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The Role of Catalysts in the Air Oxidation of Aliphatic Aldehydes

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Under preparative conditions, the liquid-phase air oxidation of 2-methylpropanal gives product profiles that differ with the catalyst. These distinctive profiles allow us to use this reaction to characterize the roles of some catalysts. The conversion of 2-methylpropanal to 2-methylpropanoic acid takes place in two stages. In stage 1 aldehyde is converted to peracid in a free radical chain reaction. In stage 2 peracid is converted to carboxylic acid. Paradoxically, noncatalyzed reactions give higher yields of 2-methylpropanoic acid than do reactions catalyzed by Mn or Co ions. The ions improve the efficiency of stage 2, but they also increase the rate of chain initiation in stage 1. Since these reactions are oxygen mass transfer limited, small increases in the reaction rate lead to oxygen starvation in the bulk liquid phase. This leads to increased formation of byproduct propane, propene, acetone, 2-propanol, CO, and CO_2. Increases in CO formation are due to decomposition of acyl radicals and are diagnostic of severe oxygen starvation. Obviously, increases in the reaction rate must also increase the amount of chain termination which is the sole source of CO_2. It is shown that Cu ion can inhibit the chain reaction and thus alleviate both conditions.

Introduction

When the air oxidation of an aldehyde is used to prepare a carboxylic acid, whether in the laboratory or in a commercial reaction system, the reaction conditions are usually far different from those used in most kinetic investigations. For practical reasons, relatively high temperatures and concentrated aldehyde solutions are used. In this paper these will be called preparative conditions. Our purpose in this work was to attempt to understand how catalysts work under these conditions. I hoped to use this information to develop better catalysts and to understand why the many different and sometimes strange catalysts reported in the patent literature were active.

A large proportion of the literature on the reaction of oxygen with aldehydes involves kinetic studies that were carried out at low temperatures (25 to −90 °C) with low concentrations (0.3 M or less) of aldehydes.[1] Under these conditions the reaction is chemically well-behaved, and reproducible kinetic data can be obtained. It is well-established that free radical chain reactions with chain lengths of 100–1000 take place. Most importantly, the reactions are chemically rate limited, i.e., oxygen mass transfer is not limiting in any way.

Reactions carried out under preparative conditions differ in several important aspects. When the aldehyde concentration or the reaction temperature is increased the intrinsic reaction rate increases. At some point the intrinsic reaction rate will be so high that it is impossible to mix the reagents more rapidly than they can react. Our experience indicates that this change-over point occurs at about 2–5 mol % aldehyde at room temperature. Under preparative conditions, the aldehyde concentrations are often 50 mol % or higher. This means that these reactions are carried out in a mass transfer limited regime.[2] The rate-limiting step is the rate of mixing of the reagents, that is, how rapidly oxygen can be transferred from gas bubbles into the liquid phase. This is not a trivial limitation and is relevant for both laboratory- and commercial-scale reactions.

It should be noted that catalysts are not really necessary for reaction to occur. Examination of a partially used bottle of an aldehyde that has been opened so that air could enter will almost certainly show that it now contains a mixture of aldehyde and carboxylic acid. This was first described by Liebig.[3] Catalysts are often considered necessary in commercial-scale reactions because traces of metal salts are present from corrosion products in the metal equipment that is used. These corrosion products can catalyze side reactions. Thus, one swamps the traces of corrosion products with larger amounts of good catalysts. These variable valent catalysts also decompose peroxides. This can be important since peroxides, peracids, and peracid–aldehyde complexes are reaction intermediates and prudent workers do not like to handle materials that contain peroxides.

The catalysts of choice usually are variable valent metallic ions like Mn or Co. As we shall see these catalysts have both desirable and undesirable effects. The good effects include directing the reaction to give desirable products. Oddly enough, the most pernicious effect of these catalysts is that they increase the intrinsic reaction rate. In a mass transfer limited reaction in which the main operational difficulty is getting oxygen into the liquid rapidly this can be a fatal defect.

Experimental Section

Equipment. A schematic diagram of the reaction system is shown in Figure 1. The reactor was a vertical 1-m section of 2-in. glass pipe surmounted by a condenser cooled with cold water. The reaction mixture was pumped out of the bottom with a centrifugal pump, heated to 45 °C in a heat exchanger, and returned to the top of the reactor. Air under a pressure of 95 psig was sparged into the bottom of the reactor through a 0.012 in. i.d. syringe needle. (This needle size gives gas bubbles with a diameter of 0.166 cm.) The air feed rate was controlled by a mass flow meter. The vent gases were let down to atmospheric pressure through a motor valve controlled by a pressure-indicator controller and then passed through a dry test meter. The majority of the vent gas was passed through a dry ice trap and then fed to two analyzers in parallel. In one, the concentration of O_2 in the vent was monitored continuously with a polarographic detector. In the other, the vent was analyzed at 15-min intervals for N_2, CO, CO_2, and O_2–Ar on a gas chromatograph equipped with molecular sieve columns. In addition, vent samples were collected at intervals from a position in front of the dry ice trap into inert plastic bags. Liquid samples were taken at 15–30-min intervals into 1-mL sealed

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[1] Reviews include: (a) McNesby, J. R.; Heller, C. A., Jr. *Chem. Rev.* **1954**, *54*, 325. (b) Sajus, L.; De Roch, S. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. H. F., Eds.; Elsevier Scientific Publishing Company: New York, 1980; Vol. 16, p 89. (d) Kochi, J. A. In *Free Radicals*; Kochi, J. A., Ed.; John Wiley & Sons: New York, 1973; Vol. 1, pp 656–659.

[2] Hobbs, C. C.; Drew, E. H.; Van't Hof, H. A.; Mesich, F. G.; Onore, M. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1972**, *11*, 220.

