

systems. If one assumes constancy for carbon, hydrogen, oxygen, chlorine and isothiocyanate, R_{Si} has the following values: in $SiCl_4$, 4.84; in $Si(CH_3)_4$, 7.14; in $Si(OCH_3)_4$, 3.88; in $Si(NCS)_4$, 6.80 ml. R_{Si} was estimated for isothiocyanates through linear interpolation between the values for the binary compounds; for example, the value for $(CH_3)_2Si(NCS)_2$ was 6.97 ml., half-way between 7.14 and 6.80 ml. To predict the molar refractions of methyl silicon *thiocyanates*, R_{Si} was taken as a constant, 7.14 ml., as in $Si(CH_3)_4$. Table II shows that the experimental molar refractions of the methyl silicon isothiocyanates agree closely with values calculated for isothiocyanates.

A previous paper¹ stated, "This issue of structure is still unsettled, and may presently be decided by examination of molar refractions of the thiocyanate group; preliminary calculations have been made, but these rest upon two compounds only." The structure of " $Si(OCH_3)_3SCN$ " mentioned in the same paper¹ and that of " $SiCl_3(SCN)$ " previously¹ isolated may now be identified as *isothiocyanate*. The observed molar refractions of 41.86 and 39.19 ml. (density adjusted from 24 to 20°) agree with values of 42.52 and 39.07 ml., respectively, calculated for isothiocyanates—in contrast with 40.22 and 36.77 ml. expected for thiocyanates.

Like the methylchlorosilanes, the methyl silicon isothiocyanates do not follow Swarts' rule⁷ of linear increase in boiling points. Boiling points calculated by the "increment method," adding 64.1° to the b. p. of the corresponding chloride for each successive replacement of one chloride² by *iso-*

(7) Swarts, *Bull. soc. chim.*, **35**, 1557 (1924).

thiocyanate, are also too low. Table III presents this comparison.

TABLE III
BOILING POINTS, °C.

Compound	Calcd. by Swarts' method	Calcd. by "increment method"	Actual
$(CH_3)_3Si(NCS)$	98	121.8 (57.7 + 64.1)	143.1
$(CH_3)_2Si(NCS)_2$	170	198.2 (70.0 + 128.2)	217.3
$(CH_3)Si(NCS)_3$	242	258.0 (65.7 + 192.3)	266.8

Like other methyl silicon halides, the vapor of $(CH_3)_3Si(NCS)$ has a disagreeable odor and a possible toxicity.

The author thanks Professor George S. Forbes of this Laboratory for helpful suggestions.

Summary

1. Each of the three methylchlorosilanes reacts with silver isothiocyanate to produce a (new) methyl silicon isothiocyanate. Trimethyl silicon isothiocyanate, $(CH_3)_3Si(NCS)$, melts at -33° and boils at 143° ; dimethyl silicon diisothiocyanate, $(CH_3)_2Si(NCS)_2$, melts at 18° and boils at 217° ; methyl silicon trisothiocyanate, $(CH_3)Si(NCS)_3$, melts at 72° and boils at 267° . These are the only known silicon compounds containing two or three isothiocyanate groups.

2. Densities, indices of refraction and vapor pressure equations are given. The observed molar refractions in ml.— $(CH_3)_3Si(NCS)$, 40.2; $(CH_3)_2Si(NCS)_2$, 49.9; $(CH_3)Si(NCS)_3$, 59.8; $Si(NCS)_4$, 70.4—agree closely with values calculated for the isothiocyanates.

CAMBRIDGE, MASS.

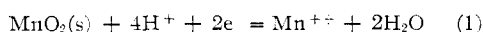
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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Manganous Ion-Manganese Dioxide Electrode

By A. WITT HUTCHISON

The July, 1930, issue of "The Journal of the American Chemical Society" contained two papers dealing with the manganous ion-manganese dioxide electrode. Brown and Liebafsky¹ in the first of these describe measurements made on the cell $H_2/HClO_4(m_1), Mn(ClO_4)_2(m_2)/MnO_2(s)$ at 25° with varying molalities of acid and manganous perchlorate. From the results of their measurements the authors reported for the molal potential of the electrode reaction



a value of +1.236 v. which they stated "is probably correct within 2 mv."

