Kinetics and Mechanism of the Thermal Decomposition Reaction of Acetone Cyclic Diperoxide in Methyl *tert*-Butyl Ether Solution

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ABSTRACT: The thermal decomposition reaction of acetone cyclic diperoxide (3,3,6,6-tetramethyl-1,2,4,5-tetroxane, ACDP), in the temperature range of 130.0–166.0°C and initial concentrations range of 0.4–3.1 $\times 10^{-2}$ mol kg^{-1} has been studied in methyl *t*-butyl ether solution. The thermolysis follows first-order kinetic laws up to at least ca 60% ACDP conversion. Under the experimental conditions, the activation parameters of the initial step of the reaction ($\Delta H^{\#} = 33.6 \pm 1.1$ kcal mol^{-1}; $\Delta S^{\#} = -4.1 \pm 0.7$ cal mol^{-1} K^{-1}; $\Delta G^{\#} = 35.0 \pm 1.1$ kcal mol^{-1}) and acetone, as the only organic product, support a stepwise reaction mechanism with the homolytic rupture of one of its peroxidic bond. Also, participation of solvent molecules in the reaction is postulated given an intermediate diradical, which further decomposes by C—O bond ruptures, yielding a stoichiometric amount of acetone (2 mol per mole of ACDP decomposed). The results are compared with those obtained for the above diperoxide thermolysis in other solvents. © 2004 Wiley Periodicals, Inc. Int J Chem Kinet 36: 302–307, 2004

INTRODUCTION

The molecules of numerous 1,2,4,5-tetroxanes substituted complexes (Scheme 1), where R_1 and R_2 can be the same or different atomic groups (Me, Et, *t*-Bu, —$(CH_2)_5$—, Ph, $PhCH_2$), have been studied by different authors in their conformational and configurational aspects [1–3] as well as their thermal decomposition reactions in different solvents [4].

The thermolysis of acetone cyclic diperoxide (3,3,6,6-tetrametyl-1,2,4,5-tetroxane, ACDP) has been investigated in many solvents with different physicochemical characteristics for e.g. hydrocarbons [5,6], alcohols [6–8], and most recently, the kinetics and mechanism of the thermal decomposition reaction in tetrahydrofurane [9], a cyclic ether type solvent. In all the case mechanisms in stages that begins with the homolytic rupture of a peroxidic bond leading to

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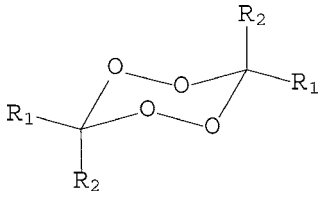
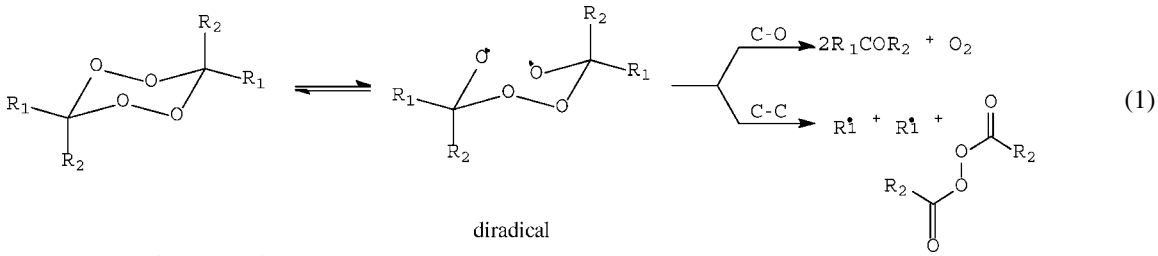


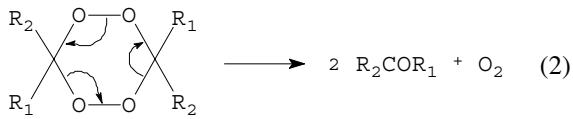
Scheme 1

the formation of an intermediate diradical, had been postulated. These constitute the rate-determining stages of the overall reactions investigated (Eq. (1); $R_r = R_2 = Me$).



