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RESEARCH ARTICLE

THERMAL DECOMPOSITION OF BENZALDEHYDE DIPEROXIDE IN ISOPROPYL ALCOHOL, EFFECT OF SOLVENT POLARITY

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ABSTRACT

The thermal decomposition reaction of 3,6-difenil-1,2,4,5-tetroxano (benzaldehyde diperoxido, DFT, 0.001M) in isopropyl alcohol solution studied in the temperature range of 130.0-166.0°C, follows a first-order kinetic law up to at least 60% DTF conversion. The organic products observed were benzaldehyde, benzoic acid and molecular. A stepwise mechanism of decomposition was proposed where the first step is the homolytic unimolecular rupture of the O-O bond. The activation enthalpy and activation entropy for DFT in isopropyl alcohol were calculated ($\Delta H^\ddagger = 13.3 \pm 0.9$ kcal mol⁻¹ and $\Delta S^\ddagger = -39.9 \pm 1.0$ cal mol⁻¹K⁻¹) and compared with those obtained in other solvents to evaluate the solvent effect.

INTRODUCTION

The importance of cyclic organic peroxides comprising a large number of chemical and biological issues mentioned in numerous works. Currently they became more important because of the peculiarity of being highly energetic compounds and release their energy content in a fast and exothermic reaction, used as explosives, forcing detection analysis and forensic investigations. (Oxley *et al.*, 2002) While there is extensive literature regarding the production of these peroxides, knowledge regarding stability and reactivity is limited. (Profeta *et al.*, 2011; Leiva *et al.*, 2008; Pila *et al.*, 2012; Reguera *et al.*, 2012; Jorge *et al.*, 2012)

In recent years there have been systematic studies to determine the kinetics and mechanism of the thermal decomposition reaction of aldehydes diperoxides derivatives (disubstituted-1,2,4,5 tetroxanes), in order to analyze the effect of the medium where the reaction takes place, thus the kinetic parameters governing the reaction solvents different physicochemical properties was obtained. Interesting is the interrelationship today of the rate of reaction with the polarity of medium. Not having a physical-chemical parameter that adequately describes this property, the literature suggests that the empirical parameter E_T (30) defined by Dimroth and Reichardt as the most appropriate. (Dimroth *et al.*, 1969) Main

objective of our group of investigation in the last years of work are the kinetic studies and mechanistic corresponding to the thermolysis in solution of the cyclic organic peroxides and all the comparisons between them. (Barreto and Eyller, 2011; Leiva *et al.*, 2010; Iglesias *et al.*, 2010). In this work we present the thermal decomposition reaction of a member of the group, 3,6-difenil-1,2,4,5-tetroxano (DFT), in a polar solvent like the isopropyl alcohol and we compared it with other studied solvents that present different physicochemical properties, for observe the effect of solvent.

MATERIALS AND METHODS

Synthesis and purification of 3,6-diphenyl-1,2,4,5-tetroxane (DFT)

DFT was prepared by dissolving 7.2 mL of benzaldehyde mark Flucka (8.85 mmol) in 20 mL absolute ethanol brand Merk. It was added to a vigorously stirred mixture of 2.3 mL of hydrogen peroxide (9.45 mmol), 50 mL of sulfuric acid (90% V / V) and 35 mL of ethanol. After stirring the mixture for 2 hours at -20 ° C, centrifuged and washed with distilled water (0°C) until the excess of acid was removed. The white solid obtained (crude product 75%) was recrystallized from boiling chloroform. Absorption bands obtained by FTIR spectroscopy (KBr): 1) 3107.6 (s) cm⁻¹ 2) 3095.0 (s) cm⁻¹ 3) 3032.1 (m) cm⁻¹ 4) 2961.8 (m) cm⁻¹ 5) 1766.8 (m) cm⁻¹ 6) 1604.0 (s) cm⁻¹ 7) 1597.0 (s) cm⁻¹ 8) 1491.9 (vs) cm⁻¹ 9) 1457.1 (s) cm⁻¹ 10) 1416.8 (m) cm⁻¹ 11) 1397.3 (m) cm⁻¹ 12)

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1271.8 (s) cm^{-1} 13) 1229.9 (m) cm^{-1} 14) 1197.0 (m) cm^{-1} 15) 1080.2 (m) 1.16 (m) 997.5 (s) cm^{-1} 17) 973.2 (s) cm^{-1} 18) 896.6 (s) cm^{-1} 19) 842.4 (s) cm^{-1} 20) 685.5 (s) cm^{-1} 21) 668.5 (s) cm^{-1} .

