INTRODUCTION

Organic peroxides derived from aldehydes and acetone had been extensively studied by several investigators. ([Baeyer et al., 1990; Criegee et al., 1949; Milas et al., 1959]) These compounds-tetroxanes- have multiple uses, such as explosive ignition, polymerization initiators and antimalarial activity. (Jones, 1999; Ando, 1992) The homolytic cleavage of the peroxodic bond (O-O) is the explaining for unusual reactivity. (Oxley et al., 2002) The study on the thermolysis of 1,2,4,5-tetroxanes were made watching on one hand the influence on it of the substituents and on the other the influence of different solvents, and have been found the kinetic parameters governing the reaction. (Profeta et al, 2011; Leiva et al., 2008; Pila et al., 2012; Reguera et al., 2012; Jorge et al., 2012) The steric effects, inductive, mesomeric, stereoelectronic of different substituents on the peroxidic ring are considered in relation to the strength of the peroxodic bond (energy bond cleavage O-O), which is weakened at the unimolecular initial stage thermolysis. The general mechanism in solution, is applicable to all members of the family of 1,2,4,5-tetroxanos,

which involves two competing mechanisms: "concerted" and "biradical", considering the interpretation found the 1,2-dioxetanes for different substituents and solvents (Pila et al., 2012; Reguera et al., 2012; Jorge et al., 2012). The numerous experimental data confirm that the mechanism by which these reactions occur is "biradical". The effect of solvent and substituent play an important role in unimolecular reactions. This paper presents the results obtained in comparative studies of thermolysis of 3,6- diphenyl - 1,2,4,5 - tetroxane (benzaldehyde diperoxide, DFT) and 3,6- dibutanal - 1,2,4,5- tetroxane (glutaraldehyde diperoxide, DPG) in solution with polar solvent. Comparison of the activation parameters of the thermolysis, the values of their constants reaction rate and analysis of the obtained products, contributing to elucidate the mechanism through which decomposition elapses.

MATERIALS AND METHODS

Kinetic methods and Product Analyses

Pyrex glass vials were filled with 0.5 mL of tetroxane solution, further degassed and closed. The closed vials were immersed in a thermostatic bath stabilized at different temperatures, further extracted at some reaction times, and cooled in a
water/ice bath to stop the reaction. The DFT an DPG remaining in the solution and the aldehydes organic product were determined by GC (internal standard method) in a HP-5 capillary column (30m length, 0.25 mm i.d., phenylmethylsilicone as stationary phase, 0.25-mm film thickness) installed in a Agilent 7890 A gas chromatograph, with nitrogen as carrier gas and flame ionization detection (FID) (300°C). Injection port was fixed at 195°C in split mode. DFT retention time under programmed conditions (50°C, 3 min, 20°C/min, 195°C, 15 min) was 12 min and DPG retention time under programmed conditions (80°C, 3 min, 20°C/min, 200°C, 15 min) was 9 min.

Calculation Methods

The corresponding first-order rate constant values were obtained by least-means-squares treatment of the GC data plotting the ln[tetraoxane] vs. reaction time values. The calculation of the activation parameters of the reactions (90% confidence limit), as well as their errors were worked out by the Arrhenius equation method using a least-means-square data treatment (Schaleger et al, 1963). The activation parameters (enthalpy and entropy of activation) were obtained by application of the Eyring equation method to the kobs values and the corresponding error limits worked out from a computational least means square data treatment considering a literature method. (Huyberetch et al, 1955)

RESULTS AND DISCUSSION

The study of the thermal decomposition of both Tetroxanes - DFT and DPG- in methanol solution, in the temperature between 130.0 166.0 ºC and 1 x 10-3 M of the initial concentration, follows a kinetics law of first order , with respect to the corresponding peroxide up to at least 60% tetroxane conversions. Typical kinetics plots for the experimental results are shown in Figure 1 and Figure 2. (Table 1)

The kinetics of thermolysis of DPG in the temperature range investigated in the methanol solvent turn out to be faster (Figures 1 and 2) compared with the corresponding reaction of the DFT (e.g. 150°C the factor is 5.3). The temperature effects on DPG and DFT thermolysis reaction in methanol solutions, evaluated through the Arrhenius equation method, show plots (Figure 3) which are linear (equation 1 and 2) over relatively large temperature intervals (36 K). This supports the fact that the corresponding activation parameters for DPG and DFT (Table 3) thermolysis belong to simple processes. (chart 1). In turn, it is evident the closeness between the energies corresponding to the decomposition reaction activation, which differ in ca. 6.5 kcal mol⁻¹.

