



RESEARCH ARTICLE

KINETIC OF THE THERMAL DECOMPOSITION OF DISUBSTITUTED TETROXANES

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ABSTRACT

The thermal decomposition of diphenyl diperoxide (DFT) and dibutanol diperoxide (DPG) were investigated over the temperature range 130 to 166°C. They were found to be first order with a high degree of conversion (60%). Arrhenius parameters were calculated: activation energy, 108 kJ mol⁻¹ and pre-exponential factor, 6.5 10⁹ s⁻¹ for DFT and 80.8 kJ mol⁻¹ and pre-exponential factor, 1.8 10⁹ s⁻¹ for DPG. The principle decomposition products were aldehyde (about 1.9 mole per mole DFT and 2.0 mole per mole DPG) and oxygen molecule. All observations were interpreted in terms of decomposition pathways initiated by O-O homolysis. The corresponding activation parameters for the reaction of DFT in methanol ($H^{0\#} = 103.8 \pm 3.3$ kJ mol⁻¹; $S^{0\#} = -69.9 \pm 7.5$ J mol⁻¹ K⁻¹; $G^{0\#} = 133.1 \pm 3.3$ kJ mol⁻¹) were compared with values obtained for PDG thermolysis in the same solvents ($H^{0\#} = 75.4 \pm 2.9$ kJ mol⁻¹; $S^{0\#} = -189.2 \pm 2.5$ J mol⁻¹ K⁻¹; $G^{0\#} = 157.4 \pm 2.9$ kJ mol⁻¹). Furthermore, the pertinent substituent effect on the peroxidic bond strength of those molecules in solution was evaluated.

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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 peroxidic bond (O-O) is the explaining for unusual reactivity. (Oxley et al., 2002) The study on the thermolysis of 1,2,4,5-tetroxanos 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 peroxidic 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- dibutanol - 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

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water/ice bath to stop the reaction. The DFT and 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, 3min, 20°C/min, 200°C, 15 min) was 9 min.

Calculation Methods

The corresponding first-order rate constant values were obtained by least-squares treatment of the GC data plotting the $\ln[\text{tetroxane}]$ 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 k_{obs} 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 ° C and 1×10^{-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)

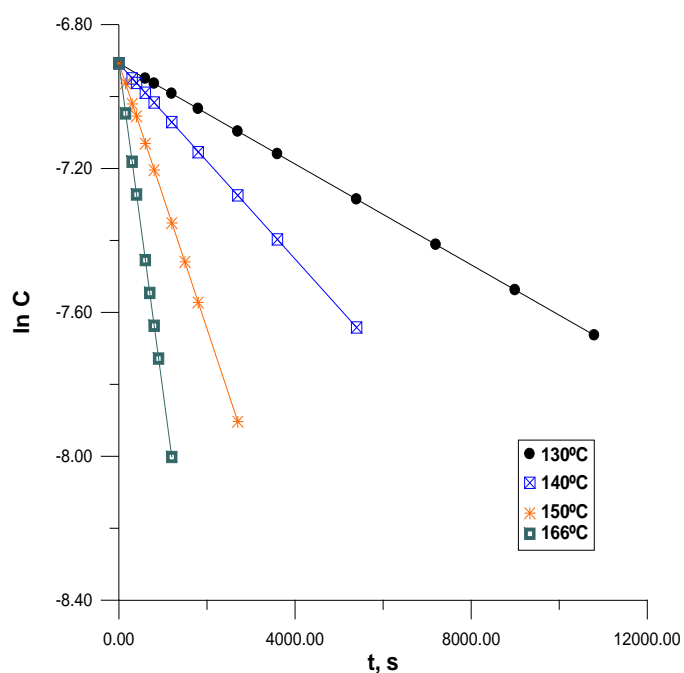


Figure 1. Representation through First-order Kinetic Plots of the Data of Typical Runs of DFT Thermolysis in Methanol Solutions at Different Temperatures

