

CHEMISORPTION AND THERMAL DECOMPOSITION OF POLYVINYLPIRROLIDONE ADSORBED BY PYROGENIC SILICA AS MODEL OF SURFACE REACTIONS ON ATMOSPHERIC MICROPARTICLES

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Abstract

Thermal decomposition of polyvinylpyrrolidone (PVP) in bulk and adsorbed on ultra-fine silica surface was studied as a model of thermal transformation of anthropogenic environmental pollutants on the surface of atmospheric micro-particles.

Three stages of polymer decomposition with maxima at 150, 280 and 360°C were observed for bulk samples of PVP of average molecular mass about 10 000. Pyrrolidone (m/z 85) was the main product resulting from elimination of side groups in main polymer chain. Rupture of main chain itself resulting in elimination of vinylpyrrolidone (m/z 111) was the main process at high temperature and occurred in single stage with maximum at 360°C.

Thermal decomposition of PVP thin layers on the surface of ultra-fine pyrogenic silica was also studied. Samples were obtained by adsorption of PVP on Aerosil A-300 surface and contained 5.8, 16.9 and 29.3 mass % of polymer. Unlike to silica-free samples, only two maxima of 85 m/z elimination (at 120 and 360°C) were observed, majority of pyrrolidone being produced during the high-temperature stage. Details of polymer decomposition depended essentially upon portion of adsorbed PVP. The conclusion was done that adsorption slows down the conformation exchange and effects the process of polymer decomposition.

Introduction

Aerosols are liquid or solid particles that are present in Earth atmosphere. They have diameters from 1 nm to over than 10 μm , most of their mass being in the size range from about 0.1 to 2.5 μm . They originate from a wide variety of natural and anthropogenic processes that exhibit a large spatial and temporal variability. The production mechanisms are: (1) direct injection of particles in the atmosphere, mostly by dispersion processes resulting in so-called primary (and coarse, that is $> 1 \mu\text{m}$ aerosols) and (2) transformations of inorganic and organic gaseous precursors into secondary (and fine, $< 1 \mu\text{m}$) aerosols. Aerosols play an important role in atmospheric chemistry, have effects on human and animal health and welfare and also influence climate. Recently, renewed interest in the health risks of aerosols had been generated by the finding correlation between increased mortality and the concentration of fine airborne particles in metropolitan areas in the United States [1].

Inadequately controlled aerosol pollution of the Earth's atmosphere by products of human industrial activity had already caused some unpredictable consequences due to shift of naturally occurring well-balanced chemical reactions in completely unexpected ways. Aerosols and dust micro-particles of industrial origin provide surfaces for heterogeneous reactions involving stages of adsorption of individual compounds from the gas phase and desorption products. Oxide micro-particles carbonized by the products of combustion are the main dust pollutants of the atmosphere in industrial areas where the coal is a fuel. Though the effect of such dust micro-particles on the human organism has not been studied in detail, it is clear that chemical reactions of

coal is a fuel. Though the effect of such dust micro-particles on the human organism has not been studied in detail, it is clear that chemical reactions of biologically neutral compounds on the surface of carbonized oxide particles may result in their catalytic transformations into toxic compounds. Despite the large body literature on the investigation of aromatic properties and their reactions a lot of questions on the mechanisms of transformation of such compounds remains.

Mass spectrometry is a method of choice in those studies since it provides ideal experimental pressure, temperature and ionization conditions for the simulation of real processes in the atmosphere. Common interest in the application of the developed powerful mass spectrometric techniques to the urgent problems of the Earth science which relate to pollution control of human environment has brought together Swiss and Ukrainian research teams in the framework of the project "Chemisorption and decomposition of toxic compounds on oxide micro-particle surfaces" co-ordinated by Prof. Renate Zenobi, Head of Analytical Chemistry Department ETH, Zurich. Results obtained in this project promoted further investigation of surface reactions on the surface of ultra-fine particles modeling atmospheric aerosols [2-11] and lead authors to understanding the necessity of investigation of thermal decomposition of polymer systems adsorbed on the ultra-fine oxide surface.

PVP was chosen as a model system. This polymer is known to possess a set of physico-chemical properties providing its efficient interaction with silica surface. On the other side, it is used in pharmaceuticals industry as a component of medicines. It stimulated our interest to studies on thermal transformation of PVP in sub-molecular layers of PVP on ultra-fine silica.

Experimental

Medical PVP produced by «Sintvita», Russia, was used in present study. Average molecular mass was 10700 Dalton. PVP produced by K-15, Fluka and another batch of PVP produced by «Sintvita», Russia, were used as reference samples. Pyrogenic silica was Aerosil A-300, with surface area 320 m²/g, produced by «Khlorvinyl», Ukraine.

