

CCLXXXI.—*The Interaction of Cuprous Chloride and the Chromates of Potassium in a Solution of Sodium Chloride.*

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ROSENFELD (*Ber.*, 1879, **12**, 958) obtained a green precipitate on adding cuprous chloride, dissolved in a concentrated solution of sodium chloride, to an excess of a solution of potassium chromate. Similar experiments are now described, and, in addition, the dichromate was used, and the order in which the reagents were mixed was sometimes reversed. Complex precipitates were obtained, differing in colour and constitution according to the method of preparation. The reaction is shown to consist essentially in the oxidation of the cuprous salt and reduction of the chromate or dichromate, with formation of basic compounds, but owing to their instability to washing, these compounds do not always give trustworthy analytical results.

EXPERIMENTAL.

*Materials.*—Cuprous chloride, prepared by the method of Wöhler (*Ann. Chem. Pharm.*, 1864, **130**, 373), was stored in the dark in a vacuum desiccator, and remained quite white indefinitely (Found : Cu, by iodometric method, 64·11, 64·06; by electrolysis, 64·08. Calc. : Cu, 64·10%). The other reagents were of A.R. quality; the chromate and dichromate were recrystallised twice and thoroughly dried. All solutions were made up free from dissolved air and stored under hydrogen, and all the experiments were carried out in an atmosphere of the same gas.

*Apparatus.*—This consisted of a wide-necked bottle, of about 1 l. capacity, fitted with a rubber stopper carrying a motor-driven stirrer, an inlet tube for hydrogen, and a burette.

The reactions were all carried out at room temperature, except in Case II, and the theoretical values in the tables are based on equations (1)—(4) on p. 2145.

*Case I.* When a dilute solution of potassium dichromate is slowly added to cuprous chloride dissolved in concentrated sodium

chloride solution, a green precipitate is continuously formed until the whole of the chloride is oxidised. If the dichromate is added too rapidly, some of it reacts with the basic products, which then become contaminated with a basic chromate. If this side reaction is avoided, reaction takes place in the molecular ratio  $\text{Cu}_2\text{Cl}_2 : \text{K}_2\text{Cr}_2\text{O}_7 = 3 : 1$ , for when known amounts of each reagent were used, complete analyses of the precipitates and filtrates gave the following values for this ratio : 2.96, 3.02, 2.99, 2.99.

Known weights of cuprous chloride were oxidised by the addition during 5 hours of the calculated volumes of a 1% solution of potassium dichromate; cupric chloride was estimated in the filtrate, the amounts of copper thus found being given below as a percentage of the cuprous chloride taken.

G. of $\text{Cu}_2\text{Cl}_2$ taken (approx.).	Conc. of sodium chloride solution used.		
	15%.	20%.	25%.
1	5.64% Cu	5.30% Cu	5.67% Cu
2.5	—	5.79	—
5	5.84	5.45	5.33

Average 5.57% Cu; theory requires 5.35% Cu.

The washed precipitates were dried to constant weight at 97°, and their analyses are given in Table I.

TABLE I.

	1.	2.	3.	4.	5.	6.	Mean.	Calc.	Atomic ratios, found. theory.	
Cu, %	43.00	42.92	42.80	42.85	42.82	42.85	42.87	42.38	11	11
Cr, %	12.85	—	—	—	12.83	12.83	12.84	12.61	4.03	4
Cl, %	—	12.90	—	13.04	—	13.05	—	—	—	—
Cl, % (corr.)*	—	12.50	—	12.55	—	12.50	12.52	12.89	5.77	6
H <sub>2</sub> O, %	18.80	—	—	18.70	—	—	18.75	18.57	—	—

\* The correction is due to the deduction of chlorine present in the precipitate as sodium chloride.

*Case II.* When an attempt was made to oxidise cuprous chloride with potassium chromate in the same way, the reaction did not go to completion, although different conditions of concentration, time of stirring, and temperature (up to 60°) were tried. In two cases the partial precipitates were filtered off, washed, dried at 97°, and analysed :

	1.	2.	Atomic ratios,		
			for 1.	for 2.	theory.
Cu, %	48.04	32.09	6	6	6
Cr, %	13.67	9.53	2.09	1.69	2
Cl, %	10.30	—	2.25	—	2

*Case III.* Known quantities (1.0—1.5 g.) of cuprous chloride were dissolved in 500 c.c. of 20% sodium chloride solution and added

more or less rapidly to excess of potassium dichromate solution; brown precipitates were immediately produced, and the filtrates contained cupric chloride (Found: Cu, as % of  $\text{Cu}_2\text{Cl}_2$  taken, 10.84, 10.80. Calc.: Cu, 10.70%). The precipitates were washed, and dried at  $97^\circ$ . They contained the chromate radical, but no chlorine. The analyses are given in Table II.

TABLE II.

	1.	2.	3.	Mean.	Calc.	Atomic ratios,	
						found.	theory.
Cu, % .....	36.30	36.42	36.44	36.38	36.30	5	5
Cr, % .....	11.60	11.70	11.75	11.68	11.87	1.96	2
$\text{CrO}_4$ as % Cr	11.71	11.78	11.76	11.75	11.87	1.97	2
$\text{H}_2\text{O}$ , % .....	14.58	14.50	—	14.54	14.40		

Although the precipitate obtained in Case I reacts with potassium dichromate, we have satisfied ourselves that, even on digestion with 1% potassium dichromate solution for 2—5 days, it cannot be made to yield a precipitate of the same composition as that obtained in Case III, for under such conditions the average composition of the final product, dried at  $97^\circ$ , was Cu, 37.86; Cr, 13.12; Cr, present as  $\text{CrO}_4$ , 8.15; Cl, 10.25%. It will be seen that although a large percentage of chromate radical is now present, very little change has taken place in the ratio Cu : Cl.

