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Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Effect of ionic liquid on the thermal decomposition of cyclic organic peroxides

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Received 22 February 2016; accepted 31 May 2016

KEYWORDS

Ionic liquid;
Solvent effect;
Thermolysis;
Cyclic organic peroxides;
Isothermal kinetics;
Thermal decomposition

Abstract The thermolysis of cyclic diethylketone triperoxide (3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane, DEKTP) and cyclic pinacolone diperoxide (3,6-diterbutyl-3,6-dimethyl-1,2,4,5-tetraoxacyclohexane, PDP) was studied in neat *N,N*-dimethylformamide (DMF) and in binary mixtures DMF/Ionic Liquid (1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM⁺][BF₄⁻]). The activation parameters for the decomposition of both peroxides in DMF, correspond to a process of homolytic cleavage of one O—O bond, generating a biradical in the initial step of radical mechanism. The rate constant values (k_d) are higher for reactions performed in mixtures. A gradual increase of [BMIM⁺][BF₄⁻] in the reaction media generates higher k_d for both peroxides (i.e. $k_{d, \text{DEKTP}}$ in DMF/[BMIM⁺][BF₄⁻] 4.0 mol L⁻¹ is 3.3 times greater than the k_d obtained for the mixture with a concentration 1.0 mol L⁻¹, under the same experimental conditions). The increase in decomposition rate can be associated with a more solvated and stabilized transition state when the ionic liquid is part of the reaction medium.

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Peer review under responsibility of King Saud University.



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1. Introduction

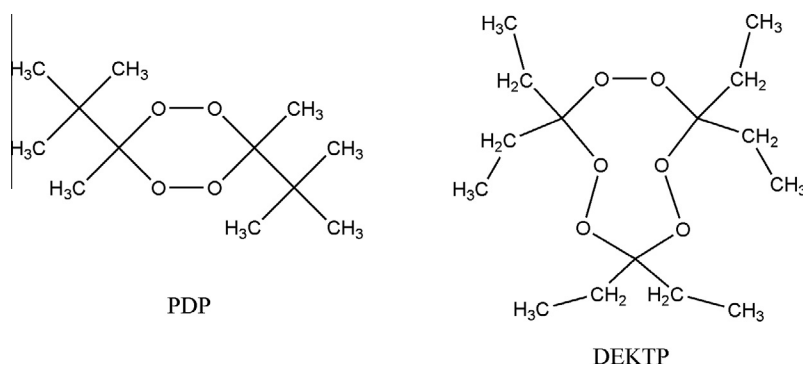
Cyclic organic peroxides, belonging to the 1,2,4,5-tetraoxacyclohexanes and 1,2,4,5,7,8-hexaoxacyclononanes substituted families have gained great importance over the last years due to their reactivity and particular behavior in different polymeric systems (Cerna et al., 2002; Sheng et al., 2004; Cañizo, 2006; Tasca et al., 2012; Nesprias et al., 2013; Barreto et al., 2014). These authors proposed the homolytic cleavage of the O—O bond during the decomposition process of these compounds, generating a biradical intermediate, which can act as an initiator in the free radical polymerization of vinyl monomers.

<http://dx.doi.org/10.1016/j.arabjc.2016.05.016>

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Please cite this article in press as: Barreto, G.P. et al., Effect of ionic liquid on the thermal decomposition of cyclic organic peroxides. Arabian Journal of Chemistry (2016), <http://dx.doi.org/10.1016/j.arabjc.2016.05.016>



Scheme 1 PDP and DEKTP structures.

Among several cyclic peroxides, two of them, the 3,6-diterbutyl-3,6-dimethyl-1,2,4,5-tetraoxacyclohexane (PDP, pinacolone diperoxide) and the 3,3,6,6,9,9-1,2,4,5,7,8-hexaethyl hexaoxacyclononane (DEKTP, diethylketone triperoxide) (Scheme 1), have been extensively studied not only from the kinetic approach but also because they have demonstrated a good performance in polymerization processes (Cerna et al., 2002; Cañizo et al., 2004a,b; Cañizo, 2006; Barreto and Eyler, 2011).

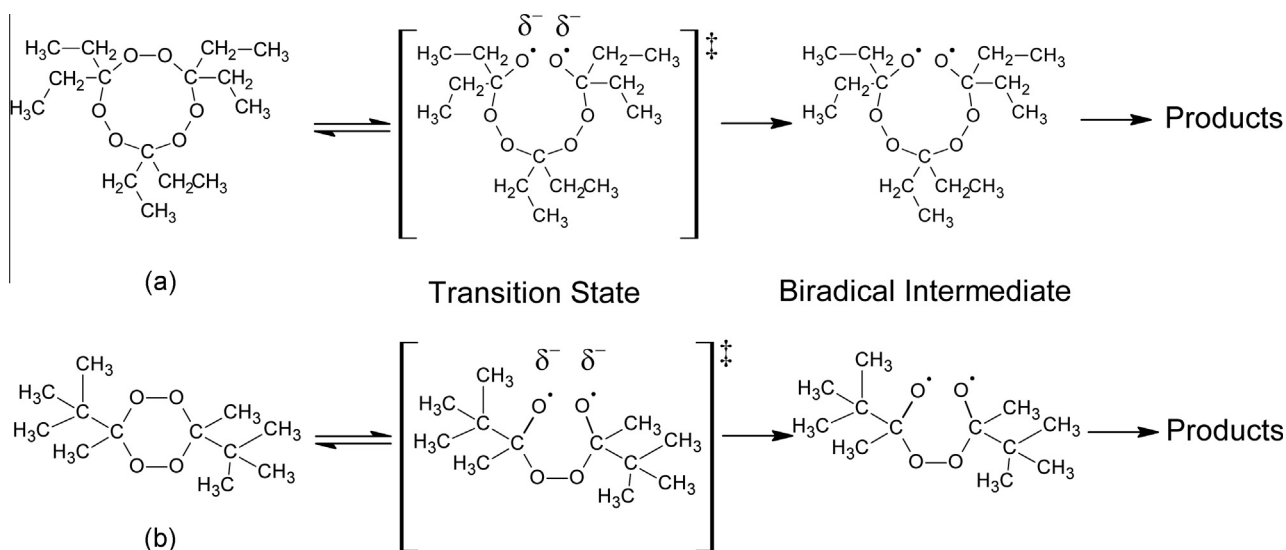
Regarding the kinetic and thermodynamic studies on the thermal decomposition of DEKTP and PDP in solution of solvents with different physicochemical properties (Eyler et al., 2002; Cañizo, 2006; Iglesias et al., 2010), the decomposition reactions obey a pseudo-first order kinetic law up to more than three half-lives for both peroxides, showing that there are no contributions from second order processes. Moreover, it was found that these cyclic peroxides thermally decomposed in solution by the homolytic cleavage of one of the O—O bonds generating a biradical intermediate (Scheme 2) which, in later stages, can decompose following different routes (Cañizo et al., 2004a,b; Cañizo, 2006). Because of radicals generation through PDP and DEKTP decomposition, these peroxides were efficiently used as *multi-functional initiators* in the radical polymerization of styrene and methyl methacrylate monomers (Cerna et al., 2002; Cañizo et al., 2004a,b; Cañizo, 2006; Barreto and Eyler, 2011).

