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## Solvent Effects in the Thermal Decomposition Reactions of Cyclic Benzaldehyde Diperoxide

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**Abstract:** The kinetics of the thermal decomposition reaction of 3,6-diphenyl-1,2,4,5-tetroxane (DFT) was investigated in various solvents at different temperatures. Linear relationships were observed between the enthalpy and entropy of activation of the unimolecular reactions of those diperoxides. The isokinetic temperature calculated by Leffler's treatment was 311.5°C, that relationship is consistent with the proposed Exner correlation between the logarithm of the rate constant values for the same reaction in each solvent at two temperatures, where the corresponding  $\beta$  value was 311.7°C. A true isokinetic relationship for the DFT thermolysis indicates that their reactions constitute a reaction series with similar interaction mechanisms. These can be related to the capacity for hydrogen bonding between the solvent and the diperoxide molecules. Then, the solvating properties of the media help the peroxidic bond rupture of this type of molecules.

**Key words:** Kinetics in solution, solvent effect, benzaldehyde diperoxide

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### Introduction

The study of organic peroxides comprehends a large number of chemical issues, from biological like themes (for example, metabolic oxidations processes) up to industrial applications (disinfections action and pigment manufacture) (Kholer, 1906; Adam and Cilento, 1982).

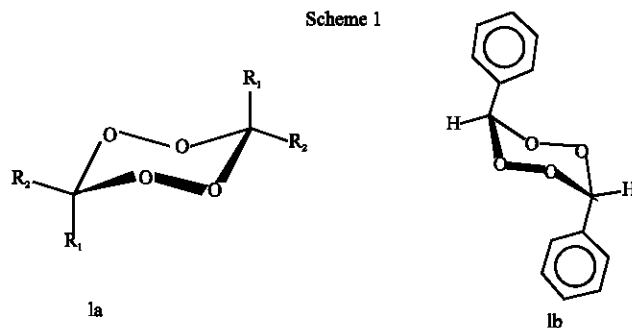
Cyclic peroxides such as the substituted 1,2,4,5-tetroxanes (Ia) undergo thermolysis, both in the gas and solution phase by a stepwise mechanism, where the activation parameters values of the initial unimolecular homolysis fall within a limited range, although significant steric and solvent effects have also been observed. Moreover, the experimental activation energies for their thermolyses are usually in good agreement with calculated values based on a peroxidic bond homolysis of the corresponding molecular rings (Cafferata and Jefford, 2001; Cafferata and Rimada, 2003).

Previous studies demonstrated a significant solvent effect in the kinetics of the unimolecular decomposition reactions of cyclic diperoxides with a tetroxacyclohexane ring in their molecules, behavior attributed to their transition states with some polar character (Cafferata *et al.*, 1991, Eyer *et al.*, 2004).

The kinetics of the thermal decomposition reactions of cyclic benzaldehyde peroxide, DFT, (Ib) provide an interesting means to learn about the nature of solvent effects on the thermolysis of this type of molecule, which is the aim of the present study.

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Scheme 1

## Materials and Methods

### Materials

The DFT diperoxide was prepared by method described elsewhere and their purity was checked by GC and IR analysis. Organic solvents were commercial analytical reagents purified by standard techniques.

### Kinetics Methods

Pyrex glass tubes (8 cm long  $\times$  8 mm o.d.), half filled with the appropriate diperoxide solution, were thoroughly degassed under vacuum at  $-190^{\circ}\text{C}$  and then sealed with a flame torch. To perform the runs, they were immersed in a thermostatic silicone oil bath ( $\pm 0.1^{\circ}\text{C}$ ) and withdrawn after selected times, stopping the reaction by cooling at  $0^{\circ}\text{C}$ . The diperoxides remaining in the reaction solution were determined by quantitative GC analysis (Internal standard method, n-octane) using a silica fused capillary column (HP-SP-2100.30 m  $\times$  0.25 mm i.d.) installed in a 5890 Model Hewlett-Packard instrument, with nitrogen as the carrier gas and FID detection. The corresponding first-order rate constant values of  $\ln(\text{diperoxide})$  vs time.

