Thus, while the above values for the dissociation constant of the acid are not to be considered as strictly accurate, the measurements nevertheless indicate a lower order of conductance for 4-methyl-2-thiazolylsulfamic acid than would be expected if this acid was not internally neutralized.

pH Values.—The values for *p*H of solutions of 4-methyl-2-thiazolylsulfamic acid, solutions (A) and (D) above, were found, respectively, to be 2.72 and 3.20. The *p*H of aqueous, 0.0960 *M*, solution of 2-thiazolylsulfamic acid at 23° was found to be 2.80, and on dilution of this solution at the same temperature to 0.0480 *M*, the *p*H found was 2.92. These values are in agreement with what would be expected of solutions of these concentrations if the 2-thiazolylsulfamic acids dissociate to approximately the same extent as does acetic acid.

Acknowledgment.—This investigation was supported by a grant from the Abbott Fund of Northwestern University. We are also grateful to Dr. E. H. Volwiler of Abbott Laboratories for determination of the sweetness of sodium 2-thiazolylsulfamate.

Summary

A series of 2-thiazolylsulfamic acids has been prepared. Evidence is presented that these acids are derivatives of sulfamic acid and not isomeric aminosulfonic acids.

The thermal and hydrolytic stabilities displayed by the 2-thiazolylsulfamic acids contrast sharply with the great instabilities of simple arylsulfamic acids such as phenylsulfamic acid and α-naphthylsulfamic acid. It is proposed that the greater stabilities of the 2-thiazolylsulfamic acids result from their existence as internal salts. Studies of the properties of these acids confirm their dipolar ion character. It was predicted that 2-pyridylsulfamic acid should also be capable of existing in a dipolar ion form and should therefore be capable of isolation. This prediction has been verified by experiment.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Application of the Principle of the Concentration Cell to Kinetic Studies. I. Hydrolysis of *t*-Butyl Chloride in 95% Water–5% Acetone Solution

BY C. GARDNER SWAIN AND SIDNEY D. ROSS

The hydrolysis of *t*-butyl chloride in solvents containing more than 50% water is too fast to be measured by the usual kinetic methods.[1] In the current investigation a kinetic technique was developed which utilizes the principle of the concentration cell. This new technique makes it possible to follow accurately reactions with half-lives as short as ten seconds, in concentrations as low as 0.001 *M*, and with solution volumes as small as 5 cc. It can be used to follow the consumption or production of H^+, Cl^-, CN^-, I_2, $KMnO_4$, Zn^{++}, etc., or, in general, of any ion or substance for which an electrode sensitive to changes in concentration is known. In the present paper it is applied to a study of the hydrolysis of *t*-butyl chloride in 95% water–5% acetone solution. Here it is used to follow the production of both chloride and hydrogen ion, independently. In a future paper it will be applied to a study of the mechanism of oxidation of oxalic acid by ceric sulfate, by following the consumption of ceric ion.

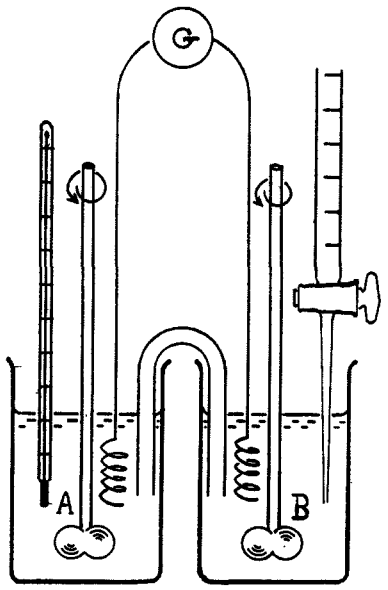

Fig. 1.—Diagram of apparatus employed in concentration cell method.

