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Thermal decomposition of 3, 6: Diphenyl: 1, 2, 4, 5: Tetroxane diperoxide in water solution

Alexander G Bordon[1], Andrea N Pila[2], Mariela I Profeta[3], Maria J Jorge[4], Lilian C Jorge[5], Jorge M Romero[6], Nelly L Jorge[7*]

[1-4, 6, 7] Laboratorio de Investigaciones en Tecnología Ambiental, Facultad de Ciencias Exactas y Naturales y Agrimensura, Iquibanea, Universidad Nacional del Nordeste. Avenida Libertad, Argentina

[5] Facultad de Ciencias Veterinarias, Universidad Nacional del Nordeste. Juan Bautista Cabral, Argentina

Abstract

We are commited to study cyclic organic peroxides with one or more peroxy functions in its molecule, motivated by the multiple utilities and application possibilities found for these compounds. In this paper we analized the kinetics of thermal decomposition of 3, 6-Diphenyl-1, 2, 4, 5-Tetroxane (DFT) in aqueous solution. At the concentration (1.0x10-3M) and temperatures studied (130-166°C), kinetic satisfactorily fulfills a first-order kinetic law until conversions of 58% of the diperoxide. From the experimentally obtained kinetic data, the activation parameters were determined in order to perform different correlations and treatments. Results obtained prior to the present work were included in the analyzes, in order to establish comparisons.

Keywords: DFT, thermolysis, kinetic, diperoxide

1. Introduction

During the last decade, the chemistry of cyclic peroxides has enjoyed a renaissance with the increasing appreciation that such compounds occur widely in nature and often possess desirable pharmacological properties. Chemical compounds having a peroxidic group play an important role in oxidation reactions of organic compounds. Usually, these reactions are developed by reacting molecular oxygen or an activated form, as singlete oxygen or the superoxide radical anion. Organic peroxides are encountered, generally in only very small amounts, as impurities in many organic compounds, where they have been slowly formed by the action of molecular oxygen. Organic peroxides are derived from alcohols and ethers, in the same way as hydrogen peroxide is derived from water [1-3].

These theoretical methods have been applied to determine the equilibrium geometry of unstable intermediates and also the transition structures of the chemical oxidation reactions of organic compounds with many compounds having attached a peroxidic group (Hehre *et al*, 1986) [4]. Recently, a large number of reaction mechanisms have been elucidated through the employment of advanced modern theoretical chemistry techniques [5-7].

It is of interest to know the effect of the medium on the thermolysis of tetroxanes, specifically cyclic Benzaldheyde diperoxide (3,6-diphenyl-1,2,4,5-tetroxane, DFT, Scheme 1). The solution thermolysis of this molecule has been studied for several years [8-14] and has shown a marked effect of the solvent among the media studied. Thus, thermolysis turns out to be almost 100 times faster in acetic acid than in benzene.

Previous work showed studies resulting from correlating the reaction rate with the polarity of the medium. It was observed that an increase in the polarity of the medium increases the DFT thermolysis rate in solution, however, some of the solvents compared: tetrahydrofuran, isopropanol, methanol and acetonitrile, are excluded from this linear correlation, showing that other factors, in addition to polarity, are conditions of Tetroxane reactivity in solution.

The present study proposes the formation of «adducts» between the DFT and the solvent, to justify the particular kinetic behavior of the DFT against certain solvents. This proposal supports both the experimental results found and theoretical calculations made for this purpose.

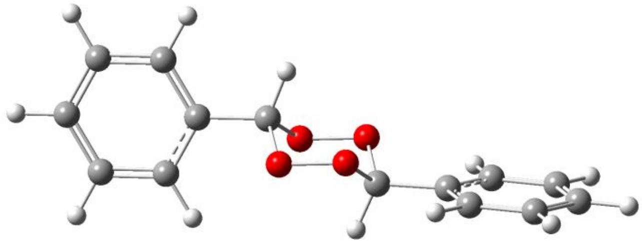

Fig 1: 3, 6-diphenyl-1, 2, 4, 5-tetroxane, DFT.