## Results

The DFT diperoxide was prepared by method described elsewhere and their purity was checked by GC and IR analysis. Organic solvents were commercial analytical reagents purified by standard techniques.

Rate measurements were made on the thermal decomposition of DFT in a variety of solvents with different physicochemical characteristics (Table 1).

The values of the activation parameters for the thermolysis of the diperoxides are given in Table 2.

In the DFT reaction the Isokinetic relationships in several solvents according to Leffler gives an isokinetic temperature of  $311.5^{\circ}\text{C}$ , (Fig. 1,  $r = 0.9679$ ) and according to Exner the corresponding  $\beta$  value was  $311.7^{\circ}\text{C}$  (Fig. 2,  $r = 0.9937$ ).

The representation of  $\ln k$  vs  $\ln T^{-1}$  must be a linear correlation according to Arrhenius equation and all the lines have to intersect at a point known as the reciprocal isokinetic temperature ( $\beta^{-1}$ ). The corresponding isokinetic temperature for the DFT thermolysis is  $303.5^{\circ}\text{C}$ , (Fig. 3).

Table 1: First-order rate constant values for DFT ( $1.3 \times 10^{-2} M$ ) thermolysis in various solvents at different temperatures

Solvent	Temp. (°C)	$K_{exp} \times 10^5 (s^{-1})$
Toluene	130	0.32
	140	0.72
	151	2.00
	166	7.90
Benzene	130	0.38
	140	1.11
	151	3.64
	166	11.70
Tetrahydrofuran	130	4.00
	140	7.90
	151	20.00
	166	67.50
Methanol	130	7.00
	140	13.60
	151	36.80
	166	91.20

Table 2: Activation parameters for DFT thermolysis in solution

Solvent	$\Delta H^\ddagger (kcal mol^{-1})$	$\Delta S^\ddagger (cal mol^{-1} K^{-1})$	$\Delta G^\ddagger (kcal mol^{-1})$
Toluene	$30.7 \pm 0.6$	$-8.3 \pm 1.5$	$34.2 \pm 0.6$
Benzene	$32.8 \pm 1.1$	$-2.3 \pm 0.3$	$33.8 \pm 1.1$
Tetrahydrofuran	$27.0 \pm 0.4$	$-12.3 \pm 0.5$	$32.2 \pm 0.4$
Methanol	$24.8 \pm 0.8$	$-16.7 \pm 1.8$	$31.8 \pm 0.8$

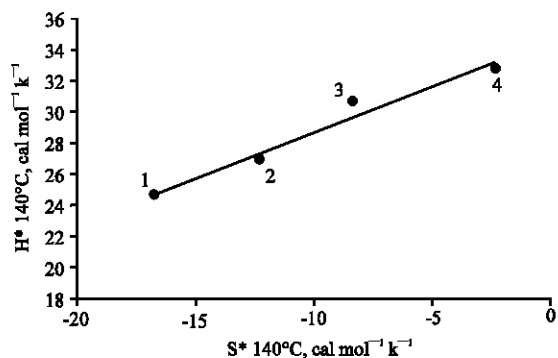


Fig. 1: Isokinetic relationships according to Leffler. (1)Methanol (2) Tetrahydrofuran (3) Toluene (4) Benzene

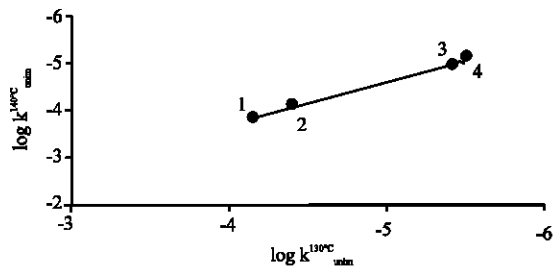


Fig. 2: Isokinetic relationships according to Exner corresponding to the unimolecular decomposition of DFT in several solvents: (1) Methanol (2) Tetrahydrofuran (3) Benzene (4) Toluene

