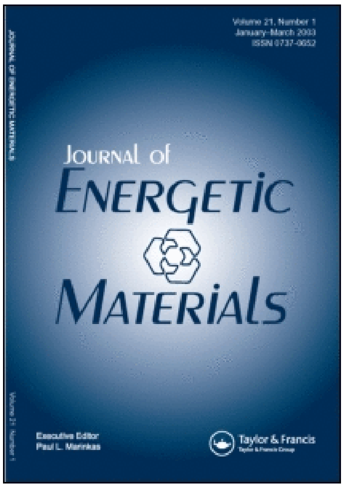

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Preparation and Thermal Decomposition Reaction of p-Chloro Benzaldehyde Diperoxide in Tetrahydrofuran Solution

Karina R. Nesprias[a]; Adriana I. Cañizo[a]; Nora Eyler[a]; Carmen M. Mateo[a]; Nelly L. Jorge[b]
[a] Department of Chemistry, Engineering Faculty, National University of the Center of Buenos Aires Province, Olavarría, Buenos Aires, Argentina [b] Laboratory of Chemistry Physic, Department of Chemistry, Exacts, Naturals and Surveying Faculty, National University of Northeast, Corrientes, Argentina

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KARINA R. NESPRIAS
ADRIANA I. CAÑIZO
NORA EYLER
CARMEN M. MATEO

Department of Chemistry, Engineering Faculty,
National University of the Center of Buenos Aires
Province, Olavarría, Buenos Aires, Argentina

NELLY L. JORGE

Laboratory of Chemistry Physic, Department of
Chemistry, Exacts, Naturals and Surveying Faculty,
National University of Northeast, Corrientes,
Argentina

Preparation and thermal decomposition studies of the title molecule (3,6-di-p-chlorophenyl-1,2,4,5-tetraoxacyclohexane) were carried out in tetrahydrofuran solution in the 52–130°C temperature range. The overall reaction follows a first-order kinetic law up to at least 60% diperoxide conversion. The activation parameters ($\Delta H^{\#} = 15.1 \pm 0.7\,\mathrm{kcal\,mol^{-1}}$ *and* $\Delta S^{\#} = -35.5 \pm 1.9\,\mathrm{cal\ mol^{-1}\,K^{-1}}$) *for the unimolecular rupture of the O–O bond in the diperoxide molecule were obtained by measuring the undecomposed diperoxide at different reaction times by the HPLC technique. P-chlorobenzaldehyde, p-chlorobenzoic acid,*

Address correspondence to Nora Eyler, Facultad de Ingeniería, UNCPBA, Avda. del Valle 5737, B7400JWI Olavarría, Buenos Aires, Argentina. E-mail: neyler@fio.unicen.edu.ar

and chlorobenzene were detected by GC as the major organic products of the reaction.

Keywords: cyclic diperoxide, di-p-chlorophenyl diperoxide, tetraoxacyclohexane, thermolysis

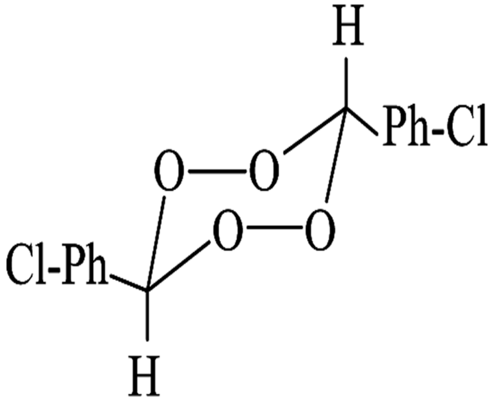
Introduction

It is commonly accepted that explosive materials, like fuels, are highly energetic compounds that, upon initiation, release their energy content in a fast, exothermic reaction. In recent years, the analysis and detection of one class of explosives, namely peroxide explosives, has become particularly important in forensic investigations because of the emergence of terrorist threats and crimes in which these explosives were used. Peroxide explosives generally can be made from hydrogen peroxide and a few other well-known chemicals, such as ketones or aldehydes. A small amount of acid (sulfuric or hydrochloric) is added as a catalyst. Intuitively, it is expected that the peroxide-based explosives would liberate much energy upon decomposition and that their energy content would depend on the carbon/oxygen ratio [1].

