

## Studies on the Aqueous Solutions of Some Chromic Salts. II. Modified Green Chromic Sulphate, Ol Green Chromic Chloride and Green Chromic Sulphate.

By Hideo SUEDA.

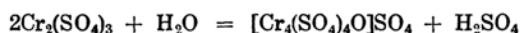
(Received October 12th, 1937.)

**I. Modified Green Chromic Sulphate.** When the aqueous solution of the violet chromic sulphate is boiled for two or three minutes, the colour of the solution changes to green and retains the colour even after it is cooled. The compound which is prepared from the violet sulphate in such a manner is generally called "modified green chromic sulphate". Many researches have already been reported on this compound. From the thermochemical point of view, A. Recoura<sup>(1)</sup> discovered the formation of sulphuric acid at the rate of one molecule per four chromium atoms in the solution, when the violet sulphate was transformed into this compound. Before Recoura, P. A. Favre and C. A. Valson<sup>(2)</sup> observed that one-third of the sulphate radical was precipitated by addition of barium chloride in the freshly prepared modified green sulphate solution. A. Recoura, having combined his results with this experiment, recognized that the following equation explains the reaction when the violet sulphate solution is heated. He gave therefore formula  $[\text{Cr}_4(\text{SO}_4)_4\text{O}]\text{SO}_4$  to the modi-

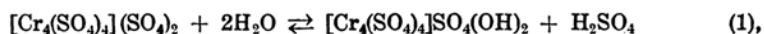
(1) *Bull. soc. chim.*, [3], **9** (1893), 586; [3], **15** (1896), 315; *Ann. chim. phys.*, [7], **4** (1895), 494.

(2) *Compt. rend.*, **74** (1872), 1023.

fied green chromic sulphate. W. R. Whitney<sup>(3)</sup> also supported this idea after his measurement of the electric conductivity of this salt.



After that, H. G. Denham<sup>(4)</sup> measured the pH-value of the solution in various dilutions, and the molecular weight of the salt was shown to be double or more that of the violet sulphate. Taking the experimental results proposed by T. W. Richards and F. Bonnet<sup>(5)</sup> as his idea, he assumed the formula  $[\text{Cr}_4(\text{SO}_4)_4](\text{SO}_4)_2$  for this salt, and the hydrolysis of this salt in the solution was expressed according to its concentration as follows:



where the reaction of equation (1) takes place in such a concentration as that experimented on by Recoura, while equation (2) is suitable for a very dilute solution. This consideration enabled him to explain his experiment, and his idea seems nowadays to have been generally adopted.

But, the complex ion  $[\text{Cr}_4(\text{SO}_4)_4]^{4+}$  is not easily deduced from Werner's co-ordination theory, and there are some questions on the number of chromium atoms in the complex radical. The salt  $[\text{Cr}_4(\text{SO}_4)_4](\text{SO}_4)_2$  which Denham assumed, should be obtained, according to his idea, when the infinitely concentrated violet sulphate solution is heated. But the compound, which is actually produced when the crystals of violet sulphate hydrate are heated, is difficultly soluble in water, contrary to the expectation from Denham's idea. Such circumstances tempted the author to study this compound.

(1) *Relation between the concentration of the modified green sulphate and the quantity of the sulphate ion precipitable by barium chloride.* According to Denham, the complex ion of the modified sulphate  $[\text{Cr}_4(\text{SO}_4)_4]^{4+}$  is not changed, whatever the concentration of the solution may be. If so, the total quantity of the sulphate radical should be three times the quantity of the sulphate ion to be precipitated by barium chloride in any concentration. As the experimental proof of it was wanting, the author has determined the quantity of barium sulphate produced on adding concentrated barium chloride to the solutions in three different

(3) *Z. physik. Chem.*, **20** (1896), 40.

(4) *Z. anorg. allgem. Chem.*, **57** (1908), 361.

(5) *Z. physik. Chem.*, **47** (1904), 29.

concentrations prepared by immediate cooling after boiling violet sulphate for three minutes, i.e. 0.06, 0.005 and 0.0006 mol/l. (molecular formula of violet sulphate being  $\text{Cr}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ ). The ratio of the precipitated sulphate ion to the total sulphate radical are shown in Table 1.

Table 1.

