

### 1116. A Spectrophotometric Study of Some Transition-metal Ions in Sulphuric Acid.

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The visible and near-ultraviolet spectra of chromium(III), titanium(III), nickel(II), and cobalt(II) have been measured in strong sulphuric acid, and are interpreted in terms of the weaker crystal field as compared with water. The spectra of vanadium(IV) and molybdenum(V) are interpreted in terms of increasing electron-donation in the  $\pi$ -component of the metal-oxygen bond of  $\text{VO}^{2+}$  and  $\text{MoO}^{3+}$  species as the concentration of sulphuric acid is increased.

THE behaviour of molybdenum(V) in hydrochloric acid solutions of various strengths has been studied by Haight<sup>1</sup> and by Simon and Souchay.<sup>2</sup> In 5–6M-hydrochloric acid, solutions of molybdenum(V) are dark brown, and the species present is a binuclear complex of molybdenum(V). Above 6M, the solutions are green, and the molybdenum is present as the ion  $[\text{MoOCl}_5]^{2-}$ . When the solvent is aqueous sulphuric acid, similar behaviour is observed, except that, as the acid concentration is increased, the initially brown solution of the molybdenum(V) species becomes not green, but green-blue. The visible absorption maxima for the concentrated hydrochloric acid solutions are at 445 and 712  $m\mu$ , but when the solvent is 91.3% sulphuric acid, they are at 392 and 675  $m\mu$ . This is surprising, since sulphuric acid or the ions sulphate or hydrogen sulphate (which, presumably, are the ligands in the sulphuric acid solution) are reputed to produce relatively weak crystal fields. Further, on increasing the concentration of sulphuric acid and eventually producing oleum solutions, the absorption maximum at 675  $m\mu$  moves to shorter wavelengths.

In attempting to account for these observations, it is necessary, first of all, to know how the spectra of transition-metal ions in general are affected when aquo-ligands are replaced in concentrated sulphuric acid solutions. Accordingly, small volumes of concentrated aqueous solutions of transition-metal sulphates were mixed with concentrated sulphuric acid, and the spectra of these solutions and corresponding aqueous solutions were compared.

#### RESULTS AND DISCUSSION

Absorption maxima and extinction coefficients for solutions of chromium(III), titanium(III), cobalt(II), nickel(II), and vanadium(IV) in water (or dilute sulphuric acid) and in concentrated sulphuric acid are shown in the Table; also included are data for solutions of

Summary of absorption maxima ( $\lambda_{\text{max}}$ ) and extinction coefficients ( $\epsilon_{\text{max}}$ ) at 25°.

Ion	Solvent	$\lambda_{\text{max}}$ ( $m\mu$ ) ( $\epsilon_{\text{max}}$ )
Chromium(III)	Water	573 (14), 407 (16)
	95.9% $\text{H}_2\text{SO}_4$ (initial spectrum)	576 (15), 410 (16), 260sh
	95.9% $\text{H}_2\text{SO}_4$ (after 6 days)	696, 668, 470, 314
Titanium(III)	0.1M- $\text{H}_2\text{SO}_4$	580sh, 510 (5.6)
	93.8% $\text{H}_2\text{SO}_4$	710 (2.5), 603 (3.3)
Cobalt(II)	Water	508 (5.0), 480sh
	98.0% $\text{H}_2\text{SO}_4$	775 (0.5), 543 (11.0)
Nickel(II)	Water	720 (2.3), 650 (1.9), 393 (5.4)
	97.0% $\text{H}_2\text{SO}_4$	826 (2.9), 673 (0.49), 431 (8.9)
Vanadium(IV)	Water	770 (18), 645sh, 235sh, ca. 200 (ca. 670)
	95.0% $\text{H}_2\text{SO}_4$	795sh, 683 (30), < 210
Molybdenum(V)	91.3% $\text{H}_2\text{SO}_4$	675 (29), 392 (15), < 210
	94.0% $\text{H}_2\text{SO}_4$ , 6.0% $\text{SO}_3^*$	630 (32), 379 (18)
	77.9% $\text{H}_2\text{SO}_4$ , 22.1% $\text{SO}_3^*$	620 (36), 387 (22)

\* Owing to the very strong absorption by the oleum itself at wavelengths below ca. 330  $m\mu$ , bands due to molybdenum(V) cannot be satisfactorily observed below this wavelength.

<sup>1</sup> G. P. Haight, *J. Inorg. Nuclear Chem.*, 1962, **24**, 663.

