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Contents

v

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

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I. INTRODUCTION

This chapter surveys the reactivities of halides
and oxyhalides of the early transition series (titan-
ium, 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 be-
cause 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 compre-
hensive 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-halogen 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 studied. Likewise, the oxychlorides MoO_2Cl_2, $MoOCl_4$, $MoOCl_3$, $MoOCl_2$, 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 $TiCl_4$ and WCl_6 to polynuclear cluster hal-
ides such as Nb_3Cl_8, Mo_6Cl_{12}, and Nb_6Cl_{14}. The rela-
tionships between structure and reactivity are particu-
larly 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., $TiCl_4$, VCl_4, WF_6, WCl_6) 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 non-
metal atoms may be associated intimately with the
cluster," then we·can conveniently classify metal hal-
ides as being of the cluster type or otherwise. Since
certain reactivity differences exist between these two
general structural classes, let us discuss them. sep-
arately. 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 sur-
vey the synthetic routes available for the preparation
of many of these halides and oxyhalides; these arti-
cles 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, princi-
pally 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 re-
cently 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
TiF_4, TiF_3	ZrF_4, ZrF_3, ZrF_2	HfF_4
$TiCl_4$, $TiCl_3$, $TiCl_2$	$ZrCl_4$, $ZrCl_3$, $ZrCl_2$, $ZrCl$	$HfCl_4$, $HfCl_3$, $HfCl$
$TiBr_4$, $TiBr_3$, $TiBr_2$	$ZrBr_4$, $ZrBr_3$, $ZrBr_2$	$HfBr_4$, $HfBr_3$, $HfBr_2$
TiI_4, TiI_3, TiI_2	ZrI_4, ZrI_3, ZrI_2	HfI_4, HfI_3

Vanadium	Niobium	Tantalum
VF_5, VF_4, VF_3, VF_2	NbF_5, NbF_4	TaF_5
VCl_4, VCl_3, VCl_2	$NbCl_5$, $NbCl_4$	$TaCl_5$, $TaCl_4$
VBr_4, VBr_3, VBr_2	$NbBr_5$, $NbBr_4$	$TaBr_5$, $TaBr_4$
VI_4, VI_3, VI_2	NbI_5, NbI_4	TaI_5, TaI_4

6

Chromium	Molybdenum	Tungsten	Rhenium
CrF_6, CrF_5, CrF_4, CrF_3, CrF_2	MoF_6, MoF_5, MoF_4, MoF_3	WF_6, WF_5, WF_4	ReF_7, ReF_6, ReF_5, ReF_4
$CrCl_4$, $CrCl_3$, $CrCl_2$	$MoCl_6$?, $MoCl_5$, $MoCl_4$, $MoCl_3$	WCl_6, WCl_5, WCl_4	$ReCl_6$,[a] $ReCl_5$, β-$ReCl_4$
$CrBr_3$, $CrBr_2$	$MoBr_4$, $MoBr_3$	WBr_6, WBr_5, WBr_4	$ReBr_5$, $ReBr_4$
CrI_3, CrI_2	MoI_3	WI_4, WI_3	ReI_4, ReI_2?, ReI

[a] An improved preparative procedure has recently been developed for this halide. The reaction of ReF_6 with BCl_3, PCl_3, and CCl_4 affords $ReCl_6$ and the appropriate non-metal fluoride [J. H. Canterford, T. A. O'Donnell and A. B. Waugh, Austral. J. Chem., 24, 243 (1971)].

TABLE II

Oxyhalides of the Early Transition Series and Rhenium

Titanium	Zirconium	Hafnium
$TiOF_2$, $TiOF$	$ZrOCl_2$	
$TiOCl_2$, $TiOCl$		
$TiOBr_2$		
$TiOI_2$, $TiOI$		

Vanadium	Niobium	Tantalum
VOF_3, VO_2F, VOF_2, VOF	$NbOF_3$,[a] NbO_2F	$TaOF_3$,[a] TaO_2F
$VOCl_3$, VO_2Cl, $VOCl_2$, $VOCl$	$NbOCl_3$, NbO_2Cl, $NbOCl_2$	$TaOCl_3$, TaO_2Cl, $TaOCl_2$
$VOBr_3$, $VOBr_2$	$NbOBr_3$	$TaOBr_3$
	$NbOI_3$, NbO_2I, $NbOI_2$	TaO_2I

Chromium	Molybdenum	Tungsten
CrO_2F_2, $CrOF_4$	$MoOF_4$, MoO_2F_2	WOF_4, WO_2F_2, WOF_2
CrO_2Cl_2, $CrOCl_3$, $CrOCl$	$MoOCl_4$, MoO_2Cl_2, $MoOCl_3$,	$WOCl_4$, WO_2Cl_2, $WOCl_3$,
	MoO_2Cl, $MoOCl_2$	WO_2Cl,[d] $WOCl_2$
CrO_2Br_2,[b] $CrOBr$	MoO_2Br_2, $MoOBr_3$	$WOBr_4$, WO_2Br_2, $WOBr_3$,
		$WOBr_2$
		WO_2I_2

Rhenium		
$ReOF_5$, ReO_2F_3, ReO_3F,		
$ReOF_4$,[c] $ReOF_3$		
ReO_3Cl, $ReOCl_4$		
ReO_3Br, $ReOBr_4$, $ReOBr_3$		

