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

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

TABLE I

MELTING POINTS, DISTILLATION TEMPERATURES, AND NEUTRAL EQUIVALENTS OF COMPOUNDS HYDROGENATED AND THEIR PRODUCTS

	Acid	Melting point, °C.	Distillation temp. °C.	Mm.	Neutral equivalent Calculated	Found
		Reactants				
1	Benzoic	121.7			122.2	122.0
2	Phenylacetic	76.7			136.1	136.1
3	β-Phenylpropionic	48.8			150.2	149.8
4	γ-Phenylbutyric	51.2			164.2	163.9
5	δ-Phenylvaleric	58.2			178.2	178.5
6	α-Phenylpropionic		189.0	48	150.2	149.9
7	α-Phenylbutyric	41.6–42.0			164.2	164.4
8	Diphenylacetic	148.2			212.2	212.0
9	Phenylcyclohexylacetic	151			218.3	217.7
10	Triphenylacetic	265.6			288.3	289.9
11	Di-(phenylpropyl)-acetic	52.5			296.4	294.2
		Products				
1	Cyclohexanecarboxylic	29.5	150.7	49	128.2	128.2
2	Cyclohexylacetic	29.7	159.8	43	142.2	142.9
3	β-Cyclohexylpropionic	17.8	170.8	37	156.2	156.5
5	γ-Cyclohexylbutyric	31.0	188.8	46	170.3	169.9
5	δ-Cyclohexylvaleric	16.5	203.0	50	184.3	184.4
6	α-Cyclohexylpropionic		175.5	49	156.2	155.9
7	α-Cyclohexylbutyric	58.5	181.0	48	170.3	169.9
8 and 9	Dicyclohexylacetic	138.6			224.3	224.8
10	Tricyclohexylacetic	235.0			306.5	305.9
11	Di-(cyclohexylpropyl)-acetic	49.0			308.5	309.9

oxide[2] in potassium hydroxide solution. The potassium salt was acidified, and the liquid acid was fractionated under reduced pressure.

γ-Phenylbutyric acid was prepared by carbonation of the Grignard reagent of γ-phenylpropyl bromide as previously described.[3] The product was fractionated under reduced pressure in a 5-ft. Vigreux column, and subsequently recrystallized from ligroin.

δ-Phenylvaleric acid was prepared by introduction of one γ-phenylpropyl radical into ethyl malonate, followed by acidification and decarboxylation in the usual manner. The acid was fractionated under reduced pressure, and subsequently recrystallized from ligroin.

Di-γ-phenylpropylacetic acid was prepared in a manner similar to that for δ-phenylvaleric acid, by introduction of two γ-phenylpropyl radicals into ethyl malonate. The crude acid was treated with Norit in acetone solution and subsequently recrystallized from freshly distilled ether.

Phenylcyclohexylacetic acid was prepared by partial hydrogenation of diphenylacetic acid in a manner to be described in a subsequent communication.[4] The acid was recrystallized from ligroin.

The platinum oxide used for the catalytic reductions was prepared from 3.5-g. portions of C. P. platinic chloride in the usual manner.[5] The pure acetic acid used as a solvent was prepared by careful fractionation of C. P. reagent glacial acetic acid in a 5-ft. spiral column. The pure product distilled at constant head temperature, and froze at 16.6°. Tank hydrogen was used directly.

The hydrogenation runs were carried out in a standard Parr low-pressure catalytic apparatus. After introduction of the solvent, the catalyst, and the material to be hydrogenated, the glass reaction bottle was alternately evacuated and filled three times with hydrogen, then brought to the desired initial pressure. The reaction bottle was shaken at a rate sufficiently fast to keep the mixture saturated with hydrogen, under which conditions the rate of hydrogenation is independent of the rate of shaking.[6] Pressures were read on the Bourdon gage with which the apparatus was equipped. This gage was graduated to 0.5 pound per square inch, and pressures were estimated to 0.1 pound. For low pressure runs (18 lb. per sq. inch or less), pressures were read on an auxiliary mercury manometer. The Bourdon gage was checked against the manometer, and also calibrated with a dead-weight gage tester.

