Mechanisms for Manganese(III) Oxidations with Alkenes

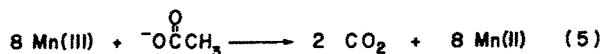William E. Fristad,* John R. Peterson, Andreas B. Ernst and Gordon B. Urbi
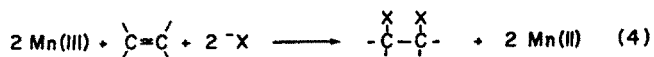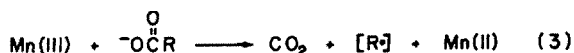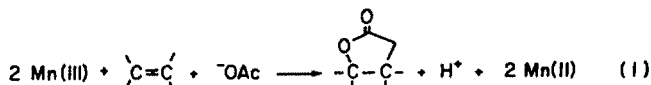
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Abstract: In the reaction of manganese(III) acetate with carboxylic acids and alkenes, three distinct processes have been identified which involve the alkene and two processes which are independent of alkene. A combination of product studies, rearrangements, dilution experiments and literature kinetic data allow the proposal of a unified mechanistic picture to describe these processes. Specifically, the role of α-H acidity of the carboxylic acid component, electron deficient radical additions, metal complexed organic radicals, and the importance of an oxo-centered manganese(III) triangle are discussed as they relate to the lactone annulation reaction. Single electron transfer oxidation of alkenes is described as a route toward 1,2-diacetates of alkenes within the 8.1–7.5 eV I.P. range. Three less common modes of Mn(III) reaction are discussed and compared with the two primary processes of lactone annulation and 1,2-diacetate formation.

Manganese(III) acetate has been employed as an oxidant for many years, yet a good understanding of the organic chemistry which it is capable of performing has remained elusive. The following discussion attempts to organize new and literature data in a way which will allow the proposal of a unified mechanistic picture which describes all the oxidation pathways available via manganese(III) as it pertains to acids and/or alkenes.

Five fundamental modes of reactions for manganese(III) are shown in eq 1–5. The lactone annulation process in eq 1 has been the most studied, and is arguably the most useful in that no

$$2\ Mn(III)\ +\ \underset{\diagup}{\overset{\diagdown}{C}}{=}\underset{\diagdown}{\overset{\diagup}{C}}\ +\ ^-OAc\ \longrightarrow\ -\underset{|}{C}-\underset{|}{C}-\ +\ H^+\ +\ 2\ Mn(II)\qquad(1)$$

$$2\ Mn(III)\ +\ \underset{\diagup}{\overset{\diagdown}{C}}{=}\underset{\diagdown}{\overset{\diagup}{C}}\ +\ 2\ ^-OAc\ \longrightarrow\ \overset{Ac\underset{\ }{O}\ \ \underset{\ }{O}Ac}{-\underset{|}{C}-\underset{|}{C}-}\ +\ 2\ Mn(II)\qquad(2)$$

$$Mn(III)\ +\ ^-O\overset{O}{\overset{||}{C}}R\ \longrightarrow\ CO_2\ +\ [R\cdot]\ +\ Mn(II)\qquad(3)$$

$$2\ Mn(III)\ +\ \underset{\diagup}{\overset{\diagdown}{C}}{=}\underset{\diagdown}{\overset{\diagup}{C}}\ +\ 2\ ^-X\ \longrightarrow\ \overset{X\ \ X}{-\underset{|}{C}-\underset{|}{C}-}\ +\ 2\ Mn(II)\qquad(4)$$

$$8\ Mn(III)\ +\ ^-O\overset{O}{\overset{||}{C}}CH_3\ \longrightarrow\ 2\ CO_2\ +\ 8\ Mn(II)\qquad(5)$$

other single-step procedure is known for this transformation. This reaction which was first discovered by Heiba et al.[1-3] and Bush and Finkbeiner,[4] has been elaborated by several groups.[5-7] Formation of 1,2-diacetates, as in eq 2, has been previously observed with stilbene.[8] The oxidative decarboxylation shown in eq 3 has been well studied, however as it will be seen, this process is relatively rare.[9] The difunctionalization of eq 4, while appearing to be similar to eq. 2, is mechanistically distinct.[10,11] Additionally, Mn(III) can oxidize acetic acid to CO_2 as shown in eq 5.
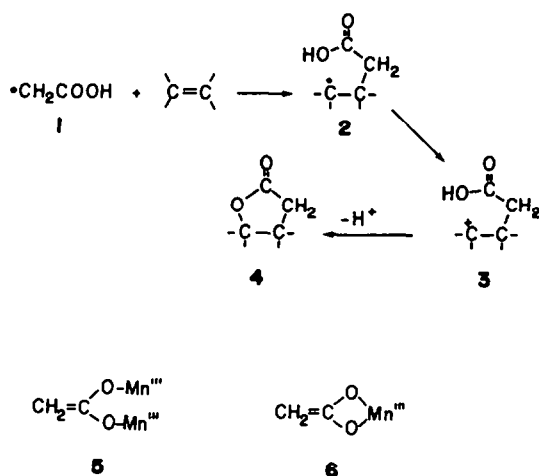
The major questions to be answered are what are the reactive species involved in all the above schemes, and how can each reaction type be controlled and predicted? This paper focuses on the processes of eqs 1, 2, and 5. However the features which control eqs 3 and 4 will be presented as well.

