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Comparative study on photocatalytic oxidation of four organophosphorus simulants of chemical warfare agents in aqueous suspension of titanium dioxide

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Abstract

Photocatalytic oxidation by oxygen of air was carried out for dimethyl methyl phosphonate (DMMP), trimethyl phosphate (TMP), triethyl phosphate (TEP), and diethyl phosphoramidate (DEPA) in different concentration. The initial rate of organophosphorus compounds consumption increases with the initial concentration at relatively low concentrations but decreases at higher initial concentrations. If the concentration is higher than the concentration in maximum, the rate decreases because of the lack of adsorbed oxygen. These summit-like dependences are well approximated by one site Langmuir–Hinshelwood equation with competitive adsorption of oxygen and organophosphorus compound. Parameters of the Langmuir–Hinshelwood equation are reported. Complete mineralization of the organophosphorus compounds at the end of reaction was evidenced by the total organic carbon concentration profiles. These profiles have sigmoidal shape. GC–MS technique was used to identify intermediates of TEP and TMP oxidation. The main intermediates are dimethyl phosphate and methyl phosphate in the case of TMP and diethyl phosphate and ethyl phosphate in the case of TEP. The set of intermediates shows that photocatalytic oxidation proceeds primarily at α carbon atoms of TEP. The distribution of intermediates corroborates that photocatalytic oxidation is initiated by reaction with hydroxyl radicals.
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Keywords: Photocatalysis; Batch reactor; Products; Rate constants; TOC; Phosphates; Phosphonates

1. Introduction

Nowadays there is a great problem of water purification from different pollutants. Many pollutants like insecticides, pesticides and detergents are organophosphorus compounds. Molecules of several chemical warfare agents (CWA) contain atoms of phosphorus (Fig. 1). Destruction of CWA is an urgent task in view of requirements of chemical weapons convention and possible emergency exposures.

One of the widespread methods of water purification is biodegradation. But in many cases biodegradation proceeds at a low rate [1,2].

Photocatalytic oxidation is a very interesting and promising method of organophosphorus compounds degradation [3]. Photocatalytic oxidation of some organophosphorus pesticides (acrinathrin, methamidophos, malathion, diazion, carbetamide) and insecticide fenitrothion was reported previously [4–7]. In some works, photocatalytic oxidation over semiconductor catalyst, TiO_2, was compared to purification with addition of oxidation agents, such as H_2O_2 and $Na_2S_2O_8$ [6–8]. Reactions with oxidation agents are faster than reactions with titanium dioxide. But complete degradation requires excess of oxidation agents. Water purification with Fenton reagent (H_2O_2/Fe^{2+}) is fast, but it requires low pH of solution (2–3), which means that products of reaction require neutralization before discharge [9]. Besides, after the reaction is finished, it is necessary to clean solution from intact reagent.

Photocatalytic oxidation works in a wide range of pH. It mostly uses cheap and non-toxic titanium dioxide as catalyst. The catalyst can be separated from solution by filtration. Solar irradiation can be used to carry out the reaction. Thus, photocatalytic oxidation is a promising method for water purification.

Some of the most dangerous CWA are organophosphorus compounds (Fig. 1) named sarin (isopropyl methylfluorophosphonate), soman (pinacolyl methylfluorophosphonate), and tabun (ethyl dimethylphosphoramidocyanidate). Due to their high toxicity it was impossible to work

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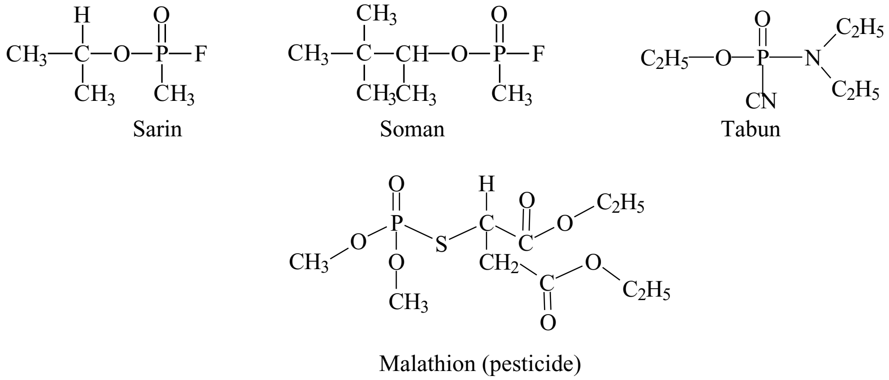


Fig. 1. Examples of organophosphorus compounds.

with these compounds in ordinary laboratory. Therefore our research was carried out with simulants of these CWA—dimethyl methyl phosphonate (DMMP), trimethyl phosphate (TMP) and triethyl phosphate (TEP) for sarin and soman and diethyl phosphoramidate (DEPA) for tabun. The bond P–F in sarin and soman is more reactive towards hydrolysis, than the bonds P–C and P–O in simulants. The bond P–CN in tabun is more labile than the bond P–O in DEPA. Therefore, the simulants are more stable in the conditions of photocatalytic oxidation in water suspension of TiO_2. The rate of degradation for tabun and sarin is expected to be higher than the rate of simulants oxidation.

