exclude the amide bond, which is known to have considerable double bond character and marked hindrance to rotation,[52] and also to exclude the phenyl-N bond, which is expected to be hindered by the porphyrin ring from carrying out free rotation. Thus, "n_{SB}" in Table VIII, the number of single bonds which can carry out free rotations in the uncoordinated side arm chain, has been adjusted for these considerations. The last column of that table gives the contribution to ΔS_1 for each of these single bonds in the side arm. This incremental ΔS per internal rotation is within the range (3–5 cal/(deg·mol)) found for cyclization of olefins and other reactions in which such internal rotations play an important role in the observed entropy of activation or reaction.[51,53] It decreases as the chain becomes longer since the coordinated pyridyl's connecting chain can undergo partial internal rotation as the chain lengthens, also consistent with results from other systems.[51,53] It is interesting but probably fortuitous that the entropy of internal rotation lost by the side arm pyridyl on coordination is so similar to the balance of the translational and rotational entropies lost by the free 3-picoline ligand on binding to zinc and the entropy gained by the solvent upon 3-picoline binding. Since this balance appears to be fairly independent of solvent (cyclohexane, $\Delta S_2 = -13.5$ cal/(deg·mol);[26] benzene, $\Delta S_2 = -13$ to -14 cal/(deg·mol);[21,23] toluene, $\Delta S_2 = -12$ to -13 cal/(deg·mol)), it appears unlikely that any side arm liganded metalloporphyrin will form a stable axial complex with its metal in solution nor would the same metalloporphyrin with a free ligand of analogous structure. However, the advantage of using side arm metalloporphyrins remains that coordination geometry may be controlled and that excess uncoordinated ligands need not be present in the solution.[54]

Acknowledgments. Support of this work by the National Science Foundation (CHE-75-20123 and 79-18217) and the National Institutes of Health in the form of a Research Career Development Award (5-KO4-GM 00227) is gratefully acknowledged. Methods of separation of metal-free **2** from other nitroporphyrin isomers and synthesis and preliminary NMR investigation of **5** were carried out by Dr. Robert S. McLeod. The Beer's law test for **5** and spectrophotometric investigation of compound **4** were carried out by Janet M. Walker.

---

(52) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(53) H. E. O'Neal and S. W. Benson, *J. Chem. Eng. Data*, **15**, 266 (1970).

(54) Reference to a company and/or product named by the Department of Agriculture is only for purposes of information and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Catalysis by Multimetallics. Catalyzed Homogeneous Oxidation of Alcohols and Ketones with Molecular Oxygen in the Presence of Hexarhodium Hexadecacarbonyl and Dirhenium Decacarbonyl

D. Max Roundhill,* Mark K. Dickson, Nagaraj S. Dixit, and B. P. Sudha-Dixit

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99164. Received February 19, 1980

Abstract: The compounds $Rh_6(CO)_{16}$ and $Re_2(CO)_{10}$ are effective catalysts for the conversion of ketones and cyclic alcohols to carboxylic acids. Cyclohexanol is converted to adipic acid via cyclohexanone as intermediate. Temperature, solvent, and pressure effects are reported and discussed. Increased acid yield with $Rh_6(CO)_{16}$ under conditions of increased CO and decreased oxygen pressure are interpreted on the basis of a lower nuclearity rhodium carbonyl being the reactive intermediate. The catalytic effect of the metal carbonyl is a consequence of the accelerated decomposition of the preformed peroxide intermediates. The side product ϵ-caprolactone is formed in the oxidation of cyclohexanone, but the yield is decreased in the presence of $Rh_6(CO)_{16}$ because of the catalyzed decomposition of its precursor peracid. The metal carbonyls catalyze the decomposition of hydrogen peroxide, but unlike ferrous ion (Fenton's reagent) do not enhance its function as an organic oxidant.

In earlier publications we described the use of the complex $Rh_6(CO)_{16}$ as a homogeneous catalyst for the oxidation, with molecular oxygen, of carbon monoxide to carbon dioxide and of ketones to carboxylic acids.[1] In that work we concluded that the oxidation of ketones was a free-radical process, but the role of the transition metal carbonyl complex was not identified. In these earlier studies we found that the compounds $Pt(PPh_3)_3$ and $IrCl(CO)(PPh_3)_2$ were also effective for increasing the yields of carboxylic acids from ketones under autoxidation conditions. The purpose of this paper is to focus interest in catalysis by clusters and to identify the role of the transition metal carbonyl in this reaction. Furthermore, we will present and discuss our new discoveries on alcohol autoxidation and the use of dirhenium decacarbonyl as an oxidation catalyst.

