Thermal Decomposition Reaction of cis-6-Phenyl-5,6-(2-phenyl-propilydene)-3,3-tetramethylene-1,2,4-trioxacyclohexane in Different Solvents

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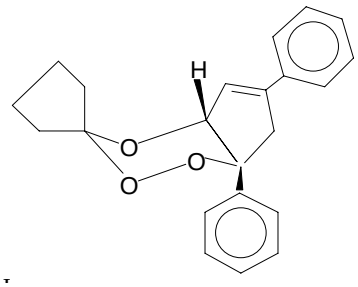
Abstract: The kinetics of the thermal decomposition reaction of cis-6-phenyl-5,6-(2-phenyl-propilydene)-3,3-tetramethylene-1,2,4-trioxacyclohexane (**I**) was investigated in the temperature range of 100-130°C in selected solvents of different physicochemical properties to evaluate a solvent effect on the reaction.

Introduction

It is interesting to mention that the antimalarial activity of the plant extract Qinghaosu is associated with the presence of the 1,2,4-trioxane ring in molecules of compounds (Artemisinin) found in its composition [1].



I

Here, available kinetic data on the thermal decomposition reaction of **I** in solvents with different physicochemical properties are presented to learn about the solvent effect on its thermolysis.

Experimental

Materials

The trioxane **I** was prepared by methods described elsewhere [2]. The organic solvents were com-

mercial analytical reagents purified by standard techniques.

Kinetic methods

Glass ampoules half filled with the appropriate **I** solution were thoroughly degassed under vaccum and immersed in a thermostatic bath at selected temperatures. The remaining concentration of **I** in the reaction solution was quantitatively determined by RP-HPLC (UV detection). In benzene solvent, kinetic data were obtained by GC analysis (FID detection). The reaction products were identified by GC-MS and RP-HPLC.

The first order rate constant values were obtained by least mean squares treatment of the data plotting the values of the [**I**] vs. time. The activation parameters were calculated according to the Eyring equation [3].

Results and Discussion

Rate measurements on the thermal decomposition of **I**, up to at least *c.a.* 60% of **I** conversion in each solvent, show an evident effect of the solvent in the temperature and initial concentration ranges of 100-130°C and 0.36-1,70 x 10^{-3} M, respectively, (Table 1). The rate constant values increase as the solvent polarity increases.

Table 1. First-order rate constant values at 120°C in solution.

SOLVENT	10^3 x [I], mol/L	10^6 x k_{exp}, s^{-1}
n-hexane	0.60	4.00
benzene	0.50	93.3
acetonitrile	0.65	173
metanol	0.36	390

The temperature effect was evaluated by the Arrhenius equation and the corresponding activation parameters for the O-O bond unimolecular homolysis of **I** were calculated. The first step of the reaction mechanism is the formation of a biradical which later decomposes.

A stepwise mechanism was confirmed by analysis of the reaction products.

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References and Notes

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