Solutions and samples were then heated to the boiling point of the solutions for several minutes. In no instance was a reaction observed on heating if none had occurred with cold solutions.

All thorium silicides reacted with concentrated hydriodic acid, concentrated hydrochloric acid, concentrated hydrofluoric acid and aqua regia. None of the silicides reacted with 20% sodium hydroxide, 30% hydrogen peroxide, 0.1 *N* potassium permanganate or 5% nitric acid. Only Th_3Si_2 reacted appreciably with 36 *N* H_2SO_4 although both Th_3Si_2 and ThSi reacted with 6 *N* H_2SO_4. Only ThSi was even slightly attacked by concentrated nitric acid. All compounds except Th_3Si_2 were attacked by 5% hydrochloric acid.

All the thorium silicides were unstable on prolonged standing in air. They disintegrated slowly to form a fine black powder which was amorphous to X-rays. Samples of ThSi sometimes reacted with air rather rapidly. Melting points were not determined, but α-$ThSi_2$ and "β-$ThSi_2$" samples showed no sign of melting when heated to 1670° while samples of Th_3Si_2 were melted at 1700°. Samples of ThSi were never obtained free of "β-$ThSi_2$" or Th_3Si_2 and may be stable over only a limited temperature range.

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The Formation of Unipositive Nickel by Electrolysis in Concentrated Salt Solutions[1,2]

BY RUSSELL H. SANBORN AND E. F. ORLEMANN

RECEIVED MAY 4, 1956

The reduction of Ni(II) at the dropping mercury electrode leads to the formation of Ni(I) where the concentration of various salts, such as $NaClO_4$, $LiClO_4$, $Ca(ClO_4)_2$, NaCl and KCl, is made sufficiently high. In general, the formation of Ni(I) becomes clearly evident at salt concentrations of about one molar and becomes the principal process where the salt concentration is made two to three molar. Evidence for the formation of Ni(I) lies in a comparison of the observed diffusion currents with directly measured diffusion coefficients, the existence of an intermediate state of nickel that reacts with bromate, and the fact that the amount of metallic nickel produced per Faraday of electricity in the concentrated solutions is much less than that obtained in dilute salt solutions. Various experiments to characterize the plus one state of nickel are described and some possible explanations of the phenomenon are presented.

In the course of a study of the mechanism of reduction of the first transition group metals at the dropping mercury electrode, it has been found that nickel shows a marked difference in behavior from the other members of this group in concentrated salt solutions. This paper is concerned with a study of the reduction of Ni(II) in concentrated salt solutions and the evidence that Ni(I) is obtained as the primary product under certain conditions.

Experimental

A Sargent Model XII Polarograph was used to record the current–voltage curves. The electrolysis cell was of the H-type, with a sintered glass disk and an agar plug separating the two arms. Oxygen was swept out of the solutions with purified nitrogen. All measurements were made at 25 ± 0.03°.

All reagents were reagent grade chemicals except $LiClO_4$ and $Ca(ClO_4)_2$, which were crystallized out of solution prepared by the action of perchloric acid on the corresponding carbonates.

Results

Current–Voltage Curves of Nickel in Concentrated Solutions of Various Salts.—Current–voltage curves of Ni(II) in NaCl solutions from 0.1 to 3.0 *M* containing 10^{-3} *M* HCl are shown in Fig. 1. Curve 1 in Fig. 1 shows a single continuous c.v. curve corresponding to the reduction of Ni(II) to the metal. Curve 2 obtained in 1 *M* NaCl shows a distinct change in slope which suggests either a stepwise reduction of Ni(II) or possibly the reduction of two Ni(II) species, that have different activation energies of reduction, which are not maintained in equilibrium. Curves 3 and 4 show the effect of increasing the NaCl concentration to 2 and 3 *M*, respectively. The change in slope becomes more marked as the salt concentration is increased and the height of the first section of the c.v curve decreases. The limiting current of the first section will be referred to as i_1. It is measured approximately by the intersection of the extrapolated slopes of the initial and second "linear" sections of the c.v. curves. Values of i_1 so obtained are quite uncertain where a curve such as 2 is analyzed and become reasonably precise for curves such as 3 and 4.

In the light of data presented subsequently in this paper the curves in Fig. 1 are to be interpreted as follows. The reduction of Ni(II) is a two-step process. In 0.1 *M* NaCl the Ni(I) initially produced disproportionates rapidly or is immediately further reduced to metal at the electrode and the total diffusion current corresponds to complete reduction to the metal. In 1 *M* NaCl, curve 2, the activation energy for electrode reduction of Ni(I) has increased so that the stepwise nature of the reduction becomes observable. Where the NaCl is made 3 *M* this kinetic "stabilization" of Ni(I) has become almost complete and the limiting current i_1 is due almost entirely to reduction to Ni(I) with only a very small contribution by further reduction to the metal. It should be noted that the Ni(I), which is about 10^{-3} *M*, need only have a half-life greater than a few milliseconds to account for curves 3 and 4.

