Reactions of Hydroperoxy Radicals. Liquid-Phase Oxidation of 1,4-Cyclohexadiene

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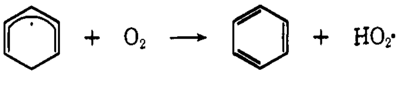
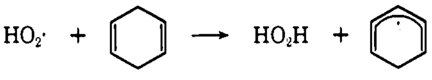
Abstract: The autoxidation of 1,4-cyclohexadiene proceeds exclusively through a free radical chain dehydrogenation to form benzene and hydrogen peroxide. The key step is the reaction of the cyclohexadienyl radical with oxygen to give benzene and hydroperoxy ($HO_2\cdot$) radicals directly. Estimated Arrhenius parameters exclude other routes. The bond energy of the active carbon-hydrogen bonds in various carbon radicals correlates directly with the amount of olefin formed in competition with organic hydroperoxide upon reaction with oxygen.

The formation of benzene and hydrogen peroxide from the oxidation of 1,4-cyclohexadiene[1,2] is one of the few cases of dehydrogenation by a simple autoxidation process at room temperature. While this oxidation is atypical because of the thermodynamic advantage associated with benzene formation, other hydrocarbons show the same behavior at higher temperatures. Because of the potential of this reaction as a source of hydroperoxy radicals near room temperature, we have made a careful study of the reaction.

The formation of benzene and hydrogen peroxide in the oxidation of 1,4-cyclohexadiene is not conclusive evidence in itself that the chain is carried by hydroperoxy radicals. The hydroperoxy radical mechanism entails the following propagation reactions:



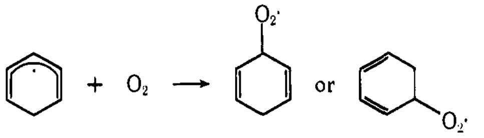
(1)



(2)

where reaction 1 could entail either an organic peroxy radical that rearranges as has been suggested[2] to form the indicated products or a direct abstraction of an H atom by O_2.

The alternative to the $HO_2\cdot$ mechanism is one involving an organic peroxy radical chain:



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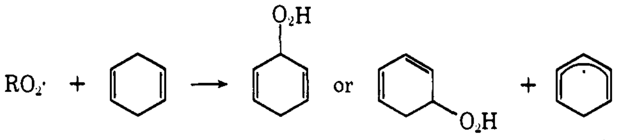
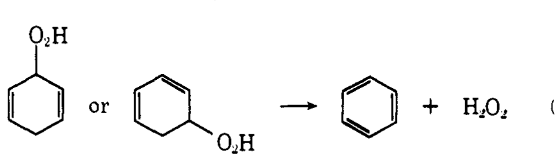


(4)

where $RO_2\cdot$ is either of the peroxy radicals formed in reaction 3. Benzene and hydrogen peroxide would be then formed by thermal or catalyzed decomposition reaction of the hydroperoxide, a highly exothermic reaction:



(5)

Since this decomposition may be fast, detection of benzene and hydrogen peroxide during the oxidation is not proof of the presence of hydroperoxy radicals. The most substantial evidence for participation of hydroperoxy radicals comes from the termination rate constants for oxidizing 1,4-cyclohexadiene.[2] These constants are very high—near diffusion control in nonpolar solvents—but much smaller in the polar solvent acetonitrile. Such a dependence on solvent suggests a chain carrier sensitive to solvation, and alkylperoxy radicals have not been observed to be this sensitive.[3] The termination of two hydroperoxy radicals most likely entails a head-to-tail interaction that is highly exothermic (~43 kcal/mol):[4]

$$HO_2\cdot + HO_2\cdot \longrightarrow HO_2H + O_2 \qquad (6)$$

This reaction is fast in the gas phase[5] and expected to be near diffusion in nonpolar solvents but, because of the HO dipole of the hydroperoxy radical, the reaction would be susceptible to interactions with polar solvents, as observed.

