Q1 4-Heptanone Cyclic Diperoxide: Improved Preparation Method and Solvent Effect on Its Thermolysis in Solution

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ABSTRACT: Cyclic organic peroxides have interesting pharmacological properties and are used at industrial level as polyfunctional initiators of polymerization, and so their preparation through novel methods has attracted the attention of numerous researchers. White crystals of 4-heptanone cyclic diperoxide (HDP) can be obtained in acidic media at $-1°C$ by a reaction between 4-heptanone and hydrogen peroxide. Its thermal decomposition was studied in acetone, cyclohexane, acetonitrile, ethyl acetate, ethanol, 2-propanol, 2-butanol, and 1,4-dioxane at temperatures higher than $120°C$, showing a behavior accordingly with a pseudo-first-order kinetic law up to at least 80% HDP conversion. It was demonstrated that an increase in solvent polarity is accompanied by an increase in reaction rates. The effect of solvent polarity on the thermal decomposition rate constant values can be associated with a reaction mechanism involving a more dipolar-activated complex than the diperoxide initial molecule. The activation parameters varied widely from 31.2 to 46.6 kcal mol^{-1} and -1.33 to 31.7 cal mol^{-1} K^{-1} when going from ethanol to cyclohexane as reaction solvents, respectively. An enthalpy–entropy compensation effect was observed in all solvents. Specific interactions between the oxygen atoms from the peroxidic bond and the hydrogen atom bonded to C2 and/or from the OH group can be taken into account to explain that the existence of the compensation effect does not mean that an isokinetic relationship consequently can be established. The kinetic results showed that an isokinetic relationship is observed only for a group of solvents. © 2011 Wiley Periodicals, Inc. Int J Chem Kinet 00: 1–10, 2011

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INTRODUCTION

During the past decade, the chemistry of cyclic peroxides has enjoyed a renaissance with the increasing appreciation that such compounds are found widely in nature and often have interesting pharmacological

properties and are used at industrial level as polyfunctional initiators of polymerization. Also, a number of studies have been undertaken concerning the examination of the behavior of cyclic organic peroxide to know the kinetics and mechanism of their decomposition reactions in different solvents. Sometimes new synthetic methods or alternative techniques that involve greater yields of peroxide compound in a shorter preparation time were reported [1–4].

The correlation between structure and reactivity has been the most relevant aim in physical organic chemistry. In that sense, the effect of solvent polarity on the thermal decomposition rate constant and activation parameter values of various cyclic diperoxides and triperoxides derived from aliphatic ketones has been carried out [3,5–9]. Information concerning substituent and solvent effects on chemical reactivity can be correlated in a variety of ways. Such relationships fall into a large class of linear free-energy relationships (LFER), also called extrathermodynamic relationships or correlation equations [10]. The observation and reporting of linear relationships between entropies and enthalpies of activation have become common in kinetic studies of groups of similar organic reactions. Such a group might comprise, for example, a series of thermal decompositions of a single compound in several different solvents, or it might be a series of reactions differing only in one of the reactants. If the enthalpy and entropy changes are temperature independent, then the enthalpy of activation changes ($\Delta H^{\ddagger}$) must be directly proportional to the entropy of activation changes ($\Delta S^{\ddagger}$) for the reaction series (this behavior has been called the "compensation effect" or "enthalpy–entropy compensation") [11]. Two extreme situations should be noted: (1) If $\Delta H^{\ddagger}$ is constant for all the reaction series, the reaction series is entirely entropy controlled; it is said to be isoenthalpic and the ln (k/T) vs. $1/T$ plots are parallel lines. (2) If $\Delta S^{\ddagger}$ is constant, the series is enthalpy controlled; it is said to be isoentropic [12].

Historically, the compensation effect and the isokinetic relationship were considered to be synonymous. Furthermore, it was demonstrated that the occurrence of one does not necessarily imply the occurrence of the other [13]. Different statistical criteria may be used to decide the existence of each effect. When the correlation coefficient for the compensation effect has a value closely to the unit, it is considered that the compensation is better. On the other hand, the only unambiguous evidence for an isokinetic relationship is the intersection of all ln k [or ln (k/T)] vs. $1/T$ plots for the series at a common point [14–16]. This isokinetic behavior is commonly found for reaction series in which only one reaction mechanism is followed [17].

In this work, an improved procedure for the preparation of 3,3,6,6-tetra-*n*-propyl-1,2,4,5-tetraoxacyclohexane (HDP; Eq. (1)) and a kinetic study of its thermal decomposition reaction in solution are reported. The reactions were carried out in solvents of different physicochemical properties at different temperatures. The solvent effects on the rate constants and on the activation parameters of the thermolysis of this organic peroxide molecule were discussed.

