# Oscillations and Mechanism: Catalyzed O₂ Oxidation of Cyclohexanone

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Abstract: A variety of oscillations has been observed in the Co, Br⁻-catalyzed O₂ oxidation of cyclohexanone. They are found in the redox potential, the concentrations of dissolved O_2, $[Co^{3+}]$, and $[Br^-]$, conductivity, and in chemiluminescence. A kinetic model based on generation of Co^{3+} by reactions of Co^{2+} with the following substituted cyclohexanone
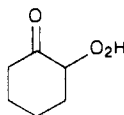
and ring-opened peracids simulates the observed oscillating behaviors.

This report presents the observation and experimental study of the oscillatory oxidation of cyclohexanone with a suggested mechanism for the time-dependent behavior. A search for possible oscillatory behavior in an aliphatic oxidation was undertaken in the hope that, if found, the understanding of the oscillations would lead to a more detailed picture of an elaborate chemical system.[1a]

In complex reactions the interrelationships of the many elementary steps can be difficult to elucidate. Where there are significant nonlinearities or autocatalysis, the difficulties may be compounded. The dependence of individual rates on higher orders of concentrations may lead to kinetics which are particularly sensitive to experimental details. However, the nonlinearities can lead to a compensating advantage in allowing the reaction to exhibit oscillations. An examination of the more general features of autoxidation had suggested that such reactions were candidates for new oscillatory systems[1b,2a,b] and that this behavior could lead to greater understanding of the reactions.

Previously, the study of the oscillatory oxidation of benzaldehyde indicated that oscillations may indeed be a powerful tool for the elucidation of a complex reaction.[2] A rich chemistry was found for the normal insertion of an oxygen atom into a C–H bond, producing benzoic acid in 98–99% yield. The mechanism exhibited new features in a well-studied reaction.[2]

In seeking other examples of oscillatory autoxidations, cyclohexanone was examined as a substrate. Unlike the clean overall reaction of benzaldehyde, the ketone gives a variety of products. Six or more may each be obtained in more than 5% yield. The relative amounts can vary substantially with changes in conditions. In a number of systems this increased complexity of the chemistry may be expected to lead to a higher probability of oscillatory behavior.[1b] Thus, although oscillation had not been reported previously the substrate seemed worthy of study. Experimentally, the conditions for cyclohexanone oxidation were varied systematically starting from those previously found appropriate for substantial conversions.[3-7] Oscillations were found as shown in Figure 1.

The overall appearance of the oscillations clearly differed from that of the benzaldehyde oxidation indicating significant differences in the mechanisms of the two reactions. A cycle of the

cyclohexanone oxidation has a long interval in which the potential remains largely constant. The mechanistic model indicates that this stage, A, involves the buildup of organic intermediates, mainly peroxides derived from cyclohexanone, to concentrations just below the thresholds required for rapidly accelerating oxidation (Figure 2). In stage B peroxides continue to be generated while converting Co^{2+} to Co^{3+} with a rapid rise in electrode potential and undergoing ring-opening reactions. Finally, in stage C accumulated Co^{3+} oxidizes organics to form radical intermediates and reverts to Co^{2+} with a rapid drop in the potential.

Experimental Section

Reactions were carried out under batch and continuous flow conditions. Batch reactions were done in either a 500-mL glass pressure bottle, equipped with mechanical stirrer, thermocouple, gas inlet, Pt and Ag electrodes, or a similarly equipped 3-mL quartz UV–vis spectrophotometric cell. The 500-mL glass pressure bottles were modified by attachment of suitable glass joints to allow use of a Br⁻ ion selective electrode, a total ion conductivity probe, a standard Ag/AgCl reference electrode, or a Clarke electrode (Beckman Instruments Corporation) for measurements of dissolved O_2. Continuous flow reactions were run in a 125-mL titanium reactor, equipped with mechanical stirrer, thermocouple, fittings for gas and liquid feeds and effluent streams as well as Pt and Ag electrodes. For measurement of chemiluminescence a 1.3-cm quartz rod was attached to the bottom of the reactor. Light signals were detected by an EMI 6255B photomultiplier tube connected to a current amplifier. Redox potential measurements were recorded as a voltage generated between Pt or Au wires and a standard Ag/AgCl reference electrode (Figure 1) or between Pt and Ag wires (Figures 2–6). Conductivity was measured by using a PP1042 probe with a Radiameter CDM83 meter. All UV–vis measurements were made with Hewlett-Packard 8450a spectrometer.

Reagent grade acetic acid, cyclohexanone, Co(OAc)₂·4H₂O, and NaBr were used as received. The alkyl hydroperoxide compounds, 2-methylcyclohexanone hydroperoxide, cyclohexyl hydroperoxide, and diisopropylketone hydroperoxide were prepared according to procedures in the literature.[8-10]

Analyses of products were made with a 0.2 mm × 25 m methylsilicone glass capillary GC column on a Hewlett-Packard 5970A instrument. The solutions were analyzed by BSTFA-derivatized GC and contained numerous peaks. The larger peaks (**3**, **5**, and **6** and adipic, glutaric, and succinic acids) were identified by GC/MS. Compared to the dibasic acids, the α-substituted cyclohexanones were too low in concentration for quantitative determination. GC/MS analyses were performed on a 16F VG-Micromass instrument with a Varian GC chromatograph. Solutions of products, concentrated about 10-fold and reduced exhaustively with LAH, were also analyzed as mixtures of mono- and dialcohol compounds, by using a Hewlett-Packard 5970A GC chromatograph. The linear mono- and dialcohols obtained from LAH reduction contain small contributions from compounds such as caproic acid, caprolactone, valerolactone, hydroxycaproic acid, and adipaldehyde. The latter compounds

(1) (a) A preliminary account of the oscillatory cyclohexanone system was presented in a poster at the fall ACS meeting, August 26–31, 1984, in the Division of Physical Chemistry. (b) Wasserman, E.; Roelofs, M. G.; Druliner, J. D., to be submitted for publication.

