Thermochimica Acta, 10 (1974) 55–61

THERMAL DECOMPOSITION OF CYCLIC ALKYLIDINE PEROXIDES (TETRAOXANES)

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(Received 6 May 1974)

ABSTRACT

Thermal decomposition of molten 6,6-bis-(4-methoxycarbonyl-butyl)-1,2,4,5-tetraoxane has kinetic parameters similar to those of the other dialkyl peroxides:

$$k = 5.8 \cdot 10^{14}\left(\exp - \frac{36.300}{RT}\right) \quad (\text{sec}^{-1})$$

A similar behaviour has also been found for 6,6-bis-(4-aminocarbonyl-butyl)-1,2,4,5-tetraoxane dissolved in dimethylformamide:

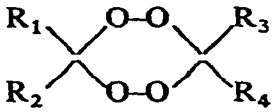
$$k = 3 \cdot 10^{13}\left(\exp - \frac{33.000}{RT}\right) \quad (\text{sec}^{-1})$$

In the absence of solvent this cyclic dimeric peroxide is uncommonly stable owing to the relatively high melting point. The increase in activation energy and frequency factor (compensation effect) at the decomposition in the absence of solvent is explained by the stabile aggregation of the amino derivative of tetraoxane in the crystalline state.

The reaction heat of the exothermic decomposition reaction equals 102 for the methoxy and 96±6 kcal mol^{-1} for the amino derivative.

The measurements of rate constants and reaction heat were carried out by the method of differential enthalpic analysis.

INTRODUCTION

Cyclic dimeric peroxides of the type tetraoxane  have been known for a long time[1,2] but the knowledge of their properties is rather poor[3,4]. Provided symbols R represent substituents with a small number of atoms (e.g. $R_1 = R_3 = H$, $R_2 = R_4 = CH_3$) the corresponding cyclic peroxides are unusually highly explosive. On the other hand, the cyclic dimeric peroxides with larger substituents are unusually stable up to the melting point of the substance which attains even

220 °C for some derivatives. In most cases these data are quoted in the literature only as qualitative statements.

We have not been able to find any quantitative data concerning the kinetic parameters of the decomposition of 3,6-bis-(alkyl)-1,2,4,5-tetraoxanes in the literature. In the case of the concrete cyclic dimeric peroxide this circumstance is not too astonishing because the description of this peroxide has been known merely for a few years[5]. But astonishing is the fact that the kinetic characteristics of this decomposition reaction have not been measured more accurately even for other analogues of dimeric peroxides of the tetraoxane type which have been known for several years[6].

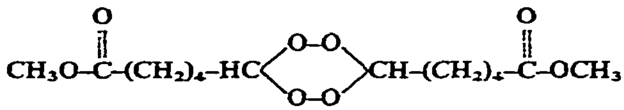
EXPERIMENTAL

A differential calorimeter, Perkin-Elmer Model DSC-1B was used. This device was calibrated for the measurements of differential enthalpic analysis by means of the melting point of anthracene (489 K). The melting point of anthracene agreed with the temperature axis of record only at a scanning speed of 4 °C $\min^{-1}$ or less. For higher scanning speeds we applied a correction, i.e. the difference between the measured melting point and its real value. Isothermal curves were taken after the manual adjustment of a chosen temperature. The samples of tetraoxane (1 mg) were sealed in volatile sample pans.

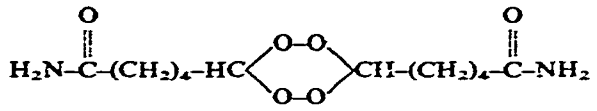
3,6-Bis(4-methoxy carbonyl-butyl)-1,2,4,5-tetraoxane and 3,6-bis(4-aminocarbonyl-butyl)-1,2,4,5-tetraoxane were prepared and purified according to ref. 5.

RESULTS AND DISCUSSION

Heating of studied tetraoxanes



(tetraoxane A)



(tetraoxane B)

leads to the exothermic decomposition (heat of decomposition: 102 kcal mol^{-1} for A: 96 ± 6 kcal mol^{-1} for B) as shown in Fig. 1. The temperature of initial decomposition of tetraoxane A is approx. 40 °C lower than that of tetraoxane B. This is evidently due to the melting of tetraoxane A ($\Delta H_f = 10.3 \pm 0.3$ kcal mol^{-1}) which takes place before decomposition. Besides the initial decomposition temperatures shift, it is worth to notice the remarkably different shape of the DSC curves.

