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### HALIDES AND OXYHALIDES OF THE EARLY TRANSITION SERIES AND THEIR STABILITY AND REACTIVITY IN NONAQUEOUS MEDIA

### By R. A. Walton

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### I. INTRODUCTION

This chapter surveys the reactivities of halides and oxyhalides of the early transition series (titanium, vanadium, and chromium subgroups) and rhenium in nonaqueous media, and it is shown that these systems undergo a fascinating variety of reactions with a wide range of donor molecules. We shall devote most of our attention to the chlorides, bromides, and iodides because these are the halides that generally exhibit the greatest variation in behavior. Fluorides are briefly mentioned, but since they have been the subject of several review articles in recent years (25, 518, 584) we discuss only a few select examples dealing with the more recent and important aspects of their reactivity.

In view of the wealth of data now available in the literature, no attempt is made to present a comprehensive literature review. Rather, examples have been chosen to illustrate specific reactivity patterns and trends.

There are three main reasons for restricting this

chapter to the halides of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, and rhenium. First, many of the halides and oxyhalides of groups IV, V, and VI show a marked sensitivity toward oxygen and moisture and consequently require similar handling techniques. This sensitivity in turn reflects both the lability of the metal-haloger. bond to solvolysis and the tendency of these metals to form strong metal-oxygen bonds via oxygen insertion. reactions involving the halides. Second, it is in this area of the periodic table that chlorine and bromine stabilize a wide range of oxidation states for certain of the transition elements. For example, molybdenum forms chlorides in all the oxidation states, ranging from VI to II; these compounds are well characterized and their reactivities have been extensively Likewise, the oxychlorides MoO<sub>2</sub>Cl<sub>2</sub>, MoOCl<sub>4</sub>, MoOCl<sub>2</sub>, MoOCl<sub>2</sub>, and MoOCl are all well documented. On the other hand, related chlorides and oxychlorides of the other transition elements (e.g., the platinum metals) are much more limited, many are poorly characterized, and often they show little reactivity. Thus we have an opportunity to follow reactivity trends in closely related series of halides as the oxidation state is changed.

Finally, it is apparent that change in the oxidation state of a metal halide is accompanied by striking structure changes. There is indeed an intriguing diversity of structure types, ranging from simple monomeric TiCl<sub>4</sub> and WCl<sub>6</sub> to polynuclear cluster halides such as Nb<sub>3</sub>Cl<sub>8</sub>, Mo<sub>6</sub>Cl<sub>12</sub>, and Nb<sub>6</sub>Cl<sub>14</sub>. The relationships between structure and reactivity are particularly interesting, and are one of the aspects covered in this chapter. In view of the close similarity of the chemistry of the rhenium halides to those of molybdenum and tungsten, it is appropriate for us to include the halides of rhenium in this review.

### A. General Considerations

Most metal halides have polymeric structures in the solid and liquid states, but several are monomeric (e.g., TiClu, VClu, WF6, WCl6) and others are of the cluster type, wherein a finite number of metal atoms are held together by metal-metal bonds. If we define the latter class of compounds along the lines proposed by Cotton (180), as "those containing a finite group of metal atoms which are held together entirely, mainly, or at least to a significant extent, by bonds directly between the metal atoms even though some nonmetal atoms may be associated intimately with the cluster," then we can conveniently classify metal halides as being of the cluster type or otherwise. certain reactivity differences exist between these two general structural classes, let us discuss them separately. Tables I to III list the halides that are

pertinent to this chapter; Tables I and II contain the halides and oxyhalides that do not possess cluster structures, whereas Table III lists the halide phases that do. No oxyhalides are yet known to possess a cluster structure.

Since we do not intend to describe in detail the preparations of the halides, reference is made to the texts by Colton and Canterford (118, 166), and several recent review articles (176, 218, 271, 292) that survey the synthetic routes available for the preparation of many of these halides and oxyhalides; these articles also contain most of the pertinent literature references.