In the second paper Popoff, Riddick and Becker² discuss their unsuccessful attempts to

obtain consistent and reproducible values for the potentials of the same cells when highly purified manganese dioxide was used. They concluded that the difference between the two studies lay in the manner of preparation and purity of the manganese dioxide and that the cell was irreversible when pure manganese dioxide was employed. These authors stated that "...serious polarization may be expected to take place at electrodes which involve reactions that take place with a change in the oxygen content..." and referred to Lewis and Randall³ for support for this generalization. The section referred to actually deals with possible polarization of an electrode process consisting of a change in the oxygen content of an

(1) Brown and Liebafsky, *THIS JOURNAL*, **52**, 2595 (1930).

(2) Popoff, Riddick and Becker, *ibid.*, **52**, 2624 (1930).

(3) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 388.

anion and consequently does not necessarily apply to the present case. The fact that reversible and reproducible potentials have been obtained with the lead dioxide, lead sulfate electrode⁴ is of interest in this connection.

Since both of these articles include comment on earlier values of the electrode potential and its general significance none is made here.

In this investigation the procedure for the preparation and analysis of the manganese dioxide recommended by Popoff and co-workers has been used and a technique of obtaining fairly reliable potentials with this material has been found. The results lead to a molal electrode potential of 1.230 volts at 25° which is in fair agreement with the value of 1.236 volts reported by Brown and Liebhafsky.¹

Experimental

Materials.—Conductivity water was used throughout. Manganous perchlorate was prepared from C.P. perchloric acid and C.P. manganous carbonate. It was recrystallized six times before preparation of a stock solution subsequently diluted to make the various cell solutions. The stock solution was analyzed by the pyrophosphate method. Manganese dioxide was prepared by decomposing similarly purified manganous nitrate exactly as described by Popoff, Riddick and Becker.² The sample contained 0.25% water and analysis by the pyrophosphate method indicated 99.8% manganese dioxide while the oxalate method yielded 99.5% manganese dioxide. The perchloric acid solution was prepared from C.P. grade 60% acid and was standardized with sodium carbonate.

Apparatus and Procedure.—The cells were constructed by joining two test-tubes by a cross arm which included a stopcock kept closed except during electrical measurements. The cells were immersed in a water thermostat maintained at 25°. Solid manganese dioxide was shaken with the solution to be studied for eight to ten hours in a mechanical shaking device before making up the cells. Sufficient manganese dioxide to provide a layer of the solid approximately 15 mm. deep at the bottom of the half-cell was added as a suspension from the bottle in which the solution had been shaken. After this had settled the half-cell was filled with the clear solution from the same bottle. Two bright platinum foil electrodes about 4 mm. square, sealed to tubes filled with mercury to provide electrical contact, were then introduced into this part of the cell. The amount of manganese dioxide was sufficient to completely cover the platinum surfaces of the electrodes.

To the second part of the cell a solution of the same concentration as that saturated with manganese dioxide was added. Two platinized platinum electrodes were inserted through the stopper of this half-cell and entry and exit tubes for circulating hydrogen gas were provided. The hydrogen was first saturated by passing it through water. Cylinder hydrogen was used without purification.

The electrical circuit consisted of a Leeds and Northrup type K potentiometer and a type R galvanometer. The standard cell was compared from time to time with ones recently calibrated by the U. S. Bureau of Standards. A Compton quadrant electrometer was used in place of the galvanometer in some of the preliminary studies.

Duplicate cells were set up at the same time for each solution studied and the measurements were carried out over a period of at least two weeks duration in each case.

Results and Discussion

In view of the possible influence of polarization on this cell mentioned above some preliminary studies were made by Voris⁵ with a Compton

quadrant electrometer to indicate the balance point of the potentiometer circuit. In these experiments the suspension of manganese dioxide was stirred mechanically during the measurements. The erratic behavior described by Popoff, *et al.*,² was found in these cells both with the electrometer and with the galvanometer in the circuit. Since electrical polarization could not take place in the measurements with the electrometer, other factors must have been responsible for the behavior of these cells.

In a continuation of these studies Schieferstein⁶ showed it was possible to obtain cell potentials which were much more stable if such a large amount of solid manganese dioxide were used that complete immersion of the platinum electrodes in the half-cell was insured. As noted above this technique was used in the present measurements.