To the best of our knowledge, comparative photocatalytic study of different organophosphorus compounds has not been undertaken before. However, there are reports on several organophosphorus simulants. Kinetic dependences of DMMP photocatalytic oxidation were described previously [10]. Dependence of rate on initial concentration has a maximum. But the decrease of oxidation rate at higher concentration was not explained satisfactorily. Intermediates of DMMP and DEPA oxidation were identified before [11]. But the nature of active oxidizing species was not determined. TMP and TEP oxidation was not investigated before. However, comparison of these compounds oxidation is helpful for understanding of organophosphorus compound oxidation mechanism.

Our work was aimed to measure and compare the oxidation rates of DMMP, TMP, TEP and DEPA as a function of their initial concentration. This can help in finding the optimal concentration of pollutants for the fastest degradation and understanding the mechanism of oxidation. Identification of intermediates of TMP and TEP oxidation lets us to suggest the probable mechanism of reactions.

2. Experimental

The photocatalyst used in this study was titanium dioxide Degussa P25, which is 75% anatase with surface area about $50\,m^2/g$. Purified water with total organic carbon content <0.2 ppm was employed for all experiments.

Oxidation of dimethyl methyl phosphonate, trimethyl phosphate, triethyl phosphate, and diethyl phosphoroamidate (all compounds 97–98%, Aldrich) by air oxygen was performed in aqueous suspension of TiO_2. Initial concentrations of the reactants were 0.31, 0.61, 1.2, 2.5, 4.9 mM, content of TiO_2 was 333 mg/l. Reaction was carried out in a 250 ml beaker with volume of suspension 150 ml. Before reaction, the suspension was treated by ultrasound during 5 min and then it was stirred on a magnetic stirrer for 10 min to keep it deagglomerated. Then, the suspension was illuminated by full irradiation of high-pressure mercury lamp “DRSh-1000” (Russia) under continuous stirring for 360 min. The reaction setup is outlined in Fig. 2.

Sampling was carried out every 30 min for initial compound concentration determination (done for DMMP, TMP, TEP), and every 90 min for total organic carbon concentration determination (done for all compounds).

Initial rate was evaluated from disappearance of initial compound using linear part of kinetic plot. Concentration of initial compound was measured by gas chromatograph “LKhM-8MD” (Russia) with a flame ionization detector. Column 0.5% OV-225 + 0.3% H_3PO_4 ($2\,m \times 2\,mm$ i.d.) was utilized. The temperature of injector was 200 °C and the temperature of detector was 100 °C. The temperature

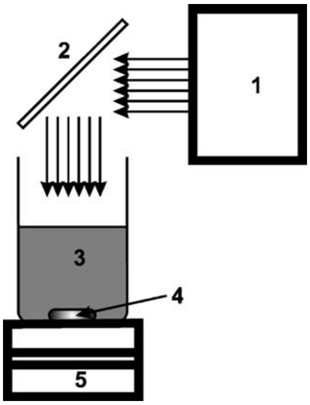


Fig. 2. The reaction setup: (1) mercury lamp; (2) mirror; (3) reaction mixture; (4) stir bar; (5) magnetic stirrer.

of column was 125 °C for DMMP, 130 °C for TMP and 140 °C for TEP. Chromatograph was calibrated by initial compound solutions. Three points calibration done before every experiment formed straight calibration line.

Mercury lamp radiance was calculated using ferrioxalate actinometry according to Parker [12]. Potassium ferrioxalate, $K_3Fe(C_2O_4)_3 \cdot 3H_2O$, was prepared of oxalic acid, potassium hydroxide and iron chloride(III) using standard method [12].

Total organic carbon concentration was measured by automatic total organic carbon analyzer TOC-VCSH (Shimadzu, Japan). The analyzer was calibrated by solution of potassium hydrophthalate (Shimadzu).

The non-volatile products of oxidation of TEP and TMP were identified using GC–MS System Saturn 2000 (Varian): gas chromatograph CP-3800 with the column WCOT Fused Silica coating CP-Sil8CD Low bleed MS, i.d. 0.25 mm, L 30 m, and mass-spectrometer Saturn 2000 with quadrupole ion trap. Time of analysis was 44 min; temperature was raised from 35 to 230 °C with gradient 8 °C/min. Non-volatile products were preliminary derivatized with BSTFA + 1% TMCS reagent (Supelco). Before derivatization, samples were evaporated until dryness at 60 °C in a flow of air. Derivatization was carried out at about 20 °C in a closed vial during 12 h. There are not spectra of many organophosphorous compounds in mass-spectra libraries. So, identification was done manually following fragmentation patterns.

