
Thermal decomposition reaction of acetone cyclic triperoxide in aliphatic alcohols

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Reacció de descomposició tèrmica del triperòxid cíclic de acetona en alcohols alifàtics
Reacció de descomposició tèrmica del triperòxid cíclic d'acetona en alcohols alifàtics

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RESUMEN

El triperóxido cíclico de acetona (ACTP) en su forma cristalina es considerado un sensible y poderoso explosivo peroxídico. ACTP ha sido preparado en el laboratorio con el objetivo de determinar su cinética y parámetros termodinámicos en algunos alcoholes alifáticos (etanol, 2-butanol, 2-propanol y 1-propanol) purificados por tratamiento con la sal disódica del ácido etilen diaminotetraacético (Na₂-EDTA), para remover trazas de iones metálicos. La reacción fue estudiada a una concentración inicial de 0,02 M, mostrando un comportamiento de acuerdo a una ley cinética de pseudo-primer orden hasta al menos un 60% de conversión de ACTP. Los parámetros cinéticos han sido correlacionados con propiedades fisicoquímicas de los alcoholes seleccionados. La reacción se acelera en alcoholes secundarios, pero la reactividad es aún mayor en los solventes no tratados con Na₂-EDTA. Probablemente opera un mecanismo diferente de reacción en presencia de iones metálicos. Los parámetros de activación fueron analizados a través de una relación isocinética.

Palabras claves: triperóxido de triacetona, cinética química, termólisis en alcoholes.

SUMMARY

Acetone cyclic triperoxide (ACTP), in its crystalline form, is considered a sensitive and powerful peroxide based explosive. ACTP has been prepared in the laboratory in order to calculate its kinetic and thermodynamic parameters in some aliphatic alcohols (ethanol, 2-butanol, 2-propanol, and 1-propanol) purified by treatment with disodium salt of ethylene diamine tetraacetic acid to remove traces of metallic ions. The reaction was studied at an initial concentration ca. 0.02 M showing a behavior according to a pseudo first-order kinetic law up to at least ca. 60 % ACTP conversion. The kinetic parameters have been correlated with the physicochemical properties of the alcohols se-

lected. The reaction is accelerated in secondary alcohols but the reactivity is still higher in solvents non-treated with Na₂-EDTA. Probably a different mechanism of reaction is operative in the presence of metallic ions. The activation parameters were investigated through an isokinetic relationship.

Keywords: triacetone triperoxide, chemical kinetic, thermolysis in alcohols

RESUM

El triperòxid cíclic d'acetona (ACTP) en la seva forma cristal·lina es considerat un sensible i poderós explosiu peroxídico. Es prepara ACTP en el laboratori amb l'objectiu de determinar la seva cinètica i paràmetres termodinàmics en alguns alcoholes alifàtics (etanol, 2-butanol, 2-propanol i 1-propanol) purificats per tractament amb la sal disòdica de l'àcid etilendiaminotetracètic (Na₂-EDTA) per eliminar traces d'ions metàl·lics. S'estudia la reacció a una concentració inicial 0,02 M, mostrant un comportament d'acord a una llei cinètica de pseudo-primer ordre fins al menys un 60% de conversió d'ACTP. Es correlacionen els paràmetres cinètics amb propietats fisicoquímiques dels alcoholes seleccionats. La reacció s'accelera en alcoholes secundaris, però la reactivitat es encara major en les solvents no tractats amb Na₂-EDTA. Probablement opera un mecanisme diferent de reacció en presència d'ions metàl·lics. S'analitzen els paràmetres d'activació mitjançant una relació isocinètica.

Mots clau: triperòxid de triacetona, cinètica química, termòlisi en alcoholes.

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INTRODUCTION

In the last few years, cyclic organic peroxides have been regaining their lost interest due their increased use as explosive materials amongst terrorist groups. Acetone cyclic triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane, ACTP) has a high capacity of detonation, and the materials for its preparation are within any body reach. ACTP and its homologue acetone diperoxide (3,3,6,6-tetramethyl-1,2,4,5-tetraoxacyclohexane, ACDP) are small cyclic molecules considered as primary explosives. ACTP is one of the most sensitive explosives known, a property that allows its employment as both primary explosive and main charge [1]. ACTP may be employed for explosive devices due to its power close to that of TNT.

