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## **Kinetics and Mechanism of Thermal Decomposition of Malonaldehyde Peroxide (DPM) in Solution**

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**Abstract** In this paper, the kinetics of the thermal decomposition reaction of 3,6-diethanal-1,2,4,5 tetroxane (malonaldehydeperoxide, DPM) is investigated in methanol solvents at different temperatures. In the temperature range of 130.0-166.0 ° C studied and at the concentration of  $2 \times 10^{-2}$  M, it follows a first order kinetic law up to at least 60% DPM conversion. The organic products observed were malonaldehyde. 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 DPM in methanol were calculated ( $\Delta H^{0\#} = 86.1 \pm 2.7$  kJ mol<sup>-1</sup> y  $\Delta S^{0\#} = -65.2 \pm 6.0$  J mol<sup>-1</sup> K<sup>-1</sup>)

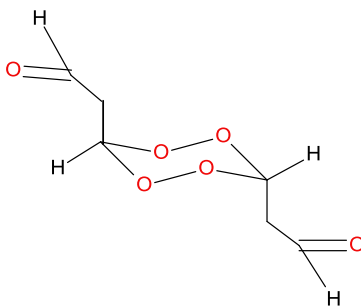
**Keywords** Diperoxide, kinetic mechanism, Gas Chromatography

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### **Introduction**

It is commonly accepted that explosive materials, such as fuels, are highly energetic compounds that, when initiated, release their energy content in a rapid exothermic reaction. In recent years, the analysis and detection of one class of explosives, namely peroxide explosives, has become particularly important in forensic investigations due to the emergence of terrorist threats and crimes in which these explosives were applied. A peroxide explosive is an organic compound that contains one or more peroxide functional groups (-O-O-) often in cyclic form. Cyclic organic peroxides can show explosive power, which can be of the same order of magnitude as high-power explosives (TNT). These compounds are generally powerful explosives, extremely sensitive to flames, heat, impact and friction. Peroxide explosives can generally be made from hydrogen peroxide and some other well-known chemicals, such as ketones or aldehydes. A small amount of acid (sulfuric or hydrochloric) is added as a catalyst. Most of these ingredients can be easily obtained at local pharmacies. On the other hand, polyfunctional cyclic organic peroxides have industrial applications because they are used as sources of free radicals in the polymerization of styrene [1,2]. The unusual reactivity of peroxides is generally attributed to the weakness of the O-O bond and the thermal decomposition thereupon is expected to be initiated by homolytic cleavage of the peroxide bond. Intuitively, peroxide-based explosives are expected to release a lot of energy when decomposed and their energy content depends on the carbon / oxygen ratio [3].

In this work a kinetic study of malonaldehydediperoxide (3,6-di-ethyl-1,2,4,5-tetraoxacyclohexane, DPM) is developed (Scheme 1). Its thermal decomposition reaction in methanol (MEOH) solution is reported.



*Scheme 1: Malonaldehyde peroxide*

## Materials and Methods

### Preparation of DPM-solvent samples for thermolysis tests

The thermolysis reaction was carried out in Pyrex glass ampoules of 14 cm in length and 7 mm in external diameter closed under vacuum. The ampoules were prepared as follows: they were filled with 1 mL of the DPM solution in the previously prepared methanol solvent, using a pasteur pipette. The open end was connected to a vacuum system ( $p < 1$  torr), containing a trap (cooled with liquid  $N_2$ ) and Teflon rods that allow the ampoule to be isolated from the rest of the system.

Then, the ampoule was immersed in a thermos with liquid  $N_2$  ( $-196^\circ C$ ), left for 2 or 3 minutes and then evacuated for another 2 or 3 minutes. The vacuum passage was closed and the ampoule was removed from the thermos until the solution had completely melted. The degassing process was repeated 3 times in order to eliminate all the gases present in the solution. At the end of degassing, keeping the ampoule submerged in liquid nitrogen, it was closed with a gas torch and  $O_2$ .

