Kinetics and Mechanism of the Thermal Decomposition Reaction of Acetone Cyclic Diperoxide in the Gas Phase

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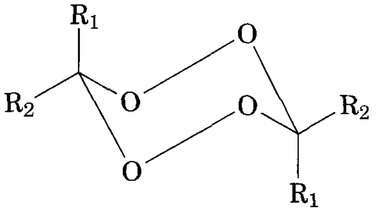
Abstract

The kinetics of the thermal decomposition reaction of gaseous 3,3,6,6-tetramethyl-1,2,4,5-tetroxane (ACDP) in the presence of *n*-octane was studied in the 403.2–523.2 K temperature range. This reaction yields acetone as the organic product. Under optimum conditions, first-order kinetics were observed, included when the S/V ratio of the Pyrex reaction vessel was increased by a nearly six-fold factor. In the range 443.2–488.2 K the temperature dependence of the rate constants for the unimolecular reaction in conditioned vessels is given by $\ln k_1/(\mathrm{s}^{-1}) = (31.8 \pm 2.5) - [(39.0 \pm 2.5)/RT]$. The value of the energy of activation in kcal/mol correspond to one O—O bond homolysis of the ACDP molecule in a stepwise biradical initiated decomposition mechanism. At the lower reaction temperatures as well in preliminary experiments participation of a surface catalyzed ACDP decomposition process could be detected. © 1994 John Wiley & Sons, Inc.

Introduction

The thermolyses of substituted tetroxanes of the general structural formula (I), where R are aliphatic, alicyclic, or aromatic substituted groups have been the subject of systematic mechanistic studies in solvents of very different physicohemical properties [1].



(I)

ACDP: $R_1 = R_2 = CH_3$
PDP: $R_1 = CH_3, R_2 = C(CH_3)_3$
CHDP: $R_1 - R_2 = -(CH_2)_5-$
BKDP: $R_1 = R_2 = C_6H_5CH_2$
BPDP: $R_1 = R_2 = C_6\,H_5$
APDP: $R_1 = CH_3, R_2 = C_6H_5$

The significant solvent effect observed in the thermolysis of those compounds was attributed to steric hindrance in the corresponding tetroxane molecules where the ACDP shows a preferential solvation [2]. The formation of an adduct in the thermolysis in 2-propanol solution ascribed to hydrogen atom bonding of the solvent molecules

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with that tetroxane, corroborates the above conclusion [3]. An important substitution effect was also demonstrated in the unimolecular decomposition reactions of those tetroxanes in benzene solution [4].

On the other hand, luminescence at 435 nm was observed during the thermolysis of gaseous ACDP at 453 K, which suggests that the decomposition of this diperoxide might be a concerted electrocyclic reaction yielding acetone molecules in singlet state [5]. However, the nature of this process could be similar to that observed in the 1,2-dioxetane family of compounds, where a homolytic initial O—O bond rupture is strongly supported [6]. The relevant problem of participation of induced processes in the mechanism of decomposition of the tetroxanes, already investigated in several solvents [1,7], can be effectively resolved through studies in the gaseous phase, only feasible with compounds sufficiently volatile at temperatures reasonably low to charge them into a reaction vessel with minimal decomposition. This is the case for the solid ACDP diperoxide (m p 133°C) with a relatively high vapor pressure (13 torr/342 K; 50 torr/362 K) here investigated, and also for APDP, BKDP, and CHDP but not, for example, for BPDP, which constitutes a practically nonvolatile compound.

Experimental

Materials

3,3,6,6-tetramethyl-1,2,4,5-tetroxane was prepared and conveniently purified as described elsewhere [8]. The *n*-octane, toluene and 1,4-cyclohexadiene employed (Sigma, USA), were purified by standard methods and their qualities, suitable for kinetic work, checked by capillary GC.

Kinetics and Analytical Methods

The gas-phase thermolysis of ACDP was studied in two types of reactors with initial partial pressures of ACDP and *n*-octane in the ranges of 11–30 and 390–1030 torr, respectively. That hydrocarbon, considered sufficiently inert at the experimental conditions of the thermolyses, was employed to introduce the ACDP in solution into the reaction vessels and because it turned to be a suitable internal standard for the GC analyses.