From the differential enthalpic curves we also determined the rate constants for corresponding temperatures as well as the supposed first order of reaction according to the procedure described by Barret[7]. The dependence of decomposition rate constant

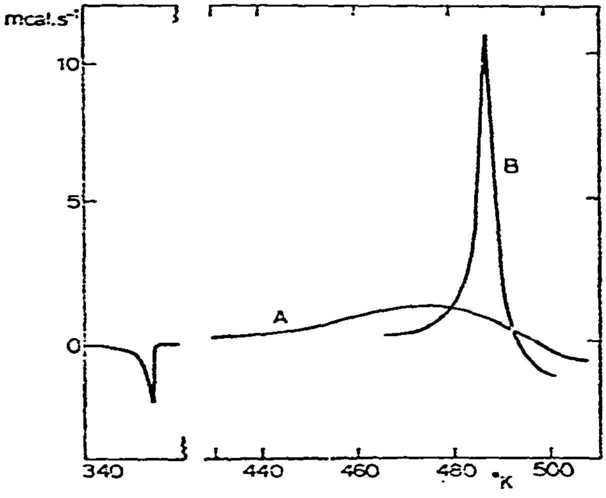


Fig. 1. Differential enthalpic curves of tetraoxane A and B at a heating rate of 8 °C min⁻¹.

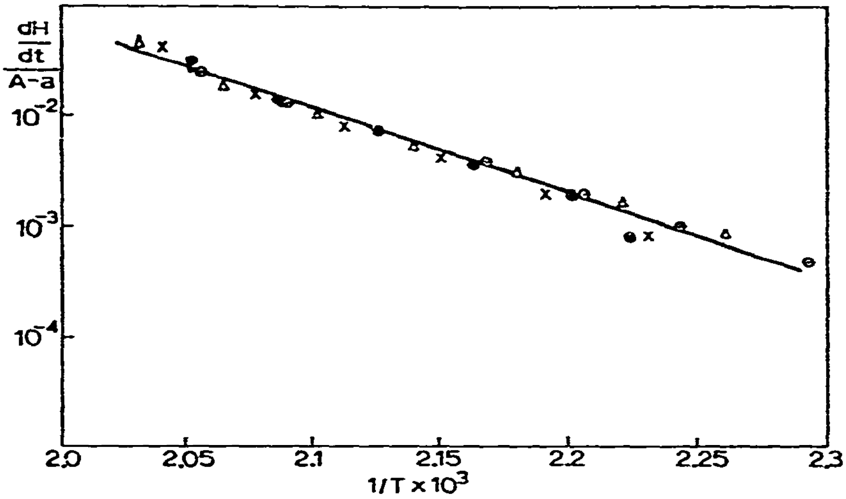


Fig. 2. Dependence of thermal decomposition rate constant (sec⁻¹) of 3,6-bis(4-methoxycarbonylbutyl)-1,2,4,5 tetraoxane on the reciprocal temperature for five independent measurements.

of tetraoxane A (Fig. 2) on the temperature

$$k = 5.8 \cdot 10^{14} \left(\exp - \frac{36.000}{RT} \right) \qquad (\text{sec}^{-1})$$

has very similar kinetic parameters with those of other alkylperoxides[8]. The obtained values of rate constants for the exothermic decomposition reaction of tetraoxane B give in the Arrhenius coordinates unusually high values of both activation energy (170 kcal mol^{-1}) and frequency factor (log $A = 74.8$ sec^{-1}) (Fig. 3).

