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Reaction of Group V and VI Transition Metal Oxide and Oxyhydroxide Anions with O_2, H_2O, and HCl

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Abstract: Negatively charged oxides and oxyhydroxides of tantalum, niobium, vanadium, and tungsten were produced, and their properties and reactivity with O_2, HCl, and H_2O were investigated in a fast-flow reactor. Importantly, the oxyhydroxide anions of niobium and tantalum are found to undergo acid-base type reactions with HCl which bear analogy to those known to occur in the condensed phase; e.g., the Cl of HCl replaces an OH unit on the metal center and H_2O is given off as the neutral product. By contrast, in cases where there are no OH units bonded to the metal atom, HCl reacts to transform a bound oxygen atom into an OH unit, with the Cl unit becoming bonded to the metal center. Quantitative rate coefficients, ranging from about 10^{-9} to 10^{-11} cm^3 s^{-1}, were measured for each of four sequential additions of HCl to the individual niobium and tantalum systems. Interestingly, only the trioxide and pentoxide of niobium and tantalum undergo observable reactions with H_2O (to form the dioxydihydroxide ion), while reaction with O_2 ($k \approx 10^{-11}$–10^{-13} cm^3 s^{-1}), in general, occurs 2–3 orders of magnitude more slowly than the observable H_2O reactions. A reversible reaction is found between the pentoxide anion reacting with H_2O and the (product) dioxydihydroxide reacting with O_2, yielding equilibrium constant values of $K = 370$ and 48 for niobium and tantalum, respectively. Comparing the reaction rates demonstrates the influence of the electronic shell of the metal atom on reactivity, where the relative ease of the period six metals to accommodate additional ligands beyond those of the initial reactant contrasts with the decreased facility for period five metals.

I. Introduction

Currently, there is extensive interest in the chemistry of metal oxides, molecular aggregates, and nanosized particles and their ions.[1-15] Molecules of the oxides are formed in oxidation reactions, and nanosized particles and thin films produced from these find application in a number of areas ranging from catalysis to microelectronics.[16] Metal oxide species usually have high electron affinities[5,6] and are important as electron scavengers in high-temperature combustion and related oxidation reactions, a fact which has also prompted further interest in their behavior and reactions. Additionally, metal oxides and oxyhydroxides are important species formed in the corrosion of iron[1] and of other transition metals such as chromium, manganese tungsten, molybdenum, and niobium.[2]

In terms of basic chemistry, there is a paucity of information on the mechanisms of the conversions of species with low oxidation states to species with different states of oxidation, and especially the extent to which these anions may undergo reactions that may bear analogy to acid-base interactions known in the condensed phase. The present paper addresses the formation of negatively charged oxides and oxyhydroxides of transition metals (i.e., V, Nb, Ta, and W) and the nature and rate of their reactions with O_2, H_2O, and HCl. Attention is focused on reactions which lead to the interconversion of the oxides and oxyhydroxides and the effect of the core electronic shell and valence on the reactions.

II. Experimental Section

The reactions of the anions are investigated at room temperature with a flow tube apparatus, employing methods and analysis described in detail previously.[17] Ions are produced by a technique originally developed by Center[18,19] for the production of tungsten and rhenium oxide anions. In the present case, a small flow of O_2 is added to 150 STP cm^3 s^{-1} or 9000 sccm (1 sccm = 1 standard cubic centimeter per minute) of He and passed over an incandescent transition metal filament (composed of the pure metal), biased at 100–200 V. The present study focuses on metals of groups V and VI (i.e., tantalum, niobium, vanadium, and tungsten). Metal oxides are either emitted from the surface of the hot filament as anions or emitted as neutrals which undergo subsequent electron attachment reactions with electrons emitted simultaneously from the same filament. The reactant ions are thermalized by means of large numbers of collisions with the helium buffer gas and then are allowed to react with reactant gases (H_2O, O_2, or HCl) added about 50 cm downstream of the filament. Reaction with the reagent gas continues until the mixture reaches the sampling orifice about 70 cm downstream of the reactant gas inlet. The HCl used is standard lecture bottle gas, the O_2 is ultra-high-purity grade (99.99%), and the distilled H_2O is subjected to several freeze-pump-thaw cycles before use.

The oxide distributions of the various metals studied all have some ions which contain hydrogen. For niobium and tantalum oxides, these ions can originate from gas-phase reaction with H_2O as the intensity of the hydrogenated ions is enhanced by addition of H_2O downstream of the ion source. This is not the case for tungsten, as the intensity of hydrogenated ions is increased when water is added at the ion source but not when it is added downstream at the reactant gas inlet. Water is not purposely added unless its reaction is under direct investigation. Therefore, the small trace of H_2O needed to form the hydrogenated ions is likely to be present as an impurity in the relatively large quantity of helium flow gas that is passed directly over the hot filament, even though the helium is 99.99% pure and is dried just prior to use.

III. Results

A. Niobium, Tantalum, and Tungsten Oxide Anions: Reactions with O_2 and H_2O. 1. Investigations of Reaction Kinetics. Rate coefficients were determined for niobium, tantalum, and tungsten oxide anions reacting with O_2 and H_2O. These values are listed in Table I, along with the reaction efficiencies and the collision

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Table I. Niobium, Tantalum, and Tungsten Oxide Anion Rate Coefficients: Dioxygen and Water Reactions[c]

reactants	products	rate coefficient $k/\text{cm}^3\ \text{s}^{-1}$	collision rate $k_C/10^{-9}\ \text{cm}^3\ \text{s}^{-1}$	efficiency k/k_C
$NbO_3^- + O_2$	NbO_5^-	$3.5 \times 10^{-12\,b}$	0.578	0.0061
$NbO_3^- + H_2O$	$NbO_2(OH)_2^-$	$1.5 \times 10^{-9\,a}$	2.29	0.66
$NbO_2(OH)_2^- + O_2$	$NbO_5^- + H_2O$	$3 \times 10^{-13\,b}$	0.572	0.0005
$NbO_5^- + H_2O$	$NbO_2(OH)_2^- + O_2$	$1.1 \times 10^{-10\,a}$	2.27	0.048
$TaO_3^- + O_2$	TaO_5^-	$2.3 \times 10^{-11\,a}$	0.557	0.041
$TaO_3^- + H_2O$	$TaO_2(OH)_2^-$	$1.6 \times 10^{-9\,a}$	2.24	0.71
$TaO_2(OH)_2^- + O_2$	$TaO_5^- + H_2O$	$2.3 \times 10^{-12\,b}$	0.555	0.0041
$TaO_5^- + H_2O$	$TaO_2(OH)_2^- + O_2$	$1.1 \times 10^{-10\,a}$	2.23	0.049
$WO_3^- + O_2$	WO_5^-	$1.5 \times 10^{-11\,a}$	0.557	0.027
$WO_3^- + H_2O$	no reaction	$\leq 10^{-13}$	2.24	$\leq 5 \times 10^{-5}$
$WO_2(OH)_2^- + O_2$	$WO_5^- + H_2O$	$3 \times 10^{-11\,a}$	0.554	0.056
$WO_5^- + H_2O$	no reaction	$\leq 10^{-13}$	2.23	$\leq 5 \times 10^{-5}$