In almost every polymeric processes where PDP and DEKTP were employed, bulk conditions were used. Although these are the simplest processes, they are associated with problems related to temperature control mixing, and increase of the system viscosity due to the produc-

tion of polymers with high molecular weights. For these reasons, at industrial scale radical polymerizations are often preferred to be performed in solution (O dian, 2004) as the use of a solvent allows a better temperature control due to heat dissipation and the decrease in the reaction mixture viscosity. In this sense, volatile organic compounds (VOCs) are the solvents most commonly used in solution polymerization due to their compatibility with monomers and ease of separating them from the final polymeric products. However, it has been well documented the negative effect on health and environment that involves the use of such solvents.

Due to contamination problems the reduction of VOCs use should be considered. In this sense, it has been emphasized in recent years the use of alternative solvents that to the environment such as water, supercritical carbon dioxide (SC-CO₂) and room temperature ionic liquids (RTILs). This last type of alternative solvents is of interest in this work.

The RTILs have been used as solvents for organic synthesis, catalysis, and in extraction processes, allowing to obtain promising results (Olivier-Bourbigou et al., 2010; Mohammad Fauzi and Amin, 2012; Almeida et al., 2014). Regarding the use of RTILs as solvents in polymerization processes to replace the conventional organic solvents, although their use in free radical polymerization is still limited, they have shown some advantages such as higher polymerization rates and molecular weights than those obtained with traditional solvents such as toluene, tetrahydrofuran, among others. This behavior has been associated with a significant increase in the ratio: propagation rate constant/termination rate constant (k_p/k_t), compared to polymer-



Scheme 2 Biradical formation through (a) DEKTP and (b) PDP thermal decomposition.

izations carried out in other polar solvents (Benton and Brazel, 2004; Li et al., 2006; Schmidt-Naake et al., 2008; Schmidt-Naake et al., 2009).

Given the results obtained independently in polymerization processes using RTIL and multifunctional initiators, the employment of multifunctional initiator-RTIL systems could generate interesting initiator-solvent systems that can give rise to polymeric materials with similar or even superior properties than those obtained with conventional systems in shorter polymerization times.

However, it must be taken into account the effects that different solvents cause (Cafferata et al., 1991; Cañizo, 2006; Barreto et al., 2014) in the decomposition of cyclic multifunctional initiators and thus, on the final properties of the obtained polymer products. So that, it is of great scientific interest to study the effects of RTILs on the decomposition of this family of peroxides, particularly on PDP and DEKTP, for their later use in the polymerization of various vinyl monomers.

Therefore, herein a complete kinetic study of the thermal decomposition of DEKTP and PDP in 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM⁺][BF₄⁻] is described.

2. Material and methods

2.1. Materials

DEKTP and PDP were prepared following the methods described in the literature (Eyler et al., 1993; Eyler et al., 2002) by the reaction of the corresponding ketone (Fluka, pro-analysis grade) with hydrogen peroxide (Riedel-de Haën, pro-analysis grade, 30%) in sulfuric acid media (Merck, 70% v/v) at -15 and -20 °C, respectively. Peroxides purity (m.p.(DEKTP) 59–60 °C and m.p.(PDP) 122–124 °C) was checked by gas chromatography (GC) and ¹H and ¹³C NMR.

Caution: peroxides must be handled with care because they can be detonated by shock.

Naphthalene used as internal standard in GC determinations (Mallinckrodt, pro-analysis grade) and *N,N*-dimethylformamide (DMF, 99.8%, Aldrich) were purified according to techniques described in the literature (Riddick et al., 1986; Perrin and Armarego, 1988) and their purity was checked by GC analysis. RTIL, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM⁺][BF₄⁻], from Aldrich) was employed without further purification.

2.2. Kinetic methods

Since it is not possible to determine the decomposition constant of the PDP and/or DEKTP initiators in [BMIM⁺][BF₄⁻], due to the insolubility of the reagents, it was necessary to include a solvent capable of dissolving both reactants. For this purpose, DMF was considered as a solvent.

Stock solutions of DMF:[BMIM⁺][BF₄⁻] with different concentration of [BMIM⁺][BF₄⁻] (1.0, 2.7 and 4.0 mol L⁻¹) were prepared with a DEKTP and/or PDP concentration of 0.01 mol L⁻¹. Thereafter, Pyrex glass tubes (7 cm in length × 4 mm i.d.) half filled with the appropriate amount of the solutions previously prepared, were degassed under vacuum at -196 °C (liquid nitrogen bath) and then sealed with a flame torch. To carry out the experiment, the ampoules were immersed in a thermostatic silicone oil bath at the desired temperature (±0.1 °C) and removed after predetermined periods of times, stopping the reaction by cooling them in an ice-water bath (0 °C).

