Direct determination of parameters of activation of the unimolecular reaction of glutaraldehyde diperoxide by gas chromatography

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Abstract
Gas phase thermolysis reaction of glutaraldehyde acid diperoxide (3,6-dibutanoic -1,2,4,5-tetroxane,DPAG) was performed in an injection chamber of a gas chromatograph as a constant time thermal flow reactor, has been applied to obtain activation parameters.($\Delta H^{\#}$=13.07 ± 0.7 Kcal mol^{-1}; $\Delta S^{\#}$=-40,28 ± 0.4calmol^{-1} K^{-1}; $\Delta G^{\#}$=35.07 ± 0.7 Kcal mol^{-1}) in the 453 – 553 K temperature range.

Keywords: DPAG, thermolysis, Kinetic, Gas phase

1. Introduction
The study of organic peroxides has emerged as a consequence of the fact that they play an important role because they are involved in combustion processes, polymerization, some biological metabolisms, and diseases such as cancer, cell aging and environmental pollution. [1-3]. It is therefore important to continue the study of its chemical properties and kinetics and reaction mechanisms in various media [5-8].

Cyclic peroxides constitute a family of compounds with interesting physicochemical properties, which has attracted the attention of various research groups [9-12].

The 1,2,4,5-Tetroxanes have been studied both in their conformational and configurational aspects and in their thermolysis reactions by various authors; In recent years, systematic studies have been carried out to know the kinetics and the mechanism of the thermal decomposition reaction of these substances.

Within the context of biological systems, peroxidic species participate in the transformations associated with cell decay caused by enzymatic autoxidation reactions. [1-3]

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Cyclic peroxides with one or more peroxide functions in the molecule (Scheme 1) can be obtained by oxidation of various types of carbonyl compounds, with hydrogen peroxide concentrated in strongly acidic medium. Initially in the literature they were called "cyclic peroxides derived from ketones or aldehydes
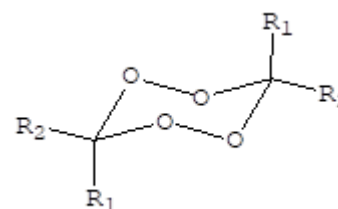
Fig 1: 1,2,4,5-tetroxanesCyclic diperoxides derived from ketones R$_2$ = R$_1$ =alkyl, aryl Cyclic diperoxides derived from aldehydes R$_2$=H R$_1$ = alkyl, aryl

The controlled oxidation reaction of aldehydes or aliphatic ketones with hydrogen peroxide produces substituted 1,2,4,5-tetroxans with variable yields (dimeric peroxides of aldehydes and ketones, cyclic diperoxydes of aldehydes and ketones). In recent years, systematic studies have been carried out to determine the kinetics and mechanism of the thermal decomposition of these substances [5-12].

The studies on the thermolysis of various 1,2,4,5-tetroxans were carried out analyzing, on the one hand, the influence on the same of the substituents present in the ring of their molecules and, on the other, the influence of the medium where the reaction takes place. In this way, the kinetic parameters governing their reactions have been established, even in the gaseous phase. [13-15].

Los estudios sobre la termólisis de diversos 1,2,4,5-tetroxanos se realizaron analizando, por un lado, la influencia en la misma de los sustituyentes presentes en el anillo de sus moléculas y por otro, la influencia del medio

donde la reacción se lleva a cabo. De esta manera, se han establecido los parámetros cinéticos que gobiernan sus reacciones, incluso en la fase gaseosa. [5-15].

In this paper, we present an experimental study by means of gas chromatography of the thermolysis reaction in gas phase of 3,6-dibutanoic-1,2,4,5-tetroxane (glutaraldehyde acid diperoxide, DAGP); and, in order to know the possible mechanisms of the unimolecular decomposition reaction.

2. Materials and methods
2.1 Synthesis
DPAG was synthesized by adding a glutaraldehyde in ethyl alcohol solution to a solution of hydrogen peroxide in strong acid medium at –20º C.The solid was isolated, washed with water and methanol 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. Methanol was used as solvent. DPAG was characterized by IR and UV spectroscopies and gas chromatography.

2.2 Kinetic
Using gas chromatographic method, which is useful, quick, and reliable to determine kinetic of reactions with small amounts of samples [16]. In this method the injection chamber was used as flow reactor, maintaining the reaction time constant and the reaction temperature as a parameter. When the compounds flow out of the injection chamber and into the gas chromatographic column, the temperature lowers enough to quench the reactions. The temperature of the column was low enough to stop the reaction, but high enough to cause the chromatographic separation of the reactants and products. [16,17]. Very diluted solutions (approximately 0.001 M solution of DPAG in methanol) were used to produce the thermolysis reaction, introducing it in the injection chamber of the gas chromatograph, which was used as reactor. Reaction is stopped when reactant reaches chromatographic column. The conversion degree of the reactant is controlled by the injector temperature that was constant taking values of 453, 473, 483, 493, 505, 513, 523 and 533 K. The reaction products and reactant were analysed by gas chromatography AGILENT 7890 A chromatograph, with an electronic device of constant flow, using nitrogen as carrier gas was operated. Flame Ionization Detector and smelt silica capillary column (25 m x 0.53 mm) coated with 5% of methyl-phenyl-silicon were used. Temperature was held at 80 °C for 2 minutes, then programmed at 30º C/min until 270 °C, and held for 10 minutes. Injector (4 mm x 80 mm) is liner Pyrex glass. Non reacted DPAG was analysed by using n-octane as internal standard. Hypothetical residence times in the injector chamber were calculated by the following equation: [16, 17]

$$t = 1 / V_L \tag{1}$$

where, l is the liner length, and V_L is the linear rate of the carrier gas. Activation energies were obtained by introducing the Arrhenius equation in the integral kinetical equation of the first order, [16] giving:

$$\ln [\ln (C_0 / C)] = - E_a / RT + \ln (A t) \tag{2}$$

Where, C_0 and C are the initial and remaining concentrations of the reactant, respectively; E_a is the activation energy; A the frequency factor; and t is the hypothetical residence time, given by equation (1).