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[1] This paper comprises a portion of the Ph.D. Thesis of Russell H. Sanborn, University of California at Berkeley, December, 1955. The research was supported in part by AEC Contract W-7405-eng-48 at the Radiation Laboratory, Berkeley, California.

[2] Presented before the Physical and Inorganic Division of the 128th National ACS Meeting, Minneapolis, Minn., September, 1955.

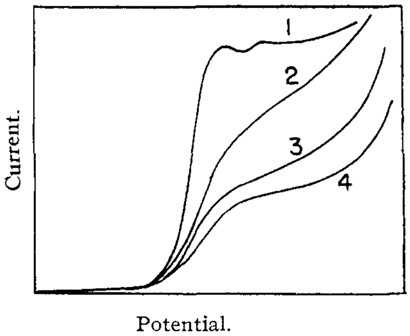

Fig. 1.—Effect of NaCl concentration on the diffusion current of 10^{-3} M Ni(II) in 10^{-3} M HCl. NaCl concentrations: (1), 0.10 M; (2), 1.0 M; (3), 2.0 M; (4), 3.0 M.

The c.v. curves of Ni(II) in $NaClO_4$ solutions from 0.1 to 3.0 M are shown in Fig. 2. The effect of salt concentration is seen to be closely parallel to that observed in NaCl solutions of the same concentrations. The only difference is that the "stabilization" of Ni(I) is not as pronounced as in 3 M NaCl and i_1 in 3 M $NaClO_4$ must include a significant contribution from the reduction of Ni(I) to the metal.

Current–voltage curves of Ni(II) have also been obtained over the concentration range 0.1 to 3.0 M in KCl, $LiClO_4$ and $Ca(ClO_4)_2$ solutions. In these cases the curves show the same general behavior as those presented in Figs. 1 and 2. In particular, the ratio of i_1 at a given salt concentration to i_1 in 0.1 M salt is almost constant at any given concentration of each of the salts. The effect of all of these salts is remarkably similar when compared at the same concentration level. This stepwise reduction of Ni(II) is also observed in 3 M NH_4Cl and 2 M NaAc.

Whatever the explanation may be it appears that the "stabilization" of Ni(I) is not a specific property of a given salt but is primarily dependent upon the magnitude of the salt concentration.

Comparison of Calculated and Observed Limiting Currents in $NaClO_4$ Solutions.—The measured diffusion coefficients of Ni(II) in 0.1 M $NaClO_4$ and 3.0 M $NaClO_4$ are 0.60×10^{-5} and 0.56×10^{-5} cm. sec.$^{-1}$, respectively.[3] From these values using the equation of Lingane and Loveridge[4] the calculated diffusion current is 7.2 ± 0.3 μamp. in 0.1 M $NaClO_4$, assuming complete reduction to the metal. The observed value is 6.8 ± 0.2 μamp. The calculated value in 3.0 M $NaClO_4$ is 6.9 ± 0.3 μamp. for reduction to the metal and 3.4 ± 0.2 μamp. for reduction to Ni(I). The observed i_1 in 3.0 M $NaClO_4$ is 2.9 ± 0.3 μamp. This is in agreement with the assumption that Ni(I) is the principal product in the concentrated salt solution.

The above result does not rule out the possibility that two species of Ni(II), reducible at different potentials, are obtained in these concentrated salt solutions although it does seem very unlikely that this would occur in such a similar fashion for the variety of salts studied.

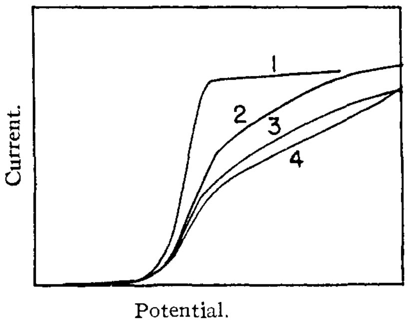

Fig. 2.—Effect of $NaClO_4$ concentration on the diffusion current of 0.8×10^{-3} M Ni(II). $NaClO_4$ concentrations: (1), 0.10 M; (2), 1.0 M; (3), 2.0 M; (4), 3.0 M.

