STRUCTURE AND REACTIVITY OF THE OXYANIONS OF TRANSITION METALS

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CONTENTS

I. INTRODUCTION

This review is concerned, primarily, with tetrahedral oxyanions of the transition metals, which are symbolized XO_4, a typical ion being permanganate. Known ions and oxides in this class are listed according to their periodic classification and electronic structure in Table I. Ions listed as "d^0" are termed "closed-shell" ions and can be depicted, formally, as X^{y+}, having a rare-gas configuration, coordinated to four oxide ligands. Then d^1 and d^2 ions have one and two "outer" electrons, respectively, these having considerable d-character on the metal (section III).

Our first concern is with the electronic structure of these ions, and their reactivity is discussed briefly in the light of our conclusions. Stress is laid primarily on the behavior of the oxyions themselves during reaction, since other aspects of mechanism, especially with respect to the complementary role of organic compounds, have been reviewed recently (59, 102).

Protonation is discussed, but polymeric ions and oxides are not included except incidentally. Solvation is considered, especially with respect to equilibria between tetrahedrally and octahedrally coordinated species, for example

$$XO_4 + 2H_2O \rightleftarrows XO_2(OH)_4 \qquad (1)$$
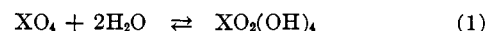
Finally the mechanism of photolysis is considered in terms of the structure of electronically excited states.

II. PREPARATION AND STABILITY

Salts of many of the ions listed in Table I are manufactured in large quantities and their preparation is covered in standard texts. The closed-shell ions represent the highest valence state of the metal under consideration and their formation is generally the result of vigorous oxidation of aqueous solutions of lower valence states. Sometimes oxyions having outer electrons are intermediates in such reactions and their salts can be isolated under appropriate conditions. Alternatively they may be prepared by controlled reduction of salts of the corresponding closed-shell ions. These salts

TABLE I

KNOWN TETRAHEDRAL OXYIONS. (FOR IONS LISTED IN PARENTHESES THERE IS UNCERTAINTY IN IDENTIFICATION)

d^0	VO_4^{3-}	CrO_4^{2-}	MnO_4^-		
d^1		CrO_4^{3-}	MnO_4^{2-}		
d^2			MnO_4^{3-}	FeO_4^{2-}	
d^3				(FeO_4^{3-})	
d^0	NbO_4^{3-}	MoO_4^{2-}	TcO_4^-	RuO_4	
d^1				RuO_4^-	
d^2				RuO_4^{2-}	
d^3					(RhO_4^{2-})
d^0	TaO_4^{3-}	WO_4^{2-}	ReO_4^-	OsO_4	
d^1		(WO_4^{3-})	(ReO_4^{2-})		
d^2			(ReO_4^{3-})		

are thermally fairly stable and the failure of many attempts to prepare some of those ions notable by their absence from Table I most probably arises because they either oxidize the solvent or disproportionate irreversibly to higher and lower valence states. Another reason may be that the desired ion is protonated by the medium. This in itself need not constitute "loss" of the ion in question, but the protonated species may either decompose thermally, with evolution of oxygen, or may undergo self condensation to give in the limit an insoluble "polymer" in which the tetrahedral environment of the metal may or may not be retained. The tendency of substituted ions to decompose with evolution of oxygen, and reactions leading to oxidation of the solvent, are considered in section IX.

To illustrate these generalizations we will consider the ions perferrate, FeO_4^-, and hypoferrate, FeO_4^{3-}. The former is unknown, while the latter, thought to be the result of certain high temperature fusions (57), has never been detected in aqueous solution.

Ferrate itself, although stable in the solid state, decomposes in aqueous solution to give oxygen and various forms of trivalent iron. The rate is an involved function of the concentration of hydroxide ion, but certainly increases rapidly as the concentration of hydroxide ion is increased. It is thus almost certain that decomposition is a result of oxidation of hydroxide ions. Since perferrate is certain to be a much more powerful oxidant than ferrate it is likely to oxidize water under all conditions, and hence attempts to prepare this ion in aqueous solutions are not likely to be successful.

Hypoferrate, on the other hand, is probably an intermediate in the decomposition of ferrate in aqueous alkali and the fact that all attempts to detect it have failed means that the disproportionation

$$3FeO_4^{3-} \rightleftarrows 2FeO_4^{2-} + 3Fe^{III} \qquad (2)$$
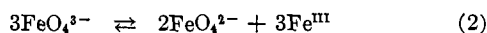
lies far to the right under all conditions. This may be because hypoferrate is protonated, but, although its basicity is unknown, comparison with hypomanganate, MnO_4^{3-}, suggests that in solutions greater than one

molar in hydroxide ion this is improbable. Rather, we are inclined to the view that this ion is very much less stable than ferrate because the latter has a special stability associated with a half-filled electronic level which is well separated from the first vacant level (section III).

IONS WITH THREE OUTER ELECTRONS

Addition of another electron to an ion with two outer electrons, such as ferrate, will either give an ion with a doublet ground state, the added electron pairing with one of those already present, or one with a quartet ground state the added electron being then in the lowest vacant orbital of the parent oxyion. Since spectrophotometric and magnetic studies of d^1 and d^2 ions reveal that in a typical case this level is about 10^4 cm.$^{-1}$ above the partially filled level, and since pairing energies are likely to be of similar magnitude, it is not clear which eventuality will transpire, and, indeed, it would not be surprising to find different results in different instances.

In either case, there is evidently a large extra factor resisting the gain of a third electron, which may well explain why disproportionations such as (2) appear to be important. Another factor requiring consideration is that the corresponding octahedrally coordinated ion, if symmetrically coordinated, would have a degenerate ground state, and hence this restriction would no longer hold. Therefore, hydration to an octahedral hydroxy derivative might well be important (see section IX) for ions with three outer electrons.

Of the possible d^3 ions three deserve special comment. Quite the most important is hypoferrate which appears to have been characterized in the solid state as its potassium and sodium salts (57). In addition to analytical data, supporting the formulations a magnetic moment of about 3.85 B.M. is reported for these salts (57), which is close to the value expected for three unpaired electrons if orbital contributions are small. Also, although in published work results of X-ray scattering studies on the powdered compounds are reported to be inconclusive, it appears that later experiments have been more successful and the results apparently confirm that the ion FeO_4^{3-} is present (58).

Preparation of these salts involves high temperature reaction between solids under carefully controlled conditons (57), a technique which has certainly proved to be successful in a number of cases in which independent and quite different methods have established the properties of the ions concerned. (Cf. hypomanganate (21, 71) and hypochromate (5).) Hitherto, however, attempts to repeat these preparations have been unsuccessful (6). The products, which are black powders, had magnetic moments, as measured by conventional techniques, close to that required for one unpaired

electron, using the "spin-only" formula. Also, our attempts to obtain well defined X-ray scattering patterns have, so far, been without success. These black solids "react" with water or aqueous alkali very rapidly to give ferrate, some form of trivalent iron, and oxygen. The diffuse reflectance spectra of solids "diluted" with potassium sulfate are ill defined, but shoulders were detected in those regions where ferrate has maxima (20, 49). Since hypoferrate is expected to have well defined absorption bands in the visible and near-ultraviolet regions we find these results most unsatisfactory. No explanation can be offered at present to account for these marked differences.

Another instance, where results are again in an unsatisfactory state, is the rhodate ion, RhO_4^{2-}. Oxidation of rhodium salts by hypochlorite, persulfate, and other oxidants in dilute aqueous alkali results in an intensely blue solution from which a blue precipitate can be obtained on addition of barium hydroxide (3, 34). Although this blue compound was thought to be rhodate, RhO_4^{2-} (34), recent spectral studies (3) have been interpreted as proving that it is a derivative of quinquevalent rhodium (3). For various reasons, we do not find this latter conclusion compelling. Preliminary magnetic studies (6) of the blue barium salt give a magnetic moment close to that required for one unpaired electron on the spin-only formulation. It is hard to reconcile this result with the concept that the compound contains quinquevalent rhodium, which should have either four unpaired electrons or be diamagnetic. Present studies of this compound are inconclusive and, while it is possible that these blue derivatives do contain sexivalent rhodium, with one unpaired electron, the evidence is, as yet, incomplete (6).

Finally, it is recalled that manganese dioxide dissolves in hot, concentrated aqueous alkali to give a clear, purple solution, apparently without change in valence state. Spectrophotometric studies (68) have revealed, however, that the solution consists of an equimolar mixture of trivalent manganese, probably $Mn(OH)_6^{3-}$, and hypomanganate, MnO_4^{3-}. This leads to the rather surprising conclusion that monomeric quadrivalent manganese oxy- or hydroxy species, whether tetrahedral or octahedral, disproportionate in alkaline solution.

III. STRUCTURE OF TETRAHEDRAL IONS

The first attempt to provide a quantitative understanding of the absorption spectra of the permanganate and chromate ions was made by Wolfsberg and Helmholz (107) in 1952. Although the orbital level scheme which they derived now appears to be incorrect, their general approach has provided a foundation for much subsequent work. They were among the first to apply molecular orbital theory to transition metal complexes and their interpretation of the spectra of permanganate and chromate as involving internal charge-transfer is undoubtedly correct.

A. THE LEVEL SCHEME OF WOLFSBERG AND HELMHOLZ

The molecular orbitals for a given molecule reflect its geometrical structure and can be classified according to their behavior under the group of rotations and reflections which leave the molecular framework unchanged. For a tetrahedral molecule or ion XO_4 (group T_d) it can be shown by group-theoretical methods that the molecular orbitals belong to one or another of five distinct types, forming bases for the five irreducible representations of T_d.

For closed-shell ions one can make the simplifying assumption that the nonvalence electrons of the metal and oxygen atoms are unaffected by the bonding and that these electrons, together with the nuclei, form an effective core into the field of which the molecular electrons are to be placed. Thus, in constructing the molecular orbitals, only the nd, $(n + 1)s$, and $(n + 1)p$ atomic orbitals of the central atom and the $2p$ atomic orbitals of the oxygen atoms are to be used. There are then twenty-four electrons to be placed in the molecular orbitals, the ground state being constructed by placing these electrons in the lowest-lying molecular orbitals.

