УДК 502/504:544.558

S.V. Olszewski, Yu.Yu. Med, V.O. Nosenko

FEATURES OF ELECTRORADIOLYTIC DESTRUCTION OF PERSISTENT ORGANOCHLORINE TOXICANTS

Annotation. *The unsatisfactory state of the specialized storage facilities of persistent organochlorine toxicants of agricultural use on the territory of Ukraine indicates the urgency of the creation of mobile systems for the destruction of mixtures of toxicants or toxicants of undetermined chemical composition. Perspective in terms of universality may be the method of electroradiolytic destruction of hazardous substances in the liquid phase. However, the expected energy consumption of the electroradiolysis method calls into question the profitability of its industrial use. The paper presents a methodology for estimating the minimum possible energy consumption during electroradiolytic decomposition of persistent organochlorine toxicants into individual atoms and it is shown that due to the structural transformations of parent molecules whithout change of their atomic composition, energy costs exceed the total dissociation energy of toxicants and of their fragments.*

Keywords*: high-energy particles, electroradiolytic destruction, persistent organochlorine toxicants.*

Introduction

Article 6.1.d of the Stockholm Convention on Persistent Organic Pollutants, to that Ukraine is a party, notes that waste such as organochlorine toxicants should be "disposed of in such a way that the content of a persistent organic pollutant is destroyed or irreversibly transformed ...". At the same time, reliable engineering and technical methods embodied in mobile systems, that are aimed to the destruction of mixtures of toxicants or toxicants of an indefinite chemical composition have not been created. The unsatisfactory state of practically all specialized storage facilities of agricultural toxicants on the territory of Ukraine unambiguously indicates both the high actualyti of the needs for these mobile systems and the state level of these needs.

A promising in this aspect is a number of plasma-chemical technologies for the distruction of toxic organe compounds in aqueous solutions based on the use of high-energy flows of plasma particles bombarding the liquid surface [1]. This influence on the processes of molecules decomposition in a liquid phase called elektroradiolytic destruction. For the design of industrial samples of plasma-liquid reactors, that use the electroradiolytic mechanism of destruction, it is important to have methods for quantifying the required power consumption for the destruction of specific toxic compounds with defined

molecular structure [2]. Particularly, that assessments are important for neutralization of mixtures of toxicants, since universal environmentally admissible methods of utilyzation of toxic mixtures are not created currently [3]. The paper considers the method of estimating energy costs for the destruction of persistent organochlorine molecules by simulating the quantum-mechanical properties of the shock dissociation reactions of the dichlorodiphenyltrichloroethane (DDT) molecule and its dissociation products.

Energy content of electroradiolytic destruction of molecules

The total energy that needs to be spent on the destruction of a complex molecule can be defined as the multiply of the destroyed molecules number by the sum of the dissociation energies of the target molecule and its fragments. For its calculation it is necessary to consider a totality of dissociation chains that include the molecule itself and all the products of the subsequent decomposition acts, except individual atoms. The dissociation energy of the *j*-th bond can be calculated as the difference in energy between the main and dissociated states of the molecule:

$$W_j = E_F - E_0 \quad (1)$$

in here E_0 – is the energy of the parent molecule in the ground state, E_F – is the energy of the dissociation state.

In fact, the task of evaluating the energy required for the complete destruction of a organochlorine stable molecule under the influence of a stream of high-energy particles is reduced to enumeration of all possible channels of dissociation of the molecule and its fragments, obtaining an array of dissociation energies and dissociation rate constants for each destruction channel and their summation taking into account the probability of the corresponding destruction channel. For reactions of order 1, that include shock dissociation, the count of destroyed molecules per unit time in volume unit is equal to the multiply of the constant of the reaction rate by the total number of primary molecules in volume unit. By definition, the probability of the j-th destruction channel will be the ratio of the number of destroyed molecules in the j-th channel to the total number of destroyed molecules by all possible channels:

$$p_j = \frac{\Delta N_j}{\sum_j \Delta N_j} = \frac{k_j N}{\sum_j k_j N} = \frac{k_j}{\sum_j k_j} \quad (2)$$

Consequently, the minimum required energy of complete destruction of complex molecules can be estimated as:

$$E_{total} = \sum_j p_j W_j \quad (3)$$

However, for polyatomic molecules, that are quantum mechanical systems, this estimate is strongly understated, since their transformation can be quite elaborate and require much greater activation energy for dissociation reactions.

