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Synthesis and Reactivity of Glutaraldehyde Diperoxide in Isopropanol Solution

Bordón AG[1], Jorge MJ[2], Jorge LC[3], Profeta MI[1], Romero JM[1] and Jorge NL[2]*

[1]Environmental Technology Research Laboratory, IQUIBA-CONICET Faculty of Exact Sciences and Nat. and Agr. Av. Libertad, Corrientes, Argentina

[2]Department of Mathematics, Faculty of Exact Sciences and Nat. and Agr. Av. Libertad, Corrientes, Argentina

[3]Faculty of Veterinary Sciences, National University of the Northeast, Juan Bautista Cabral, Argentina

ABSTRACT

We have committed ourselves to the study of cyclic organic peroxides with two peroxy functions in their molecules, motivated by the multiple uses and application possibilities found for these compounds. In this paper, we analyze the thermal decomposition kinetics of 3, 6-dibutanal-1, 2, 4, 5-tetroxane (DPG) in isopropanol solution. At the concentration (1.06×10^{-3}M) and temperatures studied (403-439 K), the kinetics satisfactorily fulfills with a first-order kinetic law up to 80% conversion of the diperoxide. From the kinetic data obtained experimentally, the activation parameters were determined $\Delta H^{\#} = 53.80$ kJ mol^{-1}± 0.6 and $\Delta S^{\#} = -170.51 \pm 0.7$ J mol^{-1} K^{-1} different correlations and treatments could be made. The results obtained prior to this work were included in the analyses, to establish comparisons.

***Corresponding authors**

Nelly Jorge, Department of Mathematics, Faculty of Exact Sciences and Nat. and Agr. Av. Libertad 5460, (3400) Corrientes, Argentina.
E-mail: nelly.jorge@gmail.com

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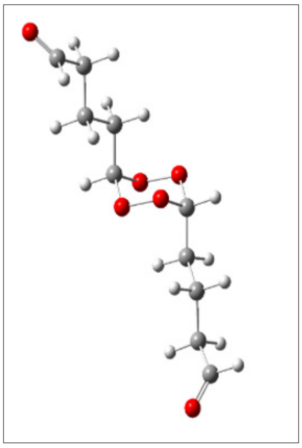
Introduction

Organic diperoxides are liquid or solid organic substances that contain two bivalent bonds –0-0- in their structure and can be synthesized with hydrogen peroxide, and ketones or aldehydes and one or both hydrogens are replaced by organic radicals [1-6].

Organic diperoxides are thermally unstable substances or mixtures, which can undergo self-accelerating exothermic decomposition. In addition, they may have one or more of the following properties: be susceptible to explosive decomposition; burn quickly; be sensitive to shock or friction and react dangerously to other substances. However, they are currently considered essential since their structure allows them to act as drugs against malaria and another action is that of herbicides [7-9].

As a contribution to these last two activities of diperoxides, we are investigating the synthesis and reactivity of diperoxides derived from aldehydes to know their possible action on different reaction media [10-12].

That is why this work focuses on the thermal decomposition of 3,6-dibutanal-1,2,4,5-tetroxane (DPG) in isopropanol solution (Figure 1)



Scheme 1: 3,6-Dibutanal-1,2,4,5-Tetroxane (DPG)