3. Results and discussion

After the mercury lamp is turned on, the concentration of organophosphorous compounds begins to decrease. Dependence of concentration of DMMP, TMP and TEP on reaction time is shown in Fig. 3 for several initial concentrations. When the initial concentration of DMMP and TMP ranged from 0.31 to 1.2 mM, and TEP from 0.31 to 2.5 mM, the concentration curves followed first order kinetics. When initial concentration of DMMP was 2.5 and 4.9 mM, TMP: 2.5 mM, TEP: 4.9 mM the concentration versus time curves fitted well to zero order dependence. Induction period is observed in dependence of concentration on time at initial concentration of TMP 4.9 mM. Hence**,** this kinetic curve was approximated by sigmoid curve. The initial rate of reaction for DMMP, TMP and TEP was calculated using program Origin 6.0. The calculation was carried out using first three–five points, which were suitable to draw a straight line.

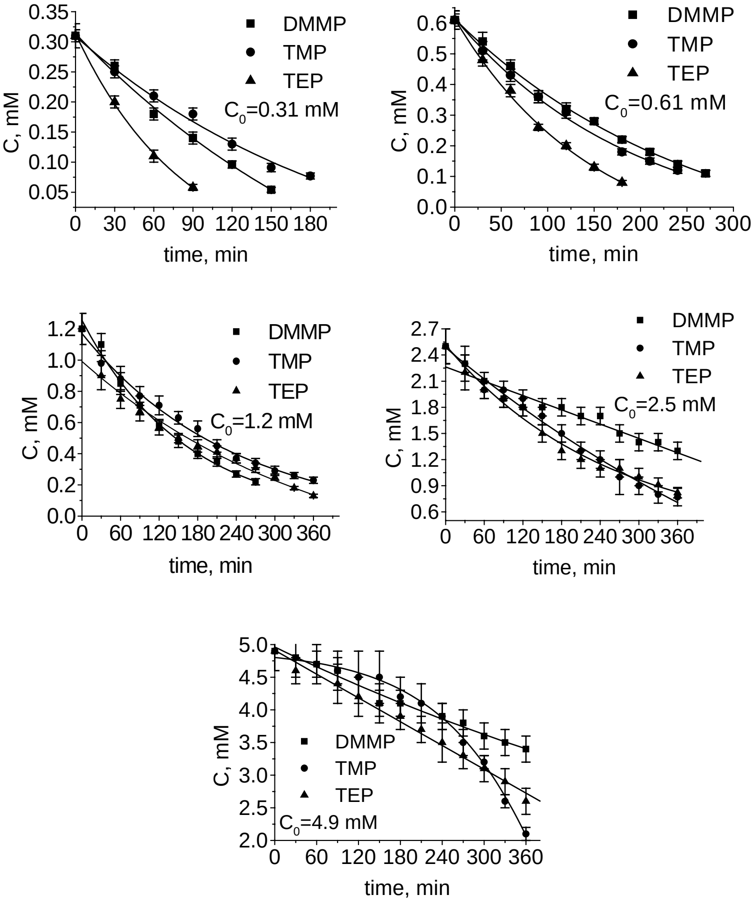


Fig. 3. Kinetic curves of DMMP, TMP and TEP oxidation at different initial concentrations.

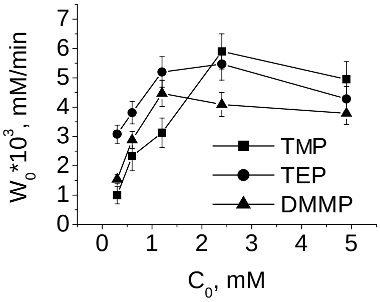


Fig. 4. Dependence of initial reaction rate of substrates on initial concentration.

Experiments for initial concentration of TMP 0.31 mM and TEP 0.31 mM were carried out twice. The obtained initial rates are within error of measurements (12%). Experiment with initial concentration of TMP 4.9 mM was carried with air bubbling at the rate 120 cm^3/min. Initial rates of TMP oxidation with air purging are higher than the rates without it. But the increase of the rate lies within the experimental error.

