QUARTERLY REVIEWS

MECHANISMS OF OXIDATION BY COMPOUNDS OF CHROMIUM AND MANGANESE

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Introduction

The Essential Problems.—Chromic acid and potassium permanganate have been regularly used as oxidising agents for well over a century both in volumetric analysis and in degradative organic chemistry, yet even today knowledge of the mechanisms of their reactions is only fragmentary. In organic chemistry few of their reactions are specific, or even quantitative.

The overall valency changes which the respective anions undergo when they are reduced to stable products (eqns. 1—3) cannot occur except by

$$(HCrO_4)^- \xrightarrow{\text{Acid}} Cr^{3+} \qquad (3\text{-electron change}) \quad . \; . \; . \quad (1)$$

$$(MnO_4)^- \xrightarrow[\text{acid}]{\text{Strong}} Mn^{2+} \qquad (5\text{-electron change}) \quad . \; . \; . \quad (2)$$

$$(MnO_4)^- \xrightarrow[\text{alkaline}]{\text{Neutral or}} MnO_2 \qquad (3\text{-electron change}) \quad . \; . \; . \quad (3)$$

a series of consecutive changes because quantum restrictions prevent more than a pair of electrons associated with any one atom from ever behaving in an identical manner. Again the electron transfers involved in these complete reductions of chromate and permanganate are not potentiometrically reversible; the redox potentials listed for them are spurious figures calculated from free-energy changes [$\Delta E = (RT/nF)\Delta G$].

Many studies of isotopically labelled ions [1] have shown that electron transfer between ions of similar atomic structure is fast and reversible (*e.g.*, eqns. 4, 5),[2, 3] whereas reactions clearly involving the rupture of covalencies (*e.g.*, eqn. 6)[4] are generally slow, for with them appreciable activation energy is needed to reach the transition state.

$$^*Mn^{2+} + Mn^{3+} \rightleftharpoons Mn^{2+} + {}^*Mn^{3+} \quad . \quad (4)$$

$$(^*MnO_4)^- + (MnO_4)^{2-} \rightleftharpoons (^*MnO_4)^{2-} + (MnO_4)^- \quad . \quad (5)$$

$$(H^{18}O)^- + (MnO_3{-}OH)^- \rightleftharpoons (H^{18}O{-}MnO_3)^- + (OH)^- \quad . \quad (6)$$

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[1] C. B. Amphlett, *Quart. Rev.*, 1953, **8**, 219; W. F. Libby, *J. Phys. Chem.*, 1952, **56**, 863; D. R. Stranks and R. G. Wilkins, *Chem. Rev.*, 1957, **57**, 743.

[2] A. W. Adamson, *ibid.*, 1951, **55**, 93; M. J. Polissar, *J. Amer. Chem. Soc.*, 1936, **58**, 1372; J. A. Happe and D. S. Martin, *ibid.*, 1955, **77**, 4212.

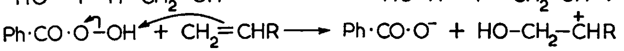
[3] W. F. Libby, *ibid.*, 1940, **62**, 1930; J. C. Sheppard and A. C. Wahl, *ibid.*, 1953, **75**, 5133; 1957, **79**, 1020.

[4] M. C. R. Symons, *J.*, 1954, 3676.

Both electron transfer and covalency breaking processes are involved in the sequence of consecutive reactions involved in the stripping of oxygen from anions of type $(MO_4)^{n-}$ to give cations M^{m+} and it is now clear that the order in which the successive valency changes occur may differ from reaction to reaction according to the nature of the substrate that is attacked. From mechanistic studies of these changes there is, for the inorganic chemist, much to be learned concerning the structure and stability of chromium and manganese ions of intermediate valency level. Here the organic chemist can give valuable help, because today a considerable body of evidence concerning the ways in which organic compounds of different structural type tend to oxidise can be used to forecast probable reaction paths. Again, only by the use of organic compounds can one readily select oxidations that are slow enough for kinetic study and the possible detection of transient intermediates. This Review will therefore deal mainly with oxidations of organic substances.

Routes of Oxidation of Organic Compounds.—Below pyrolysis temperatures, oxidations are all bimolecular, or concerted, reactions. These can be classed as (*a*) 1-electron transfers (*e.g.*, 7; Fenton's reaction), or (*b*) 2-electron transfers of type S_E2 (*e.g.*, 8; epoxidation of an olefin).

$$HO\cdot + H-CH_2-OH \longrightarrow HO-H + \cdot CH_2-OH \quad . \quad . (7)$$



$$Ph\cdot CO\cdot O-OH + CH_2{=}CHR \longrightarrow Ph\cdot CO\cdot O^- + HO-CH_2-\overset{+}{C}HR \quad . \quad (8)$$

Processes (*a*) necessarily generate free radicals and often lead to chain reactions, with very distinctive kinetics, whilst processes (*b*) involve transient ions and are rarely chain reactions. Thus kinetic studies can often be discriminatory, but may be difficult to interpret when consecutive reactions are involved. Detection of a free radical by a characteristic reaction, *e.g.*, catalysis of vinyl polymerisation or direct combination with oxygen, is diagnostic of (*a*), whilst recognition of reactions typical of carbonium ions, *e.g.*, 1:2-molecular rearrangement, can point to (*b*).

Recognising that favoured reactions take the path requiring the least activation energy, one can, taking solvent conditions into account, forecast the route of oxidation from structural considerations. 1-Electron transfers become exothermic and require little activation energy only if the immediately resulting radical is a resonance-stabilised system. Related studies with several 1-electron abstractors (Ce^{4+}, $\{Fe(CN)_6\}^{3-}$, Cu^{2+}, etc.), of which the complexed ions of Mn^{III} are typical (p. 296), indicate the general sequence of oxidisability to be: 1:4 or 1:2-dihydric phenols > monohydric phenols > aldehydes and ketones (as enols), 1:2-glycols > allylic systems, ethers > monohydric alcohols, olefins.

Olefins, other than allylic systems, are not easily attacked, except by very powerful oxidisers such as Co^{3+},[5] especially if of catio-enoid type (C:C·C:O or C:C·CN), since radical-ions, $=\overset{+}{C}-\overset{\bullet}{C}=$, are entities of high energy level. Olefins however are easily attacked by electrophilic reagents of type (*b*), *e.g.*, peracids or halogens, particularly in solvents such as water

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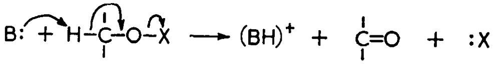
[5] C. E. H. Bawn and J. A. Sharp, *J.*, 1957, 1866.

which can co-ordinate and then react with carbonium ions. Again removal of hydrogen from H–C is greatly facilitated by a base-catalysed, concerted 2-electron movement (9, cf. p. 284), whereas homolytic hydrogen abstraction



$$B: + H-\overset{|}{\underset{|}{C}}-O-X \longrightarrow (BH)^+ + \overset{|}{\underset{|}{C}}=O + :X \quad . \; . \; . \; . \; . (9)$$

(*e.g.*, 7) needs free radicals of very high energy, such as hydroxyl or atomic chlorine, unless the resulting organic radical has a high degree of resonance stabilisation, as in Aryl–C•.

By inductive reasoning along these lines, tentative oxidation mechanisms can now be inferred with a sufficient degree of success to aid considerably the interpretation of experimental results. However, much of the published evidence for propounding the foregoing generalisations comes from studies of oxidation by means of chromium or manganese compounds that are described more explicitly in the following paragraphs.

Valency states of chromium and manganese

Since oxidations by chromic acid and permanganate involve the eventual stripping of oxygen from anions, $(CrO_4)^{2-}$, $(MnO_4)^-$, to give cations, Cr^{3+}, Mn^{2+}, it is important to know when, and how, this removal of oxygen occurs. To this end it is helpful to consider structurally similar ions of the whole transition group Ti, V, Cr, Mn, Fe, Co. With manganese and vanadium each valency between that of a stable (XO_4) anion and a cation X^{2+} is known, and hence suggestions can be made concerning possible structures and properties of chromium ions of the intermediate valencies Cr^{V} and Cr^{IV}, it being recognised that the stability and structure of any ion in solution depends on the acidity or alkalinity of its environment.

The Ions of Manganese.—The purple permanganate ion $(MnO_4)^-$ is symmetrically tetrahedral and the anion of a strong acid. In solution it does not exchange oxygen with water,[4] but in strong alkali it slowly decomposes to manganate and oxygen.

$$4(MnO_4)^- + 4(OH)^- \longrightarrow 4(MnO_4)^{2-} + 2H_2O + O_2 \quad . \; . \; . (10)$$

$$(MnO_4)^- + (OH)^- \rightleftharpoons (MnO_4)^{2-} + \cdot OH \quad . \; . \; . \; . (11)$$

$$\cdot OH + (OH)^- \rightleftharpoons (\cdot O)^- + H_2O \quad . \; . \; . \; . \; . \; (12)$$

$$(MnO_4)^- + (OH)^- + (\cdot O)^- \rightleftharpoons (MnO_4)^{2-} + (HO_2)^- \text{ etc.} \quad . (13)$$

Symons,[4] using $H_2{}^{18}O$, has shown that in equation (10) all the oxygen comes from the water and therefore favours a reaction sequence commencing with the electron transfer (11), first postulated by Stamm,[6] and continuing with further electron-transfer oxidation of dissociated hydroxyl $(\cdot O)^-$, through $HO_2\cdot$ and $(O_2\cdot)^-$, to oxygen (eqns. 11—13). Following Stamm, he has suggested that oxidations brought about by *strongly* alkaline permanganate are really effected by hydroxyl radicals, or their

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[6] H. Stamm, "Newer Methods of Volumetric Analysis", trans. by Oesper, Van Nostrand & Co. Inc., New York, 1938.

more active anions $(\cdot O)^-$. However this simple theory cannot suffice for those permanganate oxidations that can be effected rapidly in weak alkali.[7]

The green manganate ion, $(MnO_4)^{2-}$, is stable only in alkali, for solutions less than N in hydroxyl ion slowly disproportionate (eqn. 14). The sky-blue

$$3(MnO_4)^{2-} + 4H^+ \longrightarrow 2(MnO_4)^- + MnO_2 + 2H_2O \quad . \quad (14)$$

$$(MnO_4)^{2-} + (OH)^- \rightleftharpoons (MnO_4)^{3-} + \cdot OH \quad . \; . \; . \; . \quad (15)$$

hypomanganate ion, $(MnO_4)^{3-}$, obtainable as a sparingly-soluble salt, K_3MnO_4, by fusing together at red heat potassium permanganate and sodium hydroxide,[8, 9] is even less stable and disproportionates similarly in solutions less than 8N in hydroxyl ion. Reaction (15) can explain its route of formation.