[a] Error estimated to be ±20‰. [b] Error estimated to be ±30%. [c] Measurements made under the following conditions: helium bulk flow rate (150 STP $cm^3\ s^{-1}$ or 9000 sccm), reaction pressure (0.32 Torr), ambient temperature; the various reaction times (time for ions to traverse the distance from the reactant gas inlet to the detector sampling orifice) were determined via ion pulsing techniques in the standard way.

rate coefficients calculated by the method of Su and Chesnavich.[20] Specifically, the prominent reactant ions are NbO_3^-, $NbO_2(OH)_2^-$, NbO_5^-, TaO_3^-, $TaO_2(OH)_2^-$, TaO_5^-, WO_3^-, $WO_2(OH)_2^-$, and WO_5^-. When O_2 is the reactant molecule, the following two reactions occur (illustrated here for niobium):

$$NbO_3^- + O_2 \rightarrow NbO_5^- \tag{1}$$

$$NbO_2(OH)_3^- + O_2 \rightarrow NbO_5^- + H_2O \tag{2}$$

When H_2O is the neutral reactant, the dioxydihydroxide anion is the product ion and the following two reactions are observed:

$$NbO_3^- + H_2O \rightarrow NbO_2(OH)_2^- \tag{3}$$

$$NbO_5^- + H_2O \rightarrow NbO_2(OH)_2^- + O_2 \tag{4}$$

The same reactions are observed for the corresponding tungsten and tantalum anions with the exception that the tungsten oxide ions do not react with water. The reactivity of HWO_3^- was also investigated, but it was found not to react with either H_2O or O_2.

The determined rate coefficients are derived from an analysis[17] of the reactant ion intensity as a function of the reactant neutral flow rate. The results are determined from the mass spectra by integrating the reactant ion peaks, making a background correction, and normalizing the resultant intensities. Since no atom or molecule is given off to remove the energy of reaction or association and thereby effect the stabilization of the product ion, all of the trioxide anion reactants presented in Table I are of necessity termolecular (with possible atomic rearrangement, bond breaking, and bond formation). At 0.32 Torr (and 298 K), it is only necessary to multiply the given effective second-order-rate coefficients by a factor of 1.0×10^{-16} to obtain the numerical value of the corresponding third-order-rate coefficients, but the effective bimolecular values are listed for comparison purposes. From eq 1–4 and Table I it is apparent that, for the experimental situation where both O_2 and H_2O are present simultaneously, the following three rate equations apply (where A represents a Nb, Ta, or W atom).

$$-d[AO_3^-]/dt = k_1[AO_3^-][O_2] + k_2[AO_3^-][H_2O] \tag{5}$$

$$-d[AO_2(OH)_2^-]/dt = k_3[AO_2(OH)_2^-][O_2] - k_2[AO_3^-][H_2O] - k_4[AO_5^-][H_2O] \tag{6}$$

$$-d[AO_5^-]/dt = k_4[AO_5^-][H_2O] - k_1[AO_3^-][O_2] - k_3[AO_2(OH)_2^-][O_2] \tag{7}$$

Here the k values represent bimolecular (or effective bimolecular) rate coefficients and the square brackets represent concentrations of the indicated species. It is obvious from these three equations that, when measuring the rate of reaction of either O_2 or H_2O with one of the metal oxide anions, the concentration of the other neutral reactant must be kept very low. This condition is met because the H_2O concentration is vanishingly small except when it is added as a reactant. This is also true for O_2, as only a very small flow of O_2 is added at the source to enable production of the reactant ions. Thus the H_2O reactions and the O_2 reactions each can be observed independently of the other. For the reactions with O_2 (for the case of niobium), NbO_3^- and $NbO_2(OH)_2^-$ are observed to decay in intensity, while there is a corresponding increase in the NbO_5^- intensity as given by eqs 1 and 2. A similar situation exists for the H_2O reactions, with the NbO_3^- and NbO_5^- intensities both undergoing simple decay while $NbO_2(OH)_2^-$ increases in intensity in accordance with eqs 3 and 4. The experiments are greatly simplified due to the pseudo-first-order reaction conditions (reactant neutral in great excess).

Note that WO_3^- and TaO_3^- react with O_2 at comparable rates to form the pertinent pentoxides, but that NbO_3^- has a corresponding rate coefficient that is an order of magnitude smaller (about $10^{-12}\ cm^3\ s^{-1}$); see Table I. This illustrates the relative ease of period of six metals (e.g., Ta and W) to accommodate extra ligands compared to the relatively decreased ability of period five metals (e.g., Nb) to undergo a similar reaction. Shell size certainly does appear to be a determining factor here as well as in the experiments with HCl (discussed later in this paper). Valence d-electron counting does not account for the findings, as the niobium and tantalum cases have the same electron count but quite different rates. Also the tungsten and tantalum cases have almost the same rate but different numbers of valence d-electrons. From niobium to tantalum to tungsten, the rate coefficients increase successively by an order of magnitude from about 10^{-13} to 10^{-12} and then to $10^{-11}\ cm^3\ s^{-1}$ for the reaction of $AO_2(OH)_2^-$ with O_2 to form AO_5^- and H_2O (where A represents a metal atom). Again this is a shell-size effect for niobium and tantalum, but for tungsten it may at least help demonstrate that tungsten has a high affinity for oxygen. Note that the rate coefficients for both the niobium and the tantalum cases are an order of magnitude smaller than those for the corresponding trioxide reaction with O_2. This is in contrast to the results for tungsten, where $WO_2(OH)_2^-$ reacts with O_2 about twice as fast as does the trioxide, WO_3^-. The instability of $WO_2(OH)_2^-$, relative to both WO_3^- and WO_5^-, is also shown by the lack of reaction between H_2O and either of WO_3^- or WO_5^- to form $WO_2(OH)_2^-$. Lane et al.[8] also observed that highly oxidized group VI transition metal anions (i.e., CrO_3^-, CrO_5^-, MoO_4^-, and MoO_5^-) tend to be unreactive and H_2O never adds in with the concomitant loss of O_2.

Considering the stability of $H_2WO_4^-$ (or $WO_2(OH)_2^-$) relative to $H_2NbO_4^-$ and $H_2TaO_4^-$, a simple argument suffices for gaining insight into its properties and behavior. In developing this argument, all hydrogens are considered to be contained in OH units which are bound to the metal atom, and all other oxygen atoms to be bound to the central metal with a double bond. That is, the structure is assumed to be representable by $W({=}O)_2(OH)_2^-$, which is compatible with the products of the reactions of HCl with these species. (Note that these structures are deduced from reaction mechanisms discussed in subsequent sections of the paper.) The formal charge for W in H_2WO_4 (i.e., $WO_2(OH)_2$) is 0, while the formal charge is −1 for both Nb in $NbO_2(OH)_2$ and

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[20] Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

Ta in $TaO_2(OH)_2$. For all other atoms in these compounds, the formal charge is 0. Thus, it would be expected that the set of favorable singly charged negative ions would include HWO_4^- for the case of tungsten and $H_2NbO_4^-$ for niobium (i.e., $W(=O)_3(OH)^-$ and $Nb(=O)_2(OH_2^-)$ because the formal charge on the metal is −1 in both situations. This is exactly what is observed, with both of these ions displaying high intensity in the mass spectrum for their respective systems.