Additional evidence for the $HO_2\cdot$ chain comes also from the results of Howard and Ingold,[2] who obtained a quantitative yield of 4-hydroperoxy-2,6-di-*tert*-butyl-4-methyl-2,5-cyclohexadienone upon oxidizing 1,4-cyclohexadiene in the presence of 2,6-di-*tert*-butyl-4-methylphenol. They concluded that the formation of this hydroperoxide excludes reactions 3 and 4, where the chain carrier should produce 4-cyclohexadienylperoxy-2,6-di-*tert*-butyl-4-methyl-2,5-cyclohexadienone. However, this latter compound might readily decompose to the observed product and benzene in the presence of trace amounts of acid.

Experimental Section

General Oxidation Procedure. All reactions were carried out in borosilicate glass reaction tubes of about 10-ml volume. Break-off seals on the tubes allowed the contents to be expanded or distilled into a standard vacuum line. To prevent decomposition of hydrogen peroxide, the tubes were treated with concentrated HCl for 1 hr at 100° and then washed thoroughly with distilled water before use. The reaction mixtures were prepared by first placing weighed amounts of initiator and solvent in the reaction tube by conventional methods. Then the tube was connected to the vacuum line through a glass joint; 1,4-cyclohexadiene was distilled from a calibrated volume, through a gold foil trap to remove mercury, and into the vessel; the mixture was degassed by repeated freezing in liquid nitrogen, evacuation, and warming of the tube. The desired amount of oxygen was measured in a gas buret coupled with a Toepler pump and then transferred to the reaction vessel, which was cooled by liquid nitrogen. The reaction tube was sealed off, and the oxygen that did not expand into the tube was measured in the gas buret. The reaction tubes were then placed in a 50.0° (±0.05°) bath and agitated with either a Burell wrist-action shaker at 330 cycles or a Vibro mixer at 7500 cycles/min. At the completion of the reaction, the contents of the tubes were cooled (−78°) and the gases, largely oxygen, were removed through the break seal and measured.

Quantitative Determination of Hydroperoxide. The liquid contents of reaction were distilled to a tube containing MnO_2. The MnO_2 catalyzes the decomposition of H_2O_2 at room temperature

Table I. Products of Oxidation of Neat 1,4-Cyclohexadiene at 50°[a]

[ABN], *M*	Oxygen pressure, Torr	Δ oxygen Exptl	Δ oxygen Corr[b]	ΔC_6H_6	ΔH_2O_2	ΔH_2O[c]
0.0092	1272–722	0.353	0.389	0.407	0.330	0.402
0	4020–3846	0.112	0.136	0.134	0.091	0.138

[a] Reaction volumes are about 1.00 ml (10.2 *M* hydrocarbon); reaction times are 1.50 and 1.00 hr, respectively. [b] Assumes that water in excess of hydrogen peroxide is due to decomposition of hydrogen peroxide to water and oxygen. [c] Total H_2O after decomposition of hydrogen peroxide to H_2O and oxygen.

by the reaction:[6]

$$H_2O_2 \longrightarrow H_2O + {}^1/_2O_2 \qquad (7)$$

The oxygen evolution is followed by degassing of the solution and measuring until no further evolution is observed (about 1 hr). This procedure was found to be quantitative by analyzing aqueous solutions of hydrogen peroxide that had been titrated by standard titration techniques. The *tert*-butyl, cumyl, tetralyl, and *sec*-butyl hydroperoxides were not significantly affected by MnO_2, with or without hydrogen peroxide present.

