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RADIOLYSIS OF TRANSFORMER OIL IN THE PRESENCE OF POLYCHLOROBIPHENYLS AND NANO-γ-Al_2O_3

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Abstract: In this work, a comparative study of the kinetics of changes in pH indicator, the formation of H_2O_2 and CO_2 concentration depending on the absorption dose during the γ-radiolysis of polychlorobiphenyl (PCB), containing transformer oil in the presence and absence of nano-Al_2O_3 was conducted. In the radiolysis of both systems (PCB + transformer oil and PCB + transformer oil + 0.1 g nano-γ-Al_2O_3), the radiation-chemical yield of CO_2 become less in the presence of nanoparticles and decreases with the increase of initial concentration of PCB. In contrast to CO_2, the radiation-chemical yield of H_2O_2 increases with an increase in the initial concentration of PCBs, but their values are lower in the presence of nano-γ-Al_2O_3.

Keywords: transformer oil, polychlorobiphenyl, nano-γ-Al_2O_3, radiolysis, radiation-chemical yield

1. Introduction

Currently, nano-oxides are widely used to increase the efficiency of radiation-chemical decomposition of substances [1-13]. It has been established that during the radiolysis of water, the hydrogen yield in the presence of nano-catalysts, such as Al_2O_3, TiO_2, SrO_2, Zr, etc. sharply increases. It has been established in [2] that the radiolytic decomposition of small phenol impurities in water increases in the presence of nano-γ-Al_2O_3 and nano-TiO_2 [3, 4]. The observed increase in the efficiency of radiolysis is due to the participation of nonequilibrium carriers formed on the surface of nano-catalysts in the decomposition of adsorbed molecules [5-7].

The abovementioned effects may be characteristic of the radiolysis of other chemical compounds. In this aspect, the use of nano-catalysts in the process of radiological decomposition of polychlorobiphenyls (PCBs) to purify transformer oils from PCBs seems to be relevant. At present, the possibilities of radiation-chemical technology for the purification of transformer oils from PCBs are widely studied [8, 13].

Chlorinated biphenyls, having high chemical and heat resistance, do not decompose in the environment and accumulate in people's adipose tissue, causing a weakening of their immune systems, they are included in the Stockholm Convention on Persistent organic pollutants. Although their production was suspended in the late 80s of the last century, they are still in use today. Also, cross-contamination of oils during repair and refining of used transformer oils is widespread. Therefore, the development of new disinfection methods is an urgent task. Although their production was suspended in the late 80s of the last century, they are still in use today. Also, “cross” contamination of oils during repair and refining of used transformer oils is widespread. Therefore, the development of new disinfection methods is an urgent issue.

In this work, we studied the laws of radiolysis of PCB-containing transformer oil in the presence of nano-γ-Al_2O_3 under the influence of γ - radiation.

2. Experimental part

Transformer oil with and without the addition of PCB oil "Sovtol-10" containing PCB isomers and analogues, as well as 10% trichlorobenzene has been used.

Aerated samples were irradiated under the influence of γ - radiation from the ^{60}Co isotope under static conditions in glass ampoules at room temperature. The absorption dose rate was determined by Ferro sulfate dosimeter [14], which was 0.21 Gy/s.

The pH indicator was measured with a *pH*-meter, CO_2 analysis was performed on an Agilent Technologies-7890 A gas chromatograph with detectors: TCD - carbon oxides, H_2O_2 - titration. Nano-γ-Al_2O_3 from Skyspring Nanomaterial's, Inc. with a purity of 99.99%, a nano-particle size of 50 nm and γ-phase content of 99.32% and a specific surface area of 262.09 m^2/g.

3. Results and its discussion

Table 1 shows a comparative study of the kinetics of changes in pH indicator, the formation of H_2O_2 and CO_2 depending on the absorption dose during the radiolysis of PCB-containing transformer oil in the presence and absence of nano-γ-Al_2O_3 under the influence of γ radiation. The presented data are the results of three measurements of the corresponding parameters. Measurement errors are in the range of 10-15%

Table 1

The dependence of pH indicator on the absorption dose during the radiolysis of PCB-containing oil and PCB + transformer oil + 0.1 g nano-γ-Al_2O_3 at different initial PCB contents.