It is interesting to note that NbO_4^{3-}, TaO_4^{3-}, and WO_4^{2-} are all found in the condensed phase.[15] Formal addition of one or two protons to these ions would give the species which are observed in the gas phase, i.e., $NbO_2(OH)_2^-$, $TaO_2(OH)_2^-$, and $WO_3(OH)^-$. Formal charges of −1 can be obtained for W in each of HWO_3, HWO_4, and HWO_5, given that the respective structures are $W(=O)_3(H)$, $W(=O)_3(OH)$, and $(\eta^2\text{-}O_2)W(=O)_2(OH)$, where $\eta^2\text{-}O_2$ is dihapto or sideways bound O_2. Assuming that the hydrogen of HWO_3^- is directly bound to the tungsten atom provides an explanation for the low reactivity of this ion with O_2. Similar reasoning reveals that there can be a formal charge of −1 on Nb for all the Nb (and Ta) species considered in this section, thereby requiring that there be six bonds to the group V transition metal atom. Structures that allow for the desired formal charge for NbO_3^-, NbO_4^-, $H_2NbO_4^-$, NbO_5^-, and $H_2NbO_5^-$ are $Nb(=O)_3$, $(\eta^2\text{-}O_2)Nb(=O)_2$, $Nb(=O)_2(OH)_2$, $(\eta^2\text{-}O_2)_2Nb(=O)$, and $(\eta^2\text{-}O_2)Nb(=O)(OH)_2$, respectively. Formal charge may indeed be a significant indicator of favorable structures for these anions, but there is not yet sufficient evidence to verify this postulation. Again it should be noted that the main arguments concerning the structure of $H_2NbO_4^-$ are presented in a later section of this paper.

For niobium and tantalum, H_2O reacts very rapidly on the order of 10^{-9} with both trioxide anions and about 10^{-10} cm^3 s^{-1} for both pentoxide anions. Thus, surprisingly a termolecular reaction (i.e., a reaction not involving the loss of a neutral molecule, i.e., NbO_3^- reacting with H_2O) is found which proceeds an order of magnitude faster than a related bimolecular reaction, i.e., NbO_5^- reacting with H_2O (refer to Table I). Indeed the trioxide reaction occurs at about 70% of the collisional rate and the pentoxide at only 5% of the corresponding rate. This is possibly a consequence of the fact that both reactions exhibit the same type and number of bonds being formed but differ in the number of bonds that dissociate. The reaction of the pentoxide anion with H_2O not only involves the necessary breaking of an H–OH bond but also requires the elimination of O_2 from the metal center. In general, adduct forming reactions described in this paper would be expected to require a third body to remove the excess reaction energy, even though extensive atomic rearrangement may occur.

2. Consideration of the O_2 and H_2O Reactions. From Table I it is apparent that the two bimolecular reactions listed for each metal system are simply the reverse of each other. These reactions can be represented by the following (A = W, Ta, or Nb):

$$AO_5^- + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} AO_2(OH)_2^- + O_2 \qquad (8)$$

For the set of reactions represented in eq 8, the equilibrium constant is given as follows

$$K = k_f/k_b = \exp(-\Delta G^\circ/RT) \qquad (9)$$

where ΔG° is the standard free energy change for the reaction. This equation, coupled with the rate data, gives K values of 370, 48, and ≤0.003 and ΔG° values of −3.5, −2.29, and ≥+3 kcal/mol for eq 8 in the case of Nb, Ta, and W, respectively. Of course the direction of reaction spontaneity is revealed by ΔG rather than ΔG°, and the preferential direction of reaction can be altered by adding either O_2 or H_2O. The reactions are conducted under pseudo-first-order conditions, which means that the concentration of the reactant neutral (either O_2 or H_2O) is in great excess relative to each of the reactant ion, the product ion, and the product neutral. Thus, for addition of (solely) either O_2 or H_2O, there should be essentially no reverse reaction, due to the infrequency with which a product ion contacts a product neutral. As already shown in Table I, this reaction can be made to proceed in either direction for the niobium and tantalum systems. The equilibrium constants, determined above, show that niobium and tantalum oxide anions have a pronounced tendency to form the oxyhydroxide anions when they are placed in water-containing environments. In contrast, tungsten oxide anions show no such tendency and remain in the pure oxide form.

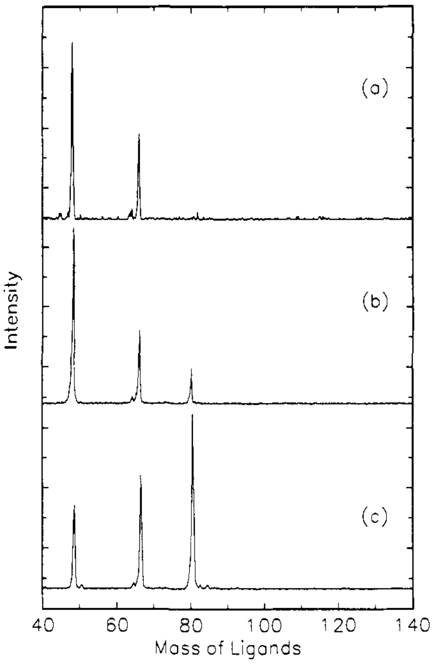

Figure 1. High-resolution spectra of (a) vanadium, (b) niobium, and (c) tantalum oxide and oxyhydroxide anions. The mass values given correspond to the mass that each species would have if the metal atoms were absent. All anions have one metal atom and three, four, or five oxygen atoms. All three spectra show the trioxide and the dioxydihydroxide, while the pentoxide is present in the niobium and tantalum spectra.

