55. *Structure and Reactivity of the Oxyanions of Transition Metals. Part VIII.* Acidities and Spectra of Protonated Oxyanions.*

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Approximate p*K* values for protonation of a variety of "closed-shell" oxyanions have been measured by spectrophotometry. Protonated ions were recognised by characteristic changes in spectra which have been interpreted theoretically. The high basicity of these ions relative to those of corresponding non-metal oxyions (*e.g.*, CrO_4^{2-} relative to SO_4^{2-}) is discussed.

Although the basicities of the oxyanions of non-metallic elements have been extensively studied and discussed, little attention has been paid to the corresponding oxyanions of the transition metals. Of these, chromate has been studied by various authors[1] who all conclude that the p*K* is in the region of 6·5. If this is correct, then chromate is a far stronger base than sulphate or selenate. This remarkable result has been questioned by Hückel[2] who suggests that the reaction studied is not protonation of chromate but dichromate formation:

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Since it is possible to correlate the basicities of very many oxyanions in terms of the number of non-protonated oxygen atoms and the formal charge on the central atom[3,4] one might conclude that oxyanions of the transition metals would be accommodated by this classification, and in fact, this has been assumed by Pauling.[3]

We have attempted to measure the p*K* values for a number of transition-metal oxyanions and conclude that in all cases the basicities are far higher than those of the corresponding non-metal oxyions. This result is discussed in terms of the electronic structure of the ions.

Basicities were estimated by comparing the visible or ultraviolet spectra of aqueous solutions of the oxyanions at various pH values with the spectra of the unprotonated ions and their conjugate acids. Whilst the spectra of the unprotonated ions are well established, those of the protonated ions, in general, have not been reported. Since a variety of reactions other than simple protonation could occur on acidification of solutions of these oxyions, we have considered in some detail the general form of the spectra to be expected for the protonated ions, particularly in relation to the spectra of the unprotonated ions. The relative spectral changes measured on acidification are remarkably similar for all the ions studied and conform well to the changes predicted by theory.

Experimental and Results

Water used in all determinations was doubly distilled from alkaline permanganate. Chemicals used were of "AnalaR" grade, apart from potassium per-rhenate which was prepared from the metal as previously described.[5] Concentrated sulphuric acid of "AnalaR" grade was further purified by distillation. Di-t-butyl chromate $(Bu^tO)_2CrO_2$ was prepared according to Leo and Westheimer's directions[6] and was recrystallised from light petroleum.

Spectrophotometric measurements were made with the Unicam S.P.600 glass or S.P.500 quartz spectrophotometers, the latter having a photomultiplier attachment.

pH measurements were made at 25° with a Doran pH meter and glass and calomel electrodes. The apparatus was standardised with 0·05M-potassium hydrogen phthalate buffer.

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* Part VII, preceding paper.

[1] Neuss and Riemann, *J. Amer. Chem. Soc.*, 1934, **56**, 2238; Tong and King, *ibid.*, 1953, **75**, 6180; Howard, Nair, and Nancollas, *Trans. Faraday Soc.*, 1958, **54**, 1034.

[2] Hückel, "Structural Chemistry of Inorganic Compounds," Elsevier, New York, 1950, p. 921.

[3] Pauling, "General Chemistry," Freeman, San Francisco, 1947, p. 394.

[4] Ricci, *J. Amer. Chem. Soc.*, 1948, **70**, 109.

[5] Carrington, Schonland, and Symons, *J.*, 1957, 659.

[6] Leo and Westheimer, *J. Amer. Chem. Soc.*, 1952, **74**, 4383.

Determination of p*K values*.—For the acid BH, pK_{BH} may be defined as:

$$pK_{BH} = \log \frac{C_{BH}}{C_{B^-}C_{H^+}} + \log \frac{f_{BH}}{f_{B^-}f_{H^+}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Provided the concentrations of B^- and BH are small, then, as the concentration of acid tends to zero, equation (1) becomes:

$$pK_{BH} = \log \frac{C_{BH}}{C_{B^-}} - \log H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Plots of $[(\log C_{BH}/C_{B^-}) - \log H^+]$ against molarity of acid were straight lines which could be extrapolated to zero acid strength (see Fig. 5). This empirical extrapolation is known to give accurate p*K* values for uncharged bases.[7]

Determination of C_{BH}/C_{B^-}.—Measurements of optical densities at a particular wavelength were made at different acid concentrations. The wavelength chosen was determined by comparison of the spectra of the acids with those of their conjugate bases such that a maximum change in optical density was obtained.

