STUDY OF EFFECT OF AEROSOL AND VAPOUR OF ORGANOPHOSPHORUS FIRE SUPPRESSANTS ON DIFFUSION HEPTANE AND PREMIXED C_3H_8/Air FLAMES

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ABSTRACT

Effect of aerosols and vapour of number organophosphorus compounds (OPC) on non premixed n-heptane and premixed stoichiometric C_3H_8/Air flame was studied using cup-burner technique and Mache-Hebra nozzle burner respectively. The high efficiency nebulizer for OPC loading in gas stream was used that allowed investigating fire suppression effectiveness in the wide range of OPC loading. Following OPC were studied: $(CH_3O)_3PO$ (TMP), $(CH_3CH_2O)_3PO$, $(CF_3CH_2O)_3PO$, $(CH_3O)_2P(O)CH_3$, $(CH_3CH_2O)_2P(O)CH_3$, $(CF_3CH_2O)_2P(O)CH_3$, $(C_3F_7CH_2O)_3PO$, $(C_3F_7CH_2O)_2P(O)CH_3$, $(HCF_2CF_2CH_2O)_3PO$, $(C_2H_5O)_2P(O)H$, $(CF_3CH_2O)_2P(O)H$, $(C_3F_7)_3PO$, $(C_2H_5O)_3P$, $(CF_3CH_2O)_3P$, $(HCF_2CF_2CH_2O)_3P$, $(CH_3O)_3P$. The tested OPC were ranked on their effectiveness. The obtained data for Mache-Hebra nozzle burner with data for OPC vapor loading and data for CF_3Br were compared. A toxicological study of OPC on laboratory mice was carried out. General parameters of toxicity of OPC under various route administration including lethality (LD_{50}) were determined.

INTRODUCTION

In connection with search of fire suppressants for replacement of Halon 1301 researchers examined a range of chemical compounds as alternatives [1]. One of perspective families of compounds is family of organophosphorous compounds (OPC). The works on their research carried out by several teams in USA in framework of the Next-Generation Fire Suppression Technology Program (NGP) [2], and in Europe [3-5]. These compounds have a number of merits: 1). do not destroy ozone layer of an atmosphere; 2). many OPC and the products of their combustion are nontoxic or low toxic; 3). they have a good compatibility with many materials; 4). they are more effective fire suppressants, than Halon 1301. There are also number of demerits

- low vapor pressure and flammability of some compounds. These problems can be solved if to use fluorinated derivative OPC [3,6]. The synthesis of such compounds represents the certain difficulties and for this reason they are still unsufficiently investigated. It was earlier shown [7], that inhibition effect of OPC on a flame is connected with catalysis by oxides of phosphorus of recombination reactions of H and OH. The main methods for screening efficiency of fire suppression and flame inhibition of these chemicals are the methods of 1). cup-burner (determination of the extinguishing concentrations of the fire suppressants), 2). non-premixed counter flow burner - the Potter burner (determination dependence of extinction strain rate on fire suppressant loading) and 3). the Bunsen burner (determination of the dependence of velocity of premixed flame propagation on inhibitor loading). These burners simulate various types of flames – premixed and non-premixed. The results of experiments on burning velocity (Bunsen burner) and on counter flow flames (Potter burner) can be compared to the data of numerical modeling [8]. For cup-burner the attempts to carry out modeling of a non-premixed flame structure are made only in conditions of microgravity [9]. In a number of the previous works [4,5,10] a number of OPC, including fluorinated their derivatives were investigated, and the extinguishing concentrations for various flames (H_2/CH_4/Air, n-heptane/Air) in cup-burner were determined. The effect of the TMP additives on structure of premixed flames (H_2/O_2, CH_4/O_2, C_3H_8/O_2) stabilized on the flat burner at atmospheric and subatmospheric pressure was investigated in [7,11-14] experimentally and by modeling. The method of the Bunsen burner for investigation of effect of OPC on propagation velocity of atmospheric CH_4/O_2 and C_3H_8/O_2 flames and that of the Potter burner for determination of fire suppression effectiveness of non-premixed CH_4/O_2 flame for a number of OPC were used. There are a little data about toxicity of OPC, in particular their fluorinated derivatives. The toxicity of $(C_2H_5O)_3PO$ is LD_{LO}=1.6 g/kg (rats, oral) [15], and that of DMMP ($(CH_3O)_2P(O)CH_3$) is LD_{50}=8.2g/kg (rats, oral) [16]. The toxicity of the phosphorus acids and their esters is highly variable [1]. Nevertheless, this family of compounds generally has, on an average, a moderately low toxicity. It seems unlikely, that phosphorus compounds would have any global environmental impact.

