temperatures, the curve may reach to a ternary eutectic involving ice and the two solid solutions in equilibrium with saturated liquid solution.

Comparison between results from the solubility studies and from the transition studies gives fairly good agreement. At 15° (point C, Fig. 5) decahydrate, dihydrate and solution are in equilibrium at a composition, mole fraction sodium chromate in dried salt from solution, 0.64, compared with 0.68 from the transition data, Fig. 9. At 19° decahydrate, hexahydrate and solution are in equilibrium at a composition 0.90 (point D, Fig. 6) compared with 0.90 from Fig. 9. (In view of the uncertainty in the location of point D, Fig. 6, this agreement is somewhat fortuitous.)

Summary

1. Solubility equilibrium relationships in the system sodium chromate–sodium molybdate–water have been investigated at 0, 8, 15, 19, 22 and 25°.
2. A discontinuity probably appears at 0°, and definitely appears at 8°, in the series of solid solutions formed by the decahydrates of the two salts. In addition to the stable solid solutions, metastable decahydrate solid solutions rich in sodium molybdate were prepared at 8°.
3. Sodium molybdate dihydrate takes up only a small amount of sodium chromate in solid solution.
4. Sodium chromate hexahydrate takes up some sodium molybdate in solid solution, and sodium chromate tetrahydrate takes up still more, at temperatures where these hydrates can exist, either as stable or as metastable phases.
5. The temperature of transition of sodium molybdate decahydrate into the dihydrate is 10.27 ± 0.05°.
6. The relationship was investigated between composition of solution and the temperature at which decahydrate solid solutions can exist in equilibrium with liquid solutions and another solid phase.
7. Decahydrate solid solutions rich in molybdate always undergo transition to dihydrate when warmed. Decahydrate solid solutions rich in chromate likewise change to dihydrate, except when chromate is in great excess, in which case the change is to hexahydrate, or, under special conditions, to tetrahydrate.

HAVERFORD, PA. RECEIVED OCTOBER 23, 1944

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1a]]

A Tensiometric Method for Evaluating Surface Wettability by Measurement of the Contact Angle

BY HELMUT WAKEHAM AND EVALD L. SKAU

The surface wettability of a solid by a liquid such as water is generally evaluated in terms of the work of adhesion between the solid and the liquid as defined by the equation $W = \gamma (1 + \cos \theta)$ where γ is the liquid to air surface tension and θ is the angle of contact between the solid and liquid.[1b] For a given value of the surface tension, γ, the work of adhesion is a function of the contact angle, θ; thus for small values of θ, W is large and the solid is more readily wet by the liquid than when θ is large.

The paper and textile industries have recognized the importance of the contact angle in the evaluation of wettability.[2-8] The method of measurement in most applications, however, requires the use of specialized and expensive optical equipment and is not conducive to rapid routine measurement. The present paper outlines the basis for a simple contact angle measurement by means of a Cenco-du Nouy interfacial tensiometer and illustrates the application of the method to several different types of samples which might be encountered when the wettability of the substance is to be measured.

In this method the sample in the form of a circular disk one-half inch in diameter is adjusted to a position parallel to the surface of the water and then pressed with gradually increasing force down into the surface (Figs. 1 and 2). As the disk is pushed down the angle which the edge of the water makes with the upper surface of the sample gradually increases. The maximum value which this angle can attain is the advancing contact angle; when the sample is pushed further down the hydrostatic pressure of the water at the edge of the sample causes the water to move across the surface of the sample. The contact angle is, thus, a function of the force or the maximum reading on the tensiometer measured at the moment that the liquid surface breaks and the sample submerges.[9]

---

(1) (a) This is one of four regional research laboratories operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(1) (b) N. K. Adam, "The Physics and Chemistry of Surfaces," Oxford University Press, New York, N. Y., 3rd ed., 1941, p. 179.

(2) R. M. K. Cobb, *Paper Trade. J.*, **100**, No. 16, 42 (1935).

(3) P. W. Codwise, *Proc. T. A. P. P. I.*, **22** 246 (1939).

(4) J. E. Foote, *Paper Trade J.*, **115**, No. 10, 31 (1942).

(5) G. H. Lafontaine, *ibid.*, **113**, No. 6, 29 (1941).

(6) N. K. Adam and H. L. Shute in International Soc. of Leather Trades' Chemists, British Section, "Wetting and Detergency," 2nd ed., Chemical Publishing Co., New York, N. Y., 1939, p. 53.

