was ignored except that the area of the end was included in the electrode area.

A number of electrolyses were performed beginning the integration some time after the beginning of electrolysis. Residual charges were noticeably lower in such cases. A series of observed diffusion charges are given in Table I, together with calculated values from equation 2.

The discrepancies between calculated and observed diffusion charges are believed to be principally due to uncertainties in the dimensions of the electrode and in the values of diffusion coefficients. For these reasons, agreements closer than a few per cent. are probably fortuitous, particularly for the larger values of ϕ, where higher terms in the equation must be included. The linear relation between concentration and diffusion charge for any one reaction is not dependent on the accuracy with which ϕ is known, and proportionality to concentration was followed more closely, within 1% for concentrations large enough so that residual charge was not a large part of the total charge. The results indicate that no significant convection effects were present and that the experimental circumstances correspond closely to equation 1.

TABLE I

DIFFUSION CHARGES

Ion	$t_1 - t_2$, sec.	q, μ coulomb Calcd.	q, μ coulomb Obsd.
I^-	0.091– 0.191	9.25	9.56
	0.691– 0.791	4.13	4.25
	2.991– 3.191	4.35	4.53
	11.99 –12.79	9.85	10.44
$Fe(CN)_6^{-3}$	0.091– 0.191	5.78	5.76
	0.691– 0.791	2.54	2.57
	2.991– 3.191	2.62	2.67
	11.99 –12.79	5.69	5.99
$Fe(CN)_6^{-4}$	0.091– 0.191	5.28	5.33
	0.691– 0.791	2.32	2.35
	2.991– 3.191	2.38	2.44
	11.99 –12.79	5.15	5.50

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SEATTLE, WASHINGTON

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

Applications of Coulometric Methods to Kinetic Studies[1]

BY PAUL S. FARRINGTON AND DONALD T. SAWYER

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The principles of coulometric analysis have been applied to the study of kinetic systems. Through coulometric generation of reactants, rate constants can be determined rapidly and precisely. A new technique for the determination of rates of hydrolysis for aliphatic esters has been developed. Rate constants have been redetermined for ethyl acetate and ethyl lactate. A procedure has also been worked out for determining the relative rates of hydrogenation of olefins in solution at a platinum-black catalyst. The relative rate constants for the hydrogenation of cyclohexene, octene-1 and decene-1 have been determined. Both methods permit the determination of reaction rates at constant concentrations of the reactants.

The coulometric generation of chemical titrants has been a subject of wide interest, especially when applied to micro-analytical methods.[2] Since the amount of titrant may be computed by Faraday's law from the number of coulombs passed through the solution, small quantities of material can be determined more accurately and conveniently than by the usual volumetric techniques.

The many advantages which coulometric methods offer for analysis prompted the investigation of adapting coulometric techniques to the study of kinetics. The two kinetic systems selected for study were chosen because they satisfied certain specific requirements. The first, the basic hydrolysis of water-soluble aliphatic esters, had the desirable features of occurring in an aqueous solution, having widely studied mechanisms and rate constants, and having a simple rate law. The second study, the hydrogenation of aliphatic olefins in solution, provided a non-aqueous system which helped to indicate the broad applicability of the coulometric method. This study was brought about by an attempt to develop a semi-micro method for the analysis of olefins. It was proposed to hydrogenate the double bonds by coulometric generation of hydrogen on platinum black catalyst. However, the slowness of the rate of reaction prevented progress in the development of an analytical procedure, and prompted a study of the kinetic factors involved.

These two systems provided ample opportunity to investigate the general applicability of coulometry to kinetics. The rate constants are of interest themselves, since there are discrepancies in the previously published ester hydrolysis data,[3-5] and since there are very few data of any nature for the rates of hydrogenation of olefins in solution.[6,7]

It should be emphasized that the purpose of the work presented herein was not to determine, or redetermine, a large body of fundamental physical

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(1) Abstracted from a thesis submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy at the University of California, Los Angeles by Donald T. Sawyer.

(2) J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953.

(3) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford, Clarendon Press, 1933, p. 86.

(4) H. Olsson, *Z. physik. Chem.*, **133**, 242 (1928).

(5) E. Tommila and S. Hietala, *Acta Chem. Scand.*, **8**, 257 (1954).

(6) National Bureau of Standards, "Tables of Chemical Kinetics," Circular of the National Bureau of Standards 510, U. S. Printing Office, Washington, D. C., 1951, p. 99.

(7) H. A. Smith and H. T. Meriwether, THIS JOURNAL, **71**, 413 (1949).

data, but rather to develop a method which would permit the evaluation of these data with greater ease and precision.

Apparatus.—The apparatus was essentially the same for the two studies. Minor differences peculiar to each specific system will be noted in the section concerned.

The construction of a precision electronic coulometer was not the purpose of the investigation. Since the goal for precision in the kinetic studies did not exceed one-half per cent., the investment in instrumentation was kept to a minimum (both in terms of time and money). A Model SR-100 Nobatron current rectifier (Sorenson and Company) was used as a power supply. This unit supplies 0–130 volts (d.c.) regulated to one-quarter per cent. It was normally operated at 120 volts with the voltage applied across sufficient variable resistance to give the desired current.