Description of the Method.—The apparatus is represented diagrammatically in Fig. 1. The "reaction cell," A, is connected to the "titration cell," B, by a salt bridge. To follow production of chloride ion from *t*-butyl chloride, electrodes of silver wire are used in each cell. These electrodes are connected through galvanometer, G. At zero time both cells contain a 95% water–5% acetone solution, which is 0.144 *M* in sodium perchlorate, but, in addition, cell A contains 0.001 *M* *t*-butyl chloride. As soon as hydrolysis occurs the galvanometer is thrown out of balance by chloride ion accumulating in cell A. Small measured additions of a solution of chloride are run rapidly into cell B every few seconds, and the time is recorded at each moment when hydrolysis in cell A again throws the galvanometer back across the null point. The concentration of the

(1) Hughes, *J. Chem. Soc.*, 255 (1935); Bateman, Hughes and Ingold, *ibid.*, 963 (1940).

titrating solution does not need to be known, because the final total addition of chloride ion required to balance the system after all reaction has ceased is taken as equivalent to 100% reaction.

To follow production of hydrogen ion, quinhydrone electrodes and a hydrogen ion titrating solution are used.

A number of considerations which would constitute errors in any method involving absolute measurement of potential can be neglected in this null method because identical effects in both half cells cancel. For example, it is not necessary that the electrodes register thermodynamic equilibrium potentials, but sufficient that they be made and treated identically. Thus, the rate of production of chloride ion was measured with an accuracy of ±3% for "points" (or ±10% for the first order rate constant), despite the fact that the silver electrodes were found to have a thirty-six second lag for 97% equilibrium and the half-life of the reaction measured was only twenty-seven seconds.

Since only the relative, not the absolute, concentrations in the two cells are important, solutions can be studied which are so dilute that ordinary analytical methods, even potentiometric titrations, would fail. Thus even if there were time for the analysis, it would be difficult accurately to titrate potentiometrically an aliquot of our solutions with silver nitrate, due to the lack of a sharp "break" in potential at the end-point at this dilution. However there is no question about the position of the end-point in the concentration cell method, because reaction is allowed to proceed each time to an "equivalence point" automatically determined by the titration cell.

The chief disadvantage of the method is that a carrier electrolyte is required to minimize liquid junction potentials between the salt bridge and the solutions in the two cells. This does not, however, represent a serious limitation, for in most kinetic studies a high inert salt concentration is desirable to prevent fluctuations in rate due to salt effects.[2]

Comparison with Other Methods.—To check the accuracy of the results, the reaction was followed by two other methods. The first was the method of Peters and Walker,[3] involving intermittent direct titration of the entire reacting solution with sodium hydroxide, to follow production of hydrogen ion. This method has restricted application since it is suitable for following only hydrogen ion, and only in reactions unaffected by the changing *p*H, dilution and ionic strength caused by the titration. The hydrolysis of *t*-butyl chloride proved to be such a reaction. The second method was a new polarographic technique, used to follow both chloride and hydrogen ion, independently. A Moll "Microgalvanometer" with a full period of only one-fifth of a second was used to follow the entire current swing during the two-second life of each mercury drop. The maximum of each swing was recorded. The relationship between galvanometer swings and chloride and hydrogen ion concentrations was obtained by standardization with known concentrations of hydrochloric acid in a separate sample of the same medium just before or after the kinetic run. The necessity for excluding air and the presence of a slight "maximum" makes this a troublesome method for hydrogen ion. Even for chloride it is less accurate than the concentration cell technique due to the necessity for a separate standardization. The equipment is rather cumbersome. However, this polarographic method does have wide applicability.

All three methods gave the same results within experimental error. Table I presents the data for four typical runs using the concentration cell method and Table II summarizes the data for representative runs of all types. Sodium perchlorate to give a total 0.144 *M* ionic strength was present in all runs except 1j, where it was 0.000 *M*. Brom thymol blue was used as an indicator for *p*H 7.0 in the intermittent titration runs. The data of run 22 were obtained with a 5-cc. microcell for the reaction half-cell. Run 25 was done at *p*H 12.0, rather than *p*H 7.0–3.0.

TABLE I

Secs.	Cc.	% Cl^-	Secs.	Cc.	% Cl^-
	Run 17			Run 22	
12	0.50	25.9	19	5.00	36.2
20	0.80	41.4	35	8.03	58.2
27	1.00	51.8	50	10.00	72.5
36	1.20	62.2	74	12.00	87.0
47	1.40	72.5	97	13.00	94.2
54	1.50	77.8	∞	13.80	100.0
65	1.60	83.0			
78	1.70	88.1		Run 24	
∞	1.93	100.0	Secs.	Cc.	% H^+
			22	0.82	39.0
	Run 25		28	1.00	47.6
30	0.90	55.9	33	1.20	57.2
44	1.10	68.3	41	1.40	66.7
62	1.30	80.8	50	1.50	71.5
83	1.40	87.0	59	1.60	76.2
111	1.50	93.2	89	1.80	85.7
∞	1.61	100.0	∞	2.10	100.0

