$3UF_4 \cdot HF$ with an over-all weight loss of 12.47% to uranium tetrafluoride

$$NH_4F \cdot 3UF_4 = 3UF_4 \cdot HF + NH_3 \qquad (9)$$

and

$$3UF_4 \cdot HF = 3UF_4 + HF \qquad (10)$$

The total weight loss for the thermal decomposition of hydrazinium(+2) bishexafluorouranate(V) to uranium tetrafluoride is 14.90%. The decomposition of $3UF_4 \cdot HF$ adduct is most probably associated with the endothermic dta peak at 350°.

The thermal decomposition of the hydroxylammonium and nitrosyl hexafluorouranates(V) is rather complicated. It has been reported[10] that nitrosyl hexafluorouranate(V) gradually decomposes above 200° with melting occurring at approximately 350°. The first decomposition step we observe appears to involve a reduction of the hydroxylammonium compound while the nitrosyl complex remains unchanged. This internal oxidation–reduction probably occurs according to the equation

$$3(NH_3OH)UF_6 + NOUF_6 = 2(NH_3OH)UF_5 + NOUF_6 + UF_4 + NO + 4HF \qquad (11)$$

The corresponding weight loss 9.65% was also observed. The slow weight loss of the intermediate product with time observed at the isothermal decomposition at 105° is most probably due to the slow decomposition of the hydroxylammonium pentafluorouranate(IV) which is known to occur at this temperature.

The nature of the next decomposition step remains uncertain. The shift of the NO^+ infrared absorption band toward lower frequencies mentioned above indicates that the formal charge on the ion was decreased. The reduction of nitrosyl hexafluorouranate(V) to a uranium(IV) compound might be caused by a secondary reaction product from the hydroxylammonium pentafluorouranate(IV) decomposition. It is also obvious from the relatively small weight loss in the last decomposition step that the product obtained at 250° contains very little thermally degradable material in addition to the bulk of uranium tetrafluoride.

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A Study of Dimolybdate and Dichromate Formation in Fused Equimolar Sodium Nitrate–Potassium Nitrate Solvent

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An electrochemical study of dimolybdate and dichromate formation from the orthooxy anions in an equimolar sodium nitrate–potassium nitrate solvent is reported. Selected values of the equilibrium constant for the reaction $2MO_4^{2-} = M_2O_7^{2-} + O^{2-}$, when M = Mo, at several temperatures are: 533°K, 2.5×10^{-8}; 583°K, 8.5×10^{-8}; 617°K, 2.1×10^{-7}. For M = Cr, selected equilibrium constants are: 544°K, 1.2×10^{-8}; 587°K, 2.4×10^{-8}; 615°K, 3.3×10^{-8}. The values of $\Delta H°$ for this reaction when M is Mo and Cr are, respectively, 17 and 10 kcal. The values of $\Delta S°$ for this reaction when M is Mo and Cr are, respectively, −4 and −17 eu. An explanation for the large difference in $\Delta S°$ is proposed which involves a mixed coordination number in the dimolybdate polymer.

Introduction

The acidic nature of the group VIb oxides CrO_3, MoO_3, and WO_3 in fused potassium nitrate has been demonstrated.[1] This acidity is easily explained in terms of the Lux–Flood acid–base theory if the polymeric nature of these oxides is considered. Generally, polymeric oxides will tend to be acidic, reacting with basic solvents and oxide ion and depolymerizing to smaller units, the ortho anion, MO_4^{2-}, representing the limit in the case of the group VIb oxides. The first step in the reverse process, the dimerization of the ortho anion, is illustrated by the occurrence of dichromate, and the formation of ditungstate, $W_2O_7^{2-}$, from orthotungstate has recently been shown.[2] Compared with orthochromate, orthotungstate is quite basic, the formation of ditungstate with the concurrent release of an oxide ion occurring rather readily. It becomes of interest, then, to know how orthomolybdate behaves in the same type of reaction. Also, the weak basic properties of orthochromate have been inferred from studies of rates of reaction of the acidic dichromate

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[1] A. M. Shams El Din and A. A. El Hosary, *J. Electroanal. Chem.*, **9**, 349 (1965).