Table II shows the symmetry behavior of the orbitals and the various combinations which transform under

TABLE II
MOLECULAR ORBITALS FOR XO_4 COMPLEXES

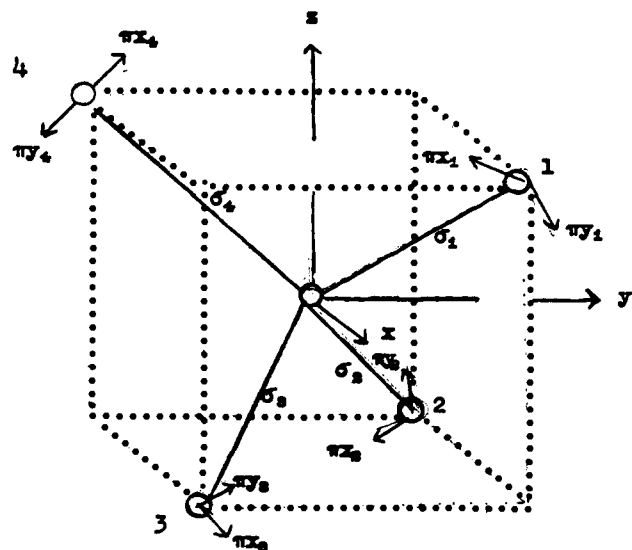| X orbitals	O orbitals	Irreducible representation
$4s$	$\frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$	A_1
d_{z^2}	$\frac{1}{4}[\pi x_1 + \pi x_2 + \pi x_3 + \pi x_4 - \sqrt{3}(\pi y_1 + \pi y_2 + \pi y_3 + \pi y_4)]$	E
$d_{x^2-y^2}$	$\frac{1}{4}[\pi y_1 + \pi y_2 + \pi y_3 + \pi y_4 + \sqrt{3}(\pi x_1 + \pi x_2 + \pi x_3 + \pi x_4)]$	
$p_{x_1}\, d_{yz}$	$\frac{1}{2}(\sigma_1 + \sigma_3 - \sigma_2 - \sigma_4)\frac{1}{4}[\pi x_4 + \pi x_2 - \pi x_1 - \pi x_3 + \sqrt{3}(\pi y_4 + \pi y_2 - \pi y_1 - \pi y_3)]$	
$p_{y_1}\, d_{xz}$	$\frac{1}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)\frac{1}{2}[\pi x_1 + \pi x_2 - \pi x_3 - \pi x_4]$	T_2
$p_{z_1}\, d_{xy}$	$\frac{1}{2}(\sigma_1 + \sigma_4 - \sigma_2 - \sigma_3)\frac{1}{4}[\pi x_3 + \pi x_2 - \pi x_1 - \pi x_4 + \sqrt{3}(\pi y_4 + \pi y_1 - \pi y_2 - \pi y_3)]$	
	$\frac{1}{4}[\pi y_2 + \pi y_4 - \pi y_3 - \pi y_1 + \sqrt{3}(\pi x_1 + \pi x_3 - \pi x_2 - \pi x_4)]$	
	$\frac{1}{2}[\pi y_1 + \pi y_2 - \pi y_3 - \pi y_4]$	T_1
	$\frac{1}{4}[\pi y_2 + \pi y_3 - \pi y_1 - \pi y_4 + \sqrt{3}(\pi x_2 + \pi x_3 - \pi x_1 - \pi x_4)]$	

Fig. 1.—Orientation of the oxygen orbitals relative to the axes on the central atom. (The direction cosines of the O_1 orbitals are: $\sigma_1 = -1/3^{1/2}, -1/3^{1/2}, -1/3^{1/2}$; $\pi x_1 = 1/6^{1/2}, -2^{1/2}/3^{1/2}, 1/6^{1/2}$; $\pi y_1 = 1/2^{1/2}, 0, -1/2^{1/2}$. The direction cosines of the other oxygen orbitals may be obtained from these by the action of the twofold axes of T_d which coincide with the x, y, and z axes shown.)

the representations A_1, A_2, E, T_1, and T_2 of the tetrahedral group, while Fig. 1 shows the orientation of the atomic orbitals used. In principle, one can now determine the energies (ϵ) and forms of the final molecular orbitals by solving a secular determinant $H_{ij} - G_{ij}\epsilon = 0$ for each representation in turn. Wolfsberg and Helmholz (107) did this by making semiempirical estimates of the H_{ij} elements. For example, there will be two pairs of molecular orbitals belonging to the E representation, one pair being of the form

$$A \; d_{z^2 - y^2} + B \; \tfrac{1}{4}[\pi y_1 + \pi y_2 + \pi y_3 + y_4 +$$
$$\sqrt{3} \; (\pi x_1 + \pi x_2 + \pi x_3 + \pi x_4)]$$

where the coefficients A and B are to be determined. Hence the secular determinant for the representation is

$$\begin{vmatrix} H_{11} - G_{11}\epsilon & H_{12} - G_{12}\epsilon \\ H_{21} - G_{21}\epsilon & H_{22} - G_{22}\epsilon \end{vmatrix} = 0$$

where the suffix 1 refers to the metal $d_{z^2 - y^2}$-orbital and suffix 2 to the combination of oxygen 2p-orbitals. In order to solve for ϵ we first need values for the H_{11} and H_{22} elements and Wolfsberg and Helmholz derived their values from experimentally determined ionization potentials. The group overlap integral G_{12} is

$$G_{12} = G_{21} = \int d_{z^2 - y^2} \tfrac{1}{4}[\pi y_1 + \pi y_2 + \pi y_3 + \pi y_4 +$$
$$\sqrt{3}(\pi x_1 + \pi x_2 + \pi x_3 + \pi x_4)]d\tau$$

This is expanded as a sum of simple atomic overlap integrals which can be evaluated if one assumes appropriate wave functions to represent the atomic orbitals.

The values of $H_{ij}(i \neq j)$ elements were approximated

by setting them proportional to the corresponding overlap integrals according to the relation

$$H_{ij} = FG_{ij} \; \tfrac{1}{2}(H_{ii} + H_{jj})$$

where F is a constant.

Finally the symmetry orbitals were normalized and so $G_{11} = G_{22} = 1$.

The molecular orbital energies of MnO_4^- and CrO_4^{2-} as calculated by Wolfsberg and Helmholz are shown in Fig. 2, the twenty-four valence electrons being placed
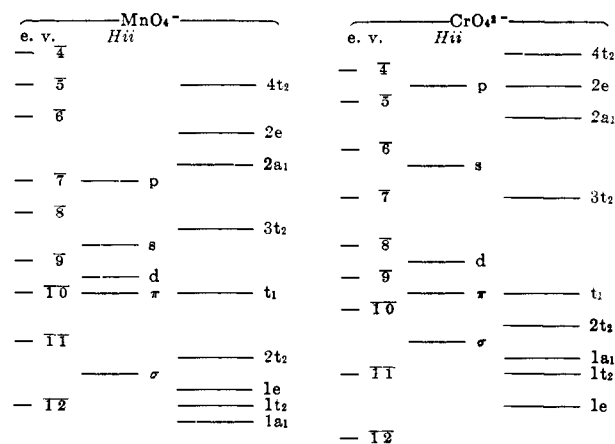

Fig. 2.—Energy level scheme for MnO_4^- and CrO_4^{2-} after Wolfsberg and Helmholz (107).

in the orbitals of lowest energy. The $1t_2$- and $2t_2$-orbitals, each capable of holding six electrons, are bonding, while $3t_2$ and $4t_2$ are antibonding. The two e-orbitals are each capable of holding four electrons, $1e$ being strongly bonding and $2e$ antibonding. t_1 is a nonbonding π-orbital located on the four oxygen atoms and is fully determined by symmetry.

The level schemes show several curious features. In particular, the stability of the $1e$-orbital is unusual in view of the fact that it is a π-orbital. As a consequence the first antibonding level is an orbital triplet, rather than the $2e$-orbital doublet. This point is fully discussed later.

B. ELECTRONIC TRANSITIONS

The ground state of MnO_4^- can be written, $(1e)^4$-$(1t_2)^6(1a_1)^2(2t_2)^6(t_1)^6$: $^1A_1$ and the lowest energy absorption band is described by Wolfsberg and Helmholz as $(t_1)^53t_2$: $^1T_2 \leftarrow \; ^1A_1$. This is the absorption band responsible for the purple color of permanganate, known to every chemist. For a tetrahedral molecule electric dipole transitions are allowed only if the product of the ground and excited states contains a term transforming under the T_2 representation of T_d; hence the transition $^1T_2 \leftarrow \; ^1A_1$ is symmetry allowed (the superior suffix giving the spin degeneracy of the state). The excited electron configuration $(t_1)^53t_2$ gives rise to E, A_2, and T_1 states also but transitions to these from the $^1A_1$ ground state are symmetry forbidden.

The ultraviolet band of MnO_4^- is interpreted by Wolfsberg and Helmholz as the transition $(2t_2)^5$-$(t_1)^63t_2$: $^1T_2 \leftarrow {}^1A_1$. Again the excited electron configuration gives rise to other states (T_1, E, A_1) transitions to which are symmetry forbidden. Wolfsberg and Helmholz's numerical results do not agree too well with the observed transition energies or intensities, but they do show the trend toward shorter wave lengths in passing from MnO_4^- to CrO_4^{2-}. Moreover they are able to explain the very weak bands found by Teltow (100) in his measurements on single mixed crystals $K(Cl,Mn)O_4$. These occur at the long wave length end of the lowest energy band and were interpreted as the normally forbidden transitions mentioned above which were enhanced as a consequence of the lower symmetry of the ion in the $KClO_4$ lattice. This lowering of the symmetry also accounts for changes in the lines arising from the $3t_2 \leftarrow t_1$ transition as the direction of polarization varies with respect to the crystal axes.

Only closed-shell ions were considered by Wolfsberg and Helmholz. However, as spectra of ions with outer electrons became available an attempt was made to use their approach for purposes of interpretation (20). This also seemed to be reasonable in a qualitative sense. However, in 1958, Ballhausen and Liehr (7) proposed an alternative level scheme, illustrated in Fig. 3, and used this to interpret the spectra of closed-shell ions with some success. In their arrangement the antibonding e orbital lies below t_2, this being the order predicted by crystal field theory.