Two roles appear to have been identified for metal complexes in oxidations with molecular oxygen. The first is the coordination and activation of molecular oxygen.[2] This role has been claimed in the conversion of phosphines to phosphine oxides,[3] alkenes to ketones,[4] CO to CO_2,[5] alkenes to epoxides,[6] and isocyanides to

---

(1) (a) Mercer, G. D.; Shu, J. S.; Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 1967. (b) Mercer, G. D.; Beaulieu, W. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 6551. (c) Roundhill, D. M. In "Proceedings of the 2nd International Workshop on Fundamental Research in Homogeneous Catalysis", Ishii, Y., Tsutsui, M., Eds.; Plenun Press: New York, 1978; pp 11–23. (d) Dickson, M. K.; Sudha, B. P.; Roundhill, D. M. *J. Organomet. Chem.*, in press.

(2) Vaska, L. *Acc. Chem. Res.* **1976**, *9*, 175.

(3) (a) Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8337. (b) Graham, B. W.; Laing, K. R.; O'Connor, C. J.; Roper, W. R. *Chem. Commun.* **1970**, 1272. (c) Hanzlik, R. P.; Williamson, D. *J. Am. Chem. Soc.* **1976**, *98*, 6570. (d) Otsuka, S.; Nakamura, A.; Tatsuno, Y. *Ibid.* **1969**, *91*, 6994. (e) Schmidt, D. D.; Yoke, J. T. *Ibid.* **1971**, *93*, 637.

(4) Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 883. (b) Read, G. *J. Mol. Catal.* **1978**, *4*, 83. (c) Tang, R.; Mares, F.; Smith, D. E. *J. Chem. Soc., Chem. Commun.* **1979**, 274. (d) Mimoun, H.; Machiran, M. M. P.; de Roch, I. S. *J. Am. Chem. Soc.* **1978**, *100*, 5437.

isocyanates.[3d] A further role identified for transition-metal compounds in catalyzed oxidations is the decomposition of preformed peroxides. Examples on the use of simple metal salts are in the oxidation of alkenes, aromatics, alkanes,[7] and cyclohexanone.[8] Similarly, complexes of heavy-metal ions in low oxidation states have been used in the oxidation of aldehydes to carboxylic acids[9] and of cyclohexene to 2-cyclohexen-1-one.[10]

Our earlier work with hexarhodium hexadecacarbonyl was the first example of the use of a transition metal carbonyl compound for catalyzed oxidations. In view of this significance, and because of the continuing interest in the use of cluster compounds in homogeneous catalysis,[11] we have studied further the scope of the chemistry. As a complementary effort we have also begun to understand the mechanistic involvement of the metal carbonyl in the reaction. In beginning to understand the chemistry of the metal carbonyl in these oxidations it is significant that there is no evidence for the complexation of molecular oxygen with $Rh_6(CO)_{16}$. In view of this fact we have presumed it unlikely that the reaction pathway involves oxygen activation by the carbonyl cluster, and have considered it more likely that the compound is involved in peroxide decomposition. This premise has been borne out by experiment. In this paper we report and discuss our supporting evidence for this claim, and also include our work both on the use of dirhenium decacarbonyl as a homogeneous oxidation catalyst and on the catalyzed oxidation of cyclic alcohols to dicarboxylic acids.

Results and Discussion

In our previous papers the only metal carbonyl we used as an oxidation catalyst was the cluster compound $Rh_6(CO)_{16}$. We now find that $Rh_6(CO)_{16}$ is not unique in functioning as a homogeneous catalyst for the oxidation of ketones. The dimer $Re_2(CO)_{10}$ is equally effective. The reaction mixture is homogeneous throughout the catalytic reaction. The carbonyl is not decomposed and can be recovered quantitatively at the end of the oxidation. This latter situation even prevails when the oxidations are carried out in the absence of carbon monoxide. Species characterization is done by isolation methods or by IR spectroscopy in the carbonyl region. This stability to autoxidation conditions differs from that found with $Rh_6(CO)_{16}$ (where a pressure of CO must be maintained in the reaction vessel) or with platinum metal phosphine or phosphite complexes. In these latter cases extensive ligand oxidation occurs and it is possible that chain processes arise from these side reactions in addition to the primary one involving the metal ion. A further problem with these complexes is that decomposition to a variety of metal intermediates can occur and it is virtually impossible to deduce the identity of the catalytic species. Much of the work in this paper uses $Re_2(CO)_{10}$ as the oxidation catalyst, principally because of its solubility and its resistance to decomposition under the experimental conditions.

In a brief survey of other simple binary carbonyls we find that the compounds $M(CO)_6$ (M = Cr, Mo, W) and $Ru_3(CO)_{12}$ have only minimal catalytic activity for the autoxidation of alcohols or ketones. The compounds $Fe(CO)_5$ and $Fe_3(CO)_{12}$ are completely decomposed on attempted use as catalysts. When the compound $Mn_2(CO)_{10}$ is used, there is a considerable enhancement in acid formation. During this reaction there is extensive decomposition to manganese dioxide, and we believe that this compound is the one primarily involved in the catalytic oxidation.