In a typical experiment for measuring a reaction rate constant value, 300 μL of a stock solution of ACDP in *n*-octane (ca. 0.15 M), were introduced in cylindrical (28 mm o.d. × 90 mm length) Pyrex vessels ($V = 44\ cm^3$; $S/V = 0.16\ cm^{-1}$) to yield by calculation the respective partial pressures at the temperature of the run. Afterward the vessels were thoroughly degassified at liquid air temperature and sealed with a flame torch. In another set of experiments the empty reactors were packed with Pyrex tubes (4 mm o.d. × 30 mm length), rendering a residual internal volume of 7 cm^3 and S/V ratio of 1 cm^{-1}. For a kinetic run at one temperature, three similar reactors previously charged with the same volume of the above stock solution were simultaneously introduced in a silicone oil thermostat (±0.1 K) and after selected times each of them periodically withdrawn and cooled in an ice-water bath to stop the reactions. The monitoring of the remaining ACDP, as well as the organic product (acetone), were performed by GC analysis of the liquid contents of the reaction vessels using the internal standard method (*n*-octane), in a 5840 A model Hewlett-Packard instrument equipped with a RSL Heliflex silica fused capillary column (30 m length,

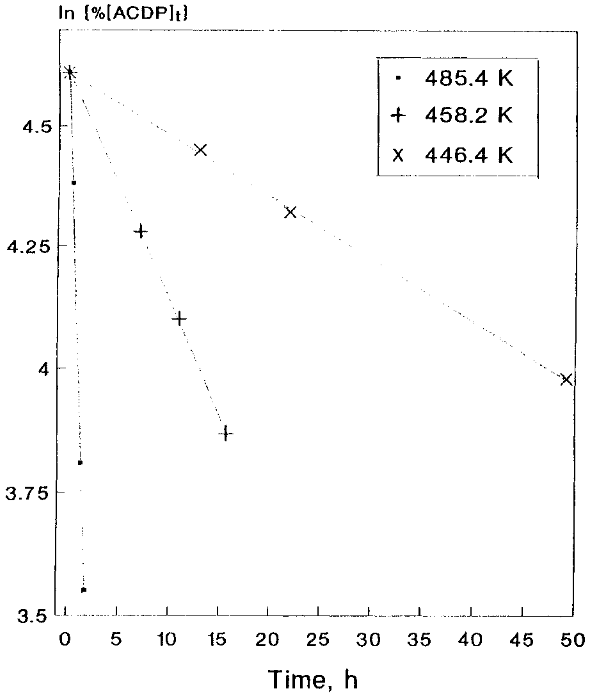


Figure 1. Representation through first-order kinetic plots of the data obtained in typical experiments of the gas-phase ACDP thermolysis in the presence of *n*-octane (unpacked reactors).

0.25 mm i.d., 0.25 μm thickness silicone stationary phase) at 65°C, with FID detection. The reaction rates were calculated in terms of a first-order kinetic law (Fig. 1), employing the data from the ACDP gas chromatographic analyses. The Arrhenius parameters of the thermolyses in the unpacked reactors were obtained by a least means square data treatment [9].

Results and Discussion

The whole temperature range chosen for the thermolysis of ACDP (403.2–523.2 K) was high enough to ensure thermal decomposition of the supposedly initially formed biradical, as concluded from studies performed in solution [2], but sufficiently low to prevent cleavage of the C—C or C—O bonds of its molecule.

In both reactors the only organic product found in the thermolyses was acetone and in preliminary experiments deviations from first-order kinetics occurred at relatively high conversions (more than ca. 70%), behavior which turned the *k* values at one temperature increasing with higher ACDP conversions. However, reliable results in the ACDP decomposition in aged reaction vessels were finally obtained [(Fig. 1) and (Table I)].

In the temperature range 443.2–488.2 K and in unpacked reactors the experiments of the ACDP thermolysis performed in the presence of a free radical scavenger as toluene, showed first-order rate constant values which are in line with those obtained without that substance addition. Furthermore, the silanization of the vessels by appropriate trimethylchlorosilane treatment, or the addition of a product of the thermolysis

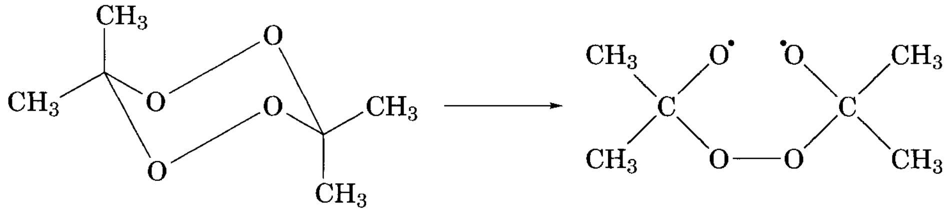
TABLE I. Kinetic data for the gas-phase thermal decomposition reaction of acetone cyclic diperoxide in unpacked vessels in the presence of *n*-octane.

