

Thermal Decomposition of Diethylketone Cyclic Triperoxide in Polar Solvents

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The thermolysis of diethylketone cyclic triperoxide (3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane, DEKTP) was studied in different polar solvents (ethanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, and acetonitrile). The rate constant values (k_d) are higher for reactions performed in secondary alcohols probably because of the possibility to form a cyclic adduct with the participation of the hydrogen atom bonded to the secondary carbon. The kinetic parameters were correlated with the physicochemical properties of the selected solvents. The products of the DEKTP thermal decomposition in different polar solvents support a radical-based decomposition mechanism.

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Introduction

The participation of organic peroxides in various processes, ranging from biological (oxidation of membrane lipids), industrial (initiation of polymerization processes, cross-linking agents, disinfectants, bleaches), and environmental (air pollutants) processes to those involved in security systems (terrorist explosives) make the chemistry of these compounds of great interest in different research fields.^[1–3]

The reaction between carbonyl compounds and hydrogen peroxide affords the formation of peroxidic compounds, both open chain and cyclic. Such reactions are carried out using an inorganic acid as catalyst and at relatively low temperatures (−20°C to 0°C). In this work, the thermolysis of diethylketone cyclic triperoxide (3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane, DEKTP, **Chart 1**) was studied in different polar solvents

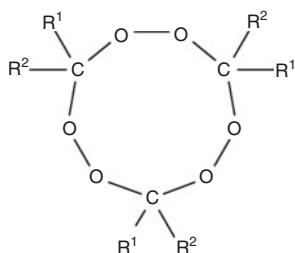


Chart 1. 1,2,4,5,7,8-hexaoxacyclononane structure. DEKTP: $R^1 = R^2 = -CH_2CH_3$.

(ethanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, and acetonitrile).

The reactivity of these compounds can be explained by the relatively low energy of the O–O bond, i.e. $\sim 45 \text{ kcal mol}^{-1}$,^[4] responsible for the instability observed in peroxides. In addition to this weak linkage, it is known that organic peroxides are very labile in the presence of some catalysts, such as traces of metallic ions, and can accelerate the decomposition process.^[5] There are several kinetic and thermodynamic data for the thermal decomposition of DEKTP in solvents of different physicochemical properties.^[3] In all cases, the decomposition reaction obeys a pseudo-first-order kinetic law, achieving a DEKTP conversion of up to $\sim 80\%$, showing that there are no contributions from second-order processes.

It is known that this type of cyclic peroxide is thermally decomposed in solution by homolytic cleavage of one of the O–O bonds, generating a biradical intermediate (**Scheme 1**), which can be decomposed by different pathways in the later stages of the decomposition process.^[3,6] Because radicals formation is possible through DEKTP, the latter peroxide has been efficiently used as a multifunctional initiator for radical polymerization process of styrene and methyl methacrylate monomers.^[3,7–9]

The pseudo-first-order rate constants (k_d s) for the decomposition of DEKTP in various solvents, reported in the literature,^[3] showed that the rate of decomposition was faster in polar solvents than in non-polar solvents. The objective of this work is to provide a more complete study of the thermal

decomposition of DEKTP in polar protic solvents (i.e. alkyl alcohols) and in aprotic solvents such as acetonitrile, which is rarely reported in the literature.

Experimental

Materials

DEKTP was prepared according to methods described in the literature report,^[10] involving the reaction between 3-pentanone (Fluka, pro-analysis grade) and hydrogen peroxide (Riedel-de Haën, pro-analysis grade, 30 %) in sulfuric acid (Merck, 70 % v/v) at -15 to -20°C . The purity of DEKTP (mp 59 – 60°C) was evaluated by gas chromatography (GC).

