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RADIATION CHEMISTRY

Effect of Chlorinated Biphenyl Admixtures on Transformer Oil Radiolysis

Z. I. Iskenderova[a], * and M. A. Kurbanov[a]

[a] *Institute of Radiation Problems, National Academy of Sciences of Azerbaijan, Baku, AZ 1143 Azerbaijan*

**e-mail: Zenfira_iskenderova@mail.ru*

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Abstract—A comparative study has been carried out on the gamma-radiolysis of waste transformer oil and oil containing polychlorinated biphenyls (PCBs) as impurities. To this end, changes in the pH and the concentrations of hydrogen peroxide, chlorine, and PCB isomers as a function of the absorbed dose have been studied. The waste transformer oil has been investigated with and without the addition of the Sovtol-10 PCB oil. It has been established that the radiolysis of the transformer oil containing admixtures of chlorinated biphenyls in results in stronger oxidation of the oil the presence of dissolved oxygen (formation of H_2O_2 and CO_2, a decrease in pH value) and oxygen has a negative effect on the radiolytic degradation of chlorinated biphenyls.

Keywords: PCB, transformer oil, γ-radiation, radiation-chemical yield

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Radiation-chemical transformations in transformer oil containing polychlorinated biphenyls (PCBs) have been investigated in many studies [1–4] aimed to explore the possibility of using ionizing radiation sources for oil purification to remove PCBs. Those studies focused on the radiolytic degradation of PCB isomers. Meanwhile, the effect of PCB components on the radiolysis of transformer oil, especially in the presence of adsorbed oxygen, has been poorly studied. It is known that during long-term operation of a transformer, the oil contained in it is strongly degraded by the heat and electric field of the windings. Oxidation products are formed, which negatively affect the dielectric quality of the oil. Similar situations can be observed in the electrical equipment of nuclear reactors in emergency conditions when the waste oil is exposed to the reactor gamma-radiation [5].

The objective of the work is a comparative study of the gamma-radiolysis of waste transformer oil and the oil containing PCB isomers. Changes in the pH and the concentrations of hydrogen peroxide, chlorine, and PCB isomers as a function of the absorbed dose have been studied for this purpose. The object of the study was waste transformer oil with and without the addition of the PCB oil Sovtol-10 containing PCB isomers and 10% trichlorobenzene [6].

EXPERIMENTAL

Irradiation was carried out using ^{60}Co γ-rays. The absorbed dose rate of γ-radiation was determined by ferrous sulfate dosimetry to be 0.21 Gy/s. Samples were irradiated under steady-state conditions at room temperature in 45-mL glass ampoules; the radiation dose was 4–140 kGy. The pH of the system was measured with a glass electrode according to the procedure described in [7]. Liquid radiolysis products of transformer oil were analyzed on an Agilent Technologies-7820A gas chromatograph. Carbon dioxide was determined chromatographically as well. The total chlorine content was determined by the colorimetric method. Analysis of the transformer oil for chlorine was carried out with a Dexsil L2000 analyzer [8]. Hydrogen peroxide was determined by the permanganatometric method [9].

RESULTS AND DISCUSSION

Two sets of experiments were carried out, including determination of changes in CO_2 concentration, pH value, and H_2O_2 concentration in the processed chlorine (PCB)-free transformer oil depending on the absorbed dose (set 1) and changes not only in the above parameters, but also in total and individual concentrations of PCB isomers and chlorine in irradiated waste transformer oil containing PCBs in an amount of 20 ppm (set 2). According to published data [10], the concentration of oxygen in adsorbed air is 30.2%. The results are presented in Table 1.

Table 1. Kinetics of changes in process parameters depending on the absorbed dose

Dose, kGy	Transformer oil			Transformer oil containing 40 ppm chlorine				
	pH	H_2O_2, 10^{-5} g/mL	CO_2	pH	H_2O_2, 10^{-5} g/mL	CO_2	total PCB concentration, ppm	chlorine content, ppm
0	5.6	0	0	4.2	0	0	19.3	41.1
4.1	4.9	5.1	0.45	3.7	8.5	5.95	20.41	33.9
27.4	4.3	6.0	2.26	3.3	11	11.0	20.16	29.6
68.4	4.0	4.3	0.3	3.2	9.0	11.4	19.16	27.1
136.8	3.5	4.0	0.4	3.1	6.5	11.8	17.01	21.8

Table 2. Changes in the concentration of individual isomers with absorbed dose during radiolysis of transformer oil containing 20 ppm PCBs

PCB	Name	Amount of PCB, ppm			
		initial	4.1 kGy	27.4 kGy	136.8 kGy
PCB 18	Trichloro	2.21	2.50	2.31	2.09
PCB 28 + 31	Trichloro	2.36	2.75	2.83	2.59
PCB 52	Tetrahloro	3.87	4.13	3.89	2.85
PCB 44	Tetrahloro	5.34	5.77	5.84	5.14
PCB 101	Pentachloro	2.30	2.36	2.62	1.95
PCB 118 + 149	Penta + hexachloro	0.86	0.81	0.78	0.73
PCB 153	Hexachloro	0.75	0.68	0.65	0.66
PCB 138	Hexachloro	1.19	1.05	0.91	0.85
PCB 180	Heptachloro	0.45	0.35	0.32	0.28

In the experiments of set 1, it was found that the pH of the waste oil decreases with increasing dose, a change that is due to the formation of acids during irradiation. The unirradiated waste oil also contains acidic compounds [7], but their formation significantly increases with absorbed radiation dose. The dose dependence of hydrogen peroxide formation is nonmonotonic in character; the maximum H_2O_2 concentration under the experimental conditions is observed at ~27 kGy. With a further increase in the dose, the concentration of H_2O_2 decreases, indicating the occurrence of secondary reactions involving the peroxide. The rate curve of CO_2 formation exhibits a concentration maximum at 27.4 kGy, and the radiation-chemical yield of CO_2 is 0.18 molecule/l00 eV.