Materials and Methods

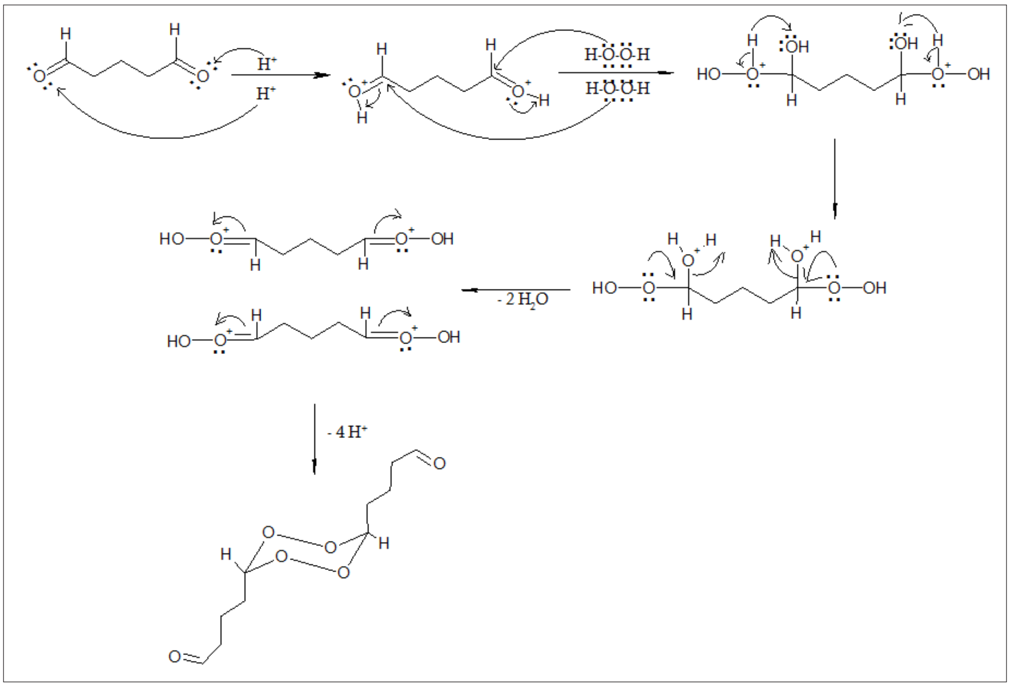
Synthesis

Glutaraldehyde diperoxide (Scheme 1) was synthesized by oxidation of glutaraldehyde with oxygen peroxide in the presence of concentrated sulfuric acid, following the Bayer and Viller method modified by Jorge et al. [10-12].

Hydrogen peroxide 60% (H_2O_2:0.051 mol, 0.975 g) and glutaraldehyde (35.4 mmol, 4.02 g) were added by consecutive dropwise addition to a stirred solution of water (15 mL), EtOH (25 mL) and H_2SO_4 (35 mL) at -10°C.

Stirring was continued for 1 h at -10°C. The resulting white precipitate was centrifuged, washed with water, and dried in a vacuum desiccator to constant weight. The precipitate was recrystallized from acetonitrile. (Scheme 2)

The synthesized compound was characterized by infrared spectroscopy and UV-visible spectroscopy. The gas chromatography technique was also carried out, which is necessary to be able to see its degree of purity and if it is possible to analyze it by this method of quantification of DPG in the kinetics in solution and in the gas phase.



Scheme 2: DPG Synthesis Mechanism

Solvent

Isopropanol: The commercial solvent Fluka (p.a.) was treated with the disodium salt of ethylenediaminetetraacetic acid (Na_2-EDTA, MercK brand p.a.), leaving it at rest in a covered Erlenmeyer flask for 24 hours with occasional stirring. It was then distilled, collecting the 83°C boiling point fraction. Its purity was controlled by Gas Chromatography.

Preparation of DPG-Solvent Samples for Thermolysis Tests

The thermolysis reaction was carried out in vacuum-closed Pyrex glass ampoules 14 cm long and with an external diameter of 7 mm. The ampoules were prepared as follows: they were filled with 1 mL of DPG in isopropanol, 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 caps that allow the ampoule to be isolated from the rest of the system. Subsequently, the ampoule was immersed in a thermos with liquid N_2 (-196 °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 flask until the solution had completely melted. The degassing process was repeated 3 times to eliminate all gases present in the solution. At the end of degassing, keeping the ampoule submerged in liquid nitrogen, it was closed with a gas and O_2 torch.

