Mechanism of Oxidation of Saturated Hydrocarbons by Cobalt(III), Manganese(III), and Lead(IV) Trifluoroacetates

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Oxidation of adamantane with lead tetra-acetate or manganese triacetate in acetic acid gives poor yields of primary products (based on the oxidant). However, oxidation of adamantane by manganese(III), cobalt(III), or lead(IV) acetates in trifluoroacetic acid gives high yields of 1-adamantyl trifluoroacetate as primary product. Other hydrocarbons are also oxidised by attack at a bridgehead carbon–hydrogen bond. Thus bicyclo[3.3.1]nonane with Pb^{4+} gives the trifluoroacetate of bicyclo[3.3.1]nonan-1-ol in 74% yield and similarly diamantane gives the two bridgehead trifluoroacetates in 93% yield. The generality of these oxidations is discussed. A product analysis shows that in contrast to anodic oxidation which gives products of fragmentation with substituted adamantanes, oxidation by Pb^{IV}, Co^{III}, or Mn^{III} leads only to products by attack at a bridgehead tertiary carbon–hydrogen bond. In further contrast, anodic oxidation of 1,3,5-trimethyl-7-t-butyladamantane (30) leads to fragmentation products in high yield, but oxidation of tetrasubstituted adamantanes such as (30) by metal salts is very sluggish and gives, in low yield, complex product mixtures. Comparison of the electrochemical oxidations with those by Co^{III}, Mn^{III}, and Pb^{IV} suggests that, in contrast to current views, oxidation of saturated hydrocarbons by metal salts does not proceed *via* cation radical intermediates. A mechanism proceeding by localised attack at a carbon–hydrogen bond is suggested. Adamantane with potassium permanganate in trifluoroacetic acid gives protoadamantanone (37) in 30% yield based on hydrocarbon consumed. A novel mechanism for this oxidation is tentatively proposed.

OXIDATION of saturated hydrocarbons by metal salts in solution is a subject of industrial interest.[1-7] In aqueous solution, reaction with, for example, cyclohexane is either sluggish, or with more powerful oxidants, yields of primary products of oxidation are low, because of secondary oxidation processes. Mechanistic studies are therefore difficult because of the substantial or dominant contribution of the secondary processes. Similarly, in acetic acid where cobalt(III),[1,3,4] manganese(III),[4] and lead (IV)[8] are sufficiently powerful to oxidise saturated hydrocarbons, mechanistic studies are greatly complicated by secondary processes. In particular, acetates formed as primary products have reactivities comparable with those of the initial hydrocarbons and, more critically in most previous studies, the choice of hydrocarbon substrate has permitted elimination from cationic intermediates to give olefins as primary products. These are substantially more reactive [4,9] than the initial saturated hydrocarbons and complicate any kinetic analysis.

Here we describe mechanistic studies which seek to avoid the above complications. By choice of adamantanes or other bridged hydrocarbons as substrates, only primary products of substitution are obtained; elimination is precluded on the basis of Bredt's Rule. By using trifluoroacetic acid, monotrifluoroacetates are obtained as reaction products; these are substantially less reactive than the initial hydrocarbons and so mechanistic studies are facilitated by observation typically of $>90\%$ of primary oxidation products. Synthetic aspects of these reactions have already been described.[10]

Little is known concerning the mechanism of oxidation of saturated hydrocarbons by metal salts. Essentially, three mechanisms require consideration: (*a*) an initial homolytic attack on a carbon–hydrogen bond leading directly to an alkyl radical subsequently oxidised to products, (*b*) an electrophilic attack upon a carbon–hydrogen bond leading to a carbocation either by effective hydride abstraction, or by collapse of an initial transition state, or intermediate, perhaps of triangular geometry,[11] to give a carbon–metal bond subsequently undergoing solvolysis, and (*c*) an initial electron transfer to give a cation radical intermediate which would collapse to give, by proton loss, an alkyl radical.

Studies with cobalt(III) and saturated hydrocarbons both in acetic acid [1-4] and in trifluoroacetic acid [6] have been described. Hanotier and his co-workers [1] have observed that cobalt(III) oxidises saturated hydrocarbons in a process accelerated by strong organic or inorganic acids to give in acetic acid under nitrogen acetates as products but under oxygen ketones as products. As attack at secondary was favoured over attack at tertiary carbon atoms, some steric hindrance between oxidant and substrate was suggested. The nature of the initial transition state or intermediate was not elucidated, but from kinetic evidence the following scheme was proposed:

$$\mathrm{RH} + \mathrm{Co^{III}} \rightleftharpoons \mathrm{R^{\bullet}} + \mathrm{Co^{II}}$$
$$\mathrm{R^{\bullet}} + \mathrm{Co^{III}} \longrightarrow \text{products}$$

