

Macrocyclic Synthesis. The Thermal Decomposition of Dicyclohexylidene Diperoxide and Tricyclohexylidene Triperoxide

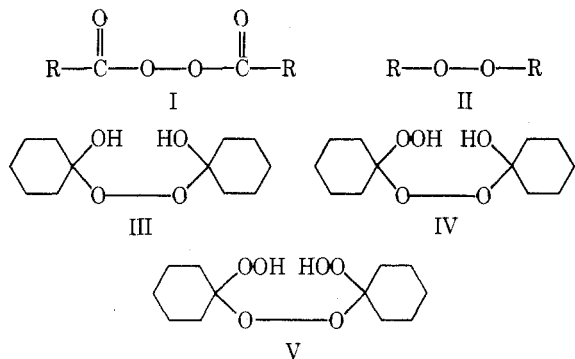
John R. Sanderson*^{1,2} and Paul R. Story¹

Department of Chemistry, The University of Georgia, Athens, Georgia 30601

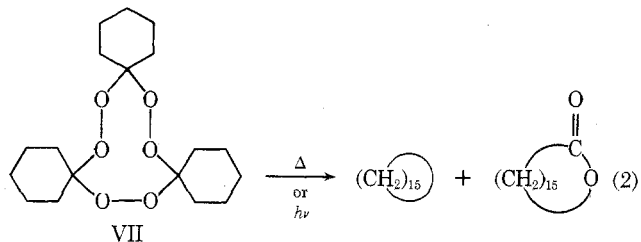
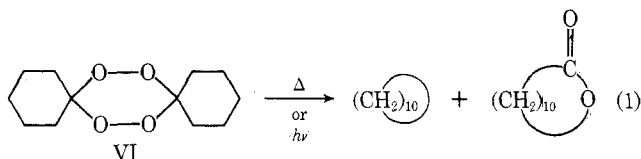
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The thermal decomposition of dicyclohexylidene diperoxide and tricyclohexylidene triperoxide has been studied in a variety of solvents. Not surprisingly, both peroxides were found to obey first-order kinetics. The activation enthalpies and activation entropies for both peroxides (calculated from the rate constants determined at three to four temperatures) show that the rate of decomposition may be influenced by the solvent.

Although there is a wealth of kinetic and decomposition data on acyl and alkyl peroxides (*e.g.* I and II)³⁻⁶ prior to 1967 there was very little kinetic and decomposition data dealing with ketone peroxides other than several papers dealing with "open" ketone peroxides such as 1,1'-dihydroxydicyclohexyl peroxide (III), 1-hydroxy-1'-hydroperoxydicyclohexyl peroxide (IV) and 1,1'-dihydroperoxydicyclohexyl peroxide (V).⁷⁻⁹



In 1967, Story and coworkers (while examining peroxides and ozonides in atmospheric pollution studies) found that the thermal and photochemical decomposition of cyclic ketone peroxides such as VI and VII produced macrocyclic hydrocarbons and lactones.¹⁰ Later Story, *et al.*, developed



better methods for the preparation of the peroxides.¹¹ Newer and safer techniques for the decomposition were reported.¹² The discovery of improved methods for the synthesis of mixed trimers gave rise to previously unavailable macrocyclics, and thus, it appeared that the only limiting factor in producing macrocyclics was the availability of the starting ketone.¹³

In an extension of this earlier work we have undertaken a detailed thermal decomposition and kinetic study of some 20 cyclic dimeric and trimeric ketone peroxides. This is the first of a series of papers in which we wish to report our results.

Results and Discussion

Rate measurements were made on the decomposition of dicyclohexylidene diperoxide and tricyclohexylidene triperoxide in a variety of solvents which differ in viscosity and dielectric constant. The concentration of the diperoxide was monitored iodometrically. Figure 1 shows some typical and atypical data for the decomposition of the dimeric peroxide. Typical data as used here refer to data which obeyed the first-order rate law throughout the time interval for which that particular run was followed. Atypical data deviate significantly from the first-order rate law. Carbon tetrachloride, chloroform, and acetic anhydride were the only solvents of those studied to exhibit autocatalytic (atypical) behavior illustrated in Figure 1. We also observed no plots in which the curvature was convex. In other words, we observed no rate plots in which the rate of decomposition decreased with time even though the peroxide concentration was followed through 80-90% decomposition for several runs.

Table I shows the rate measurements for dicyclohexylidene diperoxide in some solvents at different initial peroxide concentrations at 160°. In all solvents in which there is a difference in rate, the peroxide solution of higher concentration shows a slightly faster rate of decomposition. The induced decomposition is not great for most of the solvents studied. The most drastic increase in rate with increase in peroxide concentration occurs in isomeric hexanes.