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

Naphthalene (Mallinckrodt, pro-analysis grade), ethanol (Merck, pro-analysis grade), 2-butanol (Merck, pro-analysis grade), 2-propanol (Merck, pro-analysis grade), 1-butanol (Dorwil, pro-analysis grade), 2-methyl-2-propanol (Merck, pro-analysis grade), and acetonitrile (Fluka, pro-analysis grade) were purified according to techniques described in the literature reports^[11,12] and their purity was assessed by GC. For alcohols whose synthesis involves metal cations, treatment with a sodium salt of ethylene diamine tetraacetic acid ($\text{Na}_2\text{-EDTA}$, Merck, pro-analysis grade) was carried out before distillation.^[5]

Kinetic Methods

Pyrex glass tubes (7 cm long \times 4 mm i.d.) were half-filled with the appropriate DEKTP solution, and degassed under vacuum at -196°C (liquid nitrogen bath), then sealed with a flame torch. The ampoules were immersed in a thermostatic silicone oil bath ($\pm 0.1^{\circ}\text{C}$) and removed after pre-determined times. The reaction was stopped by cooling the mixture-containing ampoules in an ice-water bath (0°C).

The pseudo-first-order rate constant values (k_d s) were calculated from the slope of the line obtained by a least mean square analysis of the experimental data by plotting the values of \ln (DEKTP concentration) vs reaction times. The activation parameters were calculated using the Eyring equation:

$$\ln\left(\frac{k_d}{T}\right) = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} + \ln\left(\frac{R}{N_A h}\right)$$

where ΔH^\ddagger is the activation enthalpy, ΔS^\ddagger activation entropy, T is the temperature at which each constant (k_d) was determined, R is the general gas constant, N_A is Avogadro's number (6.02×10^{23} molecules mol^{-1}) and h is Planck's constant (6.63×10^{-34} J s).

Analytical Techniques

GC analyses were performed on a Konik KNK 2000 C equipped with a DB-5 capillary column (5 % biphenyl, 95 %

dimethylpolysiloxane; 30 m long, 0.32 mm i.d., 0.25- μm film thickness). Nitrogen was used as carrier gas at a constant pressure of 23.5 psi at the top of the column. The linear velocity through the column was 29.4 cm s^{-1} at 60°C . The injector operated in the split mode at 150°C and flame ionization detector (FID) at 250°C , with nitrogen as the make-up gas (30 mL min^{-1}). The oven temperature was maintained at 80°C for 5 min and then programmed at a heating rate of $20^{\circ}\text{C min}^{-1}$ to achieve a final temperature of 160°C that was maintained for 10 min. Under these experimental conditions, the retention time of DEKTP was 13.8 min.

The reaction products were determined by gas chromatography mass spectrometry (GC-MS), using a BPX70 capillary column (70 % cyanopropyl polysilphenylene-siloxane; 30 m long, 0.25 mm i.d., 0.25- μm film thickness), a Thermo Quest Trace 2000 CG model gas chromatograph with helium as carrier gas (1 mL min^{-1}), and an injection port operating in split mode at 150°C (split ratio: 1:33; split flow: 33 mL min^{-1}). The detection was carried out with a Finnigan Polaris Ion trap MS with a transfer line at 210°C and ion source at 200°C . The oven temperature was maintained at 50°C for 4 min then programmed at $10^{\circ}\text{C min}^{-1}$ to achieve a final temperature of 205°C that was maintained for 5 min.

