Conference Paper

Study of the Effect of Radiation Dose Rate on the Stability of Various Organochlorine Pesticides

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Abstract

The radiolysis of organochlorinated pesticides (OCP) is studied in dilute solutions irradiated at a dose of 10 kGy with a dose rate varied from 8.3 · 10⁻³ up to 2.33 Gy/sec. It is found that the shape of the degradation degree relationship on dose rate is similar for different OCPs in polar and non-polar solvents (hexane, 2-propanol) and does not depend on the concentration of the initial substance. The maximum of the OCP degradation degree is registered in the dose rate range of 0.23-0.43 Gy/sec. A lognormal distribution is considered as a function best fitting the experimental data. The OCP degradation mechanism could be explained by the ratio of active and recombined particles along the gradient of ionizing radiation intensity.

Keywords: organochlorinated pesticide; irradiation, dose and dose rate of gamma-radiation; radiation degradation; functional dependence

At the present time, certain knowledge and experience have been accumulated and results have been obtained from studies of the effect of high-energy ionizing radiation on biologically active substances, such as organochlorineted pesticides (OCPs). Actual problems of studying consequences of radiation impact on the OCPs and other chemicals, similar to them in composition and toxicity (listed among the persistent organic pollutants (POPs)) were discussed in [1-2]. In radiation-chemical studies of these organochlorine compounds, which microconcentrations are contained in environmental media and foodstuffs, a dependence of degradation degree (P) on dose (D) is most often analyzed [3-5]. Information about the effect of low dose rate (D) radiation on the stability of pesticides is scarce and incomplete. At the same time, to provide the radiation safety requirements to such a field of radiation technologies (RT) applications as agricultural and food products treatment, a determination of dosimetric characteristics of radiation exposure is of special importance.
In the previous studies [6-7], the dependence was found for the γ-HCH (γ-hexachlorocyclohexane) degradation degree in 2-propanol on irradiation dose rate, as well as the influence of dose rate was revealed not only on quantitative but also qualitative composition of the DDT (dichlorodiphenyltrichloroethane) radiolysis products. We also studied this relationship on the example of various OCPs (α-, γ-HCH, DDT and DDE (dichlorodiphenyltrichloroethylene)) in solutions at the concentration of 0.100 (1.00) μg/ml in hexane and 2-propanol [8]. Samples irradiated with the same dose (10 kGy) but different dose rates of 0.43, 0.70 and 1.35 Gy/s were compared. This choice of the dose rate values was attributed to real technological parameters of foodstuff radiation treatment [9]. It was found that the \( P(\cdot) \) value, calculated from the experimental data, has the character of hyperbolic function within the studied range of \( \dot{D} \) values. Simultaneously, the same dependence of \( P(\dot{D}) \) was revealed for systems including various pesticides and polar (non-polar) solvents. It was shown that an increase of the pesticide concentration in solution by an order of magnitude did also not change the dependence of \( P(\dot{D}) \).

Our results about reducing of \( P \) in the studied range of \( \dot{D} \) values do not contradict to conclusions regarding the mechanism of organic matter degradation under irradiation, presented in [10]. However, there is no published information about an effect in OCPs from irradiation with dose rate less than 0.43 Gy/sec. Preliminary results of our study of the DDE radiolysis carried out at small \( D \) values required a confirmation. Thus, the range of \( \dot{D} \) levels was extended to obtain new data concerning a shape of \( P(\dot{D}) \) dependence for the various OCPs.

1. Materials and methods

The dose rate effect on the OCP degradation degree was studied at exposure to a dose of 10 kGy of solutions of DDE, alpha-, gamma-HCH in hexane and 2-propanol with concentrations of 0.100 and 1.00 μg/ml.

The model solutions of the individual OCPs were irradiated at doses of 10 kGy at dose rate varied from 0.0083 up to 1.35 Gy/sec (“Issledovatel” \(^{60}\text{Co} \), “Luch-1” \(^{60}\text{Co} \) and Gammacell \(^{60}\text{Co} \) installations).