Purification of solvents

Isopropyl alcohol

The commercial solvent was tested with peroxides test to verify the absence of them. It was dried with anhydrous K_2CO_3 , filtered and purified by distillation, collecting the fraction boiling from 125 ° C. Its purity was monitored by Gas Chromatography.

n-octane

It was chosen n-octane like internal standard because it is chemically stable in working conditions. The commercial product (Baker, pa) was washed twice with concentrated H_2SO_4 then with water, dried with K_2CO_3 , filtered and distilled, to collecting the fraction boiling from 126 ° C. The purity of this substance was also controlled by Gas Chromatography.

Kinetic Method

We worked with Pyrex glass ampoules closed at one end 8 cm long x 4 mm internal diameter that were full with 0.5 mL of the solution of known concentration in isopropyl alcohol of DFT. These vials were cooled to -196°C with liquid nitrogen approximately 1 min to ensure solidification and were degassed in vacuum line, were removed from liquid nitrogen and they reached room temperature again, to allowing the slow melting of the contents of the ampoule. This operation to extract gas was repeated three times. Finally, the ampoules were sealed to the flame of a torch who works with a mixture of natural gas and oxygen. The sealed ampoules were immersed in an oil bath thermostated silicone ($\pm 0.1^\circ\text{C}$). Reaction times and temperatures for the kinetic were chosen, according to data available studies for DFT in other solvents that were researched by our work team and by other authors.

After the stipulated time the decomposition reaction is stopped by immersing the vials in a water bath / ice at 0°C . Quantitative determination of the concentration of remaining DFT each reaction time and / or the products generated in the decomposition of diperoxide compound is carried out using gas chromatography analysis (GC) (internal standard method, n-octane). GC: Agilent Technologies, Model: 7890 A equipped with a capillary column HP5 (30 m, 0.25 mm id and methylphenylsilicone as the stationary phase) equipped with an FID detector, using nitrogen as a gas chromatograph. Experimental data were obtained from the relationship between the absolute remaining areas of the analyzed species and the Standard and were analyzed with the EZChrom software. Analyses were performed to maintain set temperature initially the column at 60°C for 4 min, and then increased the temperature at 20°C per minute to a temperature end of 190°C . The injector temperature was set at 155°C k experimental (k_{EXP}) values of the first order were calculated by the method least squares as the slope of the line determined when it represented $\ln [\text{DFT}]$ versus time.

Using the Arrhenius equation analyzed the effect of k experimental and temperature on the activation energy was calculated and the corresponding pre-exponential factor. The activation parameters ΔH^\ddagger and ΔS^\ddagger were calculated using the Eyring representation.

RESULTS AND DISCUSSION

Thermal decomposition of DFT has been studied in solution of isopropyl alcohol, in the field of temperatures of 130.0 to 166.0°C and initial concentrations of 0.001 mol L^{-1} . The decomposition of DFT, performs a first-order law until 60% conversion diperoxide. (Table 1, Figure 1)

Table 1. Rate constants of the first order at different temperatures corresponding to thermal decomposition of DFT in isopropyl alcohol

T ($^\circ\text{C}$)	$k \cdot 10^3 \text{ (s}^{-1}\text{)}$
130	1.06
140	1.58
150	2.76
166	4.27