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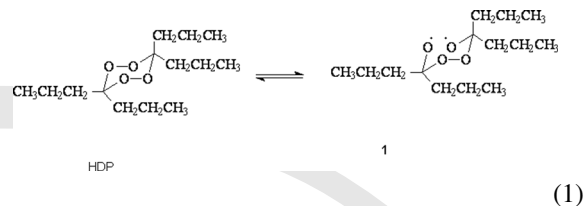
EXPERIMENTAL

Preparation of 3,3,6,6-Tetra-*n*-propyl-1,2,4,5-petraoxacyclohexane

This cyclic peroxide was prepared by an alternative method to that reported in the literature [18]. In this work, HDP was obtained by dropwise addition of 5.7 mL of hydrogen peroxide (30%, 0.056 mol) to a vigorously stirred mixture of 14 g of sulfuric acid (70%, v/v) and 7 mL of 4-heptanone (0.050 mol) cooled at $-1°C$.

After 2 h of reaction, the mixture was extracted twice with 50 mL of purified light petroleum ether (35–60°C) and the organic phase was freed of exceeding hydrogen peroxide with aqueous saturated solution of ammonium chloride, washed with cold distilled water (0°C) until the exceeding acid was eliminated, and then dried over anhydrous sodium sulfate. The organic solvent was evaporated at ambient temperature, and the residue was left overnight in a desiccator.

The white solid obtained (54.4% crude product) was twice recrystallized from boiling methyl alcohol. The colorless crystals (m.p., 47.0–47.5, 47.0–48.0°C [18]) actually correspond to HDP molecule prepared by an improved method. Its purity was also checked by gas   **Q3** chromatography (GC) and Fourier transform infrared (KBr) absorption bands.

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

Materials

Acetone, cyclohexane, acetonitrile, ethyl acetate, ethanol, 2-propanol, 2-butanol, and 1,4-dioxane were purified with the appropriate techniques [19,20], and

their purity was checked by GC analysis. Alcohols used as solvents were distilled from ethylenediaminotetraacetic acid disodium salt to remove traces of metallic ions [21]. Sublimed naphthalene was employed as an internal standard in quantitative GC determinations.

Kinetic Methods

Q4   Pyrex glass tubes (7 cm long × 4 mm internal diameter [i.d.]) half filled with the appropriate HDP solution were thoroughly degassed under vacuum at $-196°C$ and then sealed with a flame torch. To carry out the experiment, the ampoules were immersed in thermostatic silicone oil bath ($\pm0.1°C$) and withdrawn after predetermined times, stopping the reaction by cooling them in an ice-water bath ($0°C$).

The HDP remaining in the solution and the 4-heptanone organic product were determined by GC (internal standard method) in a DB-5 capillary column (5% biphenyl–95% dimethyl polysiloxane, 30 m × 0.32 mm i.d., 0.25-mm film thickness) installed in a Konik-2000C gas chromatograph, with nitrogen as carrier gas and flame ionization detection ($250°C$). Injection port was fixed at $150°C$ in split mode. HDP retention time under programmed conditions ($80°C$, 3 min, $10°C$/min, $170°C$, 15 min) was 20.3 min.

The corresponding pseudo-first-order rate constant values were calculated from the slope of the line obtained by a least-mean-square treatment of the reaction data when plotting the values of the ln [HDP] concentration vs. reaction times.

Enthalpy and entropy of activation were obtained from the experimental rate constant values at different temperatures in intervals of at least $30°C$ in each solvent. Linear regression analysis of $\ln (k/T)$ vs. $1/T$, according to the Eyring equation, allowed the calculation of the enthalpy of activation from the slope and the entropy of activation from the intercept. The errors on the activation parameters were worked out by the Arrhenius equation method using a least-mean-square data treatment [22].

