the circles represent the observed results. The curve below the graph of the observed results was obtained by assuming the mobility, term, $(\overline{\mathfrak{M}}/c)$, to be constant and equal to P, its value at zero concentration. The difference between this curve and the upper curve represents the calculated effect of electrophoresis. The lowest curve was obtained from the limiting law of the theory which for lanthanum chloride becomes

$$\mathfrak{D} = \mathfrak{D}_0 - \mathcal{S}_{(\mathfrak{D})}\sqrt{c} = 1.2937 - 6.354\sqrt{c} \quad (11)$$

It is clear from these graphs that fair agreement with theory is obtained as the concentration of the salt approaches zero. On the other hand, the difference between the calculated and observed results is considerably greater than the estimated error in the determination of the diffusion coefficient. This fact we believe to be significant.

A comparison of the diffusion coefficients of calcium and lanthanum chloride is illustrated by Fig. 2 in which these quantities are plotted against the square root of the concentration. The upper curves represents the complete theory and the lower straight lines the limiting law. These results show that the deviation from theory of the diffusion coefficient of calcium chloride is about twice the magnitude of the deviation for lanthanum chloride. In both cases, the observed results approach the theoretical values as the concentration decreases.

For lanthanum chloride, very close conformity with theory at molar concentrations below 0.0005 molar or 0.003 ionic strength is indicated. For calcium chloride, it appears that agreement between theory and observed results will only occur in extremely dilute solutions.

NEW HAVEN, CONN. RECEIVED APRIL 13, 1951

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Studies in the Theory of the Polarographic Diffusion Current. VI. The Effect of Ionic Strength on the Diffusion Current Constant in the Absence of Gelatin

BY LOUIS MEITES

Data are presented on the effect of acid concentration on the diffusion current constant of thallium(I) in 0.01–4.1 F hydrochloric acid and in 0.01–0.4 F perchloric acid, and of iodate in 0.01–4.2 F hydrochloric acid. At ionic strengths between about 0.1 and 0.8, I is equal within 1% to the value calculated from the Ilkovič equation using the appropriate values of D^0. At lower ionic strengths, however, I increases, so that the diffusion current constant at infinite dilution is much higher than that predicted. This is considered to represent a failure of the diffusion coefficient dependence expressed by the Ilkovič equation.

Introduction

For want of any convenient and precise method for the determination of ionic diffusion coefficients under polarographic conditions, the values of D^0 calculated from the Nernst equation have commonly been applied to diffusion current data secured in the presence of a large excess of supporting electrolyte. Lingane and Kolthoff[1] compared the diffusion currents of a number of ions with the values calculated from the Ilkovič equation on the basis of this assumption. Although no large systematic discrepancy was apparent, the differences were occasionally as large as 8%.

The work here described was intended to make possible a more direct test of the Ilkovič equation by extrapolating diffusion current constant values to infinite dilution for comparison with the predicted values.

Experimental

Hydrochloric and perchloric acid solutions were prepared by volume dilution of solutions standardized against carefully purified sodium tetraborate decahydrate. A known volume of an acid solution of the desired concentration was placed in a modified H-cell[2] and deaerated. When the residual current had become constant, a weighed portion of a solution of thallium(I) chloride or potassium iodate was added, the solution was deaerated again, and the total current was measured. These measurements were made at four or five potentials between −0.8 and −1.0 v. *vs.* S.C.E. (except with 2 or 4 F acid, where slightly more positive potentials were used to obviate interference from the discharge of hydrogen ion), using three or four concentrations of the reducible ion between 0.1 and 0.35 mM. Consequently each diffusion current constant is the mean of twelve to twenty individual values: the mean deviation of each such series was about ±0.25%.

All measurements were made with the manual polarograph previously described,[3] with the cell in a water thermostat at 25.00 ± 0.01°. One capillary was used throughout this work: at −0.9 v. *vs.* S.C.E. it gave a drop time of 3.0 sec., which is well within the range in which the diffusion current constant is independent of drop time in the absence of gelatin.[4]

Thallous chloride was twice recrystallized from water and dried at 140°. The preparation of the potassium iodate has been described elsewhere.[5] Stock solutions of these materials were prepared by weight.

It has recently been shown[3,6] that the diffusion current of an ion at very low concentrations may be affected by a phenomenon related to maximum formation, especially if the measurement is made at a potential not very far removed from the half-wave potential. In this work it was always found that the diffusion current constants at the most negative and most positive potentials used agreed within the limits of experimental error, so that any contribution from the above effect must have been negligibly small.

