$^3/_2O_2$ occurs with formation of violet-black crystals of calcium chromite, which are green when finely ground. Vasenin,[13] in a study of thermal decomposition of calcium chromates, cites a decomposition of $CaCr_2O_7$ to form $CaCr_2O_4$ at 1112° following evolution of hydrate water at 150°, but the intermediate decomposition at 500° is not described. The failure of the data to show exactly 3 atoms of O evolved per mole of $CaCr_2O_7$ is probably due to slight reoxidation of $CaCr_2O_4$ on cooling in air.

Solubility in Organic Liquids.—Solubility characteristics of both hydrates are similar. They are insoluble in ether, carbon tetrachloride and hydrocarbon solvents, dissolve in alcohol with immediate reduction of the dichromate and precipitation of brown hydrous chromic chromate, and dissolve in acetone, with subsequent precipitation of calcium chromate. In this respect, the calcium dichromates resemble lithium dichromate dihydrate.[9e]

Summary

1. A procedure has been outlined for the preparation of calcium dichromate solutions.
2. Two crystalline hydrates of the salt $CaCr_2O_7 \cdot 3H_2O$ and the previously unknown $CaCr_2O_7 \cdot 4.5H_2O$, have been prepared. The latter is orthorhombic in external symmetry.
3. The system $CaCr_2O_7$–H_2O has been investigated. Two invariant points exist at atmospheric pressures: $CaCr_2O_7 \cdot 4.5H_2O$–$CaCr_2O_7 \cdot 3H_2O$–solution at 63.02% $CaCr_2O_7$ and 42.1°; ice–$CaCr_2O_7 \cdot 4.5H_2O$–solution at 49.3% $CaCr_2O_7$ and −31.3°.
4. The density of calcium dichromate solutions has been determined at 30° for concentrations up to saturation.
5. On heating the hydrates, partial decomposition to $CaCrO_4$ and CrO_3, due to hydrolysis, occurs. There is no evidence of the existence of anhydrous $CaCr_2O_7$ as a pure crystalline phase. Further heating results in the loss of oxygen at 500° to give a mixture of Cr_2O_3 and $CaCrO_4$, which loses oxygen at 1100–1200° to form $CaCr_2O_4$.
6. The qualitative solubility in common organic solvents has been reported.

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(13) F. I. Vasenin, *Zhur. Priklad Khim.*, **21**, 429–436 (1948).

[CONTRIBUTION FROM THE DIVISIONS OF CHEMISTRY AND VITICULTURE, COLLEGE OF AGRICULTURE, AND THE RADIATION LABORATORY, DEPARTMENT OF PHYSICS, UNIVERSITY OF CALIFORNIA]

The Reaction of Wolfram Dioxide with Dichlorodifluoromethane[1]

BY A. DINSMOOR WEBB AND HERBERT A. YOUNG

It has been known for several years that carbon tetrachloride could be used as a chlorinating agent for several of the heavy metal oxides, including those of wolfram and uranium.[2] Only recently, however, has the use of a simple freon type compound been reported for the halogenation of a metallic oxide.[3] Booth and co-workers found that dichlorodifluoromethane would reduce and fluorinate uranium trioxide to produce uranium tetrafluoride in nearly quantitative yields.

Because of recent interest in the comparison of the chemical properties of wolfram and uranium, it was though to be of some interest to study the reaction between wolfram dioxide and freon, particularly since such a reaction might produce the unknown wolfram tetrafluoride.[4]

The experimental procedure developed was the simple one of leading the pure gaseous freon over the heated metallic oxide, held at temperatures up to 525°, and collecting and analyzing the products. A condensing unit, as shown in Fig. 1, was constructed with several separately removable collecting units which could be maintained at successively lower temperatures. In operation, this allowed for the separate collection of samples with differing volatilities.

