

DSC Study of Thermal Decomposition of Partially Ozonized Diene Rubbers

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SYNOPSIS

The thermal decompositions of partially ozonized 1,4-*cis*-polybutadiene (E-BR), 1,4-*cis*-polyisoprene (E-IR), 1,4-*trans*-polyisoprene (Z-IR), 1,4-*trans*-polychloroprene (Z-PCh), and of polybutadiene elastomer (BR) (microstructure: 1,4-*cis*, 47%; 1,4-*trans*, 42%; 1,2, 11%) were studied. The respective thermograms were described by the presence of an intense and relatively broad exothermic peak in the 60–200°C range, which is the result of thermolysis of functional groups of the peroxide type. The measured values of the enthalpy of the reaction, normalized with respect to the amount of reacted ozone (kJ/mol O₃), were as follows: 337 (E-BR), 260 (BR), 197 (E-IR), 180 (Z-IR), and 239 (Z-PCh). Values of the activation energy and reaction order were also determined: 122.6, 118.5, 108, 113, 101.5 and 1.0, 0.96, 1.04, 1.08, and 1.25, respectively. The enthalpy values, obtained by means of differential scanning calorimetry, should be used for quantitative determination of ozonides from polydienes and polyisoprenes. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Ozonides are the basic product of ozonolysis of most diene elastomers.^{1,2} Studies of the thermal decomposition of ozonides and other peroxide type products under conditions of partial ozonolysis of rubber macromolecules are of interest for the effect on the aging processes in vulcanizates,^{3,4} and for the possibilities for elastomer modification and/or oligomerization.^{5,6} Until now, works reported in this field have been preliminary and include only a few polydiene elastomers.^{7,8} Practically no studies have been published so far in which thermal analysis methods are applied.⁹

In the present paper we report on a differential scanning calorimetry (DSC) investigation of the thermal decomposition of five diene rubbers that were partially ozonized in solution.

EXPERIMENTAL

Materials

Commercial samples of 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); and 1,4-*trans*-polychloroprene (Denka M 40) were used in the experiments. The 1,4-*trans*-polyisoprene samples were kindly supplied by Dr. A. A. Popov (Institute of Chemical Physics, Russian Academy of Sciences). All rubbers were purified by threefold precipitation from CCl₄ solutions with excess methanol. The above-mentioned elastomer structures were confirmed by means of ¹H-NMR spectroscopy.

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

Ozonation of Elastomer Solutions

The ozonolysis of elastomers was performed by passing an ozone–oxygen gas mixture at a rate of $v = 1.6 \times 10^{-3} \pm 0.1 \text{ L s}^{-1}$ and ozone concentration of

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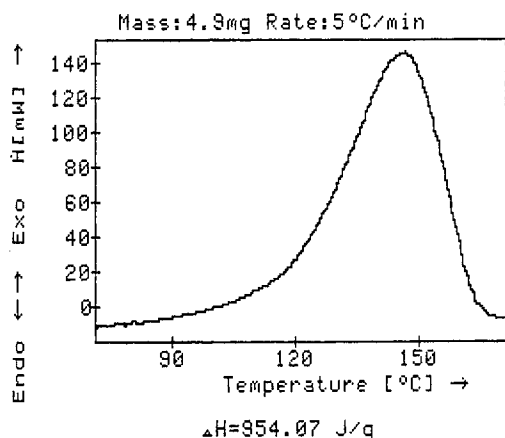


Figure 1 DSC curve of 1,4-*cis*-polybutadiene rubber (E-BR) with 17.8% ozonized C=C double bonds.

$1.1 \times 10^{-4} \pm 0.06 \text{ mol/L}^{-1}$ through a bubbling reactor containing 10 mL of polymer solution (1 g/100 mL CCl_4) at 293 K. Ozone concentrations in the gas phase at the reactor inlet ($[\text{O}_3]_i$) and outlet ($[\text{O}_3]_u$) were measured spectrophotometrically at 254 nm.² The amount of consumed ozone (G , mol) was calculated by the equation

$$G = v([\text{O}_3]_i - [\text{O}_3]_u)t, \quad (1)$$

where t is the ozonation time (s). The degree of conversion of double C=C bonds was determined on the basis of the amount of reacted ozone and the reaction stoichiometry (1 : 1),¹⁰ and varied between 15 and 30%.