Results and Discussion

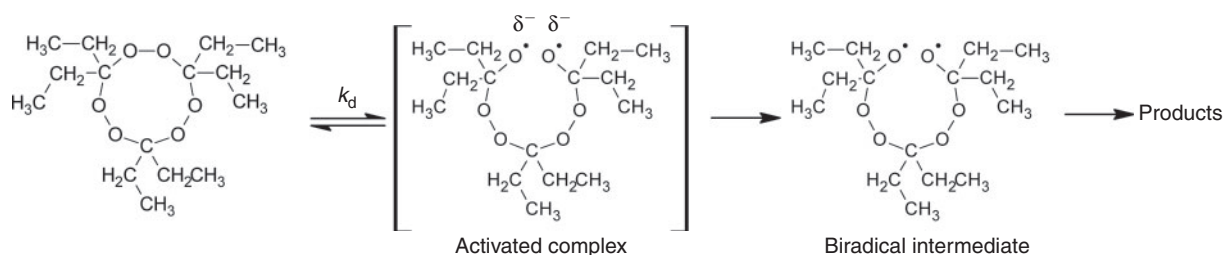
Thermal Decomposition of DEKTP

Thermal decomposition of DEKTP ($\sim 10^{-2} \text{ mol L}^{-1}$) was studied at 150°C in polar protic and aprotic solvents. Two primary alcohols (ethanol and 1-butanol), two secondary alcohols (2-propanol and 2-butanol), and one tertiary alcohol (2-methyl-2-propanol) were selected as polar protic solvents, and acetonitrile as polar aprotic solvent (Table 1). All reactions followed a pseudo-first-order kinetic law, with a DEKTP conversion of 65 % or more.

The kinetic data obtained in this work and other results described previously by other authors for different cyclic peroxides^[3,6,9,13–20] confirm that the rate constant corresponds to the mono-molecular rupture process of one peroxidic bond as the rate-determining step of the decomposition process (Scheme 1).

The thermal decomposition of DEKTP in acetonitrile at 150°C and in 2-butanol was evaluated by varying the initial concentration of DEKTP from 0.01 to 0.05 mol L^{-1} and 0.01 to 0.02 mol L^{-1} , respectively (Table 1). The rate constant values are mostly unaffected by the initial triperoxide concentration.

The rate constant values obtained for reactions involving the secondary alcohol were slightly higher (~ 18 – 28 %) than those obtained for reactions using primary alcohols as solvents. This behaviour is similar to that reported for the thermal decomposition of triacetone triperoxide in alcohols (TATP: $\text{R}^1 = \text{R}^2 = -\text{CH}_3$, Chart 1),^[21] whereby a solute–solvent



Scheme 1. DEKTP homolytic decomposition.

interaction mechanism through the formation of cyclic species was proposed. In the case of thermal decomposition of DEKTP in 2-methyl-2-propanol, the rate constant was twice as low as the rate constants obtained when secondary alcohols were used as solvents. Other authors reported the same behaviour for different peroxides in 2-methyl-2-propanol^[22,23] that could be attributed to the large size of the *tert*-butyl substituent that inhibited the formation of specific interactions.

In all cases, a change in ΔH^\ddagger in the thermolysis reaction of DEKTP was accompanied by a change in ΔS^\ddagger (compensation effect). The values of ΔG^\ddagger are mostly constant within the experimental errors (Table 2). These results indicate that the reaction mechanism is the same in all solvents.

The values of the activation parameters of DEKTP thermolysis show linear correlations according to the Leffler treatment,^[24] indicating an isokinetic relationship. In these cases, the corresponding plot gives an isokinetic temperature of 445.4 K (172.25°C), which is outside the temperature range that was used for the kinetic measurements. This correlation is valid for a wide temperature range ($\sim 32^\circ\text{C}$) and activation parameter range ($\Delta\Delta H = 18.2 \text{ kcal mol}^{-1}$, $\Delta\Delta S = 40.3 \text{ cal mol}^{-1} \text{ K}^{-1}$).

In previous studies,^[3] it has been found that k_d values obtained from kinetic determinations in some solvents with different physicochemical properties are sensitive to an increase in solvent polarity and are well correlated with the Dimroth–Reichardt solvent polarity parameter ($E_T(30)$)^[25] (Fig. 1). The

$E_T(30)$ scale is based on the extremely solvatochromic character of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridiniumyl) phenoxide whose strong basic character is known to instigate significant shifts in hydrogen-bond donor solvents.^[26] When the rate constant values obtained in solution of alcohols are inserted to the graph in Fig. 1, it can be observed that those values fall outside the trend established for other solvents including acetonitrile. The reaction in alcohols is slower than expected considering the polarity parameter mentioned earlier. On the other hand, in polar aprotic solvents, such as acetonitrile and acetone, the k_d values are comparable and higher than those obtained in alcohols.

