

**CATALYTIC DECOMPOSITION OF  
3,3,6,6-TETRAMETHYL-1,2,4,5-TETROXANE.  
EFFECT OF FERRIC IONS (Fe<sup>3+</sup>)**

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ABSTRACT: Thermal decomposition of 3,3,6,6-tetramethyl 1-1,2,4,5-tetroxane in presence of iron (III) salts takes place through a coordination mechanism, involving the metal ion as a Lewis acid, and it's completely consistent with the counter ion effect observed. The activation parameters of the reaction initial step ( $\Delta H^\ddagger = 10,96 \pm 0.8$  kcal/mol ;  $\Delta S^\ddagger = -34,4 \pm 0.6$  kcal/mol;  $\Delta G^\ddagger = 25,48 \pm 0.8$  kcal/mol) are compared with those reported for the unimolecular thermolyses of the 3,3,6,6-tetramethyl-1,2,4,5-tetroxane in presence of other metallic ions.

## 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 [1]. In the past decade remarkable progress has been made in theoretical chemistry, particularly in computational procedures for elucidation of the structures of unstable molecules and transition states and those of stable molecules [2]. These advanced theoretical methods have been applied to the determination of fully optimized geometries of unstable intermediate species and also to the location of structures in oxidation reaction of organic compounds with various peroxy compounds.

The mechanisms of many newly developed oxidation reactions have been elucidated by the use of such modern techniques [3].

Peroxides present some interesting chemical reactions, due to the characteristic of being initiators on free radicals reactions. Recent works have shown that they intervene on biological processes [4].

On the other hand, the electronic characteristics of the become oxygenated molecules turn out to be modified when they are coordinated with transition metals, what allows to suppose that ions can catalyze also the decomposition of the peroxide compounds [5,6].

Previous works about tetramethyl 1,2 dioxetane decomposition in methanol solution, showed a much higher reaction velocity, due to the presence of metallic impurities that act as a catalyst. Thermal decomposition of 3,3,6,6-tetramethyl 1,2,4,5-tetroxane (ACDP) in methanol solution with the aggregate of cupric chloride shows an increase in their velocity. Thus, cupric ions have a catalytic effect on peroxide decompositions [7].

This work studies the effect of Fe(III) ions on thermal decomposition of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane that are considered to possess in their structure two endoperoxide groups [8].

## EXPERIMENTAL SECTION

### *Materials*

3,3,6,6-tetramethyl-1,2,4,5-tetroxane was prepared and conveniently purified as described elsewhere and its purity checked by GC. CAFFERATA L. F. R *et al.* [9]. Methanol (Merck<sup>®</sup>, p.a.), a single and narrow chromatographic peak was detected for that solvent.

n-Octane (Fluka<sup>®</sup> p.a.) was employed as internal standard in quantitative determinations of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane concentration and reaction products.

### *Kinetic Methods*

Pyrex glass tubes (4mm i.d., 70 mm length) filled with the appropriate volume (c.a.3mL) of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane in methanol solution, with addition of n-octane (internal standard) and ferric salt, were thoroughly degassed under vacuum line at -196°C and then sealed with a flame torch. To perform the runs, the ampoules were immersed in a thermostated silicone oil bath (+ 0.1°C) and withdrawn after selected times, stopping the reaction by cooling at 0°C. Quantitative determinations of the 3,3,6,6-tetramethyl-1,2,4,5-tetroxane and the organic reaction products in the solution after the runs (acetone) were performed by quantitative GC analysis (from 40°C to 150°C) at 30°C/min rate in HP5 capillary column (30m length, 0.250mm i.d., with methylphenylsilicone stationary phase) installed in a 5890 model series II Hewlett Packard Gas Chromatograph, using FID detection, nitrogen carrier gas and employing the internal standard method (n-octane).

### ***Products Identification***

It was performed by comparison of the retention time data with the corresponding to authentic samples.

### ***Calculations Methods***

First-order rate constant values were determined using a least-means-square data treatment ( $r > 0.995$ ) and the activation parameters values of the reactions obtained from computational method employing the Eyring equation parameters.

## **RESULTS AND DISCUSSION**

The thermal decomposition reactions of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane in methanol solution with the addition of  $\text{FeCl}_3$  ( $3.92 \times 10^{-4}$  M), at the temperature range of  $130.0^\circ\text{C}$ - $166.0^\circ\text{C}$  and initial concentration of  $1.87 \times 10^{-2}$  mol/L, follows first order kinetic laws with regard to the 3,3,6,6-tetramethyl-1,2,4,5-tetroxane (Figure 1).

