Solvent Effects in the Thermal Decomposition Reactions of Cyclic Ketone Diperoxides

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The kinetics of the thermal decomposition reactions of acetone, pinacolone, and cyclohexanone cyclic diperoxides were investigated in various solvents at different temperatures. Linear relationships were observed between the enthalpy and entropy of activation of the unimolecular reactions of those diperoxides. The acetone cyclic diperoxide (ACDP) reaction is relatively more sensitive to solvent changes, behavior attributed to a reduced steric hindrance of the methyl groups of its molecule. Qualitatively different ground or transition states for the corresponding unimolecular reactions of the ACDP may be postulated according to the strong solvent dependence.

Introduction

In a previous work[1] a significant substituent effect was demonstrated in the kinetics of the unimolecular decomposition reactions in benzene solution of cyclic diperoxides with a tetroxacyclohexane ring in their molecules, behavior attributed to steric hindrance.
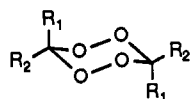
ACDP: $R_1 = R_2 = CH_3$
APDP: $R_1 = CH_3$; $R_2 = C_6H_5$
BKDP: $R_1 = R_2 = C_6H_5CH_2$
BPDP: $R_1 = R_2 = C_6H_5$
CHDP: $R_1-R_2 = -(CH_2)_5-$
PDP: $R_1 = CH_3$; $R_2 = tert$-C_4H_9

On the other hand, the unimolecular thermolysis of some open chain diacyl peroxides exhibit solvent effects because their transition states have some polar character.[2] In the case of diaroyl peroxides such as benzoyl peroxide that effect is very important even though the products derive from benzoyloxy radicals rather than ion pairs.[3] Furthermore, the reaction of that peroxide on silica clearly shows the importance of ion-pair structures in the rate-determining transition state.[4] The kinetics of the thermal decomposition reactions of cyclic diperoxides as acetone cyclic diperoxide (3,3,6,6-tetramethyl-1,2,4,5-tetroxane, ACDP), pinacolone cyclic diperoxide (3,6-di-*tert*-butyl-3,6-dimethyl-1,2,4,5-tetroxane, PDP), and cyclohexanone cyclic diperoxide, (7,8,15,16-tetroxadispiro[5.2.5.2]hexadecane, CHDP) provide an interesting means to learn about the nature of solvent effects on the thermolysis of this type of molecules, which is the aim of the present study.

Results and Discussion

Rate measurements were made on the thermal decomposition of ACDP, PDP, and CHDP in a variety of solvents with different physicochemical characteristics (Table I). At each temperature the observed rate constant values, k, are practically independent of the initial diperoxide concentrations, and in our work the thermolyses follow first-order kinetic laws up to at least ca. 50% conversions. However, many runs showed that type of behavior for more higher decomposition of the diperoxides.

The effect of the temperature on the k values according to the Arrhenius method gives the activation parameters for the ACDP, PDP, and CHDP unimolecular reactions (Table II).

In general, a significant variation is evident in the observed values of the activation parameters. These parameters are associated with the corresponding unimolecular reactions, since induced decomposition pathways in the thermolyses of those substances were not detected. Activation enthalpies near 33 kcal mol⁻¹ correspond to the peroxidic O–O bond strength for homolytic types of ruptures[5] although lower activation parameters for the decomposition of peroxides were attributed to ionic reactions in solution.[6]

The values of the activation parameters for the thermolysis of the diperoxides (Table II) show linear correlations ($\Delta H^{\ddagger} = \Delta H^{\circ} + \beta \Delta S^{\ddagger}$) according to Leffler's treatment[7] for the postulate of an isokinetic relationship, going from *n*-octane or toluene to acetic acid or acetophenone as reaction solvents. In the ACDP reaction the corresponding plot (Figure 1, $r = 0.998$) gives an isokinetic temperature of 217 °C, which is well outside the temperature range where the kinetic measurements were performed (90–166.6 °C). That relationship is consistent with the proposed[8,9] Exner correlation between the logarithm

