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A Ruthenium(III) Analogue of the Udenfriend System: Ru(III)-EDTA-Ascorbate-Molecular Oxygen in the Effective Oxygen Atom Transfer Reaction of Saturated and Unsaturated Organic Compounds

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The oxidation of cyclohexane, cyclohexanol, and cyclohexene by a ruthenium(III) analogue of the Udenfriend system, involving Ru(III)-EDTA-ascorbic acid and molecular oxygen, was investigated at 30 °C and μ = 0.1 M KNO_3 in a 50% (v/v) mixture of 1,4-dioxane and water in acidic medium. The kinetic parameters of the complicated oxidation reactions were determined by potentiometric, spectrophotometric, and manometric techniques. The rates of oxidation of the substrates are first order with respect to the Ru(III)-EDTA complex, ascorbic acid, and molecular oxygen concentrations and inverse first order with respect to the hydrogen ion concentration. A first-order dependence with respect to cyclohexene and cyclohexanol and a fractional-order dependence in cyclohexane concentration were observed. The oxidation of cyclohexane gives cyclohexanol, *cis*-1,3-cyclohexanediol, and cyclohexanone whereas the oxidation of cyclohexene gives 100% of the epoxide. The hydroxylation of cyclohexanol gives exclusively *cis*-1,3-cyclohexanediol. The rate of oxidation of substrates with the Ru(III)-EDTA complex in the absence of ascorbic acid is slower than that of the Ru(III)-EDTA-ascorbate system. On the basis of kinetics and experimental results, the rate laws for all the oxidation reactions were derived and their mechanisms discussed. The order of the reactivity of the substrates is cyclohexane < cyclohexanol < cyclohexene.

Introduction

The oxygenation reactions of organic compounds through metal-oxo[1-7] and metal-peroxo[8] intermediates have become an important class of reactions in chemistry. The reactions involve iron(III) porphyrins,[1,4,8] chromium porphyrins,[2] manganese(III) porphyrins,[6] and molybdyl complexes.[7] In these reactions the catalytically active metal-oxo species is generated by the oxidants H_2O_2, iodosylbenzene, peroxy acids,[8] and amine oxides.[4] An important advance in the reaction is the selective hydroxylation of alkanes by regioselective iron(III) porphyrins.[9] The metal-oxo catalyzed reactions have become important prototypes of reactions catalyzed by cytochrome P-450 oxidase[10] or xanthine oxidases.[7]

In the options available to date for the oxygenations catalyzed by metal ions of group 3d, 4d, and 5d, the oxidants are restricted to the oxygen atom transfer agents cited earlier.[1-8] Catalytic oxygen atom transfer reactions that are performed directly with molecular oxygen as an oxidant have been studied[11] only in a few cases.

One of the interesting systems for the oxidation and oxygenation of organic compounds directly by molecular oxygen is the Udenfriend system,[12-14] consisting of Fe(II)-EDTA-ascorbic acid and molecular oxygen. The reaction was used for the oxidation of a number of saturated and unsaturated compounds.[15-24] In most of the cases the studies were restricted to the report of the yield of the product without a detailed kinetic and mechanistic investigation of the reaction. Bruice[25] has recently used Fe^{III}-(EDTA) as catalyst in the oxidation of organic substrates by *m*-chloroperbenzoic acid.

Recently we have studied[26-35] the oxygenation and oxidation

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of organic compounds by molecular oxygen catalyzed by Ru(III)–EDTA. The Ru(III)–EDTA catalyzed oxidation of ascorbic acid by molecular oxygen[33,34] and H_2O_2[35] were also reported. Since the Ru(III)–EDTA–ascorbate system is more stable than Fe(III)–ascorbate system[36–38] we considered the possibility of its use as an oxygenation catalyst for a variety of substrates. In this paper we report the oxidation of cyclohexane, cyclohexanol, and cyclohexene by the Ru(III)–EDTA–ascorbate–molecular oxygen system referred to as the ruthenium(III) analogue of the Udenfriend system.

Experimental Section

Materials. Ruthenium(III) trichloride trihydrate (Johnson Mathey) was prepared in 1 M hydrochloric acid and estimated spectrophotometrically by the thiourea method.[39,40] All organic solvents (AR) were obtained from BDH and were purified prior to use by known methods.[41] AR grade samples of the disodium salt of ethylenediaminetetraacetic acid were used in the investigation. The ionic strength of the solution was maintained at 0.1 M by AR grade KNO_3 used as a supporting electrolyte. The solution of ascorbic acid (AR) was freshly prepared for each experiment with deaerated double distilled water. The Ru(III)–EDTA complex was prepared in situ in the reaction mixture in a 1:1 molar ratio, and the concentration was calculated from the reported stability data.[42] Double-distilled AR grade 1,4-dioxane was used as a cosolvent. AR grade cyclohexane, cyclohexanol, and cyclohexene were distilled and purified to remove trace impurities before use.

Analytical Data. The purity of the solvent and substrates was checked by a Shimadzu gas chromatograph GC-9A assembled with the programmed and computerized chromatopac CR-3A using a stainless-steel column, 3 mm i.d. × 4 mm o.d. × 2.00 m, containing 10% Carbowax 20M on 90–100 mesh Anakrom on TCD. A synthetic standard of the oxidation products of the substrates was used to determine the yields by a comparison of peak areas and their corresponding retention times under identical experimental conditions at the column temperature of 120–200 °C. A thermal conductivity detector at 200 °C using hydrogen as carrier gas was used for product analysis. Infrared spectra were recorded on a Shimadzu IR-435 instrument for the characterization of products formed after the oxidation of various substrates used in the present study. Also, the ^{18}O-labeled products were characterized by the same technique using the said model.

Potentiometric Measurements. The first and second dissociation constants of ascorbic acid were computed by an earlier reported method[36,37] at 30 °C, μ = 0.1 M KNO_3. The desired constant temperature (±0.1 °C) was maintained in the reaction cell with a circulating water bath while the pH was maintained (±0.01 pH) with a digital pH meter with combined glass and calomel electrodes. The electrode system was calibrated in terms of hydrogen ion concentration at the constant ionic strength of 0.1 M KNO_3 by direct titration of HCl and carbonate-free sodium hydroxide in the acidic and alkaline medium. During the potentiometric titrations, the reaction mixture in the cell was continuously stirred by a magnetic stirrer and purified nitrogen was bubbled. Nitrogen was purified by passing it in turn through vanadous sulfate and alkaline pyrogallate solutions prior to bubbling it through the experimental solution.