B. Niobium, Tantalum, and Vanadium Oxide Anions: Reactions with HCl. 1. Mechanistic Studies. Oxide anions of all three group V transition metals react with HCl in a similar manner. The ions produced are NbO_3^-, $NbO_2(OH)_2^-$, and NbO_5^- for niobium as shown in Figure 1b, TaO_3^-, $TaO_2(OH)_2^-$, and TaO_5^- for tantalum as shown in Figure 1c, and VO_3^- and $VO_2(OH)_2^-$ for vanadium as shown in Figure 1a. Note that in Figure 1, the metal atoms have arbitrarily been assigned a mass of zero in order to facilitate comparison between the vanadium, niobium, and tantalum systems. Each of the three (two for vanadium) reactant ions, for a given metal system, reacts with HCl to give the same primary product ion. The initial products are $VO_2(OH)Cl^-$, $NbO_2(OH)Cl^-$, and $TaO_2(OH)Cl^-$ for vanadium, niobium, and tantalum, respectively. This is illustrated for niobium in eqs 10–12. The

$$NbO_3^- + HCl \rightarrow NbO_2(OH)Cl^- \qquad (10)$$

$$NbO_2(OH)_2^- + HCl \rightarrow NbO_2(OH)Cl^- + H_2O \qquad (11)$$

$$NbO_5^- + HCl \rightarrow NbO_2(OH)Cl^- + O_2 \qquad (12)$$

fact that all three reactant ions yield the same product ion is not a totally surprising result, as $NbO_2(OH)_2^-$ is formed by addition of H_2O to NbO_3^- and NbO_5^- is formed by addition of O_2 to NbO_3^-. Yet, these reactions (i.e., eqs 11 and 12) are not simple ligand-switching reactions as might be inferred from an initial analysis. For instance, the species designated as $NbO_2(OH)_2^-$ in eq 11 would have to be $NbO_3^-\cdot H_2O$ for simple ligand switching to be involved.

In order to determine the nature of $H_2NbO_4^-$, in particular to ascertain whether it is $NbO_3^-\cdot H_2O$ or more appropriately representable as $NbO_2(OH)_2^-$, studies were also conducted with deuterium chloride. Even though NbO_3^-, NbO_5^-, and $H_2NbO_4^-$ are simultaneously present and all have the same initial ionic product, $NbO_2(OH)Cl^-$, they would differ in deuterium content depending on the possible neutral product. With NbO_3^- and NbO_5^-, the initial product should be deuterated, $NbO_2(OD)Cl^-$, since no hydrogens are donated to a neutral product from the

Table II. Niobium Oxide Anion Rate Coefficients: HCl Reactions

reactants	products	rate coefficient k/cm^3 s^{-1}	collision rate $k_C/10^{-9}$ cm^3 s^{-1}	efficiency k/k_C
NbO_3^- + HCl	$NbO_2(OH)Cl^-$	$6.5 \times 10^{-10\,a}$	1.24	0.52
$NbO_2(OH)_2^-$ + HCl	$NbO_2(OH)Cl^-$ + H_2O	$5.9 \times 10^{-10\,a}$	1.22	0.48
NbO_5^- + HCl	$NbO_2(OH)Cl^-$ + O_2	$5.9 \times 10^{-10\,a}$	1.21	0.49
$NbO_2(OH)Cl^-$ + HCl	$NbO_2Cl_2^-$ + H_2O	$5.3 \times 10^{-10\,b}$	1.21	0.44
$NbO_2Cl_2^-$ + HCl	$NbO(OH)Cl_3^-$	$2.0 \times 10^{-11\,a}$	1.20	0.017
$NbO(OH)Cl_3^-$ + HCl	$NbOCl_4^-$ + H_2O	$2 \times 10^{-10\,b}$	1.19	0.2
$NbOCl_4^-$ + HCl	no reaction	$<10^{-14}$	1.18	$<10^{-5}$
$NbO_3Cl_2^-$ + HCl	$NbO_2(OH)Cl_3^-$	$\leq 10^{-13}$	1.19	$\leq 10^{-4}$

[a] Error estimated to be ±20%. [b] Error estimated to be ±30%.

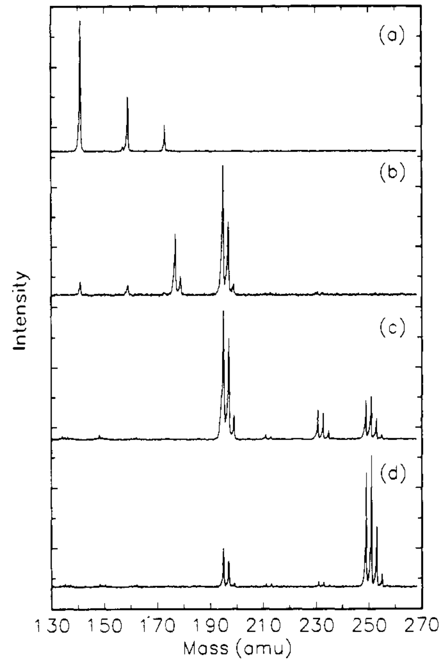

Figure 2. HCl added to a distribution of NbO_3^-, $NbO_2(OH)_2^-$, and NbO_5^- at mass flow rates of (a) 0.0, (b) 1.0, (c) 6.1, and (d) 20.4 sccm at 9000 sccm (0.32 Torr) helium. The initial product for all three initial anionic reactants is $NbO_2(OH)Cl^-$ at 177 and 179 amu. Thereafter, sequential products show up as a triplet, a quartet, and a quintet of peaks beginning at 195, 231, and 249 amu, corresponding to $NbO_2Cl_2^-$, $NbO(OH)Cl_3^-$, and $NbOCl_4^-$, respectively.

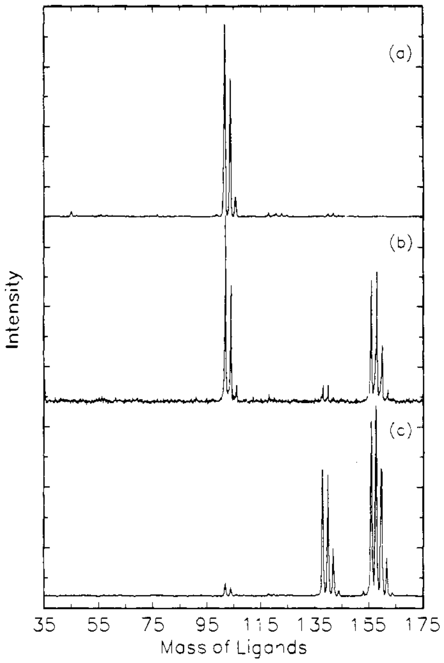

Figure 3. Comparison of (a) vanadium, (b) niobium, and (c) tantalum oxide and oxyhydroxide anions reacting with 50.9, 15.1, and 6.1 sccm HCl, respectively, at 0.32 Torr helium. The mass values given correspond to the mass that each species would have if the metal atoms were absent. Note that the vanadium reaction stops at $VO_2Cl_2^-$ at about 105 amu above the mass of a bare metal atom. $NbO_2Cl_2^-$ reacts at a moderate rate, and $TaO_2Cl_2^-$ reacts very rapidly with HCl.

reaction pair. For $H_2NbO_4^-$, the initial product would be deuterated if $H_2NbO_4^-$ is $NbO_3^-{\cdot}H_2O$ (ligand switching to form $NbO_3^-{\cdot}DCl$) and nondeuterated if it is $NbO_2(OH)_2^-$ (reaction with DCl forms $NbO_2(OH)Cl^-$ and HOD). Our experiments produced a ratio of nondeuterated to deuterated initial product which points to $H_2NbO_4^-$ being, in fact, $NbO_2(OH)_2^-$.

