SOME EFFECTS OF HYDROCARBON GROUPS ON THE STRENGTH OF CARBOXYLIC ACIDS

BY J. O. HALFORD[1]

In the preceding paper,[2] the quantitative relation between relative strengths of acids in different solvents has been discussed. The relative strength of two acids has been found, in general, to vary from one medium to another. The magnitude which this variation can attain becomes important, particularly to the organic chemist, for it determines the limits within which measurements of acid strength may be interpreted as truly characteristic of the acids. It has been useful, in correlating the properties of organic compounds, to consider the effect of substitutions and structural modifications on acid strength, to know, for example, how the dissociation varies through an homologous series, or how it is changed by the substitution of one group for another within the molecule. The use, for this purpose, of acid strengths measured by our present methods, involves the assumption that they evaluate a property of the acids. The variation of relative strength with the solvent shows that acid strength, as measured, depends on the solvent as well as the acid. It follows that the variation of acidity through a series of substances cannot be expressed in terms of other measured properties, such as distances between atoms, without taking into account the specific nature of the interaction of substance and solvent.

However, it should not be concluded that acid strengths, measured in one solvent, are entirely without significance in the correlation of the properties of series of related compounds. There can be little doubt that trichloroacetic acid is intrinsically stronger than acetic acid, or that phenol is weaker than benzoic acid. Our problem, then, is to decide what minimum difference of measured acidity may be interpreted as indicating a characteristic difference between the acids compared, or what is the maximum value of the uncertainty introduced by the irregular character of the solvent effect. An idea of the magnitude of this quantity can be obtained by measuring the strength of a sufficient number of acids in several solvents.

As an addition to the available experimental data, we have measured the strength of a number of acids, including some which are not readily studied in water because of low solubility, under conditions which permit the comparison of a relatively large number of substances. Following Michaelis and Mizutani,[3] we have employed 50% ethyl alcohol by volume

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[1] Alfred H. Lloyd, Fellow in the Graduate School, University of Michigan.

[2] Halford, THIS JOURNAL, 53, 2939 (1931).

[3] Michaelis and Mizutani, Z. physik. Chem., 116, 135 (1925); Mizutani, ibid., 116, 350 (1925).

as solvent in some of the measurements, partly for the purpose of checking our procedure against theirs. However, we have given more attention to a solvent containing 60% by volume of butyl carbitol (diethylene glycol mono-butyl ether) and 40% of water. This solvent was selected because butyl carbitol–water solutions have somewhat more general solvent power than the corresponding alcohol–water solutions. For example, a solution of myristic acid and potassium myristate, each at a concentration of 0.0025 N, shows a precipitation in 50% alcohol, but does not come out of the butyl carbitol–water solution until the butyl carbitol content is reduced below 20%. The butyl carbitol content may be as high as 80% without serious interference with electrometric measurement. The selection of the 60% solution is arbitrary, but this figure is in the neighborhood of the optimum for high solvent power and ease of measurement.

Experimental

Procedure.—All measurements were made at 23 $\pm$ 1°. In order to examine the applicability of a titrimetric method, a set of titration curves was obtained, using the antimony or quinhydrone electrode against a saturated aqueous calomel cell. Having demonstrated in this way the greater reliability of the antimony electrode, it was adopted for the determination of acid strength. To obtain a measure of the strength of an acid, two solutions were made up, the one containing acetic acid, the other the unknown, each at a concentration of five millimoles per liter. To provide conductance, and standardize the salt effect, all solutions were 0.1 molal in lithium chloride. Each acid was then half neutralized with potassium hydroxide. The acetate buffer was introduced into the cell with the antimony electrode, and the potential against a saturated aqueous calomel cell determined. The procedure was repeated with the buffer of the unknown acid, followed by a repetition with the acetate buffer. In this way the electrodes were checked against previous measurements, and chance variation of electrode behavior directly following a determination was guarded against. Stirring was employed, but with the antimony electrode this was always gentle enough to prevent mixing large quantities of air through the solution.

Electrodes.—The hydrogen, antimony and quinhydrone electrodes were tested. None of these proved entirely satisfactory, at least by comparison with the precision attainable in aqueous solutions. The hydrogen electrode was too readily poisoned in the solutions containing butyl carbitol, the average life of those tried being about fifteen minutes. The quinhydrone electrode was better, but extraneous effects which cause small variations in water tend to introduce large errors in the mixed solvents, and it was difficult to obtain reproducibility within 20 mv. It was found possible to prepare sets of platinum electrodes by slightly different methods, such that satisfactory agreement within each set could be obtained, but large differences between different sets appeared. When used for the purpose of measuring equivalent weights, which depends on the sharpness of the break at the point of equivalence, the quinhydrone electrode was entirely satisfactory.