[a] Not yet fully characterized as definite compounds.
[b] Thermally unstable below room temperature.
[c] Isostructural with $MoOF_4$.
[d] It has recently been claimed that MoO_2Cl and WO_2Cl can be prepared by the tin(II) chloride reduction of MO_2Cl_2 according to the equation $2MO_2Cl_2 + SnCl_2 \rightarrow 2MO_2Cl + SnCl_4$. 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. Inorg. Chem.*, 15, 1158 (1970)].
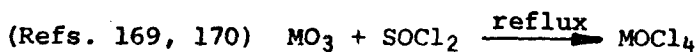
9

R. A. Walton

TABLE III

Anhydrous Cluster Halides of the Early
Transition Series and Rhenium

Niobium	Tantalum
Nb_6F_{15}	
Nb_3Cl_8, Nb_6Cl_{14}	Ta_6Cl_{15}, Ta_6Cl_{14}
Nb_3Br_8	Ta_6Br_{15}, Ta_6Br_{14}
Nb_3I_8, Nb_6I_{11}	Ta_6I_{14}

Molybdenum	Tungsten
Mo_6Cl_{12}	W_6Cl_{18}, W_6Cl_{12}
Mo_6Br_{12}	W_6Br_{18},[a] W_6Br_{16}, W_6Br_{14}, W_6Br_{12}
Mo_6I_{12}	W_6I_{15}, W_6I_{12}

	Rhenium
	Re_3Cl_9
	Re_3Br_9
	Re_3I_9

[a]Two different clusters have this composition, namely,
$[W_6Br_8]Br_2(Br_4)_{4/2}$ and $[W_6Br_{12}]Br_6$.

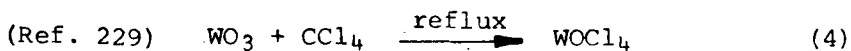(218); these procedures range from the halogenation of
the oxides to the carefully controlled reaction of the
halides with oxygen and oxygen-containing compounds.
Equations 1 through 10 illustrate several such prepar-
ative routes which have been used to prepare certain
representative oxyhalides.

$$(Refs. 169, 170) \quad MO_3 + SOCl_2 \xrightarrow{\text{reflux}} MOCl_4$$

$$\text{where } M = Mo \text{ or } W \tag{1}$$

(Ref. 169) $Mo + Br_2 + O_2 \xrightarrow[\text{flow system}]{\text{ca. } 250\text{-}300°C} MoO_2Br_2$ (2)

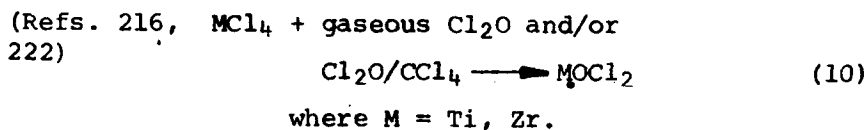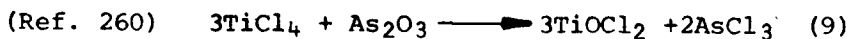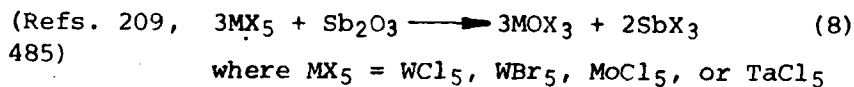(Ref. 613) $W + 2WO_3 + 3I_2 \xrightarrow[\text{gradient}]{\text{temperature}} 3WO_2I_2$ (3)

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

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

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

(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 = Cl 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) $3TiCl_4 + As_2O_3 \longrightarrow 3TiOCl_2 + 2AsCl_3$ (9)

(Refs. 216, $MCl_4 + \text{gaseous } Cl_2O \text{ and/or}$
222)
$Cl_2O/CCl_4 \longrightarrow MOCl_2$ (10)

where M = Ti, Zr.

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 oxygen-
containing nonaqueous solvents. The high metal-
oxygen bond energies are clearly the driving force in
such reactions. However, although Eqs. 1 to 10 repre-
sent fairly general preparative procedures there are,
as might be expected, many exceptions to the rules.
Thus $ReCl_5$ does not react with liquid sulfur dioxide
to give $ReOCl_3$ (260), and vanadium(IV) chloride gives
a mixture of VCl_3 and $VOCl_3$, rather than the expected
$VOCl_2$ (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
$WOCl_2$ has been prepared by thermal decomposition of
$WOCl_3$ (209, 483)

$$2WOCl_3 \xrightarrow{\Delta} WOCl_2 + WOCl_4 \tag{11}$$
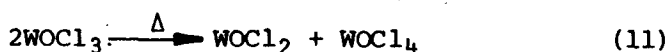
This same halide, nevertheless, has been reported to
be prepared as golden-brown crystals by the stannous
chloride reduction of $WOCl_4$, followed by sublimation
at 500°C (267), and by the reaction

$$W + WO_3 + WCl_6 \longrightarrow 3WOCl_2 \tag{12}$$
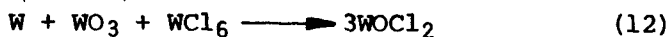
from which $WOCl_2$ can be obtained in crystalline form
by chemical transport (616). X-Ray powder diffraction
data for these various products are not in particu-
larly good agreement (209, 267, 616), although it has
been claimed (209, 483, 616) that $WOCl_2$ and $MoOCl_2$ (561)