species, and one is tempted to conclude that the copper(II) complex is being reduced *via* the +1 state.

At *p*H 11.5 in 0.24 *F* carbonate, or *p*H 11.0 in 0.91 *F* carbonate, a gelatinous blue precipitate begins to separate out (Fig. 7). A portion of this precipitate, filtered on a sintered Pyrex Buchner-type funnel, washed with water and acetone, and air-dried overnight, lost 32.0% at 100°. The material thus dried was ignited to cupric oxide; it contained 80.0% (calcd. for $Cu(OH)_2 \cdot 2.25\ H_2O$: 31.6% H_2O, 81.5% CuO).

According to Pickering,[9] solutions of copper(II) in excess sodium carbonate contain "α-cupricarbonate," which he represented as $Na_2Cu(CO_3)_2 \cdot Na_2CO_3$. Assuming that the copper is actually present as the $Cu(CO_3)_3^{-4}$ ion, we have

$$Cu(CO_3)_3^{-4} + 2OH^- \longrightarrow Cu(OH)_2 + 3CO_3^=$$

$$K = [CO_3^=]^4/[Cu(CO_3)_3^{-4}][OH^-]^2 \quad (15)$$

But the carbonate concentration also depends on *p*H: letting $[CO_3^=] + [HCO_3^-] = C$

$$K = C^3[OH^-]/[Cu(CO_3)^{-4}]([OH^-] + K_W/K_2)^3 \quad (16)$$

In 0.915 *F* carbonate the calculated value of K is $(1.15 \pm 0.2) \times 10^7$, and in 0.240 *F* carbonate it is $(1.85 \pm 0.3) \times 10^7$. In mean, therefore, $K = (1.5 \pm 0.4) \times 10^7$.

As the *p*H is raised to still higher values, the hydrous oxide redissolves, giving waves identical with those found in the absence of carbonate,[1] and hence presumably due to the $Cu(OH)_4^=$ ion.

Summary

The following new thermodynamic data have been derived from polarographic measurements.

$Cu(C_2O_4)_2^= \longrightarrow Cu^{++} + 2C_2O_4^=$	$K = 4.8 \times 10^{-11}$
$Cu(C_2O_4)_2^=$	$F^0 = -315.5$ kcal.
$Cu + 2C_2O_4^= \longrightarrow Cu(C_2O_4)_2^= + 2e$	$E^0 = -0.04$ v.
$Cu_4(OH)_6(C_2O_4) \longrightarrow 4Cu^{++} + 6OH^- + C_2O_4^=$	$K = 2.6 \times 10^{-68}$
$Cu_4(OH)_6(C_2O_4)$	$F^0 = -413.1$ kcal.
$Cu_4(OH)_6(C_2O_4) + 4OH^- \longrightarrow 4Cu^{II}$	$K = 4.5 \times 10^{-4}$
$Cu(NH_3)_{a-2}(C_2O_4)_y^{1-2y} + 2NH_3 \longrightarrow Cu(NH_3)_a(C_2O_4)_y^{2-2y} + 2e$	$E^0 = +0.01$ v.
$Cu(NH_3)_{b-2}(C_2O_4)_m^{1-2m} + OH^- + 2NH_3 \longrightarrow Cu(OH)(NH_3)_b(C_2O_4)_m^{1-2m} + e$	$E^0 = +0.15$ v.
$K_2Cu(HCO_3)_4 \longrightarrow 2K^+ + Cu^{++} + 4HCO_3^-$	$K = 0.3 \times 10^{-11}$
$K_2Cu(HCO_3)_4 + HCO_3^- \longrightarrow 2K^+ + Cu(HCO_3)_5^-$	$K = 0.0105$
$Cu(CO_3)_3^{-4} + 2OH^- \longrightarrow Cu(OH)_2 + 3CO_3$	$K = 1.5 \times 10^7$

NEW HAVEN, CONNECTICUT RECEIVED MAY 24, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES, AND THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarography of Chromium(II)

BY ROBERT L. PECSOK[*] AND JAMES J. LINGANE[†]

The anodic wave of chromous ion in sulfuric acid has been used for the determination of chromium in steel,[1] and the reversible behavior at the dropping mercury electrode of the chromo-chromicyanide couple has been studied by Hume and Kolthoff.[2] These are the only data available concerning the polarography of +2 chromium.

