1,5-(bistrimethylammonium)-pentamethylene dibromide $\lambda^0_2 = 77.3$ while for compound IV $\lambda^0_2 = 79.4$. Higher mobility for the substituted ethers presumably means a more compact structure. This readily can be obtained if we assume that the ether oxygen is pulled toward one of the cationic nitrogens; molecular models show that there is ample space between methyl groups for near N^+O^- contact. The presence of the negative oxygen near the nitrogen weakens the attraction of the latter for an approaching anion, *i.e.*, acts in the direction of increasing k_2. Increase of R also increases k_2. Hence we conclude that the NC_2OC_2N chain is shorter than the NC_5N chain and that the near equality of the k_2's is the result of compensating effects.

NEW HAVEN, CONNECTICUT

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

The Gluconate Complexes. I. Copper Gluconate Complexes in Strongly Basic Media[1]

BY ROBERT L. PECSOK AND RICHARD S. JUVET, JR.

RECEIVED JUNE 12, 1954

The copper gluconate chelates have been studied polarographically, spectrophotometrically, potentiometrically and amperometrically. From the data obtained the structures of some of the chelates have been postulated and the equilibrium constants at various ionic strengths have been measured. Evidence is given for the existence of at least five species—a 2:4, a 2:2, and a 2:1 copper gluconate species in strongly basic solution and two other different 2:2 complex species in less concentrated basic solutions. The pK for the 2:2 complex in strongly basic solution is 18.2_9, independent of ionic strength, and the pK's for the 2:4 species vary from 20.0_6 to 19.4_3 as ionic strength varies from 3 to 0.45 molar.

The present study is the first of a series of papers dealing with the metal chelates of gluconic acid. Gluconic acid forms very strong complexes with most of the transition elements. These complexes are being investigated polarographically, potentiometrically and spectrophotometrically, where applicable. The polarograph was used in the present investigation for the determination of the dissociation constants of the copper gluconate chelates and for obtaining valuable information concerning their structure.

Traube, Kuhbier and Schröder[2] have prepared solid compounds of barium copper gluconates which analysis showed had empirical formulas close to $(C_6H_8O_7Cu)Ba\cdot 3H_2O$ and $[(C_6H_9O_7)_2Cu]Ba_2\cdot 9H_2O$. Mehltretter, *et al.*,[3] have compared the sequestering capacity of gluconic acid for copper with several other sugar acids in 3% sodium hydroxide on a gram per gram basis.

Cannan and Kibrick[4] have measured the dissociation constants of the gluconate chelates of several Group II elements using ordinary potentiometric measurements, but found that only weak complexes are formed with these elements. No previous measurements have been reported on the dissociation constants of the transition metal gluconate complexes.

Experimental

Polarograms were recorded according to usual technique[5] with a calibrated Sargent Model XXI automatically recording polarograph. Since the strongly basic solutions used in this work were found to attack agar salt bridges, it was necessary to design a new type of polarographic cell.[6] The resistance was found to be *ca.* 265 ohms when measured through the dropping mercury electrode in a 0.1 M potassium chloride solution. Corrections for IR drop were made where necessary, and corrections were made for residual currents in determining all diffusion current data. The rate of flow, m, was 1.452 mg. sec.$^{-1}$, and the drop time was 5.18 sec. on open circuit and 5.80 sec. at -0.65 v. *vs.* S.C.E. at which most measurements of the diffusion current were made. Temperatures were maintained at 25.0°.

Spectrophotometric investigations were run either on a Cary Model 11PMS automatically recording spectrophotometer (Applied Physics Corp., Pasadena, California) or on a Beckman DU quartz spectrophotometer.

