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Effect of Cupric Ions on Thermal Decomposition of 3,6-Diphenyl-1,2,4,5-Tetroxane

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Abstract: The thermal decomposition reaction of 3,6-diphenyl-1,2,4,5-tetroxane (DFT), within the temperature range of 130.0-150.0°C and initial concentrations equal to 1.69×10^{-3} mol L^{-1} with addition of the copper-compound $CuCl_2$ (4.0×10^{-4} M) has been studied in methanol solution. The thermolysis follows a first-order kinetic law up to ca 60% DFT conversion. Under the experimental conditions, the activation parameters of the initial step of the reaction ($\Delta H^{\#} = 19.0\pm0.8$ kcal mol^{-1}; $\Delta S^{\#} = -20.1\pm1.8$ mol^{-1} K^{-1}; $\Delta G^{\#} = 27.3\pm0.8$ kcal mol^{-1}) and benzaldehyde, as the organic product, supports a stepwise reaction mechanism with the homolytic rupture of one of its peroxidic bonds. Also, the participation of cupric ions in the reaction is postulated to give an intermediate diradical, which further decomposes by CO bond ruptures, yielding a stoichiometric amount of benzaldehyde. The results are compared with those obtained for the above diperoxide thermolysis in methanol whitout the presence of the copper-compound.

Key words: 3,6-Diphenyl-1,2,4,5-tetroxane, cupric ions, thermal decomposition

INTRODUCTION

The study of organic peroxides comprehends a large number of chemical issues, from biological like themes (involving, for example, the metabolic oxidation processes), up to disinfectant action and pigment manufacture (Adam and Cilento, 1982; Vennerstrom *et al*., 1992).

Peroxides are widely used in several chemistry areas due to their high reactivity with organic and inorganic substrates (Schulz and Kirschke, 1972). Their specific properties as free radicals reaction initiators are amply employed in synthetic chemistry, especially in polymerization processes (Wilt, 1973). Unfortunately, several members of these kind of compounds are very unstable and just a small number of them are easy to manipulate with a sensible degree of security and just few of them are available as commercial products.

Although the importance of these compounds is well known in the chemistry area, several structural aspects and reactivity modeling need to be precisely defined (Turro and Devaquet, 1975; Wilsey *et al*., 1999). Chemical reactivity of these molecules, in thermal decomposition or induced by metals through an electronic-transfer process decomposition, probably involves an homolytic breakdown of the O-O bond with free radicals formation as a critical reaction step (Richardson *et al*., 1974; Wilsey *et al*., 1999; Castro and Jorge, 2003). These chemical species, or their decomposition products, are normally involved in rapid chemical reactions with several substrates (Wilt, 1973).

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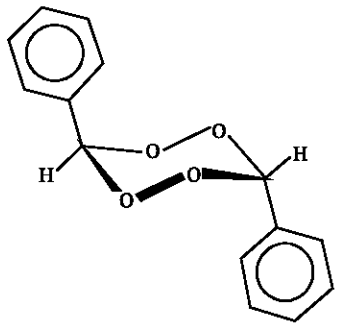


Scheme 1

During the last decade, the chemistry of cyclic peroxides has enjoyed a quite interesting renaissance with the increasing appreciation that such compounds occur widely in Nature and often they possess desirable pharmacological properties (McCullough and Nojima, 2001).

The kinetics and mechanism of the thermal decomposition reaction of cyclic diperoxides, show a significant substituent and solvent effects that have been interpreted as a transition state with separation of charges that confers them a certain polar character (Cafferata and Furlong, 1995).

Probably, in the case of the thermal decomposition of cyclical peroxides, in presence of metallic ions, the reaction would pass forming an intermediary complex between the diperoxide molecule and the metal.

The formation of a complex of coordination with the metallic ion intervener would facilitate the breaking of the peroxide molecule on having diminished restrictions of orbital symmetry, or alternative, having produced a change in the electronegative character of one or both atoms of oxygen of the heterocyclic ring of these molecules.

On the other hand, it is well known that some metallic ions of transition series (i.e., cuprous and cupric) catalyze this type of reactions in non-cyclical peroxides (Bartlett *et al*., 1974; Moryganov *et al*., 1962).

