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Note

DSC study of the thermal decomposition of 1-decene ozonide

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Abstract

The kinetics of thermal decomposition of 1-decene ozonide has been studied by means of differential scanning calorimetry. It was found that the enthalpy of the reaction ΔH was 349 ± 9 kJ mol^{-1}. Values of activation energy, kinetic order, and pre-exponential factor, determined from thermograms, give the following expression for the reaction rate constant: $k/(\mathrm{s}^{-1}) = 1.66 \times 10^{15} \exp(-129000/RT)$.

INTRODUCTION

Ozonides are the basic product of the reaction of ozone with olefins [1]. In contrast with the thermal decomposition of a great number of organic peroxides, such as dialkyl peroxides [2], 1,2,4,5-tetraoxanes [3], and 1,2,4-trioxanes [4], this reaction has not been sufficiently studied in the case of 1,2,4-trioxolanes. There are considerable differences in the activation energy data E [5–7]. For this reason, there are two hypotheses concerning the rate-controlling step of the thermolysis, namely, the homolytic or heterolytic scission of the ozonide cycle [8–11]. Although thermal analysis methods offer great opportunities for the investigation of these types of reactions, no studies have been published so far for 1,2,4-trioxolanes. In this work we present an attempt to determine the activation parameters of the thermal decomposition of 1-decene ozonide by means of differential scanning calorimetry (DSC).

EXPERIMENTAL

The ozonolysis of 1-decene was performed by passing an ozone–oxygen gas mixture at a rate of 1.6×10^{-3} l s^{-1} and ozone concentration of 1.1×10^{-4} mol l^{-1} through a bubbling reactor containing 10 ml of a 0.5 M solution of the respective olefin in hexane at −70°C. The ozonide was

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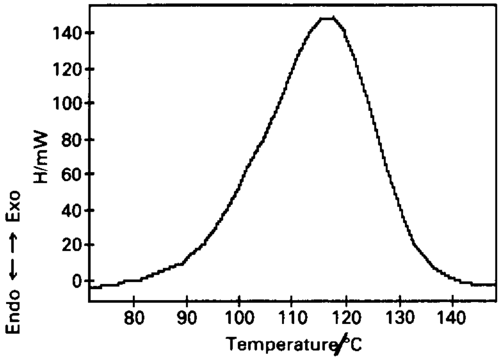


Fig. 1. A DSC curve of 1-decene ozonide: mass, 2.1 mg; heating rate, 5°C min^{-1}; $\Delta H = 1854.04$ J g^{-1}.

isolated by chromatographic separation (silica gel; *n*-hexane/diethyl ether 10:1). The structure and purity of the colourless liquid ozonide were confirmed by ^1H and ^{13}C NMR, IR spectroscopy, and by elementary and mass spectral analyses.

Differential scanning calorimetry was carried out in a Mettler calorimeter Model FP 800, equipped with a computer. Samples (1.5-4.0 mg) were encapsulated in aluminium crucibles under argon. At least three measurements were performed at every heating rate.

RESULTS AND DISCUSSION

A highly intense exothermic peak was present in the thermograms of 1-decene ozonide (Fig. 1). Data displayed in Table 1 show that the enthalpy ΔH of the reaction of thermal decomposition was 349 kJ mol^{-1}, which is about 62% higher than the respective value for dicumene peroxide ($\Delta H = 215$ kJ mol^{-1}) [12].

TABLE 1

DSC analysis of the thermal decomposition of 1-decene ozonide

Heating rate/ °C min^{-1}	T_m/K	ΔH/kJ mol^{-1}	E/kJ mol^{-1}	n
3	384.4	341	129	1.02
5	390.0	349	127	0.98
10	396.0	353	131	1.01
15	401.0	345	129	0.99
20	403.0	347	128	0.98
Average values		349 ± 9	129 ± 4	1.00 ± 0.06

TABLE 2

Thermolysis of organic peroxides

Compound	E/kJ mol^{-1}	lg A	Reference
RO–OR	155 ± 5	15.3 ± 0.5	17–20
Dicumyl peroxide	140 ± 8		12
Acetone diperoxide	153 ± 5	13.8 ± 1.1	3
Benzylketone diperoxide	128		3
Pinacolone diperoxide	128	12.6 ± 1.3	3
Ethylene ozonide	115.1	13.6	7
Hexene-1 ozonide	99.2	10.8	7
Heptene-1 ozonide	95.4	10.2	7

Key: R is Me, Et, *n*-Pr, i-Pr, *sec*-Bu, *t*-Bu radicals.