T, K	$10^5 \times k$, s^{-1}	% conversion[a]
523.2	48.8	69
523.2	32.4[b]	69
493.2	15.3	58
488.2	16.6	70
488.2	13.8	62
485.4	16.0	65
480.2	8.5	36
475.2	5.7[d]	48
475.2	5.7[f]	46
467.2	2.4	13
467.2	3.2[e]	13
463.0	1.7[b]	20
463.0	1.0[e]	28
458.2	1.3	52
453.1	0.83[c]	26
453.0	0.80	17
450.2	0.46	24
446.4	0.37	48
443.2	0.35	39
443.2	0.26	33
439.4	1.3[b]	37
423.2	0.34	12
423.2	0.48	22
423.1	0.34[b]	14
403.2	0.08	16
403.2	0.18	19

[a] Maximum ACDP conversion value in the run.
[b] Toluene added (ca. 6 torr).
[c] Reactor previously silanized.
[d] Acetone added (ca. 13 torr).
[e] 1,4-cyclohexadiene added (ca. 9 torr).
[f] di-*tert*-butyl peroxide added (ca. 5 torr).

as acetone or a convenient source of methyl free radicals as di-*tert*-butyl peroxide, did not changed significantly the kinetic data obtained (Table I). The Arrhenius equation plot of the rate constant values in the conditioned nonpacked reactors and in the above temperature range (Fig. 2) exhibits no curvature ($r = 0.9898$), with the following values of its parameters: $E_a = 39.0 \pm 2.5$ kcal/mol; $A = 10^{(13.8 \pm 1.1)}$ s^{-1}. The energy of activation approach to the theoretically calculated value for one O—O bond homolysis in the ACDP molecule (= 38.3 kcal/mol [2]), a reaction which can be represented by eq. (1).

(1)



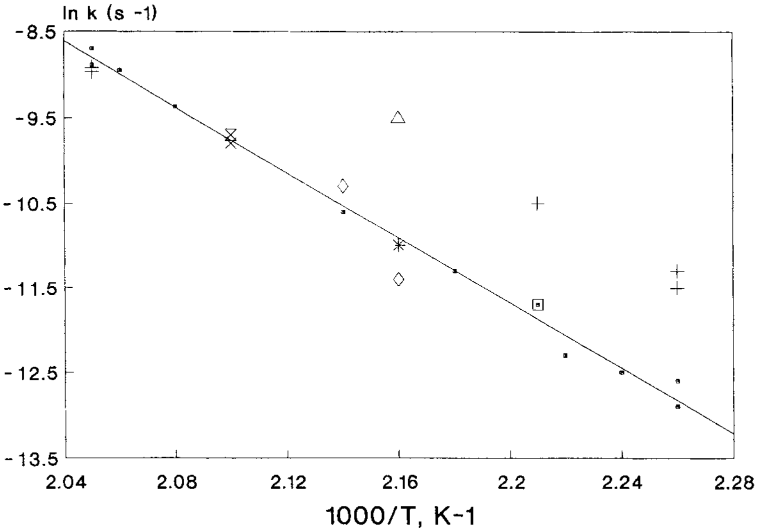


Figure 2. Arrhenius equation plot for the gas-phase ACDP thermolysis in the presence of *n*-octane, in the 443–488 K temperature range. Symbols: (⊡) unpacked vessels; (+) packed vessels; (*) toluene added (ca. 8 torr); (◇) 1,4-cyclohexadiene added (ca. 9 torr); (×) acetone added (ca. 13 torr); (⊠) Di-*tert*-butyl peroxide added (ca. 5 torr); (△) 1,4-cyclohexadiene added, packed reactors (ca. 40 torr); and (□) reactor previously silanized.

At reaction temperatures lower than ca. 454 K, a heterogeneous contribution is evident for the ACDP thermolysis in experiments performed in packed reactors (Table II), because the rate constant values are ca. 2.6 times as fast as expected from inter- or extrapolation of the data obtained in unpacked vessels in the range 443–488 K (Fig. 2).

The acetone molar yield in the ACDP thermolysis in unpacked reactors increases with the reaction temperature (Fig. 3). This corresponds with the already proposed decomposition pathways of the initially formed biradical [eq. (2)] in the ACDP thermolysis in benzene solution [2].

TABLE II. Kinetic data for the gas-phase thermal decomposition of acetone cyclic diperoxide in packed reaction vessels ($S/V = 1\ \mathrm{cm}^{-1}$) in the presence of *n*-octane.

T, K	$10^5 \times k$, s^{-1}	% conversion[a]
523.2	32.0[b]	65
488.2	12.7	60
488.2	13.4	62
463.0	8.0[c]	25
453.1	2.7	62
443.2	1.2	39
443.2	1.0	33

[a] Maximum ACDP conversion value in the run.

[b] Toluene added (ca. 8 torr).

[c] 1,4-cyclohexadiene added (ca. 40 torr).