Fig. 4 shows the obtained dependences of initial rates on initial concentrations. One can see in Fig. 4 that the curves have a maximum and the highest rate is observed in the case of TMP, the lowest—in the case of DMMP. The initial rates are well approximated by Langmuir–Hinshelwood equation with competitive adsorption of substrate and oxygen on the same type of catalytic sites:

$$W_0 = k_\mathrm{p}\frac{K_\mathrm{OP}C_0K_{\mathrm{O}_2}C_{\mathrm{O}_2}}{(1+K_\mathrm{OP}C_0+K_{\mathrm{O}_2}C_{\mathrm{O}_2})^2},$$

where W_0 is the initial rate, K_OP and K_{O_2} are adsorption constants of initial organophosphorus compounds and oxygen, k_p is the reaction rate constant, C_{O_2} the oxygen concentration, C_0 the initial concentration of organophosphorus compound.

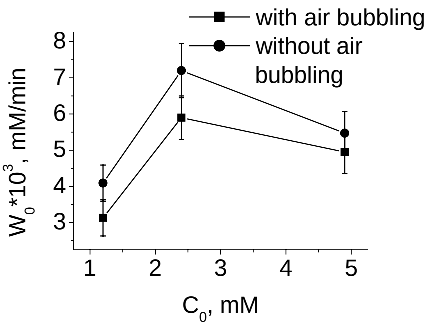


Fig. 5. Effect of air bubbling on initial rates of TMP oxidation at different initial concentrations.

One can speculate that the maximum in initial rates is associated with insufficient supply of oxygen at higher substrate concentrations. To check on this possibility, a set of experiments was carried out with air passing through suspension. Fig. 5 shows the initial rates of TMP oxidation versus initial concentrations with air bubbling and without it. The oxidation rate increases in the case of air bubbling because the concentration of dissolved oxygen rises. However, the shape of the kinetic dependence remains the same. Thus, the appearance of maximum is not associated with the limitation of reaction rate by oxygen transport rate to the photocatalyst surface.

Fig. 6 shows how Langmuir–Hinshelwood equation approximates the experimental points. One can see that the deviation from the experimental points is within the experimental errors. There is a maximum in all dependences of

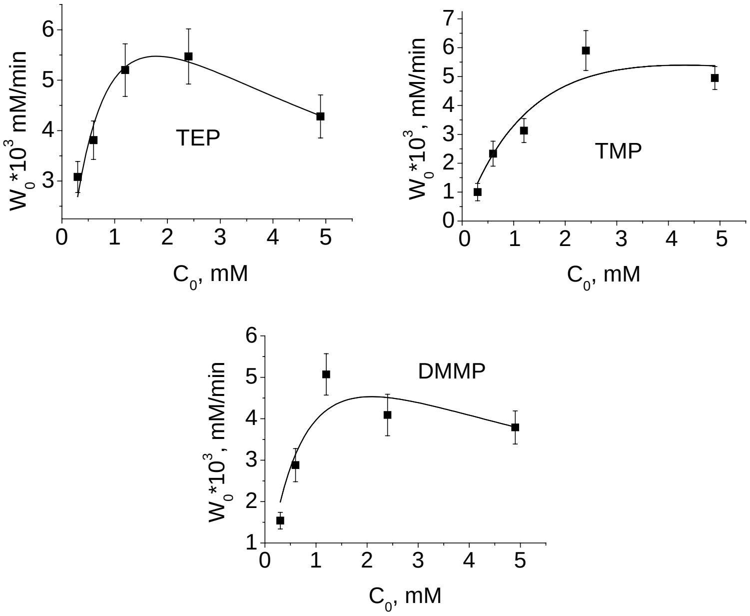


Fig. 6. Approximation of initial rates of TEP, TMP, and DMMP oxidation by one site Langmuir–Hinshelwood model.

Table 1
Constants found by approximation of experimental points by Langmuir–Hinshelwood equation

Compound	k_p (mM/min)	K_A (mM^{-1})	$K_{O_2} \times C_{O_2}$
DMMP	250 ± 42	0.60 ± 0.04	0.08[a]
TMP	290 ± 64	0.25 ± 0.04	0.08[a]
TEP	300 ± 24	0.5 ± 0.1	0.08 ± 0.01[a]

[a] $K_{O_2} \times C_{O_2}$ was calculated in the case of TEP, and it was taken as constant for DMMP and TMP.

initial rate on initial concentration. If the concentration is higher than the concentration in maximum, the rate decreases because of the lack of adsorbed oxygen. It is necessary to emphasize that the appearance of maximum in the dependence of initial rate on initial concentration cannot be linked to competitive adsorption of reaction products and the initial compound. In the first period of reaction, the concentration of products is low, so they are unable to affect the rate of reaction. Besides, initial compounds and products can have different adsorption sites.

Approximation by the Langmuir–Hinshelwood equitation can be used to calculate adsorption constants and rate constants for DMMP, TMP, and TEP. Table 1 shows these data. Rate constants are different but lie within the limits of error for all compounds. TMP adsorption constant is less than the adsorption constants of DMMP and TEP. So, the TMP oxidation rate is the highest in the case of higher concentration, because the lack of adsorbed oxygen occurs at higher concentration of trimethylphosphate.