Conc. of the solution (mol/l.)	0.06	0.005	0.0006
Precipitated sulphate (%)	34.6	50.5	64.6

These results show that the percentage of sulphate ion depends on the concentration of the solution, and cannot be deduced from Denham's idea. In other words, the concentration of the solution controls the quantity of the sulphate radical in the complex ion of the modified green sulphate, and the quantity was between one-third and two-thirds of the total sulphate in the range of these concentrations.

(2) *The relation between the concentration of the solution and the quantity of sulphuric acid formed in the solution.* As described above, Recoura and Whitney showed that one molecule of sulphuric acid was liberated for four chromium atoms, when the violet sulphate was transformed into the modified sulphate. The concentrations of the solutions employed by them were moderately great, i.e. 1/12 and 1/30 mol/l., and the case of a smaller concentration has not yet been studied. The present author has examined such a case. Electrometric titration has been applied for this purpose, by using the antimony electrode<sup>(6)</sup>. A sodium hydroxide solution was added to 1/200 mol/l. violet and modified green sulphate solutions. The latter green sulphate solution was prepared from the former violet sulphate solution by the usual method. The titration curves are shown in Fig. 1. The curve of violet sulphate (I) smoothly rises, while that of modified green sulphate (II) begins at a lower *pH*-value than curve I, the increase of *pH* is not considerable till the molecular ratio of sodium hydroxide and chromic sulphate becomes equal, and it becomes noticeable after the point of equilibrium is passed. This result shows that one sulphuric acid molecule is liberated for four chromium atoms, even when a modified sulphate is formed in such a dilute solution. As described in (1), the relative quantity of sulphate ion increases when the

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(6) T. Uemura and H. Sueda, this Bulletin, **8** (1933), 1.

concentration of the solution changes from 6/100 to 1/200 mol/l., but the relative quantity of the liberated sulphuric acid is independent of the concentration of the solution.

(3) *Absorption spectra.* The absorption spectra, given by the following six solutions, were measured with the concentration of 1/100 N: (a) solution immediately cooled after heating, (b) solution prepared to pH 1.0 by adding sulphuric acid, (c) solution standing for 24 hours, (d)

solution standing for several days, (e) solution in which the liberated sulphuric acid was neutralised with sodium hydroxide, and (f) solution in which the sulphate ion was removed by filtering off barium sulphate after the addition of the equivalent amount of barium chloride. These solutions show similar curves which can be represented by one curve (I in Fig. 2). Curve I compares with that given by  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]\text{Cl}_2$ , but

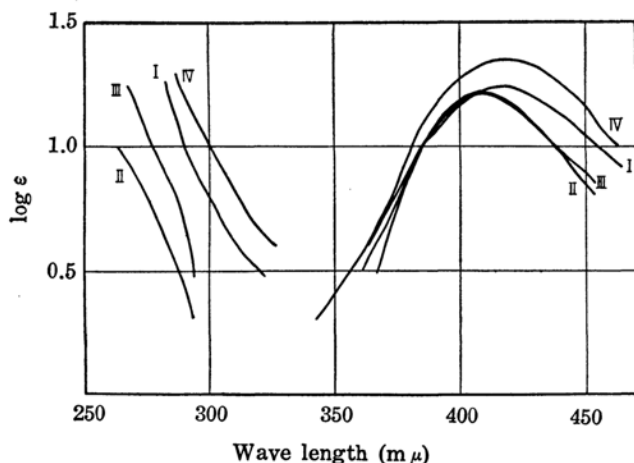
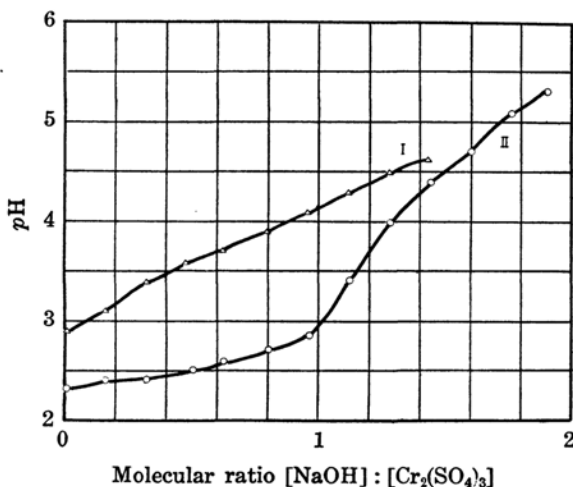


Fig. 2.



I: Violet chromic sulphate.  
II: Modified green chromic sulphate.