The use of two hydrogen and two platinum electrodes permitted four combinations in each cell. In general the difference between these combinations did not exceed one millivolt in any set of measurements. The variation between the two independently prepared cells, or of a given cell measured at different times, was somewhat greater. The values reported below represent the average of a large number of closely agreeing measurements taken on the pair of cells over the entire period of observation. Replacing the hydrogen electrodes failed to change the potential. In several cells the platinum electrodes in the manganese dioxide side were replaced, or were deliberately disturbed. This frequently produced a change in potential of as much as 1 mv. but on standing the potential generally returned to a value near that shown prior to the change.

The values obtained are listed in Table I. As may be seen three series of cells were studied.

TABLE I

Concn. HClO ₄	Concn. Mn(ClO ₄) ₂	<i>E</i> ^F	<i>E</i> ^G	
0.5000	0.5000	1.234	1.242	1.231
.2000	.2000	1.220	1.241	1.231
.1000	.1000	1.209	1.239	1.231
.0500	.0500	1.199	1.237	1.230
.0250	.0250	1.191	1.238	1.232
.0125	.0125	1.181	1.237	1.232
.1000	.0500	1.217	1.238	1.230
	.0250	1.224	1.236	1.229
	.0100	1.234	1.234	1.228
	.0050	1.241	1.232	1.226
	.0025	1.247	1.230 ^a	1.224 ^a
	.0010	1.256	1.230 ^a	1.224 ^a
.0250	.010	1.200	1.236	1.230
	.005	1.208	1.234	1.230
	.002	1.214	1.230 ^a	1.226 ^a

^a Potentials have been corrected for manganous ion concentration resulting from the manganese dioxide saturation.

(4) Hamer, *THIS JOURNAL*, **57**, 9 (1935).

(5) Voris, M.S. Thesis, The Pennsylvania State College, 1936.

(6) Schieferstein, B.S. Thesis, The Pennsylvania State College, 1937.

In the first the molalities of the two electrolytes were varied simultaneously over the range 0.5 to 0.0125 *m*. In the second and third series the acid was kept constant while the concentration of the salt was varied. The values listed under *E* are the measured potentials, in volts, corrected to a hydrogen partial pressure of 1 atm.

In the fourth column are listed values of the formal electrode potential, E^F , calculated by the equation

$$E^F = E + RT/nF \ln (m_2)/(m_1)^2 \quad (2)$$

A variation of the values of E^F with the concentration is expected in view of the size of the ionic strengths of these solutions.

The evaluation of the molal potential for the cell requires a knowledge of the activity coefficients of the ions and of the activity of the water as may be seen from the equations

$$E = E^0 - RT/nF \ln (a_{Mn^{++}} + a_{H_2O}^2/a_{H^+}^2) \quad (3)$$

or assuming the activity of water unity throughout

$$E = E^0 - RT/nF \ln (m_2)/(m_1)^2 - RT/nF \ln \gamma_2/\gamma_1^2 \quad (4)$$

The last term in (4) may be approximated by making use of the Debye-Hückel equation

$$-\log \gamma = \frac{0.506Z^2\sqrt{\mu}}{1 + 2\sqrt{\mu}} \quad (5)$$

to estimate the ion activity coefficients of the Mn^{++} and H^+ ions, respectively. Introducing this expression into equation (4) yields for 25°

$$E^0 = E^F - \frac{(0.0296)(0.506)(4 - 2)\sqrt{\mu}}{1 + 2\sqrt{\mu}} \quad (6)$$

or

$$E^0 = E^F - \frac{0.030\sqrt{\mu}}{1 + 2\sqrt{\mu}} \quad (7)$$

In these equations μ is the ionic strength of the solutions. The coefficient of $\sqrt{\mu}$ in the denominator in these equations was chosen on the assumption that the distance of closest approach of ions in these solutions might be about 6 Å. This figure is mentioned by Harned and Owen⁷ in discussing the activity coefficients of a group of 1-2 type electrolytes. It may be noted that as used in equation (6) expression (5) becomes the same as would be applied in the calculation of the mean ion activity coefficient of a 1-2 type electrolyte. As a test of the validity of this expression values of the activity coefficients of manganese chloride solutions were calculated with it as follows: 0.1 *m*, 0.545; 0.3 *m*, 0.465; 0.5 *m*, 0.438. Experimental values for the solutions are 0.522, 0.454 and 0.446, respectively, according to the measurements of Robinson and Stokes.⁸

