

Fig. 4.—Turbidity, τ , as a function of time for a solution 0.025 M in sodium tungstate and having a H^+/WO_4^{2-} ratio of 2 to 1. The arrow indicates the point when cloudiness was first noted in the solution.

2/3 ratio agreed remarkably well with the theoretical value for a trimer. This indication of an intermediate between the monomer and the hexa-

mer is most evident in the solutions of high total tungsten concentration.

On treating a tungstate solution with sufficient acid to convert the Na_2WO_4 to tungstic acid precipitation takes place. If the total tungsten concentration is small enough the solution remains clear even after adding sufficient acid to convert the Na_2WO_4 to tungstic acid and precipitation ensues only after a period of time has lapsed. Introductory studies of solutions having a H^+/WO_4^{2-} ratio of 2 to 1 or in other words sufficient acid to convert all the Na_2WO_4 to tungstic acid indicate that it is possible to use the light scattering technique to study the rate of polymerization of freshly prepared tungstic acid to the point where actual precipitation commences. Figure 4 is a plot of τ versus time for a solution 0.025 M in Na_2WO_4 and having a H^+/WO_4^{2-} ratio of 2 to 1. The turbidity increase with time is indicative of increasing polymerization of the tungsten containing species as the solution ages. In Fig. 4 the arrow indicates the point where visible cloudiness was first noted in the solution. Beyond this point τ began to decrease and actual precipitation commenced. In the case of a solution 0.05 M in tungstate 24 hours passed before visible cloudiness was observed while with a 0.10 M solution cloudiness ensued immediately.

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Chemistry of Rhenium and Technetium. I. Synthesis of $ReCl_5$, $TcCl_4$ and Related Compounds

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A general method for the synthesis of anhydrous metal chlorides has been developed. It is a modification of the method of Michael and Murphy in which the metal oxide and carbon tetrachloride are heated to 400° in a sealed glass tube. The glass tube is contained in a metal bomb with carbon tetrachloride or water in it to equalize the pressure. Pure preparations of $ReCl_5$, $TcCl_4$, $MoCl_5$, WCl_6 and $TaCl_5$ have been made. Preliminary results also indicate that Fe, Zr, Be and V oxides are completely converted to chlorides; that Zn, Al, La, Th and Nb oxides are partially converted; and that Co and Ni oxides are not converted. The highest chloride formed by the metal is found in all known cases. Technetium yields a blood-red powder identified by analysis as the tetrachloride. Thus, under ordinary conditions, the highest chloride of Tc is different from that of Re, which forms a pentachloride.

Introduction

The general methods of preparing anhydrous metal halides have been reviewed earlier.² The method of Michael and Murphy,³ in which the metal oxide and carbon tetrachloride react in a sealed tube, has been modified to overcome the difficulty of frequent breaking of the glass tubes at higher temperatures. At the temperature required to bring about the complete conversion of some oxychlorides to the chlorides, high pressures are generated which must be balanced by an external pressure. The balancing pressure is supplied by placing the sealed tube inside a high-pressure steel reaction vessel with heater⁴ containing the proper amount of

a liquid. Then the whole assembly is heated. If water is used as the external liquid, heavy wall tubes must be used, because although the pressure at the reaction temperature can be made equal inside and outside the glass tube, the pressure difference at intermediate temperatures is great enough to break standard wall tubing. If carbon tetrachloride is used outside, standard wall glass tubing can be used. In the latter case, however, corrosion of the containing steel vessel is more rapid, but not alarmingly so.

Experimental

Method.—The standard conditions used in this Laboratory are 8 cc. of liquid carbon tetrachloride at room temperature for every 26 cc. of volume in the glass reaction vessel. The amount of metal oxide is that calculated to have a five-fold excess of carbon tetrachloride present, according to the equation for the reaction; e.g., $Re_2O_7 + 7CCl_4 \rightarrow 2ReCl_5 + 7COCl_2 + 2Cl_2$. The excess CCl_4 is needed to dissolve and

(1) Bell Telephone Labs., Inc., Murray Hill, N. J.

(2) S. Y. Tyree, Jr., *Inorg. Syntheses*, **4**, 104 (1953).