Since a peroxide may undergo a decomposition by a first-order cleavage and by an induced chain process, an at-

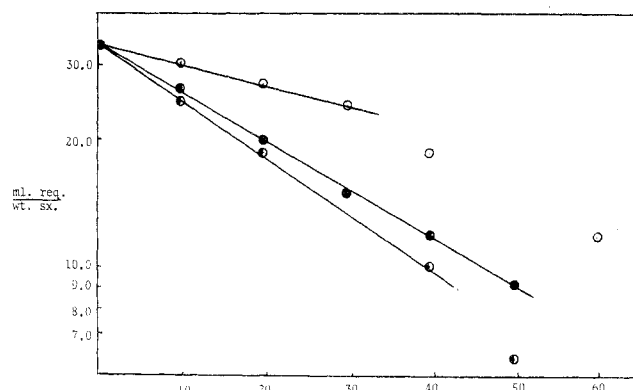


Figure 1. Typical and atypical plots for the decomposition of dicyclohexylidene diperoxide in ethyl acetate, ●; carbon tetrachloride, ○ ($k = 25.2 \times 10^{-5} \text{ sec}^{-1}$ from first three points); and acetic anhydride, ○ ($k = 51.4 \times 10^{-5} \text{ sec}^{-1}$). The initial peroxide concentration for all three runs was 0.03 *M*.

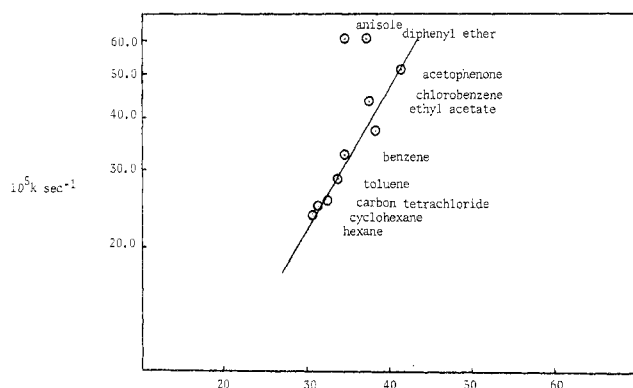


Figure 2. Semilog plot of rate constant vs. *E* (Dimroth's solvent polarity parameter) for dicyclohexylidene diperoxide in some solvents at 160°.

tempt was made to separate the induced decomposition (k_i) from the unimolecular decomposition (k_d) in the following equation.

$$\frac{-dp}{dt} = k_d P + k_i P^x \quad (3)$$

This is important in a study of the decomposition of a peroxide since the first-order process and the induced process are somewhat solvent dependent. Using the method of Nazaki and Bartlett, an attempt was made to separate k_d and k_i in eq 3 for several solvents.¹⁴ We were thwarted, however, because the analytical method used was not sensitive enough. Within experimental error, the extrapolated k_d values and the k_{obsd} values were the same.

Acetophenone is the solvent which exhibits the least induced decomposition on VI, although the rate (probably due to increase in the polarity of the solvent) is three times that in nonane when the 0.02 *M* concentrations are compared. This is not surprising in view of the fact that acetophenone was found to be an excellent solvent for the suppression of induced decomposition in substituted benzoyl peroxides.¹⁵

Rate measurements were also made on tricyclohexylidene triperoxide (VII) in various solvents; however, the study was in less detail than the study on dicyclohexylidene diperoxide (VI). It was necessary to use quantitative infrared analysis to monitor the concentration of the trimeric peroxide since it did not reproducibly liberate iodine from an iodide solution (see Experimental Section). Table II shows some rate data obtained by monitoring the disappearance of the band at $\sim 965 \text{ cm}^{-1}$ in the infrared.

If one examines Table II, the second and third runs in

Table I
Rate Constants for the Thermal Decomposition of Dicyclohexylidene Diperoxide in Various Solvents at 160°

Solvent	P_0^a	$t_{1/2}$, min	$10^5 k, \text{ sec}^{-1}$
Hexanes (mixture)	0.02	48.9	23.6 (± 0.9)
	0.03	22.5	51.3 (± 0.5)
	0.06	37.8	30.6 (± 0.8)
<i>n</i> -Nonane	0.02	62.6	18.5 (± 1.2)
	0.03	49.0	23.6 (± 0.6)
	0.06	37.8	30.6 (± 0.8)
Cyclohexane	0.01	46.2	25.0 (± 0.9)
	0.02	41.6	27.7 (± 0.8)
	0.03	42.5	27.2 (± 1.4)
Benzene	0.01	34.9	33.1 (± 0.6)
	0.02	29.0	39.9 (± 2.3)
	0.03	28.0	41.2 (± 1.5)
Toluene	0.01	40.3	28.7 (± 1.4)
	0.03	39.6	29.2 (± 2.3)
	0.06	30.1	38.4 (± 0.9)
Chlorobenzene	0.01	26.2	44.1 (± 2.0)
	0.03	24.5	47.1 (± 1.8)
	0.04	21.5	53.7 (± 1.2)
Diphenyl ether	0.02	18.9	61.1 (± 2.9)
	0.04	18.8	61.6 (± 2.5)
	0.06	18.0	64.2 (± 1.1)
Anisole	0.04	18.7	61.9 (± 2.6)
	0.02	32.4	37.5 (± 1.8)
	0.03	27.5	42.1 (± 1.4)
Ethyl acetate	0.04	24.5	47.2 (± 1.0)
	0.01	22.2	52.1 (± 3.1)
	0.02	22.7	51.0 (± 1.7)
Acetophenone	0.03	20.5	56.4 (± 1.3)
	0.06	18.0	64.2 (± 1.1)
	0.01	22.2	52.1 (± 3.1)
Nonane ^e	0.065	153	7.56 (± 0.37)
Nonane ^{b,e}	0.065	198	5.83 (± 0.28)
Chlorobenzene ^e	0.065	97.9	11.8 (± 0.7)
Acetophenone ^e	0.065	93.4	12.4 (± 0.6)
Acetic acid ^{c,f}	0.065	21.7	53.2 (± 0.6)
Neat ^d		27.0	42.8 (± 0.1)