The method of Ellerstein [13] was used to determine the values of the activation energy E and the kinetic order of the reaction n at different heating rates. Calculations were made according to the equation proposed by Crane et al. [14]

$$T^2(S/h) = (E/R) - nT^2(h/r) \tag{1}$$

where $S = \mathrm{d}H^2/\mathrm{d}T^2$, $h = (\mathrm{d}H/\varphi \mathrm{d}t) = \mathrm{d}H/\mathrm{d}T$, $r = \Delta H - H_\mathrm{p}(T)$, ΔH is the total enthalpy of the reaction, $H_\mathrm{p}(T)$ is the partial enthalpy evolved up to temperature T (absolute temperature), t is reaction time, and $\varphi = \mathrm{d}T/\mathrm{d}t$, the heating rate. A linear plot of the left-hand side of eqn. (1) against $T^2(h/r)$ yielded E/R as the intercept and n as the slope. Linear regression analysis of eqn. (1) for the data displayed in Table 1 resulted in correlation coefficients above 96%.

The Kissinger relationship between the peak maximum temperature T_m and E for data obtained at different heating rates was used as an alternative method to determine the value of E [14, 15]

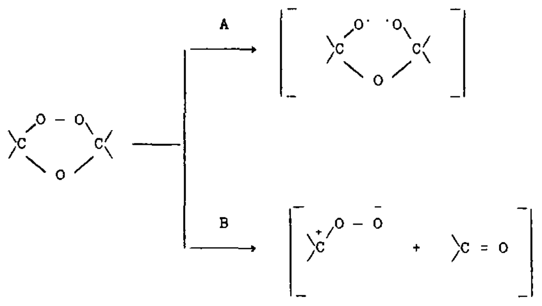
$$\mathrm{d} \ln \varphi/\mathrm{d}(1/T_\mathrm{m}) = -E/R - 2T_\mathrm{m} \tag{2}$$

In this case, a plot of ln φ versus $1/T_\mathrm{m}$ gives a straight line with slope $-E/R$ when $E/R \gg 2T_\mathrm{m}$. The value of E was 132 kJ mol^{-1} for a correlation coefficient in excess of 0.999.

Taking into account the first-order of the reaction, the pre-exponential factor A in the Arrhenius equation was calculated from the equation [16]

$$A = \frac{E\varphi(\mathrm{d}T/\mathrm{d}t)}{RT_\mathrm{m}^2} \exp(E/RT_\mathrm{m}) \tag{3}$$

according to which $A \approx 1.66 \times 10^{15}$. On the basis of the values of E, n, and A thus determined, the following expression for the rate constant of the thermal decomposition of 1-decene ozonide can be written: $k/(\mathrm{s}^{-1}) = 1.66 \times 10^{15} \exp(-129000/RT)$.



Scheme 1.

Kinetic data on the thermolysis of three different classes of peroxide compounds are collected in Table 2. It is well known that the rate-controlling step in the thermolysis of dialkyl peroxides and ketone diperoxides is the homolytic scission of the peroxide bond [2, 3, 12]. In the case of 1,2,4-trioxolanes, in addition to this (pathway A of Scheme 1), there is also another hypothesis, according to which this class of peroxide compounds is subjected to heterolytic cleavage by forming a carbonyl oxide intermediate and the respective carbonyl compound (pathway B of Scheme 1) [8, 9]. One of the important arguments for this suggestion are the lower E and A values obtained for the ozonides presented in Table 2. However, the proximity of the E and A values of 1-decene ozonide with those of the dialkyl peroxides and 1,2,4,5-tetraoxanes corroborate with the more widely accepted hypothesis of homolytic cleavage of the O–O bond. As far as the ozonide data mentioned in Table 2 are concerned, the lower E and A values in this case are probably a result of the applied method of investigation which is based on manometric measurements of the gaseous products of the ozonide decomposition.

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