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THERMAL DECOMPOSITION OF THE ACETONE CYCLIC DIPEROXIDE IN 1-OCTANOL SOLUTION

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Abstract

The thermal decomposition reaction of acetone cyclic diperoxide (ACDP) in 1-octanol (OCT) solution, at the temperatures and initial concentration ranges of 130° -166 ºC and (0.94-3.00) x 10^{-2} mol/L , respectively, follows a pseudo-first order kinetic law. Acetone is the main organic decomposition product observed. The activation parameters values of the initial reaction step ($\Delta H^{\#}$ = 25.8 ± 0.3 kcal/mol; $\Delta S^{\#}$ = -19.1 ± 0.6 cal/mol K; E_a = 26.6 ± 0.3 kcal/mol), support a reaction mechanism which includes a homolytic rupture of one peroxidic

bond of the ACDP molecule with participation of the solvent and involving a biradical intermediate.

Keywords: tetroxane, thermal decomposition, ACDP, diperoxide

Resumen

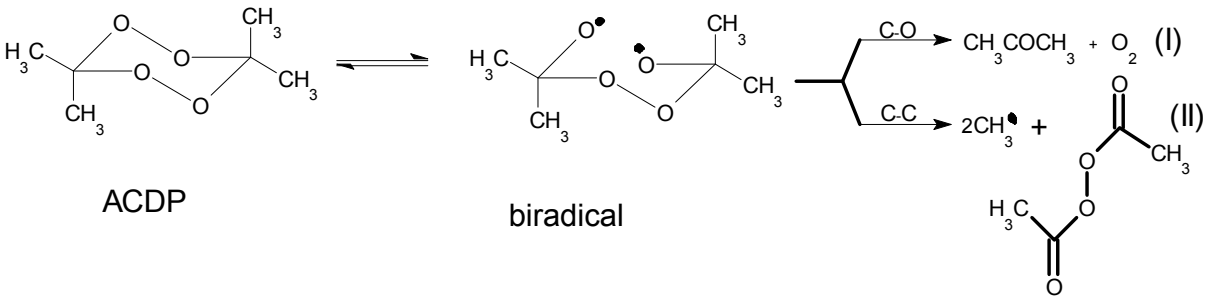
La reacción de descomposición térmica del diperóxido de acetona cíclico (ACDP) en solución de 1-octanol (OCT), en los rangos de temperatura y concentraciones iniciales de 130° -166 ºC y (0.94-3.00) x 10^{-2} mol/L respectivamente, sigue una ley cinética de seudo primer orden. La acetona es el principal producto de descomposición observado. Loa valores de activación de la etapa inicial ($\Delta H^{\#}$ = 25.8 ± 0.3 kcal/mol; $\Delta S^{\#}$ = -19.1 ± 0.6 cal/mol K; E_a = 26.6 ± 0.3 kcal/mol) apoyan un mecanismo de reacción que incluye una ruptura homolítica de un enlace peroxídico en la molécula del ACDP con participación del solvente y que involucra un birradical intermediario.

Palabras claves: tetroxano, descomposición térmica, ACDP, diperoxido

Introduction

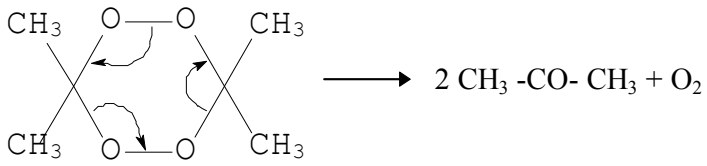
Actually peroxides are receiving great attention and are considered very important molecules since a) they play a relevant role in oxidation reactions of organic compounds, b) they are intermediate species in combustion and polymerization processes [1-3], biological metabolism reaction, cancer, pollution and aging phenomena, [4,5] etc., active oxygen atoms and free radicals react with lipids, carbohydrates, enzymes and DNA, causing an oxidative damage [6-9]. Some derivatives have antitumoral and antimicrobian effects and it is recognized the antimalarial action of tetroxanes [10-16]. For the thermolysis of acetone cyclic diperoxide (3,3,6,6-tetramethyl-1,2,4,5-tetroxane, ACDP) it has been reported further solvent effects [17, 21-22]. In particular, that effect was observed on the rate constant values of the activation parameter values. In fact, the unimolecular decomposition of those molecules can take place by two different kinds of mechanisms:

a) a stepwise homolysis initiated by one peroxidic bond rupture with a biradical as intermediate which further decomposes by either C-O or C-C bond ruptures, originating different final products:



Scheme 1

b) a concerted type of mechanism where the bond breaking and the bond making may occur simultaneously:



Scheme 2

For this process, acetone and oxygen are the only expected reaction products. In this work, the probable mechanism involved in the ACDP thermal decomposition in OCT solution is postulated. The data were compared with those results obtained in previous studies to learn about the effect of the solvent both on the kinetic and the product yields during the course of the reaction.

