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# OZONE AND ITS REACTIONS WITH DIENE RUBBERS

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**Abstract.** The reactions of ozone with 1,4-*cis*-polybutadiene (SKD); Diene 35 NFA (having the following linking of the butadiene units in the rubber macromolecules: 1,4-*cis* (47 %), 1,4-*trans* (42 %), 1,2- (11 %); 1,4-*cis*-polyisoprene (Carom IR 2200), 1,4-*trans*-polychloroprene (Denka M 40), and 1,4-*trans*-polyisoprene have been investigated in $CCl_4$ solutions. The changes of the viscosity of the polymer solutions during the ozonolysis have been characterized by the number of chain scissions per molecule of reacted ozone ($f$). The influence of the conditions of mass-transfer of the reagents in a bubble reactor on the respective $f$ values has been discussed. The basic functional groups-products from the rubbers ozonolysis have been identified and quantitatively characterized by means of IR-spectroscopy and $^1$H NMR spectroscopy. A reaction mechanism that explains the formation of all identified functional groups has been proposed. It has been shown that the basic route of the reaction of ozone with elastomer double bonds – formation of normal ozonides – does not lead directly to a decrease in the molecular mass of the elastomer macromolecules, because the respective 1,2,4-trioxolanes are relatively stable at ambient temperature. The most favourable conditions for ozone degradation emerge when the cage interaction between Criegee's intermediates and respective carbonyl groups does not proceed. The amounts of measured different carbonyl groups have been used as an alternative way for evaluation of the intensity and efficiency of the ozone degradation. The thermal decomposition of partially ozonized diene rubbers has been investigated by DSC. The respective values of the enthalpy, the activation energy and the reaction order of the 1, 2, 4-trioxolanes have been determined.

**Keywords**: ozone, ozonolysis, diene rubber, mechanism, degradation.

## 1. Introduction

The interest in the reaction of ozone with polydienes is due mainly to the problems of ozone degradation of rubber materials [1-4] and the application of this reaction to the elucidation of the structures of elastomers [5-8]. It is also associated with the possibilities of preparing bifunctional oligomers by partial ozonolysis of some unsaturated polymers [9-12]. Usually the interpretation of experimental results are based on a simplified scheme of Criegee's mechanism of C=C-double bond ozonolysis, explaining only the formation of the basic product – ozonides [13, 14].

In most cases, quantitative data on the functional groups formed during the reaction are missing [15-18]. At the same time alternative conversion routes of Criegee's intermediates, which lead to the formation of carbonyl compounds and some other so-called "anomalous products" of the ozonolysis, are of great importance for clarifying the overall reaction mechanism [19-21]. The mechanism of ozone degradation of rubbers is also connected with the non-ozonide routes of the reaction, because the formation of the basic product of ozonolysis, normal ozonide, does not cause any chain scission and/or macromolecule cross-linking [22].

In this work the changes in the molecular mass of different types of diene rubbers during their partial ozonolysis in solution have been investigated. By means of IR and $^1$H NMR spectroscopy ozonolysis products of the elastomers have been studied. The effects of the nature of the double bond substituents and its configuration on the degradation mechanism have been considered. By using differential scanning calorimetry thermal decomposition of the functional groups of peroxide type has also been investigated.

# 2. Experimental

## 2.1. Materials

Commercial samples of 1,4-*cis*-polybutadiene (SKD; E-BR); polybutadiene (Diene 35 NFA; BR); 1,4-*cis*-polyisoprene (Carom IR 2200; E-IR), and polychloroprene (Denka M 40; PCh) were used in the experiments (Table 1).

The 1, 4-*trans*-polyisoprene samples were supplied by Prof. A.A. Popov, Institute of Chemical Physics, Russian Academy of Sciences. All rubbers were purified by threefold precipitation from $CCl_4$ solutions in excess of methanol. The above mentioned elastomer structures were confirmed by means of $^1$H NMR spectroscopy.

Ozone was prepared by passing oxygen flow through a 4–9 kV electric discharge.

*Table 1*

**Some characteristics of polydiene samples**

| Elastomer | Monomeric unit | Unsaturation degree, % | 1,4-*cis*, % | 1,4-*trans*, % | 1,2-, % | 3,4-, % | $M_v \cdot 10^{-3}$ | *n* |
|---|---|---|---|---|---|---|---|---|
| SKD | -CH=CH- | 95–98 | 87–93 | 3–8 | 3–5 | - | 454 | 2.1 |
| Diene 35 NFA | -CH=CH- | 97 | 47 | 42 | 11 | | 298 | 2.63 |
| Carom IR 2200 | -C($CH_3$)=CH- | 94–98 | 94–97 | 2–4 | - | 1–2 | 380 | 2.0 |
| 1,4-*trans* PI | -C($CH_3$)=CH- | 95–97 | | 95–97 | | | 310 | 2.3 |
| Denka M40 | -C(Cl)=CH- | 94–98 | 5 | 94 | - | - | 180 | 1.8 |

*Notes*: $M_v$ is the average molecular weight, determined viscosimetrically from equation $[h] = k \cdot M_v^{a'}$, where $[h] = (h_1/C)(1+0.333h_1)$; $h_1 = h_{rel} - 1$; $h_{rel}$ is the intrinsic viscosity; $C$ – solution concentration; $k = 1.4 \cdot 10^{-4}$ – Staudinger's constant and $a' = 0.5–1.5$ – constant depending on the rubber type, being one for natural rubber; $M_v \approx M_w$; $n = M_w/M_n$ ($M_w$ and $M_n$ are the average weight and number average molecular mass, respectively) [22].

## 2.2. Ozonation of the Elastomer Solutions

The ozonolysis of elastomers was performed by passing an ozone-oxygen gaseous mixture at a flow rate of $v = 1.6 \cdot 10^{-3} \pm 0.1$ l·s$^{-1}$ through a bubbling reactor, containing 10–15 ml of polymer solution (0.5–1g in $CCl_4$) at 293 K. Ozone concentrations in the gas phase at the reactor inlet ($[O_3]_i$) and outlet ($[O_3]_u$) were measured spectrophotometrically at 254 nm [23]. The amount of the consumed ozone ($G$, mol) was calculated by the Eq. (1):

$$G = v \cdot ([O_3]_i - [O_3]_u) \cdot t \qquad (1)$$

where $t$ is the ozonation time, s.

The degree of conversion of the double C=C bonds was determined on the basis of the amount of reacted ozone and the reaction stoichiometry [23].

# 3. Results and Discussion

P. Florry [24] has shown that the reactivity of the functional groups in the polymer molecule does not depend on its length. It is also known that some reactions of the polymers proceed more slowly, compared with their low molecular analogues (catalytic hydrogenation). The folded or unfolded forms of the macromolecules provide various conditions for contact of the reagents with the reacting parts [4, 25]. By using the modified version of this principle [26] it was possible to explain the proceeding of reactions without any specific interactions between the adjacent C=C bonds and the absence of diffusion limitations. The study of the mass-molecular distribution (MMD) is in fact a very sensitive method for establishing the correlation between molecular weight ($M_w$) and the reactivity. The theory predicts that the properties of the system: polymer-solvent can be described by the parameter of so-called globe swelling ($g$), which defines the free energy ($F$) of the system and thus the rate constant of the reaction. For a reversible reaction, *i.e.* polymerization – depolymerization, the dependence of the rate constant of the chain length growing on the molecular weight is expressed by the following equation:

$$\ln k_{pj}/k_{p\infty} = -\text{const} \cdot (5g - 3/g) \cdot (dg/dM) \cdot M_0 \qquad (2)$$

where $M_0$ is the molecular weight of the studied sample and $k_p$ is the rate constant for infinitely long macromolecules. A good correlation between the theoretical and experimental data for polystyrene solutions in benzene has been found in [27].

