

Physicochemical Transformations and Kinetics of Photochemical Reactions Inherent in High-Disperse State of Matter

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Abstract

Chemical substances in high-disperse phase state (in the form of small aerosol particles 0.1–10 μm in diameter and very thin films 0.01–1 μm thick) exhibit specific chemical and physicochemical properties. The processes inherent in such substances differ to a considerable extent from the processes occurring in rather coarsely dispersed aerosols and thick films and, particularly, from the reactions proceeding in usual liquid or solid solutions. This specificity is connected with the fact that the values of evaporation, hardening and stratification (segregation) rates for a disperse material depends on the sizes of disperse objects in a reciprocal square manner. In turn, all this results in crucial distinctions in the bulk structures of chemical material for fine and coarsely dispersed objects and, hence, in different mechanisms of chemical reactions occurring.

Key words: photochemistry, photosensitization, photolysis, aerosols, pesticide, atmosphere

INTRODUCTION

High-disperse aerosol state of matter represents a phenomenon widely occurring in the nature. Hundred million tons of aerosols are annually coming in the atmosphere. Their source is formed by the emission of aerosol particles from fires in forests and savannas, from volcanic eruptions, sea spray and blowing dust, as well as by the atmospheric emission of gaseous metabolic products from terrestrial vegetation and the subsequent formation of an aerodisperse phase. The man-caused contribution is connected with chemical and mining industry, heat-and-power engineering, motor transport exhausts as well as with the application of pesticides in agriculture.

Chemical reactions occurring in the atmosphere (oxidation reactions, the reactions with OH radicals, ozone, with nitrogen and sulphur oxides, as well as photochemical and catalytic reactions), result in the chemical transformations of atmospheric pollutants, including the destruction of the latter to yield rather safe chemical compounds. There are strong grounds for believing that photochemical reactions due

to sunlight could play a very important role. It is the photochemical stage of destruction representing a multistage process, which often determines the mechanism and rate for chemical transformation of atmospheric pollutants.

What the lines of investigations are connected with the photochemistry of disperse-state substances? Many works [for example, 1–5] were devoted to the studies on the reactions of atmospheric chemical impurities with reactive species occurring in the atmosphere (OH radicals, nitrogen oxides, ozone). These species are formed under sunlight; therefore all the processes with the participation of such species are referred to as “photochemical reactions”. However, these processes include not only light-induced formation of primary radicals, but also they could be accompanied by a number of so-called dark chemical reactions, as well as by meteorophysical processes (such as the formation of the temperature and concentration distributions throughout the height, convection reagent transportation within the atmosphere).

In this connection the reactive species and their reactions occur not only under sunlight, but also during the dark time, *i. e.* at night,

thus these processes could be considered as photochemical ones only by convention. Moreover, these reactions use to proceed in the gas phase (for example, the reactions with the chemical compounds in the form of vapour) so formally they are not inherent in the aerodisperse state. However, these gas phase reactions could result in the formation of low-volatile substances those might represent a material for the nucleation and growth of aerosol particles in the atmosphere. Another research field is connected with the ability of OH radicals and other species to react with the molecules adsorbed on the surface of so-called atmospheric aerosols those are permanently present in air [6–8]. In this case the surface of a particle plays the role of a substrate which the substrate can be either chemically inert or catalytically active one. In the case of the (photo)catalytic activity the reactions on the surface of aerosols could be considered as an essential factor for atmosphere detoxification from chemical pollutants [9, 10].

The research work carried out at the Institute of Chemical Kinetics and Combustion (ICKC), SB RAS (Novosibirsk, Russia) during last decade was devoted to the studies on the photolysis of disperse objects when light absorbed by an aerosol particle or very thin film initiates chemical reactions directly within the volume of an object. There are only scarce publications available in the literature concerning the investigation of intra-aerosol light absorption and chemical reactions proceeding inside the object [5]. To a certain extent, this research field includes the works concerning photodegradation of polymeric films [11, 12] where (photo)chemical reactions in the bulk occur, and impurities (for example, (photo)sensitizers) and oxygen diffusing within the volume of a particle play an important role. However, the processes proceeding in polymeric films essentially differ from those under our investigation, since the films represent rather “thick” objects (the thickness amounting to 5–10 μm and more) with a known chemical composition and the immobile bulk structure. On the contrary, chemical and bulk structures of real fine-dispersed objects, especially as applied to natural atmospheric conditions, are variable and difficult to predict.

