nylethylamine, respectively, by methylation with formaldehyde. *N*-Methylprolinol, 1,2-dimethylpyrrolidine, *N*,*N*-dimethyl-2-aminobutanol, and *N*,*N*-dimethyl-2-aminobutane were prepared by known procedures[14] from L-proline and 2-amino-1-butanol. All catalysts used were dried prior to use. Solvents used (toluene, $CHCl_3$) were dried and distilled over P_2O_5 and stored over molecular sieves. Chloral was distilled [bp 96 °C (765 mmHg)] under N_2 and stored at −25 °C. Ketene was prepared by pyrolysis of acetone vapors in an apparatus described by Williams and Hurd.[15] Residual acetone vapors were removed as thoroughly as possible by cooling the vapors to −40 °C (ketene bp −42 °C). No further purification of the ketene was performed. With the equipment used, after 0.75–1 h about 0.01 mol of ketene is formed, as was established by leading ketene through an aniline solution and isolating the acetanilide formed. All chloral–ketene addition reactions were performed under an inert atmosphere of dried nitrogen.

(*S*)-β-(Trichloromethyl)-β-Propiolactone (3). In a three-necked round-bottom flask (100 mL) equipped with a thermometer, a ketene inlet under the surface of the toluene, and a dropping funnel was dissolved 83 mg (0.25 mmol) of purified quinidine in 50 mL of toluene. The solution was cooled to −50 °C. Ketene was bubbled through the solution with magnetic stirring while 1.47 g (0.01 mol) of anhydrous chloral in 20 mL of toluene was added dropwise during 0.75–1 h. Excess of ketene should be avoided in order to minimize formation of diketene. After the reaction was complete, the mixture was warmed to room temperature and transferred to a separatory funnel. The catalyst was removed by repeated (2×) washing with 4 N HCl. The toluene layer was washed with saturated NaCl solution and dried over $MgSO_4$. After removing $MgSO_4$ by filtration, the toluene was removed under reduced pressure. The residue was purified by bulb to bulb distillation: 120 °C (0.5 mmHg), yield 1.67 g (89%); $[\alpha]^{20}_{578}$ −15.3° (*c* 1, cyclohexane) corresponding to an ee of 98%; NMR 3.7 (2 H, m), 5.0 ppm (1 H, t).

Optically Pure (*R*)- and (*S*)-β-(Trichloromethyl)-β-propiolactone. Lactone 3 (18 g) (ee 95%) was dissolved in 41 mL of methylcyclohexane by warming. The solution was filtered and allowed to cool to room temperature. After filtration and washing with a little cool methylcyclohexane, 15.5 g of (*S*)-lactone product could be isolated (85% recovery), $[\alpha]^{20}_{578}$ −15.6° (*c* 1, cyclohexane), mp 51–52 °C. The specific rotation did not change after another crystallization. The same procedure starting with 19.7 g of lactone 3 (72% ee) from 110 mL of methylcyclohexane yielded 12.8 g (*R*)-lactone (65% recovery), $[\alpha]^{20}_{578}$ 15.4° (*c* 1, cyclohexane), mp 51–52 °C. Again the rotation did not change after another crystallization. Racemic lactone 3 has mp 36–37 °C.[15]

4,4,4-Trichloro-3-hydroxybutanoic Acid (4). Lactone 3 (9.7 g), mp 51–52 °C, $[\alpha]^{20}_{578}$ −15.6° (*c* 1, cyclohexane), was suspended in 150 mL of 4 N HCl and heated under reflux for 3 h. The water/HCl was removed by distillation under reduced pressure, furnishing 11.24 g (100%) of acid after drying; $[\alpha]^{20}_{546}$ +26.1° (*c* 1, acetone).

Malic Acid. To a solution of 2.12 g (10 mmol) of 4,4,4-trichloro-3-hydroxybutanoic acid, $[\alpha]^{20}$ + 26.1 (*c* 1, acetone), in 15 mL of water was added dropwise at 0 °C a solution of 2.2 g of NaOH (55 mmol) in 15 mL of water. The solution was stirred, with the exclusion of carbon dioxide, for 24 h at 20 °C. The solution was passed through a Dowex 50W column (3-cm diameter, 20-cm length, 150 g of Dowex 50W-X8). The resulting solution was evaporated to dryness. The residue was dissolved in 1 mL of water and filtered to remove the fumaric acid formed during the hydrolysis (about 5%). After evaporation of the solvent and drying under vacuum, 1.14 g of malic acid could be obtained, $[\alpha]^{20}_D$ −28.4° (*c* 5.5, pyridine) (lit. $[\alpha]^{20}_D$ −28.6° (*c* 5.5, pyridine).[16]

Acknowledgment. The cooperation and advice both on the mechanism of the reaction and the ^{13}C NMR work by Professor I. Agranat, Jerusalem University, Jerusalem, Israel is gratefully acknowledged.

Registry No. 1, 463-51-4; **2**, 75-87-6; (*S*)-**3**, 16493-62-2; (*R*)-**3**, 16493-63-3; (*S*)-**6**, 97-67-6; (*R*)-**6**, 636-61-3; quinine, 130-95-0; acetylquinine, 18797-86-9; quinidine, 56-54-2; cinchonidine, 485-71-2; cinchonine, 118-10-5; epichlorocinchonidine, 79769-63-4; deoxycinchonidine, 5808-37-7; epiquinine, 572-60-1; *N*-methylephedrine, 552-79-4; (*S*)-*N*,*N*-dimethyl-α-phenylethylamine, 17279-31-1; (*S*)-*N*-methylprolinol, 34381-71-0; (*R*)-1,2-dimethylpyrrolidine, 40170-49-8; (*S*)-*N*,*N*-dimethyl-2-amino-1-butanol, 79769-64-5; (*R*)-*N*,*N*-dimethyl-2-aminobutane, 40916-66-3; brucine, 357-57-3.

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(15) Williams, J. W.; Hurd, C. D. *J. Org. Chem.* **1940**, *5*, 122.