Because the concentration of supporting electrolyte was always at least 35 times that of the reducible ion, and because of the high mobility of the hydrogen ion, no interference from the migration current was expected, and the diffusion current constants always appeared to be independent of the concentration of reducible ion.

Data and Discussion

Table I summarizes the values of I of thallium(I) and iodate found at various ionic strengths. At

---

[1] J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).

[2] L. Meites and T. Meites, *Anal. Chem.*, in press.

[3] L. Meites and T. Meites, THIS JOURNAL, **72**, 3686 (1950).

[4] L. Meites, *ibid.*, **73**, 1581 (1951).

[5] L. Meites and T. Meites, *ibid.*, **73**, 395 (1951).

[6] F. Buckley and J. K. Taylor, *J. Research Natl. Bur. Standards*, **34**, 97 (1945).

TABLE I

DIFFUSION CURRENT CONSTANTS OF THALLIUM(I) AND IODATE IN ACID SOLUTIONS

[HCl], F	I_{Tl^+}	[HClO$_4$] F	I_{Tl^+}	[HCl], F	$I_{IO_3^-}$
4.09	2.085	0.435	2.722	4.21	(4.0)
2.04	2.503	.217	2.728	2.11	9.96
1.02	2.631	.109	2.739	1.05	12.14
0.613	2.693	.0782	2.804	0.548	12.28
.327	2.693	.0564	2.851	.295	12.10
.204	2.652	.0361	2.885	.169	12.04
.123	2.711	.0261	2.907	.112	12.00
.0818	2.780	.0152	2.920	.0813	11.97
.0572	2.837	.0096	2.949	.0610	12.22
.0409	2.857			.0437	12.23
.0245	2.887			.0305	12.30
.0163	2.932			.0203	12.41
.0102	2.958			.0142	12.43
				.0102	12.49

ionic strengths between 0.1 and 0.8 in hydrochloric acid, I for thallous ion is 2.687 ± 0.015; and at ionic strengths between 0.1 and 0.45 in perchloric acid I for thallous ion is 2.730 ± 0.006. In 0.1 F potassium chloride Lingane and Kolthoff[1] found I = 2.68, and Buckley and Taylor[6] reported I = 2.71 in the same medium with 0.008% gelatin. The mean value for I of iodate at ionic strengths between 0.08 and 0.6 is 12.08. In 0.1 F potassium chloride–0.1 F hydrochloric acid the author previously found 12.035,[4] while Loveridge[7] found 12.05 in an 0.2 F phosphate buffer of pH 7.0, and Kolthoff and Lingane[1] secured the value 12.0_2 in 0.1 F potassium chloride. In agreement with the conclusions of Lingane and Kolthoff, all of these values are close to those computed from the Ilkovič equation using the diffusion coefficients of the ions at infinite dilution. These values, it may be noted, are 2.707 for thallous ion and 11.99 for iodate.

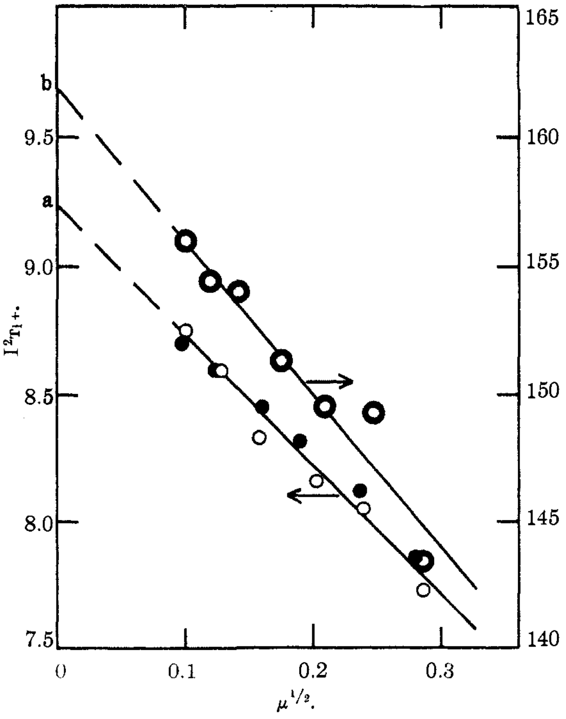


Fig. 1.—Onsager–Gosting–Harned extrapolation function for diffusion current constant data on (a) thallium(I) in hydrochloric acid (open circles) and in perchloric acid (solid circles), and (b) iodate in hydrochloric acid.

The decrease in I at high ionic strengths may be due to a viscosity effect, at least in the measurements with thallium(I). In the 4 F hydrochloric acid solutions containing iodate, a visible amount of free iodine formed at the top of the solution. This may have been due to a small impurity in the acid used. No iodine could be detected in solutions more dilute than this even after several hours of standing.