Spectrophotometric Measurements. The stability constant K_1 for the Ru(III)–EDTA–ascorbate complex (1:1:1) was determined spectrophotometrically at 30 °C (μ = 0.1 M KNO_3) by using a DU-7 high-speed UV–visible spectrophotometer by the reported[43] method. The stoichiometry of the ascorbic acid and Ru(III)–EDTA reaction was studied by a spectrophotometric titration technique.[44,45]

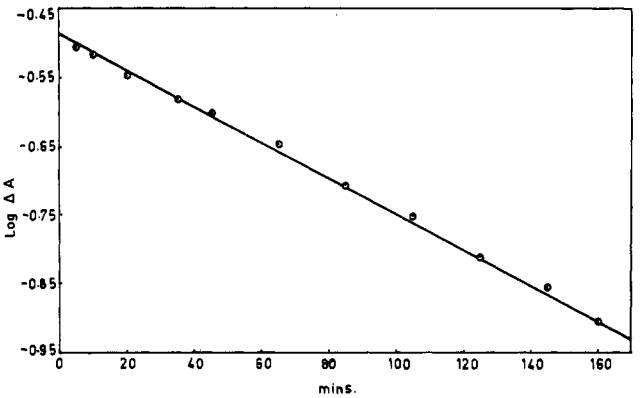

Figure 1. First-order kinetic plot of the oxidation of cyclohexane by the Ru(III) analogue of the Udenfriend system in terms of concentration of ascorbic acid at 30 °C, μ = 0.1 M (KNO_3), pH = 2.50, [Ru(III)–EDTA] = 5×10^{-4} M, [ascorbic acid] = 5×10^{-3} M, [cyclohexane] = 5×10^{-3} M, and O_2 pressure = 1 atm.

Table I. Equilibrium Data for the Species Involved in the Ru(III) Analogue of the Udenfriend System for the Oxidation of Cyclohexane, Cyclohexanol, and Cyclohexene at 30 °C and μ = 0.1 M (KNO_3)

constant	equilibrium quotient	log K
K_a	$[HA^-][H^+]/[H_2A]$	−3.95[a]
K_{2a}	$[A^{2-}][H^+]/[HA^-]$	−11.18[a]
$K_1 = K^{ML}_{ML[HA]}$	$[ML(HA)]/[ML][HA^-]$	3.48[b]
$K_2 = K^{ML(HA)}_{ML(HA)O_2}$	$[ML(HA)O_2]/[ML(HA)][O_2]$	3.18[c]
$K_3 = K^{ML(HA)(O_2)}_{ML(A)(O_2)(C_6H_{12})}$	$[ML(A)(O_2)(C_6H_{12})][H^+]/[ML(HA)(O_2)][C_6H_{12}]$	0.83[c]
$K_4 = K^{ML}_{ML(B)}$	$[ML(C_6H_{11}OH)]/[ML][C_6H_{11}OH]$	−0.61[c]
$K_5 = K^{ML(HA)}_{ML(HA)B}$	$[ML(HA)(C_6H_{11}OH)]/[ML(HA)][C_6H_{11}OH]$	2.99[c]
$K_6 = K^{ML(HA)B}_{ML(A)BO_2}$	$[ML(A)(C_6H_{11}OH)O_2][H^+]/[ML(HA)(C_6H_{11}OH)][O_2]$	0.95[c]
$K_7 = K^{ML(HA)}_{ML(HA)D}$	$[ML(HA)(C_6H_{10})]/[ML(HA)][C_6H_{10}]$	1.50[c]
$K_8 = K^{ML(HA)D}_{ML(A)DO_2}$	$[ML(A)(C_6H_{10})O_2][H^+]/[ML(HA)(C_6H_{10})][O_2]$	1.14[c]

[a] Potentiometrically. [b] Spectrophotometrically. [c] Kinetically.

Kinetic Measurements. The kinetics of the oxidation reaction was followed by spectrophotometric and manometric methods as reported elsewhere.[33,34] The experiments were carried out with a DU-7 high-speed UV–visible spectrophotometer by following the progress of the reaction at the absorption maximum of Ru(III)–EDTA–ascorbate complex by monitoring the peak at 510 nm. First-order kinetic data in terms of the concentration of ascorbic acid were computed from slopes of the plot of log ΔA versus time (multiplied by −2.303) (Figure 1) where ΔA is the difference in absorbances at zero and experimental time. The value of the absorbance at zero time was selected after examining the absorbance versus time plot for each set of runs.

The rate constants of the oxidation reactions were also examined by oxygen absorption manometric techniques and were found to be reproducible within ±2%. The rate of absorption of oxygen was measured by using a glass manometric apparatus provided with leak-proof Springham stopcocks. High-vacuum silicon grease was applied to stopcocks to keep the system airtight. The temperature of the reaction mixture was maintained constant by circulating water at a particular temperature (±0.1 °C) through a jacketed glass cell. The system was evacuated and flushed with oxygen several times to ensure that a complete oxygen atmosphere prevails in the reaction cell. Molecular oxygen was presaturated with water vapor by streaming through a wash bottle containing an electrolyte concentration identical with that of the reacting solution. All the substrates were dissolved in sufficient quantity of dioxane to maintain a 1:1 water–dioxane ratio in the reaction mixture. In order to minimize the effect of solvent vapor, a blank was run simultaneously under the same conditions of temperature, pressure, and volume. The absorption of oxygen was measured manometrically by noting the change in the levels of the indicator solution in the measuring buret at suitable intervals of time. The stirrer was operated in such a manner that the rate of dissolution of gas was much faster than the rate of absorption by the

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catalyst, and there was no limitation due to diffusion control. In order to get a desired partial pressure of molecular oxygen, mixtures of molecular oxygen and nitrogen varying in composition, as well as pure oxygen, were employed. In all the cases it was assumed that Henry's law is obeyed since the dissolution of oxygen in reaction mixture to keep up a desired concentration is much faster than the rate of reaction. The solubility of molecular oxygen in solution at 1 atm was determined from the physical data[46] of solubility of molecular oxygen. The data at other partial pressures were computed from the solubility data at 1 atm pressure of molecular oxygen.