In the present paper, the results of a systematic investigation of the anodic wave produced by the oxidation of +2 chromium to the +3-state in various supporting electrolytes are reported.

Experimental

Apparatus.—Earlier measurements were made with a manual instrument based on a circuit previously described.[3] Later measurements, including most of those described herein, were made with a modified Fisher Elecdropode. Since this instrument is not suitable for measuring anodic currents, a reversing switch was placed across the galvanometer terminals and the damping condenser was removed. An auxiliary variable resistance was placed across the galvanometer terminals so that the galvanometer sensitivity could be adjusted to correspond to convenient multiples of microamperes. This resistance was correctly adjusted for each shunt value by measuring the potential drop across a precision resistance with a potentiometer and applying Ohm's law. The polarizing slide wire was calibrated with a potentiometer.

All measurements were made in an H-cell with a saturated calomel electrode at 25.0 ± 0.1°. The drop time of the capillary was 5 sec. on open circuit and 3.5 sec. at an applied potential of 1.7 volts. The rate of flow of mercury was measured automatically.[4] Purified nitrogen was used to remove dissolved oxygen from the test solutions. Residual currents were measured and the proper corrections have been made for all diffusion current constants reported. The *p*H of the solutions was measured with a glass electrode.

All potentials were measured against the saturated calomel electrode (S. C. E.).

Reagents.—Standard solutions of chromous sulfate were prepared as previously described.[5] This method introduces zinc into the solution which is reduced at a more positive potential than the anodic wave of chromous ion in many supporting electrolytes and thus interferes. Although zinc can be separated by precipitating the chromium as chromous acetate,[6] other methods of reduction were investigated. Reduction by pure aluminum metal

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[*] Harvard University Ph.D., 1948.

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[1] A. M. Zan'ko and F. A. Manusova, *Zavodskaya Lab.*, **10**, 565 (1941).

[2] D. N. Hume and I. M. Kolthoff, THIS JOURNAL, **65**, 1897 (1943).

[3] J. J. Lingane and I. M. Kolthoff, *ibid.*, **61**, 825 (1939).

[4] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 329 (1944).

[5] J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **20**, 425 (1948).

[6] E. Zintl and G. Rienäcker, *Z. anorg. allgem. Chem.*, **161**, 374 (1927).

proved to be entirely satisfactory. About 20 g. of aluminum turnings and 600 ml. of solution containing 0.1 *M* chromic chloride hexahydrate and 0.05 *M* hydrochloric acid were placed in a one-liter round-bottom flask. Neutral solutions are not reduced by aluminum and heating to boiling is necessary even with acid solutions. Reduction is complete after fifteen minutes of boiling. Solutions so prepared are not stable when stored over aluminum as is possible with zinc.[6] However, if cooled under a stream of nitrogen and transferred to a Stone type storage apparatus,[7] they are stable for long periods. A 0.1145 *M* solution has remained constant in titer for six months.

Supporting electrolytes were prepared as required from reagent grade chemicals.

Results and Discussion

Chloride Solutions.—Polarograms were studied in solutions of 0.1 *M*, 1.0 *M* and saturated potassium chloride. Typical polarograms plotted in Fig. 1 and curve b in Fig. 4 show a well defined anodic wave for the oxidation of chromous to chromic ion, and a well defined cathodic wave for the reduction of chromous ion to the metal.

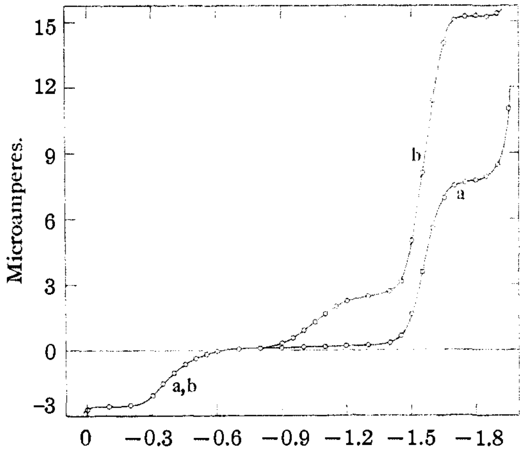

Fig. 1.—Polarograms of: (a) 1 millimolar chromium(II); (b) 1 millimolar chromium(II)–1 millimolar chromium(III) in 1.0 *M* potassium chloride (0.005% gelatin).

