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SUBJECT: The Oxidation of Chromium(III) to Chromium(VI) in the Presence of Platinum Metals

TO: Distribution

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SUMMARY

Ruthenium, either as soluble salts, powdered metal, or oxide, catalyzed the oxidation of Cr(III) to Cr(VI) in dilute oxygenated sulfuric acid solutions. Under the same conditions, in the absence of ruthenium Cr(VI) was not produced.

In a 2 M $\text{Al}(\text{NO}_3)_3$ -1 M HNO_3 solution at the atmospheric boiling point, ruthenium and compounds of ruthenium, platinum, palladium, rhodium, and osmium very markedly increased the rate at which Cr(III) was oxidized to Cr(VI). Very low concentrations of ruthenium were capable of causing the oxidation to proceed at an appreciable rate.

In boiling 65% nitric acid, Cr(III) was oxidized to Cr(VI) if reduced oxides of nitrogen were removed from solution either in the presence or absence of ruthenium; without removal of the oxides of nitrogen, detectable quantities of Cr(VI) were not formed in either case.

Cr(VI) was not produced in boiling and aerated uranyl sulfate solutions containing ruthenium.

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The Oxidation of Chromium(III) to Chromium(VI)
in the Presence of Platinum Metals

N. E. Wisdom,* R. S. Greeley, and J. C. Griess

INTRODUCTION

The ability of low concentrations of ruthenium to catalyze the oxidation of Cr(III) to Cr(VI) in either uranyl sulfate or sulfuric acid at high temperatures has been demonstrated on several occasions.¹ Since Cr(VI) is a corrosion inhibitor in many environments, it was of interest to see if ruthenium or other platinum metals would catalyze the oxidation of Cr(III) to Cr(VI) in several different environments.

The environments investigated were oxygenated sulfuric acid at 250°C, a boiling solution containing 2 M Al(NO₃)₃ and 1 M HNO₃, boiling 65% HNO₃, and a boiling uranyl sulfate solution containing sulfuric acid and copper sulfate. The first environment was chosen because in the absence of ruthenium or other platinum metals Cr(III) is not oxidized to Cr(VI). In the second environment Cr(III) is oxidized to Cr(VI) at a very slow rate--only a few ppm Cr(VI) is formed after several thousand hours of boiling.² Hence in this environment the effectiveness of the catalysts could be easily judged. In the absence of ruthenium, boiling 65% HNO₃ is capable of oxidizing Cr(III) to Cr(VI) if reduced oxides of nitrogen are removed, but if the oxides of nitrogen are retained in the acid, Cr(VI) is not formed.³ In boiling uranyl sulfate solutions Cr(III) is not oxidized to Cr(VI) in the absence of ruthenium.

The following sections describe the experiments that were conducted and the results that were obtained. The experiments were of an exploratory nature and no attempt was made to determine the kinetics of the reactions involved.

EXPERIMENTAL PROCEDURES AND RESULTS

Sulfuric Acid Tests. All tests were conducted at 250°C in quartz-lined autoclaves equipped with valves so that the autoclave could be pressurized with oxygen. A stock solution containing 1230 ppm Cr(III) (0.0118 M Cr₂SO₄) and 0.037 M H₂SO₄ (pH = 1.3) was prepared, and in each test 20 ml of this solution was added to an autoclave. The substance whose catalytic activity was to be tested was then added, and after closing the autoclave an oxygen pressure of 100 psi was applied. After 48 hr at 250°C, the autoclaves were cooled, opened, and the solution and any solids analyzed. Table 1 shows the catalysts that were tested and the concentrations in solution at the end of the tests.

*Summer participant.

Table 1. The Effect of Catalysts on the Oxidation of Cr(III) to Cr(VI) in Sulfuric Acid

Conditions: Temperature, 250°C; initial Cr(III) concentration, 1230 ppm; sulfuric acid concentration, 0.037 M; oxygen pressure, 100 psi at 25°C; test time, 48 hr.

Catalyst	Cr Conc. at End of Test (ppm)		Catalyst Concentration ^a (ppm)	
	Cr ⁺³	Cr ⁺⁶	Initial	Final
None	263	<2	- ^b	-
RuCl ₃	<10	730	100 ^b	46
(RuNO) ₂ (SO ₄) ₃	63	953	100 ^b	13
Pwd Ru metal	406	54	c	16
Pwd Ru metal and RuO ₂	486 ^d	133	c ^b	22
RhCl ₃	4200 ^d	<2	50 ^b	c
PdCl ₃	384 ^d	<2	100 ^b	13

^aRefers to concentration of metal ion.

^bBased on weight of material added.

^cNot determined.

^dLeak in autoclave caused concentration.