On the other hand, organic peroxides have industrial applications; they are used as active components of cosmetics and pharmaceuticals, as sources of free radicals in styrene polymerization [2,3], as hardener and curing agents for plastics such as unsaturated polyester and fiber glass resins, and they have biochemical effects related to gastric necrosis, metabolic acidosis, and homolysis [4].

The unusual reactivity of peroxides is generally attributed to weakness of the O−O bond linkage, and it is expected that their thermal decomposition would be initiated by homolytic dissociation of the peroxide bond.

Here we report an alternative method for preparation of the cyclic diperoxide derived from p-chlorobenzaldehyde (3,6-di-p-chlorophenyl-1,2,4,5-tetraoxacyclohexane, DClPT) (Scheme 1). To our knowledge, there are no vibrational analysis and kinetic studies published for this compound, so we consider it of great interest to examine in depth the experimental IR spectra for absorption



Scheme 1. Ph-Cl represent p-Chloro Phenyl group.

bands of this molecule and to carry out a kinetic study of its thermal decomposition reaction in tetrahydrofuran (THF) solution.

Experimental

Preparation of p-Chlorobenzaldehyde Diperoxide

In this work is presented an alternative technique of synthesis of p-chlorobenzaldehyde diperoxide. It is prepared by drop-wise addition of p-chlorobenzaldehyde (8.85 mmol) in ethanol (10 mL) to a vigorously stirred mixture of hydrogen peroxide (9.45 mmol) and 12.5 mL of sulfuric acid (90% V/V) in ethanol (8.75 mL), cooled at -18°C.

After stirring for 2 h at -18°C the mixture was filtered and washed with cold distilled water (0°C) until the excess of acid was eliminated.

The white solid obtained (45% product crude) was recrystallized from boiling carbon tetrachloride. **Caution**: DClPT must be handled with care because it can be detonated by shock.

The product obtained by this improved method is the same as that obtained by the technique described in the literature [5]. Its purity was also checked by HPLC and the FTIR (KBr) absorption bands were obtained with a Nicolet spectrometer.

Solvents

Tetrahydrofuran solvent employed in the reaction was purified with the appropriate techniques [6,7] and its purity was checked by HPLC analysis.

Kinetic Methods

Pyrex glass tubes (7 cm long × 6 mm o.d.) half filled with the appropriate DClPT solution were thoroughly degassed under vacuum at -196°C and then sealed with a flame torch. To perform the runs, the ampoules were immersed in a thermostatic silicone oil bath ($\pm 0.1^\circ$C) and withdrawn after predetermined times, stopping the reaction by cooling them in an ice-water bath (0°C). The DClPT remaining and the reaction products were determined by quantitative analysis with high-resolution liquid chromatography (HPLC Hewlett-Packard instrument series 1050 C), making use of a reverse-phase column (ODS Hypersil, 5 μmm, 100 mm long × 4.6 mm), UV detection ($\lambda = 254$ nm), and gradient elution. The starting mobile phase employed to analyze the diperoxide was an elution system: 0 min acetonitrile/water (60:40), and the linear gradient is run over 3.5 min to a final proportion of acetonitrile/water/tetrahydrofuran 60:20:20 with a flow rate of 1 mL/min. Under these conditions, the retention time of DClPT was 7.4 min. The solvents employed were of HPLC quality.

The corresponding first-order rate constant values were calculated from the slope of the line obtained by a least-mean-squares treatment of this reaction data when plotting the values of ln [DClPT] concentration vs. reaction times. The activation parameters were calculated according to the Eyring equation, and the errors were worked out by the Arrhenius equation method using a least-mean-squares data treatment [8].

Product Analyses

The qualitative determination of the organic reaction products was performed by GC in a DB-5 capillary column (5% biphenyl, 95% dimethyl polysiloxane, 30 m × 0.32 mm I.D., 0.25 mm film thickness) installed in a Konik 2000C gas chromatograph with nitrogen as carrier gas and flame ionization detection.

