with the previously reported results for carbonyl systems[10] which suggest that the ligands having phosphorus as donor atom react better than the ligands of the same basicity having nitrogen as donor atom. Such a behavior could be explained on the basis of the polarizability of the ligand atom, which will affect its nucleophilic strength toward these substrates. In fact, the metal in our system is of the class b[11] or soft acid type,[12] and it therefore will react with a P atom ligand easier than with a N atom ligand.

The activation parameters for reaction 1 are given in Table III: negative entropies of activation are in agreement with a bimolecular process in which there is considerable bond formation with the entering reagent in the transition state. The nature of the solvent appears to have little effect on the rate of reaction 1: this has been observed also for several other bimolecular reactions[13] in which the carbonyl derivatives of the transition metal are involved.

Finally, the carbonyl stretching frequencies of the isolated compounds are collected in Table IV. The four absorption bands observed in the range 2150–1900 cm^{-1} strongly support a *cis* structure; in fact, *cis*-$Re(CO)_4XL$ has C_s symmetry, which gives rise to four stretching frequencies ($3\ A' + A''$). The $A'(1)$ mode can be assigned to the band at lowest frequency, the $A'(3)$ mode to the band at highest frequency, and the $A'(2)$ and A'' modes to the bands at intermediate frequency.

Acknowledgments.—This work was supported by the Italian Consiglio Nazionale delle Ricerche (C.N.R. Roma).

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A Study of the Orthotungstate Condensation in Fused Equimolar Sodium Nitrate–Potassium Nitrate Solvent

BY R. N. KUST

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An electrochemical study of the orthotungstate condensation to ditungstate in an equimolar sodium nitrate–potassium nitrate solvent is reported. Selected values of the equilibrium constant for the reaction $2WO_4^{2-} \rightleftarrows W_2O_7^{2-} + O^{2-}$ at several temperatures are: 589°K, 3.3×10^{-3}; 621°K, 7.6×10^{-3}; 643°K, 1.8×10^{-2}. The values of the thermodynamic quantities $\Delta H°$ and $\Delta S°$ for this condensation are, respectively, 21.0 ± 0.3 kcal and 24.8 ± 0.4 eu.

Introduction

In aqueous solutions many oxy anions, such as silicate, are capable of condensing to form polyanionic species when the acidity of the solution is increased. Although phosphate oxy anions behave somewhat differently in aqueous solutions, polyphosphates being depolymerized at low pH values, Audrieth and co-workers[1] have pointed out that reactions analogous to the pH-dependent condensation of silicates occur with phosphates in certain high-temperature, solid-state processes. In general, condensed oxy anions can be considered acidic in terms of the Lux–Flood concept of acidity wherein an acid is defined as an oxide ion acceptor.

The group VIb oxides—CrO_3, MoO_3, and WO_3—have been shown to have acidic character when dissolved in a molten salt such as potassium nitrate.[2] This is in keeping with the infinite chain structure attributed to these oxides in the solid states.[3-5] Also the simplest condensed chromate, dichromate, has been shown to have acidic properties in fused alkali nitrate melts.[6] Presumably, then, it would be expected that in molten nitrates or similar high-temperature melts, the ortho oxy anions CrO_4^{2-}, MoO_4^{2-}, and WO_4^{2-} would tend to condense stepwise as the acidity of the melt were increased. However, potentiometric titrations in molten potassium nitrate[2] indicate that the species in equilibrium with the orthotungstate ion is tungstic oxide, WO_3, successive neutralization steps not being evident in the titration curves. This apparent absence of intermediate condensed species is unexpected in light of the relatively stable nature of dichromate in nitrate melts. This paper is a report of an investigation of the possibility of existence of ditungstate species in alkali nitrate melts.

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Experimental Section

Reagent grade $Na_2WO_4 \cdot 2H_2O$ was recrystallized from an aqueous solution at a pH of about 10. The recrystallized salt was dried at 150° for several hours. Infrared analysis of the dried product corresponded to published spectral data for sodium orthotungstate[7] and indicated that no water or condensed tungstate species were present. X-Ray powder diffraction patterns also indicated that only orthotungstate was present.[8]

Tungstic oxide, WO_3, was made by dropping concentrated sodium tungstate solution into hot concentrated hydrochloric acid, digesting for several hours on a steam bath, and filtering. The filtrate was washed with dilute ammonium nitrate until free of chloride ion. The washed filtrate was then dried at 120° for several hours and finally at 600° for 2 hr.