(2) (a) Roelofs, M. G.; Wasserman, E.; Jensen, J. H.; Nader, A. E. J. Am. Chem. Soc. 1983, 105, 6329. (b) Roelofs, M. G.; Wasserman, E.; Jensen, J. H. Ibid. 1987, 109, 4207. (c) Jensen, J. H. J. Am. Chem. Soc. 1983, 105, 2639.

Catalyzed O₂ Oxidation of Cyclohexanone

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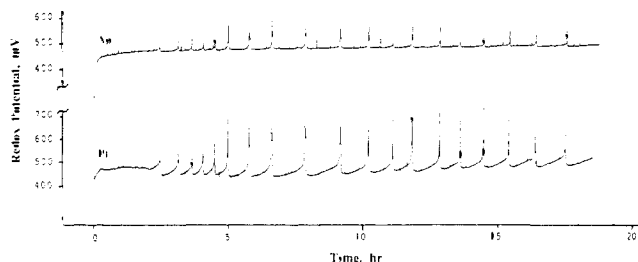**Figure 1.** Redox potential behavior measured with Au and Pt electrodes versus Ag/AgCl reference accompanying batch oxidation of cyclohexanone (0.5 M) in the system: $Co(OAc)_2$ (0.02 M), NaBr (0.01 M), O_2 (~507 Torr) in acetic acid/H_2O (90/10) at 110 °C and 50 rpm stirring in a 3-mL glass cell.
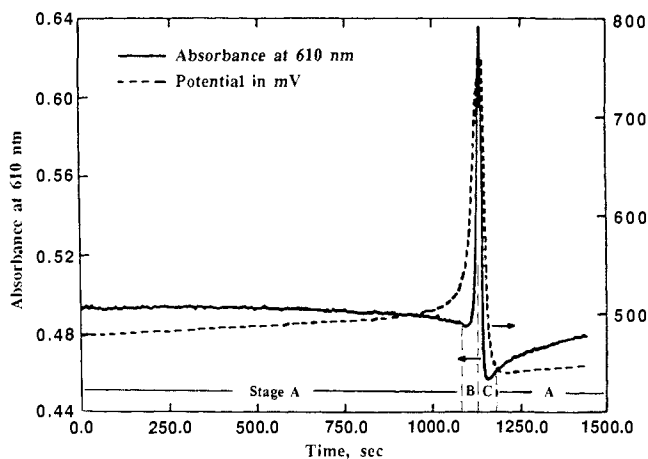

Figure 2. Redox potential and visible absorbance measurements during one oscillation cycle accompanying batch oxidation of cyclohexanone at 99 °C under 711 Torr O_2 in a 3-mL quartz cell and 400 rpm stirring. Other conditions as shown in Figure 1.

have been reported in previous studies,[3-7] but were detected in only trace amounts in this study.

A typical experiment with a 3-mL quartz cell is the following. The contents are 2 mL of a solution containing 0.02 M $Co(OAc)_2$, 0.01 M NaBr, and 0.5 M cyclohexanone in acetic acid/water (90/10). The reactor was placed in a temperature-controlled oil bath. An atmosphere of 10 psig O_2 was established, stirring was adjusted to 50 rpm, and the solution was brought to a temperature of 110° within 30 min. Over a period of 18 h the redox potential was recorded with Pt and Au electrodes (Figure 1).

Because of potentially hazardous reaction mixtures, all reactions were done in a barricade constructed of heavy steel walls. The exceptions were reactions in 3-mL quartz cells which were shielded with Lucite barriers or the tempered glass windows of the laboratory fume hood.

Results and Discussion

Examples of the oscillatory behaviors are presented in Figures 1–6. The rapid changes associated with the different measurements are essentially in phase.

The first observations were the oscillations in redox potential. Au and Pt electrodes do not have the same response (Figure 1), with much of the difference due to the greater sensitivity of the Pt potential to the surface absorption of organic or halide species.[11] Co^{3+} does make a small contribution to the changes as determined
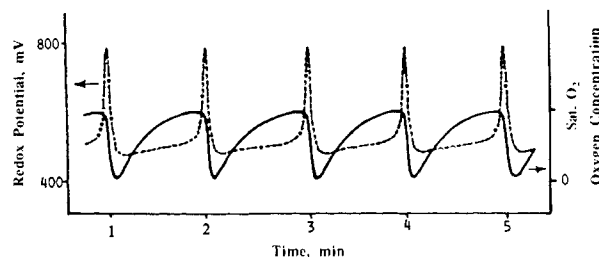

Figure 3. Redox potential and dissolved O_2 behavior accompanying batch oxidation of cyclohexanone at 105 °C under 627 Torr O_2 in a 500-mL glass bottle and 450 rpm stirring. Other conditions as shown in Figure 1.

from the time variation of its absorption spectrum (Figure 2). For cobalt, the changes in absorbance at 610 nm (Figure 2) showed that [Co^{3+}] changed from 0.002 to 0.003 M, while the redox potential changed from about 400 to 750 mV. The increase in [Co^{3+}] would, according to the Nernst eq 1, contribute only ~15 mV to the change in redox potential.

$$\Delta E = 0.074 \log \frac{([Co^{3+}]/[Co^{2+}])_{high}}{([Co^{3+}]/[Co^{2+}])_{low}} \quad (1)$$

To anticipate some of the conclusions of the kinetic model, the long periods of nearly constant potential at the beginning of each cycle, particularly with Au electrodes (Figure 1), are associated with the slow buildup of organic intermediates, probably including
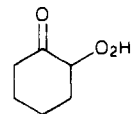
(KO₂H). Hendry et al. have provided strong evidence that KO_2H is a primary intermediate in the Co catalyzed O_2 oxidation of cyclohexanone in acetic acid.[5] While KO_2H is too unstable to isolate, *tert*-α-carbonyl hydroperoxide compounds are quite stable.[12] They were used in measurements of rates of reaction of a peroxide with Co^{2+} to generate Co^{3+}.