Whereas dilute aqueous (alkaline) solutions of hypomanganate can be prepared, manganites, X_2MnO_3 (with Mn^{IV}) and permanganites $XMnO_3$ (with Mn^V) are known only as solid products of alkali fusion of manganese dioxide. However there is now strong evidence (see p. 292) for the separation of transient (MnO_3) anions in several oxidations.

Charge transfer between manganate and permanganate (eqn. 5) is fast [3] and permanganate appears to convert hypomanganate very rapidly into manganate.[9] Disproportionation of metastable solutions of $(MnO_4)^{2-}$ and $(MnO_4)^{3-}$ to stable $(MnO_4)^-$ and hydrated manganese dioxide can be explained as occurring by electron transfer in this way, for, like $Ti(OH)_4$, a compound $Mn(OH)_4$ would be far too weak an acid to exist in any solution as $(MnO_4)^{4-}$ and would immediately be dehydrated to an insoluble product. The dissociation constants of H_2MnO_4 and H_3MnO_4 are probably of the same order as those of H_2CrO_4 and H_3VO_4, and it can well be therefore that the disproportionations of compounds of Mn^{VI} and Mn^V involve the ions $(HMnO_4)^-$ and $(HMnO_4)^{2-}$.[10] These ions undoubtedly undergo displacement reactions involving hydroxyl, for Symons[4] has found that alkaline manganate in isotopic water, $H_2{}^{18}O$, slowly exchanges oxgyen with the water. This has been visualised as an S_N2 substitution at the manganese centre (eqn. 6). By using this equilibration, and subsequently the disproportionation of manganate (eqn. 14) in more acid solution, K. Wiberg has been able to prepare ^{18}O-labelled permanganate and therewith trace the route of the oxygen atoms in several of the oxidation reactions of permanganate solutions.

Electronic structures, absorption spectra, and thermodynamic properties of ions $(MnO_4)^{n-}$ have been studied by Symons and his colleagues.[10, 11] The oxidising powers of the MnO_4 anions decrease markedly in the order $(MnO_4)^- > (MnO_4)^{2-} > (MnO_4)^{3-}$. This is to be expected, for oxidation

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[7] A. Y. Drummond and W. A. Waters, *J.*, 1953, 435.

[8] H. Lux, *Z. Naturforschung*, 1946, **1**, 281; R. Scholder, D. Fischer and, H. Waterstradt, *Z. anorg. Chem.*, 1954, **277**, 234.

[9] J. S. F. Pode and W. A. Waters, *J.*, 1956, 3373.

[10] A. Carrington and M. C. R. Symons, *J.*, 1956, 3373.

[11] A. Carrington, D. J. E. Ingram, D. Schonland, and M. C. R. Symons, *J.*, 1956, 4710; A. Carrington, D. Schonland, and M. C. R. Symons, *J.*, 1957, 659.

involves electron gain, which has to be effected by electron movement contrary to the charge on the anion.

With the metals from vanadium to iron the quadrivalent state marks the transition between stability as oxyanions and as cations; this can be associated with the symmetry of electrically neutral $M^{IV}(OH)_4$, and the tendency of such substances to be dehydrated to insoluble materials.

Although manganese dioxide is a well-known oxidising agent, long used in the presence of sulphuric or other mineral acids, yet no homogeneous oxidations involving Mn^{IV} are known; the fairly specific heterogeneous oxidations that can be effected by activated manganese dioxide in aprotic solvents [12] cannot yet be related to reactions of dissolved manganese compounds.

Tervalent manganese gives a cherry-red cation, Mn^{3+}, in concentrated ($>$ 9N) sulphuric acid.[13] At lower acidities this cation rapidly disproportionates (eqns. 16*a*, 16*b*) but Mn^{III} can be stabilised in solutions of much lower acidity by chelating agents, as, for example, pyrophosphate. Such solutions of Mn^{III} are useful volumetric reagents.[14] Their colours are not sufficiently intense to provide direct end-points, but for this starch–iodide solutions can be used. The complexed ions, *e.g.*, $\{Mn(H_2P_2O_7)_3\}^{3-}$, are structurally similar to the octahedral co-ordination compounds of Cr^{III}, Fe^{III}, and Co^{III} and have easily-displaced ligands.[15] The reactions of Mn^{III} complexes are therefore similar to those of free Mn^{3+} but the redox potential of Mn^{III}–Mn^{II} solutions naturally depends on the nature and concentration of the complexing agent. For the simple Mn^{3+}–Mn^{2+} system this has the very high value of + 1·15 v.

$$2Mn^{3+} \rightleftharpoons Mn^{2+} + Mn^{4+} \quad \ldots\ldots\ldots\ldots (16a)$$

$$Mn^{4+} + 2H_2O \longrightarrow MnO_2 + 4H^+ \quad \ldots\ldots (16b)$$

In neutral or weakly acid solutions Mn^{2+} is oxidised by permanganate to manganese dioxide. This Guyard reaction, usually written as (17), is not truly a reversible equilibrium, for dissolution of hydrated manganese dioxide requires very much stronger acid than that which can completely prevent oxidation of manganous salts by permanganate. Again, isotope exchange does not seem to occur between permanganate ions and manganous ions in the absence of a precipitate or colloid of manganese dioxide.[2] Several suggestions as to the mechanism of the Guyard reaction have been propounded, all of which depend on postulates concerning the structures of transient manganese ions of intermediate valency. The first

$$2(MnO_4)^- + 3Mn^{2+} + 4(OH)^- \rightleftharpoons 5MnO_2 + 2H_2O \quad . . (17)$$

$$(MnO_4)^- + Mn^{2+} \rightleftharpoons (MnO_4)^{2-} + Mn^{3+} \quad . . . (18)$$

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[12] See *Ann. Reports*, 1952, **49,** 142; 1953, **50,** 170.
[13] A. R. J. P. Ubbelohde, *J.*, 1935, 1605.
[14] I. M. Kolthoff and J. I. Watters, *Ind. Eng. Chem. Anal.*, 1943, **15,** 8.
[15] H. Taube, *Chem. Rev.*, 1952, **50,** 47.

stage is probably the reversible electron transfer (18). Reference to the published redox potentials, $(MnO_4)^{-}$-$(MnO_4)^{2-}$ = + 0·6 v,[10] Mn^{3+}-Mn^{2+} = + 1·51 v shows that oxidation of Mn^{2+} can proceed significantly only (i) if the acidity is low enough for the subsequent disproportionation of Mn^{3+} (eqn. 16) to follow, with removal of Mn^{4+} as hydrated manganese dioxide, or (ii) if a selective complexing agent has been added to lower the concentration of free Mn^{3+} to a requisite extent. In the presence of pyrophosphate for example manganous salts can be quantitatively titrated (electrometrically) at pH 6 to the Mn^{III} stage with aqueous permanganate.[14] Somehow the rapid reduction of $(MnO_4)^-$ to Mn^{3+} in an acid solution must be possible by a route that does not involve formation of any significant amount of $Mn(OH)_4$. This is conceivable if compounds of Mn^{V} and Mn^{IV} have amphoteric character and can form cations analogous to VO_2^+ and VO^{2+}. Such ions have been postulated by A. W. Adamson,[16] F. C. Tompkins, and E. Abel.[17]

The Ions of Chromium.—Chromic acid is a fairly strong acid ($K_1 = 0{\cdot}18$; $K_2 = 3{\cdot}2 \times 10^{-7}$) [18] and in dilute aqueous solution largely exists as $(HCrO_4)^-$. In more concentrated solutions the dehydration (19) occurs extensively.

$$2(HCrO_4)^- \rightleftharpoons (Cr_2O_7)^{2-} + H_2O \quad \ldots\ldots\ldots\ldots (19)$$

This vitiates any chance of using ^{18}O in studies of the mechanism of chromic acid oxidations. Alkaline chromate, *i.e.*, $(CrO_4)^{2-}$, is devoid of oxidising power and it has been established that $(Cr_2O_7)^{2-}$ is a much weaker oxidiser than $(HCrO_4)^-$.[19] Though the anhydride, CrO_3, and the acid chloride, CrO_2Cl_2, are both powerful oxidisers, particularly valuable since they can be used in organic solvents, the chlorochromate anion, $(CrO_3Cl)^-$, is much less active than $(CrO_3\text{-}OH)^-$.[20] Since strong acids enhance the oxidising powers of Cr^{VI} it has been suggested that cations such as $(HCrO_3)^+$ can exist (cf. HSO_3^+). In this way, too, one can explain the solubility of chromium trioxide in acetic acid.

In 1957 Bailey and Symons [21] prepared green K_3CrO_4 by alkali fusion, following the procedure for making K_3MnO_4. Its solutions in very strong alkali rapidly absorb oxygen and immediately disproportionate on dilution with water. Earlier, Weinland and Fiederer [22] had prepared a series of salts, such as Rb_2CrOCl_5 and $C_5H_5N,HCrOCl_4$ (C_5H_5N = pyridine), that appear to contain the anion $(Cr^{V}OCl_4)^-$. They will oxidise neutral solutions of iodide, whereas neutral $K_2Cr_2O_7$ does not do so, and are at once decomposed by water, behaving stoicheiometrically as if they contained Cr^{V}.

Quadrivalent chromium is known in CrF_4 and $CrCl_4$. The dioxide, CrO_2,

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[16] A. W. Adamson, *J. Phys. Chem.*, 1951, **55**, 293; F. C. Tompkins, *Trans. Faraday Soc.*, 1942, **38**, 131.

[17] E. Abel, *Monatsh.*, 1949, **80**, 455 and later notes.

[18] J. D. Neuss and W. Riemann, *J. Amer. Chem. Soc.*, 1934, **56**, 2238.

[19] F. H. Westheimer and A. Novick, *J. Chem. Phys.*, 1943, **11**, 500.

[20] M. Cohen and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1952, **74**, 4387.

[21] N. Bailey and M. C. R. Symons, *J.*, 1957, 202.