Thermolysis Reaction

The reaction ampoules, containing the DPG solution in the appropriate solvent, were immersed in a thermostatic bath of stabilized silicone oil at the chosen temperature (±0.2°C); and they were removed at conveniently determined times, stopping the reaction by immersion in a water/ice bath at 0°C. The remaining DPG of the pyrolyzed solutions was quantified by Gas Chromatography using the external standard method.

Results and Discussions

Figure 1 shows the IR spectrum obtained experimentally for DPG. It is interesting to observe about this spectrum the presence of an absorption peak corresponding to the peroxide O-O bond and the C=O bond, characteristic of this type of compounds.

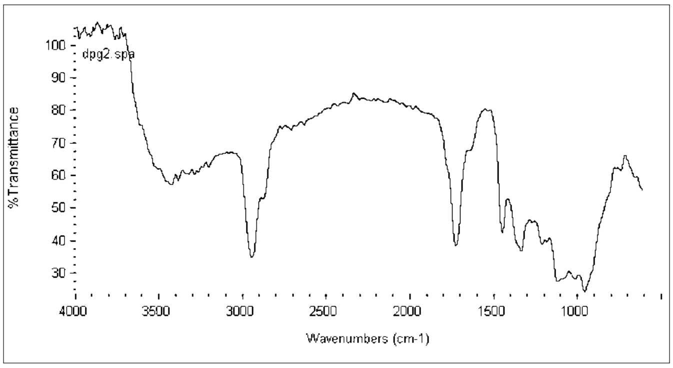


Figure 1: Experimental IR Spectra Obtained from the DPG

The assignment of vibrational frequencies was carried out by comparison with the density functional method (DFT) with the functional BhandHlyp and the base 6-311+G**. The calculated frequencies and the corresponding assignment are for the most stable isomer, which is the one where the butanal groups are in the axial-axial position.

The symmetric and asymmetric C-H stretching of the CH_2 group generally appear at 2926 and 2853 cm^{-1}, respectively. The symmetric modes in DPG are located at 2870 and 2877 cm^{-1} and the asymmetric modes at 2960 and 3047 cm^{-1}. The largest changes observed in the CH_2 stretching bands must be associated with the nearby presence of peroxide. The calculated asymmetric stretching modes are in the range of 3094 cm^{-1}. The calculated symmetric CH_2 stretching modes, on the other hand, are at 2984 cm^{-1}.

The carbonyl groups of aldehydes absorb at slightly higher frequencies than those of the corresponding methyl ketones. The C = O groups in the DPG absorb at 1708 and 1729 cm^{-1} and the corresponding calculated values are 1903 and 1905 cm^{-1}, the values have a high shift with respect to the experimental ones, it could be due to the fact that the diffuse ones were coupled and that it could affect the calculation of this group. The experimental bands at 1445, 1404,1371, 1348, 1346, 1333, 1270, 1250,1209,1206 and calculated at 1439, 1399, 1371,1345, 1343, 1340, 1265, 1256, 1209, 1206, respectively, are assigned as, movement of the hydrogens of the CH_2 group: wagging, bending and twisting, CC stretching, symmetric stretching of the H CH_2, bending of the H of the ring, stretching CO, asymmetric out of phase of the CCC, bending and δOCH, out of phase symmetric of the CCC, respectively. The band at 1333 cm^{-1} is due to the C-H aldehyde bending vibration, the calculated one is 1304 cm^{-1}.