The procedure of sample preparation was as follows. 10% aqueous solution of PVP in distilled water was prepared as well as dispersion of silica. The calculated amount of PVP solution was added to dispersion, thoroughly mixed, and after one-hour-pause deposited as a thin layer on glass surface. Then samples were dried at the temperature 80 °C for 4-5 hours. The product was then dispersed and additionally treated for 1 hour at the temperature 80 °C.

Carbon contents was measured by express analyzer AN-7529, Russia, by burning samples in oxygen flux at 800 °C. Specific surface area of thus prepared samples was estimated by low temperature argon desorption.

IR spectral measurements were conducted on M-80 apparatus (Karl Zeiss, Jena). Spectra of individual PVP samples were measured being preliminarily pressed with KBr (2.5 mg of PVP in 300 mg of KBr); silica-containing samples were pressed at 30 atm to obtain pellets of density 12-15 mg/cm².

Thermal decomposition of adsorbed polymer in oxygen-free atmosphere was analyzed according to the procedure described previously [2, 11]. Samples of about 1mg weight were placed in a quartz-molybdenum tube, evacuated at 10⁻¹ Pa and then attached to the inlet system of a MX-7304 (Ukraine) mass spectrometer. The reactor-to-mass spectrometer interface included a high-vacuum valve with an orifice of diameter 5 mm and the inlet tube of 20 cm length, which was kept at 150 °C. The reaction space was open in the ion-source direction, and at the heating rate used (about 0.1 K s⁻¹) the observed intensity of the ion current was expected to be proportional to desorption rate so that diffusion inhibition might be neglected. We assumed that quasi-stationary conditions were achieved when the shape and position of desorption peaks did not depend on the

Results and discussion

Good solubility of polymer in water allows obtaining water dispersions silica-PVP in wide range of component ratios. Presence of silanol groups on the silica surface as well as tertiary nitrogen and carbonyl groups in polymer molecule provided for strong adsorption interaction. It also has been shown that in the hybrid PVP-silica material the hydrogen bond formation has been observed binding silanol and carbonyl groups.

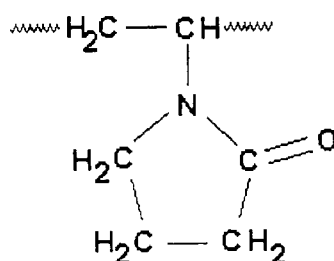
Properties of PVP-silica samples synthesized in accordance with previously described procedure are summarized in Table 1.

Table 1
Characteristics PVP-silica samples

Sample number	1	2	3
Content of carbon	3.8	11.0	19.0
Content of PVP (weight %)	5.8	16.9	29.3
Content of PVP (mmole/g)	0.52	1.52	2.64
Surface area, m ² /g.	258	183	65

It is clear from the table that specific surface area of the samples PVP depended upon amount of polymer on the silica surface. While amount of polymer increased, SiO₂ particles became larger and surface area decreased.

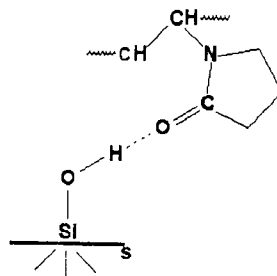
The molecular mass of PVP used in present study having average molecular mass was 10700, which corresponded to approximately 94 elementary links shown (see Scheme I), plus terminal groups



Scheme I. Elementary link of polyvinylpyrrolidone

The number of elementary links in Sample 1 (see Table 1) was chosen to be equal to the number of silanol groups on ultra-fine silica surface. But, as all the links of polymer cannot be distributed uniformly throughout the surface, IR spectra showed the presence of free valence SiO-H bonds (3750 cm⁻¹), not bound with carbonyl groups of PVP. Increase of polymer amount in Samples 1-3 resulted in increase of carbonyl group line intensity of IR specter and, simultaneously, in decrease of SiO-H line intensity up to its complete disappearance. Scheme II below illustrates the probable mechanism of interaction of elementary link with silanol group of the ultra-fine silica surface.

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Scheme II. Adsorption of elementary link on silanol group

Two mass spectra of adsorbed PVP decomposition are presented in Fig. 1.