[22] R. F. Weinland and M. Fiederer, *Ber.*, 1906, **39**, 4042.

is thought to result from many chromic acid oxidations and has been isolated as a brown powder that immediately decomposes in water.[23] By analogy with vanadium it can be suggested that CrO_2 should be basic rather than acidic. Westheimer [24] has inferred that Cr^{IV} must be a stronger oxidising agent than Mn^{III} (this has had some recent confirmation [25]) and yet a powerful reducing agent. He considers that Cr^{IV} can oxidise iodide to iodine, this being consistent with a cation ($Cr^{4+} + I^- \longrightarrow Cr^{3+} + I^0$) whilst Cr^V oxidises iodide to hypoiodite, as would be expected for an oxyanion. However the main evidence for transitory Cr^V and Cr^{IV} ions comes from the study of chromic acid oxidations of organic compounds. Analogies between chromium and the two adjacent elements, vanadium and manganese, are helpful in formulating hypotheses concerning mechanisms of reduction of chromate to Cr^{III}. The strong reducer Cr^{2+} will not be considered in this Review.

Chromic acid oxidations—inorganic reactions

The mechanism of chromic acid oxidation was reviewed in 1949 by F. H. Westheimer [24] who had previously shown [19] that the only active oxidising species in acidic aqueous solution is the acid chromate ion, $(HCrO_4)^-$. He pointed out that transient ions having intermediate valency states must be postulated to explain the occurrence of induced oxidations, such as (20) and (21) under conditions in which direct oxidation of the second oxidisable component (I^-, Mn^{2+}) did not occur.

$$(HCrO_4)^- + Fe^{2+} + 2I^- + 7H^+ \longrightarrow Cr^{3+} + Fe^{3+} + I_2 + 4H_2O \text{ (at pH 3)} \quad (20)$$

$$2(HCrO_4)^- + 2H_3AsO_3 + Mn^{2+} + 6H^+ \longrightarrow 2Cr^{3+} + 2H_3AsO_4 + MnO_2 + 4H_2O \quad (21)$$

$$(HCrO_4)^- + Fe^{2+} \rightleftharpoons (HCrO_4)^{2-} + Fe^{3+} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (22)$$

In reactions such as (20), two equivalents of the second component can, in the limit, be oxidised per mole of chromic acid; this is indicative of oxidation through quinquevalent chromium. Kinetic study of the oxidation of ferrous ion by chromic acid indicates that the initial step is rapid and reversible, a later reaction being rate-controlling. Thus the redox potential for the Cr^{VI}–Cr^V equilibrium must be similar to that of the Fe^{III}–Fe^{II} system, and by analogy with the chemistry of manganese (eqn. 18) reaction (22) can be postulated as a rapid equilibrium, the ion of Cr^V resembling that of hypomanganate, or of vanadate, as recent work has verified.[21] It may be noted that the inorganic reactions proceeding through Cr^V are those in which the primary reducing agent is an ion that can provide *one electron*, *e.g.*, Fe^{2+}, Ti^{3+}, Ce^{3+}, V^{2+}, VO^+, VO_2^+.

In reactions such as (21) only one equivalent of the second component is oxidised per chromate ion. This indicates that the reaction proceeds through quadrivalent chromium (reaction 23). Oxidations of alcohols,

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[23] A. Leo and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1952, **74**, 4383.

[24] F. H. Westheimer, *Chem. Rev.*, 1949, **45**, 419.

[25] A. E. Ogard and H. Taube, *J. Phys. Chem.*, 1958, **62**, 6.

$$(HCrO_4)^- + (H_2AsO_3)^- \longrightarrow Cr^{IV} + (H_2AsO_4)^- \quad . \; . \; . \; . \quad (23)$$

$$Cr^{VI} + Cr^{IV} \longrightarrow 2Cr^{V} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (24)$$

$$Cr^{V} + As^{III} \longrightarrow Cr^{III} + As^{V} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (25)$$

hydroxy-acids, and probably many other types of organic compound, such as aromatic aldehydes, are of this character and it may be noted that all these reactions involve the rupture of a covalency, *i.e.*, of *an electron-pair* bond. Kinetic analysis of oxidations of type (21) indicates however that both the valency levels of Cr^{VI} and Cr^{V} are probably involved in the absence of the second oxidisable component and Westheimer has therefore postulated, as a fast reaction, the re-oxidation of Cr^{IV} and the 2-electron reduction of Cr^{V} (reactions 24 and 25), reaction (25) presumably being similar in type to reaction (23) as would be expected of an ion $(H_2CrO_4)^{2-}$.

Chromic acid oxidations—organic reactions

(i) **Oxidation of Alcohols.**—This reaction has been studied in great detail. In 1943 Westheimer and Novick [19] established that the oxidation of *iso*propyl alcohol resembles reaction (21) ; in the presence of manganous salts one equivalent of manganese dioxide can be obtained for every two equivalents of *iso*propyl alcohol oxidised. In 1949, Westheimer and Nicolaides, by comparing the rates of oxidation of $H–CMe_2·OH$ and $D–CMe_2·OH$, established that the H(D)–C bond of the alcohol is broken in the rate-determining stage of the oxidation.[26] Westheimer [24] therefore concluded that a rapid, reversible, acid-catalysed esterification of the alcohol preceded the slower oxidation, which he wrote as a concerted base-catalysed process giving quadrivalent chromium ($(HCrO_3)^-$ or CrO_2] that would rapidly oxidise Mn^{2+}, but was usually destroyed by reaction (24). His reaction mechanism (eqns. 26, 27) has been so widely applied as a model for other oxidations that it merits further consideration.

$$(HCrO_4)^- + 2H^+ + HO\text{–}CMe_2\text{–}H \rightleftharpoons H\text{–}CMe_2O{\cdot}CrO_2\text{–}OH_2^+ + H_2O \quad . \; . \quad (26)$$

$$H_2O{:} + H\text{–}CMe_2\text{–}O\text{–}CrO_2\text{–}OH_2^+ \xrightarrow[\text{Slow}]{} H_3O^+ + CMe_2{=}O + H_2CrO_3 \quad . \; . \quad (27)$$

Dependence of the oxidation rate on $[HCrO_4^-]$ and on $[H^+]^2$ (in moderately dilute acids) is consistent with an acid-catalysed esterification involving un-ionised H_2CrO_4.

Chromate esters are now well known, *tert.*-butyl chromate having been introduced by Oppenauer and Oberrauch [27] as a specific oxidiser for alcohols. It has been shown [23] that this reagent acts by rapid trans-esterification with primary and secondary alcohols: this esterification and its reverse [28] usually involve electron-pair displacements at the chromium atom, *i.e.*, acyl–oxygen bond fission. Di*iso*propyl chromate, which can be extracted by benzene from

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[26] F. H. Westheimer and N. Nicolaides, *J. Amer. Chem. Soc.*, 1949, **71,** 25.

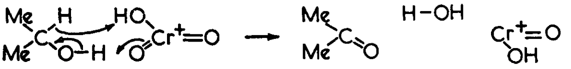
[27] R. V. Oppenauer and H. Oberrauch, *Anal. Asoc. Quim. argentina*, 1949, **37,** 246.

[28] M. Anbar, I. Dostrovsky, D. Samuel, and A. D. Yoffe, *J.*, 1954, 3603; H. H. Zeiss and C. N. Matthews, *J. Amer. Chem. Soc.*, 1956, **78,** 1694.

chromic acid–*iso*propyl alcohol mixtures, decomposes under anhydrous conditions in the latter solvent by a first-order reaction, depositing a brown powder containing Cr^{VI} and Cr^{III} in the ratio 42:58 (*i.e.*, slightly more Cr^{VI} than that required for Cr^{IV}).[23] This decomposition is catalysed by pyridine, as would be expected for a base-catalysed fission of a C–H bond as shown in equation (27). However, one can question whether neutral chromate esters, R_2CrO_4, are exact models for all reactions of chromic acid, since solvents have a very great effect on the reaction velocity. In 86·5% acetic acid the rate of oxidation of *iso*propyl alcohol is 2500 times as fast as in water,[29] a difference that can be ascribed to solvent displacement of the ionisation of H_2CrO_4 or to the formation of a highly reactive acetyl–chromic anhydride, $CH_3{\cdot}CO{\cdot}O{\cdot}CrO_2{\cdot}OH$, whilst chloride markedly retards reaction by formation of the more stable chlorochromate ion, $(Cl{\cdot}CrO_3)^-$.[20]

In glacial acetic acid chromic acid oxidations exhibit autoretardation, owing to the formation of brown, undissociated chromic–chromate complexes such as $Cr^{III}(HCrO_4)(O{\cdot}CO{\cdot}CH_3)_2$,[30] that could easily be mistaken for chromium compounds of valency intermediate between Cr^{VI} and Cr^{III}. These however may be broken up by the addition of an acid stronger than H_2CrO_4, *e.g.*, sulphuric acid which markedly accelerates oxidations, water and acetates being retarders that favour this complex formation. The effect of phosphoric acid is similar,[31] but more complex on account of its stepwise dissociation.

For oxidations in strongly acid aqueous solutions Westheimer has suggested that proton addition to the acid chromate ester, giving the cation shown in equation (27), favours the electron switch from the water molecule that acts as base catalyst. Roček and Krupicka,[32] by showing that the logarithm of the oxidation rate is linearly dependent on Hammett's acidity function H_0, argue that a molecule of water need not be required as catalyst and suggest that the oxidation proceeds by a bimolecular cyclic electron switch as in reaction (28), involving molecular H_2CrO_4 at low acidities and a protonated species, $(H_3CrO_4)^+$ or $(HCrO_3)^+$, at higher acidities.



. . . (28)

However Graham and Westheimer question the above argument,[29] since stoicheiometrically a reaction of rate dependent on the product [Ester of Cr^{VI}][H_2O][H^+] is equivalent to the measured rate which depends on the product [H_2CrO_4][Alcohol][H^+] and no extra water molecule. They concede however that in very strong acid a cyclic process such as (28) may operate. Roček and Krupicka consider that the cyclic mechanism explains more satisfactorily than the catalysed mechanism the relative rates of oxidation

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[29] G. E. T. Graham and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 3030.

[30] R. Slack and W. A. Waters, *J.*, 1948, 1666; 1949, 599.