D, kGy	pH					
	5 ppm PCB	15 ppm PCB	40 ppm PCB	5 ppm PCB + 0.1g nano-A_2O_3	15 ppm PCB + 0.1g nano-A_2O_3	40 ppm PCB + 0.1g nano - A_2O_3
0	5.5	4.7	4.5	5.3	5.1	4.2
4.1	5.2	4.6	4.15	4.92	5	3.72
27.4	4.8	4.3	3.9	4.35	4	3.3
68.4	4.5	3.9	3.7	4	3.6	3.2
136.8	4.4	3.7	3.5	3.5	3.2	3.11
Degree of conversion	20%	21.2%	22.2%	37.7%	37.2%	26%

It has been established that the acidity of the oil increases in both cases: in the first case (without the presence of nano-γ-Al_2) the degree of acidity growth is 20-22%, and in the second case (in the presence of nano-γ-Al_2) it increases and amounts to 26-38% at different concentrations of PCBs in the mixture.

An increase in acidity from the absorption dose during the irradiation of the abovementioned systems can also occur due to the oxidation of the main components of the transformer oil mixture with dissolved oxygen. Moreover, oxygen not only dissolves but also chemically combines with oil, forming oxidation products [15]. The presence of dissolved oxygen in transformer oil when exposed to gamma radiation, leads to the formation of carbon dioxide and hydrogen peroxide, which we have identified experimentally.

Figure 1 shows the dependences of the concentration of carbon dioxide during the radiolysis of PCBs containing transformer oil in the presence and absence of nano-γ-Al_2O_3 at different concentrations of PCBs. As can be seen from fig. 1 (a) the concentration of the resulting CO_2 rapidly increases with increasing dose and reaches a stationary concentration at doses of ~ 4 kGy at PCB concentrations in the range of 5–40 ppm. A similar course of kinetic curves is also observed in the presence of nano-*γ-Al_2O_3* (Fig. 1 (b)), but stationary CO_2 concentrations are lower than the radiolysis of a homogeneous PCB – transformer oil system, i.e. the presence of nano-*γ-Al_2O_3* leads to a decrease in the rate of the oil oxidation reaction.

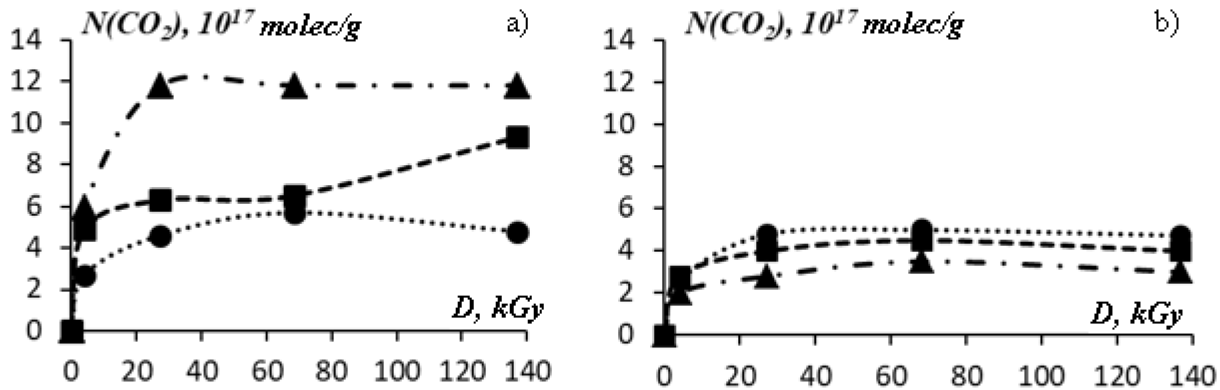

Fig. 1. Dependence of CO_2 concentration on the absorption dose a) during radiolysis of PCB containing oil and b) PCB + transformer oil + 0.1 g nano-γ-Al_2O_3 (5- (●), 15- (■), 40- (▲)) ppm PCBs.

Another oxidation product is hydrogen peroxide, the kinetics of formation of which is shown in Figure 2 a, b. As can be seen, after a sharp increase in the concentration of hydrogen peroxide up to an absorption dose of ~ 30 kGy, its values decrease with increasing dose, apparently, due to the participation of hydrogen peroxide in secondary reactions.