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 recrystallization from ethyl acetate until a constant melting point was attained (133°C). The product purity was checked by capillary GC and FTIR. [23]

1-Octanol (OCT) was purified by standard technique [24] (bp 194.5°C). The purity was checked by GC analysis.

Kinetic Methods. Pyrex glass tube (4 mm i.d., 70 mm long) filled with the appropriated volume (c.a. 0.2 mL) of ACDP solution and octane (internal standard), were thoroughly degassed in the vacuum line at -196°C and then sealed with a flame torch. To perform the runs, they were immerse in the thermostatic silicone oil bath ($\pm$ 0.1°C) and withdrawn after selected times, stopping the reaction by cooling at 0°C. Quantitative determinations of the ACDP remaining in the solution and the organic reaction products were performed by GC programmed temperature analysis (from 40°C to 150°C) using a silica fused capillary column (HP5, 30m length, 0.25 mm i.d., with phenylmethylsilicone as stationary phase) installed in a 5890 series II - Hewlett Packard Gas Chromatograph, using FID detection, nitrogen as carrier gas and employing the internal standard method (octane).

*Calculating Methods***.** The first-order rate constant values were calculated from the slope of the line obtained by a least mean-square treatment of this reaction data when plotting the values of ln [ACDP] concentration vs. reaction times ($r \geq 0.997$). The activation parameters values were calculated according to the Eyring equation and the errors were worked out by Arrhenius equation method using a least-mean-squares data treatment [25].

Results and discussion

The thermal decomposition reaction of acetone cyclic diperoxide (ACDP) in OCT, at the temperatures and initial concentration ranges of 130°-166 ºC and (0.94-3.00) x 10^{-2} mol/L, respectively, follows a first order kinetic law (Figure 1) up to 75% diperoxide conversions.

To discard a radical – induced decomposition reaction as a competing mechanism, the kinetics of the ACDP thermal decomposition reaction in OCT was studied at 166°C and at higher initial diperoxide concentration, 0.3 M. (Table I). The results show that the rate constant values are independent of the initial ACDP concentration.

These results suggest that there are no contributions from second-order processes inducing the decomposition of ACDP at higher conversions. A similar behavior was observed in the ACDP thermal decompositions but in another alcohol solvent such as 2-propanol [19]. The values for the thermolysis of ACDP in OCT solution (Table 1) are similar to those obtained with other solvents.

