

has been presented recently by Kolthoff and Medalia<sup>13</sup> from studies of the reaction of ferrous iron and cumene hydroperoxide in the absence of oxygen.

(3) The kinetic order of the decomposition reaction as regards the initial step is believed to be bimolecular with the solvent. In the one pertinent reaction studied, of hydroperoxide decomposition in xylene containing styrene, the initial step of the decomposition was difficult to specify directly in view of the fact that important subsidiary reactions occur which lead to the  $3/2$ -order dependence on hydroperoxide and  $1/2$ -order dependence on styrene.

In order to explain the large accelerating effect of methanol on the decomposition of potassium persulfate in buffered aqueous solution, Bartlett and Cotman<sup>7</sup> arrived at the conclusion that a radical chain reaction was operative in which solvent radicals were formed by bimolecular reaction of methanol with persulfate ion and that these solvent radicals effected considerable induced decomposition of persulfate ion. By analogy, one may

derive an expression for hydroperoxide decomposition in xylene containing styrene as

$$-d(\text{ROOH})/dt = K'(\text{ROOH})(\text{Styrene}) + K''(\text{ROOH})^{1/2}(\text{Styrene})^{1/2} \quad (\text{E})$$

If the induced effect predominates, then only the second term on the right side of equation (E) is important. This type of kinetic behavior appears to occur in the case of styrene and is evidenced in the Figs. 2-4.

Under conditions where chain-induced decompositions are not important, then the rate of decomposition of hydroperoxide is bimolecular with the solvent as represented by the first term on the right side of equation (E). This may be the case for the decomposition in mesitylene at low concentrations of hydroperoxide.

### Summary

Studies are presented on the kinetics of the decomposition of *t*-butyl hydroperoxide and dimethylphenyl methyl (cumene) hydroperoxide in several organic solvents and in the temperature range 50 to 150°.

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(13) Kolthoff and Medalia, *This Journal*, **71**, 3789 (1949)

[CONTRIBUTION FROM THE SUGAR RESEARCH FOUNDATION LABORATORY, DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

## Stability of Carbonate Buffered Cupritartrate Reagents of Low pH for Estimating Micro and Macro Quantities of Reducing Sugars

BY LAWRENCE J. HEIDT AND KENNETH A. MOON

Recent studies in this Laboratory<sup>1</sup> of the method devised by P. A. Shaffer, A. F. Hartman and M. Somogyi for estimating reducing sugars have led to improvements in the reliability of the method and in the yield of cuprous oxide, and to the adaptation of the method to the estimation of macro as well as micro quantities of reducing sugars. The best results are obtained when the carbonate buffered cupritartrate micro and macro reagents are at pH 9.0 and 8.7, respectively. It was pointed out, however, that the reagents at these pH values sometimes deposit an azure blue crystalline precipitate, and that when this occurs, the supernatant solutions give lower yields of cuprous oxide.

The present study was made primarily to determine the effect of the accumulation of the precipitate upon the yield of cuprous oxide produced by the supernatant solution and upon the pH and optical density of the solution. The composition of the precipitate and the effect of pH upon the reproducibility of the results were also determined. In the remainder of this article the copper reagent will be called reagent and the

mildly alkaline solution of sodium thiosulfate will be called thio.

**Materials, equipment and procedures** were for the most part the same as in the earlier work.<sup>1</sup>

All measurements were made at  $24 \pm 1^\circ$ . The temperature of the vigorously boiling water-bath, in which the reagent was reduced by sugar, was  $100 \pm 0.5^\circ$ .

The pH measurements were made with a Cambridge Electron Ray Research Model pH Meter equipped with the Standard Electrode ensemble. The pH values were reproduced to  $\pm 0.005$  unit.

Optical densities,  $D = \log_{10}(I_0/I)$ , were measured with the Beckman DU quartz spectrograph serial 3249. The light source was a tungsten lamp. The wave length scale was calibrated with a mercury arc lamp and with a didymium glass filter previously calibrated. The transmission and optical density scales were calibrated with mildly alkaline solutions of potassium chromate. The length of the light path in the solutions was in all cases 1.000 cm. The measurement of optical densities was confined to the region between  $D = 0.4$  and 1.2 unless otherwise noted. The densities are referred to an equal depth of water.