Onopchenko and Schulz [2-4] have studied the oxidation of cyclohexane and n-butane in acetic acid by cobalt(III). In both cases it was concluded that alkyl radicals are obtained in a two-step process, implying cation radical intermediates:

$$\mathrm{RH} + \mathrm{Co^{III}} \rightleftharpoons \mathrm{RH^{\bullet+}} + \mathrm{Co^{II}}$$
$$\mathrm{RH^{\bullet+}} \longrightarrow \mathrm{R^{\bullet}} + \mathrm{H^{+}}$$

However, measurement of kinetic isotope effects [3] for cyclohexane *versus* [$^2H_{12}$]cyclohexane showed a negligible isotope effect, and it was concluded that collapse of

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[1] J. Hanotier, P. Camerman, M. Hanotier-Bridoux, and P. de Radzitzky, *J.C.S. Perkin II*, 1972, 2247.

[2] A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.*, 1973, **38**, 909.

[3] A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.*, 1973, **38**, 3729.

[4] A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.*, 1975, **40**, 3338.

[5] T. A. Cooper and W. A. Waters, *J. Chem. Soc. (B)*, 1967, 687.

[6] R. Tang and J. K. Kochi, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3845.

[7] E. I. Heiba, R. M. Dessau, and W. J. Koehl, *J. Amer. Chem. Soc.*, 1969, **91**, 6830.

[8] W. H. W. Lunn, *J. Chem. Soc. (C)*, 1970, 2124.

[9] C. E. H. Bawn and J. A. Sharp, *J. Chem. Soc.*, 1957, 1866; R. M. Dessau, *J. Amer. Chem. Soc.*, 1970, **92**, 6358; J. R. Gilmore and J. M. Mellor, *J. Chem. Soc. (C)*, 1971, 2355.

[10] S. R. Jones and J. M. Mellor, *J.C.S. Perkin I*, in the press.

[11] G. A. Olah, *Angew. Chem. Internat. Edn.*, 1973, **12**, 173.

any cation radical intermediate is fast relative to formation of the ion radical. Onopchenko and Schulz suggest formation of cation radicals by electron transfer from a carbon–hydrogen σ-bond and state that the importance of electron transfer will depend on the ionisation potential of the hydrocarbon substrate. Results obtained by photoelectron spectroscopy [12] indicate that the electron most readily removed from most saturated hydrocarbons is from a HOMO of mainly σ_{CC} character. A simple electron transfer mechanism of type (*c*) above, and having analogy with the established electron-transfer mechanism operative with alkylaromatic compounds,[13] would be expected to proceed by removal of an electron from the HOMO. Hence in the studies of oxidation of saturated hydrocarbons by cobalt(III) there is some evidence that attack is localised at a carbon–hydrogen bond, yet a mechanism of electron transfer involving cation radical intermediates has been proposed.[2,4,6]

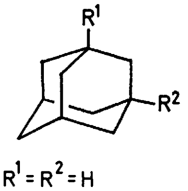
Manganese(III) acetate is a less powerful oxidant than cobalt(III) acetate, and at the more elevated temperatures required for reaction with saturated hydrocarbons a number of homolytic mechanisms become possible. However, it has been concluded [4] that in oxidation of cyclohexane by manganese(III) acetate in acetic acid, electron transfer, implying cation radical formation, is a probable contributing process.

The reaction of lead(IV) with saturated hydrocarbons has been little studied. In acetic acid lead tetra-acetate oxidises adamantane,[8] but the mechanism has not been elucidated. Lead tetra-acetate in trifluoroacetic acid and lead tetrakistrifluoroacetate are more powerful oxidants,[14] but until our recent study [10] of the synthetic interest reactions with hydrocarbons had not been studied.

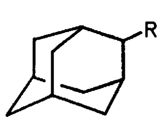
With reference to the mechanisms (*a*)—(*c*) proposed above for cobalt and manganese, an electron-transfer mechanism of type (*c*) has been proposed.[2,4,6] These proposals are founded on kinetic data involving complex and little understood processes and on product studies in reactions where yields of primary oxidation products are not high. We have studied the oxidation of various bridged hydrocarbons with cobalt(III), manganese(III), and lead(IV), where product yields are high. In a previous paper [15] we describe the electrochemical behaviour of a series of substituted adamantanes and, in particular, the competitive fragmentation and deprotonation from anodically derived cation radicals. In this product study, from the absence of fragmentation products which might originate from a cation radical we conclude that an electron-transfer mechanism of type (*c*), leading to cation radical intermediates, is unimportant with these inorganic oxidants in reactions with saturated hydrocarbons.