$NbO_2(OH)Cl^-$, the primary product of all three reactions in eqs 10–12, undergoes three sequential additions of HCl and the loss of two H_2O molecules to yield $NbOCl_4^-$, a well-known stable ion in solution-phase chemistry.[21] Tantalum oxide anions likewise react with HCl to yield a final product of $TaOCl_4^-$. But the reaction sequence for vanadium ends at $VO_2Cl_2^-$, with two less additions of HCl than that for the corresponding sequential reactions of niobium and tantalum. Starting from $NbO_2(OH)_2^-$, the characteristic reaction sequence is

$$NbO_2(OH)_2^- \xrightarrow[-H_2O]{HCl} NbO_2(OH)Cl^- \xrightarrow[-H_2O]{HCl} NbO_2Cl_2^- \xrightarrow{HCl} NbO(OH)Cl_3^- \xrightarrow[-H_2O]{HCl} NbOCl_4^- \quad (13)$$

Whenever an OH unit is bound to the metal center, HCl adds in with loss of H_2O; the net result is replacement of an OH unit with a Cl unit. Also note that when OH units are not present, HCl addition results in an additional Cl becoming attached to the metal center, along with formation of an OH group. A similar stepwise addition–dehydration sequence has been observed for reaction of various Bronsted acids with a cyclopentadienylcobalt oxide anion.[9]

In Figure 2a, the initial reactants NbO_3^-, $NbO_2(OH)_2^-$, and NbO_5^- appear at masses 141, 159, and 173 amu, respectively. It is easy to see from Figure 2b,c, that the initial product at 177 and 179 amu, $NbO_2(OH)Cl^-$, undergoes further reaction with HCl to form $NbO_2Cl_2^-$ at 195, 197, and 199 amu. The third and fourth products, $NbO(OH)Cl_3^-$ and $NbOCl_4^-$, show up as a quartet and a quintet of peaks beginning at 231 and 249 amu, respectively. The intensity is low for the right-most (high-mass side) peak of both of the last two products, and they are distinguished by a triplet and a quartet of peaks, respectively.

Figure 3 is useful for gaining insight into the relative reactivity of vanadium, niobium, and tantalum dioxy dichloride anions. As in Figure 1, the metal atoms have been assigned a mass of zero in Figure 3 to facilitate comparison. $VO_2Cl_2^-$ and its Nb and Ta analogs show up at the center of Figure 3a, 3b, and 3c, respectively, with reaction conditions of 0.3 Torr helium and 50.9 sccm HCl for the V case, 15.1 sccm HCl for Nb, and 6.1 sccm HCl for Ta oxides. Even though the HCl concentration is greatest for the vanadium system and least for the tantalum system, the extent of reaction is greatest for $TaO_2Cl_2^-$ and least for $VO_2Cl_2^-$. It is clear that the order of reactivity with HCl for the three dioxy dichloride species is $TaO_2Cl_2^- > NbO_2Cl_2^- > VO_2Cl_2^-$, with the $TaO_2Cl_2^-$ reaction being quite fast and the $VO_2Cl_2^-$ reaction not

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(21) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1980.

Table III. Tantalum and Vanadium Oxide Anion Rate Coefficients: HCl Reactions

reactants	products	rate coefficient k/cm^3 s^{-1}	collision rate $k_C/10^{-9}$ cm^3 s^{-1}	efficiency k/k_C
TaO_3^- + HCl	$TaO_2(OH)Cl^-$	$8 \times 10^{-10\,a}$	1.19	0.7
$TaO_2(OH)_2^-$ + HCl	$TaO_2(OH)Cl^-$ + H_2O	$7 \times 10^{-10\,a}$	1.18	0.6
TaO_5^- + HCl	$TaIO_2(OH)Cl^-$ + O_2	$6 \times 10^{-10\,a}$	1.18	0.5
$TaO_2(OH)Cl^-$ + HCl	$TaO_2Cl_2^-$ + H_2O	$6 \times 10^{-10\,b}$	1.18	0.5
$TaO_2Cl_2^-$ + HCl	$TaO(OH)Cl_3^-$	1.3×10^{-10}	1.17	0.11
$TaO(OH)Cl_3^-$ + HCl	$TaOCl_4^-$ + H_2O	$5 \times 10^{-11\,b}$	1.16	0.04
$TaOCl_4^-$ + HCl	no reaction	$<10^{-14}$	1.16	$<10^{-5}$
$VO_2Cl_2^-$ + HCl	no reaction	$<10^{-14}$	1.23	$<10^{-5}$
$V_2O_4Cl_2^-$ + HCl	$V_2O_3(OH)Cl_3^-$	$9 \times 10^{-11\,b}$	1.18	0.07

[a] Error estimated to be ±20%. [b] Error estimated to be ±30%.

occurring. It should be noted that none of the peaks to the high-mass side of $VO_2Cl_2^-$ are at the correct position for an HCl reaction product and they are all rather small anyway.

2. Kinetic Studies. Rate coefficients, collision rates, and reaction efficiencies are given in Tables II and III for HCl reaction with niobium and tantalum oxide anions, respectively. Data for $VO_2Cl_2^-$ and $V_2O_4Cl_2^-$ are also given in Table III. The majority of the rate coefficients in these two tables were determined as described earlier; i.e., the decay of the reactant ion as a function of reactant gas concentration was determined directly from a computer integration of spectra collected at a number of different flow rates of reactant gas under pseudo-first-order conditions. As can be seen from eq 13, the anions listed in Table II from $NbO_2(OH)Cl^-$ to $NbOCl_4^-$ (and Table III from $TaO_2(OH)Cl^-$ to $TaOCl_4^-$) are all part of a reaction sequence and are not subject to ready determination of the individual rate coefficients without the use of curve-fitting routines. However, it is possible to set conditions for each of $VO_2Cl_2^-$, $NbO_2Cl_2^-$, $TaO_2Cl_2^-$, $NbOCl_4^-$, $TaOCl_4^-$, $V_2O_4Cl_2^-$, and $NbO_3Cl_2^-$ such that all previous anions in the reaction sequence have reacted away and the ion of interest is still of high intensity. An example of this condition can be seen for the data plotted in Figure 2c for $NbO_2Cl_2^-$. For the niobium (and tantalum) system, it is easy to see that this arises due to the reaction of $NbO_2Cl_2^-$ (and $TaO_2Cl_2^-$) with HCl being roughly an order of magnitude slower than each of the preceding reactions in the sequence. Back-reaction from sequential products is not considered to be a problem under the pseudo-first-order reaction conditions of the present experiments. Note that $NbO_3Cl_2^-$ arises from two additions of HCl to $H_2NbO_5^-$ (or $NbO_3(OH)_2^-$). $H_2NbO_5^-$ is only present under certain conditions and is not seen in either Figure 1b or Figure 3.