<div align="center">**Results and Discussion**</div>

Lactone Annulation (Eq 1)

Heiba, Dessau and Rodewald have proposed the mechanism in Scheme I.[2] Okano has proposed a similar path except with a direct oxidative conversion of 2 → 4. Bush and Finkbeiner did not propose an entire process, but suggested that a manganese complexed radical 5, or 6, was the key intermediate involved.[4]
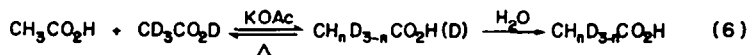
<div align="center">**Scheme I**</div>

$$\cdot CH_2COOH \; + \; \underset{1}{\diagup}C=C\underset{\diagdown}{\diagdown} \longrightarrow \underset{2}{-\overset{\cdot}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-}$$

(Scheme I shows intermediates **2**, **3**, **4** with the transformation 2 → 3 and 3 → 4 via $-H^+$, and manganese-complexed radical structures **5** and **6**)

The mechanism in Scheme I provided a starting point for the analysis of this reaction. However, there were two questions to be answered. (a) Do the intermediates remain complexed to the metal? (b) Does the multimetallic nature, an oxo-centered triangle,[12] of the Mn(III) oxidant impart a unique influence on the course of the reaction? The initial intermediate in the lactone annulation sequence proposed by Heiba et al. is a free radical. The evidence for a radical was strong, and quite logical as Mn(III) is a well-known one-electron oxidant. We previously have demonstrated that a radical intermediate similar to 2 was involved and have also shown that a carbocation similar to 3 was <u>not</u> involved.[7] The question to be settled, however, was still whether this radical, 2, and its precursor were free or metal complexed species?

We first sought to define the initially produced reactive intermediate and the method of its formation. We have shown previously that the inclusion of KOAc shortened the lactone annulation reaction time and increased the yield. The effect of base was more directly shown by the linear relationship of the log (rel. rate of oxidation) vs. $p\underline{K}_a$ of the α-H on a series of substituted acetic acids, $X-CH_2COOH$.[7] These data were consistent with rate determining α-H removal from either a complexed acetate or enolization of acetic acid solvent followed by oxidation to some type of an acetic acid radical species.

These two possible environments for α-proton removal were distinguished by two sets of kinetic experiments. In the first experiment, eq 6, H/D-exchange between HOAc/HOAc-d_4 was monitored by measuring the appearance of HOAc-d_2 over time by mass spectrometry. H/D-exchange was

$$CH_3CO_2H \; + \; CD_3CO_2D \; \underset{\Delta}{\overset{KOAc}{\rightleftharpoons}} \; CH_nD_{3-n}CO_2H(D) \; \xrightarrow{H_2O} \; CH_nD_{3-n}CO_2H \qquad (6)$$
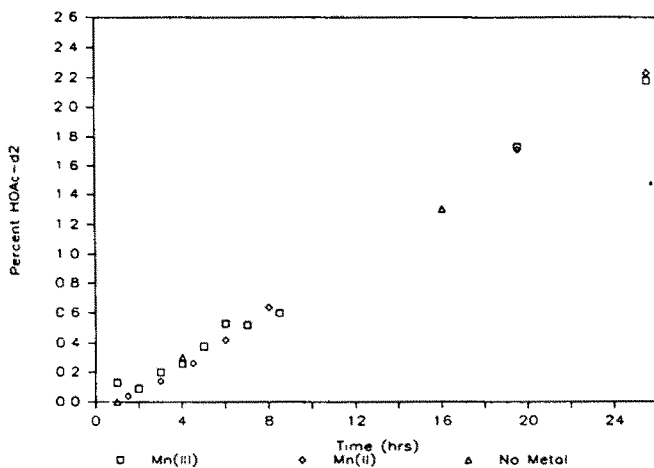
Figure 1. H/D exchange study with HOAc/HOAc-d₄.

measured with 0.5 M KOAc in HOAc/HOAc-d$_4$ at reflux in the presence of (a) no Mn, (b) 0.25 M
Mn(OAc)$_2$ and (c) 0.083 M [Mn$_3$O] and plotted in Figure 1. It was readily apparent that the metal
in either oxidation state had no effect on the observed H/D-exchange. This result necessitated
that either (a) sufficient enolization was occurring in the solvent to account for HOAc oxidation,
and hence lactone formation, or (b) the enolization of a complexed acetate which went on to
product was essentially irreversible, and that no H/D-exchange would be observed to be due to
[Mn$_3$O].

