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Kinetic solvent effects on the thermal decomposition reaction of acetone triperoxide†

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ABSTRACT: The kinetic data of the thermal decomposition reaction of acetone cyclic triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane, ACTP) are reported for a wide range of organic solvents (acetone, toluene, 2-propanol, 2-methoxyethanol, *n*-butylamine, diethylamine, triethylamine, and chlorobenzene) at 0.02 M initial concentration and in the temperature range of 135.0–172.0 °C. The thermolysis reaction follows pseudo first-order kinetic laws up to at least *ca*. 70% ACTP conversion. The results indicate the importance of solvent polarity and specific solvent-peroxide interactions in governing the rates of the reactions. The activation enthalpy and entropy of the thermal decomposition reaction of this triperoxide in several organic solvents were correlated through ''isokinetic relationships'' to verify the existence of a genuine solvent effect on this reaction. Other cyclic organic di- and triperoxides and some cyclic trioxanes showed a similar behavior, in contrast to the pinacolone cyclic diperoxide (PDP), probably due to a relatively great steric hindrance of this molecule. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: acetone cyclic triperoxide; solvent effects; thermal decomposition

INTRODUCTION

Cyclic organic peroxides have reached great importance through the years because of O—O bond linkage whose decomposition in free radicals makes them applicable in polymerization, an essential operation in synthetic polymer fabrication.

Recently, their capacity as initiators in the polymerization of styrene has been evaluated.[1]

In previous studies kinetic data[2–9] and solvent effects[2,3,5,7] related to the thermal decomposition reaction of cyclic peroxides of the families of substituted 1,2,4,5-tetroxanes,[2,3,5,9] 1,2,4-trioxanes[6,9] and 1,2,4,5,7,8-hexaoxacyclononanes[3,6–8] have been evaluated. An evident substituent effect on the O—O homolytic rupture during the thermolysis of the 1,2,4,5-tetroxanes was found in benzene solution.[4] Recently, we have published some results regarding the kinetics of the thermal decomposition of substituted cyclic mono, di and tri-organic peroxides in toluene solution[9] (substituent and ring size effects).

Acetone cyclic triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane, ACTP) and acetone diperoxide (3,3,6,6-tetramethyl-1,2,4,5-tetraoxacyclohexane, ACDP) have found few civilian or military applications[10,11] due to their low chemical stability, sensitivity to mechanical stress and high volatility. Unfortunately, the straightforward synthesis of these cyclic organic peroxides from readily available materials has made them popular components of explosive devices improvised by terrorists worldwide. As such, there is a great demand for an analytical methodology capable of detecting these materials[12] and designing additives that could improve their detection possibilities. The nature of these peroxides hampers a detailed experimental study of these initiation steps and, thus, experimental observations on peroxide-based materials are limited to analysis of post-blast residues or thermal decomposition studies.[3,6,13]

An alternative to experimental studies of thermal decomposition[6] is atomistic-scale computational simulation methods.[13] Quantum mechanics (QM) methods[14] and a series of molecular dynamics (MD) simulations[15] have been successfully employed to study several possible unimolecular ACTP-decomposition pathways and have provided valuable insights into the chemistry of these materials.

A significant variation is evident in the observed values of the activation parameters. Activation enthalpies near 33 kcal mol^{-1} correspond to the peroxidic O—O strength for homolytic types of ruptures[16] although lower activation parameters for the decomposition of peroxides

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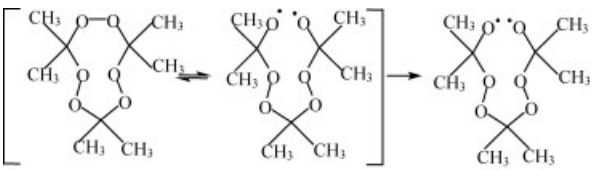
have been attributed to ionic reaction in solution[17] or a marked solvent effect.[2] However, through an estimate[18] of the average O—O bond energy for a series of peroxides it has been suggested that the expected average bond energy should be increased from 34 to 45 kcal mol^{-1}.

In a previous study[6] it was demonstrated that the activation parameters for the thermolysis of ACTP in toluene correspond to the unimolecular reaction of this triperoxide molecule (Eqn (1)). It was also demonstrated that the biradical decomposes thermally to form free methyl radicals that react with the solvent (toluene) to generate different products such as methane, bibenzyl, and ethylbenzene.



