

Thermal Decomposition of 3,6-Diphenyl-1,2,4,5-Tetroxane in Nitromethane Solution

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Abstract

The thermal decomposition reaction of benzaldehyde diperoxide (DFT; 0.001 mol L^{-1}) in nitromethane solution studied in the temperature range of $130.0\text{-}166.0 \text{ }^\circ\text{C}$, follows a first-order kinetic law up to at least 60% DFT conversion. The organic products observed were benzaldehyde and benzoic acid. 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 DFT in nitromethane were calculated ($\Delta H^\ddagger = 106.3 \pm 1.0 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -58.6 \pm 1.1 \text{ J mol}^{-1}\text{K}^{-1}$) and compared with those obtained in other solvents to evaluate the solvent effect.

Keywords: DFT; Kinetic; Gas chromatography; Activation energies.

1. Introduction

Organic peroxides are compounds that have great importance in numerous combustion reactions and important industrial applications such as polymerization initiators, bleaches, disinfectants, antimalaric, etc. [1,2]

The kinetic and mechanistic studies corresponding to the thermolysis in solution of cyclic organic diperoxides and the comparisons between them that arise, have been the initial objective of this research group.[3,4] However, in recent years the application of this type of compounds as preemergent herbicides has been of great interest. [5]

Tetroxanes are thermally decomposed through a mechanism of reactions in stages, in which the speed determining stage is assigned to the unimolecular homolysis of the peroxide bond. The dissociation energy determined for the OO rupture of different peroxy compounds is close to 45 kcal / mol [6], however, the value of this energy can be affected by steric effects caused by the different ring substituents [7] or by the change in physicochemical properties of the solvent used to carry out the kinetic studies [8,9].

In this work we present the thermal decomposition reaction of a member of the group, 3,6-diphenyl-1,2,4,5-tetroxane (DFT), in a aprotic polar solvent, like the nitromethane and we compared it with other studied solvents that present different physicochemical properties, for observe the effect of solvent.

2. Materials and Methods

2.1. Síntesis del dipéroxido de benzaldehyde

DFT was prepared by dissolving 7.2 mL of benzaldehyde mark Flucka (8.85 mmol) in 20 mL absolute ethanol brand Merk. It was added to a vigorously stirred mixture of 2.3 mL of hydrogen peroxide (9.45 mmol), 50 mL of sulfuric acid (90% V / V) and 35 mL of ethanol. After stirring the mixture for 2 hours at $-20 \text{ }^\circ\text{C}$, centrifuged and washed with distilled water (0°C) until the excess of acid was removed. The white solid obtained (crude product 75%) was recrystallized from boiling chloroform. Absorption bands obtained by FTIR spectroscopy (KBr): 1) $3107.6 \text{ (s) cm}^{-1}$ 2) $3095.0 \text{ (s) cm}^{-1}$ 3) $3032.1 \text{ (m) cm}^{-1}$ 4) $2961.8 \text{ (m) cm}^{-1}$ 5) $1766.8 \text{ (m) cm}^{-1}$ 6) $1604.0 \text{ (s) cm}^{-1}$ 7) $1597.0 \text{ (s) cm}^{-1}$ 8) $1491.9 \text{ (vs) cm}^{-1}$ 9) $1457.1 \text{ (s) cm}^{-1}$ 10) $1416.8 \text{ (m) cm}^{-1}$ 11) $1397.3 \text{ (m) cm}^{-1}$ 12) $1271.8 \text{ (s) cm}^{-1}$

cm⁻¹ 13) 1229.9 (m) cm⁻¹ 14) 1197.0 (m) cm⁻¹ 15) 1080.2 (m) 1.16 (m) 997.5 (s) cm⁻¹ 17) 973.2 (s) cm⁻¹ 18) 896.6 (s) cm⁻¹ 19) 842.4 (s) cm⁻¹ 20) 685.5 (s) cm⁻¹ 21) 668.5 (s) cm⁻¹.

2.2. Solvents

Nitromethane used as solvent and n-octane (internal standard) were purified according to appropriate techniques and their purity controlled by GC.

2.3. Kinetic method

Pyrex tubes closed at one end (7 cm long x 4 mm ID) were loaded with ca. 0.5 mL of the DFT solution in the nitromethane solvent, some sealed in the presence of oxygen with the flame of a torch and others conveniently degassed in the vacuum line (-196°C) and closed in the same way. These ampoules were immersed in a thermostated silicone oil bath ($\pm 0.1^\circ\text{C}$) at the chosen temperature, extracted at conveniently determined times and stopping the decomposition of the DPP at 0°C, in an ice and water bath.