Product Analysis

The reaction products were identified by GC–MS analysis in a Rtx-5MS capillary column (5% biphenyl–95% dimethyl polysiloxane, 30 m × 0.25 mm i.d., 0.25-μm film thickness) installed in a Thermo Quest Race 2000 CG model gas chromatograph with helium as carrier gas (0.5 mL min^{-1}) and the injection port at $150°C$ in split mode (split ratio 1:33). The detection was carried out with a Finnigan Polaris ion-trap MS detector with the transfer line at $275°C$ and the ion source at $200°C$. The oven was maintained at $50°C$ for 3 min and then

heated up to $200°C$ at a rate of $20°C$/min. Only 4-heptanone organic product was identified by GC with FID detection, as was described in the Kinetic Methods section.   **Q6**

RESULTS AND DISCUSSION

This paper describes a new and alternative method of preparation of 4-heptanone cyclic diperoxide (HDP) to that reported in the literature [18]. This improved technique obviated the addition of acetanhydride as reaction solvent. The reaction was initiated by drop-wise addition of H_2O_2 to a mixture of 4-heptanone in acidic media at $-1°C$ instead of adding ketone to the acidic H_2O_2 at $15°C$. The molar yield of white crystals of 4-heptanone diperoxide raised with the present method was ca. 54.4% in 2 h of reaction, whereas Dilthey et al. [18] obtained only a yield of 35.2%.

The thermal decomposition reaction of HDP has been studied in solution at a temperature range of 120–170°C (Table I) and at an initial concentration of ca. 2×10^{-2} M. It was found that the kinetic behavior of this system agrees with a pseudo-first-order kinetic law up to at least 80% of HDP conversion. It seems that under the experimental conditions of the present work, there are no contributions from second-order processes inducing the decomposition of HDP. The experimental rate constant values, k_{exp}, obtained in solvents with different physicochemical properties are shown in Table I.

The temperature dependence of the k_{exp} values for the thermal decomposition reaction of HDP in solution follows the Arrhenius equation with good accuracy for most solvents investigated. The linearity of the Arrhenius equation plots in a relatively large temperature interval (ca. 30°C, Table I) suggests that the calculated activation-parameter values for the HDP reaction in solution belong to a single process, which could be its unimolecular thermal decomposition through the O–O bond cleavage to form the intermediate biradical **1** (Eq. (1)) as the initial bond-breaking step [5].

The biradical species **1** (Eq. (1)) can reform the diperoxide molecule or undergo either C—O bond cleavage to give 4-heptanone (Eq. (2)) or O—O bond cleavage to give a biradical species **2** (Eq. (3)), which can undergo C—C bond cleavage to give n-propyl and butanoate radicals (Eq. (4)). Butanoate radicals can abstract a hydrogen atom from solvent to give butanoic acid (Eq. (5)) or take part in some radical reaction to form n-propylbutanoate (Eq. (6)). A radical–radical coupling reaction between two n-propyl radicals may explain the detection of n-hexane as a product (Eq. (7)).

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Table I Pseudo-First-Order Rate Constant Values (k_{exp}) for the Thermal Decomposition Reaction of HDP in Different Solvents

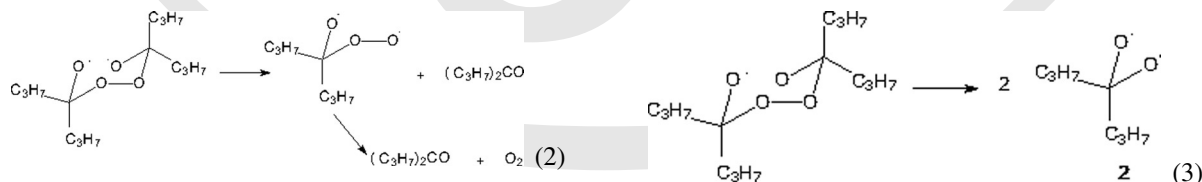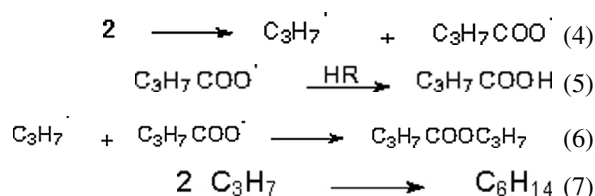| Solvent[a]	Temperature (°C)	$k_{exp}(\times 10^4 s^{-1})$	r[b]
Cyclohexane (E_T^N: 0.006)	140.0	0.167	0.981
	150.0	0.896	
	160.0	1.47	
	170.0	9.59	
1,4-Dioxane (E_T^N: 0.164)	140.0	0.170	0.999
	150.0	0.730	
	160.0	2.16	
	170.0	7.99	
Acetone (E_T^N: 0.355)	130.0	0.220	0.999
	140.0	0.620	
	150.0	1.83	
	160.0	5.23	
Acetonitrile (E_T^N: 0.460)	130.0	0.17	0.998
	140.0	0.67	
	150.0	2.36	
	160.0	5.83	
Toluene[c] (E_T^N: 0.099)	130.0	0.116	0.993
	141.4	0.563	
	145.0	0.590	
	151.0	1.68	
	166.0	6.51	
Ethyl acetate (E_T^N: 0.228)	140.0	0.350	0.989
	150.0	1.17	
	155.0	1.86	
	160.0	2.30	
	165.0	5.60	
Ethanol (E_T^N: 0.654)	120.0	0.190	0.999
	130.0	0.500	
	140.0	1.38	
	150.0	3.41	
2-Propanol (E_T^N: 0.546)	130.0	1.85	0.992
	140.0	4.65	
	150.0	16.7	
	160.0	27.3	
2-Butanol (E_T^N: 0.506)	130.0	1.47	0.994
	140.0	5.66	
	150.0		13.4
	160.0		29.1
1-Propanol[d] (E_T^N: 0.617)	150.0		5.91

