[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

CALCIUM PERCHROMATE. A NEW TYPE OF RED PERCHROMATE

BY J. A. RAYNOLDS AND J. H. REEDY

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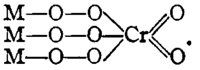
In spite of the very painstaking work of Riesenfeld[1], Wiede,[2] and others, our knowledge of the constitution of the perchromates is far from satisfactory. Their instability makes their isolation difficult, and no theory of the mechanism involved in their formation from chromates and peroxides has been advanced to prove their structure. The supposition that blue perchromic acid is formed in acid medium by a hyper-oxidation of chromates by means of hydrogen peroxide is hardly conclusive, when it is recalled that chromic acid is one of the strongest oxidizing agents and hydrogen peroxide in acid medium tends to behave as a reducing agent.

The red perchromates, which are formed when chromates and peroxides react in neutral medium, are more stable than the blue perchromic acid, and for this reason are better suited for isolation and analysis. Riesenfeld[3] has been the principal contributor to our knowledge of the red perchromates. From his analysis of the perchromates of the alkalies, he has proposed the type formula  $\begin{matrix}M{-}O{-}O\\M{-}O{-}O\\M{-}O{-}O\end{matrix}\!>\!Cr\!<\!\begin{matrix}O\\O\end{matrix}$.

Experimental Part

Red Perchromic Acid.—A solution of what may be considered to be perchromic acid was prepared by the action at 0° of 30% hydrogen peroxide on freshly precipitated chromic hydroxide. The reaction is slow, an hour or more being required for its completion. The solution thus prepared has a brown to grape-juice color, and decomposes slowly upon standing at 0°, and very rapidly if the temperature is allowed to rise, giving a yellow solution of chromic acid. Up to this time, the product has not been isolated in a crystalline form. It is insoluble in organic solvents, and for this reason cannot be extracted from its water solution. Upon attempting to separate the excess water by freezing, the whole mixture congeals to a mushy mass. Upon acidification, the acid changes to the blue perchromic acid, and upon adding alkalies chromates are formed.

Calcium Perchromate.—This compound was first prepared by adding very slowly one volume of 30% hydrogen peroxide to three volumes of saturated calcium chromate, cooled to slightly below 0° by means of a bath of ice and salt. The mixture was allowed to stand at about −5° for an hour, and then the calcium salt was filtered off in a Gooch crucible. The product was washed with several portions of ice water, and finally with acetone, and dried on a clay plate in a desiccator. The yield was from 15 to 20% of the weight of the original calcium chromate.

Later it was found that calcium perchromate could be prepared by the action be-

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[1] Riesenfeld, *Ber.*, **38**, 1885, 3059, 3380, 4068 (1905); **39**, 3181 (1906); **41**, 2826, 3536, 3941 (1908); **44**, 147 (1911); *Ber. Naturforsch. Ges. Freiburg*, **17**, 1 (1906); *Z. anorg. Chem.*, **74**, 48 (1912).

[2] Wiede, *Ber.*, **30**, 2178 (1897); **31**, 516, 3139 (1898); **32**, 378 (1899).

[3] Riesenfeld, *ibid.*, **41**, 3947 (1908).

tween calcium acetate solution and the red perchromic acid as prepared above. The products obtained by these two methods are identical in every respect.

Calcium perchromate is a buff-colored, fluffy powder, slightly soluble in water with slow decomposition, and practically insoluble in ether, alcohol and acetone. It is stable at ordinary temperatures, but decomposes explosively at about 100°, leaving a greenish residue of calcium oxide and chromic oxide. The purity of the salt is indicated by the failure of its water solution to give a precipitate with barium or lead acetate solutions. Upon acidification, the blue perchromic acid is formed.

Calcium perchromate prepared in this way was analyzed as follows. The calcium was determined by dissolving about 0.2 g. in dilute hydrochloric acid and boiling to destroy any peroxides. The calcium was then precipitated as calcium oxalate, and determined by titration with standard potassium permanganate solution.

The chromium was determined as barium chromate by the following procedure. About 0.2 g. was dissolved in very dilute acetic acid, the solution heated to boiling, and the chromium reconverted into the chromate form by means of sodium peroxide. After neutralization with acetic acid, barium acetate was added, and the precipitated barium chromate was filtered, ignited and weighed.

The available (or peroxide) oxygen was determined by dissolving about 0.1 g. in a mixture of potassium iodide and dilute sulfuric acid solutions and titrating the iodine liberated with standard sodium thiosulfate solution.