Fig. 1.

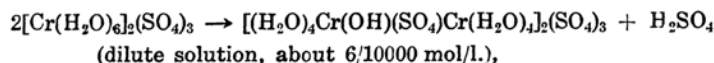
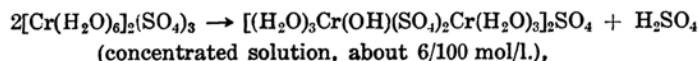
the absorption capacity of the former is higher than that of the latter in shorter wave length. The absorption of the modified sulphate solution does not show any change by the addition of acid, while the colour of the hydroxopentaquo chromic chloride solution becomes bluish violet. The properties of these two salts were

essentially different at this point, and the author cannot accept the idea of H. T. S. Britton<sup>(7)</sup>.

As an addition of acid to the modified green chromic sulphate solution does not influence the absorption, the compound must be ol-salt. The removal of sulphate ion or the neutralisation of the liberated acid does not show any effect nor does it change the curves, so they are independent of the complex ion.

(4) *Constitution of the modified green chromic sulphate.* Denham considered that the modified sulphate should contain four chromium atoms in its complex radical. This consideration came from his confirmation that the molecular weight of its cation could be double that of violet sulphate which was assumed as  $[\text{Cr}_2-]^{6+}$ . As the author, however, indicated in the previous paper that the cation of violet sulphate should be  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , the cation of modified sulphate must be considered to contain two chromium atoms, since it has about double the molecular weight of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ .

It has been shown that in (1) one-third of the sulphate radical of modified sulphate can be found as ion in the solution of 6/100 mol/l., but when the concentration decreases to 6/10000 mol/l., the quantity of the sulphate ion becomes two-thirds of whole sulphate radical, while in (2) ratio of the liberated sulphuric acid to the chromium atom does not show any relation with its concentration, that is, one sulphuric acid molecule is produced for four chromium atoms, and in (3) the modified green sulphate must be ol-compound. After all, the author considers the following schema for the formation of the modified green sulphate:



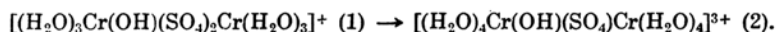
and when the concentration of the solution is intermediate between the above-mentioned, a mixture of both salts can be obtained. The reason for giving the  $\mu$ -sulphato form to the modified green sulphate will be explained later. The number of water molecules in the complex radical has been selected in order to comply with the demand of Werner's co-ordination theory.

(5) *Relation between the time of standing of the modified green chromic sulphate and the quantity of the sulphate radical precipitated by*

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(7) *J. Chem. Soc.*, **127** (1925), 2120.

*barium chloride*. As mentioned above, 50.5% of the sulphate radical was precipitated by barium chloride in the fresh modified sulphate solution, but after standing for 24 and 130 hours, 53.6 and 59.1% of sulphate could be respectively precipitated. This shows that the sulphate radical in the complex radical decreases proportionally to the time of standing of the solution. This can be expressed as follows:



From the quantity of the sulphate ion in the fresh solution, the ratio of the quantity of compound (1) to that of (2) should be 1:1.07, while it becomes 1:3.44 after standing for 130 hours. In spite of such a change, the absorption spectra do not differ. This result cannot be explained unless the absorption spectra of these two compounds are quite similar.

**II. Ol Green Chromic Chloride.** As described in the previous section, when the colour of the violet chromic sulphate solution is once changed to green by heating, the latter colour does not easily change even at a low temperature. But, the violet chromic chloride solution returns to bluish violet, in proportion to the depression of the temperature, though it is green in the hot state producing  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]\text{Cl}_2$  according to Bjerrum<sup>(8)</sup>. It is very interesting to note that sulphate and chloride behave differently in spite of the same cation<sup>(9)</sup>. The author already published a paper<sup>(10)</sup> of an analogous example, i.e. diaquo-tetramine-cobaltic sulphate changes to ol-compound by the addition of an alkali, while the corresponding chloride has not a similar reaction.

Although the violet chromic chloride solution changes reversibly by heating and cooling, the hydroxo-pentaquo-chromic chloride solution given by adding equivalent sodium hydroxide to violet chloride solution does not return to the original hydroxo-compound when it is cooled after heating, but is transformed into another salt which is called, in this paper "ol green chromic chloride".