At this stage there did not seem to be much to choose between these alternatives. A new criterion was
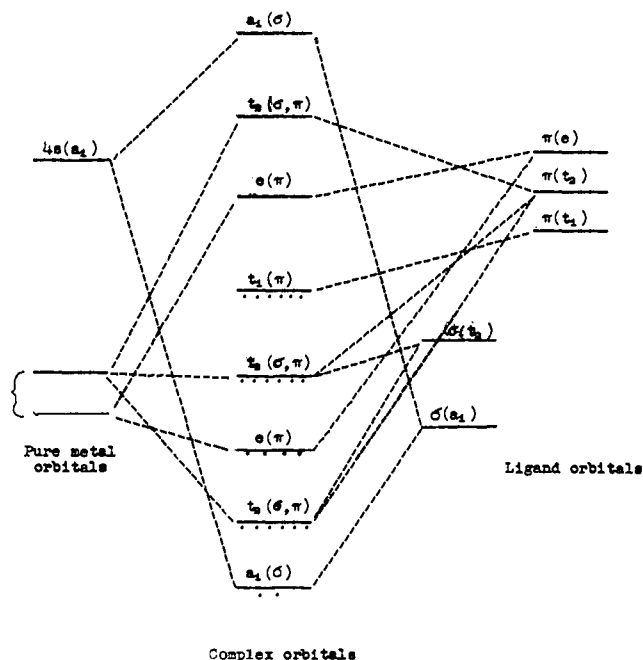

Complex orbitals

Fig. 3.—Molecular orbital scheme for tetrahedral ions after Ballhausen and Liehr.

needed, and this was forthcoming in the form of electron-spin resonance spectra for certain d^1 and d^2 ions. Initial experiments on polycrystalline materials (16) were not very informative, but detailed studies of single, diluted, crystals gave the required information, which showed convincingly that the unpaired electrons were in the antibonding e level rather than the t_2 level. Because of their key position, the results of these studies are described in some detail.

c. ELECTRON SPIN RESONANCE OF FERRATE AND HYPOMANGANATE

The detailed crystal structure of potassium ferrate has not been determined, but Retgers (81) examined microscopic crystals of potassium ferrate, potassium chromate, and potassium sulfate and concluded that they were isomorphous, while Carrington, et al. (15), were able to grow quite large mixed crystals of potassium chromate and potassium ferrate. The e.s.r. spectrum obtained from a potassium chromate crystal containing about 1% of potassium ferrate was fully consistent with the known details (112) of the potassium chromate crystal structure. Two electronic transitions were observed, showing an effective spin of 1 and confirming the conclusions of Hrostowski and Scott (40) which were based on a magnetic susceptibility study.

The angular variation of the e.s.r. spectrum could be well represented by a spin Hamiltonian of the form

$$\mathcal{K} = g\beta H \cdot S + D_x S_x^2 + D_y S_y^2 + D_z S_z^2$$

with $S = 1$ and the g-value isotropic at $g = 2$. The zero-field splittings of the spin triplet are given by $D_x = 0.0504$ cm.$^{-1}$, $D_y = 0.0180$ cm.$^{-1}$, and $D_z = 0.0684$ cm.$^{-1}$.

The isotropic g-value, the very small zero-field splitting, and also the fact that the e.s.r. line widths are temperature-independent, show that the ground state of the ion must be well separated from the first excited state so that spin-orbit coupling is relatively ineffective in mixing higher excited states into the ground state (10, 18). These conclusions strongly indicate that the ion possesses a $^3A_2$ ground state, formed by two electrons occupying a doubly degenerate e-orbital with their spins parallel. An example of the alternative arrangement in which two electrons occupy an initially triply degenerate orbital is provided by octahedrally coordinated V^{3+} ion. In this case (115) the zero-field splittings are so large ($\sim$8 cm.$^{-1}$) that the usual electron resonance transitions in which the electron spin quantum number changes by unity are not observable with the microwave frequencies normally used. Although the orbital degeneracy of an orbital triplet in ferrate would be partially removed by the rather low site symmetry in the potassium chromate crystal, spin-orbit coupling would still be relatively important.

The e.s.r. results obtained from single crystals of sodium vanadate containing 1–2% of hypomanganate are also consistent with a $^3A_2$ ground state, well separated from the lowest excited state. The extreme complexity of the sodium vanadate crystal structure (24) prevented a complete analysis from being carried out. However, the g-value was found to be isotropic at 2.0 and the well resolved Mn^{55} hyperfine structure was also isotropic. The general form of the anisotropic electronic splitting suggested that the zero-field splittings were comparable with those measured for the ferrate ion, and again the line width was found to be almost temperature-independent.

D. ELECTRON SPIN RESONANCE OF MANGANATE

Preliminary investigations (16) on pure polycrystalline potassium manganate showed the presence of a single asymmetric line, observable only at 20°K. Single crystals of potassium chromate containing 1% potassium manganate gave a very well resolved spectrum, again observable only at 20°K. The anisotropic g-value and Mn^{55} hyperfine structure was well represented by the spin Hamiltonian

$$\mathcal{H} = \beta(g_x S_x H_x + g_y S_y H_y + g_z S_z H_z) + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z + A_{yz} S_y I_z + A_{zy} S_z I_y$$

the experimental values of the constants being

$$g_x = 1.970 \quad g_y = 1.966 \quad g_z = 1.938$$

$$A_z = 0.0135\epsilon \text{ cm.}^{-1} \quad A_x = 0.0025\epsilon \text{ cm.}^{-1} \quad A_y = 0.0033\epsilon \text{ cm.}^{-1}$$
$$A_{yz} = -0.0022\epsilon \text{ cm.}^{-1}$$

where ϵ is $+1$ or -1. In addition to the normal hyperfine structure extra lines owing their intensity to the perturbing effects of the Mn^{55} electric quadruple moment were observed. These effects are not represented in the above spin Hamitonian.

The extra terms in the spin Hamiltonian reflect the very low symmetry of the ion in the potassium chromate lattice. This lack of symmetry complicates the theoretical evaluation of the spin Hamiltonian constants

because the axes of the hyperfine and g-tensors are different. Readers interested in details of evaluating the results are referred to Schonland's paper (88).

The main conclusions can be summarized as follows:

1. The unpaired electron in the unperturbed tetrahedral manganate ion is in a doubly degenerate orbital.

2. The unpaired electron is concentrated mainly on the manganese atom.

3. The lowest excited orbitals of t_2 symmetry in the unperturbed ion are spread over the whole ion.

It should be stated that conclusions 2 and 3 depend directly on the chosen form of the manganese 3d atomic orbital wave functions and indirectly on the value of the spin-orbit coupling constant for sexivalent manganese. These are matters of some uncertainty which frequently arise in the interpretation of electron spin resonance data.

One could undoubtedly learn more about the importance of π-bonding in the e-orbitals by studying the MnO_4^{2-} ion enriched in O^{17} and looking for oxygen ligand hyperfine structure (33). Such a study would be both difficult and costly. The most important result of the e.s.r. studies is in their discrimination between the alternative orbital level arrangements and in our subsequent discussion we shall follow the scheme suggested by Ballhausen and Liehr.

We should perhaps digress for a moment to discuss the possibility of a Jahn–Teller effect in the manganate ion. One might have hoped to observe some of the consequences of this effect in the electron spin resonance spectrum, remembering the results obtained for the Cu^{2+} ion in cubic crystalline fields (1, 78). However, the chromate ion, which is diamagnetic having a closed shell ground state, is itself highly distorted in the crystal and the orbital degeneracy of the manganate ion is certainly removed in the mixed crystals. The electron spin resonance measurements made so far give no evidence for or against the operation of the Jahn–Teller effect.

TABLE III

DETAILS OF THE VISIBLE AND ULTRAVIOLET SPECTRA OF VARIOUS OXIDES AND OXYANIONS

	VO_4^{3-} (20)	CrO_4^{2-} (20)	CrO_4^{3-} (5)
Band max (ν, cm.$^{-1}$)	36,900	26,810:36,630	16,000:28,200
Oscillator strengths (f)	0.150	0.089:0.110	

	MnO_4^- (21)	MnO_4^{2-} (21)	MnO_4^{3-} (21)
ν	18,320:32,210	16,530:22,940 + 28,490 + 33,440	14,810:30,800
f	0.032:0.070	0.025 ca. 0.12	0.017 : 0.112

	FeO_4^{2-} (20)	MoO_4^{2-} (20)	TcO_4^- (103)	RuO_4 (20)
ν	12,720:19,600	44,500	34,900:40,700:49,500	26,000:32,200
f	0.009:0.035	0.106	0.040:0.095:0.013	0.020:0.044

	RuO_4^- (110,103)	RuO_4^{2-} (110,103)	WO_4^{2-} (20)	ReO_4^- (20)
ν	26,000:31,700	21,600	ca. 50,300	44,000:49,000
f	0.027:0.037	0.031		

	OsO_4 (103, 60)	CrO_3F^- (108)	CrO_3Cl^- (108)
ν	33,500:41,500	22,500:28,500	22,500:27,900
		0.003:0.016	0.003:0.025

E. ELECTRONIC SPECTRA OF CLOSED-SHELL IONS

According to the orbital level diagram illustrated in Fig. 3, the lowest-energy electronic transition is the promotion of a nonbonding electron from t_1 into the e-orbital. The excited electron configuration $(t_1)^5e$ gives rise to a T_1 and a T_2 state, the $^1T_1 \leftarrow {}^1A_1$ transition being symmetry forbidden. Attempts to calculate the oscillator strength of the absorption band have been made (7, 19). If the e-orbitals are taken as pure metal d-orbitals (7), the "charge-transfer" character of the transition is immediately apparent. In common with other sorts of charge transfer spectra (76), however, the absorption bands will be intense only if there is some overlap between the donor and acceptor orbitals. Carrington and Schonland (19) found that the calculated intensity of the lowest energy absorption band in MnO_4^- and CrO_4^{2-} depends strongly on the amount of mixing between the metal d-orbitals and ligand π-orbitals in the e molecular orbitals.

The ultraviolet absorption band found for MnO_4^- and CrO_4^{2-} is interpreted in terms of the electronic transition $(t_1)^53t_2$: $^1T_2 \leftarrow {}^1A_1$, and again the intensity of the band is governed mainly by the amount of ligand π-orbital admixture in the t_2-orbitals. The detailed calculations (19) suggest that the amount of such admixture required to account for the experimental oscillator strengths is quite small for both the ultraviolet and the visible absorption bands.

F. ELECTRONIC SPECTRA OF d^1 AND d^2 IONS

In terms of the orbital level scheme used for permanganate, the ground state electron configuration of the manganate ion is $(t_1)^6e$: ^2E, while that of the hypomanganate ion is $(t_1)^6e^2$: $^3A_2$. In the case of the manganate ion, the two electronic transitions considered in the case of permanganate give rise to the excited electron configurations (and states) $(t_1)^6e^2$: $(2T_1 + 2T_2)$ and $(t_1)^5et_2$: $(T_1 + T_2 + E + A_1 + A_2)$. In this case electric dipole transitions are allowed to both $^2T_1$ and $^2T_2$ states. For a particular excited electron configuration the T_1 and T_2 states will have different energies because of electron repulsion terms, so that one might expect to observe two absorption bands associated with each electron jump, making a total of four bands. The visible and ultraviolet absorption spectrum of the manganate ion indeed shows four bands.

For the hypomanganate ion the corresponding excited electron configurations are $(t_1)^5e^3$ and $(t_1)^5e^2t_2$. The only allowed electric dipole transitions are to $^3T_1$ states so that we would now expect to observe only two absorption bands associated with the two electron jumps. This again is consistent with the experimental measurements.

