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THERMAL DECOMPOSITION OF POLYURETHANE ELASTOMERS CONTAINING ANTIPYRENE

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Thermal analysis, IR and emission spectroscopy were used to study the influence of phosphorus and phosphorus/chlorine-containing antipyrenes on the thermal decomposition of polyurethane elastomers based on 4,4'-diphenylmethane diisocyanate and polytetraoxymethylene. The introduction of P-containing antipyrene into the structure of polyurethane elastomers induces changes in the mechanism and kinetics of thermal decomposition towards inactivation of the exothermal reactions of oxidative decomposition. It causes a shift of the first exothermal peak towards higher temperatures by 100° and helps the formation of temporarily stabilized structures. P/Cl-containing antipyrene has a smaller positive effect towards inactivation of the exothermal decomposition reactions and the formation of temporarily stabilized structures.

The use of antipyrene is one of the most common methods of reducing polymer flammability. For most antipyrenes the flame-proofing mechanism has not yet been explained. It is probable that the thermal decomposition of modified polymers is affected in a specific way. Study of the thermal decomposition of similar systems in a sufficiently wide temperature range would clarify the nature of the reactions proceeding and would help in the choice of a suitable antipyrene.

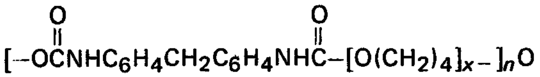
There have been quite a number of reports on the thermal analysis of various polyurethane polymers [1–5], including elastomers [6]. We have no information concerning thorough studies on the influence of flame-proofing additives on the thermal decomposition processes of polyurethanes. The directly proportional relations recently found between flammability tests and thermogravimetric and differential thermal analysis results [7] recommend a wider utilization of these methods for evaluation of the influence of antipyrene on different polymers.

In an earlier work [8] on the same polyurethane elastomers (PUE) modified with phosphorus and phosphorus/chlorine, a connection was found between their thermal behaviour (shift and intensity reduction of the first thermal peak) and the value of the oxygen index. This correlation gives information on the optimum concentration of antipyrene as concerns its effectiveness for combustion retardation. The aim of this work is a more detailed study of the transformations these polymers undergo upon heating, and the influence of antipyrenes on the thermal decomposition mechanism.

Experimental

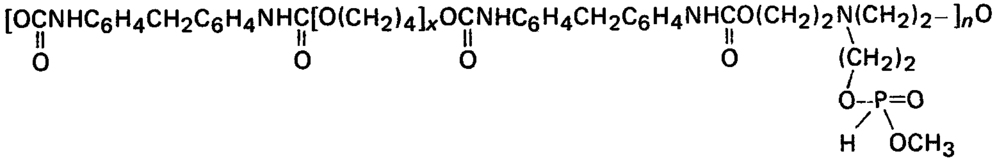
Initial polymers

(a) The initial polyurethane elastomer (IPUE) was based on 4,4′-diphenylmethane diisocyanate and polytetraoxymethylene:

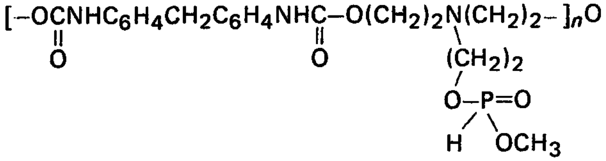


$$[-O\overset{\overset{O}{\|}}{C}NHC_6H_4CH_2C_6H_4NH\overset{\overset{O}{\|}}{C}-[O(CH_2)_4]_x-]_nO$$

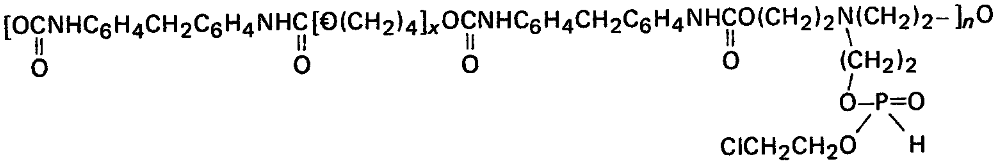
(b) Modified polyurethane elastomer based on IPUE, containing 0.8, 1.4 or 3.8 weight per cent phosphorus (MPUE—P):