The variable resistance was provided by the rheostat system shown in Fig. 1. For currents in excess of 15 milliamperes, the 100,000 ohm rheostat was switched out of the circuit to protect it from damage. The same was true for the 5000 ohm rheostat for currents above 100 milliamperes. A continuous range of currents from 1 to 150 milliamperes was conveniently provided by this circuit. To maintain temperature equilibrium in the resistors, a dummy resistance was used when the coulometric cell was not operating. Thus, current was continuously passing through the circuit. Currents were stable to within one-quarter of one per cent. over periods of several hours. Three standard resistors; 10, 50 and 100 ohms, were placed in series in the circuit. Measurement of the potential across one of these resistors with a Leeds and Northrup Type K potentiometer gave a convenient means of determining the current passing through the circuit.

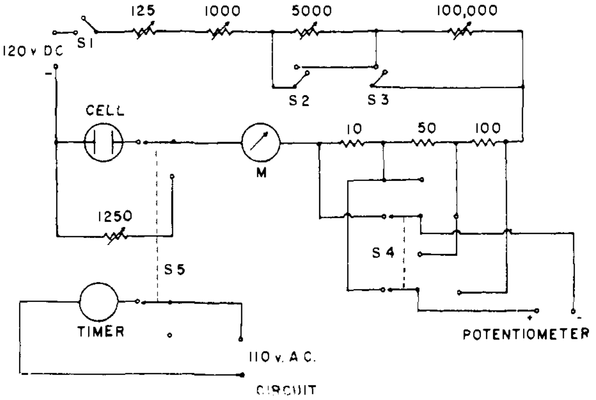

Fig. 1.—Circuit for continuously variable constant current generator.

Meter, M	Milliameter (0–150 ma.)
Resistors	
10, 50, 100	Precision resistors, ±0.1%
1250 variable	Dummy resistor used to substitute for cell resistance
Switches, S1	On-off s. p. s. t. switch
S2	Bypass s. p. s. t. switch for currents above 100 ma.
S3	Bypass s. p. s. t. switch for currents above 15 ma.
S4	3-position double-pole switch for potential measurements across precision resistors
S5	Cell-timer on-off d. p. d. t. switch
Timer	Electric clock, Type S 10, The Standard Electric Time Co., Springfield, Mass., (± 0.1 sec.)
120 v. d.c.	Model SR-100 Nobatron d.c. power supply, Sorenson and Company, Inc., Stamford, Conn., (± 0.25%)

A Beckman Model GS *p*H meter was used for the measurement of indicator potentials and *p*H. This meter is identical to the familiar Model G, except that the sensitivity for the detection of changes of *p*H may be increased 10-fold by switching out a shunt on the galvanometer. The latter arrangement was used for the ester hydrolysis study. In the hydrogenation study, the Model GS was used to indicate potentiometrically the molecular hydrogen concentration in solution.

The temperature of the reaction cells was controlled by a thermostatic bath insulated with plaster of Paris. The bath was stirred continuously and heated with a 50-watt heating coil. The heater was actuated by a toluene–mercury regulator (approximately 40 times as sensitive as the conventional mercury regulator). The temperature was controlled to 0.002° over 24-hour periods. The cell was either placed directly in the thermostatic bath, or the bath water was pumped to a small external reservoir placed around the cell. The latter arrangement was used in most cases since it provided greater accessibility to the cell. The temperature of the external reservoir was controlled to 0.01°.

Figure 2 illustrates the cells used for the two kinetic studies. The cell bottom for both studies is shown in part III. Section A is a saturated calomel electrode protected by an agar plug saturated with potassium chloride. The reference electrode is further protected by section B, which provides a means of placing a buffering solution between the agar plug and the cell. Strong bases and organic solvents have a tendency to attack agar. This attack, as well as the entrance of chloride ions into the cell, is pre-