[31] J. Roček, *Coll. Czech. Chem. Comm.*, 1955, **20**, 1320.

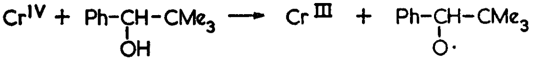
[32] J. Roček and J. Krupicka, *Chem. and Ind.*, 1957, 1668; *Chem. Listy*, 1958, **52**, 1735.

of *para*-substituted 1-phenylethanols, found by Kwart and Francis[33] to follow the order MeO- > Me_3C- > Me- > H- > Cl- > NO_2-, electron-donating substituents favouring oxidation.

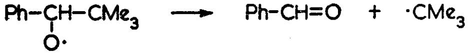
Barton,[34] accepting the validity of Westheimer's mechanism, has suggested that for cyclic (*e g.*, steroid) secondary alcohols molecules with accessible (equatorial) hydrogen atoms should be oxidised more readily than their hindered epimers (with axial H). This hypothesis assumes that the esterification equilibrium (26) is not markedly affected by steric conditions. Though qualitatively true, and valuable for structural diagnosis, Barton's conclusion is not quantitatively correct[35] and the cyclic mechanism (28) is in much better accord with observations.

Oxidation of tertiary alcohols is more difficult than that of primary or secondary alcohols but can be effected in the presence of sulphuric acid. Though of first order with respect to the alcohol, it is of zero order with respect to chromic acid and seems to involve the slow formation of an olefin which is then rapidly oxidised, mainly to a ketone.[36] Esters of tertiary alcohols appear to be oxidised in a similar way. Chromic acid will also effect glycol fission, and from the reaction between pinacol and chromyl chloride, Slack and Waters[37] isolated an intermediate containing two atoms of chromium per pinacol molecule. This they supposed to decompose to give Cr^V: however, in view of later evidence of acid and base catalysts of glycol fission by lead tetra-acetate, a concerted electron-pair mechanism may be more plausible.

Compounds of Cr^V cannot however entirely be neglected in considering steps in alcohol oxidation. W. Mosher and his collaborators[38] noted that some C–C bond cleavage occurs during chromic acid oxidations of alcohols of type $R_3C{\cdot}CHR'{\cdot}OH$. This phenomenon has been investigated more closely by Hampton, Leo, and Westheimer[39] for α-*tert.*-butylbenzyl alcohol $Me_3C{\cdot}CHPh{\cdot}OH$, which yields benzaldehyde and *tert.*-butyl alcohol as well as pivalophenone, $Me_3C{\cdot}COPh$. Up to 67% of C–C cleavage may occur, but this is sharply reduced by adding Mn^{2+} or Ce^{3+} ions to remove any



$$\mathrm{Cr^{IV} + Ph\text{-}\underset{OH}{CH}\text{-}CMe_3 \longrightarrow Cr^{III} + Ph\text{-}\underset{O\cdot}{CH}\text{-}CMe_3} \quad . \; . \; . \; . \; . (29)$$



$$\mathrm{Ph\text{-}\underset{O\cdot}{CH}\text{-}CMe_3 \longrightarrow Ph\text{-}CH{=}O + \cdot CMe_3} \quad . \; . \; . \; . \; . (30)$$

$$\mathrm{Cr^{VI} + \cdot CMe_3 + H_2O \longrightarrow Cr^{V} + HO{\cdot}CMe_3 + H^+} \quad . \; (31)$$

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[33] H. Kwart and P. S. Francis, *J. Amer. Chem. Soc.*, 1955, **77**, 4907.

[34] D. H. R. Barton, *Experientia*, 1950, **6**, 316.

[35] J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, 1955, **38**, 1529.

[36] W. F. Sager, *J. Amer. Chem. Soc.*, 1956, **78**, 4970; J. Roček, *Coll. Czech. Chem. Comm.*, 1958, **23**, 833.

[37] R. Slack and W. A. Waters, *J.*, 1949, 594.

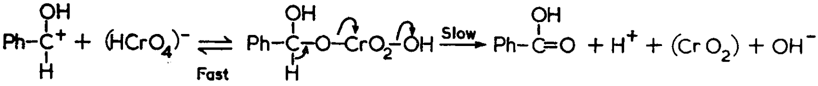
[38] W. Mosher and F. Whitmore, *J. Amer. Chem. Soc.*, 1948, **70**, 2544; W. Mosher and E. Langerak, *ibid.*, 1949, **71**, 286; 1951, **73**, 1302.

[39] J. Hampton, A. Leo, and F. H. Westheimer, *ibid.*, 1956, **78**, 306.

Cr^{IV} intermediate as soon as it is formed. It has been suggested therefore that the C–C cleavage is an oxidation involving Cr^{V} [formed from Cr^{IV} by reaction (24)], but a sequence of 1-electron changes such as (29)—(31) cannot altogether be excluded, if it is granted that reaction (24) may be reversible. Deuterium labelling, by use of $Me_3C{\cdot}CDPh{\cdot}OH$, indicates that chromic acid itself does not effect C–C fission.

(ii) **Oxidation of Aromatic Aldehydes.**—This is now well understood.[29, 40] The oxidation of benzaldehyde is of first order with respect to both [Ph·CHO] and $[HCrO_4^-]$ and in the acid range 0·018—0·3M the logarithm of the rate constant varies linearly with the Hammett function H_0. Comparison with Ph·CDO shows that the rate-determining stage involves H–C cleavage ($k_H/k_D = 4{\cdot}3$) as required by the mechanism

$$\mathrm{Ph{\cdot}CHO} + \mathrm{H^+} \rightleftharpoons \mathrm{Ph{\cdot}\overset{+}{C}H{-}OH} \qquad \ldots\ldots\ldots\ldots\ldots \quad (32)$$



$$\mathrm{Ph{-}\overset{OH}{\underset{H}{C}}{}^{+}} + (\mathrm{HCrO_4})^- \underset{\mathrm{Fast}}{\rightleftharpoons} \mathrm{Ph{-}\overset{OH}{\underset{H}{C}}{-}O{-}CrO_2{-}OH} \xrightarrow{\mathrm{Slow}} \mathrm{Ph{-}\overset{OH}{C}{=}O} + \mathrm{H^+} + (\mathrm{CrO_2}) + \mathrm{OH^-} \quad (33)$$

Electron-attracting groups (*e.g.*, NO_2) accelerate the oxidation, as would be expected for the shift of the equilibrium of reaction (32) in formation of cations $(Ar{\cdot}CH{\cdot}OH)^+$, and effects of substituents have magnitudes according with Hammett's σ function.

With benzaldehyde, as with *iso*propyl alcohol oxidation, it has been shown that the addition of manganous or cerous ions reduces the oxidation rate by 30—40% by eliminating secondary reactions due to Cr^{IV}.[29] Oxygen greatly increases the oxidation rate.[40] Uptake of oxygen is quite common in oxidations of organic compounds by chromic acid and, naturally, has been regarded as indicative of free-radical formation.[41] However it is now thought that the oxygen absorption may be caused either by direct reactions of Cr^{IV} or Cr^{V} compounds with oxygen,[24] or by traces of organic free radicals formed by reactions between Cr^{IV} and organic molecules.

Oxidations of aliphatic aldehydes have not received detailed study, but may well occur by a different mechanism, because oxidations of aliphatic ketones are thought to occur by way of their enols (cf. p. 297) to give mixtures of α-hydroxy-ketones and $\alpha\beta$-unsaturated ketones.[42] In cyclic systems axial attack of the chromic acid is thought to occur. It is significant that aliphatic aldehydes are oxidised less easily than the corresponding primary alcohols.[43]

(iii) **Oxidation of Olefins.**—Chromic acid oxidation of olefins eventually leads to carbon–carbon fission at the olefinic link with formation of ketones and carboxylic acids, but a very complex mixture of products can result from controlled reactions with limited amounts of oxidant, *e.g.*,

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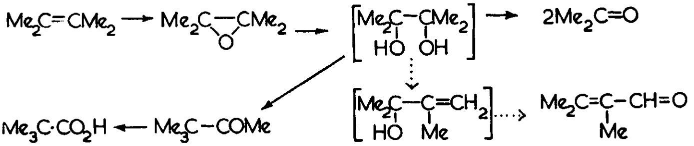
[40] K. B. Wiberg and T. Mill, *J. Amer. Chem. Soc.*, 1958, **80**, 3022.

[41] W. A. Waters, (*a*) *J.*, 1946, 1151; (*b*) *Trans. Faraday Soc.*, 1946, **42**, 184.

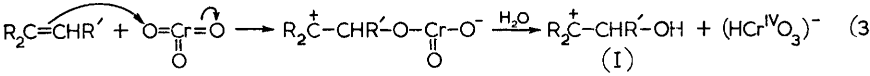
[42] E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.*, 1958, **80**, 211.

[43] W. Mosher and D. M. Preiss, *ibid.*, 1953, **75**, 5605.



The systematic studies of products by W. J. Hickinbottom and his collaborators, both with chromic acid in aqueous sulphuric acid and with chromium trioxide in acetic anhydride, have led to the conclusion that aliphatic olefins give mixtures that " can easily be explained by the initial formation of an epoxide, 1 : 2-diol, or of some polar product easily converted into one of the latter ".[44, 45] As the above example shows, pinacolinic rearrangement products are often formed; this in fact was one of the main bugbears of early interpretations of oxidative degradations of terpenes. With alicyclic compounds, allylic oxidation is a frequent side reaction; thus 1-phenyl*cyclo*hexene gives up to 25% of 3-phenyl*cyclo*hex-2-enone,[46] and *cyclo*hexene 37% of *cyclo*hex-2-enone.[47] In natural-product research this has been used for diagnosis of the $-C{=}C{-}CH_2-$ system and, like oxygen uptake during the oxidation, has been regarded as an indication of some homolytic attack on the methylene group. Even if this hypothesis is correct the reaction may be due to Cr^{IV} rather than Cr^{VI}, and in any case it does not represent the main oxidation route.