The study of the polymer degradation is complicated by their structural peculiarities on molecular and supramolecular level and diffusion effects. It is difficult to find simple model reactions for clarification of particular properties and for the express examination of the proposed assumptions. An exception in this respect is the ozone reaction with C=C bonds, whose mechanism has been intensively studied and could be successfully applied upon ozonolysis of polymeric materials [28].

Table 2 summarizes the rate constants of the ozone reactions with some conventional elastomers and polymers and their low molecular analogues, synthesized by us. It is seen that the reactivities of elastomers and polymers and their corresponding low molecular analogues, as it is demonstrated by their rate constants, are quite similar, thus suggesting similar mechanisms of their reaction with ozone. This statement is also confirmed by: 1) the dependence of $k$ on the inductive properties of substituents: for example $k$ of polychloroprene is higher than that of vinylchloride due to the presence of two donor substituents and 2) the dependence of $k$ on the configuration of the C=C bond in *trans*-isomer (gutta-percha) and *cis*-isomer (natural rubber).

*Table 2*

**Rate constants of ozone reactions with polymers and low molecular analogues in $CCl_4$, 293 K**

| Compound | $M_w$ | $k\cdot10^{-4}$, $M^{-1}\cdot s^{-1}$ |
|---|---|---|
| Polychloroprene | $8\cdot10^5$ | $0.42 \pm 0.1$ |
| Vinylchloride | 62.45 | 0.18 |
| 2-Bromopropene | 121 | $0.28 \pm 0.05$ |
| Polybutadiene | $3.3\cdot10^5$ | $6.0 \pm 1$ |
| Cyclododecatriene-1,5,9 | 162 | $35 \pm 10$ |
| Poly(butadiene-co-styrene) | $8\cdot10^4$ | $6 \pm 1$ |
| Gutta-percha | $3\cdot10^4$ | $27 \pm 5$ |
| Natural rubber | $1\cdot10^6$ | $44 \pm 10$ |
| 2-Me-pentene-2 | 85 | $35 \pm 10$ |
| Squalene | 410 | $74 \pm 15$ |
| Polystyrene | $5\cdot10^5$ | $0.3\cdot10^{-4}$ |
| Cumene | 120 | $0.6\cdot10^{-4}$ |
| Polyisobutylene | $1.7\cdot10^5$ | $0.02\cdot10^{-4}$ |
| Cyclohexane | 84 | $0.01\cdot10^{-4}$ |

It has been found out that the effects, related either to the change in the macromolecule length or to the folding degree, do not affect the ozonolysis in solution. Probably this is due to the fact that the reaction is carried out in elastomeric solutions, in which the macromolecules are able to do free intramolecular movements and they do not react with adjacent macromolecules. Moreover, the rate of macromolecules reorganization is probably higher than the rate of their reaction with ozone as the experiment does not provide any evidence for the effects of the change in the parameters pointed above [29].

However, it should be noted that $k$ values of the elastomers are about 2-6 times lower that those of the low molecular analogues. The accuracy of activation energy ($E_a$) determination does not allow to estimate the contribution of the two parameters: pre-exponential factor ($A$) or $E_a$ for the decrease in $k$. If we assume that the mechanism of ozone reaction with monomers and elastomers is similar, *i.e.* the reactions are isokinetic, then $A_{mon} = A_{pol}At\cdot k_{mon}/k_{pol} = 2–6$ the difference in $E_a$ at 293 K will be 2.9–4.19 kJ/mol. At the low experimental values of $E_a$, these differences will become commensurable and thus the determination of $E_a$ is not sufficiently accurate. In this case two assumptions could be made, which can give a reasonable explanation for the lower values of $k_{pol}$: 1) the reorientation of the macromolecules is a slower process than that of olefins, which would result in $A_{pol}$ lower than $A_{mon}$ and 2) the addition of ozone to C=C bonds is accompanied by the rehybridization of the C-atoms from $sp^2$-$sp^3$ and the movements of the polymer susbstituents during the formation of activated complex (AC) will be more restricted than those in olefins, mainly because of their greater molecular mass and sizes. This will ultimately result in decrease of the rate constant.

Table 2 shows some examples of ozonolysis of saturated polymers - polystyrene and polyisobutylene. These reactions take place not via the mechanism of ozone reaction with the double bonds but through a hidden radical mechanism with the rate constants of 4-5 orders of magnitude lower.

## 3.1. Polybutadienes

Because of the high viscosity and high value of rate constants the reaction takes place either in the diffusion or in the mixed region. In order to obtain correct kinetic data we have used the theory of boundary surface [30]:

$$[O_3] = a[O_3]_0\cdot\exp[-d(k\cdot c\cdot D)^{1/2}] \quad (3)$$

where $[O_3]$ is the ozone concentration at the distance $d$; $a$ – Henry's coefficient; $[O_3]_0$ – equilibrium ozone concentration in the gas phase at the reactor inlet; $d$ – penetration depth of ozone from the interphase surface [22]; $k$ – rate constant of the ozone reaction with double bonds; $c$ – concentration of the monomeric units; $D$ – diffusion coefficient of ozone in the liquid phase.

It was found out that the relative viscosity decreases exponentially upon ozonation of SKD solutions (Fig. 1). As the viscosity is proportional to the molecular weight it follows that the polydiene consumption should be described by the first or pseudo first order kinetics.

The value of $f$, corresponding to the number of degraded polymeric molecules per one absorbed ozone molecule can be used to calculate the degradation efficiency. The value of this parameter ($f$) may be estimated using the following equation:

$$f = 0.5\,[(M_{vt})^{-1} - (M_{v0})^{-1}]\cdot P/G \quad (4)$$

where $M_{vt}$ is the molecular weight at time moment $t$; $M_{v0}$ – the initial molecular weight; $P$ – the polymer amount; $G$ – amount of consumed ozone.

The dependence of $f$ on $G$ is a straight line for a given reactor and it depends on the hydrodynamic conditions in the reactor. It is seen from Fig. 2 that the *f* values are increasing linearly with the reaction time and decreasing with increase in ozone concentration. The corresponding dependences for Carom IR 2200 and Denka M40 ozonolysis are similar. The *f* values for $G \rightarrow 0$ were used to avoid the effect of hydrodynamic factors on them.

The values of *f* found for SKD, Carom IR 2200 and Denka M40 at $[O_3] = 1 \cdot 10^{-5}$ M amount to $0.7 \cdot 10^{-2}$, $0.78 \cdot 10^{-2}$ and 0.14, respectively, and the slopes are: -40, -70 and 200 $M^{-1}$, respectively. Substituting the known values for the parameters in Eq. (3) we have obtained *d* within the range of $1 \cdot 10^{-3} - 2 \cdot 10^{-4}$ cm, which indicates that the reaction is taking place in the volume around the bubbles, and hence in the diffusion region.