The experimental rate constant values corresponding to the kinetics carried out in methanol with the addition of ferric ions are bigger than those corresponding to the reaction in methanol without the ferric ions. This indicates a great catalytic effect of the ferric ions (Table 1). The present metallic ions in solution would facilitate the decomposition of the molecule 3,3,6,6-tetramethyl-1,2,4,5-tetroxane forming coordination connections with the free electron pairs of the oxygen atoms. In methanol solution, the dissociated ferric ion will be solvated forming a complex type of  $\text{Fe}^{3+}(\text{MeOH})_x$ . [6]. Consequently, it can be settle down that could exist a competition between the solvent and the diperoxide for the metallic ion (Figure 1).

Table 1: First order rate constant values respect to the 3,3,6,6-tetramethyl-1,2,4,5-tetroxane for the Thermal Decomposition Reaction on methanol solution with addition of  $\text{FeCl}_3$  ( $3.92 \times 10^{-4}$  M) at different temperatures.

Temp °C	[3,3,6,6-tetramethyl-1,2,4,5- tetroxane]. $10^2$ mol/L	$k_{\text{exp}} \cdot 10^{5a}$ $\text{s}^{-1}$	$k \cdot 10^{5b}$ $\text{s}^{-1}$
130	1.87	0.40	303.14
135	1.87		398.50
140	1.87	1.00	428.32
155	1.87		761.00
166	1.87	6.59	984.17

<sup>a</sup> without the Fe(III), <sup>b</sup> added of Fe(III)

The temperature effect on the rate constant values corresponding to the studied reaction can be represented by the following Arrhenius equation:

$$\ln k (\text{s}^{-1}) = (8.59 \pm 0.4) - (11531.71 \pm 1000) / T$$

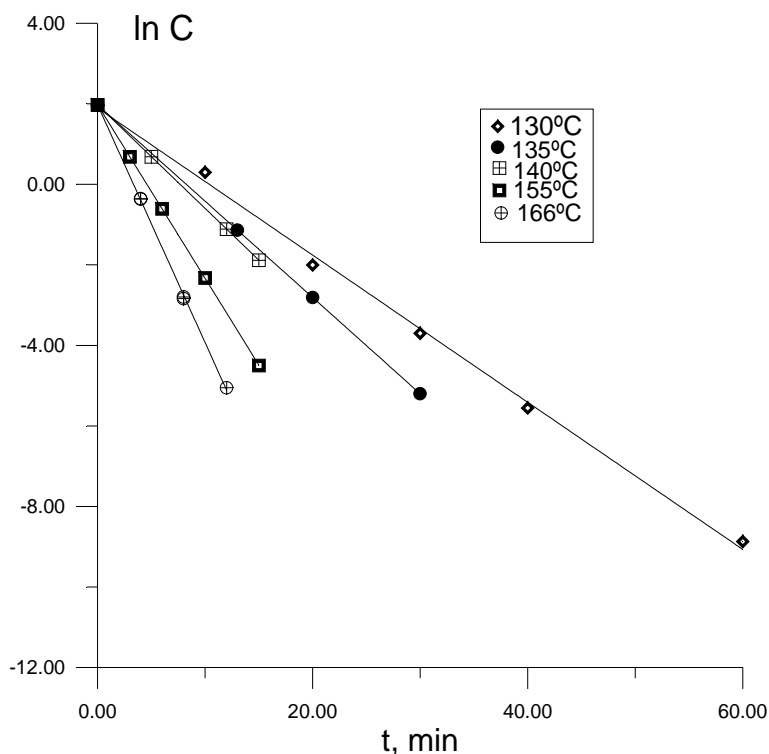


Figure 1. Kinetic of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane ( $1.87 \times 10^{-2}$  M) Thermal Decomposition Reaction in methanol solution with addition of  $\text{FeCl}_3$  ( $3.92 \times 10^{-4}$  M) at different temperatures.

The linearity of that equation ( $r \geq 0.999$ ) over a relatively large temperature range ( $36^\circ\text{C}$ ) suggests that their parameters belong to a single process. The value of the activation energy observed ( $E_a$  ca 12 kcal / mol) support that the metallic ion catalyzes the decomposition of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane [10, 11, 12, 13]. At the same time we can postulate the formation of a very orderly transition state through the negative value of the activation entropy [13, 14].

Table 2: Iron (III) ion catalyzed decomposition of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane in treated methanol.