TABLE II

Run no.	Remarks	Analytical method	Half life, secs.
1i	0.144 *M* $NaClO_4$	Int. titr. for H^+	28
1j	No inert salt	Int. titr. for H^+	28
1o	0.144 *M* NaCl	Int. titr. for H^+	27
5	...	Polarog. for Cl^-	28
6	...	Polarog. for H^+	30
17	...	Concn. cell for Cl^-	26
22	Microcell used	Concn. cell for Cl^-	26
25	*p*H 12.0	Concn. cell for Cl^-	26
24	...	Concn. cell for H^+	27

(2) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., pp. 128–129.

(3) Peters and Walker, *Biochem. J.*, **17**, 260 (1923).

This run used 0.01 *M* sodium hydroxide and 0.0001 *M* sodium chloride to prevent silver oxide precipitation. The caption "cc." refers to cc. of 0.0499 *M* hydrochloric acid. Runs by all methods gave very satisfactory straight lines on a logarithmic plot, the average deviation of points in run 17, for example, being less than 0.5% of the total reaction.

Discussion of Results.—At 25° in 95% water–5% acetone 0.001 *M* *t*-butyl chloride liberates both chloride and hydrogen ions by a first order reaction, the half-life being 27 ± 3 seconds. Within experimental error the rate is unaffected by *p*H (between 3 and 12), by ionic strength (between 0.000 and 0.144 *M* sodium perchlorate), or by sodium chloride concentration (between 0.000 and 0.144 *M*). The absence of a second order nucleophilic displacement by hydroxyl ion and of reversal by chloride ion is not surprising, because such reactions were not observed with certainty in 90% acetone by Bateman, Hughes and Ingold,[1] in which medium they would certainly be far more important than in ours. However, it is interesting that whereas Bateman, Hughes and Ingold found a 40% acceleration on adding 0.1 *M* salt (sodium chloride, bromide or azide) to *t*-butyl bromide in 90% acetone, we observed no such salt effect. This may be due to the fact that the percentage increase in dielectric constant caused by the same addition of salt to 95% water is much less.

In one experiment 0.048 *M* sodium thiosulfate was added instead of 0.144 *M* sodium perchlorate to give a 0.144 *M* ionic strength. The total hydrogen ion liberation was the same as in a parallel run with sodium perchlorate. It should have been less by the amount of reaction with thiosulfate. The apparent absence of such reaction, or of reaction with chloride or hydroxyl ions, certainly indicates a low degree of discrimination by the *t*-butyl carbonium ion between the various nucleophilic substances with which it might react. This may be due to the fact that it is so poorly stabilized by resonance that it combines with very nearly the first molecule with which it collides. Since water is present in over three hundred times the concentration of any other reactive substance under our conditions, combination with water is the only reaction observed.

Experimental

Reagents.—*t*-Butyl chloride was prepared by the reaction of *t*-butyl alcohol with hydrochloric acid[4] and fractionated through a four-foot glass helices column. A middle fraction boiling at 51.0–51.5° was saved for kinetic purposes. A 0.21 *M* stock solution was made by diluting 0.974 g. to 500 cc. with Merck reagent acetone.

The acetone stock solution was kept at 4° in a cold room when not in use and showed no detectable hydrolysis over a period of nine months, although the acetone must have contained more than equivalent water.

Apparatus.—A potentiometer in series with the galvanometer was used to determine, if desired, the magnitude of voltages developed. Our galvanometer was a Leeds and Northrup No. 2420-B enclosed lamp and scale type, with a sensitivity of 2×10^{-7} amp. per mm. on the ±25 mm. ground glass scale after critically damping with a 300-ohm variable resistor across its terminals. Knife switches were used in place of tapping keys, so that the galvanometer could be connected in continuously when near endpoints. A double-pole double-throw knife switch was connected for reversing the polarity of leads from the cell.

