Reviews

Kinetics of Aerobic Liquid-Phase Oxidation of Organic Compounds

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Abstract:
The work discussed the role of cobalt and manganese complexes in the liquid-phase catalytic benzylic oxidation in polar and apolar media. Evidence that hydrocarbon is involved during oxidation with the transition metal ion is presented. It is supposed that reaction acceleration caused by bromide salts is due to the increase in the rate of the electron transfer and no initiation by bromine atoms exist. The reasons for different product selectivity in the presence of cobalt and manganese are explained and the synergistic effects of mixed catalysts are discussed. Thus cobalt is active in the oxidation of hydrocarbons and alcohols, while manganese is active in oxidation of carbonyl compounds. These assumptions allowed to build a system of differential rate equations.

Introduction

Aerobic liquid-phase catalytic oxidation of organic compounds is widely applied in the production of oxygen-containing substances. These oxidation processes use inexpensive oxidant, are selective, and produce but a small amounts of unrecoverable or toxic wastes. The study of oxidation mechanism and kinetics is necessary for the successful scale-up and commercialisation of these processes. A vast amount of literature starting from the 1930s was devoted to the theory and practice of liquid-phase oxidation. Nevertheless, a literature review of the basic dependencies of catalytic oxidation of various hydrocarbons and their oxygen-containing derivatives is virtually absent. The authors attempt such a generalisation in the present review.

Most of large-scale oxidation processes are run without a solvent or using lower aliphatic carboxylic acids as the solvents. So, we will define as reactions in nonpolar reaction media those run without a solvent or in nonpolar solvents (i.e., in dichlorobenzene). Under polar media acetic acid is usually assumed. Reaction mechanisms in both these media have a lot in common; nevertheless the rate ratios of individual steps are different.
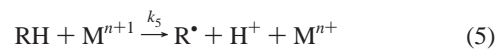
Hydrocarbon Oxidation in a Nonpolar Media

Noncatalysed Oxidation. Let us consider a typical noncatalytic hydrocarbon oxidation. It is a commonplace that

organic peroxides are the first molecular products of C−H bond oxidation. These compounds containing a weak O−O bond are prone to homolytic breakage which produce radical species.

Carefully purified hydrocarbons react with molecular oxygen only after a more or less lasting induction time. Then the reaction rate increases autocatalytically and significant amounts of peroxides accumulate in the reaction mixture. Introduction of peroxides into the reaction mixture at the beginning eliminates the induction time. Rate acceleration coincides with the accumulation of peroxides. These observations gave rise to the theory describing liquid-phase aerobic oxidation as a radical-chain process with degenerate chain branching due to hydroperoxide radical decomposition. The hydroperoxides are so potent a source of free radicals that one can neglect the thermal initiation due to the direct oxidation of RH with O_2. This theory of radical chain oxidation was used in developing of a number of liquid-phase oxidation processes. Compounds with O−O bond (hydroperoxides, peroxoacids) serve in these processes as branching agents.[1]

Catalysed Oxidation. It is known that soluble salts of transition metals catalyse oxidation processes. The mechanism of C−H bond oxidation in the presence of these salts can be illustrated by the following reactions:[2]

$$R-H + O_2 \xrightarrow{k_1} R^\bullet + HO_2^\bullet \tag{1}$$

$$R^\bullet + O_2 \xrightarrow{k_2} ROO^\bullet \tag{2}$$

$$RH + ROO^\bullet \xrightarrow{k_3} R^\bullet + ROOH \tag{3}$$

$$ROOH + M^{n,n+1} \xrightarrow{k_4} \text{radicals} + M^{n+1,n} \tag{4}$$

$$RH + M^{n+1} \xrightarrow{k_5} R^\bullet + H^+ + M^{n+} \tag{5}$$

$$2ROO^\bullet \xrightarrow{k_6} \text{molecular products} \tag{6}$$

$$ROO^\bullet + M^{n+} \xrightarrow{k_7} \text{molecular products} \tag{7}$$

where R−H is an oxidisable hydrocarbon, alcohol, aldehyde, etc., $M^{n,n+1}$ is a transition metal ion in its lowest and highest oxidation states, respectively.

(1) Emanuel, N. M.; Denisov, E. T.; Maizus, Z. K. *Tsepnye Reaktsii Okisleniya Uglevodorodov v Zhidkoi Phaze* [Hydrocarbon liquid-phase chain oxidation]; Nauka Publishers: Moscow, 1965.
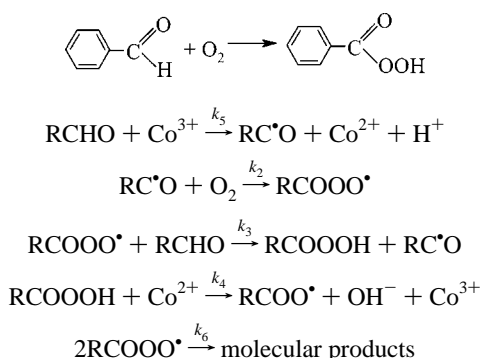(2) Partenheimer, W. *Catal. Today* **1995**, *23*, 69.

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The above scheme shows that the oxidation state of the transition metal during the reaction changes all the time. Frequently either metal oxidation or reduction prevails, and the catalyst exists in its highest or lowest oxidation states, respectively. In that case a rate law can include an analytical concentration of a catalyst. However, in many cases in the course of the reaction the ratio of concentrations of catalytic species in different oxidation states varies. This fact was observed quite a long time ago, and its possible consequences on oxidation kinetics were discussed.[1] Nevertheless, all attempts to build kinetic models taking into account this phenomenon failed so far. The main cause of this failure is the binding of the catalytic species into various complexes. Thus, the actual concentrations of the catalytic species strongly differ from their analytically determined values. Therefore, despite the same sequence of the elementary steps, different kinetic equations were frequently obtained. The interpretation of these equations was complicated, and their adequacy was strongly doubted.

Let us consider the catalytic oxidation of hydrocarbons. It is initiated by a degenerate decomposition of a peroxide compound just as in a noncatalysed process. A catalytic metal ion accelerates this decomposition. The overall rate r of the substrate consumption is the sum of rates of steps 1, 3, and 5. The rates of steps 1 and 5 are usually assumed to be negligible compared to that of step 3, so $r = r_3$. Under these conditions one would observe a radical-chain oxidation of RH.

The oxidation can be initiated by steps 1, 4, and 5. The rate of step 1 r_1 also would be lower than r_4 and r_5. Step 4 is a radical hydroperoxide decomposition catalysed by a metal in its highest and lowest oxidation states just like in the Haber-Weiss scheme.[3] It is evident that reaction of ROOH with M^{n+1} proceeds with a significant rate when the hydroperoxide has readily oxidisable C−H bonds. If no such bonds are available, then M^n is regenerated in the reaction of RH with M^{n+1}. If reactions of ROOH with M^n and M^{n+1} proceed with the same rates, then the rate law would include the overall analytic concentration of a catalytic metal. When the rate of step 5 prevails, then the variations in the catalyst oxidation state would influence the overall process rate.

