of the tendency of these compounds to vitrify. Of the four compounds only n-butyl trifluorosilane gave a definite, reproducible freezing point, and even it showed a tendency to supercool considerably (15°). The other three substances on cooling became more and more viscous, finally forming transparent glasses. As a result of their investigation of the freezing points of several alkyl halides, Turkevich and Smyth[19] have concluded that irregularity of molecular form contributes toward a tendency to vitrification. Furthermore, a small difference in the size of an atom or group in a molecule may make a great difference in this tendency. It is possible that these conclusions may apply in explaining the formation of glasses by the n-butyl trihalosilanes.

Acknowledgments.—This investigation was carried out under the sponsorship of the Naval Research Laboratory. We are deeply indebted to members of the staff of the Chemical Division for valuable suggestions and encouragement during its progress.

(19) A. Turkevich and C. P. Smyth, THIS JOURNAL, **64**, 737 (1942).

Summary

n-Butyl trichlorosilane (n-$C_4H_9SiCl_3$) was prepared by the reaction of n-butylmagnesium bromide with excess silicon tetrachloride. Its fluorination by antimony trifluoride to yield n-butyl dichlorofluorosilane (n-$C_4H_9SiCl_2F$), n-butyl chlorodifluorosilane (n-$C_4H_9SiClF_2$), and n-butyl trifluorosilane (n-$C_4H_9SiF_3$) was studied in the absence and presence of catalyst and under varying conditions of pressure and temperature in order to determine the conditions for optimum production of the two intermediate chlorofluorides. Of the four compounds, only the n-butyl trichlorosilane had been reported prior to this work.

A number of the physical constants of the compounds were determined, and a brief study was made of a few of the chemical properties of the four compounds, particularly their solubilities, their action on metals and glass, and their reaction with water and organic compounds containing oxygen.

The Polarographic Analysis of Nitrite and of Nitrite–Nitrate Mixtures[1]

BY BERTRAM KEILIN AND JOHN W. OTVOS[2]

A method for the polarographic determination of nitrate in the presence of uranyl ion in acid solution has been described by Kolthoff, Harris and Matsuyama.[3] Since in the earlier methods studied by Tokuoka and Ruzicka[4,5] in which other cations were used as "activators," the reduction potentials for nitrate and nitrite were always found to be identical, it was of interest to us to examine the polarographic behavior of nitrite in the presence of uranyl ion.

At the acid concentrations necessary for suppressing the hydrolysis of uranyl ion, all but a few per cent. of nitrite exists as nitrous acid and the similarity between nitrate and nitrite is thus greatly decreased. Nevertheless the waves for the two substances are very similar in appearance and occur at the same potential.

A method for the separate estimation of nitrate and nitrite in solutions containing both ions is described in this paper. Use is made of the additivity of the waves, and of a simple chemical conversion of nitrite to nitrate without the in-

troduction of new ions which might interfere with the determination.

Experimental

Apparatus and Materials.—A Heyrovsky Type XII Polarograph was used in all experiments. Measurements were made at 25°. Dissolved oxygen was removed by passing nitrogen through the solutions. All chemicals were of reagent grade. The sodium nitrite used in quantitative experiments was standardized against permanganate in acid solution, the primary standard being sodium oxalate.[6]

Decomposition of Nitrous Acid.—It is known that in cold dilute solutions and in the absence of air nitrous acid decomposes to nitric acid and nitric oxide; in the presence of oxygen, nitric acid alone is produced. Because of the instability of nitrous acid, a polarographic procedure for the determination of nitrite in acid solution must involve some error. Experiments performed in connection with this investigation have shown that in air and at concentrations which are of interest in polarography the decomposition of nitrous acid[7,8] is first order and that about six per cent. decomposes in a half hour at room temperature. If the nitrite solution is polarographed as soon as possible after it is acidified, the error arising from nitrous acid decomposition can be kept below 3%.

Comparison of the Nitrous Acid and Nitrate Waves.—Figure 1 shows a nitrous acid wave and a nitrate wave, each obtained with a solution 4×10^{-4} M in the nitrous acid[9] or nitrate, 2 $\times$

(1) This paper is based in whole or in part on work done for the Office of Scientific Research and Development under Contract OEMsr-881 with the California Institute of Technology.