Quantitative Determination of Water. After the hydrogen peroxide analysis, the contents were distilled to a reaction tube containing calcium hydride. The reaction[7]

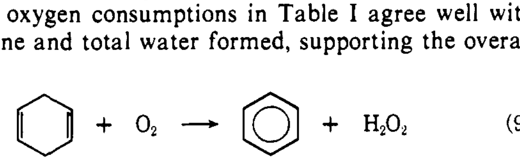
$$2H_2O + CaH_2 \longrightarrow Ca(OH)_2 + 2H_2 \qquad (8)$$

requires from 1 to 3 hr for completion. Analysis of known amounts of water tended to give values about 4% high, possibly through atmospheric contamination. The rate of the reaction is a function of particle size of the CaH_2 and its prior exposure to the atmosphere. Because of the sensitivity of the method, all reagents used in the oxidation were carefully dried over calcium hydride.

GLC Analysis of Organic Products. The analysis of the organic phase from the reaction was performed by GLC using a Carbowax on Chromosorb W column at 70°. Benzene was quantitatively measured by comparing it with an internal standard and correcting for relative response. The 1,4-cyclohexadiene contained 0.1 to 0.5% benzene initially, and it was necessary to correct the benzene measurements accordingly.

Results

Products of Oxidation. Table I presents product balances for an oxidation of 1,4-cyclohexadiene catalyzed by azobis(methylpropionitrile) (ABN) and an oxidation with no added initiator. Although benzene and hydrogen peroxide should be formed in equal amounts, less hydrogen peroxide than benzene is recovered. However, the total water analysis after the decomposition of the hydrogen peroxide agrees very well with the benzene formed. The differences (−1.22% and +2.98%) are within the limits of experimental uncertainty. Thus, as the hydrogen peroxide forms in the oxidation reactor, it partly decomposes by the time reaction 8 takes place, regenerating oxygen. The values of consumed oxygen in Table I have been corrected by attributing the difference between the total water and hydrogen peroxide to decomposition during the reaction and adding one-half the difference to the experimental oxygen consumption. The corrected oxygen consumptions in Table I agree well with the benzene and total water formed, supporting the overall reaction:



(9)

Kinetics of Oxidation. Data on the effects of 1,4-cyclohexadiene concentration, ABN concentration, and oxygen pressure are summarized in Table II. In the absence of an initiator, the following kinetics are observed:

$$\text{rate} = C[C_6H_8]^{1.43\pm0.07}[O_2]^{0.57\pm0.07}$$

With ABN as a free radical initiator, the experimental rate expression is:

$$\text{rate} = C[C_6H_8]^{1.03\pm0.04}\{C'[\text{ABN}]^{0.98\pm0.08} + C''[C_6H_8]^{0.80\pm0.22}[O_2]^{0.14\pm0.14}\}^{1/2}$$

The nature of oxygen pressure dependence is consistent with a thermal initiation reaction and not with the typical dependence observed at low oxygen pressure which is due to appreciable concentrations of nonoxygenated hydrocarbon radicals. In the latter case, the order of the reaction in oxygen would decrease from one to zero with increasing oxygen pressure, in the presence or absence of ABN. In Table II, the order of reaction in oxygen is essentially constant over the oxygen pressure range studied; the addition of ABN decreases but does not eliminate the oxygen pressure dependence, because the oxygen-dependent initiation is comparable to the ABN initiation.

In slow reactions at longer reaction times, product balances were less satisfactory, and there was evidence of a nonvolatile residue. The reason for this variation is not clear, but there was no evidence of residue at low conversions in slow reactions or at high conversions in faster reactions. The residue might arise from an isomerization of 1,4-cyclohexadiene to the more stable 1,3-cyclohexadiene by some catalyst generated in the system. The 1,3-cyclohexadiene would copolymerize with oxygen to form a polyperoxide $HO_2(C_6H_8O_2)_xH$. Such a complication could account for the reported[2] organic hydroperoxide in the oxidation.