[a]Normalized solvent polarity parameter values E_T [30] are informed between brackets.
[b]Correlation coefficient according to the Arrhenius equation.
[c]Rate constant value from [7].
[d]Rate constant value from [23].

$$2 \longrightarrow C_3H_7^\cdot + C_3H_7COO^\cdot \quad (4)$$

$$C_3H_7COO^\cdot \xrightarrow{HR} C_3H_7COOH \quad (5)$$

$$C_3H_7^\cdot + C_3H_7COO^\cdot \longrightarrow C_3H_7COOC_3H_7 \quad (6)$$

$$2\ C_3H_7^\cdot \longrightarrow C_6H_{14} \quad (7)$$

The presence of 4-heptanone as one of the peroxide decomposition products was recognized through the interpretation of mass spectrum and also by comparison of its retention time with that obtained by injecting an authentic sample of this compound in a gas chromatograph with FID detection. Hexane, n-propylbutanoate, butanoic acid, and propane were identified qualitatively by interpretation of their mass spectrum.

Organic chemists have usually attempted to understand the solvent effects in terms of solvent polarity. In 1968, Reichardt and Dimroth [24] proposed an empiric solvent-polarity parameter, denominated as E_T [30], which is based on the transition energy for the longest wavelength solvatochromic absorption band of the pyridinium-N-phenoxide betaine dye. A classification of the solvents according to their normalized E_T^N values [25] gives three groups related with specific solute/solvent interactions: 1-protic hydrogen bonding donor (HBD) solvents (E_T^N ca. 0.5–1), 2- dipolar non-HBD solvents (E_T^N ca. 0.3–0.5), and 3-apolar non-HBD solvent (E_T^N ca. 0–0.3). In the present work, various solvents included in these groups were used as reaction media (Table I), showing that HDP is less reactive in apolar solvents (cyclohexane, toluene [7], and 1,4-dioxane) than in protic-HBD solvents (ethanol, 1-propanol, 2-propanol, and 2-butanol) according to the k_{exp} values at 150°C (Table I, Fig. 1). Probably, these differences in the kinetic behavior of HDP in alc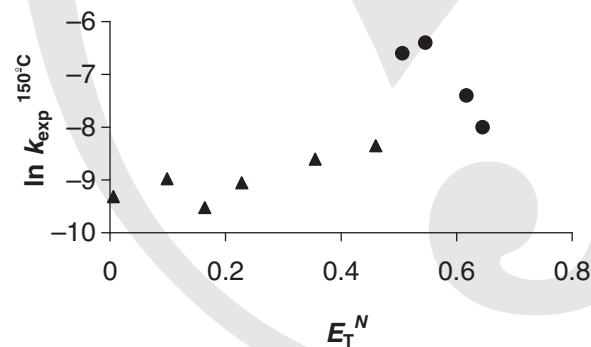ohols are responsible for the specific interactions between protic-HBD solvents and the O—O bond in the HDP molecule. Although the correlation between reactivity of HDP at 150°C and E_T^N is not exactly linear, the trend demonstrates that an increase in the solvent polarity is accompanied by an increase in reaction rates (Fig. 1). This trend could be considered as evidence in support of a reaction mechanism involving a more dipolar-activated complex than the diperoxide initial molecule. **Q7**