This scheme is realised in some of the cases. Let us consider the kinetics of the cobalt catalysed benzaldehyde oxidation to perbenzoic acid and corresponding radical-chain mechanism proposed by Bawn:[4]

$$RCHO + Co^{3+} \xrightarrow{k_5} RC^{\bullet}O + Co^{2+} + H^+$$

$$RC^{\bullet}O + O_2 \xrightarrow{k_2} RCOOO^{\bullet}$$

$$RCOOO^{\bullet} + RCHO \xrightarrow{k_3} RCOOOH + RC^{\bullet}O$$

$$RCOOOH + Co^{2+} \xrightarrow{k_4} RCOO^{\bullet} + OH^- + Co^{3+}$$

$$2RCOOO^{\bullet} \xrightarrow{k_6} \text{molecular products}$$

Perbenzoic acid is rapidly reduced to benzoic one due to its reaction with Co^{2+}. That allows us to neglect the Bayer-

Villiger reaction: $RCOOOH + RCHO \rightarrow 2RCOOH$. Thus the final oxidation product is benzoic acid. Virtually all cobalt is present in the form of Co^{3+} due to the fast oxidation of Co^{2+} to Co^{3+}. Possibly at the beginning Co^{3+} is produced in the same reaction because benzaldehyde oxidation gives a sufficient amount of perbenzoic acid. The catalyst is present mainly in the highest oxidation state and concentration of Co^{3+} is constant. According to the steady-state approximation Co^{3+} generated in the reaction with perbenzoic acid should be continuously reduced to Co^{2+}. Reduction proceeds according to the following reaction:

$$RCHO + Co^{3+} \xrightarrow{k_5} RC^{\bullet}O + Co^{2+} + H^+$$
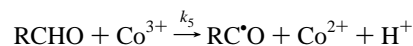
as only benzaldehyde has an oxidisable C−H bond.

It is evident that $k_5[RCHO][Co^{3+}] = k_4[RCOOOH][Co^{2+}]$.

The overall rate of peroxide generation would be the sum of $k_5[RCHO][Co^{3+}]$ and $k_4[RCOOH][Co^{2+}]$ or $2k_5[RCHO]-[Co^{3+}]$. As the rates of chain initiation and termination are equal, we obtain:
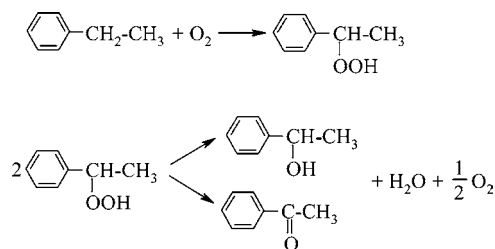
$$2k_5[RCHO] = 2k_6[RCOOO^{\bullet}]$$

or

$$[RCOOO^{\bullet}] = \sqrt{\frac{k_5}{k_6}[Co^{3+}][RCHO]}$$

The rate of benzaldehyde consumption is described by the following equation:

$$r = k_3\sqrt{\frac{k_5}{k_6}[Co^{3+}][RCHO]}[RCHO] =$$

$$k_3\sqrt{\frac{k_5}{k_6}[Co^{3+}]}[RCHO]^{3/2} \quad (I)$$

Oxidation of Hydrocarbons in Nonpolar Media

Let us consider the oxidation of ethylbenzene in the presence of a manganese catalyst in the absence of a solvent:
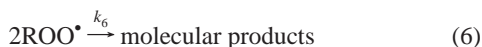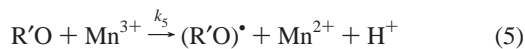

This reaction is somewhat more complicated than the previous one as the concentration of Mn^{3+} changes with time due to its binding with reaction intermediates.[5] The simplified

(3) Haber, F.; Weiss, J. *Naturwissenschaften* **1932**, *20*, 1.
(4) Bawn, C. E. H.; Jolley, C. *Proc. R. Soc. London, Ser. A* **1956**, 237.
(5) Bukharkina, T. V.; Grechishkina, O. S.; Digurov, N. G.; Krukovskaya, N. V. *Org. Process Res. Dev.* **1999**, *3*, 400.

reaction scheme is presented below (interactions of the catalyst with reaction intermediates are omitted):

$$RH + O_2 \xrightarrow{k_1} R^\bullet + HO_2^\bullet \qquad (1)$$

$$R'O + Mn^{3+} \xrightarrow{k_5} (R'O)^\bullet + Mn^{2+} + H^+ \qquad (5)$$

$$(R'O)^\bullet + O_2 \xrightarrow{k_9} (R'O)OO^\bullet \qquad (9)$$

$$(R'O)OO^\bullet + RH \xrightarrow{k_8} (R'O)OOH + R^\bullet \qquad (8)$$

$$R^\bullet + O_2 \xrightarrow{k_2} ROO^\bullet \qquad (2)$$

$$ROO^\bullet + RH \xrightarrow{k_3} ROOH + R^\bullet \qquad (3)$$

$$2ROO^\bullet \xrightarrow{k_6} \text{molecular products} \qquad (6)$$

In this scheme acetophenone is designated as R'O. The reaction is initiated at the start by the direct interaction of ethylbenzene with oxygen. As acetophenone is accumulated in the reaction mixture, the initiation is caused by its interaction with Mn^{3+} according to the above Bawn scheme. As the result, ethylbenzene consumption is described by the following rate law:

$$r = k_3 \sqrt{\frac{k_5}{k_6}[Mn^{3+}][R'O][RH]}$$

where [RH] is the ethylbenzene concentration. Oxidation of ethylbenzene occurs due to its reaction with peroxide radicals. Mn(III) is regenerated in the reaction of Mn^{2+} with peroxides.

However, when the rate of substrate oxidation by a transition metal ion in its highest oxidation state is much higher than the rates of chain initiation and propagation ($r_5 > r_1$, $r_5 > r_4$, and $r_5 > r_3$) the picture changes drastically. The process is no longer a radical-chain one but a catalytic radical one, i.e., the reaction of M^{n+1} with RH gives one molecule of product. The acetophenone oxidation in the presence of a manganese catalyst is an example. The kinetic study[6] of aerobic and anaerobic oxidation of acetophenone
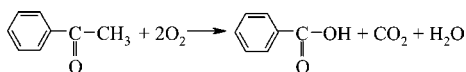

by manganese triacetate showed that both reactions obey the
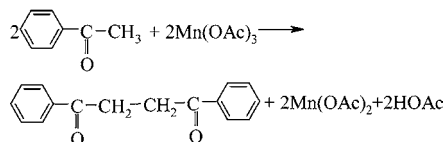
same rate law: $r = k[R'CO][Mn^{3+}]$, where k is the rate constant of the reaction of Mn^{3+} with acetophenone. Moreover, the rates of acetophenone consumption under aerobic and anaerobic conditions are equal.[6]

From the above it follows that acetophenone is oxidised in a nonchain pathway, and the rate-limiting step is a one-electron transfer from acetophenone molecule to Mn^{3+}.

$$R'CO + Mn^{3+} \rightarrow (R'CO)^{\bullet+} + Mn^{2+}$$
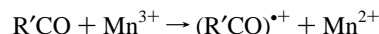
In this case one molecule of a reaction product is formed in every single act of acetophenone interaction with Mn^{3+}. The product of decomposition of acetophenone radical cation participates in the reaction initiation according to steps 8 and 9.

In all the previous examples initiation steps, or more generally, substrate involvement into an oxidation, constitutes a one-electron transfer from a substrate molecule onto a catalytic metal ion in its highest oxidation state. Indeed, this step in a catalytic oxidation is more important than it was thought earlier and, certainly, more significant than catalysed radical-forming decomposition of hydroperoxides. Undeniably, the introduction of peroxides into a reaction mixture in some cases accelerates the oxidation thus eliminating or significantly shortening the induction time. However, if peroxides are introduced *after* the induction time, they do not exert any effect, as in oxidation of ethylbenzene in the presence of a manganese catalyst.[5] When there is no induction time, like in the oxidation of p-nitroethylbenzene catalysed by $Mn(OAc)_2$, introduction of peroxides into a reaction mixture exerts no effect. It was also established that in ethylbenzene oxidation Mn^{3+} accumulates in the reaction mixture during induction time and the acceleration of the reaction corresponds to this accumulation. In the case of p-nitroethylbenzene virtually all the Mn present transforms to Mn^{3+} at the start of the reaction.[7] Addition of peroxides at the start of ethylbenzene oxidation results in a rapid conversion of all present Mn ions to Mn^{3+}, and thus reaction profiles are obtained that coincide with those after the induction time.