Results

The various equilibrium constants calculated potentiometrically, spectrophotometrically, and kinetically, represented by eq 1–10

$$H_2A \overset{K_{a_1}}{\rightleftharpoons} HA^- + H^+ \quad (1)$$

$$HA^- \overset{K_{a_2}}{\rightleftharpoons} A^{2-} + H^+ \quad (2)$$

$$\underset{ML}{[Ru^{III}L(H_2O)]^-} + HA^- \overset{K^{ML}_{ML(HA)}}{\rightleftharpoons} \underset{ML(HA)}{[Ru^{III}L(HA)]^{2-}} + H_2O \quad (3)$$

$$\underset{ML(HA)}{[Ru^{III}L(HA)]^{2-}} + O_2 \overset{K^{ML(HA)}_{ML(HA)O_2}}{\rightleftharpoons} \underset{ML(HA)O_2}{[Ru^{III}L(HA)(O_2)]^{2-}} \quad (4)$$

$$\underset{ML(HA)O_2}{[Ru^{III}L(HA)(O_2)]^{2-}} + C_6H_{12} \overset{K^{ML(HA)O_2}_{ML(A)(O_2)(C_6H_{12})}}{\rightleftharpoons} \underset{ML(A)(O_2)(C_6H_{12})}{[Ru^{III}L(A)(O_2)(C_6H_{12})]^{3-}} + H^+ \quad (5)$$

$$\underset{ML}{[Ru^{III}L(H_2O)]^-} + C_6H_{11}OH \overset{K^{ML}_{ML(B)}}{\rightleftharpoons} \underset{ML(B)}{[Ru^{III}L(C_6H_{11}OH)]^-} + H_2O \quad (6)$$

$$\underset{ML(HA)}{[Ru^{III}L(HA)]^{2-}} + \underset{B}{C_6H_{11}OH} \overset{K^{ML(HA)}_{ML(HA)B}}{\rightleftharpoons} \underset{ML(HA)(B)}{[Ru^{III}L(HA)(C_6H_{11}OH)]^{2-}} \quad (7)$$

$$\underset{ML(HA)B}{[Ru^{III}L(HA)(C_6H_{11}OH)]^{2-}} + O_2 \overset{K^{ML(HA)(B)}_{ML(HA)(B)O_2}}{\rightleftharpoons} \underset{ML(A)(B)O_2}{[Ru^{III}L(A)(C_6H_{11}OH)O_2]^{3-}} + H^+ \quad (8)$$

$$\underset{ML(HA)}{[Ru^{III}L(HA)]^{2-}} + \underset{D}{C_6H_{10}} \overset{K^{ML(HA)}_{ML(HA)D}}{\rightleftharpoons} \underset{ML(HA)(D)}{[Ru^{III}L(HA)(C_6H_{10})]^{2-}} \quad (9)$$

$$\underset{ML(HA)(D)}{[Ru^{III}L(HA)(C_6H_{10})]^{2-}} + O_2 \overset{K^{ML(HA)(D)}_{ML(HA)(D)O_2}}{\rightleftharpoons} \underset{ML(A)(D)O_2}{[Ru^{III}L(A)(C_6H_{10})(O_2)]^{3-}} + H^+ \quad (10)$$

are given in Table I. Quantitative yield of the products of oxidation reactions and their distribution are listed in Table II. In eq 1–10, H_2A, HA^-, A^{2-}, and L are ascorbic acid, the ascorbate monoanion, the ascorbate dianion, and the tetraanion of EDTA, respectively.

Kinetic Studies

Dependence of the Rate on Ascorbic Acid Concentration. The rates of oxidation of all the substrates, cyclohexane, cyclohexanol, and cyclohexene increase in the presence of ascorbic acid. First-order kinetic plots (Figure 1) of log ΔA versus time were linear in each case, which indicates that the reaction is, in fact, first order with respect to ascorbic acid concentration. A first-order dependence in ascorbic acid concentration for the oxidation of cyclohexane is shown in Figure 1.

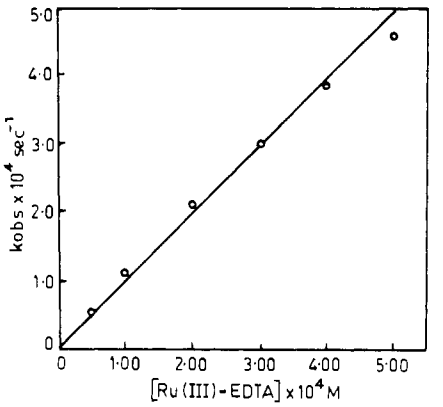

Figure 2. Plot of [Ru(III)–EDTA] versus first-order rate constants k_{obs} at 30 °C, μ = 0.1 M (KNO_3), pH = 2.50, [ascorbic acid] = 5×10^{-3} M, [cyclohexane] = 5×10^{-3} M, and O_2 pressure = 1 atm.

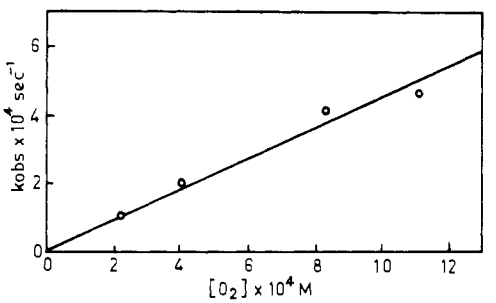

Figure 3. Molecular oxygen concentration dependence of first-order rate constants k_{obs} for the oxidation of cyclohexane by the Ru(III) analogue of the Udenfriend system at μ = 0.1 M (KNO_3), T = 30 °C, pH = 2.50, [ascorbic acid] = 5×10^{-3} M, [Ru(III)–EDTA] = 5×10^{-4} M, and [cyclohexane] = 5×10^{-3} M.

Dependence of the Rate on Catalyst Concentration. The oxidation of a given substrate was studied by conducting the experiments at different concentrations of Ru(III)–EDTA, keeping the concentration of other reactants constant. The rate of the reaction in each case was found to be first order with respect to Ru(III)–EDTA concentration. Figure 2 shows the first-order plot of rate constants (k_{obs}) versus Ru(III)–EDTA concentration (d log k_{obs}/d log [Ru(III)–EDTA] = 1) for the oxidation of cyclohexane. Kinetic data for the catalyst concentration dependence for the oxidation of cyclohexanol and cyclohexene are given in Table III.

Dependence of the Rate on Molecular Oxygen Concentration. In the concentration range $(2.20–11.10) \times 10^{-4}$ M of molecular oxygen, the rates of oxidation of the substrates increase with increasing concentration of molecular oxygen. A plot of the rate constants k_{obs} versus the concentration of molecular oxygen (d log k_{obs}/d log $[O_2]$ = 1) shows a first-order dependence of the reaction on molecular oxygen concentration. One of the plots is presented in Figure 3 for the oxidation of cyclohexane. The kinetic data for molecular oxygen dependence for cyclohexene and cyclohexanol are given in Table IV.