The purpose of this research is to report the thermal decomposition reaction of benzaldehyde cyclic diperoxide (3,6-diphenyl-1,2,4,5-tetroxane, DFT, scheme 1), in methanol solution with the addition of the copper-compound $CuCl_2$ in order to examine in a homogeneous medium the effect of metallic ions that would bring a decrease of the strength of the O-O bond and the breaking of the molecule. A comparison with kinetic data from the thermal decomposition reaction of the DFT in methanol solution without metallic ions is also included. On the other hand, the conclusions of this study might be extended to the knowledge of the behaviour of analogous molecules and to be of biochemical interest in biological mediums.

MATERIALS AND METHODS

Reagents and Solvents

The 3,6-diphenyl-1,2,4,5-tetroxane was prepared by methods described elsewhere (Jorge *et al*., 2000) and its purity was checked by GC.

The methanol solvent was commercial analytical reagent (Merck, p.a.) and purification was made via standard techniques (Weissberger, 1965) (bp: 65°C). n-Octane (Fluka pa) was employed as internal standard in quantitative determinations of DFT concentration and reaction products.

Kinetic Methods

Pyrex glass ampules (12 cm long×4 mm i.d.) filled with 0.2 mL of the diperoxide solution with addition of the copper-compound were thoroughly degassed under vacuum line at -196°C and then

sealed up with a flame torch. To perform the runs, they were immersed in a thermostatic silicone oil bath (±0.1°C) and withdrawn after predetermined times (5-8 at each temperature), stopping the reaction by cooling at 0°C.

The remaining diperoxides (DFT) in the reaction solution and the reaction products were determined by quantitative GC analysis (Internal standard method, n-octane) using a silica fused capillary column (HP5, 30 m length, 250 mm i.d.) impregnated with 5% phenylmethylsilicone as stationary phase, in a Hewlett-Packard model 5890 series II gas chromatograph with nitrogen as carrier gas and FID detection.

The analyses were carried out with the injector port at 125°C and using programmed oven temperature (30° min^{-1}) from 40 to 190°C. The identification of the products was carried out for comparison of their retention times with those of authentic samples, or by comparison of the corresponding MS spectra. In this case it was used helium as carrier gas and a Hewlett-Packard model 5972 A selective detector, connected to the chromatograph.

Calculation Methods

The corresponding first-order rate constant values (k_{exp}) were calculated from the slope of the one obtained by plotting the values of ln (DFT) concentration vs reaction time values. In all the cases the reaction was followed at least through one half-life. The corresponding activation parameters were worked out from the Arrhenius equation (Eq. 1) and their errors determined using a least-means-square data treatment (Machado and Machado, 2001; Schaleger and Long, 1963; Huyberetch *et al*., 1955).

The other activation parameters values of the reactions obtained from computational methods employing the Eyring equation parameters.

RESULTS

The study of the thermal decomposition of DFT methanol solution with the addition of the copper-compound ($CuCl_2$, 4×10^{-4} M), in the range of temperature equal to 130.0-150.0°C (Table 1) and initial concentration of 1.69×10^{-3} mol L^{-1} allowed us to check that under these conditions the reaction follows a first order kinetics law with regard to the DFT, up to a conversion degree of 60% (Fig. 1).

The observed rate constant values (k_{exp}) are larger than the corresponding k_0 values obtained in the methanol solution without the copper-compound (Castellanos *et al*., 1999) (Table 1).

It seems that Cu ions facilitate the peroxide decomposition by forming coordination bonds with free electronic pares from the oxygen belonging to the diperoxide bond.

The temperature effect on the rate constant values (k_{exp}) for the unimolecular reaction can be represented by the Arrhenius equation (Eq. 1) where the errors shown are standard deviations from a least mean square data treatment (Machado, 2001; Schaleger and Long, 1963; Huyberetch *et al*., 1955) of the kinetic data.

$$\ln k\ (s^{-1}) = 20.7\pm0.7-(9978.35\pm0.8)/T\ (CuCl_2\ 4.0\times10^{-4}M) \quad (1)$$

Table 1: First order rate constants values for DFT in methanol solution with the addition of the copper-compound $CuCl_2$

Temp°C	(DFT) 10^3 (mol L^{-1})	k_0 10^4 (sec^{-1})	(k_{exp} 10^4 sec^{-1})
130	1.69	0.70	168.36
140	1.69	1.40	306.67
150	1.69	3.70	542.83

k_0 experimental constants obtained at each temperature corresponding to DFT decomposition on methanol at the initial concentration of 1.69×10^{-3} M; k_{exp} observed constants at each temperature corresponding to DFT decomposition on methanol with the addition of the copper-compound $CuCl_2$ 4×10^{-4} M