In 0.1 *M* potassium chloride, the amount of gelatin present is a critical factor in determining the shape of the wave and its half-wave potential. With no gelatin, a small negative maximum is observed in the anodic wave. Increasing amounts of gelatin eliminate this maximum and cause a shift of the anodic wave to more positive potentials. In saturated potassium chloride, the polarograms are identical with or without gelatin. Except for the above experiments 0.005% gelatin was added to all solutions.

The anodic half-wave potential is shifted in a negative direction with increasing concentrations of potassium chloride, indicating that the oxidation becomes more nearly reversible with increasing chloride ion concentration. The slope of the wave in saturated potassium chloride indicates that the oxidation proceeds irreversibly.

In saturated calcium chloride (*ca.* 10 *M* chloride ion) the anodic half-wave potential is −0.51 v. *vs.* the S.C.E., the same as in saturated potassium chloride (4.7 *M* chloride ion), but the oxidation proceeds reversibly as shown in Fig. 2. The reciprocal slope for the graph of log $[(i - i_d)/-i]$ *vs.* E is 0.0588, in good agreement with the theoretical value 0.0592 for a reversible one-electron oxidation. Furthermore, the polarogram of a mixture of 1 millimolar each of chromous and chromic chlorides (curve c in Fig. 2) has no inflection at zero current. A similar analysis of the slope of the combined wave yielded a value of 0.074. The latter slope is identical with that obtained for 1 millimolar chromic ion alone in saturated calcium chloride. It appears that while chromous ion in saturated calcium chloride is reversibly oxidized at the dropping electrode, the reduction of chromic ion is slightly irreversible.

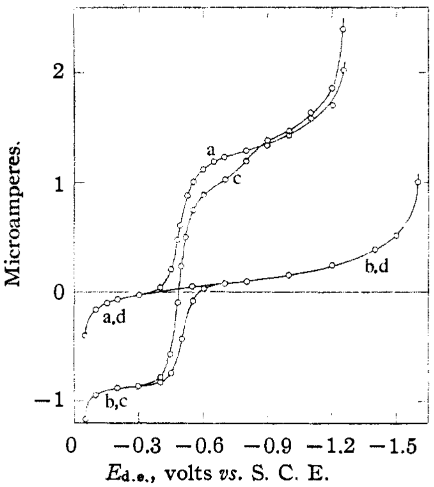

Fig. 2.—Polarograms of: (a) 1 millimolar chromium(III); (b) 1 millimolar chromium(II); (c) 1 millimolar chromium(II)–1 millimolar chromium(III); (d) residual current in saturated calcium chloride (0.005% gelatin).

The cathodic half-wave potential of chromic ion in saturated calcium chloride obtained in this study is −0.51 v. *vs.* the S.C.E. This has been previously reported as −0.55 v. *vs.* the S.C.E. by Kalousek.[8] In a previous study of chromic ion,[9] we observed that the first reduction wave is shifted with increasing concentrations of calcium chloride to more negative potentials, becoming completely suppressed in a saturated solution. The solutions polarographed earlier contained a smaller concentration of hydrogen ion (*p*H 6), than that produced by the hydrolysis of chromic ion. Apparently, this was because the calcium chloride contained basic impurities, *e. g.*, calcium hydroxide. In the present study, the calcium chloride was obtained from another source and recrystallized from water, yielding a saturated solution of *p*H 5.5. Solutions of 1 millimolar chromic ion in

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(7) H. W. Stone, *Anal. Chem.*, **20**, 747 (1948).

(8) M. Kalousek, *Coll. Czech. Chem. Commun.*, **11**, 592 (1939).

(9) J. J. Lingane and R. L. Pecsok, THIS JOURNAL, **71**, 425 (1949).

saturated solutions of this purified salt had a *p*H of 3.0. The polarogram of chromic ion in this medium is very sensitive to *p*H. Between *p*H 3 and 5, the wave is gradually suppressed and finally completely eliminated at a *p*H greater than 5 because of the precipitation of hydrous chromic oxide.