The goal of the present work consists in determination of the fire suppression and inhibition efficiency of the large number of OPC. The data about toxicity of some OPC also will be presented.

EXPERIMENTAL

In the previous work [7] the effect of different OPC on velocity C_3H_8/Air flame propagation was investigated. In the present work the study of the efficiency of flame inhibition by the additives of OPC have been carried on. Unlike [7] OPC have been introduced in combustible mixture by nebulizer. List of OPC under investigation and their boiling points are presented in Table 1. Also $POCl_3$ and 60 % a water solution of H_3PO_4 were investigated.

Table 1. The boiling point of investigated OPC

OPC	Boiling point [^{0}C] at pressure [torr]
$(CH_3O)_3PO$, TMP	180/760
$(C_2H_5O)_3PO$	215/760
$(CF_3CH_2O)_3PO$	187/760
$(HCF_2CF_2CH_2O)_3PO$	90/0,5
$(C_3F_7CH_2O)_3PO$	97/2,5
$(CH_3O)_2$ $P(O)CH_3$, DMMP	181/760
$(C_2H_5O)_2P(O)CH_3$	194/760
$(CF_3CH_2O)_2P(O)CH_3$	193/760
$(C_3F_7CH_2O)_2P(O)CH_3$	92/9
$(C_3F_7)_3PO$	144/760
$(CH_3O)_3P$	111/760
$(C_2H_5O)_2P(O)H$	204/760
$(CF_3CH_2O)_2P(O)H$	194/760
$(C_2H_5O)_3P$	158/760
$(CF_3CH_2O)_3P$	131/760
$(HCF_2CF_2CH_2O)_3P$	95/3

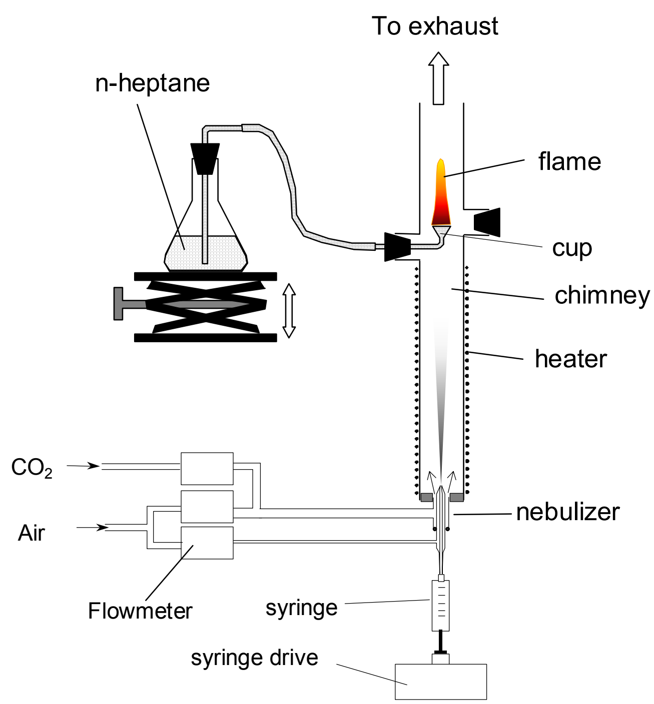

Fig. 1. Cup-burner setup

The efficiency of suppression non-premixed flame was determined by a cup-burner technique (Fig. 1). It represents the reduced variant of the standard cup-burner with small constructive changes. N-heptane was used as fuel. The cup-burner consists of a pyrex tube of an internal diameter 5.5 cm and length about 65 cm. The bottom part of the tube was heated by electrical