There are no known industrial or military applications of ACTP [2] due of its tendency to sublime rapidly and the fact that its danger significantly increases if is allowed to dry. As such, there is a great demand for an analytical methodology capable of detecting these materials [3, 4] 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 [4] or thermal decomposition studies in solution [5-7].

It has been shown that radicals generated among the products derived from the ozonolysis of tetramethylene (TME) are useful in the polymerization of vinyl monomer such as methyl methacrylate (MMA). These products are ACDP and ACTP plus other peroxidic species which may be open-chain oligomers [8]. However, the polystyrene (PS) obtained by reaction of styrene in the presence of ACTP at 423 K during three hours [9] has presented the same performance and characteristic properties if compared with that obtained by pure thermal initiation. Those results have shown that ACTP is not efficient as initiator of styrene polymerization. Nevertheless, in the same work, it has been shown that diethylketone cyclic triperoxide (DEKTP) and pinacolone cyclic diperoxide (PDP), tri and bifunctional initiators respectively, present typical multifunctional initiator behavior, and in their presence it was possible to obtain PS with high molecular weight at high reaction rates. On the contrary, up to the present, DEKTP has not been found in traces analysis of explosives, which is a very important subject in forensic investigations.

In solution, the ACTP molecule is highly stable so its thermal decomposition reaction has been investigated over the temperature range of 403.0 to 445.0 K in solvents of different physicochemical properties [5]. The kinetic results demonstrated that the reaction follows a pseudo-first order kinetic law up to a high degree of conversion. The activation parameters of the thermolysis of ACTP in solution [5-7] have been assigned to the unimolecular homolytic reaction of this triperoxide molecule and it has been reasonably assumed that the biradical intermediate formation is the rate determining step (Eq. 1, $R_1=R_2=CH_3$). The literature [10] has reported that the main decomposition reaction products in solution were acetone and carbon dioxide. Quantitative analysis of acetone indicated that the molar yield of acetone per mole of ACTP decomposed was about 2 in the gas-phase and 2.5-2.6 in condensed-phase [10]. Other authors [6, 7, 11] have found some products derived from methyl radical hydrogen abstraction (methane) and radical-radical reactions (ethane, 2-butanone in

acetone as solvent [7], or ethylbenzene in toluene as solvent [6]). The presence of those methyl radicals has been explained through the decomposition of the biradical initially formed (Eq. 1) by C-C bond ruptures.

The kinetic data in solution showed that protic solvents accelerate 2-3 times the thermal decomposition of ACTP [5], so the objective of this study was to provide a more complete investigation of the thermolysis of ACTP in some alcohols solution, a subject on which no information was found in the literature. Kinetic data of the thermal decomposition reaction of ACTP in different cyclic organic solvents and data obtained for different cyclic organic peroxides in some aliphatic alcohols were compared.

MATERIALS AND METHODS:

Materials: ACTP was prepared by the reaction of acetone (- 271 K) with concentrated hydrogen peroxide in concentrated sulfuric acid media. The translucent solid obtained was purified by twice recrystallization from light petroleum ether (p.f. 369.5 – 370.0 K)[7]. The solvents employed in the reaction were purified using standard methods [12], and they were distilled from disodium salt of ethylene diamine tetraacetic acid (Na_2 -EDTA) to remove traces of metallic ions [13]. In all cases, the suitability of the purity for kinetic studies was checked by GC analysis. 1-octanol was employed as internal standard in quantitative GC determinations.

Caution: ACTP must be handled with care because can it be detonated by shock.