The data for chloride solutions are summarized in Table I. The half-wave potential shifts to more negative values with increasing chloride ion concentration up to about 4 *M* (saturated potassium chloride) and then remains constant. The diffusion current constant is virtually independent of the concentration of potassium chloride between 0.1 and 4 *M*. In saturated calcium chloride (5 *M*) the diffusion current constant is only about one-third the value in the other supporting electrolytes, probably because of the relatively great viscosity, and correspondingly small diffusion coefficient in the former solution. For the following solutions the ratio of the viscosity to the viscosity of water at 25° is: 0.1 *M* potassium chloride, 0.999: saturated potassium chloride, 1.050: 0.1 *M* calcium chloride, 1.030: and saturated calcium chloride, 8.5.[10]

TABLE I

POLAROGRAPHIC CHARACTERISTICS OF CHROMIUM(II) AT 25°

$m^{2/3}t^{1/6}$ = 1.610 mg.$^{2/3}$ sec. $^{-1/2}$; 0.005% gel. added to all solutions

Supporting electrolyte	$E_{1/2}$ volts *vs.* S. C. E.	$\frac{i_d}{Cm.^{2/3}t^{1/6}}$
0.1 *M* KCl	−0.34	−1.54
1.0 *M* KCl	− .40	−1.54
Satd. KCl	− .51	−1.55
Satd. $CaCl_2$	− .51	−0.47
0.05 *M* KSCN	− .71	−1.55
0.5 *M* KSCN	− .78	−1.78
1.0 *M* KSCN	− .80	−1.64
2.0 *M* KSCN	− .82	−1.55
9.0 *M* KSCN	− .85	−1.20
0.1 *M* NH_4OH–5 *M* NH_4Cl	− .85	−1.14
0.5 *M* HCOOH	− .30	−1.54
0.1 *M* $(CH_3)_4NBr$	− .43	−1.54
0.1 *M* $NaC_7H_5O_3$–0.1 *M* NaOH	−1.23	−1.17

Thiocyanate Solutions.—Chromous ion was studied in solutions varying from 0.05 to 9 *M* potassium thiocyanate in which a deep blue complex ion is formed.[11] The polarograms show a well defined but irreversible anodic wave. Typical polarograms are shown in Fig. 3 and curve e in Fig. 4, with the data included in Table I. The half-wave potential becomes more negative with increasing concentration of thiocyanate ion. The half-wave potential of the first reduction wave of chromic ion is −0.91 v. *vs.* the S.C.E. in 0.1 *M* potassium thiocyanate and −0.99 v. *vs.* the S.C.E. in 1.0 *M* potassium thiocyanate, and thus considerably more negative than the anodic chromous wave. The diffusion current constants are not very reliable because it is difficult to measure the current accurately at concentrations of chromic ion greater than one millimolar. The curve has a negative maximum immediately preceding the current rise. It is not certain whether this is a true maximum or whether the current is suppressed prior to this point. The latter is more likely since the galvanometer fluctuations were very erratic when the full diffusion current should have been developed. This anomalous behavior was reproducible.

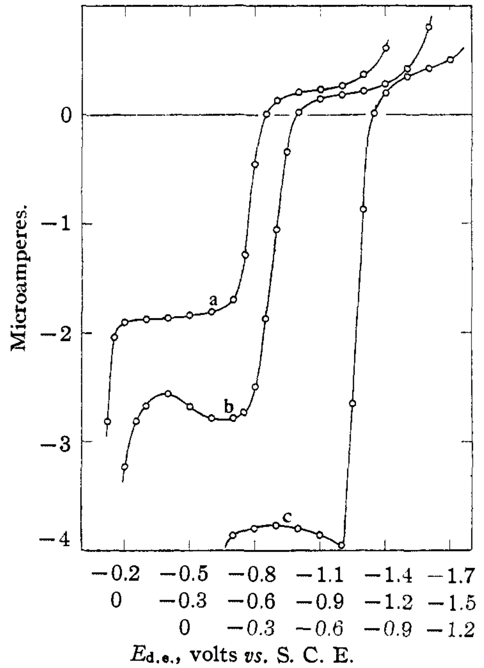

Fig. 3.—Polarograms of: (a) 0.72 millimolar chromium(II) in 0.5 *M* potassium thiocyanate; (b) 1.22 millimolar chromium(II) in 0.05 *M* potassium thiocyanate; (c) 1.55 millimolar chromium(II) in 0.5 *M* potassium thiocyanate. All solutions contained 0.005% gelatin. Curves (b) and (c) are shifted 0.2 and 0.5 volt to the right, respectively.

