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Kinetics of the thermal decomposition reaction of diethylketone cyclic triperoxide in acetone–toluene and acetone–1-propanol binary solvent mixtures

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The thermal decomposition reaction of diethylketone triperoxide (DEKT) *ca*. 0.02 M was studied in binary mixtures of acetone–toluene and acetone–1-propanol at 150 °C. Products of DEKT thermolysis in solution, detected by GC analysis, were diethylketone, bibenzyl and butane. The reactions were explored by GC at different solvent compositions and in each case the reactions followed a pseudo first order kinetic law, up to at least 90% peroxide conversion. The rate coefficient value of the reaction is affected by the solvent properties, showing an increase in the k_{obs} values with increases in the polarity of the solvent mixture in acetone–toluene systems. Changes in the rate coefficient values are probably caused by the presence of the apolar toluene solvent, which dominates the preferential solvation around the DEKT molecule through non-specific interactions. In acetone–1-propanol mixtures the solvation effect is slightly dominated by the specific interactions between the 1-propanol and a polar intermediate specie represented by the biradical, initially formed. The rate coefficient value increases *ca*. 6% in the mixture with 0.1 mole fraction of 1-propanol in comparison with the value in pure acetone; but no more changes in rate coefficient values are observed when the amount of the alcohol increases. The critical state of the reaction (intermediate biradical) is preferentially solvated by the 1-propanol instead of acetone, but in mixtures of different composition, it is not possible to detect any effect on the reactivity for homolytic rupture of the O—O bond. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: diethylketone triperoxide; kinetics in solution; binary mixtures

INTRODUCTION

It is well known that the rates and courses of many chemical reactions are deeply influenced by the solvent used in these processes.[1] These effects are understood as a result of changes in the specific and non-specific polar interactions which cover the overall solvent capability of the solvent. The unimolecular homolysis of diethylketone cyclic triperoxide (1,2,4,5,7,8-hexaoxa-3,3,6,6,9,9-hexaethylcyclononane, diethylketone triperoxide (DEKT), Reaction 1) has been investigated in both polar and non-polar solvents. In previous works,[2–4] it was demonstrated that the thermal reaction of DEKT (Reaction 1) is affected by the solvent polarity. As an example, the rate coefficient at 150 °C in pure acetone (mildly polar aprotic solvent) is *ca*. three times higher than in pure toluene (non-polar aprotic solvent) (Table 1).

The experimental pseudo first order rate coefficient, k_{obs}, for the unimolecular homolysis of DEKT in different pure solvents[4] is well correlated with the Dimroth–Reichardt solvent polarity parameter[1,5] $E_T(30)$ according to the relationship ln k_{obs} *versus* $E_T(30)$ ($r^2 = 0.9643$). The k_{obs} values were sensitive to an increase in solvent polarity showing how complex the interactions of the solvent molecules are with the peroxide molecule and/or with the intermediate biradical formed in the solvent cage reaction. The rate-determining first step of the mechanism (Reaction 1) is the rupture of the O—O bond which is influenced by the

physicochemical characteristics of the solvent cage or the microsphere of solvation of the triperoxide. Physicochemical studies of solvent properties normally include an interest in mixed solvents, which have increased in recent years.[4,6,7] For kinetic and mechanistic studies, mixed solvents have the advantage of providing the opportunity to continuously vary the reaction conditions, in contrast to the most abrupt changes arising from studies of solvent effects in pure solvents or substituent effects. The main disadvantage of mixed solvents is that the interpretation of the data is more complex than in pure solvents. In binary solvents, solvent–solvent interactions should be considered together with solute–solvent interactions. As it is known, in solvent mixtures the solutes can interact, to a different degree, with the components of the mixture, and this difference in the interaction is reflected in the composition of the

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Table 1. Pseudo first order rate coefficient values (k_{obs}) of the thermal decomposition reaction of DEKT at 150 °C in acetone–toluene binary mixtures and its refractive indexes