Sodium ditungstate was prepared by fusing equimolar quantities of sodium orthotungstate and tungsten(VI) oxide at 850° for 4 hr in a platinum crucible. The melt was then quenched by pouring onto cold porcelain. After grinding, it was stored over magnesium perchlorate. Infrared analyses with KBr disks and Nujol mulls gave spectra which were in good agreement with published spectra.[7] There were no indications that any orthotungstate or tungstates more condensed than the ditungstate were present.

An oxygen electrode previously described[9,10] was used in conjunction with an $Ag-Ag^+(1\ m)$ glass reference electrode to measure oxide ion concentration. A high-impedance electrometer amplifier was used as a series null indicator in a potentiometric measuring circuit.

The experimental procedure consisted of adding small amounts of sodium orthotungstate either to a pure solvent consisting only of equimolar sodium nitrate–potassium nitrate or to a similar solvent containing a known quantity of sodium ditungstate. The dissociation of the tungstate was observed electrochemically by measuring the oxide ion concentration.

Results and Discussion

When small amounts of sodium orthotungstate (*ca.* $10^{-5}\ m$) were added to the equimolar sodium nitrate–potassium nitrate melt, the potential of the electrochemical cell increased. The potential developed by the electrochemical cell to which the cell reaction

$$2Ag^+ + O^{2-} \rightleftharpoons 2Ag + {}^1/_2O_2$$

applies is related to the oxide ion concentration through the Nernst equation which can be written as

$$E = E^{\circ\prime} + \frac{2.3RT}{nF} \log [O^{2-}] \tag{1}$$

where $E^{\circ\prime}$ incorporates the standard emf, the oxygen pressure, and the reference electrode characteristics. When the potentials obtained above were plotted against $\log [WO_4{}^{2-}]_T$ for a constant temperature, where $[WO_4{}^{2-}]_T$ represents the total amount of sodium orthotungstate added, straight lines were obtained whose slopes were within 2 mv of those calculated from the Nernst equation. Several such lines are illustrated in Figure 1. This agreement indicates that the oxide ion concentration is proportional to the total tungstate ion concentration.

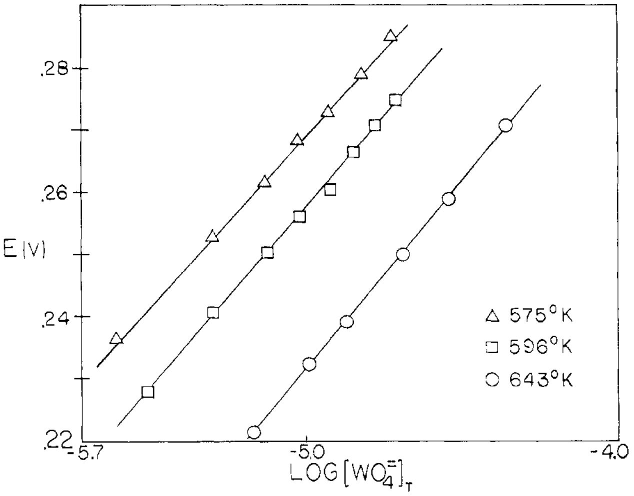

Figure 1.—Oxygen electrode potentials as a function of total tungstate concentration at several temperatures. Observed and calculated slopes for the different temperatures are, respectively: 575°K, 0.0576 v, 0.0569 v; 596°K, 0.0593 v, 0.0590 v; 643°K, 0.0625 v, 0.0638 v.

If a small amount (*ca.* $10^{-4}\ m$) of sodium ditungstate is first added to the solvent and then successive quantities of the ortho salt are added, the oxide ion concentration shows a different dependence on the quantity of the ortho salt added. When the potentials obtained in this manner were plotted against $\log [WO_4{}^{2-}]_T$, straight lines were obtained whose slopes were within 2 mv of being twice the calculated Nernst slope. Potential variations with $\log [WO_4{}^{2-}]_T$ for this situation are shown for two temperatures in Figure 2. These lines indicate that the oxide ion is proportional to the square of the total amount of orthotungstate added.