The first-order k_{exp} values were calculated by the least-squares method as the slope of the determined line when $\ln [DFT]$ is plotted against time. Using the Arrhenius equation, the effect of the temperature on the k_{exp} was analyzed and the activation energy and the corresponding preexponential factor were calculated. The activation parameters (ΔH^\ddagger and ΔS^\ddagger) were calculated using the Eyring representation:

$$\ln \frac{k_{exp}}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}$$

Where k_B is the Boltzman constant, h is Planck's constant, T is the temperature in K, ΔH^\ddagger is the activation enthalpy and ΔS^\ddagger activation entropy.

The quantitative determinations of the remaining DFT in the pyrolyzed solutions, the quantification of the benzaldehyde and the qualitative determination of other formed products (benzoic acid, diphenyl) were determined by GC using the internal standard method (n-octane). An Agilent gas chromatograph, model 7890 A, equipped with FID detector, filled column type HP5 (methyl phenyl silicon) was used and nitrogen was used as carrier gas.

The injector operated in the split mode at 155°C and the flame ionization detector at 300°C, with nitrogen as the make-up gas (40 mL min⁻¹). The oven temperature was initially maintaining at 50°C for 2 min and then programmed increasing the temperature at a rate of 30°C per minute until reaching a final temperature of 190°C that was maintained for 15 min. Under these experimental conditions, the retention time of DFT was 9 min.

3. Results and Discussion

The decomposition of the DFT has been studied in nitromethane solution, in the temperature range of 130.0 - 166.0°C and initial concentrations of 0.001 mol L⁻¹. The thermolysis of the DFT in nitromethane complies with a kinetic law of first order until conversions of the peroxide of ca. 60 percent. Although at low concentrations of the DFT the effects of decomposition secondary reactions induced by free radicals originated in the reaction medium, can be considered minimal or negligible, some experiences were performed in the presence of oxygen.

The results obtained indicate that there are practically no differences in the values of the rate constants (Table 1) when the oxygen is present or when it was removed from the medium, which would indicate that the generated free radicals do not induce the decomposition of the DFT.

In order to corroborate that the calculated speed constants do not include a contribution of reactions induced by radical species derived from peroxide, the effect of the concentration of DFT on the value of k_{exp} at 150°C

was investigated (Table 1). Because of the low solubility of the DFT in nitromethane, the highest concentration prepared was ca. 0.01 mol L⁻¹, observing that there is no effect of the concentration on the reaction rate.

Table 1.

To observe the effect of temperature on the velocity constant we have used the arrhenius equation:

$$\ln k_{exp} = (23.72 \mp 1.00) - \frac{(13255,00 \mp 1.00)}{T}$$

The corresponding plot is linear ($r = 0.999$) over a relatively wide temperature range ($\approx 36^\circ\text{C}$); therefore, the calculated activation parameters for DFT reaction in nitromethane solution belong to a single process which could be unimolecular homolysis. The results of density functional calculations with full geometry optimization also supported the stepwise mechanism of formaldehyde diperoxide and the methyl diperoxide decomposition through intermediate diradical species. [9, 10]

The values of the activation parameters ($\Delta H^\ddagger = 102.9 \pm 1 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -49.8 \pm 1.1 \text{ J mol}^{-1} \text{ K}^{-1}$) were determined using the Eyring equation, whose graphical representation is linear ($r^2 = 0.9990$) in the temperature range ($\approx 36^\circ\text{C}$). the negative value of ΔS^\ddagger observed (Table 2) reflects the decrease that occurs in the degrees of freedom of the molecules of the DFT reagent when passing to a rather rigid «transition state». This allows to suppose that its thermolysis takes place with rupture of a peroxidic bond of the molecule assisted by the nitromethane solvent, where it could form, for example, hydrogen bonds with the peroxygen oxygen atoms. Obviously, nitromethane in the thermolysis of DFT has an intermediate behavior among the other solvents studied so far (Table 2).

In previous studies, it has been found that k_{exp} values obtained from kinetic determinations in some solvents with different physicochemical properties are sensitive to an increase in solvent polarity. When studying the effects of solvent on the thermolysis reaction rate of the DFT, it is not sufficient to consider only the change in the activation free energy (ΔG^\ddagger) corresponding, since it is determined by the contributions of the enthalpic and entropic terms and the correlation between both parameters is linear for that series of reactions in particular.