(1)

Cage reaction

In this study the effect of different solvents on the O—O bond homolysis of ACTP (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane) was investigated to assess the kinetic behavior of a representative of a family of nine-membered ring cyclic peroxides.

EXPERIMENTAL

Materials

ACTP was prepared and purified as described elsewhere.[8] The solvents employed in the reaction were purified using standard methods,[19] except 2-propanol and 2-methoxyethanol, solvents which were distilled from ethylene diamine tetracetic acid (EDTA) to remove traces of metal ions.[20] In all cases, the suitability of the purity for kinetic studies was checked by GC analysis.

Kinetic methods

Pyrex glass ampoules (10 cm long × 6 mm o.d.) half filled with ACTP solution and spiked with octanol as an internal standard were thoroughly degassed under vacuum at −196 °C and then sealed with a flame torch. To perform the runs, the ampoules (6 at each temperature) were immersed in a thermostated silicone oil-bath (±0.1 °C) and withdrawn after predetermined times. The reaction was stopped by cooling to 0 °C. The concentration of ACTP remaining in the solution was determined by quantitative GC analysis in a DB-5 capillary column (5% biphenyl-95% dimethyl polysiloxane, 30 m × 0.32 mm ID, 0.25 μm film thickness) installed in a Konik -2000C gas chromatograph with nitrogen as the carrier gas and flame ionization detection.

The corresponding first-order rate constants were calculated from the slope of the line obtained by plotting the values of ln [ACTP] against reaction time. The corresponding activation parameters were deduced from the Eyring equation and the errors were determined using a least mean squares data treatment.[21,22]

RESULTS AND DISCUSSION

The thermal decomposition reaction of ACTP in different solvents (acetone, toluene, 2-propanol, 2-methoxyethanol, *n*-butylamine, diethylamine, triethylamine, and chlorobenzene) at a 0.02 M initial concentration and in the temperature range of 135.0–172.0 °C follows pseudo-first order kinetic law up to at least 70% ACTP conversion. The corresponding rate constant values of ACTP thermolysis in different solvents at 140 °C are shown in Table 1.

In Table 1 a variation in the rate constant values can be observed. The pseudo-first-order reaction rate constant for the thermolysis of ACTP in solution showed that the rate of decomposition was somewhat faster in polar and protic solvents than nonpolar solvents. The rates of ACTP decomposition at 140.0 °C, however, did not vary by more than a factor of about five in these solvents.

The lowest activation enthalpy and entropy values were found for the protic solvents (2-methoxyethanol and 2-propanol, Table 1), and can be attributed to the hydrogen bonds formed between them and the O—O bond of the ACTP. In these cases the rate constant values are the highest. In *n*-butylamine it is possible to assume that the ACTP-solvent interaction process is more complex.

Table 1. Activation parameters for the unimolecular thermal decomposition reaction of ACTP in solution

Solvent	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ cal mol^{-1}K^{-1}	$\Delta G^{\neq}$ kcal mol^{-1}	$k^{140.0\,°C} \times 10^5$, s^{-1}
Acetone	41.7 ± 2.5	18.3 ± 5.6	34.1 ± 2.5	0.30
Toluene	41.8 ± 1.6	18.5 ± 3.8	34.2 ± 1.6	0.30
2-propanol	36.7 ± 0.6	7.0 ± 1.3	33.8 ± 0.6	1.1
2-methoxyethanol	25.1 ± 1.5	−20.3 ± 3.2	33.4 ± 1.5	1.5
n-butylamine	49.2 ± 2.4	37.7 ± 5.7	33.6 ± 2.4	1.2
Diethylamine	41.3 ± 0.5	16.0 ± 1.3	34.7 ± 0.5	0.40
Triethylamine	40.7 ± 3.4	14.1 ± 4.0	34.9 ± 3.4	0.30
Chlorobenzene	41.4 ± 1.4	16.9 ± 1.2	34.4 ± 1.4	0.60

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Table 2. Activation parameters for the unimolecular thermal decomposition reaction of different cyclic organic peroxides in 2-methoxyethanol