Oxidation of Hydrocarbons in Acetic Acid

It was shown[8] that the rate laws of anaerobic toluene oxidation by Co^{3+}

$$-\frac{d[Co^{3+}]}{d\tau} = k'\frac{[RH][Co^{3+}]^2}{[Co^{2+}]}$$

and oxygen consumption during Co^{3+}-catalysed aerobic toluene oxidation in acetic acid

$$-\frac{d[O_2]}{d\tau} = k''\frac{[RH][Co^{3+}]^2}{[Co^{2+}]}$$

are identical with ratio $k'/k'' = 1.7$.[8]

It proves that the rate of the reaction of the transition metal ion in the highest oxidation state with toluene is quite close to the overall oxidation rate. Consequently, the rates of hydrocarbon−radical interaction both in acetophenone and toluene oxidations are negligible compared to rates of hydrocarbon−M^{n+1} interaction.

(6) Bukharkina, T. V.; Grechishkina, O. S.; Digurov, N. G.; Krukovskaya, N. V. *Org. Process Res. Dev.* **2003**, *7*, 148.

(7) Bukharkina, T. V.; Digurov, N. G.; Mil'ko, S. B.; Shelud'ko, A. B. *Org. Process Res. Dev.* **1999**, *3*, 404.

(8) Kamiya, Y.; Kashima, M. *J. Catal.* **1972**, *25*, 326.

In this connection there appears a problem of increasing the concentration of M^{n+1} and the rate of one-electron transfer from substrate molecule onto M^{n+1}. In the existing large-scale oxidation processes these problems were solved empirically. The addition of ketones and aldehydes leads to an increase in M^{n+1} concentration.[9] It is possible to recover M^{n+1} by the electrochemical oxidation of M^n or by adding ozone as an oxidant.[10]
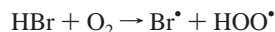
The most convenient and cost-effective way is the addition of a mixture of different transition metals ions or, for example, Zr.[12] In the latter case the increase in reaction rate is not linearly dependent on the initial concentration of metal ions that gave rise to discussion of their so-called "synergistic" action.

Currently one of the most efficient ways of increasing the rate of liquid-phase hydrocarbon oxidation (especially of aromatic hydrocarbons) is the addition of bromide ions to one or more of transition metals.[2]
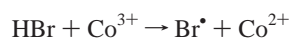
Ravens[13] proposed the first scheme of cobalt bromide catalysis. On his opinion, a hydrocarbon is involved into an oxidation by its reaction with the bromine radical:

$$Ar-CH_3 + Br^\bullet \rightarrow Ar-CH_2^\bullet + HBr$$
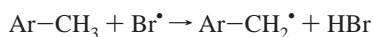
that is obtained by oxidation of HBr by oxygen

$$HBr + O_2 \rightarrow Br^\bullet + HOO^\bullet$$

or Co^{3+} cation

$$HBr + Co^{3+} \rightarrow Br^\bullet + Co^{2+}$$

Although this scheme explained the promoting effect of bromine ions, some experimental facts did not fit into it. For example, it did not account for the extremely low reaction rate in the presence of bromine radicals without transition metal ions.

It is thought presently that the promoting effect of bromide ions is the result of their ability to form complexes with a catalytic metal ion. Bromine in this complex has a partly-full[14] or full[15] radical nature due to partial or complete transfer of electron density from a bromide anion to a metal cation. Such a low electron density ligand alleviates electron transfer from a substrate to a catalyst. During the elementary catalytic act bromine radical can leave the coordination sphere[15] or can remain inside it,[14] as was proposed by Kamiya:[14]

$$Co^{3+}Br^- \rightleftarrows Co^{2+}Br^\bullet$$
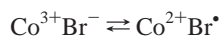
All these mechanisms explain the role of transition metal ions during oxidation, and do not consider the hydrocarbon

reaction with peroxide radicals, thus making quite doubtful the existence of the chain-radical oxidation pathway in the presence of cobalt bromide catalyst. It was shown[15] that the highest possible rate of free-radical hydrocarbon oxidation is lower by 2 orders of magnitude than that observed in the experiment. The termination rate (recombination of free radicals) was determined by chemiluminescence, and propagation rate was calculated independently as the rate of reaction 3 ($ROO^\bullet + RH$). The elucidation of the reaction mechanism and building of the kinetic model was quite difficult as just initial nearly linear segments of S-like concentration profiles were under consideration. The variations in the composition of the reaction mixture and, most important, in the catalyst composition, were neglected.

Oxidation in the Presence of Cobalt Bromide and Manganese Bromide Catalysts. The necessity of studying of at least some of the reactions in a "pure form" was caused by a highly complicated composition of a reaction mixture and an enormous number of possible interactions between reaction components. Thus, some of the current authors studied the interaction of Co^{3+} and Mn^{3+} with Br^- and organic compounds under anaerobic conditions.[15]

The reaction of Mn^{3+} with Br^- in acetic acid according to the equation
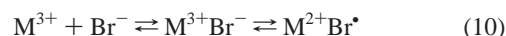
$$2M^{3+} + 2Br^- \rightarrow 2M^{2+} + Br_2$$
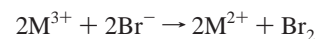
was monitored by the titration and a stopped-flow method using EPR. It was established that the reaction has a first-order on $[M^{3+}]$ and $[Br^-]$ and is inhibited by Mn^{2+}. This was described by the following rate law:

$$-\frac{d[M^{2+}]}{d\tau} = \frac{k_{10}[M^{3+}][Br^-]}{[M^{2+}]} \tag{II}$$

where k_{10} is an effective rate constant.

The proposed mechanism is shown below:

$$M^{3+} + Br^- \rightleftarrows M^{3+}Br^- \rightleftarrows M^{2+}Br^\bullet \tag{10}$$

$$2M^{2+}Br^\bullet \rightarrow 2M^{2+} + Br_2 \tag{11}$$

$$M^{2+} + Br^- \rightleftarrows M^{2+}Br^- \tag{12}$$

Bromide ion bonded with Mn^{2+} ions cannot participate in the equilibrium in eq 10, thus decreasing the concentration of $M^{2+}Br^\bullet$ and inhibiting the overall reaction.

One can propose a mechanism including formation of free bromine radical analogous to Ravens' scheme:

$$M^{3+} + Br^- \rightleftarrows M^{2+} + Br^\bullet \tag{13}$$

$$2Br^\bullet \rightarrow Br_2 \tag{14}$$
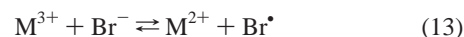
It is highly doubtful that the first step is reversible as no Co^{3+} was observed when $Co(OAc)_2$ was UV-irradiated in the presence of Br_2. Thus, the free $Br^\bullet$ radical can be

(9) Tupitskaya, S. L.; Shkalkova, V. I.; Bukharkina, T. V.; Digurov, N. G. *Neftekhimiya* **1979**, *19*, 441.
(10) Yakobi, V. A. *Proc. Mendeleev Moscow Inst. Chem. Technol.* **1978**, *103*, 66.
(11) Gipe, R. K.; Partenheimer, W. Catalysts by Rational Design: Prediction and Confirmation of the Properties of the Co/Ce/Br Liquid-Phase Autoxidation Catalyst Based on the Kinetic Similarity to the Co/Mn/Br Catalyst. 3rd World Congress on Oxidation Cataysis; 1997.
(12) Chester, A. W.; Landis, P. S.; Scott, E. I. Y. *CHEMTECH* **1978**, *8*, 366.
(13) Ravens, D. A. S. *Trans. Faraday Soc.* **1959**, *55*, 1768.