Table I. Solvent Effects in the Oxidation of Cyclohexanone to Adipic Acid[a]

solvent	time, h	adipic acid, mmol	yield, %	catalyst, mg
CH_2Cl_2 (10 mL)	20	15.3	30	$Re_2(CO)_{10}$ (25)
$(CH_3)_2CO$ (10 mL)	25	11.1	22	$Re_2(CO)_{10}$ (25)
C_6H_{12} (5 mL)	24	18.4	36	$Re_2(CO)_{10}$ (25)
t-BuOH	24	2.1	4	$Re_2(CO)_{10}$ (25)
CH_3CN	24	2.2	4	$Re_2(CO)_{10}$ (25)
C_6H_6 (10 mL)	24	2.9	5	$Re_2(CO)_{10}$ (25)
CH_2Cl_2 (10 mL)	24	0.34	0.7	none
$(CH_3)_2CO$	24	0.48	1.0	none
none	18	10.6	42	$Re_2(CO)_{10}$ (17)[b]

[a] Reaction conditions: cyclohexanone (5 mL), oxygen (500 psi), temperature 96 °C. Yield based on cyclohexanone. [b] This reaction is with CO (600 psi) and O_2 (300 psi).

Table II. Temperature and Oxygen Pressure Effects in Oxidation of Cyclohexanone to Adipic Acid[a]

solvent	time, h	temp, °C	oxygen pressure, psi	adipic acid, mmol
$(CH_3)_2CO$	20	115	300	10.7
$(CH_3)_2CO$	18	115	400	15.4
$(CH_3)_2CO$	15.5	115	500	20.8
$(CH_3)_2CO$	5	130	500	17.9
C_6H_{12}	22	100	500	12.8
C_6H_{12}	5	122	500	18.7

[a] Reaction conditions: cyclohexanone (5 mL), $Re_2(CO)_{10}$ (50 mg), solvent (10 mL).

Oxidation of Cyclohexanone. Our data on the catalyzed oxidation of cyclohexanone are shown in Tables I–III. Yields of acid have been measured under conditions of changing solvent, temperature, and oxygen pressure. Solvent effects on the yield of adipic acid formed in the oxidation are significant. When benzene, acetonitrile, or *tert*-butyl alcohol are used as solvent, the conversion to acid is very low; however, when the solvents cyclohexane, acetone, or dichloromethane are used, the acid yield increases by approximately a factor of 10. These tabulated yields are based on initial cyclohexanone. No attempt has been made to optimize the yield of adipic acid in a commercial sense. It is apparent from Table II that the quantity of adipic acid produced is increased considerably on increasing the oxygen pressure; similar improvements in yield can be obtained by increasing the temperature of the reaction over 100 °C. Thus from Table II we find that, whereas only 12.8 mmol of adipic acid is formed in 22 h at 100 °C, upon raising the temperature to 122 °C the amount of adipic acid obtained in only 5 h is 18.7 mmol. We believe that higher acid conversions could be obtained by making further changes in these reaction conditions, as well as making technical improvements to increasing yield by using improved mechanical features such as a stirrer design.

The solvent effects on adipic acid yield require comment. Although solvent effects are often considered to be small in free-radical chemistry, we find our data to be consistent with the published solvent effects on the decomposition rate of benzoyl peroxide.[12] Our high yield of adipic acid correlates with the faster rates of peroxide decomposition. Thus our data in Table I showing smaller yields of adipic acid in the solvent sequence cyclohexane > dichloromethane > benzene correlate with the respective decreasing rates of benzoyl peroxide in these solvents. From Table I the highest yield of adipic acid is formed in the absence of solvent. This observation may be simply due to chain termination reactions occurring in the solvent media.

All our data point to the reaction pathway following a similar one to those found for hydrocarbon autoxidation.[13] If the metal

---

(5) Chin, C-S.; Sennett, M. S.; Vaska, L. *J. Mol. Catal.* **1978**, *4*, 375.

(6) Chen, M. J. Y.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1977**, 204.

(7) (a) Sheldon, R. A.; Kochi, J. K. *Adv. Catal.* **1976**, *25*, 272. (b) Black, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 527.

(8) Kamiya, Y.; Kotake, M. *Bull. Chem. Soc. Jpn.* **19738** *46*, 2780.

(9) (a) Hojo, J.; Yuasa, S.; Yamazoe, N.; Mochida, I.; Seiyama, T. *J. Catal.* **1975**, *36*, 93. (b) Sakamot, H.; Funabiki, T.; Tarama, K. *Ibid.* **1977**, *48*, 427.