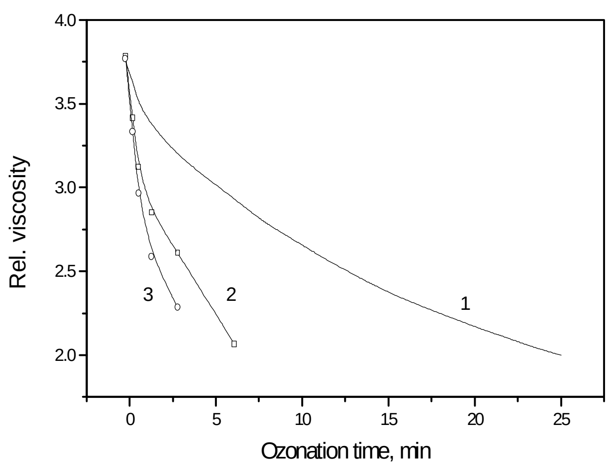



**Fig. 1.** Dependence of the relative viscosity ($h_{rel}$) of SKD solutions (0.6 g in 100 ml $CCl_4$) on reaction time at ozone concentrations of $1 \cdot 10^{-5}$ M (1); $4.5 \cdot 10^{-5}$ M (2) and $8.25 \cdot 10^{-5}$ M (3)

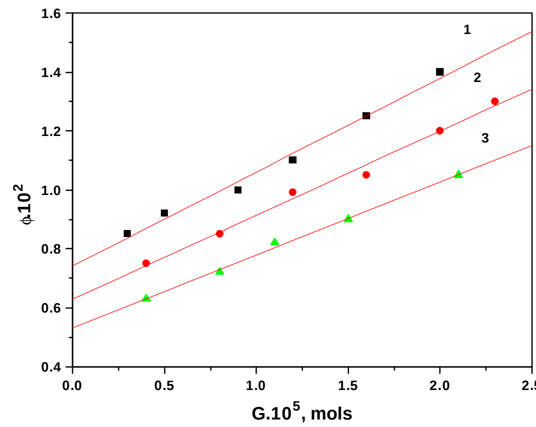
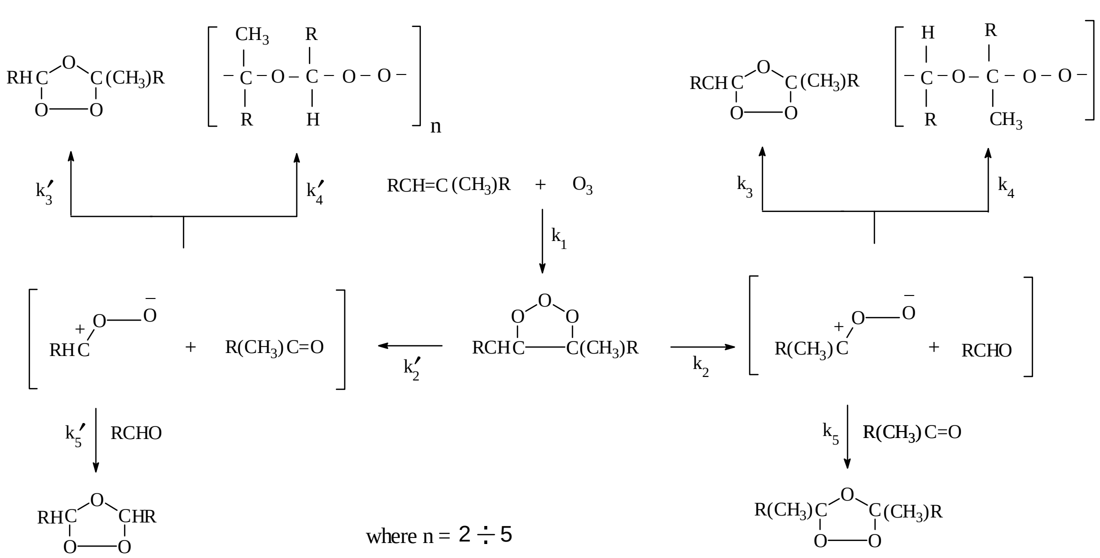



**Fig. 2**. Dependence of *f* on *G* for SKD (0.6/100) at various ozone concentrations: $1 \cdot 10^{-5}$ M (1); $4.5 \cdot 10^{-5}$ M (2) and $8.25 \cdot 10^{-5}$ M (3)

The ozonolysis of polydienes in solutions is described by the Criegee's mechanism. The C=C bonds in the macromolecules are isolated as they are separated by three single carbon-carbon bonds. According to the classical concepts, the C=C bonds configuration and the electronic properties of the groups bound to them, also affect the polymer reactivity; similarly they do this in case of the low molecular olefins. The only difference is that the polymer substituents at the C=C bonds are less mobile, which influences the $sp^2$-$sp^3$ transition and the ozonides formation. In the first stage, when primary ozonides (PO) (Scheme 1, reaction 1) are formed, the lower mobility of the polymer substituents requires higher transition energy, the rate being respectively lower, compared to that with low molecular olefins and the existing strain accelerates the PO decomposition to zwitterion and carbonyl compound.




**Scheme 1**. Criegee's mechanism of ozonides formation

The lower mobility of the polymer parts impedes the further ozonide formation and causes the zwitterion to leave the cage and pass into the volume, which in its turn accelerates the degradation process. The latter is associated either with its monomolecular decomposition or with its interaction with low molecular components in the reaction mixture. The efficiency of degradation is determined by the C=C bonds location in the macromolecule, for example, at C=C bond location from the macromolecule center to its end, it is in the range from 2 to 1.

$$M_1 = (1/g)\cdot M_0 \qquad (5)$$

and $M_2 = M_0 - M_1$; where $1 \le g \le 2$ – coefficient pointing the C=C bond location; $M_0$, $M_1$ and $M_2$ – the molecular weights of the initial macromolecule and of the two degradated polymer parts, respectively.

At $g = 2$, *i.e.* when the broken C=C bond is located in the macromolecule center, the values of $M_1$ and $M_2$ will be exactly equal to $M_0/2$, at $g \to 1$, *i.e.* at terminal C=C bond in the polymer chain, the value of $M_1$ will be approximated to $M_0$ and thus the value of $M_2$ will be practically insignificant. For example, $M_2$ may be 50–1000, which is 3-4 orders of magnitude less than that of the macromolecule and in fact degradation process will not occur. The viscosimetric determination of the molecular weight, which we have applied in our experiments, has the accuracy of ± 5 % and does not allow the differentiation of molecular weights of 22700, 19000 and 9000 for the corresponding types of rubbers. This suggests that the cleavage of C=C bonds, located at the distances of 420, 280 and 100 units from the macromolecule end, would not affect the measured molecular weight.

Since the reaction of elastomers ozonolysis proceeds either in the diffusion or in diffusion-kinetic region, at low conversions each new gas bubble in the reactor would react with a new volume of the solution. On the other hand, the reaction volume is a sum of the liquid layers surrounding each bubble. It is known that the depth of the penetration from the gas phase into the liquid phase is not proportional to the gas concentration and thus the rise of ozone concentration would increase the reaction volume to a considerably smaller extent than the ozone concentration. This leads to the occurrence of the following process: intensive degradation processes take place in the micro-volume around the bubble and one macromolecule can be degraded to many fragments, while the macromolecules out of this volume, which is much greater, may not be changed at all. Consequently with increase in ozone concentration, one may expect a reduction of coefficient MMD and increase in the oligomeric phase content. This will result in apparent decrease of $f$ in case of the viscosimetric measurements. The discussion above enables the correct interpretation of the data in Fig. 3.