### Thermolysis Reaction

The reaction ampoules, containing the DPM solution in the methanol solvent, were immersed in a thermostatic bath of stabilized silicone oil at the chosen temperature ( $\pm 0.2^\circ C$ ); and they were removed at conveniently determined times, stopping the reaction by immersion in a water / ice bath at  $0^\circ C$ . The remaining DPM of the pyrolyzed solutions was quantified by Gas Chromatography.

### Analysis Methods Used

#### Qualitative and quantitative determination of DPM in solution

The remaining DPM of the pyrolyzed solutions was quantified by Gas Chromatography.

An Agilent 7890A gas chromatograph was used, with an injection port and a flame ionization detector.

The equipment has an oven temperature programmer, as well as a pressure regulator, thus allowing the linear speed to be varied, with  $N_2$  as carrier gas. With a capillary column 30 m in length, 0.320 mm internal diameter and 0.25  $\mu m$  thick of stationary phase (5% phenyl, 95% methylpolysiloxane; HP-5).

The chromatographic conditions under which the determination of reagent and products involved in thermolysis was carried out are:

Injector temperature:  $180^\circ C$

Detector temperature:  $300^\circ C$

Carrier gas pressure: 25 psi

Oven temperature (programmed)

Initial temperature:  $40^\circ C$  initial time: 3 min

Final temperature:  $190^\circ C$  End time: 6 min.

Heating speed:  $20^\circ / min$ .



Thermal decomposition was carried out in a temperature range of 130 to 166°C.

Injected sample volume: 1µL

The retention time of the DPM in these conditions was 11 min.

The measurement of the areas of the chromatographic peaks was carried out using the EZ-Chrom software

The qualitative analysis was carried out by determining the relative retention times of the observed chromatographic peaks, comparing them with those obtained using authentic samples. The quantitative analysis of the remaining DPM as well as the products formed in the reaction was carried out applying the technique of the external standard, for which calibration curves were constructed for each of the analyzed compounds.

The experimental data were obtained from the relationships between the absolute areas of the remaining species analyzed, values that were previously converted in terms of molar concentration for the peak obtained from the species of interest in each particular chromatogram.

In all cases, the chromatographic data used for kinetic studies were the result of averaging the determinations made in triplicate

### Qualitative and Quantitative Determination of Reaction Products

For the analysis of the products of the thermal decomposition reaction of the DPM, pyrolysis was performed in each solvent at a certain temperature up to total decomposition of the DPM (ca. 10 half-lives).

Using the CG technique, glutaraldehyde was identified by comparing the retention time of the product obtained with the reference reagent.

### Calculation Methods Used

#### Determination of the speed constant of the thermal decomposition of the DPM.

In all the systems studied the solvent is in excess of the concentration of the peroxide therefore it is considered that it remains constant throughout the decomposition process of the studied species. For the reaction considered the mathematical expression of the law of serious velocity:

$$\frac{dC_{DPM}}{dt} = -k \cdot C_{DPM} \quad (1)$$

Where  $C_{DPM}$  is the remaining diperoxide concentration.

Thus the order of the reaction is determined only by the concentration of the diperoxide. Reordering the previous expression yields:

$$\frac{dC_{DPM}}{C_{DPM}} = -k \cdot t \quad (2)$$

Integrating the reaction, it remains:

$$\ln C_{DPM_t} = \ln C_{DPM_0} - k \cdot t \quad (3)$$

Where  $C_{DPM_0}$  is the initial concentration of diperoxide and  $C_{DPM_t}$  is the concentration of the remaining diperoxide at the different reaction times (t) in the solution.

In a first-order reaction this equation gives a line whose slope determines the value of the velocity constant,  $k = k_{exp}$ , whose unit is  $s^{-1}$ .

#### Calculation of Activation Parameters

The reaction rate and specifically the experimental velocity constant, depends on the temperature (T), the mathematical expression of this relationship is known as the Arrhenius Equation and is as follows:

$$k_{exp} = A e^{-E_a/RT} \quad (4)$$

Where A is the preexponential factor,  $E_a$  represents the activation energy, in Joule, R is the general constant of gases (8,314 Joule  $mol^{-1} K^{-1}$ ),  $k_{exp}$  is the experimental velocity constant corresponding to the unimolecular thermal decomposition of peroxide in solution at absolute temperature T.