Fig. 2 shows the relationship between the rate constant values of DEKTP decomposition at 150°C in different solvents and the solvent polarity/polarizability parameter (SPP).^[27] This parameter is not influenced by specific solvent interactions. The rate constant values for the decomposition of DEKTP in different aprotic solvents show a good trend; an increase in solvent polarity (in accordance to the SPP scale) allows increased rate constant values (Fig. 2). However, the behaviour differs when thermal decomposition is carried out in alcohols; the constants obtained are lower than those expected according to the trend observed for the other solvents.

Because of the similar values of SPP for the alkyl alcohols (0.841 ± 0.012), a linear correlation between $\ln k_d$ and SPP is not observed (Fig. 2). In addition, as observed from Fig. 2, SPP and k_d values for acetone and acetonitrile are greater than the corresponding values for alkyl alcohols.

Considering the acidic character of the alcohols, different specific interactions with the peroxide molecule are expected

Table 1. Pseudo-first-order rate constant values of the thermal decomposition of DEKTP in polar solvents

Solvent	$T [^\circ\text{C}]$	Concentration of DEKTP [mol L^{-1}]	$k_d^A \times 10^4 [\text{s}^{-1}]$	r^{2B}
Ethanol	120.0	0.02	0.052	0.973
	130.0	0.02	0.163	0.991
	140.0	0.02	0.834	0.988
	150.0	0.02	2.47	0.998
	150.0	0.01	2.70	0.997
1-Butanol	150.0	0.01	3.11	0.999
2-Propanol	150.0	0.01	1.11	0.998
2-Butanol	140.0	0.01	3.04	0.998
	150.0	0.01	3.33	0.995
	160.0	0.02	7.90	0.997
2-Methyl-2-propanol	150.0	0.01	1.48	0.997
	150.0	0.05	4.63	0.999
Acetonitrile	120.0	0.01	0.19	0.997
	130.0	0.01	0.52	0.997
	140.0	0.01	1.44	0.999
	150.0	0.01	4.79	0.999
	150.0	0.05	4.63	0.999

^APseudo-first-order rate constant values for thermal decomposition of DEKTP.

^BLinear correlation coefficient of the corresponding kinetics plots.

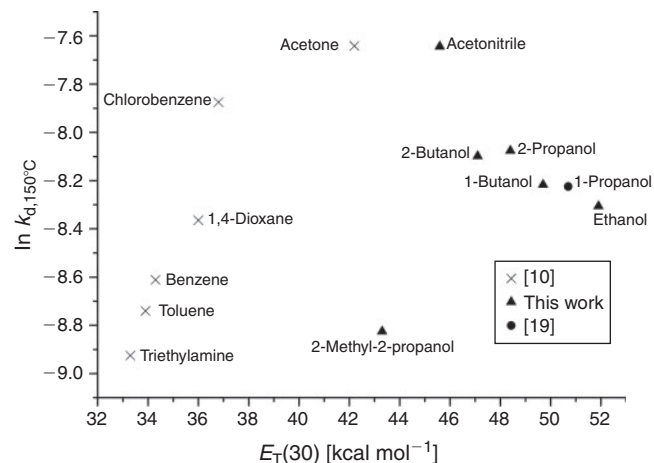


Fig. 1. Relationship between DEKTP decomposition rate constant values and empirical Dimroth's parameter at 150°C in different solvents.