Kinetic methods: Pyrex glass ampoules (10 cm long x 6 mm o.d.) half filled with ACTP solution were spiked with 1-octanol as an internal standard, thoroughly degassed under vacuum at 77 K 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 ($\pm 0.1^\circ$). The reaction was stopped after predetermined times by cooling them at 273 K. 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 x 0.32 mm I.D., 0.25 μ m film thickness) installed in a Konik -2000C gas chromatograph with nitrogen as the carrier gas, injection port at 423 K in split mode, and flame ionization detection (523 K). The experiments were carried out under programmed conditions (333 K, 3 min, 5 %/min, 433 K, 15 min). Retention times of internal standard and ACTP were ca. 11.2 min and 12.5 min, respectively.

The corresponding experimental pseudo first-order rate constant values (k_t), with 5 % accuracy, were calculated from the slope of the line obtained by plotting the values of $\ln [ACTP]_t$ against reaction time in seconds. The corresponding activation parameters were deduced from the Eyring equation and the errors were determined using a least-means-square data treatment [14, 15].

RESULTS AND DISCUSSION

The thermal decomposition reactions of ACTP in different solvents (2-butanol, 1-propanol, 2-propanol, and ethanol) were studied at an initial concentration ca. 0.02 M, and in the temperature range of 403.0 – 445.0 K. The reactions followed a pseudo first-order kinetic law up to at least

60 % ACTP conversion. The corresponding rate constant values of ACTP thermolysis (k_1) in different alcohols are shown in Table I, where some data obtained in a previous work were included [5].

Table I: Pseudo-First-Order Rate Constant Values for the Thermal Decomposition Reaction of ACTP (0.02 M initial concentration) in solvents with $\text{Na}_2\text{-EDTA}$ treatment.

Solvent	Temp., K	$k_1 \cdot 10^5, \text{s}^{-1}$	r
2-butanol	413.0	1.50	0.999
	423.0	5.30	0.999
	438.0	15.0	0.995
Ethanol	403.0	0.14	0.999
	413.0	0.90	0.998
	423.0	2.40	0.997
	433.0	4.70	0.999
	443.0	17.9	0.999
2-propanol	413.0 ^a	1.12	0.990
	423.0 ^b	3.25	--
	433.0	9.02	0.993
1-propanol ^c	438.0	15.5	0.997
	423.0	2.50	0.995
	423.0	0.78	0.999
Acetone ^e	423.0	0.91	0.999

^{a)} ref [5]; ^{b)} interpolated value; ^{c)} ACTP conversion : 92%; ^{d)} at 424.65 K; ref [6]; ^{e)} ref [7]

Kinetic data of the thermal decomposition reaction of ACTP in different aliphatic alcohols demonstrated that the investigated reactions depend directly on some solvent properties. In general, it has been found that the rate constant values (k_1) are higher in more polar solvents [6], but in the series of alcohols studied in this work it is evident that the cause of an increment in the reaction rate is not only due to the alcohol polarity, reflected in their $E_T(30)$ values. Figure 1 presents the plot of $\ln k_1$ in aliphatic alcohols with and without $\text{Na}_2\text{-EDTA}$ treatment [13] as a function of $E_T(30)$ parameter values [16] for the ACTP thermal decomposition reaction at 423 K. In ethanol the k_1 value was at least three times higher than the k_1 value in acetone [7] or toluene [6], but it was lower than the values obtained in the other alcohols. The alcohols in Table I may be classified as primary and secondary, and in that sense, the results have shown that the reaction is accelerated in the secondary ones.

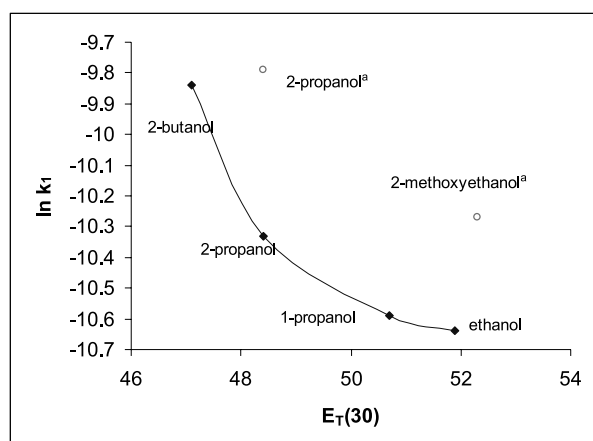


Figure 1: Correlation of $\ln k_1^{423 \text{ K}}$ vs. $E_T(30)$ for aliphatic alcohols. (^e-solvent without $\text{Na}_2\text{-EDTA}$ treatment).