For both tantalum and niobium, two of the anions were not amenable to the direct treatment mentioned in the previous paragraph. Each of $NbO_2(OH)Cl^-$, $TaO_2(OH)Cl^-$, $NbO(OH)Cl_3^-$, and $TaO(OH)Cl_3^-$ either reacts away too quickly or is immediately preceded by a relatively slow reaction (or both). In this case a sequential kinetic analysis must be used. For the case of the dioxyhydroxy chlorides, $TaO_2(OH)Cl^-$ and $NbO_2(OH)Cl^-$, a consecutive two-stage irreversible reaction analysis can be used. The rate coefficient, k_1, for the appearance of $NbO_2(OH)Cl^-$ (neglecting the reaction of this ion with HCl) is taken to be the weighted average of the disappearance rate coefficients of NbO_3^-, $NbO_2(OH)_2^-$, and NbO_5^-, and the determined value is used to derive the rate coefficient, k_2, for reaction of $NbO_2(OH)Cl^-$ with HCl. The weighted average with respect to concentration is taken because each of these three reactant ions yields the same product ion, and the three reactant ions have different intensity values. Note from Table II that the rate coefficient for the disappearance of each of these three reactant anions is about 6×10^{-10} cm^3 s^{-1}, which means that the weighted average rate coefficient is also about the same value. The tantalum case is treated in the same manner.

The basic kinetic model for a two-stage bimolecular irreversible sequential reaction conducted under pseudo-first-order conditions, where [R] represents the number density of neutral reactant, is given by

$$A \xrightarrow{k_1[R]} B \xrightarrow{k_2[R]} C \qquad (14)$$

For this situation, the expressions[22] for the concentration of A and of B are

$$[A] = [A_o] \exp(-k_1[R]t) \qquad (15)$$

and

$$[B] = [A_0]\left\{\frac{k_1}{k_2 - k_1}\right\}\{\exp(-k_1[R]t) - \exp(-k_2[R]t)\} + [B_0] \exp(-k_2[R]t) \qquad (16)$$

Here the various k values represent rate coefficients for the sequential reactions, t is reaction time, and the terms with square brackets represent number densities of the respective species. Equation 15 is the expression used in the usual kinetic analysis, while eq 16 gives the concentration of B for the general case of both A and B being present initially (where again, A and B are as defined in eq 14). Equation 15 is used to find k_1, and then eq 16 can be used to find a value for k_2.

The above analysis can also be used to determining the rate coefficients for the HCl reactions of $NbO(OH)Cl_3^-$ and $TaO(OH)Cl_3^-$. That is, these reactions can be treated as though the entire reaction sequence (illustrated here for the niobium case) is as follows

$$NbO_2Cl_2^- \xrightarrow{HCl} NbO(OH)Cl_3^- \xrightarrow[-H_2O]{HCl} NbOCl_4^- \qquad (17)$$

This is allowed because the dioxy dichloride anion reacts relatively slowly and the preceding reactants have already reacted away at the reactant gas concentration chosen as the initial value in the present analysis.

Note from Tables II and III that the trioxide, the dioxydihydroxide, and the pentoxide anion of both tantalum and niobium react with HCl with a rate coefficient in the range 6–8 × 10^{-10} cm^3 s^{-1} and with a reaction efficiency of about 50%, where the efficiency is defined as the ratio of the reaction rate coefficient to the calculated collision rate coefficient. The next reaction listed in both tables, that of the dioxyhydroxy chloride anion, and the seventh reaction, that of the oxy tetrachloride, also have rate coefficients that are comparable for both tantalum and niobium. $NbO_2(OH)Cl^-$ and $TaO_2(OH)Cl^-$ both react with HCl at about 50% of the collisional rate, while $NbOCl_4^-$ and $TaOCl_4^-$ both show no reaction with HCl. However, $NbO_2Cl_2^-$ and $NbO(OH)Cl_3^-$ have reactivities very different than that of the corresponding Ta anions. $TaO_2Cl_2^-$ reacts relatively fast with a rate coefficient of 1.3×10^{-10} cm^3 s^{-1}, while the rate coefficient for $NbO_2Cl_2^-$ is smaller by an order of magnitude. In contrast, $TaO(OH)Cl_3^-$ reacts moderately slowly at 5×10^{-11} cm^3 s^{-1}, and the reaction of $NbO(OH)Cl_3^-$ with HCl is about 4 times faster.

3. Consideration of the HCl Reactions. It is of interest to compare the various termolecular reactions discussed in this section, both with regard to a particular metal oxide system and also in terms of system to system similarities and differences. The electronic configurations for V, Nb, and Ta are [Ar]$3d^34s^2$, [Kr]$4d^45s^1$, and [Xe]$5d^36s^2$. Each of the termolecular reactions listed in Tables II and III leads to an increase by one in the number of atoms directly bound to the central metal atom. Thus, an

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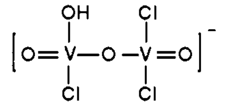
[22] Rodiguin, N. M.; Rodiguina, E. N. In *Consecutive Chemical Reactions*; Schneider, R. F., Ed.; D. Van Nostrand: Princeton, NJ, 1964.

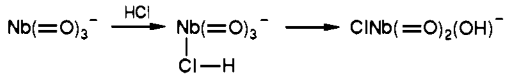
opportunity is afforded for observing reactivity as a function of electronic shell size. Tantalum, niobium, and vanadium trioxide anions all react quite fast with HCl. The rate coefficient for VO_3^- was not quantitatively determined, but the experimental evidence (i.e., VO_3^- was observed to disappear totally via reaction at relatively low reactant gas concentrations) points to it having an effective second-order-rate coefficient in the $10^{-10} \times 10^{-9}$ cm^3 s^{-1} range at 0.3 Torr helium pressure. Vanadium resists addition of a fifth ligand, and the reaction sequence stops at $VO_2Cl_2^-$. Compared with the majority of the other rate coefficients in Tables II and III, the rate coefficient for reaction of $NbO_2Cl_2^-$ is relatively slow at 2.0×10^{-11} cm^3 s^{-1}. On average, only about 2 per 100 of the capture collisions between HCl and $NbO_2Cl_2^-$ actually lead to the $NbO(OH)Cl_3^-$ product (11 per 100 for the tantalum case). However, the reaction is actually termolecular and the three-body rate is quite fast (compared to other termolecular reactions) at 2.0×10^{-27} cm^6 s^{-1}, where the effective second-order-rate coefficient divided by the helium number density (1.0×10^{16} cm^{-3} at 0.32 Torr helium) yields the three-body rate. $TaO_2Cl_2^-$ reacts almost 10 times faster with HCl than does $NbO_2Cl_2^-$. Thus vanadium does not allow for a change from four to five bound entities, while niobium and tantalum demonstrate no such impediment. This is probably due to the relative ease with which the metal atom d-orbitals can participate in bonding. $V_2O_4Cl_2^-$ may appear, at first, to be an exception. Table III reveals that it reacts very quickly with HCl ($k \approx 10^{-10}$ cm^3 s^{-1}) to form $V_2O_3(OH)Cl_3^-$. However, this still corresponds to four or less ligands per vanadium atom. $V_2O_4Cl_2^-$ should have one[14,21] or two[23] μ-O oxide bridges joining the two vanadium atoms. An example of a possible candidate for the product of the reaction with HCl (whether there are two or just one oxide bridge in the reactant ion) is the following:



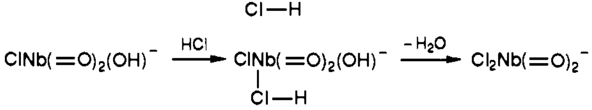
None of the observed metal oxide anions readily increase the number of bound entities from five to six. $NbOCl_4^-$ and $TaOCl_4^-$ show no evidence of reaction, while $NbO_3Cl_2^-$ reacts at a rate ($k \leq 10^{-13}$ cm^3 s^{-1} at 0.3 Torr) that is just barely discernible with the present experimental technique. The low rate could be attributable to steric hindrance (kinetic effect) or reluctance of extra d-orbitals from the metal atom to become involved in the bonding. In summary, both kinetic and thermodynamic considerations are in agreement with the fact that group V transition metals tend to have a coordination number of five or less.