Table 2. Activation parameters for the thermal decomposition of DEKTP in different solvents

Solvent	SPP	ΔH^\ddagger [kcal mol^{-1}]	ΔS^\ddagger [$\text{cal mol}^{-1} \text{ K}^{-1}$]	ΔG^\ddagger [kcal mol^{-1}]	$k_{d,150} \times 10^4 [\text{s}^{-1}]$
Ethanol	0.853	42.9 ± 1.6	25.8 ± 4.0	32.4 ± 1.6	2.47
Acetonitrile	0.895	34.4 ± 0.8	6.70 ± 1.9	31.7 ± 0.8	4.71
2-Butanol	0.842	34.8 ± 0.8	7.1 ± 1.9	31.8 ± 0.8	3.18 ± 0.14
Acetone ^[9]	0.881	30.0 ± 2.3	-3.10 ± 0.9	31.3 ± 2.3	4.80
Toluene ^[3]	0.655	48.2 ± 1.7	37.2 ± 4.2	32.5 ± 1.7	1.60
1,4-Dioxane ^[10]	0.701	45.0 ± 1.9	30.1 ± 4.6	32.3 ± 1.9	2.33

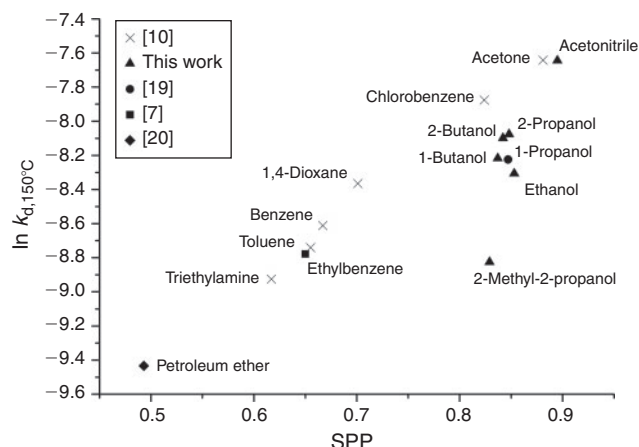


Fig. 2. Relationship between DEKTP decomposition rate constant values and SPP at 150°C in different solvents.

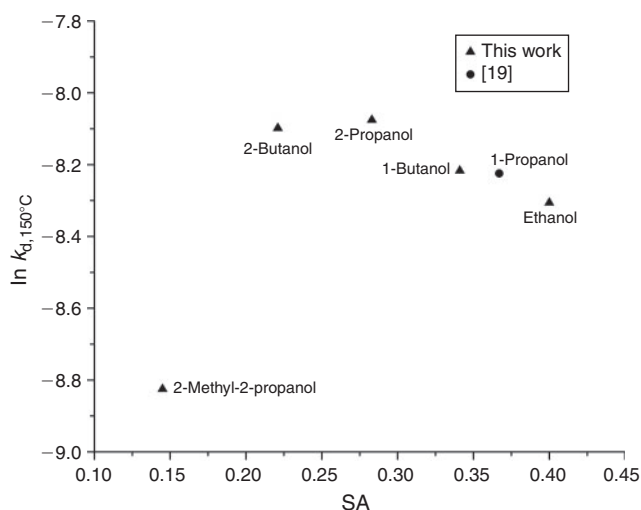


Fig. 3. Dependence of the rate constant values of DEKTP on SA at 150°C in different alcohols.

consequently, the kinetics parameters should be different. For this purpose, the relationship between the rate constant and the solvent acidity (SA)^[27] is examined to analyze the effect of possible specific interactions on the rate constant of DEKTP decomposition, as shown in Fig. 3.

The reactivity of DEKTP in 2-methyl-2-propanol appears to be unusually low. In contrast, an increase in the acidity appears to decrease the decomposition rate constant, as observed for the other five alcohols that feature a higher acidic character. Also, every secondary alcohol molecule is capable to form two hydrogen bonds with the O–O bond in the peroxide molecule, forming a cyclic adduct (Chart 2).

This species promotes O–O cleavage as the initial step in the thermal decomposition of DEKTP (Scheme 1). On the other hand, only one hydrogen bond can be formed between primary alcohols and the peroxidic bond; thus, a slower triperoxide decomposition reaction is obtained.