Toluene mole fraction (X_T)	Refractive index (η)	$E_T^N(30)^a$	k_{obs} (10^{-4} s^{-1})
0	1.3596	0.355	2.55
0.05	1.3714	0.349[b]	2.28
0.10	1.3837	0.343	2.30
0.20	1.4071	0.327	2.19
0.30	1.4217	0.309	2.17
0.50	1.4477	0.275	1.85
0.70	1.4764	0.241	1.69
1	1.4970	0.099	1.52[c]

[a] From Reference 12.
[b] Interpolated values from data in Reference 12.
[c] From Reference 3.

microsphere of solvation, the so-called cybotatic region, which is different from the composition of the bulk solvent.

Up to now, few systematic studies in mixed solvents have been carried out with DEKT. In a first attempt to systematize the study of the solvent effects in binary mixtures, we reported the kinetic data in acetone–water mixtures of different composition.[8] In the present work, it was of interest to evaluate the solvent effects of some reported non-synergetic and synergetic binary mixtures on the thermal decomposition of diethylketone cyclic triperoxide. We now report the study of the above reaction in binary mixtures of acetone–toluene (aprotic + aprotic solvent system) and acetone–1-propanol (aprotic + protic solvent systems) in order to investigate the influence on the rate of this reaction with the continuous change of the polarity of the medium and the microenvironment of the reactants. The results are interpreted in terms of preferential solvation (PS) alternatively referred as a solvent sorting, in which one or more solvation shells significantly differ in molar composition from the bulk solvent mixture. Solvation of solute and transition state will contribute to a change in the intrinsic barrier of the reaction. In other words, changes in the rate of reaction may be evaluated since the solute and/or the transition state are species with different charge distributions, each one having in its microenvironment, a higher amount of one kind of solvent of the mixture than the other.

MATERIALS AND METHODS

Materials

DEKT was prepared by methods described elsewhere[9] (m.p. 59–60 °C) and its purity was checked by GC. The acetone (Merck, analytical grade) was purified following methodologies described in the literature[10] (b.p. 56 °C). The toluene (b.p. 110.0–111.0 °C) and 1-propanol (b.p. 97 °C) solvents were purified by standard methods.[11] Sublimed naphthalene (Mallinckrodt AR) was employed as an internal standard in quantitative GC determinations of DEKT concentration.

Kinetic methods

Pure solvent was mixed by volume to give binary solvent mixtures of various mole fraction compositions. Kinetic solutions

of DEKT were about 0.02 M and 1% naphthalene was added as an internal standard to perform quantitative analyses. The appropriate solution of DEKT in acetone–toluene and acetone–1-propanol mixtures were placed in a Pyrex glass ampoule (10 cm long × 4 mm OD), thoroughly degassed under vacuum at −196 °C and then sealed with a flame torch. These ampoules were immersed in a thermostated silicone oil bath (±0.1 °C), at 150 °C. After predetermined times (15, 30, 60 and 120 min) the reaction in the ampoule was stopped by cooling at 0 °C in an ice-water bath. The concentrations of DEKT remaining in the solution were determined by quantitative GC analysis (internal standard method) in an Rtx-5MS capillary column (5% biphenyl–95% dimethyl polysiloxane, 30 m, 0.25 mm ID, 0.25 μm film thickness) installed in a Thermo Quest Trace 2000 GC model gas chromatograph with helium as carrier gas (0.5 mL min^{-1}), FID detection (250 °C) and injection port in split mode at 150 °C. The experiments were carried out under programmed conditions (80 °C, 5 min, 10 °C min^{-1}, 160 °C, 20 min). Retention time of DEKT is *ca.* 15.7 min.

The corresponding pseudo first-order rate coefficient values, in s^{-1}, were calculated from the slope of the straight line obtained by plotting the values of ln[DEKT]$_t$ *versus* reaction time at 150 °C; correlation coefficients (r) obtained by a least-mean-square program were better than 0.996 for all kinetic runs.