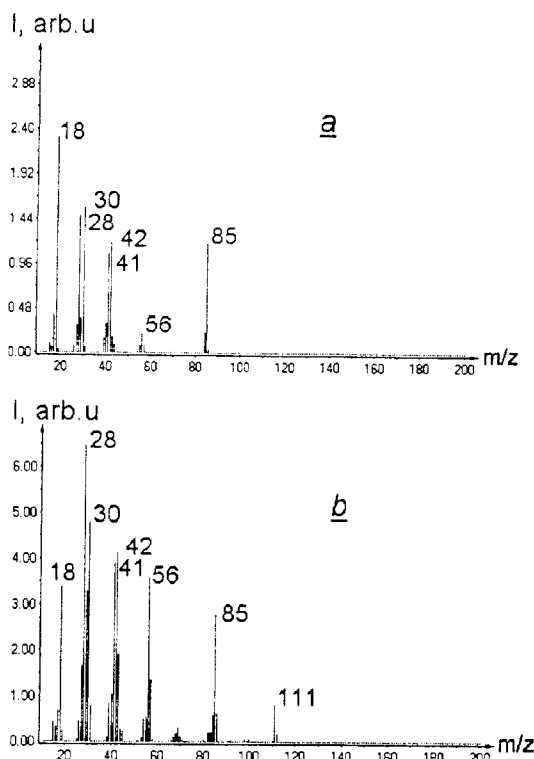


Fig.1. Typical mass spectra of adsorbed polymer decomposition at characteristic temperatures of about 130 (a) and 360 °C (b) corresponding to low-temperature and high-temperature maximum rates, as it is shown in Fig. 2 (a, b, c) below.

In Fig. 2. thermograms are presented of pyrrolidone (at 85 m/z) and vinylpyrrolidone (at 111 m/z) desorption in the whole temperature interval for six samples, three of which (a, b, c) are silica-PVP mixtures with different ratios of components, three others (d, e, f) are bulk PVP samples of different origin.

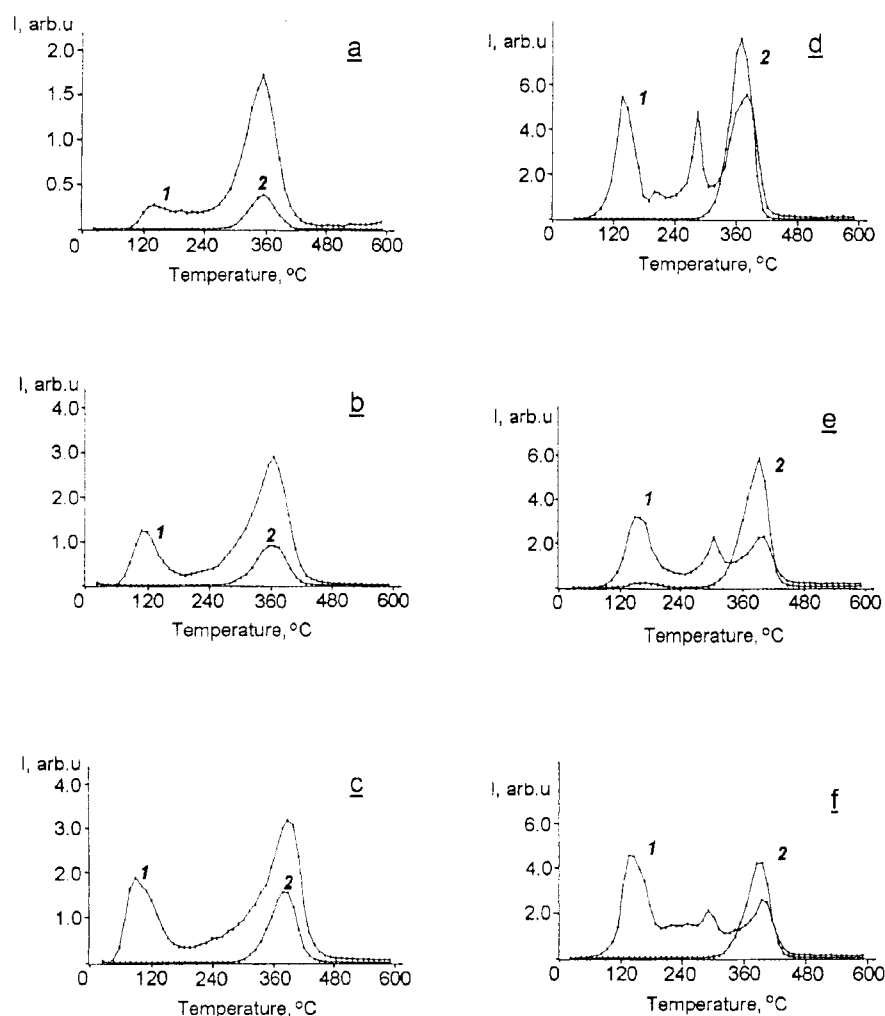


Fig. 2. Thermograms of pyrrolidone (1, $m/z = 85$) and vinylpyrrolidone (2, $m/z = 111$) resulting from PVP destruction: *a* - Sample 1; *b* - Sample 2; *c* - Sample 3; *d* - «Sintvita», Russia; *e* - K-15, Fluka; *f* - another batch of «Sintvita», Russia.