Anion or salt	$[\text{Anion}]/[\text{Fe}^{3+}]$	$K_{\text{cat}} 10^5$ [ $\text{s}^{-1}$ ]
None		428.32
$\text{NaO}_2\text{CCH}_3$	2.1	94.10
$\text{Na}_2\text{EDTA}$	1.2	34.24

A counterion effect was observed for iron (III) ion catalysis (Table 2) [15]. Data in Table 2 indicates that the greater the complexation of the metal ion, the less effective the catalysis. These experimental results indicate that the metal ion was necessary for a most efficient catalysis. Thus, the effect will be stronger with a major concentration of iron (III). A coordination mechanism, involving the metal ion as a Lewis acid, is completely consistent with the counter ion effect and the linear free energy relationship. Complexation of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane by a metal ion might facilitates decomposition by removing positive character to one or both oxygen atoms (in one of the two peroxides

bonds); thereby destabilizing the peroxy bond and allowing for more facile ring cleavage [16,5] (Figure 2).

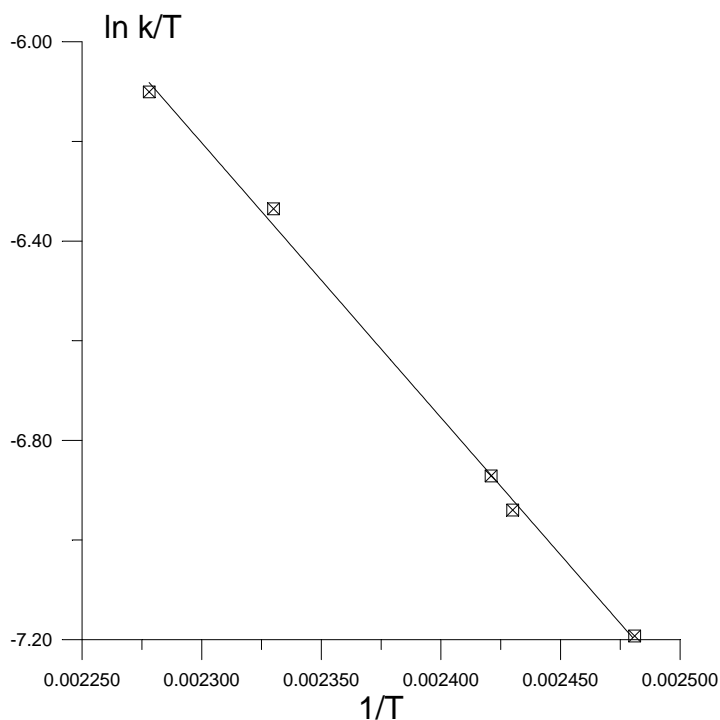


Figure 2. Eyring equation plot for the 3,3,6,6-tetramethyl-1,2,4,5-tetroxane for the Thermal Decomposition Reaction in methanol solution with added of FeCl<sub>3</sub> ( $3.92 \times 10^{-4}$  M).

In Table 3, kinetic parameters, shows that methanol with the addition of metals, presents a similar behavior to the acetic solvent and methanol with addition of Cu (II).

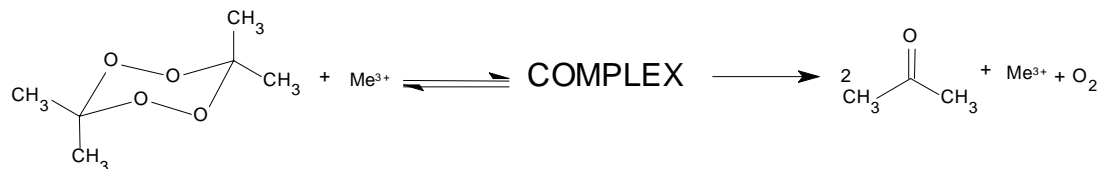
Table 3. Activation parameters for the thermal decomposition reaction of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane in different solvent

Solvent	$\Delta H^\ddagger$ kcal/mol	$\Delta S^\ddagger$ cal/mol °K	References
Methanol	25.8	-17.9	[17]
Methanol (added Cu II)	21.8	-10.8	[13]
Methanol (added FeIII)	10.96	-34.4	this work
2-Propanol	19.4	-31.4	[6]
Acetic acid	13.3	-43.7	[13]

## CONCLUSION

The thermal decomposition reactions of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane in methanol solution with addition of FeCl<sub>3</sub> ( $3.92 \times 10^{-4}$  M), at the temperature range and initial concentration of 130.0°-166°C and  $1.87 \times 10^{-2}$  mol/L, respectively, follows first order kinetic laws with regard to the 3,3,6,6-tetramethyl-1,2,4,5-tetroxane.

Postulated reaction mechanism begins by the rupture of a peroxy bond of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane with participation of alcohol molecules and the corresponding metallic ions that conduces finally to the formation of reaction products and the recovery of the metal. A high catalytic effect was observed on Discussion this mechanism is demonstrated by the counter ion effect.



Currently, research is in progress to determine whether the complexation involves one or both oxygen atoms of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane. We shall report on the rearrangements of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane by strong Lewis acids.

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