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Table I. First-Order Rate Constant Values for ACDP, PDP, and CHDP Thermolyses in Various Solvents at Different Temperatures

diperoxide	$10^3 m,^a$ mol kg^{-1}	solvent	temp, °C	$10^6 k,^b$ s^{-1}
ACDP	(50–230)	benzene^c	135.5	0.62 ± 0.01
	(50–250)		140.5	1.19 ± 0.07
	(50–180)		145.5	2.09 ± 0.03
	(17–100)		150.5	2.83 ± 0.08
	(20–60)		165.0	14.1 ± 0.2
	55	toluene	140.0	1.73
	55		147.7	3.44
	(20–90)		165.0^c	13.7 ± 0.0
	40	acetonitrile	132.6	0.88
	55		146.8	4.9
	40		150.0	6.0
	55		160.5	15.6
	40		165.0	19.0
	40	*n*-octane	135.0	0.24
	40		145.0	0.76
	20		155.0	2.30
	98		165.0	10.1 ± 0.2
	41	acetophenone	137.5	2.86
	41		150.0	11.40
	41		166.6	59.8
	13	2-propanol	90.0^d	1.22
	13		105.0^d	3.29
	(13–81)		120.0^d	10.3 ± 0.1
	19		140.0^e	49.6
	19		148.0^e	79.0
	19		160.0^e	154
	50	acetic acid^e	130.0	57.8
	50		150.0	99.6
	50		160.0	212
PDP	(15–92)	benzene	120.0	34.8 ± 0.8
	(7–170)		140.0	274 ± 16
	(7–170)		160.0	1300 ± 50
	9	acetonitrile	130.0	38.8
	(3–33)		140.0	307.5 ± 14
	(6–73)		160.0	2593 ± 37
	22	*n*-octane	110.2	6.31
	(15–112)		120.0	17.5 ± 1.4
	(15–112)		120.0	17.5 ± 1.4
	15		140.0	232
	(15–112)		160.0	1485 ± 5
	38	acetic acid	100.0	6.12
	(23–85)		120.0	48.5 ± 0.5
	(9–83)		140.0	434 ± 4
CHDP	55	benzene^f	108.0	1.7
	40		120.5	7.6
	41		135.0	23
	55		150.0	220
	(23–121)		160.0	360 ± 2
	(10–20)	toluene^g	149.1	85.4 ± 1.1
	(10–20)		160.1	292 ± 23
	(10–20)		165.1	512 ± 41
	(10–20)	ethyl acetate^g	149.1	113 ± 9
	(10–20)		154.1	183 ± 4
	(10–20)		160.1	357 ± 18
	(10–20)		165.1	615 ± 23
	(10–20)	chlorobenzene^g	149.1	141 ± 4
	(10–20)		160.1	441 ± 20
	(10–20)		165.1	697 ± 8
	(10–20)	acetophenone^g	149.1	158 ± 7
	(10–20)		154.1	310 ± 11
	(10–20)		160.1	510 ± 17
	(10–20)		165.1	839 ± 33

^{a} Initial diperoxide concentrations. ^{b} Errors as mean standard deviations. ^{c} From ref 12. ^{d} From ref 18. ^{e} From ref 13. ^{f} From ref 15. ^{g} From ref 14.

of the rate constant values for the same reaction in each solvent at two temperatures (Figure 2, $r = 0.995$), where the corresponding β value (221 °C) is in agreement with that calculated according to Leffler's treatment. In fact,

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Table II. Activation Parameters for ACDP, PDP, and CHDP Unimolecular Thermolysis in Solution

diperoxide	solvent	$\Delta H^{\ddagger},^a$ kcal mol^{-1}	$\Delta S^{\ddagger},^a$ cal mol^{-1} K^{-1}
ACDP	*n*-octane	43.0 ± 2.7	17.8 ± 6.4
	acetophenone	36.6	6.8
	benzene^b	35.5 ± 1.2	1.4 ± 0.3
	acetonitrile	33.0 ± 2.2	-3.2 ± 5.2
	toluene	28.9 ± 0.4	-13.7 ± 1.0
	2-propanol	19.3 ± 0.1^c	-30.2 ± 0.4^c
		19.5 ± 1.3^d	-30.4 ± 3.5^d
	acetic acid^c	13.3 ± 4.4	-43.7 ± 10.5
PDP	*n*-octane	37.5 ± 0.2	12.3 ± 0.5
	acetonitrile	34.6 ± 0.6	10.8 ± 1.5
	acetic acid	32.2 ± 1.4	5.3 ± 3.6
	benzene	29.8 ± 0.6	-1.5 ± 1.5
CHDP	toluene^e	40.0 ± 0.3	16.9 ± 0.8
	ethyl acetate^e	38.1 ± 0.5	12.9 ± 1.0
	chlorobenzene^e	35.8 ± 0.3	8.0 ± 0.7
	benzene^f	33.8 ± 1.0	5.2 ± 1.5
	acetophenone^e	32.4 ± 1.0	0.5 ± 2.0

