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Kinetic study of the thermal decomposition reaction of pinacolone diperoxide in the presence of styrene

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Introduction

The synthesis and chemical behaviour of the organic cyclic peroxides, in which the O-O function is included within the molecular ring is interesting because the peroxidic function is directly related to oxidative processes of other organic compounds, such as alcohols (Nesprías *et al.*, 2004) and hydrocarbons (Bailey, 1958; Loan *et al.*, 1965). Besides these molecules participate in the formation of free radicals able to initiate styrene polymerization (Cafferata *et al.*, 1989) in industrial processes. Other large uses of peroxidic substances are related to industries of perfumes, pharmaceuticals and textiles.

Industrially, the action of other cyclic peroxides, such as the diethylketone triperoxide (3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane, DEKTP), has been tested as chain initiator for styrene polymerization, which carries great complexities at the time to synthesize it in low yield. Therefore, it is of interest to analyse the use of other multifunctional initiators.

In this paper the kinetics of the thermolysis reaction of pinacolone diperoxide (3,6-dimethyl-3,6-diterbutyl-1,2,4,5-tetraoxacyclohexane, PDP) is studied in solution of ethylbenzene with and without styrene addition. It was worked at low peroxide concentrations, and high monomer (styrene) concentrations for simulating industrial practice, where the system is highly concentrated and viscous.

Methodology

Reagents and solvents

Pinacolone diperoxide was synthesized using the previously described technique (Eyler *et al.*, 2002) of pinacolone reaction with hydrogen peroxide in acid medium (mp: 123-124 ºC).

Ethylbenzene was used as solvent, which was purified according to suitable techniques (Perrin and Armarego, 1988) and naphthalene as internal standard. Styrene was purified by distillation under reduced pressure as reported in the literature (Perrin and Armarego, 1988).

Kinetic determinations

Pyrex-glass ampoules (10 cm length x 6 mm ext. diameter) were filled with 1 ml of solution. An initial PDP solution in ethylbenzene with the addition of naphthalene (0.3% m/v) as internal standard (IS) was used. In some assays a known amount of styrene was added. Ampules filled with the initial solution were placed in liquid N_2 (-196 ºC) and degassed ($P \leq 133$ Pa). Finally, maintaining the solution at low temperature, the ampoules were heat-sealed using a torch. Thermolysis of PDP in solution was carried out immersing the sealed ampoules in a thermostized bath at a chosen temperature (± 1 ºC) between 110.0 and 150.0 ºC. The ampules were drawn at the previously established reaction times and immediately cooled in a water/ice bath in order to stop the reaction of peroxide decomposition. In all cases the solution contained in the ampule, where thermal decomposition was carried out, was injected into the chromatograph.

Quantitative determinations of the remaining PDP in the pyrolized solutions were analysed by GLC using the internal standard (naphthalene) method. A Konik gas chromatograph, KNK 2000 model, was used equipped with FID detector, a DB-5 capillary column, 30 meters length x 0.32 mm diameter and 0.25 microns thick of stationary phase (5% biphenyl 95% dimethylpolysiloxane). Analyses were performed with the following temperature program: 2 minutes at 110 ºC, 10 ºC/min heating rate until a final temperature of 220 ºC, injector at 150 °C and detector at 250 °C for the ampules without styrene, while for those that contained styrene the temperature program was: 5 minutes at 100 ºC, 10 ºC/min heating rate until a final

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temperature of 200 ºC, injector at 150 °C and detector at 250 °C.

Results and discussion

The experimental conditions, under which the reaction of thermal PDP decomposition in solution was studied, are such that the solvent is found in great excess regarding the peroxide, therefore concentration variation during the reaction will be very small and could be considered constant. Therefore, the followig kinetic behaviour of this system is only related to the quantitative peroxide determination in the course of the reaction.

Kinetic data obtained in this work keep an approximately linear correlation according to a first order kinetics law. It could be considered that, under these conditions, the reactions are of *pseudo*-first order. Kinetic experiments were carried out at low peroxide concentrations (0.02 M for the system without styrene) and in the temperature range of 120-150 ºC (Table 1) for minimizing the effects of induced decomposition processes. In the system with styrene concentrations of 0.01 M and a temperature range of 110-130 ºC (Table 1) were used to avoid thermal polymerization, and thus, to be able to assess only the effect of peroxide as chain initiator of styrene polymerization. In all cases the behaviour has shown to be of *pseudo*-first order.