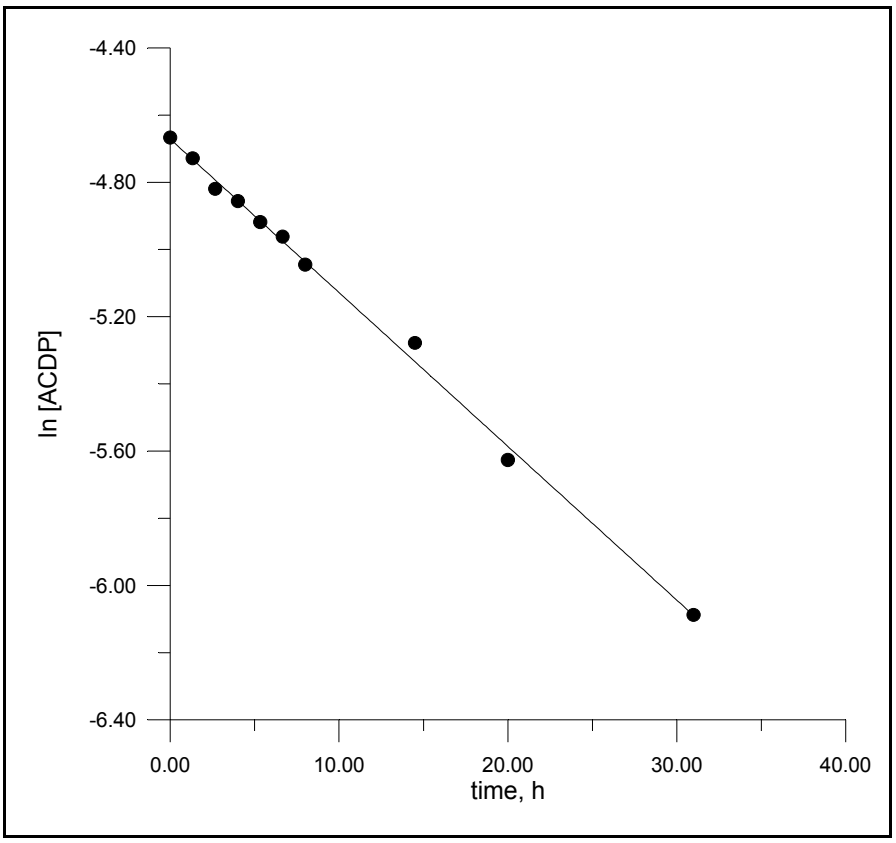


Figure 1. Representation through first order kinetics plots of the data obtained in typical thermolysis experiments of ACDP (0.94 x10^{-2} mol/L) in OCT solution at 140°C.

In order to evaluate the effect of the solvent polarity in the ACDP thermolysis data, the reaction was analyzed in solvents of different dipole moment, dielectric constant, and empirical parameter ET(30) (Table 2). Although some of these parameters describe the medium polarity, from different aspects [26, 27] it is possible to classify the solvents (Table 2) methanol, THF, and 2-propanol as polar solvent, while benzene, toluene, octane are considered as no polar solvents.

Table 1: First order rate constant of values for ACDP thermal decomposition in OCT solution

Temperature (ºC)	**[ACDP].10** ^{2} (mol/L)	**k** 10^{5} [a] (s^{-1})	**r** [b]
130	0.94	0.602	0.9949
140	0.94	1.27	0.9976
150	0.94	2.71	0.9966
166	0.30	9.18	0.9850
	0.94	9.13	0.9937
	3.00	9.08	0.9890
		9.13[a]	

[a] Experimental mean rate constant values.

[b] Correlation coefficients from a least mean square data treatment.

A comparison of the mentioned parameters (Table 2) with the corresponding k values obtained in the different solvents indicates that in low-polarity solvents ACDP exhibit slow kinetics process, while in the most polar solvents it shows the fastest rate constant value. Therefore, the kinetics of the thermolysis of ACDP in OCT was found to be similar to the one taking place in methanol.

The temperature effect on the experimental rate constant values (k) for the unimolecular reaction investigated can be represented by the following Arrhenius equations (1) where the errors shown are standard deviation from a least mean-squares data treatment [25] and the activation energy is expressed in cal mol^{-1}.

$$\ln k\ (s^{-1}) = 21.2\ (\pm\ 0.6) - 26589.0\ (\pm\ 0.3) / R\ T \quad (1)$$

The linearity of this equation over a relatively large temperature range (36ºC) suggests that the calculated activation parameters values for the ACDP thermal decomposition reaction (Table 2) belong to a single process, which could be the unimolecular thermal cleavage of the O-O bond as the initial bond breaking step (Scheme 1) or a concerted type process (Scheme 2). It is not probable that both processes have identical activation parameters. The theoretically calculated value (38.3 kcal mol-1) for one O-O bond homolysis of the ACDP molecule was also corroborated by experimental measurements in the gas phase [28], where the activation energy value obtained (39.0 ± 2.5 kcal mol^{-1}) supports a stepwise mechanism of reaction given a biradical as the intermediate specie.

Besides, theoretical calculations performed via uBHandLYP method of the decomposition reaction in gas phase of ACDP following both reaction paths in stages and concerted, respectively, confirm the fact that the mechanism takes place in stages with an activation energy equal to 29.0 kcal/mol which is lower than the corresponding activation energy for a concerted mechanism (i.e. 78.7 kcal/mol) [29].

Table 2. First-Order Rate Constant Values and Activation Parameters for ACDP Thermolysis in Solvents Dielectric Constants, Dipole Moments, and Empirical Parameter ET(30) of the Reactions Organic Solvents.