From Hickinbottom's studies the nature of the main initial reaction is now evident; it is electron-pair donation by the olefin to $O{=}Cr$, giving a product that with water promptly yields the conjugate acid of an epoxide (I) [45, 48] (reaction 34). 1 : 2-Diol formation is certainly a secondary reaction for epoxides can be isolated in high yields from olefins by the use of chromium trioxide in acetic anhydride diluted with carbon disulphide.[45] Moreover pinacolinic products cannot be formed from 1 : 2-diols nearly as rapidly as the latter are oxidised, under comparable conditions of acidity, to C–C bond fission products. Even the epoxides cannot be the initial products for they can be oxidised by chromic–sulphuric acid mixtures more rapidly than they can be hydrolysed or isomerised by sulphuric acid of the same concentration.[48]



$$R_2C{=}CHR' + O{=}\underset{\underset{O}{\|}}{Cr}{=}O \longrightarrow R_2\overset{+}{C}{-}CHR'{-}O{-}\underset{\underset{O}{\|}}{Cr}{-}O^- \xrightarrow{H_2O} \underset{(I)}{R_2\overset{+}{C}{-}CHR'{-}OH} + (HCr^{IV}O_3)^- \quad (34)$$

For aqueous chromic acid the oxidation is of first order with respect to both the olefin and chromic acid.[49] Representation as (35), giving a carbonium ion and not necessarily a cyclic intermediate such as (III), satis-

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[44] W. J. Hickinbottom, D. R. Hogg, D. Peters, and D. G. M. Wood, *J.*, 1954, 4400.

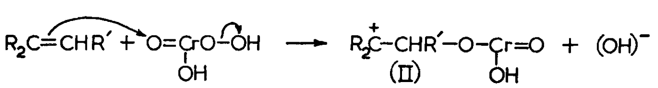
[45] W. J. Hickinbottom, D. Peters, and D. G. M. Wood, *J.*, 1955, 1360, and earlier papers of the series.

[46] D. Ginsberg and R. Pappo, *J.*, 1951, 516; L. F. Fieser and J. Szmuszkovicz, *J. Amer. Chem. Soc.*, 1948, **70**, 3352.

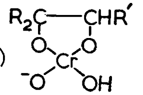
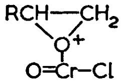
[47] F. C. Whitmore and G. W. Pedlow, *ibid.*, 1941, **63**, 758.

[48] M. A. Davis and W. J. Hickinbottom, *J.*, 1958, 2205.

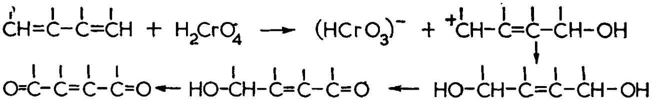
[49] H. H. Zeiss and F. R. Zwanzig, *J. Amer. Chem. Soc.*, 1957, **79**, 1733.

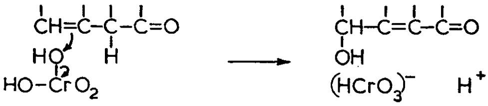

(35)

factorily explains the difference between chromic acid oxidation and the attack on olefins of osmium tetroxide or potassium permanganate (p. 293); all subsequent stages can be adequately represented as passing *via* (I).[48]

(III)


(IV)

Mechanism (35) can be extended to oxidations of conjugated dienes, which easily yield unsaturated 1 : 4-diketones or ketols,[50] and also to oxidation with double-bond shift of $\beta\gamma$-unsaturated ketones,[51] reactions often encountered with terpenes and steroids possessing structures that could not yield cyclic Cr^{IV} intermediates:


(36)


. . . . (37)

The initial lead for the formulation of mechanisms (34) and (35) for chromic acid oxidations of olefins came from a study by Cristol and Eiler of the addition of chromyl chloride to olefins.[52] In carbon tetrachloride solution *cyclo*hexene reacts rapidly to give C_6H_{10},CrO_2Cl_2 and then much more slowly to form a brown solid, $C_6H_{10}(CrO_2Cl_2)_2$. Hydrolysis gives 30–40% of *trans*-2-chloro*cyclo*hexanol, whilst olefins, $R{\cdot}CH{=}CH_2$, by similar treatment yield chlorohydrins, $R{\cdot}CHCl{\cdot}CH_2{\cdot}OH$. This indicates that chromyl chloride acts as an electrophilic reagent, adding by an oxygen atom to the π-electrons of the double bond giving a carbonium cation $(R{\cdot}CH{\cdot}CH_2{-}O{-}CrO{-}Cl)^+$ (cf. II) for which various cyclic mesomeric or non-classical structures such as (IV) must be written so as to explain the eventual *trans*-combination of the chloride ion.

(iv) **Oxidation of Saturated Hydrocarbons.**—This requires vigorous conditions and preferentially occurs at tertiary C–H groups or similar sites of reactivity, such as α-CH_2 groups of aromatic side-chains. This, of course, is the site of homolytic oxidation and possibilities of 1-electron transfer have been considered by Slack and Waters.[30] Oxidations of hydrocarbons are retarded by bases and catalysed by acids, the effect of the latter being proportional

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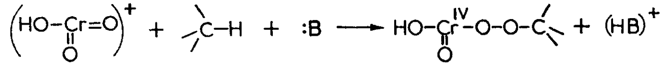
[50] J. Elks, R. M. Evans, A. G. Long, and G. H. Thomas, *J.*, 1954, 451.

[51] D. H. R. Barton, N. J. Holness, K. H. Overton, and W. J. Rosenfelder, *J.*, 1952, 3751.

[52] S. J. Cristol and K. R. Eiler, *J. Amer. Chem. Soc.*, 1950, **72**, 4353.

to H_0.[53] This indicates attack by a cation, *e.g.*, $(HCrO_3)^+$. By comparing the rates of oxidation of Et_3C–H and Et_3C–D, Sager and Bradley [54] have shown that the rate-determining stage ruptures the C–H(D) bond. They find that the alcohol Et_3C–OH is an early product and conclude that it is not formed from the free cation Et_3C^+ since this would promptly yield the much too easily oxidised olefin $Et_2C{=}CH{\cdot}Me$. A concerted electrophilic substitution followed by cleavage of an O–Cr link, as in hydrolysis of chromate esters, thus seems to be indicated:


(38)

For such a mechanism steric factors should be important: in H–C bridgehead molecules, such as camphane which yields *epi*camphor,[54] oxidative attack is transferred to a CH_2 group.

Undoubtedly the Étard reaction [55] of chromyl chloride has a similar mechanism, and it is significant that the Étard complexes which generally contain *two* molecules of chromyl chloride per molecule of hydrocarbon are formed by direct addition and not by elimination of hydrogen chloride. It is suggested that they should be formulated as salts.[56]

Chromic acid oxidations of CH_2 groups give high yields of ketones: oxidations in acetic anhydride usually give their diacetyl derivatives $\rangle C(OAc)_2$, which usefully afford protection against subsequent oxidation. The oxidation may occur in stages but, under the conditions that have to be used, the isolation of easily-oxidised primary or secondary alcohols or their esters would clearly be impracticable.

(v) **Oxidations of Aromatic Hydrocarbons.**—Though benzene is resistant to oxidation, polycyclic aromatic and heterocyclic hydrocarbons, such as anthracene and phenanthrene, are easily oxidised to quinones. Qualitatively, the order of reactivity of these compounds is that of their electron availability and this is wholly consistent with attack by a cation such as $(HCrO_3)^+$. Again, chromic acid easily destroys ring systems containing electron-donating substituents such as OH or NH_2.

Permanganate oxidations

General Features.—The literature of oxidation by permanganate was reviewed in 1958 by Ladbury and Cullis.[57] Consequently the following pages aim at giving a broad picture of reaction mechanisms and show the very limited extent to which similarities can be traced between the chemistry of chromium and manganese.

Enough has been said about the Guyard reaction (p. 281) to make it clear that it is only when the selection of experimental conditions allows of oxidation of Mn^{2+} and of the equilibration (16) that permanganate be-

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[53] J. Roček, *Coll. Czech. Chem. Comm.*, 1957, **22,** 1509, 1519.

[54] W. F. Sager and A. Bradley, *J. Amer. Chem. Soc.*, 1956, **78,** 1187.

[55] M. Étard, *Ann. Chim. Phys.*, 1881, **22,** 218.

[56] C. C. Hobbs and B. Houston, *J. Amer. Chem. Soc.*, 1954, **76,** 1254.

[57] J. W. Ladbury and C. F. Cullis, *Chem. Rev.*, 1958, **58,** 403.

comes a 5-electron acceptor. In mineral acid solution where this oxidation of Mn^{2+} to Mn^{3+} can occur easily the manganic ions have a higher redox potential than $(MnO_4)^-$ anions, so many substrates are then oxidised by manganic cations and not directly by the permanganate. This is the case with those permanganate oxidations which exhibit autocatalysis, the best known examples of which are the oxidations of hydrogen peroxide and of oxalic and malonic acids. By adding fluoride or pyrophosphate to remove *free* Mn^{2+} and Mn^{3+} these oxidations can be inhibited almost completely.[58] Side-chain oxidation of aromatic hydrocarbons seems to be largely, though not exclusively, of this type.[59] Consequently the mechanisms of oxidations effected by manganic salts, considered separately below (p. 296), are of particular relevance to the understanding of the modes of action of solutions of permanganate in mineral acid.

For oxidations in which the $(MnO_4)^-$ ion is directly involved there are two distinct paths, (*a*) mere electron transfer, *e.g.*, $(MnO_4)^- + e \longrightarrow (MnO_4)^{2-}$, and (*b*) direct oxygen transfer; both of these can be investigated experimentally.

Modes of Electron Transfer to $(MnO_4)^{n-}$ ions.—Oxidations by electron transfer can be studied only in alkaline solutions in which the anions $(MnO_4)^{2-}$ and $(MnO_4)^{3-}$ are reasonably stable. Following Stamm,[60, 6] who introduced alkaline permanganate as a volumetric reagent and used baryta to prevent bulk reduction beyond the manganate stage ($BaMnO_4$ is very insoluble), Drummond and Waters [61] verified that organic compounds of many types were rapidly and extensively attacked by cold alkaline permanganate, often giving oxalate as the end-product. A significant feature of these oxidations was the repeated stepwise degradation of hydrocarbon chains, occurring by oxidations of aldehydes and ketones through their enol anions. Of aliphatic compounds only ethers, tertiary alcohols (excluding 1 : 2-diols), and the anions of saturated acids resisted attack. However the quantitative conversion of $(MnO_4)^-$ into $BaMnO_4$ under these conditions does not indicate invariable 1-electron abstraction, since the immediate electron transfer (39) destroys any evidence for the transient existence of a Mn^V valency level.[9]

$$(MnO_4)^{3-} + (MnO_4)^- \longrightarrow 2(MnO_4)^{2-} \quad . \; . \; . \; . \; . \; . \quad (39)$$

Later work by Pode and Waters,[9] who studied oxidations effected by sodium manganate in 10N-potassium hydroxide, in which the blue anion $(MnO_4)^{3-}$ has a reasonably long life, showed that whilst $(MnO_4)^{2-}$, like $(MnO_4)^-$, was not a specific oxidiser for particular organic groups, yet its reactions could be divided into two categories, according to whether they yielded dissolved blue $(MnO_4)^{3-}$ as a visible product or immediately gave brown hydrated manganese dioxide (Mn^{IV}). These are tabulated.