^a Initial peroxide concentration in moles per liter. ^b Decomposed in the presence of atmospheric oxygen. ^c Decomposed in the presence of 0.065 *M* perchloric acid. ^d Pure neat peroxide decomposed in evacuated sealed vials. The rate constant was determined from three points since several vials exploded when placed in the bath at 160.1°, 146.1°, 60.0°. ^e Standard deviation in parentheses.

the solvents cyclohexane and benzene show that the infrared method for the determination of rate constants is reproducible within experimental error. Furthermore, there is only a slight increase in rate when the initial concentration of the peroxide is increased. In every case in which there is a significant difference in rate (at any given temperature and in any given solvent), the rate of decomposition is faster when the initial peroxide concentration is higher. It is reasonable to postulate that the slight increase in rate is caused by radical-induced decomposition.^{16,17}

A naive view of a radical reaction might indicate that since neutral radicals are formed, they would not be subject to the same influences that affect the reactions of ions. Thus, radical reactions would show no solvent or substituent effect, whereas ionic reactions should show large differences in behavior. As a matter of fact, the lack of sensitivity of a reaction to solvent is frequently used as a criterion for proving whether this new reaction is ionic or free radical.³

Many radical reactions, of course, show polar influences similar to those in ionic reactions. Cross termination reactions are favored over homotermination in the copolymerization of two olefins.¹⁸ The well-known work of Swain, Stockmayer, and Clarke is another example of a free radical reaction with polar character.¹⁹

Table II
Rate Constants for the Decomposition of
Tricyclohexylidene Triperoxide in Various Solvents

Solvent	$T, ^\circ\text{C}$	P_0^a	$10^5 k, ^b \text{sec}^{-1}$	$t_{1/2}, \text{min}$
Cyclohexane	140.1	0.03	4.96 (± 0.24)	233
	145.1	0.03	9.15 (± 0.34)	126
	145.1	0.03	9.16 (± 0.48)	126
	150.1	0.03	13.5 (± 1.1)	85.3
	150.1	0.10	16.8 (± 0.4)	68.6
	155.1	0.06	43.0 (± 2.0)	26.8
<i>n</i> -Hexane	140.1	0.03	4.25 (± 0.19)	272
	145.1	0.03	7.90 (± 0.95)	146
	145.1	0.06	9.14 (± 0.30)	126
	150.1	0.10	14.4 (± 0.03)	80.1
	150.1	0.03	14.3 (± 1.0)	81.1
<i>n</i> -Decane	140.1	0.03	4.38 (± 0.22)	264
	145.1	0.03	7.40 (± 0.01)	156
Toluene	140.1	0.03	8.59 (± 0.21)	134
	145.1	0.03	14.0 (± 0.5)	82.3
	145.1	0.10	14.7 (± 0.2)	78.6
	150.1	0.03	30.3 (± 2.6)	38.2
Benzene	150.1	0.03	35.4 (± 0.7)	33.6
	140.1	0.03	9.55 (± 0.43)	121
	145.1	0.03	17.3 (± 1.7)	66.9
	145.1	0.03	18.5 (± 0.4)	62.6
Acetone	150.1	0.03	35.4 (± 1.0)	32.6
	140.1	0.03	14.2 (± 0.8)	81.4
	145.1	0.03	29.3 (± 1.1)	39.5
	150.1	0.10	52.8 (± 1.0)	21.9
150.1	0.03	57.1 (± 2.1)	20.2	

^a Initial peroxide concentration in moles per liter. ^b Standard deviation in parentheses.

In Figure 2, the semilog of the rate constants for the decomposition of dicyclohexylidene diperoxide is plotted against E (Dimroths solvent polarity parameter).^{20,21} It can be seen immediately that the effect of solvent polarity on rate of decomposition is not great. The correlation is poor, but the trend is evident. The rate increases with an increase in the polarity of solvent.

In Figure 3, the semilog of the rate constant for the decomposition of tricyclohexylidene triperoxide is plotted vs. E . Again, the trend is evident. The rate of decomposition of the trimeric peroxide increases as the polarity of the solvent increases.

It must not be assumed that there is similarity between the decomposition of above ketone peroxides (VI and VII) and the model reactions from which the above solvent polarity parameters were derived. The plots serve to illustrate the effect of solvent polarity on rate of decomposition.

It is very improbable that a radical or radical-like transition state would be solvated to the same extent as the initial state since differences in the electronic configuration (and therefore polarizability) should exist. The relative solvation of a radical or radical-like transition state in a radical reaction should lead to a difference in the rate and therefore the energy of activation. There are several detailed discussions on this concept.²²⁻²⁴

Viscosity might also be considered a factor which affects the rate of decomposition of VI and VII.²⁵ The viscosity test, however, is generally not applicable to studies of cyclic systems which produce diradicals. The situation arises because the rate of diffusion of diradicals is insignificant compared to the rate of cage reactions. The problem is discussed by Neuman.^{26,27}

