due to S_4^+ and S_8^+ respectively either trapped in the crystals or adsorbed on the surfaces. It is noted that $(C_2F_5)_2S_5$ and $(C_2F_5)_2S_6$ were observed as reaction products in the C_2F_4-$S_8(AsF_6)_2$ reaction and that they can be simply derived from **1**, $S_8C_2F_4^+$, but not $S_4C_2F_4^+$.

The reaction of $S_8(AsF_6)_2$ and tetrafluoroethylene in SO_2 gave in addition to arsenic trifluoride and bis(perfluoroethyl) polysulfides, $C_2F_5S_xCF_3$, $C_2F_5S_xCF_2COF$ ($x = 2, 3$), CF_3COF, and SOF_2. The reaction is clearly more complicated than the neat reaction and would appear to involve reaction with the solvent. The reaction using sulfur dioxide was carried out in well-dried glass and Kel-F apparatus and in a thoroughly passivated metal vessel, the results being essentially the same in all cases. It appears highly unlikely, therefore, that moisture or adhering oxides could have provided the oxygen for the carbonyl species. The sulfur dioxide itself was carefully dried over fresh P_4O_{10} and in other cases over CaH_2 for several weeks. The presence of thionyl fluoride supports the claim that sulfur dioxide participates in the reaction, perhaps in a manner analogous to the reaction between carbon tetrachloride and sulfur dioxide in the presence of aluminum chloride. In this reaction, thionyl chloride is formed in good yield along with phosgene and, presumably, other products.[18]

$S_8(AsF_6)_2$ is very soluble in sulfur dioxide, and it has been shown that in solution S_8^{2+} is in equilibrium with a paramagnetic species, most probably S_4^+.[4,16,17,19] This could, wholly or in part, be the species involved in the initial reaction with tetrafluoroethylene in sulfur dioxide forming the intermediate $S_4C_2F_4^+$. This, or intermediate **1**, may react as in the neat reaction yielding bis(perfluoroethyl) polysulfides or undergo reactions, some of which involve sulfur dioxide, leading to $CF_3S_xC_2F_5$, $C_2F_5S_xCF_2COF$ ($x = 2, 3$), CF_3COF, and SOF_2. A study of the mechanism of this reaction and the isolation and characterization of the interesting perfluoroethyldi- and trisulfanylperfluoroacetyl fluorides will be the subject of further investigation.

While our work was in progress, Belen'kii, *et al.*, reported a reaction between tetrafluoroethylene and sulfur in sulfur dioxide in the presence of antimony pentafluoride giving compounds of the type $C_2F_5S_xC_2F_5$ and $C_2F_5S_xCF_3$ ($x = 2, 3, 4$).[5] Sulfur poly cations were postulated as intermediates, and it was suggested that they react with the olefin to form a cationic intermediate. They did not, however, report carbonyl-containing products.

Registry No. $S_8(AsF_6)_2$, 33248-05-4; C_2F_4, 116-14-3.

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The Platinum-Oxygen Electrode in Dichromate–Chromate Solutions of Alkali Nitrate Melts

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A platinum electrode dipping into a nitrate melt buffered with respect to oxide ions and bathed in an atmosphere of dry nitrogen follows Nernstian behavior toward oxide ions. It is proposed that the platinum–oxygen electrode in the absence of oxygen gas is an electrode of the second kind, *i.e.*, $Pt|PtO|O^{2-}$, in dichromate–chromate solutions of alkali nitrate melts. The standard emf of this indicator electrode *vs.* $Ag|Ag^+$ (1.0 *m*) reference electrode is 0.547 V at 250° and its temperature dependence is −0.111 mV/deg. Replacing Pt with Au gives potential readings 80 mV larger and approximate Nernst behavior is observed with Au. In $Cr_2O_7^{2-}$–CrO_4^{2-} solutions of nitrate melts, these indicator electrodes are electrodes of the second kind and the half-reaction is the oxidation of the metal to its oxide.