(10) (a) Fusi, A.; Ugo, R.; Fox, F.; Pasini, A.; Cenini, S. *J. Organomet. Chem.* **1971**, *26*, 417. (b) Cenini, S.; Fusi, A.; Porta, F. *Gazz. Chim. Ital.* **1978**, *108*, 109.

(11) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 759. (b) Muetterties, E. L. *Science* **1977**, *196*, 839. (c) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(12) Nozaki, K.; Bartlett, P. D. *J. Am. Chem. Soc.* **1946**, *68*, 1686.

Table III. Acid Yields from Cyclic Ketones[a]

ketone (mL)	solvent (mL)	acid, mmol	time, h	catalyst (mg)	O_2, psi	CO, psi
cyclopentanone (5)	acetone (20)	10.1	17	$Re_2(CO)_{10}$ (50)	450	0
cyclohexanone (5)	none	21.2	18	$Re_2(CO)_{10}$ (17)	500	0
cycloheptanone (10)	none	9.3	22	$Re_2(CO)_{10}$ (22)	500	0
acetone (10)	none	0.8	29	$Rh_6(CO)_{16}$ (44)	170	330

[a] Reaction conditions: temperature 98 °C.

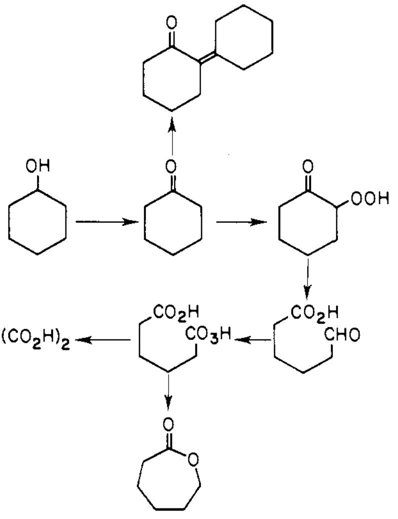
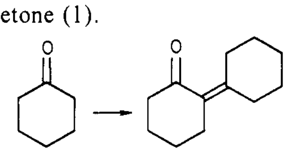


Figure 1. Intermediates and products in the oxidation of cyclohexanol to adipic acid.

carbonyl were involved in oxygen activation and lowering the activation energy of alternate catalytic pathways, we would expect a change in the distribution of side products. Comparison of gas chromatographic analyses from reaction mixtures of both the rhenium carbonyl catalyzed and the uncatalyzed reactions shows the same species to be present in each reaction mixture. Separation of the volatile reaction products from both cyclopentanone and cyclohexanone autoxidations in the GLC column shows no *qualitative* differences in the side products formed in the reaction. This indicates that the rhenium carbonyl is involved in changing the rate of one or more steps in the reaction pathway, but that there is no fundamental new chemistry being generated by the metal carbonyl activation of molecular oxygen. A similar situation is found with $Rh_6(CO)_{16}$ as catalyst. Of the volatile side products of cyclohexanone autoxidation, one of the few components to show significant *quantitative* change in the presence of $Rh_6(CO)_{16}$ is 2-(1-cyclohexenyl)-1-cyclohexanone.[14] The yield of this condensation product is increased by a factor of 4 in the catalyzed reaction. This product has been reported previously in the autoxidation of cyclohexanone, and arises from a self-condensation reaction of the ketone (1).



(1)

Table IV. Solvent Effects in the Oxidation of Cyclohexanol to Adipic Acid[a]

solvent (5 mL)	time, h	adipic acid, mmol	catalyst (40 mg)
none	22	7.8	$Re_2(CO)_{10}$
none	22	1.1	none
$(CH_3)_2CO$	22	10.0	$Re_2(CO)_{10}$
$(CH_3)_2CO$	22	1.8	none
C_6H_{12}	22	14.2	$Re_2(CO)_{10}$
C_6H_{12}	22	4.4	none
C_6H_6	22	4.1	$Re_2(CO)_{10}$
C_6H_6	22	1.0	none

[a] Reaction conditions: cyclohexanol (5 mL), oxygen (500 psi), temperature 98 °C.

Table V. Acid Yields from Cyclic and Acyclic Alcohols[a]

alcohol	acid, mequiv	catalyst (mg)	oxygen, psi	CO, psi
cyclohexanol	15.6	$Re_2(CO)_{10}$ (40)	500	0
ethanol	0.2	$Re_2(CO)_{10}$ (14)	500	0
ethanol	0.15	$Rh_6(CO)_{16}$ (15)	300	500
diethylcarbinol	0.7	$Re_2(CO)_{10}$ (17)	500	0
diethylcarbinol	0.4	$Rh_6(CO)_{16}$ (11)	300	600
2-propanol	0.08	$Rh_6(CO)_{16}$ (10)	330	320[b]
1-phenylethanol	0.05	$Rh_6(CO)_{16}$ (10)	325	315[c]

[a] Reaction conditions: alcohol (10 mL), time 22 h, temperature 98 °C. [b] Time 12 h, temperature 86 °C. [c] Time 24 h, temperature 86 °C.