As observed in dynamic tests, Cr(III) was not oxidized by oxygen-containing sulfuric acid. However, with ruthenium in almost any form added to the solution, a significant amount of Cr(VI) was formed during the 2-day tests. The soluble ruthenium salts, ruthenium nitroso sulfate, and ruthenium chloride, were considerably more effective than either the metal or the mixture of the metal and dioxide. During the tests with rhodium chloride and palladium chloride the autoclaves leaked, and a substantial concentration of sulfuric acid and Cr(III) occurred. Both the concentration of the acid and the loss of oxygen as a result of the leak would tend to prevent the oxidation of Cr(III) and the fact that Cr(VI) was not formed should not be taken to mean that rhodium and palladium are catalytically inactive. It is possible that under the conditions that prevailed in the ruthenium tests some Cr(VI) might have been formed.

In all cases some solids were found in the quartz liners at the end of the tests. The solids were anhydrous chromic oxide containing low concentrations of the catalyst.

2 M Al(NO₃)₃-1 M HNO₃ Tests. In this series of tests 500-ml aliquots of the 2 M Al(NO₃)₃-1 M HNO₃ solution containing at least 700 ppm Cr(III) (as chromic nitrate) and the catalyst were boiled in a flask containing a reflux condenser open to the air for several days with air bubbled through the solution. At the end of the test the solutions were analyzed. No stainless steel was present in the test vessel. The test conditions and results are given in Table 2.

Table 2. The Effect of Several Catalysts on the Oxidation of Cr(III) to Cr(VI) in 2 M Al(NO₃)₃-1 M HNO₃ Solution

Catalyst	Time (days)	Chromium Concentration (ppm)			Catalyst Conc. ^a (ppm)	
		Cr(III) Initial	Cr(III) Final	Cr(VI) Final	Initial	Final
None	12	700	700	1	-	-
RuCl ₃	7	1140	1470	179	100	78
(RuNO) ₂ (SO ₄) ₃	7	1210	1240	222	100	69
Pwd Ru metal	7	1240	1460	444	b	34
PtCl ₄	18	700	530	54	100 ^c	91
OsO ₄	18	700	570	444	100 ^c	<2
RhCl ₃	18	700	393	337	50 ^c	b
PdCl ₂	18	700	310	365	100 ^c	132

^aRefers to concentration of metallic ion.

^bNot determined.

^cBased on weight of material added.

All of the platinum metal compounds added to the 2 M Al(NO₃)₃-1 M HNO₃ solution were effective in causing the oxidation of some of the Cr(III) to Cr(VI). In this environment ruthenium metal was more effective than either ruthenium nitroso sulfate or ruthenium chloride. Osmic acid produced the same amount of Cr(VI) as did the ruthenium metal, although the time of refluxing was about two and one-half times greater with the osmium than with ruthenium. Apparently most of the osmium tetroxide added to the solution was volatilized during the test, since osmium was not detected in the solution at the end of the test. The chlorides of platinum, rhodium, and palladium were catalytically active in the solution, with platinum chloride being substantially less active than the other two.

In the 2 M Al(NO₃)₃-1 M HNO₃ system, Cr(III) and Cr(VI) are soluble and the only solids found in solution were small amounts of the platinum metals which were apparently formed from the salts. Why the sum of Cr(III) and

Cr(VI) at the end of the test did not equal the Cr(III) at the beginning of the test (except in the absence of a catalyst) is not known definitely, although it is probable that the low concentrations of platinum metals in solution interfered with the chemical analyses. That Cr(VI) did form in the presence of the platinum metals was evidenced by the fact that the solutions gradually changed from near colorless to an orange color as the tests progressed.

One of the flasks in which the ruthenium catalyst was used was cleaned with soap and water at the end of the test. Then a fresh portion of the test solution containing about 1200 ppm Cr(III) (but no ruthenium) was added, and the solution was refluxed. At the end of two days the solution contained 150 ppm Cr(VI). The flask was cleaned with sodium hypochlorite solution in which ruthenium and ruthenium dioxide are soluble. A trace of ruthenium was found in the cleaning solution even though no deposit had been visible before cleaning. After the hypochlorite cleaning, the flask was used for another fresh portion of solution with no ruthenium added; this solution was boiled for 12 days, at the end of which time only 1 ppm of Cr(VI) was found in the solution.

Tests in 65% HNO₃ and Boiling UO₂SO₄ Solutions. Only the effect of 100 ppm ruthenium as ruthenium trichloride was determined in boiling 65% HNO₃. In this case 300 ppm Cr(III) as chromic nitrate was added to the nitric acid. When the solution was aerated during boiling Cr(VI) was formed both in the presence and absence of ruthenium chloride. When the solution was not aerated and a closed system with a cold-finger condenser was used, no detectable amount of Cr(VI) was found in solution even with ruthenium present. The oxidation of Cr(III) to Cr(VI) leads to the formation of oxides of nitrogen which prevent further oxidation of Cr(III). If the oxide initially formed is allowed to escape from the boiling solution, Cr(VI) is readily formed even in the absence of ruthenium.

One test was also made in which 30 ppm ruthenium as ruthenium chloride was added to a solution containing 0.04 M UO₂SO₄, 0.025 M H₂SO₄, 0.01 M CuSO₄, and 500 ppm Cr(III) as chromic sulfate. The solution was boiled and aerated with oxygen for 15 days, during which time no Cr(VI) formed.

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