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Kinetics of Destruction of Diisopropyl Methylphosphonate in Corona Discharge

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ABSTRACT

The kinetics of the destruction of diisopropyl methylphosphonate (DIMP) in corona discharge has been studied using a tubular coaxial wire dielectric barrier corona discharge reactor. The identification and quantitative determination of DIMP, the intermediates of the destruction and the phosphorous containing destruction products (PCDP) were performed using molecular beam sampling mass-spectrometry (MBMS) and gas chromatography mass-spectrometry (GC/MS). The dependence of the extent of the destruction, D , ($D = 1 - x/x_0$, where x and x_0 are DIMP mole fractions at the outlet and the inlet of the reactor) on the specific energy deposition, E_x , ($E_x = PF^{-1}x_0^{-1}$, F is the carrier gas flow, P is the discharge power, x_0 is the initial mole fraction of DIMP) was measured over the DIMP mole fraction range 60 – 500 ppm at pressure 1 bar. Over the range of the experimental conditions studied the destruction obeys the "pseudo-first order" kinetic law: $\ln(1-D) = -k E_x$. Plausible mechanisms of the destruction are discussed.

INTRODUCTION

Recently, corona discharge emerged as a promising novel technology for the treatment of low concentration of pollutants (VOCs, NO_x, SO_x) from stack emissions. During the last years a significant progress was achieved in application of the corona discharge plasma for conversion of VOCs [Nunez et al (1993), Krasnoperov and Krishtopa (1994-1995, 2001), Evans et al (1993), Yamamoto et al (1992)], silicon containing compounds (SiH₄) [Kushner (1993)], oxides of nitrogen (NO_x) [Dinelli et al (1990), Krasnoperov and Krishtopa (1994-1995), Ohkubo (1994), Masuda (1988, 1994), Chang (1989, 1992)], oxides of sulfur (SO_x) [Chay (1991), Sardij (1990), Kushner (1992)] and in the understanding of the kinetics of destruction of these pollutants. Initial research on the decontamination of organophosphorus compounds in corona discharge was performed in the mid-80s [1-4]. Fraser, Sheinson et al [] determined hydrocarbons as DMMP destruction products. But phosphorus containing compounds (exempt phosphine) have not been detected as destruction products and therefore balance on phosphorus have not been determined. Krasnoperov et al (1994-2001) developed approach based on determination of the kinetics of pollutant destruction and measurement of electrical power consumed by discharge. He presented obtained data using coordinates: X_{out}/X_{in} and $P/(FX_{in})$ (X_{out} , X_{in} - concentrations of pollutant at the inlet and outlet of reactor, ppm, P - consumed power, J/cm³, F - flow rate, cm³). Obtained data for many investigated compounds follow the law: $X_{out}/X_{in} = \exp(-KP/(FX_{in}))$. It was concluded that ion mechanism is major one responsible for destruction processes. Krasnoperov et al concluded that ion mechanism is major one responsible for destruction processes. [Potapkin et al (1989) for SO₂, Green et al (1996) for VOCs, Chang (1989) for NO_x] came to the same conclusion. In contrast, other groups of researchers consider that the radical mechanism is major one responsible for destruction of pollutants: [Fitzmmons et al (Cambridge, 2000)] for toluene, dichloromethane [Whitehead et al (Cambridge, 2000)] for hydrocarbon and NO_x. We have initiated a systematic study on the conversion of volatile organic compounds (VOCs), NO_x and SO_x [5] and simulants of sarin [6] in corona discharge. However, the research on the destruction of actual Chemical Warfare Agents as well as their surrogates is still very limited. In the current study, the kinetics and the products of the destruction of a simulant of sarin - diisopropyl methylphosphonate – in a dielectric barrier corona discharge was studied over a range of experimental conditions. To apply for destruction of OPC in corona discharge approach based on determination of kinetics of OPC destruction and measurement of power consumed by discharge. Objectives of this research:

- To apply for destruction of OPC in corona discharge approach based on determination of kinetics of OPC destruction and measurement of power consumed by discharge.
- To determine intermediate and final destruction products of OPC as a function of parameter $E_{v,o}$ and to check out the balance on phosphorus.
- To study destruction kinetics of OPC in corona discharge, to measure OPC destruction extent as a function of parameter $E_{v,o}$.
- To determine whether the law $(1-D) = \exp(-KP/FX_0)$ describe the destruction of OPC in corona discharge
- To use obtained data for discussion of possible mechanism of destruction of OPC in corona discharge.