Experimental

Since dichlorodifluoromethane is extremely corrosive at temperatures near 500°, it was necessary to use nickel vessels[5] for all equipment that came in contact with the freon at high temperatures and the reaction products at all temperatures. The reaction chamber was constructed from a piece of two inch i. p. s. nickel pipe three feet long with flanges and removable cover plates at each end. The pipe was heated for a distance of eighteen inches from one end by an electrical resistance tube furnace, the power being regulated by a thermocouple mounted within a thin walled nickel tube so located that the thermocouple was about one-half inch above the surface of the reacting wolfram dioxide. A large variable autotransformer and potentiometer type off-on controller completed the power regulating assembly. The unheated portion of the nickel pipe reactor was wrapped with asbestos cloth to help maintain a constant temperature gradient. The cooler end of the nickel pipe reactor was wrapped with a copper tubing

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(1) Scheduled but not presented because of illness at the meeting of the American Chemical Society in Atlantic City, September, 1949, Taken in part from report BC-70 revised to the Radiation Laboratory, University of California, and based on the dissertation submitted by A. Dinsmoor Webb to the Faculty of the Graduate Division of the University of California in partial fulfillment of the requirements for the degree, Doctor of Philosophy.

(2) A. Michael and A. Murphy, *Amer. Chem. Jour.*, **44**, 382 (1910).

(3) H. S. Booth, W. Krasny-Ergen and R. E. Heath, THIS JOURNAL, **68**, 1969 (1946).

(4) The preparation and characterization of wolfrom tetrafluoride was reported by H. F. Priest and W. C. Schumb, *ibid.*, **70**, 3378 (1948), during the course of this investigation.

(5) R. Landau and R. Rosen, *Ind. Eng. Chem.*, **39**, 281 (1947), show nickel metal to be most resistant to action of fluorine.

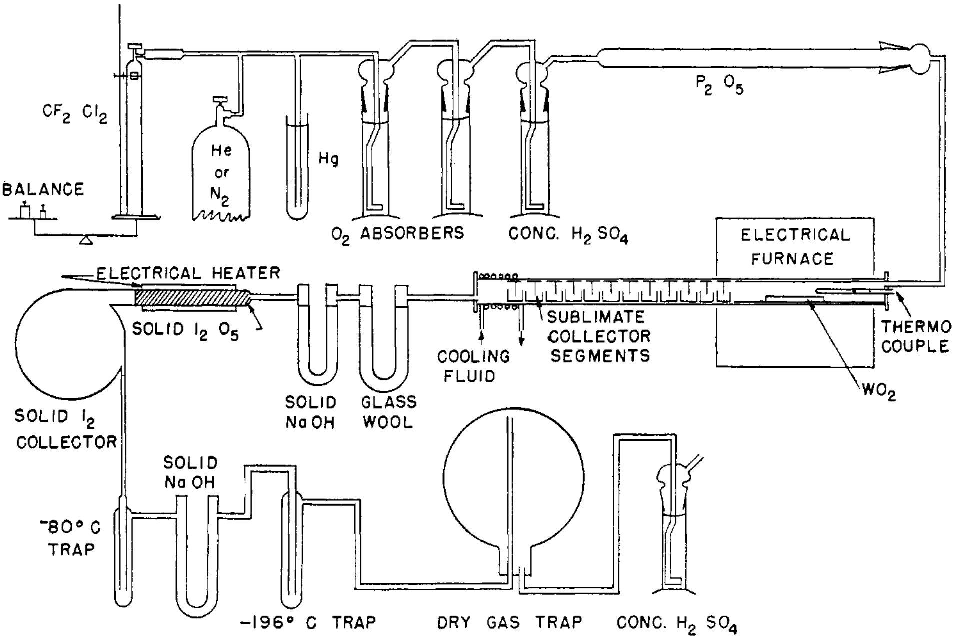

Fig. 1.—Experimental arrangement.

coil for a distance of two inches from the end. A temperature near zero was maintained at this end of the nickel pipe reactor by circulating ice water or other coolant through the copper tubing coil. The cooler end of the nickel pipe reactor protruded into a large "dry-box" in which water vapor was maintained at a very low concentration by continuously circulating the air through an activated alumina dryer.

The portion of the nickel pipe reactor in which a temperature gradient was maintained was filled with product collector units made by welding semi-circular baffles over the ends of one and one-half inch long pieces of nickel pipe which fitted snugly inside the reactor pipe. A third baffle covering three-quarters of the cross section area was welded in the center of each product collector unit so that the gas stream was caused to impinge on three surfaces in passing through each unit. As a total of twelve product collector units was used, the average temperature difference between centers of units was 44° when the reactor was maintained at 525°. Known quantities of dichlorodifluoromethane were introduced into the reactor from a small lecture bottle which was mounted on a laboratory scale.