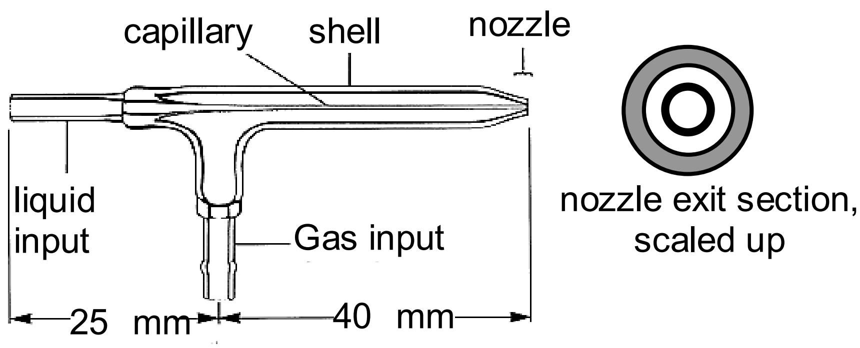

Fig .2. Construction of nebulizer

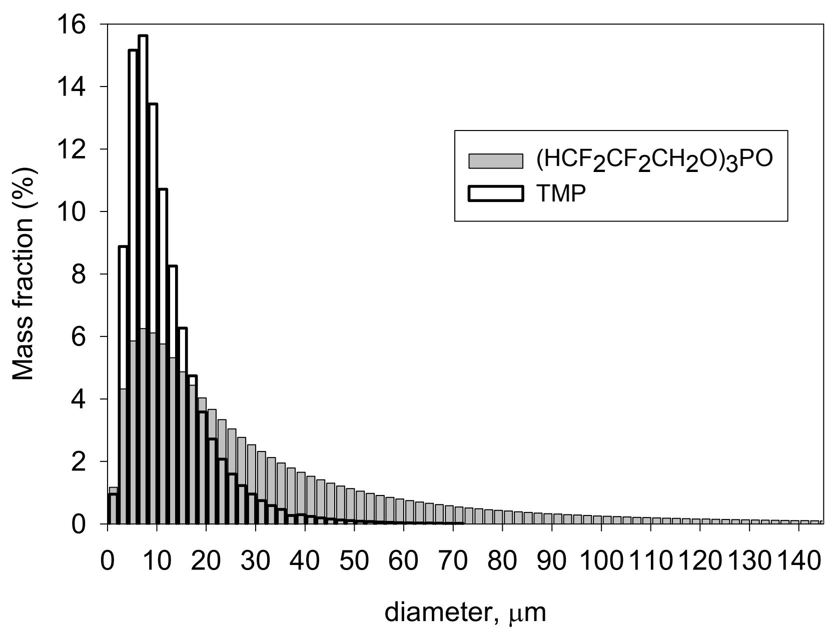

Fig. 3. Mass fraction distribution of the aerosol particles diameter of OPC

furnace. The flow rates of air 10 slpm. OPC was introduced into the air flow using a nebulizer. OPC feeding in to the nebulizer was performed by a syringe pump that made it possible to vary the flow rate of the liquid OPC in the wide range. The nebulizer is shown in Fig. 2. Inner diameter of the nebulizer - 0.1 mm, the thickness of the walls of the central capillary - 0.04 mm, and the width of the annular gap - 0.05 mm. Working pressure of the nebulizer was 5 atm.

At these conditions the mass-median diameter of the aerosol particles was about 10-20 microns that was determined by use of five-stage cascade impactor for 30 and 80% solution of glycerin in water, which viscosity corresponds to viscosity of TMP and $(HCF_2CF_2CH_2O)_3PO$ (Fig. 3).