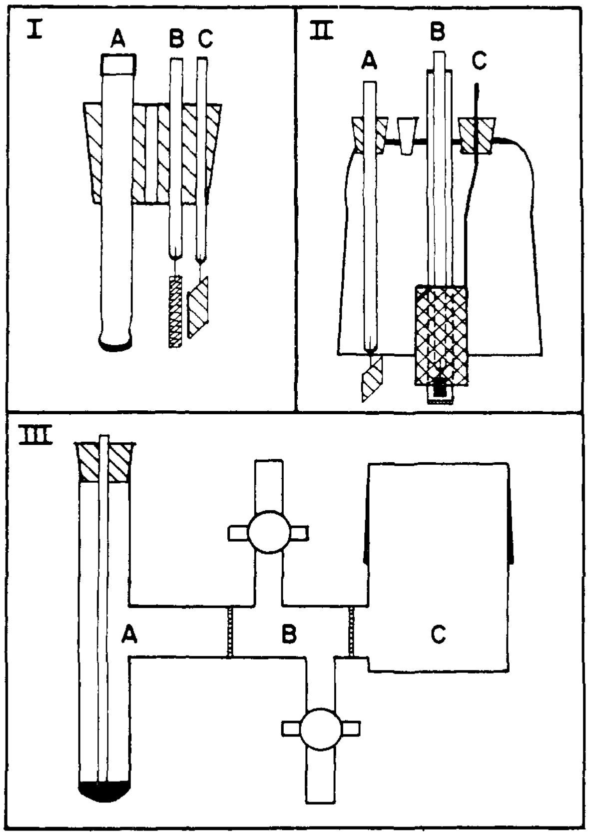

Fig. 2.—Coulometric cell for kinetic studies: Part I, top for ester hydrolysis studies: A, Beckman clinical type glass electrode; B, silver wire generator anode; C, platinum generator cathode. Part II, top for olefin hydrogenation studies (Standard Taper 40/35): A, platinum indicator electrode; B, shielded platinum generator anode; C, gauze platinum-black generator cathode. Part III, cell bottom for both studies: A, saturated calomel reference electrode with agar plug; B, buffer solution compartment, with two Pyrex fine sintered discs; C, cell compartment, capacity approximately 32 ml. (Standard Taper 40/35).

vented by introducing an inert electrolyte through the two stopcocks. Two Pyrex, fine-porosity, sintered discs retard diffusion into and from section B. The cell proper, section C, was fabricated from a 40/35 standard taper male joint. It has a capacity of approximately 32 ml. A 1″ × 5/16″ stirring bar is normally placed in the cell for use with a magnetic stirrer.

The cell top for the ester hydrolysis work, part I, was prepared from a number 7 rubber stopper. The stopper was drilled to provide an airtight fit for a Beckman clinical type glass electrode (section A), a silver electrode (section B) and a platinum electrode (section C). Holes were also drilled for deaeration and introduction of sample.

For the hydrogenation studies, a cell top that would be inert to organic solvents was required. Using the cell of Furman, Cooke and Reilley[8] as a guide, an all glass cell top was designed (part II). A standard taper 40/35 female joint was closed and fitted with small standard taper female joints. The small joints provided entries for a gas bubbler, sample introduction, a platinum indicator electrode (section A) and a gauze platinum–black generator cathode (section C). In addition, the top was fitted with a shielded compartment for the platinum anode (section B). This compartment was made from a glass tube closed with a Pyrex, fine, sintered glass disc, which prevented oxygen produced at the anode from entering the cell solution. Since platinum electrodes can only be sealed in soft glass, the male joints were fashioned from Teflon and the electrodes pressure-fitted into drilled holes. The supporting wire of the gauze platinum black electrode was fitted directly into the Teflon.

Efficient stirring is essential to maintain equilibrium in the cell solution. Although a mechanical stirrer was used for some of the preliminary work, a magnetic stirrer was found to be preferable. It permitted the cell to be sealed easily, and provided greater accessibility to the electrodes and cell openings.

Because carbon dioxide would interfere with the ester hydrolysis studies and oxygen would react with hydrogen on platinum black, it was necesary to deaerate the sample solutions. Nitrogen purified over heated copper was used for deaeration of the solutions with its rate of flow regulated by a glycerol head meter.

Rates of Hydrolysis of Water-soluble Esters.—The kinetics of ester hydrolysis probably have been studied more intensively than those of any other system in the liquid phase.[3] Because of this broad background of study, the system was ideal for the development of a new method for determining rate constants. Of the many esters subjected to thorough rate analysis, ethyl acetate has received the most attention, hence the alkaline hydrolysis of this ester in aqueous solution was selected for study in the development of the coulometric method. The hydrolysis of ethyl lactate also was studied for comparison with ethyl acetate.

The coulometric method developed here is based on the following conditions: (1) a large known excess of ester in solution, (2) a means of accurately measuring the hydroxyl ion concentration and (3) a method for producing hydroxyl ion at a known rate to maintain a constant concentration. Condition (1) permits the ester concentration to remain essentially constant over short periods of reaction time. Condition (2) is necessary because the hydroxyl ion concentration appears in the equation for the evaluation of the rate constant. With condition (3) it is possible to determine the rate of disappearance of the ester, which is also needed to evaluate the rate constant. When these three conditions are satisfied, hydrolysis rate constants can be determined for esters.

After the present work was initiated a note in the literature indicated the possibility of applying the coulometric method to hydrolysis studies.[9] Details were not indicated, nor were specific results presented. The reaction cell contained a generator anode isolated in a cation-exchange resin whose function was to adsorb the generated hydrogen ions. No details of instrumentation or of the procedure for making a determination were mentioned.

More recently an automatic instrument has been developed for the study of the activity of enzymes through a hydrolysis reaction.[10] A two-compartment reaction cell was used to prevent diffusion of hydrogen ions from the anode compartment.

Experimental

The generator circuit has been discussed above and is shown in Fig. 1. The reaction cell consisted of parts I and III shown in Fig. 2. Compartment B in the cell bottom was filled with a saturated aqueous solution of potassium chloride for the ester studies. All *p*H measurements were made with the Beckman Model GS *p*H meter.

Eastman Kodak white label grade ethyl acetate and ethyl lactate were used without further purification. All other materials were reagent grade.