Identification of the reaction products was done by GC analysis by comparing the retention time of each product in a sample prepared with the corresponding reagents with the retention time of that compound in the reaction mixture. The identification was checked by co-chromatography.

Refractive index (η) determinations

A standard ABBE refractometer was used to measure the corresponding refractive index of each mixture at ambient temperature.

RESULTS AND DISCUSSION

General considerations of the selected solvent systems

Acetone–toluene system

The aprotic non-polar co-solvent toluene possesses a small permanent dipole moment ($\mu = 0.36$ D) and a π-electron system which contains neither an electron pair donor centre nor an electron pair acceptor centre. Acetone is an aprotic mildly polar solvent ($\mu = 2.88$ D, $\varepsilon_{25} = 20.7$) which may participate in donor–acceptor interactions. Acetone weakly interacts with toluene[12] but they are both miscible in all concentrations. The $E_T(30)$ parameter for aprotic + aprotic binary solvent systems with acetone as solvent and toluene as co-solvent, have been reported by Mancini *et al.* in 1995. There is a relatively large increase in $E_T(30)$ values when small amounts of acetone are added to toluene (Table 1) providing strong evidence for PS by acetone. Acetone–toluene mixtures yield non-synergetic effects on the $E_T(30)$ polarity parameter.[12] The normalized $E_T^N(30)$ polarity parameter values of each mixture for binary mixtures of acetone–toluene (Table 1) were worked out from an equation using tetramethylsilane ($E_T^N = 0$) and water ($E_T^N = 1$) as extreme reference solvents.[1]

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Acetone–1-propanol system

Acetone–1-propanol mixtures may be considered as synergetic binary solvent systems,[13] where the interaction through hydrogen bonds between the solvents, generate a complex with E_T values higher than those of the two pure mixed solvents. In this mixture, acetone is the dipolar hydrogen bond acceptor solvent. The so-called normalized $E_T^N(30)$ parameter values, for aprotic + protic binary solvent systems, with acetone as solvent and 1-propanol as co-solvent were determined by Ortega *et al.* in 1996.

Kinetic determinations

Rate measurements were made on the thermal decomposition of diethyl ketone triperoxide molecule (1,2,4,5,7,8-hexaoxa-3,3,6,6,9,9-hexaethylcyclononane, DEKT Equation 1) in acetone–toluene (Table 1) and acetone–1-propanol (Table 2) binary solvent systems at 150 °C and at an initial concentration of DEKT *ca.* 0.02 M. In all the studied cases, the reaction was followed up to at least 90% DEKT decomposition, showing a consistent behaviour with a pseudo first order kinetic law.

The experimental rate coefficients k_{obs} were determined in binary solvent mixtures prepared at different mole fractions of co-solvent to vary the composition systematically (Tables 1 and 2).
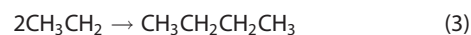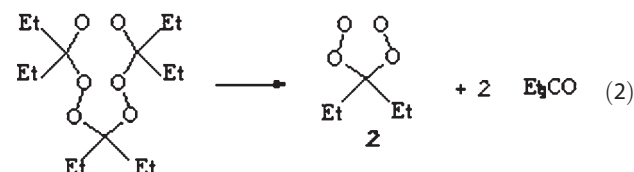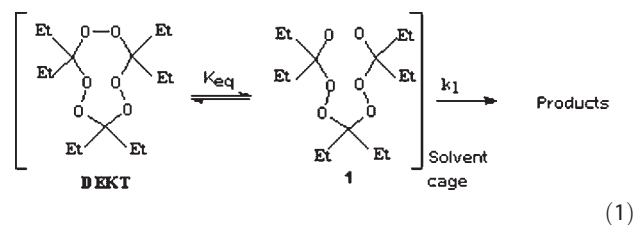
The formation of the organic products derived from thermolysis of DEKT in solution may be understood in terms of initial O—O bond homolysis to give the intermediate biradical **1**, which may reform the triperoxide molecule (Reaction 1) or undergo either C—O or C—C bond cleavage. Diethylketone and a diperoxy radical (3,3-diyldioxy-pentane diradical, **2** in Reaction 2) are products derived from C—O bond cleavage. On the other hand, the C—C bond cleavage gives ethyl radicals which may form butane by coupling reaction (Reaction 3). Benzyl radicals (Reaction 4) come from a hydrogen atom abstraction between toluene and some radical species generated '*in situ*'. These benzyl radicals take part in radical–radical reactions to give bibenzyl (Reaction 5).

