XLIV.—*Oxidation of Oxalic Acid by Potassium Dichromate.*

By EMIL A. WERNER, F.I.C., Assistant in the Chemical Laboratory,
Trinity College, University of Dublin.

IN a preliminary notice on the above subject (Abstr., December, 1887), I pointed out that the oxidation of oxalic acid by potassium dichromate was limited by the formation of a chromoxalate, even in presence of sulphuric acid, provided the latter was not present in a concentrated form.

In the present paper, I propose to give the results of a study of the oxidation of oxalic acid by potassium dichromate, *per se*, and in varying molecular proportions. A paper on the same subject has been quite recently communicated to the Society by Mr. C. H. Bothamley (this vol., p. 159), but as the writer has overlooked the formation of a chromoxalate in the interactions, I believe that he has been misled in the interpretation of his results.

In short, for a complete and successful solution of the problems presented in the interactions of oxalic acid and potassium dichromate, a previous knowledge of the properties of the chromoxalates is absolutely necessary, more particularly of Croft's red potassium compound, whose precise composition and relations I have recently studied (this vol., p. 404).

Whether in the solid state, or in aqueous solution, 7 mols. of oxalic acid are required for the complete reduction of 1 mol. of potassium dichromate, the *sole* products of the interaction being Croft's salt, carbonic anhydride, and water, thus :—

The experimental data proving the correctness of this equation are given under Experiment I, further on.

Bearing in mind this equation, it seemed highly probable that all cases of the interaction of potassium dichromate and oxalic acid, between 1 and 7 mols., might be represented by one general equation, and the outcome of the present investigation has been to give complete corroboration to this view, and to prove that when dichromate on the one hand, or oxalic acid on the other, is used in excess beyond the proportions required by the foregoing equation, that excess is found in the residue on completion of the reaction.

The general method adopted in the experiments was the following:—An intimate mixture of the two substances, both in fine powder, was slowly heated in a dry, weighed, conical flask to the temperature of interaction, after which the flask with its contents was heated in an air oven at 110—120°, until the weight was constant, and the loss determined. This does not represent, as Mr. Bothamley assumed, “the *complete* dehydration of the oxalic acid and its partial oxidation by the dichromate,” but its partial oxidation together with its *partial* dehydration, for the red potassium chromoxalate formed (*not chromic oxalate*) retains, as I have shown (Trans., 1888, 404), 2 mols. H_2O , at the temperature and under the conditions of the interaction. The residue was dissolved in water, diluted to a definite volume, and the chromium and oxalic acid determined in aliquot portions. The estimations of the carbonic anhydride by absorption in ammoniacal calcic chloride solution were made in separate experiments carried out in presence of water; the spontaneous nature of the reaction, accompanied as it is by considerable development of heat when the substances interact in the solid state, rendering the correct estimation of the carbonic anhydride by any absorption method very difficult.

The potassium dichromate and oxalic acid used in these experiments were both purified by recrystallisation, the latter carefully air-dried, whilst the former was heated to 150—160°, and allowed to cool in a desiccator.

A. Potassium Dichromate (1 mol.), Hydrated Oxalic Acid (7 mols.)

In this case the dichromate is completely reduced, and the interaction takes place according to the equation already given.

$$\text{Expt. I.—} 5.1895 \text{ grams } \begin{cases} = 1.2973 \text{ gram } \text{K}_2\text{Cr}_2\text{O}_7 \\ = 3.8922 \text{ „ } \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}. \end{cases}$$

Temperature of interaction, 28—30°.

At 110—120°—

Loss 2.6445 grams = 50.95 per cent. of total weight.

Theory .. 2.6741 „ = 51.53 „ „

$\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$ (unoxidised as chromoxalate in residue)—

			Acid taken.	Acid unoxidised.
Found..	2.2570 grams.	Ratio..	100	: 57.98 or 7 : 4.05.
Theory..	2.2241 „	Ratio..	100	: 57.14 or 7 : 4.

The residue when dissolved in water yields a rich purple-red solution, perfectly free from any unaltered dichromate.

A series of experiments had previously shown that water, in whatever proportion it may be present, is entirely without influence on the nature of the interaction.