The release of an oxide ion when an orthotungstate salt is dissolved in the alkali nitrate melt can be visualized as a simple dissociation

$$WO_4{}^{2-} \rightleftharpoons WO_3 + O^{2-}$$

or as a condensation leading to higher polymeric species

$$nWO_4{}^{2} \rightleftharpoons aW_2O_7{}^{2-} + bW_3O_{10}{}^{2-} + \ldots + mO^{2-}$$

where only the formation of linear polymers is assumed for simplicity.

The simple dissociation process, which might be suggested by the absence of intermediate neutralization steps in the potentiometric titration data,[2] would be characterized by an equilibrium constant of the form

$$K = \frac{[WO_3][O^{2-}]}{[WO_4{}^{2-}]}$$

Combined with the mass balance equation

$$[WO_4{}^{2-}]_T = [WO_3] + [WO_4{}^{2-}]$$

and the stoichiometric equation, the equilibrium expression becomes

$$K = \frac{[O^{2-}]^2}{[WO_4{}^{2-}]_T - [O^{2-}]} \tag{2}$$

Since in most of the measurements that were made $[WO_4{}^{2-}]_T$ was usually about two orders of magnitude larger than the $[O^{2-}]$ eq 2 can be simplified to

$$K = \frac{[O^{2-}]^2}{[WO_4{}^{2-}]_T} \tag{3}$$

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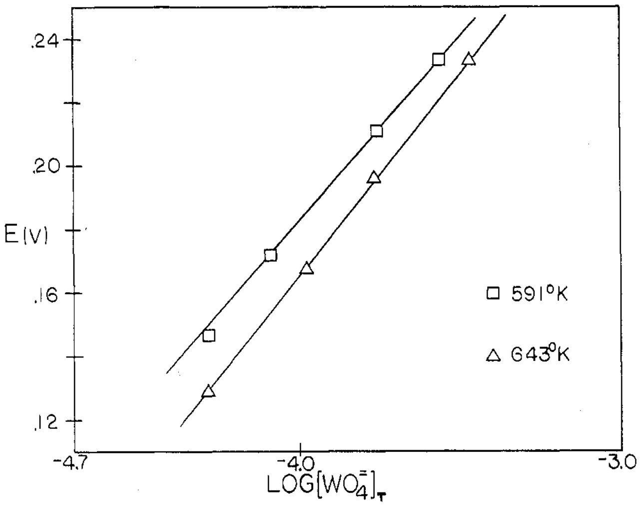

Figure 2.—Oxygen electrode potentials as a function of total tungstate concentration at several temperatures with an initial concentration of ditungstate. The temperature, ditungstate concentration, observed slope, and calculated slope are, respectively: 591°K, 2.78 × 10^{-4} *m*, 0.1188 v, 0.0585 v; 643°K, 2.68 × 10^{-4} *m*, 0.1293 v, 0.0638 v.

When eq 3 is combined with the Nernst expression (1) in such a manner as to eliminate the oxide ion concentration, the following expression is obtained

$$E = E^{\circ\prime} + \frac{2.3RT}{nF}\log\,\{K[\mathrm{WO_4^{2-}}]_\mathrm{T}\}^{1/2} \qquad (4)$$

Thus the potential should vary as the log of the square root of the total amount of orthotungstate added. Even if the simplifying approximation is not made, the square root dependence would be a limiting form. This relationship between potential and total orthotungstate added is not observed.