RESULTS AND DISCUSSION

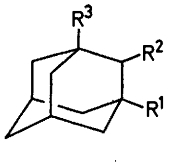
We now describe the oxidation of bridged hydrocarbons by salts of Co^{III}, Mn^{III}, Pb^{IV}, and Mn^{VII} (MnO_4^-),



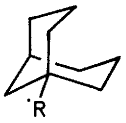
(1) $R^1=R^2=H$
(2) $R^1=H$, $R^2=OAc$
(4) $R^1=H$, $R^2=O_2C\cdot CF_3$
(5) $R^1=H$, $R^2=OH$
(8) $R^1=H$, $R^2=Cl$
(19) $R^1=H$, $R^2=Bu^t$
(20) $R^1=O_2C\cdot CF_3$, $R^2=Bu^t$
(21) $R^1=OH$, $R^2=Bu^t$
(22) $R^1=Cl$, $R^2=Bu^t$



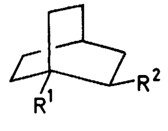
(3) $R=OAc$
(6) $R=OH$
(7) $R=O_2C\cdot CF_3$



(9) $R^1=R^2=R^3=H$
(11) $R^1=O_2C\cdot CF_3$, $R^2=R^3=H$
(12) $R^1=R^2=H$, $R^3=O_2C\cdot CF_3$
(13) $R^1=R^3=H$, $R^2=O_2C\cdot CF_3$



(10) $R=H$
(14) $R=O_2C\cdot CF_3$



(15) $R^1=O_2C\cdot CF_3$, $R^2=H$
(16) $R^1=H$, $R^2=O_2C\cdot CF_3$

first in acetic acid, and then in trifluoroacetic acid, and finally we compare the results with those of anodic oxidation.[15]

Preparatively, the reaction of adamantane (1) with either manganese(III) acetate (dihydrate) or lead tetra-acetate in acetic acid is of little value. Mixtures of products are obtained, as the initially formed monoacetates have a reactivity comparable with that of the starting hydrocarbon. Our results (Table 1) show that with lead tetra-acetate, in spite of the earlier claim [8] that 1-adamantyl acetate (2) is the only monosubstituted product, adamantane gives both 1-adamantyl acetate (2) and 2-adamantyl acetate (3). Diacetates are also obtained. As reaction only proceeds at elevated

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[12] W. Schmidt, *Tetrahedron*, 1973, **29**, 2129.

[13] P. J. Andrulis, M. J. S. Dewar, T. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, 1966, **88**, 5473; E. I. Heiba, R. M. Dessau, and W. J. Koehl, *ibid.*, 1970, **92**, 412; J. K. Kochi, R. T. Tang, and T. Bernath, *ibid.*, 1973, **95**, 7114; W. S. Trahanovsky and D. W. Brixius, *ibid.*, p. 6778.

[14] J. R. Campbell, J. R. Kalman, J. T. Pinhey, and S. Sternhell, *Tetrahedron Letters*, 1972, 1763; H. C. Bell, J. R. Kalman, J. T. Pinhey, and S. Sternhell, *ibid.*, 1974, 857; R. E. Partch, *J. Amer. Chem. Soc.*, 1967, **89**, 3662; D. Westphal and E. Zviral, *Monatsh.*, 1975, **106**, 679; R. E. Partch, *J. Amer. Chem. Soc.*, 1976, **89**, 3662.

[15] G. J. Edwards, S. R. Jones, and J. M. Mellor, *J.C.S. Perkin II*, 1976, preceding paper.

temperatures, at which the decomposition of lead tetra-acetate by homolytic pathways is well established,[16] the probability of such processes participating in the oxidation of adamantane is high.

With manganese(III) acetate, as shown in Table 1, the reaction of adamantane in acetic acid in the absence of added strong acids is slow. When activated by added mineral acids reaction gives poor yields of primary products. However, loss of oxidant is rapid even in the absence of added hydrocarbon. Competitive side reactions preclude a satisfactory mechanistic analysis of these hydrocarbon oxidations in acetic acid. Such activation could arise from formation of a new complex in solution of higher electron affinity or higher electrophilicity or by catalysis of a homolytic process.

Further results (Table 3) established that relative to adamantane, diamantane (9) is more reactive.

With cobalt(III) acetate similar results were obtained although reactions were generally faster. In particular, addition of sulphuric acid led to marked activation. Whereas the reaction of adamantane with cobalt(III) in the absence of added acid requires many hours at 75 °C, in the presence of sulphuric acid reaction requires minutes at room temperature. Again a number of mechanistic possibilities might explain this result.