The variety of mixed halides and oxyhalides which are known do not appear in Tables I and II, principally because for the most part their reactivities have not been thoroughly investigated. However, it is important to realize that they can be readily prepared and, although their existence is not particularly remarkable, many are rather interesting species. Among the mixed halides and oxyhalides that have recently been prepared are  $[MCl_nF_{5-n}]$  (M = Nb or Ta) (439, 525), cis- and trans- $WCl_2F_4$  (341),  $MoBrF_4$  (484),  $TiBrF_3$  (446),  $WOBrCl_3$  (69),  $WOBr_2Cl_2$ , and  $W_2O_2Br_3Cl_3$  (427).

There are generally numerous methods available for the synthesis of the oxyhalides listed in Table II

TABLE I

Noncluster Halides of the Early Transition Series and Rhenium

Titanium	Zirconium	Hafnium
TiFt, TiF3	ZrF4, ZrF3, ZrF2	HEFL
TiCl4, TiCl3, TiCl2	ZrClu, ZrCl3, ZrCl2, ZrCl	HfCl $_{\mu}$ , HfCl $_{3}$ , HfCl
TiBr4, TiBr3, TiBr2	ZrBru, ZrBr3, ZrBr2	HfBr <sub>μ</sub> , HfBr <sub>3</sub> , HfBr <sub>2</sub>
TiIt, TiI3, TiI2	ZrI4, ZrI3, ZrI2	Hflu, Hfl3
Vanadium	Niobium	Tantalum
VF5, VF4, VF3, VF2	· NDF5, NDF4	TaF5
VCl4, VCl3, VCl2	NbCl <sub>5</sub> , NbCl <sub>4</sub>	TaCls, TaClu
VBru, VBr3, VBr2	NDBr <sub>5</sub> , NDBr <sub>4</sub>	TaBrs, TaBru
VI4, VI3, VI2	Nb15, Nb14	Tals, Talu

Tungsten	WF6, WF5, WF4	WBr6, WBr5, WBr4	Wit, Wis	Rhenium	ReF7, ReF6, ReF5, ReF
Molybdenum	MoF6, MoF5, MoF4, MoF3 WF6, WF5, WF4 MoC167, MoC15, MoC14, MoCl3 WC16, WC15, WC14	MoBru, MoBra	MoI3		
Chromium	CrF6, CrF5, CrF4, CrF3, CrF2 MOF6, MOF5, MOF4, MOF3 CrCl4, CrCl3, CrCl2 MOC167, MOC15, MOC14, N	CrBr3, CrBr2	CrI3, CrI2		

The reaction of ReF with BCl3, PCl3, and  $CCl_{\psi}$  affords ReCl6 and the appropriate non-metal fluoride [J. H. Canterford, T. A. O'Donnell and A. B. Waugh, Austral. An improved preparative procedure has recently been developed for this halide.

Recle, Recls, B-Reclu

ReBr<sub>5</sub>, ReBr<sub>4</sub> ReI<sub>4</sub>, ReI<sub>2</sub>?, ReI

J. Chem., 24, 243 (1971)].

# PABLE II

Oxyhalides of the Early Transition Series and Rhenium	
and	-
Series	
Transition	•
Early	
the	
of	
Oxyhalides	,
÷	

Titanium	Zirconium	Hafnium
TiOF2, TiOF		
Tiocl2, Tiocl	zroc12	
TiOBr2		
Tiol2, Tiol		
Vanadium	Niobium	Tantalum
VOF 3, VO,F, VOF , VOF	NbOF3, a NbO2F	racF3, TaC2F
VOC13, VO2C1, VOC12, VOC1	Nbocl3, Nbo2cl, Nbocl2	raccl3, rac2cl, raccl
VOBr3, VOBr2	Nbobr 3	TaOBr3
	NbOI3, NbO2I, NbOI2	$\mathtt{TaO}_2\mathtt{I}$
		ı