The latter two possibilities were distinguished by monitoring γ-lactone (product) formation
on the same time scale as H/D-exchange (enolization). If γ-lactone production exceeded total
solution H/D-exchange, then option (a) above would be untenable, and irreversible deprotonation
must have occurred in the formation of product. Figure 2 shows that this was exactly the result.
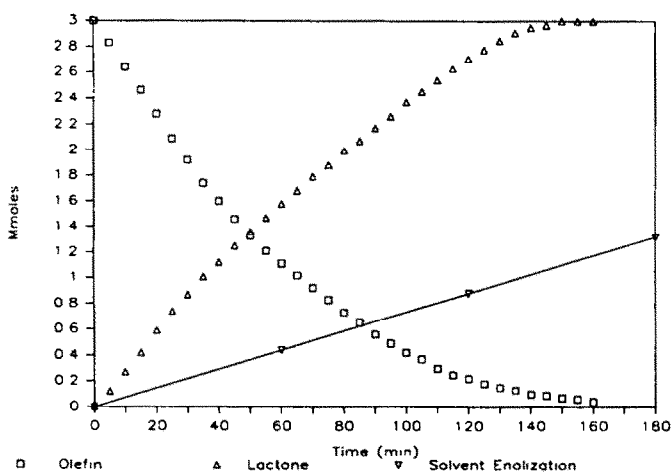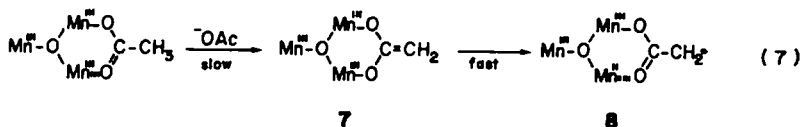

Figure 2. Lactone formation and solution enolization (H/D-exchange) versus time.

These results are compatible only with a rate determining step involving loss of an α-proton from
a complexed acetate, eq. 7. Deprotonation of a bridging acetate ligand would produce formally a

$$8 \quad \text{(eq 7)}$$

complexed acetic acid dianion, **7**. This very electron rich ligand should then suffer electron loss to the oxo-centered   metal system to give formally a $[Mn_3^{III,III,II}O]$ triangle bearing a bridging acetate radical centered on the α-carbon **8**.

Enolization of bidentate acetate ligands has not been previously proposed to our knowledge, but the strong enhancement of C-H acidity by metal complexation to organic molecules has been well established. Amino acids undergo facile α-H exchange and aldol-like condensation with aldehydes when chelated to Co^{3+} [13] Al^{3+} or Fe^{3+}. [14] No condensation occurred under similar conditions without the trivalent metal species. Cobalt(III) acetylacetone (acac) complexes also undergo rapid H/D-exchange at the methyl groups of the chelated acac when treated with base, and again the free ligand is stable to these conditions.[15] In the present case, coordination of an acetate in a bidentate fashion to two oxidized metal ions should greatly enhance the α-proton acidity. The stability of the complexed radical **8** in acetic acid solution relative to a free acetate/acetic acid radical would be anticipated. Gritten and Patmore have demonstrated that H-abstraction from the Me group of transition metal acac complexes by $\underline{t}$-BuO· was more rapid than H-abstraction from sodium acetylacetonate,[16] and the good coorelation between kinetics of H-atom abstraction and product radical stability is well known.[17]

Thus far the data indicate that a Mn complexed acetate radical was initially produced. Did this complexed radical add to an olefin to initiate lactone formation (eq 8) or did it produce free acetic acid or acetate radicals which initiated lactone formation (eq 9)? We favor eq 8 over eq 9 based on several experiments. Free acetic acid or acetate ester radicals are known to add to

$$(8)$$

$$(9)$$
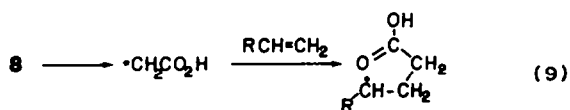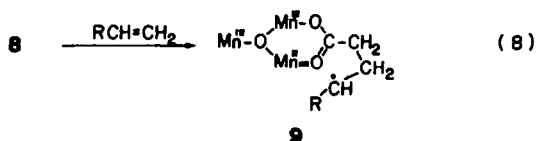
alkenes. However, the process is often not very efficient,[18] and dimerization can become the predominant product in the absence of an acceptor alkene.[19] We saw absolutely no succinic acid from reductive decomposition of $[Mn_3O]$ in glacial acetic acid in the absence of alkene.[20] The only product observed was CO_2 in quantitative yield based on the oxidant required to oxidize $CH_3COOH \rightarrow 2 CO_2 + 4H^+$.[7] The lack of dimer argued against the presence of free acetic acid or acetate radicals. Also under our usual reaction concentrations, the formation of free acetic acid radicals via H-abstraction after thermal decomposition of one mole equivalent of phenylazotriphenylmethane resulted in 67% recovery of octene as the alkene, and no decanoic acid was isolated.[21] Again, addition of free acetic acid radicals to alkenes under our reactant concentrations did not appear to be as efficient as required in the Mn(III) lactonization sequence.