Initial quantum efficiency of every reaction was calculated as the ratio of initial rates of organophosphorus compound consumption and mercury lamp irradiance (5×10^{-5} E/min), which was determined by ferrioxalate actinometry. Table 2 shows that the quantum efficiency is quite high and varies from 3 to 18% depending on the compound's initial concentration.

Table 2
Initial quantum efficiency in oxidation of DMMP, TMP and TEP

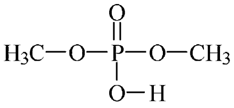
Compound	Concentration (mM)	Quantum efficiency (%)
DMMP	0.31	4.7
	0.61	8.7
	1.2	15.4
	2.5	12.5
	4.9	11.6
TMP	0.31	3.0
	0.61	7.1
	1.2	9.5; 12.5[a]
	2.5	18.0; 21.9[a]
	4.9	15.1; 16.7[a]
TEP	0.31	9.4
	0.61	11.6
	1.2	15.8
	2.5	16.7
	4.9	13.0

[a] Experiments with air bubbling.

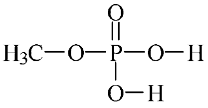
Total organic carbon (TOC) concentration was measured for all experiments in order to trace the overall oxidation into inorganic products. Fig. 7 shows the dependence of TOC on reaction time for different initial concentrations. The shape of most TOC decreasing kinetic curves is sigmoid. Complete mineralization occurred at low concentration (0.31 mM for DMMP and TEP, 0.31 and 0.61 mM for TMP, in the case of DEPA complete mineralization was not observed). So, we can observe just the initial part of the sigmoid curve at low initial concentrations. Fig. 8 shows the dependence of average rates of TOC disappearance on initial concentration, which was calculated from data presented in Fig. 7.

Average TOC decrease rate depends on the initial compound oxidation rate and the intermediates oxidation rate. At low initial concentrations, the TOC decrease rate is the highest in the case of TEP, because the rate of initial compound oxidation is quite high. At high initial concentrations, TMP oxidation rate is the highest among all studied compounds, because TMP oxidation intermediates oxidize to inorganic substances quite fast. Average TOC decrease rate in the case of diethyl phosphoroamidate is low compared to other compounds. The nitrogen of DEPA and its oxidation intermediates is probably protonated as a result of acids release in reaction, so adsorption constant decrease because of electrostatic repulsion of positively charged TiO_2 surface and protonated compounds. If initial concentration increases, the average TOC decrease rate generally increases too. High scattering of experimental points in Fig. 8 should be linked to difference between shapes of TOC decrease curves for different initial concentration.

Identification of non-volatile intermediates of TMP oxidation reaction in trimethylsilyl form after 6 h of reaction gives only two products: trimethylsilyl dimethyl phosphate and bis(trimethylsilyl)methyl phosphate. Their structure formulas without trimethylsilyl groups are shown below.



$$\mathrm{H_3C{-}O{-}}\underset{\underset{\mathrm{O{-}H}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}\mathrm{{-}O{-}CH_3}$$

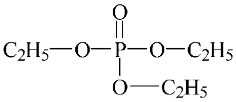
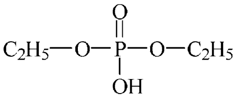
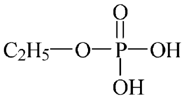
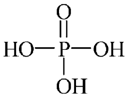
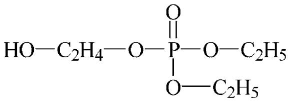
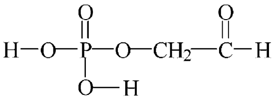
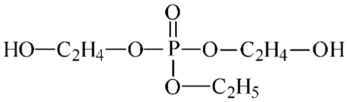
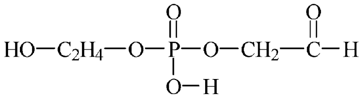


$$\mathrm{H_3C{-}O{-}}\underset{\underset{\mathrm{O{-}H}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}\mathrm{{-}O{-}H}$$

These products are formed by oxidation of one or two methyl groups of trimethyl phosphate, respectively. The hydroxymethyl dimethyl phosphate is presumed to be formed in the first stage of reaction. This compound is a hemiacetale. Thus, it hydrolyzes in water to dimethyl phosphate and formaldehyde. If aldehyde group forms in the first stage of reaction, the formed compound is anhydride and it is transformed in water to dimethyl phosphate too. Methyl phosphate forms, like dimethyl phosphate, by oxidation of the second methyl group.