Peroxide	$\Delta H^{\#}$ kcal mol^{-1}	$\Delta S^{\#}$ cal mol^{-1} K^{-1}	$\Delta G^{\#}$ kcal mol^{-1}	$C(K_{exp}^{-150°C}) \cdot 10^5$, s^{-1}
ACTP	25.1 ± 1.5	-20.3 ± 3.2	33.4 ± 1.5	5.2
ACDP[a]	22.5 ± 1.2	-25.6 ± 3.0	33.3 ± 1.2	5.8
T[5]	24.6 ± 1.8	-18.3 ± 4.3	32.6 ± 1.8	6.6
PDP[23]	43.8 ± 1.0	31.9 ± 2.6	30.7 ± 1.0	137

[a] Leiva, L. Doctoral Thesis, Universidad Nacional del Nordeste, 2004.

The reactivity and activation parameters of ACTP, acetone cyclic diperoxide (ACDP) and *trans*- 3,3-dimethyl-5,6-tetramethylene-1,2,4-trioxacyclohexane (T) in 2-methoxyethanol (Table 2) are similar, in contrast to the pinacolone cyclic diperoxide (PDP), probably due to the relatively strong steric hindrance of this molecule.

Examination of the activation parameters shows that a change in $\Delta H^{\neq}$ is always accompanied by a change in $\Delta S^{\neq}$ (compensation effect). The values of $\Delta G^{\neq}$ within the series are almost constant and comparable with the experimental errors (Table 1).

The values of the activation parameters for the thermolysis of ACTP (Table 1) show linear correlations ($\Delta H^{\#} = \Delta H^{\circ} + \beta \Delta S^{\#}$) according to Leffler'[24] treatment for the postulation of an isokinetic relationship, changing from 2-methoxyethanol to *n*-butylamine as reaction solvents. In these cases, the corresponding plot (Fig. 1, dashed line, $r = 0.996$) gives an isokinetic temperature of 420 K (147 °C), which is within the experimental temperature range in which the kinetic measurements were performed. This correlation is valid for a wide temperature range ($\Delta T = 32.0$ °C) and activation parameter range ($\Delta\Delta H = 24.1$ kcal mol^{-1}, $\Delta\Delta S = 58.0$ cal mol^{-1} K^{-1}).

Leffler and Grunwald[25] have reported that the isokinetic relationships in which the solvent is the variable often have

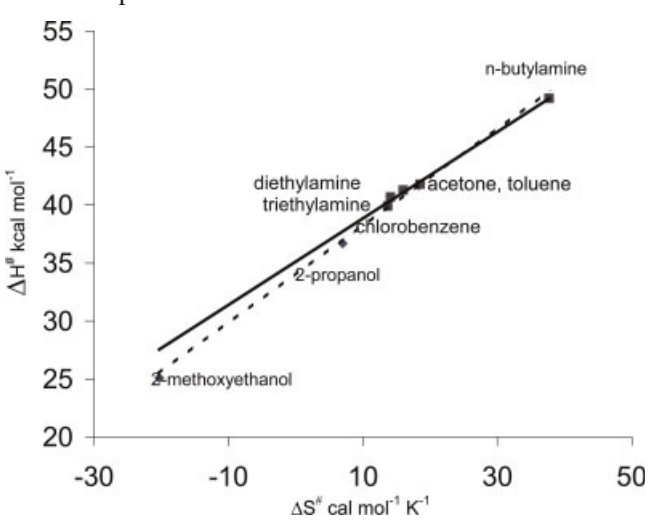

Figure 1. 'Isokinetic Relationship' according to Leffler for the thermal decomposition of ACTP in solution. Isokinetic temperature: dashed line 420 K (147 °C, with 2-propanol and 2-methoxyethanol included), solid line 372 K (99.0 °C)