EXPERIMENTAL

The set-up is a molecular beam sampling mass-spectrometry (MBMS) based experimental facility [6] modified for the kinetic studies on the destruction of diisopropyl methylphosphonate

(DIMP) in a corona discharge flow reactor. A tubular dielectric barrier AC powered corona discharge flow reactor coupled to an on-line molecular beam sampling quadrupole mass-spectrometer was used. The reactor consists of a quartz tubing 115 cm long, 1.2 cm OD, 0.9 cm ID, with a coaxial nichrome wire 0.5 mm in diameter which serves as one of the electrodes. The tube was wrapped with nickel copper braid which is the second, grounded, electrode. The active length of the reactor determined by the wrapped length is 105 cm. The reactor tube was located inside a water jacket. The reactor temperature was kept at 340 K by circulating water from a bath circulator. Carrier gases (N₂, He) were supplied from cylinders ("SibTechGas", purity 99.7%). A mass-flow controller (MKS Instruments) controlled the carrier gas flow. The organophosphorus compound (DIMP in this study) was introduced to the reactor by passing the carrier gas above the surface of the liquid reactant in an evaporator. The mass flow of the reactant was established by measuring the mass loss of the evaporator to the accuracy of 0.1 mg. Typical mass loss at the gas carrier flow rate of 2.5 scems was 20 mg/hour. The mole fraction of DIMP was varied in the range 60 - 500 ppm. Organophosphorus compounds were obtained from Aldrich chemical company diethylmethylphosphonate (DEMP) 97%(683-08-9), orthophosphoric acid (OPA) 85%(7664-38-2), methylphosphonic acid (MPA) 98%(13590-71-1). The DIMP 98%+ was purchased from Alfa AESAR (Johnson Matthey). N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA, 99.5% (25561-30-2), was obtained from Supelco Inc.

The output voltage from a 1 kW high voltage AC power supply was controlled by a variac. The active power measurements were based on the electrical measurements. The maximum amplitude of the output voltage was 20 kV, frequency 50 Hz. The voltage and the current are recorded using a digital oscilloscope (LeCroy, Model 9310AL). The measurements were performed by summing up of five hundred 100 ms (5 periods) sweeps of the voltage and current. The voltage and current obtained in this way were multiplied and averaged. The active power (P) dissipated in

the plasma reactor was determined by subtracting the measured power without load from that measured with load.

The samples were analysed using a molecular-beam sampling system with a quadrupole mass-spectrometer MC7302 produced by the Experimental Plant of the Russian Academy of Sciences. The detection system allows determination of the extent of DIMP destruction at mole fractions as low as 1 ppm. The mole fractions of DIMP and the destruction products were determined via measuring their parent ion peak intensities and the calibration coefficient. In addition, DIMP mole fractions at the inlet (x_0) and the outlet (x) of the reactor were measured using gas chromatography mass spectrometry (GC/MS). In these measurements, the gas was passed through a system of three liquid nitrogen traps. A glass wool filter was placed in the last trap to trap possible aerosols. To control the initial mole fraction of DIMP it was measured twice, before and after the experiment. To increase accuracy of measurements of the initial mole fraction of DIMP the gas was passed through the trapping system for one hour and more. After that the traps were removed and rinsed with acetone. The resulting solution was evaporated using a rotor evaporator producing a residue. The volume of the residue 0.3-0.4 ml was determined in additional test experiments. The efficiency of the trapping and recovery of DIMP under the conditions of trapping and the solution evaporation used was better than 95%. The typical scatter of the experimental data was ca. 5-20% for molecular beam sampling mass-spectrometry (MBMS) and 7-30% for GC/MS analysis depending on their mole fractions.