The reaction pathway and product distribution observed in the $Re_2(CO)_{10}$- and $Rh_6(CO)_{16}$-catalyzed autoxidation of cyclohexanol and cyclohexanone are shown in Figure 1. An important proposed intermediate in this scheme is the peracid. In this sequence the peracid is the final intermediate; adipic acid results from the final reaction between this compound and the aldehyde. Because of the robust reaction conditions used for the oxidation it is not feasible to try to isolate or identify directly any reaction intermediates. An alternate approach to identify transients is to analyze the final reaction mixture for stable compounds which must result from transformations of the intermediate. Thus we have assayed lactone formation as a means both of identifying peracid as an intermediate and of probing any changes in peracid concentration caused by the presence of $Rh_6(CO)_{16}$. In the case of cyclohexanone we have used the yield of ε-caprolactone (**4**) as a measure of this intermediate peracid.[13e] In both the absence and presence of $Rh_6(CO)_{16}$, the product mixture contains ε-caprolactone. Analysis of the oxidation products for the uncatalyzed and $Rh_6(CO)_{16}$-catalyzed oxidation of cyclohexanone shows the respective ratios of ε-caprolactone to be 1.00 and 0.43 when measured against an added aliquot of dodecane. Thus there is a decrease in ε-caprolactone formation in the presence of $Rh_6(CO)_{16}$. This observation is consistent with the premise that the metal carbonyl accelerates the decomposition of peroxides. In the presence of $Rh_6(CO)_{16}$ it is to be expected that the increased decomposition rate of peracid will lead to a lower steady-state concentration of this species, and hence its transformation to ε-caprolactone will be reduced. These data support a reaction pathway proceeding via hydroperoxide **1** and its subsequent conversion to the peracid **2**. Adipic acid results from final reaction between peracid and aldehyde **3** (2). The latter steps in the chemistry thus resemble those found in Baeyer–Villiger oxidations.

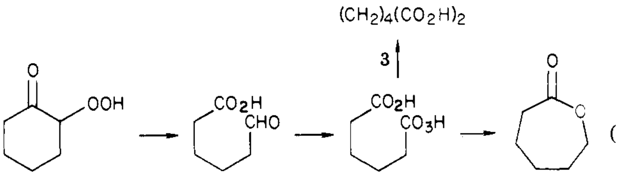
We have also done similar experiments in the oxidation of cyclopentanone. In this case the lactone formed from peracid is δ-valerolactone. In the catalyzed reaction with $Rh_6(CO)_{16}$ the quantity of δ-valerolactone is decreased by a factor of 45 over the

---

(13) (a) Kochi, J. K. In "Free Radicals", Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, Chapter 11. (b) Scott, G. "Atmospheric Oxidation and Anti-Oxidants"; American Elsevier: New York, 1965; Chapters 2 and 3. (c) Reich, L.; Stivala, S. S. "Autoxidation of Hydrocarbons and Polyolefins"; Marcel Dekker: New York, 1969; Chapter 4. (d) Denisov, E. T.; Mitskevich, N. I. "Liquid-Phase Oxidation of Oxygen-Containing Compounds"; Consultants Bureau: New York, 1977. (e) Berezin, I. V.; Denisov, E. T.; Emanuel, N. M. "The Oxidation of Cyclohexane"; Pergamon Press: Elmsford, N.Y., 1966.

(14) The peak assigned to this product shows no decrease in size on washing with base or treating with iodide. Refluxing the reaction mixture with strong base increases the peak. The retention time correlates with an authentic sample (mixed solution).

(15) (a) Hassall, C. H. *Org. React.* **1957**, *9*. (b) Davies, A. G. "Organic Peroxides"; Butterworths: London, 1961; pp 151–154.

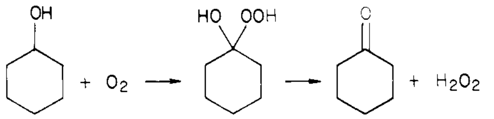


1 3 2 4 (2)

amount formed in the absence of $Rh_6(CO)_{16}$.

Oxidation of Alcohols. The compounds $Rh_6(CO)_{16}$ and $Re_2(CO)_{10}$ are also effective homogeneous catalysts for the autoxidation of cyclic alcohols to dicarboxylic acids. Solvent-effect data for cyclohexanol are shown in Table IV. Again low yields are found in benzene solvent, and considerably higher conversions in cyclohexane. In Table V are shown the yields of carboxylic acids obtained from both cyclic and acyclic alcohols. It is apparent that the acid yields are small for acyclic alcohols. There is no difference in catalytic activity whether the compound $Rh_6(CO)_{16}$ or $Re_2(CO)_{10}$ is used and low yields are obtained from both primary and secondary alcohols.