In the spectra of the ozonized polybutadienes the appearance of bands at 1111 and 1735 $cm^{-1}$, that are characteristic of ozonide and aldehyde groups, respectively, is observed [22, 31]. It was found out that the integral intensity of ozonide peak in the 1,4-*cis*-polybutadiene (E-BR) spectrum, is greater and that of the aldehyde is considerably smaller in comparison with the respective peaks in the Diene 35 NFA (BR) spectrum, at one and the same ozone conversion degree of the double bonds. The mentioned differences in the aldehyde yields indicate that, according to IR-analysis, the degradation efficiency of the BR solutions is greater.

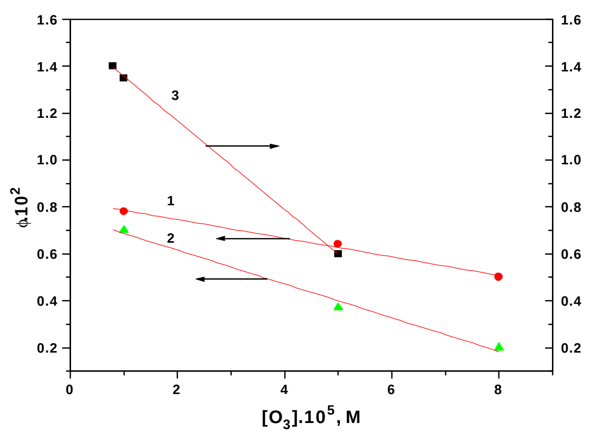



**Fig. 3.** Dependence of $f$ on ozone concentration for elastomer solutions: SKD (0.6/100) (1); Carom IR 2200 (0.6/100) (2) and Denka M40 (1/100) (3)

*Table 3*

**Assignment of the signals in the $^1$H NMR spectra of partially ozonized E-BR and BR rubbers**

| Assignment of the signals (according Fig. 4) | Chemical shifts (ppm) | | Ref. |
|---|---|---|---|
| | E-BR | BRA | |
| a | 5.10–5.20 max 5.12, 5.16 | 5.05–5.18 max 5.10, 5.15 | [19, 34] |
| b | 1.67–1.79 max 1.72, 1.76 | 1.66–1.80 max 1.73 | [7, 19] |
| c | 9.75 | 9.74 | [33] |
| d | 2.42–2.54 max 2.47 | 2.42–2.54 max 2.50 | [33] |
| e | 2.27–2.42 max 2.35 | 2.27–2.42 max 2.35 | [33] |
| f | | max 2.81 | [33] |

The $^1$H NMR spectroscopy provides much more opportunities for identification and quantitative determination of functional groups, formed during ozonolysis of polybutadienes [32]. Fig. 4 shows spectra of ozonized E-BR. The signals of the ozonolysis products are decoded in Table 3 on the basis of Fig. 5. The ozonide: aldehyde ratio, determined from NMR spectra, was 89:11 and 73:27 for E-BR and BR, respectively. The peak at 2.81 ppm is present only in the spectra of ozonized Diene 35 NFA. It is usually associated with the occurrence of epoxide groups [33]. The integrated intensity of that signal compared to the signal of aldehyde protons at 9.70–9.79 ppm, was about 10 %. Similar signal at 2.75 ppm has been registered in the spectra of ozonized butadiene-nitrile rubbers, where the 1,4-*trans* double bonds are dominant [31].

According to [2, 10] two isomeric forms of 1, 2, 4-trioxolanes exist. The ratio between them is a function of the double bond stereochemistry, steric effect of the substituents and the conditions of ozonolysis. It was fond out only on the low molecular weight alkenes [19, 21]. The $^{1}$H NMR spectroscopy is the most powerful method for determination of the *cis/trans* ratio of ozonides (in the case of polymers it is practically the only method that can be applied). The measuring is based on the differences in the chemical shifts of the methine protons of the two isomers: the respective signal of the *cis* form appears in lower field compared to the *trans* one [19, 21]. The multiplet in Fig. 4 in the area of 5.1–5.18 ppm could be interpreted as a result of partial overlapping of triplets of *trans*- and *cis*-ozonides: 5.12 ppm (t, J ≈ 5 Hz, 2H) and 5.16 ppm (t, J ≈ 5 Hz, 2H), respectively. It is interesting to note that the *cis/trans* ratio of the E-BR 1, 2, 4-trioxolanes is practically equal to that obtained from *cis*-3-hexene [19, 34]. The resolution of the respective BR spectrum does not allow consideration in detail of the multiplicity of the signals at 5.10 and 5.15 ppm. In this case the area of the signals is widened, most probably due to the presence of ozonide signals of the 1, 2-monomer units [20].

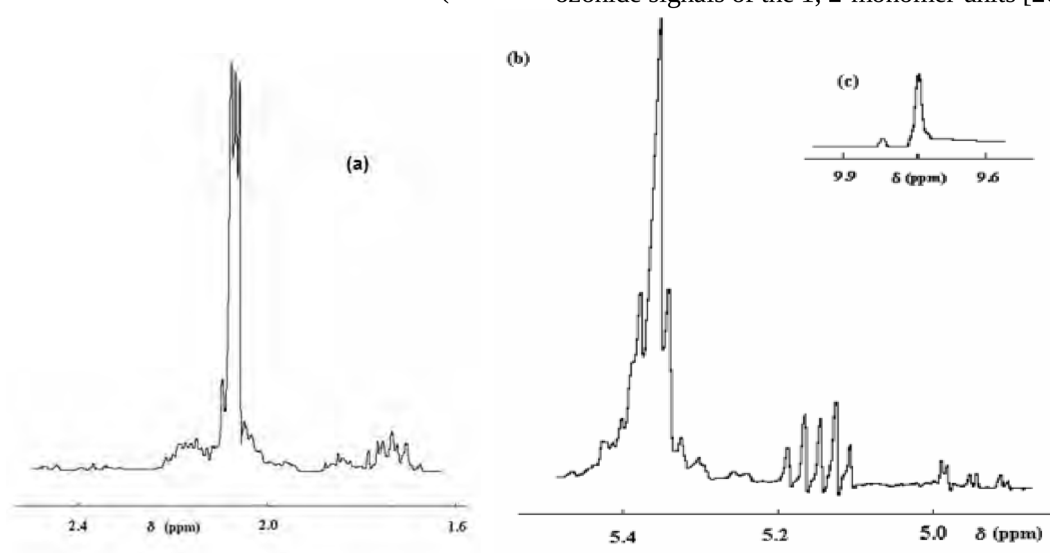



**Fig. 4.** $^{1}$H-250 MHz NMR spectra of E-BR solutions (0.89 g / 100 ml CCl4) ozonized to 18 % conversion of the double bonds (external standard TMS; digital resolution 0.4 Hz, 293 K): at 1.6–2.5 ppm region (a); at 4.8–5.6 ppm (b) and 9.5–10 ppm (c)

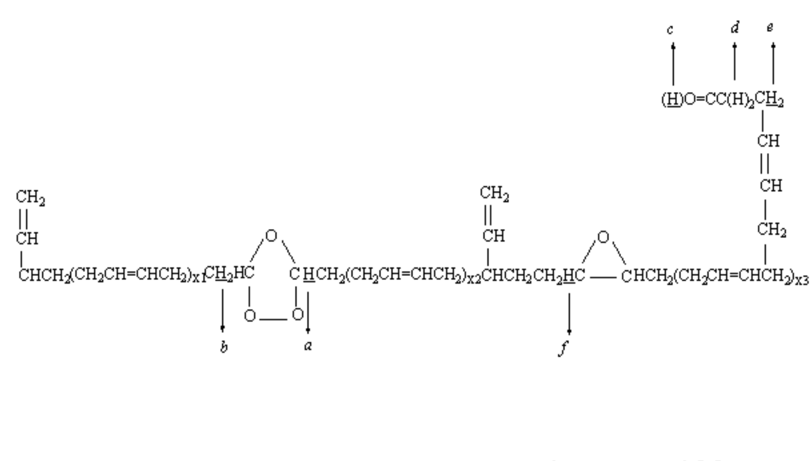



**Fig. 5.** Selection of protons with characteristic signals in the $^{1}$H-250 MHz NMR spectra of partially ozonized polybutadiene macromolecules