Hydroxide was produced coulometrically by the procedure of Lingane and Small.[11] The reaction,

$$2Ag + 2Br^- + 2H_2O = 2AgBr + H_2 + 2OH^-$$

produces one mole of hydroxide per faraday of electricity passed through the cell. The anode reaction produces AgBr on a helical silver wire electrode, while water is reduced on the platinum foil cathode. The electrolyte solution contains 0.03 F KBr, 0.1 F K_2SO_4 and 1.25×10^{-5} F H_2SO_4. The KBr concentration must be kept low to prevent the formation of $AgBr_2^-$ at the anode; good conductance is provided by the K_2SO_4. Removal of CO_2 from the solution is aided by the presence of H_2SO_4.

The generator electrodes, A and B of part I in Fig. 2, are placed as near as possible to each other. This close proximity prevents field effects from disturbing the *p*H readings.

The data for a rate constant determination are obtained by the following procedure: approximately 20 ml. of the above electrolyte solution are pipetted into the cell, the cell top is put in place and the magnetic stirrer is turned to maximum speed. A stream of purified nitrogen is bubbled through the cell for 5 minutes to free the solution of carbon dioxide. Deaeration is stopped, the cell is sealed, and hydroxide is generated until the desired *p*H is obtained (usually *p*H 9 or 10). A very slow rate of bubbling is again started, and the ester sample, approximately 0.7 ml., is introduced into the cell with a micropipet. The cell is sealed and generation of hydroxide is started immediately. The generation current is adjusted until the desired *p*H is obtained. *p*H is maintained at a constant value by adjustment of the current. When the current becomes essentially constant, the *p*H meter is switched to the GS scale (giving a 10-fold increase in sensitivity). Generating-current measurements are made at 250, 500, 750 and 1000 seconds with the potentiometer.

After each run the silver electrode is placed in concentrated KCN to remove the AgBr coating. This coating tends to increase the cell resistance, which in turn causes increased electric fields. A new solution is used for each run.

Results and Discussion

Ester hydrolysis in basic solutions may be expressed by the reaction

$$RCOOR' + OH^- = RCOO^- + R'OH \qquad (1)$$

It has been established that the rate law for the reaction is

$$\frac{-d(RCOOR')}{dt} = k(RCOOR')(OH^-) \qquad (2)$$

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(9) R. G. Pearson and L. H. Piette, THIS JOURNAL, **76**, 3087 (1954).

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(11) J. J. Lingane and L. A. Small, *ibid.*, **21**, 1119 (1949).

For this hydrolysis the rate of disappearance of hydroxyl ions is exactly equal to the rate of disappearance of ester molecules. Therefore, if the hydroxide concentration is kept constant by coulometric generation, then the rate of production of hydroxide is equal to the rate of disappearance of the ester. Expressed in another way, the rate of disappearance of ester is directly proportional to the generation current necessary to maintain the hydroxide concentration at a constant value.

These considerations may be expressed mathematically by the equation

$$\frac{-\mathrm{d}(\mathrm{RCOOR'})}{\mathrm{d}t} = \frac{\mathrm{d}(\mathrm{OH}^-)}{\mathrm{d}t} = \frac{i}{VF} = k(\mathrm{RCOOR'})(\mathrm{OH}^-) \quad (3)$$

Rearrangement of terms gives

$$k = \frac{i}{(\mathrm{OH}^-)\,(\mathrm{RCOOR'})\,VF} = \frac{i}{(\mathrm{OH}^-)\,M_\mathrm{e}F} \quad (4)$$

where

k is the rate constant in liters mole^{-1} sec.$^{-1}$
i is the current in amperes
F is the faraday
V is the volume of the solution in liters
M_e is the number of moles of ester added to the solution

If several conditions are fulfilled, equation 4 may be used for the evaluation of rate constants. First, the number of moles of ester, M_e, must not change during the determination (or at least, the value must be corrected for any change). Second, the rate of generation must be within the limits of the instrument. In addition, the rate constant has to be sufficiently large to permit rapid detection of changes of pH arising from incorrect generation rates. The last condition is affected by the solubility of the ester, since the rate of generation is directly proportional to the ester concentration.

The minimum rate constant value that can be determined by the method may be calculated if the following limitations are made: 1, maximum ester concentration, 0.2 F; 2, minimum pH change detectable, 0.003 pH unit; 3, maximum time allowed for a pH change of 0.003, 60 seconds; 4, maximum relative error for the rate constant, 1%. A change of 0.003 pH unit corresponds to 0.7% of the hydroxide concentration. The number of moles of hydroxide needed to cause this pH change in a volume, V, is given by the expression

$$\text{moles} = 0.007\,(\mathrm{OH}^-)\,V \quad (5)$$

For the above limitations, 1% of the minimum current must produce this pH change in 60 seconds. This may be expressed by the equation

$$i_\mathrm{m} = \frac{0.007(96{,}500)\,(\mathrm{OH}^-)\;V \times 100}{60} \quad (6)$$

when i_m is the minimum current. Therefore, the minimum rate constant that can be determined is

$$k_\mathrm{m} = \frac{-\mathrm{d}(\mathrm{RCOOR'})}{\mathrm{d}t}/(\mathrm{OH}^-)\,(\mathrm{RCOOR'}) = \frac{i_\mathrm{m}}{VF(\mathrm{OH}^-)(\mathrm{RCOOR'})} = 5.8 \times 10^{-2}\ \mathrm{l.\ mole^{-1}\ sec.^{-1}} \quad (7)$$

for the limitations set forth. This seriously limits the number of esters that can be studied. However, the method is very satisfactory for fast reactions, which is one of its main advantages over conventional techniques.