$$(1)$$

$$(2)$$

$$2CH_3CH_2 \rightarrow CH_3CH_2CH_2CH_3 \quad (3)$$

$$R + CH_3C_6H_6 \rightarrow RH + CH_2C_6H_6 \quad (4)$$

$$2CH_2C_6H_6 \rightarrow C_6H_6CH_2CH_2C_6H_6 \quad (5)$$

The rate of ring cyclization to rebuild the peroxide molecule within the cage reaction after the initial O—O homolysis (Reaction 1) would be relatively fast[14] so it may be considered as a non-rate determining process in the proposed mechanism. The lifetime of the biradical **1** as initial intermediate for the triperoxide homolysis would depend on the physicochemical characteristics of the solvent cage.

For the reaction represented by Eqn (1) the rate of decomposition of DEKT shows that

$$\frac{-d[DEKT]}{dt} = k_{obs}[DEKT] \quad (6)$$

and

$$\frac{d[Products]}{dt} = k_1[\mathbf{1}] \quad (7)$$

The equilibrium constant in the solvent cage is

$$K_{eq} = \frac{[\mathbf{1}]}{[DEKT]}$$

therefore

$$[\mathbf{1}] = K_{eq}[DEKT]$$

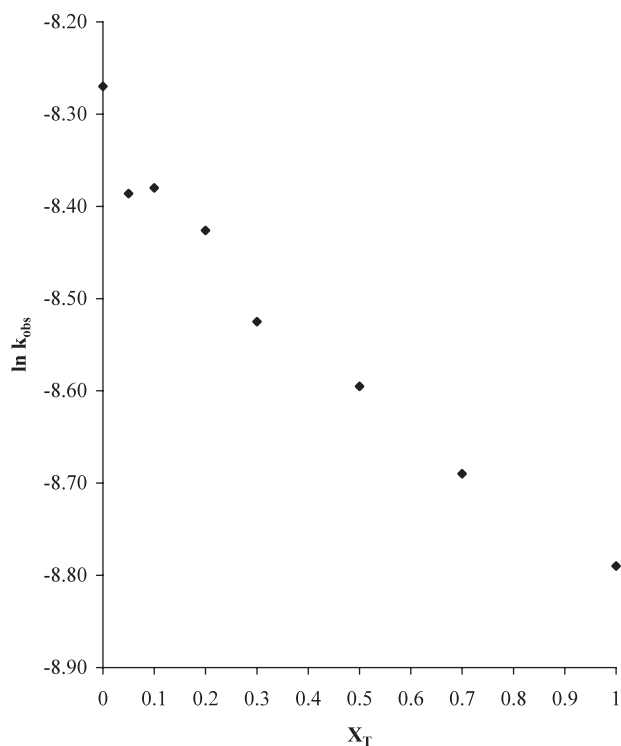Substitution into Eqn (7) gives

$$\frac{d[Products]}{dt} = K_{eq} k_1[DEKT]$$

where

$$k_{obs} = K_{eq} \, k_1$$

Consequently the differential rate Eqn (8) may be written as in Eqn (6):

$$\frac{d[Products]}{dt} = k_{obs}[DEKT] \quad (8)$$

The reaction product analysis is not enough to elucidate the real mechanism of reaction but supports the generation *in situ* of radical species according to a general stepwise mechanism.

