Thermal Decomposition of Cyclic GlutaraldehydeDiperoxide.UV.Spectroscopic Analysis

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Accepted: April 08, 2015

Abstract: The thermal decomposition reaction of Cyclic GlutaraldehydeDiperoxide (3,6-dibutanal-1,2,4,5-tetroxane) in solution of methanol in the temperature range of 130.0-166.0°C and initial concentration of 1.69 x10⁻³ mol/L, follows first-order kinetic laws. Under the experimental conditions, the activation parameters of the reaction are bigger than the obtained ones for other tetroxanos with different substituent’s in the same solvent, which indicates us that the substituents stabilize the condition of transition decreasing the energetic barrier.

Keywords: DPG, thermal decomposition, solvent.

Introduction

In the last years, systematic studies have been performed to study the kinetics and the mechanism of thermal decomposition reaction of 1, 2, 4, 5-tetroxanes, cyclic diperoxides which today have an important role in oxidation reactions of organic compounds with biological interest. [1-3]. These kinetic studies are intended to analyze the effect of substituents and solvents on the parameters governing the rate of reaction Steric, inductive, mesomeric and stereoelectronic effects of the different substituents on peroxodic ring are considered in relation by the force of peroxodic link (energy of

break of the link brought into play), which is debilitated in the initial step unimolecular of thermolysis. The general mechanism in solution belongs applicable to all the members of the family of them 1,2,4,5-tetroxanos, the unimolecular thermal decomposition can take place by two different kinds: a) a stepwise homolysis initiated by one peroxodic bond rupture with a biradical as intermediate. b) a concerted type of mechanism where bond breaking and bond making may occur simultaneously. However, for both processes in the thermolysis of tetroxanes give the corresponding ketone or aldehyde and molecular oxygen as reaction products. 1,2,4,5-tetroxanes shows the most significant solvent effect, in this work its thermal decomposition of 3,6-dibutanal-1,2,4,5-tetroxano (DPG, figure 1) in methanol solution have been studied examining the influence of this relatively polar medium.DPG presents a beak of absorbance to low lengths of wave presenting stable readings and fulfilling of Lambert Beer's Law to 204 nm, up to concentrations of the order of 10⁻⁶ M [4].In this paper a study of the thermal decomposition of this cyclic diperoxide in methanol is approached by UV spectroscopy, as an alternative methodology for the determination of kinetic parameters governing the thermolysis reaction of such compounds.

Materials and Methods

Purification of Solvents

Methanol (Merck, p.a.) was purified by fractionated distillation from disodium salt of ethylenediaminetetraacetic acid (disodium EDTA) in order to eliminate traces of metal ions that could be present in the commercial solvent [7]. CG analysis did not reveal the presence of organic impurities.

Synthesis Dipeoxide

DPG was prepared by dropwise addition of glutaraldehyde in ethanol solution to a vigorously stirred and cooled (-20°C) mixture of 60% hydrogen peroxide and sulfuric acid (18M). After stirring for 2h more at the same temperature, the microcrystalline solid obtained was repeatedly washed with water and further purified by recrystallizing from methanol until a constant melting point was attained (192°C). The DPG purity was checked by GC in methanol solution.

Kinetic Methods

Pyrex glass tubes (4mm i.d., 70 mm length) filled with the appropriate volume of DPG in methanol solution, with added n-octane (internal standard) were thoroughly degassed in the vacuum line at -196°C and then sealed with a flame torch. These ampules were submerged in a thermostated silicone oil bath (+ 0,1°C) to different temperatures and withdrawn after selected times, stopping the reaction cooling rapidly to 0°C. The closed ampules were conserved to 18ºC up to his analysis for UV spectroscopy.

Analysis of Remaining Reagent.

The remaining DPG was performed by UV spectrophotometer; it marks CamSpec M330 at 204 nm.

Calculation Methods

The first order rate constant values were calculated by a least mean square data treatment (r> 0.995) and the activation parameters values of the thermal decomposition obtained from computational method employing the Eyring and Arrhenius equation parameters.

Results and Discussion

The thermal decompositions reaction of DPG in methanol solution in the range of temperature from 130,0 to 166,0 °C and initial concentration 1.55x10⁻³ mol L⁻¹ follow first order kinetic laws up to ca. 60 % dipeoxide conversions (Fig. 2). In Table 1 we present values of the rate constants of reaction of DPG in methanol and in other tetroxanes (Table 2) indicate nearly ΔGº values in the same studied solvent.