The antimony electrode, in the form of sticks of the metal, gave the most reproducible results. Regardless of age or previous treatment, it was exceptional to find two electrodes which differed by more than 2 mv. or failed to reproduce measurements by more than 5 mv. This statement applies to the measurement of acid strength by means of buffered solutions. We have no explanation of the behavior of these electrodes in

titrations. The titration curves up to the point of equivalence were entirely satisfactory, but thereafter a drift back toward the initial readings set in, partially masking the break. However, the same electrodes gave good results, before or after such titrations, when used with buffered solutions in either the acid or alkaline range.

The experience of others[4] with the antimony electrode in aqueous solutions indicates that in the form of sticks it does not give the correct reversible potentials. However, it should be satisfactory in comparative work. In changing from water to a water–alcohol system, the potentials of the antimony electrode cannot be expected to follow those of the hydrogen electrode, for the latter is independent of the water activity, except for its influence on the hydrogen-ion activity, while with the former, water enters into the electrode reaction. If a given buffer in water shows a considerable difference of potential against the same buffer in 50% alcohol with hydrogen electrodes, a smaller potential should be observed with antimony electrodes. The difference between two buffers at constant water concentration, however, is practically the same with the two electrode systems.

Cells.—The cells were of the same type as those employed by Conant and Werner,[5] with a saturated potassium chloride–agar bridge, except that the junction from the bridge to the calomel cell was not stoppered. Antimony electrodes were suspended by copper or platinum wires.

Butyl Carbitol.—Commercial butyl carbitol was allowed to stand over lime for several days, then distilled at a pressure of 30 mm. No difficulty was experienced in obtaining a large fraction boiling within one degree, a 90% recovery from the commercial product being readily attained. This purification was made because the solvent, when mixed with water, was frequently 0.001 to 0.002 molar in an acid of about the strength of acetic acid. Even the purified solvent, when mixed with water and allowed to stand for several days, showed slight acidity. Apparently the acid was formed only in the solutions containing water, for the anhydrous solvent could be kept at least for several weeks without deterioration. Consequently, butyl carbitol–water solutions were made up shortly before use.

Acids.—The acids were mainly Eastman Kodak Co. products. Melting points of most of them are recorded in Table I. Stearic acid, a sample of unknown origin, gave the correct equivalent weight within one per cent. An attempted purification of tridecylic acid, which melts twelve degrees below the value given in "International Critical Tables," produced no increase of the melting point.

Results

Titrations with the Antimony Electrode in 60% Butyl Carbitol.—In order to obtain sufficiently sharp end-points with the antimony electrode it was necessary to employ acid concentrations of 0.05 to 0.1 molal, titrated with 1.0 molal potassium hydroxide. The results of several such titrations are plotted in Fig. 1, with potential as the ordinate against the function $\log(X/1 - X)$ as abscissa, where X represents the fraction of the acid neutralized. The slope of the lines is slightly higher than that obtained in aqueous solutions. Stearic acid was titrated at a smaller concentration, because of its low solubility. The order of the curves is the

[4] Uhl and Kestranek, *Monatsh.*, **44**, 29 (1923); Kolthoff, *Rec. trav. chim.*, **44**, 113 (1925); Franke and Willaman, *Ind. Eng. Chem.*, **20**, 87 (1928); Roberts and Fenwick, This Journal, **50**, 2125 (1928); Britton and Robinson, *J. Chem. Soc.*, 458 (1931).

[5] Conant and Werner, This Journal, **52**, 4436 (1930).

same as in water, with the exception of benzoic acid, which in the water scale lies half-way between formic and acetic acids.