[2] R. N. Kust, *Inorg. Chem.*, **6**, 157 (1967).

with the solvent nitrate ions[3] and from potentiometric titrations of dichromate with sodium peroxide in fused potassium nitrate.[1] The direct observation of the dimerization of chromate in fused equimolar sodium nitrate–potassium nitrate would contribute necessary thermodynamic data needed for a comparative study of the group VIb orthooxy anions. This paper is a report of the electrochemical investigation of the dimerization of orthomolybdate, MoO_4^{2-}, and orthochromate, CrO_4^{2-}.

Experimental Section

Analytical reagent grade K_2CrO_4 and $K_2Cr_2O_7$ were dried at 150° and were used without further purification.

Reagent grade $Na_2MoO_4 \cdot 2H_2O$ was dried at 150° for 24 hr. Infrared analysis of the dried product using a Nujol mull corresponded to published spectral data for sodium orthomolybdate[4] and indicated that no water or condensed molybdate species were present. X-Ray powder diffraction patterns agreed with published data.[5]

Molybdenum(VI) oxide was prepared by allowing ammonium molybdate to react with hot nitric acid, crystallizing H_2MoO_4, and dehydrating the H_2MoO_4 by heating at 180° for 24 hr. X-Ray powder diffraction patterns agreed with published data.[6]

Sodium dimolybdate, $Na_2Mo_2O_7$, was made by two different methods. In one method, equimolar amounts of molybdenum(VI) oxide, MoO_3, and sodium orthomolybdate were intimately mixed in a porcelain crucible and were fused at 800° for 12 hr. The melt was then quenched by pouring onto cold porcelain and after grinding was stored over magnesium perchlorate. The second method consisted of mixing intimately molybdenum(VI) oxide and sodium carbonate in a mole ratio of 2:1. This mixture was then fused at 850° for 0.5 hr and at 800° for 12 hr, quenched, ground, and stored over magnesium perchlorate. Infrared spectra, using both KBr disks and Nujol mull techniques, were obtained for the products of both preparative methods. The spectra of both products agreed exactly with each other and with published spectra for sodium dimolybdate.[7] X-Ray powder patterns were obtained from both samples; the patterns were identical and agreed with published structural data.[5,8]

An oxygen electrode, previously described,[9,10] was used in conjunction with a silver–silver(I) glass reference electrode to measure oxide ion concentration. A high impedance electrometer amplifier was used as a series null detector in a potentiometric measuring circuit.

The experimental procedure consisted of adding small amounts of sodium orthomolybdate or potassium orthochromate to a pure solvent consisting of equimolar sodium nitrate–potassium nitrate or to a similar solvent containing a known quantity of sodium dimolybdate or potassium dichromate. The dimerization of the molybdate or chromate was observed electrochemically by measuring the oxide ion concentration.

Results

When small amounts of the orthooxy anions (*ca.* 10^{-3} *m*) were added to the equimolar sodium nitrate–potassium nitrate solvent, the potential of the electrochemical cell increased. The cell reaction for the electrochemical measuring system can be written

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

The relation between the electrode potential and the oxide ion concentration is given by the Nernst equation which can be written for the above cell reaction as

$$E = E^{\circ\prime} + \frac{2.3RT}{2F} \log\,[O^{2-}] \qquad (1)$$

where $E^{\circ\prime}$ incorporates the standard emf, the oxygen pressure, and the reference electrode characteristics. When the potentials obtained were plotted against log $[MO_4^{2-}]_T$ for a constant temperature, where $[MO_4^{2-}]_T$ represents the total amount of orthooxy anion added, straight lines were obtained whose slopes were within 0.4 mv of those required by eq 1. Several such lines are shown in Figure 1 for the molybdate system. These slopes indicate that the oxide ion concentration is proportional to $[MO_4^{2-}]_T$. Similar lines were also obtained for the chromate system.