In 1963 Kust and Duke[1] reported that a platinum electrode bathed in an atmosphere of oxygen responds reversibly to both oxide ion and oxygen gas in alkali nitrate melts according to the half-reaction $^1/_2O_2 = O^{2-} + 2e^-$. Their findings have most recently been confirmed by Temple, *et al.*[2] Shams El Din and coworkers[3-6] have been using this electrode as an indicator electrode to carry out Lux–Flood titrations in molten nitrates and they have based many of their arguments concerning the stable polymeric species of chromate, molybdate, arsenate, phosphate, etc., upon the reversibility of the above half-reaction in distinctly basic nitrate melts as well as in acidic nitrate melts. However, Jordan and his group[7] have used voltammetry at a rotating platinum disk electrode to show that oxide ion is not stable [except possibly at very low concentrations] in fused nitrates because the addition of Na_2O to the nitrate melts results in its oxidation by NO_3^- to give an "equilibrium mixture" of O_2^{2-} and O_2^-. In view of their findings and a report by Inman[8] that a one-electron process involving O_2 and O^{2-} occurs at a gold electrode in molten halides, Jordan[9] sug-

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[7] P. Zambonin and J. Jordan, *J. Amer. Chem. Soc.*, 91, 2225 (1969).

gested that the oxygen electrode is best represented by the one-electron process $O_2 + e^- + O_2^-$. Zambonin and Signorile[10] have studied the oxygen electrode in basic nitrate melts and found that both Pt and Au [or the oxides of these metals] serve as supporting electrodes for the half-reaction $2OH^- = {}^1/_2O_2 + H_2O + 2e^-$. Recently our laboratory[11] made another interesting observation concerning the oxygen electrode in molten nitrates. We found that a platinum electrode dipping into a nitrate melt buffered with respect to oxide ions and bathed in an atmosphere of dry nitrogen follows Nernstian behavior toward oxide ions. Since all gases which could conceivably be in equilibrium with oxide ions, namely, oxygen and water, are eliminated, we propose that the platinum-oxygen electrode in the absence of oxygen is an electrode of the second kind, *i.e.*, $Pt|PtO|O^{2-}$. We have made a study of this electrode and have measured its temperature dependence in dichromate-chromate solutions of alkali nitrate melts.

Experimental Section

Chemicals. The solvent was a eutectic melt [100 g] of reagent grade sodium and potassium nitrates [supplied by Baker]. Initially we found it necessary to purify the nitrate salts by recrystallizing the salts and drying them in a vacuum oven. We have also filtered the eutectic melt at 280° to remove insoluble impurities. However, we found that if Baker Chemical was the supplier, our sodium and potassium nitrates did not need further purification other than purging the melt with dry nitrogen to remove water. Reagent grade $K_2Cr_2O_7$ and K_2CrO_4 were dried at 120° and stored in a desiccator until needed. The melt was kept under a flux of dry nitrogen.

Apparatus and Procedure. The Pyrex reaction vessel was heated with a beaker heating mantel and the temperature of the melt was maintained within ±0.3°. The reference electrode was a silver-silver ion electrode in which the silver ion concentration was varied from 0.08 to 1.0 *m*. This electrode was separated from the bulk melt by a thin glass membrane. The impedence of the cell was approximately 1 megohm. Therefore a Keithley 601 electrometer was used in conjunction with a Keithley digital multimeter to measure the potential of the cell within ±1 mV. A magnetic stir bar was used to stir the melt and the gases were passed over the indicator electrode at a rate of 50 cm^3/min.

Results and Discussion

A platinum foil dipping into a dichromate-chromate solution of an alkali nitrate melt which is continuously saturated with dry nitrogen gas responds to oxide ion concentration much the same way as the platinum-oxygen electrode described by Kust.[12] Since oxygen gas is completely removed from the melt, we propose that the silver-silver nitrate reference electrode in conjunction with the above indicator electrode describes an electrochemical cell having the cell notation

$$\mathrm{Pt|PtO|O^{2-}, Na, KNO_3 \underset{glass}{\vdots} Ag^+, Na, KNO_3|Ag}$$

for which the cell reaction is

$$\mathrm{Pt + O^{2-} + 2Ag^+ = PtO + 2Ag} \qquad (1)$$

Relatively large amounts of chromate and dichromate ions were added to 100 g of $NaNO_3$-KNO_3 melt such that the equilibrium concentrations of these ions are essentially their analytical concentrations and the oxide ion concentration is equal to $K[CrO_4{}^{2-}]^2/[Cr_2O_7{}^{2-}]$ where K is the equilibrium constant for the reaction $2CrO_4{}^{2-} = Cr_2O_7{}^{2-} + O^{2-}$. The Nernst equation for the cell reaction can be written

$$E = E^{\circ\prime}(\mathrm{Ag^+|Ag}) - E^{\circ\prime}(\mathrm{Pt|PtO}) + RT/F \ln\,[\mathrm{Ag^+}] + RT/2F \ln\,\{[\mathrm{CrO_4{}^{2-}}]^2/[\mathrm{Cr_2O_7{}^{2-}}]\} + RT/2F \ln K \qquad (2)$$