Most of the experiments were performed at room temperature, although a few were made at higher temperatures. For the latter, the reaction bottle was immersed in an air-bath the temperature of which was controlled to ±0.5°. The bottle and contents were preheated to the desired temperature before the run was started. Checks on the temperature of the reaction mixture before and after a run generally indicated a rise of about two degrees. This was caused by the heat of hydrogenation which was evolved.

When the hydrogenated compound was easily separated as a crystalline solid, the procedure for recovery was simply to filter off the platinum catalyst, dilute the acetic acid solution with water, and filter off the product. This was then washed with water, and recrystallized from freshly distilled ether.

When the hydrogenated compound was a liquid or low melting solid, the platinum was filtered off, and the acetic acid distilled from the product in a small 10-inch Vigreux column. The product was subsequently fractionated in the same apparatus, usually at reduced pressure.

Melting points were taken on all solid reactants and hydrogenated products. Equivalent weights of the acids were found by titration with standard, carbonate-free base. Table I gives the significant data on the unhydrogenated and hydrogenated acids.

Experimental Calculations and Results

Some preliminary runs were made on benzoic and phenylacetic acids in order to determine the effect of certain variables on the rate of hydrogena-

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[2] *Cf.* Delépine and Bonnet, *Compt. rend.*, **149**, 39 (1909).

[3] Smith, THIS JOURNAL, **61**, 1176 (1939).

[4] *Cf.* Miescher, Hoffmann and Panizzon, *Helv. Chim. Acta*, **24**, 458 (1941); also Sandoval, *Ciencia* (Mex.), **4**, 107 (1943).

[5] Adams, Voorhees and Shriner, "Org. Syntheses," **8**, 92 (1928).

[6] Adams and Voorhees, *ibid.*, **8**, 10 (1928).

tion. It was established that the rate of hydrogenation under the experimental conditions employed was (a) first order with respect to hydrogen pressure, (b) zero order with respect to concentration of the compound to be hydrogenated, (c) directly proportional to the amount of catalyst used. These facts are clearly demonstrated by Fig. 1.

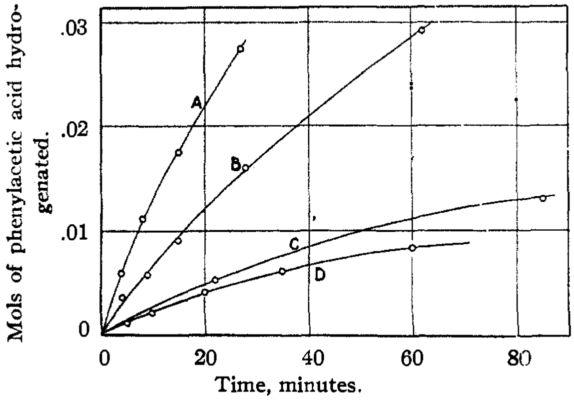

Fig. 1.—Effect of variables on rate of hydrogenation of phenylacetic acid.

Curve	Moles of phenylacetic acid	Grams of PtO_2	Initial pressure p. s. i.	Initial rate mol./min.
A	0.05	0.2	63.3	0.00122
B	.05	.2	33.3	.00059
C	.05	.05	63.3	.00030
D	.125	.05	63.3	.00029

Since the amount of catalyst is constant throughout any given run, the pressure change should follow the equation

$$-dp/dt = kp$$

where p represents total pressure (atmospheric plus gage reading) and t represents time. The integrated form of this equation is

$$\log p_0/p = kt/2.303$$

where p_0 represents the initial pressure. Thus if a plot of log p_0/p *versus* time is made, the value of k can be calculated by multiplying the slope of the line thus obtained by 2.303. Furthermore, if these values of k are all referred to the same amount of catalyst, the magnitude of the constant at a given temperature will depend only on the nature of the phenyl-substituted acid which is being hydrogenated.