(16) The Aldrich-Europe Catalog Handbook of Fine Chemicals, 1981–1982. The original reference [*Beilstein* **1921**, *3*, 419. Walder, P. *Ber.* **1899**, *32*, 2859: $[\alpha]_D^{18}$ 38.0° (*c* 5, pyridine)] is misleading. The rotation cited by Aldrich $[\alpha]_D^{20}$ 28.6° (*c* 5.5, pyridine) is correct, checked by ourselves.

Reaction of Cyclohexane and Cyclohexyl Radicals with Atomic and Molecular Oxygen

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Abstract: The reaction of oxygen atoms with cyclohexane in a fast-flow system was studied with a photoionization mass spectrometer. Cyclohexyl radicals formed by the initial hydrogen abstraction were detected directly. The subsequent reaction of the cyclohexyl radicals with atomic oxygen proceeds by both hydrogen abstraction (52%) and an oxygen atom addition reaction (48%). The product in the hydrogen abstraction reaction was cyclohexene. Most of the products in the oxygen atom addition reaction resulted from ring cleavage of the vibrationally hot cyclohexyloxy radicals. (The yield of cyclohexanone was just 3%.) Competition experiments show that cyclohexyl radicals react $(5.0 \pm 1.3) \times 10^{-2}$ times as fast with O_2 as with $O(^3P)$. In the presence of an excess of O_2 both cyclohexene and cyclohexanone are observed but in decreased yields—cyclohexene (25%) and cyclohexanone (2%). These results could be explained by the reaction of oxygen atoms with cyclohexylperoxy radicals produced by the recombination of cyclohexyl radicals with O_2.

When alkyl radicals react with oxygen atoms, two typical processes are conceivable: (1) formation of olefins by hydrogen abstraction; (2) formation of aldehydes or ketones by oxygen atom addition. For example, the reaction of the *tert*-butyl radicals[1] with atomic oxygen forms isobutene (80%) and acetone (20%). In the case of the cycloalkyl radicals, formation of cycloalkene and cycloalkanone are expected by analogy. However, since four hydrogen atoms in the cycloalkyl radical can be abstracted to form cycloalkene as compared to nine equivalent hydrogen atoms in the *tert*-butyl radical to produce isobutene, the branching ratios to produce cycloalkene and cycloalkanone are expected to be different from the case of the *tert*-butyl radical. Further, ring

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Table I. Pseudo-First-Order Decay Rates for Reactions of Cyclohexane and Cyclohexene with Atomic Oxygen[a]

reaction	pressure			lamp (window)	k, cm^3 $molecule^{-1}$ s^{-1}
	total[b]	cyclohexane[c]	$[O]_0$[c]		
$O + c\text{-}C_6H_{12}$	3.90	0.010	13.70	Ar (LiF)	$(9.5 \pm 0.8) \times 10^{-14}$
	3.81	0.028	16.14	Kr (MgF_2)	$(9.8 \pm 0.8) \times 10^{-14}$
					av $k_1 = (9.7 \pm 0.6) \times 10^{-14}$
$O + c\text{-}C_6H_{10}$	3.73	0.012	0.560	Kr (MgF_2)	$(1.94 \pm 0.07) \times 10^{-11}$
	3.70	0.004	0.266	Kr (MgF_2)	$(2.05 \pm 0.06) \times 10^{-11}$
					av $k_3 = (2.00 \pm 0.05) \times 10^{-11}$

[a] Reaction times are 1-8 msec in all cases. [b] Pressure in torr. [c] Pressure in mtorr.

cleavage may compete with the process forming cycloalkanone.

The same two products have been observed but in a different proportion (isobutene (27%) and acetone (73%)) in the reaction of *tert*-butyl peroxy radicals with atomic oxygen.[1] In the case of the reaction of cycloalkyl peroxy radicals with oxygen atoms, reaction probably occurs in a different manner because cycloalkanones were not major products in the photooxidation of cycloalkanes (C_5–C_7) in the NO–H_2O–air system[2] (instead the major products were carbonyls produced by ring rupture processes).

In the present study, cyclohexyl radicals were generated in the reaction of cyclohexane with atomic oxygen in a fast-flow reactor. Radicals formed and reaction products produced by the subsequent reactions were measured by a photoionization mass spectrometer.[3,4]

Experimental Section

The experimental setup of a fast-flow reactor and a photoionization mass spectrometer was as described previously.[5,6] Measurements of the total and partial pressures and the linear flow velocity within the reactor were also as described before.[6] Oxygen atoms were generated by a microwave discharge in a helium–oxygen mixture (0.05–2% in helium), and their concentration was determined by titration with NO_2 according to the reaction $O + NO_2 \rightarrow NO + O_2$. Then known partial pressures of NO were added to calibrate the instrument sensitivity. Cyclohexane (Wako Pure Chemical Ind., 99.8%) was diluted in helium (about 5% cyclohexane in He) and entered the main flow through a movable inlet with six small radially directed holes. The various photoionization lamps used to ionize radicals and molecules were powered by a microwave discharge. All measurements were done at room temperature, 298 ± 3 K.

The gases O_2 (Nippon Sanso, 99.99%), He (Nippon Sanso, 99.9999%), NO_2 (Matheson, 99.5%), and NO (Matheson, 99.0%) were used without further purification. Cyclohexane, cyclohexene, and cyclohexanone (all from Wako Pure Chemical Ind.) were used without further purification except degassing.

Measurements were done under the conditions [O] > 2[cyclohexane].[7]

Results

Cyclohexyl radicals were observed when oxygen atoms reacted with cyclohexane. The radical was detected using a Xe resonance lamp with a sapphire window (8.44 eV). Mass spectra measured are shown in Figure 1. Other products produced by subsequent reactions and the parent molecule were not photoionized by this lamp.