Copper solutions were made from Merck reagent grade copper sulfate and were standardized electrolytically by the method of Kolthoff and Sandell.[7]

Sodium gluconate solutions were prepared from D-glucono-δ-lactone (Matheson, Coleman and Bell) which was recrystallized twice from ethylene glycol monomethyl ether and dried at 110° for 1 hour. The purified lactone was then standardized by titration with standard sodium hydroxide. Care must be taken in this titration since the lactone hydrolyzes rather slowly a few ml. before the equivalence point and the pH slowly decreases as hydrolysis takes place. At the end-point, however, a very definite increase in pH is found. An alternate standardization procedure is to add an excess of standard sodium hydroxide solution followed by a back-titration with standard hydrochloric acid solution. The D-glucono-δ-lactone was found to be 99.7% pure.

Theoretical Discussion

Lingane[8] has pointed out the inherent usefulness of the polarograph for the determination of stability constants and formulas of metal complexes. We have adapted his analysis of the polarographic wave to fit the situation at hand. Two modifications are required: hydroxide ion is involved in the half reaction, and in some cases the concentration of free gluconate is not in large excess.

We may write for the general reaction of the reduction of copper gluconate

$$\text{Complex} + yH_2O + Hg + 2e^- = Cu(Hg) + pGH_4^- + xOH^- \quad (1)$$

where HGH_4 is gluconic acid and GH_4^- is the gluconate ion (H's refer to the secondary hydroxyl hy-

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[1] Presented before the Regional Meeting of the Southern California Section of the American Chemical Society, Los Angeles, May 8, 1954.

[2] W. Traube, F. Kuhbier and W. Schröder, *Ber.*, **69B**, 2655 (1936).

[3] C. L. Mehltretter, B. H. Alexander and C. E. Rist, *Ind. Eng. Chem.*, **45**, 2782 (1953).

[4] R. K. Cannan and A. Kibrick, THIS JOURNAL, **60**, 2314 (1938).

[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishing Co., New York, N. Y., 1952.

[6] R. L. Pecsok and R. S. Juvet, *Anal. Chem.*, in press.

[7] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1952, p. 407.

[8] J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

drogens), p is the number of gluconate ions associated with each copper, and x is the number of hydroxide ions entering into the reaction. Thus, if we can determine p and x, important information concerning the structure of the chelate will be obtained.

This general equation may be written, for convenience, as the sum of two partial reactions

$$\text{Complex} + y\text{H}_2\text{O} = \text{Cu}^{+2} + p\text{GH}_4^- + x\text{OH}^- \quad (2a)$$

$$\text{Cu}^{+2} + \text{Hg} + 2\text{e} = \text{Cu(Hg)} \quad (2b)$$

Using the symbolism of Lingane,[8] the potential of (2b) at any point on the wave should be given by

$$E_{\text{d.e.}} = E^0_{\text{a}} - \frac{0.0591}{2} \log C^0_{\text{a}}/C^0_{\text{Cu}}\, a_{\text{Hg}} = \epsilon - 0.0296 \log C^0_{\text{a}}/C^0_{\text{Cu}} \quad (3)$$

where we assume that the concentrations are equal to the activities, and where the superscript "0" refers to the concentration of the particular species at the surface of the electrode as distinct from the concentration in the body of the solution.

If the dissociation of the complex ion is rapid so that equilibrium is maintained at the surface of the electrode with respect to equation 2a, then

$$C^0_{\text{Cu}} = \frac{K(C^0_{\text{complex}})}{(C^0_{\text{GH}_4})^p(C^0_{\text{OH}^-})^x} \quad (4)$$

where K is the "apparent" equilibrium constant which differs from the thermodynamic equilibrium constant in that concentrations are used instead of activities. The following relations also hold

$$i = k_{\text{c}}\,(C_{\text{complex}} - C^0_{\text{complex}}) \quad (5)$$

$$i_{\text{d}} = k_{\text{c}}\, C_{\text{complex}} \quad (6)$$

$$C^0_{\text{a}} = i/k_{\text{a}} \quad (7)$$

Since gluconate ion is a product of the electrode reaction, its concentration at the electrode surface increases with increasing current. Therefore we may write for the concentration of gluconate ion at the surface of the electrode

$$C^0_{\text{GH}_4} = C_{\text{GH}_4} + p(i/k_{\text{GH}_4^-}) \quad (8)$$

where $k_{\text{GH}_4^-}$ is proportional to the square root of the diffusion coefficient of GH_4^- and is, to a fair approximation, equal to k_{complex}. A similar expression is found for the concentration of hydroxide ion at the surface of the electrode. However, in this case the second term becomes negligibly small compared with the concentration of hydroxide in the body of the solution. This simplification can also be made when high concentrations of gluconate are used.