Titrations with the Quinhydrone Electrode in 60% Butyl Carbitol.— In Fig. 2 are shown the results of a number of titrations with the quinhydrone electrode. In this case, to show the character of the end-point, the potential is plotted as a function of the volume of standard alkali. The breaks are sharper, for the weaker acids, than those obtained with water as solvent.
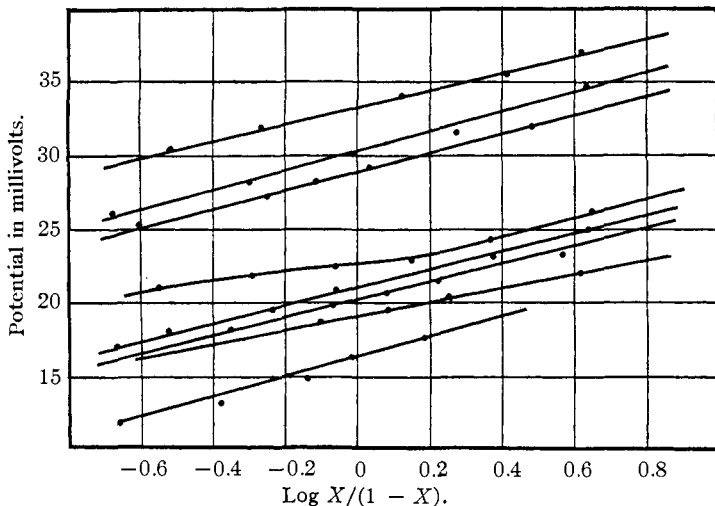

Fig. 1.—Titration curves with the antimony electrode in 60% butyl carbitol. 0.05 M acids titrated with 1.0 M KOH. In order, from the top, stearic, benzoic, acetic, formic, salicylic, chloroacetic, malonic, dichloroacetic (stearic acid at 0.005 M, titrated with 0.1 M KOH).

Strength of Acids.—In Table I the results of the determination of comparative strengths are summarized. The first column shows the acid, the second and third the melting point, measured and taken from "International Critical Tables,"[6] the fourth the pK value in water from the same source and the fifth the potential in volts, against a saturated aqueous calomel cell, of the half-neutralized solution of the acid in 60% butyl carbitol, as measured with the antimony electrode. The sixth column shows the strength, in pK units, on a scale in which the pK of acetic acid is arbitrarily taken as zero. The rate of change of potential with P_H in water was determined with several electrodes to be 54 mv. per P_H unit. The values of column six were obtained on the assumption that 54 mv. corresponds to one P_H unit in the mixed solvent as well. Columns seven and eight are similar to five and six, for 50% alcohol.

6 "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. I, p. 176, 1926; Vol. VI, p. 261, 1929.

TABLE I

RESULTS OF DETERMINATIONS

Acid	M. p., "I. C. T.," °C.	M. p., °C., measd.	pK (aq.)	60% Bu. carbitol E	ΔpK	50% Alcohol E	ΔpK
Acetic			4.74	0.298	0	0.285	0
Formic			3.68	.235	−1.2	.215	−1.4
Valeric			4.81	.332	0.6	.302	0.3
Isovaleric			4.78	.333	.6	.302	.3
Methylethylacetic			4.78	.333	.6	.305	.4
Trimethylacetic			5.02	.354	1.1	.318	.6
Caproic	− 9.5	−10	4.85	.336	0.7	.305	.4
Isocaproic			4.84	.337	.7	.304	.4
Heptylic	−10	−10.5	4.89	.340	.8	.307	.4
Cyclohexane carboxylic	31	29.7	4.9	.338	.8	.319	.6
Caprylic	16	14.5	4.85	.343	.8	.309	.4
Pelargonic	12	10.3	4.96	.346	.9	.313	.5
Capric	31	31– 2		.347	.9	.312	.5
Undecylic	29.3	22		.348	.9	.317	.6
Lauric	48	42– 3		.352	1.0	.314	.5
B		129–129.5		.405	2.0	.377	1.7
G		88– 9		.384	1.6	.345	1.1
Campholic				.387	1.6	.358	1.3
Tridecylic	51	39– 40		.342	0.8	.319	0.6
Myristic	58	54		.346	.9		
Pentadecylic	54	48– 49		.351	1.0		
Palmitic	64	62– 63		.350	1.0		
Stearic	69.3	55– 56		.345	0.9		
Benzoic	121.2	122	4.22	.315	.3	.285	0
Hydrocinnamic	48.7	48– 49	4.65	.305	.1	.292	0.1
Diphenylacetic	148	146–147		.305	.1	.275	−0.1
Salicylic	158	158–159	3.00	.220	−1.4	.195	−1.7
o-Nitrobenzoic	148	147–148	2.20	.215	−1.4	.179	−2.0
α-Naphthoic	160	161–162	3.7	.304	0.1	.266	−0.4
p-Nitrophenol	114	113–114	7.2	.412	2.1	.383	1.8
Phenol	42–3	42– 43	9.98	.575	5.1	.566	5.2
Chloroacetic	62–3	62– 63	2.82	.206	−1.6	.185	−1.9
Dichloroacetic			1.2	.173	−2.5	.152	−2.5

