head-to-head cis-syn-cis isomer, the maximum distance between ortho positions on the two phenyl rings is 3–4 Å; in the H–H, cis-syn-cis isomer the maximum separation is ~1.5 Å.

(15) Yang[12] found that the rate of self-quenching did not vary with temperature in the same manner as does the calculated diffusion control rates, a result indicating an excimer. Davidson and Whalen [R. S. Davidson and T. D. Whalen, *J. Chem. Soc., Chem. Commun.* **1977**, 361] have reported studies which indicate that fluorescence self-quenching occurs only when an excimer is formed and that dimerization only occurs when an excimer is present (not all excimers photodimerize).

(16) The constant *a* is the quantum yield for the formation of ether from the carbocation.

(17) The constant *b* is the product of the quantum yield for the formation of the intermediate and for the formation of the ether from the carbocation. The constant *c* incorporates the analogous quantum yields as well as the efficiency of sensitization in the triplet manifold.

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Organic Photochemistry with 6.7-eV Photons: Irradiation of Molecular Oxygen in Hydrocarbon Solution

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Abstract: Irradiation of a solution of oxygen gas in cyclohexane with 185-nm light from a mercury resonance lamp leads to cyclohexyl hydroperoxide as the principal product. Control experiments show that (i) the radiation is absorbed by oxygen to give the observed product, (ii) there is no impurity in the solvent that is responsible for either the initiation or propagation of the process, (iii) a chain reaction is not involved, (iv) the reaction is distinct from thermal autoxidation, and (v) ozone is not an intermediate in the process. It is mostly likely that, on absorption of a photon, oxygen is excited to the $^3\Sigma_u^-$ state and reacts directly with the solvent. Irradiation of oxygen in methylcyclohexane under identical conditions leads to mixtures of nearly all possible methyl cyclohexyl hydroperoxides. The product composition changes very little over the temperature range −10 to +41 °C. The lack of selectivity in the formation of these products also supports the intermediacy of an energy-rich species. Photolyses of these solutions with the unfiltered light from a mercury resonance lamp lead not only to hydroperoxides but also to the corresponding alcohols and ketones. The latter are mostly, if not exclusively, formed by the secondary photolysis of the hydroperoxides at long wavelength.

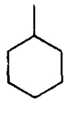
Introduction

The intense absorption of oxygen gas which lies in the wavelength range 176–195 nm (Schumann-Runge bands) has been extensively studied by both spectroscopists[1] and photochemists.[2] The reactions which take place in this region will be mentioned later. The photochemistry of solutions of oxygen in the same wavelength region in solvents which are transparent to the light has attracted little attention. In this investigation, we demonstrate that, in such a system, a photochemical reaction takes place which can be attributed to the electronic excitation of the oxygen and its subsequent reaction with the solvent. Although the process gives rise to product(s) which are common to both the thermal autoxidation of the solvent[3–5] and the reaction of the solvent with ozonized oxygen,[6,7] we show that the process at 185 nm is distinctly different.

Interest in the concurrent action of light and air (oxygen) on organic compounds has attracted attention for nearly 100 years. Very early work using ultraviolet light in which the systems were not clearly defined has been summarized elsewhere.[8] More recent work which has concentrated on the O_2 ($^1\Delta_g$) state has given rise to a vast literature which has been reviewed.[9–11] It is only necessary to mention that O_2 ($^1\Delta_g$) is inert with respect to saturated hydrocarbons such as cyclohexane.

Results

Products. Irradiation of cyclohexane saturated with oxygen at 185 nm led to the rapid formation of cyclohexyl hydroperoxide (**1**) and lesser amounts of cyclohexanol and cyclohexanone. The yields of these products at conversions of the order



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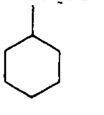

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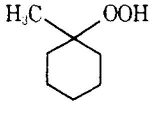

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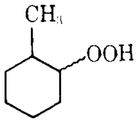

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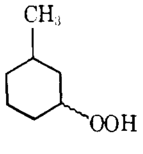

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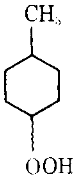

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Table I. Product Yields from Irradiation of Oxygen-Saturated Hydrocarbons[a]

hydrocarbon	time, min	hydroperoxide	cyclohexanol	cyclohexanone
cyclohexane	60	8.4×10^{-5} (±5%) M	2.2×10^{-5} (±62%) M	1.4×10^{-5} (±10%) M
methylcyclohexane	180	1.10×10^{-4} (±3%) M **2**, 1.9%; **5**, 22.7% **3**, 31.5%; **6**, 22.7% **4**, 21.2%	0.07×10^{-4} (±54%) M	0.10×10^{-4} (±12%) M

[a] Mercury resonance lamps: 185-nm band-pass filter.