The rate constants determined for ethyl acetate and ethyl lactate are shown in Table I. Some values from the literature are also presented. Data are given at 25.08 and 30.02° for ethyl acetate and at 25.08° for ethyl lactate. The rate constants are corrected for depletion of ester, although the correction is usually less than 1%.

TABLE I

RATE CONSTANTS FOR THE BASIC HYDROLYSIS OF ETHYL ACETATE AND ETHYL LACTATE IN WATER

A. ETHYL ACETATE

1. 25.08°, 3.69 × 10^{-1} F, pH 10.00

Generation time, sec.	k, l. mole^{-1} sec.$^{-1}$ × 10^1	Av. dev. × 10^1
250	1.26	±0.02
500	1.21	± .01
750	1.17	± .01
1000	1.15	± .02
Literature	1.11[6] 0.96[a,4] 0.98[a,4] 1.19[a,5] 1.08[b,5] 0.87[b,4] 1.19[b,4]	

2. 30.02°, 5.00 × 10^{-1} F, pH 9.00

Generation time, sec.	k, l. mole^{-1} sec.$^{-1}$	Av. dev.
1000–2000	1.41 × 10^{-1}	±0.05 × 10^{-1}

B. ETHYL LACTATE

1. 25.08°, 3.17 × 10^{-1} F, pH 9.00

Generation time, sec.	k, l. mole^{-1} sec.$^{-1}$	Av. dev.
500	1.7	±0.2
750	1.24	± .04
1000	1.12	± .03

2. Ratio of $k_{(\text{ethyl lactate})}/k_{(\text{ethyl acetate})}$, 25.08°

Generation time, sec.	Ratio
1000	9.8
Literature	9.68[5]

[a] Data adjusted to 25.08°; [b] Values calculated from empirical equations.

The generation rate for ethyl lactate is unusually high during the first 400 seconds but becomes normal after 500 seconds; this effect is thought to be due to a small amount of lactic acid in the ester sample. The rate constant is determined at 1000 seconds to avoid any interference.

The above results indicate that rate constants for water-soluble esters can be determined coulometrically by generation of hydroxyl ions. For esters with the necessary solubility and reaction rate, the method is both convenient and rapid. A rate constant may be determined with a precision of 1–2% relative error in less than one-half hour.

For sufficiently active esters, the method could be extended to non-aqueous systems. However, the concentrations of base could not be calculated from pH meter readings. Therefore, it would not be possible to determine absolute rate constants, but only relative values. The non-aqueous system selected must be a solvent for the electrolyte and must conduct current. The major limitation would be that rates of hydrolysis decrease significantly in non-aqueous solvents in comparison to those in water.

Rates of Hydrogenation of Olefins.—The methods for determining the rate of hydrogenation of unsaturated materials have become somewhat standardized. For studies in solution, Adams catalyst (platinum oxide) is added to the solvent and reduced with hydrogen gas. After the sample is introduced, hydrogen is brought in contact with the stirred solution. The change in volume of hydrogen gas at constant pressure is noted with respect to time. In another variation, a constant volume of gas is maintained and the change of pressure with respect to time is measured.[7,12,13] These methods, although workable, have several disadvantages. Rather large samples and long periods of time are required for a determination. Also, the accuracy and precision of the rate constants are less than might be desired.

An attempt was made by the authors to develop a semi-micro procedure for the analysis of olefins by coulometric generation of hydrogen on a catalytic surface. During the course of the investigation it became necessary to determine the rate-controlling factors for the hydrogenation reaction. It was desirable to study the variables under the conditions proposed for the analytical procedure. This led to the development of a new coulometric method for the determination of reaction rates for the hydrogenation of olefins. The studies with this new method indicated that a satisfactory analytical procedure was not possible under the proposed conditions. However, the coulometric method developed for the kinetic studies has several advantages as a general technique for determining hydrogenation reaction rates.

The method is based on conditions similar to those used for the ester hydrolysis studies. These are (1) a large known excess of olefin in solution; (2) a means of accurately measuring the concentration of hydrogen on the catalytic surface; and (3) a method for producing hydrogen at a known rate to maintain a constant concentration. Condition (1) permits the olefin concentration to remain essentially constant over short periods of reaction time. It turns out that condition (2) is not easily realized. Since the hydrogen concentration on the catalytic surface appears in the rate constant calculations, absolute rate constants cannot be determined without this quantity. However, it is possible to maintain a constant hydrogen concentration in solution with a potentiometric indicator electrode. Therefore, relative hydrogenation rate constants can be determined. With condition (3) it is possible to determine the rate of disappearance of the olefin, which is also needed for the calculation of the rate constant. Under these conditions relative pseudo first-order rate constants can be determined for olefins.