Substituting equations 4 through 8 into equation 3, one obtains

$$\frac{E_{\text{d.e.}} - \epsilon}{0.0296} = \log K \frac{k_{\text{a}}}{k_{\text{c}}} - p \log \left(C_{\text{GH}_4^-} + p \frac{i}{k_{\text{GH}_4^-}} \right) - x \log C_{\text{OH}^-} - \log \frac{i}{i_{\text{d}} - i} \quad (9)$$

Since the half-wave potential is defined as that point at which $i = i_{\text{d}}/2$, equation 9 may be expressed

$$E_{\text{d.e.}} = (E_{1/2})_{\text{c}} - 0.0296 \log (i/(i_{\text{d}} - i))$$

where the half-wave potential of the complex $(E_{1/2})_{\text{c}}$ is expressed by

$$\frac{(E_{1/2})_{\text{c}} - \epsilon}{0.0296} = \log K \frac{k_{\text{a}}}{k_{\text{c}}} - p \log \left(C_{\text{GH}_4^-} + p \frac{i_{\text{d}}}{2k_{\text{GH}_4^-}} \right) - x \log C_{\text{OH}^-} \quad (10)$$

This equation will be useful for the determination of the structure of the copper gluconate chelate.

von Stackelberg[9] and Lingane[8] have shown that the half-wave potential of an uncomplexed metal ion, $(E_{1/2})_{\text{s}}$, is given by

$$(E_{1/2})_{\text{s}} = \epsilon - 0.0296 \log k_{\text{s}}/k_{\text{a}} \quad (11)$$

if we assume that activities equal concentrations. Combining equations 10 and 11, we obtain

$$(E_{1/2})_{\text{c}} - (E_{1/2})_{\text{s}} = 0.0296 \log K \frac{k_{\text{s}}}{k_{\text{c}}} - 0.0296 \log \left(C_{\text{GH}_4^-} + p \frac{i_{\text{d}}}{2k_{\text{GH}_4^-}} \right)^p (C_{\text{OH}^-})^x \quad (12)$$

This equation will be used to determine the dissociation constants of the copper complexes.

Discussion and Results

Before the equations derived above can be used, it is necessary to establish the reversibility of the system. The conventional log plot[8] was used to prove the reversibility of the reduction of copper gluconate in 0.1 *M* sodium gluconate and 0.34 *M* sodium hydroxide (a concentration of gluconate which will be shown to correspond to a 1:2 complex). A plot of log $i/(i_{\text{d}} - i)$ *vs.* $E_{\text{d.e.}}$ gave a straight line whose slope was 0.034 which is in fair agreement with the theoretical value of 0.030. In the region of small gluconate concentration (corresponding to the reduction of a 1:1 species), it was necessary to establish the reversibility of the complex in a different manner since the concentration of gluconate is changing at the surface of the electrode as reduction proceeds. A solution of 1 m*M* copper in 8 m*M* sodium gluconate and 1 *M* sodium hydroxide was polarographed and the cathodic half-wave potential was noted. A 1 m*M* copper amalgam was prepared and was polarographed in a 8 m*M* sodium gluconate solution in 1 *M* sodium hydroxide containing no copper, and the anodic half-wave potential was compared with the first polarogram. After corrections were made for *IR* drop through the cell, the half-wave potentials were found to agree within 4 millivolts. Thus, the reduction of both the 1:1 and the 1:2 complexes are essentially reversible.