PHYSICOCHEMICAL FEATURES OF CHEMICAL REACTIONS OCCURRING IN THE HIGH-DISPERSE STATE OF MATTER

As it was mentioned above, there are extremely few works on the photolysis of aerosol-state substances available from the literature. It is partly connected with the fact that only extremely low volatile organic substances (with the saturation vapour pressure value ranging within 10^{-4} – 10^{-10} Pa and lower at standard temperature) can form fine-dispersed aerosol particles (for example, of 1 μm in size and smaller) with the lifetime in the atmosphere amounting to hours, days and years.

Micrometer-sized particles those consist of more volatile substances use to evaporate during a very short time such as minutes, seconds, fractions of a second. In this connection, “usual” organic substances with the molecular mass less than 200–250 and a relatively high volatility, as a rule, do not form a long-living high-disperse phase. In turn, it should be noted that the data obtained under the photolysis of substances in the form of usual liquid and solid samples (so to speak, in a “test tube”) ought not be directly extended over the processes proceeding within fine-dispersed particles and films. This also concerns relatively thick dispersed objects in the form of particles and films with size/thickness of several tens and hundreds micrometers since the high-disperse state itself can in a critical manner influence the rate and mechanism of physicochemical transformations and chemical reactions in matter.

Firstly, the size of aerosols determines the character of light dispersion and absorption, this dependence being nonmonotonic. As a rule, aerosol systems are polydisperse (*i.e.* they consist of the particles of different sizes), which complicates the measurement of total and, especially, of partial the amounts of light absorbed by aerosols of different size.

Secondly, for a chemical reaction within the volume of a particle to proceed, diffusion of oxygen and of other reacting molecules is sometimes required. The diffusion rate is to a considerable extent dependent on the size of aerosol particles (according to a reciprocal square law, *i.e.* inversely proportional to the square of particle diameter).

Thirdly, the evaporation rate of individual chemical components from the particles depends on the sizes of aerosol in a reciprocal square fashion. During the evaporation of relatively volatile substances (for example, solvents) from initially multicomponent aerosols the chemical composition and the size of the latter are progressively changing and the most rapid changes can be observed for most fine particles. Consequently, an aerosol system that is non-uniform with respect to particle size (polydispersed system), but originally homogeneous with respect to the chemical composition of the particles tends to become chemically non-uniform one in the course of time. On the other hand, it results both in simplifying the chemical composition of particles and in simplifying chemical reactions within.

Fourthly, if a reactive species (for example, an OH radical) penetrates inside a fine object from air, one can consider the possibility of its reiterated contact within the bulk with the molecules of condensed matter forming the particle (film). In other words, for a disperse particle a kind of "cage effect" well-known for radical reactions in the condensed phase is observed. The effect of dispersity in this case is manifested by the fact that the surface-to-volume ratio value (for the surface area the reactive radicals penetrate inside the particle and the particle volume where a chemical reaction occurs), increases as decreasing the object size/thickness.

Fifthly, during the evaporation of solvents the phase state of a particle can change from an initial liquid composition to a final viscous or solid one. As it is well-known, the diffusion rate value for reacting molecules (for example, oxygen) in the solid or viscous media is on several orders of magnitude lower as compared to the diffusion rate in the liquid. On the other hand, within the porous structure of the formed solid aerosol, to all appearance, the diffusion of oxygen and other gaseous reagents through pores directly inwards the particle occurs more rapidly. Such opposite diffusion rate dependences on the phase state and the structure of a material can in a complicated manner influence chemical reactions of aerosol matter.

Sixthly, relatively "light" products formed in the course of a chemical reaction (for example, due to the destruction of the molecule of

an initial "heavy" component) exhibit an increased volatility and can quickly evaporate from a high-disperse object. Thus, these products cannot be kept inside and therefore cannot be further involved in chemical and physicochemical transformations.

Seventhly, after the evaporation of solvents the residuary particle usually represents a composition consisting of one, two or three the most low-volatile components of an initial preparation. For example, in the case of sensitized photolysis this final solution could consist of the sensitizer substance and the component under photolysis. In such a solution both the molecules of the sensitizer (the donor of excitation) and the substance under photolysis (the acceptor of excitation) constantly contact each other, which results in the excitation transfer from donor to acceptor according to the resonant exchange mechanism. It is obvious, that such a process is impossible for usual solutions in a "test tube" where the molecules of a solvent serve as buffer agents and to prevent a direct contact between donor and acceptor molecules.