DSC

DSC was carried out in a Mettler calorimeter Model FP 800, equipped with a computer, in argon flow at a rate of 60 mL min^{-1} . Samples (4–7 mg) were prepared by evacuation of the solvent from the respective rubber solutions. At least three measurements were performed at every heating rate.

RESULTS AND DISCUSSION

Enthalpic analysis

An intense and relatively broad exothermic peak was present in the thermograms of 1,4-*cis*-polybutadiene (E-BR), polybutadiene Diene NFA (BR), 1,4-*cis*-polyisoprene (E-IR), 1,4-*trans*-polyisoprene (Z-IR), and 1,4-*trans*-polychloroprene (Z-PCh) in the 60–200°C range (Figs. 1–3). These peaks could not be

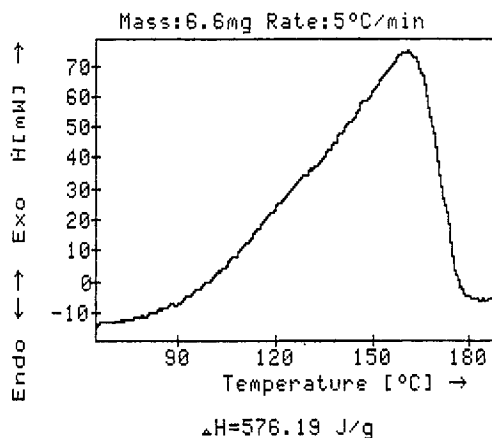


Figure 2 DSC curve of 1,4-*cis*-polyisoprene rubber (E-IR) with 24.4% ozonized C=C double bonds.

resolved upon varying the heating rate within 1–10°C min^{-1} .

Values of the enthalpy changes of the examined samples, normalized with respect to the amount of reacted ozone (ΔH_1), are given in Table I. The highest values were found with E-BR. Lower values were measured for BR and Z-PCh. The lowest ones were observed with the polyisoprenes. Experiments conducted at various conversions of the double bonds showed that the values of ΔH_1 were independent of the conversion degree in the range investigated (15–30%).

The modern concepts about the mechanism of the reaction of ozone with C=C double bonds is summarized in Scheme 1.^{10,11} It is seen that besides the basic reaction product, ozonides, other functional groups of the peroxide type, and carbonyl and carboxylic groups are also formed. The ratio between

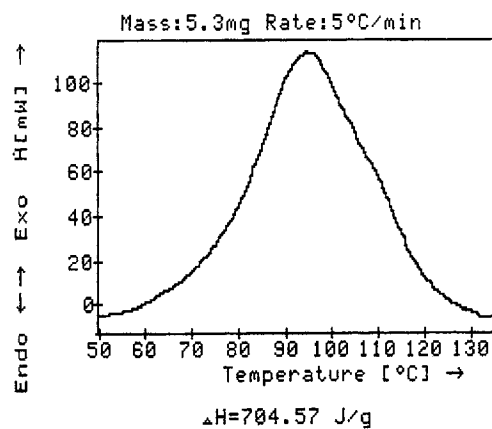


Figure 3 DSC curve of 1,4-*trans*-polychloroprene rubber (Z-PCh) with 28.6% ozonized C=C double bonds.