The oven temperature was maintained at 60°C for 1 min and then programmed at a rate of 10°/min to 150°C.

Results and Discussion

Vibrational Analysis of DClPT

It is of interest to examine in depth the experimental IR spectra for absorption bands of the molecule 3,6-di-p-chlorophenyl-1,2,4,5-tetraoxacyclohexane, which might be related to the O−O linkages.

Table 1 gives the position of the characteristics vibrations by IR spectroscopy of the DClPT. Bands between 679 and 480 cm^{-1} (679, 625, 550, 523, 517, 507, and 480) correspond to skeletal deformations, OCC, COO, OCO, and OCH.

Bands located between 550 and 507 cm^{-1} correspond to torsion angles coupled with CH rocking modes.

The bands at 841–801, 750–737, 679, and 625 cm^{-1} are assigned as COO deformation modes, out-of-phase ring substituted aromatic, CO stretching; out-of-plane ring, CCl out-of-plane deformation, CCl out-of-phase deformation, bending of the ring, H out-of-plane; asymmetric and symmetric ring deformation O1, 2, 4, 5 and OCO deformation modes, respectively.

Because of the similarity of the masses of the carbon and oxygen atoms, there may be no bands due to vibrations exclusively of the O−O bond, and instead complicated skeletal vibrations of the systems would probably be observed. The corresponding O−O stretching modes of the ring are located at 951–905 cm^{-1} as single modes, the bands at 951 and 905 cm^{-1} correspond to the asymmetric and symmetric O−O coupled stretching modes, respectively.

Bands at 1005, 1016–1027 cm^{-1} correspond to C−O and C−C stretching modes, respectively. The OCO deformation mode at 1090 cm^{-1} is coupled with wag and CH rocking modes. The COO stretching modes located at 1197 cm^{-1} are coupled with CH bending and twisting (tetraoxacyclohexane ring) modes.

The skeletal vibrational wave numbers involving C−C and C−O stretches show a small shift from those of *n*-alkanes. The C−O bond force constant is nearly the same as that of the C−C

Table 1
Characteristic vibrational frequencies and assignments of the 3,6-di-p-chlorophenyl-1,2,4,5-tetraoxacyclohexane

IR vibrational frequencies cm^{-1}	Assignments
480	Out of plane bending ring, δOCC
507	δOCH, τOCOO, τHCOO
517	τOCOO, τHCOO, δOCH, νCO
523	τHCOO, δOCH
550	δOCH, δOCC, CH rocking
625	Sym ring deformation O1,2,4,5, δOCO, CH rocking, νCO, CH out of plane deformation
679	Asymmetric ring deformation O1,2,4,5, CH rocking, CH bending, νOCO, δOCO
737	CCl out of phase deformation, bending of ring, out of plane H.
750	Out of plane ring, CCl out of plane deformation
801–841	Out of phase ring substituted aromatic, δOOC, νCO
905	Sym νOO
951	Ring deformation, Asym νOO, CH twisting, CH rocking, νCCC
1005	Ring deformation, νCO, CH wagging, CH rocking
1016–1027	νCO, νCC, CH wagging, CH rocking
1090	νCO, νCC, CH wagging, CH rocking, δOCO
1197	CH bending (tetraoxacyclohexane ring), νCO, sym νCH, νCOO, CH twisting
1282	Out of phase ν CCO, out of phase sym ν CCC
1290	Out of phase ν CCO, out of phase asym ν CCC, out of phase ν HCO
1332–1352	CH bending, δOCO, CH wagging, CH rocking, sym ν CH
1412	CH bending (tetraoxacyclohexane ring)
1485	Sym νC=C
1578–1597	Asym νC=C
2956	Sym ν CH (aromatic ring)
3091	Asym ν CH (aromatic ring)

bond since the masses of O and C do not differ greatly. This means that C−O and C−C bonds interact strongly. The bands between 1290 and 1282 cm^{-1} correspond to CCO out-of-phase stretching, symmetric and asymmetric CCC out-of-phase stretching, and HCO out-of-phase stretching.