In the oxidation of cyclohexanol the product adipic acid is formed via cyclohexanone as intermediate. The steady-state concentration of this species is sufficiently high to be measurable by GLC. The reaction follows a free-radical pathway with cyclohexanol being first converted into cyclohexanone and hydrogen peroxide (3). The cyclohexanone formed can then undergo the autoxidation reaction described in the previous section. An alternative oxidation route would involve the formed peroxide as oxidant. We have therefore carried out a series of experiments to test whether such a pathway must be given serious consideration. Our data for the oxidation of cyclohexanol and cyclohexanone with hydrogen peroxide as oxidant are shown in Table VI. These data show that there is rather minimal oxidation of cyclohexanol to adipic acid with hydrogen peroxide under the experimental conditions used. The added $Re_2(CO)_{10}$ does not enhance significantly the yield of acid, and there is no evidence that it functions as a Baeyer–Villiger catalyst[16] or Fenton's reagent in cyclohexanol oxidation. From these hydrogen peroxide results we consider the oxidation of cyclohexanol with molecular oxygen to involve rhenium carbonyl catalyzed hydroperoxide decomposition, and not to be primarily due to oxidation by the hydrogen peroxide formed from oxygen.[17]



(3)

From Table VI it is apparent that the hydrogen peroxide formed in the conversion of cyclohexanol to cyclohexanone is an effective oxidant for converting the cyclohexanone into adipic acid. This will likely be a contributing pathway to the formation of adipic acid from cyclohexanone, but the data over the solvent range do not lead to a consistent argument that rhenium carbonyl catalysis of this reaction is the reason behind the increased autoxidation of cyclohexanol in the presence of this compound. Nevertheless the reaction is a complex one and it may be a significant factor in solvents such as cyclohexane.

Table VI. Acid Yields from the Oxidation of Cyclohexanol and Cyclohexanone with Hydrogen Peroxide[a]

hydrocarbon (5 mL)	solvent (10 mL)	catalyst (mg)	adipic acid, mmol
cyclohexanol	none	$Re_2(CO)_{10}$ (50)	0.08
cyclohexanol	none	none	0.09
cyclohexanol	benzene	$Re_2(CO)_{10}$ (50)	0.12
cyclohexanol	benzene	none	0.02
cyclohexanol	acetone	$Re_2(CO)_{10}$ (50)	2.67
cyclohexanol	acetone	none	2.07
cyclohexanol	cyclohexane	$Re_2(CO)_{10}$ (50)	0.70
cyclohexanol	cyclohexane	none	0.81
cyclohexanone	none	$Re_2(CO)_{10}$ (50)	13.8
cyclohexanone	none	none	24.0
cyclohexanone	benzene	$Re_2(CO)_{10}$ (50)	15.6
cyclohexanone	benzene	none	3.2
cyclohexanone	acetone	$Re_2(CO)_{10}$ (50)	10.4
cyclohexanone	acetone	none	15.2
cyclohexanone	cyclohexane	$Re_2(CO)_{10}$ (50)	16.1
cyclohexanone	cyclohexane	none	7.6

[a] Reaction conditions: hydrogen peroxide (17 mL of 30%), bath temperature 98 °C, time 8 h.

Table VII. Acid Yields from the Oxidation of Cyclopentanone with Hydrogen Peroxide[a]

solvent (5 mL)	catalyst (mg)	adipic acid, mmol
none	$Re_2(CO)_{10}$ (50)	33.0
none	none	25.8
benzene	$Re_2(CO)_{10}$ (50)	12.5
benzene	none	14.4
acetone	$Re_2(CO)_{10}$ (50)	13.4
acetone	none	10.2
cyclohexane	$Re_2(CO)_{10}$	21.7
cyclohexane	none	22.4

[a] Reaction conditions: hydrogen peroxide (17 mL of 30%), bath temperature 98 °C, time 8 h.

Table VIII. Catalyzed Decomposition of H_2O_2[a]

	$Re_2(CO)_{10}$ (25 mg)	none
benzene	64	19
acetone	9	2
cyclohexane	57	26

[a] The data are expressed as percent decomposition for a solution of 30% H_2O_2 (2 mL) in solvent (15 mL) and a reaction time of 2 h at 90 °C.