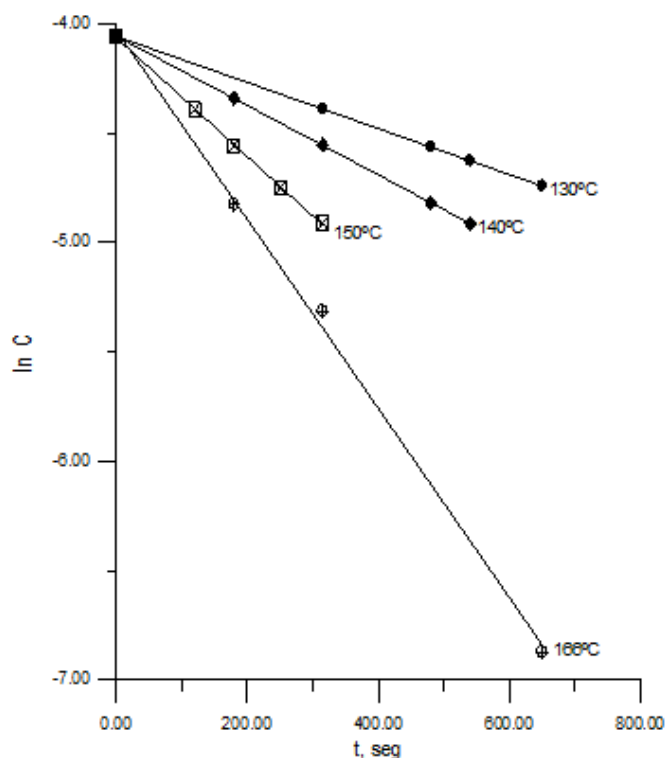
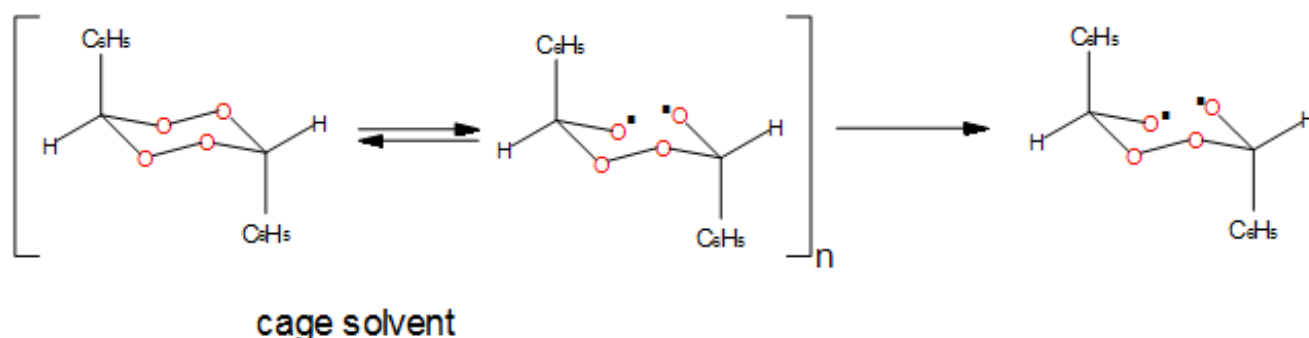


Figure 1. Thermal decomposition of DFT in isopropyl alcohol at different temperatures $1.00 \times 10^{-3}\text{M}$

The influence of temperature on the values of the rate constant (k_{EXP}) corresponding to the unimolecular reaction can be represented by the following Arrhenius equation,

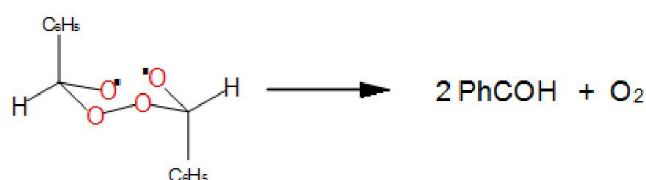
$$\ln k = \ln (10.7 \pm 1) - (14069.4 \pm 0.9) / RT$$

Where the activation energy is in cal mol^{-1} and errors correspond to standard deviations arising from treatment of the kinetic data by the method of least squares.