Dependence of the Rate on Substrate Concentration. Kinetic measurements of rate dependence with respect to each substrate indicate a fractional-order dependence in cyclohexane and a first-order dependence on cyclohexanol and cyclohexene concentrations. A plot of rate^{-1} versus [cyclohexane]$^{-1}$ reflecting a fractional-order dependence in cyclohexane concentration is shown in Figure 4. Similar plots for a first-order rate dependence (d log k_{obs}/d log [substrate] = 1) on cyclohexene and cyclohexanol concentrations were also obtained; the data are given in Table V.

pH Effect on the Rate of Oxidation. In the pH range 1.50–2.50, a rapid increase in the rate of oxidation was observed with increasing pH. A plot of k_{obs} versus $[H^+]^{-1}$ gives a straight line in each case passing through the origin. One such plot is depicted in Figure 5, indicating an inverse first-order dependence in hydrogen ion concentration for the oxidation of cyclohexane. The

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Table II. Percentage Yield and Distribution of the Products Formed from the Oxidation of Cyclohexane, Cyclohexanol, and Cyclohexene

catal syst	substrate	products	% absolute yield[a]	% distribn
Ru(III)-EDTA-ascorbate	cyclohexane[b]	cyclohexanol	5.45	66.50
		cis-1,3-cyclohexanediol	2.56	31.30
		cyclohexanone	0.18	2.20
Ru(III)-EDTA-ascorbate	cyclohexanol[b]	*cis*-1,3-cyclohexanediol	24.3	97.90
		cyclohexanone	0.50	2.10
Ru(III)-EDTA-ascorbate	cyclohexene[c]	epoxide	65	100
Ru(III)-EDTA	cyclohexanol[b,d]	cyclohexanone	11	100
Ru(III)-EDTA	cyclohexene[c,e]	epoxide	45	100
Fe(II)-EDTA	cyclohexane[f]	cyclohexanol	<1	
		cyclohexanone	<1	
Fe(II)-EDTA	cyclohexene[f]	epoxide	<1	

[a] Yield based on initial amount of the substrates. [b] Reactions were carried out in a homogeneous mixture containing [Ru(III)-EDTA] = 5×10^{-4} M, [ascorbic acid] = 5×10^{-3} M, and [substrate] = 5×10^{-2} M, with pH 2.50 and μ = 0.1 M (KNO_3) at 30 °C and where molecular oxygen was bubbled for 4 h. [c] Same as conditions as in footnote b, but molecular oxygen was bubbled for 3 h. [d] Detailed kinetics and mechanism are discussed in ref 32. [e] Detailed kinetics and mechanism are discussed in ref 53. [f] Reference 17; reactions were carried out in a mixture containing 31.5 mL of 0.058 M acetate buffer (pH 4.5) 30 mL of acetone, 5 mL of substrate, 1.1 mmol of ascorbic acid, and 0.04 mmol of Fe^{2+} and shaken under an atmosphere of air for 2 h.

Table III. Variation of the Rate of Oxidation of (a) Cyclohexene and (b) Cyclohexanol Catalyzed by the Ru(III)-EDTA-Ascorbic Acid-O_2 System with Catalyst Concentration at 30 °C, μ = 0.1 M (KNO_3), and O_2 Pressure = 1 atm

cyclohexene[a]		cyclohexanol[b]	
10^4[Ru(III)-EDTA], M	$10^4 k_{obs}$, s^{-1}	10^4[Ru(III)-EDTA], M	$10^4 k_{obs}$, s^{-1}
5.75	4.63	1.20	0.80
8.63	8.12	2.50	1.79
12.00	10.40	4.00	2.40
17.30	15.62	5.00	2.65
20.00	17.44	10.00	5.22
23.00	20.80		

[a] [cyclohexene] = 1.0×10^{-2} M; [ascorbic acid] = 1.0×10^{-2} M; pH = 2.00. [b] [cyclohexanol] = 5×10^{-3} M; [ascorbic acid] = 5×10^{-3} M; pH = 2.50.

Table IV. Variation of the Rate of the Oxidation of (a) Cyclohexene and (b) Cyclohexanol Catalyzed by the Ru(III)-EDTA-Ascorbate-O_2 System with O_2 Concentration at 30 °C and μ = 0.1 M (KNO_3)

cyclohexene[a]		cyclohexanol[b]	
$10^4[O_2]$, M	$10^4 k_{obs}$, s^{-1}	$10^4[O_2]$, M	$10^4 k_{obs}$, s^{-1}
2.67	9.30	2.20	0.49
5.35	13.90	5.50	0.90
8.00	17.10	8.32	1.86
11.10	24.10	11.10	2.65

[a] [cyclohexene] = 1.00×10^{-2} M; [Ru(III)-EDTA] = 8.63×10^{-4} M; [ascorbic acid] = 1.00×10^{-2} M; pH = 2.00. [b] [cyclohexanol] = 5.0×10^{-3} M; [Ru(III)-EDTA] = 5.0×10^{-4} M; [ascorbic acid] = 5.0×10^{-3} M; pH = 2.50.

Table V. Variation of the Rate with Substrate Concentration of the Oxidation of (a) Cyclohexene and (b) Cyclohexanol Catalyzed by the Ru(III)-EDTA-Ascorbate-O_2 System at 30 °C, μ = 0.1 M (KNO_3), and O_2 Pressure = 1 atm

10^2[cyclohexene],[a] M	$10^4 k_{obs}$, s^{-1}	[cyclohexanol],[b] M	$10^4 k_{obs}$, s^{-1}
1.50	6.90	1.00	4.20
2.50	9.27	2.00	7.86
3.50	12.70	2.50	8.60
5.00	18.50	5.00	17.00
6.00	23.10	7.50	24.25
7.00	27.80		

[a] [Ru(III)-EDTA] = 8.63×10^{-4} M; [ascorbic acid] = 1.00×10^{-2} M; pH = 2.00. [b] [Ru(III)-EDTA] = 5×10^{-4} M; [ascorbic acid] = 5×10^{-3} M; pH = 2.50.

experimental data for pH dependence are given in Table VI.

^{18}O Labeling Studies. In order to ensure the source of the oxygen atom incorporated in the products formed, ^{18}O labeling experiments were carried out for the oxidation of substrates by using a 50:50 isotopic mixture of $^{18}O_2$ and $^{16}O_2$ as supplied by Nakarai Chemicals, Japan. The mixture of $^{16}O_2$ and $^{18}O_2$ was then passed through the experimental solution for a sufficiently

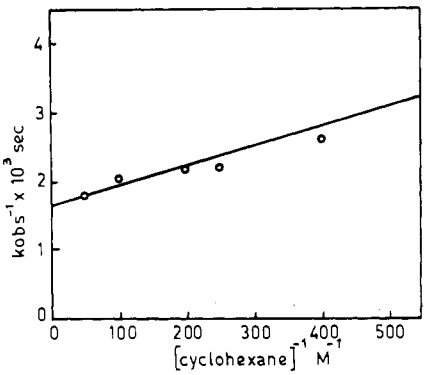


Figure 4. Plot of k_{obs}^{-1} versus [cyclohexane]$^{-1}$ for the oxidation of cyclohexane by the Ru(III) analogue of the Udenfriend system at μ = 0.1 M (KNO_3), T = 30 °C, pH = 2.50, [Ru(III)-EDTA] = 5×10^{-4} M, [ascorbic acid] = 5×10^{-3} M, and O_2 pressure = 1 atm, showing a fractional order dependence in cyclohexane concentration.