Figure 1 presents the plot of ln k_{obs} in acetone–toluene mixtures as a function of co-solvent (toluene) mole fraction for

Table 2. Pseudo first order rate coefficient values (k_{obs}) of the thermal decomposition reaction of DEKT at 150 °C in acetone–1-propanol binary mixtures and its refractive indexes

1-Propanol mole fraction (X_P)	Refractive index (η)	$E_T^N(30)^a$	k_{obs} (10^{-4} s^{-1})
0	1.3596	0.364	2.55
0.10	1.3644	0.500[b]	2.67
0.30	1.3688	0.592[b]	2.64
0.50	1.3739	0.625[b]	2.66
0.70	1.3802	0.634[b]	2.70
0.90	1.3849	0.621[b]	2.62
1	1.385	0.617	2.68

[a] From Reference 13.
[b] Interpolated values from Reference 13.

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Figure 1. Correlation of $\ln k_{obs}$ *versus* co-solvent mole fraction for acetone–toluene solvent systems at 150 °C (including pure solvents)

the thermal decomposition reaction of DEKT analysed at 150 °C. The k_{obs} values decrease with the toluene content. In mixtures with 1-propanol, practically, no changes in rate coefficient values were obtained from 0.1 to 1 mole fraction of co-solvent (Table 2).
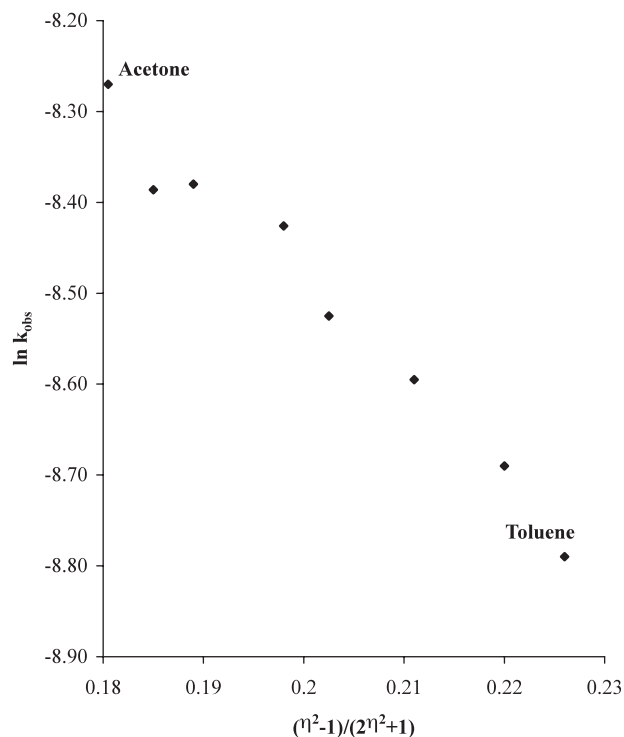
Figure 2. Correlation of $\ln k_{obs}$ with a function of refractive indexes in acetone–toluene solvent systems at 150 °C (including pure solvents)
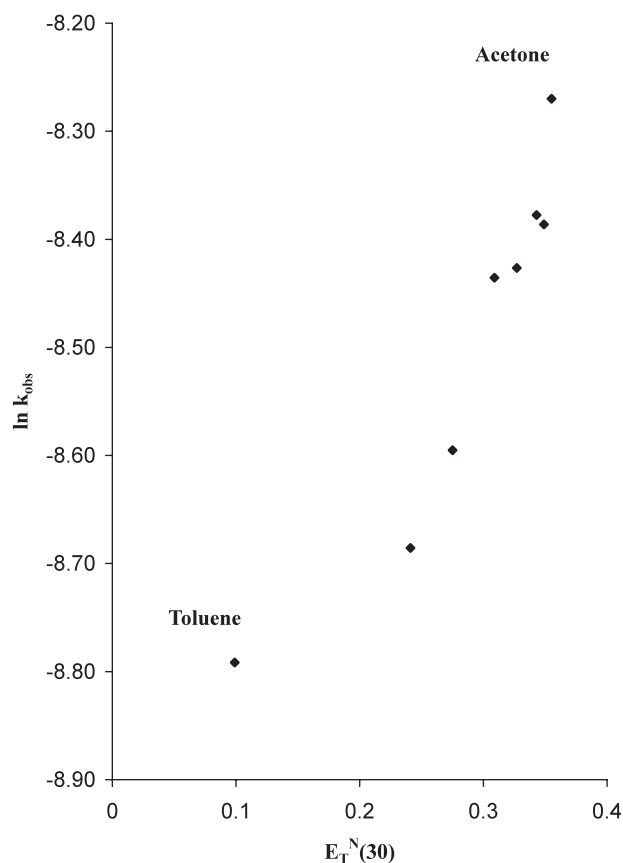
Figure 3. Correlation of $\ln k_{obs}$ *versus* $E_T^N(30)$ for acetone–toluene solvent systems at 150 °C (including pure solvents)