3. Results and Discussion
In table 1, temperatures, first member in equation (2) and experimental constant rates are reported. Figure 1 gives a linear representation between ln [ln (C_0 / C)] and the T^{-1}. Minimal square fitting gives E_a, the activation energy and (At) the frequency factor and the hypothetical residence time. From the intercept ln (At), and using the residence time (eq. (1)) the frequency factor of the Arrhenius equation can be extracted, giving the reaction rate constant, k_{exp}, for each temperature (Table 1). Known the frequency factor and the activation energy we come to the following equation of Arrhenius:

$$\ln k = (8.91 \pm 0.6 - (14600.0 \pm 0.5) / RT$$

with a correlation coefficient of 0.999. Activation energy turns out to be 14.6 kcal/mol, less than the gas phase activation energy of the diphenyl substituted derivative (21.6 kcal/mol), obtained with the same method used in this work [16].

Taken into account previous experimental works [5-12] a stepwise mechanism can be reasonably assigned. However, a deeper study is required to know the truth reaction mechanism, therefore a computational study should increase our knowledge of this subject.
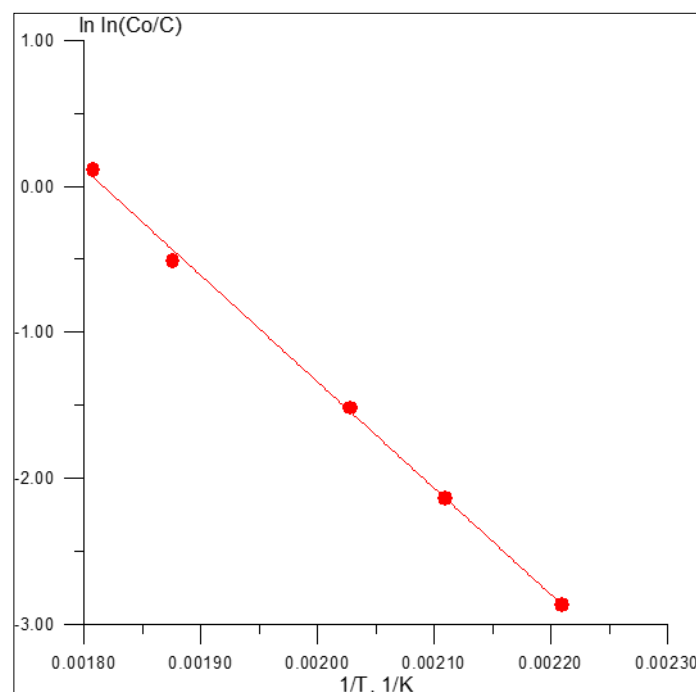
Fig 2: ln ln C_0/C of DPAG 0.001 M in solution of methanol as a function of inverse of temperature, in K. Linear rate of the carrier gas in the injector, V_L=14.2 cm/s; and carrier gas flow, Q=9.47 cm³/s.

**Table 1:** Temperature (K), first member of equation (2), and rate constant (sec^{-1}) of DPAG 0.001 M in solution of tetrahydrofurane. Linear rate of the carrier gas in the injector, V_L=14.2 cm/s; and carrier gas flow, Q=9.47 cm^3/s.

T (K)	ln [ln C$_0$/C]	k$_{exp x}$X 10^4(s^{-1})
453	-0,5779136	7,70
473	-0,2392032	15,1
483	-0,1986745	20,8
493	0,0831658	28,2
505	0,2940047	37,5
513	0,0831658	50,2
523	0,5855308	65,9
533	0,9738912	140,0

The thermolysis of DPAG (0.001 M) injected into the chromatograph in methanol solution, allows to verify the presence of glutaraldehyde acid as a product. The reaction is fast and with a very high conversion. A single reaction product is observed indicating that there are no secondary reactions. The kinetic results of this work, which reflect excellent precision for this type of studies, are comparable with those obtained by calculations, for the same reaction with formaldehyde diperoxide (DFT) [13]

The mechanism of DPAG decomposition indicates the initial rupture of a peroxy bond. An intermediate biradical is formed as accepted for analogous reactions of this type of substances.

This intermediate then experiment a rupture of C-O bonds obtaining glutaraldehyde acid and molecular oxygen. (Scheme 2).
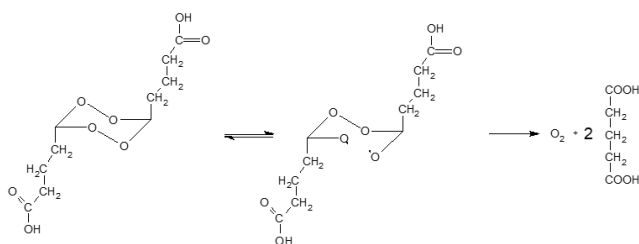
Fig 3: Mechanis.

4. Conclusions

The study of the thermal decomposition reactions of DPAG in the injector of a gas chromatograph is a fast and precise method to determine kinetic parameters of unimolecular reactions. It is useful 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.

Generally, no secondary reactions occur because the short residence time in the injection chamber.

5. Acknowledgments

6. References

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