[3] Liebig, L. *Justus Liebigs Ann. Chem.* **1987**, *14*, 139.

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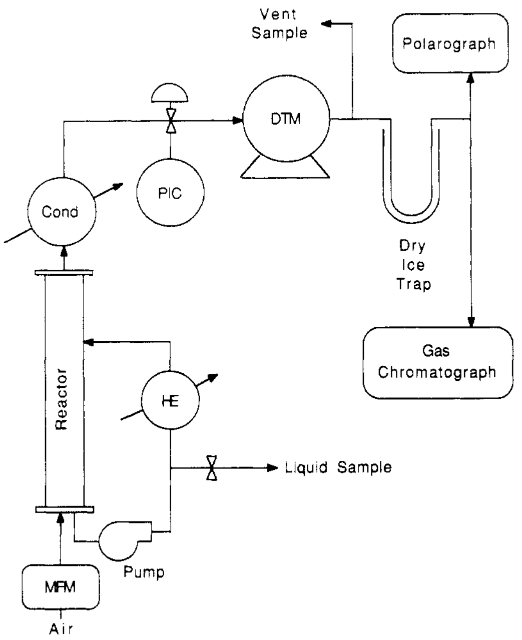

Figure 1. Diagram of reaction system showing arrangement of reactor, mass flow meter (MFM), pressure-indicator controller (PIC), dry test meter (DTM), condenser (Cond), centrifical pump (Pump), and heat exchanger (HE).

ampoules and stored above mercury.

Safety Considerations. The reaction system was enclosed in a protective Plexiglas box. The box was connected through a length of tubing to a CO_2 fire extinguisher that could be activated by remote control. The polarographic oxygen analyzer activated an automatic shutdown system when the oxygen in the vent reached 8%. An excess flow valve was placed in the air line leading to the reactor.

Reaction Charge. The reaction charge consisted of about 1300 g of a 50 wt % solution of 2-methylpropanal in propanoic acid plus an appropriate amount of catalyst. All catalysts were added as the metal(II) acetates. The propanoic acid solvent was needed to allow control of the initial reaction temperature. A temperature of 45 °C gave convenient rates.

Analyses. Off-line samples were analyzed on a Varian 2700 instrument equipped with a flame ionization detector. For liquid samples, 0.25-μL injections were made into a 3-ft $^1/_8$ in. diameter column of Porapak S that was programmed from 130 to 250 °C at 6°/min. The vent samples that were collected in the plastic bags were analyzed for propane, propene, acetone, 2-propanol, and 2-methylpropanal on the same column used for the liquid samples using 1-mL injections from a gas syringe. The initial column temperature was lowered to 80 °C so that propane and propene could be separated. All peak areas were electronically integrated.

Data Workup. A computer program was used to make both a mass and a redox balance[4] across the reaction for each conversion level.

Efficiency of Mass Transfer. The reaction system used in this work gives extremely good mass transfer. As an example, rates of propionaldehyde oxidation approximately 100 times that given in the literature[5a] were obtained under the literature conditions. Yet we have never observed a chemically rate-limited aldehyde oxidation at 45 °C when the aldehyde concentration was above 0.4 M.[5b]

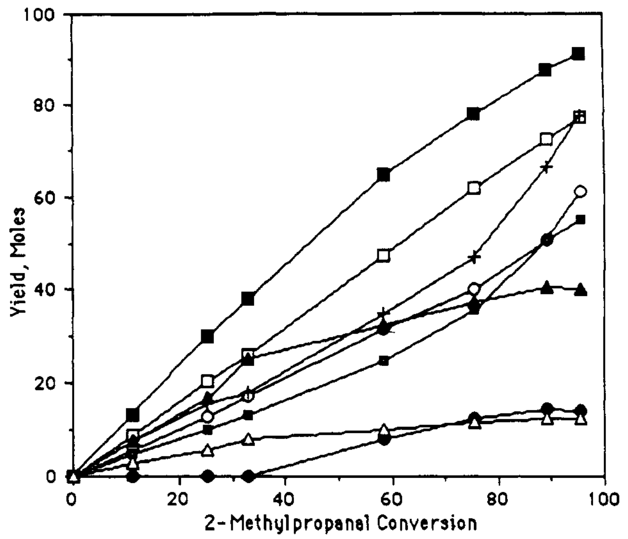

Figure 2. Product yields as a function of aldehyde conversion in the presence of 300 ppm of Mn ion: (■) carbon monoxide (×10), (□) 2-methylpropanoic acid, (+) carbon dioxide (×10), (○) acetone (×10), (▣) 2-propanol (×10), (▲) propane (×10), (●) 2-propyl formate (×10), (△) propene (×10).

By all of the usual criteria[6] all of the reactions described in this paper were mass transfer limited. An additional simple test when using glass equipment is to observe the color of the reaction mixture. In our system the color within a centimeter of the air sparger is usually different from that of the remainder of the solution. For instance if manganese is being used as the catalyst the reddish color of Mn(III) is seen near the sparger; the remainder of the solution contains predominantly the light-brown color of Mn(II).

***tert*-Butyl-2-picolinic Acid.** A mixture of *tert*-butyl-2-cyanopyridines was prepared by the homolytic alkylation technique of Minisci.[7] This intermediate was then treated with caustic,[8] acidified and the product extracted into ether. Evaporation of the ether left a brown powder which according to Minisci would consist mainly of 4-*tert*-butyl-2-picolinic acid and 6-*tert*-butyl-2-picolinic acid. The NMR and IR spectra were compatible with this identification, and the crude product was used without further purification.