On the other hand, when the alcohols were purified only by distillation without a previous $\text{Na}_2\text{-EDTA}$ treatment, as it was the case of 2-propanol and 2-methoxyethanol, the rate constant values were higher than the expected (Table II and Fig. 1). In these cases, the acceleration of the reaction was probably caused by trace impurities such as tran-

sition metal ions. These compounds have catalytic activity and can not be eliminated by distillation. The k_1 value in 2-propanol at 423 K with $\text{Na}_2\text{-EDTA}$ treatment was 2 times lower than the value obtained in the same solvent without $\text{Na}_2\text{-EDTA}$ treatment.

Table II: Pseudo-First-Order Rate Constant Values for the Thermal Decomposition Reaction of ACTP (0.02 M initial concentration) in solvents without $\text{Na}_2\text{-EDTA}$ treatment.

Solvent	Temp., K	$k_1 \cdot 10^5, \text{s}^{-1}$	r
2-propanol	413.0	2.19	0.992
	423.0	5.60	0.990
	438.0	18.0	0.995
2-methoxyethanol	413.0 ^a	1.48	0.980
	423.0 ^b	3.47	--
	425.0	5.21	0.999
	438.0	8.00	0.990
	445.0	17.3	0.990

^{a)} ref [5]; ^{b)} interpolated value

The temperature effect on the k_1 values evaluated according to the Arrhenius method showed a linear correlation over a relatively large interval of temperatures (at least 25 K). These results have suggested that the calculated activation parameters (Table III) are representative of a single process as the O-O bond homolysis (Eq. 1).

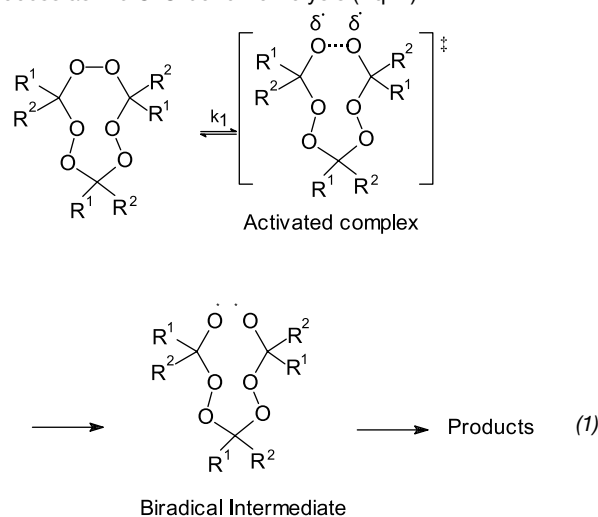


Table III: Activation Parameters for the Thermal Decomposition Reaction of ACTP in solution.

Solvent	$\Delta T, \text{K}$	$\Delta H^\ddagger, \text{kJ} \cdot \text{mol}^{-1}$	$\Delta S^\ddagger, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\Delta G^\ddagger, \text{kJ} \cdot \text{mol}^{-1}$	r
2-propanol ^a	25.0	122.47 \pm 5.02	-30.5 \pm 7.5	76.5 \pm 23.4	0.999
2-propanol ^b	25.0	153.41 \pm 2.51	29.3 \pm 5.4	141.0 \pm 2.51	0.999
2-butanol	25.0	130.83 \pm 7.94	-22.2 \pm 18.8	140.2 \pm 7.94	0.990
2-methoxyethanol ^{a, b}	32.0	104.92 \pm 6.27	-84.9 \pm 13.4	140.8 \pm 6.27	0.980
Ethanol	40.0	168.04 \pm 7.52	57.7 \pm 16.7	143.8 \pm 7.52	0.999
Toluene ^d	32.0	174.72 \pm 6.69	77.3 \pm 15.9	142.0 \pm 6.69	0.993
Acetone ^e	32.0	174.72 \pm 10.45	76.5 \pm 23.4	142.4 \pm 10.45	0.998