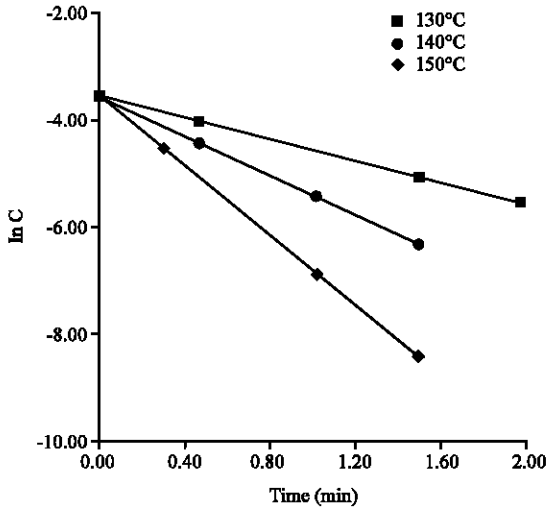


Fig. 1: Representation through first-order kinetic plots of the data obtained in typical thermolysis experiments of DFT (1.69×10^{-3} M) in methanol with the addition of the copper-compound ($CuCl_2$ 4.0×10^{-4} M) at different temperatures

The corresponding equation plot is particularly linear (r = 0.995) in a relatively wide temperature range. It suggests that the calculated activation parameter values for the DFT decomposition in methanol solution with the addition of the copper-compound belong to a single process and this could be also an unimolecular homolysis.

Furthermore, a significant catalytic effect takes place in the DTF thermolysis in methanol solution with the addition of the copper-compound. The catalitic effect of the media would help the peroxidic bond rupture, showing activation parameters lower than 6 kcal mol^{-1} in the methanol with the addition of the copper compound.

The corresponding value of the activation enthalpy ($\Delta H^{\#}$ = 19.0±0.8 kcal mol^{-1}) is similar to that one informed for the homolytic rupture mechanism of different dialkyl peroxides in solution (Cafferata *et al*., 1990), which suggests that the decisive stage of the reaction rate in the DFT thermolysis, is the rupture of a peroxidic bond in the molecule with formation of an intermediary birradical.

The value of the activation entropy ($\Delta S^{\#}$ = -20.1±1.8 cal mol^{-1} K^{-1}) compared with that one obtained in the thermolysis in methanol solution without addition of the copper-compound ($\Delta S^{\#}$ = -15.3±1.8 cal mol^{-1} K^{-1}), suggests a moderate influence of the solvent in the rupture of the peroxidic bond (Table 2 and Fig. 2). However, the negative value for activate entropy variation is in agreement with the decrease of freedom degrees from reactive molecules by passing from a rather rigid transition state, which supports the supposition that thermolysis in methanol is favored by solvent molecules as well as by the presence of metallic ions in the solution.

The main products of the thermal decomposition of DFT, have been identified as benzaldehyde and benzoic acid and a lower quantitys of formic acid, benzene, dimethyl acetal of the benzaldehyde and biphenyl. Since benzaldehyde is the main reaction product it is sensible to understand the occurrence of its posterior oxidation chemical reaction with formation of benzoic acid. However, the formation of benzoic acid whose maximum concentration is larger than that corresponding to benzaldehyde, seems to suggest that they appear in a nearly simultaneous process and not in the way that it happens in the serial reactions.

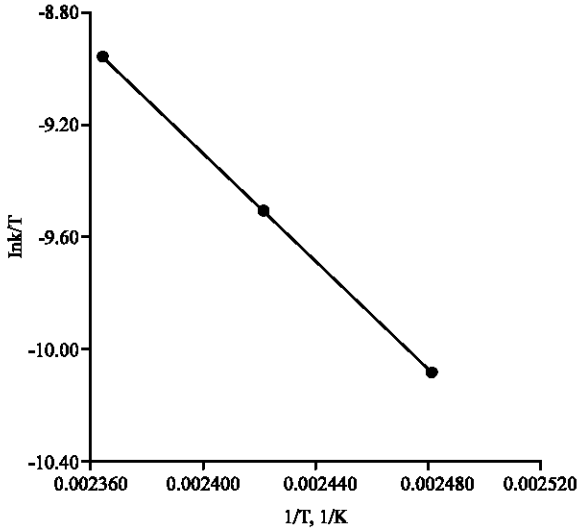
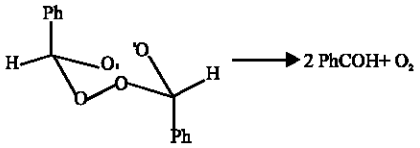