(14) Kamiya, Y. *J. Catal.* **1974**, *33*, 480.
(15) Digurov, N. G.; Bukharkina, T. V.; Lebedev, N. N. *Nefetkhimiya* (Russ.) **1986**, *26*, 787.

$C_{Mn^{2+}}$, mol·L^{-1}
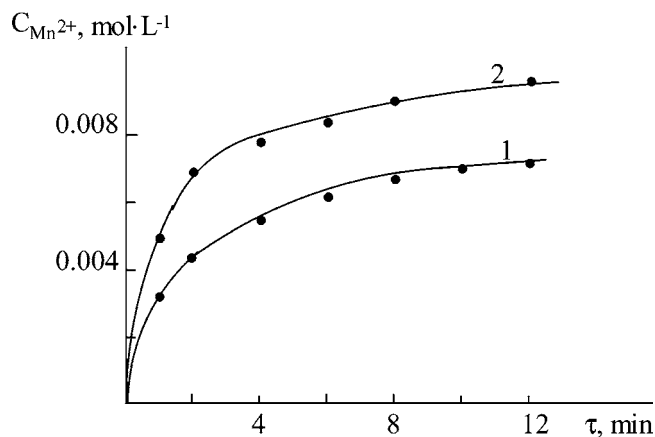
Figure 1. Accumulation of Mn^{2+} ions according to reactions: (1) Mn^{3+} + Br$^-$; (2) Mn^{3+} + Br$^-$ + toluene. Initial concentrations: (mol·L^{-1}): [Mn^{3+}] = 0.01; [Br$^-$] = 0.02; [toluene] = 1.0; t = 40 °C. Points − experiment, curves − least-squares fit.

produced only by the irreversible reaction

$$M^{3+} + Br^- \rightarrow M^{2+} + Br^\bullet \qquad (15)$$

or

$$M^{3+}Br^- \rightarrow M^{2+} + Br^\bullet \qquad (16)$$
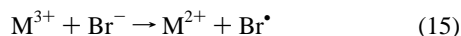
In this case the rate of $C_{Mn^{3+}}$ variation should be independent of consumption of Br$^\bullet$. Also, schemes including equations 13−16 do not allow the development of an adequate kinetic equation.

The addition of a hydrocarbon (toluene) promotes reaction 16 of manganese and cobalt triacetates (Figure 1). Results[15] suggest that Mn^{2+} Br$^\bullet$ species is consumed by two parallel pathways with formation of molecular bromine and hydrocarbon radicals and the consequent recombination of R$^\bullet$ and bromine radicals into benzyl bromide according to the following scheme:

$$RH + M^{3+}Br^- \xrightarrow{slowly} M^{2+} + R^\bullet + H^+ + Br^- \qquad (17)$$

$$R^\bullet + M^{3+}Br^- \rightarrow RBr + M^{2+} \qquad (18)$$
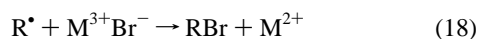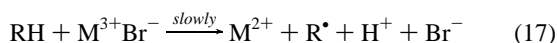
It should be noted that under the reaction conditions (40−60 °C) the rate of oxidation of RH with M^{3+} is negligible. The acceleration of Mn^{3+} consumption in the presence of toluene under anaerobic conditions is compelling evidence of toluene participation in the rate-limiting step. Thus, the abstraction of an electron from a hydrocarbon by Mn^{3+} proceeds both in the presence and in the absence of Br$^-$. There are no grounds for supposing that the change of a bromine ligand in the coordination sphere of a central ion for the acetate one would alter the mechanism of aerobic benzylic oxidation.
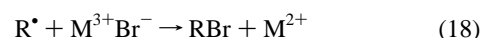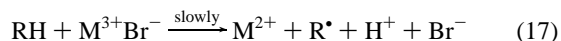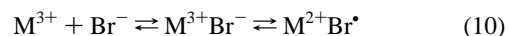
The equality of initiation (slow reaction 17) and toluene oxidation reaction rates was demonstrated in ref 17 where these processes were described by identical equations with the same rate constants. Thus, bromine-promoted and non-

(16) Gabdrakhmanov, M. N.; Geletii, Yu. V.; Zakharov, I. V. *Nefetkhimiya* (Russ.) **1984**, *24*, 496.
(17) Kashirsky, V. F.; Digurov, N. G.; Shevyreva, E. V.; Lebedev, N. N. *Kinet. Katal.* **1981**, *22*, 364.

promoted oxidations both proceed by the same nonchain mechanism.

The study of benzyl alcohol anaerobic oxidation by Co(OAc)$_3$ and Mn(OAc)$_3$ showed the similarity of this reaction to hydrocarbon oxidation, the only difference being the higher alcohol reactivity and, consequently, the higher rate of M^{3+} consumption.

The metal-catalysed aerobic liquid-phase oxidation of benzaldehyde and acetophenone proceeds by the same mechanism in both the presence and an absence of Br$^-$. No promoting effect of Br$^-$ was observed in the oxidation of carbonyl compounds.

Thus, the general scheme of a steady-state process of aerobic benzylic oxidation in the presence of a metal bromide catalyst can be presented by the following scheme:

$$M^{3+} + Br^- \rightleftarrows M^{3+}Br^- \rightleftarrows M^{2+}Br^\bullet \qquad (10)$$

$$RH + M^{3+}Br^- \xrightarrow{slowly} M^{2+} + R^\bullet + H^+ + Br^- \qquad (17)$$

$$R^\bullet + M^{3+}Br^- \rightarrow RBr + M^{2+} \qquad (18)$$

$$R^\bullet + O_2 \rightarrow RO_2^\bullet \qquad (2)$$

$$RO_2^\bullet + M^{2+} + H^+ \rightarrow ROOH + M^{3+} \qquad (19)$$

ROOH + M^{3+} ——→

$$[M^{3-} + OH^- + R'CH_2O^-] \Big\langle \begin{array}{l} R'CHO + H_2O + M^{2-} \qquad (20) \\ R'CH_2\dot{O} + \bar{O}H + M^{3+} \qquad (21) \end{array}$$

(where R is R′CH$_2$)

$$R'CH_2O^\bullet + M^{2+} + H^+ \rightarrow R'CH_2OH + Mn^{3+} \qquad (22)$$

$$2M^{2+}Br^\bullet \rightarrow 2M^{2+} + Br_2 \qquad (11)$$

$$M^{2+} + Br^\bullet \rightleftarrows 2M^{2+} + Br^\bullet \qquad (13)$$
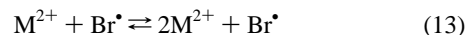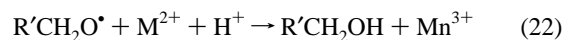
The rate-limiting step is a one-electron transfer (17) just as in the absence of Br$^-$. Then, the radical undergoes a number of transformations, resulting in the formation of a hydroperoxide, which decomposes by parallel pathways into alcohol and aldehyde. The oxidation of alcohol proceeds by a nonchain mechanism, the limiting step being an abstraction of an electron by a metal bromide complex:

$$M^{3+}Br^- + R'CH_2OH \rightarrow R'C^\bullet HOH + M^{2+} + H^+ + Br^- \quad (23)$$

$$R'C^\bullet HOH + M^{3+}Br^- \rightarrow R'CHO + M^{2+} + H^+ + Br^- \quad (24)$$

It is evident that at low concentrations of M^{3+}, R′C$^\bullet$HOH can react with oxygen:

$$R'C^\bullet HOH + O_2 \longrightarrow R'-\overset{\overset{\displaystyle OO^\bullet}{|}}{CH}-OH \qquad (25)$$

and then yields aldehyde by reaction with M^{2+}.

$$R'-\overset{\overset{\displaystyle OO^\bullet}{|}}{CH}-OH + M^{2+} + H^+ \longrightarrow R'CHO + M^{3+} + H_2O_2 \qquad (26)$$

Benzaldehyde is oxidised to perbenzoic acid according to the mechanism not much different from that proposed by

Bawn (described previously). The only difference is the presence of high concentrations of M^{2+} in the reaction mixture. This results in the chain termination by oxidation of M^{2+} to M^{3+}.

$$RCHO + M^{3+} \xrightarrow{k_5} RC^{\bullet}O + M^{2+} + H^{+}$$

$$RC^{\bullet}O + O_2 \xrightarrow{k_2} RCOOO^{\bullet}$$

$$RCOOO^{\bullet} + RCHO \xrightarrow{k_3} RCOOOH + RC^{\bullet}O$$

$$RCOOO^{\bullet} + M^{2+} \xrightarrow{k_7} RCOOO^{-} + M^{3+}$$

Under these conditions the chain termination by radical recombination is negligible. In all possibility the rate of the following reaction

$$R'C^{\bullet}HOH + RH \rightarrow R'CH_2OH + R^{\bullet}$$

is also very low.

