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Thermal Decomposition Reaction of Acetone Triperoxide in Toluene Solution

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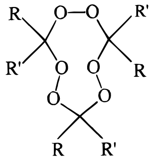
The thermal decomposition reaction of acetone cyclic triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane, ACTP) in the temperature range of 130.0−166.0 °C and an initial concentration of 0.021 M has been studied in toluene solution. The thermolysis follows first-order kinetic laws up to at least ca. 78% acetone triperoxide conversion. Under the experimental conditions, a radical-induced decomposition reaction as a competing mechanism may be dismissed, so the activation parameters correspond to the unimolecular thermal decomposition reaction of the ACTP molecule [$\Delta H^{\ddagger} = 41.8\ (\pm 1.6)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 18.5\ (\pm 3.8)$ cal mol^{-1}K^{-1}]. Analysis of the reaction products are not enough to elucidate the real mechanism for the thermolysis of the acetone triperoxide in toluene solution.

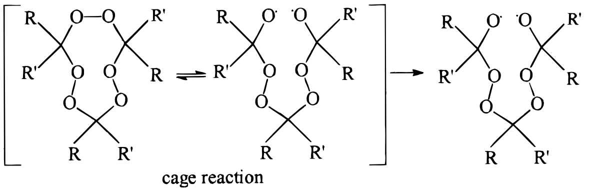
Introduction

The chemistry of organic peroxides, which entails the synthesis, characterization, and transformation of derivatives of hydrogen peroxide, has a long history and strong tradition.[1,2] The unusual reactivity of peroxides is generally attributed to weakness of the O−O bond linkage and hence the case with which it is homolytically cleaved. Cyclic di- and triperoxides derived from aliphatic ketones which were prepared in this laboratory are the object of numerous studies related to their application as initiators for the polymerization of vinyl monomers. Up to this moment, DEKTP[3,4] ($R = R' = C_2H_5$; 3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane, Scheme 1) and 3,6-di-*tert*-butyl-3,6-dimethyl-1,2,4,5-tetraoxacyclohexane are currently of special interest for the radical polimerization of styrene at high temperatures. The effects of the nature of these peroxide initiators on polystyrene conversion and molecular weight are being evaluated.[5]

Simultaneously with the studies related to the potential application of cyclic peroxides as initiators of polymerization, we have been investigating the thermal decomposition reactions in solution of other members of this family of compounds. The kinetic of the triperoxanes (Scheme 1) thermal decomposition reaction for cyclohexanone triperoxide ($R-R' = -(CH_2)_5-$; 3,6,9-tricyclohexylidene-1,2,4,5,7,8-hexaoxacyclononane, CHTP)[6] and DEKTP[4] have been studied, and it was demonstrated that the different products obtained are related to the characteristics of the respective molecule's substituents. The absence of a significant solvent effect on the products of the thermal decomposition reaction of CHTP[6] and DEKTP[4] suggest that the product-forming step and the rate-determining step are separated events. Thus, the rate-determining step is the biradical (dialkoxy radical) formation by homolytic cleavage of one of the O−O bonds (eq 1).

Scheme 1





(1)

It is reasonable to assume that the biradical recombination[7] to rebuild the triperoxide molecule in a cage reaction (eq 1) is a fast, nondetermining process. On the other hand, the biradical formed can react with the solvent and/or decompose thermally to generate several different product sets and free radicals derived from β-scission reaction (C−C and C−O bond ruptures).

In this work, we report the thermal decomposition reaction of acetone cyclic triperoxide ($R = R' = CH_3$, 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane, ACTP) in toluene solution under experimental conditions where a radical-induced decomposition reaction as a competing mechansim may be dismissed. A comparison with kinetic data from the thermal decomposition reaction of ACTP in acetone[8] is included.

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Table 1. First-Order Rate Constant Values for ACTP in Toluene Solution

temp (°C)	[ACTP], mol L^{-1}	$10^6 \times k_{exp}$, (s^{-1})	r[a]
130.0	0.021	0.644	0.9980
135.0	0.021	1.62	0.9940
141.4	0.021	3.27	0.9850
151.5	0.021	7.82	0.9995
151.5	0.200	7.52	0.9970
166.0	0.019	37.9[b]	0.9940
166.0	0.021	58.4	0.9922

[a] Correlation coefficient from a least mean square data treatment. [b] Up to at least 78% ACTP conversion.