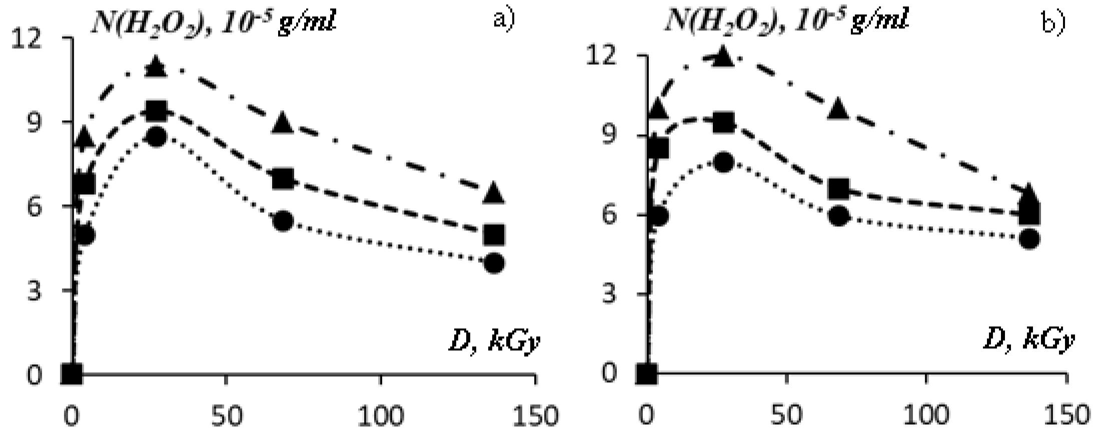

Fig. 2. Dependence of the H_2O_2 concentration on the absorbed dose a) during radiolysis of PCB containing oil and b) PCB + transformer oil + 0.1 g nano-γ-Al_2O_3 (5- (●), 15- (■), 40- (▲)) ppm PCBs.

Table 2 shows the radiation-chemical yields of CO_2 and H_2O_2 during the radiolysis of a homogeneous mixture of PCB containing transformer oil and a heterogeneous system of the abovementioned mixture in the presence of nano-*γ-Al_2O_3* at various initial PCB concentrations in the range of 5-40 ppm.

Table 2

Radiation-chemical yields of H_2O_2 and CO_2 during radiolysis of PCB + transformer oil and PCB + transformer oil + 0.1 g nano-γ-Al_2O_3 systems.

PCB, ppm	*G*, molec/100 eV			
	PCB + transformer oil		PCB + transformer oil + 0.1 g nano-γ-Al_2O_3	
	CO_2	H_2O_2	CO_2	H_2O_2
5	1.1	3.9	1.0	4.1
15	1.9	4.7	1.1	5.9
40	2.3	5.9	0.79	6.9

As can be seen, during the radiolysis of both systems, the radiation-chemical yields of H_2O_2 increase with an increase in the initial concentration of PCBs. In contrast to the radiolysis of a homogeneous system, the radiation-chemical yields of CO_2 decrease when nano-γ-Al_2O_3 is added to the system.

4. The discussion of the results

The investigated system is a system consisting of many components. Therefore, an explanation of the results is hypothetical.

Transformer oil has a complex hydrocarbon composition with an average molecular weight of 220-340 a.e, and contains the following main components: paraffins 10-15%; naphthenes or cycloparaffins 60-70%; aromatic hydrocarbons 15-20%; asphalt-resinous substances 1-2%; sulfur compounds <1%; nitrogenous compounds <0.8%; naphthenic acids <0.02; antioxidant additive (ionol) 0.2-0.5% [15]. When irradiating transformer oil, the energy of ionizing radiation is absorbed in proportion to the electron density of each component. Since the main components of the oil are alkanes, cycloalkanes, and aromatic hydrocarbons, energy is mainly absorbed by the molecules of these compounds.

In the radiolysis of such a complex system, because of the possibility of transferring electron excitation energy and charge, the composition and yields of radiolysis products change. The molecules of hexane (alkanes), cyclohexane, (cycloalkanes) and benzene (aromatic hydrocarbons) have an ionization potential of 10.4, 9.9, and 9.2 eV, respectively [16]. A comparison of the ionization potential shows the possibility of charge transfer from the “parent” ions of hexane and cyclohexane to benzene molecules. Benzene molecules also effectively capture hydrogen atoms and hydrocarbon radicals. Also, electron excitation can be transferred from alkane and cycloalkane molecules to benzene molecules, since they have more high-energy electron states, for example, the energy of the singlet state of benzene and hexane molecules is 9.13 and 9.84 eV. It has been previously established that the hydrogen yield during the radiolysis of binary mixtures of hexane (cyclohexane) + benzene decreases with increasing concentration of benzene, which is explained by the transfer of charge and electron excitation from hexane (cyclohexane) molecules to benzene molecules [17]. The ongoing chemical processes lead to the formation of gases, the decomposition of the main components of oil and the course of oxidative processes. The formation of hydrogen peroxide is associated with the presence of dissolved oxygen in oil [18]. According to [19], when air dissolves in oil, the ratio between the air constituents changes. So, air contains 78% and 21% by volume of nitrogen and oxygen, but if it is dissolved in oil, it contains 69.8% by volume of nitrogen and 30.2% oxygen.