(3) A. Michael and A. Murphy, *Am. Chem. J.*, **44**, 365 (1910).

(4) Obtainable from the American Instrument Company, Silver Spring, Md.

thereby reduce the final pressure of the product gases, COCl_2 and sometimes Cl_2 , and to dissolve the solid chlorocarbon by-products which would otherwise contaminate the product. If standard wall glass tubes are used, the same proportion of CCl_4 to free volume is maintained in the steel bomb. If heavy wall tubes are used, 66 cc. of liquid water at room temperature is used for every 1410 cc. of outside volume. The metal oxide and C.P. CCl_4 without further purification are placed in the glass reaction vessel shown in Fig. 1. The neck is sealed and heated carefully to give a uniformly thick seal. After flame annealing of the neck, the glass tube is placed inside the steel bomb with the proper amount of balancing fluid in it (commercial grade CCl_4 is satisfactory here). Closure is made, and the assembly is heated to 400° for a few hours, the pressure developed being about 100 atmospheres. There is no danger of an explosion here with a properly selected metal bomb, but the usual precautions taken in high-pressure, high-temperature work should be observed. If a leak should develop in the seal, obnoxious gases will be given off. The heater is turned off and the assembly allowed to cool to room temperature. It is opened in a hood or out of doors.

The glass tube now contains gases under pressure, estimated to be about 1–2 atm. excess at room temperature, and so it should be handled carefully. It is opened in a hood by playing an oxy-gas flame on the sealed tip, which blows out because of the pressure inside the tube. (Caution: Heat the tip on a side which will make it blow out in a safe direction.) The whole top of the tube is then taken off in order to facilitate removal of the contents in the dry box. This is done by scratching the side of the tube with a sharp file just below the shoulder (the scratch is most easily made before opening the tip with the flame) and leading the scratch around the tube with a red-hot glass rod. These operations should be carried out as rapidly as possible so as to be completed before effervescence ceases and air enters the tube. The tube is then placed inside another tube fitted with a ground-glass joint and stopcock at the top, shown in Fig. 2. The stopcock is joined to a vacuum system by a rubber tube through a Dry Ice-acetone trap and a NaOH tower. It is partly opened very carefully, adjusting the stopcock so as to give a steady but not violent ebullition. The rapid boiling causes cooling which tends to slow down the rate of boiling to the point where bumping can be very bad. The external application of sufficient heat by means of an infrared lamp has been found very effective in overcoming the trouble and in maintaining a steady ebullition. About one-half of the volume of the liquid is slowly pumped away in order to remove dissolved COCl_2 and Cl_2 . It is not all pumped away, otherwise the solid chlorocarbons deposit. The tube is removed to an efficient dry-box, opened, the product filtered and washed with CCl_4 .

Rhenium Pentachloride.—Rhenium metal is burned in oxygen to the heptoxide⁶ which is sublimed into the glass reaction vessel previously sealed onto the oxidation apparatus. The oxygen pressure is brought to just above atmospheric pressure, the connecting tube cut, and the CCl_4 quickly poured in through a funnel. The tube is sealed and heated as above. The product is large green-black crystals of ReCl_5 beneath a green liquid. The over-all yield is about 90%: in one preparation, 1.2 g. of Re gave 2.0 g. of ReCl_5 , 87%; in another starting with the heptoxide, 9.0 g. of Re_2O_7 gave 13.4 g. of ReCl_5 , 99%. Rhenium pentachloride can be kept indefinitely in the sealed tube, but once this is opened, the product must be used promptly because it slowly decomposes, probably losing chlorine.

For analysis, samples of about 200 mg. are weighed out in a dry box, removed and dissolved in a sodium hydroxide-hydrogen peroxide mixture. The solution is evaporated to dryness in a platinum casserole to decompose any hexachlororhenate(IV) formed. If the residue is not colorless, more sodium hydroxide-hydrogen peroxide solution is added and evaporation repeated. This treatment is sometimes required as many as three times to break up this robust complex. The residue is taken up with water, neutralized and made slightly acidic with nitric acid, and titrated potentiometrically with standard silver nitrate, care being taken not to go too far over the end-point. Hydrochloric acid is then added to remove excess silver. The precipitate is digested and filtered off. Since nitrate interferes with tetraphenylarsonium perchlorate precipitation, it is removed by

(5) A. D. Melavan, J. N. Fowle, W. Brickell and C. F. Hiskey, *Inorg. Syntheses*, **3**, 188 (1950).