(2) Present address Shell Development Company, Emeryville, California.

(3) I. M. Kolthoff, W. E. Harris and G. Matsuyama, THIS JOURNAL, **66**, 1782 (1944).

(4) M. Tokuoka, Coll. Czechoslov. Chem. Comm., **4**, 444 (1932).

(5) M. Tokuoka and J. Ruzicka, ibid., **6**, 339 (1934).

(6) J. S. Laird and T. C. Simpson, THIS JOURNAL, **41**, 524 (1919).

(7) Abel, Z. physik. Chem., **148**, 337 (1930).

(8) Bray et al., Chem. Rev., **10**, 161 (1932).

(9) Concentrations of nitrous acid, as given in this paper, include both un-ionized and ionized forms.

10^{-4} M in uranyl acetate, 0.01 M in hydrochloric acid, and 0.1 M in potassium chloride. The two waves are almost identical in shape. There is no trace of the nitric oxide wave at -0.77 volt (vs. S.C.E.) reported by Heyrovsky and Nejedly[10] for acid solutions of nitrite, probably because nitrogen was bubbled through the solutions immediately before the polarograms were made.

In neutral or alkaline solutions the reduction potentials of nitrate and nitrite are known to become more positive in the presence of polyvalent cations.[5] This effect has been attributed to the formation of loose "ion pairs" which, because of their positive charge, facilitate the access of nitrate or nitrite to the negative electrode. Presumably the same phenomenon occurs with nitrate in acid solution in the presence of uranyl ion. Nitrous acid, however, is uncharged and should not require the assistance of polyvalent cations for its approach to the cathode. In preliminary experiments in this Laboratory, nitrous acid in the absence of uranyl ion has indeed been found to produce a wave at about -1.0 volt (vs. S.C.E.), which is approximately the half-wave potential of the uranyl-activated nitrite wave. This wave may correspond to that reported by Schwarz[11] for nitrite in acetic acid solution, which extends from -0.6 to -1.6 volts. Although the uranyl ion has little effect on the half-wave potential of the nitrous acid wave, its presence causes an increase in the nitrous acid diffusion current.
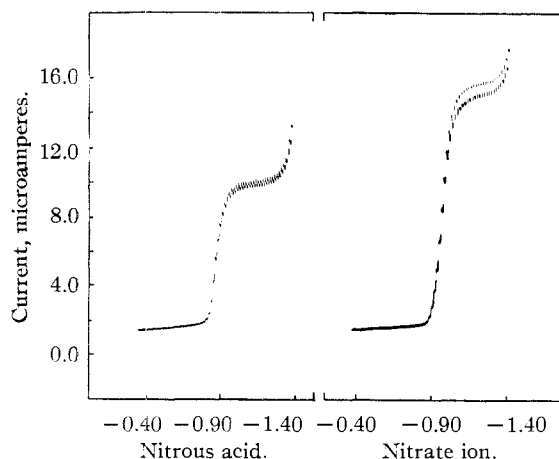
Potential of dropping mercury electrode, volts vs. S.C.E.

Fig. 1.—Comparison of nitrous acid and nitrate waves. Solutions are 0.1 M in hydrochloric acid, 0.1 M in potassium chloride, 2×10^{-4} M in uranyl acetate, and 4×10^{-4} M in nitrous acid and nitrate, respectively; $m^{2/3}t^{1/6} = 2.08$ mg.$^{2/3}$ sec.$^{-1/2}$.

The nitrous acid wave shown in Fig. 1 is a little over half as high as the nitrate wave, after correction has been made for the blank uranyl wave. The diffusion current constants for nitrous

(10) J. Heyrovsky and V. Nejedly, Coll. Czechoslov. Chem. Comm., 3, 126 (1931).

(11) K. Schwarz, Z. anal. Chem., 115, 161 (1939).

acid at several concentrations are given in Table I. For the more dilute solutions the concentration of uranyl ion was reduced to 5×10^{-5} M from the usual value of 2×10^{-4} M. Over a hundred-fold concentration range of nitrous acid (2×10^{-5} M to 2×10^{-3} M), the mean value of $i_d/Cm^{2/3}t^{1/6}$ is 7.45 and the average deviation of the points from the mean is 4.5%. Probably a large part of the deviation is due to the instability of nitrous acid and variations in the time required to run a polarogram.