diradical (1)

In the final stages of the reaction, acetone and oxygen are the expected products, but in particular solvents C—C bond cleavage of ACDP molecule is evident. Furthermore, it was reported that ACDP thermolysis in solvents such as alcohols [7] or tetrahydrofurane [9] release 2 mole of acetone per mole of ACDP decomposed. This supports a C—O scission of an initial diradical intermediate. However, when the reaction is carried out in hydrocarbon like solvents (as benzene or toluene) [5], acetone and oxygen are the main products detected but with minor yields of methane and methyl acetate. These results support recombination reactions of intermediate radicals produced in the initial dirradical fragmentation through their C—C linkages breakdown. As mentioned above, a stepwise reaction mechanism has been postulated for ACDP thermolysis in different solvents, although it is recognized that concerted type decomposition could take place:



(2)

It is, instead, this type of reaction that has been suggested for thermal decomposition of other cyclic peroxides [5,7] but not mentioned for the thermolysis of tetroxanes.

On the other hand, a kinetic effect of the solvent reaction has also been reported for the thermal decomposition ACDP [6].

In this work, the kinetics of the thermal decomposition reaction of ACDP (Scheme 1) in methyl *t*-butyl ether (MTBE) solution has been studied to assess the influence of this oxygenated low-polarity solvent on the initial stage of the reaction. The data were compared with those obtained in previous studies to learn about the effect of the solvent polarity both on the kinetic and the product yields during the course of the reaction.

EXPERIMENTAL SECTION

Materials

ACDP was prepared by methods described elsewhere [8] and its purity checked by GC.

The MTBE solvent was commercial analytical reagent (Fluka pa) purified by standard techniques [15] (bp: 55.2–56.0°C). *n*-Octane (Fluka pa) was employed as internal standard in quantitative determinations of ACDP concentration and reaction products.

Kinetic Methods

Pyrex glass ampules (12 cm long × 4 mm o.d.) filled with 0.2 mL of the diperoxide solution were thoroughly degassed under vacuum at −196°C and then sealed with a flame torch. To perform the runs, they were immersed in a thermostatic silicone oil bath (±0.1°C) and withdrawn after predetermined times (5–10 at each temperature), stopping the reaction by cooling at 0°C. The remaining ACDP and the reaction products were determined by quantitative GC analysis (internal standard method, *n*-octane), using a silica fused capillary column (HP5, 30 m length, 250 mm i.d.) impregnated with 5% phenylmethylsilicone as stationary phase, in a Hewlett-Packard model 5890 series II gas chromatograph with nitrogen as carrier gas and FID detection.

The analyses were carried out with the injector port at 105°C and using programmed oven temperature (30°/min) from 40 to 150°C. The identification of the products was carried out for comparison of its retention times with those of authentic samples, or by comparison of the corresponding MS spectra. In this case it was used helium as carrier gas and a Hewlett-Packard model 5972 A selective detector, connected to the chromatograph.

The corresponding first-order rate constant values were calculated from the slope of the one obtained by plotting the values of ln [ACDP] concentration vs reaction time values. In all the cases the reaction was followed at least through one half-life. The corresponding activation parameters were worked out from the Arrhenius equation [Eq. (2)], and their errors determined using a least-means-square data treatment [12,13].

RESULTS AND DISCUSSION

The ACDP thermolysis in MTBE solution in the 0.4–3.1 $\times$ 10^{-2} mol kg^{-1} initial concentration range and in temperature range of 130.0–166.0°C (Table I), fulfill first-order kinetic laws until ca. 60% ACDP conversions (Fig. 1).

The observed rate constant values (k_{exp}) are practically independent of the initial ACDP concentration, which shows that there are no contributions from second-order processes inducing the decomposition of ACDP at higher conversions. A similar behavior was observed in the ACDP decompositions but in another ether solvent such as THF [9]. The values for the thermolysis of ACDP in MTBE solution (Table I) are similar to those obtained with other solvents (Table II).