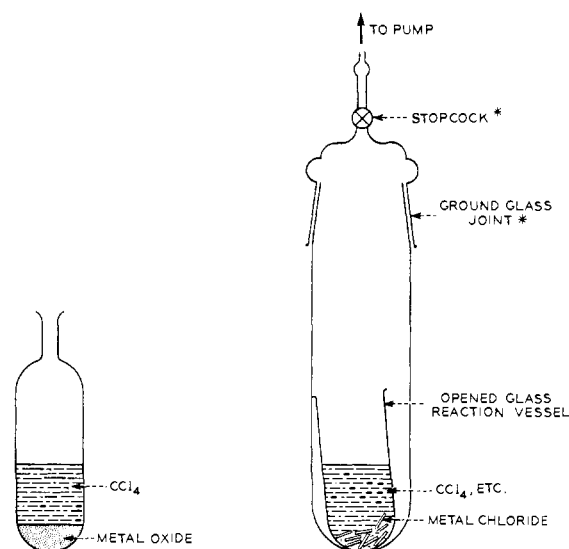


Fig. 1 (Left).—Glass reaction vessel.

Fig. 2 (Right).—Container for removal of opened reaction vessel to dry-box. *The best grease to use here is holocarbon chemically inert stopcock grease, obtainable from Holocarbon Products Corp., 2012–88th St., North Bergen, N. J.

adding concentrated hydrochloric acid and evaporating a few times. Then tetraphenylarsonium perchlorate is precipitated and weighed according to the method previously described for perchlorate analysis.⁶ The results on several preparations are

% Re (theory 51.24)	% Cl (theory 48.76)	Cl/Re
51.69	47.90	4.87
50.85	48.25	4.99
51.61	48.12	4.90
51.59	48.17	4.91

Technetium Tetrachloride.—This synthesis is exactly the same as that for rhenium; 0.14 g. of Tc gave 0.27 g. of TcCl_4 , 79%. The product is, in this case, small blood-red crystals. The analytical procedure is essentially the same, except that considerable Tc is lost for some unknown reason upon evaporation with concentrated HCl, and so this step is omitted. In addition, the halo-complexes of Tc are more easily hydrolyzed than those of Re, and so ammonia can be used as the base for the dissolution of the chloride. Thereby, only a small amount of nitric acid is needed after evaporation, and so no interference occurs in the precipitation of tetraphenylarsonium pertechnetate.⁷ The technetium is easily recovered as the metal from the analytical precipitate in quantitative yield by reduction in hydrogen according to a method described for the reduction of ammonium perchlorate.⁸ The results of triplicate analyses on two different preparations are

% Tc (theory 41.09) ⁹	% Cl (theory 58.91)	Cl/Tc
41.00	58.00	3.95
41.28	58.91	3.98

Molybdenum Pentachloride.—In this case a weighed amount of reagent grade MoO_3 is placed directly into the reaction vessel, CCl_4 is added, and the synthesis is carried out as above; in one synthesis, 5.1 g. of MoO_3 gave 8.1 g. of

(6) C. S. Patterson, S. Y. Tyree, Jr., and K. Knox, *This Journal*, **77**, 2195 (1955).

(7) Elision of the -et- in naming technetium anions is recommended for consistency with the names of the parent acids, such as pertechnic acid. As with molybdenum, the names of the anions and particularly of the acids are then much easier to pronounce.

(8) L. C. Hurd and E. Brimm, *Inorg. Syntheses*, **1**, 177 (1939).

(9) The mass spectroscopic chemical atomic weight of 98.913 is used for Tc: M. G. Inghram, D. C. Hess, Jr., and R. J. Hayden, *Phys. Rev.*, **72**, 1269 (1947).