Chromium	Molybdemun	Tungsten
CrO2F2, CrOF4	MOOF4, MOO2F2	WOF4, WO2F2, WOF2
CrO2Cl2, CrOCl3, CrOCl	MOOCI <sub>4</sub> , MOO <sub>2</sub> Cl <sub>2</sub> , MOOCl <sub>3</sub> ,	WOC14, WO2C12, WOC13,
	MoO <sub>2</sub> C1, MoOC1 <sub>2</sub>	WO2C1, d WOC12
${\tt CrO_2Br_2}$ , croBr	MoO <sub>2</sub> Br <sub>2</sub> , MoOBr <sub>3</sub>	WOBIL, WO2BI2, WOBI3,
		WOBr <sub>2</sub>
		WO2I2
		Rhenium
		ReOF5, ReO2F3, ReO3F,
		ReOFu, C REOF3
		ReO3Cl, ReOCl4
		ReO3Br, ReOBru, ReOBr3
Not yet fully characterized as definite contremally unstable below room temperature.  Thermally unstable below room temperature.  Isostructural with MoOF4.  It has recently been claimed that MoO <sub>2</sub> Cl a chloride reduction of MO <sub>2</sub> Cl <sub>2</sub> according to the SnCl4. However, the analytical data report satisfactory [S. S. Eliseev, I. A. Glukhov, Chem., 15, 1158 (1970)].	Anot yet fully characterized as definite compounds.  Compared the state of MO <sub>2</sub> Cl and WO <sub>2</sub> Cl can be prepared by the tin(II) chloride reduction of MO <sub>2</sub> Cl <sub>2</sub> according to the equation 2MO <sub>2</sub> Cl <sub>2</sub> + SnCl <sub>2</sub> + 2MO <sub>2</sub> Cl + SnCl <sub>4</sub> . However, the analytical data reported for these two oxyhalides are not very satisfactory [S. S. Eliseev, I. A. Glukhov, and N. V. Gaidaenko, Russ. J. Phorg. Chem., 15, 1158 (1970)].	be prepared by the tin(II) 2MO <sub>2</sub> Cl <sub>2</sub> + SnCl <sub>2</sub> + 2MO <sub>2</sub> Cl + two oxyhalides are not very aidaenko, Russ. J. Inorg.

TABLE III

Anhydrous Cluster Halides of the Early
Transition Series and Rhenium

Niobium	Tantalum
Nb <sub>6</sub> F <sub>15</sub>	
Nb3Cl8, Nb6Cl14	Ta <sub>6</sub> Cl <sub>15</sub> , Ta <sub>6</sub> Cl <sub>14</sub>
Nb <sub>3</sub> Br <sub>8</sub>	Ta <sub>6</sub> Br <sub>15</sub> , Ta <sub>6</sub> Br <sub>14</sub>
$Nb_{3}I_{8}$ , $Nb_{6}I_{11}$	Ta <sub>6</sub> I <sub>14</sub>
Molybdenum	Tungsten
Mo <sub>6</sub> Cl <sub>12</sub>	W <sub>6</sub> Cl <sub>18</sub> , W <sub>6</sub> Cl <sub>12</sub>
No <sub>6</sub> Br <sub>12</sub>	W <sub>6</sub> Br <sub>18</sub> , W <sub>6</sub> Br <sub>16</sub> , W <sub>6</sub> Br <sub>14</sub> , W <sub>6</sub> Br <sub>12</sub>
Mo <sub>6</sub> I <sub>12</sub>	$W_6I_{15}$ , $W_6I_{12}$
	Rhenium
	Re <sub>3</sub> Cl <sub>9</sub>
	Re <sub>3</sub> Br <sub>9</sub>
	Re3I9

Two different clusters have this composition, namely, [W6Br8]Br2(Br4)4/2 and [W6Br12]Br6.

(218); these procedures range from the halogenation of the oxides to the carefully controlled reaction of the halides with oxygen and oxygen-containing compounds. Equations 1 through 10 illustrate several such preparative routes which have been used to prepare certain representative oxyhalides.

