBN cumyl oxidation at 110^{0}C in the presence of the synthesized compounds inhibited the oxidation of studied inhibitors react with radicalscumylperoxide. Studies have shown that all compound shaving as a part of metal complexes fragment inhibit initiated oxidation.

It has been shown the antioxidant measurements in the table. Largest induction period (τ) calculated stoichiometric factor ψ, equal to the number of oxidation chains terminating in one molecule of the inhibitor and its transformation products. To calculate the rate constants for the interaction of inhibitors with peroxide radicals-k_7 kinetic curves of oxygen uptake of the transformed coordinates into $[O_2]^{-1}$t to $[O^-]^{-1}$ t.

Table 1. Antioxidan properties of azomethines and its metal complexes

№ com-pounds	**Formula of the compounds**	**T= 60^{0}C**		**T= 110^{0}C**		**τ, minutes**
		f	**$K_7$10^{-4}l/mol san**	**K,10^{-4}l/mol san**	**v**	
1	[NH_2-C_6H_4-C=N-C_6H_4-OH]	6,0	5,22	16	32000	250
2	Cu-2[NH_2-C_6H_4-C=N-C_6H_4-OH]$_2$	1,8	2,2	11	22000	110
3	Ni-2[NH_2-C_6H_4-C=N-C_6H_4-OH]$_2$	1,6	1,8	9	18000	60

Fig. 2 has shown cumene oxidation in the presence of the initiator kinetic curves metal complexes listed derivatives. We can see from the picture, the curves of compounds with cumolhidroperoxide. In addition to the compounds studied has not been going at a steady pace and induction period of oxidation of cumene is not

observed. However, in response to a concentrated environment metal complexes into derivatives when the absorption rate of 5 10-4 moll reduced.

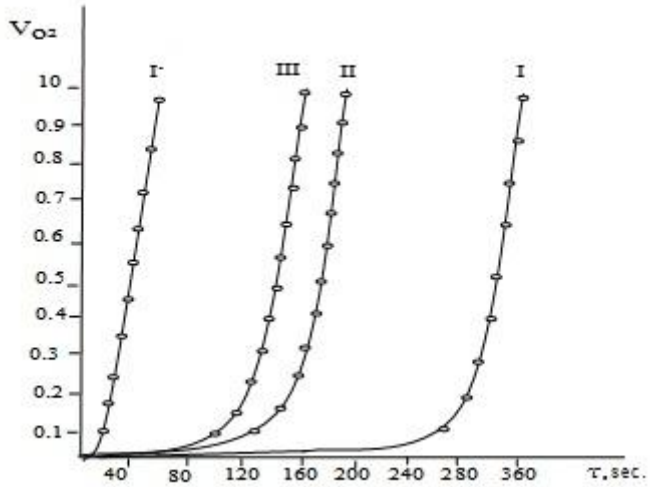

Figure 2. Cumene oxidation kinetic curves in the presence of synthesized compounds (I, II III) with initiator T = 60 0 C: 11 [lnH] = 0; [AIBN] = 2 10-2 mol / l, O_2-absorbing oxygen volume (ml); τ-induction period

Fig. 3 under the influence of the synthesized compounds were cumeneautooxidation kinetic curves. As shown in the picture cumene induced cycle inhibitor for 40 minutes. In comparison with the first picture we can see that the decomposition of cumene without initiator the period of induction equal 20 minutes. As can be seen, the highest result determined nikkel derivatives.

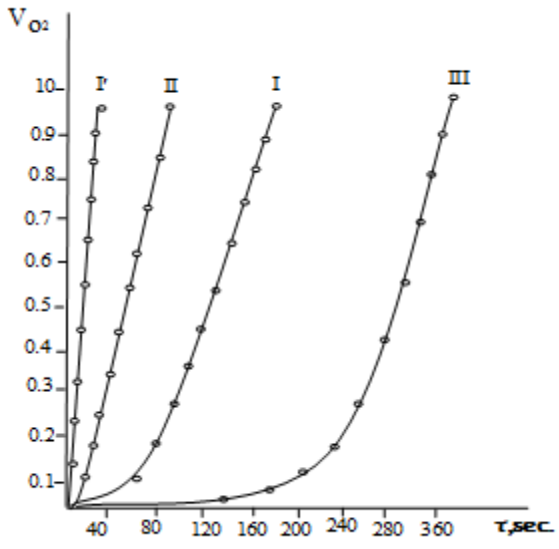

Figure 3. The kinetic curves of cumeneautooxidation with prescence of synthesized compounds (I, II and III) T = 110 0 C: 11, [ln H] = 0: [lnH} = 5 10-5 mol / l:VO_2-absorbed oxygen volume (ml); τ-induction period.

As a result of studies have found that all the tested compounds (1-5) actively decomposed HPC figure 4. Kinetic curve of HPC decomposition under the action of the compound consists of two parts. At the beginning of the reaction revealed some induction period during which there is very little decay HPC and then goes fast catalytic decomposition of HPC.

This suggest that the reaction of the compound (1) of HPC is complex. First antioxidant reacts with cumylhidroperixide turning into active products which are then catalytic decomposition of HPC.

The catalytic decomposition of hydroperoxide in the presence of metal complexes flows under the influence is not the source of the antioxidant and its conversion products.

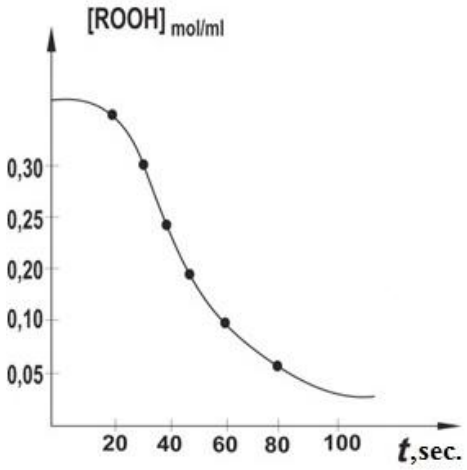

Figure 4. Kinetic curves of kumil hidroperoxide division with synthesis compounds

The results showed that one molecule of the compound capable of decomposing to a few tens of thousands of molecules HPC. The value of the kinetic parameters of the catalytic decomposition of HPC by the action of the compounds are shown in Table 2.

3. Results and discussion

In model reactions, we studied the reactions of different metal complexes with cumylperoxide and cumylperoxide radicals established that they have exhibit high antioxidant activity. Continuing studies on the synthesis of various derivatives metal complexes and studied the relationship between structure and antioxidant properties in this paper the synthesis metal complexes based on the reaction of benzaldehyde with p-aminophenol

Analysis of the kinetic parameters of the HPC cleavage is seen that the catalyst factor is observed for the compound which in the molecule, together with aazomethinemoity also contains a primary amine fragment. From the table we can easily see that high antioxidant properties, along with its inherent high catalyst factor also has a high value of the reaction rate constant. For example, the value for the compounds (1) is 9 and for compounds (2-4) 2,2-5,22 l/mols.

Thus studies have shown that the investigated metal complexes are effective inhibitors of the oxidation of complex action:Terminated chain oxidation reaction with peroxide radicals and hydroperoxides are catalytically decomposed.

4. Conclusion

From the result of antioxidant effect we can conclude that all compounds exhibited strong to moderate activity. Metal complexes derivatives have been found to be more effective standards oxidants as the process dominantly affects the overall antioxidant behavior of.

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