Any chemical transformation of the molecular system, associated with a change in the mutual arrangement of its constituent atoms, can be considered as its phase motion along the coordinate of the reaction to the hypersurface of potential energy $E\left(\vec{\xi}\right)$. Here and thereafter E – is the potential energy of the system, $\vec{\xi} = \left(r_1, \varphi_1, \vartheta_1, r_2, ...r_N, \varphi_N, \vartheta_N\right)$ – is the vector of the internal coordinates of the *N*-atomic molecule. As the reaction coordinate, it is understanded the trajectory of motion on the hypersurface of potential energy, along which the energy has a minimal value. In order to predict the direction and rate of conversion of the molecular system, one must know the dependence of the energy of the system *E* on the relative position of the atoms. Depending on the distance between the atoms, the value of *E* corresponds either to non-interacting atoms **X** and **Y** (region $U = 0$) or to a stable **XY** molecule ($U = U_{\min}$), or to intermediate formations that are realized in the process of recombination of **X** and **Y** atoms or to the excitement of internal states of the **XY** molecule in dissociation. All elementary chemical reactions can be divided into two groups. The first group is the reaction for which the maximum on the hypersurface of the potential energy along the coordinate of the reaction is absent. This case is characteristic for many processes of homolytic destruction of a chemical bond with the formation of two radicals. For this reactionary group, the bursting energy of **XY**

 ISSN 1562-9945

bonds can be calculated as the difference between the sum of the energies of individual fragments **X**, **Y** and the energy of the molecule **XY**.

The second group is the reactions for which the hypersurface of potential energy pass through maximum during motion along the coordinate of reaction. The location of this maximum are accepted as the transition state of the reaction.

For a radical decay, the activation energy coincides with the enthalpy of the reaction, which, in turn, can be calculated in accordance to the expression:

$$\Delta_r H^0\left(R_1 - R_2\right) = \left(\Delta_f H_{opt}\left(R_1\right) + \Delta_f H_{opt}\left(R_2\right)\right) - \Delta_f H_{opt}\left(R_1 - R_2\right) \qquad (4)$$

here $\Delta_f H_{opt}\left(R_1 - R_2\right)$, $\Delta_f H_{opt}\left(R_1\right)$ and $\Delta_f H_{opt}\left(R_2\right)$ – the enthalpy of the formation of the parent compound and the corresponding radical fragments, that born during the breakdown of the chemical bond. The criterion for the rightfulness of the use of expression (4) is the absence of transitional states of the initial molecule in the process of its dissociation. The absence of such transitional states can be established in the absence of a clearly expressed maximum on the dependence curve of the potential energy of the molecule on the coordinate of reaction. For reactions of non-radical transformation of molecules instead of enthalpies of the final and initial states it is necessary to use the enthalpies of the transitional and initial states.

The calculation of the main kinetic and thermodynamic parameters of chemical reactions that must occur in the liquid phase can be carried out under the conditions of the Arrhenius law. Using the basic ideas of the theory of transition state (activated complex) and quantum-mechanical methods, one can calculate the constant of the speed k_t of an elementary chemical reaction. An important role in these calculations is played by the Eyring equation that binds the constant of the reaction rate and the equilibrium constant of the formation of the activated complex [4], expressed through the concentration $k_t = \frac{ek_BT}{h} K_c^{\neq}$, where k_B is the Boltzmann constant, h is Planck's constant.

Results of simulation and discussion

The potential energy of the system was found from the solution of the Schredinger equation for the wave function of the polyatomic molecule in the *n*-th state $\Phi_n\left(\vec{\xi}\right)$, also called the molecular orbital.

$$\hat{\boldsymbol{H}}\left\{\Phi_n\right\} = E_n \Phi_n\left(\vec{\xi}\right) \tag{5}$$

here $\hat{\boldsymbol{H}}\left\{\cdots\right\}$ – Hamilton's operator, E_n is the energy of the molecule in the *n*-th state.

According to the LCAO method, the molecular orbitals $\Phi_n\left(\vec{\xi}\right)$ were represented by a linear combination of atomic orbitals:

$$\Phi_n\left(\vec{\xi}\right) = \sum_{i=0}^{M} c_{n,i}\varphi_i\left(\vec{\xi}\right) \tag{6}$$

where M is the number of functions that is determined by the necessary accuracy and was a free parameter of the task. The explicit form of atomic orbitals $\varphi_i\left(\vec{\xi}\right)$ was approximated by a linear combination of basic functions from the standard Pople basis sets:

$$\varphi_i\left(\vec{\xi}\right) = \sum_{j=0}^{J} b_{i,j} G_j\left(\vec{\xi}\right) \tag{7}$$

Here $G_k\left(\vec{\xi}\right)$, in explicit form, there are functions from the Pople basis set: $G_{nlm}(\boldsymbol{r},\theta,\varphi) = N_n(\alpha)\boldsymbol{r}^{n\text{-}1}e^{-\alpha \boldsymbol{r}^2}Y_{lm}(\theta,\varphi)$, where $Y_{lm}(\theta,\varphi)$ – are spherical functions.