C. Discussion. 1. HCl Reactions. In part 1 of section B above, experimental evidence from labeling studies was discussed for group V transition metal oxides with which hydrogen atoms are incorporated, showing that the hydrogens are contained in OH groups. Also, eq 13 gives a typical sequential reaction sequence, beginning at $NbO_2(OH)_2^-$, for HCl reacting with group V metal oxides. The experiments reveal that when there are both M—OH and M═O bonds simultaneously present on one metal center, M, H_2O is eliminated after addition of one molecule of HCl. Whenever there are M═O but no M—OH bonds, nothing is given off when HCl is added; however, H_2O is eliminated after the next HCl addition. This implies that, in the absence of an OH unit on the metal atom, an M═O bond may become Cl—M—OH, either by direct addition of HCl to the M═O bond[9] or by means of a four-centered intermediate in a concerted reaction. Also implied here is that, in the presence of at least one OH group attached to the metal atom as well as one or more bare O atoms bound to the metal atom with a double bond, HCl exclusively adds across an M—OH bond to form Cl—M—OH_2, followed by loss of H_2O. Likewise, this may occur by direct addition to the indicated bond or by means of a four-centered interaction. For a four-centered interaction, the reaction may be concerted or it may occur with dative coordination of Cl to the metal atom followed by transfer of the HCl proton to an oxygen atom.

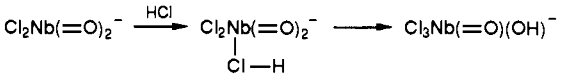
To the best of our knowledge, no one actually has observed the intermediates in these types of reactions. The products of each reagent molecule addition are seen, but the intermediates of each addition are not observed. Wang and Squires[9] invoke direct addition across a Co═O double bond, but they also suggest that Co inserts into a H—A bond when there is no Co═O bond present. In the situation with group V metal oxides, there is always an M═O double bond whenever there is a M—OH bond, but the OH group always receives the HCl hydrogen. Thus, intuitively it makes sense to have dative coordination of Cl to the metal atom followed by proton transfer to either a bare oxygen atom or an OH group, depending on the availability and energetics of each transfer pathway. Equations 18–21 give the mechanism for conversion of NbO_3^- to $NbOCl_4^-$ by means of four additions of HCl and the loss of two H_2O molecules. For illustration purposes only, eq 22 gives the mechanism for the reaction of HCl with $NbOCl_4^-$, if it were to occur.



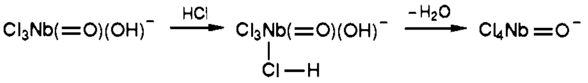
$$\mathrm{Nb(=O)_3^-} \xrightarrow{\mathrm{HCl}} \underset{\mathrm{Cl{-}H}}{\underset{|}{\mathrm{Nb(=O)_3^-}}} \longrightarrow \mathrm{ClNb(=O)_2(OH)^-} \qquad (18)$$



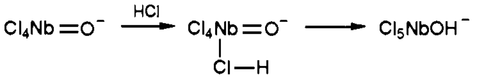
$$\mathrm{ClNb(=O)_2(OH)^-} \xrightarrow{\mathrm{HCl}} \underset{\mathrm{Cl{-}H}}{\underset{|}{\mathrm{ClNb(=O)_2(OH)^-}}} \xrightarrow{-\mathrm{H_2O}} \mathrm{Cl_2Nb(=O)_2^-} \qquad (19)$$



$$\mathrm{Cl_2Nb(=O)_2^-} \xrightarrow{\mathrm{HCl}} \underset{\mathrm{Cl{-}H}}{\underset{|}{\mathrm{Cl_2Nb(=O)_2^-}}} \longrightarrow \mathrm{Cl_3Nb(=O)(OH)^-} \qquad (20)$$



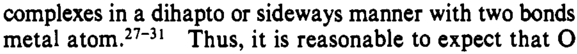
$$\mathrm{Cl_3Nb(=O)(OH)^-} \xrightarrow{\mathrm{HCl}} \underset{\mathrm{Cl{-}H}}{\underset{|}{\mathrm{Cl_3Nb(=O)(OH)^-}}} \xrightarrow{-\mathrm{H_2O}} \mathrm{Cl_4Nb{=}O^-} \qquad (21)$$



$$\mathrm{Cl_4Nb{=}O^-} \xrightarrow{\mathrm{HCl}} \underset{\mathrm{Cl{-}H}}{\underset{|}{\mathrm{Cl_4Nb{=}O^-}}} \longrightarrow \mathrm{Cl_5NbOH^-} \qquad (22)$$

The bonding for NbO_3^- in eq 18 is taken to be representable by $Nb(=O)_3^-$ because one of these Nb═O double bonds is converted to Nb—OH in each of eqs 18 and 20 and one doubly bound oxygen needs to be left for $NbOCl_4^-$.[24-26] Note that, as discussed above, the reaction sequence terminates when the number of atoms directly bound to the metal atom of the product ion exceeds a set number (i.e., four for V and five for each of Nb and Ta). This difference in reactivity between vanadium and niobium illustrates the effect of shell size. When the product ion has five atoms directly attached to an Nb center, the reaction proceeds favorably; however, at six such atoms there is no reaction.

2. O_2 and H_2O Reactions. Water adds to NbO_3^- (TaO_3^-) in much the same way as does HCl in eq 18. In fact, H_2O is one of the Bronsted acids that Wang and Squires[9] added to their cyclopentadienyl cobalt complex with similar results. NbO_3^- adds H_2O to form $NbO_2(OH)_2^-$ in accord with eq 23.



$$\mathrm{Nb(=O)_3^-} + \mathrm{H_2O} \longrightarrow \underset{\mathrm{HO{-}H}}{\underset{|}{\mathrm{Nb(=O)_3^-}}} \longrightarrow \mathrm{Nb(=O)_2(OH)_2^-} \qquad (23)$$

It is well-known that dioxygen adds to many organometallic complexes in a dihapto or sideways manner with two bonds to the metal atom.[27-31] Thus, it is reasonable to expect that O_2 adds in this manner to NbO_3^-, forming NbO_5^- (the same should also be true for tantalum oxides). Note also that all of the reactant

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[23] Fairbrother, F. *The Chemistry of Niobium and Tantalum*; Elsevier: Amsterdam, The Netherlands, 1967; p 55.