TABLE 1

Oxidation of adamantane by manganese(III) acetate dihydrate and $Pb(OAc)_4$ in acetic acid

	No. of mmol [a]					
Oxidant	Oxidant	Adamantane	Temp. (°C)	Reaction time (h)	Activator	% Oxidant consumed
$Mn(OAc)_3,2H_2O$	2	2	50	4	M-H_2SO_4	86
$Mn(OAc)_3,2H_2O$	2	0	50	4	M-H_2SO_4	33
$Mn(OAc)_3,2H_2O$	2	2	50	7	M-$HClO_4$	99
$Mn(OAc)_3,2H_2O$	2	2	50	7	M-$NaClO_4$	4
$Mn(OAc)_3,2H_2O$	2	2	50	14	M-H_2SO_4	100 [b]
$Pb(OAc)_4$ [c]	20	20	Reflux	1	None	100 [d]

[a] Reactions performed in acetic acid (10 ml). [b] Products are 1-adamantyl acetate (24%), adamantan-1-ol (17%), and products of longer retention time (yields based on oxidant consumed). [c] Reaction performed in acetic acid (12 ml). [d] Products are monoacetates (57%) and diacetates (24%); g.l.c. analysis shows the monoacetate fraction to be a mixture of 1-adamantyl acetate and 2-adamantyl acetate in the ratio 4.5 : 1 and the diacetate fraction to be a mixture of four isomers.

TABLE 2

Oxidation of adamantane by manganese(III) acetate dihydrate in trifluoroacetic acid–dichloromethane

No. of mmol					% Adamantane lost (based on oxidant)	Products and yields (%) based on adamantane consumed					
Oxidant	Adamantane	Temp. (°C)	Reaction time (h) [a]	Activator		(5)	(6)	(4)	(7)	(8)	Others
0	2	75	48	None	0						
2	0	75	48	None		28% Mn^{III} consumed					
2	2	75	48	None	88	7	0	80	6	0	0
2	2	100	8	None	90	9	0	73	8	0	0
4	1	75	41	None		12	1	74		0	6
2	2	20	24	$h\nu$	104	7	0	53	10	0	2
2	2	50	40	0.5M-$HClO_4$	91	8	0.3	80	2	0.3	0
2	2	50	96 [b]	0.5M-H_2SO_4		10	1	62	12	12	2 [c]

[a] Time required for loss of brown colour of Mn^{III}, in trifluoroacetic acid (5 ml) and dichloromethane (5 ml). [b] Much Mn^{III} unchanged. [c] Ratios of products.

In trifluoroacetic acid, in contrast, simpler product distributions are obtained and the reactions have preparative value. Preliminary experiments with adamantane and manganese(III) acetate are shown in Table 2. Dichloromethane was added as a co-solvent to maintain a homogeneous solution, but did not otherwise affect the reaction. In the absence of any mineral acid conversion of adamantane into 1-adamantyl trifluoroacetate (4) at 75 °C in a sealed tube was efficient. To effect reaction, either an elevated temperature (75 °C), at which background loss of oxidant in the absence of added hydrocarbon was considerable, or irradiation was required. However, as in related oxidations, activation could be achieved by addition of mineral acid. Such activation could arise from formation of a new complex

The reaction of adamantane with lead(IV) in trifluoroacetic acid is particularly efficient. The results in Table 3 show that loss of lead(IV) in the absence of added hydrocarbons is slow, and that acyclic hydrocarbons (3-methylhexane) and monocyclic hydrocarbons (methylcyclohexane) are unreactive relative to adamantane, but that other bridged hydrocarbons are converted into monotrifluoroacetates in high yield. In these reactions of preparative value we have already noted [10] that purified lead tetra-acetate is relatively unreactive but that activation is readily achieved by addition of a metal halide—most efficiently a metal chloride, *e.g.* lithium chloride.

In the reactions described in Tables 2 and 3 a number of features are common. In no case is the identity of the oxidant clear. Complex equilibria involving solvent, added ions, and possible polymeric species associated with several inorganic atoms preclude further comment.

[16] J. B. Aylward, *Quart. Rev.*, 1971, **25**, 407; D. J. Rawlinson and A. Sosnovsky, *Synthesis*, 1973, 567; R. O. C. Norman and C. B. Thomas, *J. Chem. Soc.* (*C*), 1970, 421.

The observed acceleration of reaction by added acid or metal salts might be achieved in many ways. One is the possibility recognised earlier that a saturated hydrocarbon might be oxidised by electron transfer to give a cation radical. To obtain evidence for this pathway a spectroscopic search for the intermediate, or product, or kinetic studies might be envisaged. In attacking the similar problem in the study of oxidations of alkylaromatic compounds by metal salts, substantial evidence [13] for the electron-transfer pathway was established by observation of spectra associated with cation radicals. A similar study with cation radicals derived from saturated hydrocarbons is more difficult, and in view of their anticipated short lifetimes no such study has been made.