^{a} Values at 140 °C from a least mean square data treatment and errors calculated as in ref 19. ^{b} From ref 1. ^{c} From ref 13. ^{d} From ref 18. ^{e} From ref 14. ^{f} From ref 15.
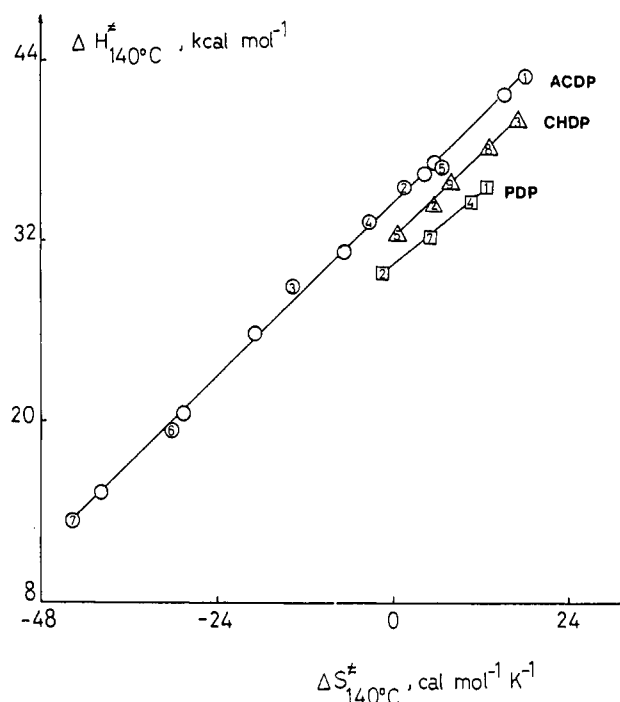

Figure 1. "Isokinetic relationships" according to Leffler: (1) *n*-octane, (2) benzene, (3) toluene, (4) acetonitrile, (5) acetophenone, (6) 2-propanol, (7) acetic acid, (8) ethyl acetate, (9) chlorobenzene. Empty circles: mapped back from the representation $\ln k(T_1)$ vs $\ln k(T_2)$ of Figure 2.

the straight line obtained by plotting $\log k(T_2)$ vs $\log k(T_1)$ can be mapped back into the representation $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$, and vice versa (Figures 1 and 2). However, the most striking aspect of the results for the ACDP thermal decomposition reactions (Table II) is the difference of nearly 30 kcal mol^{-1} in the activation enthalpy values and 61 entropic units in going from *n*-octane to acetic acid as the solvents. All of these findings suggest that its thermolysis conforms to a genuine "reaction series",[10] where the solvent affects the tetroxacyclohexane ring O–O bond rupture of the ACDP molecule.

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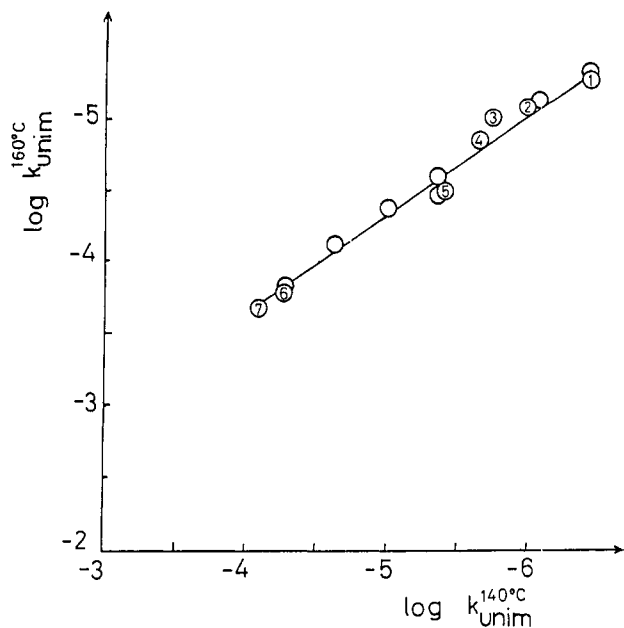
Figure 2. "Isokinetic relationship" according to Exner corresponding to the unimolecular decomposition of ACDP in several solvents: (1) *n*-octane, (2) benzene, (3) toluene, (4) acetonitrile, (5) acetophenone, (6) 2-propanol, (7) acetic acid. Empty circles: mapped back from the representation ΔH^{*} vs ΔS^{*} of Figure 1.
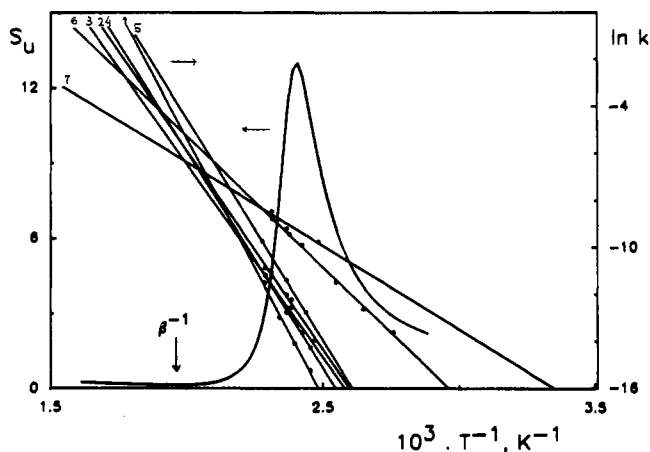

