TABLE I

EXPERIMENTAL FREE ENERGY VALUES FOR REACTION (1) COMPARED WITH THOSE GIVEN BY ROSSINI FOR THE CORRESPONDING REACTION INVOLVING CARBON IN THE FORM OF β-GRAPHITE

	ΔF^0, kcal./mole	
T, °K.	Rossini	Authors' data
298.16	12.140	12.353
300	12.105	12.318
400	10.048	10.284
500	7.841	8.092
600	5.490	5.764
700	3.050	3.345
800	0.550	0.854
900	−2.010	−1.691
1000	−4.610	−4.280
1100	−7.220	−6.901

is such as to indicate that the carbon used in the present work is thermodynamically unstable with respect to β-graphite, and that the free energy change per mole for the conversion of the carbon here used to β-graphite is about 300 calories. This seems reasonable since one would not have expected the carbon used in the present work to have graphitized at even the highest experimental temperature employed. The numerical value for the free energy change for the conversion of the carbon used in the present work to graphite must, however, be considered as only approximate since it is the difference between two large values for free energy.

Since the completion of this work it has been noted that Troesch[10] has obtained equilibrium values for reaction (1) for carbon supported on a nickel catalyst at temperatures as low as 143°. The equilibrium constants obtained by Troesch in the range 143–252° are low compared to Rossini's values by a factor of about 2. The present data extrapolated to these low temperatures give values of the equilibrium constant which are low compared to Rossini's values by a factor of about 1.5.

Summary

Equilibrium constants for the reaction $CH_4 = C + 2H_2$ have been measured in the temperature range 380–838°, the carbon present being formed from the decomposition of Fe_3C. The values obtained are close to those for the reaction in which the carbon form is β-graphite.

[10] Troesch, International Conference on Heterogeneous Kinetics at Lyon, France, September, 1949.

PITTSBURGH 13, PENNSYLVANIA RECEIVED JULY 31, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF LOUISVILLE]

Chelate Formation between Copper and 8-Quinolinols

BY J. P. PHILLIPS AND F. J. O'HARA

As part of a study of practical applications of chelate stability principles the lines of investigation described here were tried, using various substituted 8-quinolinols as the chelating agents. Cupric ion was selected as the chelating metal because it apparently forms more stable chelates than other common metals.

Experimental

Reagents.—The preparation and purification of the 8-quinolinols have been previously described.[1,2] Standard solutions of cupric ion were made from weighed amounts of copper foil dissolved in nitric acid; for the conductometric titrations solutions of copper sulfate were used after standardization by electrodeposition.

Complex Formula Determination.—The formula of the soluble complex between copper and 8-quinolinol-5-sulfonic acid was determined spectrophotometrically by the method of continuous variations.[3] All measurements were taken with a Beckman model DU spectrophotometer, using 1.00 cm. cells. The experiment was made with 0.0158 M solutions in 2 M ammonium hydroxide at 460 mμ, and again with 0.0119 M solutions in a potassium acid phthalate buffer of pH 4.0 at 560 mμ. After the formula was determined, the extinctions of 0.0053 M solutions of the complex at various pH values were measured at 620 mμ, where the components of the complex had a negligible absorption, in order to obtain an estimate of the range of pH over which the complex formed.

Conductometric Titrations.—A standard solution of 8-quinolinol in isopropyl alcohol was added from a microburet to known volumes of 0.0166 M copper sulfate diluted to a total volume of 200 ml. The conductivities were measured after each addition of the standard solution using a dip type cell (having a cell constant of about 0.44) with an Industrial Instruments Conductivity Bridge, Model RC-1B. Since the amount of standard solution added was less than 2% of the total volume, no dilution corrections were made.

Mohr-type Titrations.—Fifty ml. of a solution containing 0.00658 g. of cupric ion in an acetate buffer of pH 4.4 and 0.1 ml. of 1% ferric iron as indicator was titrated with a 0.0201 M solution of 8-quinolinol in 50% alcohol until a black coloration persisted in the solution. A blank correction amounted to less than 0.1 ml.

A similar titration was carried out using 0.5 ml. of a 1% aluminum solution as indicator, the end-point being detected by the appearance of a fluorescence under ultraviolet light. The blank correction amounted to 0.25 ml. for a total solution volume of about 50 ml.