(1) (a) L. J. Heidt, F. W. Southam, J. D. Benedict and M. E. Smith, *This Journal*, **71**, 2190 (1949); (b) L. J. Heidt and F. W. Southam, *ibid.*, **72**, 589 (1950).

The stability of the reagents was determined by following the changes in the optical densities as the reagents were shaken with an excess of finely ground crystals of the blue precipitate. At intervals the shaking was stopped, the suspension was allowed to settle, and samples of the supernatant solution were withdrawn, after which the shaking was resumed.

The solutions were shaken by placing 100-ml. portions of them with excess of the blue precipitate in glass-stoppered 250-ml. erlenmeyer flasks completely covered with light tight aluminum foil. The flasks were clamped to a shaft that moved back and forth on its axis through an angle of  $20^\circ$  with a period of a half-second. The clamps held the flasks by their necks from three to six inches from the axis of the shaft. Care was taken to prevent loss of water by evaporation.

**Composition of the reagents** was the same as recommended in the earlier work.<sup>1</sup> The micro reagents were all made up from a large batch of double strength stock solution that contained only enough bicarbonate to produce a solution of  $pH$  slightly greater than 9.4 when a portion of it was diluted with an equal volume of water. The double strength solution contained the following ingredients per liter at  $25^\circ$  besides water: 10.00 g.  $CuSO_4 \cdot 5H_2O$ , 34.00 g.  $NaKC_4H_4O_6 \cdot 4H_2O$ , 50.00 g.  $Na_2CO_3$ , 38.00 g.  $NaHCO_3$ , 1.400 g.  $KIO_3$  and 2.00 g.  $KI$ . The solution was made up in the manner previously described for the micro reagent.<sup>1</sup> It was filtered through a clean sintered glass filter of medium porosity after it was one day old. The filtered solution was stored in the dark in a Pyrex bottle and remained unchanged. Every micro reagent was made by adding the appropriate amount of sodium bicarbonate to a portion of the double strength solution which was then diluted with water until the final volume was twice the original volume of the double strength solution.<sup>2</sup>

### Results and Discussion

The deep azure blue crystalline precipitate was found to be very insoluble in water at  $25^\circ$ , but it dissolved in 0.1 *N* hydrochloric acid with effervescence of carbon dioxide. When the blue crystals were gently heated, their color changed to greenish-blue and water was liberated. When the heating was stronger, the crystals suddenly changed from greenish-blue to reddish-brown, more water was liberated, and a strong

(2) It was found in making up reagents from the double strength stock solution that the  $pH$  could be reproduced to 0.01 unit simply by reproducing within  $\pm 0.2\%$  the ratio of bicarbonate to stock solution, provided the same batches of stock solution and bicarbonate were used. A different lot of bicarbonate gave a different (although reproducible)  $pH$ , the difference being 0.06  $pH$  unit at all  $pH$  values between 8.9 and 9.4. This was rather surprising, since both lots of bicarbonate were of analytical reagent grade and from the same manufacturer. These observations re-emphasize the fact that one cannot rely upon the formal concentration of the reagent to fix its  $pH$  within 0.01 unit, especially when new lots of chemicals are employed.

odor of burnt sugar was given off, indicating the presence of tartrate. Stronger heating produced a black residue.

The precipitate contained by weight 30.6% Cu, 11.3% C, 2.9% H, 7% Na, 17%  $CO_3^{=}$ . The formula which comes closest to satisfying the observations is  $Na_2(CuC_4H_2O_6) \cdot 2CuCO_3 \cdot 7H_2O$ . This new compound contains 30.31% Cu, 11.46% C, 2.56% H, 7.31% Na, 19.09%  $CO_3^{=}$ . The agreement between the calculated and observed values is not bad when one considers that the blue solid cannot be recrystallized or properly dried.