The gas streams were passed through two bubblers filled with solutions of alkaline pyrogallol to remove traces of oxygen, and then through concentrated sulfuric acid and over phosphorus pentoxide to remove water vapor before being led into the reactor.

The dichlorodifluoromethane was diluted with either nitrogen or helium gas in some experiments, and, in all cases, the reactor and analytical train were flushed out with one of the inert gases before and after the introduction of the dichlorodifluoromethane.

The gas stream from the reaction zone, after being passed over the baffles of the product collector units, was brought outside the dry-box and through a train of absorption bulbs designed to collect different possible reaction products. Powdered antimony metal was used to trap any free halogens, solid sodium hydroxide flakes were used to absorb traces of wolfram hexafluoride that passed out of the reactor as well as to trap phosgene, carbonyl fluoride and carbon dioxide. Carbon monoxide was determined by oxidation to carbon dioxide with iodine pentoxide heated to 160 ± 5°. The iodine produced by the reduction of the iodine pentoxide was dissolved in potassium iodide solution and titrated with standard sodium thiosulfate solution and the carbon dioxide produced was absorbed in a tube of sodium hydroxide flakes and weighed. Finally, the unreacted dichlorodifluoromethane was removed from the inert carrier gas stream by condensation in a trap cooled by liquid nitrogen.

After cooling of the nickel pipe reactor at the termination of a reaction, the cover plate was removed from the dry-box end of the reactor and the product collector units were removed one at a time. Solid products collected on the units were transferred by means of a spatula to previously tared weighing bottles.

The weighing bottles containing the solid reaction products were weighed and the contents dissolved in dilute sodium hydroxide solution within a half hour as some of the products showed a tendency to decompose upon standing for a period of days. Dissolution in the basic solution without loss of hydrohalides was accomplished by sliding the weighing bottle with loosened cover down the inside wall of a large-mouthed Erlenmeyer flask containing the dilute alkali solution and which was closed with a large rubber stopper. The weighing bottle floated in the alkali solution until opened by gentle shaking, after which a rapid hydrolysis occurred giving a yellow precipitate of wolfram trioxide which was then slowly dissolved by further shaking. Aliquots from the basic solution thus obtained were analyzed for wolfram,[6] for fluorine,[7] and for chlorine. The chlorine was distilled as hydrochloric acid from the perchloric acid solution along with the fluosilicic acid for the fluorine determination. After titration and precipitation of the thorium fluoride, the solution was filtered through a sintered glass disc and chloride was determined in the filtrate by titration with acidified mercuric nitrate solution to the turbid end-point with sodium nitroprusside as indicator. It was found, alternately, that chloride could be determined in the presence of fluosilicate ions or fluoride ions by this method providing the weakness of the corresponding acids were taken advantage of by acidification of the solution. In calculating compositions

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[6] F. S. Grimaldi and N. Davidson, "U. S. Geol. Sur. Bull. No. 950," 135-138 (1946).

[7] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933); and W. B. Huckabay, E. T. Welch and A. V. Metler, **19**, 154 (1947).

of the solid products the difference between the sum of the amounts of wolfram, chlorine, and fluorine found analytically and the total weight was assumed to be oxygen.

Experimental Results and Discussion.—Analyses of materials collected on the removable product collector units in four typical experiments are presented in Table I. In addition, calculated compositions for the mixtures assuming that only wolfram hexachloride, wolfram oxytetrachloride and wolfram oxytetrafluoride are components are presented. These three components were chosen for calculating mixture compositions because they are well known stable products, and because the characteristics of the mixtures were such as to make this choice reasonable. That all of the wolfram was present in the plus six oxidation state was shown by the absence of blue or brown colors in the hydrolysis products when the material was added to sodium hydroxide solutions. The crystal form and color was more nearly characteristic of that of pure wolfram oxytetrachloride than that of any of the other wolfram compounds possible.