Results and Discussion

Relative Stabilities.—The relative stabilities of the copper chelates formed by 8-quinolinol, 2-methyl-8-quinolinol, 4-methyl-8-quinolinol and 8-quinolinol-5-sulfonic acid were established by means of a series of competitive reactions. Equivalent amounts of 8-quinolinol and the 2-methyl derivative were added simultaneously to an ammoniacal solution containing insufficient cupric ion to react with both; the resulting precipitate was filtered off, dissolved in chloroform and the ultraviolet absorption spectrum determined. Since the spectrum was that of the 8-quinolinol copper salt rather than that of the 2-methyl-8-quinolinol salt,[4] it appeared that 8-quinolinol formed the more stable chelate. A similar competition between 8-quinolinol and the 4-methyl derivative was won by the 4-methyl compound. The determination of the

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[1] Phillips, Elbinger and Merritt, THIS JOURNAL, **71**, 3986 (1949).

[2] Matsumura, *ibid.*, **49**, 810 (1927).

[3] Vosburgh and Cooper, *ibid.*, **63**, 437 (1941).

[4] Phillips and Merritt, *ibid.*, **71**, 3984 (1949).

relative stability of the chelate with 8-quinolinol-5-sulfonic acid was simplified by the fact that this complex is soluble, so that the formation of a precipitate on addition of 8-quinolinol or of 2-methyl-8-quinolinol indicated that these compounds formed the more stable chelates.

The order of decreasing stability of these complexes is then: 4-methyl-8-quinolinol > 8-quinolinol > 2-methyl-8-quinolinol > 8-quinolinol-5-sulfonic acid. It is noteworthy that this is also the order of decreasing basicity[5] for these compounds with the exception of 2-methyl-8-quinolinol, whose anomalous position may be attributed to the known steric hindrance[6] to chelate formation by this compound.

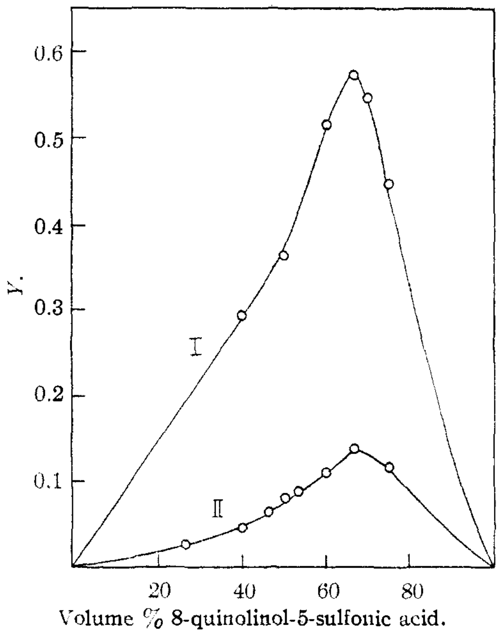

Fig. 1.—Formula of complex between 8-quinolinol-5-sulfonic acid and copper: I, at 460 mμ in ammonia; II at 560 mμ in a phthalate buffer of *p*H 4.0.

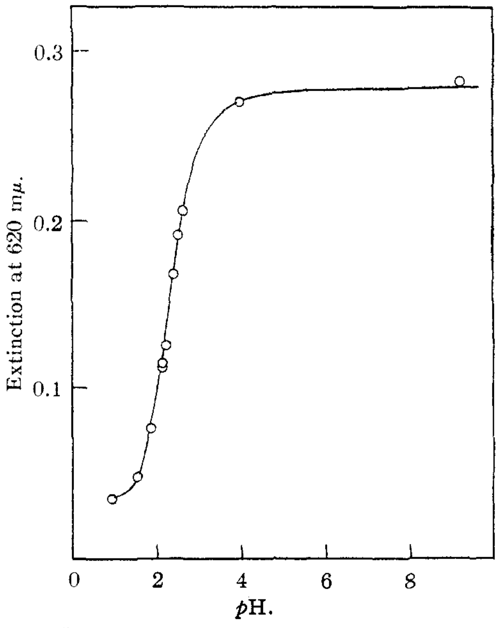

Fig. 2.—Complex formation between 8-quinolinol-5-sulfonic acid and copper as a function of *p*H.

