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STUDIES ON THE SELF-IGNITION OF HIGH-MOLECULAR SUBSTANCES AT LOW TEMPERATURES

PART I

THERMOOXIDATIVE DEGRADATION OF A POLYSTYRENE SORBENT AND OF A METHACRYLIC ACID POLYMER

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Degradation of the resins was investigated both in air and in nitrogen by means of simultaneous TG and DTA. A régime of slow oxidation and a régime of burning process were realized. Some stages of the thermal and oxidative degradation could be identified based on the examination of the composition and the IR spectra of the residues obtained by heating the resin up to different temperature levels. Self-ignition occurs in air at about 300° parallel to the process of depolymerization.

Studying the oxidation and ignition of coal, Oreshko [1] and Weltner [2] have shown that the thermogravimetric and differential thermal analytical devices are especially suitable for investigation of the interaction between a solid organic substance and molecular oxygen. Under these conditions, the ignition occurs at a temperature characteristic to the substance [1]. In a special vessel [2], however, the ignition was prevented, recording the weight changes and the thermal effects of coal oxidation up to the total conversion into gaseous products. This technique can also be used for determination of chemical processes in self-ignition of high-molecular substances at low temperature.

Experimental

Materials

Amberlite XAD-1 is a styrene polymer copolymerized with divinylbenzene. It is characterized as a sorbent by a macroreticular porosity with high surface area (about 100 m^2/g).

Amberlite IRC-50 is a non-porous, weak cation-exchange resin polymerized from some organic acids (acrylic or methacrylic) and their derivatives and cross-linked with divinylbenzene or ethylendimethacrylate. When using esters and anhydrides as initial products, polymerization should be followed by hydrolysis [3]. IR spektra of Amberlite IRC—50 exhibits the features distinguishing poly-metacrilic acid. For this investigation the resins were ground to pass a 0.2 mm sieve.

Methods

The behaviour of the resins at constant heating rate (5°/min) was established by a MOM Derivatograph using various original sample-holders. Heating under nitrogen was carried out in platinum crucibles. In air, either a series of flat platinum plates or the platinum crucible was used without cover. A bulk of the sample in six plates is suitable for investigation of burning. Smaller amounts of resin distributed onto 10 plates, do not ignite. It is useful for investigation of slow oxidation. Aluminium oxide, preheated at 1200°, was used as a reference material. TG and DTA curves recorded in this way are shown in Figs 1, 3, 5, 7, 9, 10 and 11. Intermediate solid products of degradation were obtained by heating the resins under nitrogen and in the régime of slow oxidation. Reaching the desired temperature, heating was stopped and the furnace was raised above the level of the vessel.

IR spectra of the resins and their residues, were obtained by a Unicam 200 PS spectrophotometer using the potassium bromide disc technique. The ratio of organic substance to potassium bromide was 1 : 100, or 1 : 200 when dark-coloured residues were examined. The IR spectra of the resins and their residues are shown in Figs 2, 4, 6 and 8.

Carbon and hydrogen content of the resin and their pyrolysis products was determined by the standard methods. The values of oxygen content were calculated as the differences to 100% weight (Tables 1 and 2).

The evolution of molecular hydrogen was established by heating the resins in a glass reactor inside a furnace flushed by a stream of purified nitrogen (99.999%) for 20 min. at constant temperature maintained within ±5° around the desired level. The escaping gas was analyzed by gas-chromatography. The yield of hydrogen was found 0.04 per cent of the dry matter for Amberlite XAD-1 at 270°, and nearly 0.02% for Amberlite IRC-50 at 320°. The yield of hydrogen from the polystyrene polymer at 370° was half of that released at 270°. Only traces of hydrogen was found in the gas evolved from Amberlite IRC-50 at 420°. Instead methane, propane and butane were detected in amount of 1.4, 1.3 and 4.4% of the initial dry material respectively.

Dried tablets of the samples were heated at a rate of 5°/min in a microscope of Leitzt. No signs of burning appeared under air stream, but a violent explosion occurred in oxygen stream (2 l/h). The explosion temperatures of the cylindric tablets with dimensions of 3 × 3 mm are indicated in Table 3.

Results and discussion

It is generally believed that the oxidation of hydrocarbons is attributed to alkyl radicals, resulted from their homolytic dissociation. Some information about the thermal homolytic processes in resins are provided by the experiments carried out under nitrogen.