Figure 3. Dependence of the residual sum of squares S_u on the supposed isokinetic temperature T^{-1} for the ACDP unimolecular thermolysis in different solvents: (1) *n*-octane, (2) benzene, (3) toluene, (4) acetonitrile, (5) acetophenone, (6) 2-propanol, (7) acetic acid.

When the isokinetic relationship is valid, its general representation, ln k vs T^{-1} (Figure 3), must be a linear correlation according to the Arrhenius equation, and all the lines have to intersect at a point known as the reciprocal isokinetic temperature (β^{-1}). The Exner statistical analysis[11] based on a least-squares method calculates a common point of intersection of regression lines in the Arrhenius plot for which the sum of squares S_u of the deviations of the experimental points from new regression lines, including that point, becomes a minimum. If this is not found in the plot representing the dependence of S_u on the supposed values of T^{-1}, the expected correlation is not valid. The corresponding isokinetic temperature for the ACDP thermolysis (Figure 3) is 238 °C, which is also in reasonable agreement with the above β value. Those results mean that a change of the solvents of that reaction

do not produce a variation in its mechanism because the existence of a true isokinetic relationship support a common "reaction series". On the other hand, the reaction products analysis for ACDP thermolysis in benzene solution in the initial concentrations range where induced decomposition is absent indicates acetone as the main organic product.[12] In the other extreme of the series of solvents investigated, the ACDP reactions in acetic acid, carbon dioxide, acetone, succinic acid, methane, and traces of ethane were qualitatively detected.[13] However, is worth noting that in general, similar type of reaction products do not demonstrate the existence of a common mechanism.

The activation parameters reported by Story et al.[14] for the CHDP thermolysis in various solvents and the corresponding values in benzene solution[15] can be also correlated ($r = 0.997$) through a ΔH^{*} vs ΔS^{*} plot (Figure 1), giving a β value of 174 °C. However, this relationship may be invalidated because of the narrow experimental temperature range (only 16 °C) of most of the pertinent kinetic data. It is recognized that rate constants should be determined over much larger temperature ranges for obtaining exact activation parameters. Then, in this case the difference of 7.6 kcal mol⁻¹ in the activation enthalpies in going from acetophenone to toluene solvents (Table II) is not sufficient to warrant a marked solvent effect in the CHDP unimolecular decomposition reaction. Also, the isokinetic temperature for that reaction is not far from the temperature range where the kinetic experiments were performed (Table I), and the most stringent Exner's treatment in the different solvents yields a poor correlation ($r = 0.928$) with a β value of 96 °C, which cannot be compared with the above mentioned value, 174 °C.

For the PDP molecule the linear correlation between ΔH^{*} and ΔS^{*} values (Figure 1, $r = 0.998$) gives an isokinetic temperature of 140 °C. This temperature is within the experimental temperature range (120–160 °C), and a satisfactory correlation according to the Exner's proposed treatment was not found.

Thus, a significant solvent effect is operative on the ACDP unimolecular decomposition reaction in contrast to the behavior of the PDP and CHDP molecules. This is probably due to a relatively reduced steric hindrance and very likely to qualitatively different ground or transition states for the ACDP unimolecular reactions. This proposal is in line with conclusions of the substituent effect study[1] on the homolytic rupture of the tetroxacyclohexane ring; in the case of the ACDP thermolysis their activation parameters ought to be excluded from the correlation obtained for other sterically hindered diperoxides.

