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XXXVIII.—Researches on Chrom-organic Acids.

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WHEN oxalic acid is used to reduce potassium dichromate, two distinct compounds can be obtained according to the conditions under which the experiment is performed.

lst. If the oxalic acid is in large excess, and partly present as acid potassium salt, the beautiful "blue oxalate of chromium and potassium" is obtained, discovered by Dr. Gregory in 1837.

2nd. If the oxalic acid used for reduction be not in very great excess, and none of it as the potassium salt, a fine red salt will be formed which was discovered by Crofts in 1842.

The compounds thus obtained have been generally treated as "double salts," that is, as molecular compounds of chromium oxalate with oxalate of potassium, or any of the other metals which can be made to displace potassium in these compounds. Malaguti, however, took a different view of their nature, and pointed out (*Compt. rend.*, 16, 456) that "the oxide of chromium, and probably all the oxides of the same formula, can, in combining with certain organic acids, give rise to compounds which, far from being salts, are veritable acids." Malaguti's view seems to have attracted little attention, as it has been almost ignored by other chemists (with the exception of Clarke and Kebler) who have worked with these remarkable chromiumderivatives.

My examination of these substances has led me to the conclusion that they are salts of complex chromoxalic acids, and that other organic acids can be more or less completely substituted for oxalic acid in some of these compounds.

In the present paper, I propose to describe the results obtained with salts of chromoxalic acid, and primarily to show that the formula of Gregory's salt, $K_3Cr(C_2O_4)_{3,3}H_2O$, must be doubled.

PART I.

On certain Chromoxalates (Blue Series).

A quantity of Gregory's salt was prepared according to its discoverer's directions, and analysed with the results stated below. The method adopted for the analysis of this salt and of the different compounds described, was as follows: the substance was ignited in a platinum crucible with free access of air, the residue consisting of a

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mixture of potassic chromate and carbonate was dissolved in water, the acidified solution reduced by boiling with alcohol, and the chromium precipitated with ammonia; the potassium was estimated in the filtrate by evaporating to dryness, igniting, and weighing as sulphate. The oxalic radicle was estimated by boiling the aqueous solution of the salt with a slight excess of potash until completely decomposed, filtering from precipitated chromic hydrate, and determining the oxalic acid in the filtrate, after acidifying with sulphuric acid, by means of potassium permanganate.

	Theory.	Í.	
K ₆	24.02 per cent.	23.84	
$Cr_2 \dots \dots$	10.68 ,,	11.08	11.14
$(C_2O_4)_{6}$	54·20 "	53.84	53.99
$(H_2O)_6$	11.10 "	11.24 (by diff.)	
	100.00	100.00	

The formation of this salt is represented by the following equation :---

 $K_2 Cr_2 O_7 + 4KHC_2 O_4 + 5H_2 C_2 O_4 = K_6 Cr_2 (C_2 O_4)_6 + 6CO_2 + 7H_2 O;$ and its decomposition on ignition as—

 $K_6Cr_2(C_2O_4)_6 + 9O = 2K_2CrO_4 + K_2CO_3 + 11CO_2$

which requires a residue amounting to 54 per cent. of the crystallised salt; 1.424 gram ignited with free access of air left a residue weighing 0.7645 gram, equal to 53.69 per cent. of the original weight.

The proof that the doubled formula used above is the correct one is afforded by the formation of the well-defined compound $K_5(NH_4)Cr_2(C_2O_4)_{6,}6H_2O$, which is obtained by replacing one molecule of KHC_2O_4 by $(NH_4)HC_2O_4$ in the equation representing the formation of Gregory's salt. The ammonium in this compound was determined by distillation with soda solution, using an apparatus somewhat similar to that described by Holmes (*Chem. News*, **52**, 49)—

		Found.	
	Theory.	Í.	<u> </u>
K ₅	20.47 per cent.	21.14	21.17
NH_4	1·88 ,,	1.75	1.88
$Cr_2 \dots \dots$	10.92 "	11.40	10.91
$(C_2O_4)_6\ldots$	55·40 "	55.61	55.40
$(\mathrm{H_2O})_6$	11.33 "	11·10 (by diff.)	11.33
	100.00	100.00	

This compound crystallises in deep-blue rhombic prisms, indistinguishable in appearance from Gregory's compound, and possessing similar properties. 0.7663 gram ignited left a residue weighing 0.3728 gram = 48.70 per cent., consisting of chromate and carbonate of potassium. The decomposition is represented by the following equation :—

$$2K_{5}(NH_{4})Cr_{2}(C_{2}O_{4})_{6} + 9O_{2} = 4K_{2}CrO_{4} + K_{2}CO_{3} + 2NH_{3} + 23CO_{2} + H_{2}O,$$

which requires a residue amounting to 47.95 per cent. of the crystalline salt.

The decomposition of these salts on ignition is given as being characteristic, and furnishing at the same time corroborative evidence of the formula of the particular compound.