*Case IV.* These experiments were carried out in the same way as those in Case III, potassium chromate being used instead of the dichromate. This was a repetition of Rosenfeld's (*loc. cit.*) experiment, as far as could be gathered from the available details. The washed precipitates were dried at  $110^\circ$ , as in his experiments, and the results are shown in Table III. Our figures are in better agreement, among themselves, than Rosenfeld's, and the atomic ratios agree better with equation (4) than do those obtained from his results.

TABLE III.

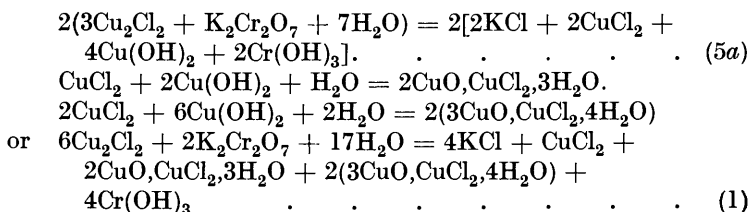
	1.	2.	3.	Mean.	Calc.	Atomic ratios,	
						found.	theory.
Cu, % .....	43.55	43.50	43.64	43.56	43.65	6	6
Cr, % .....	11.60	11.72	11.70	11.67	11.91	1.97	2
$\text{CrO}_4$ as % Cr	6.14	6.01	6.13	6.09	5.95	1.03	1
Total Cr, %	17.74	17.73	17.83	17.76	17.86	3.00	3
$\text{H}_2\text{O}$ , % .....	16.01	—	16.62	16.31	16.50		

### Discussion.

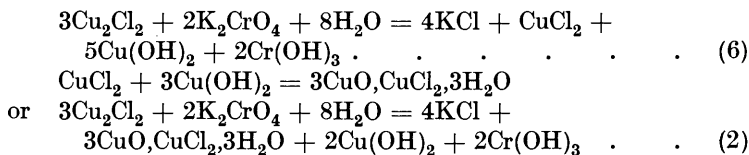
It is noteworthy that, in spite of variations in the concentration of the sodium chloride solution and of casual alterations in the time and other conditions, the analytical results are so constant for each set of experiments. Another point of interest is the fact that the reagents are not used up in every case in the proportions given by

the simplest equations by which the reactions can be expressed, viz., (5) and (6). The results of the analyses show that further reactions have taken place, and we give below equations for these secondary reactions. Equations (1), (2), (3), and (4) express, for the respective cases, the sum of all the reactions, and it is from these equations that the theoretical values in the tables have been calculated.

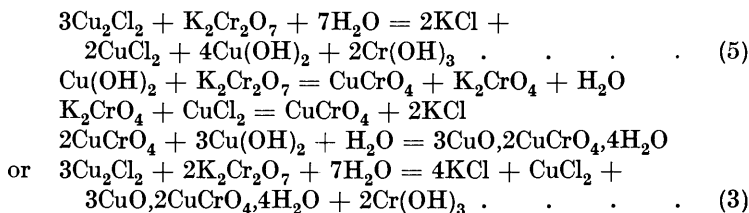
*For Case I.*



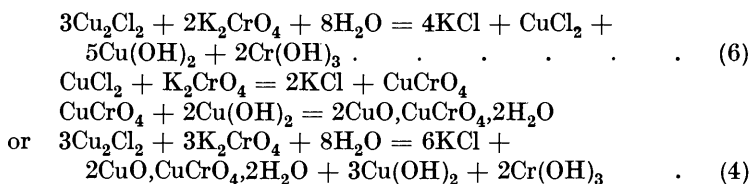
*For Case II.*



*For Case III.*



*For Case IV.*



Chromates of chromium have been intentionally ignored, on account of the doubt as to their existence in presence of water. The basic chlorides and chromates of copper given above are all known, except  $3\text{CuO}, 2\text{CuCrO}_4, 4\text{H}_2\text{O}$ ; Rosenfeld (*Ber.*, 1880, **13**, 1470), however, has described the compound  $5\text{CuO}, 2\text{CuCrO}_4, 5\text{H}_2\text{O}$ .

The compound  $3\text{CuO}\cdot\text{CuCl}_2\cdot 4\text{H}_2\text{O}$  has been characterised by Britton (J., 1925, 127, 2803).

In the equations for the secondary reactions, cupric hydroxide is imagined as behaving at the moment of formation like an electrolyte, and this supposition explains the interesting fact that the reaction proportions and products vary with the manner of mixing the reactants.

*Summary.*

(1) The interactions of cuprous chloride, dissolved in a solution of sodium chloride, with potassium chromate and dichromate have been studied.

(2) The colour and composition of the precipitates formed depend on the chromate used and on the manner of precipitation.

(3) The precipitates have been analysed, and equations involving basic copper salts have been proposed, according to which the formation of these basic salts is ascribed to secondary reactions.

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