A condensation process leads to a different form for the equilibrium expression. For such a polymeric system the material balance becomes

$$[\mathrm{WO_4^{2-}}]_\mathrm{T} = [\mathrm{WO_4^{2-}}] + 2[\mathrm{W_2O_7^{2-}}] + 3[\mathrm{W_3O_{10}^{2-}}] + \ldots$$

again assuming only linear structures. It would be expected that only two or three species would be of primary importance at any one total tungstate concentration. Assuming that only the ortho- and ditungstates are important when adding pure orthotungstate, the material balance becomes

$$[\mathrm{WO_4^{2-}}]_\mathrm{T} = [\mathrm{WO_4^{2-}}] + 2[\mathrm{W_2O_7^{2-}}]$$

and the stoichiometric relation is

$$2\mathrm{WO_4^{2-}} = \mathrm{W_2O_7^{2-}} + \mathrm{O^{2-}} \qquad (5)$$

Consequently the equilibrium expression takes the form

$$K = \frac{[\mathrm{W_2O_7^{2-}}][\mathrm{O^{2-}}]}{[\mathrm{WO_4^{2-}}]^2}$$

and when combined with the material balance and the stoichiometric equation, becomes

$$K = \frac{[\mathrm{O^{2-}}]^2}{[[\mathrm{WO_4^{2-}}]_\mathrm{T} - 2[\mathrm{O^{2-}}]]^2}$$

When this relation is combined with the Nernst equation the following expression is obtained

$$E = E^{\circ\prime} + \frac{2.3RT}{nF}\log\frac{K^{1/2}}{1 + 2K^{1/2}}[\mathrm{WO_4^{2-}}]_\mathrm{T} \qquad (6)$$

Hence the potential should vary linearly with log $[\mathrm{WO_4^{2-}}]_\mathrm{T}$. This is the dependence that is observed as is illustrated in Figure 1.

If sufficient ditungstate ion is added initially to the solvent so that the increase in ditungstate ion concentration with the addition of orthotungstate becomes insignificant, the equilibrium expression takes the form

$$K = \frac{[\mathrm{W_2O_7^{2-}}]_0[\mathrm{O^{2-}}]}{[\mathrm{WO_4^{2-}}]^2}$$

where $[\mathrm{W_2O_7^{2-}}]_0$ indicates the initial ditungstate concentration. The initial ditungstate addition lowers the oxide ion concentration so that to a good approximation $[\mathrm{WO_4^{2-}}]_\mathrm{T} = [\mathrm{WO_4^{2-}}]$. Therefore

$$K = \frac{[\mathrm{W_2O_7^{2-}}]_0[\mathrm{O^{2-}}]}{[\mathrm{WO_4^{2-}}]_\mathrm{T}^2} \qquad (7)$$

The Nernst equation can now be written

$$E = E^{\circ\prime} + \frac{2.3RT}{nF}\log\frac{K[\mathrm{WO_4^{2-}}]_\mathrm{T}^2}{[\mathrm{W_2O_7^{2-}}]_0} \qquad (8)$$

This indicates that the potential should vary as the square of the total orthotungstate added. This relation is observed and is demonstrated in Figure 2.

The equilibrium constant K can be calculated using both eq 6 and 8. The values for E° have been previously published.[10] Values of K_obsd, calculated from observed potentials at different temperatures, are listed in Table I. Each value of K_obsd is the average of five and in some cases six measurements obtained both with and without the presence of an initial amount of sodium ditungstate. From the variation of K_obsd with temperature, the standard enthalpy for reaction 5 was determined from a least-squares analysis. The value of ΔH° obtained in the temperature range 575–643°K was 21.0 ± 0.3 kcal. ΔS° for reaction 5 was calculated with this value of ΔH° and the observed values of K. ΔS° was constant over the range of temperatures and has the value 24.8 ± 0.4 eu.

TABLE I

VALUES OF THE OBSERVED EQUILIBRIUM CONSTANT FOR THE REACTION $2\mathrm{WO_4^{2-}} \rightleftarrows \mathrm{W_2O_7^{2-}} + \mathrm{O^{2-}}$ AT VARIOUS TEMPERATURES

T, °K	E°, v	10^3K_obsd
575	0.6286	2.7 ± 0.4
589	0.6253	3.3 ± 0.6
591	0.6248	4.0 ± 0.4
596	0.6235	4.7 ± 0.5
603	0.6217	5.3 ± 0.5
621	0.6171	7.6 ± 0.4
633	0.6141	15.2 ± 0.8
643	0.6115	18.0 ± 0.7