The recovery of M^{3+} is provided by the oxidation of M^{2+} by perbenzoic acid.

$$RCOOOH + 2M^{2+} + 2H^{+} \xrightarrow{k_4} RCOOH + 2M^{3+} + H_2O$$

Reaction 4 prevails both at high concentrations of M^{3+} and under anaerobic conditions. At low concentrations of M^{3+} radical $R'C^{\bullet}HOH$ is consumed according to reactions 25−26. Benzaldehyde is the single product of a benzyl alcohol oxidation up to 90% conversion. Its further radical-chain oxidation is inhibited because the rate of termination (7) is higher than the initiation rate (5).

The sequence of product formation is described by the scheme:

$$RH \rightarrow ROOH \begin{array}{c} \nearrow R'CHO \longrightarrow R'COOH \\ \quad\quad\uparrow \\ \searrow R'CH_2OH \end{array}$$

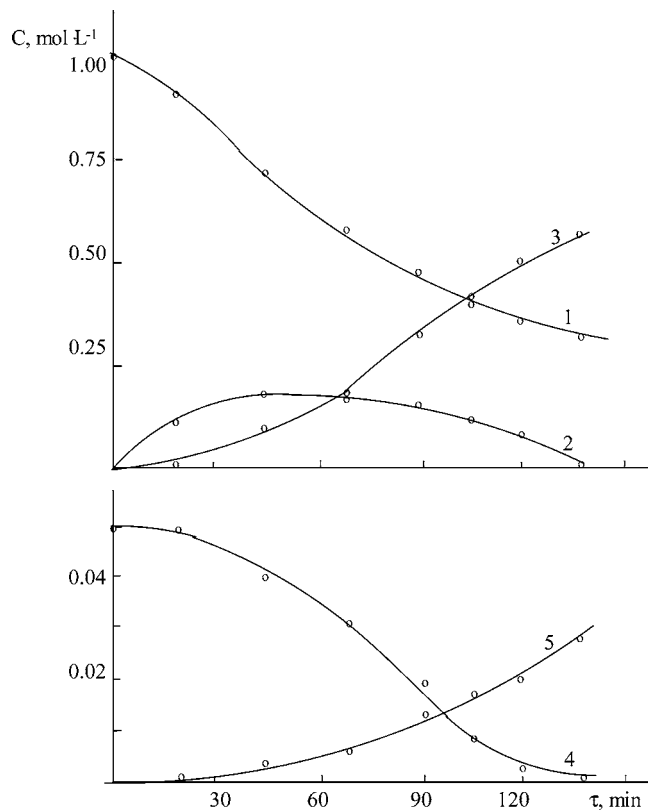This system of differential equations describes the oxidation of alkylbenzenes up to a high degree of conversion:

$$-\frac{d[RH]}{d\tau} = \frac{k_1[RH][M^{3+}][Br^{-}]}{[M^{2+}]} \quad\quad (III)$$

$$\frac{d[R'CH_2OH]}{d\tau} = \frac{\Phi \cdot k_1[RH][M^{3+}][Br^{-}]}{[M^{2+}]} -$$
$$\frac{k_2[R'CH_2OH][M^{3+}][Br^{-}]}{[M^{2+}]} \quad\quad (IV)$$

$$\frac{d[R'CHO]}{d\tau} = \frac{(1-\Phi)k_1[RH][M^{2+}][Br^{-}]}{[M^{+2}]} +$$
$$\frac{k_2[R'CH_2OH][M^{3+}][Br^{-}]}{[M^{2+}]} -$$
$$-\frac{k_3[R'CHO]^2[M^{2+}]}{[M^{2+}]} \quad\quad (V)$$

$$\frac{d[R'COOH]}{d\tau} = \frac{k_3[R'CHO]^2[M^{3+}]}{[M^{2+}]} \quad\quad (VI)$$

Here Φ is the partial yield of alcohol in hydroperoxide decomposition and is assumed to be constant. The rate constants in the above equations are effective and could not be attributed to any isolated elementary step. They are complicated functions of elementary step rate constants.

The above oxidation scheme explains the role of oxidation intermediates: the decomposition of a hydroperoxide does not change the catalyst oxidation state, and therefore, its addition has virtually no effect on a steady-state oxidation rate (III), alcohols inhibit oxidation because they reduce Mn^{3+}, the accumulation of aldehyde accelerates oxidation as the Mn^{3+} concentration is quickly increased due to chain oxidation of a carbonyl compound.

Oxidation in the Presence of Mixed Transition Metal Catalysts. These considerations can be applied for the explanation of a so-called "synergism" of Mn and Co catalysts in a low-temperature benzylic oxidation when the RH consumption rate reaches its maximum at ratio $[Mn^{2+}]_0/[Co^{2+}]_0 = 1-10$ mol %. It is explained by a formation of mixed Co−Mn complexes[17] or by oxidation of Co^{2+} to Co^{3+} by Mn^{3+}, although in acetic acid the following reaction is virtually instant and irreversible.

$$Co^{3+} + Mn^{2+} \rightarrow Co^{2+} + Mn^{3+}$$

Thus, Mn^{3+} and not Co^{3+} would be recovered first. The authors do not consider the possibility of $Mn^{3+}Br^{-}$ formation, although it was shown[16] that quite frequently this complex is more reactive than a cobalt bromide one.

It was already noted that the ratio $[M^{3+}]/[M^{2+}]$ plays a major role in a benzylic oxidation. The rates of toluene and p-xylene oxidation in the presence of a mixed cobalt manganese bromide catalyst are also determined by $[Mn^{3+}]/[Mn^{2+}]$ ratio, and the concentration of Co^{3+} in the reaction mixture is extremely low. The accelerating effect of manganese is more pronounced when its concentration is lower than that of cobalt. Obviously, when Mn concentrations are high, an accumulation of Mn^{2+} that inhibits the reaction occurs. The experimental data on toluene oxidation are described by the following scheme

$$Mn^{3+} + Br^{-} \rightleftarrows Mn^{3+}Br^{-} \rightleftarrows Mn^{3+}Br^{\bullet} \quad\quad (27)$$

$$Mn^{3+}Br^{-} + RH \xrightarrow{slowly} Mn^{2+} + R^{\bullet} + Br^{-} + H^{+} \quad\quad (28)$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \quad\quad (2)$$

$$RO_2^{\bullet} + Mn^{2+}(Co^{2+}) + H^{+} \rightarrow ROOH + Mn^{3+}(Co^{3+}) \quad\quad (29)$$

$$Mn^{2+} + Br^{-} \rightleftarrows Mn^{2+}Br^{-} \quad\quad (30)$$

$$Mn^{2+} + Mn^{2+}Br^{-} \rightleftarrows Mn^{2+}Br^{-}Mn^{2+} \quad\quad (32)$$

$$Co^{2+} + Br^{-} \rightleftarrows Co^{2+}Br^{-} \quad\quad (30)$$

$$Co^{3+} + Mn^{2+} \xrightarrow{fast} Co^{2+} + Mn^{3+} \quad\quad (33)$$

$$ROOH + Mn^{2+}(Co^{2+}) \begin{array}{c} \nearrow R'CHO + H_2O + Mn^{2+}(Co^{2+}) \quad (34) \\ \searrow R'CH_2O^{\bullet} + OH^{-} + Mn^{3+}(Co^{3+}) \quad (35) \end{array}$$