The bands calculated between 1206-1445 cm^{-1} to the different bending modes of H of CH_2, which are twisting, wagging, and rocking. The peak at 1270 cm^{-1} corresponds to the stretching of the CO bond, the calculated value corresponds to 1265 cm^{-1}. The value of 1206 cm^{-1} corresponds to the stretching of the CC bond close to the carbonyl and the calculated value is 1209cm^{-1}. The bands at 1117 and 1114 cm^{-1} and calculated 1137, 1114 cm^{-1}, respectively, correspond to the stretching coupling modes of the C=O, CH, and CC bonds and to the bending modes of the CH of CH_2. The calculated CO bond stretching bands 1155 and 1165 cm^{-1} are correlated with the experimental peaks 1178 and 1182 cm^{-1}. The bands at 1007, 1025 and 1078 cm^{-1} correspond to the stretching modes of the CO and CC bonds and their calculated values are 1002, 1022 and 1056 cm^{-1}, respectively.

The stretching of the O-O bond is characterized by being present within the range of 900 - 700 cm^{-1}. The stretching modes corresponding to the O-O bond of the ring are found to be 910-952 cm^{-1} and calculated to be 911-952 cm^{-1}. The bands in the range 810 to 570 cm^{-1}, calculated at 819 to 578 cm^{-1}, are assigned to COO deformation modes, symmetric and asymmetric ring deformation, and OCO deformation modes, respectively.

The bands located between 570 and 415 cm^{-1} and calculated between 578 and 428 cm^{-1} correspond to the couplings between the torsion angle and the bending modes of H of CH_2.

Symmetric and asymmetric stretching CCC appears at 1080 and 1078 cm^{-1}, theoretical at 1082 and 1056 cm^{-1}. The electronic bands that appear between 400 and 600 cm^{-1} experimental and theoretical between 428 and 601 cm^{-1} correspond to deformations of the HCO skeleton.

Thermal Decomposition

To determine the amount of DPG remaining or unreacted in the thermal decomposition kinetics, the external standard method was used. The calibration curve was made by plotting the area of diperoxide (DPG) as a function of the concentration of the DPG, which turned out to be linear. (Figure 2)

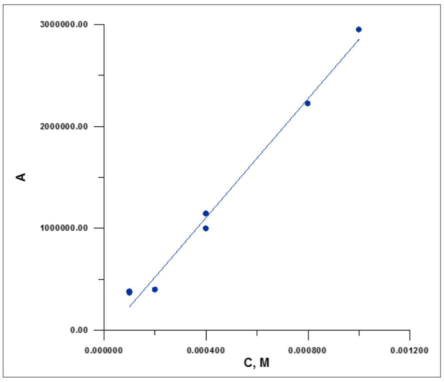


Figure 2: Calibration Curve of DPG in Isopropanol

The decomposition of **DPG** has been studied in isopropanol solution, in the temperature range of 403-439 K and at an initial concentration of 1.06 x10^{-3} M. The thermolysis of DPG in isopropanol solution complies with a first-order kinetic law of peroxide conversion from ca. 80%. At the concentration studied, the effects of secondary decomposition reactions induced by free radicals originating in the reaction medium can be considered minimal or negligible.

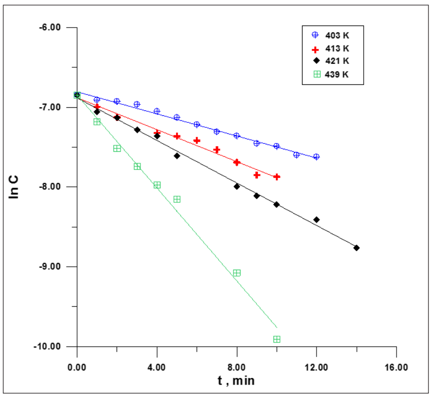


Figure 3: Thermal Decomposition Kinetics of DPG (1.06 x10^{-3} M) in Isopropanol Solution at Different Temperatures

The rate constant values of the thermal decomposition reaction of DPG show that the reactivity of this compound at a temperature of 403 K increases up to two times with respect to the protic polar solvent methanol ($k_{isoprop}$/ k_{met} = 2). With respect to acetonitrile 13 times. (kisoprop / kaceto = 13), decreasing slightly at other temperatures.. Therefore, it is evident that in polar aprotic solvents the reaction occurs more slowly than in polar protic solvents, and the rate constant increases as the polarity of the solvent increases.