The linearity of the graphical representation of the Isokinetic Ratio according to Leffler's criterion, ΔH^\ddagger vs. ΔS^\ddagger ($r = 0.989$) would confirm the enthalpy-entropy compensation also known as the "compensation effect", defining for the DFT studied, the existence of a genuine "series of reactions" in the different solvents.

The correct interpretation should be that ΔG^\ddagger is approximately constant within the reaction series and, from it, a mathematically necessary correlation arises between ΔH^\ddagger and ΔS^\ddagger . Therefore, the representations of enthalpy variation versus entropy variation may have a meaning, but in reality, they can only express the trivial fact that ΔG^\ddagger is approximately constant. The slope of the graph gives us the value of the Isokinetic temperature for that series of reactions, which is $\beta = 428 \text{ K}$, included within the experimental work range. From a physical point of view, it is the temperature at which in all the solvents the thermal decomposition reaction of DFT would proceed at the same speed. (Figure 1)

Table 2

Figure 1.

Another point of view according to the criterion of Exner, it is observed that there is a point of intersection between three of the studied solvents, the straight lines are cut within the range of experimental temperatures, making it possible to apply the statistical treatment to determine the value of $\beta = 458 \text{ K}$, close to that obtained according to the previous treatment. (Figure 2)

Figure 2.

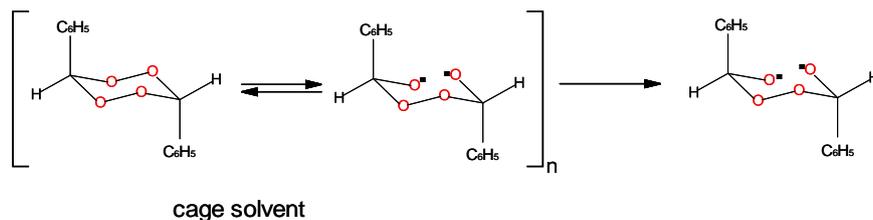
It is evident that the reaction of thermal decomposition of the DFT is affected by different mechanisms of solute / solvent interaction due to its physicochemical characteristics, in this case Acetonitrile does not meet this criterion.

Regarding the analysis of the reaction products, the formation of benzaldehyde as the main product could be verified, expressing the results by means of the relationship:

$$\text{molar aldehyde yield} = \text{moles of aldehyde formed} / \text{moles of decomposed DFT}$$

If the DFT molecule produces in its thermolysis exclusively aldehyde and oxygen, as it is proposed in the reaction pathways mentioned in this work, the molar yield of aldehyde should be 2. However, the values (comprised between 0.9 - 1.0, which can be reached if the kinetics is allowed to run out until the DFT is depleted, at a value of 1.6 at the lowest temperatures of 130 ° and 140 ° C, to rule out the possibility of a single path of decomposition of the intermediary biradical. On the other hand, this also supports the postulated decomposition mechanism.

The identification of the products obtained in the thermolysis reaction of the DFT, allows to postulate for its thermal decomposition in solution, a mechanism in stages initiated by the homolytic breakdown of the OO bond of the molecule, with the formation of the corresponding intermediate biradical as can be seen in the following scheme (Scheme 1)



Scheme 1. Rupture of the peroxidic bond (O-O).

In this first stage the biradical generated remains transiently enclosed in an environment of molecules of the solvent commonly known as "reaction box". It is possible that the biradical can recombine to give the cyclic peroxide again, before diffusion occurs from the reaction box. However, this process is very fast, so it is accepted that the initial stage of formation of the biradical would then be the determinant of the speed of the reaction. Later this species will suffer C-C or C-O ruptures originating the products observed for each particular system.

This behavior is comparable to that observed in other 1,2,4,5-tetroxanes and it is logical, taking into account that the dissociation energy of the O-O bond is considerably lower than the energies corresponding to the remaining bonds C-O, C-C or C-H.

4. Conclusions

The thermal decomposition of DFT in nitromethane solution follows a pseudo-first order kinetic law until a conversion of 60%. The rate constant values are higher for reactions performed in protic polar solvent because of the formation of hydrogen bonds with the peroxidic bond contributes to the fast decomposition reaction. The nitromethane is an aprotic polar solvent with a high characteristic polarity that can help break the O-O bond.

the kinetics of the thermal decomposition of the DFT is affected by the nature of the solvent used as a reaction medium, which is checked in the well-marked values of the activation parameters.

A reaction mechanism is proposed based on the analysis of the reaction products, whereby the initial step involves the formation of a diradical intermediate via rupture homolytic of the O-O bond.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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