Effect of Gluconate.—From equation 10, log $(C_{\text{GH}_4^-} + pi_{\text{d}}/2k_{\text{GH}_4^-})$ *vs.* $E_{1/2}$, or to a good approximation log $C_{\text{GH}_4^-}$ *vs.* $E_{1/2}$, should produce a straight line whose slope is 0.0296(p). Figure 1 is a plot of log $C_{\text{GH}_4^-}$ *vs.* $E_{1/2}$ at various concentrations of hydroxide. In each case two straight lines whose average slopes are 0.054 and 0.034 may be drawn through the experimental points. These slopes are in fair agreement with the theoretical values 0.059 and 0.030 for a 1:2 and a 1:1 copper gluconate species, respectively. The slope for the 1:1 complex in curve A differs slightly from the other curves since for those three points it was necessary to add gelatin to suppress maxima. No maxima appeared in the other solutions, and consequently no maximum suppressor was added. When the concentration of copper is 10^{-3} *M*, a 1:1 complex predominates at a gluconate concentration below *ca.* 0.012 *M* and a 1:2 copper gluconate complex predominates at concentrations of gluconate greater than 0.012 *M*.

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[9] M. von Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939).

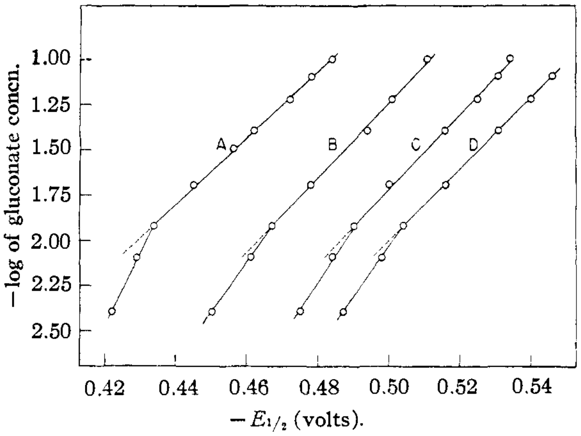
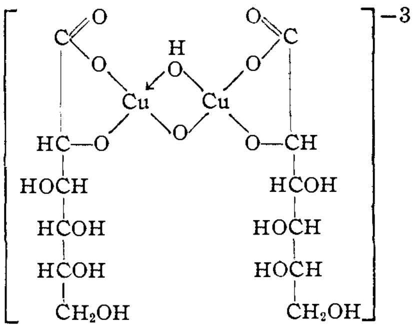


Fig. 1.—Effect of gluconate concentration on half-wave potential at various hydroxide concentrations: A, 0.378 *M*; B, 0.968 *M*; C, 1.94 *M*; D, 2.96 *M* NaOH.

Effect of Hydroxide.—If a plot is made of log C_{OH^-} *vs.* $E_{1/2}$ for concentrations of gluconate corresponding to both the 1:1 and the 1:2 complexes, a series of parallel straight lines are obtained whose slopes average 0.076_2. The slope corresponds to 2.5_7 hydroxide ions per copper. This indicates the complexes are probably dimers and 5 hydroxide ions enter into the reduction reaction. Larger polymers are not likely since the reduction is reversible and diffusion controlled.

The structure which best fits the polarographic data in strongly basic solution and which is consistent with other observations discussed below contains an oxygen bridge.



I

A structure for the 1:2 complex is more difficult to postulate. Two gluconates are associated with each copper and 2.5 hydroxides per copper enter into the reduction equation as in the case for the 1:1 complex. Consequently two coppers are probably associated with four gluconate radicals in the complex. The second two gluconates are apparently weakly bound since the stability constant data given below show the stability of the 1:1 and the 1:2 complexes are quite similar.

Amperometric Titration.—Twenty-five ml. of 0.002 *M* sodium gluconate in 1 *M* sodium hydroxide was titrated with 0.012 *M* copper sulfate, and the current was followed amperometrically. After correction for dilution effects, three poorly defined breaks at concentrations of copper corresponding to a 1:2, a 1:1, and a 2:1 copper gluconate complex were obtained. This is our only evidence for the existence of complexes with greater than a 1:1 copper to gluconate ratio.

