

group of the acid and formation of 1 : 1 hydroxo complex in accordance with the equations 3 and 4.

The breaks at $m=2$ and $m=6$ in the 2 : 1 mixture of ligand and metal (curve 3') further confirms the above formation.

The present investigation clearly reveals the formation of 1 : 1 hydroxo complex above pH 7.0.

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Studies on 6-Heteropoly Vanadomolybdate

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A few heteropoly vanadates have been reported^{1,2} but with the exception of 12-vanadophosphate anion, none of them has been well characterised^{3,4}. The present short communication deals with the preparation, characterisation and X-ray crystal diffraction studies of a new 1 : 6 heteropoly complex of vanadium with molybdenum as the heteroatom.

Water solutions of molybdic acid and potassium metavanadate were taken in the molar ratio of 1 : 12 and refluxed for nearly 4 hr. The solution was left in atmosphere for a few hours and then crystallised under vacuum when small needle shaped red crystals came out which were recrystallised thrice from hot water. The complete analysis of the compound was done by chemical and colorimetric analysis, from which the percentage of potassium, vanadium and molybdenum were found to be 10.62, 27.88, 8.70 against the theoretical calculated values 10.70, 27.99, 8.78. The percentage of water together with oxygen was calculated by difference which came to 37.434. From these percentage composition data the ratio between Mo : V came to 1 : 6, which agreed with the formula $K_8 [MoV_6O_{19}] 11H_2O$. The representation of the formula was according to the views of Keggin⁵.

X-ray Crystallographic data and determination of molecular weight : A single crystal of the compound was mounted along its longer dimension : a axis. The oscillation photographs did not show mx, my and mm

symmetry. Zero level, first level and second level Weissenberg photographs were taken. The absence of Weissenberg photographs of OKO for $K \neq 2n$ and hol for $K \neq 2n$ identified the space group as P_{21}/C . The angle was determined by the method of 'level offsets'. The final values of cell dimensions are : $a = 9.42 \text{ \AA}$, $b = 15.38 \text{ \AA}$, $c = 10.12 \text{ \AA}$ and $\beta = 105^\circ$, hence the system is monoclinic. The volume 'V' per unit cell was calculated to be 1416.18 \AA^3 . The number of molecules per unit cell 'Z' was fixed to be 2. The observed density measured by flotation method $\rho_{obs} = 2.53 \text{ gml}^{-1}$. From the relation $\rho_{obs} = \frac{1.66MZ}{V}$, the molecular weight 'M' of the compound came to 1081 against the theoretical value 1092.95, calculated from its stoichiometric formula. This definitely shows that the compound is monomeric.

Acknowledgement

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Determination of Oxidizing Powers of Tinperoxychromate and its Water Decomposition Product

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RIESENFIELD and Coworkers¹ have shown the existence of two classes of peroxychromate, blue and red, derived respectively from $HCrO_5$ and H_3CrO_5 . Raynold and Reedy², Klemm and Werth³, Beltron Martinez and Rea⁴ have prepared the perchromate of calcium, potassium and magnesium respectively.

Schwarz and Giese⁵, Prakash and Rai⁶ on the basis of their studies formulated chromium peroxychromate as CrO_4 and $Cr_2(Cr_2O_{10})_8$ respectively.

The present paper consists of the study of tinperoxychromate and its water decomposition product. It throws light on the constitution of tinperoxychromate and thus explains the formation of decomposition product.

Experimental

Tinperoxychromate was prepared by the action of ethyl acetate extracted H_2O_2 (anhydrous) on dry solid tin chromate.

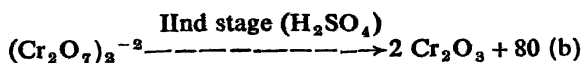
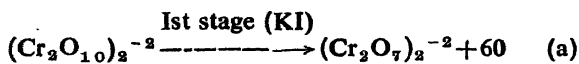
To determine the oxidizing powers of tinperoxychromate 5 ml. or 2 ml. of tinperoxychromate was titrated iodometrically in two stages against $N/100 Na_2S_2O_3$ solution.

The 1st stage includes iodometric titration of tinperoxychromate to a light yellow coloured end point. In the 2nd stage, the above light yellow coloured solution was titrated iodometrically in presence of $2 N H_2SO_4$ (10 ml.) to a characteristic light green coloured end point.

To determine the oxidizing powers of water decomposition product of tinperoxychromate iodometric titrations were done in two stages as above against the same hypo solution. The oxidized water decomposition product of tinperoxychromate (oxidation was done with $N NaOH$ 10 ml. plus 30% H_2O_2 5 ml.) was titrated only in one stage to a green end point in presence of $2 N H_2SO_4$.

Discussion

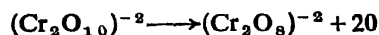
The experimental results reveal that tinperoxychromate and its water decomposition product contain $(Cr_2O_{10})^{-2}$ and $(Cr_2O_8)^{-2}$ ions respectively. Their iodometric titrations are two stage titration. The presence of these two ions and idea of two stages titration can be formulated on the basis of following equations :



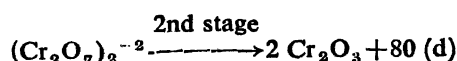
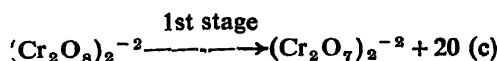
The ratio $a : b = 6 : 8$ or $0.75 : 1$ is in agreement with experimental values.