We may assume in this case that the slight variation observed may be a consequence of experimental errors in the rate determinations (*ca.* 3%). The rate coefficient value in pure acetone shows a decrease of *ca.* 6% in k_{obs}.

The determination of the experimental refractive index (η) of all binary mixtures makes possible the consideration of the polarizability of each system, measured by the function $f(\eta) = (\eta^2 - 1)/(2\eta^2 + 1)$. For the entire set of binary acetone–toluene mixtures, the variation of $f(\eta)$ is ± 0.0225, around an average value of 0.2033 including pure acetone and pure toluene. In acetone–1-propanol mixtures, the variation of $f(\eta)$ is ± 0.0047, around an average value of 0.1852 including pure acetone and pure 1-propanol. In conclusion, a slight variation in the polarizability may be considered when the co-solvent is toluene (Fig. 2), but in binary mixtures with 1-propanol as co-solvent (Table 2) the contribution from polarizability is nearly constant. A relatively good correlation between the kinetic data and the refractive index through the function $f(\eta)$ is observed in acetone–toluene mixtures (Fig. 2). The k_{obs} values decrease with toluene content.

Most of the mixtures behave almost as non-ideal solvent binary mixtures. Their $E_T(30)$ values are not related to their composition in a simple manner. A monotonous, but not always linear change in $E_T(30)$ with mole fraction of one component (X_c) was obtained for those binary mixtures used in this work.[12,13] Figure 3 presents the plot of $\ln k_{obs}$ in acetone–toluene mixtures as a function of normalized $E_T^N(30)$ parameter values for the thermal decomposition reaction of DEKT analysed at 150 °C. The k_{obs} values increase with $E_T^N(30)$ parameter values being the highest in pure acetone.

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In acetone–1-propanol mixtures the constancy of k_{obs} values within the experimental error does not make possible the evaluation of the effect of the solvent, neither according to $E_T^N(30)$ parameter values nor the refractive indexes (Table 2).

CONCLUSIONS

The rate of the thermal decomposition reaction of DEKT is affected by the solvent properties, showing an increase in the k_{obs} values with increases in the polarity of the solvent mixture in acetone–toluene systems. The decrease in the rate coefficient values with the increase in the mole fraction of toluene support this conclusion. Changes in rate coefficient values are probably caused by the presence of the apolar toluene solvent, which dominates the PS around the DEKT molecule through non-specific interactions. In this case, PS really influences solvent effects on reactivity.

In acetone–1-propanol mixtures the solvation effect is slightly dominated by the specific interactions between the 1-propanol and the more polar transition state represented by the biradical, initially formed (Reaction 1). As it may be observed, at 0.1 mole fraction of 1-propanol the reaction is accelerated in comparison with pure acetone; but no more changes in rate values are observed when increasing the amount of the alcohol. These binary systems with alcohol are synergetic mixtures but that effect is not operative in the reaction considered in the present work. The critical state of the reaction (intermediate biradical) is preferentially solvated by the 1-propanol instead of by the structure formed by intersolvent hydrogen-bonded specie. We may assume that PS is not an influencing reactivity factor for homolytic rupture of the O—O bond in these mixtures of different composition with 1-propanol.

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