Evidence for Ni(I) by Reaction with Bromate.—The current–voltage curves of Ni(II) in 0.1 M $NaBrO_3$ are the same as in 0.1 M $NaClO_4$. This shows that there is no direct catalysis of bromate reduction by Ni(II) nor any reaction between bromate and the Ni amalgam formed. However, in more concentrated $NaClO_4$ solutions with bromate present there is a reaction, as shown by the curves in Fig. 3. The greatly increased current observed in the presence of bromate in curve 3 of Fig. 3 combined with the fact that no such effect is found when Ni amalgam is produced in the dilute salt solutions seems to be good evidence that the reactive intermediate Ni(I) is formed in the more concentrated salt solution. If the bromate concentration is reduced below 0.01 M the rate of reaction with Ni(I) apparently becomes too slow for this effect to appear.

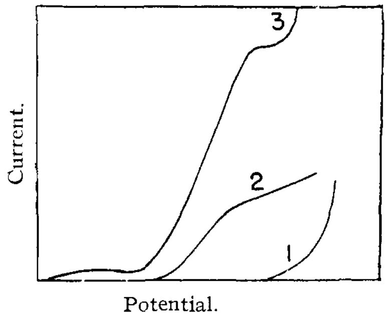

Fig. 3.—Current–voltage curves of Ni(II) in the presence of bromate: (1), 2.425 M $NaClO_4$, 0.075 M $NaBrO_3$; (2), 2.5 M $NaClO_4$, 10^{-3} M Ni(II); (3) 2.425 M $NaClO_4$, 0.075 M $NaBrO_3$, 10^{-3} M Ni(II).

The augmented diffusion current may be analyzed by equations developed by Koutecky[5] for diffusion currents produced by a combination of diffusion and reaction. It is assumed that the observed current is due to nickel only, and none to intermediate bromate reduction products. This assumption probably is not correct, but it sets an upper limit on the rate constant. With the total sodium ion concentration 2.5 M, and bromate and perchlorate as anions, an average bimolecular rate constant of 43 ± 10 liters mole^{-1} sec.$^{-1}$ was calculated. This theory also predicts that the total current should be linear with Ni(II) concen-

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(3) R. H. Sanborn and E. F. Orlemann, THIS JOURNAL, **77**, 3726 (1955).

(4) J. J. Lingane and B. A. Loveridge, *ibid.*, **72**, 438 (1950).

(5) J. Koutecky, *Collection Czechoslov. Chem. Commun.*, **18**, 597 (1953).

tration at a given bromate concentration, and this was found to be so. It was also found that there is no apparent reaction of Ni(I) with bromate in concentrated NaCl solution. This may reflect the influence of chloride ion on the rate of reaction of bromate with Ni(I).

Determination of the Amount of Nickel Metal Produced in Electrolysis.—Appropriate salt solutions containing 0.01 *M* Ni(II) were electrolyzed with the dropping mercury electrode for about two hours. The mercury was collected and analyzed for nickel content. The nickel was extracted with concentrated HCl overnight, with intermittent stirring. The solution was taken and analyzed for nickel by the polarographic method with 0.1 *M* KCl as the supporting electrolyte. The amount of Ni found was compared to that calculated from the observed average current, at potentials corresponding to i_1, and the time of electrolysis. If metallic nickel is the reduction product 100% of the calculated amount of Ni should be recovered. If Ni(I) is the only product and no metallic nickel is formed by reaction at the mercury surface before actual collection of the drops, no Ni should be observed. It is probable that metallic nickel is formed by disproportionation at the surface of the Hg as the drops fall and are collected and that varying amounts of Ni will be found even if Ni(I) is the primary product. The present experimental techniques are subject to several per cent. error due to uncertainty in the quantity of electricity employed and in the efficiency of the Ni recovery method. The results are given in Table I.

TABLE I

PER CENT. RECOVERY OF NICKEL FROM AMALGAMS, CURRENT EQUIVALENCE BASIS

Salt	Ni, %
0.1 *M* $NaClO_4$	96
3.0 *M* $NaClO_4$	68
2.5 *M* $NaClO_4$ and 0.5 *M* $NaBrO_3$	5
0.1 *M* NaCl	96
3.0 *M* NaCl	89
2.9 *M* NaCl and 0.1 *M* $NaBrO_3$	28

The data in Table I indicate that Ni(I) is the principal reduction product in the concentrated salt solutions studied. The direct measurements are complicated by disproportionation of Ni(I) during the fall and collection of the mercury drops, with the result that a large fraction of the Ni(I) initially produced is converted to the metal. In the presence of bromate there is rapid removal of Ni(I) by reaction and consequently more definitive experimental evidence of Ni(I) as the primary product.