To evaluate the effect of the solvent polarity in the ACDP thermolysis data on solvents of different dipole moment, dielectric constant, and the empirical parameter $E_T(30)$, were considered (Table II). Although, these parameters describe the medium polarity, but from different aspects [10,12] they could allow to classify the solvents (Table II) methanol, THF, and 2-propanol as polar solvent, while benzene, toluene, octane, and MTBE as low-polar solvents.

Table I First-Order Rate Constants Values for ACDP in MTBE Solution

Temp. (°C)	[ACDP] (10^3 mol Kg^{-1})[a]	k_{exp} (10^6 s^{-1})	r[b]
130.0	4.0	0.545	0.9967
130.0	10.0	0.626	0.9952
130.0	20.0	0.553	0.9980
130.0	31.0	0.500	0.9996
140.0	4.0	1.47	0.9989
140.0	10.0	1.56	0.9990
140.0	21.0	1.72	0.9915
140.0	30.0	1.49	0.9991
150.0	10.0	4.62	0.9994
150.0	20.0	4.17	0.9995
150.0	21.0	4.55	0.9970
150.0	30.0	4.42	0.9996
166.0	4.0	19.5	0.9956
166.0	10.0	18.8	0.9993
166.0	21.0	19.2	0.9990
166.0	30.0	18.1	0.9975

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

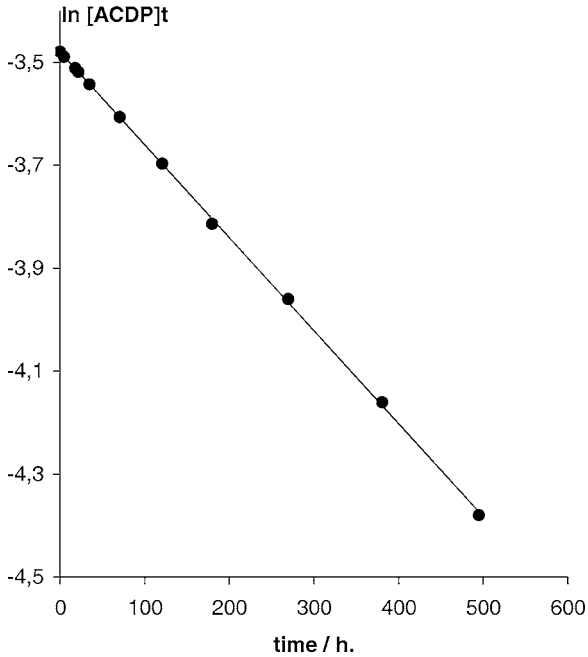


Figure 1 Representation through first-order kinetic plots of the data obtained in typical thermolysis experiments of ACDP in MTBE solution at 130°C.

A comparison of the mentioned parameters (Table II) with the corresponding k_{exp} values obtained in the different solvents indicates that low-polarity solvents exhibit slow kinetics, while the most polar solvents show the fastest rate. Therefore, the kinetics of the thermolysis of ACDP in MTBE was found to be similar to those in solvents with low polarity, such as hydrocarbons (although it is an oxygenated solvent).

The temperature effect on the rate constant values (k_{exp}) for the unimolecular reaction can be represented by the Arrhenius equation [Eq. (3)] where the errors shown are standard deviations from a least mean square data treatment [13,14] of the kinetic data.

$$\ln k_{exp}(s^{-1}) = (28.8 \pm 0.8) - (34471 \pm 1100)/RT \quad (3)$$

The corresponding equation plot is particularly linear ($r = 0.9990$) in a relatively large temperature range (ca 36°C). It suggests that the calculated activation parameter values for the ACDP decomposition in MTBE solution belong to a single process, this could be either