If ${}^{\lambda}\varepsilon_{B^-}$ represents the extinction coefficient of a solution of the oxyanion at wavelength λ and ${}^{\lambda}\varepsilon_{BH}$ the extinction coefficient of its conjugate acid at the same wavelength, then the ratio $C_{BH} : C_{B^-}$, for a solution containing both species, whose extinction is ${}^{\lambda}\varepsilon$, is given by:

$$C_{BH}/C_{B^-} = ({}^{\lambda}\varepsilon_{B^-} - {}^{\lambda}\varepsilon)/({}^{\lambda}\varepsilon - {}^{\lambda}\varepsilon_{BH}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

To reduce the extrapolation to a minimum, readings were obtained in the acidity regions in which protonation was slight. To detect the small changes in optical density that occur, test solutions were compared with solutions containing identical concentrations of the oxyanions present entirely as the conjugate bases. This procedure is preferable to that in which pure solvent is used for comparison since several inherent inaccuracies of spectrophotometry are thereby greatly reduced.[8] This reasoning would be incorrect if the spectra under consideration changed with environment. For several ions it has been established that changes in solvent and ionic strength do not detectably alter the spectra.

System CrO_4^{2-} $HCrO_4^-$.—The spectrum of chromate, measured in aqueous M-sodium hydroxide and shown in Fig. 1, curve I, is identical with that reported by others.

The spectrum of acid chromate was investigated in the pH region 3—5, with concentrations of Cr^{VI} between 1×10^{-4}M and $2{\cdot}5 \times 10^{-5}$M; extinction coefficients were constant under these conditions, showing that dichromate formation is negligible and that neither H_2CrO_4 nor CrO_4^{2-} contributes appreciably. The spectrum is remarkably similar to that of CrO_3Cl^- and CrO_3F^- [9] and monoalkyl esters $ROCrO_3^-$,[10] and is of the form expected for $HCrO_4^-$ (see below).

The conclusion that dichromate is not a constituent of these solutions can be predicted from the data of Davies and Prue,[8] and shows that the high basicity of chromate cannot be ascribed to dichromate formation.

To avoid the difficulties involved in extrapolation to zero ionic strength, the p*K* value was estimated in the following manner. The optical density of a $2{\cdot}5 \times 10^{-5}$M-solution of potassium chromate in purified water was determined and the pH of the solution was measured before and after this determination, measurements being made in a nitrogen atmosphere. By means of equation (2) and the data given in Table 1, a p*K* of 6·49 was estimated, in agreement with results of others.[1]

TABLE 1.

λ (mμ)	pH	${}^{\lambda}\varepsilon_{\text{solution}}$	${}^{\lambda}\varepsilon_{HCrO_4^-}$	${}^{\lambda}\varepsilon_{K_2CrO_4}$	p*K*
373	6·19	2310	1050	4800	6·49

System $HCrO_4^-/H_2CrO_4$.—Spectra of Cr^{VI} in 72% perchloric acid and 100% sulphuric acid are quite different from that expected for H_2CrO_4. This we tentatively ascribe to the formation of CrO_2^{2+} by analogy with the behaviour of vanadate in strongly acid solution.[11] However,

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[7] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

[8] Davies and Prue, *Trans. Faraday Soc.*, 1955, **51**, 1045.

[9] Helmholz, Brennan, and Wolfsberg, *J. Chem. Phys.*, 1955, **23**, 853.

[10] Kläning, *Acta Chem. Scand.*, 1958, **12**, 576.

[11] La Salle and Cobble, *J. Phys. Chem.*, 1955, **59**, 519.

with increasing concentration of perchloric acid, the spectrum of an aqueous solution of $HCrO_4^-$ changed until a new spectrum was obtained which did not change appreciably with further addition of acid up to about 8M. This spectrum, shown in Fig. 1, curve III, is close to that expected for H_2CrO_4 and resembles the spectra of CrO_2Cl_2 [9] and $(Bu^tO)_2CrO_2$.

FIG. 1.

