PACS: 82.50.Rx

COMPARATIVE STUDY OF THE RADIOLYSIS AND PHOTOLYSIS OF THE HEXANE SOLUTIONS OF POLYCHLORINEBIPHENYLS

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Abstract: Model solutions of polychlorinebiphenyls, containing 12 congeners in hexane were irradiated by γ–rays at 14 – 140 kGy absorption doses, as well as by UV-rays for 2 – 30 minutes using middle pressure mercury lamp (PRK-4, λ = 253 ÷ 546 nm), and the kinetics of the radiolytic PCBs degradation processes was investigated. The PCBs identification was conducted using a Gas Chromatography (Agilent Technologies 7820A).

Keywords: Polychlorinebiphenyls (PCBs), radiolysis, γ-rays, photolysis, UV-rays, degradation

1. Introduction

Polychlorinebiphenyls (PCBs) containing oils are being used at existing power facilities (transformer, capacitor, electric switches) though its production has been banned during 1987 – 1990. This case causes a "cross" pollution of "PCB clean" transformers. PCBs were included to the list of the Stockholm Convention on Persistent Organic Compounds, where it was stated that oils containing more than 50 ppm PCBs must be discontinued and utilized by the members states by 2028.

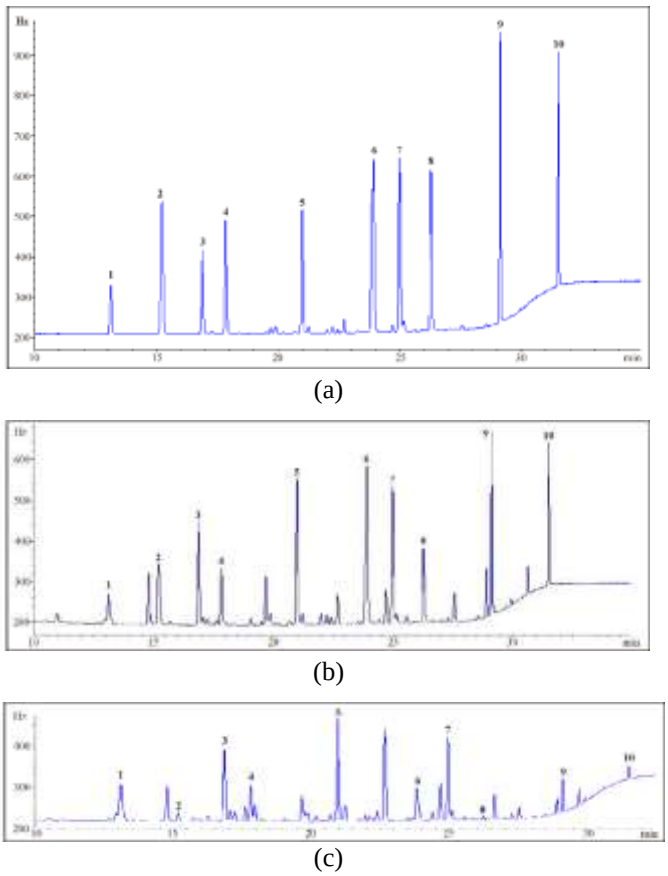
Several methods exist in the utilization of oils containing PCBs. These methods are divided into 2 major groups: full fractioning of PCBs (pyrolysis or high temperature incineration processes) and dechlorination (low temperature processes). Among second group processes the application of radiation technology has a special importance. By this method the processes are made at room temperature, one-phased, without additional reagents and in the result, biphenyls and chloride acid are generated. Some research works have been conducted in this sphere [1 – 4]. One of the limitations of the application of the radiation chemical method is relatively week studies of radiation stability of PCBs.

2. Results and discussion

The comparative radiolysis and photolysis process of the hexane solutions of PCBs have been presented in this work. For this purpose, model solutions of PCBs containing 12 congeners in hexane were irradiated by γ–rays at 14, 30 and 140 kGy absorption doses, as well as by UV-rays for 2, 5, 10, 15, 20 and 30 minutes using middle pressure mercury lamp (PRK-4, λ = 253 ÷ 546 nm, f = $1{,}5\cdot10^{15}$ quant/(sm^3·sec), and the kinetics of the PCBs degradation processes was investigated.