Figure 2 shows some typical hydrogenation plots. For some experiments, a falling off of the rate was noted as the hydrogenation proceeded. This was particularly true for some of the slower runs. That this is due to poisoning and not to a deviation from zero order was shown by means of experiments employing different initial concentrations of the acids. It is also shown by the fact that, when the rate has fallen off considerably so that the reaction has almost stopped, a new addition of catalyst is effective in causing hydrogenation. This was also demonstrated by Adams and Marshall.[1]

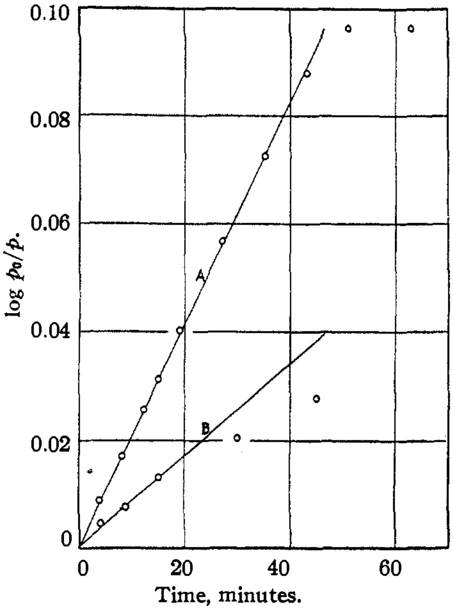

Fig. 2.—Hydrogenation plots for phenyl-substituted aliphatic acids. For each run, 0.05 mole of phenyl-substituted acid, 0.2 g. of PtO_2, 50 ml. of acetic acid, and 64.3 lb. initial H_2 pressure were used: A, phenylacetic acid; B, hydratropic acid.

As noted earlier, the catalyst was made up in small batches. In order to allow for variation in catalyst activity in the different preparations, each batch was standardized with phenylacetic acid, and referred to a common basis. Table II gives the actual rate constants as calculated for each of the five batches using 0.2 g. of platinum oxide catalyst. The average value at 30° is approximately 0.005 or 0.025 when referred to one gram of catalyst. This value was taken as the standard, and rate constants referred to this standard are designated as "k^0."

TABLE II

VARIATION IN RATE CONSTANTS WITH DIFFERENT BATCHES OF CATALYST

For each standardization, 0.2000 g. of platinum oxide, 0.05 mole of phenylacetic acid and 50 ml. of acetic acid were used.

Catalyst no.	Temp., °C.	"k" (reciprocal minutes)
1	31	0.00518
2	31	.00557
3	30	.00506
4	30	.00506
5	30	.00483

TABLE III

VARIATION IN RATE CONSTANT OF PHENYLACETIC ACID WITH TEMPERATURE

For each run, 0.2000 g. of platinic oxide, 0.05 mole of phenylacetic acid and 50 ml. of acetic acid were used.

Temp., °C.	"k" (reciprocal minutes)
50	0.0101
30	.0048
20	.0032

A few runs were made with phenylacetic acid to determine the effect of temperature on the rate constants. The results are shown in Table III.

Table III shows that, in the neighborhood of 30°, a variation of one degree causes an error of not more than 5%. Based on the figures in this table, the heat of activation of this reaction is only about 8000 calories per mole. This approximate figure was used to correct all rate constants to 30°. These corrections are small since the runs were made at temperatures which varied only one or two degrees from 30°.

Table IV gives the values of k^0_{30} for the acids which were studied.

TABLE IV

STANDARD HYDROGENATION RATE CONSTANTS FOR PHENYL-SUBSTITUTED ALIPHATIC ACIDS

Acid	$k^0_{30} \times 10^4$
Benzoic	250
Phenylacetic	250
β-Phenylpropionic	217
γ-Phenylbutyric	248
δ-Phenylvaleric	241
α-Phenylpropionic	87
α-Phenylbutyric	28
Diphenylacetic	41
Phenylcyclohexylacetic	43
Di-(γ-phenylpropyl)-acetic	125
Triphenylacetic	0.3 (approximate)

Discussion

Several interesting observations may be made on the basis of Table IV. In the first place, all of the normal acids with a phenyl group substituted in the terminal position have essentially the same rate of hydrogenation. It is particularly noteworthy that benzoic acid and higher acids show no difference, since, in benzoic acid, the carboxyl group is in resonance with the benzene ring, while this is not true for phenylacetic and higher acids. The effect of such resonance is readily observable in reactions involving the carboxyl group. For instance, benzoic and phenylacetic acids show marked differences in their rates of acid-catalyzed esterification. The effect is shown in the actual rate of esterification, in the activation energies, and in the relative entropies of activation.[7] One might also expect such differences in reactions involving the benzene ring, since it is part of the same resonating system. One explanation for their absence seems to be that the resonance in the benzene ring, and hence that with the carboxyl group, is destroyed when the phenyl group is adsorbed on the catalytic surface. Another possible explanation for the similar rates of benzoic and phenylacetic acids might be that the rate-determining step is one in which resonance between the carboxyl group and the unsaturated ring is essentially unaffected.