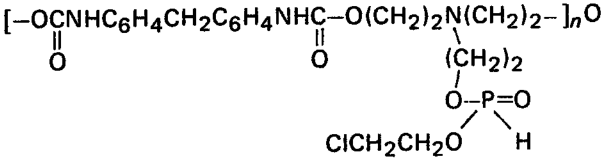
(c) MPUE containing 5.2% phosphorus, which has no polyoxymethylene fragment as an extender of the chain:



(d) MPUE bases on IPUE, containing 1.35/1.42, 2.20/2.34 or 3.40/4.04 weight percent phosphorus and chlorine (MPUE—P/Cl):



(e) MPUE containing 4.80/5.50% phosphorus/chlorine, without an extender of the chain:



MPUE without an extender of the chain was studied with regard to the influence of the structure on the thermal transformation.

All compounds concerned were in a nascent state. Their formation is reported in ref. [9].

Methods

The measurements were carried out with an OD-102 derivatograph (MOM, Budapest) under the following conditions: temperature range: 20–900°; average heating rate: 6 or 9 deg/min; initial weight of samples: 100 mg; error for weight loss allowed: ±0.5 mg; inert substance: Al_2O_3 (ignited); medium: air (static) or a continuous flow of nitrogen at 17 l/h was maintained during all measurements; sample holder: a platinum cone-like crucibel with diameters of 9.5 and 6.5 mm; the thermocouple was Pt/PtRh in the centre of the sample.

Taking into consideration the weight changes in the characteristic temperature ranges, the effective activation energy (E_{ef}) of thermal and thermooxidative degradation was calculated as in ref. [10].

Infrared spectra were recorded on an IR-20 instrument (Carl Zeiss, Jena, GDR), the samples being compression-moulded in a tablet of KBr.

Emission spectra were obtained on an ISP-30 instrument (Soviet Union).

Results and discussion

Thermal decomposition of IPUE

Figure 1 shows DTA, TG and DTG curves of IPUE in air and in an inert atmosphere. Thermal decomposition under these conditions is characterized by three stages:

Stage I. The first step of decomposition occurs up to 300° in air, with an exothermal peak maximum at 205°. In the temperature range of the exothermal peak, the TG curve indicated a weight increase of the sample by 0.5%. In a nitrogen atmosphere the exothermal peak becomes lower and is shifted towards higher temperatures, while no weight increase is observed.

Stage II. The region of the maximum rate of decomposition is 350–470°, with an extreme point at 405°. Figure 1 shows that the total thermal peak up to this temperature is exothermal, after which it abruptly changes its direction and becomes an endothermal peak with a maximum at 420°. Unlike the other recorded thermal peaks of IPUE, the intensity of the latter depends highly on the conditions of analysis (heating rate and weight of the sample), which is proof of its complex diffusion nature. Moreover, in this region the system loses 75% of its weight. In an inert atmosphere the quantity of the gaseous products decreases to some extent, while the total exothermal peak and therefore the quantity of heat evolved is several times less.

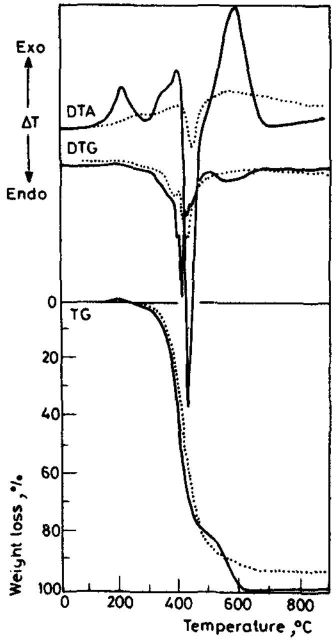


Fig. 1 DTA, TG and DTG-plots of IPUE: (———) in air, (– – –) in nitrogen; rate of heating 9°/min