Fig. 2: Eyring equation representation for thermal decomposition of DFT in methanol with the addition of the copper-compound $CuCl_2$ 4×10^{-4} M

Table 2: Activation parameters corresponding to DFT thermolysis in methanol solution with addition of the copper-compound $CuCl_2$ (4.0×10^{-4} M)

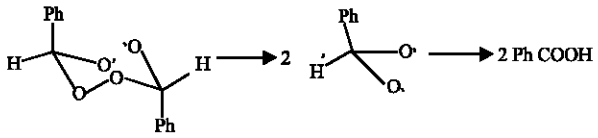
Solvent	$\Delta H^{\#}$ kcal mol^{-1}	$\Delta S^{\#}$ cal mol^{-1} K^{-1}	$\Delta G^{\#}$ kcal mol^{-1}
Methanol	25.3±0.8	-15.3±1.8	31.7±0.8
Methanol (Cu II)	19.0±0.8	-20.1±1.8	27.3±0.8

Benzaldehyde results from the fragmentation of the initially formed biradical through the rupture of its C-O linkage (Eq. 2).



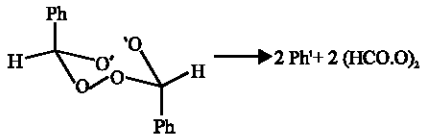
(2)

It may be conceded that the posterior benzaldehyde oxidation to form the benzoic acid observed experimentally can be understood on the basis that formation of both products is practically simultaneous and it suggests that the previously mentioned products would be formed in parallel reactions with similar reaction rates, being possible the rupture of the second peroxidic linkage O-O of the birradical, formed in the rate determining step of the reaction giving two birradicales species (Eq. 3) that in this case and after a rearreagament process would form the observed benzoic acid.



(3)

Benzene and diphenyl result from the hydrogen abstraction and combination reaction, respectively of the phenyl radicals produced in the biradical fragmentation through the ruptures of the C-C linkages (Eq. 4 and 6).

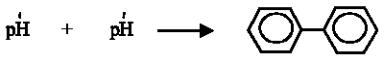


(4)

Formil diperoxide is unstable in the experimentally conditions so that it decomposes easily forming carbon dioxide and formic acid, as shown in Eq. 5.

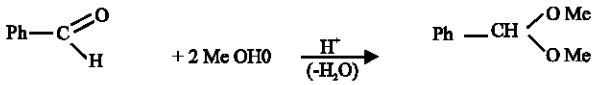
$$(H\ CO.\ O)_2\ CO_2 + HCO.OH \tag{5}$$

Biphenyl comes from phenyl radicals recombination reactions (Eq. 6).



(6)

Dimethyl acetal of the benzaldehyde results from the reaction of benzaldehyde with solvent molecules (Eq. 7). This process is favoured by the presence of acids (formic and benzoic acids) and birradical fragmentation products (Eq. 3 and 4).

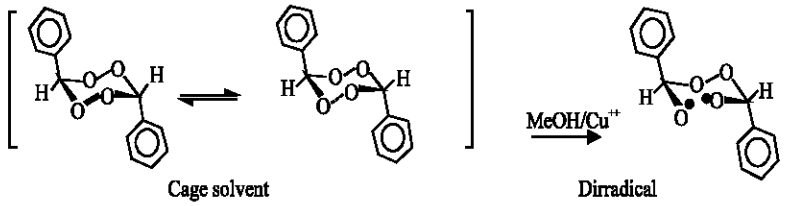


(7)

DISCUSSION

Experimental results give evidence of the catalytic effect of cupric ions on DFT thermolysis in methanol solution, while no changes were detected in the reaction products with respect to the ones registered on thermal decomposition of this tetroxane in pure methanol. These findings, together with the $\Delta G^{\#}$ variation (around 4 Kcal mol^{-1}), show that cupric ions do not influence the reaction mechanism.

According to this, a stepwise mechanism could be postulated with a diradical as intermediate product, where the presence of cupric ions would facilitate the breaking of the peroxidic bond forming coordination bonds with the free pairs of the peroxidic oxygen atoms and thus the complex DFT-ion-alcohol would stabilize the transition state (Scheme 2).



Scheme 2

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