Studies at Lower *p*H.—At low concentrations of hydroxide ion, polarographic data were of little value since maxima appeared and the waves were irreversible. However, in a 0.08 *M* sodium gluconate solution at *p*H 11.38 containing 0.01% gelatin, two irreversible waves were obtained with half-wave potentials −0.33 and −0.64 v. *vs.* S.C.E. This is consistent with our interpretation given below based on spectrophotometric evidence of two species being present at this *p*H.

Potentiometric determinations of *p*H were used to help establish the structure in less basic solutions. Figure 2 shows the titration of copper gluconate (1:1) in excess sodium hydroxide with standard hydrochloric acid solution. The titration was performed from high to low *p*H in order to avoid difficulties from the slow lactone hydrolysis. The titration curve has been marked at intervals in the reverse direction, in terms of "*a*," the moles of hydroxide ion added per mole of copper present. Two breaks in the titration curve are obvious. The first, at *a* = 1, corresponds to the titration of the acid to the salt. The second, at *a* ~ 2.7, corresponds to the titration of the hydrogen ions liberated by chelate formation. Careful observation of the second break in the titration curve shows that a small hump is present at about *p*H 9 and that the break actually consists of two inflection points—one at exactly 2.5 and the other at exactly 3.0. This would indicate that at least two different species are present in the *p*H range 6–11. Further evidence for the existence of two species in this range is obtained from spectrophotometric data. In order to compare these values of *a* to the polarographic data, we must subtract one hydroxide ion since in

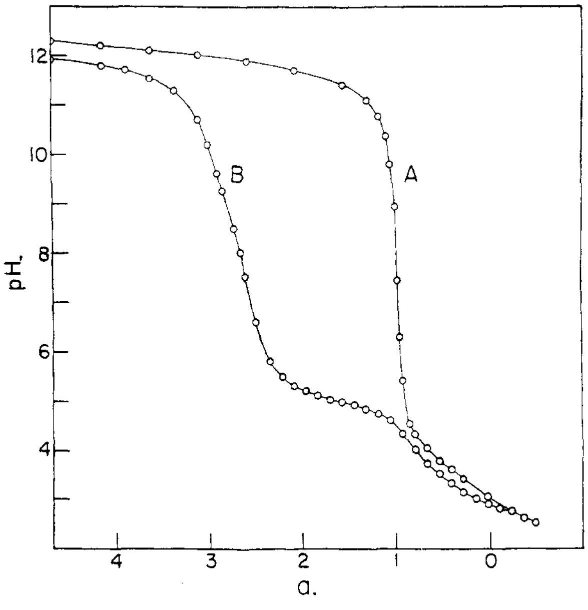
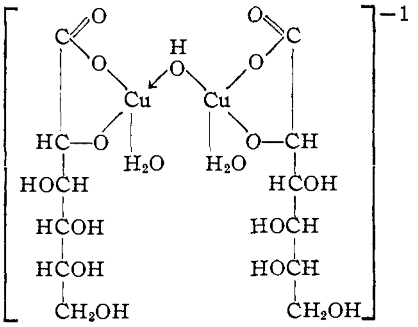
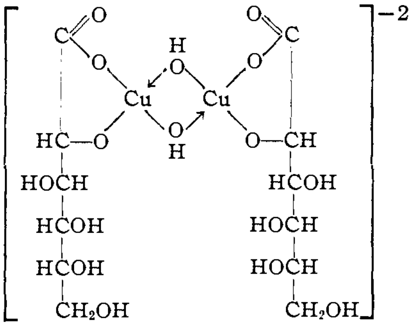


Fig. 2.—Curve A, titration of sodium gluconate containing excess base with standard HCl; curve B, titration of 9.63 m*M* copper gluconate (1:1) in excess base with standard HCl. *a* is moles of base per mole of copper; ionic strength $\mu = 0.1$.

the highly alkaline solutions, gluconate ion and not the acid is the product of reduction. Apparently the complex at pH values less than about 9 has a different structure than in more basic solutions since 1.5 hydrogen ions per copper are liberated in chelate formation rather than 2.0 at pH values greater than 9 and 2.5 in strongly basic solutions. The two structures which best fit the experimental data are given below. Structure II corresponds to an a value of 2.5 and liberates 1.5 hydroxide ions per copper upon dissociation. Structure III corresponds to an a value of 3.0, liberating 2.0 hydroxide ions per copper.