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[58] H. F. Launer and D. M. Yost, *J. Amer. Chem. Soc.*, 1934, **56**, 2571; A. Y. Drummond and W. A. Waters, *J.*, 1954, 2456.

[59] J. W. Ladbury and C. F. Cullis, *J.*, 1955, 555, 1407, 2850, 4186.

[60] H. Stamm, *Z. angew. Chem.*, 1934, **47**, 579, 791.

[61] A. Y. Drummond and W. A. Waters, *J.*, 1953, 435.

Classification of oxidations effected by alkaline manganate

Group A. Substances oxidised by 1-electron transfer ($Mn^{VI} \longrightarrow Mn^{V}$).

Hydrogen peroxide, sulphite,[8] thiosulphate.[8]
α-Hydroxy-acids, formic acid.[8]
Ketones, ketonic acids, phenols.

Group B. Substances oxidised by direct conversion of $(MnO_4)^{2-}$ *into* Mn^{IV}.

Arsenite. Alcohols, olefins, unsaturated acids.

The scope of this survey was naturally limited by considerations of solubility and stability in strong alkali; thus aldehydes could not be tested. It is significant however that whilst manganate can attack, though much more slowly, all the types of molecule that are attacked by alkaline permanganate, only the compounds of Group *A*, which yield $(MnO_4)^{3-}$ from $(MnO_4)^{2-}$, are easily oxidised by undoubted 1-electron-abstracting ions such as Mn^{3+} or $[Fe(CN)_6]^{3-}$. Other analogies support the general conclusion that substances of Group *A*, but not those of Group *B*, are oxidised by both $(MnO_4)^-$ and $(MnO_4)^{2-}$ by mere 1-electron abstraction. Thus the stepwise 1-electron transfer is the invariable course of oxidation of hydrogen peroxide to oxygen, as established for example with Ce^{3+}.[62] In acid permanganate (free H_2O_2) it needs trace catalysis by Mn^{3+}, but in alkali both $(HO_2{:})^-$ and $(O_2\cdot)^-$ lose electrons directly with $(MnO_4)^-$, $(MnO_4)^{2-}$, and $(MnO_4)^{3-}$. Sulphites, it may be recalled, undergo autoxidation that can be catalysed by cupric salts (eqn. 40) and radical dimers of sulphur compounds, *e.g.*, R_2S_2, $Na_2S_2O_6$, $Na_2S_4O_6$, are well known. In contrast, $(AsO_3)^{3-}$ oxidises only to $(AsO_4)^{3-}$ and is not directly attacked by Mn^{3+}.[63] Phosphites and hypophosphites, which are rapidly attacked by manganate, may however react by 1-electron transfer.

$$Cu^{2+} + (HSO_3)^- \rightleftharpoons Cu^+ + HSO_3\cdot \quad \ldots\ldots\ldots (40)$$

Other noteworthy experimental features are the stability of phenoxide anions to $(MnO_4)^{3-}$, probably a matter of relative redox potentials, and the rapid oxidations of 1:2-diols.

Though it is possible to formulate oxidations of Group *B* as 2-electron transfers, the evidence given below shows that most of them involve oxygen transfer as the prime reason for the valency change of the manganese. There may of course be oxidations in which the mechanistic course depends on the pH of the environment and it does seem as if, even amongst organic reactions, the direct electron transfer process occurs only in reactions between two ions (cf. aldehyde oxidation, p. 297).

Oxidations known to involve Oxygen Transfer.—(i) *Permanganate oxidation of olefins.* It is well known that dilute aqueous permanganate very rapidly oxidises olefins to *cis*-1:2-diols. More recently, alkaline manganate has been shown to exhibit the same stereospecificity of attack.[9, 64] How-

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[62] S. Baer and G. Stein, *J.*, 1953, 3176.

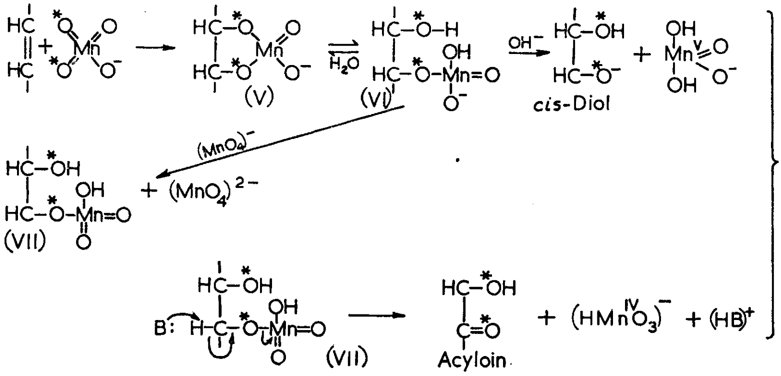
[63] H. Land and W. A. Waters, *J.*, 1957, 4312.

[64] W. Rigby, *J.*, 1956, 2452.

ever a careful selection of experimental conditions is imperative if good yields of diol are required. By rapid addition of permanganate to a neutral solution of an olefin an acyloin R·CH(OH)·CO·R′ is at once formed [65] whereas in decidedly alkaline solution (pH 12 or over), even in the presence of an excess of permanganate, the diol predominates and, when once formed, is further oxidised only slowly.[66] Organic co-solvents (acetone or alcohol) favour diol formation.[67] Again glycol fission and Wagner rearrangement can both occur as side reactions.

To explain *cis*-hydroxylation the formation of a primary cyclic adduct (V) containing Mn^{V}, suggested by Wagner [68] and then Boeseken,[69] has long been favoured, particularly since from spatially similar osmium tetroxide the analogous cyclic intermediates have been isolated.[70] Only recently has clear support for this hypothesis come from the work of Wiberg and Saegebarth [67] who, by using ^{18}O-labelled permanganate under favourable conditions for diol formation, have been able to establish that in the oxidation of oleate up to 1·5 (*i.e.*, virtually 2) atoms of oxygen can be transferred from permanganate anions to each olefin molecule. Thus the intermediate (V) must have two C–O–Mn bonds, both of which hydrolyse between the manganese and the oxygen atoms.

To explain the formation of either the 1 : 2-diol or the acyloin, Wiberg and Saegebarth suggest that the cyclic intermediate rapidly hydrolyses to (VI), and then, by bimolecular attack of hydroxyl anion on the manganese centre, to hypomanganate and the *cis*-diol (41). Acyloin production is thought to involve oxidation of the Mn^{V} ester (VI) by permanganate anion to (VII), containing Mn^{VI}, which then by a concerted base-catalysed process, similar to that operating in chromic acid oxidation of secondary alcohols (p. 284), gives the acyloin and Mn^{IV}. An alternative attack of a base on



(41)

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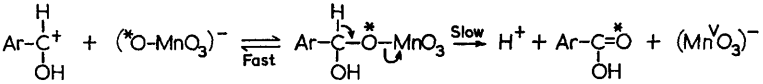
[65] G. King, *J.*, 1936, 1788.
[66] A. Lapworth and E. N. Mottram, *J.*, 1925, **127**, 1628.
[67] K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, 1957, **79**, 2822.
[68] G. Wagner, *J. Russ. Phys. Chem. Soc.*, 1895, **27**, 219.
[69] J. Boeseken, *Rec. Trav. chim.*, 1921, **40**, 553; 1928, **48**, 683.
[70] R. Criegee, *Annalen*, 1936, **522**, 75.

the hydroxyl hydrogen of (VII) can lead to glycol fission. The electron transfer stage of oxidation of (VI) to (VII) is introduced to avoid postulating reduction of manganese below the valency level of Mn^{IV}. An alternative route of diol formation is of course hydrolysis of ester (VII) by O–Mn bond fission, but this like the hydrolysis of (VI) presumably needs free hydroxyl anions.

(ii) *Oxidation of aromatic aldehydes.* This has also been proved to involve oxygen transfer from manganese to carbon in neutral or acid media.[71] It is a bimolecular reaction showing general acid catalysis and has been assigned the following mechanism (42, 43) because substitution of Ph·CDO for Ph·CHO decreases the reaction velocity 7-fold. A Hammett plot can be

$$\mathrm{Ar{-}CHO + (H_3O)^+ \underset{Fast}{\rightleftharpoons} Ar{-}\overset{+}{C}H{-}OH + H_2O} \quad \ldots\ldots\ldots\ldots (42)$$



$$\mathrm{Ar{-}\underset{OH}{\overset{H}{C}}{}^{+} + ({}^{*}O{-}MnO_3)^- \underset{Fast}{\rightleftharpoons} Ar{-}\underset{OH}{\overset{H}{C}}{-}\overset{*}{O}{-}MnO_3 \xrightarrow{Slow} H^+ + Ar{-}\underset{OH}{C}{=}\overset{*}{O} + (\overset{V}{Mn}O_3)^-} \quad . (43)$$

drawn for relative oxidation rates of substituted aromatic aldehydes, showing that electron-attracting substituents by preventing the formation of the organic cation in reaction (42) decrease the rate of oxidation. A similar mechanism to (43) was earlier suggested by Merz, Stafford, and Waters,[72] for oxidation of alcohols by permanganate; they thought however that in this case a valency change from Mn^{IV} to Mn^{II} was concerned. The scheme (42, 43) is exactly similar to that operating in oxidation of aromatic aldehydes by chromic acid (eqns. 32 and 33).

In very alkaline solution, when manganate results, a more complex mechanism is involved since (i) the deuterium effect decreases and (ii) the overall rate rises only about 3-fold per unit change of pH, indicating a rough reaction order of $[\mathrm{Ar{\cdot}CHO}][\mathrm{MnO_4}^-][\mathrm{OH}^-]^{\frac{1}{2}}$. For this a free-radical chain mechanism involving the anion $\mathrm{Ar{\cdot}CH(OH){-}O^-}$ and possibly hydroxyl radicals has been tentatively proposed.