Discussion

Kinetics and Mechanism. The observed kinetics are consistent with the following reactions:

$$\text{initiation: ABN} \xrightarrow{ek_d} R\cdot \xrightarrow{O_2} RO_2\cdot \xrightarrow{C_6H_8} RO_2H + C_6H_7\cdot \qquad (10)$$

$$C_6H_8 + O_2 \xrightarrow{k_{io}} C_6H_7\cdot + HO_2\cdot \qquad (11)$$

$$\text{propagation: } C_6H_7\cdot + O_2 \xrightarrow{k_o} C_6H_6 + HO_2\cdot \qquad (12)$$

$$HO_2\cdot + 1{,}4\text{-}C_6H_8 \xrightarrow{k_p} H_2O_2 + C_6H_7\cdot \qquad (13)$$

$$\text{termination: } 2HO_2\cdot \xrightarrow{k_t} H_2O_2 + O_2 \qquad (14)$$

The nature of reaction 12 will be discussed later when further argument is presented for $HO_2\cdot$ being the chain carrier.

Since the formation of cyclohexadienyl radical (reaction 13) is rate determining for oxygen consumption for long chain lengths, the rate of oxygen absorption is

$$R_0 = k_p[HO_2\cdot][C_6H_8]$$

Since the rate of initiation must equal the rate of termination

$$2ek_d[\text{ABN}] + 2k_{io}[O_2][C_6H_8] = 2k_t[HO_2\cdot]^2$$

Solving for $[HO_2\cdot]$ and substituting in the above equation gives the following rate expression:

$$R_0 = k_p[C_6H_8]\left\{\frac{ek_d[\text{ABN}] + k_{io}[O_2][C_6H_8]}{k_t}\right\}^{1/2} \qquad (15)$$

Thus, in the absence of ABN, the rate is 1.5 order in hydrocarbon concentration and 0.5 order in oxygen, in agreement with the experimental result. In principle, at sufficiently high ABN concentrations, the oxygen concentration term the square root term should become unimportant, and the rate should become first order in hydrocarbon and zero order in oxygen concentration. However, we have not been able to attain this situation experimentally; instead, an intermediate condition is observed where the oxygen dependence is between zero and one-half order.

Table II. Oxidation of 1,4-Cyclohexadiene in Chlorobenzene Solution at 50°

Reactants			Reaction time, hr	Rates, m*M*/hr				
							$-O_2$	
[ABN], *M*	$[C_6H_8]$, *M*	O_2 range, Torr		C_6H_6	H_2O_2	H_2O[a]	Exptl	Calcd[b]
0	1.03	502–430	7.32				5.36	5.7
0	1.02	644–586	5.25	5.40			6.11	6.5
0	1.09	2500–2230	4.52				16.2	14
0	1.10	5974–5888	2.08			23.5	22.6	22
0	3.15	531–457	1.78	26.5	23.0		23.0	32
0	4.35	410–310	1.30		43.5		38.7	44
0	10.20	511–405	1.18	39.8	80.3		88.2	176
0.0100	0.979	280–94	4.80	19.2			19.8	20
0.0107	1.05	547–340	5.35	22.8	19.4	23.4	22.0	23
0.0100	0.974	499–405	2.63				17.5	20
0.0100	1.03	6718–6480	3.06				40.9	30
0.0094	1.98	577–311	2.92		34.7		44.1	41
0.0100	4.14	560–340	1.33	86.5		87.4		95
0.0100	10.20	650–450	0.90		161.0		161.0	282
0.033	1.02	508–276	3.40	39.1			38.0	38
0.102	1.00	519–419	1.87				64.7	68
0.101	1.02	387–487	0.94				57.5	66

[a] These values include H_2O_2 that was decomposed to water in the H_2O_2 analysis. [b] Rates are calculated from eq 16 using rate constants evaluated for 1.0 *M* cyclohexadiene in chlorobenzene solution.