Solvent	**k 10^6 (s^{-1}) 150 °C**	**$E_T(30)^a$ kcal/mol**	**ε^b**	**μ^c (10^{30}Cm)**	**$\Delta H^{\#}$ kcal/mol**	**$\Delta S^{\#}$ cal/mol K**	**$\Delta G^{\#\,e}$ kcal/mol**	**Ref.**
Octane	1.05	31.1	2.00	0.04	43.0 ± 2.7	17.8 ± 6.4	35.6 ± 2.7	17
Benzene	2.83	33.9	2.28	0.00	34.3 ± 1.2	1.4 ± 0.3	34.9 ± 1.2	17
Toluene	3.44	34.5	2.38	1.43	28.9 ± 0.4	-13.7 ± 1.0	34.6 ± 0.4	17
Methyl t-butyl ether	4.44	34.3	4.50	4.23[d]	33.8 ± 1.1	-4.06 ± 0.7	35.0 ± 1.1	31
Methanol	22.2	55.4	32.79	6.07	26.9 ± 0.3	-16.9 ± 0.6	33.9 ± 0.3	21
Octanol	**27.1**	**48.3**	**10.4**		**25.8± 0.3**	**-19.1 ± 0.6**	**33.8 ± 0.3**	**This work**
THF	75.0	49.2	7.58	5.84	21.5 ± 0.3	-27.3 ± 0.6	32.9 ± 0.3	32
2-Propanol	85.8	37.4	19.92	5.54	19.4 ± 1.3	-31.4 ± 3.5	32.6 ± 1.3	19
Acetic acid.	99.6	55.2	6.15	1.74	13.3 ± 4.4	-43.7 ± 10.5	31.6 ± 4.4	33

[a] Empirical solvent polarity parameter: transition energy at 25ºC for the long wavelength absorption band of a standard pyridinium-*N*-phenoxide betaine dye [33].
[b] Dielectric constant for the pure liquid at 25 ºC [10].
[c] Dipole moments in Coulombmeter (Cm) values [10].
[d] Dipole moments in Coulombmeter (Cm) obtained by theoretical calculations (density function B3LYP with 3-21 G base set level.
[e] calculated values at the average temperatures of the experiments.

Moreover, calculated values [30] even support that the rate determining step is the homolytic rupture of the O-O bond. Calculations through the AM1 semiempirical method with geometry optimization for analogous tetroxanes, with halogen atoms as substituents, were carried out. The values of the activation energy for the concerted processes and for the

stepwise mechanism, were obtained. The results showed that the energy barrier for the unimolecular concerted decomposition turn to be *ca.* 20 kcal mol^{-1} higher than the one obtained for the unimolecular homolytic rupture of one O-O bond (a stepwise biradical initiated decomposition) with an average value of 22 kcal mol^{-1}.

Besides, of the two alternative mechanism postulated in the introduction to interpret the thermolysis of ACDP in OCT, the concerted mechanism can be discarded.