The lack of a neutralization step corresponding to the formation of the ditungstate species in the published potentiometric titration curves[2] may be due to the slowness with which equilibrium was reached. Several of the measurements reported above required 4–6 hr for the electrode potentials to become stable. Also, the potentiometric titration work was done in pure potassium nitrate solvent whereas the data reported above were obtained in an equimolar sodium nitrate–potassium nitrate solvent. The phase diagram for the K_2WO_4–WO_3 system[11] does not show the existence of a compound corresponding to $K_2W_2O_7$, whereas the phase diagram for the Na_2WO_4–WO_3 system[12] does show the formation of a compound corresponding to $Na_2W_2O_7$. It is not known whether this predilection against formation of the ditungstate species in the potassium tungstate system carries over to solutions of the tungstates. Further investigation of the cation effect in these nitrate solvents is presently underway.

Attempts to detect electrochemically species more condensed than the ditungstate have so far been unsuccessful. The primary difficulty lies in the slowness with which equilibrium is attained.

Acknowledgment.—The author gratefully acknowledges the financial support obtained from the University of Utah Cooperative Research Fund.

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Notes

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A Novel Arylboron Dihalide and the Corresponding Boronic Acid

By C. A. Eggers and S. F. A. Kettle

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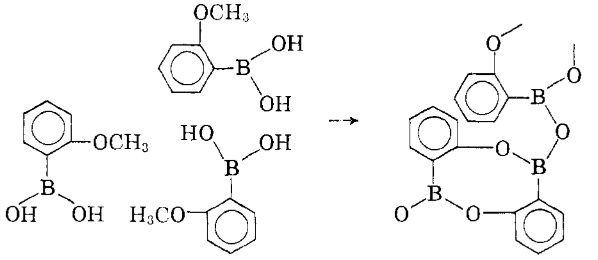
o-Anisylboron dichloride was first prepared by Michaelis and Behrens[1] by the action of boron trichloride on *o*-anisylmercuric chloride, a preparative technique which has recently been more fully studied.[2] In the course of an investigation into π bonding in the arylboron dihalides by variation of ring substituent we have repeated Michaelis and Behren's preparation. These authors did not, in fact, isolate *o*-anisylboron dichloride but identified it by the boronic acid formed when a solution of the halide was hydrolyzed. We have confirmed their work and find that when the solvent is removed from a solution of the halide a tar results. This is in contrast to the behavior of the corresponding *meta* and *para* anisyl derivatives which may be obtained in good yield. The tar formed in the *o*-anisyl case may be coordination polymer (it does not fume in moist air, for example, although the original solution did), but we have been unable to regenerate the original halide from it. It is far from clear why this behavior should be confined to the *ortho* derivative if only simple polymerization is involved and it appears that polymerization is a result of methyl group cleavage.

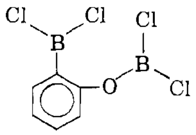
Since the *o*-anisylboronic acid may be readily prepared by the method of Bean and Johnson,[3] we attempted to prepare the dichloride from it. The most reliable method for this is by the action of boron trichloride on the boronic anhydride, although yields are not particularly good.[4]

Although *m*- and *p*-anisylboronic acids dehydrate readily at 40–50° under vacuum, the *ortho* acid sets to a hard resin (I) under these conditions. Comparison of the pmr spectra of the *ortho* acid with that of I showed that dehydration was accompanied by methanol elimination, possibly as shown below.

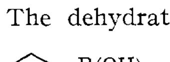


A somewhat similar reaction has been found to occur when *p*-anisylboron dichloride is heated, methyl chloride being eliminated and a resin left.[5]

When I was refluxed with boron trichloride in benzene the product was the novel compound *o*-(oxyboron dichloride)phenylboron dichloride (II). In accord with this the ^{11}B magnetic resonance spectrum of II showed two peaks. II, when hydrolyzed, gave the diboronic acid III. The dehydration of III did not proceed cleanly. It was not possible to isolate the corresponding anhydride; the infrared spectrum of the product suggested that I was among the products.



II



III

It is clear that when an alkoxide group is substituted *ortho* or *para*[5] to BCl_2 the O–alk bond is labilized, the effect of an *ortho* substituent being the greater. So,

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