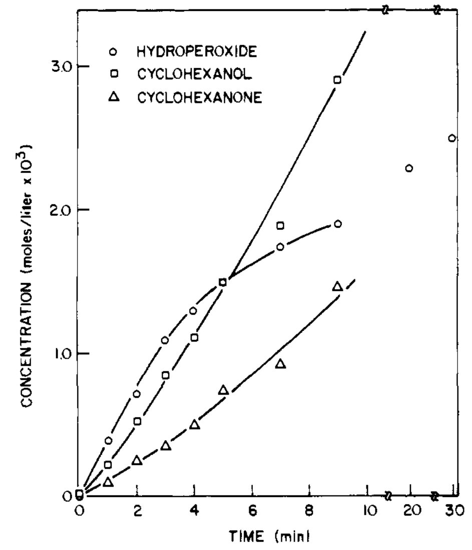

Figure 1. Product concentration vs. time in the photolysis of cyclohexane:oxygen; mercury resonance lamp; no filter.

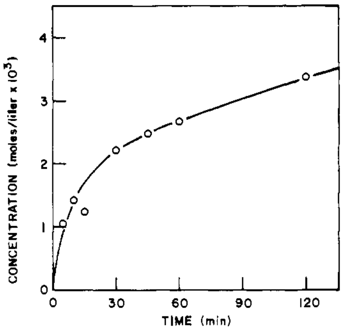

Figure 2. Total hydroperoxide yield vs. time in the photolysis of methylcyclohexane:oxygen; mercury resonance lamp; no filter.

of a percent are given in Table I. Photolysis of methylcyclohexane under identical conditions gave a similar product composition which is also listed in Table I.

Photolyses of solutions of oxygen in cyclohexane and methylcyclohexane with the entire light output of a mercury resonance lamp gave the data shown in Figures 1 and 2. The leveling trend in the concentrations of the hydroperoxide which set in rapidly suggested that the secondary photolysis of this compound may be an important consideration. This was confirmed when a deoxygenated solution of cyclohexyl hydroperoxide (which was prepared by conventional synthesis)[12] at a concentration (2.7×10^{-3} M) which corresponded to the inflection point in Figure 1 for this compound was photolyzed with a mercury resonance lamp. The concentration of the hydroperoxide decreased steadily, while those of cyclohexanol and cyclohexanone increased at rates comparable to those shown in Figure 1. The mass balance was ~100%.

An important point to consider is whether or not the hydroperoxides are the *only* primary products at 185 nm. The band-pass filter that was used to isolate the 185-nm radiation was designed to transmit only 0.1% of the intense line at 254 nm while passing 27% of the 185-nm radiation. However, its transmission between 185 and 254 averaged 30%. Therefore, secondary photolysis of the hydroperoxide from the weak mercury lines between 185 and 254 nm could well have occurred to give the observed yield of alcohols and ketones. Again the slopes of the rate curves in Figure 1 also suggest that the hydroperoxide is the only primary product and that both cyclohexanol and cyclohexanone are secondary photoproducts. This point will be discussed further in the next section.

Nature of the Absorbing Species. Three tests were undertaken to decide on the nature of the species that absorbed the 185-nm radiation to bring about the observed oxidation.

(i) Cyclohexane was highly purified by repeated passage through silver nitrate-alumina. The optical densities of this sample at 185 nm with and without oxygen were 0.31 and 0.05 (1-mm path), respectively. It follows that, in a solution saturated with oxygen, the latter will absorb 86% of the absorbed radiation. This should be viewed as a minimum value because of experimental difficulties which are detailed in the last section. Commercial spectroscopic grade cyclohexane had an optical density of 0.1-0.3 at 185 nm (1-mm path).

(ii) If a light-absorbing "initiator" was present in cyclohexane, it should be possible to decrease its concentration or eliminate it completely by extended photolysis of the solution in the presence of oxygen. The concentrations of cyclohexyl hydroperoxide that were produced by successive 30-min irradiations of a sample of spectroscopic grade cyclohexane (see Experimental Section for details) were $1.7 \pm 0.1 \times 10^{-3}$, $1.6 \pm 0.1 \times 10^{-3}$, and $1.6 \pm 0.1 \times 10^{-3}$ M, respectively. This indicates that there is no depletion of an "active" species if one is present or there is no "active" species present at all in the solvent.