(iii) *Formic acid oxidation.* This is more complicated. Formic acid is more easily oxidised by strongly alkaline than by acid permanganate and is scarcely attacked by manganic cations. Early work of Holluta, in 1922,[73] showed that both $(MnO_4)^-$ and $(MnO_4)^{2-}$ oxidised formate anions and gave the first indication of the transient existence of blue $(MnO_4)^{3-}$. In neutral or weakly alkaline solution the reaction is approximately bimolecular, shows a primary salt effect, and is not dependent upon pH,[73, 74, 75] so that the initial reaction is one between two similarly charged ions:

$$(HCO_2)^- + (MnO_4)^- \rightarrow CO_2 + (MnO_3)^- + (OH)^- \quad \ldots . \quad (44)$$

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[71] K. B. Wiberg and R. Stewart, *J. Amer. Chem. Soc.*, 1955, **77**, 1786.

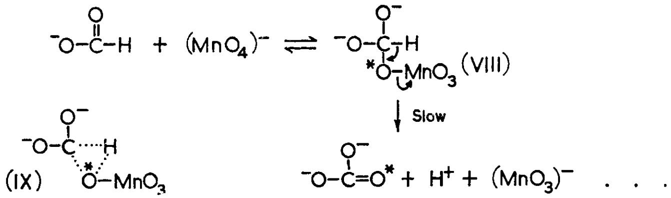
[72] J. Merz, G. Stafford, and W. A. Waters, *J.*, 1951, 638.

[73] J. Holluta, *Z. phys. Chem.*, 1922, **101**, 34, 489; **102**, 32, 276.

[74] F. C. Tompkins, *Trans. Faraday Soc.*, 1941, **37**, 201.

[75] K. B. Wiberg and R. Stewart, *J. Amer. Chem. Soc.*, 1956, **78**, 1214.

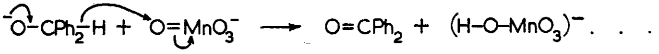
A deuterium effect ($k_H/k_D = 7{\cdot}4$) has been noted by Wiberg and Stewart who also showed, by using labelled permanganate, that there is a definite (18—30%) transfer of ^{18}O to the resultant carbon dioxide.[75] This could be explained by a reversible addition to a carbonyl bond, as in eqn. (43), followed by a slow concerted rearrangement involving both C–H and O–Mn links, as in sequence (45), but they regard this as improbable, since the



. . . (45)

$(MnO_4)^-$ anion would be expected to add to un-ionised formic acid (with a fairly definite C=O bond) more rapidly than to formate anion, whereas formic acid is oxidised less easily than formate.[73] To avoid this argument they suggest the partly-bonded transition state (IX), from which hydrogen-bonding to the whole (MnO_4) can be thought to promote the chemical change.

A structure similar to (IX) has been proposed by Stewart to explain the mechanism of permanganate oxidation of diphenylmethanol [76] in dilute alkali. This is a base-catalysed, second-order reaction in which there is a clear deuterium effect ($k_H/k_D = 6{\cdot}6$) but no oxygen transfer. A concerted



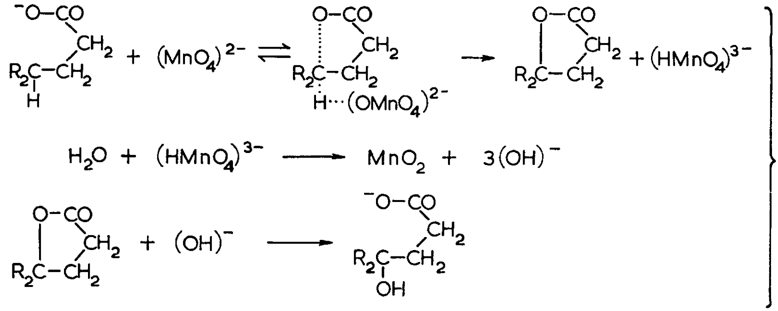
$$^-O-CPh_2-H + O=MnO_3^- \longrightarrow O=CPh_2 + (H-O-MnO_3)^- \quad . \; . \; . (46)$$

hydride-ion removal (46) would explain these observations, though it does not suffice in the case of formic acid.

(iv) *Oxidations of tertiary* C—H *in aliphatic acids* $R_2CH{\cdot}[CH_2]_2{\cdot}CO_2H$. Though most saturated carboxylic acids are inert to cold alkaline permanganate, or manganate, solutions, Kenyon and Symons,[77] found that acids of the general structure given above can be converted into hydroxy-acids $R_2C(OH){\cdot}[CH_2]_2{\cdot}CO_2H$ in preparative yields. With permanganate in concentrated (> 5N) alkali the yields can reach 70—90%, and optically active carboxylic acids give racemic products, whereas with manganate in dilute (*ca.* 0·5N) alkali equally effective oxidation occurs, but with complete retention of optical activity. The latter reaction must therefore be a hydride removal involving an Mn^{VI} to Mn^{IV} valency change and the transient formation of an optically inverted γ-lactone.

Kenyon and Symons suggest that the strongly alkaline permanganate may remove a hydrogen atom *via* hydroxyl radicals [formed as in eqn. (11)], but this does not explain the selectiveness of attack on a γ-C–H group. The sequence (47) can be compared with mechanism (38), suggested for chromic acid oxidation of saturated hydrocarbons.

[76] R. Stewart, *J. Amer. Chem. Soc.*, 1957, **79**, 3057.
[77] J. Kenyon and M. C. R. Symons, *J.*, 1953, 2129, 3580.



(47)

A point of general interest to be noted from inspection of these oxygen transfers is that they show that both manganite, $(MnO_3)^{2-}$, and permanganite, $(MnO_3)^-$, anions must be entities capable of transient existence, though they must be far less stable than anions of form $(MnO_4)^{n-}$.

Oxidations involving manganic ions

On account of the disproportionation (16) free manganic cations cannot exist in significant concentration in aqueous solution, though the sulphate, probably in the form of a complex ion, is stable in sulphuric acid of over 60% concentration.[78] Since most chelating agents form much more stable complexes with tervalent than with bivalent cations, many complex manganic salts, *e.g.*, oxalates, malonates,[79] and pyrophosphates, have been prepared and studied. Most of these have rapidly displaceable ligands.[15] The various manganic pyrophosphates, ranging from $Mn(H_3P_2O_7)_3$ to $\{Mn(H_2P_2O_7)_3\}^{3-}$ according to the degree of ionisation of the pyrophosphate groups, yield stable solutions at acidities down to pH 6 and are clearly the most suitable of these complexes for use in oxidation studies. The redox-potential measurements of Watters and Kolthoff[80] give values, dependent on pH, in the range + 1·1 to 1·2 v, showing that manganic pyrophosphate is decidedly a more potent oxidiser than ferric salts but inferior to ceric salts.

Towards organic compounds manganic pyrophosphate is quite a selective oxidant: it attacks aliphatic aldehydes and ketones, 1:2-diols, α-hydroxy-acids, malonic and oxalic acids, and phenols, often at rates suitable for kinetic study.[61] In general, monohydric alcohols and olefins are not attacked though allyl and crotyl alcohols can be oxidised very slowly.[81] On account of the resistance towards oxidation of vinyl cyanide and methyl methacrylate the induced polymerisation of these monomers can be used to establish the presence, and something of the nature, of the organic free radicals generated by the initial stages of Mn^{III} oxidations.[82] The distinctive features of several of these oxidations, which have been examined by Waters and his collaborators, are noted below.

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[78] L. Domange, *Bull. Soc. chim. France*, 1939, **6**, 594.

[79] G. H. Cartledge and P. M. Nichols, *J. Amer. Chem. Soc.*, 1940, **62**, 3057.

[80] J. I. Watters and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1948, **70**, 2455.

[81] H. Land and W. A. Waters, *J.*, 1958, 2129.

[82] A. Y. Drummond and W. A. Waters, *J.*, 1953, 2836.

Oxidation of Aldehydes and Ketones.—These regularly seem to occur through the enols or enolate ions. Thus the oxidation rates of propionaldehyde and butyraldehyde are of zero order with respect to Mn^{III} and of first order with respect to both aldehyde and hydrogen ion.[83] With ketones the same features emerge only at high Mn^{II} concentrations, for the oxidation step (eqn. 50) becomes measurable at low Mn^{III} concentrations.[84]

$$R{\cdot}CH_2COR' + (H_3O)^+ \rightleftharpoons R{\cdot}CH_2\overset{+}{C}R'(OH) + H_2O \quad \text{(Immediate)} \quad . \; . \; . \tag{48}$$

$$B{:} + R{\cdot}CH_2{\cdot}\overset{+}{C}R'(OH) \rightleftharpoons (BH)^+ + R{\cdot}CH{=}CR'(OH) \; \text{(Measureable)} \; . \; . \; . \tag{49}$$

$$R{\cdot}CH{=}CR'(OH) + Mn^{3+} \longrightarrow R{\cdot}CH{=}CR'{-}O{\cdot} + Mn^{2+} + H^+ \quad . \; . \; . \tag{50}$$

α-Hydroxy-aldehydes or ketones are the first detectable molecular oxidation products, and these are easily oxidised further. It has been suggested therefore that the true oxidation step is the removal from an enolate anion of an electron, since this would leave a mesomeric, resonance-stabilised radical that can then lose a second electron from the α-carbon atom, or, as in the case of *cyclo*hexanone oxidation,[84] disproportionate rapidly. It is noticeable that chloral hydrate, formaldehyde, and formic acid, which cannot yield enols, are not easily oxidised [83] (reactions 51—53).

$$B{:} + R{\cdot}CH{=}CR'OH \rightleftharpoons (BH)^+ + R{\cdot}CH{=}CR'{-}O^- \quad . \; . \; . \; . \; . \; . \tag{51}$$

$$Mn^{3+} + R{\cdot}CH{=}CR'{\cdot}O^- \longrightarrow Mn^{2+} + R{\cdot}CH{=}CR'{-}O{\cdot} \longleftrightarrow R{\cdot}\dot{C}H{-}CR'{=}O \quad . \tag{52}$$

$$R{\cdot}\dot{C}H{-}CR'{=}O + Mn^{3+} \longrightarrow R{\cdot}\overset{+}{C}H{-}CR'{=}O \longrightarrow R{\cdot}CH(OH){-}CR'{=}O \; . \; . \tag{53}$$

$$H_2O + R{\cdot}CH{=}CR'{-}CH{=}O \xrightarrow{H^+} HO{\cdot}CHR{-}CR'{=}CH{-}OH \quad . \; . \; . \tag{54}$$

However acraldehyde, α-methylacraldehyde, and crotonaldehyde, which cannot form normal enols, also oxidise at rates independent of the Mn^{III} concentration; in these cases oxidation through a 1 : 4-conjugated enol hydrate (54) is suggested.[63] This can be hydroxylated in the α-position, as in equations (52) and (53), and further oxidation can then occur as for a typical 1 : 2-diol.