TABLE I

DIFFUSION CURRENT CONSTANT FOR NITROUS ACID AT 25°

$m^{2/3}t^{1/6} = 2.08$ mg.$^{2/3}$ sec.$^{-1/2}$ at -1.2 volts vs. S.C.E.; diffusion current is measured at -1.2 volts vs. S.C.E.; residual current at -1.2 volts = 2.00 microamperes

Concn. of nitrous acid, millimoles/liter. C	Diffusion current of nitrous acid, microamperes. i_d	$K = i_d/Cm^{2/3}t^{1/6}$

A. Solutions 0.1 M in KCl, 0.01 M in HCl, and 2×10^{-4} M in UO₂(OOCCH₃)₂

5.125	47.8	4.50[a]
2.050	31.5	7.40
1.025	15.6	7.30
0.820	12.3	7.20
.512	7.52	7.06
.205	2.92	6.87
.102	1.56	7.35
.082	1.17	6.87
.0512	0.87	8.16

B. Solutions 0.1 M in KCl, 0.01 M in HCl, 5×10^{-5} M in UO₂(OOCCH₃)₂

0.102	1.66	7.83
.082	1.32	7.74
.0512	0.83	7.78
.0205	.324	7.60
.0102	.214	10.1[a]
.00512	.111	10.4[a]

C. Average diffusion current constant   7.45

[a] Not included in the average.

The number of electrons involved in the reduction of nitrous acid can be calculated with the use of Ilkovic's equation:

$$i_d = 605nD^{1/2}Cm^{2/3}t^{1/6} \qquad (1)$$

where i_d is the average diffusion current obtained at the dropping mercury electrode in microamperes, n is the number of faradays transferred per mole, D is the diffusion coefficient of the reducible substance in cm.^{2} sec.$^{-1}$, C is its concentration in millimoles per liter, m is the rate of flow of mercury in mg. sec.$^{-1}$ and t is the drop time in seconds. The diffusion current constant, $K = i_d/Cm^{2/3}t^{1/6}$, as given in Table I, is 7.45. The value of D for nitrite ion, calculated from its equivalent conductance,[12] is 1.92×10^{-5} cm.^{2} sec.$^{-1}$. With the assumption that the diffusion coefficient for nitrous acid is the same as that for nitrite ion, n can be calculated from these figures

(12) Niementowski and Roszkowski, Z. physik. Chem., 22, 147 (1897).

The value obtained for the electron transfer, n, is 2.8 faradays per mole.

Kolthoff, Harris and Matsuyama[3] report a five-electron reduction for nitrate in the presence of uranyl ion. The present result of 2.8 or 3 electrons for nitrous acid indicates that it, as well as nitrate, is reduced to nitrogen at the dropping mercury cathode in acid solution in the presence of uranyl ion.

It is interesting to compare this value of the electron transfer for nitrous acid, $n = 3$, with the value obtained by direct analysis of the nitrous acid wave according to the fundamental equation for a polarographic wave, first derived by Heyrovsky and Ilkovic.[13]

$$E_{d.e.} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \qquad (2)$$

In this equation $E_{d.e.}$ and i are corresponding values for the potential of the dropping mercury electrode and the current at any point on the wave, $E_{1/2}$ is the half-wave potential, and n is the number of electrons involved reversibly in the reduction. When $\log i/(i_d - i)$ is plotted against the voltage, a slope is obtained which corresponds to a value of $n = 1$ (Fig. 2). An electron transfer of $n = 1$ was also obtained by Kolthoff, Harris and Matsuyama in an analysis of the nitrate wave, although the over-all reduction of nitrate appears to involve 5 electrons. It may be inferred that, under these conditions, neither the reduction of nitrous acid nor that of nitrate is reversible. A similar effect has been found by Orlemann and Kolthoff[14] in the irreversible reduction of iodate and bromate.