The volume rate of air through nebulizer was 1.0-0.95 slpm. The air flow with OPC particles went upwards and was heated. Thus OPC usually evaporated but for low volatile OPC or for solution of H_3PO_4 complete evaporation did not occur. The "cup" has conic expansion upwards with an angle 30^o. Temperature of air close to the "cup" - 75^{o}C, airflow velocity ~10 cm/s. The diameter of the "cup" at the top edge - 13 mm. The feeding of OPC through nebulizer was begun after ignition of a flame and establishment of its stationary height 4.5-5 cm through 2 min. The CO_2 flow was introduced in flow of air in discrete steps so long as the flame was not extinguished. Such method of the test experiment similar described in work [17], allows to compare suppression efficiency of different fire suppressants in a wide range of concentrations and more precisely to determine extinguishing concentrations of fire suppressants. The investigation of flame suppression by the volatile OPC did not require the account their deposition on internal walls of tube, as the drops were evaporated in a flow at the temperature ~75 ^{o}C. The concentration of TMP saturated vapor at this temperature is 1.4 %. But in case of study of flame suppression by a 60 % water solution of H_3PO_4 latter was deposited on the walls of the tube. To take into account these losses the concentration of an acid (as aerosol) in the location of "cup" were was measured. For this purpose the dye was added in a solution, and the probe with the aerosol filter was set in place of a "cup". The analysis of the deposited quantity of aerosol on the filter has allowed to calculate the real concentration of H_3PO_4 in experiment. Important parameter determining distribution of particle size of liquid is the ratio of flow rates of air and liquid. It imposed restrictions on the upper level of concentrations of OPC, which were investigated in the present work. Burning velocity was measured using Mache-Hebra nozzle burner and total area method from the flame image as described elsewhere [18]. The design of the burner and technique of measurement of flame spread was described in detail in [12]. The combustible mixture included dry air and C_3H_8, containing about 4 % C_4H_{10}, and was prepared by three-channel regulator of gas flow rates (MKS Instruments Inc., model 1299S). Volumetric flow rate of the combustible mixture was 55 cm^3/s. The temperature of the burner was maintained at 95 ^{0}C with the help of thermostat. OPC were introduced into the gas flow using a nebulizer, which was installed in the lower part of the burner. Unlike the previous work [7], where OPC were introduced from saturator as vapor, in the present work the feeding of OPC was carried out

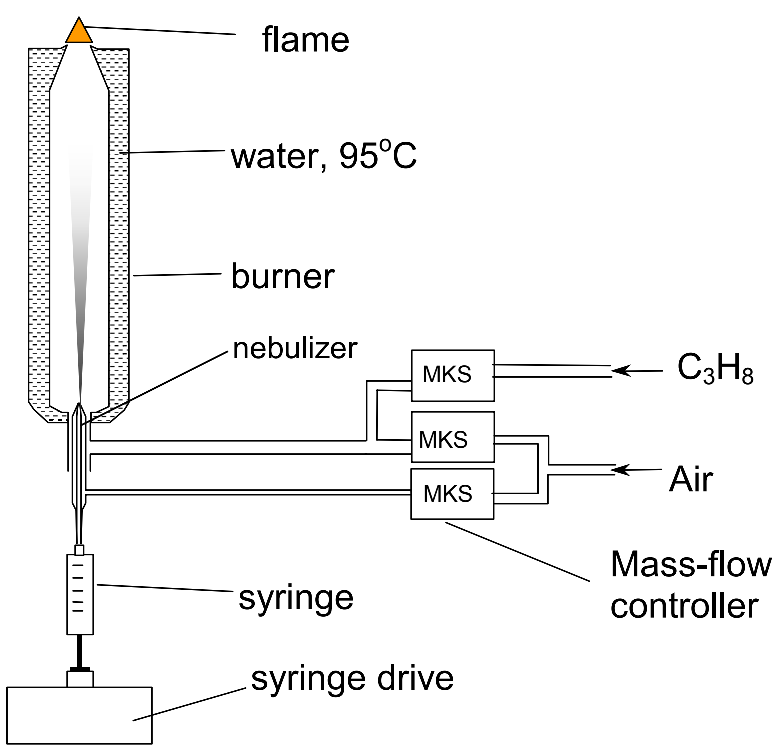

Fig.4. Mache-Hebra burner setup

as aerosol by use of nebulizer. It has allowed more precisely and in the wide range to set OPC concentrations. The experimental setup is presented in fig. 4. The feeding of OPC was performed in a similar way as in the case of cup burner. The estimations showed that evaporation time of OPC drops was less than drop residence time in a heated flow. So OPC were introduced in a flame as vapor. At temperature 25°C the combustible mixture contained both saturated vapor, and aerosol of OPC. To take into account deposition of OPC in tube of the burner a flow was passed through the filter which entrapped vapor and aerosol particles. This allowed to determine the real OPC concentration in a flame.