Two 200-cc. tall form beakers were used for cells, connected by a salt bridge consisting of a 20 cm. long 8-mm. tube bent into a simple inverted U and filled with a 3% agar gel, 0.15 *M* in sodium perchlorate. A small bulb blown in the center of the salt bridge prevented the gel from sliding out of the tube. The salt bridge was kept in a large beaker of 0.15 *M* sodium perchlorate solution when not in use.

Stirrers in each cell were driven at the same speed from one belt. Each consisted of a glass propeller blown on the end of a glass tube which fitted as a sleeve over the end of a 1/4" steel shaft held in place by a short length of rubber vacuum tubing at the upper end of the glass tube. Only glass was exposed to the solution. The steel shaft was held by two 1/4" ball bearings, clamped in bunsen clamps, with their jaws covered with rubber tubing to prevent electrical shorting to the vertically sliding ringstand support. A 3" pulley was mounted on the steel shaft between the ball bearings. Either silver or platinum wire was wound around the glass tube in a number of turns just above the propeller and connected to a clamp on the steel shaft just below the lower ball bearing. The upper end of the shaft was drilled with a 1/8" hole to a depth of over an inch to serve as a mercury well into which single copper lead wires from the potentiometer circuit were dipped to make good electrical contact with the electrodes.

The two electrodes were always made from the same piece of wire. Shiny platinum wire was cleaned with concentrated nitric acid, washed with distilled water, and heated its entire length to a bright red heat with a bunsen burner before winding on the shaft. In the absence of this "glowing" procedure galvanometer deflections were only one-hundredth of their normal value. Once treated the platinum electrodes were satisfactory through several runs. When using the platinum electrodes the solution in each cell was saturated with powdered quinhydrone to make them sensitive to hydrogen ion concentration. The silver electrodes were conditioned by chloridizing in a sodium chloride solution. Before starting a run the electrodes were always shorted in the reaction media for a few minutes to eliminate any slight difference of potential. If any difference greater than 0.1 mv. still persisted it was compensated by addition of a drop or two of dilute hydrochloric acid to the proper cell.

Procedure.—Initially each cell contained 100 cc. of 0.150 *M* sodium perchlorate at 23.7°. Acetone (5 cc.) was added to the titration cell, then immediately afterward, at zero time, 5 cc. of acetone stock solution at 25° to the reaction cell. The latter was added in less than three seconds with a glass jointed syringe pipet combination. The midpoint of the addition was taken as zero time. This gave 104.5 cc. of approximately 0.001 *M* *t*-butyl chloride solution at 25°. The buret, cells, stirrers and motor were all mounted on the same vertically sliding pipe and were dropped down so that the cells were three-quarters immersed in the 25.00 ± 0.01° thermostat immediately after this addition. The temperature was read periodically from a thermometer in the reaction cell but was always stable within a few hundredths of a degree and within one tenth of 25.0° after the first few seconds. The solution was invariably clear and homogeneous from the start. Addition of 0.0499 *M* hydrochloric acid was made with a 2-cc. microburet with a capillary tip below the surface.

The microcell was a short stubby tube 3.5 cm. tall and 1.7 cm. in inside diameter with a rather flat bottom. At one edge of the bottom a 2-mm. bore capillary tube was sealed on vertically, and bent up a short distance at its end for a total capillary length of 3 cm. This capillary bore was filled with 3% agar gel, 0.150 *M* in sodium per-

(4) "Organic Syntheses," Coll. Vol. I, p. 144.

chlorate. This salt bridge presented a very small cross section (0.03 sq. cm.) to the solution in the cell, so that diffusion of chloride into it during a five-minute run was negligible. It was short enough so that the resistance drop was not serious. The electrode for this cell was a chloridized silver wire wound around a 4-mm. glass rod, and it provided sufficient stirring for the small cell without a propeller. A small Anschütz thermometer was used to read the temperature inside the microcell. Four cc. of 0.150 *M* sodium perchlorate was placed in it. The microcell was clamped so that it was three-quarters immersed in one liter of solution in the titration cell. The latter cell consisted of a $1^1/_2$-liter beaker hung on the vertically sliding assembly with a large ring. Its electrode was wound on a stirrer with a large glass propeller. At zero time, with the solutions at 23.7°, 0.20 cc. of acetone stock solution was added to the microcell from a graduated 1-cc. pipet. Simultaneously 50 cc. of pure acetone was poured into the titration cell from a graduate. The solution in the titration cell was "titrated" with a 25-cc. buret.