Identification of triethyl phosphate oxidation reaction intermediates is more interesting than trimethyl phosphate oxidation intermediates because the TEP molecule has two unequal types of carbon atoms, thus, oxidation can proceed by different routes. Identification of the non-volatile TEP oxidation intermediates in trimethylsilyl form as expected gives much wider variety of compounds than trimethylphos-

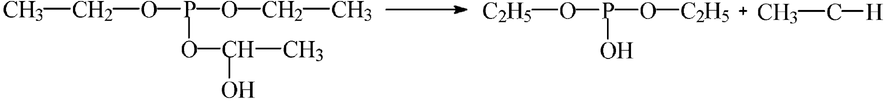
Table 3
Intermediates of TEP oxidation and the initial compound

No.	Retention time (min)	Compound without trimethylsilyl groups	*m*/*z* of main ions	Content of compounds (%)
1	12.11	$HO{-}CH_2{-}COOH$	45, 73, 103, 147	0.4
2	13.93	 $C_2H_5{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O{-}C_2H_5}{|}}{P}}{-}O{-}C_2H_5$ Initial compound	45, 155, 167, 183	61.6
3	14.97	 $C_2H_5{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}O{-}C_2H_5$	45, 73, 155, 227	15.2
4	15.72	 $C_2H_5{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}OH$	45, 73, 255, 271	13.6
5	16.49	 $HO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}OH$	45, 73, 299, 315	1.8
6	19.31	 $HO{-}C_2H_4{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O{-}C_2H_5}{|}}{P}}{-}O{-}C_2H_5$	73, 155, 255, 271	1.1
7	20.83	 $H{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O{-}H}{|}}{P}}{-}O{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$	45, 73, 241, 269	1.4
8	21.61	 $HO{-}C_2H_4{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O{-}C_2H_5}{|}}{P}}{-}O{-}C_2H_4{-}OH$	45, 73, 343, 357	0.6
9	25.03	 $HO{-}C_2H_4{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O{-}H}{|}}{P}}{-}O{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$	45, 73, 385, 401	4.3

phate oxidation. Table 3 shows the identified compounds. Diethyl phosphate, ethyl phosphate and phosphoric acid prevail. Smaller amounts of the following products were also detected: glycolic acid, 2-hydroxyethyl diethyl phosphate, bis(2-hydroxyethyl)ethyl phosphate, 2-oxyethyl phosphate, 2-oxyethyl-2-hydroxyethyl phosphate.

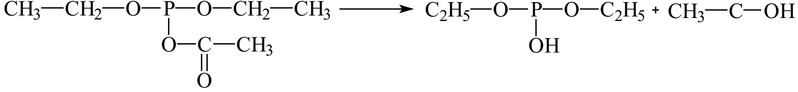
Proportions of TEP oxidation products can be estimated from peak areas of products in chromatogram. Fig. 9 shows how peak areas of the main stable intermediates changes during TEP oxidation. From this figure, we notice that the highest concentration of intermediates is at the fourth hour of reaction, when much triethylphosphate has decomposed, but intermediates did not oxidize to phosphoric acid and carbon dioxide yet. Prevalence of diethylphosphate and ethylphosphate allow to conclude that oxidation mainly proceed at the α carbon atom of triethyl phosphate.

Hemiacetales or anhydrides are assumed to be formed at the first stage of CH_2 group oxidation. Hemiacetales are decomposed by water in the following way:



$$CH_3{-}CH_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}CH_3}{|}}{P}}{-}O{-}CH_2{-}CH_3 \xrightarrow{H_2O} C_2H_5{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}O{-}C_2H_5 + CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H \tag{1}$$

Anhydrides are decomposed analogously:



$$CH_3{-}CH_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}CH_3}{|}}{P}}{-}O{-}CH_2{-}CH_3 \xrightarrow{H_2O} C_2H_5{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}O{-}C_2H_5 + CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \tag{2}$$