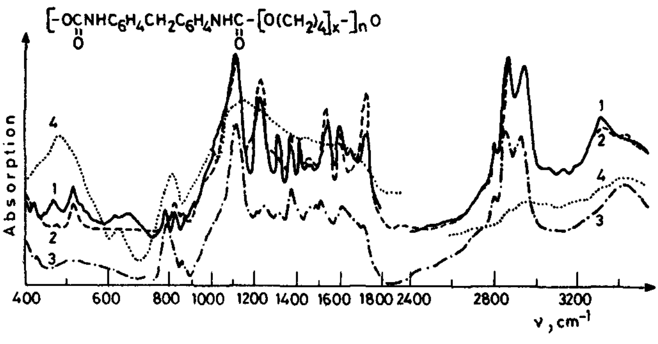


Fig. 2 IR-spectra of IPUE: 1 (———) IPUE; 2 (– – –) IPUE heated to 220°C; 3 (–·–·–) IPUE heated to 350°C; 4 (. . . . .) IPUE heated to 450°C

Stage III. After 470° a wide intensive exothermal peak is detectable, with a maximum at 580°. It is highly rounded on analysis in nitrogen atmosphere, however, the weight loss being insignificant in this temperature range.

In order to study the chemical transformations in each outlined stage of decomposition, IR spectra of IPUE were recorded before and after heating to characteristic temperatures (Fig. 2). Curves 1 and 2 show that the C=O group absorption at

Table 1 Values obtained for effective activation energy (E_{ef}) of thermal decomposition of the IPUE and MPUE–P

P-contain, %	E_{ef} – I stage, J		E_{ef} – II stage, J		E_{ef} – III stage, J	
	air	nitrogen	air	nitrogen	air	nitrogen
0	74.0	88.0	158.4	182.0	106.8	–
0.8	117.5	–	166.4	198.0	–	–
1.4	111.6	104.4	88.8	132.0	–	–
3.8	85.6	108.4	104.0	110.8	61.2	–
5.2	77.6	73.6	160.0	132.0	–	–

1720 cm^{-1} [11] increases after the first exothermal peak; in support of the thermogravimetric analysis (Fig. 1), this proves that oxygen from the air is involved. Up to 300°, only 3% of the weight of the product is lost. Therefore, if any decomposition reactions occur in this region, they result in solid products [3]. The main processes here are incorporation of peroxide and other radicals unstable at high temperatures into the polyester block [12], oxygen being the catalyst.

At 350° (Fig. 2, curve 3), C=O group absorption almost vanishes. This shows that with rise of temperature the oxidation products obtained decompose into radicals [5, 12], which determine to a great extent the rate of combustion. It is also evident from the IR spectra that on the heating of IPUE it is the urethane group that is mostly affected. The characteristic bands of CONH [13] at 1540 cm^{-1}, of C=O in a urethane group at 1735 cm^{-1}, and of NH in CONH at 1610 cm^{-1} are highly reduced, while the absorption of benzene nuclei in this region remains. The intensity of the NH band at 3300 cm^{-1} is reduced. The other bonds are little affected. The values obtained for the total E_{ef} of the first step of decomposition, conditionally established up to 350° and given in Table 1, correlate with the above description of IPUE thermal decomposition.

In the IR spectra recorded after the second stage of decomposition, at 450° (Fig. 2, curve 4), only very weak absorptions of an aromatic structure remain at 1600 cm^{-1}. As a result of oxidation processes, absorption bands of the C–C bond appear at 800 cm^{-1}, with a wide plateau at 1140 cm^{-1} due to oxidation products [14]. From these results as well as from the larger values of E_{ef} (Table 1), it follows that during the second stage of decomposition, besides heterolytic decomposition, processes of deep homolytic decomposition of the main structure occur.

Stage III is characterized by a complete combustion of the carbon residue in air, and incomplete combustion in an inert atmosphere.

Thermal destruction of MPUE–P

Phosphorus-containing antipyrenes are believed to influence mainly the solid-phase polymer, quickening the formation of protective layers on its surface. This would probably affect the tendency of the material towards oxidative decomposition.

Stage I. With MPUE–P the first exothermal peak is greatly reduced and shifted towards higher temperatures (Fig. 3). On the other hand, the IR spectra (Fig. 4, curves 1 and 2) do not reveal the increase in the C=O group absorption at 1720 cm^{-1} which was recorded for IPUE. Further, it was established (Table 1) that with samples containing the optimum concentration of antipyrene [8] the E_{ef} values are higher than those for IPUE and the other MPUE–P. Since each additive in the polymer usually results in a decrease of E_{ef} due to a break in the polymer structure, what is to be noted in this case is that the above antipyrene influence on the oxidative decomposition is exerted in its first and very important stage.