The effectiveness of the fractionating condenser is apparent from an examination of the mixture compositions for Run 10 as shown in Table I. Pure wolfram oxytetrafluoride boils at 187.5° while pure wolfram oxytetrachloride boils at 227.5°. Run 10 shows that the mixture collected at 200° is almost 75% of the higher boiling compound whereas at a collection temperature of 155° the mixture consists of 56% of the wolfram oxytetrachloride. The only significant difference between Runs 8 and 9 and Runs 10 and 11 shown in Table I was in the rate of addition of freon gas to the reactor. The first two runs had a freon addition rate only one-half as great as the latter two. The first two runs also had a total halogen to wolfram ratio greater than four and an oxygen to wolfram ratio less than unity, which can most reasonably be explained by the presence of a small amount of wolfram hexachloride in the higher boiling mixture. The vapor pressure of wolfram hexafluoride is so high at the temperatures of solidification of these mixtures that it is not considered possible as a component; in fact, wolfram hexafluoride was collected either in the first absorber tube filled with sodium hydroxide flakes or in a special low temperature filter tube which was used in one experiment.

Table I

Analyses of Materials Collected on Product Collector Units in Different Runs

Run	Collector unit temp., °C.	Analytical results in wt. % W	F	Cl	O	Calculated compositions of mixtures, mole % WCl_6	$WOCl_4$	WOF_4
8	110	57.5	9.8	27.8	4.9	7.7	51.1	41.2
	200	53.7	1.3	40.8	4.2	8.6	85.6	5.8
9	110	58.9	12.1	23.2	5.8	0	50.8	49.2
	155	55.4	4.9	35.1	4.6	7.3	71.1	21.6
10	155	58.2	10.6	25.5	5.8	0	56.4	43.6
	200	56.1	5.9	32.6	5.4	0	74.9	25.1
11	155	59.1	12.0	22.7	6.2	0	50.1	49.9
	200	58.9	11.1	25.1	4.9	0	54.9	45.1

In other experiments the quantities of the non-wolfram containing materials involved in the reactions were determined. It was observed that the wolfram dioxide charge was completely replaced by—or in other cases covered by—elemental carbon which was deposited in mechanical form identical with the wolfram dioxide reacted. The amount of carbon formed was determined by weighing the total residue in the charge boat, burning off the carbon at 600°, and subtracting from the total residue weight the weight of wolfram dioxide equivalent to the amount of wolfram trioxide formed during the oxidation. Table II presents the results of analytical determinations of the materials involved in a number of experiments where total wolfram, total chloride, and total fluoride in the reactor and samples was determined.

An examination of the molar ratios of the reactants and products as shown in Table II indicates that there is no one simple reaction involved when dichlorodifluoromethane is passed over heated wolfram dioxide in a nickel metal reactor. The fact that the much higher ratio of total halides to wolfram in the wash and sample solutions and the higher ratios of dichlorodifluoromethane reacted to wolfram reacted both occur in Run 16 suggests that there is a reaction between the freon and the nickel reactor surfaces with the production of nickel halides, as well as the main reaction between the freon and the wolfram dioxide. This effect is most marked in Run 16 because of the ten-fold smaller amount of wolfram dioxide present in the reactor.

An attempt to show a correlation between the amounts of carbon, carbon monoxide, and carbon dioxide found is not very successful and suggests that while the carbon and carbon dioxide probably result mainly from decomposition of the carbon monoxide on the surface of the wolfram dioxide, there are probably other secondary reactions involved also.

The fact that, while the ratio of carbon produced to wolfram reacted is about two-tenths, the ratio of carbon monoxide produced to wolfram reacted is near unity, combined with the facts that the fluoride and chloride ions are found in nearly equal amounts and together constitute four times the molar amount of wolfram reacted, suggests that the principal reaction may be represented by the equation

$$2WO_2 + 2CCl_2F_2 = WOF_4 + WOCl_4 + 2CO$$

The various other substances found to result in small amounts are thought to arise from secondary reactions within the system. Phosgene and carbonyl fluoride could result from reduction of the nickel halide films on the inside surfaces of the reactor by carbon monoxide. It seems reasonable then that some of the phosgene

TABLE II

THE STOICHIOMETRY OF THE MATERIALS INVOLVED IN THE REACTION BETWEEN WOLFRAM DIOXIDE AND DICHLORODIFLUOROMETHANE; ALL RUNS AT 525°