This interpretation of the spectra seems, at first sight, rather satisfactory, but there are at least two important objections to it. First, an electronic transition $t_2 \leftarrow e$ is possible for both ions and will certainly occur in the visible or near-ultraviolet region of the spectrum. Carrington and Schonland attempted to calculate the dipole moment of the transition and decided it would be too low. However, they did not take into account the possibility of mixing metal d- and p-orbitals in the t_2 level and such mixing is known to lead to enhanced intensity.

The second objection is that, if the above interpretation is correct, the energy of the charge-transfer $e \leftarrow t_1$ transition decreases as one passes from septivalent to quinquevalent manganese (Fig. 4). This cer-
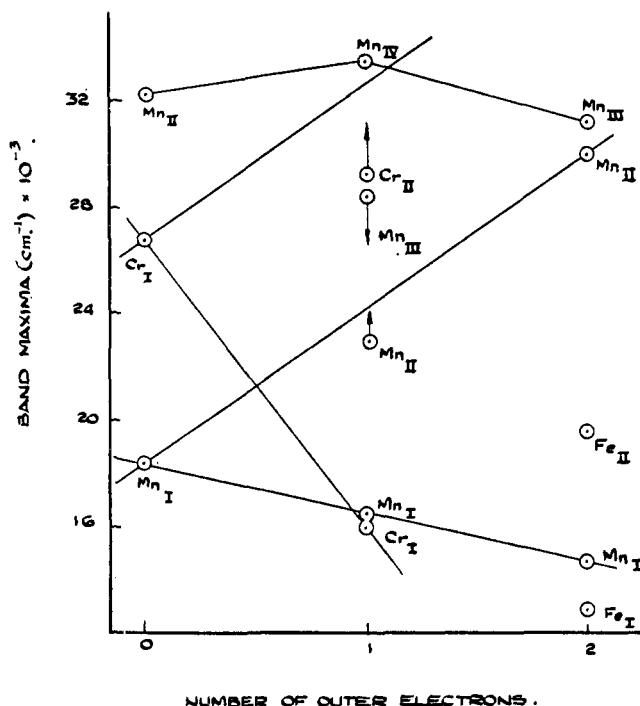

Fig. 4.—Band energies for tetrahedral oxyions as a function of the number of "outer" electrons. (XI, XII, and XIII denote maxima for the first, second, and third bands of the relevant oxyions XO_4.)

tainly is not what one would expect and alternative interpretations which seem more reasonable chemically have been made (17, 96). Without further experimental evidence however, it is difficult to be absolutely certain of any assignment; the fact that the charge-transfer and d–d transitions are expected to have rather similar energies inevitably makes the issue more involved.

G. HYBRID ORBITAL APPROACH

Giacometti (29) has explored the possibilities of describing the σ- and π-bonding of tetrahedral complexes by constructing appropriate central atom hybrid orbitals. One of the central atom σ-orbitals is

$$\sigma = \frac{1}{2} s + \left[\left(\frac{1}{4} - b^2 \right)^{1/2} (p_x + p_y + p_z) + b(d_{yz} + d_{zx} + d_{xy}) \right]$$

The constant b is chosen to give the maximum projection of the angular part of the function along the bond direction. The axes system used is the same as that indicated in Fig. 1.

Giacometti shows how one may construct central atom hybrid orbitals suitable for forming π-bonds with appropriate ligand orbitals. One of these hybrid orbitals is

$$\pi = \sqrt{\frac{1}{2}} \left[(1 - a^2)^{1/2}(p_x + p_y) - \sqrt{\frac{a}{3}} (d_{yz} + d_{zy} + 2d_{z^2-y^2}) \right]$$

The interesting and satisfactory feature is that the values $a = \sqrt{3/2}$, $b = \sqrt{1/8}$ give σ- and π-orbitals which are orthogonal and whose "strength" is very nearly a maximum. Thus the conclusions are that the σ hybrids are composed of 25% s-, 37.5% p-, and 37.5% $d(t_2)$-orbitals, while the composition of the hybrid π-orbitals is 25% p-, 25% $d(t_2)$-, and 50% $d(e)$-orbitals.

H. TEMPERATURE-INDEPENDENT PARAMAGNETISM

Despite the fact that the permanganate and chromate ions have closed-shell ground states, they are feebly paramagnetic (80). This "temperature-independent" paramagnetism is of considerable interest because it provides some information about covalent bonding in these complexes (14).

Temperature-independent paramagnetism (tip) arises from nonvanishing matrix elements of the orbital angular momentum operator 1 between the ground and excited states. It is particularly important in octahedral Co^{3+} complexes where the ground state is $(t_{2g})^6$: $^1A_{1g}$, with all the electrons paired. The lowest excited state is $(t_{2g})^5e_g^1$: $^1T_{1g}$ and 1 connects this with the ground state, giving a large contribution to tip. The magnitude of the effect can be correlated with the energy separation between the $^1A_{1g}$ and $^1T_{1g}$ states and is thus related to the strength of the coordinating ligands (32).

Now in the case of the permanganate and chromate ions, the metal d-orbitals are vacant in the ionic configuration. However, electrons are delocalized from oxygen 2p-orbitals into metal d-orbitals and possible contributions to tip arise from electrons in metal d- and oxygen p-orbitals. Estimates of these contributions have been made (14). The significant point is that if there were no covalent bonding, the tip terms would be negligible.

IV. ELECTRONIC SPECTRA OF MONOSUBSTITUTED IONS

Replacement of one oxide ligand of a closed-shell ion by another ligand such as halide, hydroxide, or alkoxide results in a highly characteristic change in the visible and near-ultraviolet spectrum. Qualitatively,
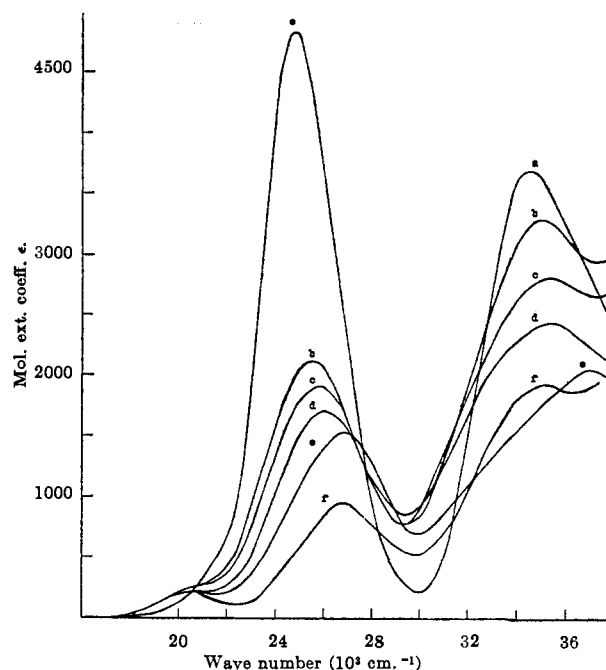

Fig. 5.—Ultraviolet spectra of monosubstituted chromates: (a) CrO_4^{2-} in H_2O, (b) t-BuOCrO$_3^-$ in t-BuOH, (c) i-PrOCrO$_3^-$ in i-PrOH, (d) MeOCrO$_3^-$ in MeOH, (e) HCrO$_4^-$ in H_2O, (f) AcOCrO$_3^-$ in AcOH.

as illustrated in Fig. 5, the first band is replaced by two new bands, one of low intensity on the low energy side and one of about one third the intensity of the "parent" band displaced to somewhat higher energies. These changes are so characteristic for a wide range of oxyions and ligands that they can be taken with some confidence as being diagnostic of the change $XO_4 \rightarrow YXO_3$. In all these cases the local symmetry at X is reduced from T_d to C_{3v}.

Wolfsberg, Helmholz, and Brennan (108) carried out a semiempirical molecular orbital calculation for CrO_3F^-, similar to that described in section III for the tetrahedral ions. A rather weak band at 22,500 cm.$^{-1}$ is ascribed to an $a_2 \rightarrow e$ transition, a_2 being a nonbonding orbital centered on the three oxygen atoms, and the e-orbital correlating with the lowest vacant e-orbital in CrO_4^{2-}. The next, more intense transition was then described as $e \rightarrow e$. In this case the excited electron configuration gives rise to A_2, A_1, and E states, transitions to the last two being symmetry allowed.

An alternative interpretation has been proposed (4) in which the energies of the filled a_2- and e-orbitals are inverted, so that the first and second transitions become $e \rightarrow e$ and $a_2 \rightarrow e$, respectively. This conclusion was reached since it gave better agreement between measured and calculated oscillator strengths for these bands.

These alternatives are depicted pictorially in Fig. 6.

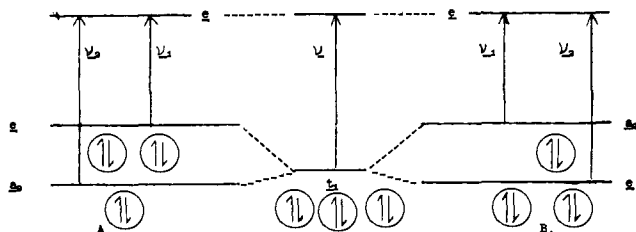In a crude first approach, it is possible to associate

Fig. 6.—Alternative orbital level schemes and electronic transitions (ν_1 and ν_2) for monosubstituted ions.

the $a_2 \rightarrow e$ transition with a charge transfer from oxygen to the vacant e level and the $e \rightarrow e$ transition with a similar charge transfer from the ligand Y (56). This is especially reasonable when the electron affinities of Y and oxygen ligands are very different. In order to distinguish between the alternative assignments, the spectra of a series of monosubstituted chromates, $ROCrO_3^-$, where R ranged from H to methyl, ethyl, isopropyl, t-butyl, and acetyl, were studied (56).

The results are shown in Fig. 5 and it was noted that there is little change in the location and intensity of the first band, but the second shifts regularly to higher energies and decreases in intensity as the electron-attracting power of the substituent increases (Fig. 7). This suggests that the lowest energy band is the charge transfer from oxygen and the second band involves charge transfer from the substituted oxygen (alternative B of Fig. 6).

Attempts at a more quantitative interpretation will be difficult since symmetry considerations are of little help when the molecular symmetry is so low.

