

853. Structure and Reactivity of the Oxyanions of Transition Metals.
Part XIV. Closed-shell Ions in Sulphuric Acid and Oleum.*

By H. C. MISHRA and M. C. R. SYMONS.

Interactions between (a) vanadates, chromates, or permanganates and (b) sulphuric acid or oleum have been studied by spectrophotometric, magnetic, conductometric, and analytical methods. The results are discussed in terms of protonation, sulphonation, dehydration, and reduction.

CHANGES in the electronic spectra of solutions of closed-shell oxyanions of transition metals upon acidification have been interpreted in terms of mono- and di-protonation, which reduces the local symmetry from T_d to C_{3v} or C_{2v} .¹ Although the theoretical interpretation¹ has been questioned,² nevertheless the spectral changes, especially for monoprotonation, are characteristic and the resulting spectra so closely resemble those for corresponding species known to have C_{3v} symmetry that the changes can confidently be taken as empirically diagnostic of the modified symmetry.

However, the local symmetry can be reduced from T_d to C_{3v} or C_{2v} by reactions other than protonation, and alternative acid-catalysed reactions, such as dehydration to give oxycations, have also been postulated. In the present study, solutions of septivalent manganese, sexivalent chromium, and quinquevalent vanadium compounds in 100% sulphuric acid and various oleums have been studied, particularly by spectrophotometric and conductometric methods, in an attempt to clarify these problems.

Green solutions obtained by dissolution of permanganates in sulphuric acid have been variously described as containing Mn_2O_7 ,³ $(MnO_3)_2SO_4$,⁴ and $HMnO_4$,¹ but the evidence is in no case compelling. Recently it has been suggested that dehydration occurs to give the oxycation MnO_3^+ ; ⁵ this is discussed below.

Little is known about the nature of solutions of chromates and dichromates in sulphuric acid. Yatsimirski and Vasiliva⁶ postulated the formation of H_2CrSO_7 , $H_2Cr_4O_{13}$, and related compounds in 50–80% sulphuric acid. Hayek and Engelbrecht⁷ reported the formation of $CrO(SO_4)_2$ and $V_2O(SO_4)_4$ when the corresponding oxyhalides were heated with sulphur trioxide, and Woolf⁸ suggested the ionic forms $(CrO_2)_2S_2O_7$ and $(VO_2)_2S_4O_{13}$ for these compounds.

The formation of a sulphate, $(VO)_2(SO_4)_3$, has been postulated⁹ for quinquevalent vanadium in sulphuric acid, but no well-defined compound has yet been isolated.

EXPERIMENTAL AND RESULTS

Materials.—"AnalaR" reagents were used, generally without further purification. Oleums were prepared as described previously.¹⁰

Measurements.—Spectrophotometric, magnetic, and conductance measurements were made as described previously.¹⁰

Spectrophotometric Results.—Solutions of permanganate in 100% sulphuric acid decompose slowly to oxygen and manganese dioxide or tervalent manganese. However, by extrapolating

* Part XIII, *J.*, 1962, 3903.

¹ Bailey, Carrington, Lott, and Symons, *J.*, 1960, 290.

² Klänig and Symons, *J.*, 1961, 3204.

³ Heslop and Robinson, "Inorganic Chemistry," Elsevier, Amsterdam, 1960, p. 458.

⁴ Franke, *J. prakt. Chem.*, 1887, **36**, 31.

⁵ Royer, *J. Inorg. Nuclear Chem.*, 1961, **17**, 159.

⁶ Yatsimirski and Vasiliva, *Zhur. neorg. Khim.*, 1956, 1983.

⁷ Hayek and Engelbrecht, *Monatsh.*, 1949, **80**, 640.

⁸ Woolf, *Chem. and Ind.*, 1954, **346**, 4113.

⁹ Ephraim, "Inorganic Chemistry," Gurney and Jackson, London, 1960, p. 608.