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

Solvent	k_{140} (10^6 s^{-1})	E_a (kcal mol^{-1})	$\Delta H^{\#}$ (kcal mol^{-1})	$\Delta S^{\#}$ (cal mol^{-1} K^{-1})	$\Delta G^{\#}$ (kcal mol^{-1})	$E_T(30)^b$ (kcal mol^{-1})	ε^d	μ^f (10^{30} Cm)	Refs
n-Octane	0.76[a]	43.7 ± 2.7	43.0 ± 2.7	17.8 ± 6.4	35.6 ± 2.7	31.1	2.00	0.04[b]	[6]
Benzene	1.19	36.6 ± 1.1	35.5 ± 1.2	1.4 ± 0.3	34.9 ± 1.2	34.5	2.28	0.00	[6]
MTBE	1.56	34.5 ± 1.1	33.6 ± 1.1	-4.1 ± 0.7	35.0 ± 1.1	34.0[c]	4.50[e]	4.23[g]	This work
Toluene	1.73	29.7 ± 0.5	28.9 ± 0.4	-13.7 ± 1.0	34.6 ± 0.4	33.9	2.38	1.43	[6]
Methanol	9.70	27.7 ± 0.3	26.9 ± 0.3	-16.9 ± 0.6	33.9 ± 0.3	55.5	32.79	6.07	[8]
THF	39.0	22.3 ± 0.3	21.5 ± 0.3	-27.3 ± 0.6	32.9 ± 0.3	37.4	7.58	5.84	[9]
2-Propanol	49.6	20.2 ± 1.3	19.4 ± 1.3	-30.2 ± 0.2	32.4 ± 0.1	48.6	19.92	5.54	[6,7]

[a] At 145°C.
[b] Empirical solvent polarity parameter: transition energy at 25°C for the long wavelength absorption band of a standard pyridinium-*N*-phenoxide betaine dye [10].
[c] Value to the corresponding one for ethers structurally related (diethyl ether = 34.6; diisopropyl ether = 34.0; di-*n*-butyl ether = 33.4) [10].
[d] Dielectric constant for the pure liquid at 25°C [10].
[e] Ref [11].
[f] Dipole moments in Coulombmeter (Cm) values [10].
[g] Dipole moments in Coulombmeter (Cm) obtained by theoretical calculations (density function B3LYP with 3-21 G base set level).

its unimolecular homolysis [Eq. (1)], or a concerted type process [Eq. (2)]. It is not probable that both processes have identical activation parameters. The theoretically calculated value (38.3 kcal mol^{-1}) for one O—O bond homolysis of the ACDP molecule was also corroborated by experimental measurements in the gas phase [15], where the activation energy value obtained (39.0 ± 2.5 kcal mol^{-1}) support a stepwise mechanism of reaction given diradical as intermediate specie.

Furthermore, a significant solvent effect is in the ACDP thermolysis in solution [6]. The solvating properties of the solvent would help the peroxidic bond rupture, showing activation parameters lower than 30 kcal mol^{-1} in the polar solvents. Low-polar solvents would not affect the intermediary transition state then, similar activation energy values to the one obtained in gas phase [15] are expected. Furthermore, the ACDP kinetics in benzene, toluene, and octane showed this behavior (Table II).

However, the activation energy value obtained for the ACDP thermolysis in MTBE [Eq. (3) and Table II] approach to the one obtained in the gas phase. According to this, a stepwise mechanism could be postulated with a diradical as intermediate, which further undergoes decomposition. By this reason the concerted process could be reasonably discarded.

If the ACDP thermolysis were of the concerted type, where the bond breaking at the transition state is partly compensated by bond making, the experimentally found activation energy would have been less than the theoretically calculated value and the corresponding activation entropy, with its highly ordered transition state, would turn to a very negative value [16].

Moreover, calculated values [17] even support that the rate determinate stage is homolytic. Calculations through the AM1 semiempirical method with geometry optimization for analogous tetroxanes, with halogen atoms as substituents, were carried out. The values of the activation energy for the concerted processes and for the in stage mechanism, were obtained. The results showed that the energy barrier for the unimolecular concerted decomposition turn to be ca 20 kcal mol^{-1} higher to the one obtained for the unimolecular homolytic rupture of one O—O bond (a stepwise diradical initiated decomposition) that it is of an average value of 22 kcal mol^{-1}.