where $E^{\circ\prime}$ represents the standard reduction potentials for the half-reactions including the appropriate activity coefficient terms. After the addition of an amount of $CrO_4{}^{2-}$ and $Cr_2O_7{}^{2-}$, we found that the cell required 1 day to equilibrate and reach a constant potential. This equilibrium potential was always approached from a lower potential. However, the cell responded rapidly to further additions of $CrO_4{}^{2-}$ and $Cr_2O_7{}^{2-}$ and constant potentials were obtained within 2-5 min and remained constant for several hours. If the $CrO_4{}^{2-}$:$Cr_2O_7{}^{2-}$ ratio was sufficiently large [a ratio of 2:1 or larger], the potential was found to remain constant for 1-2 days.

The potential of the cell was recorded at various $CrO_4{}^{2-}$-$Cr_2O_7{}^{2-}$ concentrations using three different reference electrodes at 250°. The slopes of the lines for Nernst plots represented in Figure 1 concur with the two-electron process for the cell reaction. The span in potential between the lines represents the difference in the silver concentration in the reference electrodes and corresponds to $2.3RT/F \log \{[Ag^+]_1/[Ag^+]_2\}$. The temperature dependence of this cell which is buffered for oxide ion by the presence of $CrO_4{}^{2-}$ and $Cr_2O_7{}^{2-}$ was found to be linear in the temperature range of 250-280°, Figure 2.

The slopes of the lines in Figure 2 are not the same because the melt was not buffered to the same oxide ion concentration. One can evaluate the temperature dependence for the standard emf of our cell using the temperature dependence for K reported by Kust.[12]

$$\log K = -7.27 - 218.5/T \qquad (3)$$

Substituting eq 3 into eq 2 and differentiating with respect to temperature, one obtains

$$\frac{\partial E}{\partial T} = \frac{\partial E^{\circ\prime}}{\partial T} + \frac{2.3R}{F} \log\,[\mathrm{Ag^+}] + \frac{2.3R}{2F} \log \frac{[\mathrm{CrO_4{}^{2-}}]^2}{[\mathrm{Cr_2O_7{}^{2-}}]} + \frac{2.3R}{2F}(-7.27)$$

where $\partial E/\partial T$ is obtained from Figure 2. An average of the $\partial E^{\circ\prime}/\partial T$ values yields a value of −0.111 mV/deg. The standard emf *vs.* $Ag|Ag^+$ (1.0 *m*) reference electrode is 0.547 V at 250°. These values are in contrast to the values reported by Kust and Duke which are −0.256 mV/deg and 0.642 V. Therefore we propose that in the presence of an atmosphere of oxygen the platinum-oxygen electrode responds to the oxidation reaction having the largest oxidation potential, namely, $O^{2-} = {}^1/_2O_2 + 2e^-$. However, when oxygen is excluded from the melt this indicator electrode becomes an electrode of the second kind and responds to the oxidation reaction $Pt + O^{2-} = PtO + 2e^-$.

It would be interesting to see if this second electrode would respond to Lux-Flood acids and bases if the PtO were destroyed. Not much thermodynamic information is known concerning PtO, but it is reported that PtO is unstable at temperatures exceeding 550° and that it is easily reduced to Pt in an atmosphere of hydrogen at room temperature.[13] Alkali nitrate melts begin to decompose significantly above 400° and therefore we chose to investigate this hypothesis

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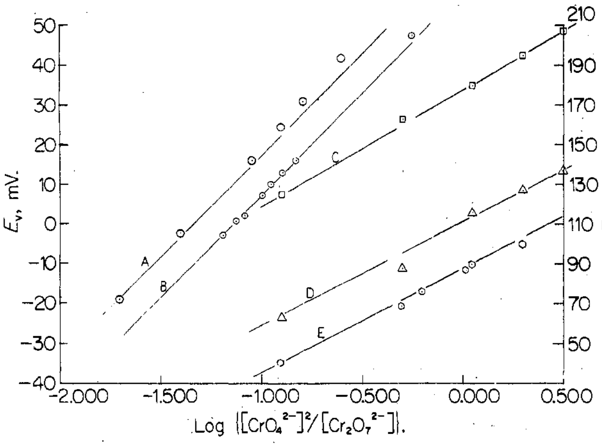