^{a)} Without $\text{Na}_2\text{-EDTA}$ treatment ^{b)} from ref [5] ^{c)} determined at 423 K, ^{d)} from ref. [6], ^{e)} from ref. [7].

A strong variation of those activation parameters values (Table III) for the thermolysis of ACTP in different solvents can be observed (e.g., in going from 2-methoxyethanol to ethanol the variations are $\Delta\Delta H^\ddagger = 63.12 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta\Delta S^\ddagger = 142.6 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ and $\Delta\Delta G^\ddagger = 8.2 \text{ kJ} \cdot \text{mol}^{-1}$). The linear

dependence between activation enthalpies and entropies (Table III) may be represented through equation (2) where the slope β (448.7 K) is called the isokinetic temperature and represents a temperature at which all reactions of the series should proceed at the same rate.

$$\Delta H^\ddagger = \beta \Delta S^\ddagger + \text{constant} \quad (2)$$

This correlation, known as the Compensation Effect or Iso-kinetic Relationship (IKR), has been much discussed [17] and widely investigated for many different physical and chemical processes [18, 19]. In Figure 2 the straight line A ($r_2 = 0.9888$) represents a correlation between ΔS^\ddagger and ΔH^\ddagger values in alcohols.

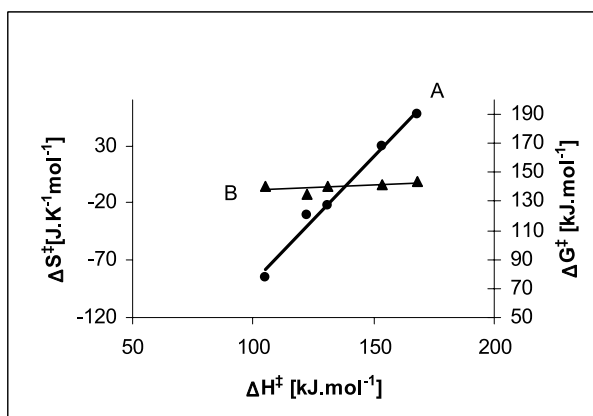


Figure 2: The enthalpy-entropy relationship for ACTP thermal decomposition in alcohol solution (Table II). A- plot of ΔS^\ddagger vs. ΔH^\ddagger ; B- plot of ΔG^\ddagger vs. ΔH^\ddagger .

The correct interpretation of the Compensation Effect should be that ΔG^\ddagger is approximately constant within a reaction series (Figure 2, line B) because enthalpy variations through the series of reaction are exactly compensated by entropy changes. In this work, the variation in ΔG^\ddagger is close to the experimental errors and these values can be considered approximately constant in comparison with the variations of ΔH^\ddagger . Nevertheless, the verification of equation (2) and determination of the constant β is, however, hindered by serious statistical problems. ΔH^\ddagger and ΔS^\ddagger (Eq. 2) have not been determined directly, these quantities are mutually dependent because both have been derived from the original kinetic data. Petersen [20] reported that in no case the linear $\Delta H^\ddagger / \Delta S^\ddagger$ plot can be taken by itself to be an adequate demonstration of the existence of an isokinetic relationship. A statistically correct solution can be achieved by returning to the original experimental quantities [16], thus a different representation of the Compensation Effect can be given in the $\ln k_i$ vs. T^{-1} , plane (or Arrhenius plane), where a family of straight lines with different slopes intersect at an ordinate position of $\ln k_i$, and at an abscissa value of T^{-1} which corresponds to β^{-1} (Fig. 3). The single point of intersection of lines in this figure could be used for a sound statistical test.