TABLE 3

Oxidation of hydrocarbons by metal salts in Trifluoroacetic acid–dichloromethane

Hydrocarbon	Oxidant	Temp. (°C)	Reaction time (h)	% Hydrocarbon lost based on oxidant	Products and yields (%) based on hydrocarbon consumed
Diamantane [a] (9)	$Mn(OAc)_3$	75	28	98	(11) 47.5, (12) 40, (13) 4.5 [d]
Bicyclo[3.3.1]nonane [a] (10)	$Mn(OAc)_3$	75	48	40	(14) 24
Adamantane [b] (1)	$Co(OAc)_3$	75	84	80	(4) 67, (7) 5.5, (5) 4, unknowns 6
Adamantane [b] (1)	$Co(OAc)_3$ [e]	20	0.05	68	(4) 80, (7) 1, (8) 4, (5) 2.5, unknowns 4.5
Diamantane [b] (9)	$Co(OAc)_3$	75	8	89	(11) 51, (12) 42, (13) 2 [d]
Bicyclo[3.3.1]nonane [b] (10)	$Co(OAc)_3$	75	48	45	(14) 24
Adamantane [c] (1)	$Pb(OAc)_4$	20	1 [f]	90	(4) 94
Adamantane (1)	$Pb(OAc)_4$ [g]	20	2 [f]	87	(4) 98
Adamantane (1)	$Pb(OAc)_4$ [h]	20	0.25	70	(4) 85
Diamantane [c] (9)	$Pb(OAc)_4$	20	0.5 [f]	84	(11) 80, (12) 9
Diamantane (9)	$Pb(OAc)_4$ [g]	20	0.5	93	(11) 81, (12) 14
Bicyclo[3.3.1]nonane [c] (10)	$Pb(OAc)_4$	20	1.75 [f]	90	(14) 74
Bicyclo[2.2.2]octane [c]	$Pb(OAc)_4$	Reflux	8 [f]	18	(15) 45, (16) 26, (17) 24, (18) 5 [d,i]
Methylcyclohexane [c]	$Pb(OAc)_4$	20	40	*j*	No products observed; 38% Pb^{IV} consumed
3-Methylhexane [c]	$Pb(OAc)_4$	20	40	*j*	No products observed; 38% Pb^{IV} consumed
None	$Pb(OAc)_4$	20	40		12% Pb^{IV} consumed

[a] 2 mmol each of hydrocarbon and of oxidant used. [b] 1 mmol each of hydrocarbon and of oxidant used. [c] 2 mmol of hydrocarbon and 1 mmol of oxidant used. [d] Products analysed after hydrolysis. [e] Activated by 0.5M-H_2SO_4. [f] Time required for complete loss of lead(IV). [g] Activated by 0.05M-LiCl. [h] Activated by 0.05M-LiBr. [i] Ratios of products. [j] Not recorded.

TABLE 4

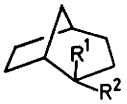
Oxidation of substituted adamantanes by oxidants in trifluoroacetic acid

Hydrocarbon	Oxidant	Temp. (°C)	Reaction time (h)	% Hydrogen lost based on oxidant	Products and yields (%) based on hydrocarbon consumed
(19)	$Pb(OAc)_4$	20	1.5	80	(20), 86; (21), 1
(19)	$Co(OAc)_3$ [a]	20	0.03	89	(20), 61; (21), 5; (22), 1; (1), 0.3; (4), 0.7
(19)	Anode	20		.	(1), 21; (4), 26; (20), 36
(23)	$Pb(OAc)_4$	20	1.5	82 [b]	(26), 0.1; (27), 0.1; (28), 0; (24), 68; (25), 11
(23)	$Co(OAc)_3$	75	6	89 [b]	(24), 76; (25), 8
(23)	$Mn(OAc)_3$	75	6	100 [b]	(24), 77; (25), 8; (26), 1.5; (27), 1.5
(23)	$Co(OAc)_3$ [a]	20	0.25	85 [b]	(26), 4; (27), 8; (28), 1; (24), 61; (25), 1; (29), 6.5
(30)	$Co(OAc)_3$	75	168	*c*	
(30)	$Mn(OAc)_3$	75	15	*c*	(31), 2 [d]; (32), 5 [d]
(30)	$Pb(OAc)_4$	20	48	*e*	(31), 4 [d]; (32), 4 [d]
(30)	$Co(OAc)_3$ [a]	20	0.25	*c*	(32), 15 [d]
(30)	Anode	20		*c*	(32), 90
(33)	$Co(OAc)_3$	75	168	*f*	
(33)	$Mn(OAc)_3$	75	96	20	(31), 8 [d]; (32), 8 [d]
(33)	$Co(OAc)_3$ [a]	20	0.25		(32), 26 [d]; (34), 0.5 [d]

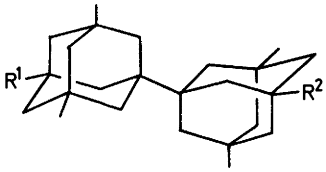
[a] Activated by 0.5M-H_2SO_4. [b] Products analysed after hydrolysis. [c] Complex product mixture formed in very low yield based on oxidant consumed. [d] Based on oxidant consumed: major products. [e] Complex product mixture (>13 peaks by g.l.c.) formed in very poor yield based on oxidant consumed. [f] No products observed by g.l.c.

