to be more stable than the corresponding hydroxide.

3. Dissociation constants of the ion–ion pair equilibrium have been computed. Salts with larger ions have larger dissociation constants.

PROVIDENCE, RHODE ISLAND RECEIVED JUNE 24, 1940

NOTES

The Sulfites of Aluminum and Iron at 30°

BY WARREN F. BARTZ

Studies of the reactions of the oxides of aluminum and of iron, respectively, with aqueous sulfur dioxide have led to many publications including patents. Several sulfites of each base have been described and it would appear that high concentrations of the metals are attained in the liquid phase. This communication reports observations on the composition of the solids formed when sulfur dioxide is injected into aqueous suspensions of the hydroxides at 30°.

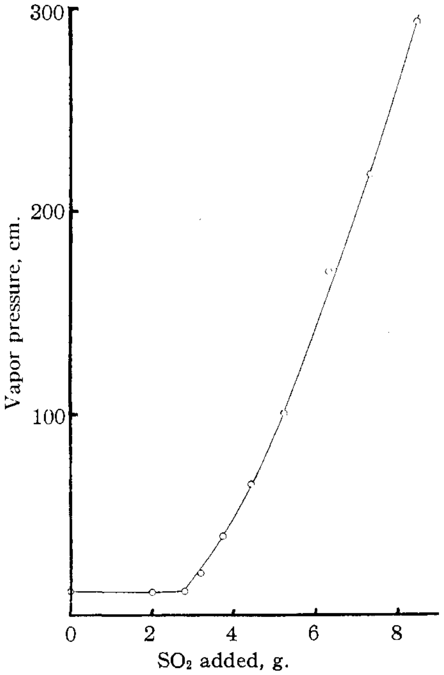

Fig. 1.—Vapor pressures in the system H_2O–SO_2–Al_2O_3.

Aluminum hydroxide was prepared by precipitation with ammonia from a solution of aluminum chloride and washing the precipitates free from chlorides. The dried precipitate with about an equal weight of water was placed in a glass absorption vessel which was attached to a manometer by a flexible copper tube, so the vessel could be agitated in a constant temperature-bath. The bath was kept at 30 ± 0.1°. Air was removed by suction and flushing with a small amount of sulfur dioxide. Measured quantities of sulfur dioxide were then introduced and the resulting pressures observed. At a pressure of about 300 cm. the process was reversed and measured amounts of sulfur dioxide withdrawn and pressures noted. Alternating the addition and withdrawal of sulfur dioxide led finally to sets of observations which all fell on a graph as shown in Fig. 1. It was not considered desirable to attain higher pressures since there was no indication that another metal sulfite would be found. The formation of the well-known hydrate of sulfur dioxide was not desired. It appeared that but one sulfite of aluminum is formed at 30°, and further additions of sulfur dioxide merely ran the vapor pressure of the suspension proportionally to the excess of added gas. Analysis of the solid formed in the absorption vessel leads to the formula $Al_2O_3 \cdot 1.86SO_2 \cdot 5.9H_2O$, while a product obtained by bubbling sulfur dioxide through a suspension for a month and then storing over sulfuric acid for two months leads to the formula $Al_2O_3 \cdot 2.03SO_2 \cdot 6.7H_2O$. It may be concluded that the product is the basic sulfite $Al_2O_3 \cdot 2SO_2 \cdot 6H_2O$. This agrees with the results obtained by Huber,[1] but Rosencranz and Hüttig[2] report but 3.3 water in the product obtained by them.

The colorless product is quite stable in dry air. Heated in a dilatometer with cottonseed oil, it was stable to 105° when it decomposed rapidly and was not reformed on cooling. The sulfite dissolves in water, but slowly, even in the presence of an excess of sulfur dioxide. Unless air be rigor-

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(1) K. Huber, *Helv. Chim. Acta*, **18**, 858 (1935).

(2) E. Rosencranz and G. Hüttig, *Gazz. chim. ital.*, **14**, 360 (1884).

ously excluded, there is oxidation of the sulfur dioxide with increased solution of alumina. The average of three determinations showed a solution containing 14.3% sulfur trioxide to contain 6.7% aluminum oxide.

Ferric sulfites have been described by several investigators. It is generally conceded that they are readily reduced in the presence of an excess of sulfur dioxide. The sulfur trioxide formed increases the solubility.