Moreover, such a situation cannot be practically realized within a "thick" particle several tens and hundreds micrometers in size, since due to the reciprocal square-law dependence of the evaporation rate on the object size a lot of days, months and even years could be required for the evaporation of buffer components from "thick" object. Hence, in this case the possibility of the formation of a two-component solution of donor and acceptor is practically excluded. Moreover, under photolysis of fine-dispersed objects in some cases, almost full absorption of photochemically active UV light is observed at particle size amounting to several tenth fractions of a micrometer. It is evident that in the case of "thick" object light cannot penetrate its depth and could not exhibit photochemical effect on internal substance layers.

Eighthly, as far as evaporation and hardening of the material of particles occurs the translational motion of molecules become complicated or completely ceased, the rotation and bending vibrations of separate molecular segments being constrained. All this could prevent the system from the formation of a required orientation of reacting molecules (such as activated complex), which might result in an in-

crease of the activation barrier, *i.e.* in the complication of chemical reaction as compared to the liquid phase. Such effects are well-known for the reactions occurring in polymeric materials [12, and references therein]. As applied to the reactions in fine-dispersed matter it should be noted that the object under investigation in this case always represents the system of polydisperse aerosols or a thin film of a relatively large area (within the range of 5–10 cm² and more rather than an individual aerosol particle or a microscopical part of the film).

The substance evaporation rate and, therefore, the rate of hardening depend on the size/thickness of disperse objects, so the real polydisperse system includes the objects with a different evaporation and hardening level, as well as with a different level of structural order or disorder of the substance under hardening. It is just the reason of the fact that the above mentioned steric effects in aerodisperse systems are difficultly predicted and could not always be reproduced.

Ninthly, the above mentioned spatial restrictions in movement, rotation and vibrations of molecules and molecular segments within (quasi)solid disperse objects can promote, on the other hand, the formation of stable energy "traps" for radicals and free electrons. Within such the traps those are not destructed due to bending vibrations or rotations of molecular segments, radicals or electrons might exist for a relatively long time, even at not-too-low temperatures. Moreover, such structural features of disperse matter could promote a singlet-to-triplet interconversion of photoexcited molecules and the subsequent triplet-triplet light quanta absorption (so-called two-quantum photochemistry [13]).

Tenthly, during the evaporation of solvents from a particle and the subsequent hardening of the latter, volume segregation (stratification) of residuary components could occur. Indeed, within an initial liquid particle these components (for example, solid substances) are dissolved in any solvent common with respect to each of them. However, after the solvent evaporation the residuary solid compounds could not be necessarily mutually soluble, in particular for any ratio values. From the point of thermodynamics, these insoluble components have

to form individual phases inside a particle, *i.e.* they should be spatially separated from each other.

Let us assume that a certain chemical reaction can proceed between these components. It is obvious that this reaction could take place within a liquid particle, but within a stratified object the possibility of the reaction occurrence is excluded due to a spatial separation of reactants. The mutual solubility of substances is, more likely, an exception rather than a rule; therefore the solid (viscous) aerosols formed during the evaporation of liquid particles would mainly be spatially stratified. The rate of chemical reactions in such objects must decrease steeply as the components undergo hardening and segregating.

Eleventhly, it was mentioned above that under the conditions of the thermodynamic equilibrium particle material under hardening must tend to the breaking down into individual components. However, practically this fact could neither take place. The point is that the formation of individual bulk phases is accompanied by the formation of the interfacial surfaces those separate the components from each other. Since energy input is required for overcoming the energy barriers necessary for their formation, the components under hardening can remain in the form of a non-equilibrium homogeneous mixture for a long time. Such non-equilibrium mixtures are referred to as "metastable solutions", they are described in physical chemistry, being sometimes observed even for vast volumes.

However, it is evident that the formation of metastable solutions is of most probability just for high-disperse objects, *i.e.* for aerosols and thin films. Really, the above mentioned energy barrier value that favours to the conservation of the metastable state is proportional to the surface of a particle, *i.e.* to the square of the particle diameter. The gain in energy connected with the spatial separation of matter, is proportional to the volume of a particle, *i.e.* to its cubed size. The surface energy/volume energy ratio would increase as the thickness of particles (films) decreased, which results in the fact that high-disperse objects could remain in the metastable state for a long time. Thus, one may draw the following conclusion: a lot of chemical reactions within fine-dispersed objects occur due to the fact that the substance

stays in a non-equilibrium solution. In the event that a metastable solution is spontaneously or forcedly transformed towards equilibrium, the reactions could be braked or stopped due to the spatial separation of reagents.