Kinetic studies were not undertaken owing to the ambiguity in the identity of the oxidant. Rather we have further examined these reactions in product studies designed to show any formation of cation radical intermediates. To discriminate amongst the original mechanisms (*a*)—(*c*) it is essential to choose a reaction in which, if a cation radical were formed, it would give products only derivable from the cation radical. We have previously [15] described the anodic oxidation of substituted adamantanes. 1-t-Butyladamantane (19) gives in trifluoroacetic acid 1-adamantyl trifluoroacetate (4) by fragmentation of the anodically derived cation radical, and also some of the trifluoroacetate of 3-t-butyladamantan-1-ol (20). The fragmentation product is a product recognisably derived from the cation radical. In Table 4 are described experiments with a number of substituted adamantanes in which the electrochemical results are compared with those in which metal oxidants were used. In reactions with metal salts we have looked for fragmentation products among the products of reaction with the view that absence of such products would indicate the lack of formation of a discrete cation radical intermediate. Electron transfer giving cation radicals by oxidation of hydrocarbons by these metal oxidants could then be discounted. Correspondingly, formation of fragmentation products would imply cation radical intermediates.

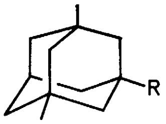
With 1-t-butyladamantane (**19**), extensive anodic fragmentation is observed, yet with the metal oxidants fragmentation is unimportant. Again with the tetramethylbiadamantane (**23**), where oxidation at a tertiary carbon–hydrogen bond or fragmentation is possible, with metal salts oxidation at the tertiary carbon–hydrogen bond is observed almost exclusively. There seem two likely explanations of these results: (*a*) cation radicals are generated in the oxidations by metal salts by electron transfer but their behaviour in an association complex with an inorganic counterion is very different from their behaviour on an electrode; or (*b*) no cation radicals are generated in the oxidations by the metal salts. We favour the second explanation, noting the following points. Electrochemically similar results[15] are obtained in acetonitrile and in trifluoroacetic acid. Solvent does not affect the dominance of the fragmentation pathway. If competing processes at the stage of the cation radical are critical in the oxidation by metal salts then prevention of attack at a tertiary carbon–hydrogen bond might be expected to lead to fragmentation. Anodic oxidation of 1,3,5,7-tetra-substituted adamantanes, for example (**30**), proceeds as expected, to give in high yield, by fragmentation, the trifluoroacetate (**32**). However, oxidation of either (**30**) or (**33**) by metal salts proves very difficult. In all cases the reaction is exceptionally slow, products are complex, and fragmentation is, except for one case, unimportant. In view of the ease of fragmentation of the ion radicals of (**30**) or (**33**), as observed electrochemically, these results suggest that oxidations by metal salts do not give the ion radicals. The possibility that steric effects prevent electron transfer between a tetrasubstituted adamantane and a metal ion is unlikely. No such steric effect is observed at the electrode, and similar effects in electron transfer reactions are not of great importance. In the most appropriate analogy to our fragmentations that we can find, it has been shown[17] that oxidation of the tetramethylbibenzyl (**35**) proceeds at a rate comparable to that of bibenzyl (**36**) by oxidants that give cation radicals. Fragmentation proceeds from the cation radical of either (**35**) or (**36**).



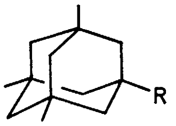
(17) $R^1 = O_2C{\cdot}CF_3$, $R^2 = H$
(18) $R^1 = H$, $R^2 = O_2C{\cdot}CF_3$



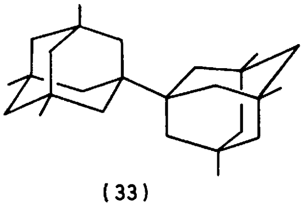
(23) $R^1 = R^2 = H$
(24) $R^1 = O_2C{\cdot}CF_3$, $R^2 = H$
(25) $R^1 = R^2 = O_2C{\cdot}CF_3$
(29) $R^1 = H$, $R^2 = Cl$



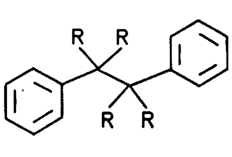
(26) R = H
(27) $R = O_2C{\cdot}CF_3$
(28) R = Cl



(30) $R = Bu^t$
(31) R = H
(32) $R = O_2C{\cdot}CF_3$
(34) R = Cl



(33)



(35) R = Me
(36) R = H

The one case where some fragmentation is observed in our study concerns the reaction with cobalt(III) acetate in trifluoroacetic acid, accelerated by addition of sulphuric acid. In these reactions conversion into products at room temperature is rapid, *e.g.* with adamantane the reaction is complete in minutes. The rate of reaction of the tetrasubstituted compound (**23**) is comparable to that of (**33**), which has tertiary carbon–hydrogen bonds. Further, the only products, (**32**) and (**34**), were obtained by fragmentation. However, the mass balance in this reaction was unsatisfactory and any mechanistic conclusion must be tentative.