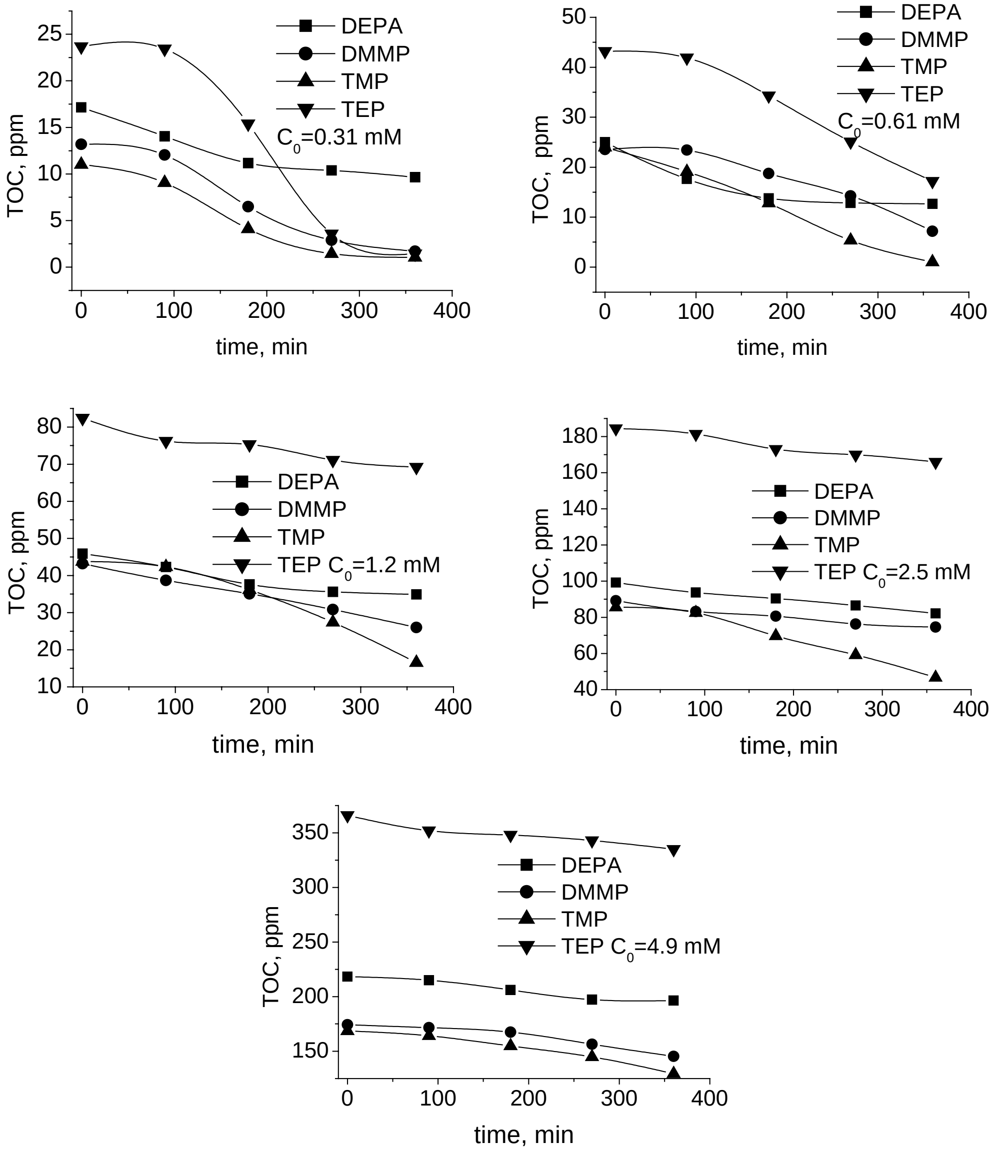


Fig. 7. Profiles of total organic carbon concentration during oxidation of DMMP, TMP, and TEP at different initial concentrations.

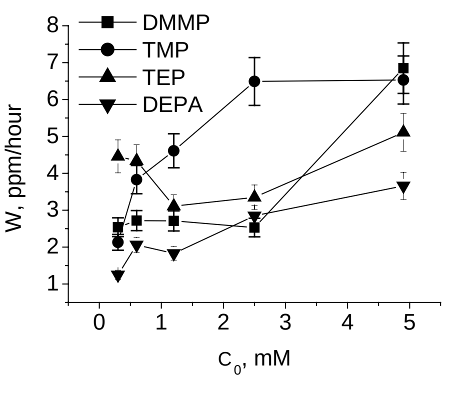


Fig. 8. Dependence of average rate of TOC concentration decrease on initial concentration of substrates.

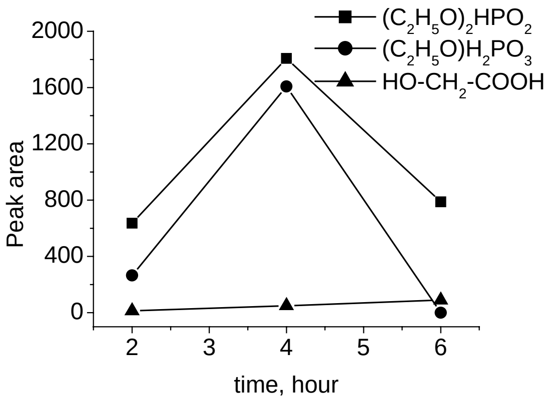
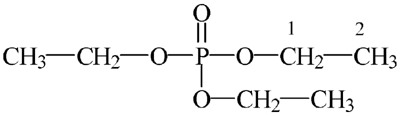


Fig. 9. Kinetic curves of main intermediates in TEP oxidation.