The very negative entropy value for the DPG thermolysis in methanol solution reflects the decrease in degree of freedoms of the DPG molecules that take place when they pass to a rather more rigid transition state, where the rupture of an O-O linkage might be assisted by the methanol solvent molecules. We believethat the interaction betweenmoleculeand the solventdiperoxidetakes place inthe initial stage of the thermal decomposition reaction.

Conclusions

The thermal decomposition of the DPG in methanol, in the area of temperatures 130 - 166°C and concentrations of the order of 1.55x10⁻³ mol L⁻¹, fulfilled satisfactorily a kinetic law of the first order up to conversions of c.a. 60 % of diperoxide. Under experimental conditions, the values of activation parameters at initial stage of the reaction (ΔHº=18.5 ± 0.9 kcal mol⁻¹ and ΔSº= -45.2 ± 0.6 cal K⁻¹ mol⁻¹) indicate us a mechanism initiated by the homolytic break of the peroxídic link for DPG that leads to the formation of an intermediary of the thermolysis (biradical), and this is determinant stage for the reaction. Thetheoreticalcalculationsalso supportthis mechanism.

The reaction products and the activation parameter values contribute to postulate the mechanism for the thermolysis of the DPG in methanol solution. The thermolysis would occur through a well known mechanism of decomposition already advanced for the tetroxanes, which begins with the homolytic
rupture of the peroxydic bond leading to the formation of an intermediate biradical and then C-O bond ruptures giving two molecules of glutaraldehyde and one oxygen molecule as final products. The large and negative activation entropy value (-45.2 cal/mol K) suggests that it makes up an interaction between solvent molecules and DPG.

References


Table 1. First order rate constant values for DPG thermal decomposition reaction in methanol solution at different temperatures.

<table>
<thead>
<tr>
<th>Temperature/ºC</th>
<th>k x 10^4 s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>6.02</td>
</tr>
<tr>
<td>140</td>
<td>8.72</td>
</tr>
<tr>
<td>150</td>
<td>19.67</td>
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<tr>
<td>166</td>
<td>40.27</td>
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</tbody>
</table>

Table 2. First order rate constant values for tetroxanes substituted thermal decomposition reaction in methanol solution at 140ºC

<table>
<thead>
<tr>
<th>Tetroxane</th>
<th>k x 10^6 s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPAG</td>
<td>6.9</td>
</tr>
<tr>
<td>ACDP</td>
<td>14.0</td>
</tr>
<tr>
<td>DFT</td>
<td>136.0</td>
</tr>
<tr>
<td>DPG</td>
<td>872.0</td>
</tr>
</tbody>
</table>

*DPAG: Glutaraldehyde acid cyclic diperoxide
*ACDP: Acetone cyclic diperoxide
*DFT: Benzaldehyde cyclic diperoxide
Figure 2. Kinetic of DPG thermal decomposition reaction (1.55 \times 10^{-3} \text{ mol L}^{-1}) in methanol solution at different temperatures

Table 2. Activation Parameters for DPAG thermolysis in methanol solution for different tetroxanes.

<table>
<thead>
<tr>
<th>Tetroxane</th>
<th>$\Delta H^#$ Kcal mol$^{-1}$</th>
<th>$\Delta S^#$ cal K$^{-1}$ mol$^{-1}$</th>
<th>$\Delta G^#$ Kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPAG</td>
<td>25.2±1.0</td>
<td>-21.8±2.6</td>
<td>34.4±1.05</td>
</tr>
<tr>
<td>ACDP</td>
<td>26.9±0.3</td>
<td>-16.9±0.6</td>
<td>34.0±0.3</td>
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<tr>
<td>DFT</td>
<td>24.8±0.8</td>
<td>-16.7±1.8</td>
<td>31.8±0.8</td>
</tr>
<tr>
<td>DPG</td>
<td>18.5±0.9</td>
<td>-45.2±0.6</td>
<td>37.6±0.9</td>
</tr>
</tbody>
</table>
Figure 3. Eyring plot corresponding to the thermal decomposition reaction of DPG in methanol.