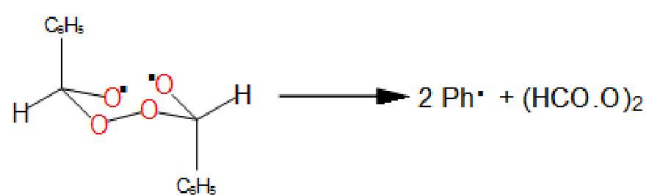


Scheme 1. The rupture (O-O) process would occur in the solvent cage. (The reactant molecules will generally be jumping from hole to hole in the solvent matrix, only occasionally finding themselves in the same solvent cage where thermal motions are likely to bring them into contact. A pair of reactants end up in the same solvent cage, where they bounce around randomly and exchange kinetic energy with the solvent molecules. Eventually the two reactants form an encounter pair. If they fail to react the first time, they have many more opportunities during the lifetime of the cage. The products form and begin to move away from each other)

The Arrhenius plot gives a straight line in the range of temperatures studied and this supports the hypothesis that it corresponds to a single simple process, it would be a unimolecular homolytic cleavage of the peroxide bond (O-O), giving a product biradical intermediate (Scheme 1). The formation of the products of the thermolysis of the DFT in solution isopropyl alcohol can be interpreted in terms of the homolytic break of the link or giving the biradical, which can cleave bonds C - O or to give the benzaldehyde and molecular oxygen (Scheme 2) or to can cleave bonds C-C to give biphenyl and phenol as secondary products (scheme 3). Also the benzoic acid has been obtained as product whose presence could be explained for the oxidation of the benzaldehyde in presence of the molecular oxygen.



Scheme 2. Formation of benzaldehyde product



Scheme 3. Eq.4. Formation of phenyl radical

The complex intermolecular interactions between solute and solvent present in the reaction solution makes it difficult to decide which of the properties of the solvent affect reaction rates. Similarly, it is not easy to define what properties of the reactant molecule must be considered when the existence is observed of a solvent effect related to reactivity. The effect of solvent on reaction rates constants of thermolysis is also reflected in the values of the parameters for activation, which are calculated using the Eyring equation. (Figure 2, Table 2))

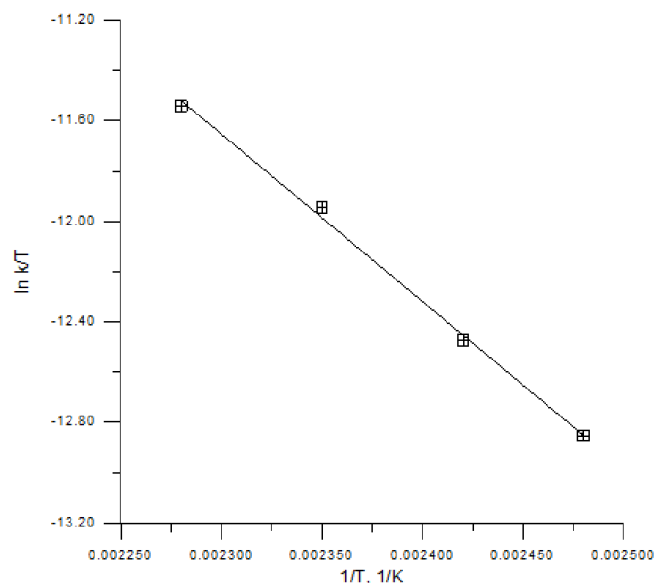


Figure 2. Graphical representation of the Eyring equation for the thermal decomposition of DFT in isopropyl alcohol solution

Table 2. Activation parameters values corresponding to thermal decomposition of DFT in solvents different

Solvent	ΔH^\ddagger Kcal mol ⁻¹	ΔS^\ddagger Cal mol ⁻¹ K ⁻¹	Ea Kcal mol ⁻¹	ΔG^\ddagger Kcal mol ⁻¹
Bencene	32.8±0.4	-5.2±1.2	32.4±0.4	34.9±0.4
Toluene	30.8±0.6	-7.9±1.5	31.6±0.6	34.1±0.6
Tetrahydrofurane	27.2±0.4	-11.8±0.5	28.1±0.4	32.5±0.4
Isopropyl alcohol	13.3±0.9	-39.9±1.0	14.0±0.9	30.0±0.9
Acetonitrile	29.5±0.6	-1.2±1.0	30.4±0.6	30.4±0.6