2. Materials and methods

2.1. Synthesis

DFT was prepared according to the literature, by reacting to solution of benzaldehyde in ethyl alcohol, dropwise addition to a stirred solution cooled to 20°C comprising hydrogen peroxide, concentrated sulfuric acid and ethanol. The solid was isolated, washed with water and ethanol and dried at the vacuum was then purified by re crystallization. The purity of the product obtained was checked by determination of the melting point, and by gas chromatography.

2.2. Kinetics

The reaction was carried out in Pyrex glass ampoules (12 cm long × 4 mm external diameter) containing 0.2 mL of the DFT in solution, completely degassed under vacuum at -196°C and sealed with flame torch. To reaction, they were immersed in a thermostatic silicone oil bath (± 0.1°C) and removed after predetermined times, stopping the reaction by cooling to 0°C. The remaining DFT and reaction products were determined by GC quantitative analysis (internal standard method, n-octane), using a capillary column (HP5, 30 m long, 250 mm internal diameter) impregnated with 5% phenyl methyl silicone as phase stationary, with nitrogen as carrier gas and FID detector. The analyzes were carried out with the injector at 150°C and the programmed oven temperature (30°C / min) from 60 to 190°C. The identification of the products was made by comparing their retention times with those of authentic samples.

2.3. Calculations

K exp values were calculated using a first-order kinetic law, estimating the goodness of the fit with the linear regression method for minimum squares (r> 0.9950).

The influence of temperature on the values of the velocity constant was represented by the Arrhenius equation. The values of the activation parameters were determined using the Eyring equation.

3. Results and Discussion

The concentration at which the thermolysis reaction was studied was very low, whereby the effects of secondary reactions of free radical-induced decomposition originating in the reaction medium can be considered negligible.

The thermal decomposition of the DFT in aqueous solution at the concentration (1.0-30.0 x10^{-3}M) and temperatures studied (130-166°C), satisfactorily complies with a first-order law until conversions of 58% diperoxide.

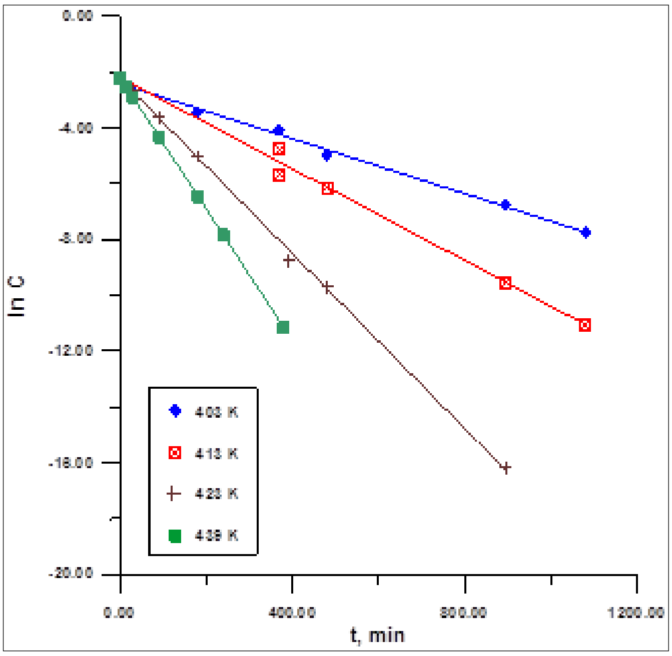

Fig 2: Kinetics of thermal decomposition of DFT in aqueous solution at different temperatures.

Table 1: Rate Constants thermal decomposition of DFT in aqueous solution at different temperatures.