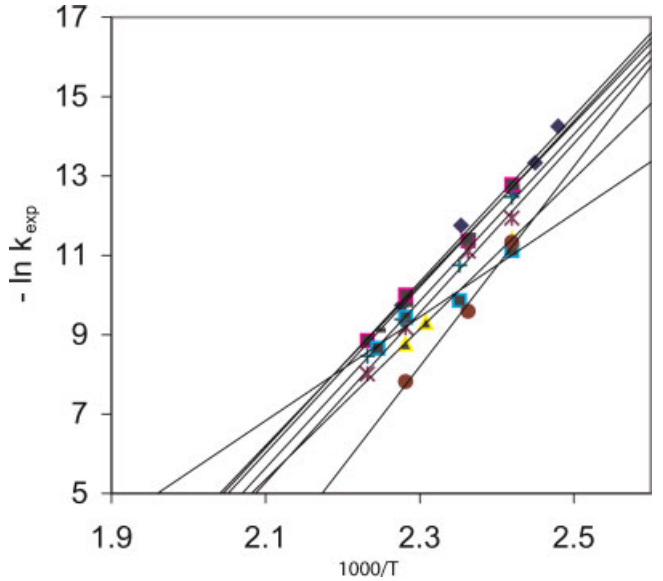

Figure 2. Arrhenius plot corresponding to the thermal decomposition reaction of ACTP in different solvents

isokinetic temperatures near the experimental temperatures.

When the isokinetic relationship is valid, its general representation, ln *k versus* T^{-1} (Fig. 2), must be a linear correlation according to the Arrhenius equation, and all the lines have to intersect at a point known as the reciprocal isokinetic temperature (β^{-1}). The Exner[26,27] statistical analysis based on a least-squares method calculates a common point of intersection of the regression lines in the Arrhenius plot for which the sum of the squares S_u of the deviations of the experimental points from new regression lines, including that point, becomes a minimum. If this is not found in the plot representing the dependence of S_u on the assumed values of T^{-1}, the

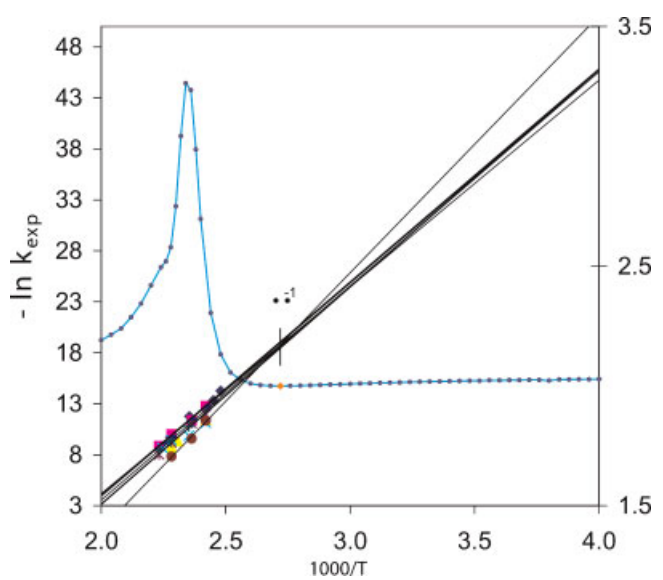

Figure 3. Dependence of the residual sum squares S_u on the isokinetic temperature T^{-1} for the ACTP unimolecular thermolysis in different solvents

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expected correlation is not valid. In Fig. 2 it can be observed that the Arrhenius plots for 2-propanol and 2-methoxyethanol (solvents that possess the alcohol function) cross each other. In these cases there is probably a different mechanism of reaction. The corresponding isokinetic temperature for the ACTP thermolysis for the other solvents (toluene, chlorobenzene, acetone, *n*-butylamine, diethylamine, and triethylamine, Fig. 3) according to Exner's treatment is 367.7 K (94.6 °C), which is also in reasonable agreement with the β value obtained by the Leffler method with the six solvents (Fig. 1, plain line $\beta = 372$ K, 99.0 °C). For these cases, the results mean that the thermolysis conforms to a genuine 'reaction series,' where the solvent affects the hexaoxacyclononane ring O—O bond rupture of the ACTP molecule.

CONCLUSIONS

The reactivity of ACTP in solution is higher when the organic solvent is 2-propanol, 2-methoxyethanol or n-buthylamine.

The results indicate the importance of solvent polarity and specific solvent-triperoxide interactions in governing the rates of the reactions.

The activation parameters of the thermolysis of ACTP in aprotic organic solvents have been correlated through isokinetic relationships (Leffler and Exner's treatments) to validate the existence of solvent effects on the unimolecular reactions.

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