RESULTS AND DISCUSSION

The results of cup-burner experiments – dependencies of CO_2 extinguishing concentrations on OPC concentration are presented in Fig. 5. The points on the diagram correspond to conditions of suppression of diffusion n-heptane flame, thus the flame can exist only at smaller concentrations of CO_2 and/or OPC. On the same figure the data for CF_3Br are shown too. It was found, that in a range of concentration from 0 up to 5000 ppm the large number of OPC, aerosol of water solution of H_3PO_4 and vapor of $POCl_3$ showed similar flame suppression efficiency. All these compounds both for premixed and diffusion flames have higher suppression efficiency than CF_3Br. At increase of OPC concentration up to 10000 ppm different relative decrease of suppression efficiency for different compounds was observed. At the increase of concentration of OPC up to concentration higher than its vapor pressure (at 75°C), the further increase of suppression efficiency was stopped (for example for TMP). For some of compounds (for example for $(CH_3O)_3P$) even a reverse effect was observed: at increase of OPC concentration CO_2 extinguishing concentration increased too. We suppose, that it is connected with a competition of two processes: 1. The increase of inhibitor concentration results in decrease speed of flame and its suppression; 2. The increase of flame temperature as result of increase of heat release at OPC addition results in increase burning velocity. At low OPC concentration (up to 5000 ppм) the first

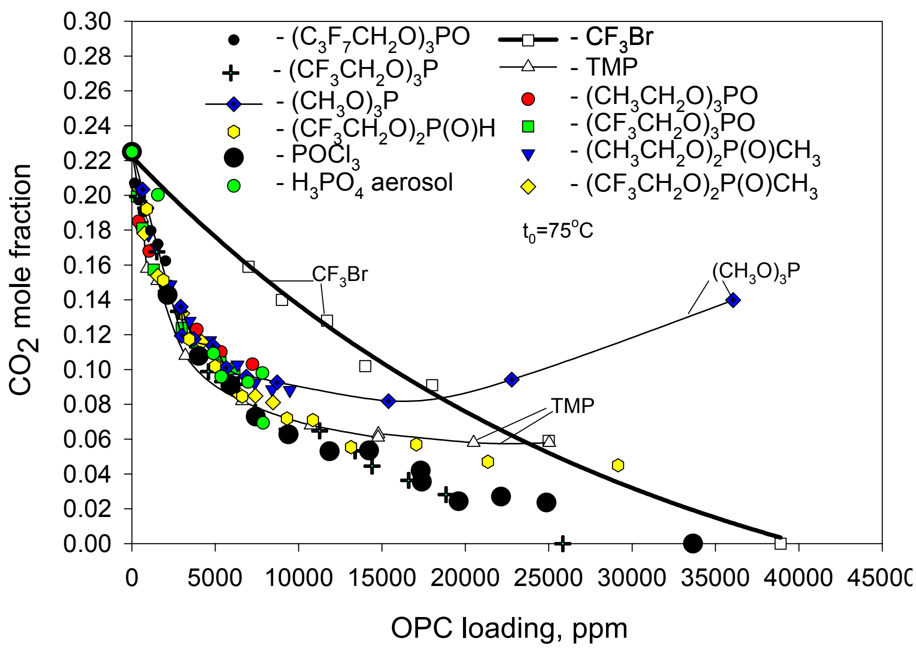

Fig. 5. The dependencies of CO_2 extinguishing concentrations on OPC loading concentration in cup-burner experiments

process prevails, but at high concentration second one has dominant role. The effect of decrease of OPC suppression efficiency at increase of its concentration was not found out in the Mache-Hebra nozzle burner and the opposed-jet burner experiments because these data were obtained in a range of lower concentrations, than in cup-burner experiments. It was not possible to obtain of OPC suppression concentration without CO_2 addition in the air flow for the most of the investigated compounds. On the basis of the data obtained it was possible to make a conclusion, that the extinguishing effect of the investigated compounds is caused by presence of atom of phosphorus in its molecule. The flame suppression efficiency of water solution of H_3PO_4, in a range of concentration up to 10000 ppм was close to that obtained for the most others OPC. Only for two compounds - $(CF_3CH_2O)_3P$ and $POCl_3$ the extinguishing concentrations without addition of CO_2 in the air flow were obtained: - 2.6±0.2 % (vol.) and 3.3±0.3 % (vol.) accordingly. The extinguishing concentration of these compounds have been determined also in [10] and [1]. They are differ from those obtained by us. This distinction is connected with different experimental conditions, such as temperature and type of fuel used in cup-burner. Similar facts were reported in [17] for extinguishing concentrations of CO_2 and CF_3Br by using as a fuel CH_4 and n-heptane (15.7 % and 19.2 % for CO_2 and 2.4 % and 2.9 %-3.2 % [10] for CF_3Br accordingly).