For each individual run ten times the half life (five minutes) was used as an infinite time point. The fact that only the solution in the titration cell is diluted 2% by the titration does not introduce any error, since the final titer is taken as representing 100% reaction and the amount by which the titration cell is diluted at any time is proportional to the percentage reaction.

Summary

Concentration cells have been adapted to permit a simple and accurate null-point method for the measurement of the rate of a chemical reaction. The method can be adapted to follow kinetically any ion or substance for which an electrode sensitive to changes in concentration is known, and should be useful in studying most oxidation, reduction, halogenation, hydrolysis and displacement reactions. The technique offers special advantages in the study of very rapid reactions, and can be applied to micro quantities or very dilute solutions for which ordinary potentiometric methods fail.

In the present paper the method has been applied to a study of the rate of production of both chloride and hydrogen ions in the hydrolysis of 0.001 *M* *t*-butyl chloride in 95% water–5% acetone. The electrode reactions selected were

$$Ag + Cl^- \overset{Ag}{\rightleftharpoons} AgCl + e$$

and

$$\text{Quinone} + 2H^+ \overset{Pt}{\rightleftharpoons} \text{Hydroquinone} - 2e$$

At 25° in 95% water–5% acetone *t*-butyl chloride liberates both chloride and hydrogen ions by a first order reaction, the half life being 27 ± seconds. Within experimental error the rate is unaffected by *p*H (between 3 and 12), by ionic strength (between 0.000 and 0.144 *M*) or by sodium chloride concentrations (between 0.000 and 0.144 *M*). The total liberation of hydrogen ion is unaffected by the presence of 0.48 *M* sodium thiosulfate. Evidently the carbonium ion formed does not accumulate to a measurable extent in solution but instead reacts immediately and indiscriminately with the most available molecule, in this case, water.

CAMBRIDGE, MASS. RECEIVED AUGUST 14, 1945

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Standard Potentials of Hydrogen–Silver–Silver Chloride Cells in Ethylene Glycol Solutions at 25°

BY SAMUEL B. KNIGHT, JOSEPH F. MASI AND DOROTHY ROESEL

In connection with other work being carried on in the Laboratory, it became necessary to determine the standard potentials of the cells

H_2 | HCl (*m*), Ethylene Glycol (x), H_2O (y) | AgCl–Ag

at 25° in solutions containing 10, 20, 40 and 60% ethylene glycol by weight. The activity coefficients of hydrochloric acid have been determined in these glycol–water solutions at acid concentrations ranging from 0 to 1 *m*. The dielectric constants of the glycol–water solutions are high enough so that hydrochloric acid may be considered completely ionized.

A number of investigators have made electromotive force measurements and activity coefficient determinations on cells of the above type using hydroxyorganic solvents other than ethylene glycol. Harned and Thomas[1] have investigated certain methanol–water mixtures, while ethanol–water solutions have been studied by Harned and Fleysher[2] and Harned and Calmon.[3] The latter have also investigated certain isopropanol–water solutions. Lucasse[4] has studied the cell in glycerol–water mixtures, and Scatchard[5] in sucrose solution. The activity coefficients of hydrochloric acid in all of these mixtures seem to conform to a pattern similar to that found in aqueous solutions, and they may be calculated from 0 to 1 *m* by means of the Debye–Hückel expression with a linear term.

Experimental

Commercial ethylene glycol was purified by fractionation at 5 mm. pressure in a slow stream of purified nitrogen. The density of the product agreed with that listed by Taylor and Rinkenback[6] for pure ethylene glycol. Stock solutions of hydrochloric acid were made by weight from

(1) H. S. Harned and H. C. Thomas, THIS JOURNAL, **57**, 1666 (1935).

(2) H. S. Harned and M. H. Fleysher, *ibid.*, **47**, 82 (1925)

(3) H. S. Harned and C. Calmon, *ibid.*, **60**, 334 (1938).

(4) W. W. Lucasse, *Z. physik. Chem.*, **121**, 254 (1926).

(5) G. Scatchard, THIS JOURNAL, **48**, 2026 (1926).

(6) C. A. Taylor and W. H. Rinkenback, *Ind. Eng. Chem.*, **18**, 676 (1926).