Relative rate constants have been evaluated for cyclohexene, octene-1 and decene-1. Benzene proved to be insufficiently reactive. Studies of styrene failed because of polymerization in the coulometric cell. The method should be generally applicable for determining relative reactivities of aliphatic olefins.

Experimental

The coulometric generator has been discussed above, and its circuit is shown in Fig. 1. The coulometric cell consisted of Parts II and III shown in Fig. 2. Compartment B in the cell bottom was filled with a saturated solution of potassium chloride in 95% ethanol.

The Beckman Model GS *p*H meter was used as a potentiometer for measuring the potential of the indicator electrode relative to that of a saturated calomel electrode. All potentials are reported on this basis.

The gauze platinum-black generator cathode, electrode C part II, was prepared from a commercial platinum electrode which had been plated with platinum black by the method of Grant.[14]

Eastman Kodak white label grade cyclohexene, benzene and styrene were used without further purification. The two other olefins investigated, octene-1 and decene-1, were obtained from Humphrey-Wilkinson, Inc., Chemical Manufacturers, North Haven, Connecticut (Lot 125 and Lot 105, respectively). Both were C.P. grade and were not purified further.

All other materials were reagent grade.

The cell reaction for the coulometric generation of hydrogen may be expressed

$$\text{anode reaction: } 2H_2O = O_2 + 4H^+ + 4e^- \qquad (8)$$

$$\text{cathode reaction: } 4e^- + 4H^+ = 2H_2 \qquad (9)$$

$$\text{cell reaction: } 2H_2O = 2H_2 + O_2 \qquad (10)$$

which indicates that two faradays of electricity produce one mole of hydrogen gas at the cathode. The oxygen produced at the anode is shielded from the cell solution by a sintered glass disc. This is necessary since platinum-black is a catalyst for the recombination of oxygen and hydrogen into water.

The two generator electrodes, B and C in part II, Fig. 2, are placed coaxially to make the field effect on the indicator electrode, A, as small as possible.

Several indicating systems were tried before the potentiometric platinum-saturated calomel electrode arrangement was selected as being most satisfactory. A platinum-black electrode substituted for the platinum foil indicator electrode gave a very insensitive response. Two identical electrodes, either platinum foil or platinum-black, when used as an amperometric indicating system,[15] gave a completely insensitive response. A large indicator current, 50–100 μ amperes, was always present. With the platinum foil–S.C.E. system a generation current of 2.00 milliamperes is required to maintain an indicator potential of 0.025 v. for a blank deaerated solution. A change of one milliampere in generation rate causes the indicator potential to change approximately 0.1 v.

The solvent is made 0.1 *F* in either perchloric acid or sulfuric acid to provide a source of hydrogen ions as well as make the solution conducting. The most satisfactory solvent of those tried (95% ethanol, absolute ethanol, and glacial acetic acid) is 95% ethanol. Its high dielectric constant makes it a good conductor, and it provides water for the anode reaction. The indicator electrode was very erratic and insensitive in glacial acetic acid. Furthermore, the low dielectric constant for this acid made it a very poor conductor for current, and caused a large field effect on the indicator electrode. Water had to be added to the shielded compartment for the anode reaction when absolute ethanol or acetic acid was used as the solvent.

The following procedure is used in obtaining the data for determining a relative rate constant: 25 ml. of 0.1 *F* $HClO_4$ in 95% ethanol are placed in the coulometric cell, the cell top is put in place, and the magnetic stirrer turned to maximum speed. A stream of purified nitrogen is passed through the cell solution for 3 minutes to free it of dissolved oxygen. The rate of bubbling is reduced to a low level and the olefin sample, approximately 0.7 ml., is introduced with a calibrated micro-pipet. Deaeration is stopped, the cell is immediately sealed, and generation of hydrogen is started. The current is adjusted to obtain the desired concentration of hydrogen gas in solution as shown by the indicator electrode. An indicator potential of 0.025 v. normally is used. This potential is kept constant by adjustment of the current. Generation currents are measured at 250, 500, 800 and 1000 seconds for each run with the potentiometer. Blanks are run before and after each rate determination. New solutions are used for each run.

The blank runs are necessary since hydrogen gas has a low solubility in the solvent,[16] and slowly escapes into the space above the solution. The current necessary to

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[16] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd Ed., Vol. 1, D. Van Nostrand Co., Inc., New York, N. Y., 1940, pp. 563, 565.

maintain the indicator potential for the blank solution must be subtracted from the current measured for the olefin hydrogenation. At an indicator potential of 0.025 v., the current for the blank is approximately 2.00 milliamperes.