Substituting (7) into (6) received:

$$\Phi_n(\xi) = \sum_{i=0}^{M} c_{n,i} \sum_{j=0}^{J} b_{i,j} G_j(\xi) = \sum_{i=0}^{M}\sum_{j=0}^{J} c_{n,i} b_{i,j} G_j(\xi) = \sum_{j=0}^{J} a_{n,j} G_j(\xi) \tag{8}$$

where $a_{n,j} = \sum_{i=0}^{M} c_{n,i} b_{i,j}$.

 ISSN 1562-9945

That is, the problem of the synthesis of wave functions was reduced to the problem of finding the coefficients $a_{n,j}$.

The coefficients $a_{n,j}$ were found by solving the optimization problem for the target function that assumed the value of the potential energy $E(\vec{x})$ in the J-dimensional space of the coefficients by the Marquardt method, where $\vec{x} = \left(a_{n,1}, a_{n,2}, \ldots, a_{n,j}, \ldots, a_{n,J}\right)^{T}$.

As a result of the calculations, it was shown that the activation energy of the radical decomposition of the DDT molecule lies within the range from 6.0 to 8.7 eV. The least energy of radical dissociation corresponds to the separation of the chlorine atom from the CCl_3 group. The greatest energy of radical dissociation corresponds to the separation of the hydrogen atom from the benzene ring. The constants of the velocity of radical dissociation lie within the limits from $3.3809 \cdot 10^{4}$ to $8.1736 \cdot 10^{-6}$ c^{-1}.

More interesting from the viewpoint of estimating the energy of DDT destruction are the channels of non-radical decay. As the simulation showed, there are channels of molecule transformation that don't change its elemental composition, but need energy expenditure for activation, which, after transformation of the molecule, dissipates to heat. We call these reactions invariant transformations (Fig. 1).

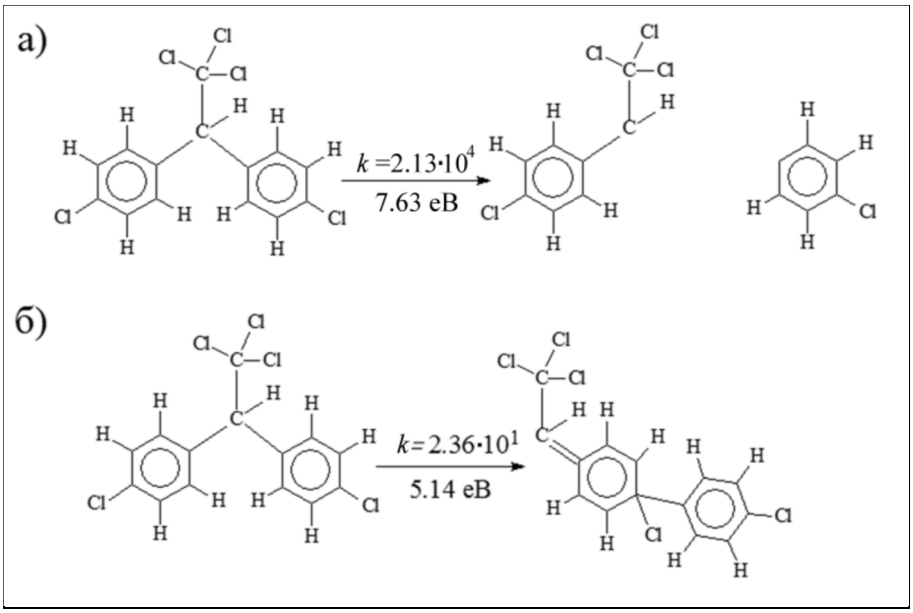

Figure 1 – Channels of radical destruction – a) and invariant transformation – b) of DDT molecules.

The calculations have shown that the activation energy of the radical decay is 7.63 eV, with the constant of the reaction rate $2.13 \cdot 10^4$ s^{-1}. At the same time, the energy of the invariant transformation is 5.14 eV, that is, it has the same order of magnitude. The rate constant of the invariant transformation is $2.36 \cdot 10^1$ s^{-1}.