II



III

Structures of type (III) have previously been reported[10] for copper chelates with some N-substituted ethylenediamines which likewise form binuclear complexes. It should be pointed out there are no doubt other structures which might be proposed for these chelates. For example, in structure II, a hydrogen ion in the water molecule coordinated with each copper could be moved to the α-hydroxyl group of the gluconate ions. Thus this hydrogen ion from the gluconate hydroxyl group would not be removed until the solution became more alkaline. Our data will not permit a decision on this matter.

Absorption Spectra.—Spectrophotometric data for the 1:1 copper gluconate chelate were obtained. All solutions were equilibrated for 2–5 days. Figure 3 shows the spectra obtained at various pH values. As the solution becomes more basic, the maximum is shifted to lower wave lengths, and the solution changes from green to deep blue. Two isosbestic points are evident: one at 813 mμ and the second at 626 mμ. The presence of two isosbestic points indicates that three copper gluconate species exist. We may compare the spectra at various pH with the titration curve in Fig. 2. Curve 1 shows the absorption of uncomplexed copper at pH 3. Curve 2, which does not pass through the isosbestic point at 813 mμ corresponds to a pH at which a equals approximately 1, the formation of the gluconate ion. Curves 3 through 6 all pass through the isosbestic at 813 mμ, and the pH range corresponds to the buffer region up to the inflection point at a = 2.5 in the titration curve. It will be noted that the absorption maximum shifts to lower wave lengths and the absorption increases reaching a maximum at approximately pH 8.5. At pH values from about 9.5 to about 12, the spectra no longer pass through the isosbestic at 813 mμ, but instead pass through an isosbestic at 626 mμ. When the concentration of base is increased to 3 M, the absorption is decreased and the spectra no longer go through the isosbestic. Curve 12 is the spectrum of the cuprate ion in 5 M sodium hydroxide in the absence of gluconate.

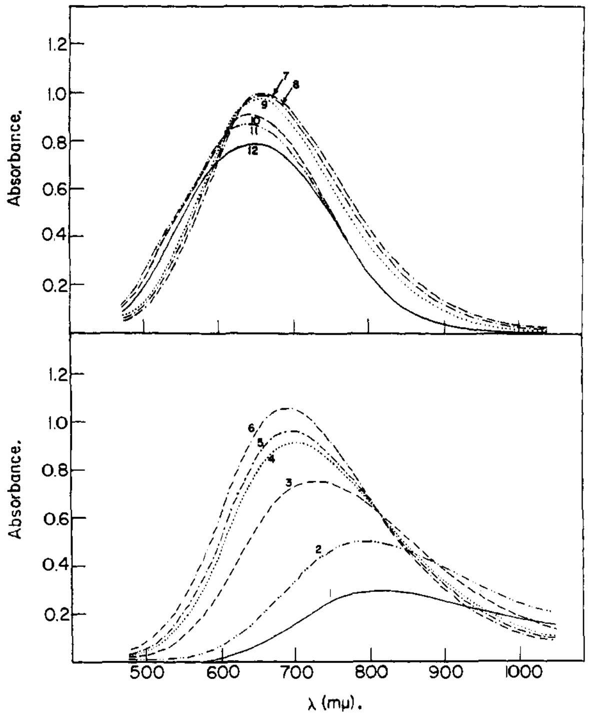


Fig. 3.—Spectra of 1:1 copper gluconate at various pH: $[Cu^{++}]_{total}$ = 9.88 mM, $[GH_4^-]_{total}$ = 12.0 mM. pH values: (1) 3.03 no gluconate; (2) 4.30; (3) 5.05; (4) 5.58; (5) 6.62; (6) 8.42; (7) 9.52; (8) 9.75; (9) 12.02; (10) 3 M NaOH; (11) 5 M NaOH; (12) 5 M NaOH, no gluconate.