T (K)	**k 10^4 (s^{-1})**
403	0.8
413	1.4
423	2.6
439	3.9

The influence of temperature on the values of the rate constant, could be represented by the Arrhenius equation, where errors show a minimum standard data processing square deviation of the kinetic data.

$$\text{Ln } k = (9.8 \pm 0.5) - (7724.1 \pm 0.8)/RT$$

The Arrhenius equation graph is particularly linear (r^2 = 0.972) in the relatively large temperature range studied (ca 36°C). This assumes that the calculated values of the activation parameter for the decomposition of DFT in the aqueous solution belong to a single process. It could be a Unimolecular homolysis or a concerted type process. It is not likely that both processes have identical activation parameters. Activation energy for the thermolysis of DFT in water is approximate to that obtained in the gas phase. A staggered mechanism could then be postulated with an intermediate birradical, which breaks down further. For this reason, the concerted process could be reasonably discarded.

The values of the activation parameters ($\Delta H\# = 60.7 \pm 0.8$ kJ mol^{-1} and $\Delta S\# = -174.2 \pm 0.7$J mol^{-1} K^{-1}) were determined using the Eyring equation, whose graph was practically linear (r2= 0.969) in the studied temperature range (ΔT: 36ºC).

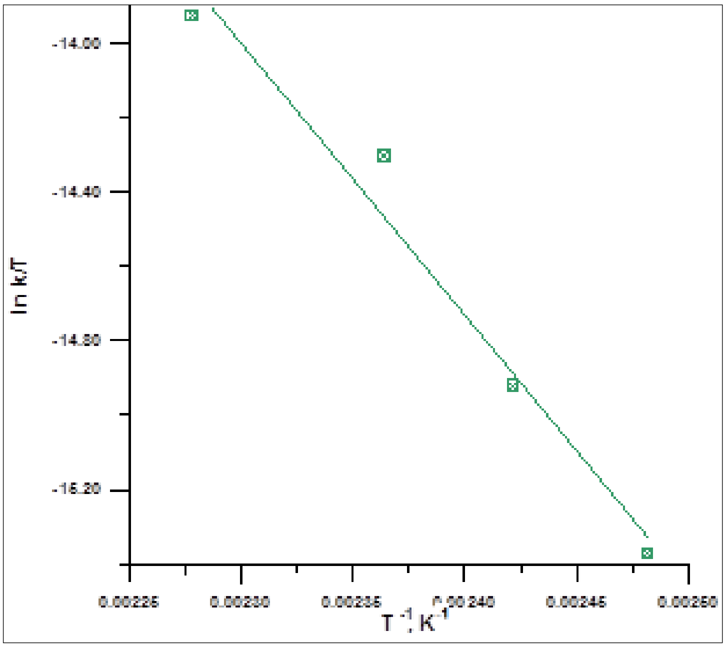

Fig 3: Graphical representation of the Eyring equation for the thermal decomposition of the DFT in water solution.

Table 2: Activation parameters of DFT thermolysis in (*) protic and (**) aprotic polar solvents.

.SOLVENT	ET$_{30}$	dielectric constant	ΔH# kJ mol^{-1}	ΔS$^{\#}$ J mol^{-1} K^{-1}	Ea kJ mol^{-1}	ΔG# kJ mol^{-1}
Acetonitrile **	45,6	37,5	122,2 ± 2,9	-8,8 ± 1,0	125,9 ± 2,9	125,5 ± 2,9
Nitrometane **	46,3	35,9	106,3 ± 1,0	-58,6 ± 1,1	109,6 ± 1,0	130,9 ± 1,0
Methylcellosolve *	52,0	10,4	83,7± 1,.0	-107,5±1.4	87,4±1.0	128,4 ±1,0
Water	63.1	80.0	60.7± 0.9	-174.2± 0.9	64.2± 0.9	133.8± 0.9
Isopropanol *	49,2	17,9	56,1 ± 0,8	-164,8 ± 0,9	59,8 ± 0,8	125,1 ± 0,8

ΔG$^{\#}$ for the thermal decomposition reaction of DFT in aqueous solution is within the range obtained in solvents of different polarities studied.

Enthalpy of activation in aqueous solution is low as in other polar protic solvents. This effect could be justified by a greater solvation of the transition state. The most negative entropy value confirms this.