(iii) Since the most logical, light-absorbing impurity in the cyclohexane would be an olefin such as cyclohexene, the change in the concentration of oxygen in an air-saturated solution of cyclohexene (10^{-2} M) during photolysis at 185 nm was monitored. No change was detectable, while the cyclohexene underwent the photoisomerizations that have been described in earlier work.[13] On the other hand, because of an internal filtering effect on the light, addition of an olefin to an oxygen-saturated solution of cyclohexane should *slow down* the build-up of the hydroperoxide on photolysis. This was found to be the case over the range 0.04-10.0% of added olefin.

Effect of Temperature. The data in Table II show that the total rate of formation of hydroperoxides from methylcyclohexane is essentially the same at −15 and +25 °C. The composition of the mixture in terms of the various hydroperoxides changes little from −15 to +25 but there is a small increase in the tertiary compound, 1-methyl-1-cyclohexyl hydroperoxide[3] at 41 °C.

Comparison with Ozone. Since irradiation of oxygen at 185 nm can give rise to ozone, it was of interest to see what effect ozone can have on this system. The following results were obtained:

Table II. Effect of Temperature on Irradiation of Oxygen in Methylcyclohexane[a]

temp, °C	total rate of formation, mol L^{-1} h^{-1}	hydroperoxides, %		
		primary	secondary	tertiary
−15	5.75×10^{-5}			
−10		4.8	69.7	25.5
+10		4.0	66.9	29.1
+25		1.9	66.7	31.5
+26	6.07×10^{-5}			
+41		1.4	56.4	42.3

[a] Mercury resonance lamp: 185-nm band-pass filter.

(i) A solution of oxygen in cyclohexane was irradiated with the entire output of a mercury resonance lamp for 5 min. The lamp was turned off, the solution was flushed with oxygen to sweep out any ozone, and the effluent was bubbled into KI solution. There was no iodine detected in the KI solution, indicating the absence of ozone. The amount of oxidation that occurred in the cyclohexane phase corresponded to that in Figure 1.

(ii) While oxygen was continuously bubbled through cyclohexane, it was irradiated (15 min) with the total output from a mercury resonance lamp. The effluent oxygen was passed through KI solution. There was no iodine liberated in the KI solution, again showing the absence of ozone.

(iii) Ozonized oxygen was bubbled into cyclohexane (which was shielded from external light). This solution was analyzed after short intervals for up to 165 min. The products and their relative yields were: cyclohexyl hydroperoxide:cyclohexanone:cyclohexanol, 1.00:2.88:7.24. This may be contrasted with the relative yields from cyclohexane + oxygen + 185-nm light as given in Table I.

Discussion

It is evident that the principal product(s) of the irradiation of oxygen at 185 nm in solution in hydrocarbons is the hydroperoxide(s). The alcohols and ketones that are also produced amount to 30% in the case of cyclohexane and 14% in the case of methylcyclohexane. Some of these products must come from the secondary photolysis of the initially formed hydroperoxide as the band-pass filter that was used could not prevent other radiation between 185 and 254 nm from being transmitted. The crucial point is if there is also a second source of these products, i.e., if these products can be formed directly by the interaction of oxygen, hydrocarbon, and 6.7-eV protons. While there is no evidence for or against such an idea, it is conceivable that the hydroperoxide, when it is formed by a mechanism such as the one discussed below, is "hot" (electronically) and decomposes a part of the time. Such electronically "hot" products have definitely been observed in solution phase photochemistry at 185 nm in the case of bicyclo[4.1.0]hept-2-ene.[14] A labile compound such as a hydroperoxide could well undergo a similar reaction. In that case, it is true that the alcohols and ketones are secondary products but they are not from biphotonic reactions.