The demonstration of the existence of the molecular complex between ACDP and isopropyl alcohol molecules,[13] stabilized probably through intermolecular hydrogen bonding, supports the observed intermediate values of the activation parameters for the unimolecular decomposition of this substance in that alcohol (Table II), with a relatively polar transition state; the kinetic results obtained in the more protonic donor acetic acid as the reaction solvent are in accord with that postulate and favor in this case the existence of a still more dipolar transition state. The reduced steric hindrance in the ACDP molecule compared with PDP and CHDP would be relevant for the formation of adducts with particular solvents. Furthermore, the

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tetroxacyclohexane ring of PDP and CHDP molecules can exhibit a certain rigidity similarly to some derivatives of cyclohexanone diperoxide molecules,[16] rendering the adduct formation less likely.

Conclusions

1. The activation parameters of the thermal decompositions of some substituted tetroxacyclohexane derivatives in organic solvents have been correlated through isokinetic relationships to validate the existence of solvent effects on the unimolecular reactions. Then, the solvating properties of the media help the peroxidic bond rupture of this type of molecules.

2. A true "isokinetic relationship" is only warranted for the ACDP thermolysis which indicates that their reactions constitute a "reaction series" with similar "interaction mechanisms". These can be related to the capacity for hydrogen bonding between the solvent and the diperoxide molecules.

3. In PDP and CHDP thermolyses the solvent effects are less remarkable because their molecules show relatively more important steric hindrance.

Experimental Section

Materials. The ACDP, CHDP, and PDP diperoxides were prepared by methods described elsewhere[17] and their purity was

checked by GC and IR analysis (KBr, Nujol). Organic solvents were commercial analytical reagents purified by standard techniques, except the 2-propanol and acetic acid solvents which were distilled from ethylenediaminetetracetic acid (EDTA) to remove traces of metallic ions.

Kinetic Methods. Pyrex glass tubes (8 cm long × 8 mm o.d.), half filled with the appropriate diperoxide solution, were thoroughly degassed under vacuum at −190 °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 selected times, stopping the reaction by cooling at 0 °C. The diperoxides remaining in the reaction solution were determined by quantitative GC analysis (internal standard method, *n*-octane) using a silica fused capillary column (HP-SP-2100, 30 m × 0.25 mm i.d.) installed in a 5840 A Model Hewlett-Packard instrument, with nitrogen as the carrier gas and FID detection. The corresponding first-order rate constant values were obtained by least mean squares treatment of the data plotting the values of ln [diperoxide] vs time. In previous isopropyl alcohol thermolysis experiments without the purification with EDTA, the reaction rate constant values were anomalously high and showed a poor reproducibility.

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Notes

ESR Detection and ab Initio Computation of the Two Rotational Barriers in (Aryloxy)methyl Radicals

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Alkoxymethyl radicals ($ROCH_2$) have been reported to display restricted rotation about the $O–CH_2$ bond.[1-5] This can be detected by ESR spectroscopy since it leads to two different hyperfine splitting constants (a_H) for the two methylenic hydrogens. In some cases, linewidth alternation at different temperatures allowed the corresponding rotational barriers to be obtained.[3,4] In particular, the free

energies of activation have been measured[3] for $MeOCH_2$ and $EtOCH_2$ ($\Delta G^* = 5.3$ and 5.7 kcal/mol, respectively).[6]

For (aryloxy)methyl radicals ($ArOCH_2$) the possibility of investigating this stereodynamical process is less favorable since conjugation between the Ar group and the oxygen is expected to reduce the OCH_2 barrier, thus making hindered rotation more difficult to detect. Indeed, in an ESR study of the $PhOCH_2$ radical and on some of its substituted derivatives, Hudson and Root[7] were unable to detect two different CH_2 splittings, which made it impossible to determine the activation energy for the OCH_2 rotational processes. However, these authors did observe[7] a broadening of the central region of the ESR spectrum with respect to the outer wings, which indicates that a dynamic process was taking place, although its rate could not be measured. In the present work we have succeeded in measuring the OCH_2 rotational barrier in $ArOCH_2$ radicals and have found experimental evidence for a second restricted motion which is rotation about the Ar–O bond. We were encouraged to undertake these experiments as a result of the predictions of ab initio calculations on some $ArOCH_2$ radicals, in which Ar was phenyl, furan, and

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