Table I DSC Analysis of Functional Groups of Peroxide Type

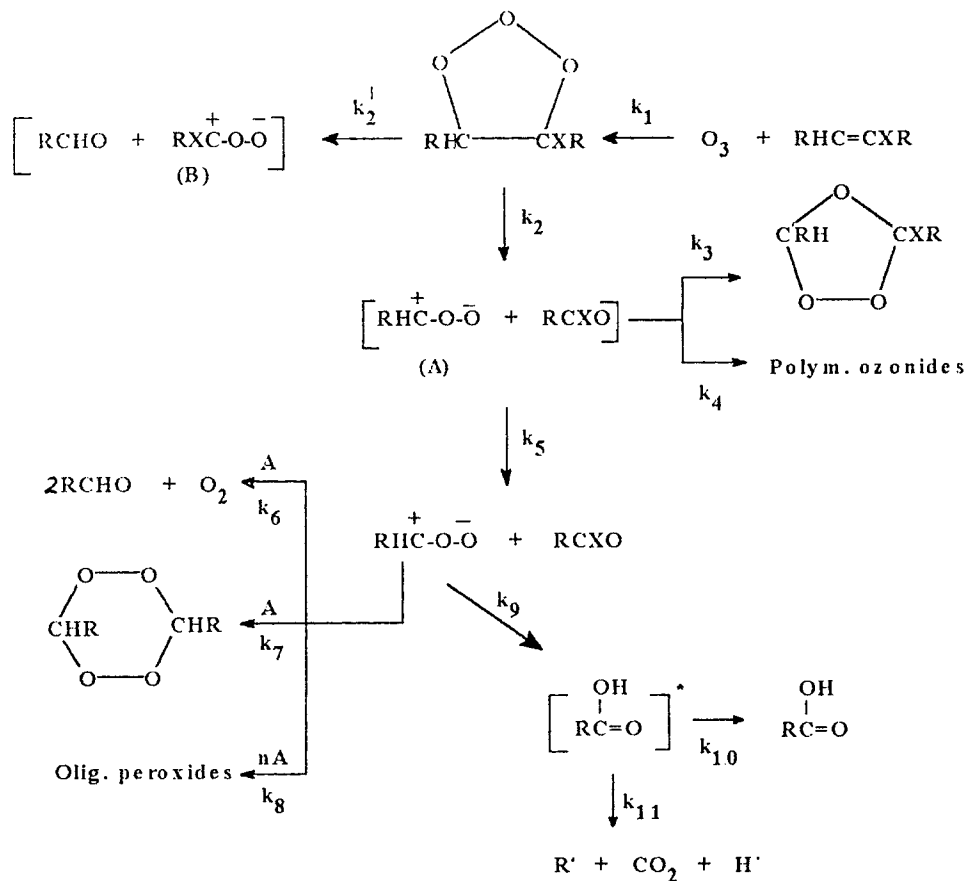
	ΔH_1 (kJ/mol O ₃)	ΔH (kJ/mol)	α_s	E (kJ/mol)		n	
				Eq. (2)	Eq. (3) ^a	Eq. (2)	Eq. (4)
E-BR	337 ± 10	370	0.67	123	127	1.0	0.75
BR	260 ± 10		0.68	118	116	0.96	0.72
E-IR	197 ± 9		0.68	108	113	1.04	0.72
Z-IR	180 ± 9		0.68	113	114	1.08	0.72
Z-PCh	239 ± 9		0.55	102	70	1.25	1.35
1-Decene ozonide		349 ± 9	0.63	129	132	1.0	0.9

^a E [eq. (3)] values were calculated assuming $n = 1$.

the different functional groups is dependent on the nature of the double bonds (their configuration and type of substituent) and the reaction conditions.¹⁰

The thermal decomposition of nonozonized elastomers in inert atmosphere has been thoroughly studied.¹² From reference data it follows that the thermal treatment of E-BR, BR, E-IR, Z-IR, and Z-

PCh in the range 60–200°C is not accompanied by changes in their structure and considerable endo- and exothermic effects. Carbonyl, acid chloride, and carboxylic groups are also stable in this range.¹³ In addition, the following experiments were carried out: thermal treatment of nonozonized sample and repeated thermal treatment of partially ozonized



Scheme 1. Mechanism of the reaction of ozone with C=C double bonds; X represents H, CH₃, or Cl.

sample. In both cases no visible changes of enthalpy were registered. It can be assumed that the above-mentioned data and the literature data on the thermal decomposition of ozonides¹⁴ and other types of organic peroxides, such as 1,2,4,5-tetraoxanes,¹⁵ 1,2,4-trioxanes,¹⁶ dialkyl peroxides,¹⁷ and polymer peroxides,¹⁷ substantiate our understanding that the observed enthalpy changes of partially ozonized polymer samples are due to decomposition of functional groups containing peroxide-bonded oxygen.