The corresponding pseudo first-order rate constant values (*k_d*) were calculated from the slope of the line obtained by a least mean square treatment of the experimental data by plotting the values of ln[DEKTP] or [PDP] concentration vs. reaction time, attending to a pseudo first order kinetic law (Eq. (1)). All experiments were performed in duplicate.

$$\ln [\text{Peroxide}]_t = -k_d t \quad (1)$$

The temperature effect and the activation parameters were worked out from the Arrhenius (Eq. (2)) and Eyring (Eq. (3)) equations, respectively.

$$\ln k_d = -\frac{E_a}{RT} + \ln A \quad (2)$$

$$\ln \left(\frac{k_d}{T} \right) = -\frac{\Delta H^\ddagger}{R} \frac{1}{T} + \frac{\Delta S^\ddagger}{R} + \ln \frac{\kappa k_B}{h} \quad (3)$$

where *R* is the gas constant, *T* is the absolute temperature, *h* is Planck's constant, *k_B* is the Boltzmann constant and *κ* is a constant known as the transmission coefficient and is often taken to have a value of unity and we have followed this convention above. This approach implies that those species that reached the transition state always proceed to products and never revert to reactants.

2.4. Analytical techniques

GC quantitative and reaction products analyses were performed in a Thermo Quest Trace 2000 CG model gas chromatograph with a BPX70 (70% Cyanopropyl polysilphenylene-siloxane, 30 m, 0.25 mm i.d., 0.25 μm film thickness) capillary column. Helium was used as the carrier gas (1 mL min⁻¹) and the injection port was at 150 °C in split mode (split ratio: 1:33, split flow: 33 mL min⁻¹). The detection was carried out with a Finnigan Polaris Ion trap MS with the transfer line at 210 °C and ion source at 200 °C. The oven temperature was maintained at 50 °C for 4 min, then programmed a ramp temperature of 10 °C min⁻¹ to 250 °C for 15 min. Solutions containing RTIL were injected in the injector port containing a cotton packed liner, to prevent the RTIL entering the capillary column. The packaging was changed every 10 injections (Figs. S1 and S2).

3. Results and discussion

3.1. Thermal decomposition of DEKTP and PDP in pure DMF

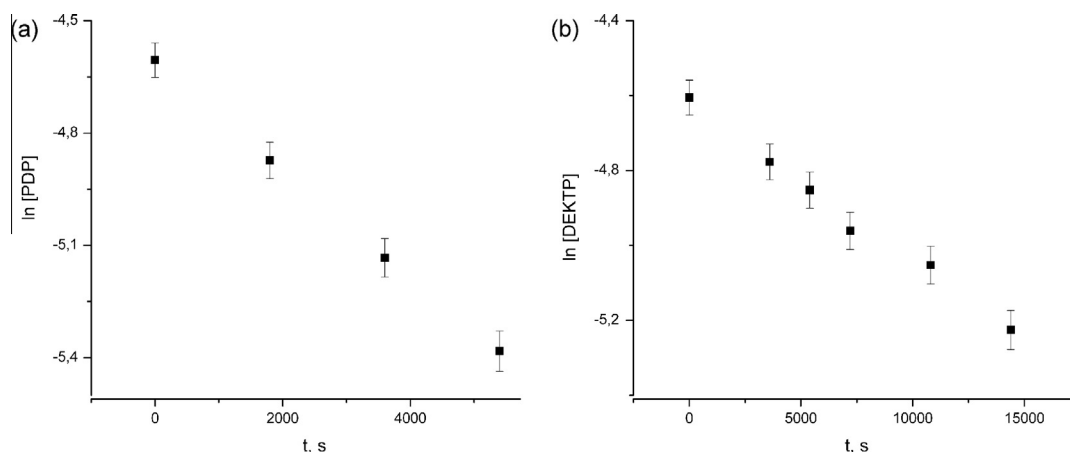
3.1.1. Kinetic studies

Thermal decompositions of DEKTP and PDP (*ca.* 10⁻² mol L⁻¹) in DMF were studied in the temperature range between 120 and 150 °C (Fig. S3). The kinetic data obtained showed, in all cases, a linear correlation according to a first order kinetic law, so it could be considered that under the experimental conditions employed, the reactions followed a pseudo-first order kinetic law up to at least 60% of DEKTP and 70% of PDP conversion, respectively (Table 1 and Fig. 1).

As it was described by other authors (Cerna et al., 2002; Eyler et al., 2002), PDP has a higher reactivity when compared with DEKTP. At each temperature, the *k_d* PDP is *ca.* 3 times higher than those obtained for DEKTP probably due to a large extent of solvation of DMF in the case of DEKTP.

Table 1 Pseudo-first-order rate constant values of the thermal decomposition of DEKTP and PDP in DMF.

Temperature (°C)	$k_{d, \text{PDP}} \times 10^5 \text{ (s}^{-1}\text{)}$	$t_{1/2, \text{PDP}} \text{ (min)}$	R	$k_{d, \text{DEKTP}} \times 10^5 \text{ (s}^{-1}\text{)}$	$t_{1/2, \text{DEKTP}} \text{ (min)}$	R^a
120	5.44	212.3	0.9981	1.48	780.6	0.9985
130	14.40	80.2	0.9997	4.21	274.4	0.990
140	42.60	27.1	0.9999	12.90	89.5	0.9998
150	101.23	11.4	0.9932	33.25	34.8	0.9897

**Figure 1** Representation through first-order kinetic plots of the data obtained in typical thermolysis experiments of (a) PDP and (b) DEKTP in DMF solution at 130 °C.

The temperature effect on the DEKTP and PDP rate constant values was evaluated using the Arrhenius equation (Eqs. (4) and (5), respectively):

$$\ln k_{d, \text{DEKTP}} = (32.88 \pm 0.71) - (34384 \pm 1000) \frac{1}{RT} \quad (4)$$

$$\ln k_{d, \text{PDP}} = (31.86 \pm 1.02) - (32563 \pm 1000) \frac{1}{RT} \quad (5)$$

The linearity of the Arrhenius equations ($R_{\text{DEKTP}} = 0.9993$ and $R_{\text{PDP}} = 0.9989$) over a wide temperature range, 40 °C, suggested that the activation parameters and the pre-exponential factor for the decomposition of both peroxides in DMF, correspond to a process of homolytic cleavage of one O—O bond (Fig. S4).