¹⁰ Arotzky, Mishra, and Symons, *J.*, 1961, 12.

results to zero time we have found that Beer's law is adequately obeyed. This strongly suggests that formation of the heptoxide is insignificant in dilute solutions. In oleum the rate of decomposition is greatly enhanced and no reliable spectra were recorded.

Number of moles of solvent anions formed per mole of solute, estimated from conductance results.

Solute	No. of HSO_4^- ions in 100% H_2SO_4	No. of ions in dilute oleum (about 5%)	No. of HS_2O_7^- ions in 65% oleum
KMnO_4	2.0—2.2	—	—
K_2CrO_4	3	3.2	—
V_2O_5	2.4	2.6	0.0—0.2

Solutions of chromates in sulphuric acid and dilute oleums (<20% SO_3) were relatively stable, but in 65% oleum, decomposition to give oxygen and quinquevalent chromium is rapid.¹¹ Spectra in 72% aqueous perchloric acid and 100% sulphuric acid are compared in Fig. 1.

Quinquevalent vanadium compounds are stable in sulphuric acid and oleums. Spectra are given in Fig. 2.

Conductance Results.—These are summarised in the Table. The precision for permanganates is low because of the relatively low stability of more concentrated solutions.

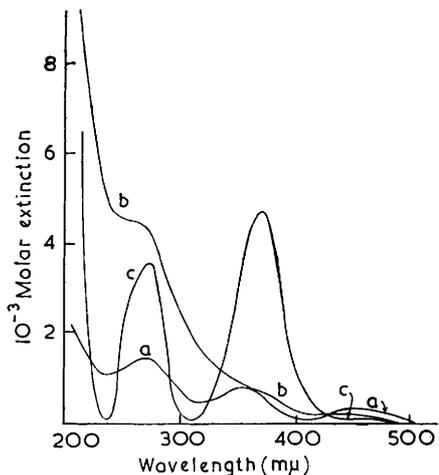


FIG. 1.

FIG. 1. Ultraviolet spectra of chromate in strongly acidic media: (a) In 72% HClO_4 ; (b) in 100% H_2SO_4 ; (c) CrO_4^{2-} in aqueous alkali.

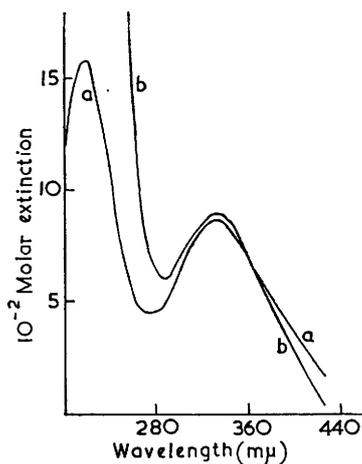


FIG. 2.

FIG. 2. Ultraviolet spectra of V_2O_5 in 100% H_2SO_4 (a) and 65% oleum (b).

Conductance results for solutions of vanadium pentoxide in sulphuric acid indicated a relative decrease in the number of bisulphate ions with increasing concentration of the pentoxide. We think that this was due to formation of polymeric species, and hence we use only the results for dilute solutions in discussion.

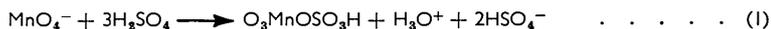
Magnetic Results.—All solutions whose properties are reported in this work were diamagnetic, their susceptibilities at room temperature being in accord with expectation for septivalent manganese, sexivalent chromium, and quinquevalent vanadium species.

Analyses.—It was confirmed that all the solutions under consideration contained manganese, chromium, or vanadium in their highest valency state, by dilution of the solutions with water followed by aqueous alkali and estimation of the concentrations spectrophotometrically.

¹¹ Mishra and Symons, *Proc. Chem. Soc.*, 1962, 23.