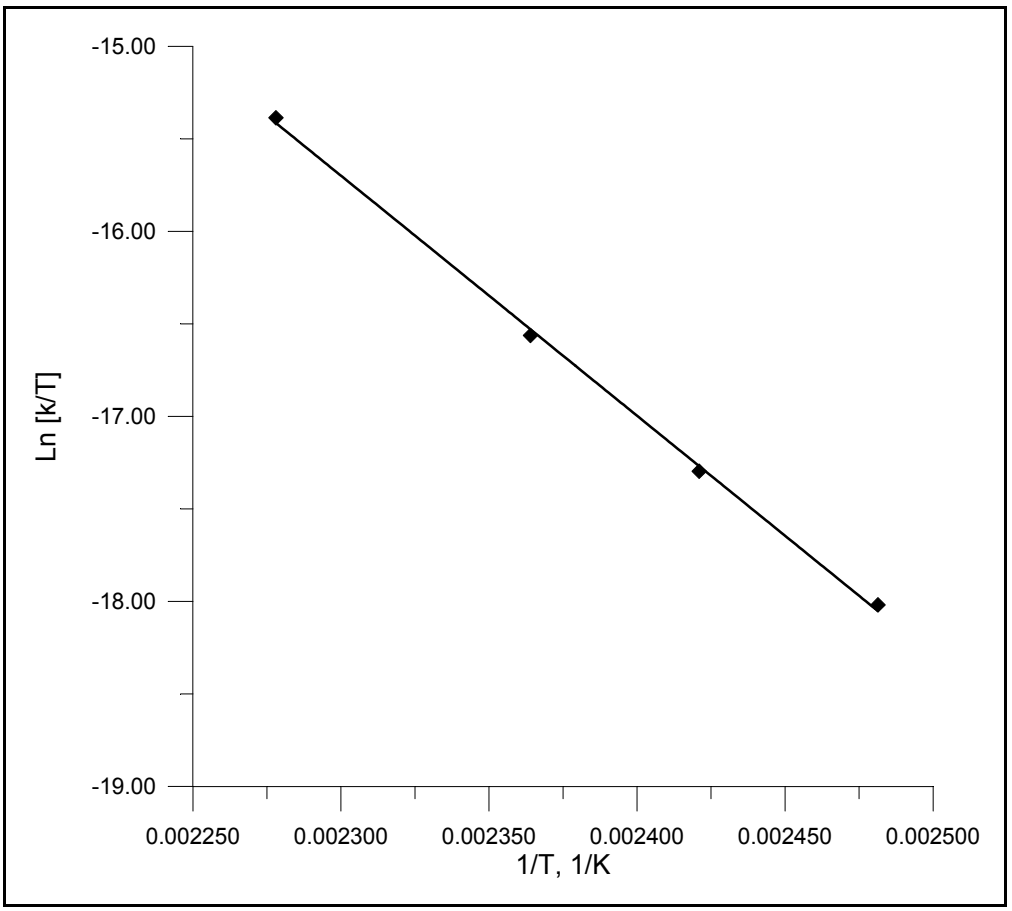
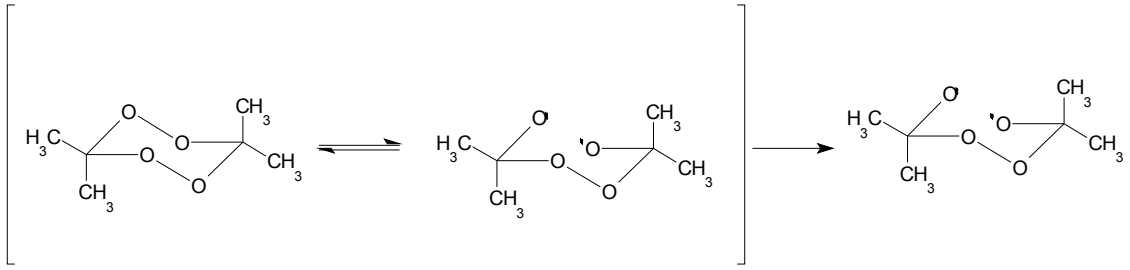


Figure 2. Eyring plot corresponding to the thermal decomposition reaction of ACDP in OCT solution.

The reaction products analysis for ACDP in OCT solution in the initial concentrations range was acetone. The value of the acetone molar yield (moles of acetone per mole of ACDP decomposed) was 2. Therefore, it is likely that the thermal decomposition of ACDP in OCT may only produce acetone and oxygen.

Since the concerted type decomposition could be discarded, these results suggests that the formation of the products of the thermolysis can be interpreted in terms of an initial O-O homolysis to give the biradical (Sheme 1, path I). Oxygen and acetone come from the fragmentation of the initially formed biradical, through the rupture of their C-O linkages

Thus, the thermolysis mechanism of the ACDP in OCT solution is initiated by a process of the following type (Scheme 3) where the rate of ring cyclization within the reaction cage should be a relatively fast step. [18].



Scheme 3.