The OCPs stability was estimated basing on their degradation under irradiation (\( P \), %):

\[
P = 100\% - \frac{C_{\text{after}}}{C_{\text{before}}} \times 100\%.
\]
where $P$ – degradation degree, %; $C_{after}$ – concentration of pesticide after irradiation, μg/ml; $C_{before}$ – concentration of pesticide before irradiation, μg/ml.

The concentrations of pesticides in solutions before and after irradiation were determined by gas-liquid chromatography. All data analysis as well as sample preparation details and irradiation parameters are presented in the earlier studies [1, 2, 5]. Statistical processing of data was carried out with MS Excel 2016 and Origin 2015.

2. Results

The effect of $D$ in the range 0.0083–1.35 Gy/sec on $P$ was considered on two examples of isomer solutions irradiation ($\alpha$- and $\gamma$-HCH), and also on the DDE solution. Initially, the $P$ values for $\alpha$-, $\gamma$-HCH were determined only for irradiation at dose rates of 0.0083, 0.43 and 1.35 Gy/sec. These data are presented in Table 1. The table shows that, at the concentrations of 0.100 and 1.00 μg/ml in two solvents (hexane and 2-propanol), a remarkable decrease in the $P$ values is observed at dose rate of 0.0083 Gy/sec, compared to the values registered at 0.43 and 1.35 Gy/sec. Thus, the maximum degradation of the OCP was likely obtained in the above range of dose rates. In this connection, this interval of $D$ values was studied in more details on the example of DDE solution. The results are also presented in Table 1 and used to show trends in a dose dependence of the degradation degree (Figure 1).

Table 1: The degradation degree (%) of OCPs depending on dose rate of gamma-radiation ($D = 10 \text{ kGy}$).

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Hexane</th>
<th>2-propanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dose rate, Gy/sec</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0083</td>
<td>0.15</td>
</tr>
<tr>
<td>$\alpha$-HCH</td>
<td>6.91</td>
<td>-</td>
</tr>
<tr>
<td>$\gamma$-HCH</td>
<td>21.80</td>
<td>-</td>
</tr>
<tr>
<td>DDE</td>
<td>15.83</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$C_{before} = 1 \mu g/ml$</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-HCH</td>
<td>9.25</td>
<td>36.57</td>
</tr>
<tr>
<td>$\gamma$-HCH</td>
<td>10.72</td>
<td>-</td>
</tr>
<tr>
<td>DDE</td>
<td>31.32</td>
<td>72.23</td>
</tr>
</tbody>
</table>
3. Discussion

The data presented in Figure 1 indicate that the dependence of the OCPs degradation degree has complex nature within the studied range of dose rates. Figure 1 shows that the DDE degradation degree increases with dose rate, reaches its maximum (at about 0.23–0.43 Gy/sec), and then decreases. This dependence is best revealed on the example of the DDE solutions, where the values of degradation degree are obtained in full range of dose rates. The shape of the degradation degree relationship on dose rate is similar in polar and non-polar solvents (hexane, 2-propanol) and does not depend on the concentration of the initial substance. From Table 1, it could be supposed that this relationship also takes place for other OCPs.

![Graph showing degradation of DDE at different dose rates](image)

**Figure 1:** Degradation of DDE (C = 0.1 or 1 µg/ml) at irradiation with different dose rate (D = 10 kGy).

The effect revealed has a clear explanation. It was noted in [11] that the radiation-chemical transformation of substance depends on the dose rate only if there is a competition between the reactions of solvent radicals with an acceptor (or solvated electrons with the same acceptor) and the recombination reactions of these radicals.