Considering that the activated complex represented by the biradical species **1** (Eq. (1)) is more polar than the diperoxide reactant molecule, it is easy to interpret through the Kirkwood formula [25] that the rate of reaction increases with the dielectric constant of the medium. This is because a higher dielectric constant favors the production of any highly dipolar species. In this way, acetone has a Kirkwood function value 2.3 times higher than cyclohexane, with a ratio $k_{exp}^{acetone}/k_{exp}^{cyclohexane}$ is close to 2. On the other hand, as seen from Figs. 1 and 2, although the four aliphatic alcohols have very similar dielectric constants, dipolar moments (E_T^N), and Kirkwood function [$(\varepsilon_r - 1)/(2\varepsilon_r + 1)$] values, when used as solvents they lead to different reaction rates (Figs. 1 and 2). The thermal decomposition of HDP can be accelerated by a factor close to 5 on going from ethanol as solvent to a secondary alcohol like 2-propanol. This observation strongly suggests that the polarizability of the solvent is an important factor in stabilizing the dipolar-activated complex of this reaction. In addition, it is possible to postulate an interaction between hydrogen atoms of the OH group (or hydrogen atoms bonded to C2 in secondary alcohols) and the oxygen atom of the O—O function, favoring this bond rupture. As it was described in a recent paper [26], when ethanol
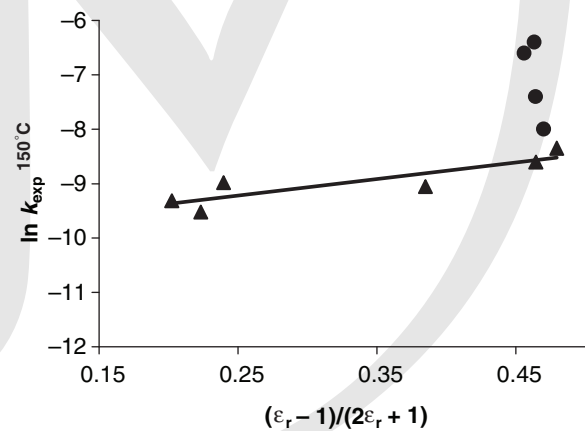

Figure 1   Correlation between the natural logarithm of the rate constant value of HPD thermolyses at 150°C, and E_T^N values of the solvents (●, aliphatic alcohols).

Figure 2   Correlation between ln k_{exp} and the Kirkwood function, $(\varepsilon_r - 1)/(2\varepsilon_r + 1)$, for the thermal decomposition reaction of HDP in solution (●, aliphatic alcohols).
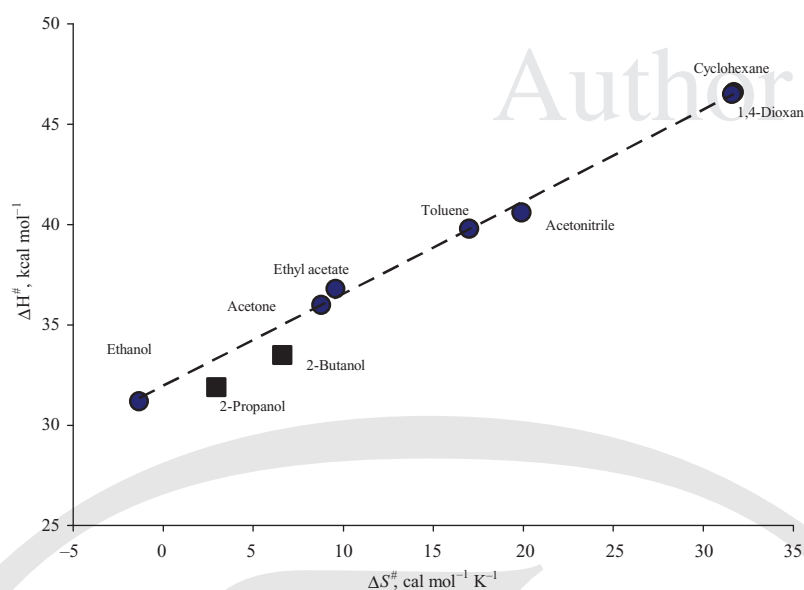
Figure 3 Enthalpy–entropy compensation for the thermal decomposition reaction of HDP in different solvents.

is the reaction solvent only the hydrogen atom of the OH group interacts with the O—O bond of the cyclic organic peroxide.

The compensation effect in the thermal decomposition reaction of HDP in solution can be observed through the linear relationship between the enthalpies and entropies of activation (Fig. 3). The experimental enthalpy and entropy of activation of HDP varied widely from 31.2 to 46.6 kcal mol^{-1} and from -1.33 to 31.7 cal mol^{-1} K^{-1}, respectively, when going from ethanol to cyclohexane as reaction solvents. These variations in activation parameters are large as compared with the probable errors of these determinations. As a consequence of this strong compensation, $\Delta G^{\ddagger}$ values remained nearly constant ($\Delta\Delta G^{\ddagger} = 2.5$ kcal mol^{-1}). The correlation coefficient of the linear plot (Fig. 3)

can be used as a criterion to judge the existence of the compensation effect; thus it is easy to deduce that the higher the correlation coefficient is the better the compensation will be. The representation of the enthalpy–entropy compensation [27] between the activation parameters for the thermolysis of HDP in nine different solvents (Table II) and Eq. (8) shows a relatively good linear dependence ($r = 0.994$; Fig. 3). It is important to emphasize that the correlation improves when the secondary alcohols are excluded ($r = 0.999$, dashed lined in Fig. 3). The slope of the line in Fig. 3 (βn Eq. (8)) is the temperature at which the rate constant is identical for all concerned reactions, and it is known as the *isokinetic temperature*. The family of reactions corresponding to the thermal decomposition of HDP in solution has a β value of 216°C (or 187°C without