Effect of Salt Concentration.—Before attempting to interpret these results, it is desirable to obtain some idea of the effect of total salt concentration on the measurements of acid strength. It is possible that the variation of relative strength between solvents, as measured, might be to some extent the result of irregular variations of the effect of total ionic strength. In the measurements an ionic strength of 0.1025 was maintained by means of lithium chloride. We have measured the relative strength, in 60% butyl carbitol, of acetic, myristic and benzoic acids, at ionic strengths from 0.0025 to 0.1025, with the result that, within the limits of error of the procedure, the total salt concentration introduces no uncertainty if it is constant through the series of measurements. Figure

3 illustrates the effect. For convenience, the curves are drawn to coincide at zero ionic strength. The coördinates are e. m. f. against the square root of the ionic strength. A small differential effect, about 0.1 pK unit, is observed, but this may not be real, since the probable error of measurement is of the same order of magnitude. If this quantity was applied as a correction to the relative strength of benzoic acid, its position with respect to acetic acid would deviate still further from that in water. In the working range the curves are nearly horizontal, showing that the potentials are not sensitive to small variations of lithium chloride concentration.
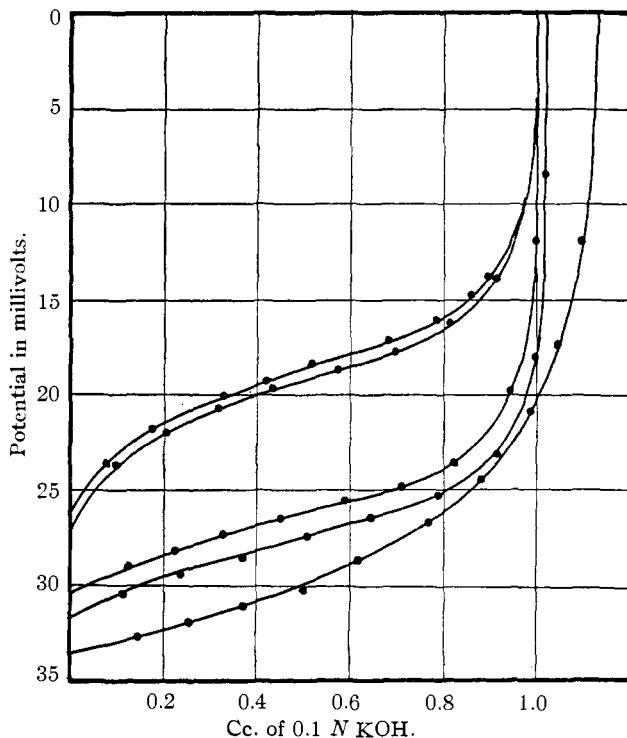

Fig. 2.—Titration curves with the quinhydrone electrode in 60% butyl carbitol. 0.005 M acids titrated with 0.1 M KOH. In order, from the top, acetic, benzoic, o-nitrobenzoic, chloroacetic, dichloroacetic.

Other Sources of Error.—The liquid junction between the aqueous calomel cell and the solution of the half-neutralized acid in the mixed solvent introduces an uncertainty of unknown magnitude. The junction potential should cancel out, in the evaluation of relative strength, if it remains constant in the separate measurements. We have attempted to minimize this error by employing a saturated potassium chloride bridge, and using the same initial acid concentration at all times. The high mole

fraction of water in the mixed solvent should produce a tendency toward small junction potentials.

The variation of the potential between successive measurements of the same system is a second source of error. This variation, which is due to the antimony electrode, has been canceled, in part, by frequent measurements of the standard acetic acid system. The total error of measurement should be less than 0.2 pK unit.
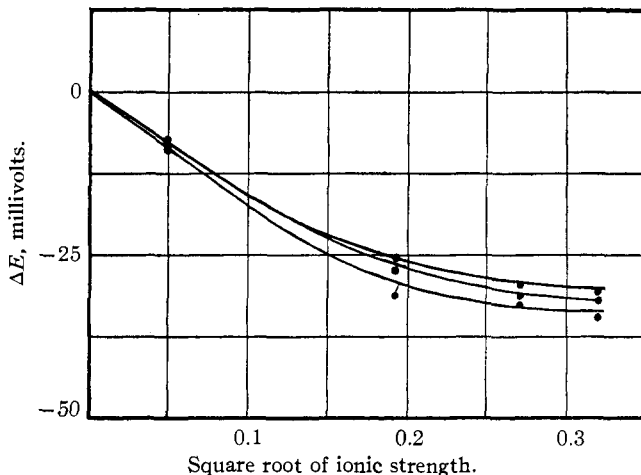

Fig. 3.—Effect of total salt concentration on apparent strength. In order, from the top, acetic, myristic and benzoic acids.