Figure 2. Kinetic profiles of toluene oxidation by oxygen. (1) toluene; (2) benzaldehyde; (3) benzoic acid; (4) Br^-; (5) Co^{3+}. Initial concentrations: $(mol \cdot L^{-1})$: [toluene] = 1.0; $[Co^{3+}]$ = 0.05; $[Br^-]$ = 0.05; oxygen flow = 0.5 $L \cdot min^{-1}$. t = 60° C. Points − experiment, curves − least-squares fit.

The rate equations were derived using the assumption that reaction 28 is the rate-limiting one and that the equilibria are strongly shifted to the right. In the case of toluene oxidation the sum of the concentration of Co^{3+} and Mn^{3+} is lower than $[Mn^{2+}]_0$. Taking into account the high rate of reaction 33 one can assume that only manganese is present in the highest oxidation state. The following rate law corresponding to experimental data was derived from the scheme:

$$-\frac{d[RH]}{d\tau} = k_1[RH][Mn^{3+}][Br^-]_f \qquad (VII)$$

$$[Br^-]_f = \frac{[Br^-]}{(1 + K_1[Mn^{3+}] + K_1 K_2[Mn^{2+}]^2)} \qquad (VIII)$$

where K_1 and K_2 are equilibrium constants for reactions 30 and 32, respectively.

At high K_1 and K_2 values the equation VII becomes similar to eqs II and III, derived above.

System III−VI satisfactorily describes the oxidation of toluene catalysed by cobalt acetate−sodium bromide in the presence of manganese or acetaldehyde or without them (Figures 2−4). It confirms the similarity of reaction mechanisms, although profiles of toluene consumption on Figure 2 look like autocatalysis, on Figure 3 are like an inhibited reaction, and in Figure 4 are like the first-order reaction. The figures show that bromine ion concentration falls during
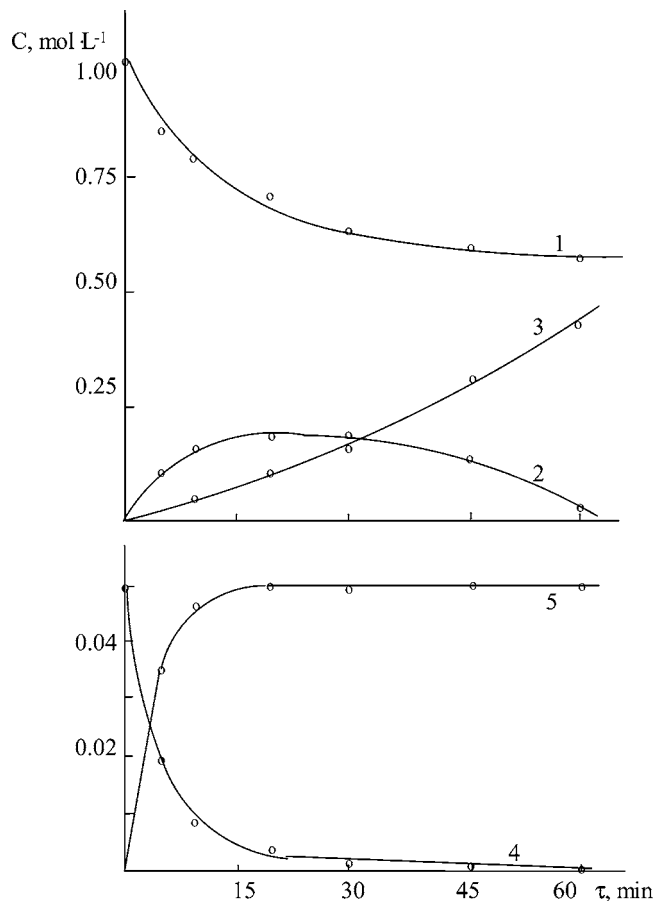
Figure 3. Toluene oxidation by oxygen in the presence of acetaldehyde. (1) toluene; (2) benzaldehyde; (3) benzoic acid; (4) Br^-; (5) Co^{3+}. Initial concentrations: $(mol \cdot L^{-1})$: [toluene] = 1.0; $[Co^{3+}]$ = 0.05; $[Br^-]$ = 0.05; acetaldehyde feed 0.1 mol/min; oxygen flow = 0.5 $L \cdot min^{-1}$. t = 60° C. Points − experiment, curves − least-squares fit.

the reaction. Partially it is due to the formation of benzyl-bromide, but mainly it is caused by the following reaction:

$$2M^{3+} + 2Br^- \rightarrow 2M^{2+} + Br_2$$
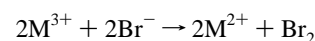
The addition of acetaldehyde results in a fast accumulation of M^{3+} that oxidises bromide ion to molecular bromine. Thus, toluene oxidation with addition of acetaldehyde runs faster at first and later is inhibited due to the loss of bromine ion.

In the oxidation of p-xylene and p-toluic acid $[Mn^{3+}]$ + $[Co^{3+}] > [Mn^{2+}]_0$ so the scheme should include the corresponding reactions of Co^{3+}. For the catalytic oxidation of p-toluic acid we obtain:

$$-\frac{d[RH]}{d\tau} = \frac{(k_1[Mn^{3+}] + k_2[Co^{3+}])[RH][Br^-]}{[Co^{2+}]} \qquad (IX)$$

In this case virtually all manganese exists as Mn^{3+}, and cobalt is present in both oxidation states.

The rate acceleration in the presence of manganese ions is due to an increase in Mn^{3+} concentration. It should be mentioned that the partial yield of benzylic alcohol is sharply increased (from 10 to 45%) in the presence of manganese. Possibly, $RO^{\bullet}$ radicals are more easily freed from the central
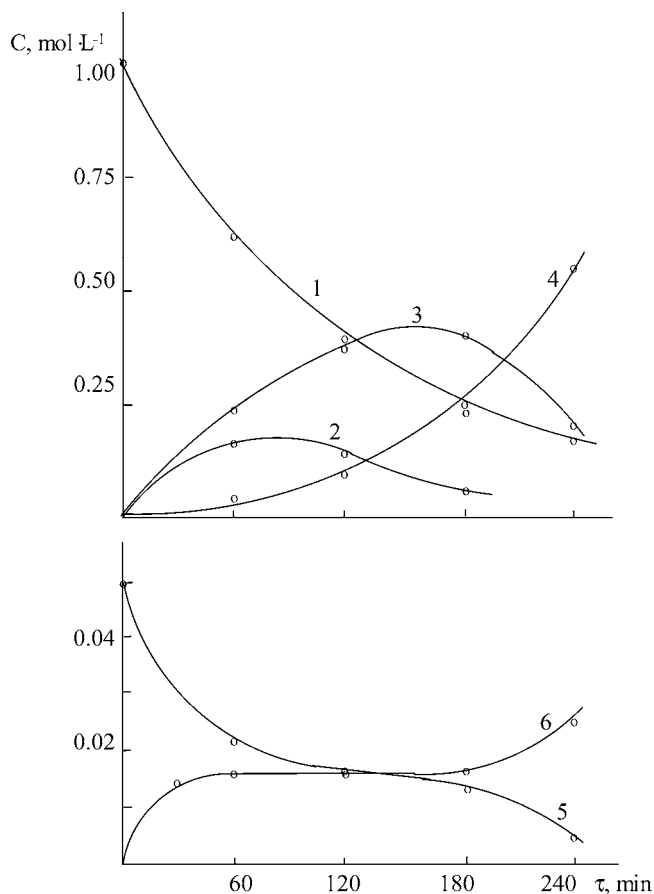
Figure 4. Toluene oxidation by oxygen in the presence of cobalt manganese catalyst. (1) toluene; (2) benzyl alcohol; (3) benzaldehyde; (4) benzoic acid; (5) Br$^-$; (6) Mn^{3+}. Initial concentrations: (mol·L^{-1}): [toluene] = 1.0; [Co^{3+}] = 0.05; [Mn^{2+}] = 0.01; [Br$^-$] = 0.05; oxygen flow = 0.5 L·min^{-1}. *t* = 60° C. Points − experiment, curves − least-squares fit.