$$\ln \frac{k_{exp}}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}$$

Table 2 shows values of activation parameters on other solvents and are compared with those obtained in isopropyl alcohol. Looking at the activation enthalpy is lower compared with those obtained in less polar and moderately polar solvents. This effect could be justified by increased of solvation of the transition state, thereby diminishing the activation enthalpy of the reaction. This is justified by the very negative value of entropy. The negative activation entropy can be explained considering that DFT is a disubstituted diperoxide with less steric hindrance, which results in a higher degree of solvation of the activated complex causing a decrease in activation entropy even more marked than that occurring in the case of tetrasubstituted like the acetone diperoxide. We can even say that there is a compensation effect between activation enthalpy and activation entropy because a small variation is observed in the value of the free energy, this allows us to say that in spite of the existence of effect solvent on the thermal decomposition of the DFT, in all cases the reaction mechanism is the same. It can be observed that the free energy decreases with increasing reaction rate.

In the literature it is given a polarity definition as the solvating ability as a result of the sum of specific and nonspecific interactions, excluding those that cause a chemical reaction between solute and solvent. The solvent polarity cannot be adequately measured with certain physical properties related to non-specific interactions such as dipole moment, the dielectric constant, refractive index, etc. The effect of solvent on k_{EXP} can be analyzed through the representation of the natural logarithm of the rate constant for the decomposition of DFT in various solvents according to some empirical polarity parameter thereof. The empirical parameter $E_T(30)$ defined by Dimroth and Reichard (Dimroth *et al.*, 1969) is the best describes the interactions present in solution. This parameter is based on the transition energy, measured in kcal mol^{-1} , associated with the solvatochromic absorption band of high length of wave of Pyridinium-N-phenolate betaine dye $E_T(30)$ (dye N° 30 in the original work of these authors) or another derivative of betaine.

This parameter is a measure of the interactions between solute / solvent in cybotactic region and has no direct equivalence with other macroscopic properties of the solvent as the dielectric constant or the dipole moment. Figure 3 shows the effect of solvent on the reaction rate constant as a function of $E_T(30)$ to a temperature of 150°C . It is observed that increasing the polarity of the solvent causes an increase in the reaction rate constant of decomposition of DFT. We observed that increasing the polarity of the solvent causes an increase in the reaction rate of decomposition of DFT, but the correlation is not linear. This allows us to suggest that the solute / solvent interactions are specific determinants of the reactivity of DFT in solution. The existence of a linear compensation between the activation parameters for the thermal decomposition of DFT in different solvents (Table 2) according to the criterion Leffler, also known as "compensation effect", can be represented by equation (5), which shows a relation approximately linear (Figure 4, $r = 0.928$), being 533 K (260°C) the value of the "isokinetic temperature" (β), or the

temperature to which in all the solvents the thermal decomposition of DFT would pass to the same speed.

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger \quad (5)$$

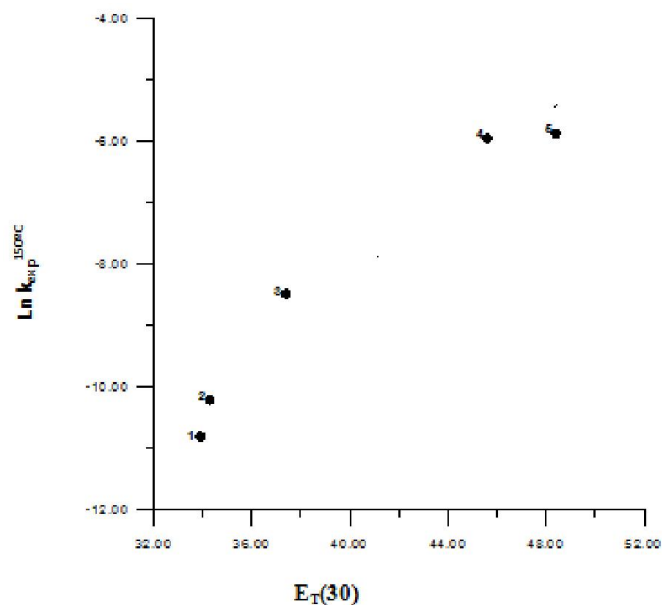


Figure 3. Graphical representation of $\ln K_{EXP}$ versus polarity parameter solvent $E_T(30)$, corresponding to the thermal decomposition of DFT in different solvents, at 150°C . 1- Toluene; 2- Bencene; 3-THF; 4-Acetonitrile; 5-Isopropyl alcohol