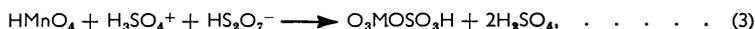
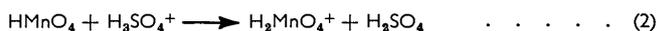
DISCUSSION

Septivalent Manganese.—The postulate¹ that the green species in 100% sulphuric acid is permanganic acid is excluded by the conductivity data. The spectrum is indicative of a species with local C_{3v} symmetry and the reaction



adequately accommodates this requirement and the conductivity data. The pK value of -2.25 estimated for permanganic acid¹ is probably valid, since this was deduced from spectral changes in dilute aqueous perchloric acid. If the spectrum in 72% perchloric acid is then assigned to permanganic acid, a significant difference between this spectrum and that now assigned to $\text{O}_3\text{MnOSO}_3\text{H}$ is worth consideration. The second band in the spectrum of the latter compound has a maximum at higher energies, and there is a considerable decrease in the oscillator strength for this band. These changes result in an unusually good resolution of the first band (Fig. 2, curve III, of ref. 1), this feature being comparable with that found in the spectrum of monoacetyl chromate (Fig. 1 of ref. 2). These trends are diagnostic of a compound O_3MnOR , where R has a relatively high electron-attracting power,² and are thus in good accord with the formulation $\text{O}_3\text{MnOSO}_3\text{H}$.

The conductometric titration data (Fig. 3) serve to eliminate the slight possibility that the species in 100% sulphuric acid is H_2MnO_4^+ , since different results are obtained depending upon whether or not a molecule of water is formed. Thus one can distinguish between reactions (2) and (3),



only reaction (3) being compatible with the results.

Since this work was completed, Royer's work on these solutions has appeared,⁵ in which cryoscopic, conductance, and spectrophotometric results are interpreted in terms of the reaction



His conductance data are closely similar to ours, giving values in the region 2.0—2.2 for the number of HSO_4^- ions formed. However, steady readings were only obtained some twelve minutes after preparation,⁵ and Royer suggests that extrapolation to zero time would give a result of 3.0, in accord with scheme (4). He attributes the decrease with time variously to decomposition and precipitation of $(\text{MnO}_3)(\text{HSO}_4)$: we find that even 30 minutes after preparation neither factor could account for a drop from 3.0 to 2.0.

It is not possible to choose between reaction (4) and (1) on the basis of cryoscopic measurements.⁵ The reported results,⁵ expressed as the number of particles produced, range from 4.2 to 6.0 for various solutions, the more dilute giving the higher values. It is suggested that results for dilute solutions are to be trusted most and hence equation (4) is favoured. On the other hand, an average of all the results gives a value close to 5, as required by equation (1).

Finally, Royer states that the optical spectrum is reasonable for the cation MnO_3^+ but that the sulphate $\text{O}_3\text{MnOSO}_3\text{H}$ would not be expected to give rise to the spectrum recorded. We consider that the very close similarity between the spectral modifications on going from aqueous permanganate to the green solutions and those observed on going from a wide range of tetrahedral ions, XO_4 , to corresponding ions, O_3XY , known to have C_{3v} symmetry,^{1,2,12} provides very strong evidence in favour of the formulation $\text{O}_3\text{MnOSO}_3\text{H}$.

Sexivalent Chromium.—By analogy with the behaviour of permanganate, the compounds $\text{O}_2\text{Cr}(\text{OH})(\text{OSO}_3\text{H})$ and $\text{O}_2\text{Cr}(\text{OSO}_3\text{H})_2$ must be considered in addition to chromic

¹² Helmholtz, Brennen, and Wolfsberg, *J. Chem. Phys.*, 1955, **23**, 853.

acid as possible constituents in sulphuric acid. The results obtained for solutions in aqueous perchloric acid,¹ including the spectrum in 72% acid, probably relate only to chromic acid. In 100% sulphuric acid the spectrum has become blurred, with no resolved maxima above 240 μ , as expected for a mixture of different species or for a compound such as the monosulphate $O_2Cr(OH)(OSO_3H)$ whose reduced symmetry will result in further multiplication of possible electronic transitions.