The basic route of the reaction – the formation of normal ozonides does not lead directly to a decrease in the molecular mass of the elastomer macromolecules, because the respective 1,2,4-trioxolanes are relatively stable at ambient temperature (by analogy with Scheme 1 of polyisoprenes, see below) [31, 32]. The most favorable conditions for ozone degradation emerge when the cage interaction (Scheme 1, reaction 3) does not proceed. Therefore, the higher ozonide yield the lower the intensity of ozone degradation of the polybutadienes and *vice versa*. As it was already determined the ozonide yields for the 1,4-*cis*- and 1,2- monomer units are close to 83–90 %, whereas that for the 1,4-*trans* units is about 50 %. The amount of aldehyde groups is usually used for evaluation of the intensity and efficiency (number of chain scissions per molecule of reacted ozone) of ozone degradation of elastomers. In this case it should be taken into account that the dominant route of degradation leads to the formation of 1 mole of aldehyde from 1 mole of ozone [32].

## 3.2. Polyisoprenes

The positive inductive effect of the methyl group in polyisoprene enhances the rate of ozone addition to the double bonds from $6{\cdot}10^4$ for SKD to $4{\cdot}10^5$ $M^{-1}{\cdot}s^{-1}$ for Carom IR 2200. The infrared spectra of ozonized 1,4-*trans*-polyisoprene (Z-IR) show two intense bands at 1100 and 1725 $cm^{-1}$, characteristic of ozonide and keto-groups, respectively [19, 35]. These spectra are identical with the well-known spectra of 1,4-*cis*-polyisoprenes (E-IR), as far as ozonide and carbonyl bands are concerned [22, 36]. It was found that the integrated intensity of the peak at 1100 $cm^{-1}$ in the E-IR and Z-IR spectra is equal for one and the same amount of reacted ozone. By analogy with the peak at 1110 $cm^{-1}$, the integral intensity of the peak at 1725 $cm^{-1}$ is also one and the same. The latter show that, according to the infrared spectra, the degradation efficiencies of E-IR and Z-IR with respect to the amount of consumed ozone practically do not differ.

The $^1$H NMR spectroscopy affords much more opportunities for identification and quantitative determination of functional groups formed on ozonolysis of polyisoprenes. Fig. 6 shows spectra of non-ozonized and ozonized E-IR. Changes in the spectra of ozonized elastomers are decoded in Table 4 on the basis of Fig. 7. It is seen that besides ketones, aldehydes are also formed as a result of ozonolysis. A comparison between methylene and methine proton signals of the non-ozonized polyisoprenes and the corresponding ozonide signals indicates a considerable overlap in the ranges 1.60–1.90 and 4.5–5.5 ppm. A signal overlap is also registered in the 2.00–2.20 ppm region, characteristic of methyl protons of keto-groups. Because of the reasons mentioned above, the ozonides and aldehydes were quantified by using the integrated intensity of the signals at 1.40 (a) and 9.70–9.79 (g) ppm, respectively. Ketone amounts were determined as a difference between the total intensity of the methylene signals from aldehydes and ketones, 2.40–2.60 and 2.35–2.60 ppm, respectively, and the doubled intensity of the aldehyde signal at 9.70–9.79 ppm. Thus the obtained ozonide:ketone:aldehyde ratio was 40:37:23 and 42:39:19 for 1,4-*cis*-polyisoprene and 1,4-*trans*-polyisoprene, respectively. The peak at 2.73 ppm, present in the spectra of both ozonized elastomers, is associated with the occurrence of epoxide groups [33, 37]. The integrated intensity of that signal compared to the signal at 9.70–9.79 ppm was 21 and 15 % for E-IR and Z-IR, respectively.

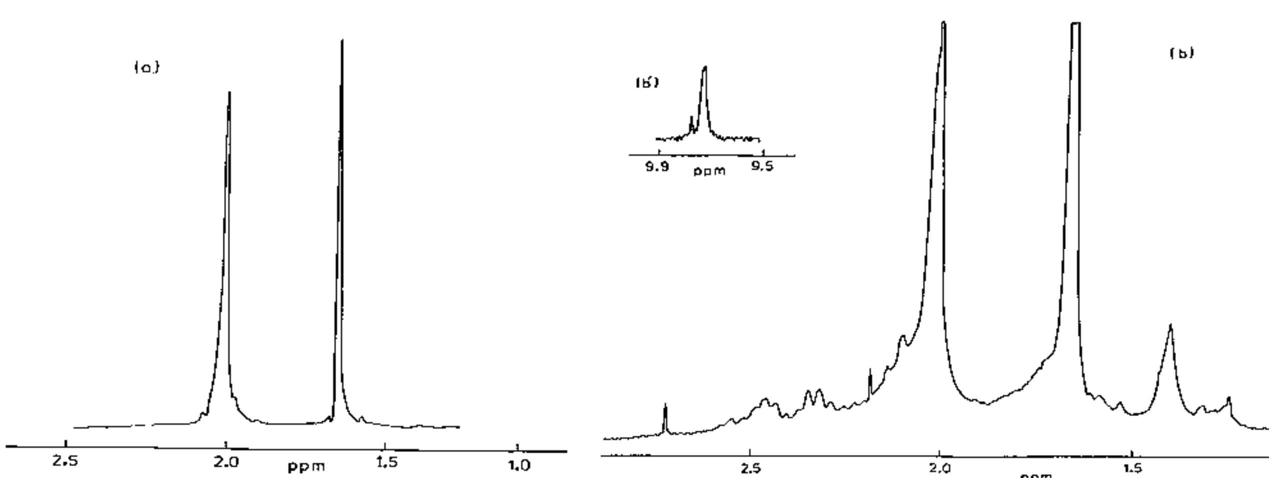



**Fig. 6.** $^1$H-250 MHz NMR spectra of 1,4-*cis*-polyisoprene solutions (1 g/100 ml $CCl_4$): non-ozonized (a) and ozonized to 23 % conversion of the double bonds (b); external standard TMS; digital resolution 0.4 Hz; 293 K

*Table 4*

**Assignment of the signals in the $^1$H-NMR spectra of partially ozonized 1,4-*cis*-, and 1,4-*trans*- polyisoprenes**

| Assignment of the signals (according Fig. 4) | Chemical shifts (ppm) | | Ref. |
|---|---|---|---|
| | E-IR | Z-IR | |
| a | max 1.41 | max 1.40 | [37, 38] |
| b | 1.70–1.78 | 1.68–1.82<br>max 1.71 | [37] |
| c | 2.10–2.20 | 2.10–2.20 | [33] |
| d | 2.22–2.40<br>max 2.33, 2.36 | 2.22–2.35<br>max 2.29, 2.33 | [33] |
| e | 2.40–2.60<br>max 2.47 | 2.35–2.55<br>max 2.48, 2.46 | [33] |
| f | max 2.73 | max 2.73 | [33] |
| g | max 9.76 | max 9.77 | [33] |