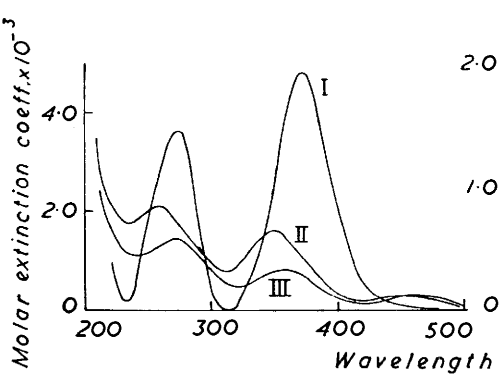

FIG. 2.

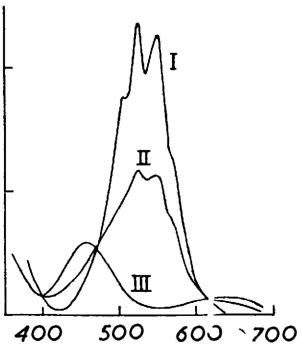

FIG. 1. *Visible and ultraviolet absorption spectra.*
(I) CrO_4^{2-}. (II) $HCrO_4^-$. (III) H_2CrO_4.

FIG. 2. *Visible and ultraviolet absorption spectra.*
(I) MnO_4^-. (II) $HMnO_4 + MnO_4^-$. (III) $HMnO_4$.

FIG. 3.

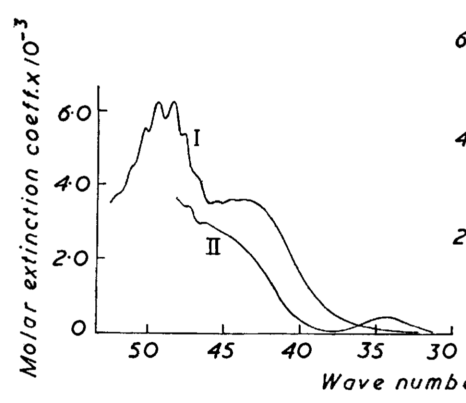

FIG. 4.

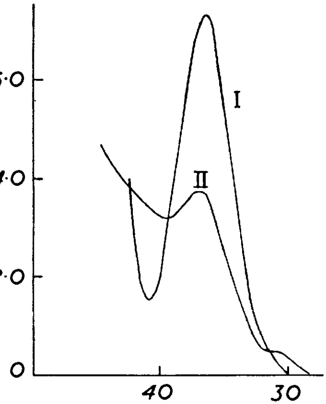

FIG. 3. *Visible and ultraviolet absorption spectra.*
(I) ReO_4^-. (II) $HReO_4$.

FIG. 4. *Visible and ultraviolet absorption spectra.*
(I) VO_4^{3-}. (II) HVO_4^{2-}.

A p*K* value of −0·98 was estimated from the results by use of the extrapolation given in Fig. 5, curve I.

System $MnO_4^-/HMnO_4$.—With increasing concentration of sulphuric acid, the colour of a solution of permanganate changes through red and brown to green. The brown solutions resemble colloidal solutions of manganese dioxide, but the spectrum may be interpreted simply as the superposition of that of permanganate and that of permanganic acid. The green colour appearing when permanganate is dissolved in concentrated sulphuric acid has been attributed [12]

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[12] Ephraim, "Inorganic Chemistry," Gurney and Jackson, London, 1948, p. 486.

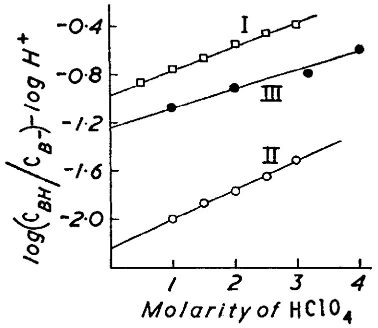
to Mn_2O_7. However, Beer's law is obeyed and since the spectrum (Fig. 2, curve III) is consistent with that expected for $HMnO_4$, we infer that in dilute solutions condensation is insignificant.

Because solutions containing permanganic acid in appreciable concentration slowly decomposed, it was necessary to extrapolate spectral readings to zero time, but during initial stages of protonation with perchloric acid (cf. Fig. 5, curve II) this was unnecessary.