Ammoniacal Solutions.—The chromous ammonia complex is oxidized at the dropping electrode, but produces abnormally extended waves of little analytical value. Best results are obtained in a solution containing 0.1 *M* ammonium hydroxide, 5 *M* ammonium chloride and 0.005% gelatin, of *p*H 7.5 (curve f in Fig. 4). A steady, reproducible diffusion current is obtained between −0.2 v. and −0.6 v. *vs.* the S.C.E. The anodic wave continues from about −0.6 v. to about −1.2 v., with a half-wave potential of about −0.85 v. *vs.* the S.C.E., independent of the concentration of chromous ion. At a higher *p*H, the chromous ion is partially precipitated yielding waves even more drawn out. Although the anodic current for solutions of *p*H 9 is easily measured between −0.2 and −0.4 v. *vs.* the S.C.E., it is not strictly propor-

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[10] "International Critical Tables," Vol. V, McGraw-Hill Book Co. Inc., New York, N. Y., 1926.

[11] K. Someya, *Z. anorg. allgem. Chem.*, **161**, 46 (1927).

tional to concentration. At a *p*H less than 7, as the ratio of ammonium chloride to ammonium hydroxide increases, the curve becomes similar to that of chromous ion in potassium chloride of the same concentration.

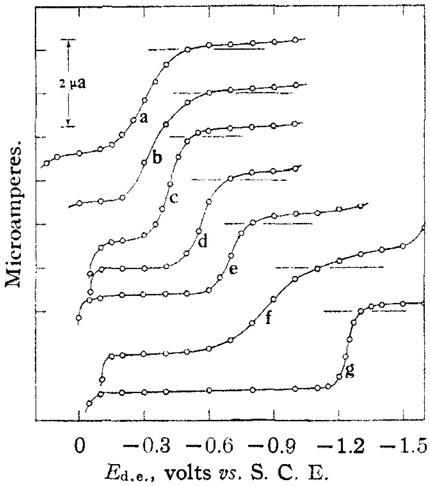

Fig. 4.—Polarograms of 1 millimolar chromium(II) in: (a) 0.5 *M* formic acid, *p*H 1.8; (b) 0.1 *M* potassium chloride; (c) 0.1 *M* tetraethylammonium bromide; (d) saturated potassium chloride; (e) 0.05 *M* potassium thiocyanate; (f) 5 *M* ammonium chloride–0.1 *M* ammonium hydroxide; (g) 0.5 *M* sodium salicylate–0.1 *M* sodium hydroxide. All solutions contained 0.005% gelatin. Zero current for each curve is indicated on ordinate axis; each curve has been shifted downward by one microampere.

Quaternary Ammonium Salts.—In 0.01 *M* tetramethylammonium bromide or tetraethylammonium bromide, chromous ion gives well defined anodic and cathodic waves, the former with a half-wave potential of −0.43 v. *vs.* the S.C.E. (curve c in Fig. 4) and the latter with a half-wave potential of −1.58 v. A polarogram of a mixture of one millimolar each of chromous and chromic ion in this supporting electrolyte shows three distinct waves; an anodic wave for the oxidation of chromous to chromic ion, a cathodic wave for the reduction of chromic to chromous ion (half-wave potential −1.14 v. *vs.* the S.C.E.), and a second combined cathodic wave for the simultaneous reduction of chromic and chromous ions to the metal. The latter wave height is slightly more than five times the height of either of the first two due to the simultaneous discharge of hydrogen ion.[9] The separation of the first two waves by 0.71 v. indicates a large degree of irreversibility. A log plot of the first wave yields a slope of 0.083.

Complexing Acid Solutions.—Neither citrate nor tartrate solutions as supporting electrolytes give well defined waves for +2 chromium. Best results were obtained in citrate solutions between *p*H 3 and 8. An abrupt wave at −1.0 v. follows a region of gradually decreasing negative current. Solutions containing excess hydroxyl ion yield only a small diffusion current, indicating that the +2 chromium is not in true solution.

The chromo–oxalate complex is not oxidized at the dropping electrode at any *p*H.