In the course of this work it was thought desirable to demonstrate that the faint green color produced between 8-quinolinol-5-sulfonic acid and copper did indeed represent a definite complex, and to investigate the *p*H range over which the complex formed. As shown in the graph (Fig. 1) the complex has a 1:2 mole ratio of copper to the reagent. The complex begins to form at a *p*H between 1 and 2, and is stable even in ammoniacal solution (Fig. 2).

Conductometric Titrations.—It was thought that the titration of copper solutions with 8-quinolinol might provide evidence, through the changes in conductivity, for the step-wise formation of the chelate. With the equipment used no such steps were detected; however, very satisfactory end-points were obtained (Fig. 3), so that this titration may be a feasible analytical procedure. The titration of 13 samples containing 5.0×10^{-5} to 16.6×10^{-5} mole of copper gave results accurate to within 3%. Some preliminary titrations using other standard copper reagents (cupferron, α-nitroso-β-naphthol, α-benzoin oxime and 2-methyl-8-quinolinol) indicated that no other common reagent gives as satisfactory a conductometric titration graph.

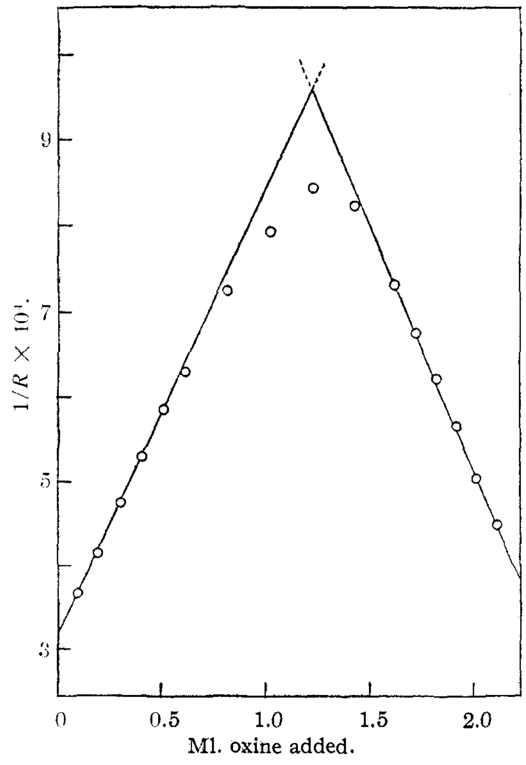

Fig. 3.—Conductometric titration of copper with 8-quinolinol (oxine). Calculated end-point at 1.16 ml., found: 1.18 ml.

Mohr-type Titrations.—It has been previously shown that copper forms a more stable chelate with 8-quinolinol than other common metal

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(5) Phillips and Merritt, THIS JOURNAL, **70**, 410 (1948).

(6) Irving, Butler and Ring, *J. Chem. Soc.*, 1489 (1949).

ions.[7] It is therefore reasonable to employ other metals forming distinctive precipitates with 8-quinolinol as indicators in the titration of copper with a standard solution of 8-quinolinol in a manner analogous to the Mohr method for determining halide. The procedure was tried using both iron and aluminum as the indicating ion; with ferric ion the end-point is observed as the appearance of a black color; with aluminum a fluorescence marks the end-point. Results of fair accuracy (Table I) on prepared samples could be obtained after a little practice by both methods. Similar titrations using zinc as a fluorescent indicator were also tried but did not give good results.

TABLE I

MOHR-TYPE TITRATIONS OF COPPER WITH 8-QUINOLINOL

Indicator	Mg. Cu taken	Mg. Cu found	No. of trials
Fe^{+3}	6.58	6.59 ± 0.05	15
Al^{+3}	6.66	6.68 ± .02	20
Zn^{+2}	6.63	6.8 ± .3	10

Acknowledgment.—This work was supported in part by a grant from the Cottrell Research Corporation.

Summary

1. A procedure for the estimation of the relative stabilities of the chelates formed by several substituted 8-quinolinols with copper has been described, and a conductometric titration method for determining copper with 8-quinolinol has been developed.

2. A volumetric method of analysis for copper based on the relative stabilities of the various metal chelates of 8-quinolinol has been shown to be satisfactory.

LOUISVILLE, KENTUCKY RECEIVED JUNE 26, 1950

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[7] Mellor and Maley, *Nature*, **159**, 370 (1947).