Through this equation it can be observed and proven experimentally, that the speed constant increases with the increase in temperature. The linear expression of the Arrhenius equation is as follows:



$$\ln k_{\text{exp}} = \ln A - \frac{E_a}{RT} \quad (5)$$

If the  $\ln k_{\text{exp}}$  vs  $1/T$  is represented graphically, a line is obtained whose ordered would give us the Preexponential Factor ( $A$ ,  $\text{s}^{-1}$ ) and the slope the Activation Energy ( $E_a$ ,  $\text{kJ mol}^{-1}$ ).

The enthalpy and entropy activation parameters ( $\Delta H^{\#0}$  and  $\Delta S^{\#0}$ ) corresponding to the initial stage of homolytic decomposition of **the DPM** are calculated using the Eyring Equation:

$$k_{\text{exp}} = \frac{k_b T}{h} \exp(\Delta G^{\#0}) = \frac{k_b T}{h} \exp\left(\frac{\Delta H^{\#0} - T \Delta S^{\#0}}{R T}\right) \quad (6)$$

where  $k_{\text{exp}}$  is the experimental velocity constant,  $T$  represents the mean working temperature (K),  $k_b$  is boltzman's constant ( $1.38064 \cdot 10^{-23} \text{ J K}^{-1}$ ), and  $h$  is Planck's constant ( $6.6252 \times 10^{-34} \text{ J s}$ ) and finally  $\Delta H^{\#0}$  and  $\Delta S^{\#0}$  are the enthalpy and activation entropy respectively.

Linearized would be:

$$\ln\left(\frac{k_{\text{exp}}}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^{\#0}}{R} - \frac{\Delta H^{\#0}}{RT} \quad (7)$$

The graphical representation of  $\ln(k_{\text{exp}} / T)$  as a function of  $1 / T$ , gives a line where it is possible to calculate the values of the activation parameters corresponding to each reaction in study analyzed, from the ordinate to the intercept  $\Delta S^{\#0}$  would be determined, and from the slope of the line  $\Delta H^{\#0}$  is obtained.

The activation free energy value ( $\Delta G^{\#0}$ ), known as the activation Gibbs energy, was calculated at the experimental mean temperature, using equation 8, which is deduced from the "Transition State Theory".

$$\Delta G^{\#0} = \Delta H^{\#0} - T \Delta S^{\#0} \quad (8)$$

The errors corresponding to enthalpy and activation entropy were calculated by the method proposed by Huyberechts et al. (1955), using a computer program created by Dr. Eduardo Borkowsky in 1986.

## Results and Discussion

The thermal decomposition of DPM into methanol solution in the studied range, as shown in Table 1 (Figure 1) fulfills a first-order kinetic law up to 60% conversion of DPM.

**Table 1:** Velocity constant values for the DPM thermal decomposition reaction in a methanol solution at different temperatures

T (K)	[DPM] $\times 10^2 \text{ M}$	$k \times 10^4 \text{ s}^{-1}$	$r^2(n)^a$
403	2,0	2,49	0,987
413	2,0	4,75	0,997
423	2,0	8,78	0,988
439	2,0	22,16	0,986

<sup>a</sup>Errors calculated in ref. [4]

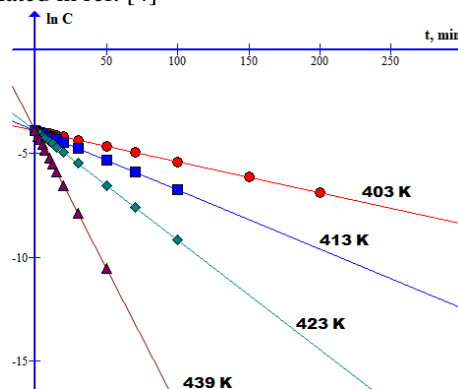


Figure 1: Kinetics of the DPM thermal decomposition reaction in a methanol solution at different temperatures