V. Interactions with Environment

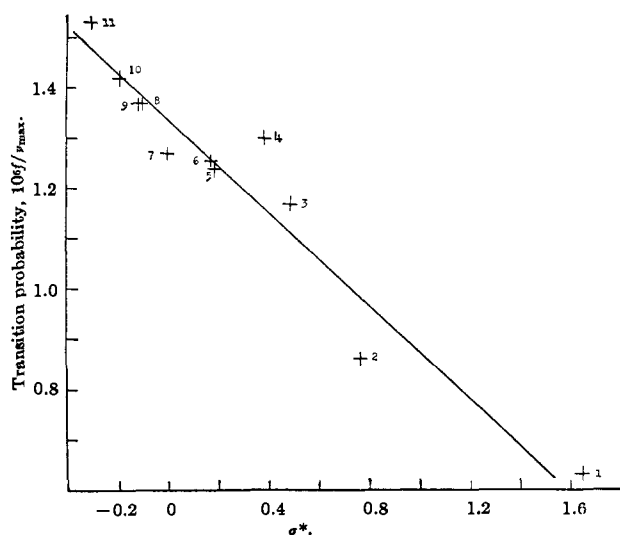Several types of interaction may be distinguished.

Fig. 7.—Correlation of the second band for monosubstituted chromates with the substituent constant σ^*: (1) $AcOCrO_3^-$, (2) $(CH_2Cl)_2CHOCrO_3^-$, (3) $HCrO_4^-$, (4) $CH_2ClCH_2OCrO_3^-$, (5) $HOCH_2 \cdot CH_2OCrO_3^-$, (6) $MeOCH_2 \cdot CH_2OCrO_3^-$, (7) $MeOCrO_3^-$, (8) $EtOCrO_3^-$, (9) n-$PrOCrO_3^-$, (10) i-$PrOCrO_3^-$, (11) t-$BuOCrO_3^-$.

In this section discussion is centered on noncovalent bonding interactions: those in which covalent bonding is involved are considered in section IX.

A. IONS IN CRYSTALS

Teltow (100) measured the spectrum of permanganate in several host crystals, retaining the cation K^+ but varying the anion. His results, showing changes in E_{max}, the energy of the 0–0 band of the $t_1 \rightarrow e$ transition and in $\Delta\nu$, the "breathing" mode frequency of the excited state, are depicted in Fig. 8, as a function of
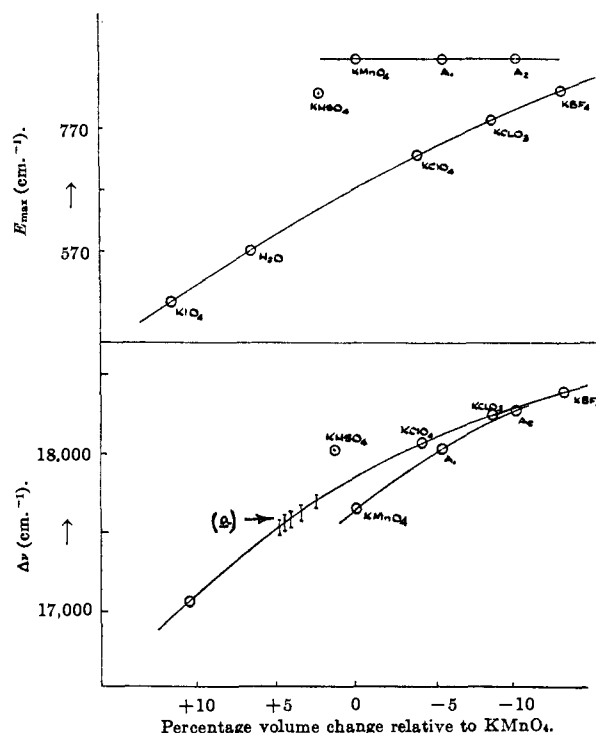

Fig. 8.—Effect of environment on the spectrum of MnO_4^-. A_1 and A_2 represent $KMnO_4$ under pressure from the data of Bentley and Drickamer (8). (a) MnO_4^- in various solvents; 200 cm.$^{-1}$ has been added to values obtained at 289°K. for purposes of comparison.

the change in volume relative to pure crystalline potassium permanganate. The shifts observed parallel those found when temperature (100) and pressure (8) are varied, and may be understood qualitatively as a progressively increasing resistance to the inward movement of negative charge as the first shell of cations is contracted by internal or external forces. Both $\Delta\nu$ and E_{max} tend to limiting values with increase in pressure, as might be expected once the "free space" is filled and repulsion forces dominate. The effect of external pressure on E_{max} for the $t_1 \rightarrow e$ transition of permanganate (8) has been indicated in Fig. 8, values for the change in volume being estimated very approximately from typical data for other salts (97). It is curious that Bentley and Drickamer (8) found no change in the breathing-mode frequency with change in

TABLE IV

STANDARD FREE ENERGIES, ΔF°_{aq}, OF OXYANIONS IN AQUEOUS SOLUTION

Species	Electron configuration	ΔF°_{aq}	Ref.	Remarks
MnO_4^-	Closed-shell	-107.4	63	Good measurement
MnO_4^{2-}	$3d^1$	-120.3	21	Good measurement
MnO_4^{3-}	$3d^2$	-127.0		Refers to concentrated KOH soln.
TcO_4^-	Closed-shell	-150.6	25	Good measurement
ReO_4^-	Closed-shell	-167.1 ± 0.8	26	Good measurement
ReO_4^{2-}	$5d^1$	-178 ± 8		Estimated by analogy
FeO_4^{2-}	$3d^2$	-77 ± 2	109	Good measurement
RuO_4	Closed-shell	-26.1	114	Refers to solid state
RuO_4^-	$4d^1$	-48.0		Good measurement
RuO_4^{2-}	$4d^2$	-61.6		Good measurement
OsO_4	Closed-shell	-68.59	63	Good measurement
CrO_4^{2-}	Closed-shell	-171.1	37	Good measurement
CrO_4^{3-}	$3d^1$	-179	5	Rough estimate
MoO_4^{2-}	Closed-shell	-238.2	30	Good measurement
WO_4^{2-}	Closed-shell	-266.6	31	Good measurement

pressure. The value for pure crystalline potassium permanganate is close to the limiting value as found, for example, in potassium tetrafluoroborate. Thus an increase in pressure effectively reduces the anomaly (Fig. 8).

B. IONS IN SOLUTION

The changes in environment discussed above are drastic and the spectral modifications small. It is therefore not surprising that the effect of polar solvents is constant, the results for solvated permanganate clustering closely about that for permanganate in a "normal" environment of cations and anions (Fig. 8). For similar reasons, we conclude that ion-pairing of any sort is unlikely to give rise to any marked spectral modifications, and results for tetraphenylarsonium permanganate in nonpolar solvents confirm this (97).

VI. THERMODYNAMIC PROPERTIES

In any problem concerned with the preparation or relative reactivity of a group of compounds it is of importance to consider over-all changes in free energy for pertinent reactions. The compilation by Latimer (63) includes data for a variety of the oxyanions under consideration as dilute solutions of their salts in water. This information is summarized, together with some more recent data, in Table IV and indication is given of the reliability of the figures, some of which might be described as useful guesses.

A major factor governing the free energy ΔF°_{aq} of an ion in solution is the solvation energy, and allowance must be made for this when comparing data. For example, although there is a steady increase in $-\Delta F^{\circ}_{aq}$ in the series MnO_4^-, MnO_4^{2-}, MnO_4^{3-}, this is entirely a consequence of the increased solvation energy and if reasonable values for the solvation energies are subtracted from $-\Delta F^{\circ}_{aq}$ for these ions, then the trend is reversed, as might be expected in view of the anti-

bonding character of the outer electrons in manganate and hypomanganate.

VII. ELECTRON-TRANSFER REACTIONS

Closed-shell ions are often strong electron acceptors, while those with outer electrons may be donors or acceptors. Thus, they often participate in electron-transfer reactions. Perhaps the simplest, and most studied is the reaction

$$MnO_4^- + MnO_4^{2-} \rightleftharpoons MnO_4^{2-} + MnO_4^- \qquad (3)$$

The results of Sheppard and Wahl (89), who studied this reaction by conventional kinetic methods using radioactive manganese, have recently been confirmed by nuclear resonance methods (13, 77). There can be no doubt that there is no exchange of oxygen under the conditions used (95) and hence this reaction must proceed by the "outer-sphere" mechanism (98). Such a description is not particularly appropriate for these systems, since it implies that "inner-sphere" mechanisms might also be found. Since the oxygens in both manganate and permanganate are bonded in manganese by strong σ and π bonds this analogy with the behavior of transition metal ions whose ligands are but weakly covalently bonded is not necessarily useful. However, such classification is always fraught with difficulty, and this point is reconsidered when hydride ion transfers are discussed (section IX).

The results for the MnO_4^-–MnO_4^{2-} exchange are summarized in Table V. The dependence of rate upon the nature and concentration of the cations is most marked, and has led Halpern (36) to suggest that there is an important pathway involving a symmetrical transition state such as $(O_3MnONaOMnO_3)^{2-}$ in which the cation acts as a bridge. There are, however, alternative explanations, and careful checks are required before this interesting concept can be accepted. This postulate should be compared with that of Adam

TABLE V

RATE CONSTANTS FOR THE PERMANGANATE-MANGANATE
EXCHANGE (89) IN AQUEOUS ALKALINE SOLUTION

Molarity of alkali	Rate constant $(M^{-1}\ sec.^{-1})$
NaOH, 0.16	730
NaOH, CsOH, each 0.08	1730
CsOH, 0.16	2470
NaOH, 0.16, Co(NH$_3$)$_6$Cl$_3$, 0.001	1860
NaOH, 0.16, Na$_3$Fe(CN)$_6$, 0.001	1180

TABLE VI

APPROXIMATE pK VALUES FOR CLOSED-SHELL OXYIONS IN
WATER (4)

System	pK
VO_4^{3-}–HVO_4^{2-}	14.4
HVO_4^{2-}–$H_2VO_4^{-}$	8.95
CrO_4^{2-}–$HCrO_4^{-}$	6.5
$HCrO_4^{-}$–H_2CrO_4	−0.98
MnO_4^{-}–$HMnO_4$	−2.25
ReO_4^{-}–$HReO_4$	−1.25

and Weissman (2), which is firmly based upon electron-spin resonance results for electron exchange between certain organic compounds and their anions in tetrahydrofuran and other solvents.

Compared with many other electron-transfer reactions, the one under consideration is relatively slow. This can be understood in terms of the principle of microscopic reversibility which, in this case, will require symmetry in the transition state, both with respect to bond lengths in the oxyions and with respect to the orientation of solvent molecules.

These requirements will be less stringent for other electron-transfer reactions, decreasing generally as the net free energy change becomes increasingly favorable.

Thus, for example, the reaction

$$MnO_4^{-} + MnO_4^{3-} \rightarrow 2MnO_4^{2-} \qquad (4)$$
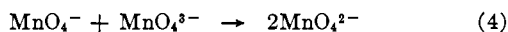
is so fast, even at 0°, that the eye cannot detect any time lag beyond that required for mixing, despite the well defined color changes associated with the reaction (21). In this case, it seems likely that neither permanganate nor hypomanganate will need to resemble manganate at all closely before the transition state is reached.