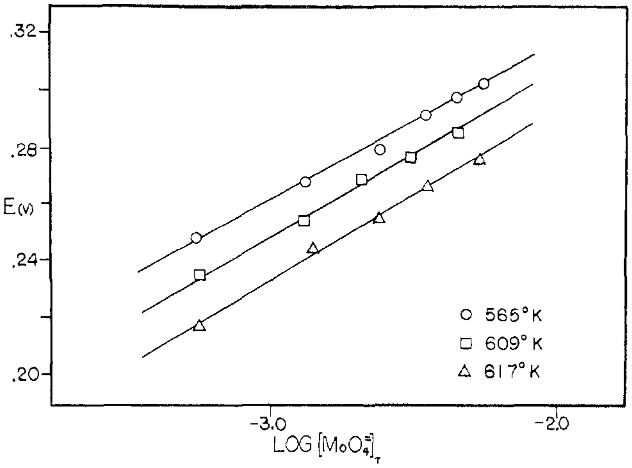

Figure 1.—Oxygen electrode potentials as a function of total molybdate concentration at several temperatures. Observed and calculated slopes for the different temperatures are, respectively: 565°K, 0.0560, 0.0559 v; 609°K, 0.0605, 0.0603 v; 617°K, 1.0615, 0.0611 v.

When small quantities (*ca.* 10^{-5} *m*) of $M_2O_7^{2-}$ (either $Na_2Mo_2O_7$ or $K_2Cr_2O_7$) were added to the melt after the first several additions of the respective orthooxy anions, the potential of the electrode system decreased, indicating a disappearance of the oxide ion. When the potentials thus obtained were plotted *vs.* log $[M_2O_7^{2-}]_T$, where $[M_2O_7^{2-}]_T$ represents the total amount of dianion added, straight lines were obtained whose slopes were within 1 mv of being equal to $-2.3RT/2F$. Several such lines are shown in Figure 2 for additions of dichromate. The slopes of these lines indicate that the oxide ion concentration is inversely proportional to $[M_2O_7^{2-}]_T$.

Further addition of the respective orthooxy anions then caused an increase in potential but in a different manner from before. A plot of potential *vs.* log $[MO_4^{2-}]_T$ for potentials obtained after the addition of the dianions also gave straight lines, but the slopes were within 1 mv of being twice the value required by eq 1. Several such lines are shown in Figures 3 and 4 for molybdates and chromates, respectively. The slopes of these lines indicate that the oxide ion concen-

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(5) I. Lindqvist, *Acta Chem. Scand.*, **4**, 1066 (1950).

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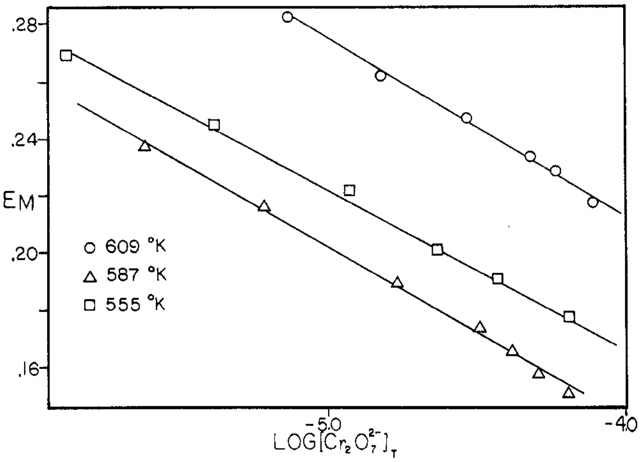

Figure 2.—Oxygen electrode potentials as a function of total dichromate concentration at several temperatures. The temperature, chromate concentration, observed slope, and calculated slope are, respectively: 555°K, 4.50 × 10^{-3} *m*, −0.0554, −0.0550 v; 587°K, 4.85 × 10^{-3} *m*, −0.0584, −0.0581 v; 609°K, 2.41 × 10^{-2} *m*, −0.0600, −0.0603 v.