B. Potassium Dichromate and Hydrated Oxalic Acid, equal Molecules.

In this case, as the experimental results show, only one-seventh of the dichromate is reduced, six-sevenths remaining unaltered.

Expt. II.—5.5965 grams $\left\{ \begin{array}{l} = 1.6789 \text{ gram } \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}. \\ = 3.9176 \text{ grams } \text{K}_2\text{Cr}_2\text{O}_7. \end{array} \right.$

Temperature of interaction, 30—32°.

At 110—120°—

Loss 1.184 gram = 21.15 per cent. of total weight.
Theory 1.153 „ = 20.61 „ „

Cr_2O_3 formed—

			$\text{K}_2\text{Cr}_2\text{O}_7$ taken.	$\text{K}_2\text{Cr}_2\text{O}_7$ reduced.
Found..	0.297 gram = 0.5744	$\text{K}_2\text{Cr}_2\text{O}_7$	100	: 14.66 or 7 : 1.02.
Theory.	0.289 „ = 0.559	„	100	: 14.26 or 7 : 1.

$\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$ (unoxidised, as chromoxalate)—

			Acid taken.	Acid unoxidised.
Found..	0.9610 gram.	Ratio..	100	: 57.23 or 7 : 4.006.
Theory.	0.9593 „	Ratio..	100	: 57.14 or 7 : 4.

Expt. III.—In presence of water, $\left\{ \begin{array}{l} = 1.78 \text{ gram } \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}. \\ 5.9335 \text{ grams } \dots \left\{ = 4.1535 \text{ „ } \text{K}_2\text{Cr}_2\text{O}_7. \end{array} \right.$

CO_2 evolved—

Found .. 0.553 gram = 0.7917 gram $\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$.
Theory.. 0.5327 „ = 0.7628 „ „

Cr_2O_3 formed—

			$\text{K}_2\text{Cr}_2\text{O}_7$ taken.	$\text{K}_2\text{Cr}_2\text{O}_7$ reduced.
Found ..	0.3110 gram	}	7	: 1.
Theory..	0.3067 „			

$\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$ (unoxidised)—

Found 1.032 gram.

Theory 1.0171 „

C. *Potassium Dichromate* (1 mol.), *Hydrated Oxalic Acid* (2 mols.).

In this case, $\frac{2}{7}$ of the dichromate are reduced, $\frac{5}{7}$ remaining unaltered.

Expt. IV.—5.3805 grams $\left\{ \begin{array}{l} = 2.4833 \text{ grams } \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}. \\ = 2.8972 \text{ „ } \text{K}_2\text{Cr}_2\text{O}_7. \end{array} \right.$

Temperature of interaction, 51—52°.

At 110—120°— Loss... 1.726 gram = 32.07 per cent.

Theory.. 1.706 „ = 31.71 „

Cr_2O_3 formed— Found .. 0.432 gram.

Theory.. 0.429 „

$\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$ (unoxidised)—

Found 1.421 gram. Theory.... 1.419 gram.

Expt. V.—5.66 grams in presence of water.

CO_2 evolved—

Found .. 0.7933 gram = 1.1358 gram $\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$.

Theory.. 0.7819 „ = 1.1195 „ „

D. *Potassium Dichromate* (1 mol.), *Hydrated Oxalic Acid* (9 mols.), corresponding to $\text{K}_2\text{Cr}_2\text{O}_7 + 7 + 2$ mols. $\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$.

In this case, the interaction takes place as in A, the excess of oxalic acid over the 7 mols. remaining unaltered.*

Expt. VI.—5.64 grams in pre- $\left\{ \begin{array}{l} = 4.479 \text{ grams } \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}. \\ \text{sence of water .. } = 1.161 \text{ „ } \text{K}_2\text{Cr}_2\text{O}_7. \end{array} \right.$

CO_2 evolved— Found .. 1.110 gram.

Theory.. 1.042 „

Cr_2O_3 formed— Found .. 0.621 gram.