Table 1: Rate constants of the thermal decomposition of DPG in isopropanol solution at different temperatures

Temperature K	C_{DPG} x 10^3 M	k_{exp}x 10^3 s^{-1}	R^2
403	1,06	1,15	0,999
413	1,06	1,64	0,996
423	1,06	2,24	0,987
439	1,06	4,72	0,991

The variations in the rate constants are probably caused by the presence of the protic solvent, which slightly dominates the preferential solvation around the cyclic diperoxide molecules. This solvation effect accounts for the specific interaction between isopropanol and the more polar activated complex represented by the biradical, initially formed (Scheme 3). As has been observed, the decomposition reaction of DPG in isopropanol is accelerated compared to that found in acetonitrile and methanol.

The effect of temperature on the k_{exp} values (Table 1, Figure 2) can be represented by the Arrhenius equation, where the errors correspond to the standard deviations obtained by treating the kinetic data with the least squares method. and the activation energy is expressed in J mol^{-1}.

$$lnk_{exp} = (10,29 \pm 0,7) - \frac{(57290,8 \pm 6)}{RT}$$

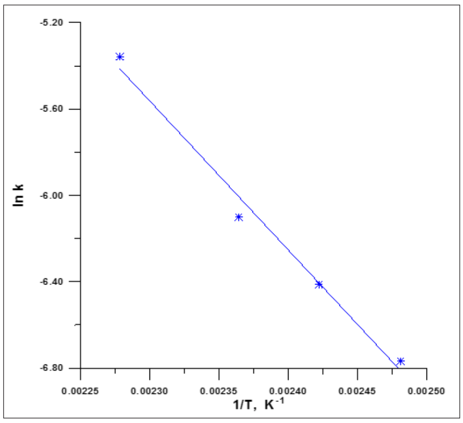


Figure 2: Graphic Representation of the Effect of Temperature on the Values of the Reaction Rate Constant Corresponding to the Thermal Decomposition of DPG in Isopropanol Solution

The kinetic parameters determined with the Eyring equation are displayed in Figure 3. Table 2 also showed the variation in the activation parameters with the change in solvent, especially between the values of activation enthalpy and activation entropy. The proximity between the activation enthalpies ($\Delta H^{\#}$) of the reaction in alcohols and the separation of acetonitrile can be appreciated, in the same way there are also contrasts between the values of the activation entropies (($\Delta\Delta S^{\#}$ = 54, 32) (isopropanol and methanol and 151.32 J mol^{-1} K^{-1} between isopropanol and acetonitrile). Among these three solvents, were the highest in acetonitrile, followed by methanol and finally isopropanol. Which indicates that there is an effect of the solvent in the thermolysis of DPG and that may be related to the difference in the polarity of these solvents; however, the values of the free energies of activation are very close to each other, which suggests that although the solvents accelerate the reaction, these thermal decompositions are equivalent [13].