Solutions Containing both Nitrate and Nitrite Ions.—In polarograms of solutions containing both nitrate ion and nitrous acid, the diffusion current, above that due to the blank uranyl wave, is the sum of the diffusion currents due to nitrate ion and nitrous acid independently. In Table II, the observed diffusion currents of some solutions containing these ions together are compared with values calculated from the additivity relationship

$$i_d = m^{2/3}t^{1/6} (7.45C_1 + 13.8C_2) \qquad (3)$$

where C_1 and C_2 are the concentrations of nitrite and nitrate in millimoles per liter and m and t are

TABLE II

ADDITIVITY OF NITRATE AND NITROUS ACID WAVES

Solutions 0.1 M in KCl, 0.01 M in HCl, 2 × 10^{-4} M in $UO_2(OOCCH_3)_2$; $m^{2/3}t^{1/6} = 2.08$ mg.$^{2/3}$ sec.$^{-1/2}$

Concn. of nitrate, millimoles/liter	Concn. of nitrous acid, millimoles/liter	Diffusion current, microamperes	
		Obs.	Calcd.
0.100	0.096	4.35	4.37
.100	.192	5.75	5.86
.100	.384	8.85	8.83
.100	.768	14.9	14.8

(13) J. Heyrovsky and D. Ilkovic. *Coll. Czechoslov. Chem. Comm.*, **7**, 198 (1935).

(14) E. F. Orlemann and I. M. Kolthoff, THIS JOURNAL, **64**, 1044 (1942).

expressed in the conventional units. The coefficients of C_1 and C_2 are the experimentally determined diffusion current constants reported here and in the paper of Kolthoff, Harris and Matsuyama.[3]
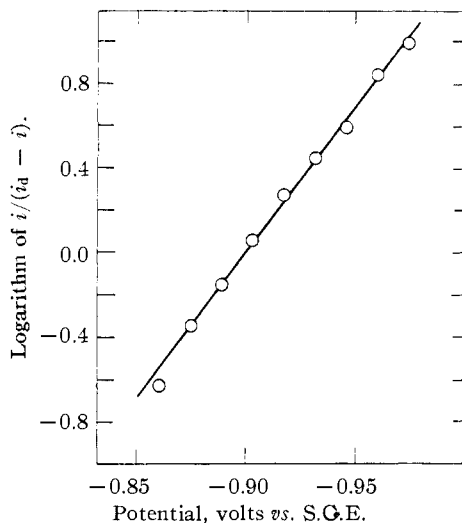

Fig. 2.—Analysis of nitrite reduction wave in 0.1 M potassium chloride, 0.01 M hydrochloric acid and 2 × 10^{-4} M uranyl acetate.

From a single polarogram of a solution containing uranyl ion, only a figure representing the weighted sum of nitrous acid and nitrate concentrations can be obtained. To obtain the concentrations of the substances separately by the methods described above it is necessary to run another polarographic experiment on an aliquot of the solution after altering the relative amounts of the two substances in a known way. It is convenient to do this by transforming one of them quantitatively to the other. A satisfactory and convenient method of achieving this transformation is the quantitative oxidation of nitrite to nitrate by hydrogen peroxide in acid solution.

$$HNO_2 + H_2O_2 \longrightarrow NO_3^- + H^+ + H_2O$$
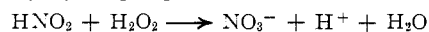
If the solution is then made basic, the excess peroxide may be catalytically decomposed with manganese dioxide. The only products of these two reactions that remain in solution are nitrate, water and oxygen; no new ionic species are produced. The uranyl ion must not be added until the reactions described above are completed and the solution is again acidified.

A polarogram of the oxidized solution, after the addition of uranyl acetate, potassium chloride and hydrochloric acid in the usual concentrations, gives a diffusion current

$$i_d' = 13.8m^{2/3}t^{1/6} (C_1 + C_2) \qquad (4)$$

since all of the nitrite has been converted to nitrate. From equations (3) and (4), the separate concentrations C_1 and C_2 of nitrite and nitrate, respectively, can be calculated.

$$C_1 = \frac{i_d' - i_{d1}}{6.35m^{2/3}t^{1/6}} \qquad (5)$$

$$C_2 = \frac{i_d'}{13.8m^{2/3}t^{1/6}} - C_1 \qquad (6)$$

Procedure for the Polarographic Determination of Nitrite.—For the determination of nitrite in solutions where its concentration is between 5×10^{-5} and 5×10^{-3} M, the following procedure is recommended.