Results and Discussion

The hydrogenation of olefins in solution can be expressed by the reaction

$$\mathrm{RHC{=}CHR'} + \mathrm{H_2} = \mathrm{RCH_2CH_2R'} \qquad (11)$$

The rate of hydrogenation, when studied on the macro-scale, has been reported[13] to follow the rate law

$$-\frac{\mathrm{d}P_{\mathrm{H_2}}}{\mathrm{d}t} = -\frac{\mathrm{d(RCH{=}CHR')}}{\mathrm{d}t} = k_\mathrm{t}\,(\mathrm{H_2})_\mathrm{c} = k_0 P_{\mathrm{H_2}} \qquad (12)$$

where k_t is the true rate constant, k_0 is the observed rate constant and $(\mathrm{H_2})_\mathrm{c}$ is the hydrogen concentration on the catalytic surface. Smith and co-workers,[7,12] have objected to this relation, and suggest the equation

$$-\frac{\mathrm{d(RCH{=}CHR')}}{\mathrm{d}t} = k_\mathrm{t}(\mathrm{H_2})_\mathrm{c} = \frac{k_0 P_{\mathrm{H_2}}}{v} \qquad (13)$$

where v is the volume of hydrogen gas in contact with the solution. Both relations indicate that the reaction is independent of olefin concentration.

The reaction rates studied coulometrically did not obey either of the above equations. From the experimental results the following rate law has been derived

$$-\frac{\mathrm{d(RCH{=}CHR')}}{\mathrm{d}t} = k'(\mathrm{RCH{=}CHR'})(\mathrm{H_2})_\mathrm{c} \qquad (14)$$

The hydrogen concentration on the catalytic surface, $(\mathrm{H_2})_\mathrm{c}$, cannot be determined easily. However, it should be directly proportional to the hydrogen gas concentration in the cell solution. The potential of the platinum indicator electrode is related to the solution concentration by the equation

$$E = E^\circ_{\mathrm{H_2,H^+}} - \frac{0.059}{2}\log\frac{(\mathrm{H^+})^2}{(\mathrm{H_2})} - E_\mathrm{ref} - E_\mathrm{j} \qquad (15)$$

The measured indicator potential is equal to $-E$. E_ref is the potential of the saturated calomel electrode. E_j is the junction potential for the cell and cannot be evaluated. However, it is essentially constant. For the non-aqueous system $(\mathrm{H^+})$ is not known, but should be constant for 0.1 F $\mathrm{HClO_4}$ in 95% ethanol. Under these conditions, E is directly related in the usual way to the hydrogen gas concentration in solution, and is therefore similarly related to its concentration on the catalytic surface. When the indicator potential is constant, the hydrogen concentration on the catalyst should be constant.

If an arbitrary potential for the indicator electrode is selected for a series of rate studies, then equation 14 may be written

$$-\frac{\mathrm{d(RCH{=}CHR')}}{\mathrm{d}t} = k(\mathrm{RCH{=}CHR'}) \qquad (16)$$

where k equals $k'(\mathrm{H_2})_\mathrm{c}$.

For the hydrogenation reaction, the rate of disappearance of hydrogen molecules is exactly equal to the rate of disappearance of olefin molecules. Therefore, if the hydrogen gas concentration is maintained at a constant level by coulometric generation, then the rate of hydrogen production will be equal to the rate of disappearance of olefin. That is, the rate of olefin disappearance is directly proportional to the generation current. With equation 16 this can be expressed in the equation

$$-\frac{\mathrm{d(RCH{=}CHR')}}{\mathrm{d}t} = \frac{\mathrm{d(H_2)}}{\mathrm{d}t} = \frac{i_\mathrm{c}}{2FV} = k(\mathrm{RCH{=}CHR'}) \qquad (17)$$

where

i_c is the corrected generation current
F is the faraday
V is the volume of the solution in liters

The 2 enters the expression since two faradays of electricity are required to produce one mole of hydrogen. Equation 17 may be rearranged to give

$$k = \frac{i_\mathrm{c}}{2FV(\mathrm{RCH{=}CHR'})} = \frac{i_\mathrm{c}}{2FM_0} \qquad (18)$$

where M_0 equals the number of moles of olefin added to the solution.

The relative rate constants, k, for several olefins are presented in Table II. All values were determined with the indicator electrode at a potential of 0.025 volt. Several potentials were tried before this value was selected as being the most sensitive to changes in hydrogen concentration. In addition the level of hydrogen concentration expressed by this potential gives an allowable range of generator currents. All values in Table II were calculated at 500 seconds generation time. The relative constants were also determined at 250, 800 and 1000 seconds; they were found to be most reproducible at 500 seconds. Olefin concentrations were corrected for depletion in all cases. Absolute rate constants could be determined if it were possible to determine the hydrogen gas concentration at a given indicator potential. No accurate method has yet been found.

TABLE II

THE RELATIVE RATES OF HYDROGENATION FOR SEVERAL OLEFINS IN SOLUTION

All values were calculated at 500 seconds generation time. The solvent was 95% ethanol, 0.1 F in $\mathrm{HClO_4}$, unless otherwise specified. The temperature was 25.08°, except for the last value.