coordination sphere into the bulk of the organic phase in the presence of a manganese catalyst.

The promoting effect of manganese ions in the oxidation of compounds with aliphatic C−C bond is not limited to rate acceleration. The oxidation in the presence of manganese yields carboxylic acid, whereas in its absence C−C bond is not oxidised and carbonyl compound is the prevailing product. Let us consider ethylbenzene oxidation. In the presence of a pure cobalt catalyst the reaction yields acetophenone,[19] whereas in the presence of a mixed manganese cobalt bromide catalyst oxidation proceeds more rapidly and yields benzoic acid.[17] The process is described by the system of equations analogous to eqs III−VI. The rate acceleration is due to the increase in the concentration of the catalyst in its highest oxidation state. In the absence of manganese the concentration of Co^{3+} ions is extremely low. In the presence of acetophenone Mn^{2+} is quickly oxidised to Mn^{3+}, which oxidises acetophenone to benzoic acid. Also, in the presence of acetophenone the reaction M^{2+} → M^{3+} proceeds only with manganese, and bromide ion inhibits oxidation, lowering the M^{3+} concentration. It shows that metal bromide complexes are not active in the oxidation of carbonyl compounds.

There are also literature devoted to oxidation of aromatic hydrocarbons having other substituents beside methyl ones, such as alkyl or those partially oxidised (keto groups). The cobalt-catalysed oxidation of *p*-methyl acetophenone and *p*-isopropyl toluene in the presence of bromides or acetaldehyde affects only the methyl group,[20,21] thus disproving the assumptions about the radical chain reaction mechanism. The authors' quantum mechanical calculations showed that the rate-limiting step is the one-electron transfer with the consequent decomposition of cation radical with the breakage of the C−H bond of the methyl group. The acetyl group remains practically untouched, confirming inactivity of cobalt catalysts in the oxidation of carbonyl compounds.

The same ratio of reaction rates was observed in acenaphthene oxidation where cobalt catalysis does not affect aliphatic C−C bonds of five-membered rings, whereas they are broken in the presence of manganese ions.[22] The mechanism of oxidation of ethylbenzene and its analogues differs from that of methyl substituted benzenes by the nonchain oxidation of an intermediate ketone. In this case M^{3+} ions can be accumulated due to chain oxidation of formaldehyde formed in acetophenone destruction. In all other aspects there are no major distinctions between oxidation mechanisms of ethylbenzene- and methyl-substituted benzenes despite different forms of reaction profiles. Particularly, the autoinhibition of ethylbenzene oxidation and autoacceleration of toluene oxidation both are the result of different variations of the concentrations of catalyst components.

The promoting role of manganese consists of acceleration of M^{2+} → M^{3+} transition. The Mn(III) species together with Co(III) participate in hydrocarbon oxidation, but do not change the reaction mechanism. The calculations according to eq IX show that there indeed exists an additive effect of Co^{3+} and Mn^{3+} ions.

Oxidation of Tetramethyl-Substituted Aryles. All the above discussion makes it clear that the rate acceleration can by attained by increasing the concentration of M^{3+} by any means available to a chemical engineer, i.e., such as by ozone addition. Thus, it appeared possible to increase the oxidation rates of both relatively reactive toluene and xylenes as well as low-reactive durene,[23] 3,3′,4,4′-tetramethyldiphenylmethane, 3,3′,4,4′-tetramethylbenzophenone,[24] and naphthalic acid.[25] It should be noted that in the case of the latter

(18) Ovchinnikov, V. I.; Nazimok, V. F.; Simonova, T. A. *Proizvodstvo Tereftalevoi Kisloty i ee Dimetilovogo Efira* [The Manufacture of Terephthalic Acid and its Dimethyl Ester]; Khimiya Publishers: Moscow, 1982.

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(22) Bukharkina, T. V.; Grechishkina, O. S.; Digurov, N. G.; Kon'kov, I. I. *Org. Process Res. Dev.* **2002**, *6*, 394.

(23) Mulyashov, S. A.; Sirovskii, F. S.; Grechishkina, O. S. *Kinet. Katal.* **1989**, *30*, 1232−1235 (Chem. Abstr. **1990**, *112*, 177792).

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(25) Bukharkina, T. V.; Grechishkina, O. S.; Digurov, N. G.; Kostin, A. B.; German, M. I.; Chibisova, T. A.; Solodar', V. L. The method of manufacturing of naphthalene tetracarboxylic acid. USSR 1536767, 1990.

**Table 1.** Composition of the reaction mixture in TMDPM oxidation in acetic acid[a]

initial concentrations, mol·L^{-1}	τ, min	[Co^{3+}] × 10^3, mol·L^{-1}	[Br$^-$] × 10^2, mol·L^{-1}	absorbed oxygen concentration, mol·L^{-1}	
				experiment	theory
[Co(OAc)$_2$] = 0.035	30	4.87	1.20	1.28	1.33
[NaBr] = 0.035	60	6.46	0.80	1.96	2.10
[TMDPM] = 0.55	90	4.00	.93	2.41	2.50
	120	1.53	1.27	2.67	2.69
	150	1.47	1.33	2.92	2.88
	180	1.53	1.40	3.00	2.96
	210	1.60	1.60	3.21	3.18
	240	-	-	3.30	3.26
[Co(OAc)$_2$] = 0.035	30	5.54	1.33	1.80	1.72
[NaBr] = 0.035	60	2.67	1.87	2.65	2.65
[Mn(OAc)$_2$] = 4 × 10^{-4}	90	3.47	2.07	2.95	2.95
[TMDPM] = 0.55	120	4.14	2.00	3.36	3.36
	150	3.67	1.60	3.56	3.57
	180	3.40	1.13	3.77	3.70
[Co(OAc)$_2$] = 0.035	15	4.01	1.73	1.42	1.41
[NaBr] = 0.035	30	7.29	1.20	2.35	2.35
[Mn(OAc)$_2$] = 4 × 10^{-4}	45	5.43	1.40	2.92	2.96
[ZrOCl$_2$] = 7 × 10^{-4}	60	3.50	1.60	3.35	3.27
[TMDPM] = 0.55	75	3.57	1.53	3.56	3.46
	90	4.42	1.40	3.60	3.52
	105	5.38	1.07	3.77	3.68
	120	4.80	0.87	3.80	3.84

[a] Pressure 1 atm, temperature 105 °C, oxidant gas: oxygen, oxygen feed rate 0.5 L·min^{-1}

compounds the rate of oxidation of first methyl groups exceeds that of toluene due to a positive *I*-effect of ring alkyl substituents:
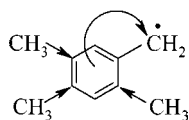
That results in the stabilisation of radical R$^\bullet$. The further oxidation occurs significantly more slowly as donor groups are transformed into acceptor ones:
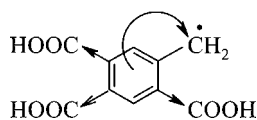
Analysis of the catalyst composition shows that M^{3+} concentration significantly falls with time. Both described effects result in the sharp decrease (virtually to zero) in the oxidation rate of the remaining methyl groups. One also observes the high product selectivity with respect to consecutive methyl groups. This decrease in reactivity of methyl groups toward the end of reaction makes it impossible to obtain tetracarboxylic acids under atmospheric pressure and temperatures not exceeding 105−115 °C. The commercial production of tetracarboxylic acids is accomplished using increased temperatures and pressures. The mixture of di- and tricarboxylic acids obtained under atmospheric pressure also can be further oxidised by potassium permanganate or other strong oxidants. However, the use of metal promoters allows obtaining tetracarboxylic acids at temperatures attainable under atmospheric pressure.