Complementary measurements were made of the response of the redox potential to additions of α-ketohydroperoxides,
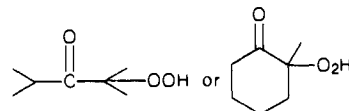
to acetic acid/H_2O solutions. In one set of measurements, injections of peroxide compounds were made to a solution of acetic acid/H_2O (90/10) at 80 °C, and the changes in redox potential were monitored by using a Pt electrode with an Ag/AgCl reference electrode. The peroxide concentrations would have been formally 0.01 M. The following compounds caused rapid (<5 s) increases in potential:
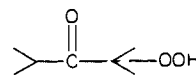
(380–475 mV),
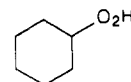
(330–600 mV), *t*-BuOOH (330–515 mV), and *m*-Cl-C₆H₅CO₃H (325–980 mV). Thus, under oscillating conditions the formation of peroxides such as KO_2H can lead to much larger changes in redox potential than can be attributed to changes in Co^{3+}/Co^{2+} alone. In addition to α-ketoalkyl peroxides, a second class of organic oxidant, namely ring-opened acyl peroxides and peracids

(3) Berzin, I. V.; Denisov, E. T.; Emanuel, N. M. *The Oxidation of Cyclohexane*; Pergamon Press: London, 1966.

(4) Onopchenko, A.; Schulz, J. G. D. *J. Org. Chem.* **1973**, *38*, 3729; **1980**, *45*, 3716.

(5) Hendry, D. G.; Gould, C. W.; Schuetzle, D.; Syz, M. G.; Mayo, F. R. *J. Org. Chem.* **1976**, *41*, 1.

(6) Tanaka, K. *Prepr. Div. Pet. Chem. Am. Chem. Soc.* **1974**, *19*, 103.

(7) Druliner, J. D. *J. Org. Chem.* **1978**, *43*, 2069.

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(9) Gersmann, H. R.; Nieuwenhuis, H. J. W.; Bickel, A. F. *Proc. Chem. Soc.* **1962**, 279.

(10) Walling, C.; Buckler, S. A. *J. Am. Chem. Soc.* **1953**, *75*, 4372.

(11) Woods, R. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1976; Vol. 9, pp 1–161.

(12) Druliner, J. D.; Hobbs, F. W.; Seidel, W. C. *J. Org. Chem.* **1988**, *53*, 700.
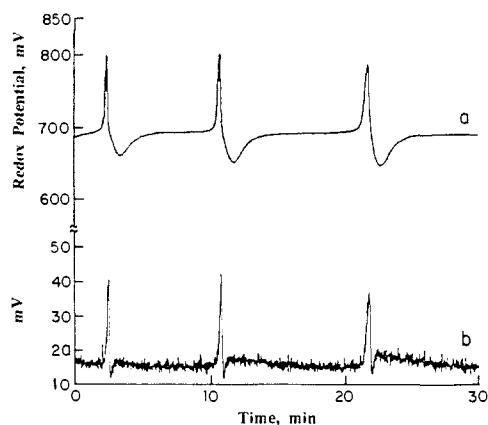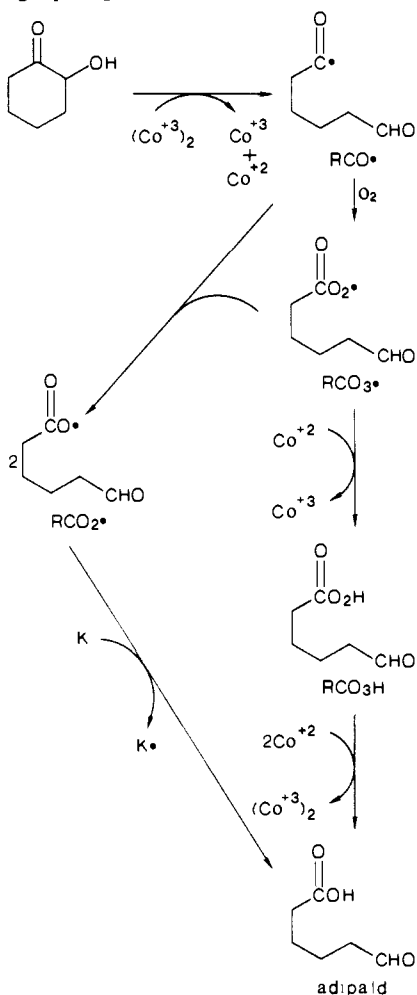
Figure 4. Redox potential (a) and chemiluminescence (b) behavior accompanying CSTR oxidation of cyclohexanone at 107 °C under 577 Torr O_2 in a 125-mL titanium reactor and 100 rpm stirring. Other conditions as shown in Figure 1.

Scheme I. Ring-Opening Reactions of 2-Hydroxycyclohexanone

$(R-CO_3^{\bullet}$ and $R-CO_3H)$ (Scheme I), is likely to be important. This conclusion is supported by our observation that Co^{3+} rapidly opens **3** and **4** to mixtures of dibasic acids. The presence of linear peracid intermediates $(R-CO_3H, R'-CO_3H)$ is also consistent with the known ability of peracids to convert Co^{2+} rapidly to Co^{3+} in $HOAc/H_2O$ solvent.[13]

The oscillations in redox potential are accompanied by corresponding changes in dissolved O_2 (Figure 3). Control mea-