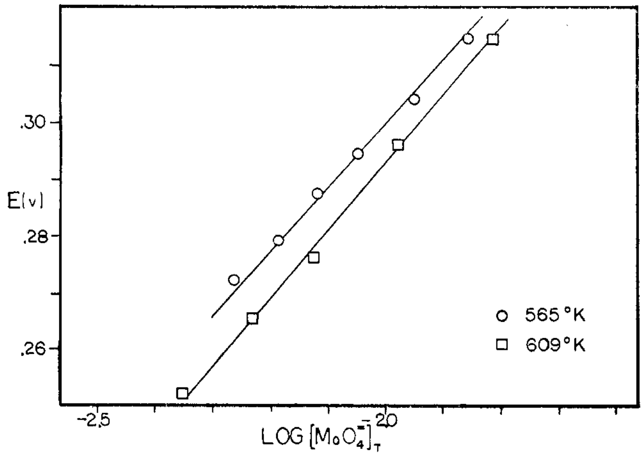

Figure 3.—Oxygen electrode potentials as a function of total molybdate concentration at two temperatures with an initial concentration of dimolybdate. The temperature, dimolybdate concentration, observed slope, and calculated slope are, respectively: 565°K, 5.38 × 10^{-6} *m*, 0.1120, 0.1118 v; 609°K, 4.14 × 10^{-6} *m*, 1198, 0.1206 v.

tration varies as the square of the total orthooxy anion concentration.

Discussion

The dependence of electrode potential on concentration of the orthooxy anion and of the dianion can be treated in the same manner as was done for the orthotungstate and ditungstate system in fused alkali metal nitrates.[2] Essentially the choice to be made is between the simple process of dissociation of the orthooxy anion into the metallic trioxide, MO_3, and oxide ion

$$MO_4^{2-} \rightleftharpoons MO_3 + O^{2-}$$

and a more complex process involving a condensation leading to higher polymeric species

$$nMO_4^{2-} \rightleftharpoons aM_2O_7^{2-} + bM_3O_{10}^{2-} + \ldots + mO^{2-}$$

where the formation of linear polymers is assumed for simplicity.

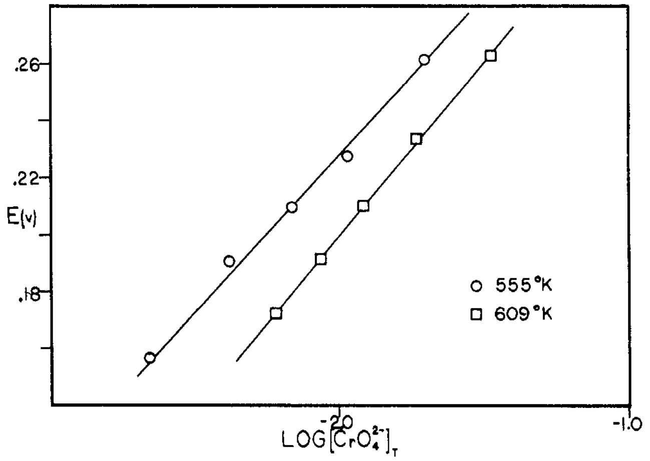

Figure 4.—Oxygen electrode potentials as a function of total chromate concentration at two temperatures with an initial concentration of dichromate. The temperature, dichromate concentration, observed slope, and calculated slope are, respectively: 555°K, 3.9 × 10^{-5} *m*, 0.1105, 1100 v; 609°K, 3.10 × 10^{-5} *m*, 0.1200, 0.1206 v.

As was shown for the orthotungstate system,[2] the simple dissociation process leads to a linear dependence of the potential on the logarithm of the square root of the total orthooxy anion concentration

$$E = E°' + \frac{2.3RT}{2F}\log\left(\{K[MO_4^{2-}]_T\}^{1/2}\right) \qquad (2)$$

As is indicated in Figure 1, this is not the potential dependence observed. Furthermore, such a process would require that species such as $M_2O_7^{2-}$ should behave as bases and dissociate also into metal trioxide and oxide ion

$$M_2O_7^{2-} \rightleftharpoons 2MO_3 + O_2^-$$

This is contrary to the evidence that the presence of $M_2O_7^{2-}$ in the melt lowers the oxygen electrode potential and hence decreases the oxide ion concentration.