The last column of the table lists the values of E^0 calculated by (7). The values obtained in this manner from the first series of measurements show good agreement. In the second and third series the agreement is not as good, especially in the cells in which the concentration of manganese

perchlorate is very small. As noted in the table a small correction has been applied to three of these values because of a possible slight increase in the manganous ion concentration resulting from the manganese dioxide saturation.⁹

The variation of E^F with the concentration of manganese perchlorate in the series of constant acid concentration seems to be greater than can be accounted for readily by inter-ion attraction effects. It is of interest to note that a similar variation was found by Brown and Liebafsky.¹ The over-all average of the fifteen values of E^0 listed is 1.229 volts. In view of possible uncertainty in the values for the three most dilute solutions studied, it is suggested that a more reliable value may be obtained by taking an average of the twelve remaining values. This yields a value of 1.230 volts for E^0 which, of course, applies also to the half-cell reaction (1).

Although the differences between the values obtained in this study and that of Brown and Liebafsky¹ for individual cells are as much as 20 mv. in certain cases it is of interest to note that the recommended molal potential differs by only 6 mv. This results in part from a difference in the method used in evaluating the ion activity coefficients. Brown and Liebafsky¹⁰ estimated values for the coefficients in the solutions containing unequal concentrations of the salt and acid by the extrapolation into regions of higher ionic strengths of data of Lewis and Randall.³ If the data of these authors for the mixed solutions are recalculated using the methods of this report a somewhat higher value for the average molal potential is obtained.

Perhaps the discrepancy between the two investigations is in part due to the factors which lead to the comment of Latimer¹¹ regarding the "variation of the thermodynamic properties of the dioxide, even when prepared under very similar conditions." This author lists for the electrode a molal potential of 1.28 volts calculated from thermal data and the third law of thermodynamics.

Summary

Potentials of cells of the type $H_2/HClO_4(m_1), Mn(ClO_4)_2(m_2)/MnO_2$ have been measured using manganese dioxide of established purity.

The reversibility of the manganese dioxide electrode has been demonstrated with manganese dioxide prepared by the method of Popoff, Riddick and Becker,² who had concluded that the electrode was irreversible.

(9) An average value of 3×10^{-4} *m*. was obtained for the concentration of manganese in 0.1 *m* perchloric acid solutions which had been shaken for a long time with solid manganese dioxide in some preliminary studies on the possible reaction between this substance and thallos perchlorate. This value was later confirmed by Kotch, B.S. Thesis, The Pennsylvania State College, 1946. The correction is 1 mv. for the 0.002 *m* solutions and 4 mv. for the 0.001 *m* solution.

(10) Private communication from Professor Brown and ref. 1, p. 2596.

(11) Latimer, "Oxidation Potentials," Prentice-Hall Inc., New York, N. Y., 1938, p. 222.

(7) Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York, N. Y., 1943, p. 423.

(8) Robinson and Stokes, *Trans. Faraday Soc.*, **36**, 1137 (1940).

From the measurements a value for the molal potential for the half cell reaction $4\text{H}^+ + \text{Mn-O}_2(\text{s}) + 2\text{e}^- = \text{Mn}^{++} + 2\text{H}_2\text{O}$ of 1.230 volts at 25° has been calculated.

This value is 6 mv. less than that computed by Brown and Liebafsky¹ from data obtained in a similar study.

STATE COLLEGE, PA.

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[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Theory and Kinetics of Specific Oxidation. II. The Periodate-Glycol Reaction

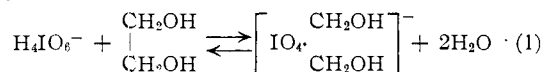
BY FREDERICK R. DUKE

Trivalent manganese has been shown to oxidize oxalate through the disproportionation of oxalate manganate complexes.¹ In order to further test the postulate that specific oxidations of glycols and related compounds generally proceed through the disproportionation of coordination complexes,¹ it was considered desirable to study as different an oxidation as possible which fits into the same category of specificity. The oxidation of glycol by periodate fulfills these conditions.