It is well established that the diffusion coefficient of an ion increases with decreasing ionic strength.[8] This being so, it is evident that the diffusion current calculated from D^0 should be higher than the experimentally measured diffusion current at finite ionic strengths. In other words, the Ilkovič equation may properly be written in either of two forms

$$I^0 = 607n(D^0)^{1/2} \text{ or } I^f = 607n(D^f)^{1/2}$$

at zero and finite ionic strengths, respectively. As D^0 is greater than D^f, it follows that, if the Ilkovič equation is correct, I^f must be less than $607n \cdot (D^0)$,$^{1/2}$ which is obviously not the case.

On extrapolation to infinite dilution, the data here presented should give an approximate value of I^0 for comparison with the known value of the diffusion coefficient at infinite dilution. This extrapolation may be made in a number of ways: *e.g.*, by plotting I against μ or against $\mu^{1/2}$, or by plotting I^2 against $\mu^{1/2}$, as suggested by the Gosting–Harned equation.[8] Of these, the last is probably the most justifiable on theoretical grounds, but, for lack of any conclusive proof of the linear dependence of I on $D^{1/2}$, the details of the extrapolation are of little theoretical moment. In any case the extrapolated value of $I°$ by any of these methods falls within the range 3.1 ± 0.15 for thallous ion and 12.7 ± 0.25 for iodate. It is curious that for both of these ions the experimental slope of the I^2 *vs.* $\mu^{1/2}$ plot is close to five times the theoretical value.

Thus the value of I at infinite dilution is some 10–20% higher than that predicted by the Ilkovič equation. Whether this is due to an error in the numerical constant in the Ilkovič equation, or to an error in the relationship between I and D, or to any of several other factors which might suggest themselves, is a question which data of this sort cannot resolve. It is apparent, however, that more study of these possibilities is required: this study should take the form of a direct comparison of values of I and D under conditions of supporting electrolyte and reducible ion concentrations such as are normally used in polarographic work. Until this has been done, however, it should be noted that attempts to calculate diffusion coefficients from polarographic data may be subject to appreciable error.

Acknowledgment.—This work was supported in part by Contract AT (30-1)-842 between the

---

[7] B. A. Loveridge, Ph.D. Thesis, Harvard University, 1947.

[8] L. J. Gosting and H. S. Harned, THIS JOURNAL, 73, 159 (1951).

U. S. Atomic Energy Commission and Yale University.

The author wishes to take this opportunity to express his appreciation of the interest and advice of Professor Herbert S. Harned.

NEW HAVEN, CONN. RECEIVED[9] FEBRUARY 7, 1951

---

(9) Original manuscript received November 8, 1950.

[CONTRIBUTION NO. 1537 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

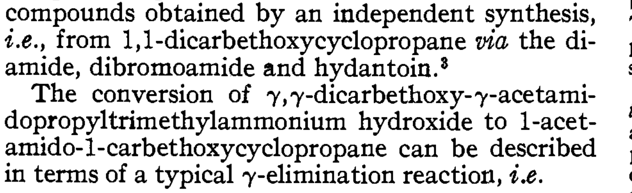
The Synthesis of a Cyclopropane Derivative through Exhaustive Methylation

BY HEINRICH RINDERKNECHT[1] AND CARL NIEMANN[2]

1-Acetamido-1-carbethoxycyclopropane has been prepared by the thermal decomposition of the quaternary base derived from the methiodide of diethyl β-dimethylaminoethylacetamidomalonate. This appears to be the first example of the synthesis of a cyclopropane ring through exhaustive methylation.

In the course of several unsuccessful attempts to prepare α-aminovinylacetic acid, diethyl acetamidomalonate was condensed with β-chloroethyldimethylamine and the resulting diethyl β-dimethylaminoethylacetamidomalonate quaternized with methyl iodide to give the expected γ,γ-dicarbethoxy-γ-acetamidopropyltrimethylammonium iodide. This latter compound upon hydrolysis and decarboxylation with aqueous hydriodic acid gave γ-carboxy-γ-aminopropyltrimethylammonium iodide hydroiodide. The γ,γ-dicarbethoxy-γ-acetamidopropyltrimethylammonium iodide was allowed to react with silver oxide, the aqueous solution of the quaternary base lyophilized, to minimize hydrolytic decomposition, and decomposed to give a distillate which subsequently crystallized. This latter substance, m.p. 79–80°, possessed the empirical formula $C_8H_{13}O_3N$, did not react with hydrogen in the presence of a platinic oxide catalyst, bromine water or aqueous permanganate, and did not give α-aminobutyrolactone hydrochloride upon hydrolysis with hydrochloric acid. Therefore, it was concluded that the product obtained by the thermal decomposition of γ,γ-dicarbethoxy-γ-acetamidopropyltrimethylammonium hydroxide was 1-acetamido-1-carbethoxycyclopropane. The above conclusion was confirmed when it was found that 1-acetamidocyclopropane-1-carboxylic acid and 1-aminocyclopropane-1-carboxylic acid prepared from the decomposition product were identical with the same compounds obtained by an independent synthesis, *i.e.*, from 1,1-dicarbethoxycyclopropane *via* the diamide, dibromoamide and hydantoin.[3]