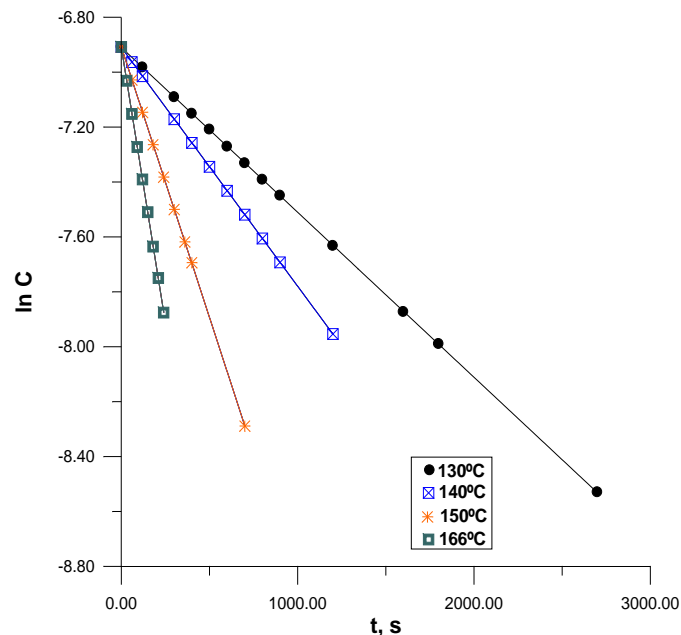


Figure 2. Representation through First-order Kinetic Plots of the Data of Typical Runs of DPG Thermolysis in Methanol Solutions at Different Temperatures

Table 1. First-Order Rate Constant Values for the Thermal Decomposition Reactions of DFT and DPG in Solution. Average values of rate constants thermal decomposition of in solution

Temp °C	$k \times 10^4 \text{ s}^{-1}$ DFT	$k \times 10^4 \text{ s}^{-1}$ DPG
130	$0,70 \pm 0,9$	$6,02 \pm 0,6$
140	$1,36 \pm 0,8$	$8,72 \pm 0,8$
150	$3,68 \pm 0,7$	$19,67 \pm 0,7$
166	$9,12 \pm 0,9$	$40,27 \pm 0,9$

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. $6.5 \text{ kcal mol}^{-1}$.

The Arrhenius equation :

$$\ln k (\text{s}^{-1}) = (22.6 \pm 1.2) - (25.8 \pm 0.8) / RT \text{ (DFT)} \quad \dots (1)$$

$$\ln k (\text{s}^{-1}) = (16.7 \pm 1.0) - (19.3 \pm 0.7) / RT \text{ (DPG)} \quad \dots (2)$$

A initial view of the thermolyses of two the diperoxides considered in this work suggests that, since birradicals 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 peroxidic bond rupture of the tetraoxane ring, and/or on the biradical-like "transition state" of these reactions. In the series of the DPG and DFT molecules

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.

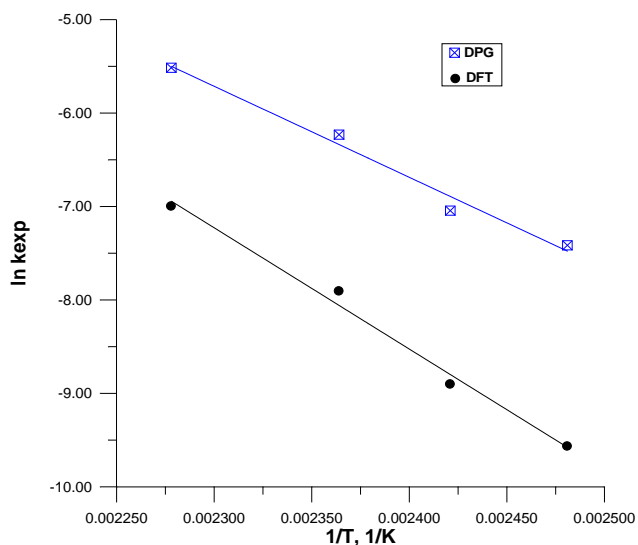


Figure 3. Arrhenius plot corresponding to the thermal decomposition reaction of DFT and DPG in methanol solution