(13) Jones, G. H. *J. Chem. Soc., Chem. Commun.* **1979**, 536. Jones, G. H. *J. Chem. Res., Symp.* **1981**, 228. Jones, G. H. *J. Chem. Res., Miniprint* **1981**, 2801.
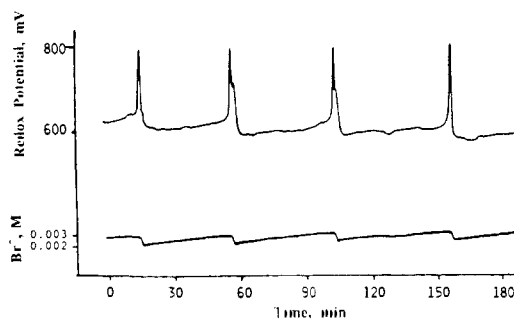
Figure 5. Redox potential and Br^- concentration behavior accompanying batch oxidation of cyclohexanone at 105 °C under 627 Torr O_2 in a 500-mL glass bottle and 450 rpm stirring. Other conditions as shown in Figure 1.
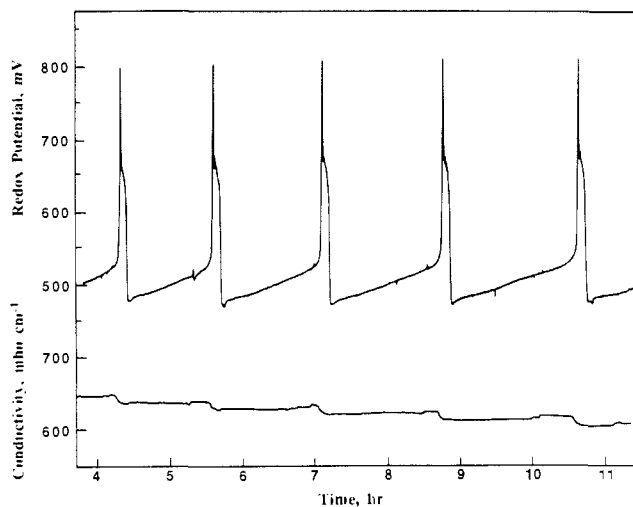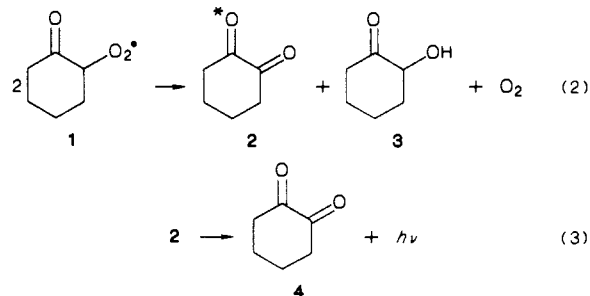

Figure 6. Redox potential and ion conductivity behavior accompanying batch oxidation of cyclohexanone at 110 °C. Other conditions as shown in Figure 1.

surements with the Clarke electrode established that dissolved O_2 varied between nearly saturated (>95%) and essentially depleted concentrations (<1%). The relatively rapid rise in dissolved O_2 during stage A of each cycle, and attainment of near saturation levels, is consistent with a slow consumption of O_2 and slow oxidation of cyclohexanone. The rapid depletion of dissolved O_2 and rapid rise in potential during stage B (Figure 3) are consequences of autocatalytic increases in Co^{3+} and hydroperoxides KO_2H and $CHO-(CH_2)_4-CO_3H$.
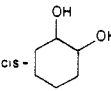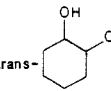
Another oscillating observable is chemiluminescence (Figure 4b). In analogy to chemiluminescence from dimerization of secondary alkylperoxy radicals, the emission observed in the oscillating cyclohexanone system may arise from the triplet excited state cyclohexanedione formed via dimerization of α-ketocyclo-hexylperoxy radicals[14] (eq 2 and 3). Although the diketone **4** rapidly undergoes oxidative ring-opening under the reaction conditions, traces of **4** are found in product solutions.

(14) For a discussion of chemiluminescence associated with dimerization of cyclohexylperoxy radicals, see: Kellog, R. *J. Am. Chem. Soc.* **1969**, *91*, 5433.

Table I. Reaction Products Produced under Oscillating and Steady-State Conditions in the Co(OAc)$_2$ (0.02 M)/NaBr (0.01 M) Catalyzed O$_2$ Oxidation of Cyclohexanone (0.5 M) in Acetic Acid/H$_2$O (90/10 at 105 °C)

entry	reactn time,[a] h	steady state (SS) or oscil condn	n-C$_5$H$_{11}$-OH	cis- OH,OH	trans- OH,OH	HO-C$_6$H$_{12}$-OH	HO-C$_5$H$_{10}$-OH	HO-C$_4$H$_8$-OH
1	52	oscil	0.030	0.029	0.075	1.0	3.32	0.64

concentrations of products (M),[c] [cyclohexanone]$_o$ = 0.5 M

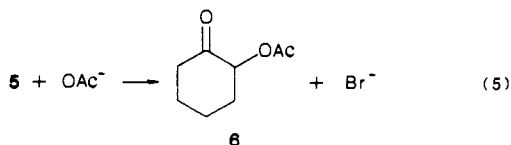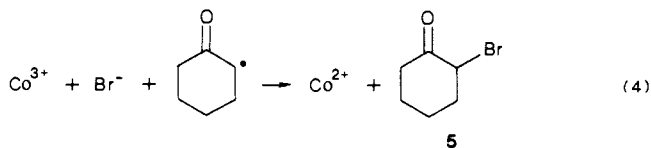|			adipic	glutaric	succinic
2	20	oscil	0.0131	0.0272	0.0046
3	22	oscil	0.0183	0.0195	0.0029
4	21	oscil	0.0189	0.0244	0.0035
5	24	SS	0.0166	0.0170	0.0016
6	21	SS	0.0153	0.0121	0.0039
7	18	SS	0.0094	0.0111	0.0037
8	9	SS	0.0076	0.0124	0.0026
9	72	SS	0.0211	0.0352	0.0069

[a] All reactions run under 10 psig O$_2$ in 3 cc glass cells. [b] Product solutions combined with pimelic acid (internal standard), concentrated by N$_2$ evaporation of solvent, reduced with 1 M LiAlH$_4$ in THF, and analyzed by GC with a methylsilicone capillary column. [c] Product solutions combined with pimelic acid (internal standard), concentrated by N$_2$ evaporation of solvent, and analyzed as methyl ester solutions with methylsilicone capillary column.