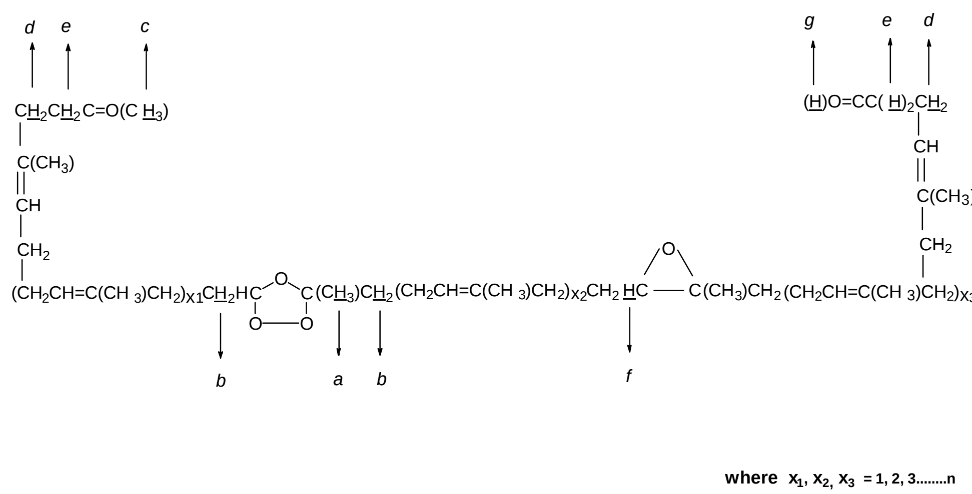
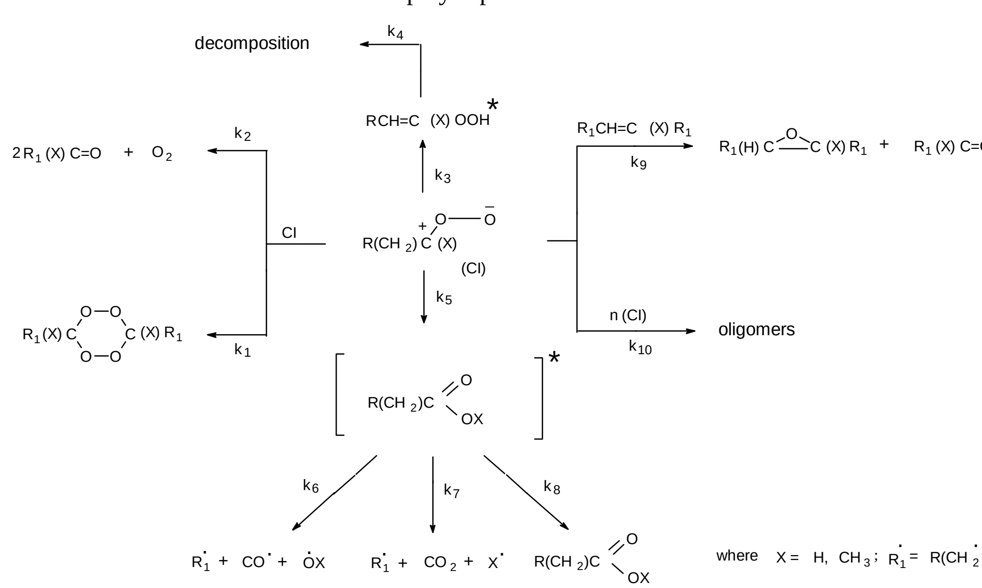



**Fig. 7.** Selection of protons with characteristic signals in the $^1$H-250 MHz NMR spectra of partially ozonized polyisoprene macromolecules




**Scheme 2**. Non-ozonide routes of deactivation of Criegee's intermediates

*Table 5*

**Intermediates and products of the ozonolysis of 1,4-*cis*-, and 1,4-*trans*- polyisoprenes**

| | DCI + aldehydes (64 %) | | | MCI + ketones (36 %) | | |
|---|---|---|---|---|---|---|
| | Ozonides, % | Aldehydes, % | DCI, % | Ozonides, % | Ketones, % | MCI, % |
| hypothese (i) | | | | | | |
| E-IR | 40 | 24 | 24 | 0 | 36 | 36 |
| Z-IR | 42 | 22 | 22 | 0 | 36 | 36 |
| hypothese (ii) | | | | | | |
| E-IR | 26 | 38 | 38 | 14 | 22 | 22 |
| Z-IR | 27 | 37 | 37 | 15 | 21 | 21 |

Current ideas about the mechanism of C=C double bond ozonolysis in solution are summarized in Schemes 1 and 2 [19, 21, 34]. As a result of the decomposition of the initial reaction product, primary ozonide (PO), zwitterionic species is formed, termed as Criegee's intermediates or carbonyl oxides (hereafter referred to as CI) (Scheme 1, reactions 2 and 2'). Two intermediates are formed from asymmetric olefins: monosubstituted CI (MCI) and disubstituted CI (DCI), if their *syn*- and *anti*-stereoisomers are not taken into account. It is known that carbonyl oxides are predominantly formed at carbon atoms with electron-donating substituents [19]. Excellent correlations of the regioselectivities of MO fragmentation with electrondonation by substituents (as measured by Hammett and Taft parameters) have been obtained, consistent with the effects expected for stabilization of a zwiterionic carbonyl oxide [20]. According to Ref. [23], for polyisoprenes the ratio between the two intermediates, DCI and MCI, is 64:36.

Ozonides are the basic product of polyisoprene ozonolysis in non-participating solvents. It is known that the dominant part of ozonides is formed through the interaction between CI and the corresponding carbonyl group, which originate from the decomposition of one and the same PO, *i.e.* a solvent cage effect is operating (Scheme 1, reactions 3 and 3') [19, 34]. With simple olefins the so-called normal ozonides are over 70 % [26]. Cross-ozonide formation is also observed (Scheme 1, reactions 5 and 5'). The amount of cross-ozonides is dependent upon the structure of the double bonds, their concentration in the solution, temperature and solvent nature. Reference data indicate that the cross-ozonide yield is strongly reduced at C=C bond concentrations of the order of 0.1 M, with non-polar solvents, and at temperatures over 273 K [19]. It is reasonable to expect that the polymeric nature of the double bonds in the polyisoprenes would additionally impede the formation of cross-ozonides. Our estimates showed that the amount of cross-ozonides, formed on ozonolysis of both elastomers, is less than 10 % of their total quantity. A very small percentage in the overall balance of reacted ozone is the share of the reaction of polymeric ozonides formation (Scheme 1, reactions 4 and 4') [22].

In the presence of two types of intermediates, DCI and MCI, it is interesting to follow their further conversion with a view to the reaction products determined by $^{1}$H NMR spectroscopy. The reaction between CI and carbonyl groups is usually considered to be 1,3-cycloaddition [20, 34]. In this connection the CI-aldehyde interaction is the most effective one: it readily precedes with high ozonide yields. Ketones are considerably less dipolarophilic and good yields of ozonides are limited to special conditions involving particularly reactive ketones, intramolecular reactions, or where ketone is used as the reaction solvent and is therefore present in large concentration [19-21]. In order to evaluate the contribution of reactions 3 and 3' (Scheme 1), it is useful to discuss two hypotheses: i) no reaction proceeds between MCI and ketone, the registered amount of ozonides being formed in reaction 3; ii) because of the solvent cage effect already mentioned, both of the reactions can be considered with practically equal rate constants. Then the ozonide yields would be proportional to the ratio between the two zwitterions (64:36). In this case the corresponding yields of the reactions DCI + aldehyde and MCI + ketone can be calculated from the following system of equations:

$$Y = x + y \qquad (6)$$

$$x/y = 64/36 \qquad (7)$$

where $Y$ is the total ozonide yield, $x$ and $y$ are the corresponding ozonide yields with the former and the latter reactions, respectively. The results are given in Table 5. A comparison between the aldehyde amounts from both hypotheses and NMR data shows that the former hypothesis leads to results that are much closer to the experimental data.