A standard (CEN PCB Congener Mix 1, 10 ug/ml in heptane, Supelco), containing 12 PCBs congeners (PCB 18 (2,2',5- trichlorbiphenyl), PXB 28+31 (2,4,4'- trichlorbiphenyl + 2,4',5- trichlorbiphenyl), PXB 52 (2,2',5,5'- tetrachlorobiphenyl), PCB 44 (2,2',3,5'- tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'- pentachlorobiphenyl), PCB 118 + 149 (2,3',4,4',5- pentachlorobiphenyl + 2,2',3,4',5',6- hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5'- hexachlorobiphenyl), PCB 138 (2,2',3,4,4',5'- hexachlorobiphenyl), PCB 180 (2,2',3,4,4',5,5'-

heptachlorbiphenyl), PCB 194 (2,2',3,3',4,4',5,5'-octachlorobiphenyl)) was used in order to prepare model solutions. Primary concentration of PCBs in the model solution was as follows: PXB 18 – $3{,}0 \cdot 10^{-7}$ mol/l, PCB 28+31 – $5{,}9 \cdot 10^{-7}$ mol/l, PCB 52 – $2{,}6 \cdot 10^{-7}$ mol/l, PCB 44 – $2{,}6 \cdot 10^{-7}$ mol/l, PCB 101 – $2{,}3 \cdot 10^{-7}$ mol/l, PCB 118 + 149 – $4{,}4 \cdot 10^{-7}$ mol/l, PCB 153 – $2{,}1 \cdot 10^{-7}$ mol/l, PCB 138 – $2{,}1 \cdot 10^{-7}$ mol/l, PCB 180 – $1{,}9 \cdot 10^{-7}$ mol/l, PCB 194 – $1{,}8 \cdot 10^{-7}$ mol/l. The PCBs identification was conducted using a Gas Chromatography (Agilent Technologies 7820A) [5]. The primary (a), after radiolysis (30 kGy) (b) and photolysis (5 min.) (c) chromatogrammies of PCB solutions in hexane are presented in Fig. 1.



(a)

(b)

(c)

Fig. 1. The chromatogrammies of the PCB solutions in hexane: a - primary, b – after radiolysis (30 kGy), c - after photolysis (5 min.) (1 – PCB 18, 2 – PCB 28+31, 3 – PCB 52, 4 – PCB 44, 5 – PCB 101, 6 – PCB 118 + 149, 7 – PCB 153, 8 – PCB 138, 9 – PCB 180, 10 – PCB 194).

As seen from the Fig. 1, in the result of PCB dechlorination process the quantity of PCBs (the area of corresponding peaks) strongly decreases during both radiolysis (b) and photolysis (c) process. The number of the peaks at the chromatographs of the photolysed and radiolysed samples is more than the number of the peaks at the chromatogrammies from the primary solution analysis. It seems, that PCBs contaning low chlorine atoms are formed during the dechlorination process of PCBs having more chlorine atoms.

Dose dependence of concentration of PCB 101, 138 and 180 at the radiolysis and at photolysis are given in Fig. 2 and Fig. 3, accordingly.

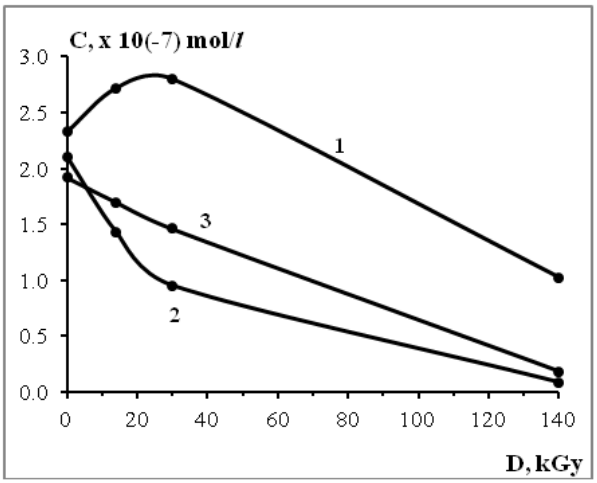


Fig. 2. The kinetics of PCBs degradation at the radiolysis of hexane solutions. 1 – PCB 101, 2 – PCB 138, 3 – PCB 180