System $ReO_4^-/HReO_4$.—The spectrum of potassium per-rhenate in sulphuric acid (Fig. 3) was taken to be that of per-rhenic acid since the expected spectral changes were found. This spectrum was reproducible and did not change appreciably during several hours. A pK value of $-1{\cdot}25$ was estimated from line III of Fig. 5, derived from measurements in aqueous perchloric acid.

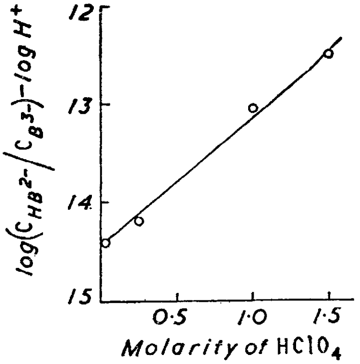
System VO_4^{3-}/HVO_4^{2-}.—Newmann and his co-workers[13] studied the spectra of vanadium(v) species in alkaline solution at an ionic strength of three and obtained an equilibrium constant of 0·097 for the reaction: $VO_4^{3-} + H_2O \rightleftharpoons HVO_4^{2-} + OH^-$. This gives a p$K$ value of about 13. For the dilute solutions of vanadate used, condensation is not expected to be important,[13] and a linear extrapolation similar to that used for acid solutions has been used to estimate pK (Fig. 6).

FIG. 5. *Graphical extrapolation for determination of* pK.



(I) $HCrO_4^-/H_2CrO_4$. (II) $MnO_4^-/HMnO_4$. (III) $ReO_4^-/HReO_4$.

FIG. 6. *Graphical extrapolation for determination of* pK.



VO_4^{3-}/HVO_4^{2-}.

The relation between the spectrum of vanadate and that ascribed to monohydrogen vanadate (Fig. 4) is as expected. Our results show that, on dissolution of Na_3VO_4 in water, conversion into HVO_4^{2-} is complete.

System $HVO_4^{2-}/H_2VO_4^-$.—Acidification of HVO_4^{2-} gave a change in spectrum similar to that for the system $HCrO_4^-/H_2CrO_4$, and pH measurements gave a pK value of 8·95, which is close to that expected by analogy with other systems (Table 2). Further acidification did not appear to give the change $H_2VO_4^- \longrightarrow H_3VO_4$ since the resulting spectrum bore no resemblance to that of HVO_4^{2-}. Conductimetric measurements showed a rapid increase in conductivity in this region, and that is tentatively ascribed to the formation of VO_2^+.

TABLE 2.

Non-metal oxyanions		Transition-metal oxyanions	
System	pK	System	pK
PO_4^{3-}/HPO_4^{2-}	12·0	VO_4^{3-}/HVO_4^{2-}	14·4
$HPO_4^{2-}/H_2PO_4^-$	7·2	$HVO_4^{2-}/H_2VO_4^-$	8·95
$H_2PO_4^-/H_3PO_4$	2·1	$CrO_4^{2-}/HCrO_4^-$	6·5
SO_4^{2-}/HSO_4^-	1·5	$HCrO_4^-/H_2CrO_4$	−0·98
HSO_4^-/H_2SO_4	−2·0 [a]	$MnO_4^-/HMnO_4$	−2·25
$ClO_4^-/HClO_4$	−7·0 [a]	$ReO_4^-/HReO_4$	−1·25

[a] Estimated from the Ricci formulation.

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[13] Newmann, La Fleur, Brousaides, and Ross, *J. Amer. Chem. Soc.*, 1958, **80**, 4491.

DISCUSSION OF BASICITIES

Although no attempt has been made to obtain very accurate results it is felt that the p*K* values recorded in Table 2 are accurate to about 0·2 unit, and that detailed comparisons with the known values for non-metal oxyions are warranted.

Comparison with Non-metal Oxyions.—Relevant p*K* values are listed in Table 2. In all cases the non-metal oxyions of similar charge-type are far weaker bases than oxyions of the transition metals, but there is considerable variation from one group to another. Thus, the p*K* values of phosphate and vanadate differ by 2·4 whilst those of sulphate and chromate differ by 5·0 units. Although the p*K* value for perchlorate is unknown, a value of —7·0 is predicted by Ricci's correlation[4] and —8·0 by Pauling's.[3] Hence perchlorate and permanganate probably differ by about 5 units.