Prepare two stock solutions, one being 0.2 M in potassium chloride, 0.02 M in hydrochloric acid, and 4×10^{-4} M in uranyl acetate; the other having the same composition except that it is only 1×10^{-4} M in uranyl acetate.

Dilute 25.00 ml. of the uranyl acetate stock solution to 50.00 ml. with redistilled water, bubble with nitrogen gas to make oxygen-free, and measure the apparent diffusion current due to the reduction of uranyl ion at a potential of -1.2 volts $vs.$ S.C.E. This current is taken as the "blank" or "residual" current for the nitrous acid wave.

Measure a suitable volume of an unknown nitrite solution into a 50-ml. volumetric flask, add 25.00 ml. of the appropriate uranyl acetate stock solution and dilute to volume with redistilled water. (It may be necessary to make a preliminary run in order to determine the concentration of uranyl ion to be used. In general, if the final concentration of the nitrite ion is to be above 1×10^{-4} M, the stock solution containing the higher concentration of uranyl acetate is used. If the concentration is below this value, the one containing the lower concentration is employed.) Make the resulting solution oxygen-free and measure the apparent diffusion current at a potential of -1.2 volts $vs.$ S.C.E. Subtract the "residual" current due to the reduction of uranyl ion from the diffusion current to obtain the diffusion current due to nitrous acid. The amount of nitrite in the unknown solution can be found from this diffusion current by referring to a standard curve, which is constructed by plotting diffusion current against concentration. Such a plot is prepared with data, such as are given in Table I, that are obtained with known solutions.

Analysis of Solutions Containing Both Nitrate and Nitrite.—Divide the solution to be analyzed into two equal portions. Add to the first portion 25.00 ml. of the appropriate uranyl acetate stock solution, and dilute to 50.00 ml. with redistilled water. Make the resulting solution air-free, measure the apparent diffusion current, and subtract the "residual" current as described above to obtain the total diffusion current due to nitrate ion and nitrous acid. To the second portion, add 2 N hydrochloric acid until it is just neutral and then add an excess of five drops. Add 1 ml. of 30% hydrogen peroxide and allow the mixture to stand at room temperature for thirty minutes. Add eight drops of 2 N sodium hydroxide and then introduce a small quantity of manganese

dioxide. After the evolution of gas has ceased, decant the solution quantitatively into a 50-ml. volumetric flask. Add three drops of 2 N hydrochloric acid and then 25.00 ml. of the appropriate uranyl acetate stock solution, and dilute to volume. Measure the apparent diffusion current as before, and again subtract the "residual" current. From the two values of the diffusion current thus obtained, the concentrations of nitrite and nitrate originally present in the unknown solution may be calculated as described above.

Interferences.—In general, interferences which have been described for the estimation of nitrate[3] will also be encountered in this determination. The presence in solution of substances such as strong bases and phosphates, which precipitate the uranyl ion, or complex-formers such as citrate or tartrate will interfere, as will also those substances, such as oxalates and strong acids, which discharge at voltages near to that of nitrous acid. Sulfate ion in a concentration twenty times that of the nitrite was found to reduce the wave height somewhat.

Summary

1. In the presence of uranyl ion, nitrous acid in dilute solutions of hydrochloric acid is reduced at the same potential at which nitrate is reduced ($ca.$ -1 volt $vs.$ S.C.E.). The diffusion current is proportional to the nitrous acid concentration when the ratio of uranyl ion to nitrous acid is above a critical minimum. The reduction of nitrous acid under these conditions involves three electrons, indicating a reduction to nitrogen, but analysis of the wave shows that the reduction is irreversible.

2. A solution containing both nitrate and nitrite ions can be analyzed for both constituents in two polarographic experiments. First, the diffusion current due to the two constituents in the original solution is measured. With another aliquot, the nitrite present is oxidized to nitrate and the diffusion current of the resulting solution is measured as before. The nitrite can be conveniently oxidized by hydrogen peroxide in acid solution, and the excess peroxide can be destroyed catalytically by manganese dioxide in basic solution.

3. Interferences are similar to those encountered by Kolthoff, Harris and Matsuyama[3] in the analysis of nitrate solutions, except that large amounts of sulfate seem to reduce the diffusion current.