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## Thermal Decomposition Reaction of Malonaldehyde Diperoxide in Gaseous Phase

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**Abstract** In the injector chamber of the gas chromatograph, the thermal decomposition of the DPM was carried out in a temperature range of 473–553 K. The average Arrhenius activation energy and pre-exponential factor were  $126.9 \pm 0.8$  kJ mol<sup>-1</sup> and  $2.1 \cdot 10^{13}$  s<sup>-1</sup>, respectively. One of the advantages of this method of performing thermal decomposition is that side reactions generally do not occur due to the short residence time in the injection chamber.

**Keywords** gas phase, diperoxide, kinetic, activation energy

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### 1. Introduction

The study of organic peroxides arises since they play an important role in combustion processes, polymerization, some biological metabolisms and diseases such as cancer, cell aging and environmental pollution. [1-3]

Therefore, it is important to continue the study of its chemical properties, kinetics and reaction mechanisms in various reaction media [5-8].

The 1,2,4,5-Tetroxanes have been studied both in their conformational and configurational aspects as well as in their thermolysis reactions by various authors. In recent years, systematic studies have been carried out to understand the kinetics and mechanism of the thermal decomposition reaction of these substances. [9-12] Within the context of biological systems, peroxide species participate in the transformations associated with decomposition cell caused by enzymatic autoxidation reactions. [1-3]

The controlled oxidation reaction of aliphatic aldehydes or ketones with hydrogen peroxide produces substituted 1,2,4,5-tetroxanes with variable yields (dimeric peroxides of aldehydes and ketones, cyclic diperoxides of aldehydes and ketones). Studies on the thermolysis of various 1,2,4,5-tetroxanes have been carried out analyzing the influence



of the ring substituents on their molecules and the effect of the medium where the reaction takes place. Hence, the kinetic parameters that govern their reactions, even in the gas phase, have been established. [5-15].

In this paper, an experimental gas chromatographic study of the gas phase thermolysis reaction of 3,6-diethanal-1,2,4,5-tetroxane (malonaldehyde diperoxide, DPM) is presented to know the possible mechanisms of the unimolecular decomposition reaction. (Figure 1)

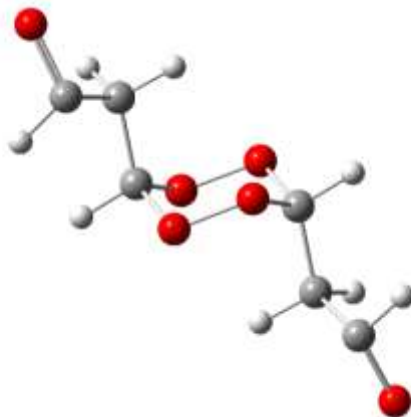


Figure 1: Structure of Malonaldehyde Diperoxide, DPM

## Materials and methods

### Synthesis of Malonaldehyde Diperoxide (DPM)

Malonaldehyde diperoxide (DPM) is synthesized by oxidation of 1,1,3,3-tetramethoxypropane with hydrogen peroxide in the presence of concentrated sulfuric acid [16].

1,1,3,3-tetramethoxypropane (2.297g, 0.0104mol) was added dropwise to a continuously stirring solution containing 60%  $\text{H}_2\text{O}_2$  (3.52 mol, 0.78g), 20 mL of ethyl alcohol and concentrated  $\text{H}_2\text{SO}_4$  (10mL) inside from a  $-10^\circ\text{C}$  bath. Once all the 1,1,3,3-tetramethoxypropane had been added, stirring was continued for 4 hours at  $-20^\circ\text{C}$ . The clear white oil obtained was extracted with petroleum ether (10mL) and then the solvent was evaporated under vacuum. A colorless oil was obtained.

The product obtained by this improved method is the same as that obtained by the technique described in the literature [17].

### Gas kinetics

Using the gas chromatography method, which is useful, fast and reliable to determine the kinetics of reactions with small amounts of samples, the gas kinetics was performed, already verified with other diperoxides [18]. In this method, the injection chamber was used as a flow reactor, keeping the reaction time constant and the reaction temperature as a variable parameter. When the compounds leave the injection chamber and enter the gas chromatography column, the temperature is low enough to stop the reaction, but high enough to cause chromatographic separation of reactants and products. [18,19].

Very dilute solutions (approximately 0.001 M solution of DPM in methanol) were used to produce the thermolysis reaction, introducing it into the injection chamber of the gas chromatograph, which was used as a reactor. The degree of conversion of the reagent is controlled by the temperature of the injector, which was constant, taking values of 473, 493, 513, 533 and 553 K.

The reaction products and the reagent were analyzed by gas chromatography in an AGILENT 7890 A chromatograph, with a constant flow electronic device, nitrogen was used as carrier gas. The detector was a flame



ionization detector and the capillary column was an HP5 (25 m x 0.53 mm) with a stationary phase of 5% methylphenylsilicone. The temperature was held at 80°C for 2 minutes, then it was programmed at 30°C/min up to 270°C and held for 10 minutes. The injector (4mm x 80mm) is a Pyrex glass liner. Unreacted DPM was analyzed using chlorobenzene as internal standard. Hypothetical residence times in the injector chamber were calculated using the following equation:

$$t = \frac{l}{v_L} \quad (1)$$

Where:  $l$  is the length of the injector (cm) and  $v_L$  is the linear velocity of the carrier gas.

The activation energy was obtained through an equation that links the first order equation of a reaction and the Arrhenius equation and is as follows:

$$\ln \ln \left( \frac{C_0}{C_i} \right) = \ln(A \cdot t) - \frac{E_a}{RT} \quad (2)$$

Where:  $C_0$  is the initial concentration of the DPM and  $C_i$  is the remaining concentration of the DPM,  $E_a$  is the activation energy,  $A$  is the frequency factor and  $t$  is the hypothetical residence time of the DPM in the injector (equation 1).