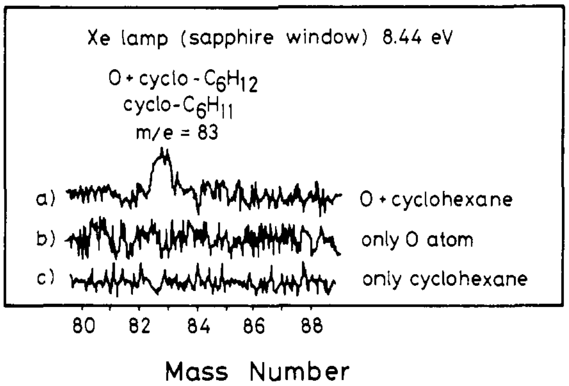


Figure 1. Mass spectra of the cyclohexyl radical produced in O + cyclohexane. A Xe lamp with a sapphire window (8.44 eV) was used for the photoionization. Conditions: partial pressure (mtorr), $[O]_0$, 4.8, [cyclohexane], 1.1; reaction time = 4.2 ms; total pressure = 4.2 torr.

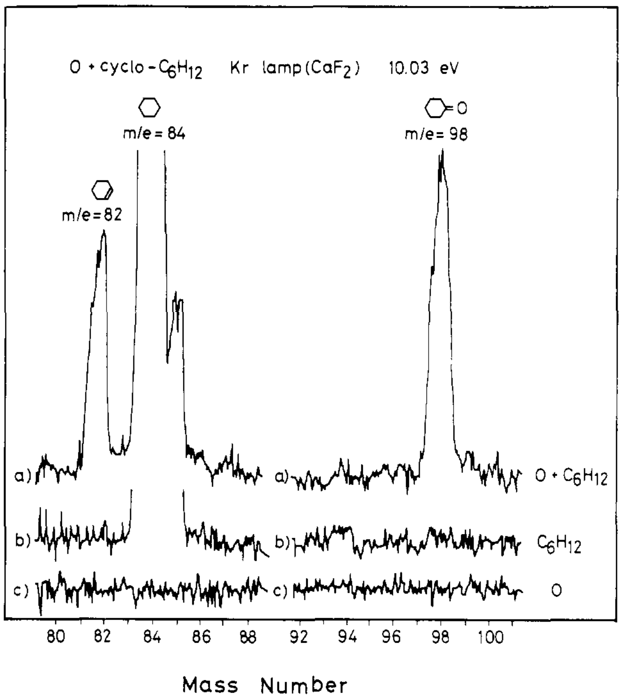
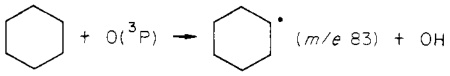


Figure 2. Mass spectra of the cyclohexene and cyclohexanone produced in O + cyclohexane. Kr lamp with a CaF_2 window (10.03 eV) was used. Conditions: partial pressure (mtorr), $[O]_0$, 8.2, [cyclohexane], 0.82; reaction time = 4.2 ms; total pressure = 4.1 torr.



ΔH = -9 kcal/mol (1)

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(1) Washida, N.; Bayes, K. D. *J. Phys. Chem.* **1980**, *84*, 1309–1314.

(2) Takagi, H.; Washida, N.; Bandow, H.; Akimoto, H.; Okuda, M. *J. Phys. Chem.* **1981**, *85*, 2701–2705.

(3) Jones, I. T. N.; Bayes, K. D. *J. Am. Chem. Soc.* **1972**, *94*, 6869–6871.

(4) Kanofsky, J. R.; Gutman, D. *Chem. Phys. Lett.* **1972**, *15*, 236–239.

(5) Washida, N.; Bayes, K. D. *Int. J. Chem. Kinet.* **1976**, *8*, 777–794.

(6) Washida, N. *J. Chem. Phys.* **1980**, *73*, 1665–1672.

(7) The reaction of cyclohexane with atomic oxygen is initiated by the hydrogen abstraction reaction to produce cyclohexyl radical and OH. The OH radicals can also be produced by subsequent radical–atom reactions and these can react with cyclohexane faster than atomic oxygen; $c\text{-}C_6H_{12} + OH \rightarrow c\text{-}C_6H_{11} + H_2O$. The rate constant for the reaction of cyclohexane with OH has been reported[8] to be $(6–8) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. OH radicals are destroyed by the reaction $OH + O \rightarrow H + O_2$. The rate constant of this reaction has been reported[9] to be $(3–4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Therefore, in order to make the effect of OH radicals on the formation of cyclohexyl radicals less than 10%, the concentration of oxygen atoms must be at least two times larger than the cyclohexane concentration.

(8) (a) Darnall, K. R.; Atkinson, R.; Pitts, J. N., Jr. *J. Phys. Chem.* **1978**, *82*, 1581–1584. (b) Atkinson, R.; Darnall, K. R.; Lloyd, A. C.; Winer, A. M.; Pitts, J. N., Jr. "Advances in Photochemistry", Pitts, J. N., Jr., Hammond, G. S., Noyes, W. A., Jr., Eds.; Interscience: New York, 1979; Vol. 11, pp 375–488.

(9) (a) Breen, J. E.; Glass, G. P. *J. Chem. Phys.* **1970**, *52*, 1082–1086. (b) Westenberg, A. A.; de Hass, N.; Roscoe, J. M. *J. Phys. Chem.* **1970**, *74*, 3431–3438. (c) Campbell, I. M.; Handy, B. J. *Chem. Phys. Lett.* **1977**, *47*, 475–478. (d) Howard, M. J.; Smith, I. W. M. *Ibid.* **1980**, *69*, 40–44.