The kinetic data obtained in this work, and other results previously described by various authors for different cyclic peroxides (Cafferata et al., 1984; Cafferata et al., 1990; Cafferata et al., 1991; Eyler et al., 1994; Eyler et al., 2000; Barreto and Cañizo, 2004; Cañizo et al., 2004a, b; Sheng et al., 2004; Cañizo, 2006; Iglesias et al., 2009), allowed to associate the rate constants with the unimolecular rupture process of one peroxidic bond as the rate-determining step of the decomposition route (Scheme 2).

The activation parameters were calculated from the Eyring equation whose representation is linear in the temperature range studied (Fig. 2).

The activation parameters determined by the Eyring equation, for both peroxides (Tables 2 and 3 for DEKTP and PDP, respectively) allowed to postulate a similar decomposition mechanism in comparison with other solvents employed. In this sense, it can be observed that a change in the value of the enthalpy of activation (ΔH^\ddagger) is accompanied by a change

in the entropy of activation (ΔS^\ddagger) in the same direction, implying a compensation effect. However, the similarity in the free energy of activation (ΔG^\ddagger) values establishes that peroxides decomposition occurs through the homolytic cleavage of one of the O—O bonds (Scheme 2).

In previous studies (Eyler et al., 2002; Cañizo, 2006), it has been found that k_d values obtained from kinetic determinations in solvents with different physicochemical properties are sensitive to solvent polarity and are well correlated with the Dimroth–Reichardt solvent polarity parameter ($E_T(30)$) (Reichardt, 1965). The results reported in Tables 2 and 3, show that an increase in solvent polarity allows to obtain a higher rate constant value for both peroxides.

3.1.2. Reaction products

The reaction products of both peroxides, DEKTP and PDP were analyzed by GC–MS. All fragmentations in the mass spectra obtained showed similar signals, typical of substituted amides structures ($m/z = 44, 58, 72, 86$). As it was demonstrated in the case of the use of other solvents (Barreto et al., 2014), it is possible to postulate a radical chain mechanism (Scheme 3) with products derived from radical couplings. The compounds identified are consistent with the initial homolytic scission of one O—O bond and a common mechanism of fragmentation of the biradical formed. The biradical formed through homolytic scission can diffuse from solvent cage to form products by various radical pathways. One possibility could be the generation of a solvent radical. These radicals derived from solvent are produced by hydrogen extraction accordingly with coupling products identified.

In case of PDP, the results show several peaks in the chromatograms that can be justified attending the formation

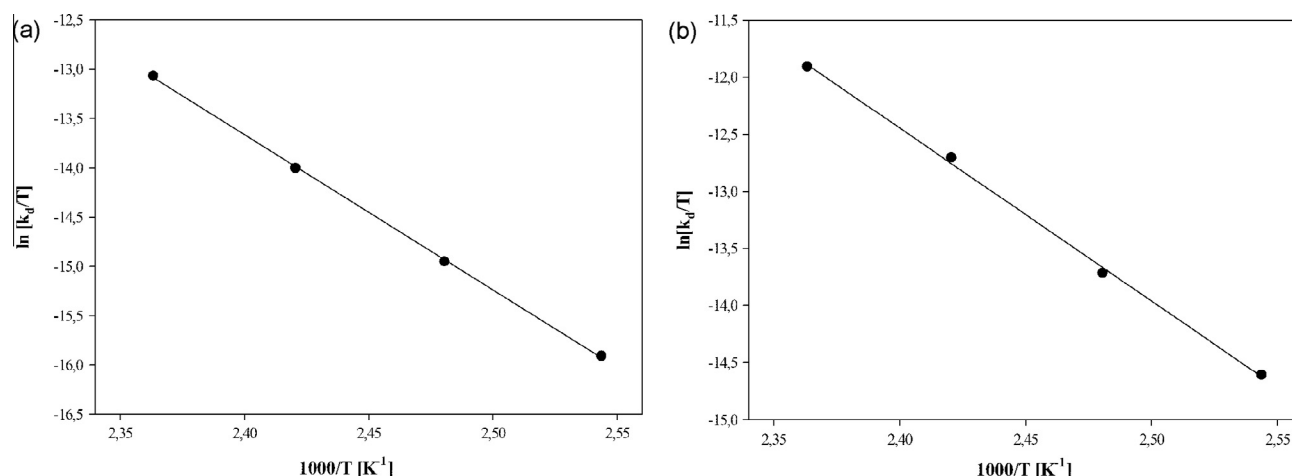


Figure 2 Eyring plots corresponding to the thermal decomposition of (a) DEKTP and (b) PDP 0.01 mol L⁻¹ in DMF.

Table 2 Thermal decomposition activation parameters for DEKTP (0.01 M) in different solvents.

Solvent	k_d 150°C × 10 ⁴ (s ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)
Ethylbenzene ^a	1.54	38.0 ± 1.1	13.0 ± 2.6	32.9 ± 1.1
DMF	3.32	33.6 ± 0.9	6.2 ± 2.1	31.1 ± 0.9
Ethanol ^b	2.47	41.0 ± 1.6	21.3 ± 4.0	32.3 ± 1.6
Benzene ^c	1.82	42.3 ± 1.4	23.6 ± 3.2	32.5 ± 1.4
Toluene ^c	1.63	48.2 ± 1.7	37.2 ± 4.2	32.5 ± 1.7

^a Barreto and Eyler (2011).

^b Barreto et al. (2014).

^c Eyler et al. (1994).

Table 3 Thermal decomposition activation parameters for PDP (0.01 M) in different solvents.

Solvent	k_d 140°C × 10 ⁵ (s ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)
Benzene ^a	27.41	29.8 ± 0.6	-1.5 ± 1.5	30.4 ± 0.6
DMF	42.63	31.7 ± 0.8	4.18 ± 1.2	30.0 ± 0.8
Acetic Acid ^b	43.42	32.2 ± 1.4	5.3 ± 3.6	30.0 ± 1.4
Acetonitrile ^b	30.53	34.6 ± 0.6	10.8 ± 1.5	30.1 ± 0.6
Toluene ^b	29.62	34.6 ± 1.2	8.8 ± 3.0	31.0 ± 1.2

^a Cafferata et al. (1990).