In the second set of experiments, it was found that the introduction of Sovtol-10 into the transformer oil decreases the pH from 5.6 to 4.2. In addition, there is a stronger decrease in the pH during radiolysis, suggesting the degradation of PCB molecules by the action of ionizing radiation. This conclusion follows from a decrease in the total chlorine content from 41.1 to 21.8 with an increase in the dose to 136.8 kGy. The change in H_2O_2 concentration depending on the dose is also nonmonotonic, similar to the case of irradiation of the waste transformer oil in the absence of Sovtol-10, although the H_2O_2 concentrations are higher by a factor of 1.8–2 in this case. In the presence of PCB admixtures, the CO_2 formation rate increases and reaches a steady-state value at a dose of 27.4 kGy. The radiation-chemical yield of CO_2 is 2.3 molecule/100 eV.

The changes in concentrations of individual isomers with the absorbed dose during the radiolysis of transformer oil containing 20 ppm of PCBs are shown in Table 2.

It was found that the main PCB components of the oil are tri-, tetra-, and pentachlorobiphenyls, making ~83% of the total amount of identified chlorobiphenyls, a finding that is consistent with the specification of Sovtol-10 [6]. Heavier isomers, such as hexa-, hepta-, and octachlorobiphenyls, make only 12–16% of the total amount of identified chlorobiphenyls. The buildup kinetics of tri-, tetra-, and pentachlorobiphenyls have maxima at ~4–27 kGy, a further increase in the absorbed dose leads to a decrease in their concen-

Table 3. Radiation-chemical yields of radiolytic processes

PCB	Name	*G*, molecule/100 eV	
		formation	consumption
PCB 18	Trichloro	2.6×10^{-3}	
PCB 28 + 31	Trichloro	3.6×10^{-3}	
PCB 52	Tetrahloro	2.1×10^{-3}	
PCB 44	Tetrahloro	3.5×10^{-3}	
PCB 101	Pentachloro	0.4×10^{-3}	
PCB 118 + 149	Penta + hexachloro		0.3×10^{-3}
PCB 153	Hexachloro		0.5×10^{-3}
PCB 138	Hexachloro		0.9×10^{-3}
PCB 180	Heptachloro		0.6×10^{-3}

tration. At ~137 kGy, the degrees of conversion for tri- (PCB 18), tetra- (PCB 44, PCB 52), and pentachlorobiphenyls (PCB 101) are 5.4, 3.7–26, and 15%, respectively.

The concentration of high-molecular-weight polychlorinated biphenyls—hexa- and heptachlorobiphenyls—decreases monotonically with increasing dose, and the conversion of hexa- and heptachlorobiphenyls at ~137 kGy is 15–28 and ~ 38%, respectively. The increase in the concentration of tri-, tetra-, and pentachlorobiphenyls at low doses is associated with the radiolytic degradation of the high-molecular-weight chlorobiphenyls and the formation of the compounds with a relatively low molecular weight.

Polychlorinated biphenyl molecules decompose in reactions with solvated electrons by the Sherman mechanism, and the electron attachment rate constant increases with increasing chlorine content in chlorobiphenyl molecules. According to [11], the electron attachment rate constants are 2.1×10^9, 3.3×10^9, and 6.9×10^9 L mol^{-1} s^{-1} for dichlorobiphenyls, tetrachlorobiphenyls, and decachlorobiphenyls, respectively.

From the data in Table 2 on to the kinetics of changes in the concentration of PCB isomers with the absorbed dose, we determined the radiation-chemical yields of the formation and consumption of individual isomers at 4 kGy, which are presented in Table 3.

As can be seen, the radiation-chemical yields of PCB (18), PCB (28 + 31), PCB (52), PCB (44), and PCB (101) vary in the range of $0.4–3.6 \times 10^{-3}$ molecule/100 eV. The total radiation-chemical yield for the formation of these isomers is 12.2×10^{-3} molecule/100 eV. The radiation-chemical yields of degradation of the identified isomers with a relatively high chlorine content are in the range of $0.3–0.9 \times 10^{-3}$ molecule/100 eV, with the total radiation-chemical yield of degradation being 2.3×10^{-3} molecule/100 eV. Apparently, part of the PCB isomers is produced from unidentified PCB isomers that have a higher chlorine content. The radiation-chemical yield of decrease in inorganic chlorine content, calculated on the basis of the data of Table 1 is ~0.5×10^{-3} molecule/100 eV.

Thus, it was found that the radiolysis of transformer oil containing admixtures of chlorinated biphenyls results in a stronger oxidation of the oil in the presence of dissolved oxygen (formation of H_2O_2 and CO_2, a decrease in pH value) and oxygen has a negative effect on the radiolytic degradation of chlorinated biphenyls.

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