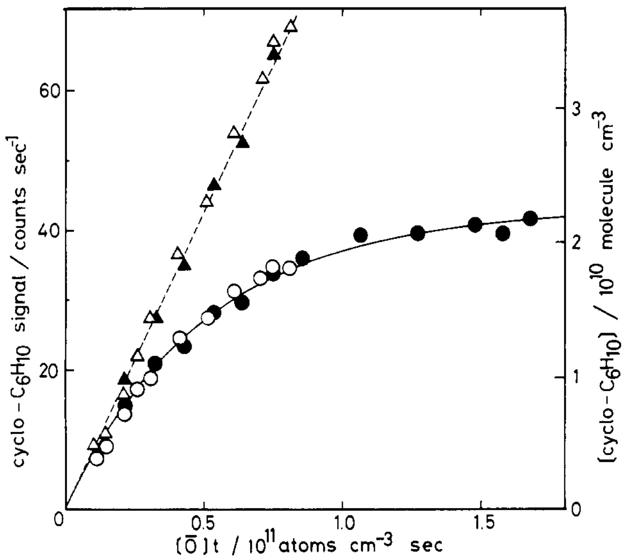
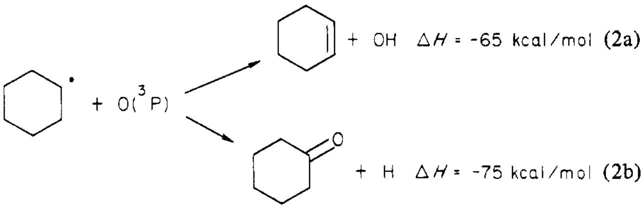


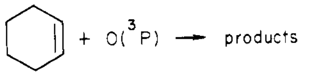
Figure 3. Time dependence of cyclohexene produced in the O + cyclohexane reaction. Conditions for the open symbols: partial pressure (mtorr), $[O]_0$, 0.33, [cyclohexane], 0.26, $[O_2]_0$, 1.04; total pressure = 3.61 torr. Conditions for the filled symbols: partial pressure (mtorr) $[O]_0$, 0.66, [cyclohexane], 0.26, $[O_2]_0$, 2.12; total pressure = 3.61 torr. $[O_2]_0$ refers the amount of O_2 added to the O_2/He discharge. Reaction times used were 1-8 ms. Values for $[\bar{O}]t$ were calculated using n = 11. Corrections for $[\bar{O}]$ were 4% or less. The cyclohexene concentrations corrected for subsequent reaction, $[\text{cyclohexene}]_T$, are indicated by triangles.

Cyclohexene (*m/e* 82) and cyclohexanone (*m/e* 98) were produced from the reaction of O + cyclohexane as expected; these were detected with a Kr lamp with a CaF_2 window (10.03 eV). Mass spectra obtained are shown in Figure 2. The signal at *m/e* 85 in Figure 2 is the isotope (^{13}C) signal of cyclohexane. The formation of cyclohexene and cyclohexanone can be easily understood by the following reaction processes subsequent to reaction 1:



Photoionization of the parent cyclohexane and the products cyclohexene and cyclohexanone by the Kr lamp with a CaF_2 window (10.03 eV) is consistent with the reported ionization potentials for these molecules—9.8, 8.7, and 9.1 eV, respectively.[10]

The pseudo-first-order decay rates of cyclohexane, reaction 1, and cyclohexene, reaction 3, were measured in a large excess of oxygen atoms. Values for k_1 and k_3 obtained are listed in Table I. The 95% confidence limits were calculated from the least-squares line using 8 points for each run and 16 points for the averaged values. In these cases, the stoichiometric factors for the number of oxygen atoms consumed per cyclohexane and cyclohexene reacted are expected to be very large. Because, as described later, about half of the total reaction of O + cyclohexane is a ring cleavage reaction and many radical fragments are produced, the product corresponding to the residual 50% is cyclohexene, which also can induce fragment radicals due to the subsequent reactions. In the present study, values of n = 11 and 8 were used[11] for the number of oxygen atoms consumed per cyclohexane and cyclohexene reacted, respectively. The values of $[\bar{O}]t$, which is a product of the average oxygen-atom concentration and the reaction time, were calculated by the integration of eq 4, where [O], $[O]_0$, k,

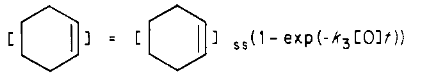


(3)

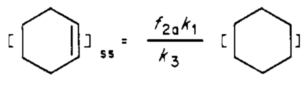
$$[O] = [O]_0 \exp(-nk[\text{c-A}]t) \qquad (4)$$

and [c-A] are the oxygen-atom concentration at the pinhole, the original oxygen-atom concentration, the rate constants for O + cyclohexane and cyclohexene, and the concentrations of cyclohexane and cyclohexene, respectively. The calculations of the pseudo-first-order decay were done by the use of $[\bar{O}]t$. The corrections for oxygen-atom consumption were less than 1% in the case of O + cyclohexane, and 12% or less in the case of O + cyclohexene. Values for k_1 and k_3 listed in Table I were used in the following kinetic analyses.

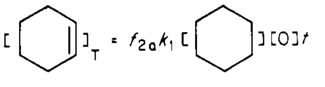
The dependence of the cyclohexene and cyclohexanone signals on the reaction time was measured. Circles shown in Figure 3 show the cyclohexene signal produced in the O + cyclohexane reaction for two different oxygen-atom concentrations. Cyclohexene approaches a constant concentration at long reaction time. This results from the fast reaction of O + cyclohexene, reaction 3. This approach to the steady-state concentration is given by eq 5 and 6, assuming that reaction 2 is much faster than reactions 1 and 3—where f_{2a} represents the fraction of reaction 2a in the total reaction of cyclohexyl radicals with atomic oxygen, reaction 2. When the plots shown in Figure 3 are fitted to eq 5, a value for k_3 of (1.95 ± 0.05) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} is calculated, which agrees well with the value obtained by the pseudo-first-order decay of cyclohexene, Table I. The best fit line for eq 5 is shown as a solid line in Figure 3. The total amount of cyclohexene produced by reaction 2a, $[\text{cyclohexene}]_T$, is given by eq 7.



(5)



(6)



(7)

Therefore, the total amount of cyclohexene can be calculated by multiplying each observed cyclohexene value by $k_3[O]t(1 - \exp(-k_3[O]t))^{-1}$. These corrected points are shown as triangles in Figure 3, and they are represented by the dashed straight line. The absolute concentrations of cyclohexene were calculated using the instrumental sensitivity as measured by adding known partial pressures of cyclohexene to the reactor. This absolute concentration is shown in the right ordinate in Figure 3. The amount of cyclohexane consumed by reaction 1, Δ[cyclohexane], is given by k_1[cyclohexane][O]t. Therefore, the ratio of $[\text{cyclohexene}]_T$ to Δ[cyclohexane] should give the value of f_{2a}, which was determined to be 0.53 ± 0.03 (95% confidence limit).