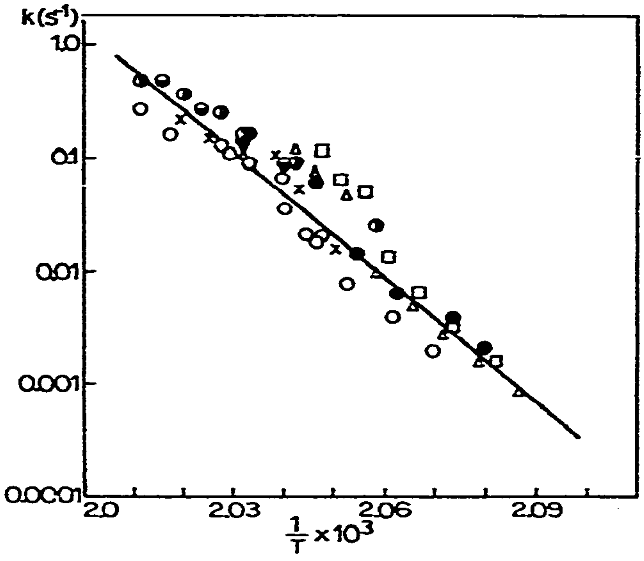


Fig. 3. Rate constants (sec^{-1}) of the decomposition of tetraoxane B calculated from differential enthalpic measurements at different heating rates (sample 1 mg). □△ 4 °C min^{-1}; ●○ 8 °C min^{-1}; ×⊗ 16 °C min^{-1}; ◑◓ 32 °C min^{-1}.

The high values of activation energy as well as frequency factor might be interpreted as a result of the decomposition reaction of tetraoxane B in solid state. The decomposition reaction can take place only if an activated complex comes into existence which means that n particles of matrix must be transported and pass the energetic barrier V. In such a case the subsequent relationship was proposed[9] for the rate constant of the reaction

$$k = 10^{12} \exp\left(\frac{n\Delta S_V}{R}\right) \exp\left(-\frac{E+nV}{RT}\right) \qquad (sec^{-1})$$

where ΔS_V is the entropy of the formation of the rotation isomer of decomposing molecule or a molecule of medium.

If we assume for rotation barrier of isomer formation a value of 4.5 kcal mol^{-1}, then ΔS_V has a value of approx. 10 entropic units and $n \doteq 30$.

The solubility of tetraoxane B in organic solvents is very small. The best results were relatively obtained with dimethylformamide. But in this case too, a higher degree of solubility is achieved only at an increased temperature. Therefore we weighed tetraoxane B (0.7 mg) and dimethylformamide (2.8 mg) directly in a measuring gas-tight capsule which could be closed. During heating an endothermic deflection appeared firstly. This effect is due to the partial evaporation of dimethyl formamide and the dissolution of tetraoxane B.

The initial temperature of decomposition is in the temperature range of tetraoxane A decomposition. Also the activation energy (33 kcal mol^{-1}) as well as the frequency factor ($3 \cdot 10^{13}$ sec^{-1}) are similar (Fig. 4). Under the experimental conditions used (20% solution of tetraoxane B in dimethylformamide) the part of non-dissolved peroxide decomposes at a higher temperature and with higher Arrhenius parameters. These high values are doubtless due to the decomposition which has already taken place in the solid phase.

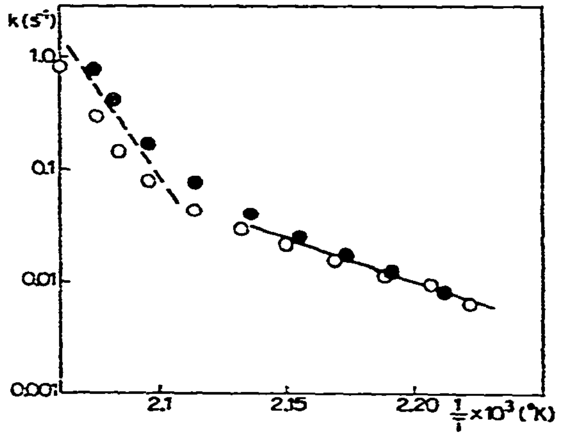


Fig. 4. Rate constants of the decomposition of tetraoxane B in the presence of dimethylformamide as a function of temperature in Arrhenius coordinates (0.7 mg of tetraoxane B and 2.8 mg of dimethylformamide in a gastight closed capsule). Two independent measurements are marked.