(Refs. 169, 170) 
$$MO_3 + SOCl_2 \xrightarrow{reflux} MOCl_4$$
  
where M = Mo or W (1)

Halides and Oxyhalides of Early Transition Series 11

(Ref. 169) Mo + Br<sub>2</sub> + O<sub>2</sub> 
$$\frac{\text{ca. } 250-300 °C}{\text{flow system}}$$
 MoO<sub>2</sub>Br<sub>2</sub> (2)

(Ref. 613) 
$$W + 2WO_3 + 3I_2 \xrightarrow{\text{temperature}} 3WO_2I_2$$
 (3)

(Ref. 229) 
$$WO_3 + CCl_4 \xrightarrow{reflux} WOCl_4$$
 (4)

(Ref. 614) 
$$2W + WO_3 + 4.5Br_2 = \frac{\text{temperature}}{\text{gradient}} 3WOBr_3$$
 (5)

(Ref. 254) 
$$MoCl_5 + liquid SO_2 \longrightarrow MoOCl_3$$

(Ref. 305) 
$$WCl_6 + \text{liquid } SO_2 \longrightarrow WOCl_4$$
 (6)

(Ref. 212) 
$$2WX_6 + WO_3 \xrightarrow{\text{sealed tube}} 3WOX_4$$
  
 $WX_6 + 2WO_3 \xrightarrow{\text{sealed tube}} 3WO_2X_2$  (7)  
where  $X = C1$  or Br

(Refs. 209, 
$$3MX_5 + Sb_2O_3 \longrightarrow 3MOX_3 + 2SbX_3$$
 (8)  
485) where  $MX_5 = WCl_5$ ,  $WBr_5$ ,  $MoCl_5$ , or  $TaCl_5$ 

(Ref. 260) 
$$3\text{TiCl}_4 + \text{As}_2\text{O}_3 \longrightarrow 3\text{TiOCl}_2 + 2\text{AsCl}_3$$
 (9)

(Refs. 216, MCl<sub>4</sub> + gaseous Cl<sub>2</sub>O and/or 222) 
$$Cl_2O/CCl_4 \longrightarrow MOCl_2$$
 where M = Ti, Zr. (10)

The oxygen-abstraction reactions represented in Eqs. 6 through 10 demonstrate the ease with which transition metal halides in this area of the periodic table will abstract oxygen from a variety of simple oxygen-containing reagents. This behavior is quite general and, as we later see, it is also observed in

the reactions of several of these halides in oxygencontaining nonaqueous solvents. The high metaloxygen bond energies are clearly the driving force in
such reactions. However, although Eqs. 1 to 10 represent fairly general preparative procedures there are,
as might be expected, many exceptions to the rules.
Thus ReCl<sub>5</sub> does not react with liquid sulfur dioxide
to give ReOCl<sub>3</sub> (260), and vanadium(IV) chloride gives
a mixture of VCl<sub>3</sub> and VOCl<sub>3</sub>, rather than the expected
VOCl<sub>2</sub> (232). Both halides and oxyhalides can exhibit
polymorphism, and this may account for differences
between halides and oxyhalides prepared by different
routes. Thus a purple-black oxyhalide believed to be
WOCl<sub>2</sub> has been prepared by thermal decomposition of
WOCl<sub>3</sub> (209, 483)

$$2WOCl_3 \xrightarrow{\Delta} WOCl_2 + WOCl_4$$
 (11)

This same halide, nevertheless, has been reported to be prepared as golden-brown crystals by the stannous chloride reduction of WOCl<sub>4</sub>, followed by sublimation at 500°C (267), and by the reaction

$$W + WO_3 + WCl_6 - 3WOCl_2$$
 (12)

from which WOCl<sub>2</sub> can be obtained in crystalline form by chemical transport (616). X-Ray powder diffraction data for these various products are not in particularly good agreement (209, 267, 616), although it has been claimed (209, 483, 616) that WOCl<sub>2</sub> and MoOCl<sub>2</sub> (561)