Previous work on the kinetics of the periodate oxidation of glycol^{2,3} is very sketchy, presumably because of the rapidity of the reaction at ordinary temperatures. Price³ concluded that the reaction is second order in periodate and glycol and suggested a cyclic ester as intermediate, the slow reaction being taken as the ester formation.

Theory

The coordination intermediate should be formed by the reaction



The kinetics, according to the theory,¹ would be expressed by the equation

$$\frac{d[A]}{dt} = \left[\frac{kK[C]}{K[C] + 1} \right] [A] \quad (2)$$

where $[A]$ is total periodate, k the rate constant and K the equilibrium constant for reaction (1) as written ($[\text{H}_2\text{O}]$ taken as unity), and $[C]$ is the concentration of uncoordinated glycol. Equation (2) may be subjected to experimental verification by measuring the rate of disappearance of periodate from solutions containing sufficient glycol to validate the assumption that $[C]$ remains constant throughout the portion of the reaction studied.⁴ Under these conditions, a series of first-order (in oxidant) pseudo-constants may be obtained, the pseudo-constant k being identified with the bracketed portion of equation (3).

(1) Duke, *THIS JOURNAL*, **69**, 2885 (1947).

(2) Criegee, Kraft and Rank, *Ann.*, **507**, 159 (1933).

(3) Price and Kroll, *THIS JOURNAL*, **60**, 2726 (1938).

(4) The stoichiometry of the oxidation is the same as that of equation (1). Thus, "sufficient glycol" concentration depends upon the magnitude of K . If K is very large, the uncoordinated glycol concentration will remain essentially constant even though $[C]$ is of the same order of magnitude as $[A]$. If K is small $[C]$ should exceed $[A]$ by ten-fold or more.

Experimental

The constant temperature baths used in the study were melting ice and melting benzene to obtain temperatures of $0 \pm 0.05^\circ$ and $5.1 \pm 0.05^\circ$, respectively. The solid phase in each case was placed into the corresponding liquid in a 2-liter wide-mouth Dewar flask, and the contents stirred. The temperature of the melting benzene is somewhat below the reported value for the melting point (5.48°) presumably because the benzene was saturated with water.

Fifty-ml. volumetric flasks with an additional 48 ml. calibration line were used for reaction vessels. The amount of 1.0 M glycol to give the desired final concentration, and 5.0 ml. of 2 M potassium nitrate were placed in the volumetric flask and the contents diluted to 48 ml. After half an hour in the constant temperature bath, 2.0 ml. of 0.20 M H_5IO_6 at the bath temperature were added and the timer started during the mixing. Five-ml. samples were removed at known times and quenched in 5 ml. of a solution saturated with sodium bicarbonate and containing 5% potassium iodide to which 1.0 ml. of 0.100 N arsenite had been added. The excess arsenite was titrated with 0.01 N I_2 .

The pH was varied by including in the original mixture in the reaction vessel 1 ml. of 0.2 M sodium hydroxide, thereby cutting the acidity in half.

Results and Discussion

Pseudo-constants obtained at 0 and at 5.1° with various concentrations of glycol, taken from the slope of plots of $\log [A]$ vs. t are recorded in Table I. The value of uncoordinated glycol concentration, $[C]$, was obtained by assuming that the periodate is completely converted to the glycol complex when the glycol concentration is 0.2 M or greater; then the amount of coordinated glycol at any concentration is the ratio of the rate at that concentration to the rate at 0.2 M multiplied by the periodate concentration. The selection of the rate at 0.2 M glycol concentration as the rate corresponding to complete coordination seems justified by the fact that the rate is nearly independent of glycol concentration in this range.

The hydrogen ion concentration was changed from 0.008 to 0.004 M without effect on the constants. Presumably, the lowering of the rate observed by Price³ in alkaline solution may be explained by the greater difficulty in displacement of the hydroxyl by the glycol

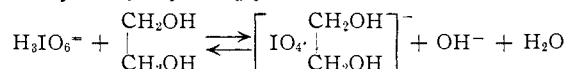


Fig. 1 is a plot of $1/k'$ vs. $1/[C]$. Reference to equation (2) shows that the slope of the straight line obtained is $1/Kk$, while the intercept is $1/k$. The large size of the constant K (130 at 0° and 80