(7) C. M. Blow and B. F. J. Moxon, *J. Soc. Chem. Ind.*, **59**, 171 (1940).

(8) R. N. Wenzel, *Am. Dyestuff Rptr.*, **25**, 505 (1936).

(9) The relation between force applied in dynes, and tensiometer reading will be the same for different interfacial tensiometers when the instruments are calibrated according to the manufacturer's directions for rings of 6.00-cm. mean circumference.

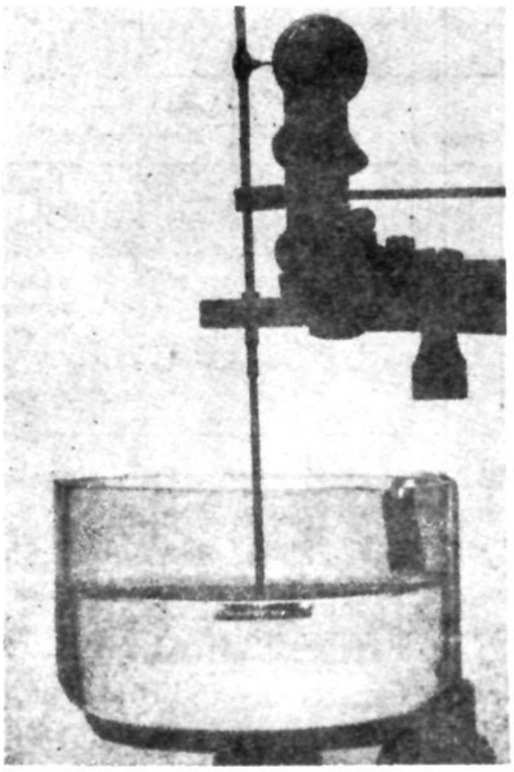

Fig. 1.—Tensiometer set up for contact angle measurement.

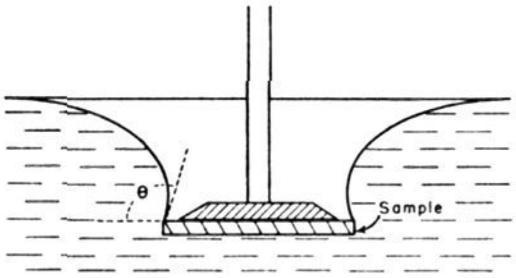

Fig. 2.—Diagram of cross-section through disk being pressed into water surface.

Contact angles corresponding to various depths of penetration and to various tensiometer readings of the force applied were obtained experimentally and are in good agreement with values deduced from theoretical considerations.

Photographs of the meniscus with the disk at various depths were taken through the plate glass observation window of a cell made especially for this purpose. Curves A, B and full curve C in Fig. 3 were constructed from the negatives (see Fig. 4) highly enlarged. These curves are all superimposable and differ only by the extents to which they curve downward to the disk. Thus the curvature of the liquid surface does not change appreciably as the disk is pushed further into the liquid; the original curve is merely extended further downward.

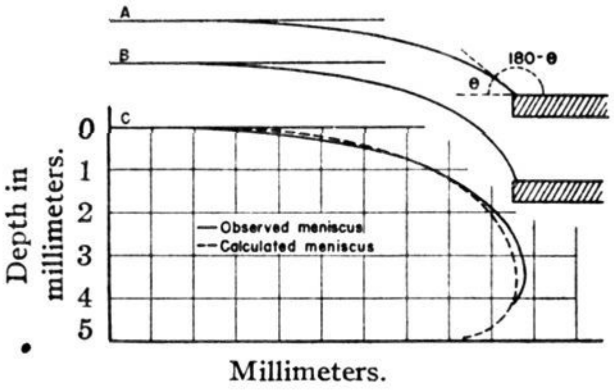

Fig. 3.—Shapes of water menisci for various depths of disk penetration: A = 1.70 mm.; B = 2.62 mm.; C = 4.10 mm.