The compensation effect could be verified since the enthalpy variation through the series of reactions is exactly compensated by the entropic changes. (Figure 3). The slope of the graph gives us the value of the Isokinetic temperature for that series of reactions, which is β = 403 K, within the range of experimental work. From a physical point of view, it is the temperature at which in all solvents the thermal decomposition reaction of DFT would proceed at the same rate.

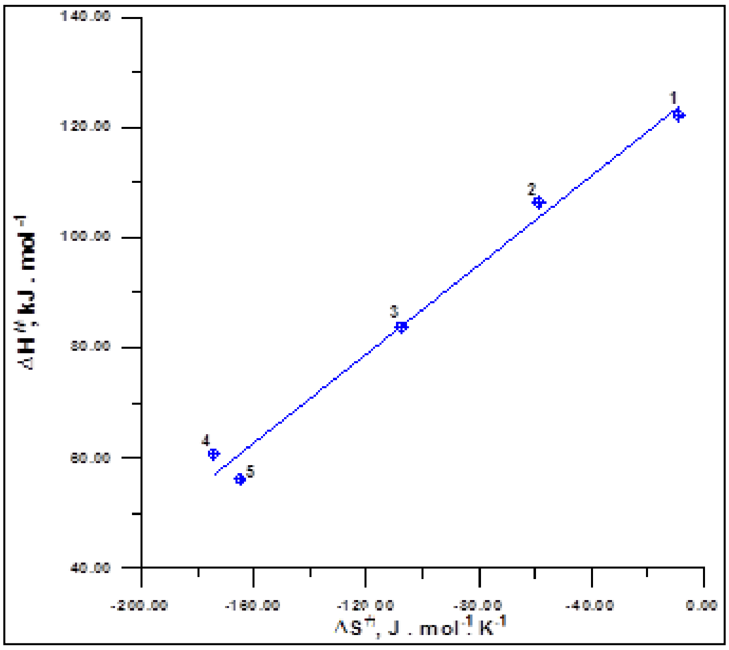

Fig 4: Representation of the "Isokinetic Ratio" according to the Leffler treatment for the unimo lecular thermolysis of DFT in 1-Acetonitrilo; 2-Nitromethane; 3- Metilcellosolve; 4-Water; 5-Isopropanol.

The values of the activation enthalpy variation correspond to a unimo lecular rupture of the per oxidic bond supporting the hemolytic mechanism in stages with the formation of a birradical intermediary common to DFT in different solvents. The results obtained also agree with those corresponding to the thermal decomposition of different diperoxides in solution studied by this group and also those obtained by other authors. Analyzing the plot plotted according to Exner's criteria, it is observed that there is not intersection point between of the solvents studied, the lines are cut within the range of experimental temperatures, making it not possible to apply the statistical treatment to determine the value of β.