Figure 1. Potential *vs.* log $\{[CrO_4{}^{2-}]^2/[Cr_2O_7{}^{2-}]\}$ at 250° to determine the Nernst slope. The Ag^+ concentration in the reference electrode was 10 times greater for the data points in C, D, and E than for the data points in A and B; therefore, refer to the right-hand ordinate legend and lower abscissa legend for curves C, D, and E. A gold indicator electrode was used to obtain the data represented by curve C. Points are experimental and lines are theoretical.

by passing hydrogen gas over our electrode which is immersed in a $Cr_2O_7{}^{2-}$-$CrO_4{}^{2-}$ solution of fused nitrate. When hydrogen gas is passed over the indicator electrode, there is an immediate change in potential of approximately 200 mV and the new potential readings are quite unstable and insensitive to the addition of acids and bases to the melt. The acids and bases we used were $Cr_2O_7{}^{2-}$, $CrO_4{}^{2-}$, MoO_3, $Mo_2O_7{}^{2-}$, and $MoO_4{}^{2-}$. When hydrogen gas is removed and swept out of the melt with nitrogen, the potential returns to its expected value and the electrode once again responds to addition of acids or bases. This observation indicates that hydrogen destroys the Pt-O_2 electrode by removing a PtO film on Pt and in the absence of oxygen the electrode does not respond to oxide ions. It appears that the hydrogen did not significantly reduce any ions in the melt which could alter the concentration of oxide ions because the potential returned to its original value when the hydrogen was removed from the melt. In addition to the above observation we found that replacing the Pt indicator electrode with a gold electrode in an atmosphere of nitrogen increased the potential at the indicator electrode by approximately 80 mV, Figure 2. This observation further demonstrates that the indicator electrode in our system does not function as an inert supporting electrode for the different half-reactions which have been proposed by several authors but that the indicator is an electrode of the second kind and the half-reaction is the oxidation of a metal to its oxide in nitrate melts.

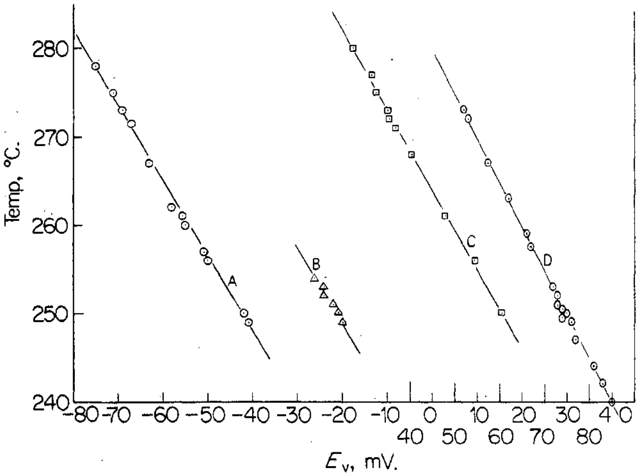

Figure 2. Temperature dependence of the galvanic cell: A, $[Cr_2O_7{}^{2-}] = 0.01\ m$, $[CrO_4{}^{2-}] = 0.01\ m$, $[Ag^+] = 0.10\ m$; B, $[Cr_2O_7{}^{2-}] = 0.005\ m$, $[CrO_4{}^{2-}] = 0.01\ m$, $[Ag^+] = 0.10\ m$; C, $[Cr_2O_7{}^{2-}] = 0.01\ m$, $[CrO_4{}^{2-}] = 0.03\ m$, $[Ag^+] = 0.10\ m$; D, $[Cr_2O_7{}^{2-}] = 0.03\ m$, $[CrO_4{}^{2-}] = 0.05\ m$, $[Ag^+] = 1.0\ m$.

The origin of the PtO is difficult to determine because the amount of oxidant required to oxidize the platinum surface exposed to the melt is immeasurably small. It is reported[14] that in aqueous systems one must distinguish between two types of platinum-oxygen electrodes. One electrode, designated as Pt(0)|O_2, is normally obtained by treating the Pt in HNO_3. This electrode is described as a Pt surface covered with a complete layer of absorbed oxygen. Perhaps the NO_3^- ion in our melts maintains an oxide film on our electrode. Other acids and bases which are not considered as strong oxidants, *e.g.*, $Mo_2O_7{}^{2-}$, $MoO_4{}^{2-}$, and $CO_3{}^{2-}$, do respond to our electrode in nitrate melts.[11,15]

Registry No. Pt, 7440-06-4; O_2, 7782-44-7.

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