Conductivity results both for solutions in 100% sulphuric acid and for titrations in dilute oleum are roughly in accord with the reaction



For solutions in more concentrated oleum the spectrum is better resolved, being similar to that in 72% perchloric acid, but the rate of decomposition is such as to preclude further

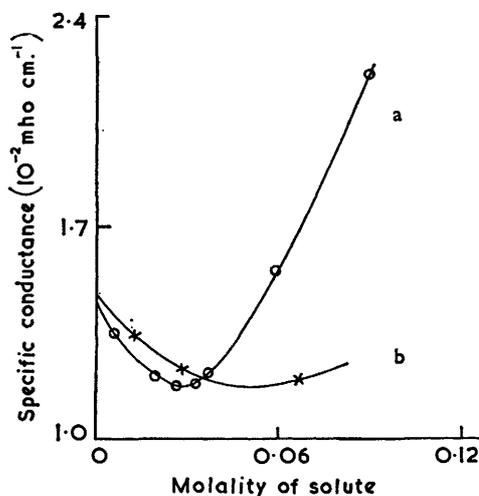


FIG. 3. Conductometric titration of solutions of potassium permanganate in dilute oleum: (a) $KMnO_4$; (b) $KHSO_4$.

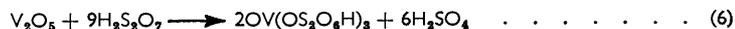
conductivity studies. We attribute this spectrum to the disulphate, which has local C_{2v} symmetry.

It was postulated earlier¹ that the cation CrO_2^{2+} might be formed in 100% sulphuric acid. This species is definitely excluded by our present results.

Quinquevalent Vanadium.—We discuss the results in terms of our findings for manganese and chromium and then attempt to reconcile our conclusions with those of others for solutions in aqueous acids.

By analogy, the covalent mono-, di-, and tri-sulphates $OV(OH)_2(OSO_3H)$, $OV(OH)(OSO_3H)_2$, and $OV(OSO_3H)_3$ should be considered, in addition to vanadic acid, H_3VO_4 , monoprotonated vanadic acid, $V(OH)_4^+$, and the cations VO_2^+ and VO^{3+} . In dilute solution in 100% sulphuric acid, Beer's law is obeyed, but this is not so for more concentrated solutions ($>10^{-2}M$), possibly because of polymerisation. We therefore confine our discussion to results for dilute solutions.

Results for solutions in 65% oleum are well accommodated by the single reaction

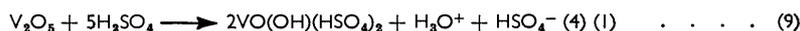
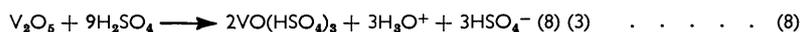
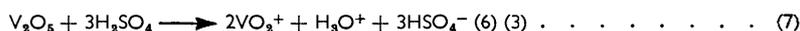


and species such as VO_2^+ or $V(OH)_4^+$ are definitely excluded. The tripyrosulphate, $OV(OS_2O_6H)_3$, has local C_{3v} symmetry and should have a spectrum of the same general form as the anion HVO_4^{2-} : in particular, relatively well-resolved bands are to be expected. The spectrum of HVO_4^{2-} is characterised by a weak band at 330 μ ,¹ associated with an electron-transfer from the oxide ligands to vanadium, and a more intense band at 260 μ which is thought to be linked primarily with an electron-transfer from hydroxide to

vanadium.² The situation for $\text{OV}(\text{OS}_2\text{O}_6\text{H})_3$ is reversed, relative to HVO_4^{2-} , and we expect a band at $330 \text{ m}\mu$ of greatly increased intensity, and a band at considerably higher energy than the $260 \text{ m}\mu$ band of HVO_4^{2-} but of reduced intensity. These predictions follow from the assignments proposed and discussed earlier,² and are closely fulfilled for vanadyl chloride, VOCl_3 , in the gas-phase.¹³

The spectrum in 65% oleum (Fig. 2) is in satisfactory agreement with these predictions in that the first band remains at $330 \text{ m}\mu$ but has far greater intensity than is normally found for the first band in the spectra of monosubstituted ions.^{1,2} Also, this band is clearly resolved, there being no sign of a band in the $260 \text{ m}\mu$ region. Unfortunately the medium is optically black below $250 \text{ m}\mu$, so that further details of the spectrum could not be obtained.