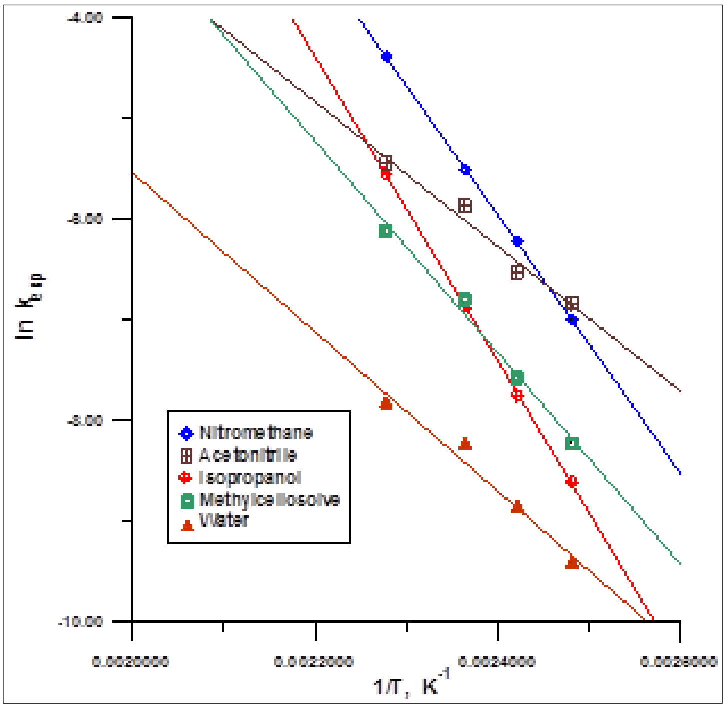

Fig 5: Graphical representation of the Isokinetic Ratio (Exner criteria) for thermal decomposition of DFT in solution.

It is evident that the thermal decomposition reaction of DFT is affected by different mechanisms of solute / solvent interaction due to its physicochemical characteristics. Another way to evaluate the effects of the solvent is to determine the rate constants of a reaction at two temperatures in Different solvents and establish a correlation between the logarithms of the same. Since the determinations of these constants are independent, their errors are also independent, therefore the existence of a linear relationship would imply an Isokinetic relationship for the series studied. [15,16] (Figure 4)

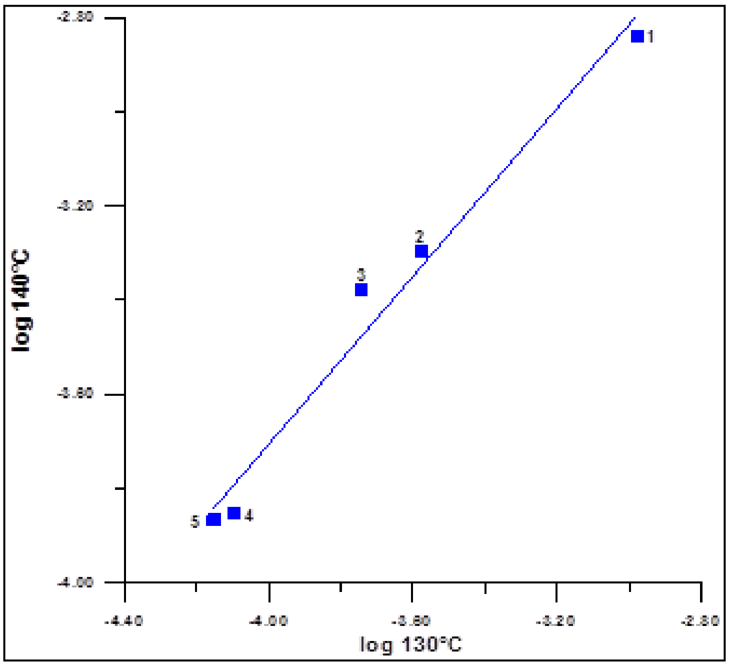

Fig 6: Graphical representation of log k (130ºC) vs log k (140ºC) corresponding to the thermal decomposition of DFT in the different solvents. 1- Isopropanol; 2-Metilcellosolve; 3- Acetonitrilo; 4- Methanol; 5- Water.

The set of reactions studied according to this treatment would confirm an Isokinetic relationship. (Figure 4) The analysis of the effect of the solvent on the k_{exp} can be carried out through the graphic representation of the natural logarithm of the velocity constant for the decomposition of the DFT in different solvents based on some empirical parameter of polarity thereof, for example the ET_{30} determined by Dimroth and Reichardt. [17-20]