Thus, the photolysis of substances in fine state of matter differs to a considerable extent from photochemical processes within usual liquid or solid solutions, and even from the photolysis occurring in "thick" disperse objects of several tens or hundreds micrometers in size. (In view of the fact that there is a reciprocal-square-law dependence of the evaporation rate on the object size observed and, hence, the components hardening and stratification rates being several orders of magnitude lower than those for fine-dispersed objects, many of aforementioned processes would be non-competitive.) Moreover, the interpretation of the results for the photolysis of dispersed systems will be always complicated by the fact that the stratification of a fine-dispersed material uses to arise spontaneously, *i.e.* in an unpredictable and difficultly reproducible manner.

SENSITIZED PHOTOLYSIS OF PESTICIDE CHEMICALS AS APPLIED TO NATURAL ATMOSPHERIC CONDITIONS

As it was emphasized in the previous section, only low-volatile substances can form long-living particles with the sizes $<1 \mu\text{m}$ or thin films with the thickness of several tenth or hundredth fractions of a micrometer. There is an additional problem in the choice of chemical reagents for studying chemical reactions within disperse objects. The point is that the mass of an individual particle of $1 \mu\text{m}$ in diameter, as estimated, is less than 10^{-12} g. At the same time, chemical changes and the change of mass could not be registered in practice for such a small object, therefore one needs to operate with the group of aerosols consisting of several hundreds thousand or millions of particles. Their total mass could amount to several fractions of a microgram or several micrograms. However, even such a relatively great amount requires for the choice of special chemical compounds as research objects.

In order to study the photolysis of chemical compounds in the disperse state, we used so-

called pesticide substances. On a global scale, the total amount of pesticides used ranges within 1.5–2 million tons per year, and the most part of them in one way or another enters the atmosphere and arrives at plants, being present as aerosols within the atmosphere and as a film/deposit on the surface of plants. In the main, pesticides represent low volatile compounds capable to exist for a long time as aerosols and thin films. Many of them could be registered with a high sensitivity using gas chromatography technique with an electron capture detector, which allows one to watch chemical transformations and the change of mass within the aerosol system or thin film under investigation.

Pesticides themselves represent either series of organic substances those do not differ from other members of these series regarding chemical properties. However, it is commonly supposed that pesticides represent environmentally hazardous pollutants of atmosphere, vegetation, soil and water. Negative consequences from the application of pesticides are often connected with their persistency, *i.e.* the stability under natural conditions. Ideally, pesticides should stay on the surface of plants only during the period of time necessary to the biological effect required then they ought to decompose into harmless substances.

The pesticides those are present in the atmosphere in the form aerosol particles should be considered as pollutants, thus they need to be rapidly destructed. There are strong grounds to believe that photochemical destruction occurs under sunlight irradiation of pesticides, thus the environmental detoxification is provided. However, the majority of pesticides use to absorb active UV light only with the wavelength value less than 290–300 nm, but it is just this wavelength range of sunlight that is completely absorbed by a stratospheric ozone layer and does not reach the atmospheric bottom layer. In this connection the majority of pesticides show rather high stability in an environment.

One of the possible ways to accelerate photodestruction consists in adding a special chemical substrate to the pesticide preparation which substrate would absorb the circumterrestrial sunlight with the wavelength values more than 290–300 nm in order to further transfer the excitation to pesticide molecules, *i.e.* to sensi-

tize the pesticide decomposition. This idea was expressed in the literature repeatedly; however, despite of a number of interesting results, there are no data concerning practical use of sensitizers for carrying out the pesticide treatment of plants in the agriculture. Perhaps, this fact is connected with the absence of a universal, inexpensive and environmentally safe sensitizer suitable for practical application.