The optical densities,  $D$ , of the micro and macro reagents before they deposited or dissolved any of the blue crystalline solid are given in Fig. 1 over the range of wave length between 525 and 700  $m\mu$ . At all  $pH$  values  $D$  increases with the wave length of the light and no sharp absorption or transmission bands are present. In the case of the micro reagent,  $D$  decreases when the  $pH$  of the reagent is raised from 8.94 to 9.4. In the case of the macro reagent,  $D$  is independent of the  $pH$  between 8.63 and 8.77. The values of  $D$  for the macro reagent have been divided by five in order to put them on the same concentration basis as the micro reagent. The decrease in  $D$  per atom of copper when the  $pH$  and formal concentrations of cupric copper and tartrate

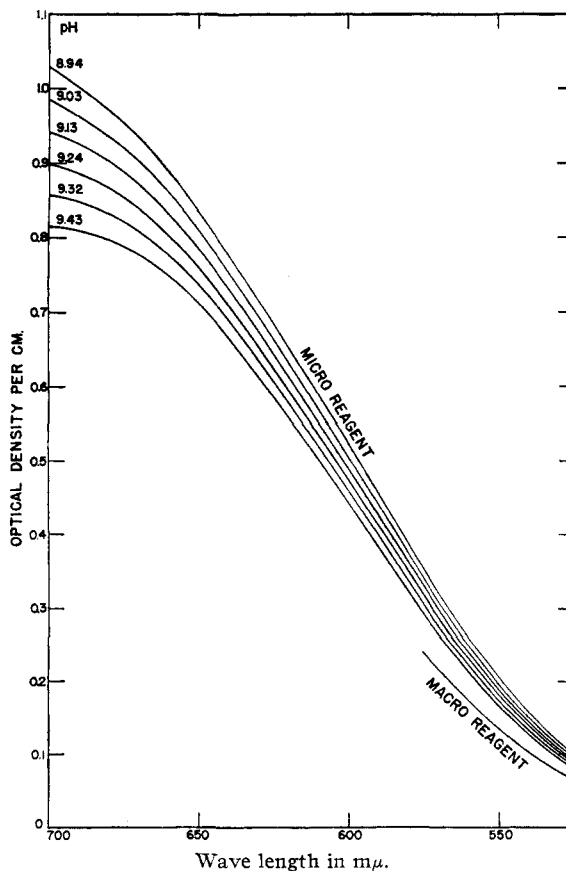


Fig. 1.—Optical densities of fresh cupritartrate reagents.

are increased indicates that these changes reduce the fraction of copper in the most strongly absorbing species in the solution.

The rate of formation of the blue precipitate is so slow that several days are required to reach equilibrium even when the reagent is shaken with the precipitate. This can be seen from the upper two sets of curves in Fig. 2. Several weeks are required to reach equilibrium when the reagent stands quietly over the precipitate.