To detect and to quantify the low volatile phosphorous containing compounds (PCC) by GC/MS the procedure of silylation was used [7, 8]. This procedure consists of the substitution of the hydrogen atom in the hydroxyl group of PCC by trimethylsilyl radical [7, 8]. Organophosphorus compounds silylated in this way are volatile and can be detected using GC/MS. The silylating solution used was a mixture of acetonitrile and N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) in the proportion 9 to 1 by volume. To account for the effect of the column ageing a reference

substance was introduced in the silylating solution of BSTFA and acetonitrile. Diethyl methylphosphonate (DEMP - $\text{PO}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$) was used as the reference compound. About 10 mg DEMP was added to 10ml of silylating solution. It gives a reproducible concentration of DEMP as reference compound in each sample. These portions of the silylating solution were added to the evaporated samples, which were obtained by rinsing the traps or the walls of the reactor. After mixing and moderate heating to accelerate the reaction these mixtures were analysed by GC/MS. For the determination of the absolute amounts of PCC in the samples the calibration was used. A small known amount of PCC was mixed with the silylating solution and analyzed by GC/MS. As a result of this procedure we obtained PCC calibrated Peak Areas which correspond to the known PCC concentrations. The washings obtained from the reactor and the traps in the experiments were evaporated, silylated and analysed using GC/MS. The calibrated PCC peak areas obtained were used to determine the PCC concentrations in the samples. For example, for DIMP: $[\text{Concentration DIMP}] = [\text{Area DIMP}] \times [\text{Calibrated Concentration DIMP}] / ([\text{Calibrated Area DIMP}] \times [\text{Area DEMP}] / [\text{Calibrated Area DEMP}])$. This formula allowed quantifying measuring PCC concentrations. The efficiency of the OPC trapping depends on the gas flow rate. At low gas flow rates (< 20 sccms, the residence time of the gas in the traps > 10 sec) the efficiency of the OPC trapping was better than 95%. The analysis of the solutions obtained by rinsing of the three traps in series showed 70% of PCC trapped in the first trap, 28% - in the second trap and ca. 1% - in the third trap at the gas flow rate of 1.66 sccms. About 1% of the PCC was precipitated on the glass wool filter. When calibrating OPC initial mole fraction the data on the PCC weight loss during the experiments were used.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Destruction products. The kinetics of DIMP destruction.

The measurements of the extent of destruction were performed after establishing steady state of DIMP concentration in the flow reactor. It was observed that the establishing of a steady state of

DIMP concentration requires a prolonged period of time (10 min) when studying low volatile organophosphorus compounds. The results below were obtained by measuring the PCC mole fractions at the inlet and the outlet of the reactor. The destruction products isopropyl methylphosphonate (IMP), methylphosphonic acid (MPA), and orthophosphoric acid (OPA) were found on the wall of the reactor. No other PCDP were detected. A small amount (< 10% of all PCDP) of organophosphorus products of DIMP destruction was found in the liquid nitrogen traps. No aerosols were collected on the glass wool when the gas flow was less than 2 sccms. The results on the DIMP destruction in nitrogen carrier gas (99.7% N₂, 0.3% O₂) are shown in Fig 1. In this figure the reactor outlet mole fractions of DIMP and the products of the destruction normalized on the initial (inlet) mole fraction of DIMP are plotted vs. the specific deposited energy, E_x. The specific deposited energy E_x was defined as energy per unit gas volume per unit mole fraction of DIMP, $E_x = P/F/x_0$, where P is the active power dissipated in the reactor, F is the gas volumetric flow rate. The previous research on VOCs and NO_x destruction demonstrated that the specific energy defined in this way is the parameter characterizing the discharge the efficiency of the corona reactor. The mass balance in phosphorous was calculated by summing the mole fractions x_i of the species containing phosphorous and comparing with the initial DIMP mole fraction. Data on balance are in Fig.1. The experimental data indicate no dependence of the DIMP destruction products on the nature of the carrier gas. The dependencies of the normalized mole fraction, x/x₀, on the specific energy for different initial mole fractions of OPC in the range 60 – 500 ppm are shown in Fig. 2. This dependency can be expressed by the equation: $\ln(x/x_0) = -K E_x = KPF^{-1}x_0^{-1} = 160 E_x$. The coefficient K was determined experimentally with the accuracy ca. 10%. The coefficient K has dimension as J⁻¹sccm ppm. Similar dependence was observed previously in the study of the destruction of VOCs in corona discharge [5].