^b Cafferata et al. (1991).

of *tert*-butyl radicals (more stable than those derived from DEKTP, ethyl radicals) which attack the solvent (*N,N*-dimethylpivalamide; *N*-methyl-*N*-neopentylformamide; Scheme 3a). Other common products for both peroxides present in the analyses seem to be the result of couplings of radicals derived from solvent (*N,N,N',N'*-tetramethyloxalamide; Scheme 3b). From the GC-MS analysis it can be concluded that only the solvent participates in the formation of the final product but also coupling between radical derived from the initiator and the solvent and radicals derived from the solvent.

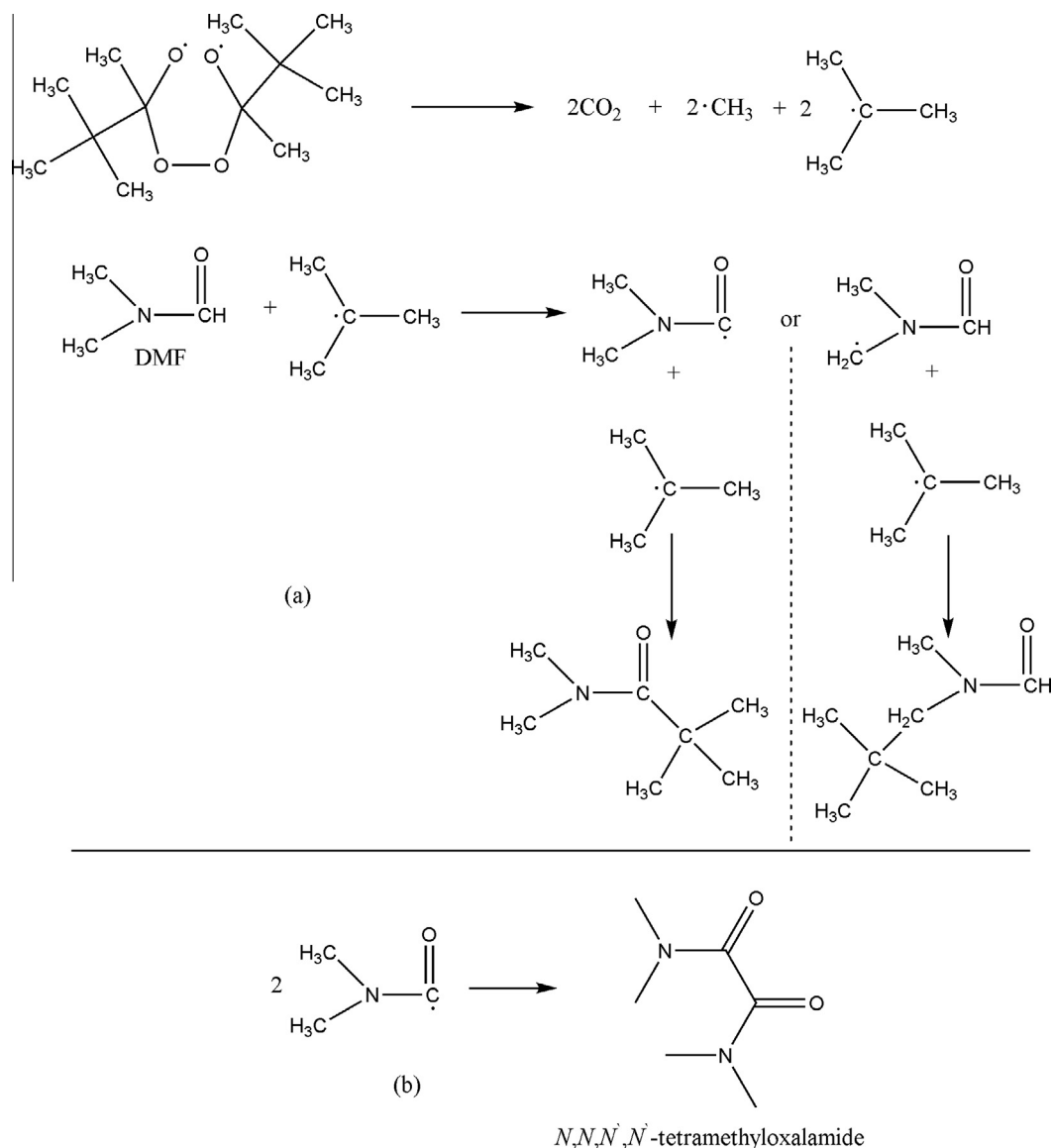
3.2. Kinetic effect of RTIL on peroxides decomposition

3.2.1. DEKTP thermal decomposition in DMF/RTIL mixtures

The determination of the decomposition rate constant (k_d) of both initiators DEKTP and PDP in the mixture DMF:

[BMIM⁺][BF₄⁻], was performed varying the concentration of [BMIM⁺][BF₄⁻] in 1.0, 2.7 and 4.0 mol L⁻¹, that correspond to a relationship DMF:[BMIM⁺][BF₄⁻] equal to 3:1, 1:1 and 1:3, respectively (Fig. S5).

The initial concentration of peroxides in the solutions was *ca.* 0.01 mol L⁻¹, so that induced decomposition was probably small enough to be neglected. The different reaction systems studied showed a consistent behavior with a pseudo-first-order kinetic law up to at least 60% peroxide decomposition. The initial transition state formed during the peroxide decomposition (Scheme 2) would not be solvated to the same extent as the starting species due to differences in the substituents, ring size and conformational isomers of both initiators. The differences in solvation of the initial and the intermediate state could cause changes in reaction rate and activation parameters.



Scheme 3 Product formation mechanism corresponding to (a) thermal decomposition of PDP and its reaction with the solvent molecule and (b) reaction between solvent radicals.

Decomposition rate constants and half-lives ($t_{1/2}$) of DEKTP (0.01 mol L^{-1}) in DMF/[BMIM⁺][BF₄⁻] mixtures are shown in Table 4.