At concentrations of antipyrene above the optimum, a decrease of E_{ef} is observed; this is probably due to a break in the structure of the initial polymer. This effect of the broken structure is particularly clearly expressed in the case of MPUE–P (5.20% P), without an extender of the chain, with a highly decreased relative thermostability (Fig. 5), a considerable shift of the first exothermal peak towards lower temperatures (Fig. 3) and a decreased value of E_{ef} (Table 1) in comparison with the other MPUE–P.

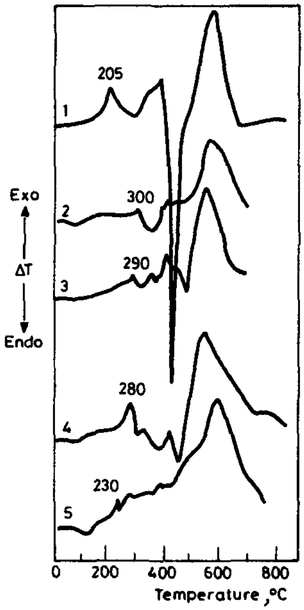


Fig. 3 DTA-plots of IPUE and MPUE–P: 1 – IPUE; 2 – 0.8% P; 3 – 1.4% P; 4 – 3.8% P; 5 – 5.2% P; heating rate 9°/min in air

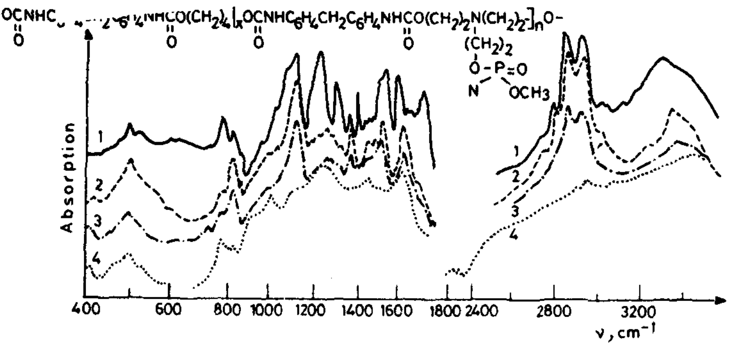


Fig. 4 IR-spectra of MPUE–P (3.8%): 1 (———) before heating; 2 (— — —) heated to 270°C; 3 (—·—·—) heated to 320°C; 4 (. . . . .) heated to 400°C

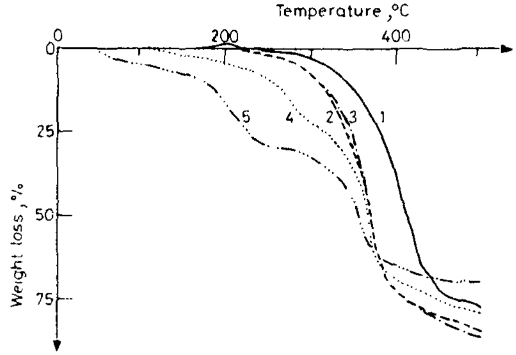


Fig. 5 TG-plots of IPUE and MPUE–P: 1 – IPUE; 2 – 0.8% P; 3 – 1.4% P; 4 – 3.8% P; 5 – 5.2% P; heating rate 6°/min in air

The decomposition of the polymer-antipyrene system begins at a lower temperature than for the initial polymer (Fig. 5). In the case of MPUE–P, decomposition starts with breaking of the weakest bonds (P–O–C) in the structure of antipyrene. From Fig. 4, curves 1 and 2 it is evident that the bands of P–O–C bond absorption at 1100–1000 cm^{-1} disappear up to the first exothermal peak [14]. The P=O bond with an absorption band at 1260 cm^{-1} is partially preserved.

Stage II. The TG curves of modified samples (Fig. 5) show that the stepwise nature of the decomposition becomes more strongly expressed with increase of the antipyrene quantity. The processes of heat evolution also decrease in intensity, breaking down into processes of weaker intensity (Fig. 3). Probably due to the influence of antipyrene, intermediate temporarily stabilized structures are formed; comparison of the IR spectra of IPUE and MPUE–P after heating to the end of stage II of decomposition (Figs 2 and 4) reveals the almost complete decomposition of IPUE and the greater abundance of absorption bands for MPUE. For the latter the aromatic structure is considerably preserved, with absorption bands at 1600 cm^{-1}, 1450 cm^{-1} and 700–900 cm^{-1}. Bands of the P=O group at 1250 cm^{-1}, of P–O–P at 930 cm^{-1} and of the P–H group at 2350 cm^{-1} are also detectable. The emission spectra of the MPUE–P residue demonstrated a 0.3% phosphorus content.