Theory.. 0.600 „

$\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$ (unoxidised)—

		Acid taken.	:	Acid unoxidised.
Found	3.003 grams }	9	:	6.03
Theory....	2.986 „ }	9	:	6.00

* In this particular case, the excess of oxalic acid combines with the red chrom-oxalate, forming the feeble compound $\text{K}_2\text{H}_4\text{Cr}_2(\text{C}_2\text{O}_4)_6$ of the blue series, which, however, is decomposed by much water.

Solutions prepared directly from potassium dichromate and red potassium chromoxalate in the proper proportions, were found in each case to be identical in every respect with the solutions of the products of the respective interactions.

With anhydrous oxalic acid, the interactions are the same as with the hydrated acid, with the exception that *anhydrous* chromoxalate is formed as the following experiments show.

Expt. VII.—Potassium Dichromate and Anhydrous Oxalic Acid equal mols. 4·9645 grams. Temperature of interaction, 40—42°.

Loss. . . . 0·7675 gram = 15·45 per cent.

Theory for hydrated chromoxalate = 13·16 „

„ anhydrous „ = 14·50 „

Expt. VIII.—Potassium Dichromate (1 mol.) Anhydrous Oxalic Acid (2 mols.). 5·28 grams. Temperature of interaction, 54—56°.

Loss. . . . 1·291 gram = 24·45 per cent.

Theory for hydrated chromoxalate = 21·33 „

„ anhydrous „ = 23·50 „

The rather high result obtained in each case is due to a loss of a small quantity of the oxalic acid by sublimation. The residue from the interaction presents the appearance of a light, bulky, porous, pale-brown mass, which develops heat when moistened with water.

From a study of the interaction of *equal* weights of potassium dichromate and hydrated oxalic acid, Mr. Bothamley deduced the following equation, as representing the change which takes place at 110—120°, viz. :—

As I have already mentioned, chromic oxalate is not formed in any of these decompositions, and neutral potassium chromate is never present as a product of the interaction of potassium dichromate and oxalic acid below 200° under any conditions.

The equation adopted by Mr. Bothamley agrees only approximately with his experimental results, and, moreover, it does not represent the molecular ratios with which he worked.

Equal weights of potassium dichromate and hydrated oxalic acid, correspond exactly with the molecular ratios :—

therefore 2 mols. of dichromate will be left unchanged, according to the equation—

and this is proved by the following experiments.

E. Potassium Dichromate and Hydrated Oxalic Acid, equal weights.

Expt. IX.—5·73 grams (= 2·865 grams $\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$). Temperature of interaction, 32—35°.

Loss 1·9395 grams = 33·84 per cent.

Theory 1·9684 „ = 34·29 „

Cr_2O_3 formed—

Found .. 0·503 gram. Theory .. 0·4937 gram.

$\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$ (unoxidised)—

Found .. 1·662 gram. Theory .. 1·637 gram.

Expt. X.—Same as above, in presence of water. 5·875 grams.

CO_2 evolved—

Found.. 0·9022 gram. Theory.. 0·8792 gram.

Mr. Bothamley's own results agree fairly well with the above equation: thus he obtained in two experiments the numbers 100 : 54 and 100 : 53 for the ratios of oxalic acid, taken to oxalic acid unoxidised, from which he concluded that half of the acid was oxidised, but the true ratio is 100 : 57 or simply 7 : 4. The absence of neutral potassium chromate in the products from any one of the preceding interactions is readily proved by the absence of any *immediate* precipitate on the addition of barium chloride or nitrate solutions to the product.

Mr. Bothamley states (referring to the solution of the product from the interaction of the dichromate and oxalic acid, in equal weights) that when mixed with ammonia, a brown precipitate of chromium chromate is formed; in my experiments, ammonia did not produce a trace of precipitate, but simply a change in colour, due to its action on the red potassium chromoxalate present.

The interactions of potassium dichromate and oxalic acid at a low red heat vary considerably with the proportions of dichromate and red chromoxalate forming the mixture, and though the decompositions are very simple, yet they require rather complex equations for their representation. The fact is, that the changes which occur under this condition are the result of the ordinary decomposition of the potassium chromoxalate complicated by the exceptional oxidising action of the dichromate on the oxalic radicle of the latter.