There are factors other than solvent polarity and viscosi-

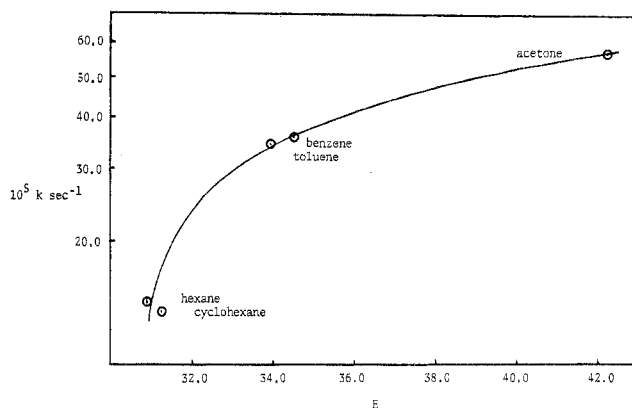


Figure 3. Semilog plot of rate constant vs. E for tricyclohexylidene triperoxide at 150° in some solvents.

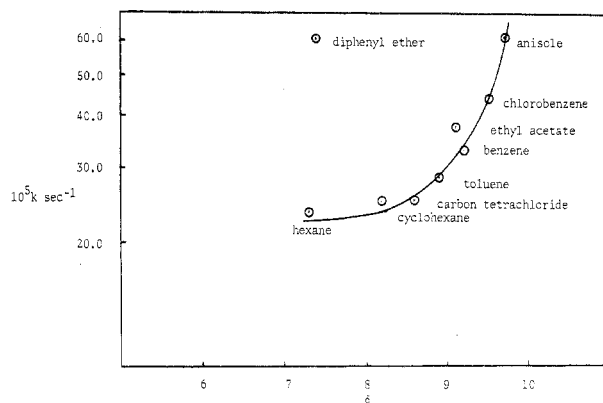


Figure 4. Semilog plot of the rate constant vs. δ (the square root of the cohesive energy density) for dicyclohexylidene diperoxide at 160° in some solvents.

ty which may affect the rate of decomposition of a peroxide. The energy necessary to form a solvent cavity in going from the initial state to the transition state must also be taken into account. This is done by considering the "cohesive energy density of the solvent."^{28,29} The square root, δ , of the cohesive energy density is a direct measure of the total molecular cohesion per cubic centimeter of a liquid and is defined by (4).

$$\delta = \sqrt{-e/v} \quad (4)$$

Here e is the molal energy of vaporization of a liquid to a gas at zero pressure and v is the molal volume of the liquid. The parameter δ is proportional to the energy necessary to form a solvent cavity. A linear relationship will be observed between $\log k$ and δ if the rate is dependent on solvent cavity requirements. The solvent cavity requirement for the transition state of a radical reaction should certainly be different (in size and shape) from that of the initial state. This difference will be reflected by a change in rate as the solvent (and therefore the cohesive energy density) is changed.

Figure 4 shows a plot of $\log k$ vs. δ for dicyclohexylidene diperoxide. The plot is not linear, but a relatively smooth curve may be drawn through the points. The conclusion to be made from this data is that the rate of decomposition may be dependent on other factors as well as the cohesive energy density.

Figure 5 is a semilog plot of rate constant vs. δ for tricyclohexylidene triperoxide. Here the plot may approach linearity.

If one now compares Figures 2, 3, 4, and 5, one may (qualitatively at least) note some similarities and differences in the rate of decomposition of the peroxides as the

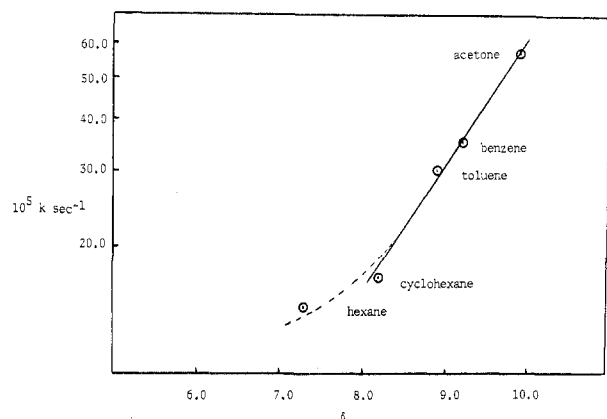


Figure 5. Semilog plot of rate constant *vs.* δ for tricyclohexylidene triperoxide in some solvents at 150°.

solvents are changed. The points in Figure 2 (a semilog plot of rate constants *vs.* solvent polarity for cyclohexanone diperoxide) approach linearity. A similar plot (Figure 3) for cyclohexanone triperoxide is strongly curved. The points in Figure 4 (a semilog plot of rate constant *vs.* cohesive energy density for cyclohexanone diperoxide) are strongly curved. A similar plot (Figure 5) for cyclohexanone triperoxide approaches linearity. Thus, the indications are that whereas the decomposition of dicyclohexylidene diperoxide is more dependent on the polarity of the solvent, the decomposition of tricyclohexylidene triperoxide is more dependent on the cohesive energy density of the solvent. The exact contributions of polarity of solvent and cohesive energy density of solvent to the rate of decomposition of the peroxides is not known.

Four representative solvents were chosen from those presented in Table I and the first-order rate constants for dicyclohexylidene diperoxide determined at three to four temperatures. The initial peroxide concentrations were between 0.01 and 0.02 *M* so that induced decomposition was probably small enough to be neglected. These data are presented in Table III.