<sup>2</sup> J. P. Simon and P. Souchay, *Bull. Soc. chim. France*, 1956, 1402.

molybdenum(v) in sulphuric acid–oleum solutions, as well as in concentrated sulphuric acid solutions.

The spectrum of chromium(III) in 95.9% sulphuric acid is almost the same as that of the hexa-aquo-ion in water. The purple colour of the sulphuric acid solution is therefore due to the hexa-aquochromium(III) ion. The crystal-field effect of the co-ordination sphere is little affected by the sulphuric acid. On standing or warming, the violet sulphuric acid solution becomes green. A similar effect has been noted for aqueous, slightly acid solutions of chromium(III) sulphate, and is accounted for by the displacement of aquo-ligands by sulphate ligands.<sup>3</sup> In aqueous solution, the resulting complexes are polynuclear, and there is no reason to suspect that they are otherwise in strong sulphuric acid solutions.

For the other transition-metal ions, replacement of aquo-ligands appeared to be instantaneous in sulphuric acid. From the data obtained in this study, it is not possible to state with certainty the constitution of the species which are produced in sulphuric acid. However, for titanium(III), cobalt(II), and nickel(II), the small change which occurs in the spectra as the concentration of sulphuric acid is increased [for example, as shown in Fig. 1 for nickel(II)]

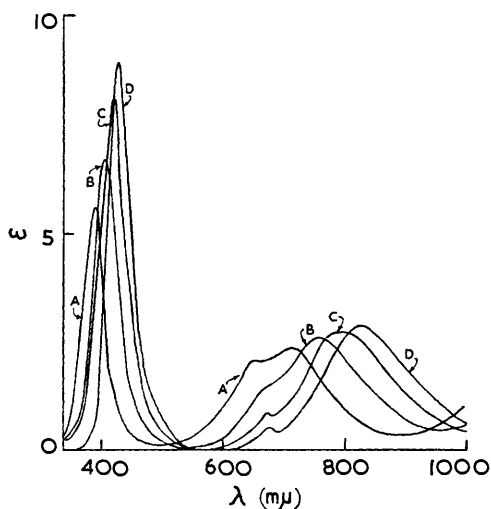


FIG. 1. Absorption spectra of nickel(II) in water (A) and in sulphuric acid solutions of the following strengths: 77.6% (B); 87.9% (C); and 97.0% (D). [Nickel(II)] = 0.074M.

suggests that the environment of the transition-metal ion is modified to only a small degree, and that it is still six-co-ordinated as in the hexa-aquo-ion. The ligands which replace the aquo-ligands are probably sulphuric acid molecules or the ions sulphate or hydrogen sulphate, and, since they bring about a shift to longer wavelength in the crystal-field bands, they thus provide a weaker crystal field.

For vanadium(IV), the maximum at 770 mμ in aqueous solution moves to shorter wavelength as the concentration of sulphuric acid is increased, being at 683 mμ in 95.0% sulphuric acid. This trend is the opposite to that observed for the ions so far considered in this discussion, but can be explained if it is assumed that the vanadyl(IV) species persists when the solvent is changed. The molecular-orbital scheme for the vanadyl ion [with six-co-ordinated vanadium(IV)] has been described by Ballhausen and Gray.<sup>4</sup> All the bands, except that producing the shoulder at 645 mμ, have been assigned to transitions which involve bonding or antibonding  $\pi$  molecular orbitals of the V–O bond. Therefore, increasing the extent of electron-donation from oxygen to vanadium in the  $\pi$ -component of the V–O bond, thereby lowering the  $e_{\pi}^b$  and raising the  $e_{\pi}^*$  orbitals, would result in a shift to shorter wavelength of the absorption maxima of these bands. As shown in Fig. 2, this is the trend observed when the solvent is changed from water to sulphuric acid, and it would thus appear that the change

<sup>3</sup> E. N. Slavnova, *Trudy Inst. Krist., Akad. Nauk. S.S.S.R.*, 1956, No. 12, 132.

<sup>4</sup> C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1962, 1, 111.

in the co-ordination sphere, which accompanies solvent change, increases electron donation in the  $\pi$ -component of the V-O bond. Moreover, the crystal-field transition  ${}^2B_2 \rightarrow {}^2B_1$ , which, in 0.1M-sulphuric acid, has its absorption maximum estimated<sup>4</sup> at *ca.* 625 m $\mu$ , moves to longer wavelength and eventually appears as a shoulder on the longer-wavelength side of the main band.