We interpret this data in the following manner: Below *ca.* pH 4 a weak chelate species probably exists which does not liberate a hydrogen ion from the alpha hydroxyl group. From pH 5 to about 8.5 there is an equilibrium between this species and another (structure II) which liberates 1.5 hydrogen ions per copper upon formation. From about pH 9.5 to about 12 there is equilibrium between this latter species and one (structure III) in which 2.0 hydrogen ions per copper are liberated. In concentrations of base corresponding to our polarographic measurements another species predominates (structure I) which liberates 2.5 hydroxide ions per copper upon reduction.

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(10) H. Irving, E. J. Butler and M. F. Ring, *J. Chem. Soc.*, 1489 (1949).

Equilibrium Constants.—The "apparent equilibrium constant" of the 1:1 and the 1:2 complexes in strongly basic solution may be determined from polarographic data for various ionic strengths. It may be seen by inspection of equation 12 that if we plot $(E_{1/2})_c - (E_{1/2})_s$ *vs.* log $[C_{GH_4^-} + p(i_d/2k_{GH_4^-})]^p\ (C_{OH^-})^x$, a straight line should be obtained whose slope is 0.0296 and whose intercept with the "*Y*" coördinate (at which the log term equals zero) is equal to 0.0296 log $K(k_s/k_o)$. The ratio k_s/k_o is equal simply to the ratio of the diffusion currents $(i_d)_s/(i_d)_c$ measured for uncomplexed and complexed copper at the same concentration and ionic strength. Thus, *K* determined in this fashion is not a true stability constant involving the formation of a complex directly from the metal and a ligand. It is the equilibrium constant for reaction 2a in which *p* is given values of 1 and 2. It must be observed that this reaction included 2.5 hydroxide ions resulting in part from the dissociation of the second hydrogen ion of gluconic acid, for which the constant is unknown. We have calculated values of *K* assuming the complex is a monomer, in order to facilitate comparison to stability constants of other chelates.

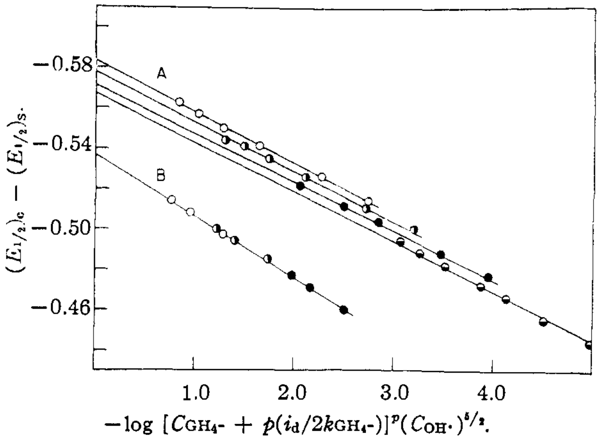

Fig. 4.—Determination of equilibrium constants: A, 1:2 complex ($p = 2$); B, 1:1 complex ($p = 1$) at various ionic strengths; ○, $\mu = 3$ *M*; ◑, $\mu = 2$ *M*; ●, $\mu = 1$ *M*; ◒, $\mu = 0.45$ *M*.

Figure 4 gives the plots used for the determination of equilibrium constants for the 1:1 complex (curve B) and the 1:2 complex (curve A). It will be noted that all experimental points for the 1:1 complex lie on one straight line with a slope of 0.031, indicating the equilibrium constant is independent of ionic strength in the region 1 to 3 *M*. However, the equilibrium constant for the 1:2 complex is dependent on the ionic strength since four straight lines with an average slope of 0.026 were obtained.