Degradation of the resins under nitrogen. Gradual heating of the Amberlite XAD-1 in nitrogen, no causes weight change between 150 and 300° (Fig. 1). However, an exothermic peak starts at about 240°. Grassie and Weir [4] found an evolution of hydrogen gas in polystyrene degradation by 253.7 nm radiation. They attributed it to a fission of tertiary hydrogen as a result of dissociation of C–H bonds forming conjugated double bonds accompanied by some cross-linking. Obviously, only the latter reaction is exothermic. It may be deduced that the hydrogen evolution mentioned and the exothermic effect refer to a similar mechanism.

Above 310°, a rapid loss in weight of polystyrene resin starts. At 380° the weight loss reaches 50% of the initial dry material. The exothermicity switches over to endothermicity in this range. On the other hand, the IR spectra of the residue, obtained at 380°, remain characteristic to polystyrene (Fig. 2). It is evident then that depolymerization is the main degradation process in this range. Two supplementary bands (at 1560 and at 1680 cm^{-1}), however, refer to some other reactions.

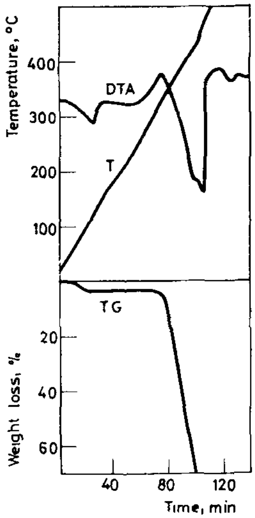
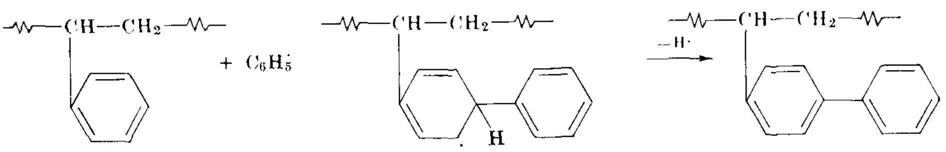


Fig. 1. TG and DTA curves of Amberlite XAD-1 heated under nitrogen

It is known that polystyrene heated at 310°, yields considerable amount of toluene and benzene [5]. The formation of the latter should be related to a dissociation of carbophenyl bonds. It is highly probable that an addition of the phenyl radical to the aromatic ring may occur forming biphenyl groups in agreement to the mechanism proposed by several authors [6]:



According to the biphenyl absorption at 1570 cm^{-1}, the new band at 1560 cm^{-1} may support the above reaction. The appearance of a band at 1680 cm^{-1} in this

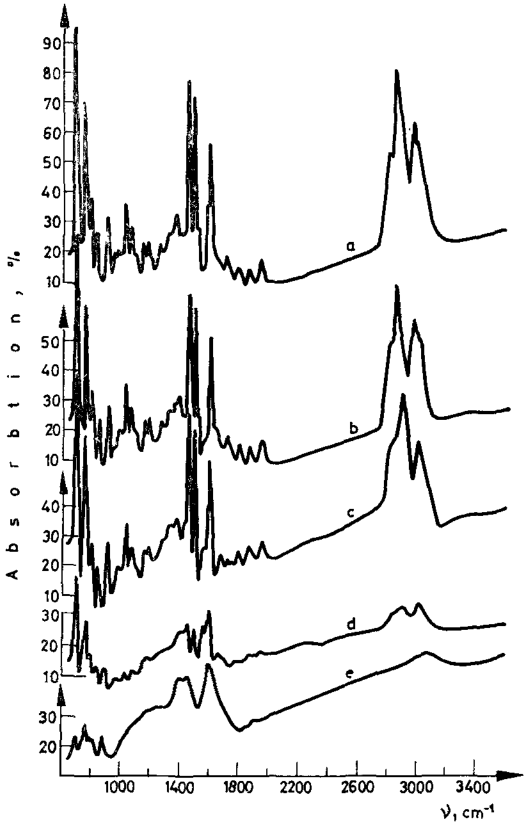
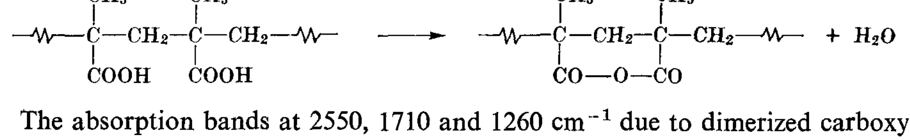


Fig. 2. IR spectra of Amberlite XAD-1 (a), its residue heated up to 280° (b), 380° (c), 430° (d) and 600° (e) under nitrogen

spectrum is therefore consistent with the change in the aromatic ring substitution pattern.