[CONTRIBUTION FROM THE FRICK CHEMISTRY LABORATORY, PRINCETON UNIVERSITY]

A Polarographic Investigation of the Alkaline Decomposition of Streptomycin

BY CLARK E. BRICKER AND W. AUBREY VAIL

A rapid polarographic method for assaying streptomycin has been reported by Levy, Schwed and Sackett.[1] These authors suggest a 3% solution of tetramethyl ammonium hydroxide for the supporting electrolyte for the polarographic determination of this compound. They also state that the wave height is a function of the *p*H of the medium and that the wave height is not constant until a *p*H of 13.6 is reached in the supporting solution. No reference was made to the polarographic behavior of the similar compound, mannosidostreptomycin.

In this investigation a more thorough study has been made of the effect of *p*H on the diffusion current obtained from streptomycin (to be called streptomycin A hereafter) and from mannosidostreptomycin (to be called streptomycin B).

Since streptomycin A or B which has been decomposed by heating an alkaline solution of these compounds was found to be non-reducible at the dropping mercury electrode, it was decided to study the rate of decomposition of these compounds polarographically. From these decomposition studies, it has been possible to calculate the energy of activation for these reactions and by comparing these values with that obtained from a similar study with α-hydroxyisobutyraldehyde, the rate determining step in the decomposition of the streptomycins has been deduced.

Experimental

Apparatus and Materials.—A Leeds and Northrup Model E Electrochemograph was employed for recording all polarograms. A polarographic cell assembly similar to that described by Furman, *et al.*,[2] was used throughout this study. This assembly was modified according to the apparatus described by Lingane[3] so that the mass of mercury flowing per second could be measured easily at any applied potential. In addition a constant temperature jacket was used to maintain the temperature of the solution being polarographed. With this jacket, the temperature of the solution was maintained to ±0.2° at as high a temperature as 75° and to ±0.05° at 25°.

Two capillaries were used in this study. All of the kinetic studies were made with a capillary that delivered 2.39 mg. of mercury per second. Those polarograms which were taken to illustrate the effect of *p*H on the reduction of streptomycin were recorded with a capillary that delivered 2.00 mg. of mercury per second. Whenever it was necessary to calculate I_D, the actual values of m and t were measured at the potential which was used for measuring i_d.

A saturated calomel electrode was used as the anode for all polarograms recorded at 25°. For the higher temperatures, a quiet pool of mercury was used. The potential of this anode was measured against a saturated calomel electrode with a Leeds and Northrup student type potentiometer. All *p*H measurements were made with a Leeds and Northrup research model *p*H meter using a No. 1199-30 glass electrode.

Tank nitrogen for removing dissolved oxygen from all solutions prior to the polarographic analysis was purified by passing it through vanadous sulfate solution as described by Meites and Meites.[4] All solutions were deaerated for 10 minutes with a slow stream of nitrogen prior to recording the polarograms. In the kinetic studies, the buffer solutions alone were deaerated ten minutes and then two minutes more after the solution of the reducible material was added.

The phosphate buffer solutions were prepared by mixing NaH_2PO_4 and Na_2HPO_4 or by mixing Na_2HPO_4 and NaOH so that the total available phosphate concentration was 0.25 *M* in all cases. The borate buffers were prepared from boric acid and sodium hydroxide with a resulting available borate concentration of 0.1 *M*.

A 1.0% gelatin solution containing a trace of mercuric iodide was used as a maximum suppressor throughout this study. This solution was perfectly stable and showed no evidence of mold growth over a period of several months.

The streptomycin A and streptomycin B were specially purified and were obtained from the Heyden Chemical Corporation.

Experiments with Streptomycin A and Streptomycin B.—A 1.53 millimolar solution of streptomycin A trihydrochloride and a 1.54 millimolar solution of streptomycin B sulfate

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[1] G. B. Levy, P. Schwed and J. W. Sackett, THIS JOURNAL, **68**, 528 (1946).

[2] N. H. Furman, C. E. Bricker and E. B. Whitesell, *Anal. Chem.*, **14**, 333 (1942).

[3] J. J. Lingane, *ibid.*, **16**, 329 (1944).

[4] L. Meites and T. Meites, *ibid.*, **20**, 984 (1948).