Reaction Products of DEKTP Thermal Decomposition in Polar Solvents

The reaction products of the DEKTP thermal decomposition in alcohols were analyzed by GC–MS (Table 3). The identified

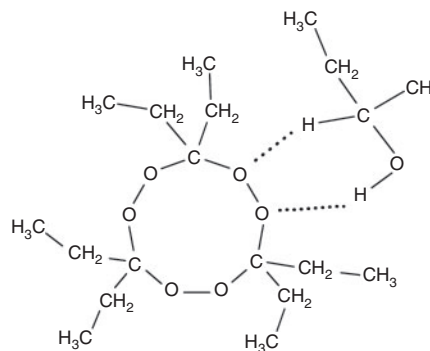


Chart 2. Cyclic adduct formation from reaction between DEKTP and a secondary alcohol (2-butanol).

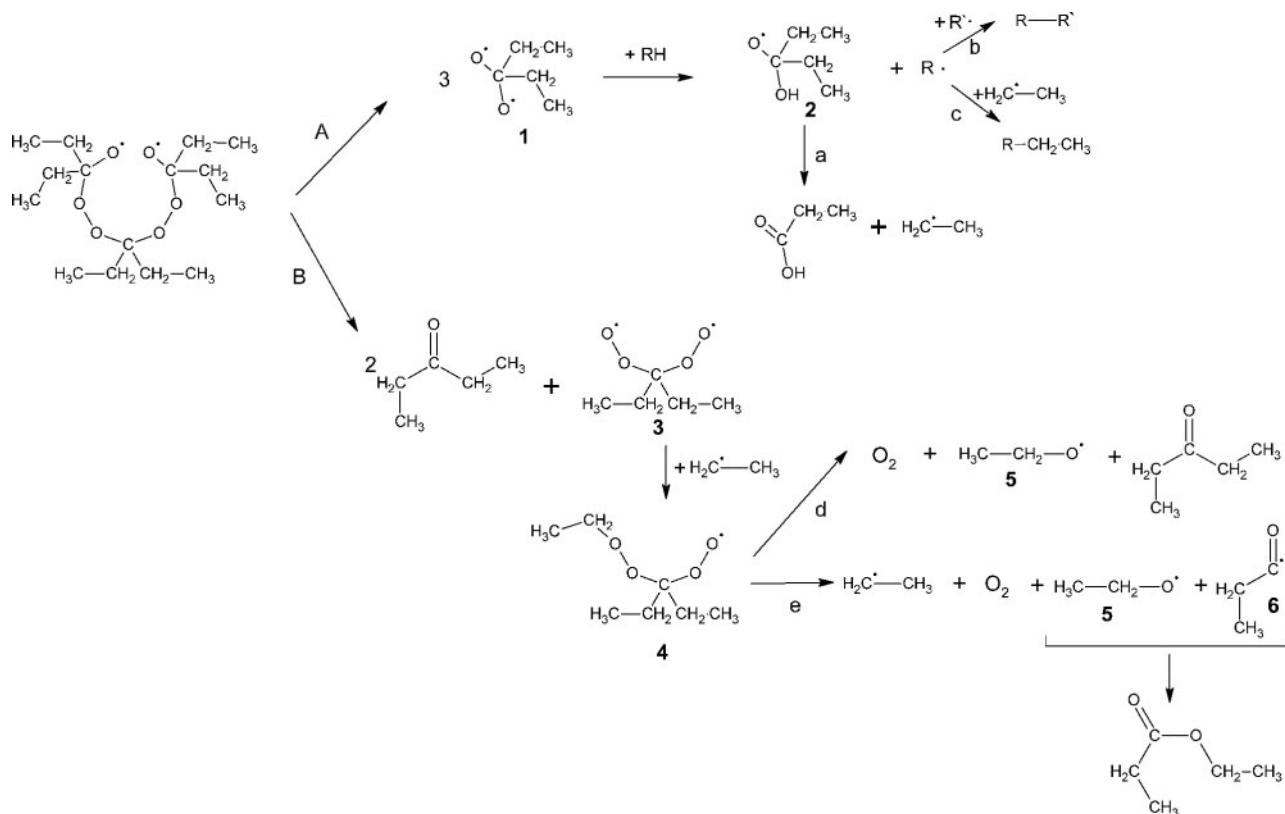
Table 3. Reaction products of DEKTP thermal decomposition in polar solvents identified by GC–MS