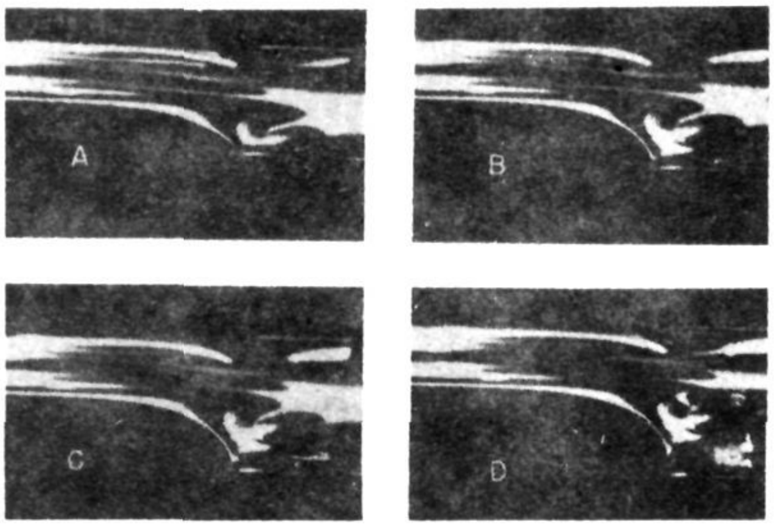

Fig. 4.—Photographs of menisci for various depths of disk penetration: A, 1.70 mm.; B, 2.62 mm.; C, 3.25 mm.; D, 3.88 mm.

The general equation for a curved liquid surface under surface tension and gravity based on the classical theory of capillarity[10] should permit calculation of the curvature of the meniscus for the case under consideration here (Fig. 3, curve C). This equation has not been found possible of solution in finite terms. A general approximate solution for the case of ellipsoid-like surfaces of revolution around a vertical axis, including the case of a drop of liquid on a plane solid surface, has been published by Bashforth and Adams.[11] This solution is not strictly applicable to the surface formed by a disk forced into the water surface. As can be seen from the photographs and drawings (Fig. 2) the lower part of this surface would be similar to a hyperboloid of one sheet. For the drop of water, the surface is such as would be produced by revolution of curve C, Fig. 3, around a vertical axis through the origin; and in the case of the disk, the surface would be produced by revolution of this same curve about a vertical axis to the right of the curve. The boundaries of the cross-section of these two surfaces would be identical in shape in the limiting case where the radii of revolution are infinite. In fact, for diameters not much greater than 4 cm. the limiting shape has probably been attained.[12] Thus if the disk used in these experiments is large, a vertical section through the liquid surface will have the same shape as that of a large drop of water on a plate. If, however, the

---

[10] N. K. Adam, *loc. cit.*, pp. 8–11 and 365–367.

[11] Bashforth and Adams, "An Attempt to Test the Theories of Capillary Action," Cambridge, University Press, 1883.

[12] It has been shown that the center of the water meniscus formed in glass tubes larger than 38 mm. in diameter is essentially flat, indicating that the limiting curvature has been attained for a surface of this size. See T. W. Richards and L. B. Coombs, THIS JOURNAL, **37**, 1651 (1915).

disk is small in diameter, the curvature of a vertical section will be less rounded than that of a large drop on a plate because of its concave curvature about a vertical axis arising from the center of the disk. That this difference is small is shown in Fig. 3, C, where the curvature (dotted) for a large drop of water on a plate as calculated from the Bashforth and Adams approximation may be compared with the photographed meniscus.

By plotting the angles of the tangents to this solid curve for various vertical depths from the normal liquid level, a relation is obtained between the contact angle and the depth of immersion of the disk, shown by the points on the experimental curve of Fig. 5. This relation between θ and the depth, k, has been derived theoretically by **Ferguson**[13] on the basis of an approximate solution of the general capillarity equation for the analogous case of a bubble of air in water underneath a solid plane surface.[14] The equation is $k = 2a \cos \theta/2$, in which $a^2 = \gamma/dg$ where d is the density of the liquid phase and g is the gravitational constant. For water at 25° $a = 2.65$ and the shape of the curve for this equation is shown in Fig. 5, dotted line. The experimental curve obtained from the photographed meniscus closely follows the same equation when $a = 2.50$.

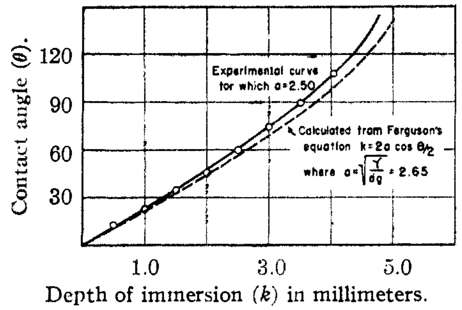

Fig. 5.—Depth of immersion *versus* contact angle.