Table IX. Acid Produced Using $Rh_6(CO)_{16}$ with Changing Pressures of CO and O_2

p(CO), atm	$p(O_2)$, atm	p(CO)/p(total)	acid, mmol	time, h
340	330	0.51	1.10	10
440	220	0.67	1.37	10
520	140	0.79	1.71	10
540	100	0.84	1.94	10
555	70	0.89	2.04	10
280	380	0.42	1.76	12
500	160	0.76	2.65	12
520	110	0.83	2.84	12
550	80	0.87	2.96	12

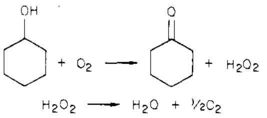
In Table VII we list the results of similar reactions with cyclopentanone. The effects of adding rhenium carbonyl to the reflux mixture are small and there is no evidence for catalytic activation of hydrogen peroxide as an oxidant to this ketone.

Decomposition of Hydrogen Peroxide. From our high-pressure data it is apparent that the carbonyls are mechanistically involved in peroxide decomposition. Using hydrogen peroxide as a model compound for the **hydroperoxide intermediates**, we have inves-

---

[16] Jacobson, S. E.; Tang, R.; Mares, F. *J. Chem. Soc., Chem. Commun.* **1978**, 888.

[17] For this conclusion it is significant that there is little formation of adipic acid from cyclohexanol in the absence of rhenium carbonyl in the closed reaction with oxygen. Since rhenium carbonyl will catalyze the decomposition of hydrogen peroxide the low acid yield in the presence of $Re_2(CO)_{10}$ could be due to the loss of hydrogen peroxide by this route. In the closed reaction with oxygen, however, the hydrogen peroxide can be re-formed from more cyclohexanol, and hence maintain a steady-state concentration. The low acid yield from the uncatalyzed reaction with cyclohexanol verifies that even in the presence of significant amounts of hydrogen peroxide the oxidation of cyclohexanol to adipic acid by this reagent is minimal.



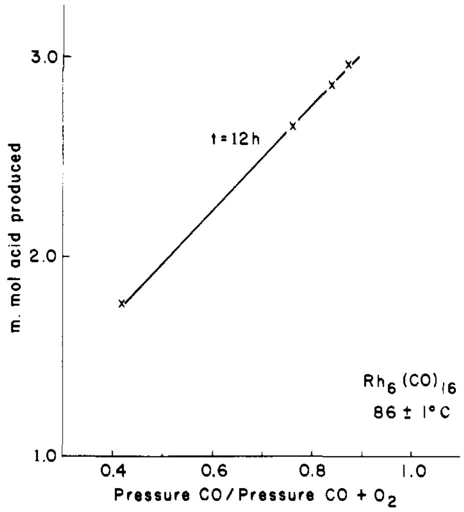


Figure 2. Plot of carboxylic acid yield with $Rh_6(CO)_{16}$ catalyst, using changing pressures of CO and O_2.

tigated catalytic effects of these metal carbonyls on hydrogen peroxide decomposition. With $Rh_6(CO)_{16}$ reaction occurs to form a product not yet characterized, but with $Re_2(CO)_{10}$ the compound is recovered unchanged. From data in Table VIII it is apparent that these compounds are catalysts for the disproportionation of hydrogen peroxide, and as such gives further credence that the mode of action in the catalytic cycle is in hydroperoxide decomposition.

Previous studies on hydrogen peroxide decomposition have focused on one-electron transition metal reagents as catalysts.[18] From the chemistry of dirhenium decacarbonyl there is little information regarding the stability of two separate carbonyl compounds having oxidation states differing by one electron. A catalytic cycle leading to free-radical chemistry involving the species $Re(CO)_5^-$ or $Re(CO)_5^+$ could be envisaged (analogous to the Fe(II)/Fe(III) pair), but we have no evidence for such chemistry, and no obvious mechanism involving mononuclear or binuclear rhenium carbonyls is apparent at this stage of our study.[19]

Pressure Effects on $Rh_6(CO)_{16}$-Catalyzed Cyclohexanone Oxidation. In an attempt to obtain some information concerning the catalytically active species in the $Rh_6(CO)_{16}$-catalyzed cyclohexanone autoxidation we have carried out a series of experiments with changing CO and oxygen pressures under isobaric conditions. The data in Table IX have been obtained at 85 ± 1 °C under the isobaric conditions of 650 ± 20 psi. This condition is created by changing the partial pressure of CO in a mixture of CO and O_2 between 0.42 and 0.89. The data in Table IX are arranged to show the effect on acid yield of changing the CO and O_2 pressure in a solution containing $Rh_6(CO)_{16}$ and cyclohexanone. Data for both 10- and 12-h reaction times are given, and in Figure 2 we plot the 12-h data for acid yield (mmol) against both oxygen pressure and the CO partial pressure. These data show that, as the oxygen pressure decreases, or concurrently as the CO pressure increases, under isobaric conditions, there is an increase in the quantity of carboxylic acid formed. This result is unexpected since lowering the partial pressure of oxygen creates a situation where its concentration becomes increasingly deficit for its function as a reactant for the conversion of both CO to CO_2 and cyclohexanone to adipic acid. It is apparent therefore that there is an increase in catalytic activity as the pressure of CO is raised.