Irradiation of oxygen in the gas phase at 185 nm gives rise to ozone by the following reactions:

$$O_2 + h\nu \rightarrow O_2\,(^3\Sigma_u^-) \qquad (1)$$

$$O_2(^3\Sigma_u^-) \rightarrow [O_2(^3\Pi_u)] \rightarrow 2O(^3P) \qquad (2)$$

$$O + O_2 \xrightarrow{M} O_3 \qquad (3)$$

Experiments have already been described here which failed to show the presence of ozone during photolysis of cyclohexane saturated with oxygen. It is nevertheless possible that ozone is an intermediate in the formation of the products as ozonized oxygen is known to react with saturated hydrocarbons to give identical products.[6] But the relative amounts of these products differ widely between the present instance with our own results on O_2:cyclohexane and the ozone:hydrocarbon (nonphotochemical) systems.[6,7] In view of this, the intermediacy of ozone cannot be entertained. Even the mere splitting of oxygen via reactions 1 and 2 can be discarded as in this event cyclohexanols should be a much more important product than is found to be the case.[15]

There are only two mechanisms that deserve serious consideration. The first is an autoxidation that is initiated by unknown absorbers in the solution and gives rise to a radical R· derived from the solvent. Then the following reactions which constitute the typical autoxidation chain can occur:

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (4)$$

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot \qquad (5)$$

The fruitless attempts that were made to pin down the unknown absorber–initiator have already been described. There are other objections to this chain mechanism which are:

(i) The abstraction step 5 needs an activation energy. Autoxidation of cyclohexane does not proceed to any extent below 60 °C[5] (when initiated by radical sources) mainly because of the slowness of this step. The present data show that the hydroperoxide yields are the same at 26 and −15 °C which strongly militates against an activated step. The ratios of hydroperoxide to alcohol + ketone also fail to provide any evidence for the operation of a chain mechanism.[5]

(ii) Owing to the activation energy needs for 5, autoxidation strongly favors the tertiary > secondary > primary positions. This selectivity tends to decrease with an increase in temperature. In the present instance, when the data on methylcyclohexane (Table II) are corrected for statistical distribution, the ratio of primary:secondary:tertiary is 0.1:1.0:4.5. While this shows the same trend as autoxidation, the degree of selectivity is an order of magnitude less.[16] Moreover, the distribution is nearly invariant with temperature between −10 and +25 °C and shows a surprising increase in the tertiary hydroperoxide at +41 °C.

The mechanism that would best explain the results is a simple one consisting of an excitation step 1 followed by an insertion.

$$O_2 + h\nu \rightarrow O_2(^3\Sigma_u^-) \qquad (1)$$

$$O_2(^3\Sigma_u^-) + RH \rightarrow ROOH \qquad (6)$$

The intermediacy of an excited state would account for the insensitivity of the reaction to temperature or the nature of the C–H which is involved. The trends seen in the data in Table II are probably due either to conformational changes in the hydrocarbon or viscosity effects (the two factors can be interrelated).

The hydroperoxide formed in eq 6 may be "hot" and decompose to give radicals which would ultimately lead to the alcohols and ketones that are observed as minor products. Thermochemical data on cyclohexyl hydroperoxide are not available but data on *tert*-butyl hydroperoxide[17] indicate that a reaction similar to eq 6 (but involving 2-methylpropane) should be exothermic by many electron volts of energy.

The formation of the upper triplet excited state of oxygen in solution at low temperature which is demonstrated in this work should open up interesting prospects in photooxidation.

Experimental Section

Materials. Cyclohexane and methylcyclohexane (Baker-Photrex) were used as obtained. For ultraviolet absorption measurements and in order to test the effect of purification on the rates, cyclohexane was purified by passage through a column of silver nitrate-alumina.[18]

A sample of cyclohexyl hydroperoxide was synthesized according to the procedure of Walling and Buckler.[12]

Oxygen (99.78%; rest nitrogen and argon; hydrocarbons $< 0.0013\%$ by volume) was passed through an "ultraire" filter (Norgren) and used in the photochemical experiments. For absorption measurements, ultra-high-purity oxygen (Matheson), 99.99%, was used as obtained.

Apparatus. For large-scale (0.1-0.5 g of products) photolysis, a 40-W hot cathode mercury resonance lamp was used in a Suprasil well as the irradiation source. For irradiations with the isolated 185-nm line, a Hanovia Ottawa-style cold-cathode spiral mercury lamp (8 W) was used in conjunction with an Acton 185 HR band-pass filter. The transmission of this filter at selected wavelengths was in nm: 185, 27%; 212, 46%; 225, 36%; 254, 0.6%; 275, 13.5%; 300, 7.0%; 350, 4.0%.