At all temperatures the same behavior can be seen. The addition of [BMIM⁺][BF₄⁻] results in an increase in the dissociation constant. In this sense, k_d in neat DMF reaches a value of $0.15 \times 10^{-4} \text{ s}^{-1}$ at $120 \text{ }^\circ\text{C}$ while when RTIL is added in concentrations 1.0, 2.7 and 4.0 mol L^{-1} the determined constants are 0.2, 0.5 and 0.9 s^{-1} , respectively. A gradual increment of DEKTP rate constant can be seen while the [BMIM⁺][BF₄⁻] concentration increases. Preliminarily, it appears to be no preferential solvation process of DMF or RTIL with the peroxide.

The temperature effect on the rate constant values of DEKTP decomposition in DMF/[BMIM⁺][BF₄⁻] mixtures can be represented by the Arrhenius equation. The Eqs. (6)–(8) correspond to the Arrhenius analysis for RTIL concentrations of 1.0, 2.7 and 4 mol L^{-1} , respectively.

$$\ln k_{d,1.0} = (35.05 \pm 2.13) - (35952 \pm 900) \frac{1}{RT} \quad (6)$$

$$\ln k_{d,2.7} = (27.01 \pm 0.90) - (28814 \pm 400) \frac{1}{RT} \quad (7)$$

$$\ln k_{d,4.0} = (24.46 \pm 2.71) - (26372 \pm 1100) \frac{1}{RT} \quad (8)$$

The linearity of the Arrhenius equation ($R = 0.9973$, 0.9995 and 0.9925 , respectively) in the relatively broad range of temperatures, $40 \text{ }^\circ\text{C}$, suggests that the calculated activation parameters (activation energy and pre-exponential factor) for the decomposition of DEKTP in the mixture DMF/[BMIM⁺][BF₄⁻], at different concentrations, correspond to a single process which can be associated with the homolytic cleavage of one O—O bond (Fig. S6(b)).

The activation parameters (ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger), corresponding to the decomposition of DEKTP in the mixtures

Table 4 Decomposition rate constants and half-lives ($t_{1/2}$) of DEKTP (0.01 mol L⁻¹) in DMF/[BMIM⁺][BF₄⁻] mixtures in the temperature range 120–150 °C.

Temperature (°C)	[BMIM ⁺][BF ₄ ⁻] (mol L ⁻¹)	$k_d \times 10^4$ (s ⁻¹)	$t_{1/2}$ (min)	R^a
120	1.0	0.2	735.07	0.9969
130	1.0	0.6	184.96	0.9978
140	1.0	1.5	74.31	0.9986
150	1.0	4.3	26.67	0.9985
120	2.7	0.5	225.28	0.9960
130	2.7	1.3	86.51	0.9937
140	2.7	2.9	39.27	0.9992
150	2.7	7.2	16.04	0.9996
120	4.0	0.9	134.40	0.9991
130	4.0	2.1	55.68	0.9988
140	4.0	5.5	20.84	0.9978
150	4.0	8.6	13.13	0.9984

Table 5 Thermal decomposition activation parameters of DEKTP (0.01 mol L⁻¹) in different mixtures DMF/[BMIM⁺][BF₄⁻] in the temperature range 120–150 °C.

Reaction media	$k_{d,130} \times 10^4$ (s ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)	R^a
DMF	0.42	33.6 ± 0.9	6.2 ± 2.1	31.1 ± 0.9	0.9999
DMF/[BMIM ⁺][BF ₄ ⁻] 1.0 mol L ⁻¹	0.62	35.1 ± 0.9	10.5 ± 2.1	30.8 ± 0.9	0.9969
DMF/[BMIM ⁺][BF ₄ ⁻] 2.7 mol L ⁻¹	1.33	28.0 ± 0.4	-5.5 ± 0.9	30.2 ± 0.4	0.9994
DMF/[BMIM ⁺][BF ₄ ⁻] 4.0 mol L ⁻¹	2.07	25.3 ± 1.1	-11.3 ± 2.7	29.9 ± 1.1	0.9910

DMF/[BMIM⁺][BF₄⁻] were calculated from the Eyring equation (Table 5).

As it was mentioned in Section 3.1 for the case of pure solvents, there also seems to exist a compensation effect between the activation parameters in the systems evaluated. The fact that the values of ΔG^\ddagger are substantially similar, allows to conclude that the same type of reaction might be taking place, i.e. the unimolecular decomposition of one O—O bond (pseudomonomolecular reaction attending to transition state theory).

On the other hand, the addition of ionic liquid to the reaction medium affects the rate constant of DEKTP increasing it as the ionic liquid content increases (Table 3). The results obtained show that the k_d in DMF/[BMIM⁺][BF₄⁻] 4.0 mol L⁻¹ is 3.3 times greater than the k_d obtained for the mixture with a concentration 1.0 mol L⁻¹, under the same experimental conditions. This increase can be associated with a change in the medium as the concentration of [BMIM⁺][BF₄⁻] increases.

Moreover, it is important to note that increasing the concentration of [BMIM⁺][BF₄⁻] to 2.7 mol L⁻¹, the effect on the activation parameters is relevant, varying ΔH^\ddagger and ΔS^\ddagger from 35.1 kcal mol⁻¹ and 10.5 cal mol⁻¹ K⁻¹ to 28 kcal mol⁻¹ and -5.5 cal mol⁻¹ K⁻¹, respectively. Thus, a high concentration of [BMIM⁺][BF₄⁻] in the reaction medium allows a greater interaction DEKTP:DMF:[BMIM⁺][BF₄⁻] causing a destabilization of the initiator molecule which leads to a faster decomposition of the initiator in the direction of formation of the bi-radical shown in Scheme 2. In addition, it can be observed (Table 4) that the ΔS^\ddagger values decrease with increasing

RTIL concentration, which is in accordance with the decrease in translational and rotational degrees of freedom of the transition state, which is mostly solvated by DMF/[BMIM⁺][BF₄⁻] mixture, with the consequent increase in k_d .