The presence and nature of acetate adduct radical **9** was the next concern. The presence of a radical adduct of some type was demonstrated by us previously,[7] by observation of predominantly cyclized products with 1,6-heptadiene (eq 10).[22] The initial adduct radical, **9**, however, did not

have to go directly on to suffer oxidative lactonization as in path a of eq 11. There was the possibility of a simultaneous equilibrium with free adduct radical, 12, as illustrated by path b
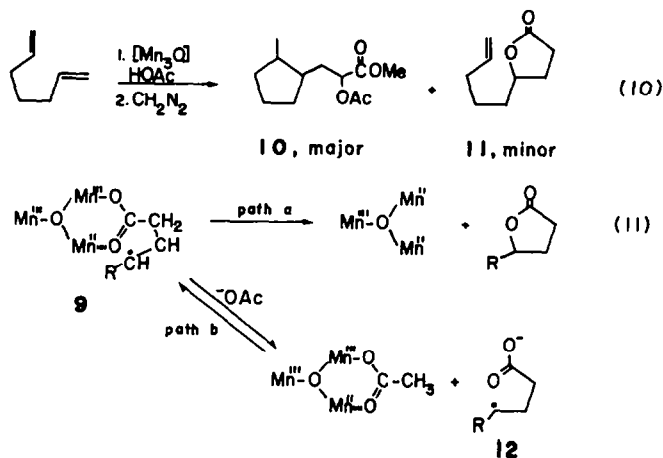
in eq 11. This equilibrium would be quite reasonable since the adduct radical 9 represented a very bulky bridging ligand, and ligand exchange within the [Mn$_3$O] species occurs very rapidly.[9,23]

This question could be settled by performing the internal radical cyclization of eq 10 at varying concentrations. If the adduct radical followed only path a (eq 11), dilution of the reaction mixture would not affect the ratio of cyclized/uncyclized (10/11) products because both processes would be intramolecular. Alternatively, if the radical dissociated away from [Mn$_3$O], path b, the product distribution was expected to change upon dilution and would result in more C-cyclized products (i.e., higher 10/11 ratio).[25] The dilution experiment of lactone annulation onto 1,6-heptadiene is illustrated in Figure 3. The observed ratios of 10/11 were 77% of that theoretically expected if all of the reaction followed path b. The free adduct radical 12 must therefore have been in equilibrium with the complexed adduct radical 9.
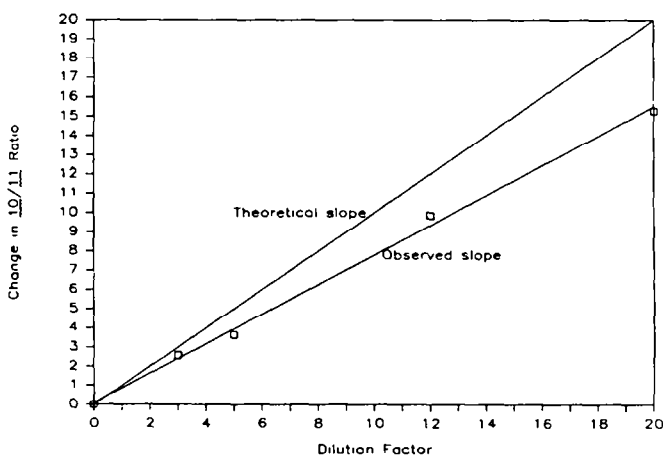
Figure 3. Dilution effect in the lactone annulation onto 1,6-heptadiene which shows the extent to which path b (eq 11) is followed. Slope = 0.77, Corr. Coeff. = 0.999.

The mechanistic conclusion from these results was that the lactone annulation process proceeded through eqs 7, 8 and 11. The important features of the reaction appear to be (1) the rate determining step involved α-H$^+$ loss, (2) a Mn complexed acetate radical was produced which (3)

added to an olefin to produce an adduct radical which could dissociate away from [Mn₃O].