I may mention here a salt prepared by replacing the KHC_2O_4 by NaHC_2O_4 ; the resulting compound, which is exceedingly soluble in water, and crystallises very imperfectly, has the formula

$$K_2Na_4Cr_2(C_2O_4)_6,8H_2O_5$$

as deduced from the following analysis :---

			Found.	
	Theory.		í.	 II.
K ₂	8·24 pe	er cent.	8.09	
$Na_4\ldots\ldots$	9.72	,,	9.37	
$Cr_2 \ldots \ldots$	10.99	"	11.37	
$(C_2O_4)_6 \ldots$	55.84	,,	56.18	56.15
(H ₂ O) ₈	15.21	,,	14.91	
	100.00		$99 \cdot 92$	

When ignited under the same conditions as the other salts, this compound, unlike them, leaves a readily fusible residue: 0.6555 gram left residue weighing 0.3162 gram, equal to 48.23 per cent. The decomposition of the salt is represented by the equation—

$$\begin{aligned} K_2 Na_4 Cr_2 (C_2 O_4)_{6} & 8H_2 O + 9O = 2Na_2 CrO_4 + K_2 CO_3 + 11CO_2 \\ &+ 8H_2 O, \end{aligned}$$

which requires a residue amounting to 48.83 per cent.

The fact of chief importance connected with these salts is that their solutions are not precipitated by calcium chloride or ammonia; moreover, when they are treated with solutions of certain of the heavier metals, as lead, silver, barium, &c., they do not yield simple oxalates by double decomposition, but salts which contain the new metal in the place previously occupied by the alkali metal. These

facts suggest a more intimate union between the chromium and oxalic groups, than that which is usually supposed to exist in what are commonly accepted as double salts; in other words, it appears that in these compounds the group $Cr_2(C_2O_4)_6$ plays the part of an acid radicle, giving rise to a complex chrom-organic acid of which Gregory's blue compound is the normal potassium salt, viz., potassium chromoxalate; the acid itself being hexabasic. On this view, I propose to represent the constitution of the salt thus:—

$$\begin{array}{c} K \cdot O(C_2O_2) \cdot O \\ K \cdot O(C_2O_2) \cdot O \\ K \cdot O(C_2O_2) \cdot O \end{array} \\ Cr - Cr \underbrace{ \begin{array}{c} O \cdot (C_2O_2) O \cdot K \\ O \cdot (C_2O_2) O \cdot K \\ O \cdot (C_2O_2) O \cdot K \end{array} \\ O \cdot (C_2O_2) O \cdot K \end{array}$$

On referring to the literature of the subject, I found, as already stated, that a somewhat similar hypothesis had been advanced by Malaguti in 1843 in a letter to Dumas (*Compt. rend.*, 16, 456); the statement concerning the constitution of these compounds, which I have given in his own words at the commencement of this paper, is, however, disputed by Löwel (*Compt. rend.*, 16, 862). He considers them to be double and triple salts, as does Rees Reece (*Compt. rend.*, 21, 1116), who prepared a number of similar salts by double decomposition, besides analogous compounds containing iron and aluminium.

When we examine the salts containing other metals, it soon becomes evident that the alkali metals occupy a position in these compounds quite distinct from that of the chromium.

Hartley's (Proc. Roy. Soc., 21, 499) calcium compound,

$\mathrm{KCaCr}(\mathrm{C_2O_4})_3, 4\mathrm{H_2O},$

termed by him "potassio-calcic chromic oxalate," was prepared according to his directions. I experienced some difficulty at first in obtaining this compound free from calcic oxalate, but by filtering a hot concentrated solution into a vessel immersed in a freezing mixture, small, but well-defined, perfectly pure crystals were obtained. After drying by pressure, and for a short time over oil of vitriol, these gave on analysis results agreeing with those obtained by Hartley, but his formula must now be doubled :—

			~ <u> </u>
	Theory.	Ι.	II.
K ₂	8.36 per cent.	8.71	
Ca ₂	8·56 ,,	8.43	8.68
$Cr_2 \ldots \ldots$	11.14 "	11.42	—
$(C_2O_4)_6\ldots$	56·53 "	57.04	56.88
$(\mathrm{H}_{2}\mathrm{O})_{8}\ldots$	15.41 "	13 ·89	
·	100.00	99.49	

The water determination in the above analysis is low, from the fact that it is impossible to obtain this salt free from moisture without its parting with a small portion of water of crystallisation, which it loses very readily over oil of vitriol.