The polymerization process, on the other hand, meets the requirements of the experimental data. Since at the beginning of an experiment only orthooxy anion is being added, the concentration of orthooxy anion is several orders of magnitude larger than the concentration of any condensed species and it can be reasonably assumed that only the concentrations of the orthooxy anion and the first condensed species to be formed are important, *i.e.*

$$2MO_4^{2-} \rightleftharpoons M_2O_7^{2-} + O_2^- \qquad (3)$$

If the equilibrium constant for reaction 3

$$K = \frac{[M_2O_7^{2-}][O^{2-}]}{[MO_4^{2-}]^2}$$

and the material balance

$$[MO_4^{2-}]_T = [MO_4^{2-}] + 2[M_2O_7^{2-}]$$

are combined and substituted into the Nernst expression (1), the equation

$$E = E°' + \frac{2.3RT}{2F}\log\left\{\frac{K^{1/2}}{1 + 2K^{1/2}}[MO_4^{2-}]_T\right\} \qquad (4)$$

is obtained. This indicates that a plot of potential *vs.* log $[MO_4^{2-}]_T$ should be a straight line with the proper two-electron Nernst slope. This is the relationship demonstrated in Figure 1.

The successive quantities of dianion which were then added to the system after the first additions of orthooxy anion were much greater in magnitude than the quantity of dianion already present as a result of dimerization of the orthooxy anion. Consequently the concentration of dianion is closely approximated by the quantity of dianion added, $[M_2O_7^{2-}]_T$. However, the increase in the concentration of the orthooxy anion from solvolysis of the dimer is negligible compared to that already present. Thus, during the addition of the dianion, the concentration of the orthooxy anion remains essentially constant. The equilibrium constant then takes the form

$$K = \frac{[M_2O_7^{2-}]_T[O^{2-}]}{[MO_4^{2-}]_T^2}$$

When this relation is substituted in the Nernst equation, the resulting form is

$$E = E^{\circ\prime} + \frac{2.3RT}{2F} \log \left\{\frac{K[MO_4^{2-}]_T^2}{[M_2O_7^{2-}]_T}\right\} \qquad (5)$$

Thus a plot of E *vs.* log $[M_2O_7^{2-}]_T$ should give a straight line with slope $-2.3RT/2F$. This is the relation demonstrated in Figure 2 for the case of dichromate.

Further addition of orthooxy anion to the system, which now contains sufficient dianion so that the amount of dianion formed from the orthooxy anion addition is negligible in comparison, will cause the potential of the system to vary according to eq 5 also. Thus a plot of E *vs.* log $[MO_4^{2-}]_T$ should give a straight line with slope $2.3RT/F$. That this is the case is demonstrated in Figures 3 and 4 for the molybdate and chromate systems, respectively.

The equilibrium constant K can be calculated from eq 4 for the first additions of the orthooxy anion and from eq 5 for additions of dianion and for further additions of orthoooxy anion. Values of $E°$ have previously been published.[10] Values of K_{obsd}, from observed potentials at various temperatures, are listed in Table I for M = Mo and in Table II for M = Cr. From the variation of K_{obsd} with temperature, the standard enthalpy of reaction 3 was determined from a least-squares analysis. The values of $\Delta H°$ obtained are listed in Table III. Values of $\Delta S°$ for reaction 3 were calculated with these values of $\Delta H°$ and the values for K_{obsd} and are listed in Table III.