Table IV also indicates that the rate of hydrogenation is diminished with substitution on the carbon atom which is alpha to the benzene ring. This is true even when the substituent is another phenyl group which may, itself, be hydrogenated. It is particularly interesting to note that phenylcyclohexylacetic acid and diphenylacetic acid hydrogenate at essentially the same rate. A comparison of diphenylacetic acid with di-(γ-phenylpropyl)-acetic acid indicates that branching further away from the phenyl group is not so effective in influencing the rate of hydrogenation.

There are several factors which might cause the variation in rate of hydrogenation as reported in this research. Differences in inductive effect of the alkyl groups, if such differences exist, can probably be ignored, since it is well known that the phenyl group is an electron sink, yet diphenylacetic and phenylcyclohexylacetic acids have the same rate.

If for no other reason than the fact that the products of the reaction do not affect the hydrogenation process, it must be assumed that saturated hydrocarbons are not materially adsorbed on the catalytic surface. Since the carboxyl group is not affected, it is probable that it also is not adsorbed. One should picture the adsorbed acid molecules with the phenyl groups toward the platinum, and the saturated hydrocarbon residues and carboxyl groups oriented outward. The reaction is zero order with respect to the phenyl groups, which is usually interpreted as indicating a continuous unimolecular layer over the active spots.

This situation would be somewhat similar to the suggestion of Harkins and Gans[8] for the adsorption of oleic acid on titanium oxide, or to that of Ewing[9] for the adsorption of methyl stearate and glycol dipalmitate on zinc oxide. Here, however, the molecules would be anchored to the solid surface by the phenyl group rather than by acid or ester groups. Such a conception is not readily compatible with a flat fit of the benzene nucleus to the substrate, but requires more of an edgewise adsorption.

On the basis of this picture, rate differences cannot be caused by differences in the individual fit of the compounds to the catalytic surface. Variations might, however, be due to steric hindrance. This may be of two types: (1) steric hindrance between the catalyst and the adsorbed molecules; (2) steric hindrance of the type which interferes with the approach of hydrogen molecules to the catalytic surface.

The first type has been postulated by Linstead and co-workers in a series of papers on the stereochemistry of catalytic hydrogenation.[10] Such a postulation, however, rests on flat adsorption of the benzene ring, and is not compatible with the picture suggested here.

Steric hindrance of the second type might be

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[7] Smith and Burn, THIS JOURNAL, **66**, 1494 (1944).

[8] Harkins and Gans, *ibid.*, **53**, 2804 (1931); *J. Phys. Chem.*, **36**, 86 (1932).

[9] Ewing, THIS JOURNAL, **61**, 1317 (1939).

[10] Linstead, *et al.*, *ibid.*, **64**, 1985 (1942).

important in governing the rate, since the hydrogen must pass through the layer of residues extending away from the catalytic surface in order to be adsorbed and subsequently react. The rate at which hydrogen is adsorbed on the catalyst may be rate-determining for the hydrogenation process. This is in line with the first-order dependence on hydrogen pressure, and would explain the fact that substituents near the phenyl groups slow down the hydrogenation process. If one assumes that, in molecules such as diphenylacetic acid or triphenylacetic acid, only one phenyl group may be adsorbed at any given instant, the slow rates observed for these compounds, and also the equality of the rates for diphenylacetic and phenylcyclohexylacetic acids are understandable.

Linstead[10] noted that the "open chain" derivatives of diphenic acid all hydrogenate in the coiled or pseudo-tricyclic phase, but was unable to explain this fact. The conception of edgewise adsorption with the carboxyl groups oriented away from the catalyst might explain this result.