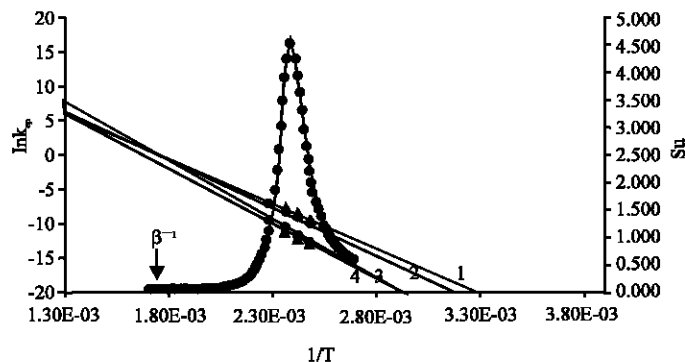


Fig. 3: Dependence of the residual sum of squares  $S_u$  on the proposed isokinetic temperature  $T^{-1}$  for the DFT unimolecular thermolysis in different solvents: (1) Methanol (2) Tetrahydrofurane, (3) Benzene (4) Toluene

### Discussion

At each temperature the observed rate constant values,  $k$ , are practically independent of the initial diperoxide concentrations and in present study the thermolyses follow first-order kinetic laws up to at least ca. 60% conversions.

In general, a significant variation is evident in the observed values of the activation parameters. Activation enthalpies near 28 Kcal mol<sup>-1</sup> correspond to the peroxidic O-O bond strength for homolytic types of ruptures although lower activation parameters for the decomposition of peroxides were attributed to ionic reactions in solution (5y6 ver ref).

The values of the activation parameters for the thermolysis of the diperoxides (Table 2) show linear correlations ( $\Delta H^* = \Delta H^\circ + \beta \Delta S^*$ ) according to Leffler's treatment for the postulate of an isokinetic relationship, going from Toluene to Methanol.

In the DFT reaction the corresponding plot (Fig. 1) gives an isokinetic temperature of 311.5°C, which is well outside the temperature range where the kinetic measurements were performed (130-151°C). That relationship is consistent with the proposed Exner correlation between the logarithm of the rate constant values for the same reaction in each solvent at two temperatures (Fig. 2), where the corresponding  $\beta$  value (311.7°C) is in agreement with that calculated according to Leffler's treatment. In fact, the straight line obtained by plotting  $\log k(T_2)$  vs  $\log k(T_1)$  can be mapped back into the representation  $\Delta H^*$  vs  $\Delta S^*$  and vice versa (Fig. 1 and 2). However the most striking aspect of the results for the DFT thermal decomposition reactions (Table 2) is the difference of nearly 8 kcal mol<sup>-1</sup> in the activation enthalpy values and 14 entropic units in going from Toluene to Methanol.

All of these findings suggest that its thermolysis conforms to a genuine reaction series, where the solvent affects the tetracyclohexane ring O-O bond rupture of the DFT molecule.

When the isokinetic relationship is valid, its general representation,  $\ln k$  vs  $\ln T^{-1}$  (Fig. 3), must be a linear correlation according to Arrhenius equation and all the lines have to intersect at a point known as the reciprocal isokinetic temperature ( $\beta^{-1}$ ). The Exner statistical analysis based on a least-squares method calculates a common point of intersection of regression lines in the Arrhenius plot for which the sum of squares  $S_u$  of the deviations of the experimental points from new regression lines, including that point, becomes a minimum. If this is not found in the plot representing the dependence of  $S_u$  on the supposed values of  $T^{-1}$ , the expected correlation is not valid. The corresponding isokinetic temperature for the DFT thermolysis (Fig. 3) is 303.5°C, which is also in reasonable agreement with

the above  $\beta$  value. Those results mean that a change of the solvents of that reaction do not produce variation in its mechanism because the existence of a true isokinetic relationship support a common reaction series.

Further studies with other family of solvents are needed to generalize this mechanism.

### **Conclusions**

Thermal decomposition of DFT follows a first kinetic order. The activation parameters and reaction products validates the existence of solvent effect on the unimolecular reaction.

A true isokinetic relationship for the DFT thermolysis indicates that their reactions constitute a reaction series with similar interaction mechanisms. These can be related to the capacity for hydrogen bonding between the solvent and the diperoxide molecules.

Then, the solvating properties of the media help the peroxidic bond rupture of this type of molecules.

### **Acknowledgment**

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