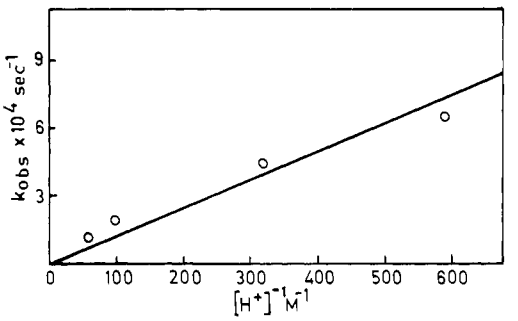


Figure 5. Acidity dependence of first-order rate constants k_{obs} at 30 °C (μ = 0.1 M KNO_3) for the oxidation of cyclohexane with [ascorbic acid] = 5×10^{-3} M, [Ru(III)-EDTA] = 5×10^{-4} M, [cyclohexane] = 5×10^{-3} M, and O_2 pressure = 1 atm, showing inverse first-order dependence in [H^+].

Table VI. Kinetic Data for the Acidity Dependence on the Observed First-Order Rate Constants k_{obs} at 30 °C and μ = 0.1 M (KNO_3)

pH	$10^2[H^+]$, M	cyclohexanol[a] $10^4 k_{obs}$, s^{-1}	cyclohexene[b] $10^4 k_{obs}$, s^{-1}
1.50	3.16	0.28	7.84
1.75	1.77	0.50	14.01
2.00	1.00	0.86	24.10
2.25	0.56	1.52	42.04
2.50	0.31	2.65	70.22

[a] [Ru(III)-EDTA] = 5×10^{-4} M; [ascorbic acid] = 5×10^{-3} M; [cyclohexanol] = 5×10^{-3} M; O_2 pressure = 1 atm. [b] [Ru(III)-EDTA] = 8.63×10^{-4} M; [ascorbic acid] = 1×10^{-2} M; [cyclohexene] = 1×10^{-2} M; O_2 pressure = 1 atm.

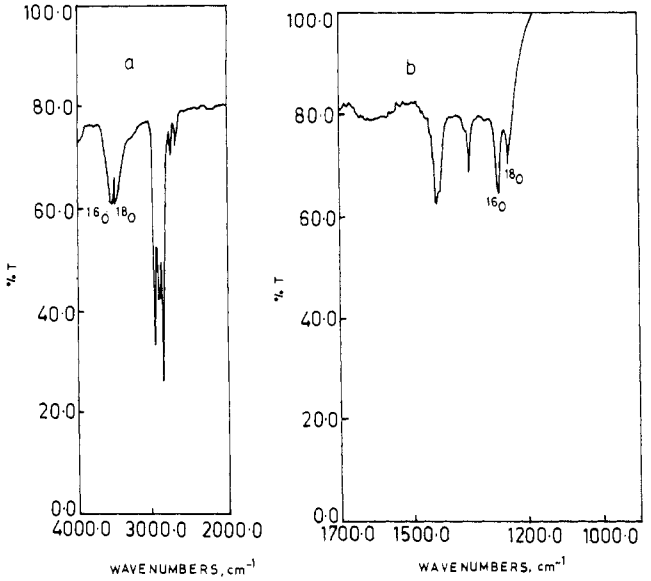


Figure 6. FT-IR spectra of the solutions that result from the oxidation of (a) cyclohexane and (b) cyclohexene by 50% $^{18}O_2$.

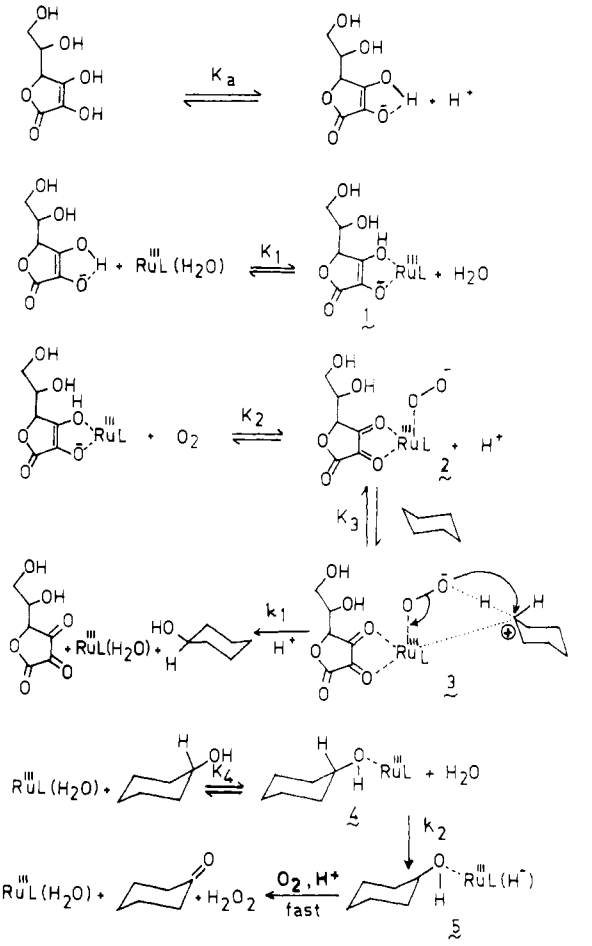
long time to ensure the oxidation of the substrates, cyclohexane and cyclohexene, to the products. The products of oxidation were then carefully separated from the reaction mixture by using microorganic techniques. The oxidation products of cyclohexane and cyclohexene, viz. cyclohexanol and cyclohexene epoxide, were characterized by the IR spectra of the neat liquid in a sodium chloride cell. One such spectrum obtained for the product of the oxidation of cyclohexane, viz. cyclohexanol, involving 50% incorporation of ^{18}O in the product is depicted in Figure 6a. The spectrum clearly shows two sharp peaks in the ν(OH) region separated by about 40 cm^{-1}, which are assigned as $\nu(^{16}O\text{–}H)$ = 3550 cm^{-1} and $\nu(^{18}O\text{–}H)$ = 3510 cm^{-1}. Similarly the infrared spectra for the epoxidation of cyclohexene by use of $^{18}O_2$ (50%) exhibits two sharp bands (Figure 6b) assignable to $\nu(C\text{–}^{16}O)$ = 1280 cm^{-1} and $\nu(C\text{–}^{18}O)$ = 1250 cm^{-1} of the epoxide. Hence, the labeling results confirm and establish that the origin of the oxygen atom incorporated in the products is certainly from molecular oxygen itself.