2. The Effect of the Carrier Gas on the Efficiency of DIMP Destruction

The corona onset voltage as well as the active power dissipated in the reactor at the same applied voltage strongly depend on the nature of the carrier gas. In the current study, helium, dry air and nitrogen (with ca. 0.3% oxygen impurity) were used as the carrier gases. The power consumed by the reactor as a function of the voltage applied for different carrier gases is listed in Table. 1. The data are also plotted in Fig. 3. The measurements of DIMP destruction in different carrier gases were performed using mass-spectrometric detection using the following set of experimental conditions: flow rate $F= 5$ scms, initial mole fraction $x_0= 250$ ppm, applied amplitude voltage $U=12$ kV. It is apparent from Table 1 that at these experimental conditions the extent of the destruction is about 60% for all carrier gases studied. However, the dissipated in reactor power P (and, subsequently, E_x) in helium is approximately 5-6 times lower than that in nitrogen. Therefore, the efficiency of the destruction in helium is ca. 5-6 times higher than in nitrogen and air.

3. Discussion

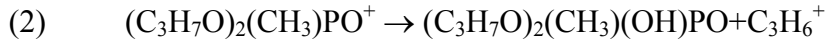
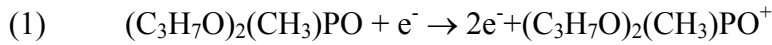
A successful mechanism of the destruction in corona discharge should explain the following experimental observations:

1. The absolute energy efficiency of DIMP destruction.
2. The fact that the same energy calculated per one DIMP molecule is required to achieve a certain extent of destruction at different concentrations
3. The difference in DIMP destruction efficiency in helium and nitrogen.
4. Only minor effect of molecular oxygen on the destruction efficiency (Air and "nitrogen").
5. Products of destruction.

The mechanisms of the destruction in corona discharge of a number of compounds currently discussed and developed. It's was based on consideration of electron beam processing, ion-molecular reactions and neutral reactions chemistry [5, 9, 10, 17].

As appears from the Fig.1. IMP is the initial and intermediate product of destruction of DIMP. This fact can be interpreted as from viewpoint both ion and radical mechanisms. Actually in works which reported features of radiolysis in nonaqueous solutions tri-n-butylphosphate (TBP) close to DIMP by structure, the main of the destruction process is dealkylation [13] leads to formation di- and mono n-butylphosphate.

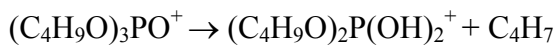
The process of breakage of bond C-O with formation di-n-butylphosphate are observed at decay exciting molecules of TBP and in reaction involving ions [14]. Similarly at radiolysis of DIMP there are expected forming IMP by the reactions:



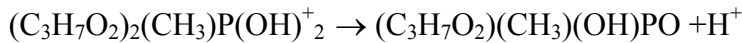
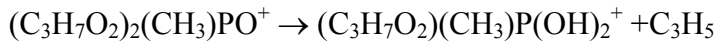
At that radicals C_4H_9 и $(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2$ are generating. The last is a precursor of di-n-butylphosphate.



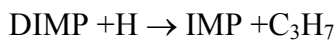
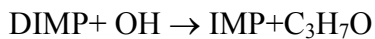
At work [14] there are postulated that the initial ion $(\text{C}_4\text{H}_9\text{O})_3\text{PO}^+$ can decompose by the reaction:



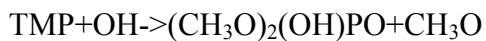
At subsequent removal H^+ from ion $(\text{C}_4\text{H}_9\text{O})_2\text{P}(\text{OH})_2^+$ di-n-butylphosphate are forming. Similar processes with forming IMP $((\text{C}_3\text{H}_7\text{O}_2)(\text{CH}_3)(\text{OH})\text{PO})$ we can expect at radiolysis of DIMP too.



There are expected [18] possibility dissociative joining electron to molecule of TBP. Leakage of bond in molecule of DIMP was observed at ionizing by electron impact in ion source of mass-spectrometer [16, 19]. Negative and positive flame ions from a premixed low-pressure ethylene/oxygen flame doped with trimethyl phosphate (TMP) were analyzed by mass-spectrometer [20]. On other side-forming IMP as initial product in reaction of DIMP with H and OH for destruction of DIMP in H_2/O_2 flames was observed [12].



Similar processes occur at destruction other organophosphorus compounds for example TMP [21]



At that rate constant of this reaction $\kappa = 5 \cdot 10^{12} \exp(-E/RT) \text{ cm}^3/(\text{s} \cdot \text{mol})$ ($E = 16.7 \text{ kJ/mol}$) is high enough for occurring this reaction at the normal conditions. Thus the most important initial stage of destruction of DIMP in corona discharge with formation of IMP can run on both radical and ion mechanisms. Question about feasible dominant role one of these mechanisms is emerged. Well-define understanding of processes of destruction in corona discharge is not. Various authors give preference to one or another process of destruction in corona discharge.