From Table 1 it is obvious that a phosphorus content over 0.8% causes a decrease of E_{ef} at this stage. With MPUE–P (5.20%) the value of E_{ef} does not tend to decrease. On the contrary, it increases quite substantially. This fact can be attributed to the favourable influence of antipyrene on cross-linking and char formation in stage II of the decomposition.

Stage III. The burning of the residue is a process involving heat generation, which is inhibited to some extent by phosphorus-containing antipyrene (Fig. 3), since phosphorous acids formed in the preceding stage inhibit exothermal oxidation of the carbon residue to CO_2.

Thermal decomposition of MPUE–P/Cl

For most polymers the presence of chlorine in a properly chosen antipyrene results in the evolution of non-combustible HCl, which insulates the polymer surface from the air. This is why Cl-containing antipyrene is considered to be more effective in the gaseous phase. For polyurethanes, P/Cl-containing antipyrenes have been found to be less effective than antipyrenes containing only phosphorus [15], but as far as their mechanism and their effect on the thermal decomposition are concerned it is expedient to make a comparative study.

Stage I. For MPUE–P/Cl, as is seen in Fig. 6, the first exothermal peak is shifted towards higher temperatures. In this particular case, however, its intensity does not diminish. On the contrary, in most cases it increases with increasing concentration of the P/Cl-containing antipyrene. It is most probable that oxidation products are formed which rapidly decompose and are not recorded in the IR spectra after the first exothermal peak.

The use of P/Cl-containing antipyrene in concentrations greater than optimum results in a decrease of E_{ef} (Table 2).

The effect of the medium in which analysis is made is similar to that for MPUE–P.

Stage II. In the stage of maximum rate of decomposition, the tendency towards compensation of the intensive exothermal peaks is clearer with P/Cl-containing MPUE. At the same time, the separate steps of the TG curves (Fig. 7) at higher concentrations of P/Cl-containing antipyrene are not so well differentiated as they are with MPUE–P. These data point to a smaller share of cross-linking reactions.

A great difference is not observed in the change of the IR spectra after the second stage of decomposition as compared to MPUE–P.

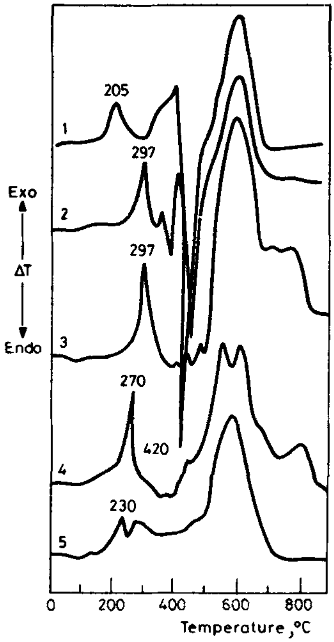


Fig. 6 DTA-plots of IPUE and MPUE–P/Cl: 1 – IPUE; 2 – 1.35/1.42% P/Cl; 3 – 2.20/2.34% P/Cl; 4 – 3.40/4.04% P/Cl; 5 – 4.80/5.50% P/Cl; rate of heating 9°/min in air

Table 2 Values obtained for effective activation energy (E_{ef}) of thermal decomposition of the IPUE and MPUE–P/Cl

P/Cl-contain, %	E_{ef} – I stage, J		E_{ef} – II stage, J		E_{ef} – III stage, J	
	air	nitrogen	air	nitrogen	air	nitrogen
0	74.0	88.0	158.4	182.0	106.8	–
1.30/1.42	92.0	124.0	95.6	127.2	–	–
2.20/2.34	74.4	87.6	82.8	101.2	–	–
3.40/4.04	63.6	95.2	72.8	110.8	68.0	–
4.80/5.51	58.0	48.0	88.8	84.0	–	–

As concerns the kinetics of the reactions at this stage, P/Cl-containing antipyrene behaves as a plasticizer of the polymer structure (Table 2). With MPUE–P/Cl without an extender of the chain, there is a certain increase of E_{ef}, probably due to the reasons discussed in connection with MPUE–P (5.20%).