In an experiment, with a view to prepare a further quantity of this salt, *cold* moderately dilute solutions of calcium chloride and the blue potash salt were mixed (Hartley recommends warm dilute solutions); the liquid was allowed to stand for a few days in a large flask, and at the end of that time a quantity of crystals had deposited, in tufts of prismatic needles; these when dried were of a fine deep-blue colour, much larger than Hartley's salt, and entirely devoid of the beautiful greenish lustre so characteristic of the latter. On analysis, this compound gave results agreeing with the formula $K_2Ca_2Cr_2(C_2O_4)_{6,6}H_2O$, differing therefore from Hartley's salt by 2 mols. of water of crystal-lisation :—

			Found.	
	Theory.		í.	л. II.
K ₂	8.68 p	er cent.	9.14	_
Ca ₂	8.90	"	8.94	8.85
$Cr_2 \ldots \ldots$	11.58	,,	10.84	
$(C_2O_4)_6$	58.79	,,	58.68	58.79
$(H_2O)_6$	12.05	,,	11.75	
	100.00		99.35	

The mother-liquor from these crystals furnished a quantity of Hartley's salt. I have since made unsuccessful attempts to obtain a further quantity of this hexa-hydrated compound; its formation appears to be entirely dependent on the degree of concentration of the mixed solutions. These two calcium salts, differing from each other in their composition by only 2 mols. H_2O , possess very different physical properties, as seen from the following table :—

1. Formula— $K_2Ca_2Cr_2(C_2O_4)_6 \cdot 8H_2O.$	Minute crystalline needles possessing a beautiful greenish lustre.	Partially decomposed by hot water, with separa- tion of calcic oxalate.
2. Formula— $K_2Ca_2Cr_2(C_2O_4)_6 \cdot 6H_2O.$	Prismatic needles, black by reflected light, blue by transmitted light.	Not evidently decomposed by water.

These salts containing calcium in combination with the oxalic radicle to the extent of over half the weight of the entire compound, are soluble in water, yet the addition of a soluble oxalate immediately

precipitates the calcium; this behaviour furnishes, I think, a striking proof that these compounds are not double salts. An attempt to prepare a salt containing calcium only, by mixing an excess of calcium chloride with the blue salt, was unsuccessful, no definite compound separating from the concentrated solution. The corresponding barium salt, which is very characteristic, is readily obtained by precipitating the blue salt with an excess of barium chloride.

This compound crystallises in fine, long, silky needles, of a pale greenish colour, slightly dichroic; sparingly soluble in cold, readily soluble in hot water, a tolerably concentrated solution gelatinises on cooling. The composition of this salt is $Ba_3Cr_2(C_2O_4)_{63}SH_2O:$

		Found.	
	Theory.	í.	<u></u> п.
Ba ₃	34.62 per cent.	34.48	34.53
$Cr_2 \ldots \ldots$	8·70 ,	8.47	
$(C_2O_4)_6$	44.49 ,,	44.29	
$({\rm H}_{2}{\rm O})_{8}$	12·19 "	12.26	—
	100.00	99.50	

When ignited, this salt leaves a residue of barium chromate and carbonate, the decomposition being--

$$Ba_3Cr_2(C_2O_4)_6 + 9O = 2BaCrO_4 + BaCO_3 + 11CO_2.$$

Two tribaric salts, containing respectively 12 and 18 mols. of water of crystallisation, are described by Rees Reece (*Compt. rend.*, **21**, 1116), while Clarke (*Ber.*, **14**, 36) describes one containing 7 mols. H_2O , the existence of which is doubtful, as it seems a peculiar property of all these salts to crystallise with an even number of water molecules.

By treating the barium salt with dilute sulphuric acid, the barium is precipitated, and a liquid is obtained possessing a deep greenishred colour, strongly dichroic, not precipitated by excess of ammonia, nor by calcium chloride; treated with potash (not in excess) it yields the original blue salt on evaporation. This liquid in all probability contains the acid $H_6Cr_2(C_2O_4)_6$ in solution, which, however, I have not yet succeeded in isolating, as the liquid decomposes on evaporation even in a vacuum, with separation of oxalic acid. A similar solution is obtained by acting on oxalic acid with a solution of chromic acid in proportions represented by the equation—

 $H_2Cr_2O_7 + 9H_2C_2O_4 = H_6Cr_2(C_2O_4)_6 + 7H_2O + 6CO_2.$

On attempting to throw the compound down by the addition of strong alcohol to the aqueous solution, it was found that it mixed readily with the latter, the compound being therefore soluble in alcohol. A

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quantity of the barium salt in fine powder was suspended in absolute alcohol, and decomposed by the calculated quantity of sulphuric acid; the complete decomposition of the barium salt in presence of the strong alcohol takes several hours, being very slow even at the boiling point of the alcohol. The mixture was allowed to stand several days, and the resulting deep greenish-red alcoholic solution filtered from the barium sulphate. On concentration, the solution refused to crystallise, but when evaporated to dryness, it left a bright green amorphous residue, exceedingly deliquescent, and possessing a peculiar ethereal odour. When ignited, this compound leaves a residue of chromic oxide, amounting to 17.48 per cent. of the original weight; for want of material it has not yet been investigated or analysed, suffice it to say here that it is not the acid $H_6Cr_2(C_2O_4)_6$, but appears to be an ethereal compound, as when treated with water it is decomposed with separation of a heavy oily liquid (ethylic oxalate?). I hope later on to fully investigate this peculiar compound, and give the results in a future communication. I have also obtained other salts of the blue series by the addition of certain oxalates to the red series; these include compounds containing various organic bases, as aniline, carbamide, &c., &c., and will be described in a future paper.

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