In the second part of my paper on the chromoxalates (Trans., 1888,

404), I have shown that the red potassium salt* decomposes at a red heat in accordance with the equation—

In the present cases, the oxygen necessary for the decomposition is wholly derived from the dichromate (which is reduced correspondingly) when the latter is in excess, whilst if the chromoxalate is in excess, the whole of the dichromate is reduced (to Cr_2O_3 and K_2CrO_4), the remainder of the oxygen being derived from the air. As this interaction is of secondary interest as compared with the more important primary change, I merely give the following two cases as examples:—

F. *Product from Interaction of $\text{K}_2\text{Cr}_2\text{O}_7$ and Hydrated Oxalic Acid, equal mols.*

$$\text{Ratio} = \frac{1\text{K}_2\text{H}_2\text{Cr}_2(\text{C}_2\text{O}_4)_4(\text{OH})_2}{6\text{K}_2\text{Cr}_2\text{O}_7}. \quad (\text{See Expt. II, B}).$$

Equation :

Expt. XI.—0.944 gram. Heated to a low red heat. Decomposition without violence.

Residue—	Found ..	0.7900 gram = 83.68 per cent.
	Theory..	0.787 „ = 83.37 „

Cr_2O_3 formed—	Found ..	0.1485 gram.	Theory ..	0.1434 gram.
---------------------------------	----------	--------------	-----------	--------------

G. *Product from Interaction of $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, equal weights.*

$$\text{Ratio} = \frac{1\text{K}_2\text{H}_2\text{Cr}_2(\text{C}_2\text{O}_4)_4(\text{OH})_2}{2\text{K}_2\text{Cr}_2\text{O}_7}. \quad (\text{See Expt. IX, E}).$$

Equation :

Expt. XII.—0.6175 gram. Heated to low red heat. Decomposition violent.

Residue—	Found ..	0.4300 gram = 69.63 per cent.
	Theory..	0.4318 „ = 69.94 „

* Omitting the water of crystallisation.

Cr_2O_3 formed—

Found .. 0.1155 gram. Theory .. 0.1215 gram.

Comparative experiments, made with an intimate mixture prepared directly from finely-powdered dichromate and red potassium chromoxalate in the proper proportions, led to the same results.

It is noteworthy that the mixed solution of potassium dichromate and red chromoxalate which results from the preceding interactions, or a directly prepared solution of the two salts, though exhibiting in every respect the properties of its constituents, refuses to crystallise under the most favourable conditions. The absorption spectrum of the mixed solution was found from a preliminary examination to be the sum of the absorption-spectra of the solutions of the separate constituents. The two compounds appear to exist in a feeble state of molecular combination just sufficient to prevent either one or the other from crystallising out. I hope to examine the solution further, later on.

The results of the present investigation may be summed up in the following conclusions:—

1. The red potassium chromoxalate, $\text{K}_2\text{H}_2\text{Cr}_2(\text{C}_2\text{O}_4)_4(\text{OH})_2$ (Croft's salt), is in all cases, *without exception*, a product of the interaction of potassium dichromate and hydrated oxalic acid, below 200° .
2. Neutral potassium chromate is *never* present as a product of the interaction of potassium dichromate and oxalic acid under any conditions below 200° .
3. When the two substances interact in the solid state, the initial temperature of the interaction, which lies between 30° and 60° , varies with the molecular proportions employed.
4. The dehydration of the oxalic acid does not affect the nature of the interaction, the anhydrous chromoxalate, $\text{K}_2\text{Cr}_2(\text{C}_2\text{O}_4)_4$, being formed in this case.
5. Water, by its solvent action, facilitates the interaction, that is, reduces the initial temperature, but is otherwise without influence on the nature of the change.
6. Seven mols. of oxalic acid is the *minimum* quantity necessary for the complete reduction of 1 mol. of potassium dichromate, and any *excess* of either above this ratio remains unchanged.
7. When the proportion of potassium dichromate to oxalic acid exceeds 1 to 7 mols., and the temperature of the mixture is raised to low redness, a secondary reaction occurs between the excess of dichromate and the red chromoxalate first formed.

University Laboratory,
Trinity College, Dublin.