A qualitative understanding of the relatively high basicities of transition-metal oxyions can be obtained by consideration of structure. Little is known about the detailed electronic structures of non-metal oxyions such as sulphate in comparison with those of oxyions of transition metals. The major differences between these classes of ions are (i) that the latter have intense electronic transitions in the visible and the near-ultraviolet region whilst the former are transparent in this region, and (ii) that the latter can accept electrons directly into low-lying orbitals whereas non-metal oxyions are unable to accept electrons and react with reducing agents by donation of oxygen.

To a crude first approximation the ions can be thought of as being built from four oxide ions and a central atom with closed-shell configuration (such as S^{6+}, Mn^{7+}, etc.) by transfer of four electrons from the oxide ions to the central atom followed by σ-bond formation using sp^3 (S^{6+}, etc.) or d^3s (Mn^{7+}, etc.) orbitals of the central atom. This will leave one negative charge on each oxygen atom and a net positive charge on the central atom. Partial charge-neutralisation will be achieved by inductive drift of the σ-bonding electrons, which should be about the same for corresponding ions in either group. Further neutralisation can be effected by π-bonding, and this has been considered in detail for transition-metal oxyions.[14] Although it has been concluded that such π-bonding is far less important than σ-bonding,[14] it is probably greater than in oxyions of non-metals.[15] Thus overlap between low-lying orbitals of the central metal atom and oxygen p-π orbitals provides a route for charge redistribution on protonation which will be less available for oxyions of non-metals. In other words, the polarisability of transition-metal oxyions will be greater because redistribution of electrons can proceed more readily through π- than through σ-bonds.

Relative Basicities.—It is noteworthy that there is a far greater difference between sulphate and chromate than between phosphate and vanadate. Although p*K* values for the latter pair of ions have to be obtained by extrapolation it is unlikely that the difference could be much greater than 2·4 units. One possible reason for this difference is the relative polarisability of chromate and vanadate. In so far as this is coupled to the availability of the low-lying vacant π-orbitals, both the greater electron-accepting power of chromate than of vanadate and the fact that the first electronic absorption band of chromate is of lower energy suggest that, were they of the same charge-type, chromate would be a stronger base than vanadate.

It might appear that the same arguments could be applied to permanganate and perrhenate: this leads to the prediction that permanganate should be the stronger base whereas, in fact, the reverse is found. This reversal may simply be due to the higher polarisability of rhenium than of manganese. An alternative explanation, that per-rhenic acid is octahedral (H_5ReO_6) rather than tetrahedral ($HReO_4$), is not favoured since the spectral changes (Fig. 3) are so well in accord with those expected on monoprotonation (see below). There is no evidence for the equilibrium $ReO_4^- + 2H_2O \rightleftharpoons H_4ReO_6^-$ in

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[14] Carrington and Symons, *J.*, 1960, in the press.
[15] Wolfsberg and Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

aqueous solution,[16] and it is likely that, if H_5ReO_6 were formed, it would be a relatively weak acid, probably weaker than periodic acid (H_5IO_6 has[17] pK $\approx$1·6).

Condensation.—Dichromate is formed far more readily than pyrosulphate. This occurs partly because protonation is a necessary step in the mechanism of condensation and partly because, in this series of ions, nucleophilic power should parallel basicity, so that chromate should be a far more powerful nucleophile than sulphate.

Our attempts to measure protonation of manganate and hypomanganate have failed, because disproportionation occurs before any spectral change can be detected. We have previously[18] suggested that, for these ions, condensation precedes disproportionation. If one further postulates that protonation precedes condensation, a rough estimate of the basicities of these ions can be given. Consideration of mechanism appears to support this reasoning, which, however, is questioned by Freedman.[19] Solutions of manganate in water containing 0·01M-sodium hydroxide and of hypomanganate in 1·0M-sodium hydroxide are stable for several minutes before onset of disproportionation. Hence the pK for manganate must be less than 12 and that for hypomanganate less than 14·4 (cf. vanadate).