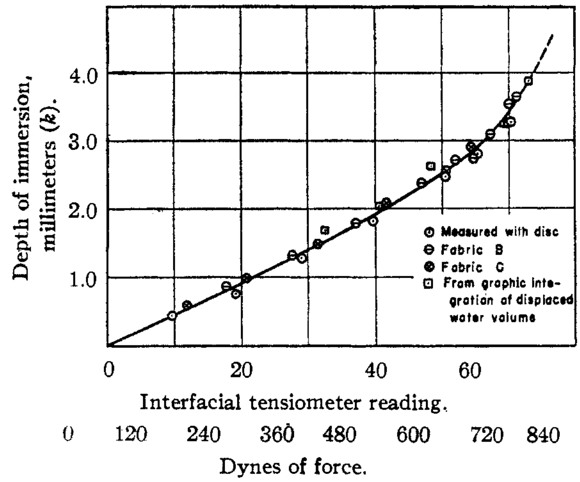

Fig. 6.—Depth of immersion *versus* tensiometer reading.

The tensiometer reading, or the force applied to the sample, depends on the value of k, since both are functions of the volume of water displaced by the disk when it is pressed into the surface. This relationship was determined experimentally by actually measuring the depths of immersion obtained with a 0.5-inch paraffined disk and with 0.5-inch disks of commercial water-repellent-treated fabric samples. Depths were determined by means of a telescope fitted with a filar-micrometer eyepiece and calibrated against an accurate steel scale. Corrections for the buoyant effect of each sample were made by calculating the volume of the sample from its measured dimensions and subtracting the weight of an equal volume of water from the tensiometer force (both in dynes). The experimental points so obtained are indicated in Fig. 6. In order to check the shape of the curve showing this relationship rough calculations of the total volume of water displaced by the disk were made by a volumetric integration using the meniscus curves obtained from photographs (Figs. 3 and 4). These values, the squares in Fig. 6, show satisfactory agreement with the experimental curve.

The curve used for directly determining the contact angle from the corrected tensiometer reading (Fig. 7, upper curve) is obtained by combining the relations of Figs. 5 and 6. Values used in plotting the curve are shown in Table I. Since the values of applied force do not take into account the buoyancy of the sample, the curve so constructed is for a disk of negligible thickness.

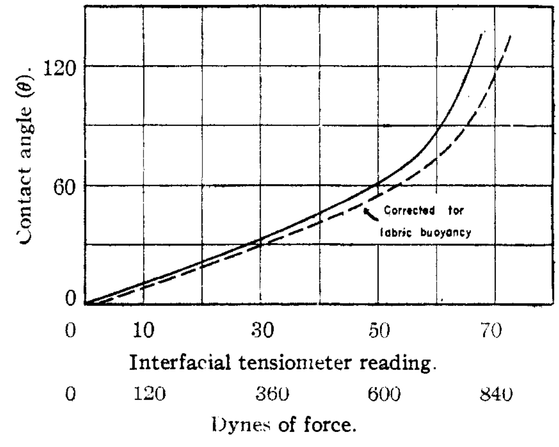

Fig. 7.—Tensiometer reading *versus* contact angle—upper curve for sample of negligible thickness.

In order to determine the accuracy of the tensiometer method of evaluating contact angle, measurements were made on two reproducible surfaces of known contact angles (previously determined by other methods). A 0.5-inch silver-plated disk with supporting stem was prepared and measured for contact angle by the tensiometric method herein described. After a twenty-four-hour aging of this silver surface, the average

---

[13] A. Ferguson, *Proc. Phys. Soc.*, **55**, 554 (1941).

[14] A bubble under a solid plane would have the same shape as a drop of the same size on a solid plane (see ref. 10).

TABLE I

TENSIOMETER READINGS AND CORRESPONDING CONTACT ANGLES

For a sample with no buoyancy correction

Tensiometer readings Scale divisions	Tensiometer readings Dynes	Contact angle, θ
20	240	21°
30	360	33
40	480	46
50	600	61
55	660	70
60	720	87
62	744	96
64	768	108
66	792	121
68	816	(142)[a]

[a] Extrapolated.

of ten tensiometer readings gave a contact angle of 91 ± 1°. This agrees reasonably well with the value of 95° found by Bartell and Cardwell[15] for the maximum advancing contact angle of water against a silver surface which had the maximum opportunity for air adsorption.

