$(RCl^{++})/(RH_2O^{+++})(Cl^-) = 1.2$[14] can be used. When this is done, the coefficient multiplying the rate function $(RH_2O^{+++})(Cl^-)(Cr^{++})$, now corresponding to reaction by the activated complex III in which chloride is a bridging group, is found to be at least 10^3. Thus, Cl^- appears in this system to be at least 50 times more effective as a bridging ligand than as a simple ligand on Cr^{++} in promoting electron transfer. It should be pointed out that the form $(RH_2O^{+++})(Cl^-)(Cr^{++})$ for expressing the rate by path III is artificial, because in actually starting with $RH_2O^{+++} + Cl^-$, the rate-determining step would be the formation of RCl^{++} from RH_2O^{+++} and Cl^-. This does not invalidate the comparison made. The calculation does show what the value of the rate coefficient for the kinetic function $(RH_2O^{+++})(Cl^-)(Cr^{++})$ would be for path III, if the substitution equilibrium were established rapidly.

A general and important implication of the present observations is this: OH^- (and probably H_2O) can transfer from oxidant to reductant during electron transfer in water, so that this mechanism must be considered a distinct possibility also for other aquo-cations undergoing electron transfer. Furthermore, at least for path 1, log a and E are similar in magnitude to values which have been observed in other systems, and therefore the agreement in the magnitude of these quantities for a variety of systems cannot be taken as diagnostic of a hydrogen atom transfer mechanism,[15] or in general of mechanisms which exclude close approach of oxidant and reductant.

It would be dangerous to generalize from the fractionation effects observed for the bridging group in the present system to other oxidizing agents. A consideration of the electron structure of Co(III), which shows that all stable orbitals are occupied, makes the existence of a marked fractionation effect in the bridging group appear reasonable, because an orbital about Co(III) must be vacated before the electron released by Cr^{++} can be accommodated. With oxidizing agents having stable orbitals vacant, the bridging group may function more nearly simply as a cement. Unfortunately, few systems of this kind can be suggested which are as amenable to direct study of fractionation effects as that chosen for the present work.

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[14] F. J. Garrick, *Trans. Faraday Soc.*, **33**, 486 (1937); $K = 1.8$ at $\mu = 0.3$. Corrected to $\mu = 1$, using variation of $K_{FeCl^{++}}$ with μ (E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942)).

[15] W. I. Reynolds and R. W. Lumry, *J. Chem. Phys.*, **23**, 2460 (1955).

CHICAGO 37, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

A New Method for the Preparation of Sodium and Calcium Nitrites

BY JAMES D. RAY AND RICHARD A. OGG, JR.

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Sodium nitrite was prepared by the reaction of nitric oxide with a mixture of sodium ferrate(III) and sodium nitrate at 400° in a vacuum system. The nitrite product was at least 99.9% pure. The reaction is quantitative with respect to nitrate, but a small percentage of nitric oxide must be recycled. Calcium nitrite was similarly prepared at 275°.

Introduction

Although the reversible reaction involving pyrolysis of sodium nitrate produces a melt containing a large proportion of nitrite contaminated with sodium oxide and peroxide,[1] isolation of pure nitrite is difficult. Even the exothermic irreversible reduction of nitrate with lead gives a product contaminated with sodium oxide.

This paper describes a method whereby very pure sodium nitrite may be prepared by means of the reversible exothermic reaction represented by the equation

$$NaNO_3 + Na_2Fe_2O_4 + 2NO = 3NaNO_2 + Fe_2O_3 \quad (1)$$

Preparation of Materials.—Nitric oxide was quantitatively prepared from potassium nitrate by a modification of the method discovered by Wagner[2] in accordance with eq. 2

$$K_2CO_3 + 2KNO_3 + Cr_2O_3 = 2K_2CrO_4 + 2NO + CO_2 \quad (2)$$

A twofold excess of chromic oxide which had been calcined at 950° under vacuum to remove higher oxides was used. The thoroughly mixed reactants were heated in a Pyrex side arm of a vacuum system to evolve the gases through a tube containing "Ascarite" in order to remove the carbon dioxide. The nitric oxide was collected in a trap cooled with liquid nitrogen for subsequent use in making nitrite. A pressure of less than 60 mm. during the course of nitric oxide and carbon dioxide evolution was not exceeded, since the Pyrex would soften at temperatures required for higher pressures.