The time dependence of the cyclohexanone signal produced in the O + cyclohexane reaction for two different oxygen atom concentrations is shown in Figure 4. Cyclohexanone rises linearly. This means that the reaction of O + cyclohexanone is slow on the time scale shown. The absolute concentration of cyclohexanone obtained from the instrumental sensitivity is also shown in Figure 4. From the slope of this line, the value for f_{2b} was determined to be 0.028 ± 0.003. The sum of the fractions of cyclohexene and cyclohexanone was only 56% of the total reaction of O +

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(10) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K. *Natl. Stand. Ref. Data Ser* (*U.S. Natl. Bur. Stand.*) **1969**, *NSRDS-NBS 26.*

(11) Although there have been a few reports on the primary reaction mechanism of O(^{3}P) + cyclic olefins,[12] the stoichiometric factor depends on the subsequent reactions. If the cyclohexenes reacted are converted to CH_2O, C_2H_2O, CO, CO_2, and H, the value of n was estimated to be 16 and 22 for O + cyclohexene and O + cyclohexane, respectively. In the present study, half of these numbers were used as the effective n.

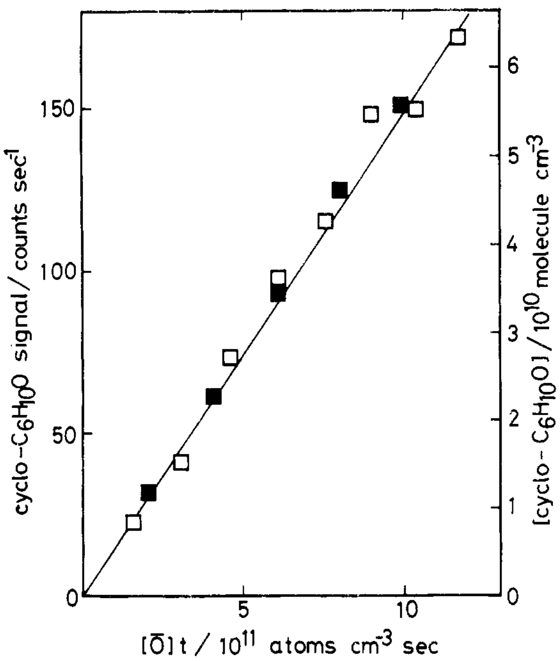
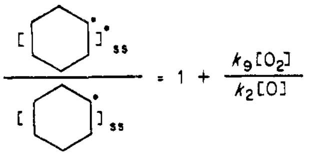


Figure 4. Time dependence of cyclohexanone produced in the O + cyclohexane reaction. Conditions for the open symbols: partial pressure (mtorr), $[O]_0$, 4.77, [cyclohexane], 0.62, $[O_2]_0$, 15.23; total pressure 3.62 torr; reaction time = 1–8 ms. Conditions for the filled symbols: partial pressure (mtorr), $[O]_0$, 6.43, [cyclohexane], 0.62, $[O_2]_0$, 24.18; total pressure = 3.62 torr; reaction time = 1–5 ms. Corrections for [Ō] using the value of n = 11 were 8% or less.

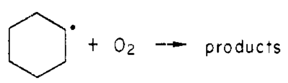
cyclohexyl radicals. Products corresponding to the residual 44% will be discussed later.

The time dependence of the cyclohexyl radical signals was measured by changing the contact time of the reaction of cyclohexane with oxygen atoms. No significant change in signal was observed under the 1–8 ms of reaction time. Signals for cyclohexyl radicals were increased in proportion to the concentrations of cyclohexane. This means that cyclohexyl radicals are in their steady-state concentration due to the balance between reactions 1 and 2. The steady-state concentration of cyclohexyl radicals was decreased when molecular oxygen was added to the system. This decrease is caused by the competition between $O(^3P)$ and O_2 for the cyclohexyl radicals and the competition results in a Stern–Volmer-type of equation;



(8)

where the superscript zero refers to the condition in the absence of O_2 and k_9 is the effective second-order rate constant for the reaction of cyclohexyl radicals with molecular oxygen.



(9)

Figure 5 shows the result of an O_2 addition experiment. A value for $[c\text{-}C_6H_{11}\cdot]^0_{ss}$ was determined by the method mentioned previously,[1] by plotting $([c\text{-}C_6H_{11}\cdot]_{ss})^{-1}$ against $[O_2]/[O]$ and then determining $([c\text{-}C_6H_{11}\cdot]^0_{ss})^{-1}$ from the intercept of a least-square fit in order to remove the effect of the O_2 surviving from the discharge. The value for k_9/k_2 calculated from the slope in Figure 5 is 0.050 ± 0.013.

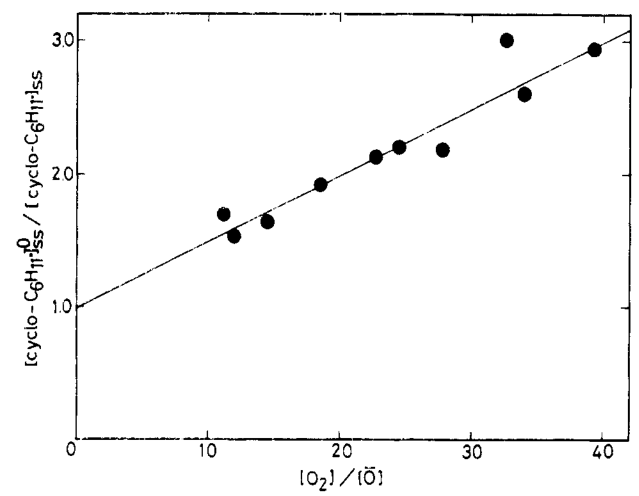


Figure 5. Stern–Volmer plot for the competition between O_2 and $O(^3P)$ for the cyclohexyl radicals. Conditions: partial pressure (mtorr), $[O]_0$, 7.92, [Ō], 7.49, [cyclohexane], 1.80; reaction time = 1.99 ms; total pressure = 3.88 torr; partial pressure of $[O_2]_0$ = 43.20 mtorr. $[O_2]$ was calculated from O_2 added + $[O_2]_0 - {}^1/_2[O]_0$.