Let us consider the kinetics of 3,3′,4,4′-tetramethyldiphenylmethane (TMDPM) oxidation:
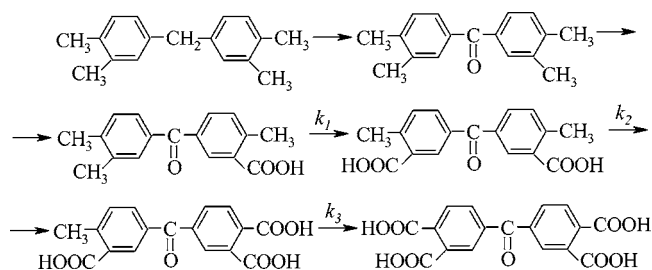

Figure 5 shows the curves of oxygen absorption in this system in the presence of cobalt bromide catalyst doped with manganese and zirconium.

The reaction conditions are listed in Table 1.

According to the amount of absorbed oxygen the available data correspond to the oxidation of intermediate mono-, di-, and tricarboxylic acids. The rate constants of these steps are designated on the scheme as k_1-k_3. The following system of differential equations describes both the consumption of intermediate acids and summary absorption of oxygen:

$$\frac{d[M]}{d\tau} = -k_1 Ct[M]$$

$$\frac{d[D]}{d\tau} = k_1 Ct[M] - k_2 Ct[D]$$

$$\frac{d[T]}{d\tau} = k_2 Ct[D] - k_3 Ct[T]$$

$$\frac{d[O_2]}{d\tau} = 1.5(k_1 Ct[M] + k_2 Ct[D] + k_3 Ct[T])$$

$$Ct = \frac{[Co^{3+}][Br^-]}{[Co^{2+}]} \qquad (VII)$$
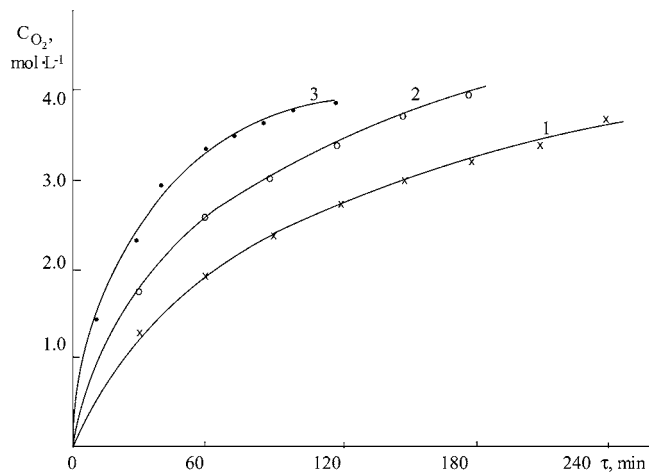
Figure 5. Consumption of oxygen in TMDPM oxidation. (1) Reaction in the presence of Co(OAc)$_2$ and NaBr. (2) Reaction in the presence of Co(OAc)$_2$, Mn(OAc)$_2$ and NaBr. (3) Reaction in the presence of Co(OAc)$_2$, Mn(OAc)$_2$ ZrOCl$_2$, and NaBr. Reaction conditions are listed in Table 1. Points − experiment, curves − least-squares fit.

Here [M] is the concentration of monocarboxylic acid, mol·L^{-1}; [D] is the concentration of dicarboxylic acid, mol·L^{-1}; [T] is the concentration of tricarboxylic acid, mol·L^{-1}; 1.5 is the stoichiometric reaction coefficient:

$$Ar-CH_3 + 1.5O_2 \rightarrow ArCOOH + H_2O$$
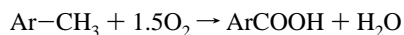
The value of Ct varied with time (see Table 1) and was approximated by a polynomial function for each single run. The constants k_1, k_2, and k_3 were obtained by a numeric solution of the system 7 with subsequent minimisation of the sum of the squares of residuals:

$$Ssq = \sum (y_{exp} - y_{calc})^2$$

where the sum is over all the experimental data, y_{exp} are the measured values of oxygen concentration, and y_{calc} are its simulated values. The following numerical values of rate constants common for all catalyst compositions were obtained (L·mol^{-1}·min^{-1}): $k_1 = 19 \pm 1$; $k_2 = 18 \pm 2$; $k_3 = 15 \pm 2$. The experimental and calculated values of oxygen concentration are listed in Table 1.

The satisfactory agreement of experimental and simulated data shows that the rate of oxidation of methyl groups in intermediate acids is determined by concentrations of catalytic metal in its highest oxidation state and bromide ion. The decrease in the values of rate constants of consecutive steps agrees with the deceleration of the process with the increase in the conversion degree. The same values of rate constants obtained for different catalytic compositions imply the existence of the same reaction mechanism in all cases,

Table 2. Production of tetracarboxylic acids from TMDPM and acenaphthalic acid

substrate	catalyst composition (mol·L^{-1})				yield of tetracarboxylic acids
	Co	Mn	KBr	Zr	
TMDPM	0.035	4×10^{-4}	0.035	7×10^{-4}	94
acenaphthalic acid	0.004	0.040	0.04	−	88

the role of Zr and Mn promoters being reduced to increasing the concentration of active catalytic species in the reaction mixture. Thus, these results allow us to state that the rate-limiting step in oxidation of TMDPM and its oxygen-containing derivatives is the transfer of an electron from the substrate to M^{3+} with chain length for peroxide radicals close to unity, which is typical for all benzylic oxidations.

Both cobalt and manganese oxidation catalysts have common and different features. Undoubtedly, they are both electron acceptors, but a lot of experimental data show that manganese salts effectively catalyse C−C bond destruction, whereas cobalt salts are more efficient in C−H bond oxidation. This is discussed in refs 5 and 22. This was further confirmed in pilot-plant and large-scale experiments on production of benzophenone tetracarboxylic acid from TMDPM and naphthalene tetracarboxylic acid from acenaphthalic acid. Both processes were run in the titanium equipment under 3−10 bar and at 120−140 °C using air as an oxidant gas in the presence of a metal bromide catalyst. In all cases the yield of tetracarboxylic acids was about 90%, but in the first case we used the cobalt-based catalyst doped by Mn and Zr, and in the second case, the manganese-based catalyst doped with cobalt (see Table 2).

Conclusions

This work has attempted to explain an enormous amount of accumulated experimental data in the framework of a single concept, thus resolving present discrepancies in various liquid-phase oxidation mechanisms. The fruitfulness of this approach is confirmed by our successes in obtaining diverse oxygen-containing products from various low reactive substrates. We do not pretend to create a completely new scheme of catalytic benzylic oxidation. We recognise that different researchers have already studied virtually all elementary and nonelementary steps discussed above, and obtained results were implemented in practice.