In 0.5 *M* formic acid, *p*H 1.8, chromous ion yields a well defined but irreversible wave (curve *a* in Fig. 4) with a half-wave potential of −0.30 v. *vs.* the S.C.E., independent of the concentration of chromous ion and with an *I* value of −1.54. The shape of the curve (similar to that obtained in 0.1 *M* potassium chloride) and the characteristic values indicate that no complex is formed. In formic acid–formate buffers, at *p*H 3.5 the wave is displaced negatively to −0.53 v., and at *p*H 7 it becomes very irregular with several inflections.

In 0.50 *M* succinic acid or lactic acid, the polarograms are similar to that in potassium chloride. When the *p*H is increased to 4 or higher, a red precipitate is formed and no oxidation wave is observed.

Chromous ion in mixtures of 0.1 *M* sodium salicylate and sodium hydroxide forms a yellow complex ion which is reversibly oxidized at the dropping electrode (curve g in Fig. 4). The half-wave potential is −1.23 v. *vs.* the S.C.E. and the *I* value is −1.17. The oxidation is shown to be reversible by a plot of log $[(i - i_a)/-i]$ *vs.* E which gives a straight line of slope 0.057. Yet when chromic chloride is added to the mixture a gelatinous precipitate is formed and the polarogram is not changed; *i. e.*, there is no reduction of +3 chromium. Since the oxidation of the chromo–salicylate complex is reversible, this behavior is explainable if a soluble chromi-salicylate complex is formed during the oxidation at the electrode surface. Apparently the soluble form is not formed when chromic chloride is added to an alkaline salicylate mixture.

When the excess hydroxyl ion of the above mixture is neutralized to *p*H 7, the solution is no longer a clear yellow, but a green gelatinous precipitate forms, yielding a gradually rising current throughout the range of applied potential. With the addition of more sodium hydroxide, the yellow complex ion is again formed.

This well defined anodic current and highly negative half-wave potential indicate that the chromo–salicylate complex is an exceptionally powerful reductant. The possibilities for potentiometric and amperometric titrations are now being investigated.

Summary

A new method for the preparation of chromous solutions by reduction with pure aluminum metal is described.

The polarographic behavior of +2 chromium has been studied in supporting electrolytes containing: potassium chloride, calcium chloride, thiocyanate, citrate, tartrate, oxalate, formate, lactate, succinate and salicylate ions, ammonia

buffers, and tetramethyl- and tetraethylammonium bromides. The following points are of special interest:

1. A reversible oxidation of chromous ion and a nearly reversible reduction of chromic ion occurs in saturated calcium chloride solutions at −0.51 v. *vs.* the S.C.E.

2. The thiocyanate complex is irreversibly oxidized with a half-wave potential of −0.85 v. *vs.* the S.C.E.; this potential is a function of the thiocyanate concentration.

3. In weak acids, no complex is formed and the wave is similar to that in potassium chloride. At higher *p*H, the oxidation wave is displaced negatively, but it becomes irregular or is suppressed completely.

4. The salicylate complex is an exception to (3), and in alkaline solution is reversible oxidized with a half-wave potential of −1.23 v. *vs.* the S.C.E. This complex is the most powerful reductant known in aqueous solution.

CAMBRIDGE, MASS. RECEIVED JULY 19, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Pseudo Halides of Silicon; Reactions of Pseudo Halides and Halides

BY HERBERT H. ANDERSON*

This article—a continuation of our earlier studies on pseudo halides of silicon—describes the preparation of three new substituted silicon isothiocyanates and one new substituted silicon isocyanate. In addition, eleven reactions involving halides and pseudo halides have been studied, five of which went to completion.

New Pseudo Halides

Preparation.—Two of the starting materials were made using the Grignard reagent, benzyltrichlorosilane and *n*-butyltrichlorosilane; triethoxychlorosilane, boiling range 154–157°, was prepared from tetrachlorosilane and absolute ethanol. The individual substituted chlorosilane was added gradually to a 25% excess of silver isothiocyanate, or silver isocyanate, suspended in benzene—with a final reflux for thirty minutes.[1] After the usual filtration and washing of the silver salts,[1] the benzene was distilled off, and center fractions of the pure pseudo halides collected under the conditions listed in Table I. In all cases the yields were approximately 80%. *n*-Butylsilicon triisothiocyanate foamed so severely during the removal of the last of the benzene that the addition of an antifoam, Dow Corning "Antifoam A," was necessary.