The silvered disk was then coated with a thin layer of paraffin from a benzene solution and again tested. The average value obtained this time gave a contact angle of 108 ± 1°. Accepted values for the advancing contact angle on paraffin vary from 105 to 113° for different methods of measurement.[16] Sumner[17] gives a mean value of 107.5° for a paraffin surface on a tilting plate apparatus. These values obtained for reproducible contact angles seem to indicate that the relations between depth of immersion, tensiometer reading, and contact angle described above are approximately correct; and that the tensiometric method is capable of giving results which agree within a few degrees with contact angles obtained by other methods.

Procedure

The following is the procedure used for tensiometric determination of contact angles.

Samples of the substance or surface to be tested (such as fabric or paper) should be of uniform diameter and are best made by stamping them out with a 0.5-inch circular die on a hard wood block. (These items may be purchased from a number of different manufacturers of cutting dies and accessories.) The die should be kept sharp to ensure flat samples with sharp, clean edges. The stocks from which the samples are cut should be smooth and flat, preferably ironed in the case of fabrics, and should be handled carefully to prevent surface contamination.

Of the various schemes tried for holding the sample in the tensiometer the method here described proved the most satisfactory. This method employs a $^3/_8$-inch metal disk soldered to the end of a 2-inch length of 16-gage wire in such a manner that the disk is perpendicular to the wire, similar to that shown in Fig. 2. This device is placed in the tensiometer so as to supplant the platinum ring normally used for surface tension measurements. The underside of the disk is then treated with a trace of adhesive (obtained by warming the adhesive on the back of surgical tape) so that when the disk, properly centered, is made to touch the flat side of the circular sample, the latter adheres to the metallic surface and protrudes uniformly beyond its periphery.

The disk with the sample is then inserted in the tensiometer so that the sample is perfectly horizontal, and the torsion on the wire of the instrument is adjusted by turning the rear setscrew until the reading on the scale is zero when the pointer indicates a balanced condition. A crystallizing dish 6–8 cm. in diameter and about 4 cm. deep is then filled to a depth of about 2 cm. with distilled water and placed on the platform of the tensiometer. The upper stage of the instrument is next lowered until the sample is just over the center of the water surface. With the torsion wire and lever arm of the tensiometer unclamped, the water surface is now gradually raised and the sample carefully forced down by increasing downward tension until the water curls over the edge of the sample, while the pointer of the lever arm is kept in a balanced position up to the moment of break. The maximum tension observed before the sample breaks through the surface of the liquid is the value used in determining the contact angle.

After one such measurement the sample is pulled off the disk with a pair of tweezers and a new sample is attached as before. If the water becomes contaminated during use, as indicated by progressively lower readings, it should be discarded and fresh water taken for each sample. Several readings are made on each fabric or other material and averaged. The contact angle is obtained from the curve in Fig. 7.

Results

Measurements have been made on a considerable number of cloth and paper samples which exhibit different contact angles. Typical results of such measurements at a room temperature of 25° are shown in Table II and illustrate the reproducibility of tensiometer readings for the same sample. Observed values of the contact angle obtained by the photographic method used by Lafontaine[5] are also shown to indicate the agreement one might expect between the tensiometric method and an optical method.

TABLE II

TYPICAL DATA FOR THE EVALUATION OF CONTACT ANGLES BY THE TENSIOMETRIC METHOD

	A. Water-repellent fabric samples			B. Paper samples		
	Fabric A	Fabric B	Fabric C	Paper A	Paper B	Paper C
Tensiometer readings	54.5	68.2	66.4	64.4	66.0	67.0
	55.2	68.8	65.7	64.3	65.2	67.7
	52.8	69.2	66.0	63.3	65.9	67.3
	53.6	68.2	66.2	64.7	64.8	67.0
	55.5	69.4	65.4	64.2	65.7	67.7
	54.2	68.8	66.4	63.8	65.8	65.7
	57.2	69.4	66.2	64.1	65.0	65.9
	53.1	68.3	66.3	62.4	66.0	65.7
	56.0	68.5	66.7	63.6	65.2	65.3
	56.4	69.1	66.0	64.4	65.6	65.7
Mean	54.8	68.8	66.1	64.0	65.5	66.5
Average deviation from mean	1.4	0.4	0.3	0.5	0.4	0.8
Corresponding contact angle deviation, in deg.	1.5	2	1.5	2.5	2.5	5
Corrected for buoyancy	51.2	64.0	61.6	62.9	64.4	64.9
Contact angle (tensiometric) in deg.	63	108	94	101	110	114
Contact angle (photographic) in deg.	62	106	96	88	104	118

---

(15) F. E. Bartell and P. H. Cardwell, THIS JOURNAL, 64, 494 (1942).