Table II Activation Parameters for the Thermal Decomposition Reaction of HDP in Different Solvents   **Q8**

Solvent	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	$\Delta G^{\ddagger a}$ (kcal mol^{-1})	$k_{exp}^{150°C b}$ ($\times 10^4$ s^{-1})
Cyclohexane	46.6 ± 0.4	31.7 ± 4.8	33.2 ± 0.4	0.896
Toluene	39.8 ± 1.2	17.0 ± 2.9	32.7 ± 1.2	1.26[b]
1,4-Dioxane	46.5 ± 0.9	31.6 ± 2.2	33.2 ± 0.9	0.73
Acetone	36.0 ± 0.5	8.79 ± 1.1	32.3 ± 0.5	1.83
Acetonitrile	40.6 ± 1.2	19.9 ± 2.8	32.2 ± 1.2	2.36
Ethyl acetate	36.8 ± 2.1	9.57 ± 4.9	32.8 ± 2.1	1.17
Ethanol	31.2 ± 0.3	-1.33 ± 0.7	31.8 ± 0.7	3.41
2-Propanol	31.9 ± 1.5	2.97 ± 3.8	30.7 ± 1.5	16.7
2-Butanol	33.5 ± 1.2	6.62 ± 2.9	30.7 ± 1.2	13.4

[a]Calculated at 150°C.

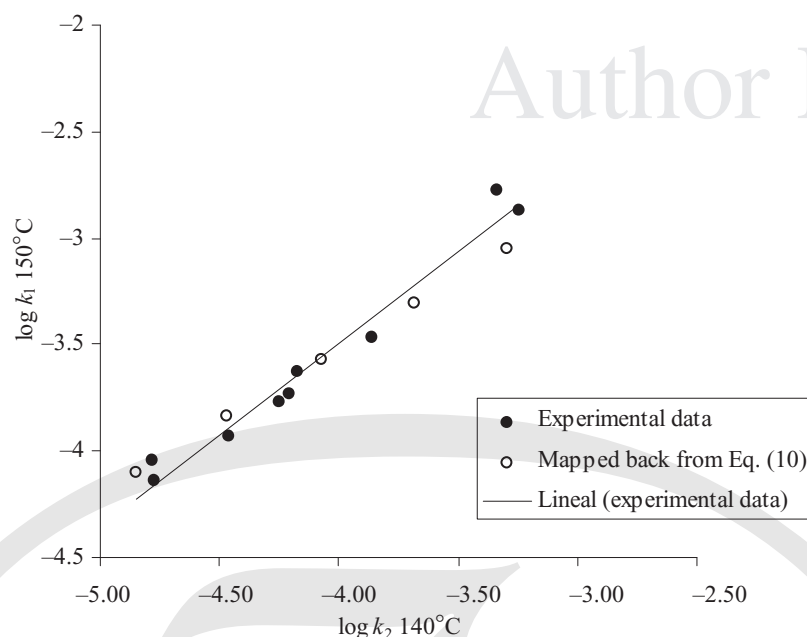[b]k_{exp} value calculated at 150°C from [7].

Figure 4 Isokinetic relationship according to Eq. (9) for the unimolecular decomposition of HDP in solution.

considering the secondary alcohols). These values are well outside of the temperature interval where the kinetic experiments have been performed (120–170°C).

$$\Delta H^{\ddagger} = \Delta H^{\circ} + \beta \Delta S^{\ddagger} \qquad (8)$$

Some authors [28,29] have suggested, on the basis of thermodynamic arguments, that the actual source of the compensation effect (Fig. 3) should be related to contributions due to solvent reorganization on forming the transition state. HDP decomposes via the formation of a more polar biradical (**1** in Eq. (1)) as an intermediate species, and the polar solvent molecules (i.e., aliphatic alcohols) should adopt specific orientations for biradical stabilization. This phenomenon may be considered as "freezing" of the solvent molecules in the transition state, and it results in lower activation entropy values than that in apolar solvents.