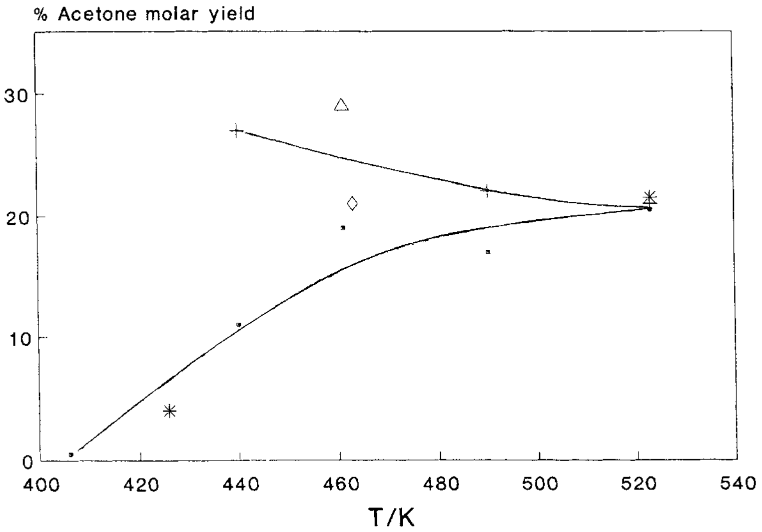
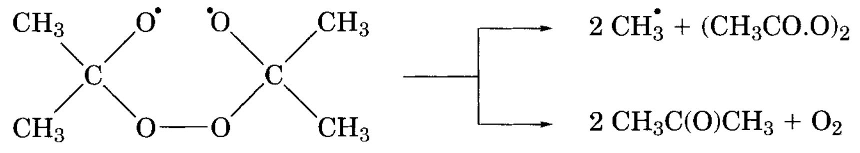


Figure 3. Temperature effect on the acetone molar yields of the gas-phase ACDP thermolysis in the presence of *n*-octane. Symbols: (□) unpacked vessel; (+) packed vessel; (∗) toluene added (ca. 6 torr); (◇) 1,4-cyclohexadiene added (ca. 9 torr); and (△) 1,4-cyclohexadiene added, packed reactor (ca. 40 torr).

(2)



The fate of the methyl free radicals as well the acetyl peroxide [eq. (2)], supposedly reaction intermediates in the gas-phase ACDP thermolysis, can be similar to that observed in the reaction in benzene solution [2], work where the methane and ethane yields were evaluated [10]. The addition of toluene to the experiments in the unpacked reactors, or still a more facile hydrogen atoms donor as 1,4-cyclohexadiene, do not affect practically the trend observed in the acetone molar yield values (Fig. 3), which demonstrates the unreactivity of the initially formed biradical [eq. (1)] to those substances. In the packed reaction vessels the yield of acetone decreases with the increase of the reaction temperature, supporting the surface reaction that renders additional acetone, contribution relatively more important at the lower temperatures (Fig. 3). The addition of 1,4-cyclohexadiene in the experiments performed in the packed vessels renders a higher rate of ACDP decomposition than the expected (Table II), which also correspond to an increment in the acetone molar yield (Fig. 3) due to enhanced catalytic activity of this reactor surface.

In conclusion, the behavior of the ACDP thermal decomposition in the unpacked and aged reaction vessels (homogeneous decomposition), correspond to the already investigated reaction in benzene solution where the induced reaction, relatively more important at higher temperatures, diperoxide concentrations, and reaction conversions, renders acetone and methyl isopropyl ether as organic products [2]. Nevertheless, according with the results of this work the ACDP thermolysis is wall sensitive. Preliminary kinetic results obtained in unconditioned reactors confirm surface initiated processes, afterward eliminated in aged reactors or by appropriate silanization procedures.

The Induced Decomposition Reactions of Substituted Tetroxanes

Because the induced decomposition of the peroxides is a generally important process its more profound investigation in the gas-phase ACDP thermolysis is a relevant matter. The whole rate constant values for the tetroxanes thermolyses in most solvents so far investigated depend on their initial concentrations in the solution in a range related to the corresponding molecular rings substitution [1]. For BKDP thermolysis the attack by benzyl free radicals yields oxygen, acetone, and benzyl phenylacetate [11]; for the BPDP thermolysis, the nature of the reaction products in benzene solution indicate a lack of induced decomposition reactions, although at high temperatures and initial diperoxide concentrations such a kind of process can not be entirely discarded [7]. The tetroxanes susceptibility to this type of reaction, probably associated with the sterically exposed peroxidic oxygens in their molecular rings, might be related to S_H2 type reactions rather than with hydrogen atom abstraction from a methyl group. However, the kinetics results for the homogeneous ACDP thermolysis (Table I), in the presence of methyl radicals (provided by the gas-phase di-*tert*-butyl peroxide thermal decomposition reaction), at least at temperatures lower than 488 K, rules out the two possible sites of attacks on that molecule, either on its methyl groups or on the ring oxygen atoms.

Acknowledgment

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