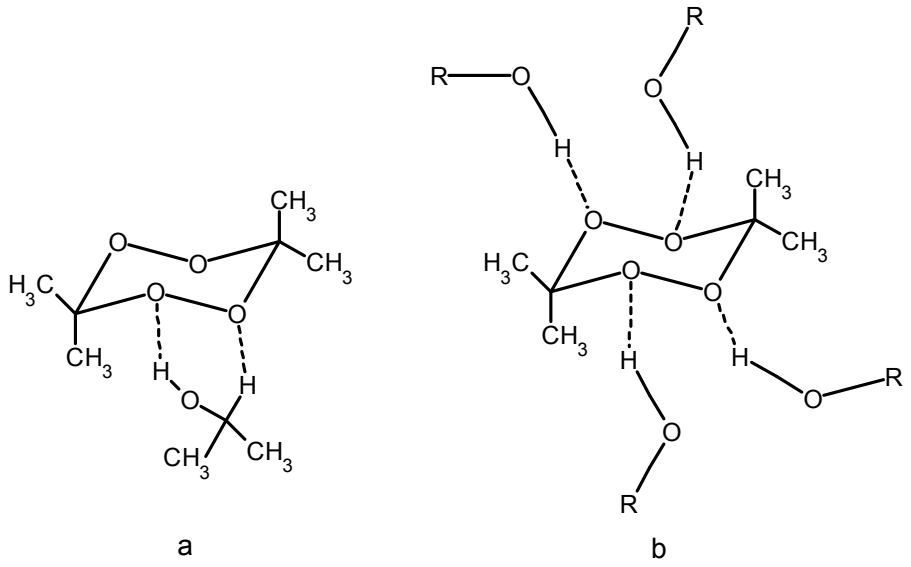
The activation parameters ($\Delta H^{\#}$=25.8 ± 0.3 kcal mol^{-1} and $\Delta S^{\#}$= -19.1 ± 0.6 cal mol^{-1}) were worked out from the Eyring equation. They are showed in the Table 2, where bibliographic data are included to be compared. The activation parameter values obtained for the thermal decomposition reaction of ACDP in OCT and in other solvents (Table 2) indicate nearly $\Delta G^{\#}$ values in the different studied solvents.

This supports that analogous qualitative interactions between solute and solvent molecules are taking place in the initial thermolysis. This means that the corresponding activation enthalpies of the reaction ($\Delta H^{\#}$, Table 2) are almost compensated by the entropies of activation.

The observed negative entropy value for the ACDP thermolysis in OCT solution reflects the decrease in degree of freedoms of the ACDP molecules that take place when they pass to a rather more rigid transition state, where the rupture of a peroxidic linkage might be assisted by the OCT solvent molecules.

The demonstration of the existence of the molecular complex between ACDP and 2-propanol molecule [19, 20] stabilized probably through intermolecular hydrogen bonding, supports the observed intermediate values of the activation parameters for the unimolecular decomposition of this substance in that alcohol ($\Delta S^{\#}$ = -31.4 cal/mol. K). Table 2, Scheme 4a, with a relatively polar transition state; the kinetic results obtained in the more protonic donor acetic acid as the reaction solvent are in accord with that postulate and favor in this case the existence of a still more dipolar transition state. The reduced steric hindrance in the ACDP molecule would be relevant for the formation of adducts with particular solvents.

The activation entropy for the decomposition reaction of ACDP in OCT is -19.1 cal/mol. Although it is not possible to form an adduct, it is supposed that 4 alcohol molecules are bonded via hydrogen bonds to the ring oxygen atoms of ACDP, making easier the O-O bond breaking off (Scheme 4b).



Scheme 4. The formation of: (a) adduct product of 2-propanol and ACDP; (b) complex ACDP-OCT.

A linear relationship between the activation enthalpies and entropies ($\Delta H^{\#} = \Delta Ho + \beta \Delta S^{\#}$, r=0.997) of the unimolecular thermolysis reactions of the ACDP can be found according to Leffler´s treatment (Figure 3). The isokinetic temperature was $\beta \cong 203$ °C. This means that the corresponding activation enthalpies of the reaction ($\Delta H^{\#}$, Table 2) are nearly compensated by the entropies of activation. All these findings suggest that the ACDP thermolysis follows a genuine reaction series [17] where the solvent affects the tetroxacyclohexane ring O-O bond rupture of their molecule.

Therefore, these values are in agreement with a stepwise reaction mechanism with homolytic rupture of one peroxidic bond of ACDP molecule yielding a biradical, as it is observed in other analogous ACDP reactions [17, 19, 21].