Formation of a dimolybdate species is not surprising since the formation of both $Na_2Mo_2O_7$ and $K_2Mo_2O_7$ has been observed in phase studies of the Na_2O–MoO_3 and K_2O–MoO_3 systems.[11,12] However, Shams El Din and co-workers[1] report that, based on potentiometric titrations of MoO_3 with Na_2O_2, the species in equilibrium with MoO_4^{2-} is the $Mo_3O_{10}^{2-}$ ion.

It is informative to compare values of thermodynamic quantities for reaction 3 when M = W, Mo, or Cr. The values for the equilibrium constant for the dimerization process indicate the order of decreasing basicity of the orthooxy anion is $WO_4^{2-} > MoO_4^{2-} > CrO_4^{2-}$ in an equimolar sodium nitrate–potassium nitrate melt, which is in agreement with the conclusions of Shams El Din and co-workers.[1] However, the $\Delta H°$ for the dimerization reaction becomes more positive in the order $CrO_4^{2-} < MoO_4^{2-} < WO_4^{2-}$. This trend indicates that the formation of an oxygen bridge bond at the cost of two metal–oxygen bonds as indicated by the reaction

$$2\text{M–O} \rightleftharpoons \text{M–O–M} + O^{2-}$$

is most endothermic for M = W. Apparently the trend in basicity of the MO_4^{2-} anion is due to some characteristic of the reaction which is related to the entropy function. The change in $\Delta S°$ from +2.5 eu in the case of tungstate to −17 eu in the case of chromate strongly suggests that the species involved in the reaction change when the central metal species changes. Most likely such a difference would involve the type and degree of solvation of the various orthooxy anions and condensed species.

It is generally accepted that the dichromate ion in aqueous solution exists as a simple dimeric unit. If the solvation of the tetrahedral chromate ion, which probably involves electrostatic and van der Waals types of interaction between solvent cations and the nucleophilic oxygen of chromate, does not change greatly when the chromate dimerizes, then the large negative entropy of dimerization of chromate most likely comes from the formation and subsequent solvation of the oxide ion. If the oxide ion is in an environment which approaches

Table I

Values of the Observed Equilibrium Constant at Various Temperatures for the Reaction $2MoO_4^{2-} = Mo_2O_7^{2-} + O_2^{-}$

Temp, °K	$E°$, v	10^8K_{obsd}
533	0.6395	2.5 ± 0.6
565	0.6314	6.3 ± 0.6
575	0.6286	6.4 ± 0.8
583	0.6268	8.5 ± 0.6
603	0.6217	16 ± 1
609	0.6202	16 ± 1
617	0.6182	21 ± 1

Table II

Values of the Observed Equilibrium Constant at Various Temperatures for the Reaction $2CrO_4^{2-} = Cr_2O_7^{2-} + O^{2-}$

Temp, °K	$E°$, v	10^8K_{obsd}
544	0.6367	1.2 ± 0.1
555	0.6340	1.6 ± 0.2
568	0.6307	1.7 ± 0.2
575	0.6286	2.1 ± 0.2
587	0.6259	2.4 ± 0.2
601	0.6223	2.8 ± 0.3
609	0.6202	3.1 ± 0.3
615	0.6187	3.3 ± 0.2
625	0.6161	4.4 ± 0.4

Table III

A Comparison of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the Reaction $2MO_4^{2-} = M_2O_7^{2-} + O^{2-}$ at 603°K for M = Cr, Mo, W

M	$\Delta G°_{603}$, kcal	$\Delta H°$, kcal	$\Delta S°$, eu
Cr	20	10	−17
Mo	19	17	−4
W	8	21	25

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(11) A. N. Zelikman and N. N. Gorovitz, *Zh. Obshch. Khim.*, **24**, 1920 (1954).

(12) V. Spitzyn and I. M. Kuleshov, *ibid.*, **21**, 1367 (1951).

being close-packed with between eight and twelve cations associated about it, then the entropy change is of the right order of magnitude.