1,2-Diacetate Formation (Eq 2)

In addition to lactone annulation, other products have been observed in the reaction of [Mn₃O] with some alkenes. In particular, electron rich alkenes tended to yield 1,2-diacetates. The products from a series of alkenes are shown in Table I. The major new products observed were vicinal diacetates or hydroxyacetates with lesser amounts of further oxidized materials (i.e. β-ketoacetates or aldehydes). Vinogradov et al have studied the oxidation of cis- and trans-stilbene and concluded that the diacetate products were a result of single electron transfer oxidation (SETO) of the alkene (eq 12).[8] This mechanistic conclusion was entirely compatible with our results. The present reaction conditions give substantially higher yields of SETO products, however, than the previous conditions.[8]

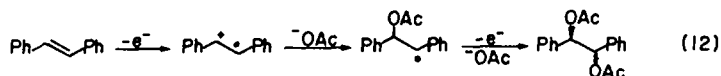$$Ph \diagdown Ph \xrightarrow{-e^-} Ph \cdot \diagdown Ph \xrightarrow{-OAc} Ph \diagdown_\bullet^{OAc} Ph \xrightarrow[-OAc]{-e^-} Ph \diagdown_{OAc}^{OAc} Ph \qquad (12)$$
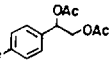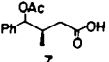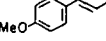
Table I. 1,2-Diacetate Formation via Single Electron Transfer Oxidation.

If 1,2-diacetate formation was in fact SETO, the fraction of SETO/LTO+SETO (LTO = ligand transfer oxidation, i.e., lactone) products should have increased with decreasing ionization potential (I.P.) of the alkene. The reported alkene ionization potentials vs SETO/LTO+SETO product ratio is shown in Table II. It was readily apparent that highly selective (>98%) lactone formation (LTO) was found with alkenes of I.P. > 8.25 eV and that highly selective (>94%) SETO was found with I.P. < 8.0 eV.[26] It should be noted that only a very small range of olefin I.P.s resulted in a mixture of SETO and LTO. The synthetically useful I.P. range for producing diacetates has a lower bound of approximately 7.5 eV. Below this value oxidative cleavage of the double bond predominated, and poor material balances were common. Thus the utilization of Mn(III) according to eq 2 was limited to a very narrow range of alkene I.P.

Table II. Alkene Ionization Potentials And Ligand Versus Olefin Oxidation Product Ratios

Alkene	IP (eV)	SETO/LTO+SETO Fraction		
		Acetic Acid	Methyl Malonate	Acetic Anhydride
n-butyl crotonate[a]	10.11	0.00		
1-hexene[b]	9.65	0.00	0.00	
1-decene[b]	9.59	0.00		
cis-4-octene[b]	9.03	0.00		
trans-4-octene[b]	9.01	0.00		
cyclohexene[c]	8.95	0.00	0.00	
norbornene[c]	8.11	0.00		
α-methylstyrene[d,e]	8.50	0.00		
1,1-diphenylethylene[d]	8.25	0.00		
4-methylstyrene[e]	8.20	0.06		
trans-β-methylstyrene[h]	8.17	0.22		
indene[f,g]	8.14	0.54	0.00	0.22
acenaphthalene[f]	8.02	0.61	0.00	0.11
trans-stilbene[d]	8.00	0.96		0.75
anethole[h]	7.68	1.00	0.00	
benzofuran[g]	7.37		0.00	

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The operation of eqs 1 and 2 illustrated that competitive oxidation of ligating acetates or unsaturated substrates was possible. It should be noted that the two processes can be manipulated by different variables. SETO depends on the alkene I.P., whereas LTO depends on the enolizability of the acetate ligand. Since ligand oxidation is related to its enolizability, other more readily

oxidizable ligands were investigated.

We have previously shown that monomethyl malonate is approximately 10^4 more reactive than acetic acid towards Mn(III) oxidation.[7] This great rate increase of LTO would be expected to diminish the amount of SETO experienced by electron rich alkenes. This was in fact born out, and in Table II it can be seen that only LTO products were characterized from all the alkenes studied. Thus a mechanistic crossover can be avoided altogether with a very strong C-H acid. Acetic anhydride had been shown to be only 250 times more easily oxidized than acetic acid.[7] This smaller rate enhancement translated into a small shift in the SETO/LTO+SETO ratio as would be expected.

