Oxidation of Vanadyl Ion by Nitrate Ion

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The reaction of HNO_3 with vanadyl ion [1, 2] and the instability of concentrated vanadyl nitrate solutions [3] have been reported in the literature. However the apparent autocatalytic behavior which can be exhibited by the reaction of vanadyl ion with nitrate ion has not. This note gives a small amount of data concerning this reaction that we have obtained at 80 °C.
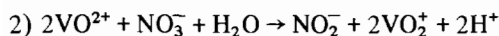
Free energy calculations [4] show that the equilibrium constants for the possible reactions involved are less than unity at 25 °C, but it is estimated that for reaction 1, $K_e = \sim$ unity at 80 °C.
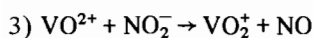
1) $3VO^{2+} + NO_3^- + H_2O \rightarrow NO + 3VO_2^+ + 2H^+$
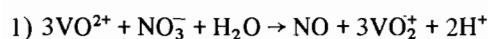
at 25 °C $\Delta G° = +3.19$ Kcal/mol, $\Delta H° = +22.4$ Kcal/mol, $K_e = 4.7 \times 10^{-3}$.

at 80 °C using $\dfrac{d\Delta G°}{dT} = (\Delta S)_{25°C}$,

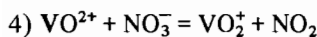$\Delta G° = -0.35$ Kcal/mol, $K_e = \sim 1.6$.

2) $2VO^{2+} + NO_3^- + H_2O \rightarrow NO_2^- + 2VO_2^+ + 2H^+$

at 25 °C $\Delta G° = +7.2$ Kcal/mol, $K_e = 5.7 \times 10^{-6}$

3) $VO^{2+} + NO_2^- \rightarrow VO_2^+ + NO$

at 25 °C $\Delta G° = -4.01$ Kcal/mol

4) $VO^{2+} + NO_3^- = VO_2^+ + NO_2$

at 25 °C $\Delta G° = +5.27$ Kcal/mol

Experimental

The experiments were carried out in a 250 ml Erlenmeyer flask containing a Teflon stirring bar operated by a magnetic stirrer. A rubber septum was attached to a side arm on the flask so that various solutions could be injected. The flask could be purged with either O_2 or A before a run, and was connected to a water manometer and a 100 ml glass syringe lubricated with water so that the volume of gas evolved or absorbed could be measured. The flask was immersed in a water bath, the temperature of which was manually controlled.

The 1 *M* $VOSO_4$ solution was made by SO_2 reduction of a V_2O_5–H_2SO_4 mixture and excess H_2SO_4 was added ($\sim$25 ml/L) until the pH was 0.40. All experiments were done by heating 25 ml of this solution to 80 °C in the appropriate atmosphere (A or O_2) and the run started by injecting 1 ml of a 5.8 *M* $NaNO_3$ solution.

Results

Argon Atmosphere

Figure 1, curve A, shows the evolution of NO from the $VOSO_4$ solution in argon following the injection of 1 ml of a 5.8 *M* $NaNO_3$ solution. The reaction has a long induction period after which it proceeds rapidly with the evolution of NO (identified as a colorless gas that turns brown with O_2 addition), and the production of a large amount of a light brown solid. The solid after recovery by filtration, washing and drying at 100 °C is amorphous (no X-ray diffraction pattern) and contained 9.8 mmol. of V^{+5} per gram. Expected for V_2O_5 is 11.0 mmol. of V^{+5} per gram so that the brown solid may contain some four valent vanadium. IR spectra of the solid showed no evidence of $SO_4^=$ or NO_3^-.

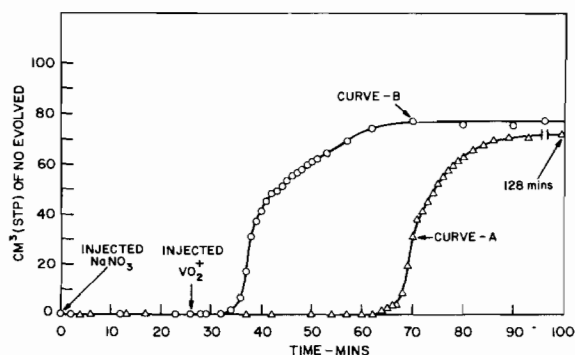
Fig. 1. Experiments in Ar Atmosphere. Curve A: NO evolution from $\sim$1 *M* $VOSO_4$ as a function of time at 80 °C following the injection of 1 ml of 5.8 *M* $NaNO_3$ solution. In curve B, 1 ml of 0.21 *M* V^{+5} (in 10% H_2SO_4) injected 26 min after the $NaNO_3$ injection.

The pH of the solution at the end of the run was 0.04, and the NO_3^- ion content of the solution determined by ion chromatography was 1.8 ± 0.2 mmol. By use of Fe^{2+} titration, the V^{+5} content of the final solution (solid and liquid) was found to be 11.78 mmol. The E.M.F. of a Pt electrode immersed in the solution (before titration) was 0.727 volts (0.97 volts *vs* H_2). This reflects the oxidation potential of V^{+5} since it decreases to 0.55 volts as the V^{+5} is titrated with Fe^{2+} (in the presence of NO_3^- which

does not change concentration during the titration). This 0.97 value is close to the value of 0.96 for the formal oxidation potential of NO_3^- producing NO as would be expected at equilibrium from the value of ~0 for the $\Delta G°$ of Eqn. 1.