3.2.2. PDP thermal decomposition in DMF/RTIL mixtures

The kinetic data obtained in all the reaction systems studied showed a consistent behavior, an approximately linear correlation according to a pseudo-first-order kinetic law at each concentration of [BMIM⁺][BF₄⁻] up to high PDP conversions (> 70%). Thus, under the established experimental conditions, the reactions can be considered as first order (Table 6). The behavior is the same as in the case of DEKTP, and an increase in RTIL concentration allows to obtain higher rate constants at all temperatures (Fig. S5).

The linearity of the Arrhenius equation (Eqs. (9)–(11)) ($R = 0.9960, 0.9998, 0.9998$, respectively) in an interval of 40 °C, suggests, as for DEKTP, that the activation energy and the pre-exponential factor for the decomposition of the PDP in DMF/[BMIM⁺][BF₄⁻] mixtures correspond to the unimolecular simple process mentioned before (Fig. S6(a)).

$$\ln k_{d,1.0} = (35.05 \pm 3.60) - (35913 \pm 1470) \frac{1}{RT} \quad (9)$$

$$\ln k_{d,2.7} = (30.78 \pm 0.77) - (30537 \pm 310) \frac{1}{RT} \quad (10)$$

$$\ln k_{d,4.0} = (28.74 \pm 0.72) - (28800 \pm 300) \frac{1}{RT} \quad (11)$$

Table 6 Decomposition rate constants and half-lives ($t_{1/2}$) of PDP (0.01 mol L⁻¹) in DMF/[BMIM⁺][BF₄⁻] mixtures in the temperature range 120–150 °C.

Temperature (°C)	[BMIM ⁺][BF ₄ ⁻] (mol L ⁻¹)	$k_d \times 10^4$ (s ⁻¹)	$t_{1/2}$ (min)	R^a
120	1.0	0.94	122.96	0.9989
130	1.0	2.17	53.11	0.9985
140	1.0	5.49	21.04	0.9980
150	1.0	16.95	6.82	0.9985
120	2.7	2.41	47.92	0.9963
130	2.7	6.66	17.36	0.9961
140	2.7	16.73	6.90	0.9971
150	2.7	38.47	3.00	0.9975
120	4.0	2.91	39.71	0.9974
130	4.0	7.65	15.11	0.9979
140	4.0	17.48	6.61	0.9989
150	4.0	40.24	2.87	0.9956

Table 7 Thermal decomposition activation parameters of PDP (0.01 mol L⁻¹) in different mixtures DMF/[BMIM⁺][BF₄⁻] in the temperature range 120–150 °C.

Reaction media	$k_{d,130\text{ °C}} \times 10^4$ (s ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)	R^a
DMF	1.44	31.7 ± 0.8	4.18 ± 1.2	30.0 ± 0.8	0.9993
DMF/[BMIM ⁺][BF ₄ ⁻] 1.0 mol L ⁻¹	2.17	30.9 ± 0.9	2.9 ± 2.3	29.7 ± 0.9	0.9952
DMF/[BMIM ⁺][BF ₄ ⁻] 2.7 mol L ⁻¹	6.66	29.7 ± 1.0	2.0 ± 0.8	28.9 ± 1.0	0.9997
DMF/[BMIM ⁺][BF ₄ ⁻] 4.0 mol L ⁻¹	7.65	27.9 ± 1.1	-2.0 ± 1.3	27.1 ± 1.1	0.9998

Also, through the Eyring equation, the ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger values at each ratio DMF/[BMIM⁺][BF₄⁻] were calculated (Table 7).

It can be observed a minor effect on the activation parameters as the content of ionic liquid increases from 1.0 to 2.7 mol L⁻¹. According to the results obtained in earlier studies, the rate constant corresponding to the thermal decomposition of DPP it is not significantly affected when the reaction is carried out in different solvents (Cafferata et al., 1990; Cañizo and Cafferata, 1992). This behavior can be attributed to the presence of tertbutyl substituents that generate impediments in interactions with the reaction medium.

Also, as a result of changes in the medium, by increasing the concentration of [BMIM⁺][BF₄⁻], it can be observed that the k_d for PDP is 3.5 times greater for a concentration 4.0 mol L⁻¹ in comparison with the k_d at 1.0 mol L⁻¹ under the same experimental conditions.

This can also be substantiated with the activation parameters where while increasing the concentration of [BMIM⁺][BF₄⁻], the activation energy for the decomposition of PDP decreases facilitating the O—O bond cleavage. Furthermore, the decrease in the values of ΔS^\ddagger as the concentration of [BMIM⁺][BF₄⁻] increases, is an indicative of the decrease in translational and rotational degrees of freedom of the PDP molecule, evidencing a greater interaction in the transition state between PDP and the mixture DMF:[BMIM⁺][BF₄⁻].

Furthermore, the decrease in the values of ΔS^\ddagger as the concentration of [BMIM⁺][BF₄⁻] increases, is an indicative of the decrease in translational and rotational degrees of freedom of the PDP molecule, evidencing a greater interaction in the tran-

sition state between PDP and the mixture DMF:[BMIM][BF₄], as the entropy of activation decreases.

3.2.3. DEKTP and PDP thermal decomposition rate constants in pure [BMIM⁺][BF₄⁻]

To obtain the extrapolated rate dissociation constant ($k_{d,ext}$) at a concentration of 5.35 mol L⁻¹ [BMIM⁺][BF₄⁻], equivalent to pure IL, for both DEKTP and PDP decomposition in [BMIM⁺][BF₄⁻], the rate constants previously calculated at each concentration (1.0, 2.7 and 4.0 of [BMIM⁺][BF₄⁻]), in the temperature range of 120–150 °C, were considered. There were also considered the values for the decomposition of both initiators in pure DMF, which were previously reported.

In this sense, Fig. 3 presents the plot of $\ln k_d$ in DMF/[BMIM⁺][BF₄⁻] mixtures as a function of [BMIM⁺][BF₄⁻] molar concentration for the thermal decomposition reaction of DEKT (Fig. 2a) and PDP (Fig. 2b) in the temperature range 120–150 °C.