Stage III. Unlike MPUE–P, with MPUE–P/Cl there is no inhibition of the exothermal peak of the burning of the carbon residue (Fig. 6) in air, which is in support of the assertion as to the smaller share of cross-linking reactions.

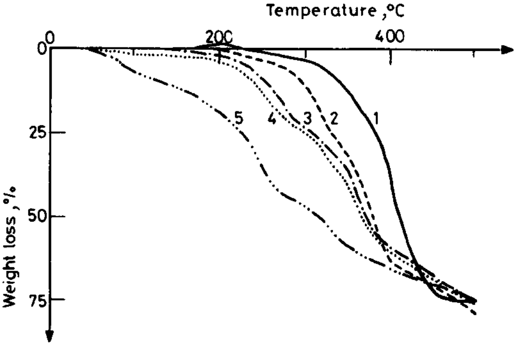


Fig. 7 TG-plots of IPUE and MPUE–P/Cl: 1 – IPUE; 2 – 1.35/1.42% P/Cl; 3 – 2.20/2.34% P/Cl; 4 – 3.40/4.04% P/Cl; 5 – 4.80/5.50% P/Cl; rate of heating 9°/min in air

Conclusion

The use of a derivatograph to study PUE systems with P- and P/Cl-containing antipyrene on gentle warming makes it possible to follow the decomposition reactions step by step; this enables us to understand the mechanism of antipyrene influence on the thermal decomposition of the polymer. The thermal decomposition of IPUE is mainly a process of heat evolution, and is particularly undesirable in the initial stage of thermal decomposition since it affects the fire-proofing properties of the product. It is confirmed that the urethane group is responsible for the instability of polyurethanes. The introduction of P-containing antipyrene into the structure of PUE induces changes in the mechanism and the kinetics of thermal decomposition, towards inactivation of the exothermal reactions of oxidative decomposition. Mostly it causes a shift of the first exothermal peak towards higher temperatures by 100° and helps the formation of temporarily stabilized structures during decomposition. Introduction of P/Cl-containing antipyrene has a less positive effect towards inactivation of the exothermal decomposition reactions and the formation of temporarily stabilized structures.

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Zusammenfassung — Zur Untersuchung des Einflusses von Phosphor und Phosphor/Chlor-haltigen Antipyrinen auf die thermische Zersetzung von auf 4,4'-Diphenylmethan-Diisozyanat und Polytetraoxymethylen ruhenden Elastomeren wurde die Thermoanalyse, die IR- und Emissionsspektralanalyse angewandt. Die Einführung von P-haltigen Antipyrinen in die Struktur der Polyurethan-Elastomere verursacht Änderungen im Mechanismus und in der Kinetik der thermischen Zersetzung in Richtung der Inaktivierung von exothermischen Reaktionen der oxydativen Zersetzung. Das verursacht eine Verschiebung des ersten exothermischen Peaks in Richtung der höheren Temperaturen um 100°, und begünstigt die Bildung von vorübergehend stabilisierten Strukturen. Die P/Cl-haltigen Antipyrine haben eine weniger positive Wirkung in Richtung der Inaktivierung der exothermischen Zersetzungsreaktionen und der Bildung von vorübergehend stabilisierten Strukturen.

Резюме — Термический анализ, ИК- и эмиссионная спектроскопия были использованы для изучения влияния фосфор- и фосфор/хлор-содержащих антипиренов на термическое разложение полиуретановых эластомеров на основе 4,4 -дифенилметандиизоцианата и политетраоксиметилена. Введение фосфор-содержащего пирена в структуру полиметановых эластомеров вызывает изменение и кинетики реакции термического разложения, приводя к дезактивации экзотермических реакций окислительного разложения. Это вызывает сдвиг первого экзотермического пика на 100° в сторону более высоких температур и способствует образованию временных стабильных структур. P/Cl-содержащий антипирен оказывает меньшее влияние как на дезактивацию экзотермических реакций разложения, так и на образование временных стабильных структур.