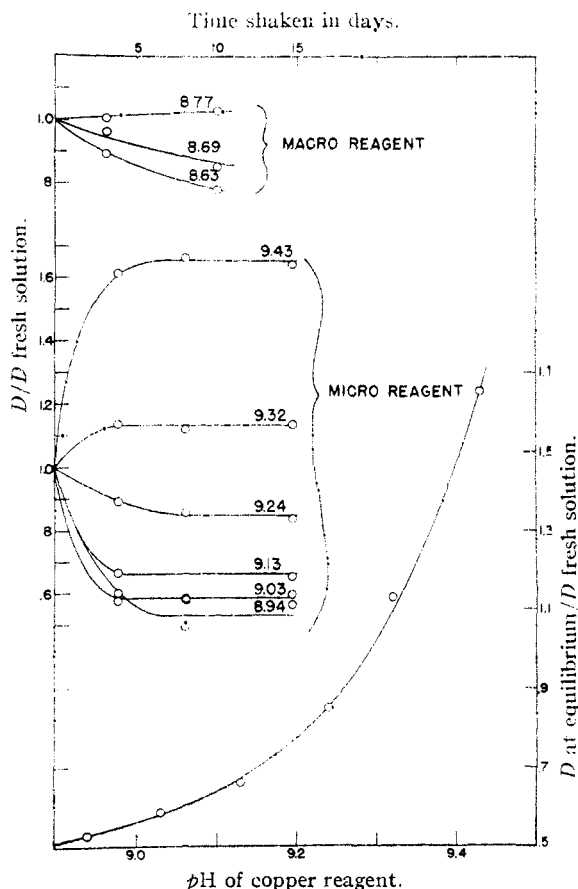


Fig. 2.—Change in optical density,  $D$ , of the copper reagents as they approach equilibrium with the blue precipitate. The initial value of the  $pH$  of the reagent is given alongside the line.

In the case of the micro reagent at  $pH$  9.0, the solid begins to appear the day after the reagent has been seeded. But precipitation can be stopped short of equilibrium at any time simply by decanting or filtering the supernatant solution free from the precipitate into a clean Pyrex bottle. Precipitation in the absence of the blue crystals often does not take place until several months or years have passed. Accidental seeding is likely to occur if either the sintered glass funnel or the bottles used for storage are not cleaned properly before use. Rinsing with dilute mineral acid, *e.g.*, 1  $N$  hydrochloric acid is a convenient way of destroying the blue solid which may be

adhering to the glass, but the acid should then be completely removed by washing with hot distilled water. The use of filter paper instead of sintered glass is not desirable for filtration because solutions filtered through paper deposit cuprous oxide on standing.

The lowest curve in Fig. 2 is a plot of the initial  $pH$  of the micro reagent against the ratio of the optical density when equilibrium is reached to the optical density before it has precipitated or dissolved any of the blue solid. The ratio equals unity at  $pH$  9.29 and 8.75 in the case of the micro and macro reagents, respectively. Below these  $pH$  values the reagents eventually deposit the blue precipitate.

**Change in Yield of Cuprous Oxide and its Reproducibility with the  $pH$  of the Micro Reagent.**—In the earlier work it was shown that the yield of cuprous oxide rose to a plateau of constant value as the heat treatment was prolonged and that the duration of the heat treatment necessary to reach the plateau had to be increased as the  $pH$  of the reagent was lowered. The reproducibility of the results obtained on the plateau was determined only for the micro reagent at  $pH$  9.00, and the macro reagent at  $pH$  8.70. We have extended this part of the study over the range of  $pH$  from 8.86 to 9.40 for the micro reagent. The experiments were carried out by employing in every heat treated sugar mixture, 5 ml. of the reagent reproduced to  $\approx 0.001$  ml.,  $4.77 \times 10^{-6}$  mole dextrose or  $5.34 \times 10^{-6}$  mole  $D$ -xylose, and enough water to bring the total volume up to  $10 \pm 0.01$  ml. About twelve experiments were carried out with each sugar at each of twelve  $pH$  values.

The time required to reach the plateau of constant yield of cuprous oxide in the case of dextrose was found to be 30, 28 and slightly less than 15 min. in the boiling water-bath when the micro reagent was at  $pH$  8.86, 9.00 and 9.40, respectively; in the case of  $D$ -xylose, 20 and less than 10 min. were required when the reagent was at  $pH$  8.86 and 9.40, respectively. In every case no change in the yield occurred when the heat treatment was prolonged an additional thirty minutes.

The yield of cuprous oxide reached on the plateau was found to increase when the  $pH$  of the micro reagent was decreased and to depend linearly upon the  $pH$  down to at least 8.90. The best straight lines representing the results were determined by the method of least squares. The equations for the lines are  $\Delta_d = 86.247 - 7.227 \times pH$  and  $\Delta_x = 65.271 - 5.156 \times pH$  for dextrose and  $D$ -xylose, respectively, where  $\Delta$  represents the difference, in ml. of 0.002  $M$  thio, between the titers for the blank and the heat treated solution that contained the sugar. A change in the  $pH$  of the reagent of 0.01 changes the yield of cuprous oxide produced by dextrose 0.33% and by  $D$ -xylose 0.26%, when employing