Decomposition under isothermal conditions

Keeping tetraoxane B at a constant temperature results in an autocatalytic decomposition of this cyclic peroxide (Fig. 5). The time necessary to reach the maximum rate of reaction as well as the maximum rate of decomposition shows a temperature dependence (Fig. 6). The apparent activation of the decomposition process varies in the proximity of 50±5 kcal mol^{-1} which is a considerably lower value than

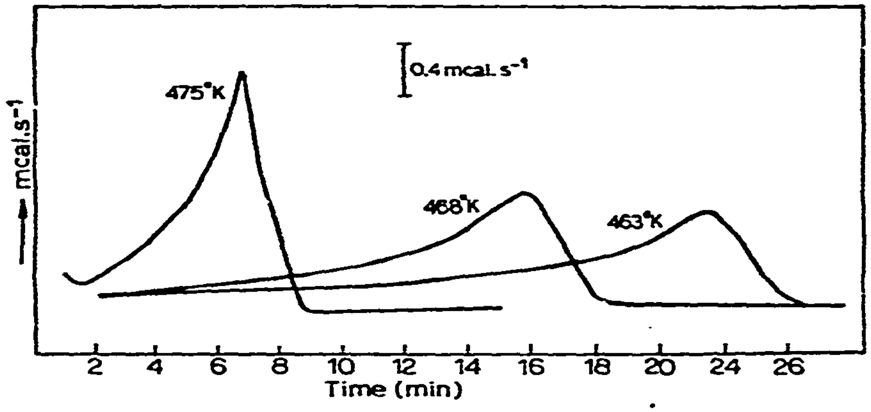


Fig. 5. Isotherms of the decomposition of tetraoxane B at different temperatures. 1 = 475 K; 2 = 468 K; 3 = 463 K.

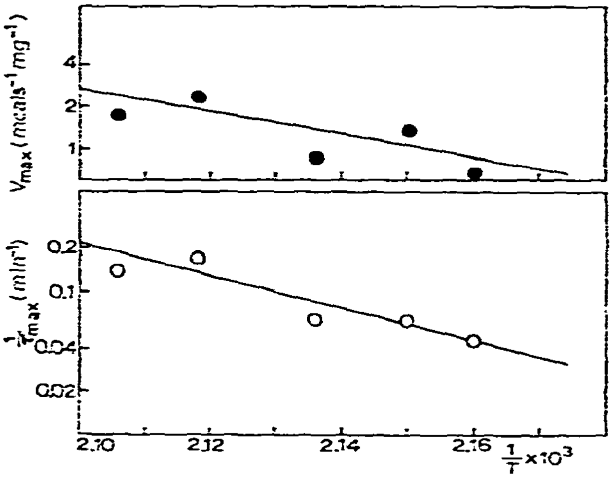


Fig. 6. Arrhenius relationship between the maximum rate of decomposition (V_{max}) and the reciprocal value of the time necessary to attain maximum rate ($1/\tau_{max}$) for isothermal decomposition of tetraoxane B at different temperatures.

we found by DEA measurements. Before discussing this apparent paradox we shall pay attention to the autocatalytic process itself of the decomposition. One of the frequent causes of the acceleration of the decomposition reaction of organic solid substances is often a gradual liquefaction of the reaction medium by decomposition products. In this concrete case this may be excluded with fairly high probability since the decomposition products formed do not melt below 600 K. Therefore it is more likely that the cause of autocatalysis at the decomposition of tetraoxane B lies in a gradual increase in the size of reaction nuclei (defects in crystal lattice). As it follows from the exponent a in the relationship[10]

$$\alpha = kt^a$$

where α is the degree of conversion of decomposition reaction at the moment t while k and a are constants, the growth of reaction nuclei proceeds in three dimensions. The formation of new reaction nuclei during the reaction is of relatively small importance because of the values of exponent a and this factor decreases with decreasing temperature

Temperature (K)	463	465	468	472	475
a	3.0	3.0	2.8	3.6	3.4

We shall also pay attention to the problem why the value of apparent activation energy of the decomposition reaction found by isothermal measurements is always lower than that found by differential enthalpic measurements. From the experimental point of view the differences are due to the higher temperature of decomposition at DEA measurements as compared with the decomposition under isothermal conditions. This fact brings about different rates of the production of new reaction nuclei as well as their growth. In view of the mechanism of individual processes it may be assumed that the activation energy of the production of reaction nuclei must be higher than the activation energy of the decomposition reaction in a defective centre of crystal. Then it follows that the isothermal decomposition takes place mainly in the original defects while the newly formed defective centres of crystal play an important part in the decomposition process at DEA measurements. The presence of the reaction nuclei in tetraoxane B is also indicated by the immeasurable induction of decomposition as well as by the values of exponent *a*.

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