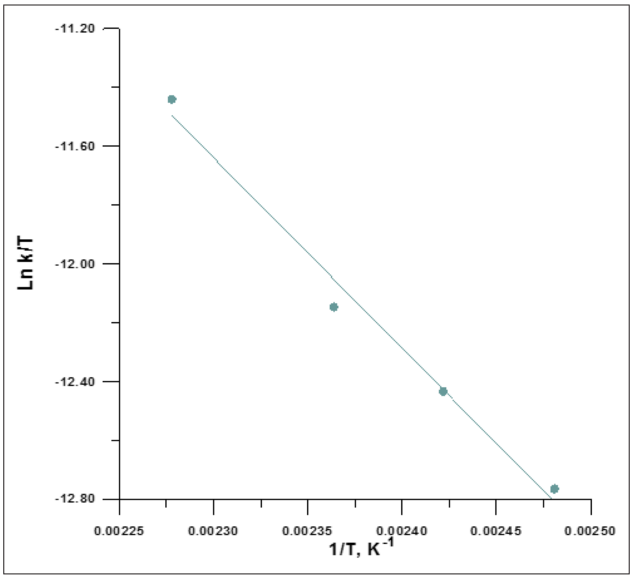


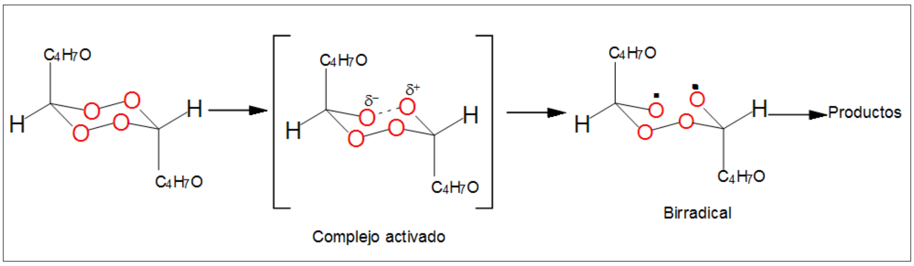
Figure 3: Graphical Representation of the Eyring Equation Corresponding to the Thermal Decomposition of DPG in Isopropanol Solution

In the isopropanol solvent, the reactive transition state and biradical species are more solvated by isopropanol. It can be assumed that preferential solvation is an influential reactivity factor for the homolytic cleavage of the O-O bond of diperoxides. Specific interactions between the O atom in the peroxide bond and the H atom in the OH of isopropanol can be taken into account. However, in addition, in this solvent an adduct is formed between DPG and isopropanol that favors more bond breaking, making the transition state more solvated than the reagents, thus the activation parameters Ea and $\Delta H^{\#}$ are lower [14].

Table 2: Activation Parameters of the Systems with Different Solvents

Solvent	E_T^N(30)	Cte. dieléctrica	ΔH# kJ mol^{-1}	ΔS# J.mol-1 K^{-1}	Ea kJ mol^{-1}	ΔG# kJ mol^{-1}
Acetonitrile	0,460	37,5	123,54	-19,12	127,03	131,56
Methanol	0,762	32,6	77,95	-116,13	81,45	126,61
Isopropanol	0,546	18,0	53,80	-170,51	57,36	125,33

The rate-determining step in the thermal decomposition reaction of cyclic peroxides is the intermediate biradical formation [13] (scheme 3). It is highly unlikely that the activated complex would dissolve to the same extent as the starting reagent, since there should be differences in the electronic configuration and thus polarization. The differential solvation of the starting material and the activated complex should lead to a difference in the reaction rate constant and subsequently in the activation parameter (eg activation energy). The solvent cavity requirement for the activated complex in a radical reaction must certainly be different (in size and shape) from that of the reactant. Changes in solvent reactions or diperoxide substituents cause changes in reaction rates.



Scheme 3: Rate-Determining Step of the Thermal Decomposition Reaction of Cyclic Peroxides (Biradical Formation)

The identification of the reaction products was carried out by GC analysis comparing the retention time of each product from a sample prepared with the corresponding products, with the retention time of that compound in the reaction mixture. Identification was confirmed by chromatography.

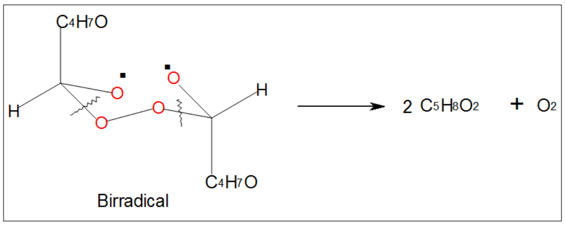
Regarding the analysis of the reaction products, it was possible to verify the formation of glutaraldehyde as the main product, expressing the results by means of the relationship:

Molar yield of product = moles of glutaraldehyde formed / moles of DPG decomposed

The molar yield of glutaraldehyde should be 2. However, the values are between 1.6 - 1.8, and if the kinetics is allowed to elapse until the DPG is exhausted, it can reach a value of 1.9 at the highest temperatures, allowing to support the postulated decomposition mechanism in all stages.