the micro reagent at  $pH$  9.00; the per cent. change is greater at higher  $pH$  values. In the earlier work<sup>1a</sup> the yield of cuprous oxide appeared to reach a maximum when the micro reagent was at a  $pH$  of about 9.0. The falling off in the yield in the case of dextrose when the  $pH$  of the reagent was less than 9.0 was caused by failure to prolong the heat treatment until the plateau had been reached; a heat treatment of 20 instead of the required 28 and 30 min. in the boiling water-bath was employed when the reagent was at  $pH$  9.00 and 8.90, respectively.

The uncertainty in the thio titers for the blanks was found to be independent of the  $pH$  of the reagent, and at every  $pH$  amounted to less than 20% of the total uncertainty in the difference between the titers for the blanks and solutions that contained the sugar. In the case of the solutions in which cuprous oxide had been produced, the uncertainty in the thio titers increased with the  $pH$  of the reagent employed. The uncertainty was independent of the nature of the reducing sugar in the case of dextrose and D-xylose and was found to be represented by the equation  $PE = -5.127 + 0.586 \times pH$  where  $PE$  represents the probable error in ml. of 0.002  $M$  thio. The probable error when the reagent was at  $pH$  9.00, therefore, was 0.15 compared to 0.12 ml. of 0.002  $M$  thio in the earlier work,<sup>1a</sup> or to 0.06 compared to 0.05 ml. of 0.005  $M$  thio. The uncertainty in measuring out delivered volumes with a good buret graduated to 0.10 ml. is about 0.02 ml.; so there is no advantage in using 0.002 instead of 0.005  $M$  thio in the titrations, and there is the disadvantage of handling larger volumes of solution. The uncertainty in the titrations is small enough so that the change in the maximum yield of cuprous oxide with the  $pH$  of the micro reagent is revealed to be significantly different for dextrose and D-xylose. The relative yields produced by the sugars, therefore, depend upon the  $pH$  of the reagent (more particularly upon the  $pH$  of the mixture of copper reagent and sugar<sup>3</sup>) as well as upon the differences in the configuration and structure of the sugars.<sup>1a</sup>

**Effect of the Extent of the Heat Treatment upon the Precision.**—There is no measurable change in the experimental error when the heat treatment is reproduced within 10% and is sufficient to reach into the plateau of constant yield of cuprous oxide. When the plateau is not reached, the error may be kept small by increasing the precision with which the heat treatment is reproduced especially when the extent of the treatment is long compared to the time required for the mixture of copper reagent and sugar to reach the temperature of the boiling water-bath.

The reproducibility of the results when the heat treatment is insufficient to reach the plateau

(3) The  $pH$  of the mixture is about two-tenths higher than the  $pH$  of the reagent employed when the volume of the mixture is twice the volume of the reagent in it and the sugar solution contains a negligible amount of acid, base or buffer.

was obtained in the case of dextrose. In these experiments, the heat treatment was for 20 instead of the 28 min. required to reach the plateau when the micro reagent is at  $pH$  9.00 and 10 to 60% of the copper is reduced. The heat treated solutions each contained 5 ml. of the micro reagent and the dextrose in a total volume of 10 ml. The yield of cuprous oxide was 4.45 moles per mole, 180 g., dextrose compared with 4.41 in the earlier work,<sup>1a</sup> when the heat treatment was for 20 min. In both cases, the probable error in the yield was 0.030 mole cuprous oxide per mole dextrose, the extent of the heat treatment was reproduced within 6 sec. or 0.5%, and  $6 \times 10^{-7}$  mole cuprous oxide was lost in every analysis.