When Amberlite IRC-50 is heated under nitrogen TG steps are accompanied by endothermic peaks. The first step is due to moisture evaporation and the second one accounts for a weight loss of 10.3% of the dry material. Based on elementar analysis (Table 1) and the IR spectra (Fig. 4), this value leads to the conclusion that this step is a decomposition of the acid into anhydride:



$$-\!\!\sim\!\!-\underset{\text{COOH}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\underset{\text{COOH}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\!\!\sim\!\!- \longrightarrow -\!\!\sim\!\!-\overset{\text{CH}_3}{\text{C}}-\text{CH}_2-\overset{\text{CH}_3}{\text{C}}-\text{CH}_2-\!\!\sim\!\!- + H_2O$$
$$\text{(ring: CO—O—CO)}$$

The absorption bands at 2550, 1710 and 1260 cm^{-1} due to dimerized carboxyl groups are characteristic of the IR spectra of the air-dried resin. When the resin

Table 1

Ultimate Composition of Amberlite IRC-50 and of Its Degradation Products

Material	Medium	Composition %			Weight loss %	C	H	O
		C	H	O		(g) in the residue of 100 g dried resin		
Original resin	—	56.0	7.0	37.0	—	—	—	—
after heating up to 380°C	nitrogen	62.4	6.5	31.1	10.3	56.0	5.8	27.8
after heating up to 380°C	nitrogen	62.7	6.4	30.8	15	53.3	5.5	26.1
after heating up to 420°C	nitrogen	69.5	7.4	23.1	31	48.6	5.1	15.9
after heating up to 280°C	air	62.4	6.4	31.2	10.3	56.0	5.8	27.8
after heating up to 380°C	air	62.5	6.0	31.5	5.5	28.1	2.7	14.0

Table 2

Ultimate composition of Amberlite XAD-1 and of its degradation products

Material	Medium	Composition %			Weight loss %	Aromic ratio H:C	
		C	H	O		residue	gaseous products
Original resin	—	92.4	7.6	—	—	—	—
after heating up to 280°C	nitrogen	92.4	7.6	—	0	1.00	—
after heating up to 380°C	nitrogen	92.6	7.4	—	50	0.96	1.03
after heating up to 430°C	nitrogen	93.8	6.2	—	69	0.79	1.21
after heating up to 280°C	air	92.3	7.6	0.0	2	1.00	1.00
after heating up to 380°C	air	75.1	3.7	21.2	63	0.59	1.10

was heated up to 200°, three new bands (at 1790, 1760 and 1020 cm^{-1}) appeared in its spectra. These frequences are peculiar to the anhydrides. This reaction starts below 200° and is finished at 280°. The absorption near 3400 cm^{-1} due to hydroxyl groups is missing in the spectra of resin heated up to this temperature level (Fig. 4). The peaks characteristic of anhydrides (near 1800 cm^{-1}, 1760 cm^{-1} and 1020 cm^{-1}) are predominant.

The thermal decomposition of polymethacrylic acid at 200° was investigated by Grant and Grassie [7]. They suppose a heterolytic mechanism of decomposition analogous to the esterification catalyzed by water. Similarly to the polymethacrylic ethers, the polymethacrylic anhydride should depolymerize above 300°. However, under our experimental conditions, the depolymerization of the anhydride resin proceeds very slowly. The weight loss between 280 and 380° is only about 3%.

An absorption band appears near 1600 cm^{-1} in the IR spectrum of the red-coloured residue after heating up to 380°. It may be related to system of conjugated double bonds formed by dissociation of secondary C–H bonds. The dehydrogenation was confirmed by the analysis of gases evolved when the resin was heated at 320°.

In this residue the absorption characteristic to anhydrides (at 1760 cm^{-1}) is reduced to some extent. In the same time the absorption of methylene and methyl groups remained unchanged. Hence it can be assumed that in the range 280–380° some loss of carbonyl takes place and its rate exceeds the rate of dehydrogenation. The small weight loss in this range indicates a relative stability of the polyanhydride, probably due to a strong cage effect in scission of the main chain.

The weight loss between 380 and 420° is about 16% of the original dry material. The composition of the black-coloured residue obtained at 420° indicates a loss of oxygen, (Table 1), thus indicating that the over-all volatile product evolved in the range 380–420° contains much more oxygen and hydrogen than it corresponds to the anhydride composition: $C_8H_{10}O_3$. It seems that in this range the depolymerization competes with formation of carbon oxides, main chain rupture and methyl groups fission. The latter is confirmed by the presence of methane in the gaseous product.