(16) N. K. Adam, *loc. cit.*, p. 186.

(17) C. G. Sumner, in International Soc. of Leather Trades' Chemists, British Section, "Wetting and Detergency," 2nd ed., Chemical Publishing Company, New York, N. Y., 1939, p. 41.

Discussion

Precautions common to surface phenomena studies must be observed in making contact angle measurements by the tensiometric method. Factors which will affect the surface tension of the water or the water-sample interfacial tension (*e. g.*, temperature, surface adsorption, or surface contamination from handling the samples) may be expected to affect the accuracy of the results. If the sample is not parallel to the surface of the water or if the edges of the sample curl, the contact angle requirement will be satisfied at an incorrect depth and the resulting measurement will be erroneous. The possible magnitude of the latter effect is illustrated in the paper sample C of Table II-B. The nature of this paper was such that upon stamping out the samples with the die the edges curled slightly downward. The first five values were obtained when the samples were tested with the curl downward; in the last five the samples were inverted and, as anticipated, gave tensiometer readings which were about 2.0 units higher. Both sides of the paper were found to have the same contact angle when the samples were flat.

If the samples are of thin, flexible fabric materials the edges of the sample will tend to bend upward when pushed into the water. The buoyancy correction would then be expected to be higher because of the slightly greater amount of water displaced. A series of observations was made, therefore, on textile materials to measure the apparent thickness for different depths of immersion; the corrected buoyancy adjustments for cotton broadcloth fabrics of about 0.3-mm. thickness were used to plot the lower curve in Fig. 7.

The tensiometric method of measuring contact angle possesses certain advantages. It permits a measurement to be made within five seconds of the time that the surface is brought in contact with the liquid. Although best results are to be expected when the surface is hard and smooth, other surfaces may be evaluated if certain precautions are followed. The method permits rapid routine measurements and requires only a tensiometer common to many laboratories.

An investigation of the application of this method to the evaluation of water-repellent fabrics is now in progress and will be reported elsewhere in the near future.

Summary

1. A tensiometric method for the evaluation of surface wettability by measurement of the contact angle using an ordinary interfacial tensiometer is described.
2. The contact angles corresponding to various tensiometer readings are derived experimentally and are shown to be in agreement with values deduced from theoretical considerations.
3. The application of the method to the measurement of contact angles of water on fabric and paper samples is illustrated and the precautions and sources of error are discussed.

NEW ORLEANS, LA. RECEIVED MARCH 6, 1944

[CONTRIBUTION NO. 41 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE, AND FROM THE WILLIAM H CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The Catalytic Hydrogenation of the Benzene Nucleus. I. The Hydrogenation of Phenyl-substituted Aliphatic Acids

BY HILTON A. SMITH, D. M. ALDERMAN AND F. W. NADIG

It is well known that the benzene nucleus can be hydrogenated at low pressures and temperatures over a platinum catalyst. The hydrogenation proceeds easily and cleanly to yield the cyclohexyl derivative. Adams and Marshall[1] studied in a qualitative manner the hydrogenation of a number of phenyl-substituted compounds including phenylacetic and hydrocinnamic acids. Their results indicate increased difficulty of hydrogenation with increased molecular complexity, the more complex molecules requiring larger amounts of catalyst and longer times than the simpler ones.

The present work was undertaken in an effort to determine in a quantitative manner the effect of structure on the rate of hydrogenation of the benzene nucleus. This necessitated not only mild conditions which would favor clean hydrogenations, but also a kinetic approach which would allow the tabulation of rate constants rather than times required for complete hydrogenation, since such times are greatly affected by catalyst poisoning. It also required a series of compounds which could be obtained in high purity. For this reason, a series of phenyl-substituted carboxylic acids was chosen, since they are mostly low-melting solids, which may be both fractionated and crystallized, and also since their purity may be readily estimated by titration with standard base.

Experimental

Benzoic, phenylacetic, β-phenylpropionic, α-phenylbutyric, diphenylacetic and triphenylacetic acids were purchased from the Eastman Kodak Company. All were found to be sufficiently pure for use directly except α-phenylbutyric acid which was fractionated under vacuum.

α-Phenylpropionic acid (hydratropic acid) was prepared from hydratropic aldehyde by oxidation with silver

---

(1) Adams and Marshall, THIS JOURNAL, **50**, 1970 (1928).