Molybdate and Tungstate.—Since the pK values for permanganate and per-rhenate are similar it is probable that molybdate and tungstate will have values close to that for chromate. Attempts to check this prediction by spectrophotometry have not been successful. Spectra attributed to monomeric unprotonated ions have been reported.[5] These were obtained from alkaline solutions: there are slight, but significant, changes in neutral solutions which might be caused by protonation, but Beer's law is not accurately obeyed and therefore condensation probably occurs concurrently. This suggests that the pK values are in the region of 6. Schwarzenbach and Meier,[20] however, consider that diprotonation takes place without the intermediate formation of monoprotonated ions and estimate pK values of about 4·5 for this process. Sasaki[21] has reported a value of about 4·0 for the pK of molybdate, and Britton[22] has estimated a value of 6·7 for tungstate. The problem is confused because of the great ease of condensation of these ions, which, since the polyions are probably octahedrally co-ordinated,[23] may well proceed by a mechanism different from that for condensation of chromate.[19]

DISCUSSION OF SPECTRA

It has been stressed above that the spectral changes which occur on protonation of a "closed-shell" transition-metal oxyanion are simple and characteristic (see Figs. 1—4). In this section we shall consider theoretically the changes in the orbital energy levels and the consequent spectral changes to be expected on protonation. Attention will be confined to changes in the lowest energy transitions, and the level scheme outlined in another paper[14] will be used as a basis for discussion.

For a tetrahedral oxyanion represented as MO_4 (symmetry T_d) it is assumed that addition of a proton gives a tetrahedral ion $MO_3(OH)$ of symmetry C_{3v}. This reduction of symmetry results in the splitting of all orbital triplets into a singlet and a doublet, $t_1 \longrightarrow e + a_2$, and $t_2 \longrightarrow e + a_1$. The degeneracy of doublet levels (e) in T_d remains unchanged although the molecular orbital form and energy may alter. This is pictured

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[16] Woodward, *Trans. Faraday Soc.*, 1952, **52**, 615.

[17] Crouthamel, Meek, Martin, and Banks, *J. Amer. Chem. Soc.*, 1949, **71**, 3031.

[18] Carrington and Symons, *J.*, 1956, 3373.

[19] Freedman, *J. Amer. Chem. Soc.*, 1958, **80**, 2072.

[20] Schwarzenbach and Meier, Symposium, Chemistry of Co-ordinate Compounds, Rome, 1957, Pergamon Press, 1958, p. 302.

[21] Sasaki, Internat. Conference on Co-ordination Chemistry, London, 1959, *Chem. Soc. Special Publ.* No. 13.

[22] Britton, *J.*, 1927, 147.

[23] Bailar, "Chemistry of Co-ordination Compounds," Amer. Chem. Soc. Monograph 131, Reinhold, New York, 1956, p. 472.

in Fig. 7, in which the $4e$ level has been arbitrarily placed above a_2. Thus the transition $e \longleftarrow t_1$, designated as ν, which gives rise to the lowest-energy absorption band for MO_4, is split into two, designated in Fig. 7 as ν_1 and ν_2 which may be written:

$$\nu_1 \ldots\ldots (4e)^3\,(a_2)^2\,5e \longleftarrow (4e)^4\,(a_2)^2 \;:\; A_1$$

$$E, A_1 \longleftarrow A_1 \quad \text{Allowed}$$

$$A_2 \longleftarrow A_1 \quad \text{Forbidden}$$

$$\nu_2 \ldots\ldots (4e)^4\,a_2\,5e \;:\; E \longleftarrow (4e)^4\,(a_2)^2 : A_1$$

Before the expected intensity of these transitions can be estimated, an approximation to the form of the molecular orbitals must be made. Helmholz, Brennan, and Wolfsberg[9] considered the molecular orbitals for CrO_3X^-, where X is halogen, and studied the behaviour of the metal $3d$, $4s$, and $4p$ orbitals and the ligand p orbitals under the symmetry operations of C_{3v}, finding the combinations which form bases for the irreducible representations (A_1, A_2, and E) of C_{3v}. On applying these results to $MO_3(OH)$, the a_2 level is found to be fully determined by symmetry and may be written as $\frac{1}{\sqrt{3}}\,(\pi y_2 + \pi y_3 + \pi y_4)$ where πy_2, πy_3, and πy_4 are the oxygen $2p$ orbitals whose orientation, relative to axes with origin at the metal atom, are given by Helmholz, Brennan, and Wolfsberg.[9]