So, the breaking of C–O bonds in TEP molecule proceeds via hydrolysis. The first stage of oxidation is carried out via radical formation. Radicals are formed by abstraction of hydrogen atom from carbon atoms 1 or 2 of TEP:



$$CH_3{-}CH_2{-}O{-}\underset{\underset{O-CH_2-CH_3}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\overset{1}{CH_2}{-}\overset{2}{CH_3}$$

Primary radical formation at α carbon atom can probably be due to the higher stability of radical number 1. According to calculations with semi-empirical method PM3, formation enthalpies of radicals are: $\Delta H_f(1) = -232$ kcal/mol, and $\Delta H_f(2) = -220$ kcal/mol. According to Buxton's data [13], ratio of quantity of radicals 1–2 in reaction with hydroxyl radical for ethanol is 6.4.

Ratio of quantity of radicals 1–2 in our study was estimated in the following way. If the reaction proceeds with radical 1 formation, products 3–5, 7, 9 in Table 3 can be formed. If reaction proceeds with radical 2 formation, products 6–9 can be formed. Adding the areas of product peaks, we can calculate comparative quantity of radicals. It is necessary to multiply the areas of peaks by the number of transformed groups. Calculating the comparative quantities of radicals 1 and 2, we have defined, that the ratio of radical 1 formation rate to radical 2 formation rate is about 4.2. This data is in agreement with Buxton's [13].

Photocatalytic oxidation of organic compounds on the surface of titanium dioxide in water suspension can be initiated by both reaction with hydroxyl radical and reaction with hole:

$$\mathrm{TEP} + \mathrm{h}^+ \rightarrow [\mathrm{TEP}]^+ \xrightarrow{+\mathrm{H_2O},\, k} \mathrm{TEP}^\bullet + \mathrm{H_3O}^+ \qquad (3)$$

$$\mathrm{TEP} + {}^\bullet\mathrm{OH} \xrightarrow{k} \mathrm{TEP}^\bullet + \mathrm{H_2O}. \qquad (4)$$

In these reactions, ratio of rate constants for the first and the second carbon atom equals to:

$$\frac{k_1}{k_2} = \frac{k_{01}}{k_{02}} \exp\left(\frac{-E_{a1} + E_{a2}}{RT}\right)$$

In reaction (3), the pre-exponential factors for reactions at the first and the second carbon atoms should be closer than in reaction (4) for the following reason. Water molecules in aqueous solutions surround the cation-radical TEP^+. Therefore, the entropy of proton transfer to water molecules from the α and β carbons should be similar. We assume that the difference between activation energies and the difference between reaction enthalpies is related by Polani– Evance equation:

$$\Delta E_a \approx (0.2 - 0.4)\Delta H_r.$$

The difference between reaction enthalpies can be calculated as difference between radical formation enthalpy. $\Delta H_r = H_f(1) - H_f(2) = -232 + 220 = -12$ kcal/mol. Accordingly, the difference between activation energies is between −2.4 and −4.8 kcal/mol. Given this difference between activation energies, ratio of rate constants at the different carbon atoms is between 59 and 3480. However, according to experimental data, this ratio is about 4.2. So, the experimental ratio of reaction intermediates does not correspond to the evaluation of reaction with hole.

In the case of reaction (4), pre-exponential factors cannot be the same, because activated complexes OH-TEP for attack of OH-radical at the first and the second atoms are quite different. The attack at the α carbon atom is sterically hindered, which decreases the pre-exponential factor. In the case of β carbon atom, the transition state intermediate is stabilized by hydrogen bond between OH-radical oxygen atom and hydrogen atom of TEP metoxy group. These facts make the formation of activated complex at the β carbon atom more advantageous. Consequently, the ratio of the rate constants is lowered. Thus, photocatalytic oxidation of organophosphorous compounds is likely initiated by reaction with hydroxyl radical.

4. Conclusions

We have measured the dependence of photocatalytic oxidation rate on initial concentration in the reaction of dimethyl methyl phosphonate (DMMP), trimethyl phosphate (TMP) and triethyl phosphate (TEP) with air oxygen in water titanium dioxide suspension. Kinetic curves are demonstrated to have a maximum and be well approximated by Langmuir–Hinshelwood competitive adsorption model.

Intermediates in oxidation reaction of TMP and TEP were identified by GC–MS method. Large variety of intermediates in the case of triethylphosphate depends upon the fact that there are two unequal types of carbon atoms in the TEP molecule, as distinct from TMP. TEP oxidation can proceed by two different ways.

Ratio of photocatalytic oxidation intermediates was defined. Oxidation mainly proceeds to α carbon atom. According to these data, probable TEP and TMP oxidation mechanism is proposed.

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