Discussion and Results

Our model reaction was the manganese-catalyzed oxidation of 2-methylpropanal to 2-methylpropanoic acid. We deliveratelv chose an aldehyde for which the reaction efficiency was poor. (The yield of acid is about 80% under conditions where at least 98% is obtained with acetaldehyde.) The reaction efficiency is poor because the 2-propyl radical is a better leaving group than a 1-alkyl radical derived from a straight-chain aldehyde. The reaction intermediates decompose with facility, and byproduct formation is easily quantified. Our basic assumption was that catalysts than can improve the efficiency of the oxidation of 2-methylpropanal will also prove useful in other aldehyde oxidations. The truth of this assumption was ultimately verified by studies of the oxidations of straight-chain aldehydes such as acetaldehyde, pentanal, hexanal, and nonanal.[9]

Numerous patent examples of catalysts for the air oxidation of 2-methylpropanal[10] were available for compar-

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[4] Hobbs, C. C. *Ind. Eng. Chem. Prod. Res. Dev.* **1970**, *9*, 497.

[5] (a) Gurumurthy, C. V.; Govindarao, V. M. H. *Ind. Eng. Chem., Fund.* **1974**, *13*, 9. (b) Many times one sees statements to the effect that stirring or shaking speeds have been increased until the reaction rate is constant. Often, the authors conclude that their reactions are in chemically rate limited regimes. A more correct conclusion may be that they have found the mass transfer limit of their equipment. Thus, this test is a necessary but not sufficient criterion for a chemically rate limited reaction.

[6] (a) Astarita, G. *Ind. Eng. Chem.* **1966**, *58*(8), 18. (b) Astarita, G. *Mass Transfer with Chemical Reaction*; Elsevier Scientific Publishing Company: Amsterdam, 1967.

[7] Minisi, F.; Mondelli, R.; Gardini, G. P.; Porta, O. *Tetrahedron* **1972**, *28*, 2403.

[8] Vaughn, H. L. *J. Org. Chem.* **1975**, *40*, 1187.

[9] Larkin, D. R. Unpublished work.

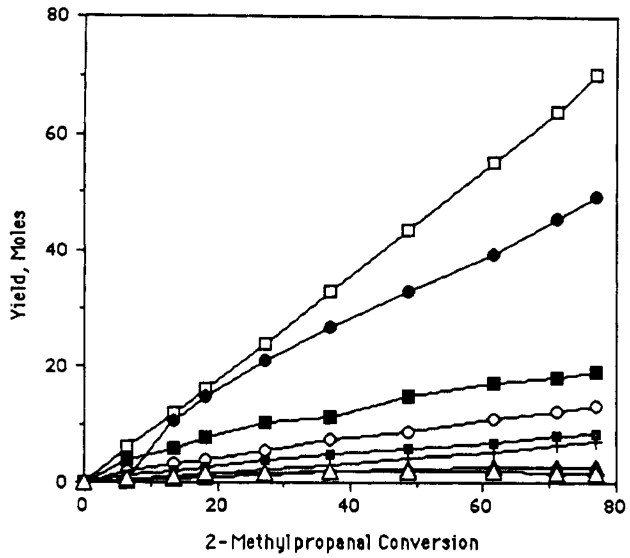


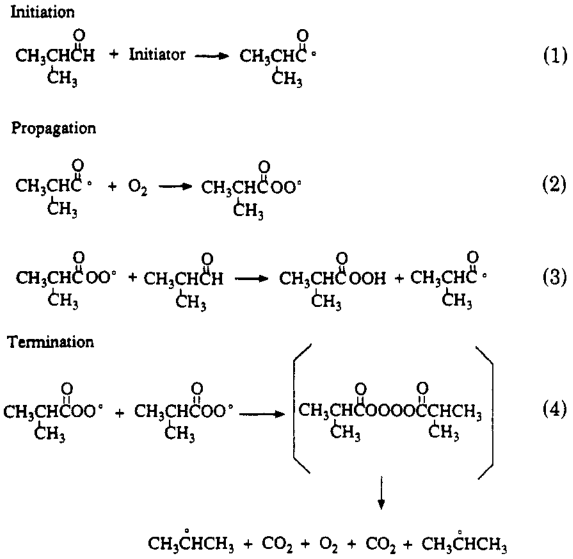
Figure 3. Product yields as a function of aldehyde conversion in the absence of a catalyst: (□) 2-methylpropanoic acid, (●) 2-propyl formate (×10), (■) carbon monoxide (×10), (○) acetone (×10), (▣) 2-propanol (×10), (+) carbon dioxide (×10), (▲) propane (×10), (△) propene (×10).

ison with our results. This literature resulted from investigations into the preparation of 2-methylpropanoic acid and its dehydrogenation as a method of producing methacrylic acid. I also wished to examine a number of very unusual catalysts that had been used for the liquid-phase oxidation of acrolein or methacrolein to the corresponding acids.[11] Manganese ion was chosen as the standard reference catalyst because it is the most widely used commercial catalyst for the oxidation of aldehydes, and many of the catalysts in the patent literature were compared to it.

Some typical results of the oxidation of 2-methylpropanal with a manganese catalyst are shown in Figure 2. The main product is of course 2-methylpropanoic acid. The other products (all 10×) include CO, CO_2, acetone, 2-propanol, propane, and propene. 2-Propyl formate, which is formed in the Baeyer–Villiger reaction, is present in trace amounts. Notice that most products are formed in an essentially linear fashion out to about 70% conversion.

Figure 3 shows results obtained in a typical noncatalytic reaction. Surprisingly, the yield of 2-methylpropanoic acid is higher than in most metal ion catalyzed reactions. The relatively large amount of 2-propyl formate produced is diagnostic of a noncatalytic reaction.

Reaction Mechanism. Some criteria have been established to characterize catalyst systems. To discuss these let us first consider the reaction mechanism. The liquid-phase oxidation of an aldehyde takes place in two stages, neither of which requires a catalyst. In stage 1 the aldehyde is oxidized via a typical free radical chain reaction to produce peracid.[1] The initiation, chain propagation, and termination steps of the chain reaction can be represented by eq 1–4.