Results for solutions in 100% sulphuric acid and dilute oleums can be related to these conclusions in terms of the mono-, di-, and tri-sulphates formulated above. The results expected for these species are given in parentheses in the following equations, the first figure referring to the total number of particles and the second to the number of bisulphate ions:



Other possible reactions, such as that giving $\text{V}(\text{OH})_4^+$, are omitted since they are eliminated by the results.

Experiment gives about 2.4 for the number of bisulphate ions, and the number of particles deduced from cryoscopy¹⁴ ranges between 5.4 for concentrated to 6.4 for dilute solutions. The results for dilute solutions are almost quantitatively correct for a combination of reactions (8) and (9), the former constituting about 65% of the total.

These results are not sufficiently precise to enable us to reject reaction (7) conclusively. However, the ultraviolet spectrum is very similar to that for solutions in 65% oleum, and for solutions in both sulphuric acid and dilute oleum the spectrum is almost identical with that for VOCl_3 ,¹³ which has the same local symmetry as that of the complexes $\text{VO}(\text{OH})(\text{HSO}_4)_2$ and $\text{VO}(\text{HSO}_4)_3$.

Pervanadyl Ion.—These conclusions must be compared with those of others who have studied quinquevalent vanadium in aqueous acids. It seems that in the pH region at which the formation of vanadic acid from H_2VO_4^+ is expected, an alternative reaction resulting in the formation of a monomeric cation occurs.^{1,15,16} This species is usually formulated as the pervanadyl ion, VO_2^+ , but the formulation $\text{V}(\text{OH})_4^+$ has also been proposed. Unfortunately no salt of the cation has been identified unambiguously and so structural information is scanty. La Salle and Cobble¹⁷ postulated that this ion is present in the salt $\text{KVO}_3 \cdot \text{H}_2\text{O}$ (which was studied by Christ *et al.*¹⁸ using X-ray diffraction methods) and concluded that it is bent, having a O-V-O angle of 105° . We consider that this conclusion requires modification since we know no reason why VO_2^+ should not take up the linear configuration to be expected on theoretical grounds for such an ion. The crystallographic data are more in accord with the formulation KH_2VO_4 , since the O-V-O bond angle is close to that expected for the H_2VO_4^- ion.

If VO_2^+ were a correct representation then one might expect to find four weakly bonded water molecules clustered round the vanadium in the xy -plane, when the z -axis is defined

¹³ Miller and White, *Spectrochim. Acta*, 1957, **9**, 98.

¹⁴ Gillespie and Robinson, personal communication.

¹⁵ Rossotti and Rossotti, *Acta Chem. Scand.*, 1956, **10**, 957.

¹⁶ Sillén, *Quart. Rev.*, 1959, **13**, 146.

¹⁷ La Salle and Cobble, *J. Phys. Chem.*, 1955, **59**, 519.

¹⁸ Christ, Clark, and Evans, *Acta Cryst.*, 1954, **7**, 801.

as the O-V-O direction. One may then ask why do the protons not rearrange to give $V(OH)_4(H_2O)_2^+$ rather than $O_2V(H_2O)_4^+$? In the former there will be four relatively short bonds in a plane and two longer bonds, whereas for the latter this situation is reversed. There is no electronic reason why the latter arrangement should be preferred, and the former is, of course, chemically more reasonable. However, the V^{5+} ion is not normally symmetrically octahedrally co-ordinated, because of its small size,¹⁹ and the former arrangement may be unstable for this reason. Normally, in these circumstances, one would expect to find tetrahedral co-ordination, and hence the ion $X(OH)_4^+$ must be considered.