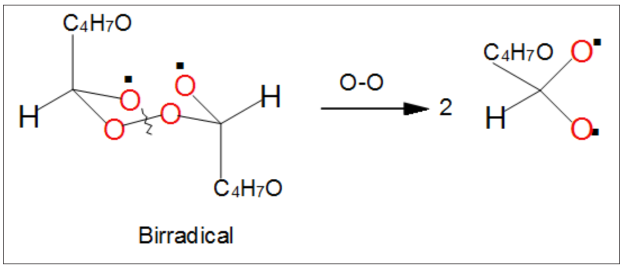
The organic products derived from the thermolysis of DPG in the different reaction media can be interpreted in terms of an initial OO bond homolysis to give an intermediate biradical (Scheme 3), which can then undergo CO bond cleavage (Scheme 4), cleavage of the OO link (Scheme 5), or subsequent CC link splits (Scheme 6).

The glutaraldehyde obtained from the decomposition of diperoxide in the solvents studied can be explained as a product derived from the breakdown of CO (Scheme 4).

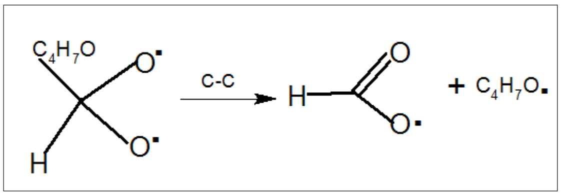


Scheme 4: Formation of Glutaraldehyde and Molecular Oxygen

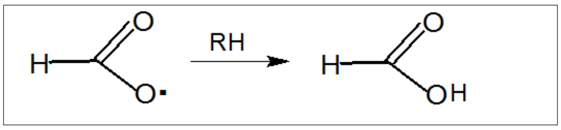
As a consequence of the O-O bond cleavage represented in Scheme 5, new highly unstable biradicals were formed. Later, the decomposition of these through C-C bond cleavage generated different free radicals (Scheme 6) capable of participating in radical-radical reactions (Scheme 7) or in the abstraction reaction of hydrogen atoms (Scheme 8). Some detected products confirm the existence of radical-radical coupling reactions (for example, 2,2,3,3-tetramethylbutane from 2c and ethane from 1a and 2a). The identified esters (butanal methanoate of 2b and tert-butyl acetate of 2c) are interpreted with the help of Scheme 6.



Scheme 5: Breaking of the O-O Bond and Formation of other Unstable Oxime Biradical



Scheme 6: Formation of the Formyl Radical and Butanal



Scheme 7: Abstraction of H and Formation of Formic Acid

$$^{\bullet}C_4H_7O \xrightarrow{RH} C_4H_8O$$

Scheme 8: Abstraction of H and Formation of Butyraldehyde

Conclusion

The thermal decomposition reaction of the DPGen compound in the different solvents studied, carried out in the temperature range between (403.15 and 439.15) K with a difference of 10 degrees, was in accordance with the pseudo-first order kinetic law, where the solvent was in excess and did not influence the reaction mechanism.

According to the products obtained in the thermolysis and the values of the activation parameters, a unimolecular mechanism with a cyclic transition state of six members, concerted and of a semipolar nature is proposed.

It was found that there is an effect of solvents, which accelerated the speed of thermolysis in solution, being higher with isopropanol, affecting the kinetics of thermal decomposition.

It can be assumed that preferential solvation is an influential reactivity factor for the homolytic cleavage of the O-O bond of this peroxide.

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Competing interests

Authors have declared that no competing interests exist.

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