The predominant product of ozonolysis of polybutadienes and polyisoprenes in inert solutions is the ozonide.^{5,18,19} It is accepted that the amount of polymer peroxides and dimmer peroxides, if formed with the polyisoprenes, is on the order of a few percent with respect to the amount of ozonides.^{2,5,20} For the present the nature of the functional groups of the peroxide type in polychloroprenes cannot be identified.²¹

The mechanism of ozonide thermal decomposition has not been clarified in detail, but from the values of the activation energy one can expect that the limiting step of the reaction is the homolytic scission of the O=O bond.^{10,14} In this connection it is important to know whether the ΔH_1 values, shown in Table I, are the result only of ozonide thermolysis or, during thermal decomposition of 1,2,4-trioxolanes, if secondary radical processes contributing to the values of ΔH_1 are also initiated. Such a process can be elastomer crosslinking. Upon peroxide vulcanization by dicumyl peroxide (DCP), the increase of enthalpy of the reaction in comparison with the enthalpy of the thermal decomposition of "pure" DCP ($\Delta H = 215$ kJ/mol) was 27-fold for E-BR and 1.7-fold for E-IR.^{12,22} Razumovskii and Zaikov made a comparative chemiluminescence analysis of ethylbenzene oxidation by using azo-bis-isobutyronitrile (AIBN) and the ozonide of 1-hexene as initiators.² The light intensity with the ozonide initiator was 1.5–3% of that observed for AIBN for one and the same decomposition rate of both initiators. Based on the aldehyde : ozonide ratio (11 : 89, unpub. results), determined from ¹H-NMR spectra, and the degree of conversion of C=C bonds, we estimated the enthalpy value of ozonide thermal decomposition of partially ozonized E-BR at 370 kJ/mol. This value is practically identical with the respective value of 1-decene ozonide ($\Delta H = 350$ kJ/mol).¹⁴ Therefore, no secondary radical processes are initiated on thermolysis of E-BR ozonides. It is unlikely that these processes may also proceed during the thermolysis of ozonized BR rubber and polyisoprenes. The absence of secondary

radical processes during ozonide thermolysis creates prerequisites to use the ΔH_1 values, obtained from DSC thermograms, for determination of the ozonide amounts.

The quantitative determination of ozonides formed during ozonolysis in solution of polydienes, polyisoprenes, and other polymers containing double C=C bonds is accompanied by considerable difficulties. The iodometric technique does not lead to satisfactory results.²⁰ On the other hand, it is not always possible to use ¹H-NMR or other alternative methods for this purpose.^{10,18,19} An essential advantage of the DSC analysis in this case is its high sensitivity due to the high values of ΔH_1 . The amount of ozonides (moles) in the BR rubber was 67% of the amount of reacted ozone, the DSC data being identical with data from ¹H-NMR spectroscopy (unpub. results). However, application of ¹H-NMR spectroscopy (250 MHz) for analysis of E-IR and Z-IR ozonides is not possible because of overlapping signals of methine, methylene, and methyl protons of the monomeric unit ozonide with signals from the initial monomeric units and aldehyde and keto groups formed during ozonolysis.^{10,23} The ozonide yield evaluated by means of DSC analysis of partially ozonized E-IR and Z-IR was 56 and 51%, respectively, of the amount of reacted ozone.