[Br⁻] (Figure 5) and total ion conductivity (Figure 6) exhibit very similar oscillating behaviors. These can be interpreted as cycling of Br between Br⁻ ion and
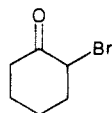
(5) (eq 4 and 5). This conclusion is consistent with GC/MS

                                                                                    (4)

                                                                                    (5)

identification of 5 and 6 among reaction products and a higher molar equivalent conductance for Br⁻ (78 mhos-cm^2) than the corresponding value for OAc⁻ (41 mhos-cm^2).[15]

The diversity and relative yields of products formed were found to be similar for both oscillating and steady-state conditions (Table I).[16] Comparison of the major products was made by LAH reduction of concentrated product solutions followed by GC analysis (Table I, entry 1). The much lower yields of c,t-cyclohexanediols from reactions at higher conversions, compared to the yields of linear C$_4$, C$_5$, and C$_6$ diols, show that 3, 5, and 6 are primarily intermediates leading to the final linear diacids, succinic, glutaric, and adipic.

Kinetic Model. A multistep model was developed to describe the main features of the oscillating cyclohexanone system (Scheme II). Some of the steps describe the autoxidation of cyclohexanone including initiation, propagation, and termination (steps 1, 2, 4, 7, 8, 26, 28, and 29). Other steps describe the generation of Co^{3+} (steps 5, 9, 19, 20, 23, and 24). Reactions also include transfer of Br between Br⁻ and 3 (steps 15 and 16).

Steps 11 and 12 describe mass transfer of O$_2$ between liquid and gas phases. Transport of oxygen was modeled with the equilibrium: $k_{11} \times [O_2g] = k_{12} \times [O_2]$. The value of $k_{12} = 1 \times 10^{-1}$ s^{-1} was based on a calculated time constant of 22 s for equilibration of oxygen between gas and liquid phases under oscillating conditions (Figure 3). This time constant represents a maximum as it includes any contribution from chemical reactions of O$_2$l during its rapid buildup. The equilibrium concentration of O$_2$l = 6 × 10^{-3} M atm^{-1} was calculated from a Henry's law constant of 3300 atm (mol fraction)$^{-1}$ for oxygen in 90/10 at 105 °C.[2b,17–19] The product of $k_{11} \times O_2g = k_{12} \times [O_2l] = 6 \times 10^{-4}$ M s^{-1}.[20] O$_2$l is also chemically produced in steps 13 and 14 but at insignificant rates compared to the rate of $k_{11} \times [O_2g]$, except for a brief period in the transition between stages B and C.[21] Steps 13 and 14 describe the termination of peroxy radicals, via a tetroxide intermediate, to give
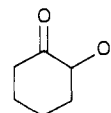
radicals and nonradical products 3 and 4.

Numerous studies have been made of the nature of Co^{3+} in acetic acid/water solvent.[13,22–27] The most detailed description, proposed by Jones[13] and further delineated by Roelofs et al.[2b]

(15) *Lange's Handbook of Chemistry*, 11th ed.; McGraw-Hill: 1973; pp 6–30.

(16) Oscillations were not always observed, depending on the purity of the cyclohexanone used and the purity of the surface of the Ag electrode. However, oscillations were observed by visible absorbance (620 nm) in bulk solution in the absence of Pt and Ag electrodes.

(17) O'Connell, J. P. *ACS Symp. Ser.* **1977**, *60*, 490–497.

(18) Rudas, A. E., et al. *Tr. Nauchno-Issled. Inst. Proekt. Monomerov* **1974**, *4*, 143–147.

(19) Wilhelm, E.; Battino, R.; Wilcock, R. *J. Chem. Rev.* **1977**, *77*, 219–259.

(20) By greatly increasing O$_2$g (1 × 10^6 atm) and making k_{11} correspondingly small (6 × 10^{-10} M atm^{-1} s^{-1}), O$_2$l was maintained at 6 × 10^{-3} M without measurably depleting O$_2$g during simulations. A constant concentration of K at 0.5 M was similarly maintained by a large reservoir of K$_{feed}$ as shown in Scheme II.

(21) Greller, L. D., private communication.

(22) (a) Lande, S. S.; Falk, C. D.; Kochi, J. K. *J. Inorg. Nucl. Chem.* **1971**, *33*, 4101. (b) Tanaka, S.; Uemura, S.; Okano, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2565. (c) Ziolkowski, J. J.; Pruchnik, F.; Szymanska-Buzar, T. *Inorg. Chim. Acta* **1973**, *7*, 473. (d) Koubek, E. E.; Edwards, J. O. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1401. (e) Scott, J. Y.; Chester, A. W. *J. Phys. Chem.* **1972**, *76*, 1520.

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(25) Ichikawa, Y.; Yamashita, G.; Tokashiku, M.; Yama, I. T. *Ind. Eng. Chem.* **1970**, *62*, 38.

(26) Wormser, Y.; Peschanski, D. *Bull. Chem. Soc. Chim. Fr.* **1962**, 876.