Unipositive Nickel in the Presence of Other Reactants.—No change was observed in the nickel wave in 2.0 *M* $NaClO_4$ when either permanganate or ceric ion was added to the solution in small concentration. These are reduced at the electrode, of course, and apparently were not present in large enough concentration about the electrode to produce a noticeable interaction. The Ni(I) might be reduced by a strong reducing agent like chromous ion. Chromous is the reduction product of chromic at potentials below the nickel reduction, and its oxidation by nickel (I) would lead to an increase in the total current observed. However, the observed total current in Ni(II)–Cr(III) mixtures was merely a summation of the chromium and nickel diffusion currents.

The Disproportionation Mechanism of Nickel Reduction.—If the normal reduction of nickel in dilute solutions of supporting electrolytes involves the disproportionation of unipositive nickel where the rate is so large that a limiting diffusion current of twice that from a one-electron reduction is obtained, then in the intermediate salt concentrations the "diffusion current" should not be linear with concentration of nickel.[6] The diffusion current of nickel in 1.0 *M* $NaClO_4$ was taken as the height of the first portion of the total wave, and was found to be linear with nickel concentration up to 0.01 *M* nickel. This result indicates that the rate of disproportionation must be slow compared to the rate of diffusion of Ni(I) away from the electrode surface.

Attempts at Electrochemical Identification.—Nickel(II) in saturated NaCl was electrolyzed with a small mercury pool at 14°, then some of the solution just above the pool was quickly pipetted into a ferric–*o*-phenanthroline solution and the transmittance was observed with a colorimeter. The Ni(I), if present, should reduce the ferric–*o*-phenanthroline complex to the highly colored ferrous–*o*-phenanthroline complex. The transmittance was the same as the solution gave before electrolysis. This indicates either that the rate of reaction of the ferric complex with Ni(I) must be slow compared to the lifetime of Ni(I), or that the lifetime of Ni(I) is shorter than one to two minutes, which is the period of transfer.

In another experiment, the above solution was electrolyzed for a short time with a small mercury pool, and an attempt was made to find an oxidizable species just above the surface of the pool with the dropping mercury electrode. There was none detectable above the potential of the dissolution of mercury.

A dropping mercury electrode with a drop time of six seconds was used with a switching device to change from a potentiometer to the polarograph. The drop was allowed to form for two seconds, with an applied potential great enough to reduce nickel; then the arrangement was switched to the polarograph at a potential just below the nickel wave With a concentrated NaCl solution, a small oxidation current was observed, but the same result was found in the dilute solution.

Discussion

The facts that clearly seem to identify Ni(I) are: (1) the nickel wave is divided into two portions of approximately the same size in the presence of a high concentration of supporting electrolyte; the diffusion current of the first wave being approximately that calculated from measured diffusion coefficients for the formation of Ni(I); (2) a definite interaction between bromate ion and a reactive nickel reduction product has been observed, but only in the presence of a large concentration

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(6) E. F. Orlemann and D. M. H. Kern, THIS JOURNAL, **75**, 3058 (1953).

of supporting electrolyte; (3) less nickel is recovered from nickel amalgams formed out of solutions containing a large excess of supporting electrolyte—when bromate is added much less is obtained.

For Ni(I) to exist in a concentration less than 0.1% that of Ni(II) in the presence of metallic Ni, the potential for the reaction Ni(I) = Ni(II) + e^- must be greater than about 0.46 v. *vs.* NHE. From the observed electrode reduction potential of Ni(II) the reversible potential for the reaction Ni(I) = Ni(II) + e^- could be no more than 0.75 v. *vs.* the NHE. Thus the potential of the couple Ni(S) = Ni(I) + e^- must be between the limits of 0.04 and −0.25 v. *vs.* NHE. In order to observe Ni(I) it is therefore necessary that it be "stabilized" kinetically with respect to direct electroreduction and with respect to disproportionation.

We have no satisfactory explanation of the role of the various salts described in this paper in stabilizing Ni(I). It would seem that one feature they have in common is the possibility of altering the activity of water to the extent that the hydration structure of Ni(I) is changed. A second possibility is that the positive ions become so concentrated in the double layer that further reduction of Ni(I) is inhibited.