Thus tinperoxychromate contains $(Cr_2O_{10})^{-2}$ ions.

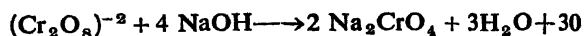
In water tinperoxychromate decomposes and forms $(Cr_2O_8)^{-2}$ ion according to the equation



The two stage titration of water decomposition product containing $(Cr_2O_8)^{-2}$ ion is represented as :



The oxidized water decomposition product contains $(Cr_2O_7)^{-2}$ ion which was formed according to the following equation



This oxidized product on titration evolves 12 atoms of oxygen.



The ratio $\frac{a+b}{c+d} : 14 : 10$ or $1.4 : 1.0$ and the ratio $\frac{c+d}{e} : 10 : 12$ or $0.83 : 1$ are in close resemblance with the experimental values given in the Table.

TABLE 1—OXIDIZING POWERS OF TINPEROXYCHROMATE AND ITS WATER DECOMPOSITION PRODUCTS

S. No.	Volume of tinperoxychromate	Volume of hypo used during titration in (ml.)		decomposition product			Ratios		
		1st stage	2nd stage	1st stage	2nd stage	decom. product after oxidation	a/b	$\frac{a+b}{c+d}$	$\frac{c+d}{e}$
		a	b	c	d	e			
1.	5ml.	6.3	8.4	6.5	3.9	13.6	0.75	1.41	0.75
2.	5ml.	6.3	8.2	7.0	3.6	14.9	0.76	1.36	0.71
3.	2ml.	3.6	4.8	4.0	3.0	9.2	0.75	1.40	0.76
4.	2ml.	5.0	7.0	4.8	3.8	12.1	0.72	1.39	0.71

Thus with these ratios it can be concluded that tinperoxychromate contains $(Cr_2O_{10})^{-2}$ ion in its constitution.

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Some Dyes as Visual Indicators for Titration of Organic Acids in Alcohol Medium

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TITRATION in alcohol is extensively used in varnish, oil and many other chemical industries for determination of acid value. Generally, phenolphthalein is used as the indicator; it is however far from satisfactory, the colour change being faint and unsharp much unlike that in water medium. Some indicators specially of sulphonaphthalein class have been recommended¹, though hardly ever used. Palit² was the earliest to introduce thymol blue (whose pK is rather unfavourable for normal aqueous titration) in non-aqueous titration; however, its sensitivity is strongly affected by the presence of small quantities of water. In this note we draw attention to the possibility of using some ordinary dyes as indicators which normally do not function as acid-base indicators in aqueous medium.

Experimental

During our studies of electrolysis of dyes in W-tubes in alcoholic solution to produce multiple boundaries³ we noted that quite a few dyes form contrasting colours between the cathodic solution (alkaline) and the anodic solution (acidic), though they do not normally behave as acid-base indicators in water. This is not at all surprising as red form of methylene blue is well-known⁴. Our results for titration of a number of weak organic acids using some such dyes, which are found satisfactory are briefly summarised in Table 1.

TABLE 1

Dyes and indicators	Colour change acid - alkali	Sharpness of colour change in absolute alcohol	
		N/10 acid	N/100 acid
Aniline blue	Red to blue	Extremely sharp	Good
Victoria blue	—do—	—do—	Good
Thionine blue	—do—	Very sharp	Fair
Methylene blue	—do—	Fair	Poor
Thymol blue	Yellow to blue	Extremely sharp	Good

A number of blue dyes whose basic form is red has been found to serve as excellent indicators. Aniline blue and victoria blue are strongly recommended for such titration. The change of colour is very sharp and occurs at the theoretical point. There is no 'blank' and neutral rectified spirit can also be used. For very precise results the titration should be done with exclusion of CO₂, as CO₂ tends to change the red form to blue. The commercial dyes can be used as such. For very precise work the dye should be used after conversion to the red form which can be obtained at the anode on electrolysis of the dye solution in a W-tube^{2,3} (the dye solution in alcohol being charged into the cathode chamber only, the rest being filled with alcohol). Commercial alcohol-soluble resins (such as resin, pale shellac, etc.) and oils, unless too dark, can be successfully titrated with precision.

Thymol blue is almost as good as the dyes mentioned above but tends to give slightly low results. Also, as mentioned earlier, its sensitivity decreases very much in presence of water and so is somewhat unsatisfactory in rectified spirit. Methylene blue is not quite as satisfactory as the aforementioned dyes; however its sensitivity increases if used in its 'red' form obtained either by electrolysis or by benzene extraction³.

It is hoped that these dyes should be used in routine industrial determination of acid value of commercial products.

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A Dye as a Catalyst for Decomposition of Hydrogen Peroxide

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THERE has lately been great revival of interest in the study of the rate of catalytic decomposition of H₂O₂ due to its evident relevance to enzyme action. In particular many metal-organic compounds have been