The picture of hydrogenation advanced in the foregoing discussion should be regarded only as a tentative hypothesis. It is advanced since it does explain the rates of hydrogenation reported in this and in the two following articles.

Summary

A study has been made of the kinetics of the catalytic hydrogenation of phenyl-substituted aliphatic acids. The reactions were carried out in acetic acid solution using Adams platinum catalyst.

It was shown that the reaction rate is first order with respect to hydrogen pressure, zero order with respect to the concentration of phenyl-substituted acid, and directly proportional to the amount of catalyst. First-order reaction rate constants, all referred to one gram of platinum oxide, are given for eleven acids.

The factors influencing the relative rates of catalytic hydrogenation are discussed.

KNOXVILLE, TENN. RECEIVED JUNE 17, 1944

[CONTRIBUTION NO. 42 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Catalytic Hydrogenation of the Benzene Nucleus. II. The Hydrogenation of Benzene and Mono-alkylbenzenes

BY HILTON A. SMITH AND E. F. H. PENNEKAMP

In the first paper of this series,[1] a study of the hydrogenation of a number of phenyl-substituted aliphatic acids was described. The purpose of the present paper is to report further kinetic studies involving the catalytic hydrogenation on platinum of a series of mono-alkylbenzenes. Since these latter compounds are liquids, their purity cannot be established readily by melting points, and, of course, neutral equivalents cannot be used. Instead, one must rely on distillation ranges and refractive indices.

Experimental

Benzene was purified by fractionation of thiophene-free Merck reagent benzene in a five-foot spiral column.

Toluene was prepared from Eastman Kodak Co. practical grade material by the method described by Fieser.[2] The hydrocarbon from this treatment was fractionated in the five-foot spiral column.

Ethylbenzene, isopropylbenzene and ***n*-butylbenzene** were purified by fractionation of the best grade of Eastman chemicals in the five-foot spiral column.

***n*-Propylbenzene, *s*-butylbenzene,** and ***t*-butylbenzene** were obtained from the best grade of Eastman chemicals by fractional distillation in a 25-cm. Vigreux column.

***n*-Amylbenzene, isoamylbenzene, *n*-hexylbenzene, *n*-heptylbenzene, and *n*-nonylbenzene** were prepared by a Fittig synthesis following the method outlined by Gattermann and Wieland.[3] These preparations were fractionated in the 25-cm. column.

Several methods were tried in the preparation of **isobutylbenzene**, none of which was satisfacotory. The material used for hydrogenation purposes was prepared by the method outlined by Wreden,[4] but the compound certainly cannot be regarded as pure.

Table I gives the distillation range and refractive index of the compounds used for hydrogenation runs. The distillation temperatures represent the temperature readings in the still-heads, all of which were of a total reflux, variable take-off construction. These readings were corrected to 760 mm. pressure by means of Trouton's rule and the Clausius–Clapeyron equation.

After each hydrogenation was complete, the acetic acid solution was separated from most of the catalyst by decantation. Water was added to the solution, and the hydrocarbon layer (with the exception of *n*-nonylcyclohexane) was steam-distilled. The hydrocarbon layer in the distillate was washed with sodium bicarbonate solution, and then fractionated in the 25-cm. Vigreux column.

Steam distillation was found to be impractical for the *n*-nonylcyclohexane. This compound was separated from the acetic acid solution by dilution with water, and subsequently distilled.

Refractive indices for the products, together with their corrected distillation ranges, are also given in Table I.

As in earlier work, the acetic acid solvent for the hydrogenation runs was prepared by fractionation, and the platinum catalyst was prepared by standard methods.[5] The hydrogenations were carried out in a low-pressure Parr catalytic reduction apparatus in the manner already described.[1]

Experimental Calculations and Results

It was established, as in previous work, that the hydrogenation reaction was first order with respect to hydrogen pressure, zero order with

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(1) Smith, Alderman and Nadig, THIS JOURNAL, **67**, 272 (1945).

(2) Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., 1941, p. 364.

(3) Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Company, New York, N. Y., 1932, p. 107.

(4) Wreden and Znatovics, *Ber.*, **9**, 1606 (1876).

(5) Adams, Voorhees and Shriner, "Org. Syntheses," **8**, 92 (1928).