Table 1. Rate constants for thermal PDP decomposition in ethylbenzene with and without styrene for different temperatures.

Solvent	[PDP] M	Temp [ºC]	$k_{exp}x10^{-5}[s^{-1}]$
Ethylbenzene/styrene (50:50)	0.01	110	12.6
Ethylbenzene/styrene (50:50)	0.01	120	16.1
Ethylbenzene/styrene (50:50)	0.01	130	30.0
Ethylbenzene	0.02	120	1.17
Ethylbenzene	0.02	130	9.16
Ethylbenzene	0.02	140	21.0
Ethylbenzene	0.02	150	65.0

The effect of temperature on the k_{exp} values for PDP thermolysis in ethylbenzene (Table 1) can be represented by the Arrhenius equation (eq. 1), where the errors account for the standard deviations obtained by kinetic data treatment with the method of least squares, and the activation energy is expressed in cal/mol.

$$\ln k_{exp}\,[s\text{-}1] = 31{,}40 \pm 6{,}0 - 33410{,}8 \pm 1400/RT \quad (1)$$

On the other hand, the graphic representation of the Eyring equation (Fig. 1) almost linear (0.997 and 0.993) for ethylbenzene and ethylbenzene/styrene, respectively, suggests that the corresponding activation parameters belong to a simple process for which the rate-determining reaction step can be attributed to the unimolecular O-O bond homolytic rupture for a giving birradical.

The activation parameters of the PDP thermolysis in ethylbenzene with and without styrene addition can be compared with those reported for thermal decomposition of this peroxide in other solvents (Table 2).

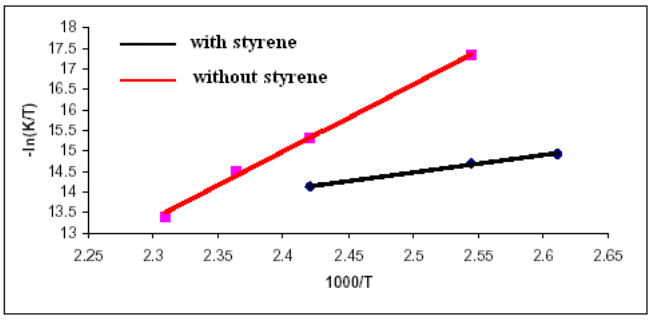

Figure 1. Effect of the temperature on the values of rate constants accounting for PDP thermolysis in solution.

The values of the activation parameters ($\Delta H^{\#}$ and $\Delta S^{\#}$) for the PDP/ethylbenzene-styrene system are lower than those obtained for various solvents. This has been observed in trials where the initiator is DEKTP.

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Table 2. Activation parameters of thermal PDP decomposition in different solvents.

Solvent	$\Delta H^{\#}$ kcal mol^{-1}	$\Delta S^{\#}$ cal mol^{-1} K^{-1}	$\Delta G^{\#}$ kcal mol^{-1}	Ref.
Ethylbenzene	32.6 ±2.4	1.2 ± 6.0	32.1 ± 2.4	This work
Ethylbenzene/styrene	8.4 ± 1.4	-55.1 ± 3.4	30.8 ± 1.4	
Toluene	34.6 ± 1.2	8.8 ± 3.0	31.0 ± 1.2	Perrin and Armarego, 1988
2-Methoxyethanol	43.8 ± 1.0	31.9 ± 2.6	30.7 ± 1.0	
Benzene	29.8 ± 0.6	-1.5 ± 1.5	30.4 ± 0.6	
n-Octane	37.5 ± 0.2	12.3 ± 0.5	32.4 ± 0.2	

Conclusions

High concentrations of styrene accelerate PDP decomposition process, which allows to check the effectiveness of this diperoxide as initiator of styrene polymerization.

However, at low monomer concentrations (*ca.* 25%) there is no influence on the specific rate constant at different work temperatures.

These preliminary conclusions are of great importance to (in a forthcoming stage and from experimental data) carry out theoretical studies and mathematical modeling of the PDP-styrene system .

Note: This study was presented at the "XXVI Congreso Argentino de Química" , San Luis, Argentina, 2006

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