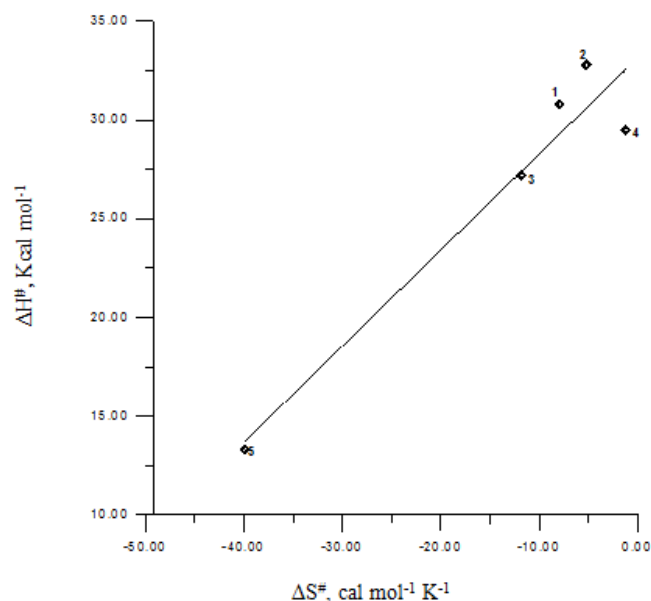


Figure 4. Isokinetic Relationship according to Leffler for the thermal decomposition of DFT in solution. 1- Toluene; 2- Bencene; 3-THF; 4- Acetonitrile; 5-Isopropyl alcohol

Comparing the activation parameters in different solvents of the thermal decomposition of DFT, we see marked differences justified by the different mechanisms of solute-solvent interaction according to the physicochemical properties of the same, which allows us to affirm that there is a marked effect of solvent. (Table 2) The values of the activation parameters obtained from the DFT in isopropyl alcohol are similar to the homolytic decomposition unimolecular for different dialkyl

peroxides diperoxides and cyclic tetrasubstituted in solution that decompose with a unimolecular peroxidic bond rupture. This suggests that the rate-determining step in the reaction in isopropyl alcohol DFT thermolysis is the homolytic cleavage of the peroxide bond with the formation of a biradical intermediate. Upon evaluation of the activation parameters (Table 2) it can be observed that a modification of the activation enthalpy value (ΔH^\ddagger) is accompanied by a change in the same sense of the corresponding activation entropy (ΔS^\ddagger), determining a compensation effect that results in a variation of activation free energy (ΔG^\ddagger) that is almost negligible ($\Delta\Delta G^\ddagger = 4.9 \text{ kcal mol}^{-1}$).

Further it should be noted that this value is in the order of the calculated experimental error for this parameter. On the other hand, the fact that the values of free energy are similar in all cases allow to establish that thermal decomposition occurs in all studied solvent via the same stepwise-type mechanism, and is initiated by the O-O bond homolytic rupture of DFT molecule. The observed differences in activation parameters can be explained taking into account that the activated complex of DFT in isopropyl alcohol is more polar than its initial state, and in turn, more polar than the activated complexes on others solvent. Therefore, the value of activation enthalpy decreases as a result of solvation, thus lowering the energy barrier that the diperoxide must overcome to be transformed into products. The association forces lead to a highly ordered activated complex, which gives rise to a significant decrease in the values of activation entropy for DFT in isopropyl alcohol. Table 2.

Conclusion

The thermolysis of DFT in isopropyl alcohol follows first order kinetic laws up to at least ca. 60% diperoxide conversion. Analysis of the reaction products and the activation parameter values contributes to postulate the mechanism for the thermolysis of the DFT in isopropyl alcohol solution. The reaction decomposition would occur through a common mechanism of decomposition, 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 benzaldehyde and oxygen as final products. The kinetics of DFT thermolysis is significantly affected by the physicochemical characteristics of the reaction medium. Probably, the high polarity of the isopropyl alcohol solvent determinates the high decomposition rates observed

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