There are no characteristic bands of anhydrides in the spectra of the residue obtained at 420° and the absorption of methyl groups is missing in the range of 1300–1400 cm^{-1}. It is rather difficult to draw any definite conclusions about the structure of this residue, but it may contain polynuclear aromatic systems, resulting from the loss of carbonyl, from the dissociation of $C-CH_3$ bonds and the abstraction of hydrogen from free radicals. The weight loss of Amberlite IRC-50 and the polystyrene resin can be followed up to 420° and 430° respectively. At higher temperatures, the evolving gases make the liquified substance spill over the vessel.

According to the analytical data (Table 2) and thermogravimetry, the composition of gaseous product of the polystyrene poyrolysis changes at about 380°. Under 380° the hydrogen to carbon atomic ratio of the over-all gas product is similar to that for polystyrene, i.e. it is close to 1. In the range of 380–430°, this ratio becomes higher than 1. It should be concluded that over 380° the depolymerization gradually gives way to other reactions of degradation. The dissociation of phenyl radicals, on the other hand, probably leads to formation of polyphenyl chains in this stage of the resin pyrolysis. Substituted bi- and triphenyls were established by Chaigneau and Le Moan in the volatile products of the polystyrene pyrolysis [8]. The absorption in the range of 1500 – 1600 cm^{-1} might be explained by the presence of such structures in the residue of the resin, heated up to 430°. Non-linear polyphenyls and polyphenyl alkanes absorb at 1600 and 1500 cm^{-1} [9]. The decreasing absorption due to methylene groups in the IR spectra of this residue probably indicates a chain rupture and a formation of free radicals abstracting hydrogen from the polystyrene backbone.

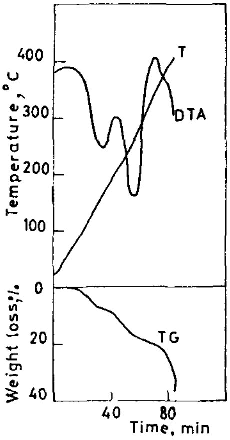


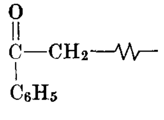
Fig. 3. TG and DTA curves of Amberlite IRC-50 heated under nitrogen

DTA curve (Fig. 1) shows that exothermic reactions take place above 440°. As the fission of aromatic hydrogen is very likely above 450° [10], the formation of molecular hydrogen and polynuclear aromatic systems by recombination of aryl radicals may be envisaged at this stage of the pyrolysis. The presence of polynuclear aromatic systems in the product, obtained by heating the resin up to 600° may explain the resemblance of its IR spectrum (Fig. 2) to that of coal.

Degradation of the resins in air. DTA curve for heating of the polystyrene resin in air under oxidation régime (Fig. 5) shows two exothermal zones: 300 – 380 and 380 – 480°, with peaks at 360 and 450°. Some information about the reactions in these zones was obtained from a respective analysis of the residues heated up to several temperature levels.

Polystyrene samples with maximum particle size of 0.200 and 0.067 mm respectively were heated in air up to 280°. No changes were observed in the IR spectra of the former sample. But the latter that developed a hardly perceptible yellow hue, showed a new absorption band between 1670 and 1690 cm^{-1} (Fig. 6).

The structure of the initial product of the oxidative degradation of polystyrene is a controversial subject. A thorough investigation on the matter leads Beachell and Smiley [11] to the conclusion that, as a result of oxidation at relatively low temperatures (200°), an acetophenone-type structure is formed having an absorption at 1685 cm^{-1}:



$$\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}-CH_2-\!\sim\!\sim-$$

The yellow residue of the resin heated up to 320° in air shows two new intensive absorption peaks: the first in the range of hydroxyl groups and the second, at 1675 cm^{-1}. Two shoulders are to be seen clearly at 1650 and 1730 cm^{-1} (Fig. 6). The absorption at 1675 cm^{-1} is characteristic to the enole [13], indicating the