In Fig. 3 the solid lines represent the kinetic data obtained in alcohols with $\text{Na}_2\text{-EDTA}$ treatment. These lines intercept in a common point, or a zone, far from the experimental interval of temperatures. A least-squares treatment to determine the two coordinates of this point and the slopes of all the lines was applied in order to achieve the minimum sum of squares of the deviations of all points. The value of

β (454 K) obtained with this treatment (Fig. 3) is comparable with that calculated from Eq. 2. This value is slightly above the highest experimental temperature. In Figure 3 it can be seen that the kinetic data in 2-propanol and 2-methoxyethanol, without $\text{Na}_2\text{-EDTA}$ treatment, are represented by parallel dotted lines and may be excluded from the correlation because they intercept the others lines within the interval of experimental temperatures. As a consequence of these results, it is possible to conclude that the ACTP thermal decomposition reaction probably proceeds by two different mechanisms. In alcohols treated with $\text{Na}_2\text{-EDTA}$, the reaction goes by a stepwise mechanism, initiated by the homolytic rupture of the O-O bond, but in those solvents where the impurities of metallic ions are present, the O-O bond rupture may be assisted by those traces, so the decomposition reaction would be accelerated following a different mechanism. Probably, this latter mechanism is comparable with that proposed for antimalarial trioxanes for the presence of the prosthetic group, heme, or Fe^{2+} ions, where the initial rupture of the peroxide bond by electron transfer is considered [21].

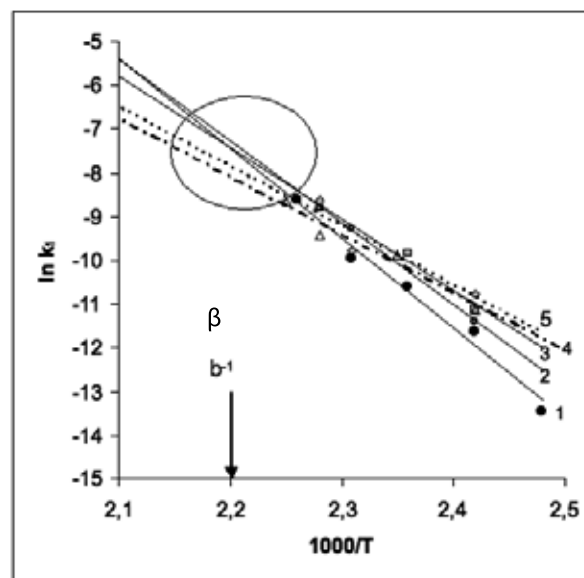


Figure 3: Arrhenius plot corresponding to the thermal decomposition reaction of ACTP in aliphatic alcohols. Solid line: solvents with $\text{Na}_2\text{-EDTA}$ treatment: 1) ethanol; 2) 2-propanol [5]; 3) 2-butanol.

Dashed line: solvent without $\text{Na}_2\text{-EDTA}$ treatment 4) 2-methoxyethanol [5]; 5) 2-propanol.

CONCLUSIONS

The thermal decomposition reaction of ACTP in aliphatic alcohols follows a pseudo first-order kinetic law. The rate constant values (k_i) are higher in secondary alcohols than in the primary ones probably because the former interacts more with the ACTP molecule favoring the biradical formation. A solute-solvent interaction mechanism through the formation of cyclic species can be postulated. The hydrogen atoms of the OH group and C2 in secondary alcohols may interact with the O-O bond in the peroxide molecule. On the other hand, the primary alcohols interact only through the hydrogen atom in the OH group. It was demonstrated that the presence of metallic ions as impurities in the alcohol solution accelerate the decompo-

sition of ACTP. Probably, the reaction mechanism in aliphatic alcohol begins with the rupture of the O-O bond of ACTP with participation of the metallic ions that finally lead to the formation of the reaction products and the recovery of the metal.

The isokinetic relationships investigated make it possible to conclude that probably different mechanisms of reaction are operative in Na₂-EDTA-treated or non-treated alcohols.

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