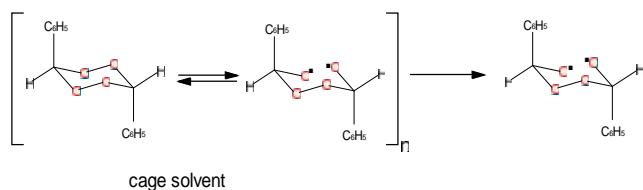


Chart 1. Cleavage of the peroxidic bond (O-O)

Table 2. Values of the parameters of thermolysis. Average values of parameters thermal decomposition in solution

Tetroxane	ΔH^{\ddagger} kJ mol ⁻¹	ΔS^{\ddagger} J mol ⁻¹ K ⁻¹	E_a kJ mol ⁻¹	ΔG^{\ddagger} kJ mol ⁻¹
DFT	103.8 ± 3.3	-69.9 ± 7.5	108.0 ± 3.3	133.1 ± 3.3
DPG	75.4 ± 2.9	-189.2 ± 2.5	80.8 ± 2.9	157.4 ± 2.9

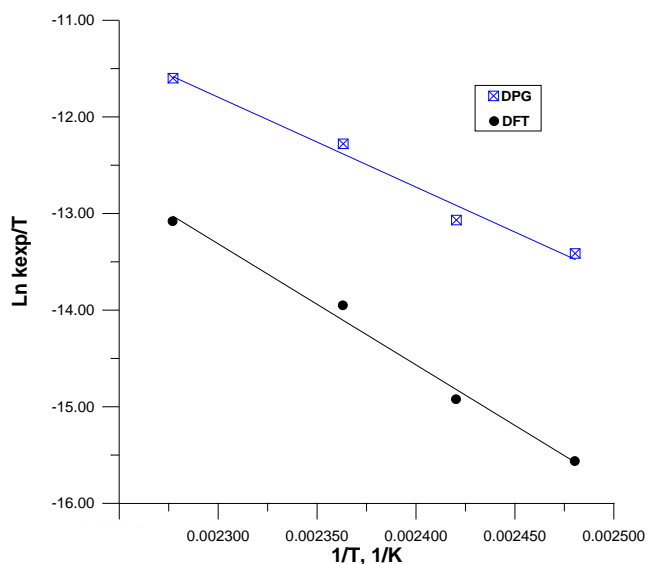


Figure 4. Eyring plot corresponding to the thermal decomposition reaction of DFT and DPG in methanol solution

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.

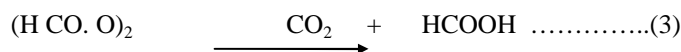
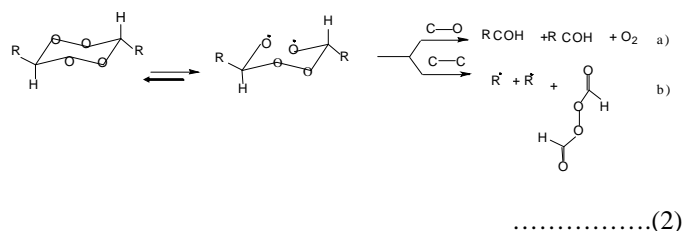


Table 3. Product Molar Yields in the Thermolyses of Diperoxides (Moles of Product per Mole of Diperoxide Decomposed) in methanol Solution (ca. 60% Conversion) at 140°C

Diperoxide	10 ³ M	RCHO	RR	Other
DFT	1.0	1.9	0.1	dimetilacetal del benzaldehído ác. formico, bifenilo. Ácido benzoico
DPG	1.0	1.8	-	

An increase in the activation energy of the reaction is offset by a less orderly transition state. The negative value for activated 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, it does not favor the breaking of the peroxidic bond. But on the other hand, a polar solvent such as dibutanol, favors breaking the O-O bond and causes a better rearrangement in the activated complex. Analysis of the reaction products of thermolysis of 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 that 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.

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