From the square of the rate expression for long chains (eq 15), the two initiation steps can be separated:

$$R_0^2 = ek_d\frac{k_p^2}{k_t}[C_6H_8]^2[ABN] + k_{io}\frac{k_p^2}{k_t}[C_6H_8]^3[O_2] \quad (16)$$

Thus at constant 1,4-cyclohexadiene and oxygen concentrations, the square of the rate is a linear function of the ABN concentration. Figure 1 is a plot of the data at 50° for 1.0 *M* 1,4-cyclohexadiene and about 450 Torr of oxygen. From the slope and a value[12] of $ek_d = 1.48 \times 10^{-6}$ sec^{-1}, the value of $k_p/k_t^{1/2}$ is calculated to be 0.0460 $M^{-1/2}$ sec$^{-1/2}$. This agrees fairly well with a value of 0.0552 at 30° reported by Howard and Ingold.

Thermal Initiation. From the intercept in Figure 1 or the measured rate with no ABN and 1.0 *M* 1,4-cyclohexadiene, the value of k_{io} is calculated to be 1.8×10^{-7} M^{-1} sec^{-1}, assuming Henry's law and an oxygen solubility in 1,4-cyclohexadiene of 0.01 *M*/atm. Reaction 11 is visualized as a hydrogen abstraction reaction by oxygen and is expected to have a frequency factor of $10^{9.0 \pm 0.5}$. The corresponding Arrhenius activation energy must be 23.3 ± 1.0 kcal/mol to give the observed rate constant. If this activation energy is equal to the heat of reaction (the back reaction having essentially no activation energy), then the dissociation energy of the carbon–hydrogen bond will equal this activation energy plus the hydrogen–oxygen bond strength in the hydroperoxy radical (47 ± 2 kcal/mol). Thus, the bond dissociation energy in cyclohexadiene is calculated to be 70 ± 3 kcal/mol, in good agreement with the literature value of 71 kcal/mol.[8]

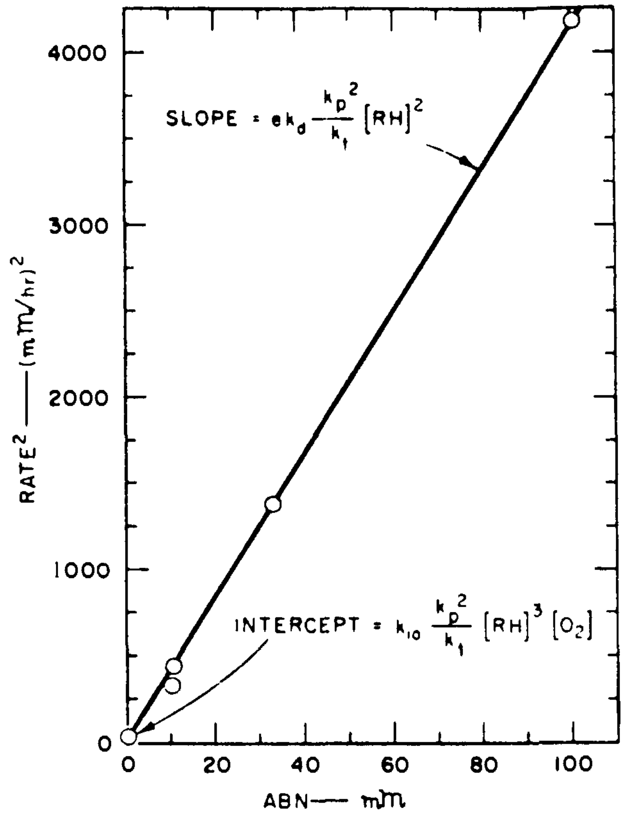


Figure 1.