The activation parameter values obtained for the thermal decomposition reaction of ACDP in MTBE and in other solvents (Table II) indicate nearly $\Delta G^{\#}$ similar values in the different studied solvents. This supports that analogous qualitative interactions between solute and solvent molecules are taking place in the

initial thermolysis. This means that the corresponding activation enthalpies of the reaction ($\Delta H^{\#}$, Table II) are almost compensated by the entropies of activation. All these findings suggest that the ACDP thermolysis conforms a genuine reaction series [6,18] where the solvent affects the tetroxacyclohexane ring O—O bond rupture of their molecule. Therefore, these values are in agreement with a stepwise reaction mechanism with homolytic rupture of one peroxidic bond of ACDP molecule given a diradical, as it is observed in other analogous ACDP reactions [6,8,9].

However a large variation in the enthalpies and entropies of activation and the rate constant values can be observed in comparing ACDP thermolysis in MTBE respect to other oxygenated solvents already investigated (methanol, THF, and 2-propanol), while small variation can be observed in the hydrocarbons (n-octane, benzene). All of these findings suggest that the low polarity of MTBE determines the low rate found in the ACDP thermolysis reaction.

Quantitative analysis of the acetone produced in the thermolysis (Fig. 2) shows a molar yield practically of 2 moles of carbonylic product for mole of ACDP decomposed, which is not dependent on the temperature and initial concentration of the tetroxane. Since the concerted type decomposition could be discarded, these results suggests that the formation of the products of the thermolysis can be interpreted in terms of an initial O—O homolysis to give the diradical [Eq. (1)], which can rebuild the ACDP molecules undergoing C—O cleavages to give exclusively acetone plus oxygen [Eq. (1)]. Thus, this suggests that solvent molecules participate in the "reaction cage solvent" formed during the diradical generation, facilitating further C—O cleavages.

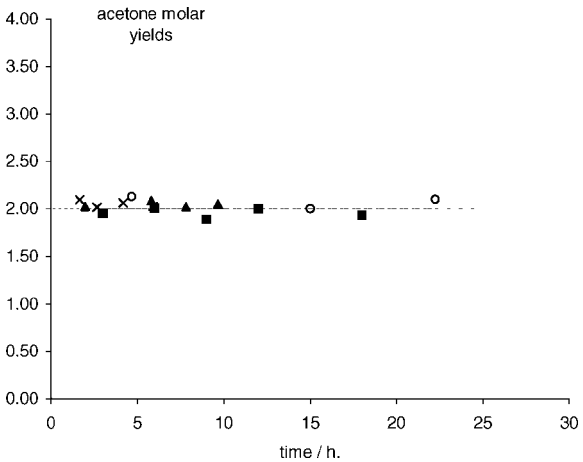


Figure 2 Acetone molar yields (moles of acetone per mole of ACDP decomposed) of acetone diperoxide in MTBE solution at different temperatures. 130°C (○), 140°C (■), 150°C (▲), and 166°C (×).

CONCLUSIONS

1. The thermolysis of ACDP in MTBE solution follows first-order kinetic law up to at least 60% diperoxide conversion.
2. Under the experimental conditions, the activation parameters correspond to the unimolecular thermal decomposition reaction of ACDP molecule.
3. Analysis of the reaction products and the activation parameter values contributes to postulate the mechanism for the thermolysis of the ACDP in MTBE solution. The thermolyses would occur through a common mechanism of decomposition already advanced for the tetroxanes, which begins with the homolytic rupture of the peroxydic bond leading to the formation of an intermediate diradical and further C—O bond ruptures giving acetone and oxygen as final products.
4. The kinetics of ACDP thermolysis is significantly affected by the physicochemical characteristics of the reaction media. Probably, the low polarity of the MTBE solvent determinates the low decomposition rates observed.

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