There must be a very large number of reactions which involve at least one step of the type depicted in (4), but few have been adequately studied as yet because of the difficulties inherent in the study of multistage reactions. Some examples which may include such steps are discussed in section IX-D.

VIII. PROTON-TRANSFER REACTIONS

Relative to the corresponding oxyions of the non-metals, closed-shell oxyions of the transition metals are surprisingly strong bases. For example, chromate has a pK value of about 6, whereas that of sulfate is about 2.5 (4). It seems that the difference is maintained for other ions of this class, if the spectrophotometric technique described is valid (4). In this work, use was made of the characteristic and large change which results on going from an ion of tetrahedral symmetry to one of C_{3v} symmetry (see section IV). That the expected change occurs on protonation is well established for chromate, since the pK value deduced from spectrophotometry (4) is the same as that derived from other techniques (39) and because the spectra of monoesters, $ROCrO_3^{-}$ are so similar (56).

However, as the example of chromate esters has shown, any change from XO_4 to O_3XOY is likely to give rise, qualitatively, to the same changes, although the spectrum is to some extent a function of the electronegativity of the group Y.

Recent cryoscopic and conductometric studies have shown that the spectrum originally assigned to permanganic acid, obtained from the green solutions of permanganate in pure sulfuric acid, is really a property of the corresponding sulfato derivative, O_3MnOSO_3H. [See, however, section IX-C and reference 39.] Nevertheless, the pK values derived from spectral changes, listed in Table VI, are thought to be authentic both for permanganic acid and others that form sulfato derivatives with concentrated sulfuric acid, since they were calculated from data obtained from dilute solutions in aqueous perchloric acid such that only slight conversion to the conjugate acid occurred (4).

This relatively high basicity, which, incidentally, results in a marked departure from the empirical rules of Pauling (79) and Ricci (82), has been tentatively explained in terms of the greater π-bonding expected for the transition metal oxyanions relative to those of the nonmetals. This, it is thought, should result in a greater polarizability for the ions of transition metals, and hence an improved power of accommodating the constraint of protonation throughout the whole molecule. The idea rests, however, on postulates that have yet to be established.

IX. NUCLEOPHILIC AND ELECTROPHILIC REACTIVITY

It is convenient to classify those reactions which do not consist simply of electron or proton transfer as electrophilic or nucleophilic. However, XO_4 cannot be regarded either as an electrophile or as a nucleophile in the traditional sense. This is because, commonly, the final result with respect to the oxyion is simply gain or loss of electrons. Some of the ambiguities which arise can be illustrated by reference to the interaction between alcoholate ions and permanganate, which have been studied extensively by Stewart and co-workers (91, 93). The reaction can be formulated as

$$R_2CHO^{-} + MnO_4^{-} \rightarrow R_2CO + HMnO_4^{2-} \qquad (5)$$
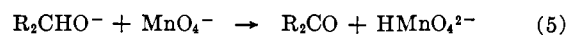
if one ignores the role of the solvent. There is a large isotope effect when rates for oxidation of R_2CHO^{-} are compared with those for R_2CDO^{-} especially when

the R groups are perfluoroalkyl (93), so that there can be little doubt that the C–H bond is broken in the rate-determining step. Nothing is known, however, about the stereochemistry of the transition state, nor about the immediate products of the first stage of reaction. In addition to simple hydride transfer, the reaction could be pictured as involving electron transfer from oxygen
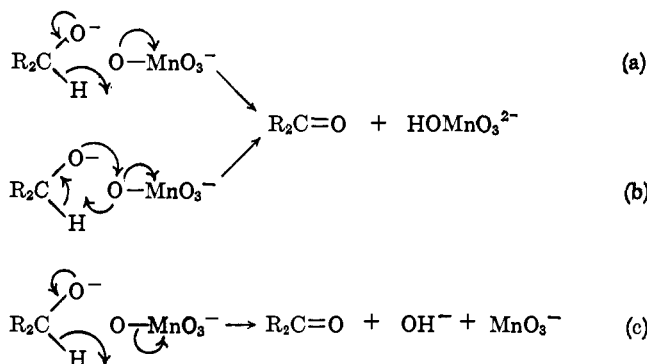

Alternatives (a) and (b) cannot be distinguished as the difference is simply one of direction of flow of electrons; this indistinguishability being characteristic of such cyclic transition states (64). In (c) the movement of oxygen σ-electrons to manganese rather than p-π-electrons results in bond breaking to give the intermediate MnO_3^-. Although such intermediates are possible and, indeed, are often postulated in reaction mechanisms, no direct evidence for their participation has been forthcoming, and, in general, it would seem that π-donation without Mn–O bond fission would be favored energetically.

Oxidations which proceed *via* an ester, for example the acid-catalyzed, thermal (38, 104), or photochemical (51, 54) oxidation of alcohols by chromate, are clearly distinguished from those presently under consideration. They do, however, add further to the multiplicity of mechanisms that are available in any particular instance, since the same sort of considerations must once again be invoked. Thus formulations such as the following have been or could be proposed
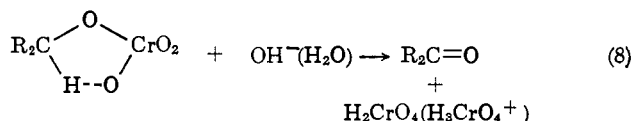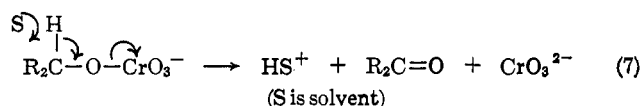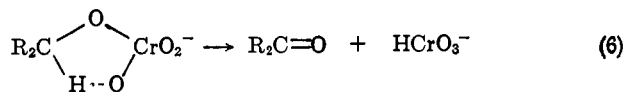
the over-all reaction being of the form

$$3R_2CHOH + 2Cr^{VI} \rightarrow 3R_2CO + 2Cr^{III} \qquad (9)$$
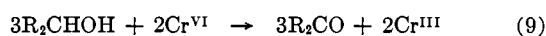
In the particular case of photolysis, in addition to considerable kinetic evidence (51), there is rather direct stoichiometric evidence for the intermediate formation of a quadrivalent chromium species (54, 55). This conclusion is based upon results derived from the photolysis of rigid solutions of the monochromate esters at 77°A. Not only did photolysis cease at a stage corresponding to complete formation of quadrivalent chromium but also on softening the alcoholic solutions became deep blue and were found to have spectra closely similar to that for the ester $(RO)_4Cr$ which has recently been synthesized (35) (section X).

These considerations show that the situation with regard to the question of electrophilic and nucleophilic reactivity of XO_4 ions is most complicated. This arises because of the propensity of XO_4 to accept electrons directly; because of the presence of multiple reactive sites; because the lone-pair electrons on oxygen are essentially nucleophilic whereas the empty d levels on the central metal are electrophilic; and because five or possibly six ligands can be attached to the metal X in the transition state or in various intermediates. Present studies can only be regarded as preliminary skirmishes which have revealed certain major pathways rather than probing details. Furthermore it is not, at present, easy to see how this greater detail can be obtained.

Detection of intermediates such as MnO_3^- would help, but, at least, in aqueous solution the rate of hydration

$$MnO_3^- + H_2O \rightarrow H_2MnO_4^- \qquad (10)$$

and of electron transfer (equation 4) must be so rapid that these intermediates will surely be very short lived and hence detection would be extremely difficult.

The situation with respect to the behavior of substrates is better understood and has been discussed extensively by Waters (102) and by Ladbury and Cullis (59). Several studies of particular interest from this viewpoint have appeared recently (19, 83, 84, 99, 105), and special mention should be made of a broadly based attack on the mechanism of oxidation of organic compounds by quinquevalent vanadium species (47, 66).

The remainder of this section is devoted to discussion of certain reactions with simple inorganic molecules. These include coordination of solvent molecules (A), complex-ion formation (B), and interaction with sulfuric acid (C). Finally, some reactions with simple anions will be discussed (D).

A. COORDINATION OF SOLVENT

Reactions of the type

$$XO_4 + 2H_2O \rightleftharpoons XO_2(OH)_4 \qquad (11)$$
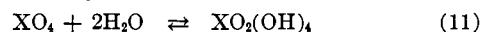
in which atom X changes its coordination from four to six, have been discussed (69). Such equilibria are very sensitive to changes in pH since the octahedral form is a proton donor, and is also

more basic than XO_4. For example, osmium tetroxide is not appreciably hydrated in aqueous solution, but is totally converted into $H_3OsO_6^-$ in dilute aqueous alkali.

In general the octahedral form is favored on going down a group in the periodic table, along a period to lower atomic number, and on increasing the number of outer electrons. The last of these has been discussed, for the particular case of osmate, $OsO_2(OH)_4^{2-}$, but the arguments made (69) are probably of general validity. The important features are thought to be the greater destabilization of appropriate metal d-orbitals by p-π-electrons of oxide than of hydroxide ligands, and the more ionic character of σ-bonds involving the latter ligands.

The trend to increased coordination on going down a group of the periodic table is to be expected. Thus ferrate and ruthenate are only known as FeO_4^{2-} and RuO_4^{2-} but osmate only as $OsO_2(OH)_4^{2-}$. Similarly, aqueous permanganate does not add even one molecule of water since it does not exchange oxygen with the solvent (95), whereas perrhenate, although present as ReO_4^- in neutral solution, readily, and reversibly increases its coordination in concentrated alkali and probably also in concentrated aqueous acid (52, 23).

The trend to increased coordination in series such as permanganate, chromate, vanadate, and titanate is also in accord with expectation since it follows a decrease in the effective charge on the central atom and an increase in the "ionic" radius. Although chromate and most of its derivatives are tetrahedrally coordinated (56), and titanates are in general octahedrally coordinated, many vanadates are of uncertain coordination (12). For example, Dunitz and Orgel (28) consider that the best way to visualize the rather unusual coordination in vanadium pentoxide is in terms of an octahedral environment of oxides around each vanadium such that the volume of the resulting cavity, determined by the oxides, is greater than that of the quinquevalent vanadium, which thus finds itself in a metastable condition when at the center of the cavity. It, therefore, moves to one side, favoring one or more oxides by a process described as "rattling" (28). As a result, one vanadium–oxygen bond is exceptionally long, and this has led some to describe the coordination as fivefold rather than sixfold.

Vanadium in the alkali metal vanadates is tetrahedrally coordinated and probably also in the monoprotonated ion O_3VOH^{2-} (4). On further acidification of aqueous solutions, however, complex interactions occur including extensive condensation to give ions such as $H_2V_{10}O_{28}^{4-}$ or $HV_{10}O_{28}^{5-}$ (85, 90), the coordination to vanadium being unknown. On further acidification the pervanadyl ion, VO_2^+, is thought to be formed (90). The evidence in favor of a monomeric, cationic

species is strong, but that in favor of the formulation VO_2^+ is largely circumstantial.