Sodium ferrate(III) was prepared in a vacuum furnace at 850° from sodium carbonate and an excess of ferric oxide (precipitated powder). This temperature was employed since it gives the optimum rate for the reaction,[3] and a product of small particle size. It was found difficult to remove the last traces of carbon dioxide, hence the mixture was removed from the furnace twice for regrinding. A final heating with a vacuum of 10^{-3} mm. for 24 hours gave a product free of carbonate. This great care was necessary since subsequent methanol extraction of sodium nitrite from the products of its use (eq. 1) would also extract the carbonate to give an impure sodium nitrite product.

Experimental

Reaction 1 was carried out by placing a mixture of sodium

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[1] K. Leschewski and W. Degenhard, *Z. anorg. Chem.*, **239**, 21 (1938).

[2] A. Wagner, *Z. Anal. Chem.*, **18**, 552 (1879).

[3] V. R. Terashkevich, R. E. Shtok and E. G. Gurova, *C. A.*, **35**, 3775 (1941).

nitrate and excess sodium ferrate(III) in a short 20 mm. i.d. tube having one end closed off and terminated in a ground glass joint at the other. This was attached to a system having a mercury displacement gas buret for maintaining the pressure at about 1 atm. while the reaction proceeded. A trap was included in the system for transferring the nitric oxide to the system by means of a liquid nitrogen bath. A furnace surrounding the reaction chamber was brought to 250° and then slowly raised to 400°. Progress of the reaction was followed by change in the mercury level of the gas buret. It was found that the rate of the reaction was strongly pressure dependent, and fell rapidly as the reaction approached completion. With the nitric oxide pressure regulated at 760 ± 200 mm., the reaction was 99% complete in 48 hours at a temperature of 400 ± 10°. The temperature was then reduced to 360° for 72 hours. The furnace was then cooled, nitric oxide removed from the system, and the reaction chamber removed for extraction of the sodium nitrite with dry methyl alcohol. The use of methyl alcohol instead of water was necessary since an excess of water-hydrolyzable sodium ferrate(III) was employed. The weight of nitrite product compared to that of the nitrate reactant indicated 99.8% conversion. Titration with permanganate confirmed the product as sodium nitrite of better than 99.9% purity.

These results are confirmed by a few rough measurements which indicate that the equilibrium constant for reaction 1 at 400° is such as to give about 99.95% nitrite under a nitric oxide pressure of one atm.

Calcium nitrite was similarly prepared as represented by eq. 3

$$Ca(NO_3)_2 + 2CaFe_2O_4 + 4NO = 3Ca(NO_2)_2 + 2Fe_2O_3 \qquad (3)$$

This reaction took place most readily at 275° under one atmosphere of nitric oxide pressure. The reaction required about 48 hours for 99% completion.

Potassium nitrite could not be prepared by this method.

Discussion

Due to the slowness of the reaction at lower temperatures and pressures and the unfavorable equilibrium constant at higher temperatures, the optimum conditions described above are incapable of giving complete quantitativeness with respect to nitric oxide. However, by having the final gas volume small, quantitative conversions with respect to nitric oxide can be very nearly attained.

STANFORD, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE UNIVERSITY OF CONNECTICUT]

The Preparation of a Strontium–Iridium Oxide Sr_2IrO_4[1,2]

BY JOHN J. RANDALL, JR., LEWIS KATZ AND ROLAND WARD

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The preparation of strontium–iridium oxide, Sr_2IrO_4, is effected by heating mixtures of iridum metal powder and strontium oxide at 1200° in air. The compound has been shown to be isotypic with K_2NiF_4 No compound of the perovskite type could be obtained in this system despite the fact that the ionic radii of strontium and iridium are favorable.