The ability to shift the SETO/LTO ratio has useful synthetic consequences. Electron rich alkenes which do not undergo the lactone annulation reaction (eq 1) with acetic acid, can be satisfactorily converted to the lactone by the use of monomethyl malonate followed by decarboxylation (e.g. anethole → lactone, 72%).[27]

Carbon Dioxide Formation (Eq 5)

When Mn(III) acetate was reduced by refluxing in acetic acid in the absence of alkene, the sole oxidation product was CO_2. The oxidation sequence is proposed to follow eq 13, and the viability of this was shown by the quantitative conversion of acetoxyacetic acid and oxalic acid to CO_2.[7] This process occurred only when the complexed acetate radical 8, initially produced, had

$$CH_3CO_2H \xrightarrow{\text{2 Mn(III)}} AcOCH_2CO_2H \xrightarrow{\text{2 Mn(III)}} (AcO)_2CHCO_2H$$

$$2 \ CO_2 \xleftarrow{\text{2 Mn(III)}} HO_2CCO_2H \xleftarrow{\text{2 Mn(III)}} \qquad (13)$$

no alternative but to be further oxidized. This could be reasonably viewed as a LTO, which involved an acetate ligand transfer to produce a complexed acetoxyacetate. The increased α-H acidity of acetoxyacetate led to the rapid further oxidation of this ligand. The net formation of only CO_2 from this process explained why the use of a small excess of Mn(III) oxidant in the lactone annulation process resulted in such clean reactions. When all the alkene had been consumed, any remaining oxidant merely produced CO_2.

Decarboxylation (Eq 3)

Two fundamental modes of simple carboxylic acid oxidation are known. Oxidation at the α-carbon is relatively rare with transition metal oxidants, and only the Mn(III) oxidations described in eqs 1 and 5 appear to follow this path with any general synthetic utility.[28] Oxidation of an acid to a carboxy radical which decarboxylates to CO_2 and a C-centered organic radical is the more prevalent mode of oxidation and this path can be achieved by Pb(IV),[29] Ce(IV),[30] or Ag(II).[31,32] Mn(III) carboxylate salts have also been shown to decarboxylate;[9] however, for this reaction mode to become dominant there must be no α-H. In this case the lower energy pathway to oxidation represented by eq 7 is unattainable, and decarboxylation is the only viable alternative. It should be noticed that the two routes to CO_2 formation, eqs 5 and 3, follow fundamentally different mechanisms.

We propose that the structure of the metal carboxylate species plays an important role in differentiating the two basic courses of oxidation. Complexes in which the carboxylate is mono-dentate or bound to only one oxidized metal we would predict to undergo decarboxylation. Pb(OAc)$_4$ decarboxylates acids and is known to have a single central metal atom surrounded by four acetate ligands.[33,34] Complexes in which the carboxylate is firmly held in a bidentate, bridging fashion between two oxidized metals can undergo enolization and we would predict oxidation at the α-carbon. This process will only occur when the acidity of the α-H is greatly enhanced by the carboxylate being bound to two oxidized metals. Mn(III) acetate is an oxo-centered triangle with six such bridging acetates. The multimetallic nature of this oxidant maintains the strong bridging interactions. Ce(IV) acetate which is known to undergo both α-oxidation and decarboxyla-tion has a crystal structure which is intermediate between Mn(III) and Pb(IV). Ce(OAc)$_4$ is an infinite chain of metal atoms held together by four bridging acetates between each pair of metal atoms.[35,36] Thus the acetate ligands are bidentate and bridging in the solid state, however in acetic acid solution the polymeric chains are presumably broken very easily. The net result would be a mixture of bridging and nonbridging ligands which is consistent with both oxidation mecha-nisms being observed.

Double Anion Addition (Eq 4)

The last remaining mode of Mn(III) reactivity with alkenes could be termed double anion addition. This could be the result of one-electron oxidation and addition of two simple anions, X$^-$, to an alkene. This process can only be observed when X$^-$ is more easily oxidized than acetate or the alkene. We have already demonstrated this mode with X=Cl$^-$ [10] and N$_3^-$ [11] and are currently trying to extend the series of acceptable X$^-$. A similar overall process is known to occur with numerous transition metal halides, although the exact mechanisms do vary (i.e. CuCl$_2$,[37] CrO$_2$Cl$_2$,[38-41] MoCl$_5$,[38,42] VOCl$_3$,[43] SbCl$_3$,[44] ReOCl$_3$,[38] CrOCl$_3$,[38] MnOCl$_3$,[38] TiCl$_3$,[45] AuCl$_3$,[46] SeCl$_4$,[44] VCl$_4$[44]).

This mode of oxidation was relatively simple to control. Either an acceptable ligand X$^-$ was available for double addition or it was not. The ligand X$^-$ need not, however, have been added externally, if a suitable internal source was available. For example, the normal lactone annula-tion process ensued when 1-octene was heated with chloroacetic acid and [Mn$_3$O], eq 14. However when KOAc was added, S$_N$2 displacement rapidly produced chloride ion and the only produce isolated was the dichloride, eq 15.[10]

$$[Mn_3O] + C_6H_{13}CH=CH_2 + ClCH_2CO_2H \xrightarrow[\Delta]{neat} \text{(lactone with } C_6H_{13}) \quad (14)$$

$$\xrightarrow[\Delta]{KOAc} C_6H_{13}\overset{Cl}{\underset{}{C}}H-\overset{Cl}{\underset{}{C}}H_2 \quad (15)$$

Conclusions

Five different modes of Mn(III) oxidation of a carboxylic acid/alkene mixture are available. While each reaction involves a number of mechanistic features, the primary controlling features are (1) the presence or absence and the acidity of an α-H on the carboxylic acid, (2) the presence or absence and the ionization potential of the alkene in the system, and (3) the presence or absence of another easily oxidized ligand which could undergo double addition to the alkene.