It is noteworthy that quinquevalent vanadium in sulfuric acid and oleum is once more tetrahedrally coordinated (75). Evidence for this stems largely from spectrophotometric studies which show that the species is spectrally very similar to the oxychloride, $VOCl_3$ (73). For this, and other reasons, it has been postulated (75) that the sulfate complex, $VO(HSO_4)_3$, or possibly $VO(OH)(OSO_3H)_2$ is formed. Thus there is, apparently, reversion to tetrahedral coordination in this medium, possibly for steric reasons (section IX-C).

B. COMPLEX FORMATION WITH TRANSITION METAL CATIONS

Although the role of tetrahedral oxyanions of nonmetals as ligands in complex compounds has been studied extensively, that of the corresponding oxyions of transition metals has received little attention. This is, in part, because oxidation–reduction reactions often result or insoluble precipitates are formed on mixing. Nevertheless, since in all instances the oxyion must coordinate primarily through oxygen lone-pair electrons, we anticipate that their relative ligand strengths will parallel, approximately, their relative basicities, so that transition metal oxyanions are likely to be far better ligands than corresponding nonmetal ions.

If this conclusion is correct, then such complexes may play an important role in the oxidation–reduction reactions which frequently occur, such as the reaction between permanganate and manganous ions which has been studied extensively.

If there is important σ-bonding between the cation and one or possibly two oxygen atoms of the oxyanion then there would be local C_{3v} symmetry with respect to the metal of the oxyanion, and as with comparable proton and alkyl derivatives, a characteristic change in the spectrum of the oxyion would be expected.

Tong and King (101) detected interaction between tri- and sexivalent chromium by spectrophotometry, but did not report the spectral envelope for the complex.

Addition of an excess of a wide range of di- and trivalent cations to aqueous permanganate was found to have a negligible affect on the spectrum of the permanganate (97). However, silver salts had a marked effect, and there can be no doubt that silver–permanganate complexes are readily formed. These complexes are, however, unstable even at 0° and decompose with evolution of oxygen and formation of colloidal manganese dioxide.

These results are curious both with regard to the specificity of silver ions and with regard to the spectral changes, which, contrary to expectation, do not resemble those for protonation or other such substitutions. However, lack of spectral change does not

prove the absence of interaction, but only of significant σ-bonding. Silver ions may differ from the others studied in their ability to back-donate electrons through d-π-bonding and permanganate will certainly act as a very strong acceptor in this respect.

It is, therefore, postulated (17) that the major effect on the spectrum is a result, not of σ-bonding, as for protonation, sulfonation, etc., but of π-bondng. This is thought to result in a lowering of the $t_1 \to e$ transition of permanganate, through a marked stabilization of the excited state. In fact, there is a shift of the first band to low energies and complete loss of fine structure, which is to be expected in view of the strong anisotropy of the effect. There is also evidence for a new, low intensity band on the low-energy side of the second transition, which may well be the result of electron transfer from silver to permanganate.

These changes are qualitatively similar to those recorded by Teltow for permanganate in single silver perchlorate crystals (100). It is noteworthy that one of the manganese–oxygen bonds is very much longer than the other three in silver permanganate (87).
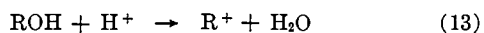
C. REACTIONS IN SULFURIC ACID AND THE FORMATION OF OXYCATIONS

Just as the possibility of solvent coordination is an important consideration with respect to nucleophilic displacements of type S_N2, so the possibility of oxycation formation is relevant to a discussion of S_N1 mechanisms.

Thus

$$MnO_4^- + 2H^+ \to MnO_3^+ + H_2O \qquad (12)$$
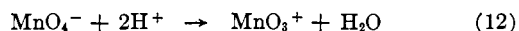
can be compared with

$$ROH + H^+ \to R^+ + H_2O \qquad (13)$$

which is the first stage in many organic nucleophilic displacements. Since reaction 13, R being alkyl or aryl, is known to be strongly favored in 100% sulfuric acid, it might be anticipated that reactions of type 12 would be similarly favored.

Green solutions which result when permanganates are dissolved in sulfuric acid are indeed thought by some to contain the ion MnO_3^+ as the major constituent (86), and solids formed by reaction of sulfur trioxide with oxyhalides of chromate and vanadate (111) are thought to contain the ions CrO_2^{2+} and VO_2^+, respectively.

Of the cations mentioned, the pervanadyl ion, VO_2^+, is widely considered to be an important constituent of acidic solutions of quinquevalent vanadium and of various solid "vanadates" (62, 90). However, recent studies suggest that, at least in 100% sulfuric acid and oleums, sulfato derivatives such as

$$O_3XOSO_3H, O_2X(OSO_3H)_2, \text{ or } OX(OSO_3H)_3$$

are formed rather than the corresponding oxycations (75). These conclusions, based largely upon spectro-

photometric, conductance, and magnetic studies, are self-consistent and seem to be in accord with the chemical reactivity of such solutions.

Spectrophotometric evidence is based largely upon analogy. Thus the spectrum of the green solutions obtained by dissolving permanganate in sulfuric acid is closely similar to that expected for a species O_3MnX having local C_{3v} symmetry (section IV).

The spectrum of solutions obtained by dissolving potassium permanganate in sulfuric acid has also been considered by Royer (86), who, on the basis of conductometric and cryoscopic studies discussed below, had concluded that the absorbing species was the oxycation MnO_3^+. Royer maintains that the spectrophotometric results strongly support this conclusion and, in particular, disprove the postulate that the species is O_3MnOSO_3H. He argues that because the lowest energy band is weak, $(\epsilon_{max} \doteqdot 100)$ it must arise from a symmetry forbidden transition. Since the lowest energy transition for a species with C_{3v} symmetry is allowed, this eliminates O_3MnOSO_3H, which has local C_{3v} symmetry.

This conclusion is incorrect. Apart from theoretical arguments, there is the indisputable fact that the ion CrO_3F^-, which is known to have C_{3v} symmetry, does show an absorption band at 22,500 cm.$^{-1}$ with a molar extinction coefficient of only 200. There is no reason why an electronic transition which, formerly forbidden, becomes symmetry allowed as a result of a small lowering of symmetry should thereby acquire a large transition moment.

Spectra for chromate in sulfuric acid are less well resolved and are thought to be due to mixed species such as $O_2Cr(OH)(OSO_2H)$. In oleum the disulfate $O_2Cr(OSO_3H)_2$ appears to be formed. In contrast, quinquevalent vanadium gives solutions having well resolved spectra which are almost identical with that for $VOCl_3$ (73, 75), and this is taken as good evidence for a trisulfate $OV(OSO_3H)_3$ (75).

Conductance studies are in good accord with these formulations and definitely exclude the possibility that the cations CrO_2^{2+} and VO_2^+ are major constituents of these solutions (75). Results for the green permanganate solutions are thought (86) to be in accord with the reaction

$$K^+ + MnO_4^- + 3H_2SO_4 \to K^+ + H_3O^+ + MnO_3^+ + 3HSO_4^- \qquad (14)$$
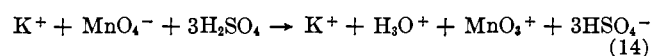
but this conclusion is based on readings obtained immediately after preparation of solutions and involves extrapolation from about 2.5 to 3.0 HSO_4^- ions at zero time (86). The estimated number of HSO_4^- ions falls to 2.0 after about 12 min., and this result, which in accord with the reaction

$$K^+ + MnO_4^- + 3H_2SO_4 \to$$
$$O_3MnOSO_3H + H_3O^+ + 2HSO_4^- + K^+ \qquad (15)$$
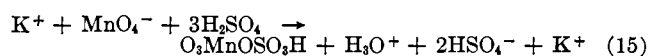
is favored by the reviewers. Again, cryoscopic results show a wide scatter, and although a ν-value of six is accepted by Royer, as required by equation 14, the average result is closer to five, as required by equation 15. Thus on balance, it appears that the green septivalent manganese species in sulfuric acid is not MnO_3^+ and is probably the monosulfate O_3MnOSO_3H. This conclusion has also been drawn by Wilmarth (106).

In general, the stability of these solutions decreases markedly on going from quinquevalent vanadium to septivalent manganese and on going from sulfuric acid to concentrated oleum. This can be rationalized in terms of reactions such as

$$O_2Mn(OSO_3H)_2^+ \rightarrow O_2 + Mn^{III}(OSO_3H)_2^+ \quad (16)$$

whereby a molecule of oxygen is directly extruded in an analogous manner to photochemical decomposition (section X). The trivalent manganese either is stabilized by coordination of solvent or reacts with septivalent manganese to give the final products. The thermal decomposition is facilitated by the great electron-attracting power of the sulfato or pyrosulfato ligands, but the net effect decreases as the electron affinity of the metal falls on going from manganese to vanadium.

In oleum, the final products of this decomposition are quinquevalent chromium and quadrivalent manganese for chromate and permanganate, respectively (74).
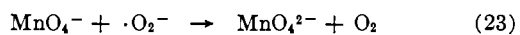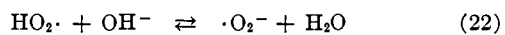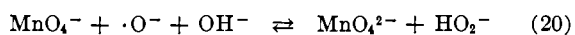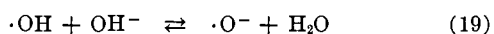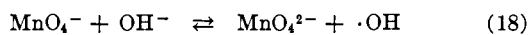
D. REACTIONS WITH REDUCING ANIONS

In this section we discuss two apparently simple reactions whose mechanisms have not been satisfactorily elucidated. They serve to illustrate the complexity of the topic and some of the ambiguities which can arise. Of these reactions, namely, the oxidation, by permanganate, of hydroxide ions and cyanide ions, the former has been studied more extensively (27, 94, 95). The stoichiometry of this reaction is accurately

$$4MnO_4^- + 4OH^- \rightarrow 4MnO_4^{2-} + 2H_2O + O_2 \quad (17)$$
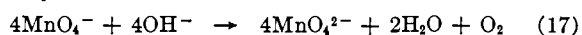
provided the pH is not allowed to fall below about 13.