MoCl₅, 85%. The product is large, very dark-colored crystals under a brown solution. Again the yield is nearly quantitative, indicative of very modest solubility in CCl₄ at room temperature. Upon sucking the crystals dry during the washing procedure in the dry box, color changes are observed on the surface of the crystals. The dry box used in this Laboratory is flushed with nitrogen which is bubbled through alkaline pyrogallol prior to drying. Since the surface to volume ratio of the crystals is so small, chemical changes manifested by these color changes are not judged to be appreciable. However, the largest deviations from stoichiometry are observed in the cases of rhenium and molybdenum pentachlorides. It is significant that no color changes are observed in handling TcCl₅, WCl₆, TaCl₅ and FeCl₃ under identical circumstances.

For analysis, samples are dissolved in 0.01 M KOH to which a little hydrogen peroxide has been added. The resulting solutions are analyzed for molybdenum by the molybdate method, ultimately weighing as PbMoO₄. The chloride content of separate samples is determined gravimetrically also, as AgCl. The results on one preparation are

% Mo (theory 35.12)	% Cl (theory 64.88)	
35.46	64.63	
35.47	64.63	
35.38	64.59	
Av. 35.44	Av. 64.62	Cl/Mo = 4.93

Tungsten Hexachloride.—Reagent grade tungsten(VI) oxide is used as starting material; in one synthesis, 6.8 g. of WO₃ gave about 10 g. of WCl₆, 86%. Large crystals of WCl₆ are obtained which are so dark as to appear black beneath a dark reddish liquid. Samples prepared by this method are not easily soluble in water, as reported of the direct synthesis product¹⁰; nor are they very soluble in CCl₄ at room temperature. It is observed that digestion with hot, aqueous ammonia for one hour is necessary to dissolve completely samples of WCl₆ prepared by this procedure.

For analysis, samples of about 275 mg. are weighed in the dry box and dissolved, after removal, by digestion in aqueous ammonia. The solutions are neutralized to a pH between 2 and 4 with nitric acid and titrated potentiometrically for chloride content, using a silver electrode with a calomel reference electrode. Samples of about 1 gram are weighed directly into platinum crucibles for the W determinations. After removal from the dry box the samples are metathesized by digestion with concentrated aqueous ammonia, carefully evaporated to dryness, ignited at 800°, and weighed as WO₃. The results on one preparation are

% W (theory 46.37)	% Cl (theory 53.63)	
46.17	53.43	
46.22	53.54	
46.35	53.52	
Av. 46.25	Av. 53.50	Cl/W = 6.000

Tantalum Pentachloride.—Reagent Ta₂O₅ is converted to TaCl₅ as above. The product is white crystals, in agreement with the color of the pure preparations of Alexander and Fairbrother¹¹ and contrary to the yellow color previously reported.¹² The supernatant liquid is yellow, due to dissolved chlorine and phosgene (CCl₄ alone turns yellow under these conditions), but the solid is white when filtered, washed and dried.

For analysis, samples of a few hundred milligrams are weighed out in a dry-box and treated with a large excess of water. The tantalum precipitation is completed by ammonia, the precipitate ignited and weighed as Ta₂O₅. Chloride is determined gravimetrically or potentiometrically as AgCl. Analysis of two samples of one preparation gave

% Ta (theory 50.51)	% Cl (theory 49.49)	Cl/Ta
50.88	49.17	4.93
50.79	49.46	4.97

(10) M. H. Lietzke and M. L. Holt, *Inorg. Syntheses*, **3**, 163 (1950).

(11) K. M. Alexander and F. Fairbrother, *J. Chem. Soc.*, S223 (1949).

(12) See *e.g.*, N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford Univ. Press, London, 1950, p. 847.

Other Metal Halides.—The method is of wider applicability than the few syntheses reported here indicate. The extensive studies of Camboulives,¹³ of Michael and Murphy,⁸ and of many others, indicate that many metal oxides are converted to chlorides by CCl₄ under a variety of conditions. In fact, we have reacted a number of other oxides with CCl₄ under these conditions, but we have not analyzed all the products yet nor, in some cases, obtained good looking products, and so only qualitative observations on other metals will be reported now.