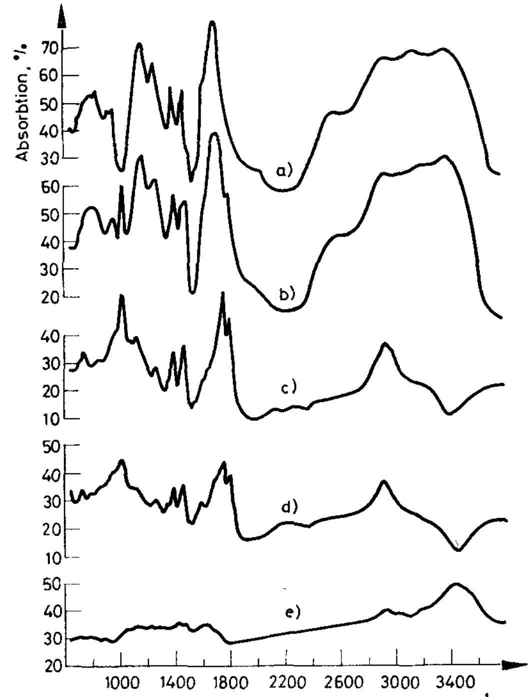


Fig. 4. IR spectra of Amberlite IRC-50 (a), its residue heated in nitrogen up to 200°(b), 280° (c), 380° (d) and 420° (e)

formation of the dicarbonyl, postulated by Zapol'skii [12] which is in equilibrium with its enolic form:

$$\underset{C_6H_5}{\overset{\overset{O}{\|}}{C}}-\overset{\overset{O}{\|}}{C}-\underset{C_6H_5}{\overset{\overset{H}{|}}{C}}-\!\!\sim\!\!- \rightleftharpoons \underset{C_6H_5}{\overset{\overset{O}{\|}}{C}}-\overset{\overset{OH}{|}}{C}=\underset{C_6H_5}{C}-\!\!\sim\!\!-$$

A less intensive band at 1720 – 1730 cm^{-1} is characteristic to the cis form of dicarbonyl. The double bond of enole absorbs at 1650 cm^{-1} as a shoulder.

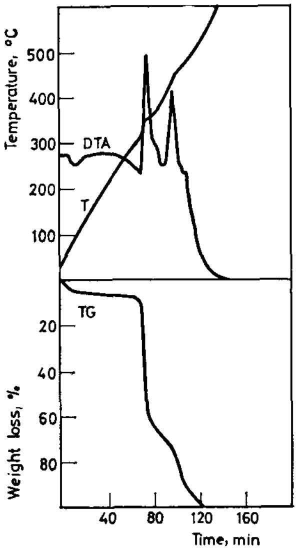


Fig. 5. TG and DTA curves of 0.2 g of Amberlite XAD-1 distributed onto 10 piled plates and heated in air

The residue of the resin, heated up to 380°, contains 21 % oxygen. Its hydrogen content is lower than that of the residue, heated up to the same temperature in nitrogen. The negligible absorption of the methylene groups in the IR spectra of the former residue (Fig. 6) suggests that between 300 and 380°, an oxidative dehydrogenation of the main chain takes place demonstrated by the first exothermal DTA peak.

The hydrogen to carbon atomic ratio of the over-all gas product, evolved during the resin oxidation under 380°, is 1.10 : 1 (Table 2). This ratio in the original resin is 1 : 1, indicating that the depolymerization is the main reaction of degradation between 300 and 380°, even in the presence of oxygen. The positive effect of the oxidation on the polystyrene depolymerization is well known [5].

The composition of the residue of the resin, heated up to 380° can be expressed as $C_8H_{4.7}O_{1.7}$. It is very likely that dehydrogenation leads to aromatization of some part of the alyphatic carbon in the resin. The oxidation of this unmelted residue causes the second exothermic peak. The rate of the oxidative degradation

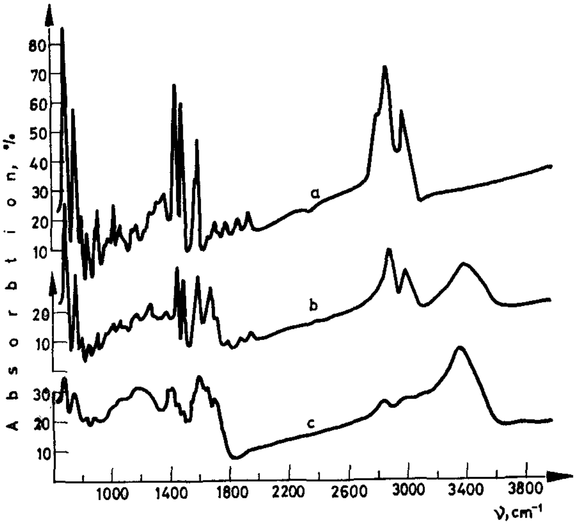


Fig. 6. IR spectra of the residue of Amberlite XAD-1 heated in air up to 280° (a), 320° (b) and 380° (c)