Solvent	Products
Ethanol	Ethyl propanoate, 3-pentanone, propanoic acid, 2,3-butanediol
1-Butanol	Butanal, 3-pentanone, propanoic acid, 4,5-octanediol, 2-ethyl-1,3-hexanediol
2-Butanol	2-Butanone, ethyl propanoate, 3-pentanone, 3-methyl-3-pentanol, propanoic acid, 3,4-dimethyl-3,4-hexanediol
2-Propanol	Ethyl propanoate, 3-pentanone, propanoic acid, 2,3-dimethyl-2,3-butanediol
2-Methyl-2-propanol	Ethyl propanoate, 3-pentanone, 2-methyl-2-pentanol, propanoic acid, 2,5 dimethyl-2,5-hexanediol
Acetonitrile	Butanenitrile, butanedinitrile, 3-pentanone, ethyl propanoate

compounds are consistent with the occurrence of an initial homolytic scission of a O–O bond, a common mechanism of fragmentation, leading to the formation of a biradical.

The biradical formed via homolytic scission can diffuse out of the solvent cage to form products via various radical pathways (Scheme 2). It can be fragmented by O–O scission (route A, Scheme 2) to produce intermediate 1 that can then react with the solvent to form intermediate 2 and a solvent radical. These radicals derived from solvent are produced by α - and, in some cases (1-propanol and 1-butanol), β -hydrogen extraction together with coupling products that were identified. Intermediate 2 can decompose by C–C cleavage to form propanoic acid (route a, Scheme 2)—the latter product was found in all solvent systems studied—and ethyl radical, which is involved in different reaction pathways. Radicals derived from solvent can react to form the coupling products discussed later (route b, Scheme 2) or they can interact with ethyl radicals (route c, Scheme 2) to produce ethyl–solvent products, as observed in the 2-butanol and 2-methyl-2-propanol solvent systems.

Contrarily, the biradical can fragment by C–O cleavage (route B, Scheme 2) to produce 3-pentanone and intermediate 3, which in turn can react with ethyl radical to generate intermediate 4. The latter intermediate may fragment via C–O and O–O scissions (route d, Scheme 2) to form oxygen, intermediate 5, and 3-pentanone or via C–O and C–C cleavage (route e, Scheme 2) to produce ethyl radical, oxygen, and intermediates 5 and 6. These last two intermediates can combine to generate ethyl propanoate, another common product found in



Scheme 2. Radical decomposition mechanism for DEKTP biradical.

the different systems. The proposed reaction mechanism correlates with the products identified in the different solvents employed.

In some cases, solvent oxidation reaction products were observed (i.e. propanal in 1-propanol, butanal in 1-butanol, and 2-butanone in 2-butanol).

Some of the products of the DEKTP thermal decomposition in acetonitrile (i.e. butanenitrile and butanedinitrile) justified the radical mechanism proposed (paths b and c in Scheme 2).

Conclusions

The thermal decomposition of DEKTP in polar aprotic and protic solvents follows a pseudo-first-order kinetic law, achieving a triperoxide conversion of 65 % or more. The rate constant values (k_d s) are higher for reactions performed in secondary alcohols probably because of the formation of a cyclic adduct via interactions between a hydrogen atom and the secondary carbon. The formation of two hydrogen bonds with the peroxidic bond contributes to the fast decomposition reaction.

A reaction mechanism is proposed based on the analysis of the thermal decomposition products, whereby the initial step involves the formation of a biradical intermediate via homolytic scission of an O–O bond.

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