The radiolytic conversion of PCBs is due to the reactions of the active particles of the radiolysis of transformer oil, which has a predominant electron density in the irradiated system. In the presence of nano-particles, nonequilibrium charge carriers — electrons and holes — occurring on the surface of nano-particles in the decomposition of transformer oil components also participate. Calculations show that under the experimental conditions ~ 40% of the radiation energy is absorbed by nano-γ- Al_2O_3, and ~60% by the components of transformer oil.

In several works, it was found that the conversion of PCB molecules occurs in a reaction with electrons, which seems likely due to the high value of the affinity of the atom for the electron.

$$e + C_{12}H_{10-n}Cl_n \rightarrow \cdot C_{12}H_{10-n}Cl_{n-1} + Cl^-,$$

where $k=(2\div3)\cdot10^9\ M^{-1}s^{-1}$ (for dichlorobiphenyl, tetrachlorobiphenyl, decachlorobiphenyl) [20]

It is likely that part of the stabilized electrons on the surface of nano -γ- Al_2O_3 also serve as the adsorption center of PCB molecules and cause their radiolytic decomposition.

5. Conclusion

1. It has been found that during the radiolysis of transformer oil in the presence of nano-γ-Al_2O_3 and PCB impurities, the hydrocarbon components of the oil are oxidized, as well as the acidity of the irradiated solutions increases due to the formation of acidic products and dechlorination of PCB impurity molecules
2. The increase of acidity in the presence of nano-γ-Al_2O_3 in the irradiated system is related with participation of stabilized electrons on the oxide surface in the dechlorination of PCB molecules.

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РАДИОЛИЗ ТРАНСФОРМАТОРНОГО МАСЛА В ПРИСУТСТВИИ ПОЛИХЛОРБИФЕНИЛОВ И НАНО-γ-Al_2O_3

З.И. Искендерова

Резюме: В данной работе проводилось сравнительное изучение кинетики изменения pH показателя, концентрации H_2O_2 и CO_2 в зависимости от поглощенной дозы при радиолизе полихлорбифенил (ПХБ) содержащего трансформаторного масла в присутствии и без нано γ-Al_2O_3 под действием излучения. При радиолизе обоих систем (ПХБ + трансформаторное масло и ПХБ + трансформаторное масло + 0.1 г нано-γ-Al_2O_3) радиационно-химический выход CO_2 уменьшается с ростом исходной концентрации ПХБ, хотя при наличии нано частиц значения радиационно-химического выхода CO_2 становиться меньше. В различие от CO_2 радиационно-химические выходы образования H_2O_2 растут с повышением исходной концентрацией ПХБ, но их значения меньше в присутствии нано-γ-Al_2O_3.

Ключевые слова: трансформаторное масло, полихлорбифенил, нано-γ-Al_2O_3, радиолиз, радиационно-химический выход.

POLİXLORBİFENİL VƏ NANO-γ-Al_2O_3 İŞTİRAKI İLƏ TRANSFORMATOR YAĞLARININ RADİOLİZİ

Z.İ. İskəndərova

Xülasə: Bu işdə tərkibində PXB olan transformator yağlarının nano-γ-Al_2O_3 -ün iştirakı ilə və iştirakı olmadan γ-şüalarının təsiri altında radiolizi zamanı pH göstəricisinin, H_2O_2 və CO_2-nin qatılıqlarının udulan dozadan asılılıqlarının yaranma kinetikası müqayisəli şəkildə öyrənilmişdir.

Hər iki sistemin radiolizi zamanı (PXB+transformator yağı və PXB+transformator yağı +0,1 q nano-γ-Al_2O_3) PXB-nin ilkin qatılıqları artdıqca CO_2-nin radiasiya-kimyəvi çıxımları azalır, sistemdə nano-zərrəcik olduğu halda CO_2-nin radiasiya-kimyəvi çıxımı daha çox azalır. CO_2-dən fərqli olaraq H_2O_2-nin radiasiya-kimyəvi çıxımının qiyməti sistemdə PXB-nin ilkin qatılığı artdıqca artır, lakin nano-γ-Al_2O_3 -ün iştirakı ilə azalır.

Açar sözlər: transformator yağı, polixlorbifenillər, nano-γ-Al_2O_3, radioliz, radiasiya-kimyəvi çıxım.