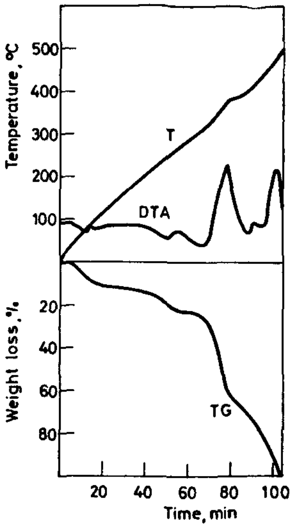


Fig. 7. TG and DTA curves of 0.2 g of Amberlite IRC-50 heated in air on 10 plates

increases at about 400°. The total decomposition into volatile substances takes place up to 550°.

The thermogravimetric curve of oxidation of Amberlite IRC-50 shows several steps accompanied by DTA peaks. Under 300° two endothermic peaks are obtained that are due undoubtedly to the loss of moisture and decomposition of the acid (Fig. 7).

The first exothermic peak above 300° corresponds to the temperature range of hydrogen formation established under nitrogen. Therefore in the range of 315 to 400°, an oxidative dehydrogenation can be supposed in air, confirmed by the data

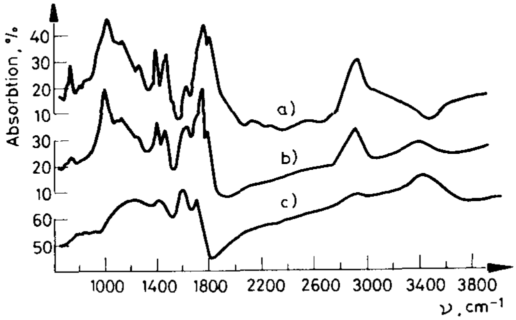


Fig. 8. IR spectra of the residue of Amberlite IRC-50 heated in air up to 280° (a), 380° (b) and 440° (c)

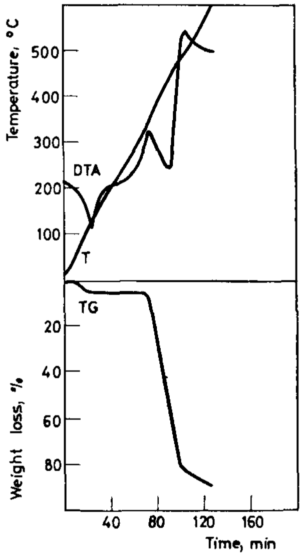


Fig. 9. TG and DTA curves of 1 g of Amberlite XAD-1 set heated in an open crucible in air

from the ultimate analysis of the residue heated in air up to 380°. The oxidation in this range leads to a strong decrease in hydrogen content (Table 1).

The hydrogen to carbon atomic ratio of the over-all gas product evolved in the range of 300 – 380° is found approximately 6 : 4, whereas this ratio for the anhydride is 5 : 4.

The small difference between both ratios indicates that the oxidative dehydrogenation catalyses the depolymerization and the latter is the main reaction in this range.

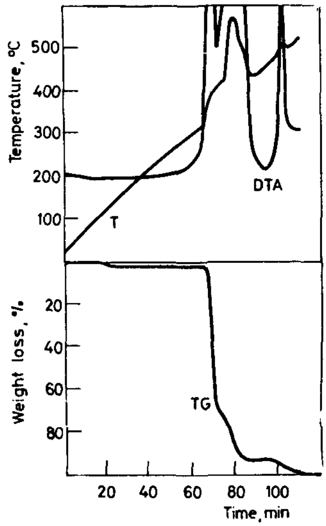


Fig. 10. TG and DTA curves of 1 g of Amberlite XAD-1 distributed onto 6 plates and heated in air

The absorption, characteristic to anhydrides, is missing in the IR spectra of the residue of resin, heated in air up to 440° (Fig. 8). The absorption of methyl groups (at 1380 and near 2900 cm^{-1}) is also of minor significance. The oxidative degradation of this product which probably has an aromatic structure, gives rise to the last exothermal peak between 430 and 470°. The complete conversion of the resin into volatile materials takes place up to about 500°.