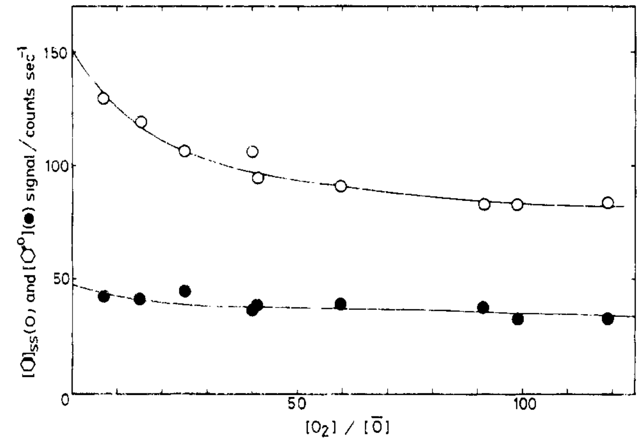
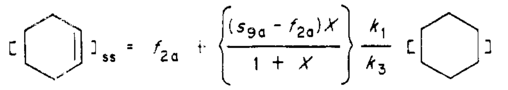


Figure 6. Decreases of signals of cyclohexene and cyclohexanone with the addition of O_2. Conditions: partial pressure (mtorr) $[O]_0$, 2.88, [Ō], 2.82, [cyclohexane], 0.34; reaction time = 4.01 ms; total pressure = 3.75 torr; partial pressure of $[O_2]_0$ = 21.1 mtorr. $[O_2]$ was calculated from O_2 added + $[O_2]_0 - {}^1/_2[O]_0$.

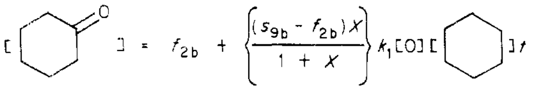
The cyclohexene and cyclohexanone signals also were measured when molecular oxygen was added in the system. Both signals decreased when O_2 was added, as shown in Figure 6. In this case, cyclohexene is in its steady-state concentration and cyclohexanone is not. If the fraction of cyclohexene produced in reaction 9 is represented by s_{9a}, the steady-state concentration of cyclohexene is given by eq 10 and 11 when both $O(^3P)$ and O_2 are present.



(10)

$$X = \frac{k_9}{k_2}\frac{[O_2]}{[O]} \qquad (11)$$

Similarly, the concentration of cyclohexanone at reaction time t is represented by eq 12; where s_{9b} refers to the fraction of



(12)

cyclohexanone produced in reaction 9. Since the value for k_9/k_2 was determined before, the concentrations of cyclohexene and cyclohexanone can be plotted against $X/(1 + X)$, as shown in Figure 7. Since the values for k_1 and k_3 were determined previously and the initial concentration of cyclohexane and the reaction time are known, values for f_{2a} and f_{2b} can be determined from the intercepts of the two lines. Values obtained are 0.52 ± 0.10 for f_{2a} and 0.030 ± 0.022 for f_{2b}, in good agreement with the values obtained from Figures 3 and 4. The values for s_{9a} and s_{9b} can be calculated from the slopes of the two straight lines in

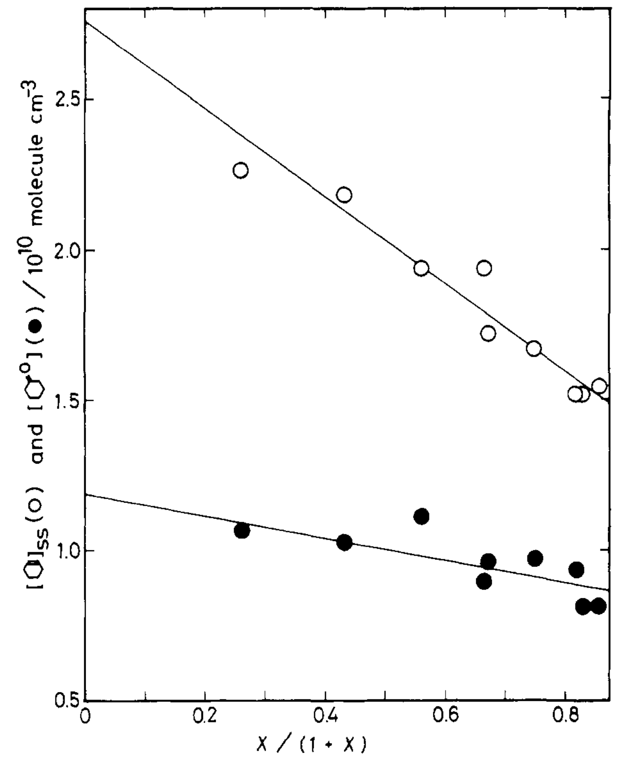
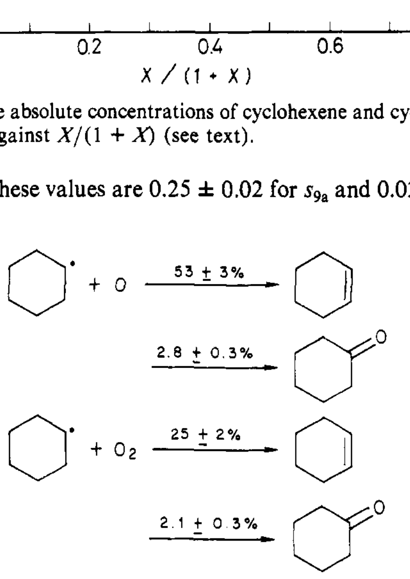


Figure 7. The absolute concentrations of cyclohexene and cyclohexanone are plotted against $X/(1 + X)$ (see text).