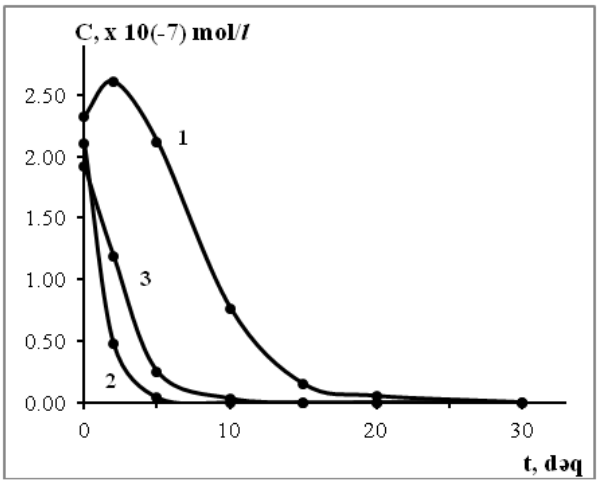
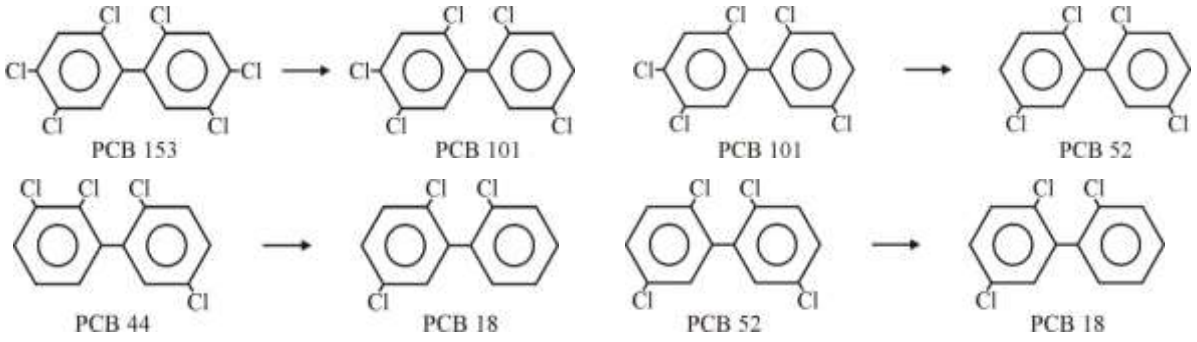


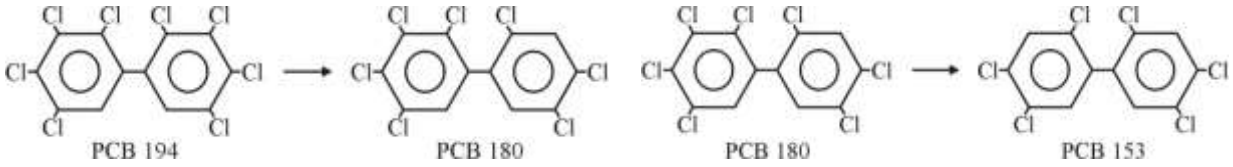
Fig. 3. The kinetics of PCBs degradation at the photolisys of hexane solutions. 1 – PCB 101, 2 – PCB 138, 3 – PCB 180

As seen from the Fig. 2, PCB 138 is dechlorinated faster than PCB 101 and 180 in hexane solution at the low irradiation doses (up to 30 kGy), but the dechlorination rate slows down by dose increasing. And the kinetics of degradation PCB 180 becomes linear. Concentration of PCB 101 at the radiolysis by small doses of irradiation (up to ~30 kGy) increases, but it decreases at further irradiation doses. The similar dose dependence was observed in [6, 7]. The kinetics of PCB 28+31, 44, 118 + 149 and 194 are analogous to PCB 138, and the kinetics of PCB 18 and 153 is analogous to PCB 180, and of PCB 52 to PCB 101.

As seen from the Figure 3, the main part of PCB 138 and PCB 180 is quickly dechlorinated during the photolysis at the low irradiation time (up to 5 min.). The kinetics of PCB 28+31, 44, 118+149 and 194 are analogous to PCB 138 and 180. The concentration PCB 101 increases at the low irradiation time (up to 2 min.) due to its formation from dechlorination of PCBs in the solution that contain more chlorine atoms. But at a later time of irradiation as a result of PCB 101 dechlorination its concentration is decreased. The kinetics of PCB 18, 52 and 153 are analogous to PCB 101. As seen, the kinetics during the photolysis of other components except PCB 180 correspond to the radiolysis.

The reason of the difference in PCBs kinetics at the radiolysis and photolysis is that another PCB is formed of a PCB in the result of dechlorination. Thus, PCB 101 may be formed when one chlorine atom comes off the PCB 153 molecule, PCB 52 when one chlorine atom comes off the PCB 101 molecule, PCB 18 from PCB 44 and PCB 52, PCB 180 from PCB 194, and PCB 153 from PCB 180.