When the resins are heated in an open crucible in air, the exothermic peak starts at 250° but becomes less intensive in the temperature range of depolymerization (300 – 400°). In this case the oxidation proceeds in lack of oxygen as the monomer vapour expels the air from the resin layer (Fig. 9). The transition of the oxidation into slow burning is observed when 1 g of resin is distributed to six plates and heated gradually in air. The exothermic peak appears about 250°. Above 310° the temperature begins to rise so rapidly that exothermicity can not be recorded by the DTA curve but directly by the heating curve (T) (Figs 10 and 11).

Some results of this investigation seem to be useful for studies of self-ignition of polymers.

When the IR spectra of the residues from Amberlite IRC-50 heated in nitrogen and in air up to 380° are compared, no difference is established at 1390 cm^{-1}. The absorption at 1460 cm^{-1}, however, is lower after the oxidation (Fig. 8), proving that primary hydrogens remain unaffected under 380° in the oxidation régime.

The hydroxyl radical is the chain carrier when hydroperoxides are formed. This radical is recognized [14] to be non-selective, even at low temperature (say 250°). The stability of the methyl groups indicates that the chain carrier in the interaction between the resin and oxygen under 380° should be a radical having a sufficiently high activation energy of hydrogen abstraction i.e. a radical of low reactivity as, for instance, $HO_2^{\cdot}$.

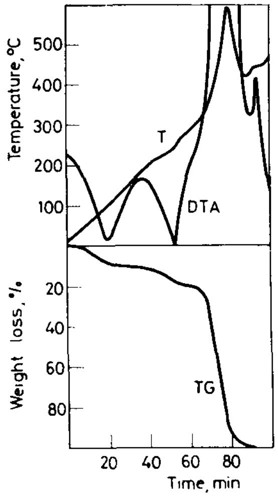


Fig. 11. TG and DTA curves of 1 g of Amberlite IRC-50 distributed onto 6 plates and heated in air

On the other hand, the temperature of intensive heat formation in air coincides with that at which the rate of depolymerization increases sharply in nitrogen. This fact is consistent with the results of Petrella and Sellers who found under the conditions of flash pyrolysis that the induction period and the period of burning are shorter for the monomer than for the polymer. Their conclusion is that the first step in the total combustion process of polystyrene involves the depolymerization of the polymer and that is the monomer which burns [15].

Under the conditions of our experiments, self-ignition does not occur in the layer of minimal thickness but in a thicker one. Obviously, the concentration of the monomer above the resin is controlled by the layer thickness.

According to the mechanism of alkane oxidation proposed by Knox [16], in the first stage of the process at low temperatures olefin or peroxy radicals are formed by the interaction between the molecular oxygen and the free radicals from the homolytic dissociation of the alkane:

$$R^{\cdot} + O_2 \rightarrow AB + HO_2^{\cdot} \qquad R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$$

At higher $HO_2^{\cdot}$ concentrations, hydroperoxydes are formed:

$$RO_2^{\cdot} + HO_2^{\cdot} \rightarrow ROOH + O_2$$

A conversion of $HO_2^{\cdot}$ into $OH^{\cdot}$ can occur above 300° as a result of its addition to the primary olefin, AB

$$HO_2^{\cdot} + AB \rightarrow {}^{\cdot}ABOOH \qquad {}^{\cdot}ABOOH + O_2 \rightarrow {}^{\cdot}OOABOOH$$
$$HO_2^{\cdot} + {}^{\cdot}OOABOOH \rightarrow HOOABOOH + O_2$$
$$HOOABOOH \rightarrow 2\,OH^{\cdot} + AO + BO$$

In the light of this mechanism the transition from oxidation to slow burning seems to be a consequence to a rapid conversion of the slightly reactive $HO^{\cdot}$ into the highly reactive $OH^{\cdot}$.

Abadie and Marchal [17] do not suppose any formation of hydroperoxides in the autooxidative destruction of polystyrene radiated by γ-rays, considering a six-membered ring as a transition state after the fission of tertiary hydrogens and the appearance of a peroxy radical, RO_2. The formation of the acetophenone-type structure in the range 250–300° may be explained in this way.

The formation of dicarbonyl in the range 300–380° then may be ascribed to a change in the mechanism resulting in the formation of double bonds and addition of $HO_2^{\cdot}$.

An evidence for the formation and accumulation of conjugated double bonds during the oxidation at 250–300° is given by the absorption at 1570–1650 cm^{-1} in the IR spectra of Amberlite IRC-50 heated up to 280° in air. There is no absorption at these frequencies when heated the resin up to the same temperature under nitrogen.