The effect of temperature on the values of the experimental velocity constant ( $k_{\text{exp}}$ ) for the investigated unimolecular reaction can be represented by the following Arrhenius equation (Ec. 9, Figure 2) where the errors shown are the standard deviation of a minimum least squares data processing and the activation energy is expressed in  $\text{J mol}^{-1}$ .

$$\ln k_{\text{exp}} \text{s}^{-1} = (18.4 \pm 1.3) - (89588.3 \pm 767)/RT \quad (9)$$

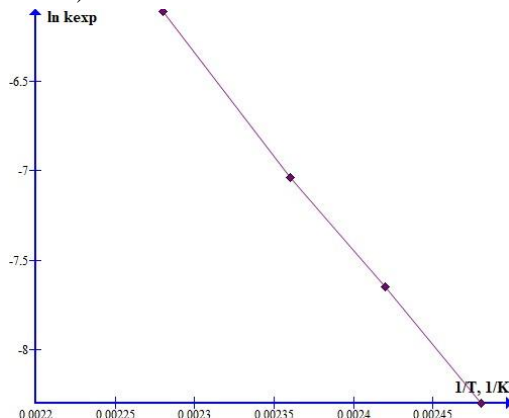
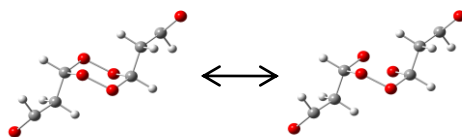


Figure 2: Representation of the Arrhenius equation

The graph of the Arrhenius equation is linear ( $r = 0.998$ ) over a relatively wide temperature range (ca.  $40^\circ\text{C}$ ) suggesting that the values of the activation parameters calculated for the DPM reaction belong to a single process, which could be its unimolecular thermal cleavage of the OO bond (Scheme 2). The step that determines the velocity is the biradical formation that is further decomposed by ruptures of C-C, C-O or O-O bonds, and originating final organic products such as malonaldehyde and etanal.



Scheme 2: Homolytic rupture of the O-O bond

In previous work, it was shown that the dissociation energy of the OO bond is influenced by the solvent [5], the substituents [6] and the size of the ring [7]. In the special case of these studies in different solvents, it was concluded that the activation parameters are higher in the most apolar solvents and the values of the velocity constant are the lowest. The values of the activation parameters ( $\Delta H^{0\#} = 86.1 \pm 2.7 \text{ kJ mol}^{-1}$  and  $\Delta S^{0\#} = -65.2 \pm 6.0 \text{ J mol}^{-1} \text{ K}^{-1}$ , Figure 3) corresponding to the unimolecular thermal decomposition reaction of DPM in methanol are in the order of the values obtained for other cyclic peroxides in polar solvents such as water, chlorobenzene, 2-propanol [8-10].

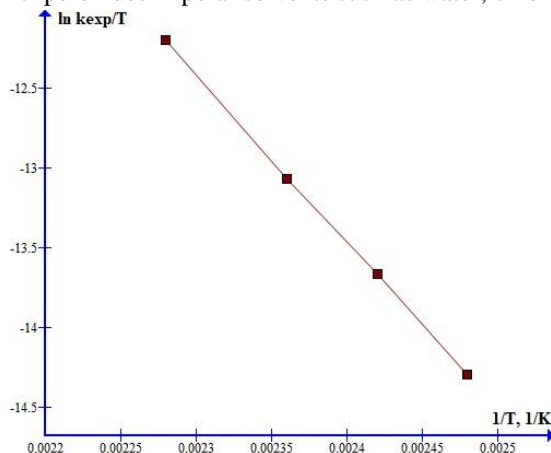


Figure 3: Representation of the Eyring equation



## Conclusions

The thermolysis of DPM in methanol solution follows the first-order kinetic law up to at least 60% diperoxide conversion. The reported activation parameters correspond to the initial homolysis of the O-O bond of the diperoxide molecule. The final organic products such as malonaldehyde and etanal.

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