Figure 7. These values are 0.25 ± 0.02 for s_{9a} and 0.021 ± 0.003 for s_{9b}.



(2)

(9)

Discussion

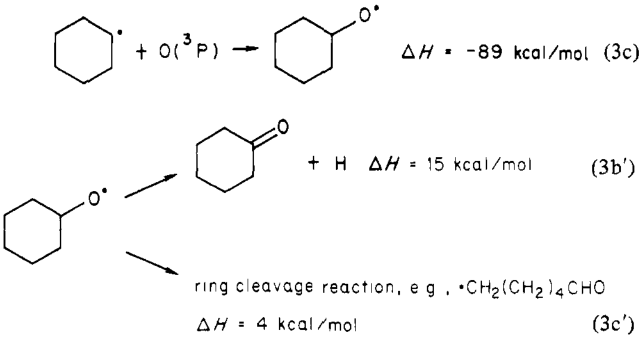
The direct observation of cyclohexyl radicals by photoionization using the Xe resonance lamp (8.44 eV) is reasonable. The ionization potentials for the cyclohexyl radicals have been reported[10] to be 7.7 eV. The radicals should be produced by the hydrogen abstraction by oxygen atoms as shown by reaction 1.

The rate constant for reaction 1 has been reported to be 1.2×10^{-13},[14] 1.5×10^{-13},[15] and 3.3×10^{-13} [16] cm^3 molecule^{-1} s^{-1} at 298 K with the activation energy of 2.8, 4.7, and 4.4 kcal/mol, respectively. The value for k_1 obtained by the pseudo-first-order decay of cyclohexane in the present study is about 30% slower than the rate constant recommended by Herron and Huie.[13,15] In the present study, the consumption of oxygen atoms was corrected using the value of $n = 11$. The effect of this correction was very small (1%) and even when the value of $n = 22$ (see ref 11) was used, the correction would be less than 2%. Therefore, the difference of 30% cannot be explained by the stoichiometric factor. One possible complication is the formation of pentenal (C_4H_7CHO) as a subsequent product of the ring cleavage reaction. The mass number of pentenal is the same at that of cyclohexane (m/e 84). Since Huie and Herron[15] measured the rate constant using a discharge flow reactor and mass spectrometer, the same question can be raised with their result. However, the reaction of oxygen atoms with an aldehyde having a double bond such as pentenal should be very fast, and consequently the steady-state concentration of pentenal should be very low. Therefore the effect of any pentenal signal on the rate measurement of O + cyclohexane by the first-order decay method should be very small. Kim and Timmons[16] measured the rate constant by observing the decay of oxygen atoms with ESR. Many subsequent reactions are possible under their experimental conditions and their estimation of the stoichiometric factor for the decay of oxygen atoms is uncertain. The value for k_1 of 9.7×10^{-14} cm^3 molecule^{-1} s^{-1}, as obtained in the present study, was used in all data analysis.

Only one value for the rate constant of the reaction of cyclohexene with atomic oxygen has been reported.[17] The value of k_3 obtained in the present study agrees well with this previous value.

There are only a few reports on the products formed in the reaction of O + cycloalkane; the formation of water and CO from O + cyclopropane[18] and CH_2O from O + cyclohexane[16] have been observed. In the present study, the formation of cyclohexene by hydrogen abstraction from cyclohexyl radicals amounted to 52%. This fraction of olefin production is clearly smaller than in the case of the O + *tert*-butyl radical reaction (80%).[1] For *tert*-butyl radicals there are nine equivalent hydrogen atoms that can be abstracted to produce isobutene. In the case of cyclohexyl radicals, only four hydrogen atoms can be abstracted to produce cyclohexene. Although the exothermicity of olefin production is larger in the case of the cyclohexyl radical than the *tert*-butyl radical, the smaller olefin yield might be explained by the effective number of abstractable hydrogen atoms.

The yield of cyclohexanone from the oxygen atom reaction was very small (3%). This yield is smaller than the corresponding formation of acetone (20%) in the reaction of O + *tert*-butyl radical. However, the formation of cyclohexanone probably competes with the ring cleavage reaction of the vibrationally hot cyclohexyloxy radical which is formed by the addition of an oxygen atom to the cyclohexyl radical. The vibrationally hot cyclohexyloxy radical has about 74 kcal/mol of energy in excess of that needed to decompose to cyclohexanone and a hydrogen atom. Probably most of the hot cyclohexyloxy radicals (45% of the total reaction of O + cyclohexyl radical) decompose by ring cleavage. The values of the heats of formation of the cyclohexyloxy and the 6-oxohexyl radical, $\cdot CH_2(CH_2)_4CHO$, were estimated[19] by the



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(19) $\Delta H_f°$[cyclohexyloxy radical] = −17 kcal/mol was deduced from group additivity tables:[21] $[C-(C)_2(H)(O)] + 5[C-(C)_2(H_2)] = 7.8 + 5 \times (-4.93)$ kcal/mol. $\Delta H_f°$[6-oxohexyl radical] = −13 kcal/mol was $[\cdot C-(C)(H)_2] + 3[C-(C)_2(H)_2] + [C-(H)_2(C)(CO)] + [CO-(C)(H)] = 35.8 + 3 \times (-4.93) - 5.2 - 29.1$ kcal/mol.