Initiation

$$\mathrm{CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}H} + \text{Initiator} \longrightarrow \mathrm{CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}\cdot} \tag{1}$$

Propagation

$$\mathrm{CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}\cdot} + \mathrm{O_2} \longrightarrow \mathrm{CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}OO\cdot} \tag{2}$$

$$\mathrm{CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}OO\cdot} + \mathrm{CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}H} \longrightarrow \mathrm{CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}OOH} + \mathrm{CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}\cdot} \tag{3}$$

Termination

$$\mathrm{CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}OO\cdot} + \mathrm{CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}OO\cdot} \longrightarrow \left[\mathrm{CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}OOOO\overset{O}{\overset{\|}{C}}\underset{CH_3}{CH}CH_3}\right] \tag{4}$$

$$\downarrow$$

$$\mathrm{CH_3\dot{C}HCH_3} + \mathrm{CO_2} + \mathrm{O_2} + \mathrm{CO_2} + \mathrm{CH_3\dot{C}HCH_3}$$

Under preparative conditions, the reaction is mass transfer limited. This means that the critical rate-limiting step is the transfer of oxygen from air into the liquid phase. The mechanism shown in eq 1–4 is a good first approximation because oxygen is a diradical and is the most common radical in the reaction liquid, even in oxygen-starved systems. However, the average oxygen concentration in the liquid phase is so low that the reaction of oxygen with the acyl radical, eq 2, is the rate-determining propagation step. Under the chemically rate limiting conditions that prevail in kinetic studies the hydrogen abstraction step, eq 3, is rate limiting.

Essentially all of the CO_2 is formed in the termination step[12] shown in eq 4. (Obviously, the termination step also destroys precursors to 2-methylpropanoic acid.) Note that as the reaction rate increases, this mechanism implies that the acyl peroxy radical concentration will increase and

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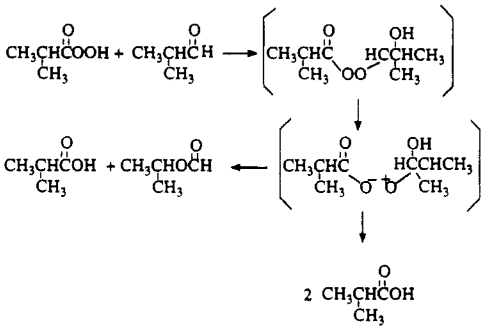
(10) (a) Sadaichi, Y.; Nakajima, H.; Kimura, H.; Nishimaru, H. Jpn. Kokai 73 97,809, Dec 13, 1973; *Chem. Abstr.* **1974**, *80*, 70348*v* (ferrocene). (b) Suzuki, Y., Okushima, H., Nitta, I. Jpn. Kokai 72 34,309, Nov 21, 1972; *Chem. Abstr.* **1973**, *78*, 97128*u* (palladium phthalocyanine). (c) Maki, T. Jpn. Kokai Tokkyo Koho 78,105,412, Sept 13, 1978; *Chem. Abstr.* **1979**, *90*, 22330*t* (alkali or alkaline earth formates). (d) Maki, T. Jpn. Kokai Tokkyo Koho 78,105,411, Sept 13, 1978; *Chem. Abstr.* **1979**, *90*, 22331*u* (alkali or alkaline earth metal compounds). (e) Maki, T. Jpn. Kokai Tokkyo Koho 78,105,413, Sept 13, 1978; *Chem. Abstr.* **1979**, *90*, 5925*y* (Li or alkaline earth metal compounds). (f) Maki, T. Jpn. Kokai Tokkyo Koho 78,108,915, Aug 8, 1978; *Chem. Abstr.* **1979**, *90*, 38538*c* (sodium isobutyrate). (g) Maki, T. Jpn. Kokai Tokkyo Koho 78,112,804, Oct 2, 1978; *Chem. Abstr.* **1979**, *90*, 54486*q* (Cu or Cu compounds). (h) Oga, A.; Goto, Y. Jpn. Kokai 77,033,614, Mar 14, 1978; *Chem. Abstr.* **1977**, *87*, 52788*d* (claimed that combination of Mn + Cu gave purer product in acetaldehyde oxidations. No indication of increased yield given). (i) Siclari, F.; Rosse, P. T. Ger. Offen. 2,649,510, May 26, 1977; *Chem. Abstr.* **1977**, *87*, 52796*e* (Ag and Ni oxides). (j) Aoshima, A.; Handa, S.; Tanaka, K.; Doi, T. Jpn. Kokai 77,005,707, Jan 17, 1977; *Chem. Abstr.* **1977**, *86*, 18911*j* (soluble Co and Mn salts in an inert solvent). (k) Sartorius, R.; Stapf, H.; Schaum, H.; Schenk, F. Ger. Offen. 2,658,043, June 29, 1978; *Chem. Abstr.* **1978**, *89*, 146430*z* (heavy metal catalysts + organic peroxides). (l) Masuko, T.; Fukaya, S.; Murai, N.; Noma, J. Ger. Offen. 2,928,002, Jan 24, 1980; *Chem. Abstr.* **1980**, *92*, 197940*k* (Alkali metal carboxylate in essentially anhydrous solution). (m) Erpenbach, H.; Gehrmann, K.; Hauser, A.; Karrenbauer, K.; Lork, W. Ger. Offen. 2,757,222, July 5, 1979; *Chem. Abstr.* **1979**, *91*, 91186*h* (Co + Cu to give acetic anhydride). (n) Erpenbach, H.; Gehrmann, K.; Hauser, A.; Karrenbauer, K.; Lork. W. Ger. Offen. 2,757,173, July 5, 1079; *Chem. Abstr.* **1979**, *91*, 107682*e* (Cu + Co + ortho-disubstituted benzenes). (o) Showa Acetyl Chemical Co. Jpn. Kokai Tokkyo Koho 80,167,242, Dec 26, 1980; *Chem. Abstr.* **1981**, *95*, 6514*d*. (p) Riesser, G. H.; Smith, R. F. French Patent 1,405,273, May 20, 1964 (Mn + boric or oxalic acid). (p) Knapsack-Griesheim A. G. French Patent 1,353,149, June 23, 1964 (metal salts of fatty acids). (q) Gobron, G.; Falize, C.; Dufour, H. U.S. Patent 3,987,103, Oct 19, 1976 (Mn, Ag, Mo, Cr, Ni, Co, V, W, Ti, Ce carboxylates. Reactions were run under severe oxygen starvation conditions to make acetone and 2-propanol).