Discussion

In the experimental pH range (1.50–2.50) ascorbic acid is dissociated and takes part in the reaction as the monoanion.[33-38,47-50] In the studies[33,34] of the oxidation of ascorbic acid by molecular oxygen catalyzed by the Ru(III)–EDTA complex, the ascorbate anion forms a mixed ligand Ru(III)–EDTA–ascorbate complex with the catalyst Ru(III)–EDTA in a preequilibrium step. In the rate-determining step, Ru(III) is reduced to Ru(II) and is reoxidized with molecular oxygen back to the Ru(III)–EDTA complex in a fast step. The major role of molecular oxygen in this system is to reoxidize the lower valent metal chelate (Ru(II)–EDTA) to the higher valent Ru(III)–EDTA and make the system catalytic; a behavior similar to that observed for the Fe(III)–EDTA–ascorbate system.[37] A zero-order dependence was observed in molecular oxygen concentration for both Fe(III)–EDTA[37] and Ru(III)–EDTA[33] systems for the oxidation of ascorbic acid. In the presence of a substrate—cyclohexane, cyclohexanol, or cyclohexene—in the system, however, the dependence of the rate on molecular oxygen concentration is first order, indicating a direct participation of molecular oxygen in the rate-determining steps.

Oxidation of Cyclohexane. On the basis of kinetic results and product analysis, a mechanism for the oxidation of cyclohexane to cyclohexanol and its further oxidation to cyclohexanone is proposed in Scheme I.

Scheme I



In the proposed mechanism, ascorbic acid first dissociates to ascorbate anion, which forms the mixed ligand Ru(III)–EDTA–ascorbate complex **1**. The formation of complex **1** has been substantiated earlier on the basis of kinetic and thermodynamic evidences.[33,34] Complex **1** reacts with molecular oxygen in preequilibrium step K_2, forming the Ru(III)–EDTA–dioxygen complex **2** with the liberation of a proton from the ascorbate anion. Complex **2** combines with cyclohexane in equilibrium step K_3 to form a carbonium ion intermediate **3** resulting from the hydride abstraction of a C–H bond. The rate-determining step k_1 involves the transfer of one of the oxygen atoms to the carbonium ion center to yield cyclohexanol and the reduction of the other oxygen atom to water followed by dissociation of the complex to give the active catalyst and dehydroascorbic acid. This is equivalent to an oxygen atom insertion in the C–H bond by an ionic route.[51] Bruice et al.[25] have also proposed a similar mechanistic route for the oxidation of organic substrates catalyzed by Fe(III)–EDTA in the presence of peracids as oxidants.

The oxygen atom insertion in the C–H bond directly from molecular oxygen is supported by the $^{18}O_2$–$^{16}O_2$ (1:1) labeling experiment, which gave evidence for the formation of the products $C_6H_{11}{}^{16}OH$ and $C_6H_{11}{}^{18}OH$ (Figure 6a) in a 1:1 molar ratio.

On the basis of the kinetic observations, the rate law (eq 11) for the oxidation of cyclohexane is derived by considering a steady-state concentration of the catalyst $[Ru^{III}(EDTA)H_2O]^-$.

$$\frac{[H_2A][[Ru^{III}L(H_2O)]_T^-]}{-d[H_2A]/dt} = \frac{[H^+]}{k_1K_aK_1K_2K_3[C_6H_{12}][O_2]} + \frac{[H_2A]}{k_1}\left(1 + \frac{1}{K_3[C_6H_{12}]}\right) \quad (11)$$

(47) Taqui Khan, M. M.; Martell, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 6011.
(48) Taqui Khan, M. M.; Martell, A. E. *J. Am. Chem. Soc.* **1969**, *91*, 4668.
(49) Maccartney, D. H.; Sutin, N. *Inorg. Chim. Acta* **1983**, *74*, 221.
(50) Davis, M. B. *Inorg. Chim. Acta* **1984**, *92*, 141.
(51) (a) Sugimoto, H.; Sawyer, D. T. *J. Am. Chem. Soc.* **1984**, *106*, 4283.
(b) Sugimoto, H.; Sawyer, D. T. *J. Am. Chem. Soc.* **1985**, *107*, 5712.

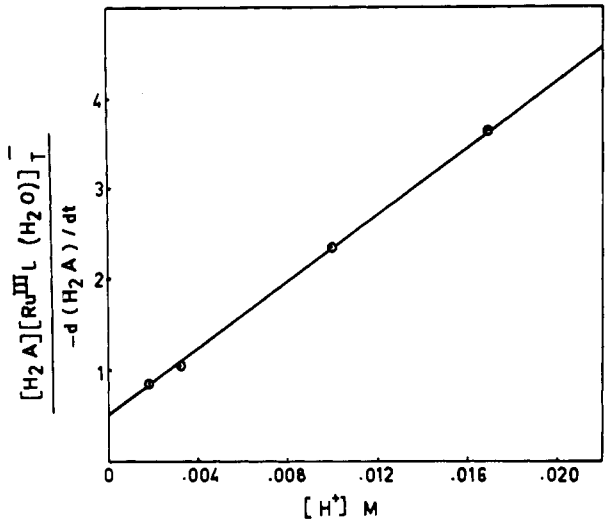


Figure 7. Plot of $[[Ru^{III}L(H_2O)]_T^-][H_2A]/(-d[H_2A]/dt)$ versus $[H^+]$ at μ = 0.1 M (KNO_3), T = 30 °C, [cyclohexane] = 5×10^{-3} M, and O_2 pressure = 1 atm verifying rate expression 11.

Table VII. Calculated Rate Constants for the Rate-Determining Steps with the Help of Slopes and Intercepts of the Plots of the Corresponding Rate Equations at 30 °C and μ = 0.1 M (KNO_3)

substrate	rate constant, k	10^4k, s^{-1}	rate eq
cyclohexane	k_1	7.8	11
cyclohexanol[a]	k_2	5.7	12
cyclohexanol	k_3	12.5	15
cyclohexene	k_4	83.7	16

[a]* In the absence of ascorbic acid, the value is taken from ref 32.

A plot of $[H_2A][Cat]/(-d[H_2A]/dt)$ vs $[H^+]$ in eq 11 gives a nonzero intercept and positive slope (Figure 7), verifying the rate expression in eq 11. Values of K_a and K_1 as described in experimental part are known. The constants k_1, K_2, and K_3 were calculated from the analysis of the kinetic data with the help of the slope and intercept of eq 11 by substituting the known values.