More complicated is the question of the other conversion routes with carbonyl oxides outside the solvent cage. It is generally accepted that the deactivation of DCI from low molecular olefins normally takes place via a bimolecular reaction mechanism. At low temperatures (below 203 K) dimeric peroxides are formed (Scheme 2, reaction 1) whereas higher temperatures give rise to the formation of carbonyl compounds and evolution of oxygen (Scheme 2, reaction 2) [20]. However, on comparing the yields of keto-groups, determined from $^1$H NMR spectra, with the amounts of ketones and DCI, presented in Table 5, it is seen that reaction 2, if occurring at all, is not dominating during DCI conversion. From kinetic evaluations of CI concentrations in solution it follows that under comparable experimental conditions these concentrations are 4-6 orders of magnitude lower than those of the C=C bonds [23]. Very likely, interactions between two or more DCI are hindered by extremely low values of CI concentration and mostly by the polymeric nature of substituent $R_1$. Under these conditions, DCI tautomerization followed by decomposition of hydroperoxides, formed in the excited state (Scheme 2, reactions 3 and 4) seems most probable.

On going into MCI conversion routes one should have in mind the lower stability and lifetime of these intermediates compared to DCI. Reference data on the proceeding of reactions 1 and 2 (Scheme 2) during ozonolysis of low-molecular olefins in solution are missing [34]. On ozonolysis of 1,4-*trans*-polychloroprene the share of CI of the MCI type is over 80 %, in agreement with the induction effect of the chlorine atom [23]. However, no aldehyde groups in the ozonized polymer solution were found [39]. It follows that the interaction between MCI entites, if any, is not the dominating deactivation reaction with these intermediates. The most probable MCI monomolecular deactivation route is assumed to be the isomerization of the MCI intermediates via hot acid to radicals (Scheme 2, reactions 5-7), because no acid groups were detected (Scheme 2, reaction 8). According to the literature reaction 5 (Scheme 2) does not occur with DCI intermediates [21].

Another route of carbonyl oxide deactivation is double bond epoxidation. Various schemes of olefin epoxidation during ozonolysis have been suggested but the epoxidation via CI (Scheme 2, reaction 9) is presumed to be the most probable with the C=C bonds in polyisoprenes [20, 21]. Since a peak at 2.73 ppm has also been observed under similar conditions on ozonolysis of acrylonitrile-butadiene copolymers [31], as well as during ozonolysis of polybutadienes, it can be assumed that the epoxidation reaction takes place with the participation of both types of CI.

## 3.3. Polychloroprene

The electron-accepting properties of the chlorine atom at the polychloroprene double bond reduces the reactivity of Denka M40 as demonstrated by its relatively low rate constant, *i.e.* $k = 4{\cdot}10^3$ $M^{-1}{\cdot}s^{-1}$. In this reaction the ratio between the zwitterions A and B, according to theoretical calculations, is in favour of A, the ratio being A/B = 4.55. The A formation is accompanied by choroanhydryde group formation and that of B with aldehyde one. In both cases the ozonides formation is insignificant and the zwitterions react predominantly in the volume resulting in enhancement of the degradation process. The intensive band detected at 1795 cm$^{-1}$ in the IR spectrum of ozonized Denka M40 solutions (Fig. 8) is characteristic of chloroanhydride group [39]. This fact correlated well with the conclusion about the direction of the primary ozonide decomposition. The band at 955 cm$^{-1}$ is also typical of chloroanhydrides. Two other bands – at 1044 and 905 cm$^{-1}$ may be attributed to the C–O vibrations. The valent vibrations characteristics of HO-groups are observed in the region of 3050–3500 cm$^{-1}$.

The iodometrical analysis of active oxygen in the ozonized Denka M40 solutions shows that the amount of O–O groups is ca. 43 %. It is of interest to note that the HI reaction with ozonized polychloroprene solutions occurs quantitatively for 3–4 h, while in SKD the same proceeds only to 20 % after 24 h. The above data, however, provide insufficient information for the preferable route of the zwitterions deactivation (*via* dimerization, polymerization of zwitterions or secondary processes).The DSC analysis of the products of Denka M40 ozonolyis reveals that the chloroprene rubber ozonolyis yields polyperoxide as the enthalpy of its decomposition is found to be very close to that of dicumeneperoxide (DCP), The higher value of $E_a$ (ca. two times of that of DCP) testifies to the possible formation of polymer peroxides [4].

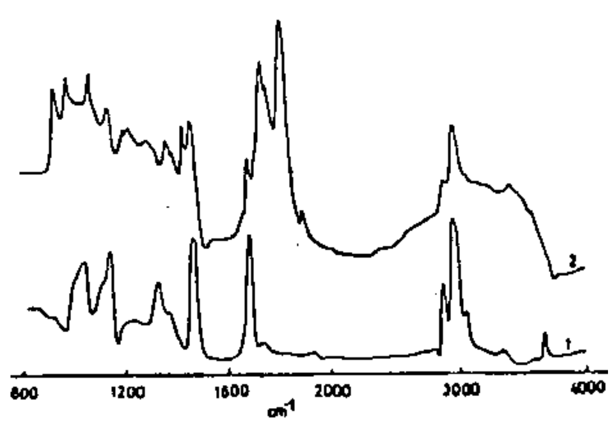



**Fig. 8.** Infra-red spectra of Denka M40 solutions: non-ozonized (1) and ozonized to 40 % conversion (2)

## 3.4. DSC Study of Thermal Decomposition of Partially Ozonised Diene Rubbers

The thermal decomposition of the ozonized diene rubbers can exercise influence on the ageing processes as an initiator of the oxidation reactions [40]. On the other hand it is of interest for the elastomers modification and oligomerization [6]. The importance of the DSC method to the investigation of 1,2,4-trioxolanes is based on high values of the enthalpy of the reaction of ozonide thermal decomposition and on the temperature range in which it takes place [41-43]. An intense and relatively broad exothermic peak is characteristic of the thermograms of the partially ozonated 1,4-*cis*-polybutadiene (E-BR), Diene 35 NFA (BR), 1,4-*cis*-polyisoprene (E-IR), 1,4-*trans*-polyisoprene (Z-IR) and 1,4-*trans*-polychloroprene (PCh), recorded in 60–200°C range (Fig. 9). Practically no thermal effects are detected in the respective thermograms of the nonozonized samples.

For an objective consideration on the enthalpy changes it is necessary to normalize $\Delta H$ values with respect to the amount of consumed ozone ($G$). It is distributed on the whole mass of the ozonated sample. The whole mass is a sum of the mass of nonozonated rubber and mass of the incorporated in diene macromolecules oxygen atoms, grouped as a moles ozone. Determination of the amounts of the incorporated ozone ($G_{inc}$) in rubber samples is performed in [43]. The corresponding values of the coefficient of incorporation of ozone ($c_{inc}$), defined as a ratio of the amounts of incorporated ($G_{inc}$) and consumed ($G$) ozone is presented in Table 6. Using $\Delta H_1$ values and ratio of the functional group, deduced from the NMR spectra, the enthalpy of the ozonide thermal decomposition ($\Delta H_2$) has been evaluated. The data of Table 6 clearly show tendency of increasing of $\Delta H_2$ values with the number of alkyl substituents of the ozonides.