The water of hydration was determined by passing a current of dried air over samples of about 0.2 g. heated in a combustion tube, and absorbing the moisture evolved in a Swartz tube containing magnesium perchlorate trihydrate. On account of the explosive nature of the material, the charge was distributed over the length of the tube, and the heating was started at one end of the tube and slowly extended toward the other end.

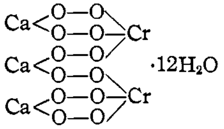
The results of these analyses have been collected in Table I.

TABLE I

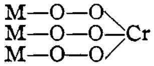
RESULTS OF ANALYSES

	Ca, %	Cr, %	Peroxide oxygen, %		H_2O, %	Oxygen (by difference), %
Experimental	18.74	16.37	15.27	15.19	34.56	
	18.70	16.42	15.25	15.26	34.46	
	18.69	16.34	15.21	15.23	34.49	
	18.70	16.39	15.22		34.57	
					34.43	
Average	18.71	16.38	15.23		34.50	15.17
Calcd. for $Ca_3Cr_2O_{12}\cdot 12H_2O$	19.01	16.45	15.18		34.18	15.18

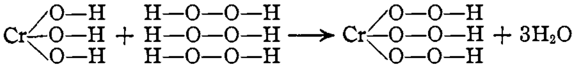
These analytical data indicate that the molecular formula for calcium perchromate is $Ca_3Cr_2O_{12}\cdot 12H_2O$. The only plausible configuration to represent this formula is



The type formula for univalent perchromates then should be

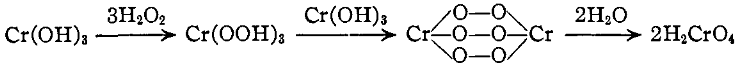


A very direct mechanism can be postulated to explain the formation of red perchromic acid:



$$\mathrm{Cr}\begin{cases}\mathrm{O{-}H}\\ \mathrm{O{-}H}\\ \mathrm{O{-}H}\end{cases} + \begin{matrix}\mathrm{H{-}O{-}O{-}H}\\ \mathrm{H{-}O{-}O{-}H}\\ \mathrm{H{-}O{-}O{-}H}\end{matrix} \longrightarrow \mathrm{Cr}\begin{cases}\mathrm{O{-}O{-}H}\\ \mathrm{O{-}O{-}H}\\ \mathrm{O{-}O{-}H}\end{cases} + 3H_2O$$

The formation of chromic acid by the action of hydrogen peroxide on chromic hydroxide may, presumably, be represented



$$\mathrm{Cr(OH)_3} \xrightarrow{3H_2O_2} \mathrm{Cr(OOH)_3} \xrightarrow{\mathrm{Cr(OH)_3}} \mathrm{Cr}\begin{matrix}\mathrm{O{-}O}\\ \mathrm{O{-}O}\\ \mathrm{O{-}O}\end{matrix}\mathrm{Cr} \xrightarrow{2H_2O} 2H_2CrO_4$$

These methods are now being used to prepare other red perchromates, with a view to ascertaining if their formulas are analogous to that of the calcium salt.

Summary

1. A solution of red perchromic acid was prepared by the action of 30% hydrogen peroxide on freshly precipitated chromium hydroxide at temperatures near 0°.

2. Calcium perchromate is formed at low temperatures, either by the action of 30% hydrogen peroxide on saturated calcium chromate, or by the action between calcium acetate and red perchromic acid solutions.

3. Analysis of calcium perchromate indicates the formula, $Ca_3Cr_2O_{12}\cdot 12H_2O$.

4. A mechanism for the formation of chromates from chromium hydroxide by means of alkaline peroxides is suggested.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA

SYNTHESIS OF PHOSGENE BY LIGHT AND BY ALPHA RADIATION

BY HUBERT N. ALYEA[1] AND S. C. LIND

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Extensive evidence shows that the initial step in a chemical reaction under alpha particle bombardment is ionization. In a great many reactions the subsequent formation of ion clusters[2] seemed sufficient to explain the resulting chemical reaction and yield per ion pair, which was in the neighborhood of two. Such a mechanism, involving ions, differs radically from the usual photochemical processes where the energy is insufficient for ionization. Among all the reactions studied, however, the union of hydrogen and chlorine was unique.[3] In this, many thousands of mole-

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[1] National Research Fellow.

[2] S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," The Chemical Catalog Co., **1928**, p. 139.

[3] S. C. Lind, *J. Phys. Chem.*, **16**, 610 (1912); *Le Radium*, **9**, 426 (1913); Bodenstein, *Z. Elektrochem.*, **22**, 53 (1916); H. S. Taylor, THIS JOURNAL, **37**, 24 (1915); **38**, 280 (1916); Porter, Bardwell and Lind, *ibid.*, **48**, 2603 (1926).