However, it is well recognized that the errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are correlated because they are calculated from the same set of data. It was Petersen [30] who postulated that a linear enthalpy–entropy relationship can never be, by itself, a sufficient demonstration of an isokinetic relationship. He analyzed the errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, showing that the error in $\Delta S^{\ddagger}$ is directly proportional to the error in $\Delta H^{\ddagger}$. Hence, a reaction series could generate an apparent isokinetic relationship solely through the operation of this error effect, which predicts that a plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ will be linear. Later, Liu and Guo [13] demonstrated

that the compensation effect and isokinetic effect are not necessarily synonymous and the occurrence of one does not necessarily imply the occurrence of the other.

On the other hand, Exner suggested a simple method to evaluate the isokinetic relationship [31]. It consists of plotting the decimal logarithms of the rate constants for the same reaction at two different temperatures ($\log k_1$ against $\log k_2$, with $T_1 > T_2$). When this representation is linear, it can be considered by itself an isokinetic relationship for the series (Fig. 4). The reason that this plot is a reliable test for such a relationship is that the errors in k_1 and k_2 are independent (unlike the errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$). Exner [31] showed that a linear function between the original coordinates ($\log k_1$ vs. $\log k_2$; Fig. 4) also required a linear function between the transformed coordinates and vice versa ($E^{\ddagger}$ vs. $\log A$; Fig. 5) according to Eqs. (9) and (10). The correlation between $\log k_{\exp}^{150°C}$ vs. $\log k_{\exp}^{140°C}$ for the thermal decomposition of HDP in different solvents constitutes a useful LFER to evaluate solvent–reactivity effects.

$$\log A = \frac{T_1}{T_1 - T_2}\left(\log k_1 - \frac{T_2}{T_1}\log k_2\right) \qquad (9)$$

$$E^{\ddagger} = \frac{2.303RT_1T_2}{T_1 + (-)T_2}(\log k_1 - \log k_2) \qquad (10)$$

According to this method, the isokinetic temperature can be obtained applying Eq. (11) [10,13], where
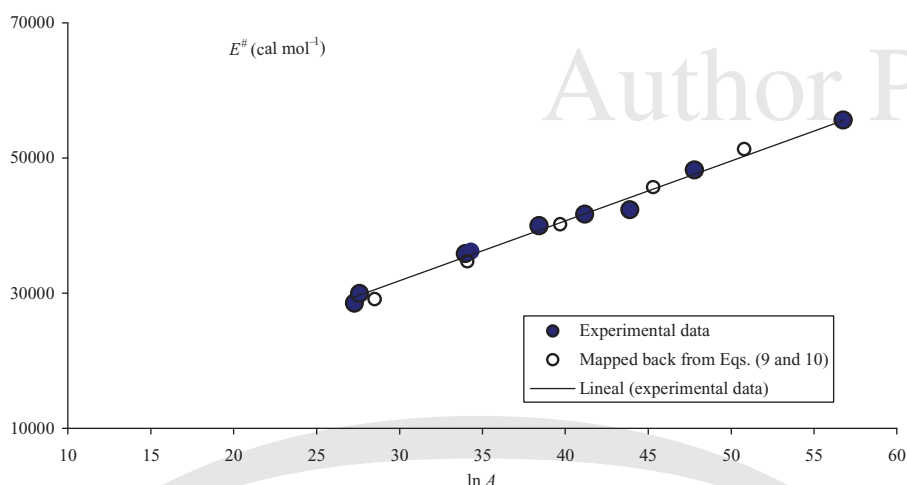
Figure 5   Isokinetic relationship according to Eq. (10) for the unimolecular decomposition of HDP in solution.
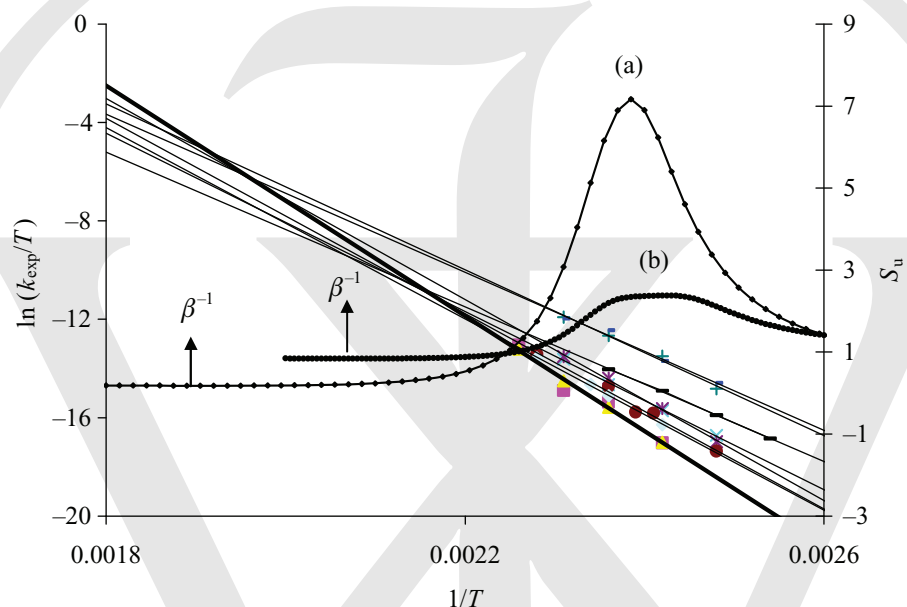