Iron(III) oxide reacts easily and completely to give large flat dark green plates that are very probably pure FeCl₃; some of the smaller crystals exhibit dichroism, being reddish brown by transmitted light.

Zirconium oxide gives white needles without any finely powdered oxide residue visible. The crystals are expected to be ZrCl₄.

Beryllium oxide appears to be completely converted also, since the finely powdered oxide is replaced entirely by white crystals.

Vanadium(V) oxide yields liquid products only; a red liquid phase under a yellow vapor appeared in the tube. From the color and the phase, it is expected that the product is VCl₄. Its separation from the excess CCl₄ would involve a fractional distillation under anhydrous conditions.

For refractory oxides the extent of reaction is quite sensitive to the history of the oxide. It appears that the activated oxides, that is, those precipitated as hydrous oxides and ignited at low temperature, will react, whereas they become inert when ignited to high temperature. Activated Al₂O₃ reacted completely to give large crystals with no residual oxide powder. Highly ignited Al₂O₃, on the other hand, gave a few small crystals but the bulk of the product was identical in appearance with the original oxide. With Nb₂O₅, two solids were present; one consisted of nice yellow needles which, when picked out, analyzed close to NbCl₅, while the other was a button of white powder which was largely, but not completely, converted to hydrous Nb₂O₅ by water. It is peculiar that we have found Ta₂O₅ more reactive to CCl₄ than Nb₂O₅, contrary to previous experience.¹⁴ The Nb case is complicated by dimorphism,¹¹ and it may be that both the low and high temperature phases of NbCl₅ were present.

For the oxides of metals with relatively non-volatile chlorides (we have made preliminary investigations on ZnO, La₂O₃, and ThO₂), a few crystals usually are produced, but the oxide appears not to have reacted completely. The material is always partially water-soluble after reaction but never completely so.

Cobalt and nickel oxides did not appear to react at all.

Preliminary experiments have also been carried out on the preparation of bromides by a similar technique. Carbon tetrabromide and bromoform have been used primarily as the brominating agents. A considerable amount of free bromine is produced in the reaction. After washing with CCl₄, however, products were obtained which analyzed close to ReBr₃ and FeBr₃.

Work is continuing in this Laboratory on the wider applicability of the method.

Discussion

The Method.—There are several advantages of this method of preparing anhydrous chlorides, when applicable, over other procedures. Oxides of the metals are generally available or easily made in pure form. The reagents need not be excessively dry because small amounts of water are converted to COCl₂ and HCl, which are easily removed from the product. Manipulation of the starting materials, except the hygroscopic Tc₂O₇ and Re₂O₇, is easy, and the subsequent operations are not difficult when a dry-box is available. The conversion is complete and the only losses are manipulative ones. In most cases rather large crystals are formed which then tend to be quite pure and are relatively insensitive to hydrolysis by virtue of their small surface to volume ratio.

(13) P. Camboulives, *Compt. rend.*, **150**, 175 (1910).

(14) Ref. 12, pp. 838, 847.

The method is especially valuable for those metals which have volatile oxychlorides, such as Nb, Ta, Mo, W, Tc and Re, thereby requiring repeated sublimation of the chloride to free it from oxychloride even when the preparation is begun with "pure" metal.

It appears to be the method of choice for Tc since direct synthesis and other methods do not work.¹⁵ In fact, interest in the method was greatly stimulated by the search for a means of synthesizing technetium chloride in pure form.

Technetium Tetrachloride.—Since previous work and these experiments prove that this reaction gives the highest known chloride of the metal in question (*cf.* MoCl₆, WCl₆, ReCl₆, etc.), it is of interest that technetium forms a tetrachloride rather than a penta- or trichloride as rhenium does. In this respect it resembles manganese more than rhenium. The fact that technetium tetrachloride can be isolated in a pure state bears out its expected greater stability over manganese tetrachloride. Thus, technetium, whose oxides differ from those of rhenium only in degree,¹⁶ has a highest chloride which differs in kind from rhenium chlorides.¹⁷ When compared to the behavior of

(15) C. M. Nelson, G. E. Boyd and W. T. Smith, Jr., *THIS JOURNAL*, **76**, 348 (1954).