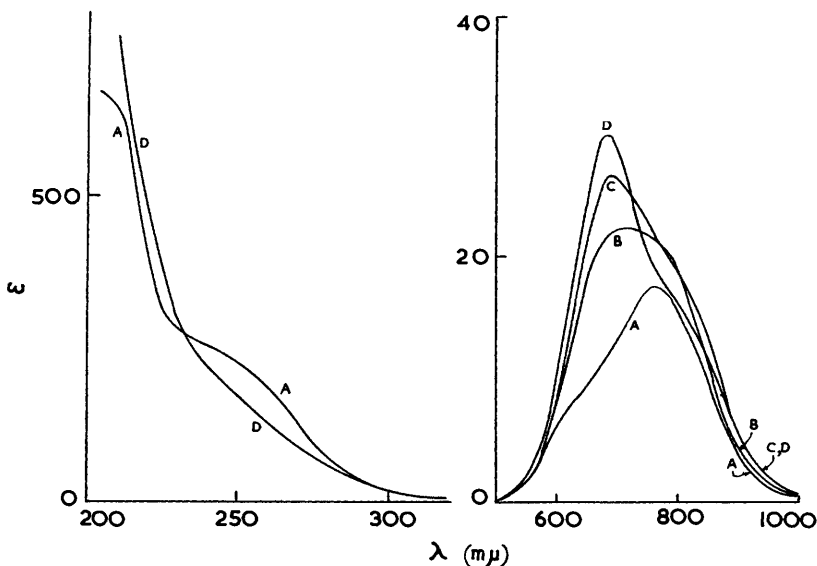


FIG. 2. Absorption spectra of vanadium(IV) in water (A) and in sulphuric acid solutions of the following strengths: 77.0% (B); 86.3% (C); and 95.0% (D). [Vanadium(IV)] = 0.040M.

The sequence of molecular-orbital energies for the  $\text{MoO}^{3+}$  species is similar to that for  $\text{VO}^{2+}$ .<sup>5</sup> In sulphuric acid solutions containing more than *ca.* 90%  $\text{H}_2\text{SO}_4$ , the effect on the spectrum of increasing the acid strength appears to be the same for molybdenum(V) as for vanadium(IV). However, it is not possible to compare molybdenum(V) with vanadium(IV) in sulphuric acids of strengths less than *ca.* 90%  $\text{H}_2\text{SO}_4$ , owing to the formation of polynuclear molybdenum(V) species at these lower acid-concentrations. If the spectrum of molybdenum(V) in sulphuric acid arises from transitions similar to those responsible for the spectrum of  $[\text{MoOCl}_5]^{2-}$ , then it seems that the band in the 600–700-m $\mu$  region and the band at *ca.* 390 m $\mu$  are due to the transitions  ${}^2B_2 \rightarrow {}^2E(I)$  and  ${}^2B_2 \rightarrow {}^2B_1$ , respectively. The extent of electron-donation in the  $\pi$ -component of the Mo-O bond is therefore greater when sulphuric acid molecules (or ligands derived from sulphuric acid) are attached to the molybdenum atom than when chloride ligands are attached. On increasing the sulphur trioxide content of the solvent, the  ${}^2B_2 \rightarrow {}^2E(I)$  band is shifted to shorter wavelength, but the  ${}^2B_2 \rightarrow {}^2B_1$  band is hardly affected. It thus appears that the conversion of ligands derived from sulphuric acid into ligands derived from disulphuric acid effects even greater electron donation in the  $\pi$ -component of the metal-oxygen bond.

#### EXPERIMENTAL

Concentrated aqueous solutions, of known strength, of titanium(III), chromium(III), cobalt(II), nickel(II), and vanadium(IV) were prepared, and either 1-ml. or 2-ml. portions were pipetted into (a) water and (b) sulphuric acid of various strengths; the resulting solution was then made up to 25 ml. with the appropriate solvent. The strength of the acid was determined by titrating a weighed

<sup>5</sup> H. B. Gray and C. R. Hare, *Inorg. Chem.*, 1962, **1**, 363.

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amount of the solution, suitably diluted, against standard alkali. The solutions of molybdenum(v) in sulphuric acid and in oleum were made from a stock solution of molybdenum(v) in dilute sulphuric acid, which was prepared as follows: molybdenum pentachloride (purified by distillation in a stream of nitrogen) was dissolved in dilute sulphuric acid and then strong ammonia solution was added to precipitate brown  $\text{MoO}(\text{OH})_3$ ; the precipitate was washed thoroughly with water and then dissolved in dilute sulphuric acid. The molybdenum(v) content of the solutions was determined by titration with standard ceric sulphate solution.

The spectra were measured on a Unicam S.P. 500 spectrophotometer.

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