(1) *Absorption spectra.* Absorption spectra of the four following solutions were observed: (a) solution prepared by cooling immediately

(8) *Z. physik. Chem.*, **59** (1907), 339.

(9) Violet nitrate solution behaves similarly to chloride: it returns to bluish violet after cooling. According to H. Brinzinger and F. Jahn, *Z. anorg. allgem. Chem.*, **229** (1936), 410,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  and  $[\text{Cr}(\text{en})_3]^{3+}$  are transformed into "zweischalige" complex salts  $[[\text{Cr}(\text{NH}_3)_6](\text{SO}_4)_4]^{5-}$  and  $[[\text{Cr}(\text{en})_3](\text{SO}_4)_4]^{5-}$  by ammonium sulphate, but ammonium nitrate cannot transform them into the salts of this kind.

(10) This Bulletin, **10** (1935), 50.

after boiling 1/100 mol/l. violet chloride  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  solution for two or three minutes (curve II in Fig. 2), and (b) solution obtained by treating 1/100 mol/l. green chloride  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$  similarly as above (curve III). As these two curves are similar to that of violet chloride, it can be said that this violet chloride at least predominated in the solutions then obtained. Their  $\text{pH}$ -values do not change before and after heating. (c) 1/100 mol/l. violet chloride solution was prepared by using 1/100 N sodium hydroxide as solvent (precipitation then occurred but was dissolved by heating the solution), and it was heated to boiling and then cooled immediately. (d) Solution obtained by adding concentrated hydrochloric acid to solution (c) to  $\text{pH}$  1.1.

As solutions (c) and (d) show similar absorption spectra, they can be represented by one curve (curve IV in Fig. 2) which is different from that given by hydroxo-pentaquo salt. As solution (c) showed no different absorption on the addition of acid, an ol-compound must be assumed to be produced when the solution of  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]\text{Cl}_2$  was heated.

(2) *Potentiometric titration.* To confirm that the "ol green chromic chloride" is actually an ol-compound, and to determine the number of OH in the complex radical in case of ol-compound, potentiometric titration was applied after heating and immediately cooling the solutions, where violet chloride and sodium hydroxide was mixed in various proportions.

When the violet chloride was dissolved to 1/100 mol/l. in 0.0053 N sodium hydroxide, the resulting solution showed  $\text{pH}$  4.1, but  $\text{pH}$  2.2 after heat treatment<sup>(11)</sup>.

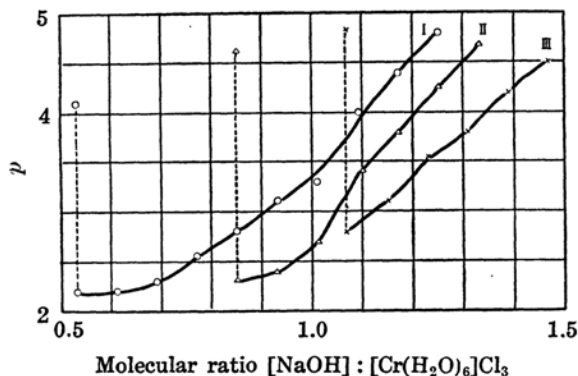


Fig. 3.

The solution was then titrated with sodium hydroxide, the titration curve being indicated in Fig. 3 (curve I). The solutions, where the molar ratios of violet chloride to sodium hydroxide were respectively 1.00 to 0.85 and 1.00 to 1.07, showed  $\text{pH}$  4.6 and 4.8 before heating. The  $\text{pH}$ -values, however,

(11) This was done as in the case of preparing the modified sulphate from the violet sulphate.

changed to 2.3 and 2.8 respectively after heat treatment. The titration curves are shown in Fig. 3 (curve II and III respectively). This decrease of pH-value of the solution of violet chloride with sodium hydroxide after heat treatment must be due to the formation of ol-compound. The change in inclination of the titration curve suggested that the number of OH contained in the complex radical is equal to that of the chromium atoms in the radical.

(3) *Constitution of the ol green chromic chloride.* Bjerrum's "latent basic salt"<sup>(12)</sup> perhaps corresponds to ol green chromic chloride discussed in this paper. But as the preparation method is somewhat different from Bjerrum's, it is probably vain to compare these two compounds<sup>(13)</sup>.