Quantitative mass spectrometric data for ten main components of mass spectra on thermal decomposition of Samples 1-3 and bulk PVP at two temperatures of maximum rate of polymer decomposition are summarized in Table 2.

As it is seen from presented data, the thermal decomposition of PVP thin layers was studied on the surface of ultra-fine pyrogenic silica in comparison with oxygen-free thermolysis in condensed state. Samples 1-3 were obtained by adsorption of PVP with average molecular mass about 10 000 on Aerosil A-300 surface and contained 5.8, 16.9 and 29.3 mass % of polymer. At least three stages of decomposition were observed for bulk, silica-free PVP, which resulted in formation of pyrrolidone ($m/z = 85$) as the consequence of elimination of side groups from main polymer chain. This process occurred in the whole temperature interval of decomposition and demonstrated maxima at 150, 280 and 360°C. Depolymerization of main

Table 2

Ten most intense components of mass spectra observed in TPD experiments of PVP-silica systems and bulk PVP at temperatures of maximum rate of polymer decomposition. Water intensity and most significant line are printed bold.

Sample PVP 1												
$T_{max}, ^\circ C$ 132												
m/z	28	30	85	42	41	40	44	29	27	56	111	H₂O
%	100	49.2	41.5	41.5	40.0	23.4	16.1	15.4	13.8	6.9	-	564
$T_{max}, ^\circ C$ 357												
m/z	28	30	41	42	85	56	27	29	40	43	111	H₂O
%	100	76.1	65.9	64.8	52.3	48.9	26.1	21.6	18.2	14.8	12.5	103

Sample PVP 2												
$T_{max}, ^\circ C$ 121												
M/z	30	28	42	85	41	29	27	40	56	84	111	H₂O
%	100	98.9	80.7	72.7	71.6	25.0	21.6	19.9	14.8	14.2	-	129
$T_{max}, ^\circ C$ 368												
M/z	28	30	42	41	56	29	85	43	27	57	111	H₂O
%	100	72.0	62.4	59.1	54.3	49.5	41.9	29.6	24.7	20.4	12.9	50.5

Sample PVP 3												
$T_{max}, ^\circ C$ 92												
M/z	28	30	42	41	85	29	27	40	56	84	111	H₂O
%	100	97.3	78.0	71.1	66.6	26.9	22.7	20.7	14.7	12.6	-	129
$T_{max}, ^\circ C$ 391												
M/z	28	56	30	41	42	85	29	27	43	40	111	H₂O
%	100	74.1	72.3	62.5	63.4	37.5	32.1	31.3	20.1	19.6	18.7	45.5

Sample PVP bulk												
$T_{max}, ^\circ C$ 151												
M/z	28	30	42	41	85	27	29	40	31	56	111	H₂O
%	100	72.1	63.9	62.8	59.9	30.2	22.1	17.4	16.2	14.0	-	23.3
$T_{max}, ^\circ C$ 393												
M/z	28	56	41	27	42	57	29	30	39	111	85	H₂O
ss%	100	88.5	41.6	40.7	39.8	32.7	27.4	26.5	25.7	20.3	11.5	7.1

chain resulting in formation of vinylpyrrolidone (m/z 111) occurred in one stage at temperature higher than 300°C and provided at this temperature main contribution to mass spectra.

Unlike to silica-free bulk samples, only two stages of 85 m/z formation were observed for PVP adsorbed on silica surface, their maxima being located at about 120 and 360°C. In adsorbed state the majority of pyrrolidone was produced in the process of the high-temperature stage. For silica-PVP samples, different to bulk samples, rupture of main chain resulting in formation of vinylpyrrolidone (m/z 111) was not the main process observed at 360°C.

It is to be noted also that, different to decomposition of bulk PVP, thermal decomposition of PVP on the silica surface resulted in carbonization. After vacuum treatment at 600 °C samples became black.

The thermal decomposition in all samples is similar as for molecular ion of vinylpyrrolidone (111 m/z). This ion appears mainly at the last high-temperature stage and is synchronized with other products of high temperature PVP decomposition.

It is interesting to note that ratio of maxima intensities 85 m/z (high-temperature/low temperature) was the greatest for sample 1 which contains the least amount of adsorbed polymer. And the ratio decreased while the amount of polymer increased. Also decreased the relative amount of other decomposition products and reached minimum for bulk samples. For example, for the ion at 41 m/z the high-temperature/low temperature ratio was 7.1, 3.4, and 3.0 for the samples 1-3 and was equal to 2.7 for the bulk sample.