The *pK* (−log equilibrium constant) calculated for the 1:1 complex is 18.29. The *pK* values calculated for the 1:2 complex at various ionic strengths at 25° are: $\mu = 3.0$, 20.06; $\mu = 2.0$, 19.85; $\mu = 1.0$, 19.48; $\mu = 0.45$, 19.43.

Los Angeles 24, California

[Contribution from the Polymer Research Institute, Polytechnic Institute of Brooklyn]

The Kinetics of the Catalyzed Decomposition of Diazohydrocarbons[1]

By Joseph Feltzin,[2] Alfred J. Restaino[3] and Robert B. Mesrobian

Received July 19, 1954

Several polymeric hydrocarbons have been prepared by the catalyzed decomposition of diazomethane, diazoethane, diazobutane, and mixtures of the former two diazohydrocarbons. The kinetics of the decomposition reaction in ether catalyzed by cupric stearate or boron trifluoride have been studied. It is observed that the reaction rate is first order with respect to the diazohydrocarbon and the catalyst concentrations. The effect of catalyst and diazohydrocarbon concentrations on molecular weight was studied with the copolymer prepared from 80 mole per cent. diazomethane and 20 mole per cent. diazoethane. The molecular weight is found to be independent of diazohydrocarbon and catalyst concentrations. A polymerization mechanism involving propagation *via* a carbonium or diazonium ion and termination by interaction of growing chains with diazohydrocarbons is presented.

The decomposition of diazomethane to yield polymethylene was first reported by Bamberger and Tchirner.[4] Recent studies of this reaction have been concerned with the efficiency of various catalysts for conversion of diazohydrocarbon to polymer, the preparation of polyhydrocarbons from a homologous series of diazohydrocarbons,[5] and the physical properties of polymethylene derived from diazomethane.[6] This paper is concerned with the kinetics and mechanism of the catalyzed decomposition reaction in ether solution.

Experimental

Materials.—Diethyl ether, U. S. P. grade, was used without further purification. Benzoic acid, toluene, hydroquinone, potassium cyanate, cupric sulfate and the various alkyl amines were reagent grade chemicals. Boron trifluoride etherate, trimethyl borate and tri-*n*-butyl borate were freshly distilled and diluted as necessary with ether. Cupric stearate was prepared by adding 6 g. of technical grade sodium stearate in 700 ml. of water to a 5% excess cupric sulfate solution. The precipitate was dissolved in ether and the solution filtered, concentrated to a small volume, and passed through a column containing 10 g. of activated alumina (Alcoa F-20 grade). The column was eluted with ether until the eluate appeared colorless. The eluate was filtered to remove traces of alumina, evaporated

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(1) This paper was presented before the Division of Polymer Chemistry at the 124th Meeting of the American Chemical Society in Chicago, Illinois, September 1953.

(2) Natvar Corporation (New Jersey) Fellow, 1951–1953. Abstracted in part from the dissertation of Joseph Feltzin, submitted in partial fulfillment of the requirements for the Ph.D. degree.

(3) Abstracted in part from the dissertation of Alfred J. Restaino, submitted in partial fulfillment of the requirements for the M.S. degree.

(4) E. Bamberger and F. Tchirner, *Ber.*, **33**, 956 (1900).

(5) (a) A. Loose, *J. prakt. Chem.*, **79**, 507 (1909); (b) K. Lorey, *ibid.*, **124**, 185 (1930); (c) H. Meerwein, *Angew. Chem.*, **A60**, 78 (1948); (d) G. D. Buckley, L. H. Cross and N. H. Ray, *J. Chem. Soc.*, 2714 (1950); (e) *ibid.*, 3701 (1952); (f) L. C. Leitch, P. E. Gagnon and A. Cambron, *Can. J. Research*, **28b**, 256 (1950).

(6) S. W. Kantor and R. C. Osthoff, This Journal, **75**, 931 (1953).