[24] Hubert-Pfalzgraf, L. G.; Pinkerton, A. A. *Inorg. Chem.* **1977**, *16*, 1895.

[25] Ebel, S.; Blanck, A.; Walther, H. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 869.

[26] Karakida, K.-I.; Kuchitsu, K. *Inorg. Chim. Acta* **1975**, *13*, 113.

[27] Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

[28] Le Carpentier, J.-M.; Schlupp, R.; Weiss, R. *Acta Crystallogr. B* **1972**, *28*, 1278.

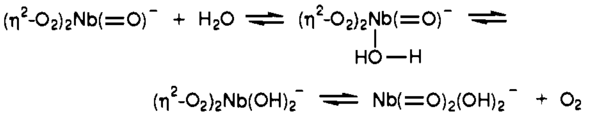
[29] Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

[30] Vaska, L. *Acc. Chem. Res.* **1976**, *9*, 175.

[31] Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348.

and product ions in eqs 18–23 have exactly six bonds to the Nb central atom. Perhaps the only way for there to be six bonds to Nb in NbO_5^- is to have two sideways bound O_2 molecules and one doubly bound oxygen atom. MoO_5 in $MoO_5(HMPT)(Py)$ and $MoO_5(HMPT)(H_2O)$ is characterized by crystallography[28] as having two dihapto sideways bound O_2 molecules and one doubly bound O atom, i.e., $(\eta^2\text{-}O_2)_2Mo({=}O)(HMPT)(Py)$ and $(\eta^2\text{-}O_2)_2Mo({=}O)(HMPT)(H_2O)$. In addition[28] the HMPT ligand is bound by means of an oxygen atom provided by HMPT, and pyridine (Py) is N atom bound while H_2O is presumably O atom bound to the metal center. Therefore, NbO_5^- may be $(\eta^2\text{-}O_2)_2Nb{=}O^-$ (a 12-electron complex).

Table I and eq 8 reveal that reactions such as that of TaO_5^- (NbO_5^-) with H_2O can be run in reverse under appropriate conditions. Dioxygen added to $TaO_2(OH)_2^-$ gives back TaO_5^- and H_2O. A mechanism for this reversible reaction that reflects the concepts expressed here is illustrated for niobium in eq 24.



$$(\eta^2\text{-}O_2)_2Nb({=}O)^- + H_2O \rightleftharpoons (\eta^2\text{-}O_2)_2\underset{\substack{|\\ HO-H}}{Nb}({=}O)^- \rightleftharpoons (\eta^2\text{-}O_2)_2Nb(OH)_2^- \rightleftharpoons Nb({=}O)_2(OH)_2^- + O_2 \quad (24)$$

For reaction with H_2O, the oxygen atom of the water molecule datively coordinates to the metal atom of the pentoxide anion followed by migration of a proton from HOH to form another OH group. Thereafter, this is followed by loss of a dihapto-O_2 molecule and conversion of $Nb(\eta^2\text{-}O_2)$ to $Nb({=}O)_2$. Again, the actual structures are unknown, but the ones described here are consistent with the evidence. The reaction proceeds in the other direction by oxidative sideways addition of O_2 to Nb of $NbO_2(OH)_2^-$. Note that $(\eta^2\text{-}O_2)_2Nb({=}O)(H_2O)^-$ is analogous to $(\eta^2\text{-}O_2)_2Mo({=}O)(HMPT)(H_2O)$.

IV. Conclusions

Negatively charged oxides and oxyhydroxides of tantalum, niobium, vanadium, and tungsten were produced, and their properties and reactivity were investigated. In contrast to the niobium and tantalum cases, tungsten oxide anions demonstrated no reactivity toward H_2O. Reaction with O_2 was observed to occur 2–3 orders of magnitude slower ($k \approx 10^{-11}$–10^{-13} cm^3 s^{-1}), in general, than the H_2O reactions that proceed. A reversible reaction was observed to occur between the dioxydihydroxide and pentoxide anions for both niobium and tantalum, and an equilibrium constant was calculated from the ratio of the forward and reverse rate coefficients in each case. Sequential reactions were observed for HCl reacting with niobium and tantalum oxide (and oxyhydroxide) anions. Interestingly, these reactions bear analogy to condensed-phase acid–base interactions along the line of NaOH and HCl reacting to give NaCl and H_2O. For the transition metal oxide anions, Cl of HCl replaces an OH unit on the metal center and H_2O is the neutral product. When there are no OH units bonded to the metal atom, HCl adds to form an OH unit and a Cl unit bonded to the metal center with no neutral reaction product being released. Rate coefficients, varying from about 10^{-9} to 10^{-11} cm^3 s^{-1}, were determined for each of four sequential additions of HCl for both the niobium and the tantalum systems. Mechanisms are proposed which utilize dative-coordination, as well as oxidative-addition/reductive-elimination concepts for the formation and decay of the transitory reaction intermediates for each reaction step. In the future, it will be desirable to expand this work to include other negatively charged metal oxide reactants such as oxides of titanium, chromium, and rhenium. Also it should be feasible to study the reactivity of the anions which have two or more metal atoms. A larger number of neutral reactant gases could be used in all of these studies to further probe the nature of the oxide.

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Kinetics of the Gas-Phase Reactions of Cl^- with CH_3Br and CD_3Br: Experimental Evidence for Nonstatistical Behavior?

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Abstract: The reactions of Cl^- with CH_3Br and CD_3Br have been studied as a function of ion-neutral average center-of-mass kinetic energy, $\langle KE_{cm}\rangle$, at several temperatures. The reactions are inefficient, proceeding at only a few percent of the collision rate. Both increasing temperature and increasing kinetic energy are found to decrease the rate constant as approximately $T^{-0.8}$ or $\langle KE_{cm}\rangle^{-0.8}$. The rate constants were found to be independent of pressure at 300 K. At a fixed $\langle KE_{cm}\rangle$, no dependence of the rate constants on temperature was found. This indicates that the rate constants for the reactions do not depend on the internal temperature of the CH_3Br or CD_3Br. By comparison with other systems, we conclude that rotational excitation of the CH_3Br should have little effect on the rate constants. Combining the apparent lack of a rotational dependence and the fact that significant amounts of the CH_3Br or CD_3Br molecules are vibrationally excited leads to the conclusion that the rate constants are also not strongly dependent on vibrational energy.

Introduction

Bimolecular nucleophilic displacement (S_N2) is one of the most basic types of chemical reaction. For this reason, numerous studies have been made to elucidate the dynamical details of the mechanism.[1-37] In contrast to many other types of gas-phase ion–molecule reactions, nucleophilic displacement reactions are often slow.[38] There has been speculation that the inefficiency results from the reaction coordinate being a double well, i.e., two ion–

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