The activation parameters in Table IV calculated from the data in Table III show that there is a marked solvent effect on the decomposition of dicyclohexylidene diperoxide. The effect might not be obvious from an examination of the rate data at one temperature, and points to the fact that lack of sensitivity of a reaction to solvent, determined by rate measurements at one temperature, is questionable.

In Table V are shown the activation parameters for tricyclohexylidene triperoxide calculated from the pertinent data in Table II. The most striking aspect of this table is the difference of 12 kcal activation enthalpy in going from decane or cyclohexane to toluene or acetone. To us, this seems quite a large difference. Indeed, at least some of this difference is probably due to experimental error and the fact that the activation parameters were calculated from rate constants determined over only 10–15°. Even though (we suspect) there is some error involved in the values of ΔH^* and ΔS^* , the trend is probably valid and the assumption is made that the trend is valid in the following discussion.

The activation parameters for dicyclohexylidene diperoxide and tricyclohexylidene triperoxide both show a linear correlation. For the diperoxide this linear correlation gives an "isokinetic temperature"³⁰ of $177 \pm 2^\circ$. This temperature is slightly higher than the temperatures where the kinetics were performed. For the triperoxide the correlation gives an isokinetic temperature of $119 \pm 4^\circ$. This temperature is not far below the temperatures where the kinetics were performed.

Table III
Rate Constants for the Thermal Decomposition of Dicyclohexylidene Diperoxide in Selected Solvents^a

Solvent	<i>T</i> , °C	<i>t</i> _{1/2} , min	10 ⁵ <i>k</i> , ^b sec ⁻¹
Toluene	149.1	135	8.54 (±0.11)
	160.1	39.6	29.2 (±2.3)
	165.1	22.6	51.2 (±4.1)
Ethyl acetate	149.1	102	11.3 (±0.9)
	154.1	63.2	18.3 (±0.4)
	160.1	32.3	35.7 (±1.8)
Chlorobenzene	165.1	18.8	61.5 (±2.3)
	149.1	81.8	14.1 (±0.4)
	160.1	26.2	44.1 (±2.0)
Acetophenone	165.1	16.1	69.7 (±0.8)
	149.1	73.0	15.8 (±0.7)
	154.1	37.3	31.0 (±1.1)
	160.1	22.7	51.0 (±1.7)
	165.1	13.8	83.9 (±3.3)

^a The initial peroxide concentrations were between 0.01 and 0.02 *M*. ^b Standard deviation in parentheses.

Table IV
Activation Parameters for Dicyclohexylidene Diperoxide in Various Solvents

Solvent	ΔH^* , ^{a, b} kcal/mol	ΔS^* , ^a eu
Toluene	40.0 (±0.3)	16.9 (±0.8)
Ethyl acetate	38.1 (±0.5)	12.9 (±1.0)
Chlorobenzene	35.8 (±0.3)	8.0 (±0.7)
Acetophenone	32.4 (±1.0)	0.5 (±2.0)

^a Standard deviation in parentheses. ^b Reference 33.

Table V
Activation Parameters for Tricyclohexylidene Triperoxide in Various Solvents

Solvent	ΔH^* , ^a kcal/mol	ΔS^* , ^a eu
Cyclohexane	33.9 (±1.8)	3.3 (±4.2)
<i>n</i> -Decane	33.4	4.1
<i>n</i> -Hexane	41.0 (±0.1)	20.0 (±0.4)
Benzene	44.4 (±0.7)	29.8 (±1.7)
Toluene	46.3 (±2.9)	34.1 (±6.9)
Acetone	45.8 (±0.9)	34.0 (±2.3)

^a Standard deviation in parentheses.

Leffler and Grunwald have pointed out that isokinetic relationships in which the solvent is the variable often have isokinetic temperatures near the experimental temperatures.³¹ This was said to be expected if the formation of molecular complexes was an important part of the solvation mechanism.

Huyser and Vanscoy have studied the effects of solvent on the decomposition of di-*tert*-butyl peroxide.²³ These workers found an isokinetic temperature of 164°. The heats of solution of the peroxide were determined and it was concluded that the differences in ΔH^* were the result of interaction of the solvent with the transition state for the decomposition.

We have likewise concluded that the difference in the values of ΔH^* for cyclohexanone diperoxide are the result of interaction of the solvent with the transition state for the decomposition rather than the initial state. By a similar argument, it must be concluded that cyclohexanone triperoxide is solvated more in the initial state than the transi-

Table VI
The Main Products of Decomposition of
Tricyclohexylidene Triperoxide in Various Solvents
at Different Temperatures^a

Solvent	T, °C	P ₀ ^b					
		Cyclopenta-decane		16-Hexa-decanolactone		Dilactone ^c	
		0.02	0.10	0.02	0.10	0.02	0.10
Hexane	145	21	20	21	18	14	13
	150	24		18			
	180	29		18			
	200	36		21			
Cyclohexane	140	20					
	145	21	21		18	12	14
	150	28		16			
Toluene	180	32		18			
	140	20					
	145		20	19	14	9	4
Benzene	150	24		18			
	180	28		15			
	200	28		16			
	145	28	25	17	14	8	9
Acetone	180	34		14			
	200	37		15			
	145		21	21	12	8	6
	150	28		10			

^a Yield in per cent. ^b Initial peroxide concentration in moles per liter. ^c Actually a mixture of two possible isomers.

tion state.³¹ These are not unexpected results from steric considerations.