The reproducibility of the results on a mole basis when the heat treatment is sufficient to reach into the plateau of constant yield of cuprous oxide can be determined in two ways under conditions otherwise the same as employed above. One way is from the equation representing the probable error in the thio differences as a function of the  $pH$  of the micro reagent. The error calculated from this equation is  $0.15 \times 10^{-6} / 4.77 \times 10^{-6} = 0.031$  mole cuprous oxide per mole of dextrose when the reagent is at  $pH$  9.00. The other way is from the uncertainty in the slope of line I in Fig. 3 which represents the results obtained when the reagent is at  $pH$  9.03. The probable error in the slope of the line is 0.030 mole cuprous oxide per mole of dextrose. The slope of the line gives a yield of 4.55 which would have been 4.59 if the reagent had been at  $pH$  9.00. The yield calculated from the equation for  $\Delta_d$  which represents the change in the yield with the  $pH$  of the micro reagent is 4.57. One, therefore, concludes that the reproducibility of the results under the above conditions is the same when the heat treatment produces 97% or more of the cuprous oxide that is obtained when the plateau is reached.

The maximum yield produced by D-xylose when the micro reagent is at  $pH$  9.00 can be estimated from the equation for  $\Delta_x$  and the loss of  $6 \times 10^{-7}$  mole of cuprous oxide in every analysis. The yield is  $(18.87 + 0.60) 10^{-6} / 5.34 \times 10^{-4} = 3.65$ . The probable error in the yield is 0.03. The yield in the earlier work was also obtained with a heat treatment sufficient to reach into the plateau of constant yield and was found to be  $3.68 \pm 0.02$  which agrees with our value within the limits of error.

**Decrease in Yield of Cuprous Oxide Brought About by Formation of Precipitate.**—The decrease in the yield of cuprous oxide brought about by the formation of the blue precipitate in the micro reagent at  $pH$  9.03 was studied in detail. The results are given in Fig. 3, along with the accompanying change in the optical density and  $pH$  of the solution.

Every heat-treated mixture, except the blanks,

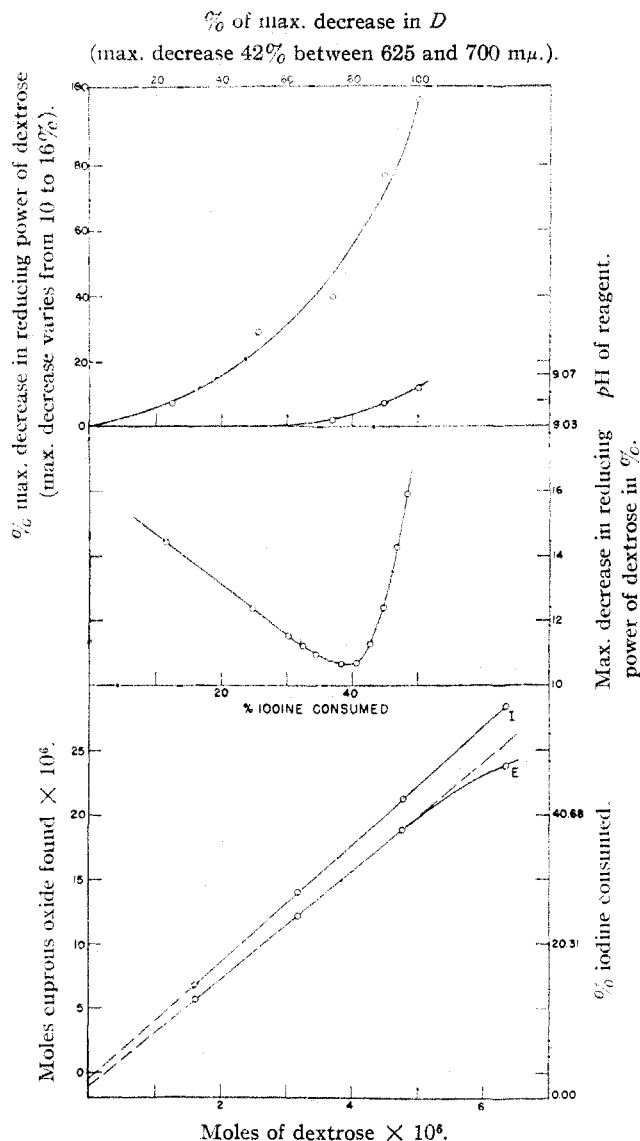


Fig. 3.—Influence of formation of blue precipitate upon micro copper reagent at pH 9.03.

contained 5 ml. of the reagent reproduced to  $\pm 0.001$  ml., dextrose, and enough water to make the total volume  $10 \pm 0.01$  ml. The blanks contained no sugar. The heat treatment consisted of 55 minutes in the  $100^\circ$  bath which was sufficient to reach into the plateau of constant yield in every case.