Determination of Activation Energy and Reaction Order

The method of Ellerstein²⁴ was used to determine the values of the activation energy (E) and reaction order (n) from thermograms recorded at different heating rates. The calculations were made according to the equation of Crane et al.,²⁵ successfully applied to polymer objects:

$$T^2(S/h) = (E/R) - nT^2(h/r), \quad (2)$$

where $S = dH^2/dT^2$; $h = (dH/\phi dt) = dH/dT$; $r = (\Delta H - H_p(T))$; ΔH is the total enthalpy of the reaction; $H_p(T)$ is the partial enthalpy evolved up to temperature T ; T is the absolute temperature; t is the reaction time; and $\phi = dT/dt$ heating rate. A linear plot of the left-hand side of eq. (2) against $T^2(h/r)$ yielded E/R as the intercept and n as the slope. Linear regression analysis of eq. (2) for data displayed in Table I resulted in correlation coefficients above 96%.

It is seen from Table I that the respective values of E and n for the polydienes and polyisoprenes are close to those of 1-decene ozonide, derived in a sim-

ilar way from DSC thermograms. The best coincidence was found for E-BR with ozonide yield about 90% of the amount of reacted ozone. Lower values of E are observed for BR samples, the amount of carbonyl compounds being considerably larger in comparison with E-BR (unpub. results).²⁰ Scheme 1 shows that the carbonyl compounds are the product of reactions that proceed parallel to the formation of ozonides. However, the problem of alternative routes of deactivation of the "Criegee intermediates" and of the structure and quantity of the other functional groups of the peroxide type and their potential effect on the values of E cannot be elucidated on the basis of DSC experiments and reference data. It is important to note the practical coincidence between the respective values of E for E-IR and Z-IR because, in agreement with current concepts of the stereochemistry of the reaction, *cis*-ozonides predominate during ozonolysis of *cis*-alkenes whereas *trans*-ozonides prevail with *trans*-isomers.¹⁰

The Kissinger relationship between the peak maximum temperature (T_m) and the activation energy (E) for data collected at five different heating rates was used as an alternative method to determine the value of E .²⁶

$$d \ln \phi / d(1/T_m) = -E/nR - 2T_m. \quad (3)$$

In this case, a plot of $\ln \phi$ versus T_m gives a straight line with slope ($-E/nR$) intercept $-2T_m$, when $E/nR \gg 2T_m$. Correlation coefficients for the values of E [eq. (3)], presented in Table I were in excess of 0.999. The practical equality between the values of E [eq. (3)] and E [eq. (2)] of polydienes and polyisoprenes should be discussed in terms of an argument to support the values for $n = 1$, obtained according to eq. (2). More considerable differences in the values of E [eq. (3)] and E [eq. (2)] are observed only with polychloroprene. If E [eq. (3)] value is corrected by the value of n obtained from eq. (2), the difference is reduced to 14%. Higher values of n for Z-Pch compared to the other polydienes are also obtained by the method of Gyulai and Greenhow,²⁷ according to which the relationship between degree of conversion at the curve maximum (α_s) and n is described approximately by the equation:

$$\alpha_s = 1 - 1.062n^{1/(1-n)}. \quad (4)$$

However, it is useless to discuss the n values and the mechanism of thermolysis without reliable information about the nature of the functional groups

of the peroxide type, which are formed during ozonolysis of that rubber.

CONCLUSIONS

DSC was used to study the thermal decomposition of functional groups of the peroxide type, which are formed during partial ozonolysis in solution of 1,4-*cis*-polybutadiene; polybutadiene elastomer Diene 35 NFA; 1,4-*cis*-polyisoprene; 1,4-*trans*-polyisoprene; and 1,4-*trans*-polychloroprene.

The following values of the enthalpy of the reaction, normalized with respect to the amount of reacted ozone (kJ/mol O₃), were obtained: 337 (E-BR), 260 (BR), 197 (E-IR), 180 (Z-IR), and 239 (Z-PCh). Values of the activation energy and reaction order were also determined: 122.6, 118.5, 108, 113, 101.5, and 1.0, 0.96, 1.04, 1.08, 1.25, respectively.

On the basis of enthalpy of the thermal decomposition of partially ozonized polybutadienes and polyisoprenes, a quantitative determination of ozonides was performed.

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