Experimental band at 1412 is assigned as CH bending (tetraoxacyclohexane ring). Those bands between 1332 and 1352, 1332 cm^{-1} correspond to CH wagging, CH bending, CH rocking, symmetric CH stretching and OCO deformation.

Bands between 1597 and 1485 cm^{-1} are assigned as C=C stretching corresponding to the aromatic ring.

In solid state, 3,6-di-p-chlorophenyl-1,2,4,5-tetraoxacyclohexane displays bands at 3091 and 2956 cm^{-1}, which are assigned as the stretching modes asymmetrical CH and stretching modes symmetrical CH, respectively.

Thermal Decomposition of DClPT in Solution

The thermal decomposition reaction of DClPT was studied in tetrahydrofuran solution at the temperature range of 52–130°C (Table 2) and initial concentration *ca.* 10^{-3} M. It was found that the kinetic behavior of this system is according to a first-order kinetics law up to at least *ca.* 60% of organic diperoxide conversion. It seems that under the experimental conditions of the present work there are no contributions from second-order processes inducing the decomposition of DClPT at higher conversions.

The temperature effect on the experimental rate constant values (k_{exp}) for the unimolecular reaction investigated can be represented by the following Arrhenius equations (Eq. (1))

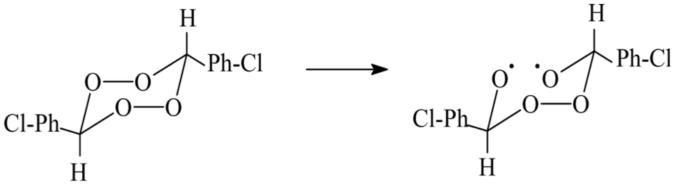
Table 2
Rate constant values for the thermolysis of DClPT in tetrahydrofuran solution

Temp, °C	$10^5 k_{\mathrm{exp}}$, s^{-1}
52	0.807
65	1.75
80	9.16
100	13.7
130	104

where the errors shown are standard deviation from a least-mean-squares data treatment [8] and the activation energy is expressed in cal mol^{-1}.

$$\ln k_{\mathrm{exp}}, \mathrm{s}^{-1} = (12.8 \pm 1.9) - (15816 \pm 667)/\mathrm{RT} \tag{1}$$

The Arrhenius equation plot is lineal ($r = 0.988$) in a relatively large temperature range (*ca.* 78°C), which suggests that the calculated activation parameters values for the DClPT reaction belong to a single process, which could be its unimolecular thermal decomposition through the O−O bond cleavage (Eq. (2)). The rate-determining step is the biradical formation that further decomposes by either C−C, C−O, or O−O bond ruptures, originating final organic products like chlorobenzene and p-chlorobenzaldehyde. The p-chlorobenzoic acid detected is formed by oxidation of p-chlorobenzaldehyde in the reaction media [9].



(2)

In previous work, it was demonstrated that the O−O bond dissociation energy is influenced by solvent [10], substituents [11], and ring size [12]. In the special case of those studies in different solvents it was concluded that the activation parameters are higher in the more non-polar solvents where the rate constant values are the lowest. The activation parameters values ($\Delta H^{\#} = 15.1 \pm 0.7\,\mathrm{kcal\,mol^{-1}}$ and $\Delta S^{\#} = -35.5 \pm 1.9\,\mathrm{cal\,mol^{-1}\,K^{-1}}$) corresponding to the unimolecular thermal decomposition reaction of DClPT in tetrahydrofuran (Eq. (2)) are of the order of those values obtained for others cyclic peroxides in polar solvents like 1,4-dioxane, chlorobenzene, and 2-propanol [10,2,13,14].

Conclusions

Experimental vibrational analysis has been performed on DClPT six-membered ring prepared in this laboratory through an alternative method. From the spectroscopic point of view, the most important contribution is the assignment of all the features of experimental IR spectra of the molecule and the prediction of the location at 951 and 905 cm^{-1} as single modes of asymmetric and symmetric O−O stretching modes, respectively.