Absorption Spectra. The absorption at 185 nm was measured with a Carey 17D ultraviolet spectrometer. Some difficulty was experienced in measuring the optical density of solutions of oxygen in hydrocarbons because the absorption was too intense to be measured in a 10-mm path cell, while, in a 1-mm path cell, the solution could not be saturated satisfactorily in situ. Some oxygen may have been lost during transfer from a saturator to the cell which would then give a minimum value for the OD. The OD of oxygen-free cyclohexane could be measured only in a 10-mm path cell as in a 1-mm path cell it was smaller than the machine correction at that wavelength.

Analysis. Cyclohexyl hydroperoxide was identified by a comparison of its spectra, and its chromatograms (thin layer, GC) were identical with those of an authentic sample. The isomeric methyl cyclohexyl hydroperoxides were identified only by the alcohols that were produced by reduction with triphenylphosphine. The composition of the isomeric mixture was taken to be the same as that of the isomeric alcohols; i.e., no rearrangement had accompanied the reduction. All of the other products (alcohols and ketones) were identified by GC mass spectrometry. Authentic samples of all of the products were available.

Quantitative analysis for hydroperoxides was conducted by iodimetry.[19] The reliability of the procedure was checked with weighed samples of authentic cyclohexyl hydroperoxide. Injection of the hydroperoxides into a gas chromatograph caused them to rearrange to the corresponding alcohols and ketones. The yield of the latter was not quantitative. Therefore, in a photolysis mixture of hydroperoxide, alcohol, and ketone, the peroxide was estimated by iodimetry. Then aliquots of the mixture were injected onto a GC before and after treatment with triphenylphosphine. These data were sufficient to evaluate the individual concentrations of the three components. However, the corrections that had to be applied to the determination of alcohol and ketone concentrations were large especially when a band-pass filter was used during irradiaton.

For methyl cyclohexyl hydroperoxide, eight isomeric structures are possible. The composition of the experimental product was determined from the alcohols that were obtained on reduction. A clean separation between cis and trans isomers of 2-, 3-, or 4-methylcyclohexanols was not realized.

Procedure. In all runs, care was taken to keep the solution close to saturation with oxygen. In qualitative or preparative experiments, oxygen was slowly bubbled through the solution during irradiation, while, in quantitative runs, the irradiation was interrrupted as many times as considered necessary (depending upon the rate of the reaction) to resaturate the solution.

Photolysis of Cyclohexene in Air-Saturated Solution. A solution of cyclohexene in pentane (10^{-2} M) was saturated with air and photolyzed with the full output of a mercury resonance lamp. The concentrations of both nitrogen and oxygen in the solution were monitored by GC, the nitrogen serving as an internal reference for oxygen. The ratios N_2/O_2 at various times were:

t, min	N_2/O_2
0	2.48
5	2.49
16	2.43
44	2.98

Similar results were obtained with cyclooctene.

Photolysis of Cyclohexane "Purified" by Irradiation. In order to eliminate possible impurities which may initiate the reaction with oxygen, cyclohexane was put through the following cycle: a volume of 150 mL of spectroscopic grade hydrocarbon was irradiated with the full radiation from a 40-W Hg resonance lamp, while oxygen was continuously bubbled through the liquid. The photolyzate from three such irradiations (i.e., 450 mL) was carefully distilled and a middle cut of 300 mL was used in the next cycle in two batches. This photolyzate was distilled again and 150 mL collected for the next irradiation. The photolyzate at the end of each irradiation was analyzed for its hydroperoxide concentration. The results were:

pass no.	volume of O_2 satd liquid, mL	irradiation time per 150 mL, min	[hydroperoxide], M
1	450	30	$1.7 \pm 0.1 \times 10^{-3}$
2	300	30	$1.6 \pm 0.1 \times 10^{-3}$
3	100	30	$1.6 \pm 0.1 \times 10^{-3}$

Photolysis of Oxygen in Cyclohexane with Olefin Added. The olefin used was tetramethylethylene. Solutions of the olefin in cyclohexane were irradiated at 185 nm with oxygen bubbling through. At the end of 1 h, the concentration of hydroperoxide was determined by titration. The concentrations of the olefin and the concentrations of the hydroperoxide were 0.0%, 0.0023 M; 0.04%, 0.0018 M; 0.5%, 0.0015 M. When the concentration of the olefin was raised to 10%, a new set of reactions was observed which gave rise to hydroperoxides derived from the olefin and not the solvent.

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