Figure 6   Dependence of S_u on the supposed isokinetic temperature β for HDP thermal decomposition in solution. (a) All solvents included, $\beta = 248°C$ and (b) secondary alcohols excluded, $\beta = 208°C$.

$b = 0.8624$ is the graphical estimated slope of the straight line determined by Eq. (9) in Fig. 4. A β value varied from $226°$ to $175°C$ with all solvents included or with secondary alcohols excluded, respectively.

$$\beta = T_1 T_2 (b - 1)/(b T_1 - T_2) \qquad (11)$$

Later, Exner [15] gave a stricter but more sophisticated method to test the isokinetic relationship based on least-squares fitting. In the method, linear regressions of experimental Arrhenius plots are done individually for each reaction of the series and under the isokinetic constraint that all regressions lines intersect

at some temperature $T = \beta$. As β is not known a priori, the residual sum of squares (S_u in Fig. 6) is calculated for trial values of β until a minimum is found. This method was often called the Exner–Linert method because Linert [17] had significantly improved the calculation procedure and the understandability of the method.

Analysis of the temperature-dependent rate constants indicates that there is no temperature such that all the rate constants of the set of reaction are close to each other. It seems that different isokinetic groups can be differentiated (Fig. 6). For example, the S_u function presents different minimum values if all solvents

were included in the calculation or when secondary alcohols were excluded. Thus the isokinetic temperature values according to this method were 248 or 208°C, respectively. It seems appropriate to consider again that the secondary alcohols have a strong interaction through two hydrogen atoms with the peroxide bond. That interaction could alter HDP reactivity, reaching the highest k_{exp} values in these solvents. The isokinetic temperature values calculated by different methods including all solvents studied or excluding secondary alcohols were higher than the experimental temperature. However, these β values obtained with Eq. (11) (Fig. 4) are subject to error problems because they were determined considering kinetic parameters at only two temperatures in a narrow temperature range ($\Delta T = 10°C$).

Q9 In summary, the compensation effect can occur when $\Delta G^{\ddagger}$ is approximately constant within the reaction series, whereas $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ vary significantly, as was observed in the present work [16]. On the other hand, the establishment of the compensation effect does not imply that the isokinetic relationship is operative at the same time, as it is shown in Figs. 3 and 6.

CONCLUSIONS

A cyclic organic diperoxide (HDP) derived from the reaction of 4-heptanone and H_2O_2 in acid media was prepared by a modified technique and appropriately purified to study its thermal decomposition in solution. The rate constant values of the thermal decomposition reaction in solution were correlated with different polarity parameters showing that they are higher in protic HBD solvents (aliphatic alcohols) than in apolar non-hydrogen donor solvents (cyclohexane, toluene, and 1,4-dioxane). This catalytic power detected when the reaction solvent is an alcohol could be explained through the existence of different and specific interaction mechanisms of alcohol/diperoxide. It was recognized that HDP decomposes via the formation of a polar biradical intermediate species, which can be stabilized by the specific orientations adopted by solvent molecules (i.e., aliphatic alcohols).

A real solvent effect affects not only the rate constant values but also the activation parameters of the thermal decomposition reaction of HDP in solution, indicating that in the studied reaction systems a dominant mechanism is operative, even so different interaction mechanisms of peroxide–solvent can be considered on the initial homolytic rupture of the O—O bond to yield the intermediate biradical species **1**. Thus, the rate of reaction is determined mainly by the environmental molecules.

Finally, the kinetic results of the thermal decomposition reaction of HDP in several solvents reveal the occurrence of the enthalpy–entropy compensation effect, whereas the isokinetic effect is observed only for a group of solvents.

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