The slightly negative entropy change in the case of molybdate and the large positive entropy change in the case of tungstate are more difficult to explain. One characteristic of the chemistries of Mo(VI) and W(VI) compounds which distinguishes them from Cr(VI) compounds is the increased tendency toward sixfold coordination. It is probably this propensity for sixfold coordination which leads to the extremely complex polyoxy anion structures observed in the aqueous chemistry of molybdenum and tungsten. Lindqvist[5] has demonstrated that solid $Na_2W_2O_7$ and $Na_2M_2O_7$ are isomorphous and do not contain discrete $M_2O_7^{2-}$ ions but are polymeric in nature, consisting of chains of MO_6 octahedra sharing corners, with additional MO_4 tetrahedra sharing corners with two adjacent octahedra. This suggests that in solution ditungstates and dimolybdates form polymeric anions of a similar configuration containing both four- and sixfold coordinated species. If solvation with the solvent occurs through cation interaction with oxygens primarily bonded to one metal species, then the effective number of sites for solvation is decreased from the number available in the orthooxy anion. This decrease in solvation would cause an increase in entropy offsetting the decrease caused by formation of the oxide ion. The enthalpy of reaction for these three systems increases in the order Cr < Mo < W, which is the order which would be expected from comparison of heats of formation of the ortho salts. Whatever the explanation for the large entropy differences observed, it is clear that the basic properties of the ortho salts must be described in terms of the solvent in which they are placed.

Further studies on these systems are indicated. At present, work is underway to determine the effect of altering the cation ratio of the solvent. This should give information regarding the solvation of the oxide ion. If extensive polymers are formed in the case of dimolybdates and ditungstates, one could expect a significant difference in solubility of the ditungstates and dimolybdates as compared to the dichromates. Such studies are being initiated.

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Structure of $IrIO_2(CO)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$, the Oxygen Adduct of a Synthetic Irreversible Molecular Oxygen Carrier

BY J. A. MCGINNETY, ROBERT J. DOEDENS, AND JAMES A. IBERS

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The system $IrX(CO)(P(C_6H_5)_3)_2$ in benzene solution adds molecular oxygen reversibly when X is Cl and irreversibly when X is I. The crystal and molecular structure of $IrIO_2(CO)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$ has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final R factor on F of 5.9% for 1255 reflections above background. The material crystallizes in space group C_{2h}^5-$P2_1/n$ of the monoclinic system, with four molecules in a cell of dimensions $a = 10.69$, $b = 22.86$, $c = 15.00$ A, $\beta = 93.05°$. The observed density is 1.80 g/cm^3, the same as that calculated for the above cell. The crystal structure consists of the packing of the discrete monomeric units $IrIO_2(CO)(P(C_6H_5)_3)_2$ and CH_2Cl_2. The molecular structure of $IrIO_2(CO)(P(C_6H_5)_3)_2$ closely resembles that reported earlier for $IrClO_2(CO)(P(C_6H_5)_3)_2$; the iridium atom, the two oxygen atoms, the carbonyl group, and the iodine atom are situated in the equatorial plane of a trigonal bipyramid, with phosphorus atoms above and below this plane. The two oxygen atoms are equidistant from the iridium atom, with an average Ir–O distance of 2.06 A. The O–O distance is 1.509 ± 0.026 A in this irreversibly oxygenated iodo compound, whereas it is 1.30 ± 0.03 A in the reversibly oxygenated chloro compound. This very significant change in the O–O bond length is consistent with the π-bonding scheme that Griffith applied to the bonding of molecular oxygen to the heme group in oxyhemoglobin.

Introduction

Previously[1,2] we reported the crystal and molecular structure of the oxygen adduct of the synthetic reversible molecular oxygen carrier $IrCl(CO)P(C_6H_5)_3)_2$.[3] As part of a continuing study of the structures of oxygenated adducts of various synthetic oxygen carriers, we have investigated the properties of the system $IrX(CO)(P(C_6H_5)_3)_2$, where X = Br, I, SCN, or N_3. This series of compounds, with the exception of the thiocyanato compound, reacts in solution with gaseous oxygen to form oxygenated species. For the halogen compounds the rate of reaction has been found[4] to increase in the order Cl < Br < I. We have found[5]

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