Run	9	10	11	12	13	14	16
W reacted, gram-atoms	0.0742	0.0666	0.1067	0.0663	0.0474	0.0709	0.0067
CCl_2F_2 reacted, moles	0.132	.....	......	......	0.0561	0.0991	0.0198
Time reactor at 525°, hours	3.8	4.0	5.0	3.3	3.0	2.8	2.0
Rate of CCl_2F_2 addition, g./hr.	11.2	27.2	24.0	11.4	6.3	6.9	5.3
Products obtained C, gram atoms	0.0106	0.0149	0.0162	0.0109	....	0.0127	0.00087
CO, moles	.....	.....	.1051	.0665	.0423	.0683	.0030
CO_2, moles	.....	.....	.0046	.0031	.0031	.00066	.00069
COF_2, moles	.....	.0013	.0022	.0011	.0023	.0014	.0024
$COCl_2$, moles	.....	.....	.00082	.00024	.0016	.0166	.00050
Totals in reactor wash and samples							
W^{6+}, g.-atoms	.....	.0475	.1019	.0622	.0456	.0649	.0052
F^-, g.-atoms	.....	.1131	.2302	.1473	.1321	.1580	.0185
Cl^-, g.-atoms	.....	.0931	.1712	.1187	.1251	.1670	.0333
Mole ratios							
X^-/W	.....	4.34	3.95	4.27	5.64	5.01	10.06
W/C	7.01	4.47	6.58	6.08	....	5.61	6.58
CF_2Cl_2/W	1.78	.....	......	......	1.19	1.40	3.48
W/CO	.....	.....	1.02	0.99	1.12	1.05	1.90

and carbonyl fluoride could interact with the corresponding wolfram oxytetrahalides to give the wolfram hexahalides and carbon dioxide.

Summary

By passing dichlorodifluoromethane over wolfram dioxide at a temperature of 525° in a nickel metal reactor with removable product collector units in a temperature gradient zone it was found that the main wolfram-containing products were solid solutions of crystal form and color similar to those of wolfram oxytetrachloride. The product compositions could be represented as wolfram oxytetrachloride in which from 14.4 to 49.9 mole per cent. of the chloride was replaced by fluoride. Very small amounts of wolfram hexafluoride and wolfram hexachloride were also found. The wolfram was in the plus six oxidation state in all of the products.

In addition to the wolfram-containing products, carbon, carbon monoxide, carbon dioxide, carbonyl chloride, and carbonyl fluoride were found.

Consideration of the amounts of the various products obtained indicated that the main reaction may be represented by the equation $2WO_2 + 2CCl_2F_2 = WOF_4 + WOCl_4 + 2CO$. The other products likely resulted from interaction of these substances with the nickel metal reactor walls and with the nickel halide films thereon.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

The Electrical Conductivities of Solutions of Potassium Bisulfate in Concentrated and Fuming Sulfuric Acid[1]

BY RICHARD A. REINHARDT[2]

The present work was carried out to study further the solvolytic equilibria of water and sulfur trioxide dissolved in sulfuric acid by observing the effect on the conductivity produced by adding potassium bisulfate to concentrated and fuming sulfuric acids. In addition, in view of the discrepancies between the results of previous workers,[3] the conductivities of fuming sulfuric acid, without added salt, have been redetermined.

Experimental

The experiments were carried out in a dry box through which passed a continuous stream of dried air and which fitted over an oil-bath maintained at 25 ± 0.02°. Pressure from the dried-air system was used to transfer liquids.

Solutions were prepared by mixing together weighed portions of two previously standardized stock solutions, one containing slightly less, the other slightly more than

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[1] Taken from the dissertation of R. A. Reinhardt presented to the Graduate School of the University of California in September, 1947, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Allied Chemical and Dye Corporation Fellow, 1946-1947. Present address: Department of Chemistry, Cornell University, Ithaca, New York.

[3] (a) W. Kohlrausch, *Ann. physik. Chem.*, **253**, 69 (1882) (b) R. Knietsch, *Ber.*, **34**, 4109 (1901); (c) A. Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); (d) F. Bergius, *ibid.*, **72**, 351 (1910).