Conclusion about dominant role of radical mechanism for destruction VOCs in nonisothermal plasma was made by comparing experimental data and modeling [17]. The destruction extent dichloromethane determines presence chlorine which forms in result of interaction between dichloromethane and exciting molecules and atoms of nitrogen was reported in this paper. The destruction extent of toluene depends on concentration of radicals OH which form in result of destruction vapor of water in discharge. The destruction of toluene practically discontinue at absence of vapor of water. In [5], only one mechanism was outlined as potentially capable of explaining all the experimental observations. This mechanism is based on the physical and chemical processes involving ions. While substantially higher energies are required for ion production (ca. 9.6 eV/molecule) compared to those required for production of free radicals (ca. 3-4 eV/molecule), the fast charge exchange reaction serve as the means of the ionisation trapping on the impurity molecules. This can explain high efficiency and concentration independence down to very low concentrations. Such a mechanism infers high efficiency of the destruction for those molecules, which have ionisation potential lower than the ionisation potential of oxygen molecules (the main source of ionisation in air). For molecules with the ionisation potential higher than the ionisation potential of oxygen (such as CH₄, SO₂) low destruction efficiency as well as the decrease of the destruction efficiency (calculated per one molecule of the contaminant) at low concentrations is anticipated.

Such a correlation was indeed observed in the study on the VOCs and SO_x destruction [5]. The results of this study are in line with such mechanism. The ionisation energies of the OPC of the study ($E_i = 9.65$ eV for DIMP are lower than the ionisation energy of oxygen ($E_i = 12.07$ eV). The measured destruction efficiency as well as the concentration dependence are similar to those previously observed for VOCs with low ionisation energy.

The higher efficiency of destruction in helium can be rationalised as follows. Helium atom has very high ionisation energy ($E_i = 24.6$ eV). Moreover, the first excited state of this atom lies at relatively high energies ($E_1 \sim 20$ eV). Therefore, the elastic collisions of electrons with helium atoms prevail at lower energies. Electrons can gain substantially high energies before they start to loose energy on excitation and ionisation in collisions with helium atoms. This is in line with substantially low corona breakdown voltage in helium compared with nitrogen and air. In such a case, an impurity with low ionisation/excitation energy can serve as the major sink of the energy gained by electrons even at very low concentration. Due to the much higher electron temperature a higher energy yield of ionisation and electronic excitations is expected. This is consistent with higher destruction efficiency in helium observed in this work.

Thus in present time the kinetics of destruction OPC in corona discharge based on only one mechanism cannot be proposed. However accordingly to modern representations about processes taking places in corona discharge Initiating of destruction of OPC occur because of emerging active particles from electron impact in volume of reactor and further occur interaction these active particles with OPC in ion-molecular and radical reactions.

CONCLUSIONS

The most efficiency of destruction OPC was achieved at using helium as a gas-carrier. The law $\ln(x/x_0) = KPF^{-1}x_0^{-1}$ proposed for destruction VOCs was confirmed for destruction OPC.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Fig.1. Dependence of mole fraction of DIMP and PCDP on parameter E_x . 1 - DIMP, 2 - IMP, 3 - MPA, 4- OPA, 5- phosphorus element balance.

Fig.2. The dependence X/X_0 on parameter E_x .

Fig.3. The dependence of discharge power on voltage for different gas-carriers.

Table 1. The data on DIMP destruction extent in flux of various gas-carriers at $X_0=250\text{ppm}$.