One of the few ternary oxides of the platinum metals to be prepared and characterized is the hexagonal $Ba_3Pt_2O_7$.[3,4] A phase with a similar structure is obtained upon heating strontium oxide and platinum dioxide at 700°. When the preparation of analogous compounds of iridium was attempted, a phase having an entirely different structure was formed in the strontium–iridium–oxygen system.

Experimental

Strontium–iridium oxide is obtained readily by the reaction between iridium metal powder and strontium oxide, carbonate, nitrate or hydroxide at 1200° in air. In using the nitrate or hydroxide, the temperature must be brought slowly to 1200° to prevent spattering. The reaction occurs rapidly compared with most solid phase reactions, a pure product being obtained upon heating for 15 min., regrinding the sample and reheating for 15 min. The reactions were carried out in platinum or zirconium silicate combustion boats.

It was found that the X-ray powder diffraction pattern of the product could be assigned to a tetragonal unit cell, a = 3.89 Å., c = 12.92 Å. The density of the product was 7.45 g./cm.^{3}. This indicated that the unit cell could contain two formula weights of Sr_2IrO_4 (calculated density 7.44 g./cm.^{3}). Examination of the products obtained by heating mixtures with atomic ratio Sr/Ir = 1.5 revealed that iridium metal had settled out of the product to form a thin layer on the surface of the zirconium boat. When mixtures of lower atomic ratio were used, some iridium remained dispersed in the sample as revealed by X-ray analysis. With mixtures containing an atomic ratio Sr/Ir = 2, the presence of strontium oxide could not be detected by X-ray analysis, nor could any change in lattice constant be observed.

Chemical Analysis.—The compound was found to be soluble upon prolonged digestion with hydrochloric acid. The iridium was determined first by the method of Delépine[5] which involves the reduction of Ir^{+4} with excess iodide and titration of the liberated iodine with thiosulfate. Calcd. for Sr_2IrO_4: Ir, 44.67. Found: Ir, 44.12.

Because of the marked color change on reducton of $IrCl_6^{-2}$ (red-brown) to $IrCl_6^{-3}$ (light yellow-green), it was thought that a photometric method would also be appropriate. The solution containing $IrCl_6^{-2}$ was treated with chlorine, the excess being removed by boiling. Using a Fisher model Electrophotometer with a filter covering the absorption peak for $IrCl_6^{-2}$ (~495 mμ), a solution containing about 1 mg. of iridium in 200 ml. was titrated with 0.004 N ferrous ammonium sulfate solution. A plot of the optical density *vs.* ml. of ferrous solution added is shown in Fig. 1. This procedure gave % Ir = 44.52.

By first separating iridium according to the method of Gilchrist (precipitation as the hydroxide, ignition to the oxide and reduction to the metal)[6] it was possible to determine strontium by titration with Versene according to the method of Cheng.[7] The percentage of strontium was 39.77% (calculated for Sr_2IrO_4, 40.53%).

From these data, the formula Sr_2IrO_4 appears to be confirmed.

Structure Determination.—The unit cell dimensions for Sr_2IrO_4 are very close to those of K_2NiF_4.[8] Sr_2IrO_4: a = 3.89, c = 12.92 Å.; K_2NiF_4: a = 4.00 Å., c = 13.07 Å. Observation of systematic absences for the X-ray powder

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(1) Taken in part from a Master's Thesis submitted by John J. Randall, Jr., to The University of Connecticut, 1956.

(2) This research was supported by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(3) M. G. Rousseau, *Compt. rend.*, **109**, 144 (1889).

(4) W. O. Statton, *J. Chem. Phys.*, **19**, 40 (1951).

(5) M. Delépine, *Ann. chim.*, **7**, 277 (1917).

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(7) K. L. Cheng, private communication.

(8) D. Balz and K. Plieth, *Z. Elektrochem.*, **59**, 545 (1951).