Discussion

We are indebted to Hall[7] for an excellent bibliography of measurements of acid strength in non-aqueous solvents. Since the variations of relative strength, as recorded by others, are of the same order of magnitude as those given here, the discussion will be sufficiently general if it is confined to the data of Table I.

The largest variation is that recorded for α-naphthoic acid, which in water is stronger by one pK unit than acetic, but in 60% butyl carbitol is weaker by 0.1 unit. Similarly, benzoic acid in water appears stronger by 0.6 unit than acetic acid, in 50% alcohol their strengths are equal, and in 60% butyl carbitol benzoic acid is the weaker by 0.3 unit. A similar variation is shown by o-nitrobenzoic acid. We are therefore unable to decide as to which of the three acids, benzoic, acetic and α-naphthoic, is intrinsically the strongest. Consequently, no specific deduction can be made concerning the relative positive or negative character of the methyl, phenyl and α-naphthyl groups. o-Nitrobenzoic acid appears in every case to be stronger than acetic acid, but we cannot say, within wide limits, how much stronger it is.

[7] Hall, *Chem. Rev.*, **8**, 191 (1931).

Any general statement about the uncertainty which variable relative strength introduces into the interpretation of measured acid strengths is based on insufficient data. However, it appears dangerous, at present, to draw conclusions about the intrinsic properties of acids from measured relative strengths which differ by less than one pK unit, or a factor of ten in the dissociation constant. This means that the specific nature of the solvent effect introduces an uncertainty of that magnitude. Any deductions which can be made are essentially qualitative. The effect of future data on this conclusion will be, of course, to change the magnitude of the uncertainty. The most probable change is an increase. However, when the rather abnormal properties of water are considered, it is possible that future measurements may show that, by omitting aqueous values from consideration, a more specific set of relations may be deduced.
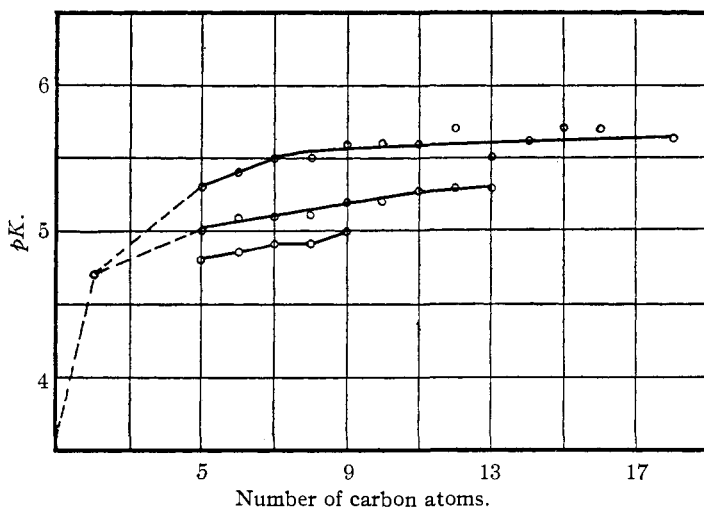

Fig. 4.—Strength (pK) of normal aliphatic acids as a function of the number of carbon atoms. Upper curve, 60% butyl carbitol; middle curve, 50% alcohol; lower curve, water.

An interesting case arises in the comparison of acetic and chloroacetic acids. Regardless of the magnitude of the measured relative strength, we should feel justified in concluding that chloroacetic acid is the stronger because of the much greater strength of trichloroacetic acid.

Normal Aliphatic Acids.—In Fig. 4 the strength relations of the normal aliphatic acids in water, 50% alcohol and 60% butyl carbitol are plotted as a function of the number of carbon atoms. The curves are drawn to coincide at the point which gives the strength of acetic acid in water. The maximum difference, the relative strength of the higher fatty acids in 60% butyl carbitol, falls just within our limit of interpretation. The

conclusion is, therefore, that, within this limit, all the normal aliphatic acids (except formic acid) have the same strength. However, this does not exclude the possibility that stearic acid may be weaker than acetic by one pK unit.