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[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Acidity of Triphosphoric Acid[1]

BY JAMES I. WATTERS, E. DAN LOUGHRAN AND SHELDON M. LAMBERT

RECEIVED MAY 31, 1956

Triphosphoric acid $H_5P_3O_{10}$, and tetramethylammonium triphosphate $((CH_3)_4N)_5P_3O_{10}$, were prepared by passing solutions of the sodium salt through cation-exchange resin columns charged with hydrogen ions and tetramethylammonium ions, respectively. The column was kept near 0° and the acid or salt was titrated with tetramethylammonium hydroxide or hydrochloric acid using a glass electrode immediately after warming the solution to 25°. One hydrogen ion was found to be largely dissociated in 0.01 *M* acid. The values obtained for the successive dissociation constants of the four remaining hydrogen ions at an ionic strength of 1.0 were $K_2 = 10^{-1.06}$, $K_3 = 10^{-2.11}$ $K_4 = 10^{-5.83}$ and $K_5 = 10^{-8.81}$. At an ionic strength of 0.1 the values of the last three constants were $K_3 = 10^{-2.15}$, $K_4 = 10^{-6.00}$ and $K_5 = 10^{-8.73}$. Extrapolated to infinite dilution the values became $K_3 = 10^{-2.30}$, $K_4 = 10^{-6.26}$ and $K_5 = 10^{-8.90}$.

Introduction

Although sodium triphosphate is available in commercial quantities there have been few published studies on the strength of the acid. This is in part due to the tendency of the triphosphate ion to form complexes with all metal ions including the alkali group and also to its rather rapid rate of hydrolysis, forming pyrophosphoric and orthophosphoric acids.

According to Monk[2] the first formation constant for the sodium complex is $10^{2.5}$. Van Wazer and Campanella[3] obtained a somewhat smaller complexity constant for sodium with several condensed polyphosphate glasses. They also investigated the complexes of other metal ions. Friess[4] found that triphosphoric acid hydrolyzes about six times faster than pyrophosphoric acid. The reaction is catalyzed by hydrogen ion. Rudy and Schloesser[5] published titration curves for triphosphoric acid in the presence of sodium ion but did not attempt to calculate the acidity constants since they were aware of the complex formation. Incidental to an anion-exchange study of condensed phosphates Buekenkamp, Rieman and Lindenbaum[6] calculated the thermodynamic acidity constants by the application of the Debye–Hückel equation to data obtained in the titration of the acid with potassium hydroxide. They mention several limitations on the accuracy of their constants which were satisfactory for their purpose. Their values were $pK_3 = 2.79$, $pK_4 = 6.47$ and $pK_5 = 9.24$.

Experimental

The sodium tripolyphosphate was prepared from anhydrous sodium tripolyphosphate, Monsanto technical grade, by recrystallizing four times to yield a 99.5% pure product according to a procedure developed by P. G. Arvon[7] in the Monsanto Laboratory. Eight hundred and forty g. of the salt was dissolved in 3.8 l. of water. The solution was filtered and treated with 1.4 l. of methanol with vigorous stirring. The crystalline $Na_5P_3O_{10}\cdot 6H_2O$ was collected on a filter, air-dried by suction and then allowed to air dry overnight. The precipitate was dissolved to produce a 13% solution by weight, and again crystallized by the addition of methanol in the same ratio. The crystals were filtered and dried as before. Four hundred and forty g. of crystalline product was leached by being thoroughly stirred with 200 ml. of water, filtered, and the filtrate discarded. Another crystallization, a leaching and a final crystallization were made using the same procedure and the same proportions as in the last steps. According to Quimby[8] the commercial 85 to 94% anhydrous salt can be made 99% pure by 3 to 5 recrystallizations from water with ethanol added to the extent of 25% by volume. Redistilled, carbonate-free water was used for all of the dilutions.

The tetramethylammonium chloride, used for the adjustment of ionic strength and for charging the column, was prepared from the Matheson Coleman and Bell 99+% product which was further purified by recrystallization from a solution containing methanol and acetone.[9]

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[1] Based in part on a thesis by E. Dan Loughran submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1955. Presented before the Division of Physical and Inorganic Chemistry, 129th Meeting of the American Chemical Society, Dallas, Texas, 1956.

[2] C. B. Monk, *J. Chem. Soc.*, 427 (1949).

[3] J. R. Van Wazer and D. Campanella, THIS JOURNAL, **72**, 655 (1950).

[4] S. L. Friess, *ibid.*, **74**, 4027 (1952).

[5] H. Rudy and H. Schloesser, *Ber.*, **73**, 484 (1940).

[6] J. Buekenkamp, Wm. Rieman and S. Lindenbaum, *Anal. Chem.*, **26**, 505 (1954).

[7] R. A. Ruerwein, private communication, Monsanto Chemical Co., Dayton, Ohio.

[8] O. Quimby, *J. Phys. Chem.*, **58**, 603 (1954).

[9] P. L. Pickard and W. E. Neptune, *Anal. Chem.*, **27**, 1358 (1955).