Line I in Fig. 3 represents the results obtained in four calibrations of the reagent with dextrose before any of the blue precipitate appeared. Every point represents the average of twelve determinations, three for each of the four calibrations. The first of the four calibrations was made before the reagent was one hour old, the last nineteen days later. The results of the four calibrations agreed within 0.20 ml. of 0.002 *M* thio.

The slope of line I corresponds to a yield of 4.55 moles cuprous oxide per mole of dextrose. The line is straight over its entire range which covers up to 60% consumption of the iodine by oxidation of the cuprous oxide. This corresponds to reduction of 60% of the cupric copper initially present since the reagent had not deposited any of the blue solid. The value of the intercept of line I at zero sugar gives the moles of cuprous oxide lost in every one of these analyses and equals  $6 \times 10^{-7}$  mole.

Line E represents the results obtained with the same lot of dextrose and the same reagent after it had come to equilibrium with the blue precipitate. The amount of iodine produced in the blanks was not changed by the formation of the blue precipitate; it was  $49.23 \times 10^{-6}$  mole in every blank. The slope of the straight portion of line E corresponds to a yield of 4.19 moles cuprous oxide per mole of dextrose and the intercept of the line at zero sugar shows a loss of  $10^{-6}$  mole cuprous oxide in every analysis. The line is straight only up to the point where 40% of the iodine is consumed by the oxidation of the cuprous oxide. This consumption of iodine corresponds to the reduction of over 75% of the cupric copper left in the reagent after it had come to equilibrium with the blue precipitate.

The maximum error that can be produced in the estimation of dextrose by ignoring the formation of the blue precipitate in the reagent at pH 9.03 is given by the plot in the middle of Fig. 3. The magnitude of the error is seen to increase rapidly when the amount of sugar in the heat treated mixture reduces most of the cupric copper; it also increases rapidly when the amount of sugar is so small that very little of the copper is reduced. The latter effect is due mainly to the larger amount of cuprous oxide lost by oxidation when the reagent has deposited blue precipitate. The maximum error percentage wise is less for the sugars producing higher yields of cuprous oxide but it is more for the sugars producing lower yields.

The effect of the formation of the blue precipitate upon the analytical results can also be given in terms of the decrease in the raw and net yields of cuprous oxide. The effect on the raw yields percentage wise is larger than given in Fig. 3 for the decrease in the reducing power of dextrose; the effect on the net yields, which include the cuprous oxide lost, is smaller percentage wise.

The increase in the error as the blue precipitate accumulates and the optical density of the reagent decreases is given by the plot at the top of Fig. 3. The initial decrease of 9% in the optical density is accompanied by slightly less than a 1% decrease in the reducing power even when the amount of cuprous oxide produced consumes 50% of the

iodine. An independent set of experiments also showed a change of less than 0.3% in reducing power at 50% or less reduction of the copper when the initial formal concentration of copper was increased or decreased 10% in the reagent at pH 9.00. The increase in the pH of the micro reagent accompanying the formation of the blue precipitate is given also in the middle part of Fig. 3; the total increase amounted to about 0.03 pH unit when equilibrium was reached.

It is worth noting that no error is made in estimating the amount of a reducing sugar even when using a reagent that has deposited blue precipitate if the solution is decanted or filtered from the precipitate and no more precipitation occurs between the time the decanted solution is calibrated and used for analysis.