The degradation degrees of PCB at the radiolysis (140 kGy) and photolysis (20 min) are presented on the Table 1.

Table 1. The degradation degrees of the hexane solutions of PCBs during radiolysis and photolysis

PCB	Primary concentration, mol/l	Degradation degree (in mol), %	
		During Radiolysis (140 kGy)	During Photolysis (15 min)
PCB 18	$3{,}0 \cdot 10^{-7}$	79,0	42,2
PCB 28+31	$5{,}9 \cdot 10^{-7}$	91,4	100
PCB 52	$2{,}6 \cdot 10^{-7}$	16,7	35,3
PCB 44	$2{,}6 \cdot 10^{-7}$	91,3	93,1
PCB 101	$2{,}3 \cdot 10^{-7}$	56,0	67,1
PCB 118+149	$4{,}4 \cdot 10^{-7}$	86,6	97,7
PCB 153	$2{,}1 \cdot 10^{-7}$	80,1	85,2
PCB 138	$2{,}1 \cdot 10^{-7}$	96,0	100
PCB 180	$1{,}9 \cdot 10^{-7}$	90,6	98,3
PCB 194	$1{,}8 \cdot 10^{-7}$	94,0	100

As seen from table 1, the degradation degree of PXB 18, 52, 101 and 153 is less than other components. Also, it's seen from the degradation degree numbers of the hexane solutions of PCBs during radiolysis and photolysis that the photolysis process is more effective than radiolysis.

At the radiolysis of the studied system γ-rays are absorbed by hexane molecules as the electronic density of hexane in solution is more than PCBs and the dissolved oxygen. And the PCBs transformation happens at the reactions of radicals derived from hexane radiolysis. The hexane molecules don't absorb UV-rays during photolysis as its absorbing spectrum is not within 253-546 nm wave length. In this range of $\lambda = 253 \div 546$ nm a selective excitation of singlet state happens in PCB molecules with the UV-irradiation of 200-300 nm wave length [8]. Excitation is transferred to a triple state with the inter-combination conversion and the PCBs are dechlorinated.

3. Conclusion

1. Kinetics of radiolytic and UV-photochemical degradation of 12 PCBs congeners was studied and the irradiation doses and UV-irradiation time for the destruction of PCBs in given solutions were calculated.
2. The specification of the degradation kinetics of the given PCBs congeners was identified. For the some congeners the analogy of the degradation kinetics at the radiolysis and UV-photolysis was observed.

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СРАВНИТЕЛЬНОЕ ИССЛЕДОВАНИЕ РАДИОЛИЗА И ФОТОЛИЗА РАСТВОРОВ ПОЛИХЛОРБИФЕНИЛОВ В ГЕКСАНЕ

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Резюме: Были исследованы модельные решения полихлорбифенилов, содержащие 12 конгенеров в гексане облученные лучами при дозах поглощения 14-140 кГр, а также УФ-лучами в течении 2-30 минут с использованием ртутной лампы среднего давления и кинетика деградационных процессов радиолитического ПХБ. Идентификация ПХБ проводилась с использованием газовой хроматографии (Agilent Technologies 7820A).

Ключевые слова: полихлорбифенилы (ПХБ), радиолиз, γ-лучи, фотолиз, УФ-лучи, деградация.

POLİXLORBİFENİLLƏRİN HEKSANDA MƏHLULLARININ RADİOLİZ VƏ FOTOLİZ PROSESLƏRİNİN MÜQAYİSƏLİ TƏDQİQİ

E.T. Abdullayev, M.A. Qurbanov, P.C. Camalov

Xülasə: Heksan məhlulunda 12 konqenerdən ibarət olan polixlorbifenilin (PXB) model məhlulları 14-140Gr udulma dozasında γ – şüaları ilə, həmçinin orta təzyiqli civə lampasından (PRK-4, λ = 253 ÷ 546 nm) istifadə etməklə UB-şüalar ilə 2-30 dəqiqə müddətində şüalandırılmış, radiolitik PXB deqradasiya proseslərinin kinetikası öyrənilmişdir. PXB-lərin təyini Qaz Xromatoqrafı (Agilent Technologies 7820A) ilə aparılmışdır.

Açar sözlər: Polixlorbifenillər (PXB), radioliz, γ – şüaları, UB - şüalar, deqradasiya.