From 1990th up till now laboratory and field investigations connected with aerosol-based using of pesticides in agriculture and forestry are being performed at the Laboratory of disperse systems of the ICKC, SB RAS. One of the research fields consists in the studies on the physicochemical mechanism of the evaporation of pesticide components from polydisperse aerosol systems and the kinetics of photochemical decomposition of pesticide aerosols and thin films as applied to natural light and temperature conditions. It is necessary for quantitative forecasting estimations of environmental consequences from aerosol application of pesticides. By the present time more than ten the modern pesticide preparations widely used in Russia and in the world have been studied [14–19]. As the properties of these preparations studied, the above mentioned features of physicochemical transformations and the chemical reactions, inherent just in the high-disperse state of matter have been found out.

Figure 1 demonstrates the temperature dependence of pesticide evaporation rate from polydisperse system of aerosols with the median mass diameter $d_m \approx 2 \mu\text{m}$ and the standard geometric deviation $\sigma_g \approx 1.8$ for pesticide propiconazole (Tilt preparation of 25 % EC). Basing on the data obtained, taking into account both the parameters of logarithmically normal aerosol distribution of aerosols throughout the particle sizes and the suggested model for pesticides evaporation from chemically multicomponent aerosols we have determined the temperature dependence for the evaporation rate of pesticides both from the system of polydisperse aerosols, and from individual particles of arbitrary size.

In addition, the temperature dependence of vapour concentration (saturation pressure) unknown earlier for propiconazole and some other pesticides [14] have been determined. Figure 2 demonstrates the dependence of the ef-

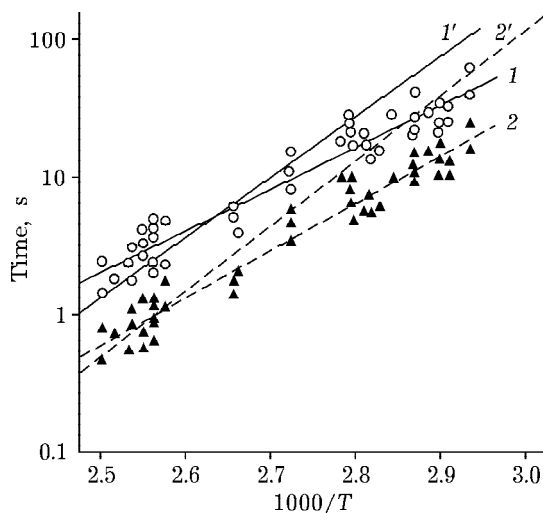


Fig. 1. Temperature dependences of the characteristic time for pesticide propiconazole evaporation from chemically multicomponent aerosols: 1, 2 – experimental data for the system of polydisperse aerosols with so-called power and exponential laws of evaporation, respectively; 1', 2' – that for the evaporation of individual particles with the median mass diameter of $2.03 \mu\text{m}$ with power and exponential laws of evaporation, respectively.

fective photosensitized decomposition rate for insecticide acrinatine (Rufast preparation of 15 % EC) on the relative amount of Shirvanol-2 sensitizer [17]. One can see that without the sensitizer there is no considerable photodecomposition of acrinatine (as well as of some other pesticides) observed under sunlight or its laboratory analogue. On the contrary, when the sensitizing substrate added, the photolysis proceeds rather quickly, this could be of practical value from the environmental point of view. Moreover, it can be seen that sometimes the photolysis rate for no apparent reason decreases several times. It is connected with an effect of spatial stratification between the Shirvanol-2 sensitizer and pesticidal substance acrinatine, which results in breaking the excitation energy transfer from the sensitizer to the pesticide molecules. Similar effects were observed, though with a different intensity, almost for all pesticide preparations under our investigation, [17, 18].

The authors of [19] revealed an effect unknown earlier in atmospheric chemistry that consists in the fact that so-called hydrodynamic viscous boundary layer influences the chemical reaction occurring between pesticide substance (in the form of either aerosols levitating in ambient air or aerosols settled on the sur-