Data have been presented which show that the lactone annulation process has a kinetic isotope

effect, and that the loss of an α–H and conversion to lactone is faster than solution enolization. These facts are consistent with enolization of a bridging acetate ligand. The initial complexed acetate radical did not appear to dissociate to free acetate radicals whereas after addition to an alkene the adduct alkyl radical was shown to dissociate from the [Mn_3O] complex. A complete description of the SETO pathway was presented along with a synthetic alternative to avoid this process and still observe lactone annulation.

Experimental Section

Melting points were determined with an Electrothermal apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a varian HFT-80 (80-MHz) or a Nicolet 300-MHz instrument. Chemical shifts are reported in parts per million relative to internal $(CH_3)_4Si$ in $CDCl_3$ unless specified otherwise. Mass spectra were obtained with an AE1 Kratos MS-30 (electron impact) or a Finnigan 4000 (chemical ionization) spectrometer. Infrared spectra were obtained on a Beckman 4250 spectrophotometer. Gas chromatography was performed with a Varian 3700 model equipped with FID's and a Hewlett-Packard 3390A integrator. The columns used were 5% Carbowax 20M on 100/120 mesh Chromosorb W, 0.3 cm x 6 m or 10% SF-96 on 80/100 mesh Chromosorb W, 0.3 cm x 6 m. Products were isolated by medium pressure liquid chromatography (FMI pump, silica gel column, refractive index detector, Altex model 156).

Starting alkenes were commercially obtained. Manganese(III) acetate hydrate was prepared by literature methods.[13,32] References after the following alkenes from Table I refer to literature spectral data which matched all the products in Table I: 1,1-diphenylethylene,[47] p-methylstyrene,[48] β-methylstyrene,[49] indene,[50] acenaphthalene,[51] stilbene,[47c,52] and anethole.[53]

Determination Of The Alkene Independence In The Manganese(III) Acetate Lactonization. Dodecane (100 μL, 0.44 mmol), potassium acetate (0.98 g, 10.0 mmol), and glacial acetic acid (20 mL) were heated to reflux in a 50-mL round-bottom flask equipped with a reflux condenser before adding [Mn_3O] hydrate (1.34 g, 1.67 mmol) and 1-decene (5.85 g, 40.0 mmol). Aliquots (1 mL) were withdrawn every 15 minutes diluted with water (5 mL), and extracted with pentane (3 mL). Lactone formation was monitored by gas chromatography and was found to maximize between 135-150 minutes. An identical reaction except for the 1-decene concentration (0.29 g, 2.0 mmol) was determined to reach a maximum lactone yield between 155-170 minutes.

Determination Of The Extent Of Solvent H/D-Exchange During Manganese(III) Acetate Reduction In Acetic Acid. A 25-mL round-bottom flask was charged with [Mn_3O] hydrate (670 mg, 0.83 mmol), potassium acetate (491 mg, 5.00 mmol), and glacial acetic acid (4.32 mL, 75.50 mmol). The mixture was heated to 110-115 °C to effect a dark brown solution before adding D_4-acetic acid (99.5 atom % D, 4.96 mL, 88.00 mmol). This solution was stirred for 1 min before removal of the t_o sample (0.3 mL). The reaction vessel was equipped with a reflux condenser and immersed into a preheated oil bath at 125 °C to maintain a steady reflux. Aliquots (0.3 mL) were regularly withdrawn, quenched with 0.1N hydrochloric acid (4.0 mL), and extracted with diethyl ether (2 x 8 mL). The combined extracts were dried ($MgSO_4$) and evaporated to afford an acetic acid sample.

The acetic acid samples were analyzed for H/D-exchange by 20 eV low resolution electron impact mass spectroscopy. The samples were injected (3 μL) at 7-8 x 10^{-6} torr source pressure, a cage temperature of 200 °C, and a gas probe temperature of 150 °C. The percent of H/D exchange was obtained by computerized calculation for masses 60-63 in the spectrum obtained by background substraction from an average t_x spectrum. Mass 62 (HOAc-d_2) was chosen in preference to 61 (HOAc-d_1) as the best indicator because random m+1 ions in the mass spectrum of carboxylic acids did not allow for accurate differentiation of HOAc-d_1 and H_2OAc^+. Results are presented in Table III.