It was observed that mechanism of thermal destruction of polymer at high-temperature also depended upon the amount of adsorbed PVP. The relative contribution of pyrrolidone in decomposition products increases with the increase of relative amount of adsorbed polymer. It means that in thin adlayer the rupture of pyrrolidone ring from main macromolecular chain is most probable. Increase of free polymer in the mixture provides increase of vinylpyrrolidone in the (111 m/z) in mass spectra as a result of destruction of main polymer chain, so that the ratio I_{85}/I_{111} becomes less than unit for bulk polymer.

The observed dependencies is most obvious from Fig. 3 in which ratios of intensities for m/z 85 and m/z 111 are presented at high-temperature maximum of decomposition as a function of PVP amount in pyrogenic silica presented in mass % of the mixture.

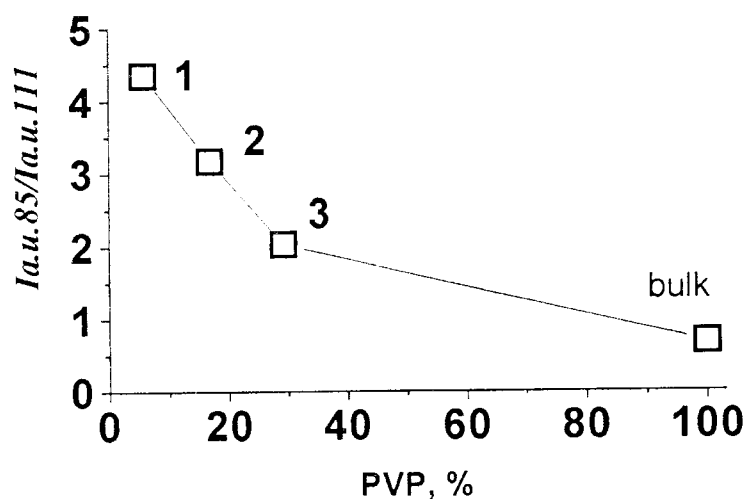
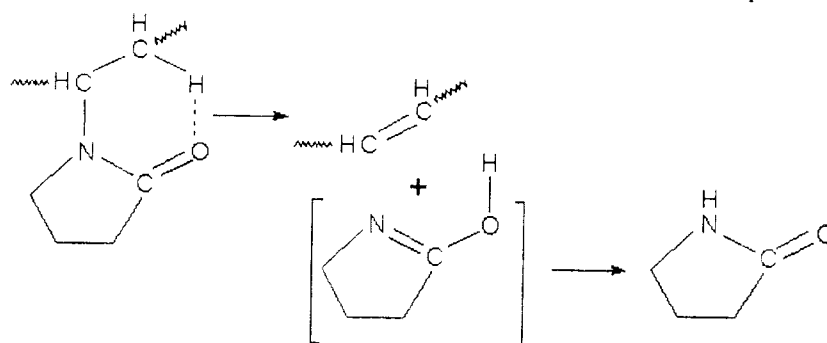


Fig. 3. Relative intensity I_{85}/I_{111} at high-temperature maximum as a function of mass percent of PVP in the mixture polymer-silica for three ratios of PVP-silica is presented (Samples 1, 2, 3). Point "bulk" corresponds to bulk PVP sample.

For polymers of vinyl containing series (polyvinyl ester, polyvinyl acetate, polyvinyl chloride) decomposition in bulk starts with rupture of side bonds in main polymer chain, as it is shown in Scheme III. Formation of hydrogenic bond between C=O group and silanol of the silica surface may block formation of such a complex and prevent from formation pyrrolidone as a product of polymer decomposition.

Summarizing obtained results, it should be stated that thermal decomposition of PVP in adsorbed state was characterized by decreased number of decomposition stages in comparison with bulk samples. Adsorption of PVP on the silica surface impeded the



Scheme III. Possible mechanism of destruction of polymer main chain.

rupture of pyrrolidone cycles from main polymer chain at low-temperature stage. Interaction of PVP with silanol groups of silica surface impeded the high-temperature depolymerization process resulting in desorption of vinylpyrrolidone. The conclusion was done that adsorption slows down the conformation exchange in PVP, thus effecting essentially the pathways of PVP thermal decomposition and displacing equilibrium to higher thermal stability of polymer chains. This fact should be taken into account in estimation of reaction pathways and rates on the surface of solid atmospheric microparticles of industrial origin.

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