(11) (a) Kao, J.-L.; Leonard, J. L. U.S. Patent 4,093,649, June 6, 1978 (Bi salts). (b) Sheng, M. N.; Kao, J.-L. U.S. Patent 4,144,399, Mar 13, 1979 (Ru or Os compounds). (c) Kao, J.-L.; Leonard, J. L. U.S. Patent 4,124,635, Nov. 7, 1978 (Zn salts). (d) Leonard, J. L.; Kao, J.-L. U.S. Patent 4,124,633, Nov 7, 1978 (Te salts). (e) Ming, M. N.; Kao, J.-L. U.S. Patent 4,115,440, Sept 19, 1978 (Se compounds). (f) Leonard, J. L.; Kao, J.-L. U.S. Patent 4,092,355, May 30, 1978 (Sb salts).

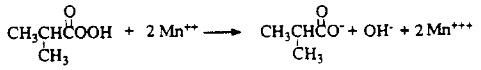
(12) (a) Clinton, N. A.; Kenley, R. A.; Traylor, T. G. *J. Am. Chem. Soc.* **1975**, *97*, 3746. (b) Clinton, N. A.; Kenley, R. A.; Traylor, T. G. *Ibid.* **1975**, *97*, 3752. (c) Clinton, N. A.; Kenley, R. A.; Traylor, T. G. *Ibid.* **1975**, *97*, 3757.

more CO_2 will be formed via the termination reaction. Although the reaction shown in eq 4 terminates a chain propagation step by destroying acyl peroxy radicals, the overall chain reaction is not greatly affected since two new free radicals are created.

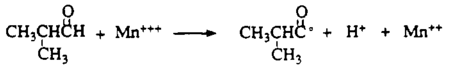
Stage 2 is the actual product formation step. In the absence of metallic catalysts a classic Baeyer–Villiger reaction of peracid with aldehyde takes place. One of the advantages of using 2-metylpropanal as substrate is that the 2-propyl group can compete with a hydrogen atom in the sigmatropic reaction shown in eq 5. From 12 to 15% of the reaction takes the path leading to 2-propyl formate.


(5)

In the presence of many metallic ions, the rate at which peracid is converted to aldehyde is increased. These catalysts may act by providing an alternative to the Baeyer–Villiger reaction. It is postulated that in the case of manganese ion, the peracid could be decomposed in a redox reaction involving Mn(II)[13] as depicted in eq 6. This is important because Mn(III) can initiate new chains as shown in eq 7. The combination of the reactions shown in eqs 6 and 7 produces two new radicals where none existed before (degenerate chain branching) so the presence of manganese ions greatly accelerates the overall reaction rate.

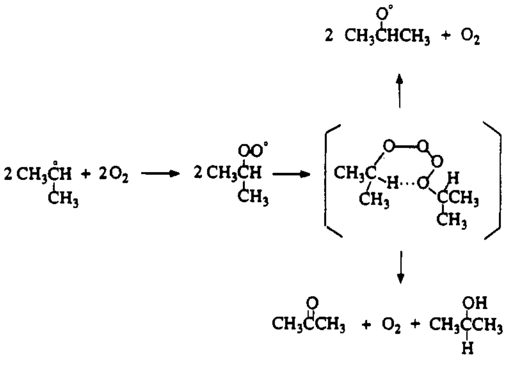


$$\underset{CH_3}{CH_3CH}\overset{O}{C}OOH + 2\,Mn^{++} \longrightarrow \underset{CH_3}{CH_3CH}\overset{O}{C}O^- + OH^- + 2\,Mn^{+++} \quad (6)$$



$$\underset{CH_3}{CH_3CH}\overset{O}{C}H + Mn^{+++} \longrightarrow \underset{CH_3}{CH_3CH}\overset{O}{C}\cdot + H^+ + Mn^{++} \quad (7)$$

The side products, acetone and 2-propanol, are formed by the two paths shown in eq 8. One path, involving the Russell mechanism,[14] gives rise to the destruction of radicals. In the second path, alkoxy radicals are formed. The alkoxy radicals can then abstract hydrogen atoms (even from alkyl side chains) to form 2-propanol or they can cleave to form acetaldehyde and methyl radicals. The methyl radicals would be converted to methanol and formaldehyde. At low conversions the second path does not appear to be too important since only traces of methanol are detected in the reaction products. After oxygen radicals, acylperoxy radicals are the most prevalent types of radical in these reactions. Thus, one would expect most (ca. 70%) of the alkylperoxy radicals to be decomposed by reaction with acylperoxy radicals as shown in eq 9. This also provides another, albeit minor, path for the production of carboxylic acid.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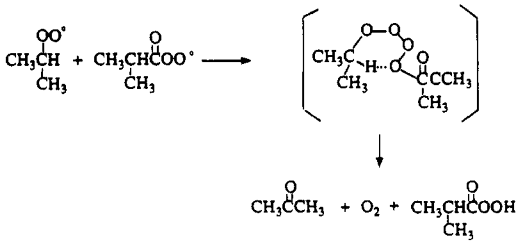
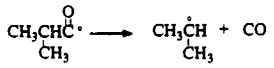