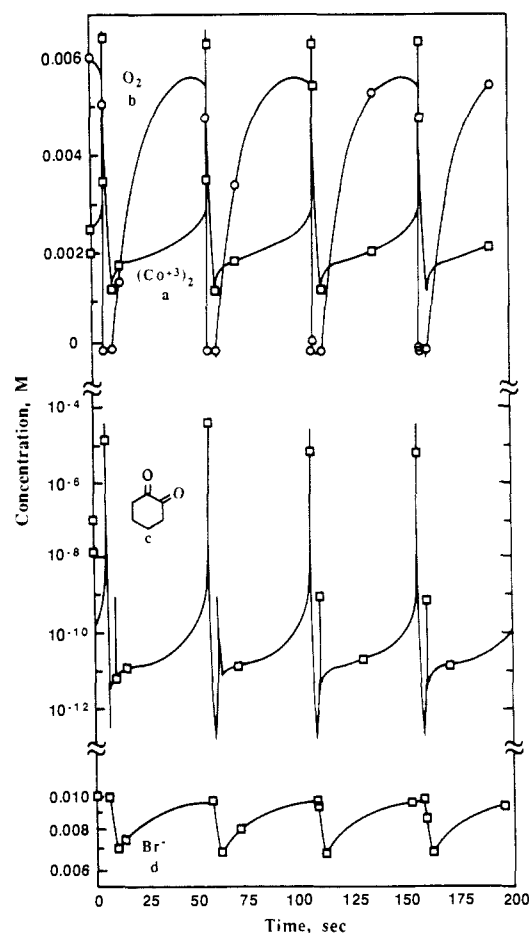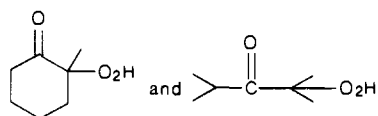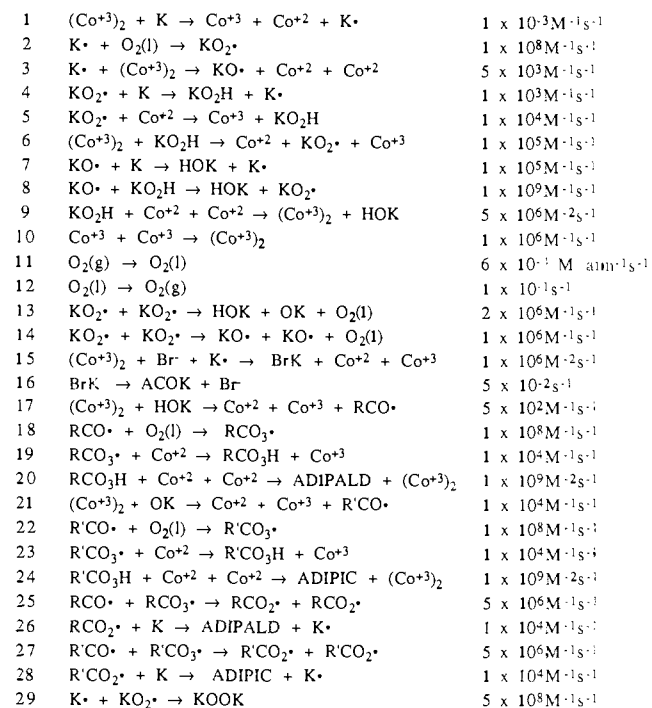(27) Sakota, K.; Kamiya, Y.; Ohta, N. *Can. J. Chem.* **1969**, *47*, 387.

Figure 7. Simulated oscillations in $(Co^{3+})_2$ (a), dissolved O_2, circles (b), 1,2-cyclohexanedione (c), and Br^- ion (d). Initial concentrations given in Scheme II.

Scheme II. Kinetics Model for Simulating Oscillating Behaviors of the $Co(OAc)_2NaBr$ Catalyzed Air Oxidation of Cyclohexanone[a]

1	$(Co^{+3})_2 + K \rightarrow Co^{+3} + Co^{+2} + K\cdot$	$1 \times 10^{-3} M^{-1}s^{-1}$
2	$K\cdot + O_2(l) \rightarrow KO_2\cdot$	$1 \times 10^8 M^{-1}s^{-1}$
3	$K\cdot + (Co^{+3})_2 \rightarrow KO\cdot + Co^{+2} + Co^{+2}$	$5 \times 10^3 M^{-1}s^{-1}$
4	$KO_2\cdot + K \rightarrow KO_2H + K\cdot$	$1 \times 10^3 M^{-1}s^{-1}$
5	$KO_2\cdot + Co^{+2} \rightarrow Co^{+3} + KO_2H$	$1 \times 10^4 M^{-1}s^{-1}$
6	$(Co^{+3})_2 + KO_2H \rightarrow Co^{+2} + KO_2\cdot + Co^{+3}$	$1 \times 10^5 M^{-1}s^{-1}$
7	$KO\cdot + K \rightarrow HOK + K\cdot$	$1 \times 10^5 M^{-1}s^{-1}$
8	$KO\cdot + KO_2H \rightarrow HOK + KO_2\cdot$	$1 \times 10^9 M^{-1}s^{-1}$
9	$KO_2H + Co^{+2} + Co^{+2} \rightarrow (Co^{+3})_2 + HOK$	$5 \times 10^6 M^{-2}s^{-1}$
10	$Co^{+3} + Co^{+3} \rightarrow (Co^{+3})_2$	$1 \times 10^6 M^{-1}s^{-1}$
11	$O_2(g) \rightarrow O_2(l)$	$6 \times 10^{-1} M$ atm$^{-1}s^{-1}$
12	$O_2(l) \rightarrow O_2(g)$	$1 \times 10^{-1}s^{-1}$
13	$KO_2\cdot + KO_2\cdot \rightarrow HOK + OK + O_2(l)$	$2 \times 10^6 M^{-1}s^{-1}$
14	$KO_2\cdot + KO_2\cdot \rightarrow KO\cdot + KO\cdot + O_2(l)$	$1 \times 10^6 M^{-1}s^{-1}$
15	$(Co^{+3})_2 + Br^- + K\cdot \rightarrow BrK + Co^{+2} + Co^{+3}$	$1 \times 10^6 M^{-2}s^{-1}$
16	$BrK \rightarrow ACOK + Br$	$5 \times 10^{-2}s^{-1}$
17	$(Co^{+3})_2 + HOK \rightarrow Co^{+2} + Co^{+3} + RCO\cdot$	$5 \times 10^2 M^{-1}s^{-1}$
18	$RCO\cdot + O_2(l) \rightarrow RCO_3\cdot$	$1 \times 10^8 M^{-1}s^{-1}$
19	$RCO_3\cdot + Co^{+2} \rightarrow RCO_3H + Co^{+3}$	$1 \times 10^4 M^{-1}s^{-1}$
20	$RCO_3H + Co^{+2} + Co^{+2} \rightarrow ADIPALD + (Co^{+3})_2$	$1 \times 10^9 M^{-2}s^{-1}$
21	$(Co^{+3})_2 + OK \rightarrow Co^{+2} + Co^{+3} + R'CO\cdot$	$1 \times 10^4 M^{-1}s^{-1}$
22	$R'CO\cdot + O_2(l) \rightarrow R'CO_3\cdot$	$1 \times 10^8 M^{-1}s^{-1}$
23	$R'CO_3\cdot + Co^{+2} \rightarrow R'CO_3H + Co^{+3}$	$1 \times 10^4 M^{-1}s^{-1}$
24	$R'CO_3H + Co^{+2} + Co^{+2} \rightarrow ADIPIC + (Co^{+3})_2$	$1 \times 10^9 M^{-2}s^{-1}$
25	$RCO\cdot + RCO_3\cdot \rightarrow RCO_2\cdot + RCO_2\cdot$	$5 \times 10^6 M^{-1}s^{-1}$
26	$RCO_2\cdot + K \rightarrow ADIPALD + K\cdot$	$1 \times 10^4 M^{-1}s^{-1}$
27	$R'CO\cdot + R'CO_3\cdot \rightarrow R'CO_2\cdot + R'CO_2\cdot$	$5 \times 10^6 M^{-1}s^{-1}$
28	$R'CO_2\cdot + K \rightarrow ADIPIC + K\cdot$	$1 \times 10^4 M^{-1}s^{-1}$
29	$K\cdot + KO_2\cdot \rightarrow KOOK$	$5 \times 10^8 M^{-1}s^{-1}$