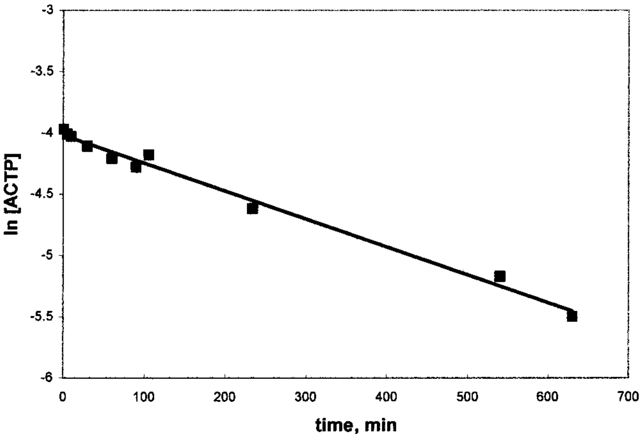


Figure 1. Representation through first-order kinetic plots of the data obtained in typical thermolysis experiments of ACTP in toluene solution at 166 °C.

Table 2. Main Products of Thermal Decomposition of Acetone Triperoxide in Toluene Solution at 173.0 °C

product	yield[a]
acetone	0.850
ethylbenzene	0.072
bibenzyl	1.54
methane, benzyl alcohol, benzaldehyde, and benzoic acid	*b*

[a] Moles of product per mole of ACTP decomposed. [b] Qualitatively determined.

Table 3. First-Order Rate Constant Values for ACTP [0.021 mol L^{-1}] in Acetone Solution

temp (°C)	$10^6 \times k_{exp}$,[a] (s^{-1})
140.0	2.80
150.0	9.10
165.0	45.6
170.0	95.8
175.0	143

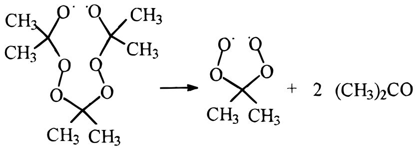
[a] From ref 8.

Results and Discussion

The ACTP thermolysis in toluene solution at an initial concentration range of 0.019−0.200 mol L^{-1} and in the temperature range of 130.0−166.0 °C (Table 1). To discard a radical-induced decomposition reaction as a competing mechanism, the kinetics of the ACTP thermal decomposition reaction in toluene was studied, at 151.5 °C, at higher initial triperoxide concentration (Table 1). The results showed that the observed rate constant values are practically independent of the initial ACTP concentration. An experiment at 166.0 °C with an initial ACTP concentration of 0.020 mol L^{-1} showed that the reaction follows first-order kinetic laws up to at least ca. 78% ACTP conversion (Figure 1). It seems that there are no contributions from second-order processes inducing the decompositon of ACTP at higher conversions.

On the other hand, toluene solvent is an excellent radical scavenger, and its large excess should inhibit radical chains; so it seems reasonable to assume that under the experimental conditions, where the rate constant values were determined, no induced decomposition reaction of the ACTP molecule must be considered. Then the observed rate constant values with an ACTP initial concentration ca. 0.021 mol L^{-1} (Table 1) can be ascribed to the unimolecular initial step of its thermolysis (eq 1, R = R' = CH_3).

The formation of the products from thermolysis of ACTP in toluene solution (Table 2) can be interpreted in terms of initial O−O bond homolysis to give the biradical (eq 1) which can reform the ACTP molecules or undergo either C−O bond cleavage, to give acetone plus oxygen and a diperoxy diradical (2,2-diyldioxypropane diradical) (eq 2), or C−C bond cleavage, to give principally methyl radicals which can abstract an hydrogen atom from toluene to give methane and benzyl radicals (eq 3) and thence bibenzyl by coupling of benzyl radicals (eq 4) and ethylbenzene by combination of methyl and benzyl radicals (eq 5).



(2)

$$CH_3^{\bullet} + PhCH_3 \rightarrow CH_4 + PhCH_2^{\bullet} \quad (3)$$

$$2\ PhCH_2^{\bullet} \rightarrow PhCH_2CH_2Ph \quad (4)$$

$$PhCH_2^{\bullet} + CH_3^{\bullet} \rightarrow PhCH_2CH_3 \quad (5)$$

The diperoxy diradical (eq 2) could abstract H from toluene to form the benzyl radical through a thermoneutral reaction or react with benzyl radical previously formed in the reaction media (for example in eq 3) which might lead to rapid formation of phenylmethoxy plus other radical species. Phenylmethoxy radical can abstract hydrogen from toluene to give benzyl alcohol.[9] Another way to explain the presence of the benzyl alcohol, benzaldehyde, and benzoic acid is the reaction of benzyl radicals with oxygen[10] formed as another reaction product.

Quantitative analysis of the acetone produced (Table 2) shows a molar yield lower than the expected (two moles per mole of ACTP decomposed) if we consider only a concerted mechanism or a decomposition reaction of the biradical by C−O bond rupture (eq 2). Thus, one might suggest that the C−C bond rupture giving methyl radicals is an important contribution in the decomposition of the biradical. But, up to this moment, analysis of the reaction products are not enough to elucidate the real mechanism for the thermolysis of the acetone triperoxide in toluene solution. Probably, the reaction can be considered as a continuum of mechanism, from stepwise to concerted.