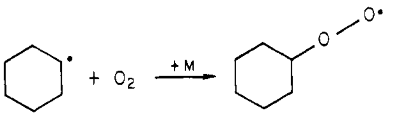
group additivity rule of free radicals.[20] If the 6-oxohexyl radical were formed, 5-hexenal could be produced by hydrogen abstraction. Since the mass number of 5-hexenal is the same as

$$\cdot CH_2(CH_2)_4CHO + O \rightarrow CH_2CH(CH_2)_3CHO + OH \quad (13)$$

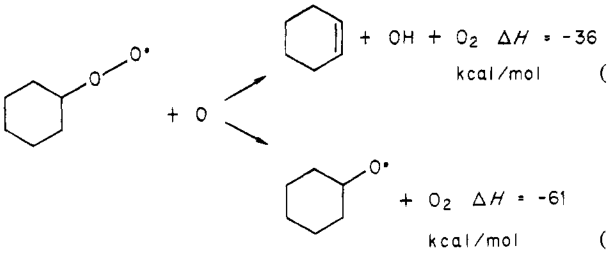
that of cyclohexanone (*m/e* 98) this represents a potential conflict. However, as shown in Figure 4, signals at *m/e* 98 increased linearly with [O]*t*. This result means that signals at *m/e* 98 are not due to significant amounts of hexenal, because 5-hexenal would be in its steady-state concentration under these experimental conditions due to its rapid reaction with oxygen atoms.

Products that could be due to the ring cleavage reaction were measured. Signals at *m/e* 28 (C_2H_4), *m/e* 30 (CH_2O), *m/e* 42 (CH_2CO), *m/e* 54 (1,3-butadiene), *m/e* 56 (acrolein ?), *m/e* 58 (glyoxal ?), and *m/e* 68 (1,4-pentadiene) were observed. However, these products also can be produced by the reaction of cyclohexene with atomic oxygen. Therefore, at this stage, the routes of the ring cleavage reaction cannot be determined.

The result of the competition experiment in Figure 5 shows that the cyclohexyl radicals react (5.0 ± 1.3) $\times 10^{-2}$ times as fast with O_2 as with $O(^3P)$. This value is about twice that observed for the *tert*-butyl radical.[1] The amounts of both of the products cyclohexene and cyclohexanone were decreased when O_2 was added, but not to zero. These products are probably also produced by the reaction of oxygen atoms with cyclohexylperoxy radicals. The heat of formation of cyclohexylperoxy radical was deduced[21] from the group additivity rule[20] and the bond dissociation energy of (ROO–H). The decrease of olefin production by the addition of O_2 was also observed in the case of the *tert*-butyl radical.[1]



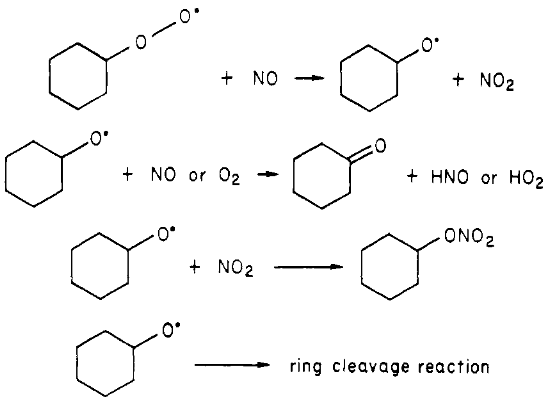
(9′)



(14)

(15)

The vibrationally hot cyclohexyloxy radical produced by reaction 15 probably decomposes to cyclohexanone or products produced by the ring cleavage reaction by reactions 3b′ and 3c′. The energy of the hot cyclohexyloxy radicals produced in reaction 15 is about 47 kcal/mol in excess of that needed for decomposition to cyclohexanone; this exothermicity is smaller than that for the reaction of cyclohexyl radicals with oxygen atoms. The yield of the products due to ring cleavage reaction is very large in the reaction of cyclohexylperoxy radicals with atomic oxygen (amounting to about 73% of the total reaction). This result is consistent with the result obtained in the photooxidation of cyclohexane in the NO–H_2O–air system.[2] In this case, the yields of cyclohexanone and cyclohexylnitrate were not large (20–30%). Both products can be produced by the reaction of NO with cyclohexyloxy radicals, which were produced by the reaction of cyclohexylperoxy radical with NO and NO_2. The major products observed are carbonyl compounds produced by the ring cleavage reaction.



(16)

(17)

(18)

(19)

Conclusion

(1) Cyclohexyl radicals are produced in the reaction of cyclohexane with atomic oxygen.

(2) The reaction of cyclohexyl radicals with atomic oxygen proceeds by hydrogen abstraction (52%) and by an oxygen atom addition reaction (48%).

(3) The product in the hydrogen abstraction was cyclohexene. The yield of cyclohexanone produced by the oxygen atom addition reaction was just 3%. Most of the products in the oxygen atom addition were products produced by the ring cleavage decomposition of the vibrationally hot cyclohexyloxy radicals.

(4) The reaction of cyclohexyl radicals with molecular oxygen was (5.0 ± 1.3) $\times 10^{-2}$ times as fast as that with atomic oxygen.

(5) In the reaction of cyclohexylperoxy radicals with atomic oxygen, the yields of cyclohexene and cyclohexanone were 25 and 2%, respectively. In this case most of the products were formed by a ring cleavage reaction (73%).

Acknowledgment. We thank Professor Kyle D. Bayes of UCLA for helpful suggestions and discussions.

Registry No. Cyclohexane, 110-82-7; cyclohexene, 110-83-8; cyclohexyl radical, 3170-58-9; cyclohexyloxy radical, 3384-35-8; cyclohexanone, 108-94-1; O_2, 7782-44-7; O, 17778-80-2; $C_6H_{11}OOH$, 766-07-4.

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[20] Benson, S. W. "Thermochemical Kinetics, Method for the Estimation of Thermochemical Data and Rate Paramenters", 2nd ed.; John Wiley & Sons: New York, 1976; pp 53–77.

[21] $\Delta H_f^0[c\text{-}C_6H_{11}\text{–}O\text{–}O\text{–}H] = -53$ kcal was deduced from [O–(H)(O)] + [O–(O)(C)] + [C–(O)(H)(C)$_2$] + 5[C(H)$_2$(C)$_2$]. The bond dissociation energy for ROO–H was estimated to be 90 kcal/mol from $CH_3OOH \rightarrow CH_3O_2 + H$ and $HOOH \rightarrow HO_2 + H$. From these values $\Delta H_f^0[c\text{-}C_6H_{11}O_2\cdot] = -15$ kcal/mol was deduced.