[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, JOHNS HOPKINS UNIVERSITY]

A New Mechanism for the Action of the Vanadium Pentoxide–Silica–Alkali Pyrosulfate Catalyst for the Oxidation of Sulfur Dioxide

BY J. H. FRAZER AND W. J. KIRKPATRICK

A mechanism for the action of this catalyst has been proposed by Bernhard Neumann.[1] His mechanism is based on the assumption that sulfur dioxide reduces pentavalent vanadium to the quadrivalent state and that silica is an inert support. He does not mention the role of the alkali pyrosulfate present in this catalyst.

Neumann states: "Die Umsetzung verlauft nach folgendem Schema:

$$2VOSO_4 \longrightarrow V_2O_5 + SO_3 + SO_2$$
$$V_2O_5 + SO_2 \longrightarrow V_2O_4 + SO_3$$
$$2SO_2 + O_2 + V_2O_4 \longrightarrow 2VOSO_4\text{''}$$

This mechanism may be possible if the silica and alkali pyrosulfate were omitted from the catalyst. Such a catalyst, however, is not active at 450° where the vanadium pentoxide–silica–alkali pyrosulfate mass is used.

Role of Alkali Pyrosulfate.—Alkali pyrosulfate is molten at 450°, the temperature at which the catalyst is used. It is a solvent for vanadium pentoxide. This solution is distributed on the silica and has sufficient mobility to cause the catalytic surface to be renewed constantly.

When dissolved in molten alkali pyrosulfate, pentavalent vanadium is reduced by sulfur dioxide to the trivalent state.

$$K_2S_2O_7 + V_2O_5 + 2SO_2 \longrightarrow 2KV(SO_4)_2$$

This was found by passing sulfur dioxide into a solution of vanadium pentoxide in potassium pyrosulfate at 450° for ten minutes. The solution was cooled rapidly and dissolved in water. Part was titrated with 0.1 *N* ferrous sulfate and part with 0.1 *N* acidified potassium permanganate. The part titrated with ferrous sulfate was treated with ammonium persulfate and then titrated with permanganate.[2]

The first titration gave the reduced vanadium, the second the oxidized, and the third the total reduced and oxidized. It was found that all the vanadium was reduced and that two equivalents of permanganate were required, showing that the vanadium was in the trivalent state, not the tetravalent.

The action of molten potassium pyrosulfate has been studied by several investigators.[3,4,5]

All of these authors agree that vanadyl sulfate disproportionates when dissolved in alkali pyrosulfate at or above its melting point. This was further confirmed by dissolving some vanadyl sulfate in molten potassium pyrosulfate, cooling, dissolving in water and titrating as above. Quadrivalent vanadium disproportionates under these conditions into the trivalent and pentavalent states.

$$2V^{IV} \longrightarrow V^{III} + V^{V}$$

Accordingly, it is impossible for tetravalent vanadium to be present in the catalyst at any stage under operating conditions.

Role of Silica.—Silica has been used since the fifteenth century for decomposing sulfates such as those of calcium or iron, the silica displacing the more volatile sulfur trioxide.[6,7,8]

The displacement of sulfur trioxide by silica can be conveniently expressed

$$2KV(SO_4)_2 + 2SiO_2 \longrightarrow V_2Si_2O_7 + K_2S_2O_7 + 2SO_3$$

F. Rivenq[9] studied the decomposition of vanadic sulfate in the absence of silica or pyrosulfate. He expressed the decomposition above 419° as

$$2V_2(SO_4)_3 \longrightarrow 2VOSO_4 + V_2O_4 + SO + SO_3$$

In the presence of alkali pyrosulfate, vanadium would remain in the trivalent state, and if silica also were present the rate of evolution of sulfur trioxide would be increased.

Oxidation of Vanadic Silicate.—Vanadic silicates of various ratios were made by adding 10% aqueous solution of potassium silicate to 10% aqueous $KV(SO_4)_2$. The silicate with a vanadium to silica ratio of 1:1 was found to oxidize most readily. This oxidation was com-

---

[1] Neumann, *Z. Elektrochem.*, **39**, 799 (1933); **41**, 589 (1935).

[2] "Standard Methods of Chemical Analysis of Alloy Steels," American Society for Testing Materials, A, 55-24, p. 18, 1924.

[3] V. Auger, *Compt. rend.*, **173**, 306 (1921).

[4] A. Rosenheim and Hsin Yu Mong, *Z. anorg. Chem.*, **148**, 25 (1925).

[5] A. Sieverts and E. L. Müller, *ibid.*, **173**, 313 (1928).