It was pointed out that the self-ignition of the polystyrene resin may occur during depolymerization in air. The lower temperature of explosion of the resin in

Table 3

Temperatures of explosion of tablets in oxygen stream

Resin	°C
Amberlite XAD-1	250; 250
Amberlite XAD-7	250; 225
Amberlite IRC-50	295; 300
Amberlite IRC-50 preheated at 280°C	290; 285

oxygen atmosphere (250°) can be explained by the catalytic effect of oxygen on the polystyrene depolymerization.

The porous polyacrylic ester sorbent (Amberlite XAD-7) explodes under oxygen at 250°. This coincidence can be ascribed to the presence of tertiary hydrogen in both resins indicating a relation between the temperature of self-ignition and chemical structure of the polymer. The higher explosion temperature of Amberlite IRC-50 (Table 3) does not contradict to this assumption, but another factor, the small surface area, is probably responsible for the weak reactivity of this resin towards the oxygen.

Further investigations are needed in order to determine the role of the chemical structure and the surface area, in formation of the minor products and the self-ignition of high-molecular substances.

References

1. V. P. Oreshko, Izvest. Akad. Nauk SSSR, Otdel Tekh. Nauk (1949), 249, 748, 1642.
2. H. Weltner, Acta Chim. Hung., 43 (1965), 89.
3. F. Helfferich, Ionenaustauscher, Verlag Chemie GMBH, Weinheim (1959), 182.
4. N. Grassie, N. A. Weir, J. Appl. Polymer Sci., 9 (1965), 963, 975, 987, 999.
5. I. P. Losev, E. B. Trostyanskaya, Khimiya sinteticheskikh polimerov. (Chemistry of synthetic polymers), Izd. Khimiya, Moscow (1971) 409.
6. M. Jackiss, M. Schwarz, Discuss. Faraday Soc., 14 (1953), 246i R. N. Milutinskaya, H. S. Bogdasaryan, E. A. Izrailevich, Zh. Fiz. Khim., 31 (1957), 1019i L. de Tat, R. Long, J. Am. Chem. Soc., 80 (1958), 4742.
7. D. H. Grant, N. Grassie, Polymer, 1 (1960) 125.
8. M.Chaigneau, G. Le Moan, Ann. pharm. franç., 28 (1971) 41.
9. C. N. R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York—London, 1963, p. 164.
10. R. Z. Magaril, Neft' i Gaz (1967), No 2, 67.
11. H. C. Beachell, L. H. Smiley, J. Polymer Sci., Part A-1,5 (1967) 1635.
12. O. B. Zapol'skii, Vysokomol. Soed., 7 (1965) 615.
13. Koji Nakanishi, Infrared Absorption Spectroscopy — Practical, Holden Day Inc., San Franc., (1962).
14. C. H. F. Tipper, A. Titchard, Combustion and Flame, 16 (1971) 223.
15. R. V. Petrella, G. D. Sellers, Combustion and Flame, 16 (1971) 83.
16. J. N. Knox, Combustion and Flame, 9 (1965) 297.
17. M. Abadie, J. Marchal, Kinetics and Mechanism of Polyreactions, Vol. 5, Preprs., Akadémiai Kiadó (1969) 239.

Résumé — On a étudié, en air et en azote, la dégradation thermique des résins par ATD et TG. On a observé un domaine d'une oxydation lente et un domaine d'ignition. On a réussi à identifier certaines étapes de la dégradation thermique et oxydative, en effectuant l'examen de la composition et des spectres IR des résidus obtenus en chauffant la résine à de différentes températures. On a établi une autoignition dans l'air à 300° parallèlement avec la dépolimerisation thermique.

ZUSAMMENFASSUNG — Die thermische Zersetzung der Harze wurde in Luft und Stickstoff durch TG und DTA untersucht. Es zeigt sich ein Gebiet der langsamen Oxydation und ein Gebiet der Verbrennung. Einige Stufen der thermischen und oxydativen Zersetzung konnten durch IR-Spektroskopie und Bestimmung der Zusammensetzung der jeweiligen thermischen Rückstände identifiziert werden. Selbstverbrennung erfolgte in Luft bei ungefähr 300° parallel mit der Depolymerisation.

Резюме — Исследован термораспад »амберлита ХАД—1 и ИРЦ—50 в воздухе и азоте с помощью дериватографа. Для регистрации потери веса и термических эффектов при квази-стационарном и нестационарном режимах взаимодействия между смолой и молекулярным кислородом использованы ячейки различной конструкции. Установлена последовательность стадий окислительного распада путем изучения сосрава и ИК-спектров остатков, полученных ступенчатым нагреванием смолы.