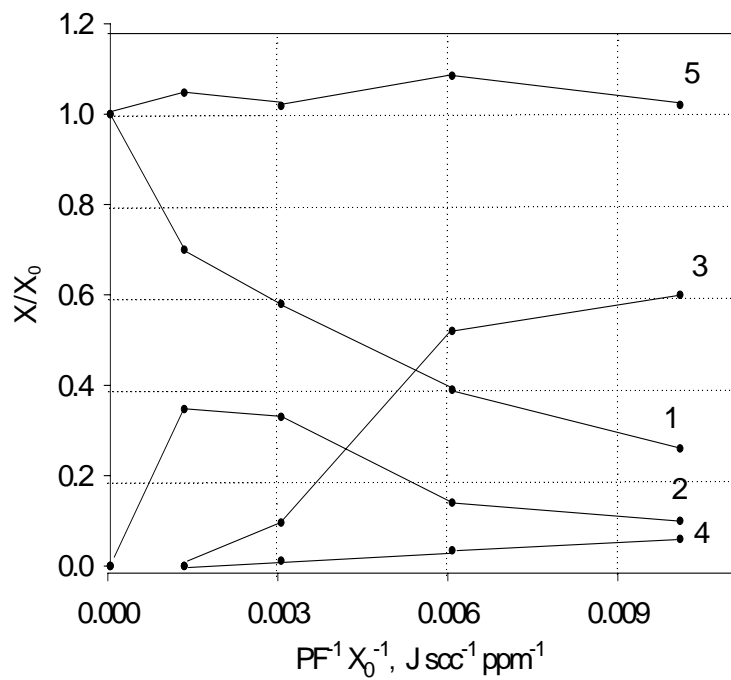


Fig. 1

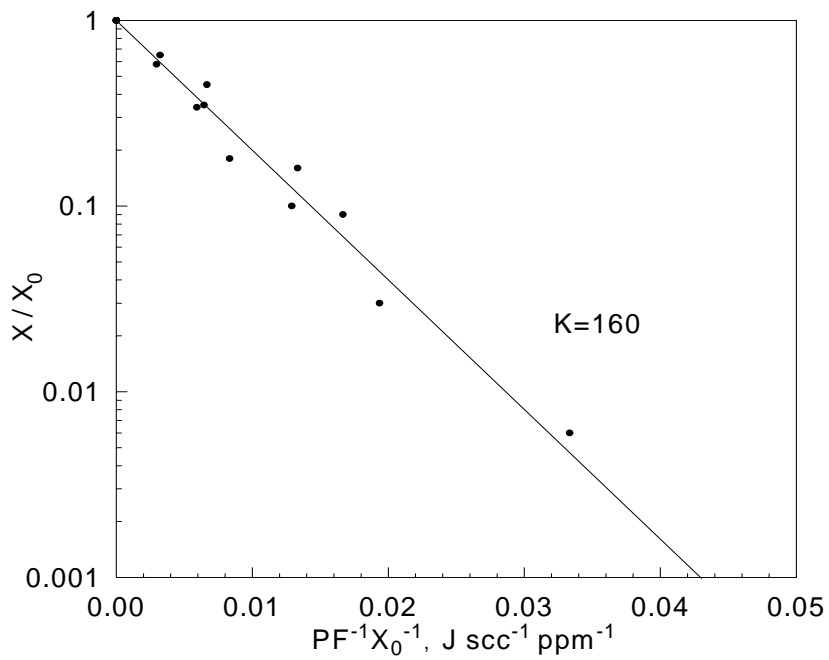


Fig. 2

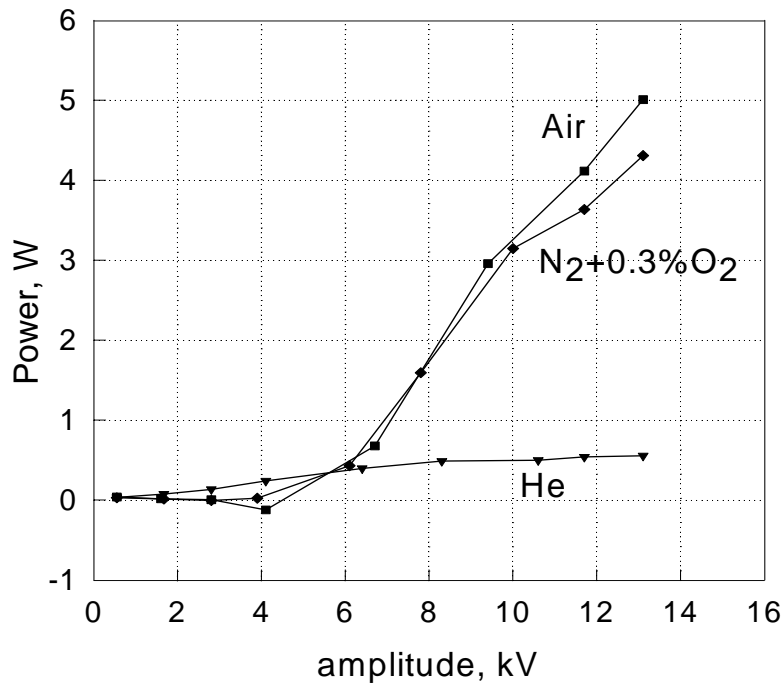


Fig. 3

Table 1. The data on DIMP destruction extent in flux of various gas-carriers at $x_0=250$ ppm.