Key:

[a] Initial concentrations: $Co^{2+} = 1.5 \times 10^{-2} M$, $Co^{3+} = 1 \times 10^{-3} M$, $(Co^{3+})_2 = 2 \times 10^{-3} M$, $O_2(g) = 1$ atm, $O_2(l) = 6 \times 10^{-3} M$, $K = 5 \times 10^{-1} M$, everything else $= 1 \times 10^{-7} M$.

involves three clusters of Co: $(Co^{3+})_2{}^a$ (active), $(Co^{3+})_2{}^s$ (stable), and $[(Co^{3+})_2Co^{2+}]^c$ (complexed). The relative strength of Co^{3+} as an oxidant in each form varies significantly. Toward H_2O_2, for example, rates of reaction in $HOAc/H_2O$ (95/5) at 0 °C decrease in the following order: $(Co^{3+})_2{}^a$ 700, $(Co^{3+})_2{}^s$ 5, $[(Co^{3+})_2Co^{2+}]^c$ 1.[13] The distribution of Co^{3+} between the three forms also varies markedly with temperature, ratio of Co^{2+}/Co^{3+}, and elapsed time from generation of $(Co^{3+})_2{}^a$, which is initially obtained by reaction of Co^{2+} with peracids. In the oscillating cyclohexanone oxidation system, with small Co^{3+}/Co^{2+} ratios, temperatures of at least 100 °C, and generally long times between the rapid generation of Co^{3+}, $[(Co^{3+})_2Co^{2+}]^c$ is most likely the predominant form of Co^{3+}. However, during the latter parts of stage B, significant concentrations of $(Co^{3+})_2{}^a$ and $(Co^{3+})_2{}^s$ could also contribute. The presence of Br^- leads to further complexity by giving many more possible clusters, each with its own activities.[2b] Thus, to simplify the model $(Co^{3+})_2$ represents all the reactive Co^{3+} species.
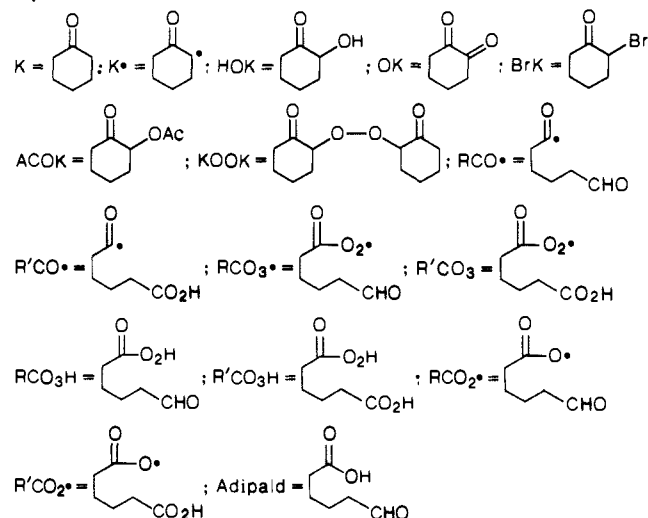
Reactions involving oxidation of Co^{2+} by peracids or acylperoxyl radicals (steps 19, 20, 23, and 24) were assigned rate constants based on studies of Jones[13] and Roelofs et al.[2b] Rate constants for reactions of $K\cdot$, $RCO\cdot$, and $R'CO\cdot$ with O_2l or for autoxidation steps which occur in the absence of Co^{2+} or Co^{3+} and involve K, $K\cdot$, $KO\cdot$, $KO_2\cdot$, and KO_2H were assigned on the basis of published rate constants for closely analogous reactions. A summary of relevant rate constants is included in the Supplementary Material. Constants for steps involving reactions of Co^{2+} and Co^{3+} with KO_2H and $KO_2\cdot$ (steps 5, 6, and 9) could not be assigned based on published model reactions. Reactions of Co^{2+} with