Ferrous hydroxide was prepared by precipitation from a hot solution of ferrous sulfate with ammonia, filtering and washing in an atmosphere of nitrogen in the device proposed by Bost.[3] Vapor pressure measurements of the suspensions in aqueous sulfur dioxide were made in the same manner as for aluminum hydroxide described above with quite similar results. One sulfite exists and addition of further quantities of sulfur dioxide produces increased pressure directly proportional to the excess sulfur dioxide.

Several samples of the solid phase were prepared. Stable in dry air, they were readily oxidized and decomposed in moist air. Analyses of the separately prepared products all gave results agreeing well with the formula of a normal salt, $FeO{\cdot}SO_2{\cdot}6H_2O$. Previous investigations have reported the normal sulfite as containing but 3 molecules of water of crystallization, and this is the figure reported by Henderson and Weiser[4] who prepared it in a quite different way.

It was not practicable to prepare aqueous solutions of ferrous sulfite which were entirely free of sulfates. Apparently ferrous hydroxide is somewhat more soluble in aqueous sulfur dioxide than is aluminum hydroxide.

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[3] A. S. Wheeler and R. W. Bost, THIS JOURNAL, **50**, 2000 (1928).

[4] W. E. Henderson and H. B. Weiser, *ibid.*, **35**, 289 (1913).

UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C.
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The Radical of Tri-*p*-tolylamine

BY S. GRANICK AND L. MICHAELIS

Tri-*p*-tolylamine on oxidation yields an intensely blue colored compound, according to Wieland,[1] which has been interpreted by Weitz and Schwechten[2] as a free radical. Direct evidence for this interpretation has never been given. Direct determination of molecular weight, which in comparable cases was sometimes used and often with misleading results,[3] could not even be attempted in this case because of insufficient stability of the substance. However, the method of potentiometric titration can be used for the purpose. It unequivocally confirms the structure of a singly charged cationic free radical.

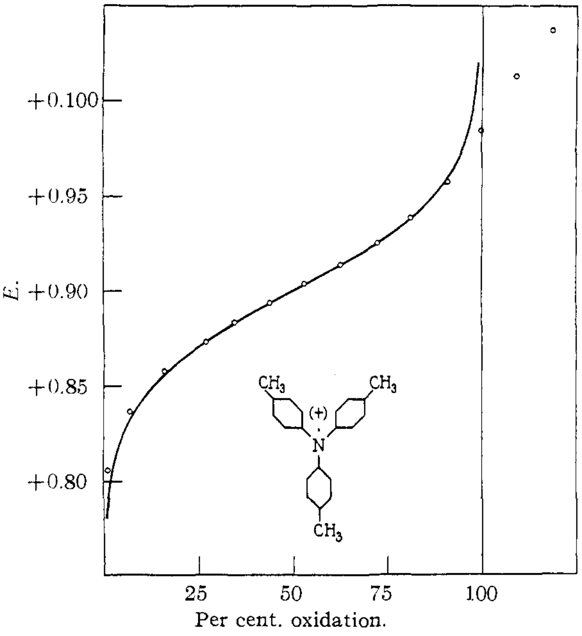

Fig. 1.

The potentiometric titration was carried out in a nitrogen atmosphere at 30°, using a potassium chloride–agar bridge. The solvent used consisted of 80 parts glacial acetic acid plus 20 parts, by volume, of water. Fifty cc. of a 1.5×10^{-4} *M* solution of tri-*p*-tolylamine in this solvent was titrated with a 3×10^{-3} *M* solution of lead tetraacetate in the same solvent. A blue color appeared and progressively increased in intensity with the addition of more oxidant. The potentials during the titration were rapidly established and were, although not perfectly stable, yet sufficiently so to yield an interpretable titration curve. As regards the stability of the potentials, the following experiment is characteristic: When the amine is mixed with about one-half equivalent of the oxidizing agent, the potential is rapidly established and drifts about 3 millivolts within ten minutes toward the negative side. Since for a regular titration experiment only a few minutes are requisite to obtain the whole curve, this drift is practically negligible. The whole titration experiment is shown in Fig. 1. As can be seen,

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[1] Wieland, *Ber.*, **40**, 4260 (1907).

[2] Weitz and Schwechten, *ibid.*, **59**, 2307 (1926).

[3] L. Michaelis, *Chem. Rev.*, **16**, 243 (1935).