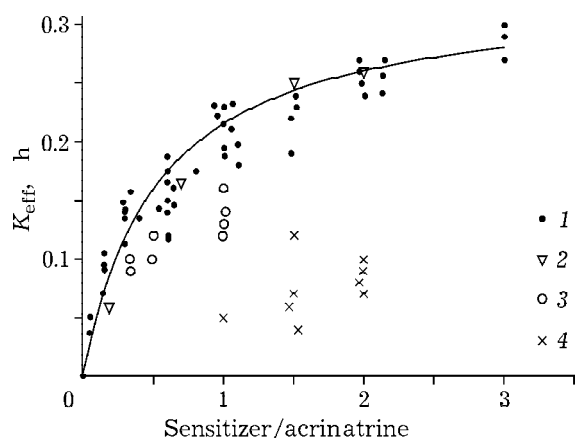
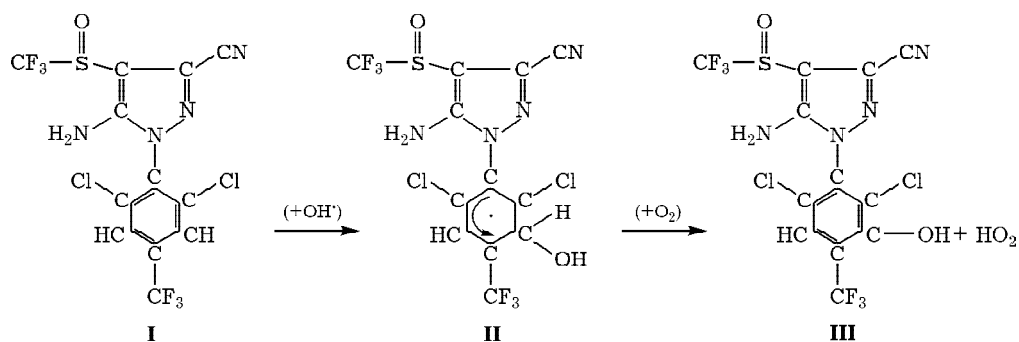


Fig. 2. Dependence of the photolysis rate constant for pesticide acrinatine on the sensitizer/acrinatine mass ratio in disperse object: 1, 3 - Rufast preparation (1 - thin film, 3 - aerosol); 2 - pure acrinatine (thin film); 4 - the experiments when a stratification of the pesticide and sensitizer spontaneously occurred; solid line is an approximating curve for the rate constants.

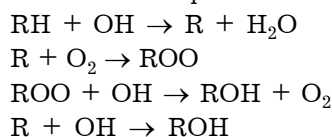
face of plant leaves, or thin films/deposits of pesticide on the surface of plants) and OH radicals penetrating into these objects from the atmosphere. It was established that thin films of pesticide fipronil (Adonis preparation of 4% EC) applied onto glass substrates (the imitation of the surface of plant leaves with a pesticide deposit) under keeping for a long time (during 3-7 days) in the open air undergo a chemical reaction with OH radicals those are always present in ambient air at the concentration of $(0.5-5) \cdot 10^6 \text{ cm}^{-3}$ depending on the time of a day and on a season.

Scheme 1 demonstrates a hypothetical chemical mechanism of this "dark" reaction; here **I** is an initial pesticide substance such as fipronil, **II** is an intermediate adduct arising due to the introduction of OH radical into the aromatic



Scheme 1.

ring, **III** is the end product identified using the chromatography/mass spectrometry assay. These reactions agree with the mechanism suggested by the authors of [1, 2], however there are also other possible routes, such as



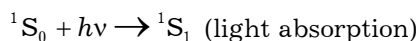
where RH is the initial molecule of fipronil **I**, ROH is the end product **III**. This mechanism is less probable due to the square-law dependence on the concentration of OH radicals. However, in this case intermediate radicals R and ROO are fixed within (quasi)solid material of an aerosol particle or thin film. The rigid structure of the material prevents R and ROO radicals from translational displacement, rotation and bending vibrations; due to this fact the radicals can stay within a solid matrix for a long time waiting for the arrival of relatively OH mobile radicals.

As seen from the reaction mechanisms, the influx of OH radicals onto the surface of a particle or of a film from ambient air is determining. This flux includes: firstly, the convection transfer of remote radicals towards the surface of an object; secondly, the diffusion transportation of these radicals across so-called viscous boundary layer of the motionless air adjoining to the surface of an object; thirdly, the diffusion of the radicals through the substance of the fine-dispersed object accompanied by chemical reaction.

Experimental measurements and theoretical calculations carried out in [19] have shown that for fipronil staying in ambient air in the form of free aerosol particles the chemical reaction rate limitation connected with the diffusion of

OH radicals through the boundary layer around of particles is insignificant. In this case chemical conversion of fipronil **I** → **II** → **III** in ambient air should occur within several minutes for the particles of 2 μm in diameter, and within 12–24 h for the particles of 20–30 μm in diameter. In the case of fipronil within aerosols settled on the surface of leaves, or of a fipronil film/deposit formed after spreading and drying the water-pesticide drops those came upon plants while spraying, the reaction rate with OH radicals will be determined by the OH diffusion through the mentioned boundary layer.