Formation of the Hydroperoxy Radical. Further information about the details of the reaction of oxygen with cyclohexadienyl radicals can be obtained from consideration of the thermodynamics of the reaction and estimates of rate parameters. Because of resonance stabilization,[8] the allylic carbon–hydrogen bonds in 1,3- and 1,4-cyclohexadiene are 23 kcal/mol weaker than the carbon–hydrogen bonds in cyclohexane. The carbon–oxygen bond in the cyclohexadiene peroxy radical must be correspondingly weaker than the carbon–oxygen bond in a secondary alkylperoxy radical, or 28 − 23 = 5 ± 2 kcal/mol.[10] The entropy change of equilibrium 17

$$C_6H_7\cdot + O_2 \underset{k_{-17}}{\overset{k_{17}}{\rightleftharpoons}} C_6H_7O_2\cdot \quad (17)$$

is 20 ± 2 gibbs/mol (1 *M* standard states), similar to that for other resonance stabilized radicals.[9] Thus the equilibrium expression is

$$K_{17} = [C_6H_7O_2\cdot]/[C_6H_7\cdot] = k_{17}/k_{-17} = 10^{-(20\pm2/4.576)+(5000\pm2000)/4.576T} = 0.1 \text{ at } 50°$$

At typical concentrations of oxygen (10^{-2} to 10^{-4} *M*), equilibrium 17 lie considerably to the left, and less than 1% of the cyclohexadienyl radicals is oxygenated. However, since our results are independent of oxygen pressure (except for the initiation terms), this equilibrium cannot be important. Thus, either there is a faster reaction competing with

Table III. Thermochemistry of Dihydro and Related Compounds

Dihydro compd (ArH_2)	Heats of formation, kcal/mol Dihydro compd (ArH_2)	Dehydro compd (Ar)	Radical (AṙH)	Bond strengths, kcal/mol ArH–H	Aṙ–H	$ArH{-}O_2\cdot$
1,4-Cyclohexadiene	26.3	19.3	45.3	71	27	5
1,4-Dihydronaphthalene	30.6	36.1	51.6	71	37	5
9,10-Dihydroanthracene	42.0	55.2	61.0	71	46	5
Cyclohexane	−29.4	−0.8	13.0	94	38	27
Cyclohexene	−0.8	26.0	29.0	82	49	15

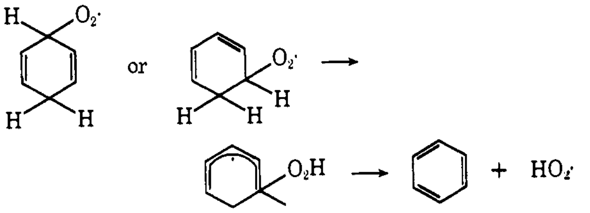
reaction 17, or $C_6H_7O_2\cdot$ can undergo a rapid reaction before the reverse reaction can occur.

Of three possible competing reactions that could prevent this equilibrium from being established, two can be ruled out. First, if propagation by a cyclohexadienyl peroxy radical (reaction 4) is faster than the reverse reaction to form a radical plus oxygen, the equilibrium will not be important. The relative rates may be expressed as follows:

$$R_{-17}/R_4 = k_{-17}/k_4[C_6H_8] = 10^{13-5000/4.576T}/[C_6H_8]10^{8-8000/4.576T} = 10^{5+3000/4.576T}/[C_6H_8]$$

This calculation uses A factors of 10^{13} for the unimolecular decomposition and 10^8 for the bimolecular propagation and expected activation energies of 5 kcal/mol for the unimolecular decomposition (equal to the bond strength) and 8 kcal/mol for propagation, consistent with a fast propagation. Evaluation of this expression at 50° indicates propagation by a cyclohexadienyl peroxy radical (reaction 4) is only 10^{-5} as fast as its dissociation in pure 1,4-cyclohexadiene at 50°; thus this propagation reaction cannot be important in the overall reaction or in affecting equilibrium 17.