The tendency, in the case of DEKTP was linear in all cases, i.e.; k_d value increases as the concentration of [BMIM⁺][BF₄⁻] increases as well. For the PDP, quadratic trends were found, where the value of k_d increases with the concentration of [BMIM⁺][BF₄⁻], but when [BMIM⁺][BF₄⁻] concentration exceeds 2.7 mol L⁻¹ the increase in k_d is almost negligible, i.e. at 150 °C $k_{d,RTIL2.7} = 38.47 \times 10^{-4} \text{ s}^{-1}$ and $k_{d,RTIL4} = 40.24 \times 10^{-4} \text{ s}^{-1}$. Moreover, the k_d increase was higher in the case of PDP in comparison with DEKTP at all temperatures when the RTIL concentration increased from 1.0 to 2.7 mol L⁻¹.

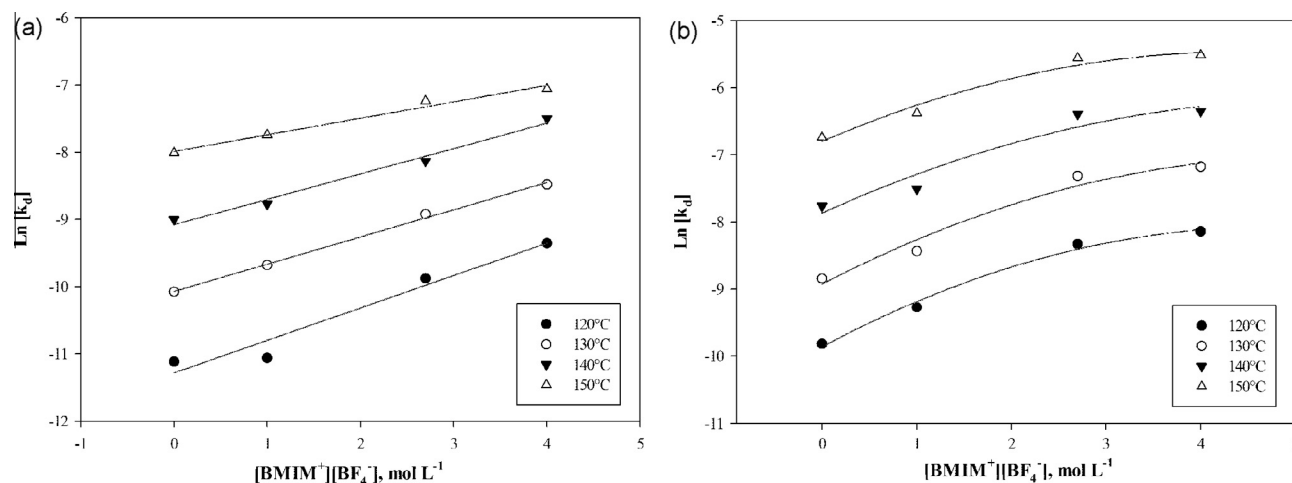


Figure 3 Graphical representation of k_d vs concentration of $[\text{BMIM}^+][\text{BF}_4^-]$ at each evaluated temperature (120–150 °C) applied to: (a) DEKTP (0.01 mol L⁻¹) and (b) PDP (0.01 mol L⁻¹) decomposition.

Table 8 Extrapolated decomposition rate constants and half-lives ($t_{1/2}$) of DEKTP and PDP (0.01 mol L⁻¹) in $[\text{BMIM}^+][\text{BF}_4^-]$ in the temperature range 120–150 °C.

Temperature (°C)	$k_{d,\text{ext DEKTP}} \times 10^4$ (s ⁻¹)	$t_{1/2}$ (min)	$k_{d,\text{ext PDP}} \times 10^4$ (s ⁻¹)	$t_{1/2}$ (min)
120	1.66	69.42	3.05	37.89
130	3.11	31.14	8.94	12.92
140	6.85	16.86	20.74	5.57
150	12.67	9.12	39.66	2.91

In each case, from the trends at each temperature, the value for the maximum concentration of $[\text{BMIM}^+][\text{BF}_4^-]$ was replaced; i.e. 5.35 mol L⁻¹, and the values for the $k_{d,\text{ext}}$ were obtained (Table 8).

From Table 8 it can be observed that the decomposition of PDP proceeds much faster than that of DEKTP which can be attributed to a lower solvation of PDP by the $[\text{BMIM}^+][\text{BF}_4^-]$, making it more susceptible to decomposition. The interactions between PDP and $[\text{BMIM}^+][\text{BF}_4^-]$ are lower than those in the case of DEKTP, stabilizing the latter in the presence of the RTIL presenting lower k_d .

4. Conclusions

The dissociation constants of PDP and DEKTP in DMF/ $[\text{BMIM}^+][\text{BF}_4^-]$ mixtures, at different concentrations of $[\text{BMIM}^+][\text{BF}_4^-]$ (1.0, 2.7 and 4.0 mol L⁻¹) in the temperature range of 120–150 °C were determined. The calculated k_d for the PDP, in the whole concentration range and temperatures tested was higher than the k_d for DEKTP. This was associated with the size of the substituents, conformation of the molecule and the size of the ring.

An increase in the concentration of $[\text{BMIM}^+][\text{BF}_4^-]$ decreases the decomposition activation energy (E_a) facilitating the cleavage of the O–O bond, PDP being more susceptible to cleavage.

Extrapolated dissociation constants in $[\text{BMIM}^+][\text{BF}_4^-]$ were determined for the first time for both initiators in the temperature range of 120–150 °C. The decomposition in the case of DEKTP presented a linear increase as a function of $[\text{BMIM}^+][\text{BF}_4^-]$ concentration, while for the PDP there is a linear increase only to a concentration of 2.7 mol L⁻¹, and exceeding this concentration linearity is lost.

Acknowledgments

Authors thank CONACyT for the Ph.D. grant to Karla Delgado and to CONACyT (Bilateral Project Mexico-Argentina No. 190268), CONICET and CICPBA for the financial support.

K. Delgado stay in Argentina was funded by the Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA). AIC and GPB are members of the Career of Scientific and Technological Research of the Scientific and Technical National Research Council (Consejo Nacional de Investigaciones Científicas y Técnicas, CONICET).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2016.05.016>.

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