The failure to react all of the nitrate with V^{+4} (only ~69% reacted) may result from the small equilibrium constant. The expected % conversion cannot be calculated using the estimated equilibrium constant of 1.6 at 80 °C since the NO partial pressure in this system is not known with precision, nor do we know the activity coefficient of the V^{+4} and V^{+5} ions in the final solution. Using the total V^{+5} content found in the final solution (both solid + liquid) of 11.8 mmol., the ratio of mmol. of V^{+5} produced to mmol. of NO_3^- consumed (3.96) is 2.98 which is close to that expected from Eqn. 1. However, the ratio of the mmol. of NO produced $(72/22.4 = 3.21)$ to the mmol. of V^{+5} made is 0.272 which is lower than the expected value of 1/3. In a repeat run, a value of 0.273 was found. The reason for this discrepancy is not known.

The long induction period followed by what appears to be an autocatalytic reaction is difficult to explain. No appreciable NO (<2 ml) evolution is observed during this time. During the induction period a buildup of NO_2^- by reduction of NO_3^- does not occur because when 1 ml of 5.8 M $NaNO_2$ is injected into 25 ml of a $VOSO_4$ solution at 80 °C there is an immediate evolution of 117 ml S.T.P. (5.2 mmol.) of gas (NO). An experiment was done (curve B, Fig. 1) in which a small amount (1 ml) of a 0.21 M VO_2^+ solution (in 10% H_2SO_4 solution) was added part way through the induction period. This small amount of VO_2^+ reduced the induction period time. This observation would be consistent with an hypothesis that the induction period ends when the brown solid, which contains V^{+5} and is not very soluble, starts to precipitate, but we have no other evidence to support this other than a visible observation of the precipitate during the initial period of rapid reaction.

O_2 Atmosphere

During the reaction of VO^{2+} with NO_3^-, the NO evolved will react with oxygen, if present above the solution, and form NO_2 which can react with water to form HNO_3 and HNO_2. The HNO_2 may decompose to HNO_3 and NO or it may oxidize VO^{2+} (a fast reaction) with the liberation of NO. The consumption of O_2 should be observed during the oxidation of VO^{2+} by NO_3^- in oxygen, and, provided no N_2 or N_2O is produced, the NO_3^- concentration should be the same at the end as at the start of the experiment.

Oxygen absorption during the reaction of NO_3^- with VO^{2+} in an oxygen atmosphere is shown in Fig. 2. There is an induction period of ~20 min, and during the period of rapid O_2 consumption, NO_2 was
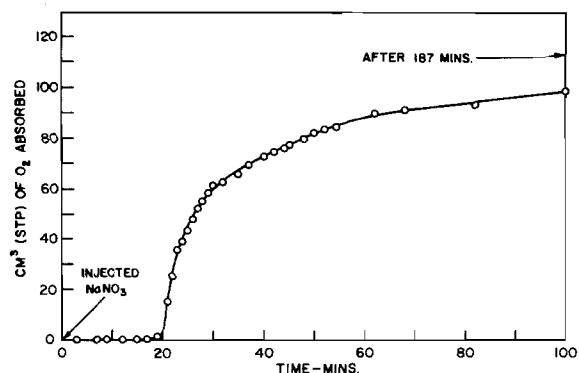

Fig. 2. Experiment in O_2 Atmosphere. O_2 absorption as a function of time at 80 °C by ~1 M $VOSO_4$ solution after injection of 1 ml of 5.8 M $NaNO_3$ solution.

visible in the gas phase. At the end of the run (187 min), the solution pH was ~0 and the E.M.F. of a Pt wire immersed in the solution vs a saturated calomel electrode was 0.78 volts. The total amount of V^{+5} found in the light brown solid product and liquid together, as determined by Fe^{2+} titration, was 20.0 mmol. This corresponds to an oxygen consumption of 112 ml S.T.P., close to the value of 113 ± 2 ml found experimentally. The total mmol. of NO_3^- found in the final solution by ion chromatography was 6.0. This is within experimental error of the initial NO_3^- value (5.8 mmol.). Thus, we have no evidence for a side reaction producing N_2 or N_2O. If the brown solid produced by an oxidation run is recovered by filtration and added to a fresh $VOSO_4$ solution, *no induction period* in oxygen absorption after $NaNO_3$ injection is noted. The brown solid will, however, not in itself, catalyze the oxidation of $VOSO_4$ by oxygen in solution at pH = 0.4.

Conclusion

The oxidation of vanadyl sulfate in acid solution at 80 °C by nitrate ion occurs as a rapid reaction after a long induction period which, in appearance, resembles an autocatalytic reaction. In the presence of oxygen, and in a closed system, nitrate ion can act as an efficient catalyst for the oxidation of vanadyl ion by oxygen.

References

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