A second reaction that could prevent equilibrium 17 from being important is the rearrangement reaction that has been suggested[2] as a main step in the formation of benzene and $HO_2\cdot$:



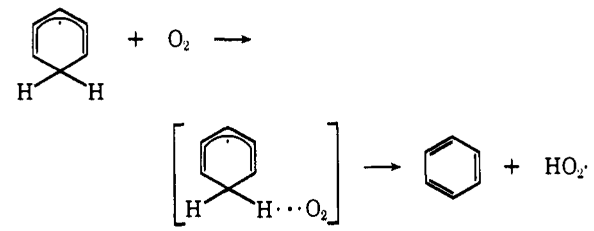
(18)

This reaction is visualized as an intramolecular reaction where the peroxy radical abstracts a hydrogen from the methylene that is either one or three carbon atoms away and then the hydroperoxy radical is eliminated to form benzene. The abstraction step[10] must have an A factor of about 10^{12} and activation energy similar to that for k_p plus about 2 kcal/mol for the strain of cyclic transition, or 10 ± 2 kcal/mol. The relative rate of this decomposition vs. dissociation is

$$R_{18}/R_{-17} = k_{18}/k_{-17} = 10^{12-10000/4.576T}/10^{13-5000/4.576T} = 10^{-1-5000/4.576T} = 10^{-4.4\pm1.3} \text{ at } 50°$$

Thus reaction 18 cannot be fast enough to prevent equilibrium 17 from being established or account for the products of the reaction.

The remaining reaction that could effectively perturb equilibrium 17 is a direct reaction of oxygen with the cyclohexadienyl radical to remove the methylene hydrogen atom:



(19)

The strength of carbon–hydrogen bonds broken in the cyclohexadiene radical has been calculated to be 24 kcal.[8] Since the strength of the hydrogen–oxygen bond formed is 47 kcal/mol,[3] reaction 19 is exothermic by 23 kcal/mol. If this reaction is one-tenth as fast as reaction 17, it will account for at least 99% of the reaction product. Thus equilibrium 17 cannot be important in controlling the concentration of the cyclohexadienyl radical; instead, its concentration will be determined primarily by reactions 13 and 19.

Comparison of Oxidations of Cyclic Hydrocarbons. While 1,4-cyclohexadiene, 1,4-dihydronaphthalene, and 9,10-dihydroanthracene are structurally similar, Howard and Ingold[2] found the tendency of these hydrocarbons in the presence of oxygen to form the corresponding aromatic system plus hydrogen peroxide to decrease in the order given. The related thermochemistry shows that these results are consistent with the mechanism we have proposed for the oxidation of 1,4-cyclohexadiene. Table III summarizes the heats of formation and bond strengths of the dihydro compounds (ArH_2), the corresponding dehydrogenated compounds (Ar), and the corresponding radicals (ȦrH). The values for heats of formation of the stable compounds are either reported or calculated values based on the group activity principle.[11] The heats of formation for the radicals have been calculated from the dihydro compounds and a carbon–hydrogen bond strength of 71 kcal/mol.[8] The bond strength of the carbon–hydrogen bond in the radical is calculated from the heats of formation of the radical and dihydro compound.

The data in Table III indicate that the addition of oxygen to the radical (reaction 17) should be reversible for each of these three compounds since $ArH{-}O_2\cdot$ bond energies are all about 5 kcal/mol. However, reaction 19 will depend on the bond strength of secondary hydrogen (Aṙ–H) and, therefore, becomes less important as the number of benzo groups is increased. The oxidation of neat 1,4-dihydronaphthalene gives high yields of 1-hydroperoxy-1,4-dihydronaphthalene although, at low concentrations, hydrogen peroxide formation is reported to predominate.[2] This observation is consistent with the higher bond strength in the 1-hydronaphthalene radical, which would be less rapidly attacked by O_2, allowing propagation corresponding to reaction 4 to become important, depending on the hydrocarbon concentration. The oxidation of 9,10-dihydroanthracene even at low concentrations (0.1–1.0 M) gives organic hydroperoxide, consistent with the higher strength of the hydroanthracene carbon–hydrogen bond.

Rearrangement 18 cannot explain the effect of structure on the ratio of hydrogen peroxide and organic hydroperoxide since the Ar(O$_2$·)-H bond strengths will all be about the same as in the parent hydrocarbons—approximately 71 kcal/mol—and the rate of reaction 18 should not vary significantly for the three systems. If breaking of the second carbon-hydrogen bond is to determine the proportion of organic peroxide, then bond breaking must occur at the point where the bond strength varies, i.e., reaction 19, not reaction 18.