The dependence of speed of premixed stoichiometric C_3H_8/air flame on OPC concentration is shown on Fig. 6. The part of these compounds was earlier investigated, but later these data were complemented and refined. On the figure the flame speed is normalized on its value for combustible mixture without OPC additive. The obtained data showed that in a range of concentration up to 4500 ppm all investigated OPC and also water solution of H_3PO_4 and $POCl_3$ have similar inhibition efficiency. Besides all OPC have higher inhibition

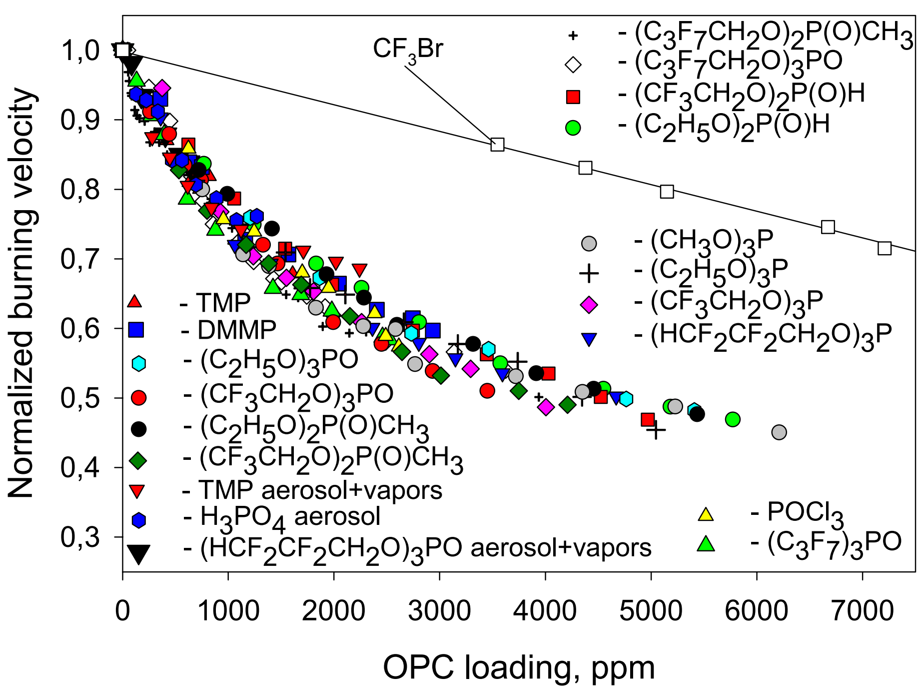

Fig. 6. Normalized burning velocity of stoichiometric premixed C_3H_8/Air flame as a function inhibitor loading

efficiency on a molecule of compound than CF_3Br. The inhibition efficiency of aerosol of TMP and $(HCF_2CF_2CH_2O)_3PO$ with the mass-median diameter of the particles 10-20 microns does not differ from inhibition efficiency of TMP (and others OPC) vapors. Comparison of OPC inhibition efficiency for premixed flame with OPC suppression efficiency for non-premixed flames (cup-burner and opposed-jet burner technique [19]) showed, that in a range of concentrations up to 5000 ppм, all OPC have a similar effectiveness. Besides all three techniques showed higher effectiveness of flame suppression and inhibition by the additives of OPC, than that of CF_3Br.