[6] J. Newton Friend "Textbook of Inorganic Chemistry," Vol. VII, part II, 144: "In the fifteenth and sixteenth centuries the alchemists obtained sulfuric acid in this manner, frequently aiding the process by the addition of silica and the process was worked on a commercial scale until the end of the nineteenth century."

[7] Trey, *Z. angew. Chem.*, **22**, 2375 (1909).

[8] G. Marchal, *Compt. rend.*, **177**, 1300 (1923); *ibid.*, **188**, 399 (1929); *Bull. soc. chim.*, **39**, 401 (1926).

[9] F. Rivenq, *Bull. soc. chim.*, **4**, 1697 (1937).

plete at temperatures as low as 100°. All other ratios tried gave products more difficult to oxidize.

Mechanism of the Action of the Catalyst.—Summing up, the over-all mechanism is

$$V_2O_5 + K_2S_2O_7 + 2SO_2 \longrightarrow 2KV(SO_4)_2$$
$$2KV(SO_4)_2 + 2SiO_2 \longrightarrow K_2S_2O_7 + V_2Si_2O_7 + 2SO_3$$
$$V_2Si_2O_7 + O_2 \longrightarrow V_2O_5 + 2SiO_2$$

Experimental

Preparation of the Catalyst.—The catalyst used in this investigation was made according to example 2 of the Slama and Wolf patent.[10]

Potassium Vanadium Sulfate ($KV(SO_4)_2$).—This sulfate was made by melting potassium pyrosulfate in a round-bottomed flask and adding 10% potassium vanadate with stirring. Sulfur dioxide was then bubbled in until the melt had a bright green color. The melt was poured on an enameled iron slab. When cool, the mixture was broken up and placed in a beaker of water. It was filtered rapidly and washed free of excess pyrosulfate. $KV(SO_4)_2$ when dry was a yellowish green powder.

Acknowledgments.—The authors are indebted to Professor J. C. W. Frazer of the Johns Hopkins University for permission to use part of the investigation that was carried out under his direction. The authors also express their gratitude to the officers of the John Hopkins University for granting permission to use their laboratory facilities during the summer of 1936.

Summary

A new mechanism for the action of the vanadium pentoxide–silica–alkali pyrosulfate is proposed. The assumption, formerly accepted, that tetravalent vanadium is an intermediate is shown to be untenable. Evidence for the existence of trivalent vanadium as an intermediate is presented. The roles of alkali pyrosulfate and silica are explained.

BUFFALO, N. Y.
MARSHALLTON, DEL.
RECEIVED APRIL 16, 1940

---

[10] Slama and Wolf, U. S. Reissue Patent No. 19,282.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Study of Heterogeneous Equilibria in Aqueous Solutions of the Sulfates of Pentavalent Vanadium at 30°

BY OSCAR E. LANFORD AND SAMUEL J. KIEHL

Introduction

Although vanadium pentoxide is known to be chiefly acid-forming in water systems, crystalline compounds containing vanadium pentoxide, sulfur trioxide, and water only were prepared long ago. Substances believed to be $V_2O_5 \cdot 2SO_3$, $V_2O_5 \cdot 3SO_3$ and $V_2O_5 \cdot 3SO_3 \cdot 3H_2O$ were reported and discussed by Berzelius, Gerland, Ditte and Munzing.

Moreover the only data available on the solubility of vanadium pentoxide in solutions of sulfuric acid, are those of Meyer and Aulich.[1] But these data are not entirely satisfactory because evidence of the attainment of equilibrium is lacking, no sulfate determinations were made, and, in addition, the only indication given of the sulfuric acid concentration of such solutions is the initial concentration of the sulfuric acid with which each solution was started. The authors conclude that, both at 25 and at 100°, the solubility curve shows two maxima, "between which lies presumably a region of colloidal solution." No information was given regarding the nature of the solid phase in contact with these vanadium pentoxide–sulfuric acid solutions.

In view of the fact that the compounds prepared by Berzelius represent more or less arbitrary stopping-points in the decomposition by heat of vanadium pentoxide–sulfuric acid solutions, a consideration of the three-component system V_2O_5–SO_3–H_2O seems likely to add significantly to the existing knowledge.

Accordingly, a study was made at 30° (and at ordinary atmospheric pressure). The effect of changes in atmospheric pressure on the solubility in such systems is negligible.

Preparation and Analysis of Material

Vanadium Pentoxide.—The starting material was a fine yellow powder, analysis of which showed a vanadium pentoxide content of 99.75% and a weight loss of 0.19% on gentle ignition. Ten-gram portions of this product

---

[1] Meyer and Aulich, *Z. anorg. Chem.*, **194**, 278 (1930).