Pyruvic acid however is oxidised quantitatively to acetic acid by a process related to that of α-hydroxy-acid oxidation and not by enolisation.[84]

Specific Oxidation of 1 : 2-Diols.—Leading to quantitative carbon–carbon bond fission, which can be brought about by several 1-electron-abstracting agents, these have several points of interest. With pinacol the initial oxidation rate is of first order with respect to total Mn^{III}, but of less than first order with respect to pinacol, the actual relationship being [85] of the form

$$-\,d[Mn^{III}]/dt \propto a[\text{Pinacol}]/(b + [\text{Pinacol}])$$

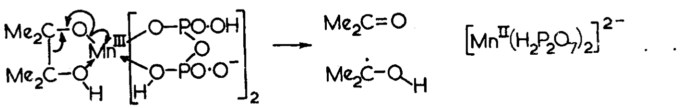
This has been explained by suggesting that the pinacol must first (reversibly) displace a chelated pyrophosphate group from attachment to the manganese atom before the electron switch (55) can occur. Some α-hydroxy-acids seem to oxidise similarly, with liberation of carbon dioxide,[86] as also does

[83] A. Y. Drummond and W. A. Waters, *J.*, 1953, 440.

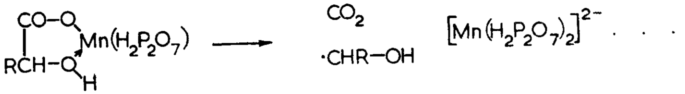
[84] *Idem, J.*, 1955, 497.

[85] *Idem, J.*, 1953, 3119.

[86] (Miss) P. Levesley and W. A. Waters, *J.*, 1955, 217.



(55)



(56)

pyruvic acid (56). When isomeric cyclic *cis*- and *trans*-glycols are examined, the relative rates of attack are not the same as for their oxidations by lead tetra-acetate or periodic acid and the reaction order with respect to Mn^{III} is not the same in all cases.[87] Evidently the stereochemistry of glycol fission by 1-electron abstraction needs further study.

Malonic acid affords another case in which oxidation by Mn^{III} occurs through a chelate complex.[88] This oxidation, like many others, is profoundly affected by the presence of oxygen, to which the initial organic free radicals are sensitive. Moreover it is specifically affected by manganous cations, the initial-rate measurements showing that the critical first oxidation step [simplified in eqns. (57) and (58) by neglecting the fact that only a manganic–malonate complex reacts] is reversible. Though the radical $\cdot CH(CO_2H)_2$ can also reduce Mn^{III} it is, as equation (57) implies,

$$Mn^{3+} + H_2C(CO_2H)_2 \rightleftharpoons Mn^{2+} + H^+ + \cdot CH(CO_2H)_2 \quad . \quad . \quad . \quad . \quad (57)$$

$$Mn^{3+} + \cdot CH(CO_2H)_2 \rightarrow Mn^{2+} + {}^{+}CH(CO_2H)_2 \quad . \quad . \quad . \quad . \quad (58)$$

$$HO\cdot CH_2\text{–}H + \cdot CH(CO_2H)_2 \rightarrow HO\cdot CH_2\cdot + H_2C(CO_2H)_2 \quad . \quad . \quad . \quad (59)$$

an oxidiser, for it can effect the oxidations of methyl and ethyl alcohols, ethers, and probably many other organic compounds (reaction 59). Here one has a novel form of induced oxidation, for manganic salts themselves, which unlike organic free radicals are merely electron abstractors, cannot directly oxidise monohydric alcohols or ethers. This induced oxidation, which is not observed with ethyl- and benzyl-malonic acids, is thought to be due to the electronic structure of the radical $\cdot CH(CO_2H)_2$ in which the two carboxyl groups are so powerfully electron-attracting that there is a marked tendency to further electron gain at the tervalent carbon centre.

Few organic free radicals as yet have been shown to exhibit this oxidising power, for in fact the great majority of carbon radicals are reducing agents. For instance the radical $\cdot CMe_2OH$, liberated during the oxidation of pinacol (eqn. 55),[82] or in other ways,[89] can reduce mercuric ions to mercurous ions, even in the presence of manganic salts or other oxidising agents.

An interesting example of this induced reduction by a transient radical is afforded by oxalic acid (60, 61), for the oxidation of oxalate by manganic

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[87] (Miss) P. Levesley, W. A. Waters, and A. N. Wright, *J.*, 1956, 840.

[88] A. Y. Drummond and W. A. Waters, *J.*, 1954, 2456.

[89] J. Merz and W. A. Waters, *J.*, 1949, S, 15.

pyrophosphate can promote the reduction of mercuric chloride by oxalate, this being a radical-catalysed chain reaction.[90]

$$(C_2O_4)^{2-} + Mn^{3+} \longrightarrow CO_2 + Mn^{2+} + (\cdot CO_2)^- \quad \dots\dots \quad (60)$$

$$(\cdot CO_2)^- + Hg^{2+} \longrightarrow CO_2 + Hg^+ \quad \dots\dots \quad (61)$$

$$(\cdot CO_2)^- + (MnO_4)^- \longrightarrow CO_2 + (MnO_4)^{2-} \quad \dots\dots \quad (62)$$

Oxygen uptake by radicals is of course another instance of induced reduction, here of the O_2 molecule.

Induced reductions and oxidations of this type are undoubtedly involved in quite a number of the oxidations that can be brought about by means of potassium permanganate in mineral acid solution. The important permanganate–oxalic acid reaction, for instance, has been investigated and discussed so frequently [57] that it needs but brief mention here, except that it should be pointed out that the initial attack on oxalic acid is effected by manganic ions, complexing of these with oxalate groups being important,[91] and that the autocatalytic nature of the overall oxidation is largely due to the rapidity with which the $(\cdot CO_2)^-$ radical-ion can attack permanganate itself (62). A similar catalysis involving the radical $\cdot CH(CO_2H)_2$ operates in the oxidation of malonic acid by acid permanganate.[88]

An important aspect of oxidations involving manganic ions is the influence of oxygen, which often changes the whole course of the reaction subsequent to the initial production of an organic free radical. Thus whereas under nitrogen the oxidation of malonic acid takes the course

$$CH_2(CO_2H)_2 \rightleftharpoons \cdot CH(CO_2H)_2 \longrightarrow HO\cdot CH(CO_2H)_2 \xrightarrow{\text{Fast}}$$

$$CO_2 + \cdot CH(OH)\cdot CO_2H \longrightarrow CO_2 + H\cdot CO_2H$$

with loss of carbon dioxide at the stage of tartronic acid and eventual production of a molecule of formic acid, the reaction in the presence of oxygen seems to have the course

$$\cdot CH(CO_2H)_2 \longrightarrow \cdot O\text{-}O\cdot CH(CO_2H)_2 \longrightarrow CO_2 + (CO_2H)_2 \longrightarrow 3CO_2$$

proceeding through oxalic acid to complete oxidation to carbon dioxide. Detailed treatment of effects of oxygen would require discussion of mechanisms of reactions between organic hydroperoxides and metallic ions; this cannot be summarised here, but it has been reviewed frequently in view of its great technical importance in hydrocarbon chemistry. It is sufficient to note that reactions of the types (63)—(66) (where X is a metal of variable

$$R\text{-}O\text{-}O\cdot + X^{2+} \rightleftharpoons (R\text{-}O\text{-}O{:})^- + X^{3+} \quad \dots\dots \quad (63)$$

$$R\text{-}O\text{-}O\cdot + X^{3+} \longrightarrow R^+ + O_2 + X^{2+} \quad \dots\dots \quad (64)$$

$$R\text{-}O\text{-}O\text{-}H + X^{2+} \longrightarrow R\text{-}O\cdot + ({:}OH)^- + X^{3+} \quad \dots\dots \quad (65)$$

$$R\text{-}O\cdot + X^{2+} \longrightarrow (R\text{-}O{:})^- + X^{3+} \quad \dots\dots \quad (66)$$

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[90] J. Weiss, *Discuss. Faraday Soc.*, 1947, **2,** 188; G. H. Cartledge, *J. Amer. Chem. Soc.*, 1941, **63,** 906.

[91] R. P. Bell and O. M. Lidwell, *J.*, 1935, 1303.

valency), can all occur, the favoured processes depending upon the redox potentials of the ions concerned in the particular environment of the reacting system.

Of the above reactions (63) and (64) are involved in the oxidation of hydrogen peroxide by manganic salts and also in the permanganate–hydrogen peroxide reaction. Oxygen undoubtedly affects the course of many oxidations in which acid or alkaline permanganate is the reagent,[41b] but its presence has rarely been taken into account or searched for experimentally. Indeed all kinetic work on oxidations involving ions of the transition elements in which cognisance has not been taken of the possible intervention of oxygen effects should be viewed with some scepticism.

Conclusions

Though this Review presents a wide range of reaction mechanisms, some substantiated in good detail but many still remaining as tentative hypotheses, it can be seen that the systematic understanding of the reactions of both chromic acid and permanganate is beginning to emerge. The major gap in experimental knowledge now concerns the inorganic chemistry rather than the organic chemistry of oxidation processes, for whilst, from other studies, it is possible to adduce relevant evidence concerning the natures of transient organic ions and free radicals, one can only make tentative suggestions concerning the structures and properties of the unstable ions of Cr^{V}, Cr^{IV}, Mn^{VI}, Mn^{V}, and Mn^{IV} in acid media. However, taking note of the present interest of quantum chemists in structures of compounds of the heavier elements, one can hope for theoretical help in the elucidation of many of these problems.