The thermolysis of DClPT in THF solution follows a first-order kinetics law up to at least 60% diperoxide conversion. The activation parameters derived correspond to the initial homolysis of the O−O bond of the diperoxide molecule. Analysis of the reaction products is insufficient to propose a complete mechanism of the thermolysis of the DClPT, but studies are in progress to clarify it.

References

[1] Dubnikova, F., R. Kosloff, J. Almong, Y. Zeiri, R. Boese, H. Itzhaky, A. Alt, and E. Keinan. 2005. Decomposition of triacetone triperoxide is an entropic explosion. *Journal of the American Chemical Society*, 127: 1146–1159.

[2] Cañizo, A. I., G. N. Eyler, G. Morales, and J. R. Cerna. 2004. Diethyl ketone triperoxide: thermal decomposition reaction in chlorobenzene solution and its application as initiator of polymerization. *Journal of Physical Organic Chemistry*, 17: 1–6.

[3] Cerna, J. R., G. Morales, G. N. Eyler, and A. I. Cañizo. 2002. Bulk polymerization of styrene catalyzed by bi- and trifunctional cyclic initiators. *Journal of Applied Polymer Science*, 83: 1–11.

[4] Mittleman, R. E., L. A. Romig, and E. J. Gressman. 1986. Suicide by ingestion of methyl ethyl ketone peroxide. *Forensic Science*, 31(1): 662–669.

[5] Bertrand, M., S. Fliszár, and Y. Rousseau. 1968. Mass spectrometry of cyclic organic peroxides. *Journal of Organic Chemistry*, 5: 1931–1934.

[6] Riddick, J. A. Y. and W. B. Bunger. 1970. In A. Weissberger (ed.), *Organic Solvents*, Vol. II. Chap. V. New York: Wiley Interscience 704–706.

[7] Perrin, P. P. and W. L. F. Armarego. 1988. *Purification of Laboratory Chemicals*. 3rd ed. Oxford: Pergamon Press.

[8] Huyberechts, S., A. Halleux, and P. Kruys. 1955. Une application de calcul statistique à la cinétique chimique. *Bulletin des Societes Chimiques Belges*, 64: 203–209.

[9] Nesprias, K., A. Cañizo, N. Eyler, and M. Mateo. 2004. Oxidación de alcoholes utilizando peróxidos orgánicos cíclicos polifuncionales. *Afinidad*, 61(514): 471–475.

[10] Cafferata, L. F. R., G. N. Eyler, E. L. Svartman, A. I. Cañizo, and E. E. Alvarez. 1991. Solvent effects in the thermal decomposition reactions of cyclic ketone diperoxides. *Journal of Organic Chemistry*, 56: 411–414.

[11] Cafferata, L. F. R., G. N. Eyler, E. L. Svartman, A. I. Cañizo, and E. J. Borkowski. 1990. Mechanism of the thermal decomposition of substituted tetraoxanes in benzene solution: effect of substituents on the activation parameters of the unimolecular reactions. *Journal of Organic Chemistry*, 55: 1058–1061.

[12] Cañizo, A. I., N. E. Eyler, C. M. Mateo, E. E. Alvarez, and R. K. Nesprias. 2004. Kinetics of the thermal decomposition of substituted cyclic organic peroxides in toluene solution: substituent effects on the reaction rates and the activation parameters of the unimolecular reaction. *Heterocycles*, 63(10): 2231–2241.

[13] Eyler, G. N., A. I. Cañizo, C. M. Mateo, E. E. Alvarez, and L. F. R. Cafferata. 1999. Solvent effect in the thermal decomposition reaction of *trans*-3,3-dimethyl-5,6-tetramethylene-1,2,4-trioxacyclohexane. *Journal of Organic Chemistry*, 64(23): 8457–8460.

[14] Cafferata, L. F. R. and M. V. Mirífico. 1982. Kinetics and mechanism of acetophenone cyclic diperoxide (*trans*-3,6-dimethyl-3,6-diphenyl-1,2,4,5-tetraoxane) thermal decomposition in benzene solution. *Anales de la Asociacion Quimica Argentina*, 74: 501–508.