From the analysis of experimental data and gas-dynamic estimations it follows that the conversion such as **I** → **II** → **III** would take place only within the range of 22–85 days. Except for reaction with OH radicals, competing photochemical reactions were revealed those provide almost comprehensive chemical transformation of fipronil films and deposited aerosols during 8–25 days [19]. One of such processes represents a sensitized oxidation such as **II** with the participation of reactive singlet oxygen. A simplified scheme of the oxidation process could be presented in the following form [20]:



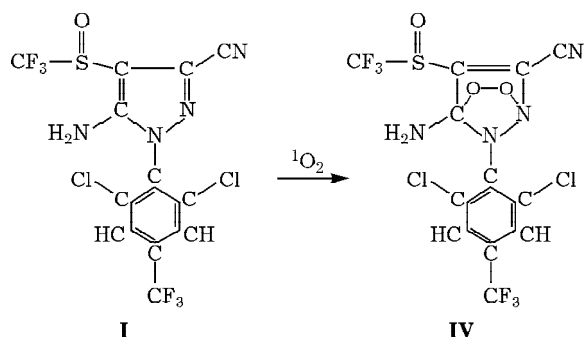
${}^1S_1 \rightarrow {}^3S_1$ (interconversion into the triplet state)

${}^3S_1 + {}^3O_2 \rightarrow {}^1S_0 + {}^1O_2$ (the formation of reactive singlet oxygen)

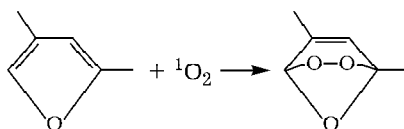
${}^1F_0 + {}^1O_2 \rightarrow {}^1(FO_2)_0$ (the formation of an oxidation product)

where S is the sensitizer molecule; 1S_0 , 1S_1 , 3S_1 are the ground singlet state of the sensitizer, the first excited singlet and the first excited triplet terms, respectively; 3O_2 is the ground triplet state of the molecule of oxygen; 1O_2 is the excited singlet oxygen (${}^1\Delta_g$ and ${}^1\Sigma_g^+$ are possible terms of excited singlet oxygen); F and FO_2 are the initial molecule of fipronil and the product formed due to the addition of a singlet oxygen molecule to fipronil, respectively. Thus, the photolysis of fipronil ultimately consists in the introduction of reactive singlet oxygen into the molecule of fipronil resulting in the formation of a new chemical compound such as **IV**. The introduction of oxygen occurs,

to all appearance, into the pyrazole ring of fipronil with the formation of a peroxide group:



The structural formula of the product **IV** is in a good agreement with the chromatography/mass spectrometry data [19]. This compound is considered to be chemically unstable; therefore it is, to all appearance, merely an intermediate product of photolysis. However, one should take into account the fact that this species being fixed within a rigid matrix formed by a (quasi)solid material of a fine-dispersed object could exist for a rather long time. This supported by our observations of thin films both of this compound and of other chemically unstable substances such as furan ozonide formed due to the introduction of singlet oxygen into the furan group of pesticide resmetrine [16]:



CONCLUSIONS

The aerodisperse state of matter represents a phenomenon widely occurring in the nature connected with atmospheric chemical, meteorological and physicochemical processes. The character and rate of these processes are to a considerable extent and in a difficultly predicted manner dependent on the dispersity level of a substance. In this connection the kinetics and mechanism of (photo)chemical reactions within high-disperse substance could crucially differ from corresponding processes within rather coarse-disperse objects.

As applied to real atmospheric conditions, kinetics and mechanism were studied for di-

rect and sensitized photo-destruction of some chemical pesticides in a high-disperse state, namely in the form of aerosol particles with the diameters ranging from several tenth fractions of a micrometer to several micrometers as well as in the form of thin films with the thickness ranging from several hundredth fractions of a micrometer to several micrometers. It has been shown that using the features of the chemical mechanism of the photolysis of these substances, one could control the photochemical destruction rate of pesticide impurities both in ambient air and on the surface of plants. The chemical destruction of substances in the nature represents a multistage process; however photochemical stages can often be a rate-determining factor for the overall process of natural environment detoxification from pesticide pollutants. In this connection the controllable (photo)destruction of pesticides can be of practical value.

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