Criegee found that trimeric ketone peroxides were extremely slow in their catalytic reduction by hydrogen and very slow in the liberation of iodine from an iodide solution.³² These workers found that dimeric ketone peroxides gave quantitative liberation of iodide at room temperature and were catalytically reduced by hydrogen under mild conditions. Criegee rationalized these results in terms of steric hindrance in the trimeric peroxides.

One may envision a similar process to account for the solvent effects observed here. The bulky alkyl groups prevent the polar solvent molecules from interacting with the radical like transition state for tricyclohexylidene triperoxide but not for the transition state of the diperoxide. Solvation would therefore be greater in the initial state for the triperoxide.

The actual process is probably a bit more complex. Models of the cyclohexanone triperoxide show that it might be possible for solvent molecules to interact with the O-O bonds. When one bond is ruptured, however, a small amount of rotation will "bury" the oxygen diradical well within a "cage" composed of the other atoms of the molecule. Thus, the solvent molecules are prevented from reacting with the transition state by the oxygen atoms of the triperoxide as well as by alkyl groups.

The yield of the main products from the thermal decomposition of dicyclohexylidene diperoxide at 160° was studied in 12 different solvents of different viscosity and polarity. The yields were as follows: cyclohexanone (5–10%), cyclodecane (40–45%), and 11-undecanolactone (30–35%). Significantly lower yields were observed in the solvent carbon tetrachloride: cyclodecane (24%) and 11-undecanolactone (20%). Thus it appears that there is no significant solvent polarity effect on the formation of the products of decomposition of dicyclohexylidene diperoxide. The low

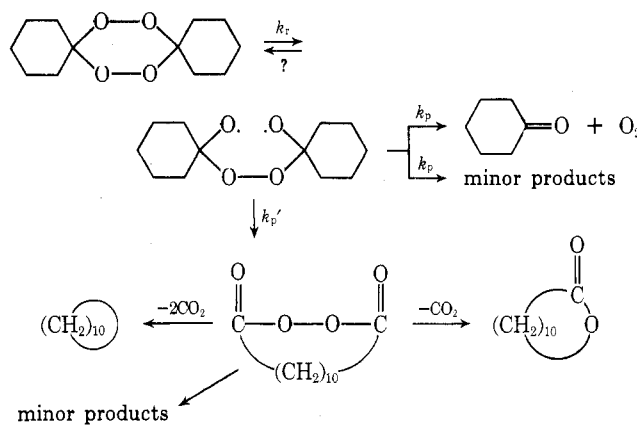
yields of products in the solvent carbon tetrachloride might be ascribed to induced decomposition but this is unsupported since no detailed studies were done.

Table VI shows the main products in the thermal decomposition of tricyclohexylidene triperoxide. In general, there is little solvent effect on the product yield or distribution. (The yields are probably accurate to about ±3%).

The products of decomposition of tricyclohexylidene triperoxide were studied in more detail than the products of decomposition of dicyclohexylidene diperoxide because the products from the former are of greater interest synthetically than the products from the latter. The data indicate that most solvents could be used for the thermolysis without a significant variation in yield. There is also some indication (Table VI) that a higher yield of macrocyclic hydrocarbon may be obtained at higher temperatures although the yield of macrocyclic lactone is not significantly affected.

The presence of a solvent effect on the rate of decomposition of dicyclohexylidene diperoxide (and tricyclohexylidene triperoxide) and the absence of a significant solvent effect on the products of formation suggest that the product-forming step and the rate-determining step are separate events. In Schemes I and II, k_r represents the rate determining step and k_p and k_p' represent the product forming steps.

Scheme I Decomposition of Dicyclohexylidene Diperoxide



Experimental Section

Solvents and Reagents. All solvents except those which were 99 mol % pure were distilled (or vacuum distilled) through a 25-cm Vigreux column. Cyclohexanone (Aldrich) was used without purification. Hydrogen peroxide was from FMC Corp.

Instrumentation. Infrared spectra were taken on a Perkin-Elmer IR-257 using a polystyrene film for calibration. Quantitative ir analysis was done with a Perkin-Elmer IR-621.

Gas chromatographic analyses were conducted on an Aerograph A90-P3 thermal conductivity instrument and an Aerograph Hy-Fi III Model 1200 with flame ionization detector.