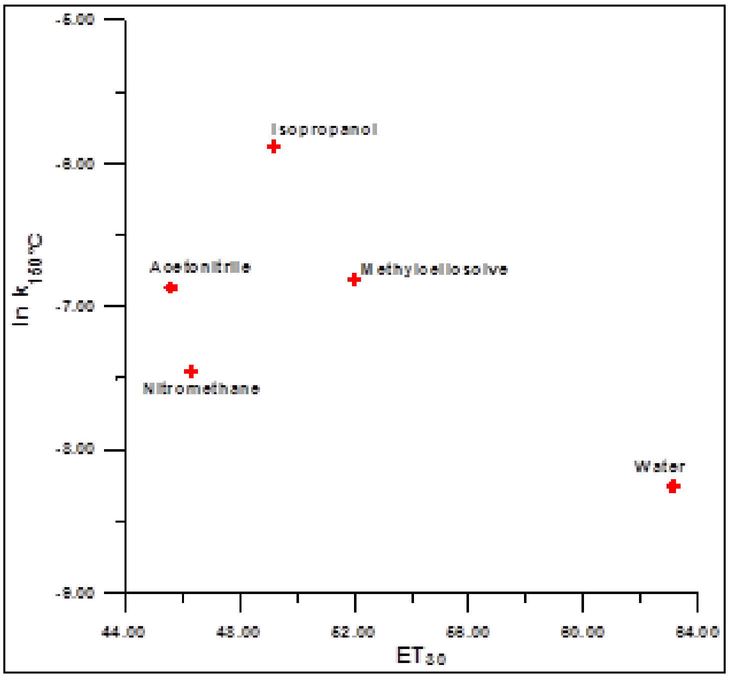

Fig 7: Relationship of the DFT thermal decomposition rate constant at 150°C with the solvent polarity parameter ET $_{[30]}$.

As the polarity of the solvent increases, determined through parameter ET $_{(30)}$, the rate of peroxide decomposition increases, however this correlation, as a whole, is not linear.

This fact allows us to suggest that the solute / solvent specific interactions are determinants of the reactivity of the DFT in solution. It has been shown in the literature that for different cyclic peroxides these interactions correspond to the hydrogen bond between the protic solvent and the O-O bond [17-20].

In Figure 5 two groups of solvents are differentiated where the correlation is linear between them. On the one hand the protic polar solvents (Isopropanol, Methylcellosolve, Water) and on the other the aprotic polar solvents (Acetonitrile, Nitro methane).

These experimental results confirm a greater reactivity of the compounds with peroxidic bond in solution of protic polar solvents, than in aprotic polar solvents, as has been demonstrated in previous studies for other cyclic organic diperoxides [21, 22].

All the treatments carried out show that the kinetics of the thermal decomposition of the DFT is affected by the nature of the solvent used as a reaction medium, which is checked in the well-marked values of the activation parameters.

As the polarity of the solvent increases, a decrease in the activation energy and in the enthalpy of activation is observed because the transition state is more solvated than the reagents. This is corroborated with the most negative activation entropy values. The free energy variation values ($\Delta\Delta G^{\#}$ = 5.85 $kJmol^{-1}$) confirm the compensation effect, whereby the series of reactions considered have a common reaction mechanism that begins with the unimo lecular homo lytic rupture of the O-O bond. The activation parameters corresponding to the kinetic determinations in Isopropanol (Table 2) are much lower than those observed in the other solvents. The low value found for the activation entropy, in comparison with the data in the other solvents, may be due to the fact that the solute-solvent interaction is high forming an adduct through hydrogen bonds. The reaction kinetics in water has the activation parameters very similar to isopropanol, however the mechanism would be given by the formation of hydrogen bonds with peroxy oxygen without the formation of an adduct favoring its breakdown.

4. Conclusions

The unimo lecular thermal decomposition of cyclic Benzaldheyde diperoxide (DFT) in solution follows a pseudo-first order kinetics, proving the existence of a solvent effect on the rate constants, the activation parameters and the products of the reaction considered, of so that an increase in solvent polarity accelerates the reaction while generating more Benzaldehyde. The changes observed in the velocity constants in the different reaction media are caused by modifications in both enthalpy and activation entropy, so that they tend to compensate and consequently the values of the activation-free energy are practically constant. The application of different criteria with respect to the treatment of the kinetic data obtained for the thermal decomposition of DFT in solution makes it possible to postulate a common mechanism of thermolysis initiated by the homo lytic rupture of an O-O bond with different mechanisms of interaction with the solvent.

5. Acknowledgments

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