(16) W. T. Smith, Jr., J. W. Cobble and G. E. Boyd, *ibid.*, **76**, 5773, 5777, 5783 (1953).

(17) As pointed out by one referee, a higher chloride of Tc may later be found under conditions other than those of this experiment, maybe

the elements near Tc and Re in the periodic table, this reduced affinity of technetium for chlorine is not surprising on an empirical basis, as can be seen by considering the highest known anhydrous chlorides in this region

NbCl ₅	MoCl ₆	TcCl ₄	RuCl ₃
TaCl ₅	WCl ₆	ReCl ₆	OsCl ₄

The affinity for chlorine definitely falls off in going up as well as across the periodic table. The fluorides of these metals follow a similar pattern. To our knowledge, no satisfactory explanation has been given for the general phenomenon; stereochemical grounds alone are not sufficient.¹⁸ We have none to offer, and regard the question as one of the interesting unsolved problems in inorganic chemistry.

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"as a constituent of the vapor phase or perhaps even as a solid at lower temperatures and higher chlorine pressures." Except for MnCl₄, the discussion refers to the highest chlorides stable at room temperature with no excess chlorine gas present. They are, in all the cases cited, the highest known chlorides under any condition thus far studied.

(18) Ref. 12, pp. 1301-1302.

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Complexes Formed between Copper(II) Ion and N,N,N',N'-Tetrakis-(2-hydroxypropyl)-ethylenediamine^{1,2}

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The compound N,N,N',N'-tetrakis-(2-hydroxypropyl)-ethylenediamine, "Quadrol" (abbreviated "Q"), reacts with copper(II) ion in aqueous solution to form the complex ion CuQ⁺². This ion reacts further with Quadrol to form Cu(Q-H⁺)⁺¹, and reacts with strong base to form successively, Cu(Q-H⁺)⁺¹ and Cu(Q-2H⁺)⁰. The ions CuQ⁺² and Cu(Q-H⁺)⁺¹ have distinctly different absorption maxima in the vicinity of 700 mμ in the visible region but the two have nearly identical absorption maxima at about 280 mμ in the ultraviolet region. The ion CuQ⁺² may be considered as a dibasic acid in solution and as such gives successive dissociation constants of 1.41 × 10⁻⁷ and 8.92 × 10⁻⁹. The formation constant for formation of CuQ⁺² from Cu⁺² and Q is of the order of 10⁹.

Introduction

This paper reports a study of the complexes of copper(II) ion with the compound N,N,N',N'-tetrakis-(2-hydroxypropyl)-ethylenediamine, "Quadrol" (abbreviated "Q"), with and without additional strong base added to the solutions. In the Quadrol molecule the nitrogen atoms and the hydroxyl radicals are in favorable position for the formation of stable five-membered chelate rings. The hydroxyl radicals of the Quadrol have nearly negligible acidic properties in solution in water

but become appreciably acidic whenever the hydroxyl radical becomes a part of the chelate ring. These complexes have been investigated in aqueous solution by spectrophotometric methods and by potentiometric and conductometric titrations.

Experimental

The Quadrol was a gift of the Wyandotte Chemicals Corporation, and was designated as being at least 99.5% pure, the principal impurity being water. It was used without further purification. The concentration of the solutions as determined by titration with acid corresponded very closely to the concentration calculated from the weight of Quadrol used. The pure Quadrol and its dilute solutions are quite stable toward change on contact with the atmosphere. An 0.5 M solution, stored in contact with air, developed a slight yellow color after a few months.

Carbonate-free sodium hydroxide solutions and solutions of hydrochloric, nitric and perchloric acids were prepared from reagent-grade stock and were standardized by the usual methods. Sodium perchlorate was prepared by neutraliza-

(1) The work upon which this paper is based was sponsored, in part, by the Office of Ordnance Research, U. S. Army.

(2) Presented before the Division of Physical and Inorganic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, Sept. 17 to 21, 1956.

(3) Abstracted, in part, from M.S. theses presented at West Virginia University by Charles W. McWilliams, 1955, and F. Robert Jones, 1956.