In (1) and (2), it has been proved that "ol green chromic chloride" is an ol-compound, and the number of OH and that of the chromium atoms in the complex radical are equal. In order to examine the existence of the chlorine atom in the radical, an excess of silver nitrate was added to cold solution of this salt, and the quantity of immediately precipitated silver chloride was measured. As all chlorine atoms was then precipitated, they cannot be contained in the complex radical. Summarising the facts observed, the author considers the following equation for the formation of this salt and gives it the formula shown below:



The author has not yet obtained any confirmation that this salt contains two chromium atoms in its complex radical. But such has been deduced from the two following points: (i) Pfeiffer<sup>(14)</sup> already proved the formation of  $[(en)_2\text{Cr}(\text{OH})_2\text{Cr}(en)_2]\text{X}_4$  on heating  $[\text{Cr}(en)_2\text{H}_2\text{OOH}]\text{X}_2$ , and (ii) the salt produced by heating the violet sulphate is di-chromium salt and the absorption spectra of the di-chromium salt is somewhat similar to that of this salt. According to Werner's co-ordination theory, eight molecules of water must exist in the complex radical in this case. Instead of ol-compound, the salt in question can be assumed to be oxo-compound which is closely related with ol-compound. But in general ol-compound is difficultly transformed into oxo-compound, except by heating or by standing for a long time. It may therefore be reasonable to take the ol-combination in this case.

(12) *Z. physik. Chem.*, **59** (1907), 336, 581; **73** (1910), 724; N. Bjerrum and C. Faurholt, *ibid.*, **130** (1927), 585.

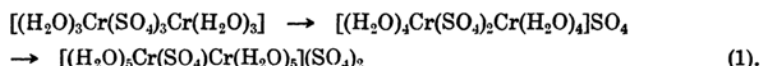
(13) Properties of the salt depend on the method of preparation, as Bjerrum has pointed out in his papers.

(14) *Z. anorg. allgem. Chem.*, **56** (1908), 261.

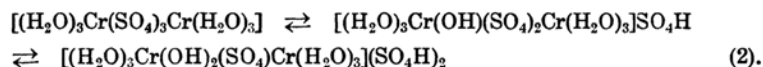


III. **Green Chromic Sulphate**  $[\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_3]$  and  $[\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_6]$ . When violet sulphate is heated in aqueous solution, a modified green chromic sulphate, i.e.  $\mu$ -ol-mono- or di-sulphato-dichromic sulphate is produced, but when it is heated in a crystalline state at  $90^\circ\text{C}$ ., it changes into the green chromic sulphate  $[\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_3]$ <sup>(15)</sup>. This green sulphate cannot be rapidly dissolved in water. It took about 100 minutes to dissolve 2 g. of this salt in 500 c.c. of water at  $25^\circ\text{C}$ . with constant stirring. The fresh solution so obtained shows an absorption analogous to that given by the solution of  $[\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_6]$ <sup>(15)</sup>, and neither solution gives immediately a precipitate of barium sulphate on the addition of barium chloride. These two salts, therefore, become the same substance in solution.

The quantity of the sulphate radical, that is precipitable by barium chloride, increases proportionally to the time of standing. In order to explain this fact, A. Colson<sup>(16)</sup> assumed three types of green chromic sulphate from his thermochemical studies: (a) all sulphate radicals, (b) two-thirds and (c) one-third, are masked in the complex radical:



On the other hand, he considered that  $[\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_6]$  is in equilibrium with the modified green chromic sulphate in aqueous solution:



The relation between these two schemata is not clear to the present author. After taking the absorption spectra, the author studied to know which of these schemata should be taken in this case, and, besides, examined some reactions of the solution with alkali and in heat treatment.

(1) *Relations found on leaving the aqueous solution of the green chromic sulphate to stand.* 1/112 mol/l. green chromic sulphate solutions was kept for 10 min., 245 min., 25.5 hours and 90 hours after the salt was completely dissolved, and their absorption spectra were observed. The absorption spectra of the first two solutions (10 min. and 245 min.) are similar to each other and are represented by one curve in Fig. 4 (curve I), and the other two solutions gave also analogous absorption curves, which

(15) A. S  n  chal, *Compt. rend.*, **159** (1914), 243.