The heats required for the formation of naphthalene from the correspond radicals are very similar to those required for the formation of cyclohexene from its corresponding radicals. However, the oxidation of cyclohexane, unlike that of dihydronaphthalene, gives no evidence of olefin formation, even at 100°, in spite of the fact that the AR-H· bond strengths are the same. Here the lack of olefin in the cyclohexane oxidation is related to the stronger ArH-O$_2$· bond, which reduces the tendency of reaction 17 to reverse and prevents reaction 19 from competing.

Acknowledgments. This research has been carried out as part of the SRI Oxidation Studies, which was supported by a group of petroleum and chemical companies.

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(12) This value of ek_d is determined by extrapolating the value in ref 3a for 60° in chlorobenzene to 50° using an activation energy of 30.8 kcal/mol.

Chemically Induced Dynamic Electron and Nuclear Polarization. VII. Simultaneous Contributions of the Radical Pair and Photoexcited Triplet Mechanisms in the Photolysis of Pyruvic Acid

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Abstract: CIDEP and CIDNP in the photoreduction of pyruvic acid in liquid by various hydrogen donors are reported and correlated. CIDNP study included both the low-field and high-field results and the method of using plane polarized light for excitation. The experimental evidence points to the co-existence of both the radical-pair and the photoexcited triplet mechanisms in CIDEP as well as in CIDNP observations. A general scheme for the simultaneous operations of the two mechanisms in a photochemical reaction is proposed.

Since the first observations of CIDEP in 1963[1] and CIDNP in 1967,[2] we have witnessed a remarkable development of a theory toward the understanding of these interesting phenomena. The initial efforts by Kaptein and Oosterhoff[3] and independently by Closs and co-workers[4] laid the foundation of the "radical-pair" theory which has now been generally established in CIDNP studies. The radical-pair theory was subsequently modified[5] with great success to account for CIDEP observations in radical systems showing the "multiplet effect". These include the original observation of H atom polarization in radiolysis,[1] the aliphatic ketyl radicals in photochemical systems,[6] and the alkyl and aliphatic ketyl radicals in radiolytic studies.[7] When a totally emissive pattern of CIDEP in the photoreduction of aromatic carbonyl compounds was reported in 1970 by Atkins, McLauchlan, and co-workers,[8] the phenomenon was explained by an extended radical-pair theory invoking the S-T$_{-1}$ mixing mechanism.[9] The importance of S-T$_{-1}$ mixing in the radical-pair theory has been beautifully demonstrated by CIDNP studies at low fields,[10] and a possible connection between CIDEP and CIDNP has also been generally recognized.[3,5,11]

In 1972 we reported the observation of totally emissive CIDEP in photochemical quinone systems.[12] The original naive proposal[12,13] of a photochemical triplet model based on the optically spin polarized triplets of the parent quinones and their subsequent hydrogen abstraction with retention of polarization in the primary radical pair has now received considerable theoretical[14-16] and experimental support.[17,18] The use of plane polarized excitation light as a test of the photoexcited triplet mechanism[16-18] in CIDEP studies was relatively successful. In some quinone systems, we have found[18] a variation factor dependent on the orientation of the polarized light to be larger than the theoretically predicted values by Adrian.[16] In view of the recent evidence that different photochemical reaction rates may result from different spin sublevels,[19] it is conceivable that even a small variation of reaction rates in the spin sublevels could lead to a much larger factor of the polarization magnitude in the plane polarized light experiments.

In a previous attempt to correlate both the CIDEP and the CIDNP results in the photolysis of *p*-benzoquinone in 2-propanol,[20] we did not obtain any conclusive evidence of the photoexcited triplet mechanism in the CIDNP observa-