Olefin	k, sec.$^{-1}$	Av. dev.	k/kc	Concn. moles/l.
Cyclohexene	$2.96 \times 10^{-5\,d}$	$\pm 0.05 \times 10^{-5}$	1.00	7.12×10^{-3}
Octene-1	2.70×10^{-5}	$\pm .03 \times 10^{-5}$	0.91	4.59×10^{-3}
Decene-1	1.60×10^{-5}	$\pm .03 \times 10^{-5}$	.54	3.83×10^{-3}
Cyclohexene[a]			.93	14.24×10^{-3}
Octene-1[a]			.89	9.18×10^{-3}
Cyclohexene[b]			.99	7.12×10^{-3}
Cyclohexene[c]			.37	7.12×10^{-3}

[a] Effect of changing olefin concentration. [b] Effect of substituting 0.1 F $\mathrm{H_2SO_4}$ for $\mathrm{HClO_4}$ in the solvent. [c] Effect of changing reaction temperature to −0.1°. [d] k_c.

The validity of equation 18 was verified by studying the same olefin at various concentrations. The data for this study, as shown for cyclohexene and octene-1 in Table II, confirm that the reaction is first order in olefin concentration. There is no noticeable effect from substituting 0.1 F sulfuric acid for 0.1 F perchloric acid in the solvent.

Since the reaction must take place at the platinum-black electrode, the hydrogenation could be diffusion-controlled rather than kinetically controlled. This possibility was checked by determining the rate constant for cyclohexene at 0° as well as at 25°. Diffusion coefficients normally change 1% per degree centigrade, while reaction rates increase much more rapidly with temperature. The data in Table II for cyclohexene at 0 and 25° indicate that the change in rate is too large to be solely diffusion controlled. Furthermore, a change in hydrogen concentration on the catalytic surface causes a like change in the rate of reaction. If the reaction were diffusion controlled, no change in rate would be observed since the reaction must take place at the electrode.

An attempt was made to study benzene, but its reaction rate was too slow to be observable above the blank generation rate. Studies of styrene were also unsatisfactory because of low solubility and polymerization.

Summary.—Relative rates of hydrogenation can be determined rapidly and conveniently with this method. It should be emphasized that the concentrations of hydrogen are much lower than with conventional methods. Rate constants which are determined coulometrically may be of more interest than those evaluated by allowing the reaction to proceed to infinite time. By determining the rate of reaction at constant concentrations of reactants the problem of change of rate law with changes of concentration is avoided. The conditions are also more closely related to industrial continuous stream processes.

The limitations for applying the method are: 1, sufficient reactivity for the olefins; 2, sufficient solubility of the olefin; 3, sufficiently low vapor pressure for the olefin to prevent loss of sample. Highly active olefins may be studied by using lower concentrations of hydrogen, and comparing the generation rate with that of a known olefin at the lower concentration. Olefins of low reactivity cannot be studied because the concentrations of hydrogen are too low to produce sufficiently rapid reaction.

The method has applications other than in the determination of the relative reactivities of olefins. By studying the same olefin, the relative effective area of different samples of a given type of catalyst and the relative reactivities of different catalysts can be determined. In a similar way, the effects of different solvents might be studied.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Reduction at the Streaming Mercury Electrode. II. Current-Voltage Curves[1]

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A method has been developed for treating current-voltage curves obtained from steady-state measurements at the streaming mercury electrode. Applications to experimental curves using thallium, cadmium and lead ions for reversible reduction and zinc ion for irreversible reduction are shown. Rate constants for the reduction of aqueous solutions of zinc ion in several concentrations of potassium chloride are reported.

In a previous paper,[2] studies of the limiting steady-state current at the streaming electrode were reported with emphasis on factors causing deviations from the Rius equation.[3] In this paper current-voltage curves obtained from steady-state measurements will be considered. Because of the short time of contact between mercury and solution, a reduction process showing a tendency toward irreversibility should give a current-voltage curve with a greater deviation from the reversible form than it gives at the dropping electrode. The streaming electrode should thus prove particularly useful in investigating kinetic features of electrode processes, providing the current-voltage measurements can be properly interpreted.

A treatment for irreversible reduction at the streaming electrode has been given by Koryta.[4] Implicit in his derivation are the assumptions, first, that the physical characteristics of the stream are those of the hypothetical "ideal streaming electrode," *i.e.*, constant radius, constant surface velocity, and negligible effects from electrode curvature and velocity gradient; second, that the reduction potential does not vary with position on the stream; and third, that the effective length of the stream remains constant. Under these conditions an element of surface neither expands nor contracts as it moves forward on the electrode, and reduction occurs exactly as at a plane, stationary, constant-voltage electrode. For an element which has been in existence for t seconds, the current density, i, is given by[5-7]

$$i = nFCk \exp\left(\frac{k^2t}{K^2D}\right) \operatorname{erfc}\left(\frac{k}{K}\sqrt{\frac{t}{D}}\right) \qquad (1)$$

in which

$$K = \left[1 + \frac{k_b}{k}\sqrt{\frac{D}{D_r}}\right]^{-1} \qquad (2)$$

and C is the bulk concentration of the reducible species, k and k_b are the first-order, heterogeneous rate constants for the forward and reverse reactions, and D and D_r are the diffusion coefficients

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[1] (1) Abstracted in part from a dissertation submitted by J. R. Weaver to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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