(16) *Bull. soc. chim.*, [4], **1** (1907), 438, 889; **3** (1908), 90; *Ann. chim. phys.*, [8], **12** (1907), 433.

are represented by another curve (curve II in Fig. 4). The absorption spectra of the modified green chromic sulphate is given as curve III. If the schema (2) can express the reaction which occurs on leaving the

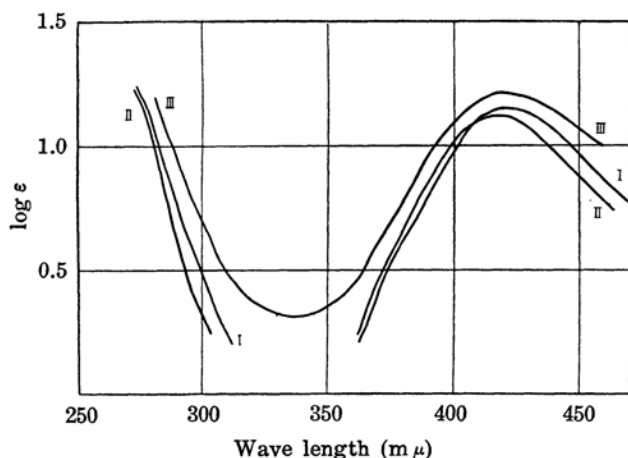


Fig. 4. The absorption spectra of green chromic sulphate.

aqueous solution of green chromic sulphate to stand, the production of the modified sulphate being recognised, curve II should come between curve I and III. However, curve II is found to be outside the other two in the ranges of wave lengths below 300  $m\mu$  and above 410  $m\mu$ . The pH-value does not change on standing, and remains at 2.5.

For these reasons, the author believes this reaction must be explained by schema (1) but not by (2).

After standing for 60 minutes and 75 hours, 1/200 mol/l. solutions of the salt precipitated respectively 14.9 and 54.6% of the sulphate radical on the addition of barium chloride. The precipitation of barium sulphate cannot be observed in the fresh solution, so the reaction  $[\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_6] \rightarrow [\text{Cr}_2(\text{SO}_4)_2(\text{H}_2\text{O})_8]\text{SO}_4$  is assumed to take place rapidly as compared with the reaction  $[\text{Cr}_2(\text{SO}_4)_2(\text{H}_2\text{O})_8]\text{SO}_4 \rightarrow [\text{Cr}_2(\text{SO}_4)(\text{H}_2\text{O})_{10}](\text{SO}_4)_2$ .  $[\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_6]$  and  $[\text{Cr}_2(\text{SO}_4)_2(\text{H}_2\text{O})_8]\text{SO}_4$  can be assumed to exist in different ratios in the solutions after standing for 10 min. and 245 min., but their absorptions are alike. This must be caused by the originally similar absorption of the two salts. In this case, as well as in the case of modified green chromic sulphate, it seems that the absorptions were not much influenced, whether the chromium combination in the radical be with two bridges or three.

(2) *Reaction with alkali.* Sodium hydroxide was added to the solutions of green chromic sulphate, which were left for 110 minutes and 90 hours respectively, in order to make the molecular ratio  $[\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_6] : [\text{NaOH}] = 1.00 : 1.26$ . The pH-values were the same and 4.2. Both solutions gave similar absorption curves represented by curve III in Fig. 4, and the curve is similar to that given by the modified

green chromic sulphate. From this result, it is evident that when the green sulphate solution is left for a time, the modified sulphate is obtained by the addition of sodium hydroxide. However, potentiometric titration is necessary to confirm it.

1/200 mol/l. green sulphate solutions were titrated with 8/100 N sodium hydroxide after standing for 3 hours and 75 hours respectively. The titration curves are shown in Fig. 5 (curve I and II). Next, sodium hydroxide was added to the solution, which was left for 75 hours, to make the molecular ratio  $[\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_6] : [\text{NaOH}] = 1.0 : 1.6$ . The solution then obtained was

titrated with hydrochloric acid, and the result is shown by curve III.

The time of standing has no relation with pH-value of the solution, when sodium hydroxide is not added ( $\text{pH}=2.5$ ). This shows that ol-compound or free acid is not produced by standing. Titration curves (I and II) do not so rapidly rise at the beginning of the process, and this is explained by assuming that a part of the green