### Results and Discussion

Table 1 reports the temperatures, the first member of equation (2) and the experimental rate constants. Figure 1 shows a linear plot between  $\ln [\ln(C_0/C_i)]$  and  $T^{-1}$ . The least squared fit gives, the activation energy ( $E_a$ ) and the frequency factor and the hypothetical residence time ( $At$ ). From the intercept  $\ln(At)$ , and using the residence time (equation (1)), the frequency factor can be extracted from the Arrhenius equation, giving the reaction rate constant,  $k_{exp}$ , for each temperature (Table 1). The length of the injector is 8 cm and the linear velocity of the carrier gas is 14.2 mL/s, giving a hypothetical time of 0.56 seconds.

Knowing the frequency factor and the activation energy, we arrive at the following Arrhenius equation:

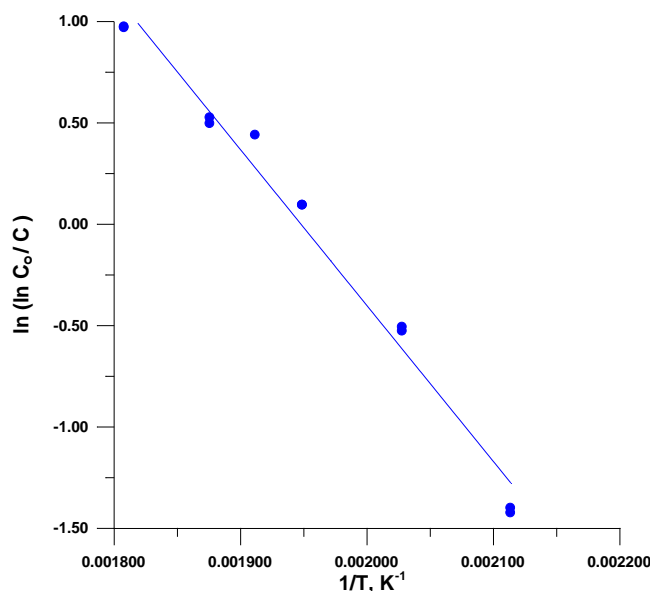
$$\ln k_{exp} = (30,7 \pm 0,7) - \frac{(15273,47 \pm 0,8)}{RT}$$

With a correlation coefficient of 0.987. The activation energy turns out to be 126.9 kJ mol<sup>-1</sup>, higher than the gas phase activation energy of the dibutanoic derivative (121.3 kJ mol<sup>-1</sup>), but lower than the substituted diphenyl derivative (179.5 kJ mol<sup>-1</sup>), both obtained with the same method used in this work [16]. Taking into account previous experimental work [5-12], a mechanism can be reasonably assigned in stages. However, a deeper analysis is required to know the true reaction mechanism, so a computational study should be conducted.

**Table 1:** Values of the experimental rate constants.

T (K)	Ln ln(C <sub>0</sub> /C <sub>i</sub> )	K <sub>exp</sub> 10 <sup>3</sup> (s)
473	-1.427354607	3.9
493	-0.5105699477	7.5
513	0.0911839858	13.8
533	0.4363821248	20.2
553	0.9664020607	40.8

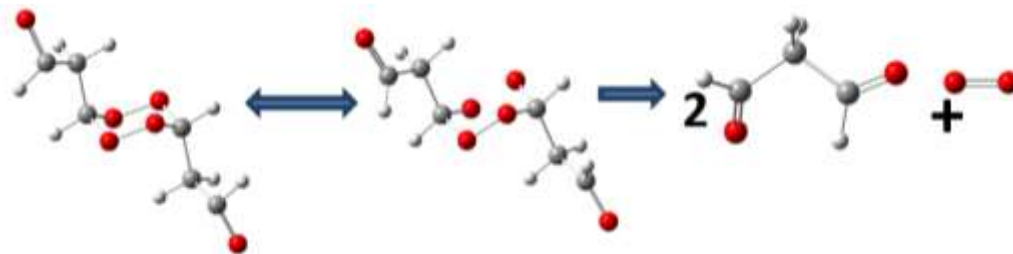




**Figure 1.**  $\ln \ln C_o/C$  of 0.001 M DPM in methanol solution as a function of inverse temperature, in K. Linear velocity of carrier gas in injector,  $V_L = 14.2$  cm/s; and carrier gas flow,  $Q = 9.47$  cm<sup>3</sup>/s.

The thermolysis of the DPM (0.001 M) injected in the chromatograph in methanol solution, allows to verify the presence of malonaldehyde as the main product. The reaction is fast and with a very high conversion. A single reaction product was observed indicating no side reactions.

The kinetic results of this work, which reflects an excellent precision for this type of study, are comparable with those obtained by calculations, for the same reaction with formaldehyde diperoxide (DFT) [14]. The decomposition mechanism of DPM indicates the initial rupture of a peroxide bond. An intermediate biradical is formed, accepted for analogous reactions of this type of substances. This intermediate then undergoes a C-O bond cleavage obtaining malonaldehyde and molecular oxygen. (Scheme 1).



*Scheme 1: Reaction mechanism*

### Conclusion

The study of the thermal decomposition reactions of DPM in the injector of a gas chromatograph is a fast and precise method to determine kinetic parameters of unimolecular reactions for organic compounds of discrete vapor pressure, using a very small amount of sample. The activation energy of the thermolysis reaction obtained is within the parameters of the activation energy of similar compounds. Side reactions do not generally occur due to the short residence time in the injection chamber.

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