The instability of the micro reagent at pH 9.00 does not mean that the reagent at this pH is not suitable for analytical purposes. Precipitation can be avoided when one uses fresh solutions made up from double strength stock solution in the manner described in this article. The reproducibility of the results is much better with the reagent at this pH than at higher values and the yield of cuprous oxide is higher.

#### Summary

1. Carbonate buffered cupritartrate reagents for estimating micro and macro quantities of reducing sugars deposit an azure blue crystalline precipitate when the pH is less than 9.29 and 8.75, respectively, the formal concentration of cupric sulfate is 0.02 and 0.10, respectively, the ratio of Rochelle Salt to copper is three, the formal concentration of sodium carbonate is 0.24 and the pH is adjusted by adding sodium bicarbonate. These values are at 25° and for concentrations in moles per liter of solution.

2. Experimental evidence indicates that the

precipitate is  $\text{Na}_2(\text{CuC}_4\text{H}_2\text{O}_6) \cdot 2\text{CuCO}_3 \cdot 7\text{H}_2\text{O}$ . It is very insoluble in water at 25°.

3. The precipitate often does not appear until the reagent has stood for several months or years. It appears overnight when the solutions are seeded, but several days are required to reach equilibrium even when the solution is shaken continuously with the crystals, and several weeks are required when the reagent stands quietly over the crystals in the dark. Precipitation can be arrested indefinitely by decanting or filtering the supernatant solution from the crystals and storing the solution in a clean Pyrex bottle.

4. The formation of the precipitate lowers the optical density of the solution and the yield of cuprous oxide produced by a sugar, and raises the pH. But an initial decrease of 9% in the optical density is accompanied by a decrease of only 1% in the yield of cuprous oxide produced by dextrose and by no measurable change in the pH of the copper reagent. The maximum error produced by ignoring the formation of the precipitate in estimating micro quantities of dextrose increases rapidly when less than 10 and more than 50% of the cupric copper is reduced.

No error is made in estimating a reducing sugar with a copper reagent that has deposited blue precipitate when the reagent is decanted or filtered from the precipitate and no more precipitation takes place between the time the decanted solution is calibrated and used for analysis.

5. The yield of cuprous oxide decreases and the probable error increases linearly as the pH of the copper reagent is increased. The yield decreases 11% and the probable error increases from 0.06 to 0.13 ml. of 0.005 M thiosulfate in an analysis when the pH of the micro copper reagent is changed from 9.00 to 9.30.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

## The Solubility of Higher Alkyl Quaternary Ammonium Salts of Fatty Acids

BY D. N. EGGENBERGER, F. K. BROOME, R. A. RECK AND H. J. HARWOOD

Inactivation of bactericidal quaternary ammonium salts by anionic colloidal electrolytes is well known.<sup>1</sup> This inactivation is assumed to be due to the formation of an insoluble quaternary ammonium salt of the surface-active anion involved. The formation of such insoluble salts is not always apparent to the eye because of their incorporation into the micelle. Precipitation has been demonstrated by surface-tension measurements as well as by bactericidal studies.<sup>2</sup>

The compatibility of quaternary ammonium

(1) Baker, Harrison, and Miller, *J. Exptl. Med.*, **74**, 621 (1941); Lawrence, *J. Am. Pharm. Assoc., Sci. Ed.*, **37**, 57 (1948).

(2) Alexander and Tomlinson, "Surface Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, p. 325.

compounds with soluble soaps depends upon the solubility of the quaternary ammonium salt of the fatty acid composing the soap. The present paper is concerned with the estimation of this solubility by the conductometric method.

#### Experimental

The preparation of trimethylhexadecylammonium chloride has been previously described.<sup>3</sup> N-Dodecyl-N-methylmorpholinium methosulfate was prepared from N-dodecylmorpholine and dimethyl sulfate according to the method of Niederl.<sup>4</sup> The morpholinium chloride was prepared in the usual manner using methyl chloride.<sup>5</sup> Solu-

(3) Ralston, Eggenberger, Harwood and Du Brow, *THIS JOURNAL*, **69**, 2095 (1947).

(4) Niederl, *ibid.*, **70**, 618 (1948).