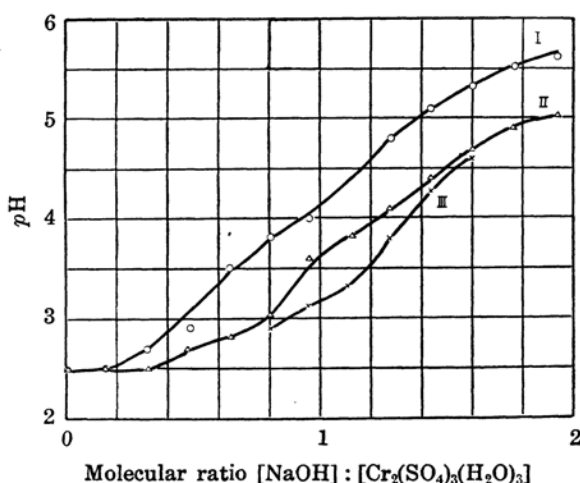


Fig. 5.

sulphate is converted into ol-compound when sodium hydroxide is added to the solution. This assumption is also confirmed by the disagreement of curves II and III. In conclusion, the green sulphate is transformed into the modified sulphate in aqueous solution by the addition of sodium hydroxide. This is the reason why the author assumed the sulphato-bridge in the formula of the modified sulphate. As shown in Fig. 5, the elevation of curve I begins earlier than that of curve II, and this means that  $[\text{Cr}_2\text{SO}_4(\text{H}_2\text{O})_{10}](\text{SO}_4)_2$  can more easily be converted into ol-compound than  $[\text{Cr}_2(\text{SO}_4)_2(\text{H}_2\text{O})_8]\text{SO}_4$  or  $[\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_6]$ .

(3) *Reaction in heat treatment.* The heat treatment<sup>(11)</sup> was performed with 1/200 mol/l. solutions, which had been left for 10 minutes and 75 hours respectively. The absorption curves given by these solutions thoroughly coincide with curve III in Fig. 4.

Titration curves of the solutions are shown in Fig. 6, where curves I and II respectively belong to the solutions left for 3 hours and 75 hours. These curves are analogous to that of modified green sulphate (Fig. 1).

The author next measured the quantity of sulphate radical which can be precipitated by barium chloride, and obtained the results summarised in Table 2. As for the solution left for one hour, the precipitated sulphate radical is smaller before the heat treatment, but it becomes larger after treatment, and for the solution left for 75

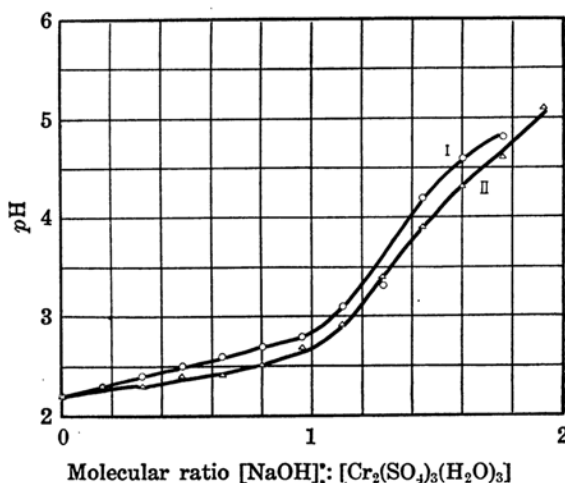


Fig. 6.

Table 2. Quantity of the precipitated sulphate radical (%).

Time after dissolution	1 hour	75 hours
Before heat treatment	14.9	54.6
After heat treatment	53.9	47.4

hours, this relation is quite contrary. The disagreement between the quantities of the precipitable sulphate radical obtained from these two solutions after heat treatment, comes perhaps from the difference of the heating intervals, and the values are approximately that obtained from the modified sulphate (50.5%). Hence, modified green chromic sulphate can always be obtained by heating the green chromic sulphate in aqueous solution.

### Summary.

(1) For the modified green chromic sulphate, the formula  $\mu$ -ol-mono- or di-sulphato-di-chromic sulphate has been deduced (i) from its absorption spectra, (ii) from the quantities of sulphuric acid produced

when this salt is formed from violet chromic sulphate, and (iii) from the sulphate ions which is precipitated by barium chloride in various dilutions.

(2) When hydroxo-pentaquo chromic chloride solution was heated, the author recognized the production of ol-compound, to which the formula di-ol-octaquo-di-chromic chloride has been given.

(3) The modification of the green chromic sulphate in aqueous solution, produced on standing, or on heating, or on adding sodium hydroxide, has been discussed.

In conclusion, the author wishes to express his sincere thanks to Assist. Prof. T. Uemura of the Tokyo University of Engineering for his kind encouragement.

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