(9)

In an oxygen-lean system, a significant portion of the acyl radicals decompose to CO and 2-propyl radical, eq 10, before they get a chance to react with oxygen, eq 2. The ratio of acyl radicals decomposing via the path in eq 10 to those reacting with oxygen via the path in eq 2 is very sensitive to the oxygen concentration in the bulk liquid. The oxygen concentration, in turn, has a marked dependence on the intrinsic reaction rate. Thus, CO formation is a sensitive indication of low oxygen concentrations which are normally caused by high intrinsic reaction rates.



$$\underset{CH_3}{CH_3CH}\overset{O}{C}\cdot \longrightarrow \underset{CH_3}{CH_3\dot{C}H} + CO \quad (10)$$

To summarize, the increase in the reaction rate brought about by ions such as manganese is harmful because: (1) It increases the radical flux and thus the rate at which the biradical termination reaction, eq 4, occurs. When the rate is doubled the rate of formation of CO_2 and other undesirable byproducts is quadrupled. (2) It depletes the oxygen in the liquid phase and so indirectly brings about an increase in CO formation via the reaction shown in eq 10.

Copper ion is a very effective reagent for converting acyl radicals into acyl carbonium ions,[15] eq 11. It was predicted a priori that adding copper ion to an aldehyde oxidation would increase the reaction efficiency to carboxylic acid by intercepting acyl radicals.[16] The acyl carbonium ion formed can react with water to give carboxylic acids, with

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[13] (a) Sheldon, R. A.; Kochi, J. A. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; p 44. (b) Hendriks, C. F.; van Beek, H. C. A.; Heertjes, P. M. *Ind. Eng. Chem. Prod. Res. Dev.* **1979**, *18*, 43. (c) Jones, G. H. *J. Chem. Soc., Chem. Commun.* **1979**, 536. The reaction of peracids with solutions of Mn(II) or Co(II) is rapid and essentially quantitative. For example, treatment of cyclohexanepercarboxylic acid with a stoichiometric amount of Co(II) acetate gives an essentially quantitative yield of Co(III) acetate and cyclohexanecarboxylic acid;[13b] the purely thermal decomposition gives cyclohexanecarboxylic acid in only 89% efficiency. However, details of the reaction represented by eq 6 are in dispute. As written it has the disadvantage of impling that the reaction is kinetically third order. Jone[13c] puts forth a similar equation in which 1 equiv of Mn(II) is oxidized to Mn(IV). Since equilibration of Mn(IV) and Mn(II) then gives Mn(III) the net reaction is the same as in eq 6. However, Jones believes that it is more likely that the major reaction is one in which $Mn(III)_2$ is oxidized to $Mn(IV)_2$. The reaction with Co(II)[13b] is written as occurring in two sequential steps. In the first step, reaction of Co(II) with peracid yields Co(III), the carboxylate ion, and hydroxyl radical. In the second step, the hydroxyl radical is oxidized by Co(II) to hydroxide ion. Again, the net reaction is the same as for eq 6, but the reactions are now kinetically second order. However, the second step may not be thermodynamically feasible in isolation. In addition, one might expect to detect products from the reaction of hydroxyl radical with the solvent. We did not detect such products.

[14] Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 3871.

[15] Reference 1d, p 659.

[16] Hobbs, C. C. Personal communication.

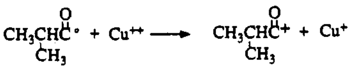
Table I. Effect of Catalyst System on Product Distribution[a]

	catalyst system[b]		
product	Mn(II)	none	Mn(II) + Cu(II)
2-methylpropanoic acid	80.80 ± 2.02	88.88 ± 1.12	87.79 ± 1.27
2-propyl formate	0.96 ± 0.49	5.77 ± 0.51	0.32 ± 0.21
oxygen in vent	0.70 ± 0.23	2.60 ± 0.24	1.02 ± 0.21
CO	12.81 ± 0.23	3.65 ± 1.02	8.33 ± 0.89
CO_2	5.40 ± 0.60	1.72 ± 0.58	3.44 ± 0.38
2-propanol	4.20 ± 0.46	1.53 ± 0.36	2.28 ± 0.17
acetone	6.85 ± 0.92	2.53 ± 0.83	4.72 ± 0.64
propene	1.38 ± 0.32	0.37 ± 0.12	3.34 ± 0.59
propane	6.59 ± 1.09	0.70 ± 0.32	1.45 ± 0.34

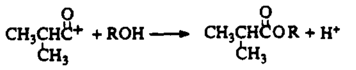
[a] Efficiencies (with 2σ error limits) are for 70% conversion and are given as moles/100 moles of aldehyde consumed. The oxidation of a solution of 50 wt % 2-methylpropanal in propanoic acid was carried out at 45 °C under a pressure of 95 psi using air as the oxidant. [b] The symbol Mn(II) indicates use of manganese ions as catalyst; Mn(II) + Cu(II) indicates use of a mixture of manganese and copper ions. Although the catalysts are added as Mn(II) acetate and Cu(II) acetate the Mn(II)/Mn(III) and Cu(I)/Cu(II) ratios existing during the reactons are controlled by the reaction conditions. The catalysts concentrations were about 300 ppm each (4.9×10^{-3} M in Mn(II); 3.9×10^{-3} M in Cu(II)).

carboxylic acids to give anhydrides, and with alcohols to give esters, eq 12. This provides an ionic alternative to the radical paths for the conversion of acyl radicals to carboxylic acid. The existence of this effect would be shown by a decrease in CO production. I now think that copper ions have a subtle and possibly more important effect. In converting the acyl radical to the acyl carbonium ion a radical chain is broken. The Cu(I) produced in eq 11 can also reduce Mn(III) to Mn(II), eq 13. This cuts the overall reaction rate by decreasing the initiation rate. Thus copper ion acts as a free-radical inhibitor or reaction moderator.

