

Thermal Decomposition Reaction of Acetophenone Cyclic Diperoxide in Solvents of Different Physicochemical Properties

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Abstract: The thermal decomposition reaction of acetophenone cyclic diperoxide (trans-3,6-dimethyl-3,6-diphenyl-1,2,4,5-tetroxane; APDP) at the initial concentration of *c.a.* 0.01 mol kg⁻¹ and temperature ranges of 135.5 to 185.0° C has been investigated in dioxane and acetonitrile solutions, and in an 2-propanol/benzene mixture.

Introduction

The aim of this work is to study the thermal decomposition of acetophenone cyclic diperoxide (APDP) in solvents of different physicochemical properties, in order to correlate the kinetic parameters of the reaction and to compare the results with the previous studies in benzene solution [1].

Experimental

The diperoxide was prepared and conveniently purified as described elsewhere [2], and the solvents employed were purified by standar methods [3]. The 2-propanol was distilled from ethylenedi-aminetetraacetic acid (EDTA) to remove traces of metallic ions.

The diperoxide remaining in the solutions and the reaction products were determined by RP-HPLC.

Results and Discussion

The APDP thermolysis was made in the temperature range of 135,0 - 185,0°C at diperoxide initial concentration *c.a.* 0.01 molkg⁻¹. The observed rate constant values for APDP thermolysis at 150,0°C in various solvent are shown in Table 1. The reaction follows a first - order kinetic law up to at least *c.a.* 50% APDP conversion. In this case, the reactivity of the APDP is higher in polar solvent than in no polar-solvent.

Table 1. First order rate constant values for APDP thermolysis in different solvents at 150,0°C.

Solvent	$10^5 k; s^{-1}$
Acetonitrile	1,46 ^a
Dioxane	1,85
2-propanol/benzene	6,9
Benzene ^b	0,51

^a 153°C^b Ref. (1)

The experimental data were statistically treated in order to verify the existence of a true isokinetic relationship and to obtain the value of the isokinetic temperature ($\beta=154,5^\circ\text{C}$). This value is compared with another obtained by a different criteria described for kinetic data treatment.

The yields of the reaction products (acetophenone, methane, ethane) supports a stepwise mechanism and make possible to discuss the nature of solvent effects on the reaction.

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References and Notes

1. Mirífico, M. V.; Cafferata, L. F. R. *An. Asoc. Quím. Argent.* **1986**, *74*, 501.
2. Mc Cullough, K. J.; Morgan, A. R.; Nonhebel, D. C.; Pauson, P. L.; White, G. J. *J. Chem. Res. Synop.* **1980**, *34*, M 0601.
3. Riddick J. A.; Bunger, W. B. In *Organic Solvent*, Vol. II; Weissberger, Ed.; Wiley Interscience: N. Y., 1970.