The Arrhenius equation :

\[ \ln k = \frac{(22.6 \pm 1.2)}{RT (DFT)} - \frac{(25.8 \pm 0.8)}{RT (DPG)} \]  … (1)

\[ \ln k = \frac{(16.7 \pm 1.0)}{RT (DPG)} - \frac{(19.3 \pm 0.7)}{RT (DFT)} \]  … (2)

A initial view of the thermolyses of two the diperoxides considered in this work suggests that, since biradicals are initially formed (chart 1), the kinetics of the corresponding unimolecular reactions would be subject to significant substituent effects. In principle, those differences observed in the activation parameters of the unimolecular thermolyses which lie well outside experimental error (Table 2, Figure 4) may correspond to inductive, electrostatic, and/or steric effects due to the substituents on the peroxoic bond rupture of the tetroxane ring, and/or on the biradical-like “transition state” of these reactions. In the series of the DPG and DFT molecules

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>k x 10³ s⁻¹ DFT</th>
<th>k x 10³ s⁻¹ DPG</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>0.70 ± 0.9</td>
<td>6.02 ± 0.6</td>
</tr>
<tr>
<td>140</td>
<td>1.36 ± 0.8</td>
<td>8.72 ± 0.8</td>
</tr>
<tr>
<td>150</td>
<td>3.68 ± 0.7</td>
<td>19.67 ± 0.7</td>
</tr>
<tr>
<td>166</td>
<td>9.12 ± 0.9</td>
<td>40.27 ± 0.9</td>
</tr>
</tbody>
</table>
the corresponding activation parameters decrease as the steric and stereoelectronic requirements of the substituents appear to increase, as well. Thus, no compensation effects are observed in the thermolyses of these diperoxide molecules, where the unimolecular reaction rate constant values, at 150°C, are in the relationship of 1:5, respectively.

The thermal decomposition reactions of the diperoxides investigated in this work (DFT and DPG) yield products (Table 3) which can best be accommodated by the general mechanism shown in chart 2-4.

\[
\begin{align*}
(H \text{ CO. O})_2 & \rightarrow CO_2 + HCOOH \\
R + R & \rightarrow RR \\
2 RCHO + O_2 & \rightarrow 2 RCOOH
\end{align*}
\]

Table 3. Product Molar Yields in the Thermolyses of Diperoxides (Moles of Product per Mole of Dioxide Decomposed) in methanol Solution (ca. 60% Conversion) at 140°C

<table>
<thead>
<tr>
<th>Diperoxide</th>
<th>10^4 M</th>
<th>RCHO</th>
<th>RR</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>1.0</td>
<td>1.9</td>
<td>0.1</td>
<td>dimetilacetal del benzaldehido ác. formico, bifenilo. Ácido benzoico</td>
</tr>
<tr>
<td>DPG</td>
<td>1.0</td>
<td>1.8</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

An increase in the activation energy of the reaction is offset by a less orderly transition state. the negative value for activate entropy variation is in agreement with the decrease of freedom degrees from reactive molecules by passing from a rather rigid transition state, which supports the supposition that thermolysis in methanol is favored by solvent molecules as well as by the presence of the substituents. The interactions between solute and solvent are favored when the substituents are smaller. In our case the two substituents have a certain volume and symmetry. Phenyl substituents are bulky and confer a certain asymmetry in the molecule that prevents an order in the activated complex. However do not favor the breaking of the peroxido bond. But on the other hand, a polar solvent such as dibutanal, favors breaking the O-O bond and causes a better rearrangement in the activated complex. Analysis of the reaction products of thermolysis DFT indicates the formation of benzaldehyde and benzoic acid as main products. Total molar yield of ca. 1.9 mol / mol diperoxide. With respect to thermal decomposition of DPG, it was found the formation of glutaraldehyde as a main product, with a molar yield of 2 mol / mol diperoxide. (Table 3)

**Conclusion**

The analysis of the reaction products of the thermolyses of DFT and DPG (substituted tetraoxanes) in methanol solution and the corresponding activation parameters for these Thermolysis reactions support a general homolytic stepwise mechanism, rather than a concerted process. DFT and DPG are structurally different substituents in their molecules however, it can be postulated that their thermolysis in methanol solution pass through a same decomposition mechanism. It starts with the homolytic cleavage of the peroxide bond with the formation of a biradical. The biradical then breaks its C-O bonds, giving rise to the corresponding aldehyde and
molecular oxygen. In the special case of the DFT, the observed benzoic acid is formed by further oxidation of benzaldehyde.

REFERENCES


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