as models for the unisolable KO_2H, revealed that α-carbonylalkyl hydroperoxides react at least 500 times faster with Co^{2+} than do normal alkyl hydroperoxides at 40 °C in dry acetic acid.[12] The order with respect to Co^{2+} is also greater than one. However, in 90/10 at 90 °C, α-carbonylalkyl hydroperoxides rapidly react with both Co^{2+} and Co^{3+}, a shuttling with no net formation of Co^{3+}. Predominantly second-order dependence on Co^{2+} concentration was reported for reaction of t-BuO_2H with Co^{2+} in acetic acid.[23] Accordingly, 2 equiv of Co^{2+} react with KO_2H (step 9) with a rate constant intermediate between those for analogous reactions involving peracids or normal alkyl hydroperoxides. Reasonable simulations of dissolved O_2 behavior were obtained with 2 equiv of Co^{2+} in step 9 but not with one.

The rate equations from Scheme II were integrated numerically by using the Gear algorithm for stiff ordinary differential equation.[28] The simulated oscillating behaviors of dissolved O_2, excited
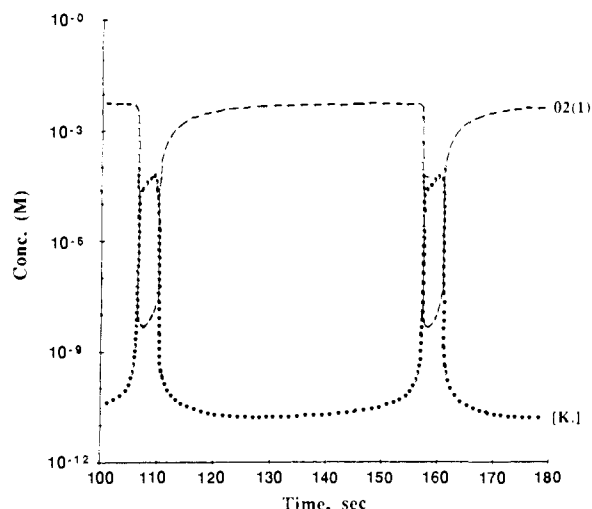
(28) Stabler, R. N.; Chesick, J. *Int. J. Chem. Kinet.* **1978**, *10*, 461.

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Figure 8. Simulated oscillations in dissolved O_2 and cyclohexanonyl radical (K*). Conditions given in Scheme II.

diketone **2**, and Br⁻, compared with $(Co^{3+})_2$ behavior, are shown in Figure 7. Analysis of the simulation showed that the three greatest contributions to oxidation of Co^{2+} to Co^{3+} during each cycle are reactions with $RCO_3^\bullet$ (step 19), with RCO_3H (step 20), and with KO_2H (step 9). The most important steps for the rapid conversion of Co^{3+} to Co^{2+} at low dissolved O_2 are steps 3 and 15 where K* and $(Co^{3+})_2$, both at relatively high concentrations, react. Figure 8 shows that the maxima of [K*] coincide with low values of $[O_2]$.

Agreement between measured and simulated behaviors is reasonable. A complete kinetics scheme, taking into account all mono- and dibasic acids, esters, lactones, hydroperoxides, and aldehydes and the various cobalt species, would require several hundred steps. The mechanism in Scheme II does contain the major steps, including the formation and reaction of ring-opened intermediates such as R'CO• and R'CO₃H which lead to adipic acid. The model was not expanded to include formation of glutaric and succinic acids. The ratios of the dibasic acids remained relatively constant under both oscillating and steady-state conditions. The constancy of the dibasic acid products suggests that all are formed from a common intermediate.[4,7] The most important sequence of reactions leading from cyclohexanone to the ring-opened species involves (a) attack on cyclohexanone (step 4), (b) α-substitution (step 2), (c) steps 9 and 13, and (d) opening of rings (steps 17 and 21), ultimately leading to formation of

carboxylic acids (steps 20 and 24). These are indicated in Scheme II.

This mechanism owes most of its considerable complexity to the desire to make it compatible with existing literature as far as possible. In fact a much simpler dynamical system, namely the Hodgkin–Huxley/FitzHugh–Nagumo equations for nerve impulses reproduce qualitatively the behavior shown in Figure 1. Those equations, however, bear little physical significance to the cyclohexanone oxidation system.[29]

A major conclusion reached in the study of the oscillating cyclohexanone oxidation involves some substantive differences in chemistry compared to the previously studied benzaldehyde system.[2] The long period of relatively flat potential in stage A in the cyclohexanone system, corresponding to slow autoxidation of the ketone, is absent in the benzaldehyde system. The primary role of Co^{2+} and Co^{3+} during this stage of the cyclohexanone oxidation is to facilitate the gradual increase in the concentrations of KO_2H and HOK (steps 5, 6, and 9), resulting in little net increase in Co^{3+}. When HOK builds to moderate concentrations, stage B begins, and a facile oxidation of HOK by Co^{3+} occurs to give RCO• and the subsequent steps in Scheme I. These steps lead to rapid generation of RCO_3H which rapidly converts Co^{2+} to Co^{3+}. Co^{3+}, in turn, then oxidizes HOK even more rapidly. Thus, there are fundamentally different roles of Co in stages A and B. In benzaldehyde A and B are combined into a single stage with rapidly rising $[Co^{3+}]$.

While the model involves the introduction of O_2 across a gas–liquid interface, replacement of that step with a solution precursor of O_2 will also yield oscillations.[21] This homogeneous O_2 analogue should exhibit essentially identical oscillatory behavior.

(29) Rinzel, J. In *Studies in Mathematical Biology*; Levin, S. A., Ed.; The Mathematical Association of American: 1978; Vol. 15, pp 1–66.