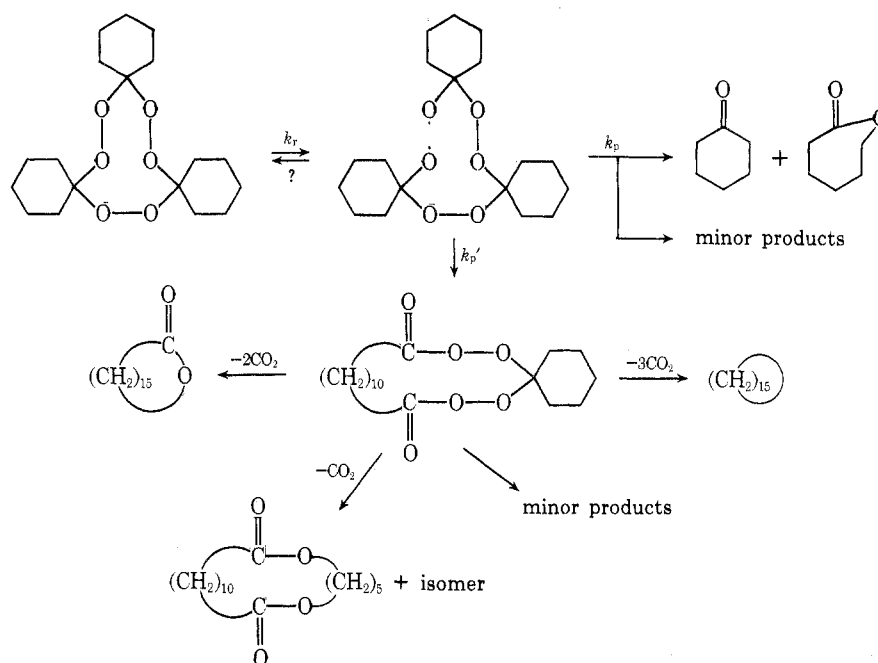
Several temperature baths were available: (a) a Sargent Model NSI-12 heater and circulator, (b) a Sargent Model NCI-33 heater with a built-in thermostat.

The IBM-360 computer was used for the least-squares treatment of the kinetic data.

Preparation of Vials. Vials were prepared in the following manner: an 18 × 150 mm Pyrex test tube was constricted about 20–30 mm from the open end. The test tube was broken at the constriction and a Pyrex glass tube of 5-mm diameter was attached. A constriction was formed 20 mm from the open end of the glass tube to be used in sealing off the vial.

Product Studies. Quantitative analysis of the peroxide decomposition products was by vpc. Yields of products were determined by measuring the response factors from standard solution. The products were identified by their retention times and mass spectrum or ir spectrum of a collected sample. The following columns

Scheme II
The Thermal Decomposition of Tricyclohexylidene Triperoxide



were used: (a) 5 ft \times 0.25 in. 20% SE 30 on Chrom W, (b) 10 ft \times 0.25 in. 20% SE 30 on Chrom W, (c) 10 ft \times 0.25 in. 10% XE 60 on Chrom W, and (d) 10 ft \times 0.25 in. 10% Carbowax 20M on Chrom G.

Beer's Law Plot for Tricyclohexylidene Triperoxide. Pure tricyclohexylidene triperoxide was accurately weighed into a volumetric flask. The flask was filled to the mark with solvent. The absorbance was then measured on the Perkin-Elmer IR-621 using standard procedures. Matched sodium chloride cells of 0.1-mm thickness were used. The data are plotted in Figure 6.

Infrared Kinetic Runs. Approximately 1-ml portions of a known concentration of peroxide solution were transferred into vials using a long stem disposable pipet. The vials were then stoppered and degassed three times.

From six to eight vials were immersed in a thermostated constant temperature bath at the desired temperature and the vials were removed (the time and number of the vial noted) usually during the first half-life of the peroxide decomposition. The vial was quenched in tap water, washed with acetone, and stored in the ice-water until it was assayed. Before the infrared analysis, all vials were allowed to come to room temperature.

Quantitative ir analysis was done using standard procedures. For tricyclohexylidene triperoxide, the band at 965 cm^{-1} was used. For all the ir studies, matched sodium chloride cells of 0.1-mm thickness were used. The rate constants were determined from a least-squares treatment of the data.

Kinetics (Iodometric). Approximately 3-5-ml portions of a known peroxide solution were transferred into weighed vials using a long stem disposable pipet. The vials were stoppered and weighed. The vials were then placed in a Dry Ice-acetone or isopropyl alcohol bath and attached to a vacuum rack. The degassing process consisted of evacuating, flushing well with nitrogen, thawing under vacuum, refreezing, and evacuating. This procedure was carried out three times. The vials were finally sealed under vacuum and stored in the ice box until the rate measurements were made.

From six to eight vials were immersed in a thermostated constant temperature bath at the desired temperature. The vials were removed (the time and number of the vial noted) usually during the first two half-lives of the peroxide decomposition. The vial was quenched in tap water, washed with acetone, and stored in ice-water until it was assayed.

The assay was conducted in the following manner. Crushed sodium iodide (1 g) was placed in a 250-ml iodine flask and 50 ml of carbonated glacial acetic acid added. One milliliter of 10% perchloric acid (in glacial acetic acid) was added along with a bit of Dry Ice. The vial was scratched with a file, broken, and the contents transferred quantitatively to the iodine flask. The vial was washed

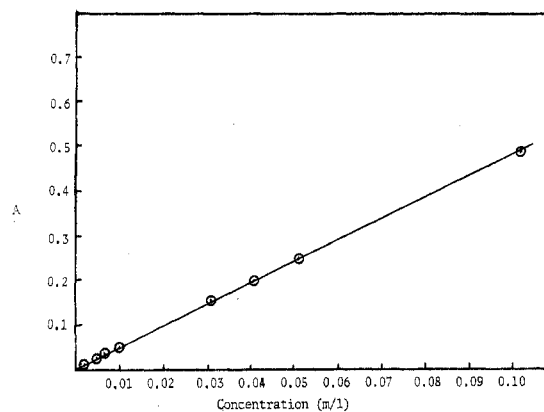


Figure 6. Plot of absorbance *vs.* concentration for tricyclohexylidene triperoxide in the solvent cyclohexane.

generously with carbonated chloroform from a squeeze bottle and the washing placed in the flask. The iodine flask was placed in the dark for 2 min. Fifty milliliters of carbonated distilled water was added and the liberated iodine titrated immediately with 0.01N thiosulfate. No indicator was used.