Gas composition	P, W	V, Jscm ⁻¹ ppm ⁻¹	D _i , %	K _i
He*	0,5	0.0008	52	900+-200
N ₂ *	3.7	0.0059	61	160+-30
N ₂ (+0.3%O ₂)	3.8	0.006	66	180+-30
Air	4.4	0.007	71	175+-30

*estimated amount O₂ ≤ 10 ppm

Bibliography

- [1] E.J. Clothiaux, J.A. Koropchak, R.R. Moore, *Plasma Chem. Plasma Process.* **4**, 15 (1984).
- [2] M.E. Fraser, *CRDC Joint Service Technical Symposium on Plasma Air Purification Technology, CRDC*, (1984).
- [3] M.E. Fraser, D.A. Fee, R.S. Sheinson, *Plasma Chem. Plasma Process*, **5**, 163 (1985)
- [4] M.E. Fraser, H.J. Eaton, R.S. Sheinson, *Environ. Sci. Technol.*, **19**, 946 (1985)
- [5] L.N. Krasnoperov and L.G. Krishtopa, Environmental Applications of Advanced Oxidation Technologies, Proceedings of the Second International Symposium, San Francisco, Feb. 28-March 2, (1996), Proceedings: Electric Power Research Institute, Section 5, pp.1,150 (1997).
- [6] O.P. Korobeinichev, A.A. Chernov, L.N. Krasnoperov, The International CW Destruction Symposium, 22-25 March, 1998, Munster, Germany. Proceedings. (Editors D.Starrock and A.Krippendorf), p.225 (1998)
- [7] D.C. Rapp, M.F.M. Nogueira, E.M. Fisher, F.C. Gouldin, *Environmental Engineering Science*, **14**, 133 (1997)
- [8] G. Bauer, W. and Vogt, Chromatographic Determination of Acids Derived from Phosphorus by Triethylsilylation with N,O-Bis(trimethyl)trifluoroacetamide, *Analytical Chemistry* **53**, 917 (1981)
- [9] Bernie M. Penetrane, Norman J. Bardsley and mark C. Hsiao, *Jpn. J. Appl. Phys.*, 1997, Vol. 36, Pt.1, No 7B, pp.5007-5017
- [10] Mark J. Kushner, *J. Appl. Phys.*, 1993, Vol. 74, No 11, pp.6538-6553
- [11] B. Eliasson, M. Hirth, U. Kogelshatz, *J. Phys. B: Appl. Phys.*, 1986, v.22, p.1241
- [12] Oleg P. Korobeinichev, Anatoly A. Chernov, Tatyana A. Bolshova, *Combustion and Flame*, 2000, v.153, No. 14, pp.
- [13] Burr J., *Radiat. Res.*, 1958, v.8, p.214-221.
- [14] R.W. Wilkinson, T.F. Williams, *J. Chem. Soc.*, 1961, pp. 4098-4105

- [15] Samuell Sass and Timothy L.Fisher, *Organic Mass Spectrometry*, 1979, v.14, No.5, pp.257-264.
- [16] Eric R.J.Wils, *J. Anal. Chem*, 1990, 338, pp.22 - 27.
- [17] C.Fitzimons, F.Ismail, J.C. Whitehead and J.J.Wilman, 16th International Symposium on Gas Kinetics, Book Abstract, Cambridge, July, 2000
- [18] Haase K.D., Shutle-Forhlinde D., Kourim P., Vacek K. – *Intern. J. Radiat. Phys. And Chem.*, 1973, Vol.1, p.105-114.
- [19] Samuell Sass and Timothy L.Fisher, *Organic Mass Spectrometry*, 1979, v.14, No.5, pp.257-264.
- [20] [] negative and positive flame ions
- [21] O.P.Korobeinichev, S.B.Ilyin, T.A.Bolshova, V.M.Shvartsberg and A.A.Chernov, *Combustion and Flame* 2000 v.121, pp 593-609.