If it is assumed that the curve for water is analogous to the others, the pK value of stearic acid in water may be estimated as about 5.2. This quantity probably cannot be checked by direct measurement. Any mixture of water, stearic acid and sodium stearate will show much greater alkalinity because of the low solubility of the acid. The mixed solvents appear to increase differences which occur in aqueous solution.

Branched Aliphatic Acids.—The measurements with isovaleric, isocaproic and methylethylacetic acids are inconclusive. However, it is improbable that such closely related substances are very differently affected by the solvent, and the measured values should be significant within rather narrow limits. Trimethylacetic acid is probably weaker than valeric.

The acids B and G, obtained from Mr. G. W. Wheland of this Laboratory, are isomers of lauric acid, and may be represented provisionally by the following structures

$$(CH_3)_3C\diagdown$$
$$(CH_3)_3C{\diagdown\atop\diagup}C—COOH \qquad\qquad (CH_3)_3C—CH_2{\diagdown\atop\diagup}C—COOH$$
$$C_2H_5\diagup \qquad\qquad\qquad\qquad CH_3\diagup$$
$$\qquad B \qquad\qquad\qquad\qquad\qquad\qquad G$$

The more highly branched B acid appears weaker than lauric acid, in the mixed solvents, by about one pK unit. The corresponding figure for the G acid is 0.6 unit. It is interesting to attempt a comparison of the three acids, acetic, lauric and B. Our limit of interpretation makes indefinite the comparison of either of the pairs, lauric and B acid, or lauric and acetic, but permits the conclusion that the B acid is definitely weaker than acetic acid. This means that either lengthening or branching the chain produces a definite weakening effect, but does not decide which of the effects is real. The probable answer is that both are significant.

Aromatic Acids.—The introduction of aromatic hydrocarbon radicals into acetic acid produces no effects large enough to be considered significant. Salicylic and o-nitrobenzoic acids are definitely stronger than benzoic acid.

The writer wishes to express his sincere appreciation of the advice and assistance of Professor James B. Conant, who suggested this problem.

Summary

The relative strength of thirty-one carboxylic acids in a solvent mixture containing, by volume, 60% of butyl carbitol and 40% of water, has been measured with the antimony electrode.

The significance of the variation of measured relative strength with the solvent has been considered, with the conclusion that a measured relative strength less than one pK unit, or a factor of ten in the dissociation con-

stant, does not necessarily indicate a difference of intrinsic acidity. Future measurements in solvents other than water may increase this uncertainty.

Aromatic hydrocarbon radicals, when introduced into aliphatic acids, produce no measurable change of acidity.

Either the lengthening or the branching of the hydrocarbon chain in the aliphatic acids produces a definite weakening effect. Probably both effects are real.

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A POTENTIOMETRIC STUDY OF WURSTER'S RED AND BLUE

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In a rather large number of cases there have been found compounds intermediary, with respect to the level of oxidation, between a compound of the quinoid type and one of the hydroquinoid type. In a previous paper[1] it could be shown by a potentiometric method for three organic dyestuffs of the oxyphenazine series, that this intermediary compound is a molecule of the same size as either the holoquinoid form or the hydroquinoid form and differs from the hydroquinoid only by one oxidation equivalent (or hydrogen atom or electron). It must be considered as a radical-like compound with an odd number of electrons. Those three dyes offered a particularly favorable opportunity for the proof of such a statement because the intermediary compounds were very stable and permitted a thorough potentiometric study of the system, there being no drift in the potentials in time. The conclusions were based on observations of systems in a true thermodynamical equilibrium and therefore were scarcely liable to a misinterpretation.

This observation suggested the idea that other examples of half-reduced quinoid substances might be accessible to a similar potentiometric analysis. The difficulty in most of these cases is the fact that these intermediary compounds are as a rule not very stable in aqueous solution but undergo irreversible reactions and so cause a drift of the potentials. An attempt to utilize the potentiometric method for such a purpose was made by Clark, Cohen and Gibbs,[2] who studied the so-called meriquinones formed from aromatic diamines. They took for granted the current idea that these intermediary compounds are meriquinones according to Willstätter's[3]

[1] Michaelis, *J. Biol. Chem.*, in press, July (1931).

[2] W. Mansfield Clark, Barnett Cohen and H. D. Gibbs, *Public Health Repts.*, Suppl. No. 54, 1 (1926).

[3] Willstätter and Mayer, *Ber.*, **37**, 1494 (1904); Willstätter and Pfannenstiel, *ibid.*, **37**, 4605 (1905); Willstätter and Piccard, *ibid.*, **41**, 1458 (1908).