In view of the low ionisation potential[12] of the hydrocarbons (HOMO) under consideration [adamantane 9.20 eV; the biadamantane (**23**) 8.50 eV] we have studied cases for which a mechanism of one-electron-transfer should be the most likely. Our tentative conclusion that this electron transfer is not important for oxidations with cobalt(III) in the absence of added sulphuric acid, with manganese(III), and with lead(IV) implies that previous reports[2-4,6] of such mechanisms with hydrocarbons of much higher ionisation potential, *e.g.* cyclohexane (10.32 eV) are probably incorrect. Again electron transfer in acetic acid is much less probable than in trifluoroacetic acid.

There remain from our study two unanswered questions. In the cases described in which we conclude that oxidation proceeding at a carbon–hydrogen bond does not involve the intermediacy of a cation radical, no mechanism has been proposed. Our results justify no further comment although we favour a mechanism involving electrophilic attack[11] at a carbon–hydrogen bond. The second problem concerns the mechanism of

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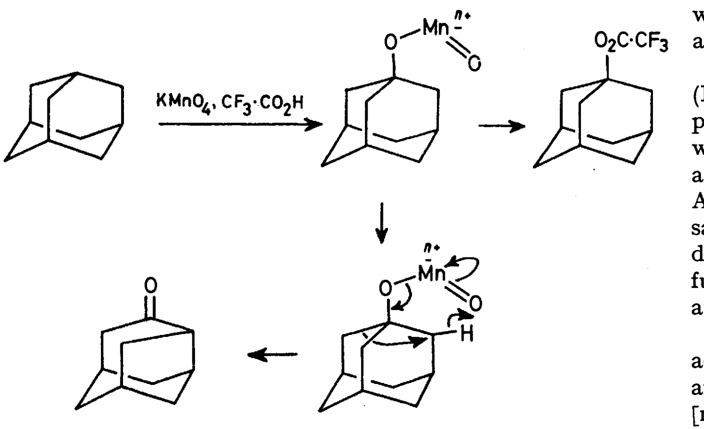
[17] P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, 1971, **93**, 4536.

oxidation with cobalt(III) activated by sulphuric acid. We are unable to discriminate between a mechanism of one-electron-transfer leading to a cation radical and hence fragmentation products, and a mechanism involving electrophilic attack [11] upon a carbon–carbon bond.

In the course of our preliminary study it was found that potassium permanganate reacted with adamantane in trifluoroacetic acid to give protoadamantanone (37) (*ca.* 30%). Although other preparations of protoadamantanone [8] are superior, this reaction has some mechanistic interest. Adamantan-1- and -2-ol and adamantanone under these conditions gave no protoadamantanone (37). A mechanism is therefore required that avoids these hypothetical intermediates. We suggest that shown in the Scheme.



(37)

SCHEME

EXPERIMENTAL

General experimental details are as reported previously.[10] Preparations of hydrocarbons and of oxidation products are described elsewhere.[10,15]

Preparation and Reactions of Managnese(III) *Acetate*.—Manganese(III) acetate dihydrate was prepared by a modification of Christiansen's procedure.[18] Analysis by iodimetric titration indicated that the manganese(III) content was 20.58 ± 0.05% [calc. for Mn(OAc)$_3$, 2 H$_2$O : 20.50%]. Analysis for manganese(III) during an oxidation was performed by adding a sample to an excess of standard iron(II) solution (Mohr's salt) in M-sulphuric acid and titrating against a standard cerium(IV) solution (Ferroin indicator). Oxidation reactions were followed visually by the change from the brown manganese(III) colour to colourless manganese(II).

All oxidations in trifluoroacetic acid were performed as follows. Manganese(III) acetate dihydrate (536 mg, 2 mmol) and the hydrocarbon (2 mmol) were heated in a sealed tube at 75 °C with trifluoroacetic acid (5 ml) and dichloromethane (5 ml). The solution was then poured into ether (50 ml) and ice–water (50 ml) containing sodium hydroxide (2 g). The aqueous layer was further extracted with ether (50 ml) and the combined ethereal extracts were washed with sodium hydrogen carbonate solution and water, and dried. The yields were measured by g.l.c. analysis (internal standards).

The same procedure was used when an acid catalyst was added, and when acetic acid was used in place of trifluoroacetic acid. The products were analysed by g.l.c.–mass spectrometric comparison with authentic compounds.