If this ion is formed, then the disproportionation



must lie well to the right, since the cationic species is detected on addition of acid to aqueous vanadates without the prior formation of a soluble neutral species.^{1,16} This is unlikely as represented in reaction (11). Rossotti and Rossotti,¹⁵ however, conclude that a well-defined polymer containing ten vanadium atoms is favoured, which is not hydrolysed on dilution. The structure of this polymer is not known. It is possible that the change on acidification is gradual, precipitation of vanadium pentoxide being the culmination of a polymerisation which starts on addition of protons to HVO_4^{2-} . The cationic species is then formed by depolymerisation on further acidification.

A consideration of ultraviolet spectra should help to elucidate this problem. Our conclusions regarding possible electronic transitions for pervanadyl ion have been outlined above. The ion $V(OH)_4^+$ has local T_d symmetry and a single, intense band should be found, at considerably higher energies than that for vanadate (VO_4^{3-}) but with comparable or slightly reduced intensity. The $t_1 \rightarrow e$ transition for vanadate is at 270 $m\mu$, with a molar extinction coefficient of 7400. Hence the spectrum given by Rossotti and Rossotti¹⁵ for the cationic species cannot be due to $V(OH)_4^+$ since there is a steadily rising absorption from 400 $m\mu$, with poorly defined shoulders in the 340 and 270 $m\mu$ regions. A similar spectrum is reported by La Salle and Cobble¹⁷ for solutions in 0.2M-aqueous perchloric acid, but they also report a peak at 225 $m\mu$ with a molar extinction coefficient of 2240.

Finally the possibility of five-fold co-ordination should be considered. Quinquevalent vanadium readily forms tetrahedral complexes such as VO_4^{3-} , $VOCl_3$, $VO(SiR_3)_3$, etc. Our experiments involving the addition of potassium pyrosulphate to $OV(OS_2O_6H)_3$ in 65% oleum suggest that in this case the five-covalent structure is only slightly less stable than the tetrahedral, since the reaction



seems to occur to a detectable extent.

We conclude that none of the formulations VO_2^+ , $V(OH)_4^+$, and $V(OH)_4(H_2O)_2^+$ is entirely satisfactory, and suggest instead the quinque-co-ordinated ions $V(OH)_4(H_2O)^+$ or $OV(OH)_2(H_2O)_2^+$.

Reactivity.—Septivalent manganese decomposes slowly in 100% sulphuric acid, where it is thought to be present as O_3MnOSO_3H , but very rapidly even in dilute oleum, to give oxygen and quadrivalent or tervalent manganese, depending upon conditions. Our evidence concerning the valency states and structures of the products has been summarised.¹¹ Here we consider a possible reason for this instability. We postulate that a disulphate is formed in low concentration, which decomposes spontaneously because of the very high electron-attraction of the ligands:



¹⁹ Dunitz and Orgel, "Advances in Inorganic and Radiochemistry," Academic Press, Inc., New York, 1960, p. 1.

The tervalent manganese either stabilises itself by further co-ordination or reacts with septivalent manganese to give the final products. This extrusion of oxygen resembles that postulated for the photochemical breakdown of permanganate,²⁰ but the transition state may involve solvent more intimately than is possible under Frank-Condon restrictions.

Similar arguments apply to species such as $O_2Cr(OS_2O_6H)_2$, though the lower electron-affinity of the metal results in greater stability. With quinquivalent vanadium, the compound $OV(OS_2O_6H)_3$ is relatively stable despite the extra sulphate group. This increased stability may also be due to an increase in activation energy of decomposition since, in this instance, unimolecular breakdown with extrusion of molecular oxygen cannot occur.

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DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY, LEICESTER.

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²⁰ Klänning and Symons, *J.*, 1960, 977.
