Chapter 7

Solvent Effect of Oxygen in the Thermolisys Decomposition of the Acetone Diperoxide

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ABSTRACT

In this paper, the kinetics of the thermal decomposition reaction of 3,3,6,6-tetramethyl-1,2,4,5 tetroxane (ACDP) is investigated in various oxygen solvents at different temperatures. Linear relationships are observed between the enthalpy and entropy of activation of the unimolecular reactions of those diperoxides. The isokinetic temperature calculated by Leffler's treatment is 527.2K, which is consistent with the proposed Exner correlation between the logarithm of the rate constant values for the same reaction in each solvent at two temperatures, where the corresponding β value was 523.5K. A true "isokinetic relationship" for the ACDP thermolysis indicates that their reactions constitute a reaction series with similar interaction mechanisms. This can be related to the capacity for hydrogen bonding between the solvent and the diperoxide molecules. The solvanting properties of the media help the peroxidic bond rupture these molecules.

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INTRODUCTION

A homogeneous reaction can turn affected according to the used solvent. Often, the solvent affects the course of a reaction because there acts really as reactive, which demonstrates for the incorporation of solvent molecules in the structure of the reaction products (Bustillo et al., 2006; Cafferata & Jefford, 2001; Cafferata & Rimada, 2003; Cafferatta et al., 1991; Eyler et al., 2004; Leiva et al., 2000, 2002, 2004).

When the solvent interacts with the state transition of a reaction, the variation of the nature of the medium is manifested in the kinetics constants of the reaction observed or in the relative proportion of the products formed.

However, it may be that the general mechanism of the reaction is not affected, this is the case where you get a "real effect of solvent, which modifies only the kinetic and sometimes determines the prevalence of some reaction products.

Leffler (1995) was one of the first authors to study this effect through the graphical comparison: $\Delta H^{\#}$ vs. $\Delta S^{\#}$, in agreement to the equation: $\Delta H^{\#} = \Delta H^{0} + \beta \cdot \Delta S^{\#}$ in the event of a solvent effect. The linearity of the graph obtained indicate an enthalpy-entropy compensation, defining for the compound studied, the existence of a genuine "series of reactions" in the medium considered. The slope of the graph gives the value of the isokinetic temperature(β) for this series of reactions. After another author, Exner (1972) showed that linear graphs the $\Delta H^{\#}$ vs $\Delta S^{\#}$ can arise either from a dependence between correlated quantities, or random experimental errors committed in the determination of these Parameters. For Exner, when the isokinetic relationship is valid, their overall representation, Ln k vs. T^{-1} must be linear and all lines must intersect at a point known as the inverse of the isokinetic temperature.

The thermolysis decomposition of acetone Diperóxido (ACDP, Figure 1), tetroxane which produces mainly acetone in their thermolysis, has been studied in different medium, sweeping a wide range of solvents with different polarity.

Cafferata and col. demonstrated a real relationship isokinetic for unimolecular descomposition the ACDP in solvents: n-octane, benzene, toluene, acetonitrile, isopropanol. More recent studies on the thermolysis of ACDP have been conducted in solvents such as methanol, tetrahydrofurane, methyl tertiary butyl ether, methyl cellosolve, all oxygenates.

In this paper we present a study of the correlation between the oxygenated solvents so far examined.

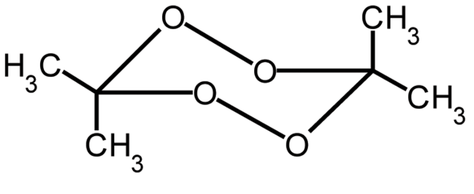
METHODS

Acetone cyclic diperoxide (ACDP) was prepared by dropwise addition of acetone in acetonitrile to a vigorously stirred cooled (-10°C) solution of 69,7% hydrogen peroxide and sulfuric acid (18M). After stirring for 1 h. at -10°C, filtration thorough water washing, and drying, the crude product was purified by recrystallizing from ethyl acetate until a constant melting point was attained (133°C). The product purity was checked by capillary GC and FTIR (Leiva et al., 1998).

The bands of absorption obtained for spectroscopy FTIR (NaC1, Nujol) are: 1)- 2910 (s) cm^{-1} 2)- 2850 (s) cm^{-1} 3)- 1200 (m) cm^{-1} 4)- 940 (w) cm^{-1} 5)- 860 (w) cm^{-1} 6)- 814 (w) cm^{-1} 7)- 682 (w) cm^{-1} (Jubert et al., 1999).

Kinetic Methods. Pyrex glass tube (4 mm i.d., 70 mm long) filled with the appropriated volume (c.a. 0,2 ml) of diperoxide solution, were thoroughly degassed in the vacuum line at - 196°C and then sealed with a flame torch. To perform

Figure 1. ACDP



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