There are no considerable differences between the values of the activation energy ($E_a$) and reaction order ($n$) of the ozonide thermal decomposition with E-IR and Z-IR (Table 7). The smaller $E_a$ values of the polyisoprene ozonides in comparison with those of E-BR ozonides and 1-decene ozonide are, most probably, due to the lower thermal stability of small amounts of oligomeric peroxides, which are present among the reaction products of E-IR and Z-IR ozonolysis [36].

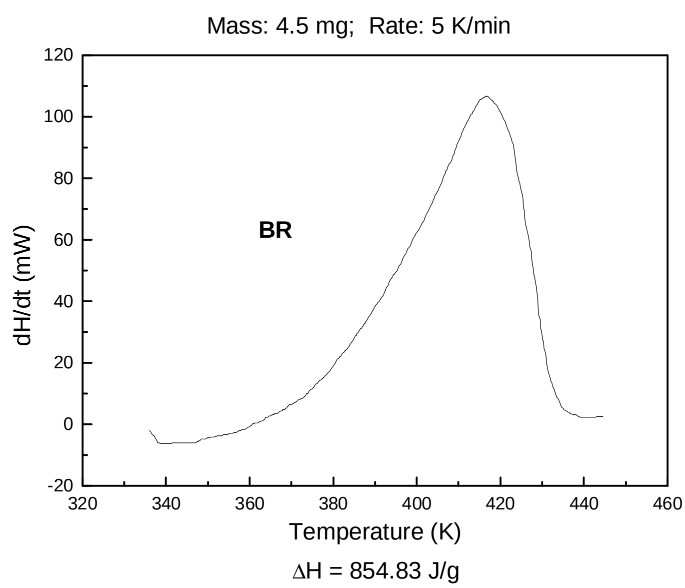



**Fig. 9.** DSC curve of partially ozonated Diene 35 NFA rubber (BR)

*Table 6*

**Enthalpy changes on the thermolysis of partially ozonated diene rubbers**

| Sample | $\Delta H$, J/g | $c_{inc}$ | $\Delta H_1$, kJ/mol $O_3$ | Ozonide (mol)/ Incorp. ozone (mol) | $\Delta H_2$, kJ/mol ozonide |
|---|---|---|---|---|---|
| E-BR | 954.07 | 0.93 | 332 | 0.96 | 373 |
| BR | 854.83 | 0.87 | 271 | 0.89 | 350 |
| E-IR | 576.19 | 0.62 | 182 | 0.65 | 453 |
| Z-IR | 576.62 | 0.62 | 178 | 0.67 | 426 |
| PCh | 704.57 | 0.81 | 254 | | |
| 1-Decene ozonide | | | | | 349 [7] |

*Table 7*

**DSC analysis of the ozonized rubbers decomposition [43]**

| | *$T_m$, K | $a_s$ | $E_a$, kJ/mol | *n* |
|---|---|---|---|---|
| E-BR | 420 | 0.67 | 125 | 1.0 |
| BR | 418 | 0.68 | 117 | 0.96 |
| E-IR | 433 | 0.68 | 111 | 1.04 |
| Z-IR | 422 | 0.68 | 113 | 1.08 |
| PCh | 369 | 0.55 | 70 | 1.25 |
| 1-Decene ozonide | 390 | 0.63 | 132 | 1.0 |

*$T_m$ and $a_s$ values at heating rate of 5 $^o$/min; $T_m$ and $a_s$ are temperature and degree of conversion at the DSC peak maximum.

## 4. Conclusions

Ozone reaction with a number of polyidienes with different configurations of the double bonds and various substituents was investigated in $CCl_4$ solution.

The changes of the viscosity of the polymer solutions during the ozonolysis were characterized by the determination of the number of chain scissions per molecule of reacted ozone (*f*). The influence of the conditions of mass-transfer of the reagents in a bubble reactor on the respective *f* values was discussed.

The basic functional groups-products from the rubbers ozonolysis were identified and quantitatively characterized by means of IR-spectroscopy and $^1$H-NMR spectroscopy. The aldehyde:ozonide ratio was 11:89 and 27:73 for E-BR and BR, respectively. In addition, epoxide groups were detected, only in the case of BR, their yield was about 10 % of that of the aldehydes. On polyisoprenes the ozonide:ketone:aldehyde ratio, was 40:37:23 and 42:39:19 for E-IR and Z-IR, respectively. Besides the already specified functional groups, epoxide groups were also detected, their yields being 8 and 7 % for E-IR and Z-IR, respectively, with respect to reacted ozone. In the case of 1,4-*trans*-polychloroprene the chloroanhydride group was found to be the basic carbonyl product.

A reaction mechanism, that explains the formation of all identified functional groups, was proposed. It has been shown that the basic route of the reaction of ozone with elastomer double bonds – the formation of normal ozonides does not lead directly to a decrease in the molecular mass of the elastomer macromolecules, because the respective 1,2,4-trioxolanes are relatively stable at ambient temperature. The most favorable conditions for ozone degradation emerge when the cage interaction between Crigee's intermediates and respective carbonyl groups does not proceed. The amounts of the measured different carbonyl groups have been used as an alternative way for evaluation of the intensity and efficiency of ozone degradation.

The thermal decomposition of partially ozonated diene rubbers was investigated by DSC. The respective values of the enthalpy, the activation energy and the reaction order of the 1,2,4-trioxolanes were determined.

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## ОЗОН І ЙОГО РЕАКЦІЇ З ДІЄНОВИМИ ЕЛАСТОМЕРАМИ

***Анотація***. *Досліджено реакції озону з: 1,4-цис-полібутадієном (SKD); дієновим еластомером 35 NFA, який містить 1,4-цис (47 %), 1,4-транс (42 %), 1,2- (11 %) бутадієнових одиниць; 1,4-цис-поліізопреном (Carom IR 2200); 1,4-транс-поліхлоропреном (Denka M40) і 1,4-транс-поліізопреном в* $CCl_4$*. Зміна в'язкості розчинів полімерів при озонолізі характеризується числом розривання ланцюга на одну молекулу поглиненого озону (φ). Досліджено вплив умов масоперенесення реагентів на значення φ в барботажному реакторі. За допомогою ІЧ- та* $^1$*Н-ЯМР спектроскопії ідентифіковані та кількісно охарактеризовані основні функційні групи продуктів озонолізу. Запропоновано механізм реакції, який пояснює формування всіх виявлених функційних груп. Показано, що основний напрямок реакції озону з подвійними зв'язками еластомерів (формування нормальних озонідів) не приводить до зниження молекулярної маси, тоді як відповідні 1,2,4-триоксолани відносно стабільні за кімнатної температури. Виявлено, що найсприятливіші умови для озонової деструкції еластомерів виникають, коли в кінетичній клітині не відбувається взаємодії між цвіттер-йоном і відповідною карбонільною групою. Кількість карбонільних груп використано як альтернативний спосіб оцінювання інтенсивності і ефективності озонової деструкції. Досліджено термічний розклад частково озонованих каучуків методом ДСК та отримано відповідні значення ентальпії, енергії активації і порядок реакції термічного розкладу 1,2,4-триоксоланів.*

***Ключові слова***: *озон, озоноліз, дієновий еластомер, механізм, розклад.*