Effect of Copper on Reaction Efficiency



$$CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}\cdot + Cu^{++} \longrightarrow CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}{}^+ + Cu^+ \qquad (11)$$



$$CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}{}^+ + ROH \longrightarrow CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}OR + H^+ \qquad (12)$$

$$Cu^+ + Mn^{+++} \longrightarrow Cu^{++} + Mn^{++} \qquad (13)$$

Table I shows reaction efficiencies from Mn ion catalysis, no catalysis, and Mn + Cu ion catalysis. First, reaction in the absence of a catalyst gives higher efficiencies to 2-methylpropanoic acid than do the reactions with catalysts. This is solely because the reaction rate is slower; thus stage 1 of the reaction, the oxidation of aldehyde to peracid, is more efficient. Secondly, it is thought that essentially all of the 2-propyl formate is formed in a noncatalytic Baeyer–Villiger reaction. Thus, 2-propyl formate production is diagnostic of a non-catalytic reaction.

The addition of copper ion to a Mn ion catalyzed reaction has two effects. It converts acyl radicals to product (shown by lower CO efficiencies) and it lowers the overall reaction rate (shown by lower CO_2 efficiencies).

Could still higher efficiencies be obtained with additional amounts of Cu(II) ion or by using complexing agents? The answer is yes as shown by the data in Table II. Here the base case is the use of 300 ppm each of Mn and Cu ion as catalyst. Increasing the Cu ion concentration by a factor of 10 gives a 5 percentage point increase in efficiency. A number of complexing agents were tested in an attempt to increase the activity of Cu ion but only picolinic acid and *tert*-butylpicolinic acid were effective.[17] These complexing agents appear to work mainly by intercepting acyl radicals rather than by reducing the reaction rate. This is shown by the lowered production of CO but not of CO_2.

Table II. Effect of Copper Ion on Product Distribution[a]

	catalyst system, ligand[b]			
product	Mn(II) + Cu(II), none	Mn(II) + 10Cu(II, none	Mn(II) + Cu(II), PA	Mn(II) + Cu(II), BPA
2-methylpropanoic acid	87.79	92.69	94.28	95.44
2-propyl formate	0.32	0.00	0.30	0.00
oxygen in vent	1.02	1.45	1.00	1.44
CO	8.33	6.06	3.74	1.73
CO_2	3.44	1.25	1.66	2.82
2-propanol	2.28	1.49	1.52	1.77
acetone	4.72	2.19	2.04	1.71
propene	3.34	3.31	1.51	0.92
propane	1.45	0.31	0.32	0.15

[a] Efficiencies are for 70% conversion and are given as moles/100 moles of aldehyde consumed. [b] The symbol Mn(II) + Cu(II) indicates use of a mixture of manganese and copper ions as catalyst. Although the catalysts are added as Mn(II) acetate and Cu(II) acetate the Mn(II)/Mn(III) and Cu(I)/Cu(II) ratios existing during the reactions are controlled by the reaction conditions. Catalyst concentrations were 300 ppm except for 10Cu, which was 3000 ppm Cu ion. PA is picolinic acid and BPA is *tert*-butylpicolinic acid.

Table III. Effect of Co and Cu Ion on Product Distribution[a]

	catalyst system			
product	Co(II)	Co(II) + Cu(II)	Co(II) + 10Cu(II)	Cu(II)
2-methylpropanoic acid	73.97	78.24	89.95	78.76
2-propyl formate	1.97	0.78	0.39	3.10
oxygen in vent	0.70	1.15	1.77	2.10
CO	20.51	18.50	6.09	9.24
CO_2	5.94	5.07	3.52	8.90
2-propanol	4.52	2.10	1.30	2.63
acetone	6.65	3.89	1.97	3.45
propene	1.30	8.47	5.97	7.07
propane	10.86	5.65	0.40	5.01

[a] Efficiencies are for 70% conversion except for Cu ion alone which is for 50% conversion and are given as moles/100 moles of aldehyde consumed. Catalyst concentrations were 300 ppm except for 10Cu(II), which was 3000 ppm Cu ion. All catalysts are added as metal(II) acetates, but the actual oxidation states existing during the reactions are controlled by the reaction conditions.

A brief examination of cobalt-catalyzed reactions was carried out. In our opinion, Co ion is a slightly worse catalyst than Mn ion because it increases the overall reaction rate more than does Mn ion. It certainly requires about 10 times more copper ion as inhibitor to give a reaction with an efficiency of about 90% (See Table III). However, this is contrary to results obtained under chemically rate limiting conditions which indicate that Mn ion is the more active catalyst.[18]

By itself, Cu ion inhibits the oxidation to such an extent that we were unable to sustain reaction out to 70% conversion because the oxygen in the vent increased to such

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[17] No stability constants are available for propanoic acid solvent. In aqueous solution the stability constants indicate that Cu(II) ion would be almost completely complexed while the Mn(II) ion would remain essentially uncomplexed. (Sillen, L. G.; Martell, A. E. *Stability Constants of Metal Ion-Complexes*; Special Publication No. 17, The Chemical Society: London, 1964). The *tert*-butyl-2-picolinic acid was a mixture of isomers and was used because its complex with Cu(II) ions is appreciably more soluble than that of picolinic acid.

[18] Bawn, C. E. H.; Hobin, T. P.; Raphael, L. *Proc. R. Soc. London, A* **1956**, *237*, 313.