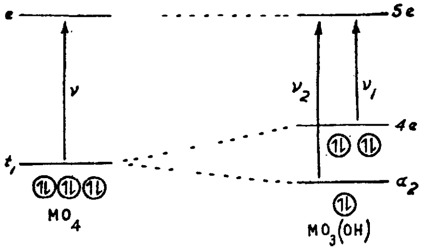

FIG. 7. *Highest filled and lowest unfilled levels for transition-metal oxyanions and their conjugate acids.*

The $5e$ level is not fully determined by symmetry, but it corresponds to the first antibonding e level for unsubstituted MO_4 ions. It has been found that this level can be treated as having " pure " metal d orbital character,[14] and the same assumption will be made for the protonated ion. It is more difficult to find a suitable description of the $4e$ level. The level could be regarded as non-bonding, since this would be the result of applying a C_{3v} symmetry perturbation to the original t_1 level of MO_4. The problem of deciding how these non-bonding electrons are distributed between the oxygen atoms and the hydroxide ligand remains, and appears to be insuperable at present.

With the above approximation to the form of the $5e$ level, the dipole strength of the ν_2 transition can be computed. By proceeding in the manner used for MO_4 ions[24] (cf. Mulliken and Riecke[25]), the dipole strength of the transition is found to be $24\alpha^2$ where α is the integral $<a_2\,|x|\,5e_a>$. When the a_2 level is taken as $\frac{1}{3}(\pi y_2 + \pi y_3 + \pi y_4)$ and admixture of ligand orbitals with $d_{x^2-y^2}$ in the $5e_a$ orbital is neglected, α is given by:

$$\alpha = \left(\frac{1}{\sqrt{3}}\right)\left\{\langle \pi y_4\,|y|\,d_{x^2-y^2}\rangle - \langle \pi y_4\,|z|\,d_{x^2-y^2}\rangle\right\}$$

In the case of the $e \longleftarrow t_1$ transition for MO_4 ions, the dipole strength was found to be $24\gamma^2$, γ being defined by

$$\gamma = 2\langle \pi y_1\,|y|\,d_{x^2-y^2}\rangle$$

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[24] Carrington and Schonland, *J. Mol. Phys.*, to be published.

[25] Mulliken and Riecke, *Reports Progr. Phys.*, 1948, **8**, 231.

Using hydrogen-like wave functions for the atomic orbitals in order to evaluate the integrals, and taking account of the choice or orientation of the oxygen *p*-orbitals,[9,15] we find that $\alpha = \gamma\sqrt{3}$.

Thus it is found that the oscillator strength should be approximately one-third of that of the original low-energy band for MO_4. More precisely,

$$f_{MO_3(OH)} = f_{MO_4} \times \tfrac{1}{3} \times \nu_2/\nu \qquad (4)$$

where f is the oscillator strength.

Of the two longer-wavelength bands found experimentally for $MO_3(OH)$, the higher-energy band has always approximately one-third of the oscillator strength of the corresponding MO_4 band, whereas the lower-energy band is very much weaker. We therefore identify the higher energy band with the ν_2 transition and hence place the a_2 level below the $4e$ level.

TABLE 3. *Comparison of experimental and theoretical oscillator strengths for protonated oxyanions.*

The values given in column 4 are based on the experimental value for MO_4 (column 2) in conjunction with the theoretical expression (equation 4).

Oxy-anion	f_{MO_4} (exp.)	$f_{MO_3(OH)}$ (exp.)	$f_{MO_3(OH)}$ (theor.)
MnO_4^-	0·032	0·015	0·013
CrO_4^{2-}	0·089	0·033	0·032
VO_4^{3-}	0·150	0·059	0·051

In Table 3, experimental and theoretical values of the oscillator strengths are compared. In view of the difficulty in describing the $4e$ level, direct calculation of oscillator strengths cannot be made and further simplification does not seem warranted.

These calculations suggest that a large increase in π-bonding on protonation would result in a corresponding increase in the relative oscillator strengths for the ν_2 transition: since this is not detected experimentally it appears that the drift of π-electrons, postulated above to explain the relatively high basicities of these ions, must be comparatively small.

One of us (A. C.) thanks the Esso Petroleum Company for a post-graduate research studentship, and another (K. A. K. L.) thanks the University of Southampton for a post-graduate research scholarship.

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[*Received, July 6th,* 1959.]