Table III. Acetic Acid H/D—Exchange Experiments: Percent CD_2HCO_2H

	Percent CD_2HCO_2H With Different Metal Species		
Time (h)	[Mn$_3$O]	Mn(OAc)$_2\cdot$4H$_2$O	No Metal
1.0	0.13		0.00
1.15		0.04	
2.0	0.09		
3.0	0.20	0.14	
4.0	0.26		0.30
4.5		0.26	
5.0	0.38		
6.0	0.53	0.42	
7.0	0.52		
8.0		0.64	
8.5	0.60		
16.0			1.30
19.5	1.73	1.71	
25.5	2.18	2.23	

Determination Of The Extent Of H/D—Exchange In An Acetic Acid Solution Of Manganese(II) Acetate. A 25-mL round—bottom flask was charged with manganous acetate tetrahydrate (613 mg, 2.50 mmol), potassium acetate (491 mg, 5.00 mmol), and glacial acetic acid (4.47 mL, 78.00 mmol). The mixture was warmed to 110-115 $^{\circ}$C to effect solution before adding D$_4$-acetic acid (99.5 atom % D, 4.96 mL, 88.00 mmol). This solution was stirred for 1 min before removal of the t$_o$ sample. The flask was equipped with a reflux condenser and immersed into a preheated oil bath at 125 $^{\circ}$C to maintain a steady reflux. Aliquots (0.3 mL) were withdrawn and subjected to the workup and mass spectral analysis described above. Results were presented in Table II.

Determination Of The Extent Of H/D—Exchange In An Acetic Acid Solution. Glacial acetic acid (3.78 mL, 66.00 mmol) and potassium acetate (393 mg, 4.00 mmol) were heated to 110-115 $^{\circ}$C in a 15-mL round—bottom flask before adding D$_4$-acetic acid (99.5 atom % D, 3.95 mL, 70.00 mmol). After stirring for 1 min and removal of the t$_o$ sample, the flask was equipped with a reflux condenser and immersed into a preheated oil bath at 125 $^{\circ}$C. Aliquots (0.3 mLO were withdrawn and subjected to the workup and mass spectral analysis described above. Results are presented in Table II.

Lactone Annulation Onto 1-Decene: Lactone Formation And Alkene Consumption Versus Time. A dark brown solution of [Mn$_3$O] hydrate (2.01 g, 2.50 mmol), potassium acetate (1.47 g, 15.00 mmol), dodecane (100 μL, 0.44 mmol), and glacial acetic acid (30.0 mL) was effected by heating the mixture to reflux in a 50-mL round-bottom flask equipped with a reflux condenser. 1-Decene (421 mg, 3.00 mmol) was added to this solution within 1 min of reaching reflux. Aliquots (0.5 mL) were withdrawn every 5 min and quenched with water (4 mL). The lactone and 1-decene were extracted with pentane (3 mL) and analyzed by gas chromatography. Results are presented in Figure 2.

Dilution Effects Upon The Lactone Annulation Onto 1,6-Heptadiene. A 15-mL round-bottom flask equipped with a reflux condenser was charged with [Mn$_3$O] hydrate (536 mg, 0.67 mmol), potassium acetate 9491 mg, 5.00 mmol), 1,6-heptadiene (96 mg, 1.00 mmol), and glacial acetic acid (5.00 mL). The dark brown solution turned colorless after 130 minutes at reflux. The reaction mixture was allowed to cool, diluted with water (45 mL), and extracted with diethyl ether (3 x 15 mL). The combined extracts were washed with water (2 x 15 mL), evaporated, and esterified with ethereal diazomethane. The 10/11 ratio was determined to be 5.37 by gas chromatography.

In other experiments, the above reaction was diluted three, five, twelve, and twenty fold with glacial acetic acid. After workup and esterification the **10/11** ratios were found to be 13.76, 19.57, 54.30, and 80.84 respectively.

General Synthetic Procedure For Alkene Oxidation With Manganese(III) Acetate. A 100-mL round-bottom flask equipped with a reflux condenser was charged with the alkene (5.00 mmol), [Mn$_3$O] hydrate (4.17 mmol), potassium acetate (25.0 mmol), and glacial acetic acid (50 mL). The mixture was refluxed until the dark brown color disappeared, cooled, diluted with water (200 mL), extracted with diethyl ether (3 x 50 mL). The combined ether extracts were washed with a saturated sodium bicarbonate solution (2 x 50 mLO, dried (MgSO$_4$), and chromatographed.

The sodium bicarbonate washes were acidified with 6N hydrochloric acid and extracted with diethyl ether (3 x 25 mL). The combined extracts were washed with water (3 x 25 mL), dried (MgSO$_4$), evaporated, and esterified with ethereal diazomethane. The esters were purified by chromatography. The fraction of total SETO/LTO+SETO products are summaried in Table III.

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