STUDY OF TMP TOXICITY

The study of TMP toxicity was carried out on uninbred white mice weighting 24-26 g. For rough determination of lethality, TMP was diluted by distilled water and administered into stomach through a stomach tube in a volume of 0.1 ml/10g body weight at doses of 10, 8, 6, 4 and 2 ml/kg (6 mice per a dose). The minimal single dose of TMP killing all of mice was 4 ml/kg. At a dose of 2 ml/kg all mice remained alive within 14 days after TMP administration. For determination of LD_{50}, some doses of TMP between 2 ml/kg and 4 ml/kg (2.0; 2.5; 3.0; 3.5 and 4.0 ml/kg) were tested. Each dose was tested on 6 animals. The results of this testing showed that LD_{50} for TMP, computed by Kerber's formula, is 2.42 ml/kg. The dose of 4 ml/kg was absolutely lethal. The clinical symptoms of poisoning occur rather quickly after TMP administration. Through 3-4 min there came some excitation of animals, there was "a shaky gait", the mice were filled up on a side. Then the excitation was replaced by slackness, the animals lie motionlessly, rare, or, on the contrary, often and superficially breathed. From lethal doses (4-2.5 ml/kg) of TMP the animals perished in 12-24 hours. The main reason of animal's death is obviously the damage of lungs: the lungs of dead mice were "red", enlarged in comparison with the lungs of control mice, apparently, as a result of a damage of vessels and edema (see Table 2).The liver and kidneys are without visible changes.

Table 2. Relative weights (% of body weight) of visceral organs of mice treated with a single intragastrical administration of different doses of TMP

Organ	4.0 ml/kg	3.0 ml/kg	2.5 ml/kg	2.0 ml/kg	0 (Control)
Liver	5.8 ± 0.17	6.3 ± 0.40	5.8 ± 0.46	5.4 ± 0.24	5.8 ± 0.40
Lungs	1.30 ± 0.056	0.98 ± 0.070	0.80 ± 0.030	1.00 ± 0.065	0.72 ± 0.019
Heart	0.67 ± 0.019	0.80 ± 0.058	0.84 ± 0.129	0.58 ± 0.034	0.54 ± 0.021
Kidney	0.62 ± 0.042	0.86 ± 0.033	0.73 ± 0.071	0.78 ± 0.031	0.73 ± 0.030
Spleen	-	0.17 ± 0.013	0.28 ± 0.015	0.56 ± 0.11	0.43 ± 0.079

At a dose of 2 ml/kg, despite of the expressed symptoms of a poisoning in nearest 2 hours after TMP administration (adynamia, slackness), in subsequent all mice remained alive without external changes during 14 and more days of observation.

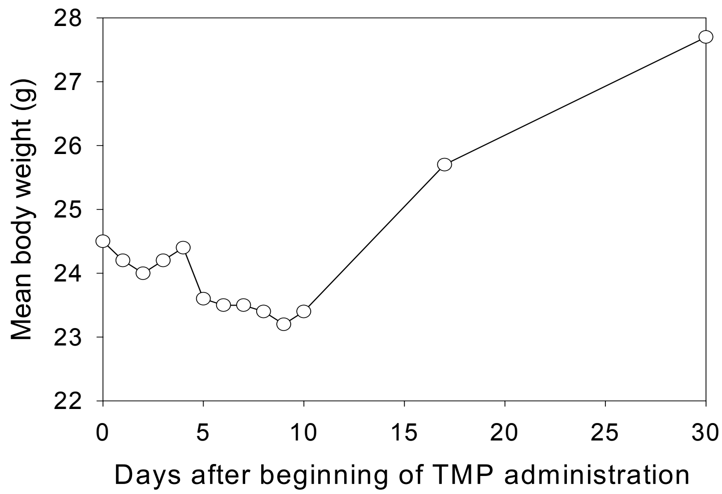

Fig. 7. Dynamics of body weight of mice in the course (1-10 days) and after TMP administration

To determine the cumulative toxicity, TMP was administered into 10 mice daily within 10 days at a dose of 1.2 ml/kg (1/2 LD_{50}). Thus, the total dose of TMP has made 5 LD_{50}. The transient weak symptoms of a poisoning (some slackness) after 8-10 TMP intubations were registered only in 2 mice of 10. The insignificant reduction (maximum 5 %) of animal's body weight is marked also (see Fig 6). After the discontinuance of TMP administration, the animals added in weight quickly, and has made 113 % of initial by the end of the experiment (30 days). The application of undiluted TMP on eye mucous or skin was without the local or general reactions of these tissues, i.e., it does not render irritating action on mucous and skin.
Thus, in mice, TMP under intragastrical administration has possess rather low general toxicity and poorly expressed cumulative effect.

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