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Table 4. Activation Parameters for the Thermolysis of Cyclic Di- and Triperoxides in Solution

cyclic peroxide	solvent	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}	$\Delta S^{\ddagger}$,[a] cal mol^{-1} K^{-1}	$k_{145°C}$, $\times 10^5$ s^{-1}	refs
ACTP	toluene	41.8 (± 1.6)	18.5 (± 3.8)	0.49	this work
ACTP	acetone	41.7 (±2.5)	18.3 (± 5.6)	0.37	8
DEKTP	toluene	48.7 (±1.5)	40.5 (± 3.4)	6.6	4
CHTP	toluene	46.3 (±2.9)	34.1 (±6.9)	14.3	6
CHTP	acetone	45.8 (±0.9)	34.0 (±2.3)	29.3	6
acetone diperoxide	toluene	28.9 (±0.4)	−13.7 (±1.0)	0.28	13
cyclohexanone diperoxide	toluene	40.0 (±0.3)	16.9 (± 0.8)	5.5	6
3,3,5,5-tetramethyl-1,2-dioxolane	benzene	43.6 (±0.9)	11.0 (±1.9)	0.0066	15

[a] Errors calculated as in ref 12.

The temperature effect on the rate constant values (k_{exp}) for the unimolecular reaction can be represented by the Arrhenius equation (eq 6) where the errors shown are standard deviations from a least mean square treatment[11,12] of the kinetic data.

$$\ln k_{exp},\ s^{-1} = (39.1 \pm 3.9) - (42667 \pm 1600)/RT \quad (6)$$

The Arrhenius equation plot for k_{exp} is linear (r = 0.993) in a relatively large temperature range (ca. 36 °C), which suggests that the calculated activation parameters values for the ACTP reaction belong to a single process, which could be its unimolecular homolysis (eq 1). The k_{exp} values obtained in acetone[8] solution (Table 3) are in reasonable agreement, within the experimental error, with those in this work for toluene solvent (Table 2). Furthermore, the activation parameters values of the thermal decomposition reaction of ACTP in both solvents are coincident (Table 4).

The activation parameter values for the unimolecular thermal decomposition of cyclic peroxides in solution are cited in Table 4. The variation in the activation enthalpy values in toluene solution for these kinds of compounds is 8.7 kcal mol^{-1} if we exclude acetone diperoxide (ACDP), which shows the lowest parameters and, on the other hand, in a previous work[14] it was demonstrated that it deviates from a correlation when studying effect of the substituents on the activation parameters of the substituted tetroxane unimolecular reaction in benzene solution. In Table 4, we include the activation parameters of 3,3,5,5-tetramethyl-1,2-dioxolane in benzene solution[15] because this compound undergoes decomposition by a stepwise biradical route. Activation parameters of cyclohexanone diperoxide are in agreement with those obtained in ACTP. A big variation in the entropies of activation and rate constants values can be observed in comparing ACTP with DEKTP and CHTP. Probably, a different mechanism is operative in the thermal decomposition reaction of ACTP.

Conclusion

1. The thermolysis of ACTP in toluene follows first-order kinetic laws up to at least ca. 78% triperoxide conversion.

2. Under the experimental conditions, a radical-induced decomposition reaction as a competing mechanism may be dismissed, so the activation parameters correspond to the unimolecular thermal decomposition reaction of ACTP molecule.

3. Analysis of the reaction products are not enough to elucidate the real mechanism for the thermolysis of the acetone triperoxide in toluene solution.

Experimental Section

Materials. ACTP was prepared by methods described elsewhere[8,16] and its purity checked by GC, FTIR (KBr), RP-HPLC, and TLC.

The toluene solvent was commercial analytical reagent (Merck p.a.) purified by standard techniques[17] (bp: 110.0−111.0 °C). Sublimed naphthalene (Mallinckrodt A. R.) was employed as internal standard in quantitative determinations of ACTP concentration and reaction products.

Kinetic Methods. Pyrex glass ampules (10 cm long × 6 mm o.d.) filled with 1 mL of the triperoxide solution were thoroughly degassed under vacuum at −196 °C and then sealed with a flame torch. To perform the runs, they were immersed in a thermostatic silicone oil bath (±0.1 °C) and withdrawn after predetermined times (5−10 at each temperature), stopping the reaction by cooling at 0 °C. The ACTP remaining and the reaction products were determined by quantitative GC analysis (internal standard method, naphthalene) in a 3% SE−30 Silicone Gum Rubber stationary phase on Chromosorb-W (1/8 in. O. D. s.s. column installed in a KONIK (KNK-2000 C model) gas chromatograph with nitrogen as carrier gas and FID detection.

The corresponding first-order rate constant values were calculated from the slope of the line obtained by plotting the values of ln[ACTP] concentration vs reaction time values. In all the cases the reaction was followed at least through one half-life. The corresponding activation parameters were worked out from the Arrhenius equation (eq 6), and their errors were determined using a least-means-square data treatment.[11,12]

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