\[ RH^* \rightarrow R^* + H^* \]  

\[ R^* + R'Cl_n \rightarrow RCl + R'^*Cl_{n-1} \]  

\[ R'^*Cl_{n-1} + RH \rightarrow R'Cl_{n-1}H + R^* \]  

\[ R^* + R^* \rightarrow RR, R'^* + R'^* \rightarrow R'R', R^* + R^* \rightarrow R(-H) + RH \]
where RH – molecules of initial aliphatic hydrocarbon (solvent); RH* - excited molecule; R* - aliphatic hydrocarbon radical; R′Cl\textsubscript{n} – molecules of initial OCP; R′* - alicyclic radical of pesticide molecules; R(-H) – olefin with hydrocarbon chain of solvent molecule; R′Cl\textsubscript{n−1} - OCP radical.

The $P(D)$ dependence in the dose rate range investigated indicates a competition between the reactions (2) and (4). Since the OCP is an acceptor, the reactions with radical replacement (2) and the formation of dechlorinated molecule (3) can be considered as the beginning of a pesticide radiation-chemical transformation. According to the experimental data, the concentration of active radicals in the OCP solutions increases (1) with increasing irradiation dose rate. Simultaneously, the process of radicals’ recombination is accelerated (4). The effect obtained in the dose rate range from 0.0083 up to the values with maximum degradation (0.23–0.43) Gy/sec could be explained in the following way. If we assume that in the region of low dose rates the yield of free radicals should be lower in comparison to their yield in the range 0.23–1.35 Gy/sec, this will result in a decrease in the number of reactions (2 and 4), as well as weakening their competition. However, along a gradual increase in $D$, reaction (2) in solutions becomes predominant which, according to our data, leads to an increase in the $P$ values. With a further increase in $D$, the advantage is likely to remain behind the reaction (4). This explains the decrease in $P$ observed in the curves in Figure 1.

It should be noted that irradiation of solutions was carried out in the presence of O$_2$, which reduces the OCP degradation because of their competition in the reaction (2). This is especially noticeable at low dose rates (0.0083–0.43 Gy/sec), when a O$_2$ “burnout” does not occur, because energy supplied to the solution could be insufficient for the full consumption of oxygen. In the range of higher dose rates (from 0.43 up to 1.35 Gy/sec), oxygen is obviously consumed at the initial stage of irradiation, and does not subsequently influence the radiation-chemical process.

To approximate the data presented in Figure 1, a lognormal distribution function can be applied. This choice is stipulated by the fact that a distribution of logarithms of $x$ (in our case, $D$) follows the Gaussian law [12] which is confirmed with the data in Figure 2.

4. Conclusions

Using the data obtained on the identity of behavior of these OCPs solutions, it can be assumed that the mechanisms underlying the changes in the radiation-chemical processes developing in the various OCPs solutions under irradiation with increasing
dose rate \((8.3 \cdot 10^{-3} \text{–} 1.35 \text{ Gy/sec})\) at a constant \(D\) value are similar. This, in turn, may indicate that, under irradiation, molecules similar in chemical structure are able of forming radicals comparable in ratio values of recombination constants and diffusion coefficients. This, then, could be considered as a supposition of the possibility to have similar products at these OCPs degradation.

At the maximum of \(P(OCP)\) values achieved in the experimental conditions, the radiolysis process ends with a formation of chemical metabolites, but not with the full substance mineralization. The solvent participation in this process complicates a total composition of the degradation products in the resulting post-radiation medium. In this regard, it is difficult to predict a detrimental potential of this medium.

Additional studies are necessary to reveal the mechanism by which the maximum radiation degradation of the various OCPs is achieved at their irradiation conditions applied in this study (dose of 10 kGy given within the tested range of \(D\) values. In particular, an important issue is a studying the \(P(D)\) dependence at larger and lower values of absorbed dose, as well as the identification of this dependence for macroconcentrations of OCPs. However, in our opinion, the important outcome of this work is an evidence for the existence of optimal parameters for the effective OCPs degradation, which should be considered when studying the toxicity of radiation metabolites.
References


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