The most reasonable explanation for these data is that under the increasing CO pressure there is a corresponding increase in the concentration of a lower nuclearity rhodium carbonyl compound which is the catalytically active species in the reaction mixture. This concept is in agreement with previous ideas that smaller aggregate carbonyl clusters are formed under high CO pressure.[20] In particular for rhodium(0), Whyman has shown that at low temperatures and under an extremely high pressure of CO there is a conversion to the dimeric compound $Rh_2(CO)_8$.[21] Under our experimental conditions it is not possible to *directly* observe such intermediates, and no attempt has yet been made to do so. We have, however, previously used the lower cluster compound $Rh_4(CO)_{12}$ as a catalyst for the oxidation of cyclohexanone. The results show that the compound is effective as a catalyst, but is converted to $Rh_6(CO)_{16}$ and is not recoverable as $Rh_4(CO)_{12}$.[1]

The chemistry and function of $Rh_6(CO)_{16}$ and $Re_2(CO)_{10}$ as oxidation catalysts for organic compounds are under continuing investigation. In particular, we are studying the role of $Rh_6(CO)_{16}$ as a labile multisubstrate oxidation catalyst for the oxidation of CO and triphenylphosphine.

Experimental Section

Alcohols and ketones were commercial samples and distilled before use. Cylinder gases were not purified. High-pressure oxidation reactions were carried out in a Parr Model 4712 high-pressure reaction vessel. The equipment was fitted with a 45-mL cup, a Model 4316 gauge block, a 2000-psi disk burst seal, muffler, and 5000-psi pressure gauge. The organic liquid was placed in a glass tube along with a clean Teflon-coated stir bar. The vessel was pressurized slowly with carbon monoxide, then with oxygen. *Caution*: There is always the possibility that an explosion may occur. This is most likely either during filling with oxygen or while the mixture is being heated; necessary precautions must be taken. The vessel was heated and stirred by placing it in an aluminum block on a stir hot plate. Temperature was measured by immersing a thermometer in a tube of oil in a second hole in the block. Carboxylic acid was analyzed by adding excess standardized base to the reaction mixture and back-titrating with standard acid.

Gas-liquid chromatographic analysis has been carried out on a Hewlett-Packard Model 5830A chromatograph. Retention times and peak areas were calculated on a Model 18850A GC terminal microprocessor. Infrared spectra were measured on a Perkin-Elmer Model 700 spectrometer.

Benzene was continuously dried over $LiAlH_4$ in a recirculating distillation apparatus. Carbonyls $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Fe(CO)_5$, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ were commercial samples. The compounds $Ru_3(CO)_{12}$ and $Rh_6(CO)_{16}$ were synthesized by published methods. Hydrogen peroxide (30%) was analyzed prior to use by the iodide/thiosulfate method. The hydrogen peroxide decomposition reactions were carried out at 90 °C for 2 h. Reactions used solvent (15 mL), hydrogen peroxide (2 mL), and catalyst (25 mg). A blank was run in parallel in the same stirred oil bath. After the reaction time, the reaction mixtures were cooled in ice and assayed for remaining hydrogen peroxide. Acetone, cyclohexane, and dichloromethane were reagent-grade purity. ε-Caprolactone, δ-valerolactone, and 2-(1-cyclohexenyl)-1-cyclohexanone were commercial samples.

The GLC method for ε-caprolactone and δ-valerolactone used constant mixed aliquots of the reaction mixtures and dodecane; data were normalized to dodecane. Reaction times are accurate to within 5% of the reported values.

Acknowledgments. We thank the Division of Basic Chemical Sciences of the Department of Energy for support of this work. Thanks are due to Mr. K. Alexander and Mr. C. Craven for their capable experimental assistance.

---

[18] (a) Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125. (b) Brown, S. B.; Jones, A.; Suggett, A. *Prog. Inorg. Chem.* **1970**, *13*, 159. (c) Melynk, A. C.; Kildahl, N. K.; Rendina, A. R.; Busch, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 3232.

[19] Work is presently underway to identify intermediates in the $Re_2(CO)_{10}$-catalyzed decomposition of peroxides. The chromophore due to $Re_2(CO)_{10}$ slowly disappears during the reaction and other carbonyl-containing compounds are formed as intermediates. The $Re_2(CO)_{10}$ chromophore returns after complete decomposition of peroxide.

[20] (a) Chini, P. *Inorg. Chim. Acta. Rev.* **1968**, *2*, 31. (b) Johnston, R. D. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 470.

[21] Whyman, R. *Chem. Commun.* **1970**, 1194.