Analyses.—Each individual isothiocyanate was decomposed in absolute ethanol, with addition of water after two minutes; thereupon thiocyanate—in this place the word has no structural implication—was determined through titration with standard silver nitrate solution in the presence of ferric nitrate as indicator. Triethoxysilicon isothiocyanate *only* was analyzed (in June, 1947) *without weighing* as follows: the contents (at 24°) of a 0.401-ml. micropipet was delivered into absolute ethanol, rinsed with ethanol and then titrated as above, requiring 18.80 ml. of 0.1 *N* silver nitrate solution.[2] Calcd. for the *n*-butyl compound: H, 3.47. Found: H, 3.45.

Properties.—The chief numerical data of the new compounds are collected in Table I. Other properties are as follows: All of these substances are colorless when pure and hydrolyze rapidly without the evolution of much heat. Benzylsilicon triisothiocyanate is easily soluble in acetone, benzene and carbon disulfide, and is moderately soluble in hexane; thus it is definitely more soluble in these solvents than is methylsilicon triisothiocyanate.[3] *n*-Butylsilicon triisothiocyanate was readily soluble in the same solvents. For the triethoxysilicon compound: vapor pressure equation, $\log p = 8.1510 - 2524/T$; λ (calcd.) 11.3 kcal./mole; λ/T_B 24.1. Supercooling below the freezing point of the liquid took place in the following amounts: benzylsilicon triisothiocyanate, 36°; benzylsilicon triisocyanate, 44°; *n*-butylsilicon triisothiocyanate, 50°.

TABLE I

NEW COMPOUNDS

Compound	Distillation range °C.	Mm.	B. p., °C.	M. p., °C., ±1.0	n^{20} ±0.0010	d^{20}_4	Mol. refr. Calcd.	Mol. refr. Found	Mol. wt. Calcd.	Mol. wt. Found	Isothiocyanate Calcd.	Isothiocyanate Found
$(C_6H_5CH_2)Si(NCS)_2$	171–172	3	348.9 ± 1.0	36.0	....	1.275[a]	...	...	293	260[b]	59.4	59.32, 59.2
$(C_6H_5CH_2)Si(NCO)_3$	111–112	3	265 ± 2	−11.0	1.5230	1.225	60.2	61.1	245	235[b]	(17.14	16.81, 16.80)[d]
$(nC_4H_4)Si(NCS)_3$	135–136	3	300.6 ± 1.0	− 0.5	1.5928	1.189	73.9	73.7	259	239[b]	67.0	67.2, 66.6
$(C_2H_5O)_3Si(NCS)$	122.2–122.8	53	205.8 ± 0.5	....	1.4431	1.036	56.6	56.67	221	235[c]	26.24	26.3

[a] Supercooled liquid. [b] Through freezing point depression of camphor. [c] Dumas method. [d] Values of nitrogen determined as Kjeldahl ammonia, at New York University in 1948.

Silver isothiocyanate and either diethoxydichlorosilane or ethoxytrichlorosilane reacted, yielding a mixture of a liquid and a solid, undoubtedly $(C_2H_5O)_3Si(NCS)$ and $Si(NCS)_4$, respectively.

Reactions of Pseudo Halides and Halides

$SiCl_4$ + HNCO.—Gaseous isocyanic acid was bubbled through tetrachlorosilane at 30° for an hour, without any elevation of the boiling point such as would occur in the presence of $SiCl_3(NCO)$.[4]

$SiCl_3(SH)$ + AgNCO.—When 14 g. of the former was added gradually to a suspension of 60 g. of the latter in 80 ml. of benzene, there was a reaction with much heat and the silver salts turned black. After thirty minutes at 90°, the solution was filtered, with washing of the black silver salts; after distillation of the benzene, the liquid product boiled at 106° under 34-mm. pressure and contained no sulfur. $SiCl_3(SH) + AgNCO \rightarrow Si(NCO)_4{}^1 + Ag_2S + AgCl$.

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* Harvard College A.B. 1934; Research Associate, 1938–1940, 1946–1947.

[1] Forbes and Anderson, THIS JOURNAL, **62**, 761 (1940).

[2] For a later, smaller-scale modification see: Anderson, *ibid.*, **71**, 1801 (1949).

[3] Anderson, *ibid.*, **69**, 3049 (1947).

[4] Anderson, *ibid.*, **66**, 934 (1944).