The rate constants were obtained from the slope of the line obtained by plotting log (milliliters of thiosulfate required/weight of sample) *vs.* time. The data given in the results and discussion section were obtained from a least-squares treatment of these data using the IBM 360 computer.

Synthesis of Dicyclohexylidene Diperoxide (VI) and Tricyclohexylidene Triperoxide (VII). The syntheses of both of these peroxides are given in detail elsewhere.¹¹

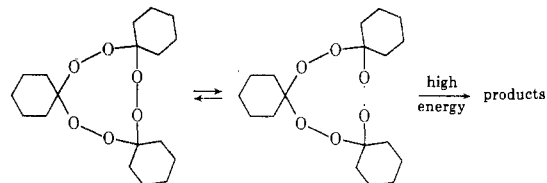
Acknowledgment. We thank the National Science Foundation for support of this work through Grant No. 34496.

Registry No.—VI, 183-84-6; VII, 182-01-4.

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The high energy process might be rupture of another O-O bond. Some of this might also occur in the decomposition of the dimeric peroxide. A parallel may be found in the decomposition of bis(trifluoromethyl) peroxide in the vapor phase.³⁵ E_a for this peroxide has been estimated to be 45 kcal/mol. The authors agree that this is a reasonable hypothesis but it still does not explain the large spread in ΔH^\ddagger observed for the trimeric peroxide. The rate constants should be determined over a much larger temperature range for the determination of the activation parameters before the mechanism above could be accepted with a modicum of certainty. By determining the rate constants of di-*tert*-butyl peroxide over a large temperature range Walling and Bristol³⁶ determined values of ΔH^\ddagger and ΔS^\ddagger which were significantly smaller than those of Huyser and Vanscoy.²³

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Micellar Effects upon the Decomposition of 3-Bromo-3-phenylpropionic Acid Effect of Changes in Surfactant Structure¹

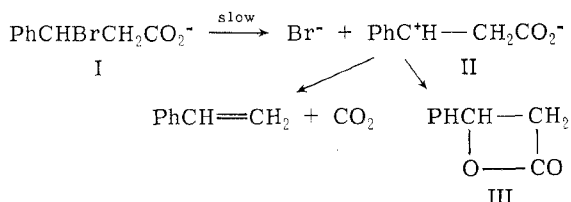
Clifford A. Bunton,* Albert A. Kamego, and Patricia Ng

Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106

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The S_N1 decomposition of 3-bromo-3-phenyl propionate ion is inhibited by cationic micelles of 1-hydroxyethyl-2-dimethylalkylammonium bromide (alkyl = *n*-C₁₂H₂₅, *n*-C₁₆H₃₃). At high surfactant concentrations an E2 elimination gives *trans*-cinnamate ion in dilute alkali (0.1 M). In the absence of surfactant¹ this E2 elimination is only found in much more concentrated alkali. Zwitterionic micelles of *N,N*-dodecyltrimethylalanine and sonicated vesicles (liposomes) of lecithin give small inhibitions and addition of hydrophobic alcohols reduces the surfactant effect.

The solvolysis of 3-bromo-3-phenyl propionate ion (I) in water involves rate limiting formation of the zwitterion (II) which rapidly undergoes both decarboxylation with elimination giving styrene and cyclization giving the β -lactone (III) as a minor product, and it was suggested that reaction

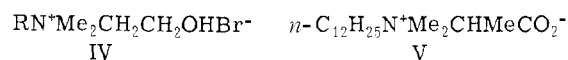


was assisted by electrostatic interaction between the carboxylate and cationic centers.² It seemed possible that this interaction would be more effective in a micelle than in water, but micelles of surfactants (detergents) inhibit this and other S_N1 reactions^{3,4} and the aim of this work was to investigate the effect of changes in the surfactant and solvent and the use of organic solvents which generate reverse micellization. (For reviews of micellar catalysis and inhibition see ref 5-7.) Using a surfactant derived from choline

we found formation of *trans*-cinnamate ion by an E2 elimination even in dilute alkali.

Experimental Section

Materials. The preparation and purification of three of the surfactants, CTABr (*n*-C₁₆H₃₃N⁺Me₃Br⁻) and 1-hydroxyethyl-2-dimethylalkylammonium bromides (IVa, R = C₁₂H₂₅; IVb, R = C₁₆H₃₃), have been described,⁸ and the other (V) was prepared by



standard methods.^{9,10} *N,N*-Dimethylalanine was prepared by the reductive methylation of DL-alanine⁹ and was quaternized with 1-bromododecane, and the zwitterionic surfactant *N,N*-dimethyldodecylalanine (V) was recrystallized from acetone. Lecithin (Schwarz Mann, egg white, highly purified) was sonicated at 0° for 5-min periods using a Biosonik IV sonicator to give a clear solution.

The organic solvents were redistilled and the sample of substrate was that used earlier.³ Redistilled deionized water was used.

Kinetics. The reaction at 25.0° was followed spectrophotometrically at 248 nm using a Gilford spectrophotometer and 5×10^{-5} M substrate.³ The observed first-order rate constants, k_{obs} , are in reciprocal seconds.