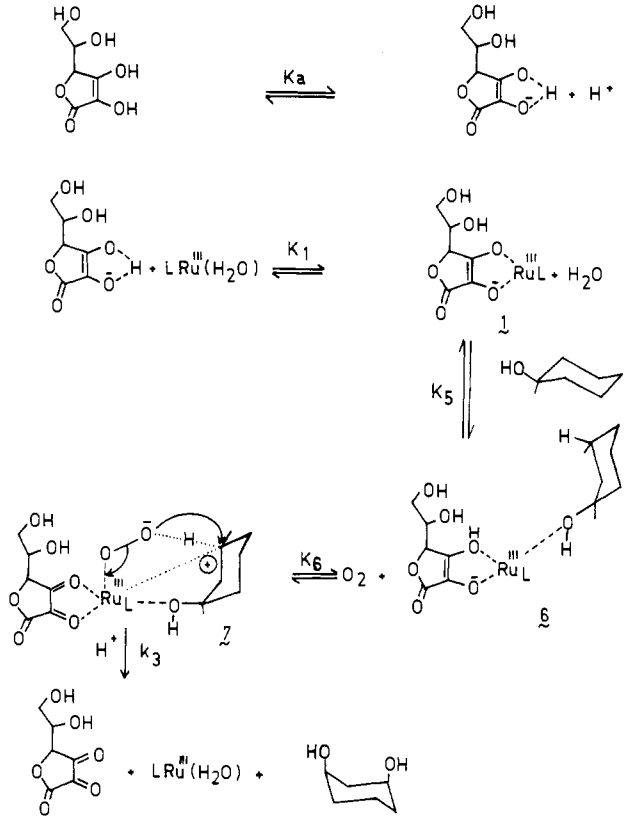
Further oxidation of cyclohexanol by molecular oxygen gives mostly *cis*-1,3-cyclohexanediol in the presence of ascorbic acid. The kinetics and mechanism of this reaction are discussed separately. A small amount of cyclohexanone is also obtained in the reaction. We believe that the oxidation of cyclohexanol to cyclohexanone proceeds by the Ru(III)–EDTA complex by a mechanism independent of oxygen concentration.[32] In this mechanism,[32] Ru(III)–EDTA forms a mixed-ligand complex (**4**) with cyclohexanol. A hydride abstraction from cyclohexanol to ruthenium(III) center gives the intermediate metal–hydride complex **5**, which is attacked by molecular oxygen in a fast step to give the catalyst, cyclohexanone, and hydrogen peroxide. The oxidation of cyclohexanol to cyclohexanone thus follows a path independent of molecular oxygen concentration. The reaction is similar to the reduction of O_2 to H_2O_2 by mixed function oxidases.[19] The rate expression for the oxidation of cyclohexanol to cyclohexanone is represented by eq 12. Values of K_4 and k_2, as per the reported data,[32] are given in Tables I and VII, respectively.

$$\frac{-d[O_2]}{dt} = k_2K_4[C_6H_{11}OH][[Ru^{III}L(H_2O)]_T^-] \quad (12)$$

The rate constant for the oxidation of cyclohexane to cyclohexanol, k_1 (7.80×10^{-4} s^{-1}), is more than that for the oxidation of cyclohexanol to cyclohexanone, k_2 (5.70×10^{-4} s^{-1}); see Table VII. The hydroxylation of cyclohexane to cyclohexanol and further to *cis*-1,3-cyclohexanediol are faster than the oxidation of cyclohexanol to cyclohexanone at our experimental condition. This is supported by product distribution (Table II), which indicates that only a small quantity (2.2%) of the cyclohexanol is oxidized to cyclohexanone in the system.

Oxidation of Cyclohexanol. In the presence of ascorbic acid, the oxidation of cyclohexanol by Ru(III)–EDTA proceeds via an oxygen-dependent (first-order) pathway with the formation of *cis*-1,3-cyclohexanediol as the main product. A mechanism for the reaction is proposed in Scheme II.

Scheme II



In the proposed mechanism, the Ru(III)–EDTA–ascorbate complex **1** reacts with cyclohexanol to form the mixed-ligand complex **6** in the preequilibrium step "K_5". Complex **6** then combines with 1 mol of dioxygen, yielding the kinetic intermediate **7**. The rate-determining step of the reaction involves a selective abstraction of an hydride ion from the tertiary carbon atom of cyclohexanol, a homolytic cleavage of an O–OH bond in dioxygen complex **7**, transfer of OH^- to the carbonium ion center, and the reduction of the other oxygen atom to H_2O to yield *cis*-1,3-cyclohexanediol, dehydroscorbic acid, and the catalyst. Groves and Van Der Puy[52] had proposed a similar mechanism for the stereospecific hydroxylation of cyclohexanol to *cis*-1,3-cyclohexanediol by the Fe(II)–H_2O_2 system, the rate data for which was not reported. The rate law for the oxidation of cyclohexanol to *cis*-1,3-cyclohexanediol can be represented by eq 13. Rate

$$\frac{-d[H_2A]}{dt} = k_3K_1K_5K_6K_a[H_2A][\text{Ru(III)–EDTA}][C_6H_{11}OH][O_2]/[H^+] \quad (13)$$

expression 13 is rearranged to eq 14, where the total concentration

$$\frac{[[Ru^{III}L(H_2O)]_T^-][H_2A]}{\frac{-d[H_2A]}{dt}} = \frac{[H^+]}{k_3K_1K_aK_5K_6[C_6H_{11}OH][O_2]} + \frac{[H_2A]}{k_3}\left(1 + \frac{1}{K_6[O_2]}\right) \quad (14)$$

$$= \frac{1}{[O_2]}\left(\frac{[H^+]}{k_3K_1K_aK_5K_6[C_6H_{11}OH]} + \frac{[H_2A]}{k_3K_6}\right) + \frac{[H_2A]}{k_3} \quad (15)$$

of catalyst, present in the form of various intermediate complexes,

(52) Groves, J. T.; Van Der Puy, M. *J. Am. Chem. Soc.* **1976**, *98*, 5290.

is considered. The rate constant k_3 (Table VII) and equilibrium constants K_5 and K_6 (Table I) were resolved kinetically from the slopes and intercepts of the plots of the lhs of the rate equation vs $[H^+]$ (eq 14) and vs $[O_2]^{-1}$ (eq 15). The rate constant k_3 (12.5×10^{-4} s^{-1}), corresponding to the hydroxylation of cyclohexanol to *cis*-1,3-cyclohexanediol (Table VII), is higher ($1^1/_2$ times) than the rate constant k_1 (7.8×10^{-4} s^{-1}) for the oxidation of cyclohexane to cyclohexanol. The oxidation of cyclohexanol to cyclohexanone by molecular oxygen catalyzed by Ru(III)–EDTA (in the absence of ascorbic acid) ($k_2 = 5.7 \times 10^{-4}$ s^{-1}) is slower than the rate of oxidation ($k_3 = 12.5 \times 10^{-4}$ s^{-1}) of cyclohexanol to *cis*-1,3-cyclohexanediol (in the presence of ascorbic acid). Hence the presence of ascorbic acid not only increases the rate of oxidation of cyclohexanol but also changes the nature of the product.

The formation of *cis*-1,3-cyclohexanediol or cyclohexanone depends on the competition between an oxygen atom transfer versus a hydride transfer in the rate-determining step. In the presence of excess ascorbic acid in the system, the reaction proceeds by a path first order in molecular oxygen concentration and the oxygen atom transfer mechanism prevails to form the diol.