The conversion of γ,γ-dicarbethoxy-γ-acetamidopropyltrimethylammonium hydroxide to 1-acetamido-1-carbethoxycyclopropane can be described in terms of a typical γ-elimination reaction, *i.e.*



$$(CH_3)_3N^+{-}CH_2{-}CH_2{-}\overset{\displaystyle CO_2C_2H_5}{\underset{\displaystyle CO_2C_2H_5}{C}}{-}NHCOCH_3 + OH^- \longrightarrow$$

$$+ C_2H_5OH + (CH_3)_3N + CO_2$$

It is of interest to note that ethyl α-benzylisocrotonate was obtained by the thermal decomposition of the methiodide of diethyl β-dimethylaminoethylbenzylmalonate.[4] In this instance it was concluded[4] that elimination of the carbethoxy group is accompanied by a 1:2 shift of one of the β-hydrogen atoms and elimination of trimethylamine. It should be noted that when the thermal decomposition of γ,γ-dicarbethoxy-γ-acetamidopropyltrimethylammonium iodide was attempted the bulk of the material resinified. While it may be argued that the acetamido group favors retention of the hydrogen atoms on the β-carbon atom over that obtaining with the benzyl derivative, the lack of comparable experimental data deprives the argument of much of its force.

1-Aminocyclopropane-1-carboxylic acid was tested in respect to its ability to function as a precursor, or as an antagonist, of methionine and threonine and γ-carboxy-γ-aminopropyltrimethylammonium iodide hydroiodide was evaluated as a methyl donor. All tests were negative.[5]

Experimental[6,7]

Diethyl β-Dimethylaminoethylacetamidomalonate (I) (A).—Diethyl acetamidomalonate (4.4 g.) was added to a solution of 0.46 g. of sodium in 50 ml. of absolute ethanol, the solvent was removed under reduced pressure and was replaced by 75 ml. of dry toluene. To this suspension was added 2.5 g. of redistilled β-chloroethyldimethylamine,[8] the reaction mixture refluxed for 6.5 hours with mechanical stirring, the sodium chloride removed by filtration and the filtrate evaporated to dryness under reduced pressure. The residue was distilled to give 5.15 g. (88%) of I, a yellow oil, b.p. 132–137° (1 mm.), which solidified upon standing. This product was repeatedly recrystallized from a benzene–petroleum ether mixture to give I, m.p. 76–78°. I is freely soluble in water, ethanol, benzene and acetone.

(B).—To a solution of 1.56 g. of potassium in 250 ml. of *t*-butanol was added 8.68 g. of diethyl acetamidomalonate and then an ethereal solution of β-chloroethyldimethylamine prepared from 11.5 g. of the hydrochloride. The remainder of the procedure was identical with that given above with the exception that it was found necessary to dissolve the crude product in dry ether and to filter the turbid solution prior to distillation. The yield of I was 8.0 g. (70%).

Anal. Calcd. for $C_{13}H_{24}O_5N_2$ (288): C, 54.2; H, 8.4; N, 9.7. Found: C, 54.2; H, 8.4; N, 9.6.

γ,γ-Dicarbethoxy-γ-acetamidopropyltrimethylammonium Iodide (II).—Methyl iodide (4.0 g.) was added to 6.9 g. of I in 50 ml. of acetone and after standing at room tempera-

---

(1) Research Associate, Cilag. Co., Schaffhausen, Switzerland.

(2) To whom inquiries regarding this article should be sent.

(3) C. K. Ingold, S. Sako and J. F. Thorpe, *J. Chem. Soc.*, 1177 (1922).

(4) C. K. Ingold and M. A. T. Rogers, *ibid.*, 722 (1935).

(5) We are indebted to Drs. N. H. Horowitz and J. W. Dubnoff for this information.

(6) Microanalyses by Dr. A. Elek.

(7) All melting points are corrected.

(8) We are indebted to the Ciba Laboratories of Summit, N. Y., for the hydrochloride of this substance.