Table IV. Effects of Catalysts on Efficiency[a]

	efficiencies		
catalyst system	CO_2	CO	2-methylpropanoic acid
Co(II)	5.94	20.5	74.0
Mn(II)	5.40	12.8	80.8
Co(II) + Cu(II)	5.07	18.5	78.2
Co(II) + 10Cu(II)	3.52	6.1	90.0
Mn(II) + Cu(II)	3.44	8.3	87.8
Mn(II) + Cu(II) (BPA)	2.82	1.7	95.4
no catalyst	1.72	3.7	88.9
Mn(II) + Cu(II) (PA)	1.66	3.7	94.3
Mn(II) + 10Cu(II)	1.25	6.1	92.7

[a] Efficiencies are in moles/100 moles of aldehyde consumed. The CO_2 efficiencies are proportional to the initiation and termination rates. Catalyst concentrations are 300 ppm except for the 10Cu cases in which it is 3000 ppm. PA and BPA are the ligands, picolinic acid and *tert*-butylpicolinic acid, respectively. All catalysts are added as metal(II) acetates, but the actual oxidation states existing during the reactions are controlled by the reaction conditions.

an extent that our safety shutdown system stopped oxygen flow to the reactor (see Table III). The reaction efficiencies are low with Cu ion because forcing conditions are needed to maintain reaction. Extreme care is recommended in using Cu ion as a catalyst because an exothermic reaction took place in the liquid product after it was drained from the reactor. This was the only time a problem with the build up of peroxidic intermediates was encountered in this work.

In Table IV the effects of many of the catalysts are listed in order of decreasing CO_2 formation. Since CO_2 efficiency and overall reaction rate are causally related this is also the order of decreasing reaction rates. The high CO efficiencies for Co and Mn catalyzed reactions also correlate with reaction rate since they are caused by oxygen starvation. There is some indication here that copper–picolinic acid complexes are more effective at intercepting acyl radicals than in reacting with Mn(III).

If one takes into account the 6–7% efficiency loss to 2-propyl formate via the Baeyer-Villiger reaction one can see that the noncatalytic oxidation is remarkably efficient.

It was mentioned that there were a number of unusual catalysts for aldehyde oxidations in the patent literature. Many of these, particularly those used for the oxidations of acrolein and methacrolein, were presumed to work only on stage 2, the decomposition of peracid and peroxidic intermediates to acid. Representative samples from most patents[10,11] have been examined. Without listing them it can be said that all of the catalysts that were evaluated gave higher efficiencies than Mn in the oxidation of 2-methylpropanoic acid but did so because they were completely inert. The reaction product distribution (including production of about 6% of 2-propyl formate) and all reaction characteristics were identical with those obtained in the absence of a catalyst.

Some of the more interesting catalysts that were tested included lithium hydroxide, ferrocene, antimony trichloride, and trifluoroacetic acid. It was thought that bases such as lithium hydroxide might form surface active salts with 2-methylpropanoic acid that could enhance oxygen mass transfer. Such was not the case; lithium hydroxide was essentially inert. At low concentrations ferrocene was also essentially inert. At high concentrations ferrocene (or its decomposition products) acted as inhibitors, and it was impossible to maintain reaction. It was hoped that trifluoroacetic acid would catalyze decomposition in the Baeyer–Villiger reaction so as to preferentially give 2-methylpropanoic acid rather than 2-propyl formate. The literature[19] indicated that it might do this. If so, a noncatalytic oxidation in the presence of trifluoroacetic acid would give extremely high efficiencies. In our hands the addition of trifluoroacetic acid appeared to increase the overall rate of the Baeyer–Villiger reaction without changing its product distribution. Thus, adding it to a Mn ion catalyzed reaction gave about 6% 2-propyl formate; adding it to a noncatalytic reaction had no apparent effect. Antimony trichloride was also tested to see if it could catalyze the desired path in the Baeyer–Villiger reaction. It had no detectable effect on either stage 1 or stage 2 of the reaction.

Conclusions

Three types of aldehyde oxidation systems can be distinguished.

Manganese-like. While Mn is widely used as a catalyst for aldehyde oxidations there is a trade-off in its use. Mn improves the efficiency of conversion of peracid to acid (stage 2) but lowers the efficiency of conversion of aldehyde to peracid (stage 1). With straight-chain aldehydes the overall efficiency is often improved with Mn. With 2-methylpropanal as substrate, Mn-catalyzed oxidations have the following characteristics. The measured vent oxygen concentrations are low, indicating that the intrinsic reaction rate is high. Reaction stage 1 is quite inefficient, and large amounts of propane, propene, acetone, 2-propanol, CO, and CO_2 are produced.

Noncatalyzed Reactions. With 2-methylpropanal as substrate the oxygen concentration in the vent is high, showing that the intrinsic reaction rate of stage 1 is low. Reaction stage 1 is efficient and relatively small amounts of radical degradation products are made. Essentially all of the acid is produced through a Baeyer–Villiger reaction. The main byproduct, produced in stage 2, is 2-propyl formate.

Inhibited Manganese. Copper ion is an effective reaction moderator. A judicious combination of manganese and copper ions should allow one to retain the beneficial effect of manganese (clean conversion of peracids to acids) and still avoid the harmful effect (acceleration of reaction rate). The data given above support this conclusion. Obviously, each aldehyde may require an optimum ratio of copper to manganese that can only be determined by experiment.

Acknowledgment. I wish to thank Dr. C. C. Hobbs, Dr. C. Walling, and Dr. H. R. Gerberich for many educational conversations about liquid phase oxidations. I also am indebted to Dr. Hobbs for allowing me to use his computer program for making material and redox balances across a reaction system. I greatly appreciate the careful help with the experimental work provided by E. E. McChristy.

Registry No. $CH_3CH(CH_3)CHO$, 78-84-2; Mn, 16397-91-4; Cu, 15158-11-9; $CH_3CH(CH_3)C{=}OOH$, 79-31-2.

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(19) (a) Royer, J.; Beugelmans-Verrier, M. *C. R. Acad. Sci., Ser. C* **1971**, *272*, 1818. (b) Hawthorne, M.; Emmons, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 6398.