Although hydroxide is a strong nucleophile, it is by no means certain that permanganate acts as an electrophile in these reactions. Thus it has been proposed that the sequence of simple one-electron and proton transfers

$$MnO_4^- + OH^- \rightleftharpoons MnO_4^{2-} + \cdot OH \quad (18)$$
$$\cdot OH + OH^- \rightleftharpoons \cdot O^- + H_2O \quad (19)$$
$$MnO_4^- + \cdot O^- + OH^- \rightleftharpoons MnO_4^{2-} + HO_2^- \quad (20)$$
$$MnO_4^- + HO_2^- \rightleftharpoons MnO_4^{2-} + HO_2\cdot \quad (21)$$
$$HO_2\cdot + OH^- \rightleftharpoons \cdot O_2^- + H_2O \quad (22)$$
$$MnO_4^- + \cdot O_2^- \rightarrow MnO_4^{2-} + O_2 \quad (23)$$

adequately describes the reaction (94). A variety of arguments for and against this reaction will be summarized but no firm conclusions will be drawn.

The major feature of this formulation which renders it improbable is the adverse free energy change for step 18, which for standard conditions would amount to about $+33$ kcal. This result would seem to be incompatible with estimates for the rate of the initial step (67), even when one allows for the fact that strongly alkaline solutions were used. Thus, attempts to extrapolate to zero time for reaction 18 gave initial rates of the order of 2×10^{-3} l. mole^{-1} sec.$^{-1}$, while similar measurements in the presence of organic substrates gave about 3×10^{-3} l. mole^{-1} sec.$^{-1}$. This result appears to make the reverse of (18) impossibly fast. Two possible explanations within the context of the mechanism are that the reducing power of hydroxide is greatly increased in strongly alkaline solutions and that the rate data are misleading in view of the exceptionally high mobility of hydroxide ions in water. The latter aspect is important in that it allows neighboring water molecules to become hydroxide "on demand" as it were, by chain proton–transfer to remote hydroxide ions. The former concept is somewhat nebulous, but it does seem to be common experience that hydroxide can act as an unexpectedly powerful reductant when the concentration of water is low. For example, manganate is readily reduced to hypomanganate (21), and chromate to hypochromate (5) under these conditions, and similarly, ozone is rapidly reduced to the ozonide ion, O_3^- (72).

The observation (50, 67) that certain compounds are oxidized by permanganate in strongly alkaline solutions but not otherwise lends support to the concept that hydroxyl or O^- radicals are formed, which can attack the substrate more readily. Detailed rate studies appear to substantiate this reasoning (67).

Perhaps the most significant observation is that, in contrast with the photochemical results discussed in section X, when solvent water is labeled with $H_2^{18}O$ all the oxygen is derived from the solvent (95). This result rules out many alternatives which the involved kinetic pattern might permit (94). Also, when relatively dilute alkaline solutions are studied containing both permanganate and manganate, but with the latter in large excess, addition of dilute hydrogen peroxide results in the reduction of *less* than an equivalent of permanganate, although the peroxide is quantitatively decomposed (70). With labeled water, the evolved oxygen was found to contain considerably more than the natural abundance of ^{18}O. These results suggest strongly that some step, such as the reverse of (20), is significant, and that this step cannot involve complete reduction of hydroperoxide to hydroxide since, under the conditions used, oxidation of hydroxide was negligible. Hence some intermediate must have been involved, which could react with solvent or hydroxide to re-form *labeled* peroxide. This conclusion is in accord with the postulated mechanism and it is not

easy to see what alternatives are available (70).

In relatively dilute alkali, Duke found that, with barium ion present to precipitate barium manganate, the reaction was zero order (27). He suggested that the reaction was heterogeneous, involving adsorption of hydroxyl radicals on the glass surface where they combined to form hydrogen peroxide. Recently a similar zero-order law has been found for the decomposition in dilute alkali, even in the absence of barium hydroxide (41). A somewhat involved mechanism put forward to explain this result has as an initial key step the formation of a complex $(MnO_4OH)^{2-}$ between permanganate and hydroxide ions.

This is an interesting suggestion and may be compared with that for the first stage of oxidation of cyanide. There are various alternative structures for such a complex: in one, the hydroxyl ion is coordinated directly to manganese, and in the other, it is coordinated to one of the oxide ligands which, in order to accept the hydroxide, must donate two electrons into the outer e-level of the manganese. This latter "complex" is, in effect, a monoperoxide of hypomanganate. Yet another hypothesis would be that a loose "charge-transfer" complex is formed.

Since the spectra of the solutions under consideration can be accounted for quantitatively in terms of permanganate and manganate as the only absorbing species, the concentration of such a complex, whatever its structure, must be very low. We are inclined to favor the peroxy–hypomanganate formulation since oxygen exchange studies would appear to rule out direct coordination (95), and complex formation via weak charge-transfer forces seems unlikely between two, strongly solvated, negative ions.

The Polish workers have also reported results of their studies of the kinetics of disproportionation of manganate

$$3MnO_4^{2-} + 2H_2O \rightleftarrows 2MnO_4^- + MnO_2 + 4OH^- \quad (24)$$
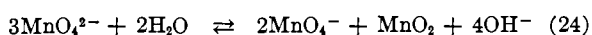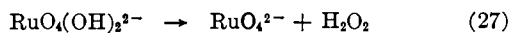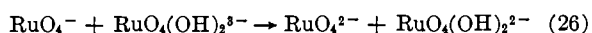
and the equilibrium thereby set up (42).

In contrast, the mechanism for decomposition of perruthenate ions in aqueous alkaline solution is thought to involve the intermediate $RuO_4(OH)^{2-}$ (22). The over-all reaction is

$$4RuO_4^- + 4OH^- \rightarrow 4RuO_4^{2-} + 2H_2O + O_2 \quad (25)$$

the product, ruthenate, being then quite stable (22, 110) under the conditions used.

The mechanism proposed (22) to fit kinetic studies was

$$RuO_4^- + RuO_4(OH)_2^{3-} \rightarrow RuO_4^{2-} + RuO_4(OH)_2^{2-} \quad (26)$$

$$RuO_4(OH)_2^{2-} \rightarrow RuO_4^{2-} + H_2O_2 \quad (27)$$

followed by rapid oxidation of peroxide to oxygen. The intermediate formation of peroxide has been postulated also by Larsen and Ross (61).

The reaction with cyanide ion varies with pH, the product being largely cyanate in solutions of pH between 12 and 14.6 but from 6 to 12, cyanogen and carbon dioxide are also formed. There is considerable transfer of oxygen from permanganate to cyanide during reaction. In strong alkali the kinetic course of the reaction is complicated, but one process, which occurs when the concentration of cyanide is low, appears to be clean cut, and is thought to involve transfer of oxygen

$$MnO_4^- + CN^- \rightarrow MnO_3^- + CNO^- \quad (28)$$
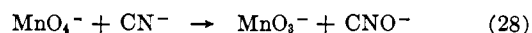
Other more obscure features of this reaction are discussed by Stewart and van der Linden (92). It seems possible that a permanganate–cyanide complex is involved in this reaction, possibly of the type suggested for hydroxide, which is better described as a cyanato derivative of hypomanganate, $(O_3MnOCN)^{2-}$. This could then undergo a variety of reactions, including displacement

$$OH^- + O_3MnOCN^{2-} \rightarrow HMnO_4^{2-} + CNO^- \quad (29)$$
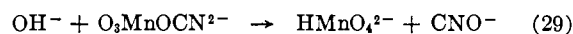
thus obviating the need to postulate MnO_3^- as an intermediate.

The complexity of the kinetic course of these two apparently simple reactions is a challenge to the progress of our understanding in this field.

X. PHOTOLYSES

An extensive study of the photolysis of aqueous permanganate was made by Zimmerman (113), who found that, over the range 2537 to 5780 Å., the quantum yield, which was very small, was independent of pH and light intensity. These results, together with the important observation, derived from studies of the isotopic content of oxygen evolved from solutions in water enriched with $H_2^{18}O$, that the oxygen is derived entirely from the permanganate, led him to postulate a direct extrusion of oxygen as the first stage in the photolysis

$$MnO_4^- + h\nu \rightarrow MnO_2^- + O_2 \quad (30)$$
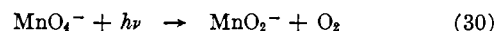
In contrast, Bowen and co-workers (11) found no photodecomposition for chromate or acid chromate with light of wave length greater than 3000 Å.

These results have been reinforced by studies of rigid solutions of oxyions in various solvents at 77°K. (53) exposed to ultraviolet light. Under these conditions chain decomposition cannot occur and, often, unstable fragments are trapped and can be studied by spectrophotometric or magnetic methods. On softening such solutions further reaction may occur, but nevertheless analysis may give information pertinent to an understanding of the reaction mechanism.

Of the ions studied, which included permanganate, manganate, hypomanganate, chromate, dichromate, and acid chromate, only permanganate was photolyzed detectably (53). In this instance photolysis proceeded smoothly until the permanganate was completely

converted to manganese(III), but no further. This result, taken together with those of electron-spin resonance studies of photolyzed solutions in alcohol glasses, which showed that not even transient amounts of oxygen atoms, superoxide ions, or hydroxyl radicals were formed, seems to confirm the formulation (113) postulated by Zimmerman.

That chromate does not decompose is not surprising in view of its far greater thermodynamic stability and smaller electron affinity, but the stability of manganate and hypomanganate is less readily understandable. Some aspects have been discussed (53) but perhaps the over-riding consideration, if a mechanism corresponding to equation 30 is operative, must be the reduced electron affinity of manganese in these ions, relative to permanganate.

It is interesting to compare these results with those for the thermal decomposition of corresponding sulfates discussed in section IX-C, which is also thought to proceed by an initial extrusion of oxygen. Thus the thermal stability increases on going from manganese to vanadium, and the sulfato derivative of quinquevalent chromium is much more stable than that of chromate.

The thermal (104) and photoinduced (51, 53) oxidations of simple alcohols may be compared similarly. As mentioned earlier, they proceed *via* the formation of esters which in the photochemical studies was the thermally stable monoalkyl chromate, O_3CrOR^-, and in the thermal studies is thought to be the conjugate acid, $O_2Cr(OH)(OR)$.

Perhaps the simplest picture for the photochemical and thermal breakdown of, for example, isopropyl chromate (or its conjugate acid), is *via* the cyclic transition state

$$\begin{array}{c} H\!\!-\!\!O \\ \diagup \qquad \diagdown \\ Me_2C \qquad\quad CrO_2 \\ \diagdown \qquad \diagup \\ O \end{array}$$
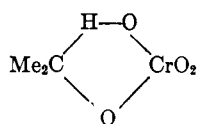
Again, the direction of flow of electrons is unspecifiable, and in the thermal decomposition, simultaneous attack by solvent to give a more highly coordinated quadrivalent chromium species is probable.

In addition to kinetic evidence in favor of the initial formation of quadrivalent chromium on photolysis (51), studies of rigid solutions exposed to ultraviolet light and of fluid solutions studied by flash photolytic techniques (86) strongly support this view.

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