Preparation and Reactions of Cobalt(III) *Acetate*.—Solid cobalt(III) acetate was prepared by the method of Dessau *et al.*[13] Analysis showed that the cobalt(III) content was 15.7% by weight. Analysis for cobalt(III) during an oxidation was performed by pouring a sample into an excess of iron(II) solution (Mohr's salt) in M-sulphuric acid and titrating against standard dichromate solution (sodium diphenylaminesulphonate as indicator). The oxidation reactions were followed visually by the change in colour from green cobalt(III) to red cobalt(II).

All oxidations were performed by a procedure similar to that described for manganese(III). Cobalt(III) acetate (378 mg; 1 mequiv. Co^{III}) and the hydrocarbon (1 mmol) in trifluoroacetic acid (2.5 ml) and dichloromethane (2.5 ml) were heated to 75 °C in a sealed tube. The solution was worked up and the products were analysed as described above.

Reactions of Lead Tetra-acetate.—Lead tetra-acetate (B.D.H. Laboratory Reagent) moist with acetic acid was partially dried by filtration under nitrogen. The sample was further dried over potassium hydroxide under vacuum and stored in a desiccator over phosphorus pentaoxide. Analysis for lead(IV) showed 95—100% purity for various samples. In oxidations allowance was made for the differences in lead content. Lead tetra-acetate could be further purified by recrystallisation from acetic acid–acetic anhydride.

In oxidations a hydrocarbon (2 mmol) and lead tetra-acetate (1 mmol) were stirred in trifluoroacetic acid (5 ml) and dichloromethane (5 ml) in the dark. Reaction rate [measured by removal of samples, which were quenched with an excess of potassium iodide solution (5%) and titrated with standard thiosulphate solution under anaerobic conditions (Vitex indicator)] varied in a manner dependent upon the history of the lead tetra-acetate used. As fully described elsewhere,[10] the reaction is accelerated by halide ion and most efficiently by chloride ion. In Tables 2 and 3 results are given for both lead(IV) which has not been further purified by recrystallisation and contains traces of chloride ion, and lead(IV) purified by recrystallisation and then activated by addition of the appropriate halide (solution 0.05M in either LiCl or LiBr). Purified lead tetra-acetate reacts very slowly with these hydrocarbons. Work-up and analysis of reaction mixtures were performed as described for the manganese(III) oxidations.

Adamantane (I) (2.75 g) and lead tetra-acetate (9.73 g) were heated under reflux in acetic acid (12 ml) for 1 h; a negative starch–iodide test then showed the absence of Pb^{IV}. The mixture was worked up as described above. Removal of the solvent and preparative t.l.c. (silica gel; 10% ether in light petroleum as eluant) gave 3 fractions: adamantane (0.74 g), a mixture of 1- and 2-adamantyl acetates (1.64 g; ratio 4.5 : 1) identified by comparison of n.m.r. spectra and g.l.c. retention times with those of authentic samples, and a mixture of at least four diacetates (0.94 g). Hydrolysis of this diacetate fraction in aqueous 5% sodium hydroxide gave a mixture of at least four diols (g.l.c.). The major component was isolated by fractional recrystallisation (CH$_2$Cl$_2$) and identified as adamantane-1,3-diol, m.p. 320—323° (lit.,[19] 325—330°), δ[(CD$_3$)$_2$SO] 1.30—1.56 (12 H, m),

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[18] O. T. Christiansen, *Z. anorg. Chem.*, 1901, **27**, 325.

[19] H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, 1968, **24**, 5369.

2.12br (2 H, s), and 4.37 (2 H, s) *m/e* 168 (26%), 112 (10), 111 (100), 95 (21), 94 (6), 43 (20), 41 (14), and 39 (9). Structures of the minor diol components were not established.

Oxidation of Adamantane with Potassium Permanganate.—Potassium permanganate (200 mg) and adamantane (272 mg) were heated under reflux in dichloromethane (5 ml) and trifluoroacetic acid (5 ml) for 30 min. The solution was worked up as described for manganese(III) oxidations. After removal of the solvent, the crude products were hydrolysed with 10% sodium hydroxide (10 ml) at room temperature. Preparative t.l.c. on silica gel (1 : 1 ether–light petroleum as eluant) gave adamantane (169 mg), a ketone fraction (34 mg, 30% based on consumed hydrocarbon), and an alcohol fraction (36 mg, 31% based on consumed hydrocarbon). The ketone fraction was a mixture of two isomers (ratio 10 : 1) and the alcohol fraction a mixture of 1- and 2-adamantan-1- and -2-ols (12 : 1). The major ketone was purified by preparative g.l.c. and identified by comparison with an authentic sample as protoadamantanone (37), m.p. 208—210° (lit.,[8] 210—212°). Under similar conditions adamantan-1- and -2-ol and adamantanone afforded no protoadamantanone.

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