In the absence of ascorbic acid however, the hydride transfer mechanism (Scheme I) prevails to give cyclohexanone. In the first phase of the oxidation of cyclohexane, the product formed is cyclohexanol. After a sufficient concentration of cyclohexanol is built up, it is further oxidized to *cis*-1,3-cyclohexanediol in the presence of ascorbic acid. Hence the rate of oxidation of cyclohexanol to *cis*-1,3-cyclohexanediol successfully competes with its oxidation to cyclohexanone. When ascorbic acid is exhausted in the system, cyclohexanol is oxidized to cyclohexanone as a main pathway.

Oxidation of Cyclohexene. In the proposed mechanism for oxidation of cyclohexene (Scheme III), a mixed-ligand Ru(III)–EDTA–ascorbate complex is formed in a preequilibrium step as in Schemes I and II. This is followed by another preequilibrium step involving the formation of the mixed-ligand Ru(III)–EDTA–ascorbate–olefin complex **8**. Reaction with molecular oxygen forms the intermediate complex **9**. In the proposed rate-determining step, k_4, heterolytic cleavage of the O–O bond in **9** with the subsequent transfer of an oxygen atom to cyclohexene results in the formation of the epoxide while the catalyst is regenerated with the elimination of dehydroascorbic acid. The oxygen atom transfer to cyclohexene in the rate-determining step is supported by $^{18}O_2$:$^{16}O_2$ labeling studies that gave the ^{18}O and ^{16}O incorporated epoxide in a 1:1 ratio.

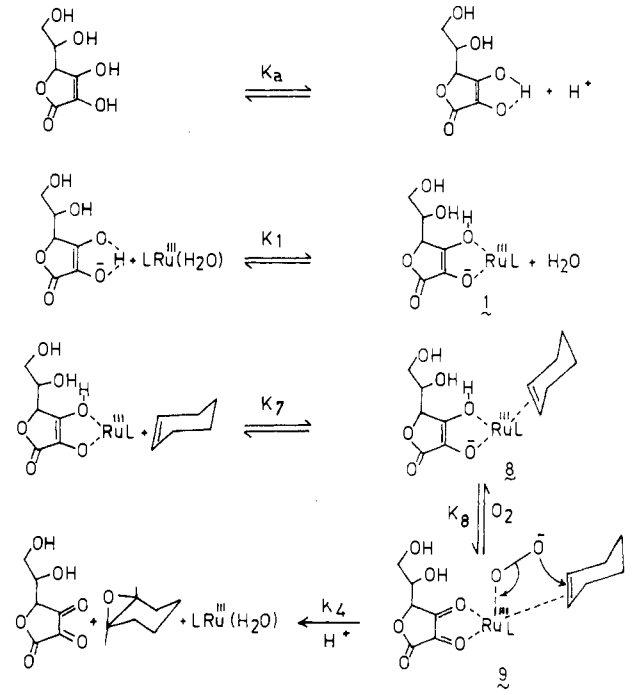
Under the steady-state concentration of the $[Ru^{III}(EDTA)(H_2O)]^-$ complex, the rate law for the oxidation of cyclohexene is given by eq 16.

$$\frac{[[Ru^{III}L(H_2O)]_T^-][H_2A]}{\frac{-d[H_2A]}{dt}} = \frac{[H^+]}{k_4K_1K_aK_7K_8[C_6H_{10}][O_2]} + \frac{[H_2A]}{k_4}\left(1 + \frac{1}{K_8[O_2]}\right) \quad (16)$$

The equilibrium constants K_7 and K_8 (Table I) and rate constant k_4 (Table VII) are calculated kinetically by slopes and intercepts of the rate expression in eq 16.

The kinetics of Ru(III)–EDTA-catalyzed oxidation of cyclohexene indicates a first-order dependence with respect to [Ru(III)–EDTA] and [cyclohexene] and a half-order dependence with respect to molecular oxygen concentration.[53] The difference in the dependence on molecular oxygen concentration in the presence and absence of ascorbic acid also indicates a difference in the mechanistic pathways for the reactions. A μ-peroxo complex $[Ru^{IV}(EDTA)(cyclohexene)]_2O_2$ is formed[53] as an intermediate in the reaction, and the proposed rate-determining step is the

Scheme III



formation of the intermediate ruthenyl species $(EDTA)Ru^V{=}O$ by the homolytic cleavage of the O–O bond in the peroxo complex followed by a transfer of an oxygen atom to cyclohexene to form the epoxide. In the presence of ascorbic acid, however, a first-order dependence on oxygen concentration is observed and the oxidation of cyclohexene is proposed to proceed through a pathway involving a heterolytic cleavage of the O–O bond (Scheme III).

The rate of oxidation of cyclohexene and the yield of the epoxide is very much enhanced in the presence of ascorbic acid (Table II). The yield of epoxide in the presence of ascorbic acid is 65%. This reflects on an easier cleavage of O–O bond by heterolytic rather than by homolytic fission.

It is of interest to compare the rates of the oxidation of saturated and unsaturated hydrocarbons by the Ru(III)–EDTA–ascorbic acid–O_2 system based on the yield and rate constants (k_1, k_2, k_3, and k_4); see Table VII. The system is very effective for the epoxidation of unsaturated hydrocarbon cyclohexene. The order of the substrate reactivity observed in this catalytic oxidation is cyclohexane < cyclohexanol < cyclohexene. Accordingly, the rate constants for the individual reactions follow the order $k_1 < k_3 < k_4$.

It is of further interest to comment on the coordination number of ruthenium in the various intermediates proposed in the mechanism. Diamantis et al.[54] have proposed a tetradentate coordination of EDTA in Ru(II) and Ru(III)–EDTA complexes. We have recently completed the X-ray structure of $[Ru(EDTA)Cl_2]^{3-}$ where it was shown[55] that EDTA is tetradentate with two long M–Cl bonds. These two are the actual labile positions on the complex that can be occupied by ascorbic acid. The substrate molecule and O_2 may be loosely coordinated to the metal ion as a kinetic intermediate with an expanded coordination number. Such intermediates have a very low value of stability constants as indicated by the data in Table I. After the catalytic reaction the kinetic intermediates revert back to thermodynamically stable coordination number six in Ru(III)–EDTA–ascorbate complex. The tendency of Ru(III) to expand its coordination number beyond six was reported.[42]

Registry No. EDTA, 60-00-4; Ru, 7440-18-8; cyclohexane, 110-82-7; cyclohexanol, 108-93-0; cyclohexene, 110-83-8; ascorbate, 50-81-7.

(53) Taqui Khan, M. M.; Prakash Rao, A. *J. Mol. Catal.* **1986**, *39*, 331 and references therein.

(54) Diamantis, A. A.; Dubrawski, J. V. *Inorg. Chem.* **1983**, *22*, 1934.

(55) Taqui Khan, M. M.; et al. Unpublished results.