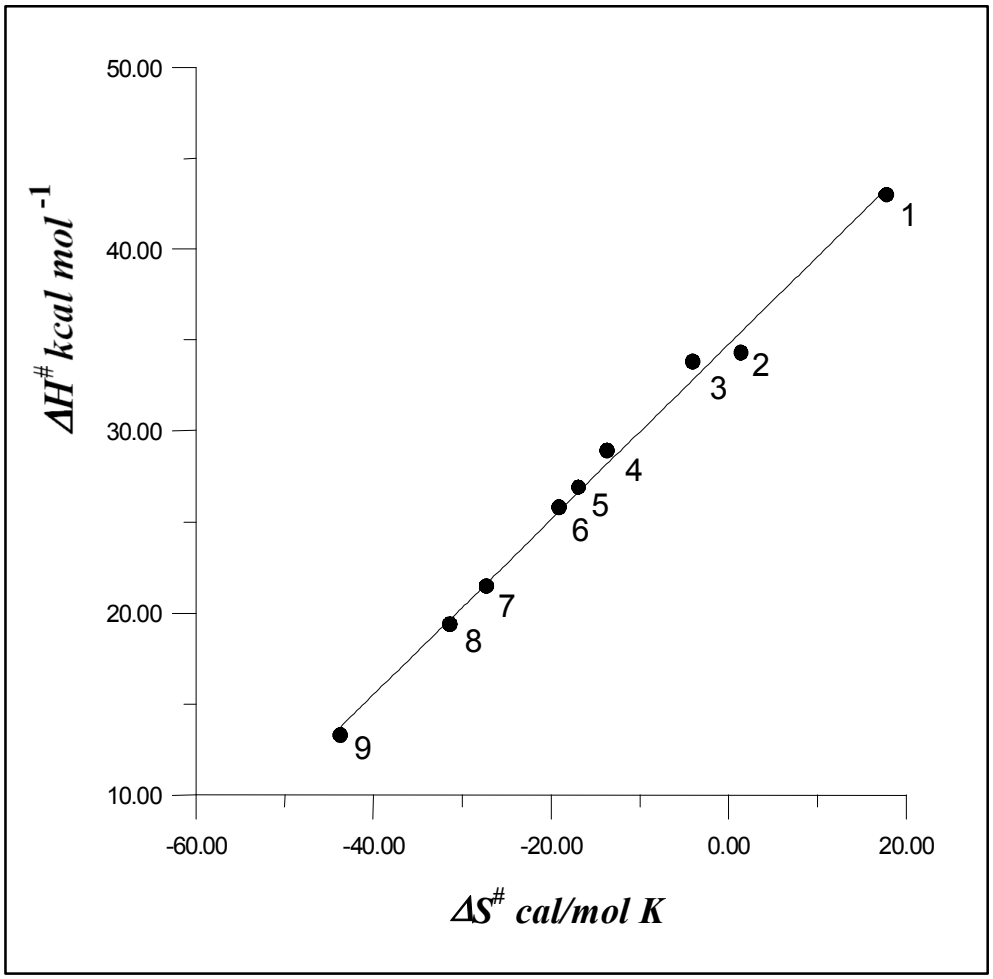


Figure 3. Isokinetic relationship according to LEFFLER for the thermal decomposition reaction of ACDP: **1:** octane; **2:** benzene; **3:** methyl t-butyl ether, **4**: toluene; **5**; methanol; **6**: 1-octanol; **7**: THF; **8**: 2-propanol; **9**: acetic acid.

Conclusions

1- The thermolysis of ACDP in OCT solution follows a pseudo-first-order kinetic law up to at least 75% diperoxide conversion.

2-Under the experimental conditions, the activation parameters correspond to the unimolecular thermal decomposition reaction of the ACDP molecule. The activation parameters values of the initial step of the reaction ($\Delta H^{\#}$ = 25.8 ± 0.3 kcal/mol; $\Delta S^{\#}$ = -19.1 ± 0.6 cal/mol K; Ea = 26.6 ± 0.3 kcal/mol), support a reaction mechanism which includes a homolytic rupture of one peroxidic bond of the ACDP molecule with participation of the solvent and it involves a biradical intermediate.

3- Analysis of the reaction products and the activation parameter values contributes to postulate the mechanism for the thermolysis of the ACDP in OCT solution. The thermolysis would occur through a well known mechanism of decomposition already advanced for the tetroxanes, which begins with the homolytic rupture of the peroxydic bond leading to the formation of an intermediate biradical and further C-O bond ruptures giving acetone and oxygen as final products.

4- The kinetic of ACDP thermolysis is significantly affected by the physicochemical characteristics of the reaction media which is noted in the $\Delta S^{\#}$ value. The large and negative activation entropy value (-19.1 cal / mol=K) suggests that it makes up an interaction between solvent molecules and ACDP.

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