The dependence of the potential energy of a DDT molecule on the reaction coordinate under radical decay and invariant transformation is shown in Fig. 2

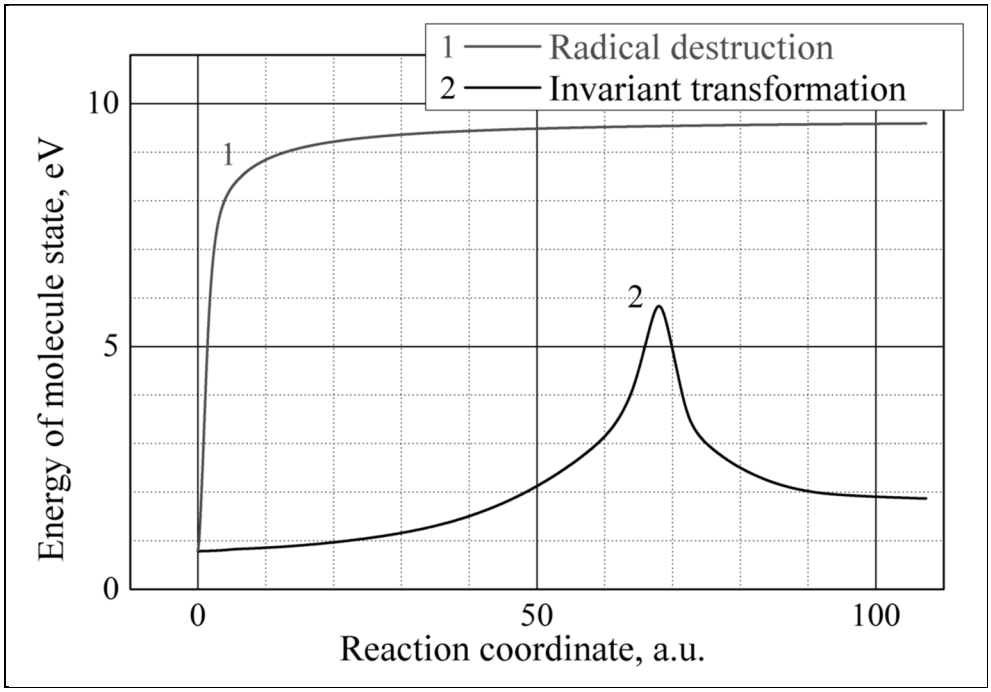

Figure 2 – Dependences of the potential energy of a DDT molecule on the reaction coordinate under radical decay – curve 1 and invariant transformation – curve 2.

Curve 1 corresponds to the trajectory of the radical decay reaction, curve 2 - the trajectory of the reaction of the invariant transformation. As can be seen from the obtained dependencies, in the case of radical dissociation, the energy of the high-energy particle is spent on the destruction of the target, and formula (1) for estimating energy costs for destruction is valid. Conversely, for an invariant transformation, the energy of the initial and final states varies little, and the energy of the high-energy particle is spent on the excitation of the transition state, and in the future, when the target passes to the final state, it dissipates in the form of heat. In this case, the elemental composition of the molecule does not change, which causes a high probability of reverse transformation into the parent toxicant.

 ISSN 1562-9945

In fact, the presence of channels of invariant transformation of target molecules and their fragments causes a significant increase in the energy that must be introduced into the solution of persistent toxicants by the flow of high-energy particles. Despite the fact that the rate constant of such reactions is much less than for radical dissociation reactions, their influence may be significant, since target molecules don't escape from the reaction zone. Thus, the method of estimation of actual energy consumption for the destruction of persistent organochlorine toxicants can not be reduced to direct summation of the activation energies of the dissociation of parent molecules and their fragments. This estimation requires the solution of the kinetic problem of scattering the flow of high-energy particles in solutions of the toxic chlororganics in the conditions of competition of invariant transformations and impact dissociation.

Conclusions

- Electroradiolytic mechanism of DDT molecules destruction includes both radical and non-radical dissociation and transformation, that invariant with respect to the molecule atomic composition. The activation energy of invariant transformations is small different from the dissociation energy.
- Despite the fact that the rate constants of invariant transformations are usually three orders less than the dissociation rate constants, it is impossible to exclude the contribution of these transformations from the total energy consumption, since the concentration of toxic reagents due to such reactions practically does not change.
- The presence of invariant transformations is a source of unproductive dissipation of the energy of the high-energy particles stream, that causes an increase in the minimum required power of plasmochemical reactors for the neutralization of persistent organochlorine toxicants by the electroradiolytic mechanism.

REFERENCES

1. Polak L.S. Neravnovesnaya himicheskaya kinetika i ee primenenie. M., "Nauka", 1979 s.
2. TerraTherm enjoys rapid growth as ISTR gains industry acceptance.// Environmental Business International Inc., Volume XXVIII No. 4, 2015.

3. USEPA. Potential Applicability Of Assembled Chemical Weapons Assessment Technologies To RCRA Waste Streams And Contaminated Media, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Technology Innovation Office, Washington, DC, EPA 542-R-00-004, August, 2000.
4. Pitzer, K.S. Energy Levels and Thermodynamic Functions for Molecules with Internal Rotation I. Rigid Frame with Attached Tops /K.S. Pitzer, W.D. Gwinn // J. Chem. Phys. - 1942. - V. 10. - P.

 ISSN 1562-9945