such chemical reactions are very common, and that their effects are masked by other physical factors having large positive temperature coefficients.

The number of chemical reactions previously known which have negative temperature coefficients is extremely small. Bodenstein cites one case, that of the reaction: $2NO + O_2 = 2NO_2$.

Strutt found that atomic nitrogen recombines to form molecules much more rapidly at low temperatures than at high, and he reasons that a high translational velocity of the molecule should in general hinder rather than hasten the reaction. He considers that rotational velocity of the molecules, on the other hand, favors the reaction and that this factor in the majority of reactions greatly outweighs that of the translational velocity. Thus reactions between atoms should always have negative temperature coefficients, since atoms cannot have rotational energy. The present work lends further support to Strutt's views.

The view-point developed as a result of this work with low pressure reactions is undoubtedly applicable to reactions at high pressures and also to reactions between solids and liquids. It is hoped that further work will lead in a similar way to a better understanding of the mechanism of homogeneous reactions.

In conclusion, the writer wishes to express his appreciation of the valuable assistance of Mr. S. P. Sweetser, who has carried out most of the experimental part of this work.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF KENTUCKY.]

CUPROUS SALTS OF OXYGEN ACIDS AND A NEW METHOD FOR PREPARING CUPROUS SALTS.

[PRELIMINARY PAPER.]

BY LLOYD C. DANIELS.

Received March 19, 1915.

The number of cuprous salts of oxygen acids is so small, and those that are known are so unfamiliar, that it is not surprising that the misstatement is often made in text-books, even in the larger number of the more modern ones, that such compounds do not exist.

The longest known and most familiar member of this class of compounds is red cuprous sulfite, $Cu_2SO_3.H_2O$, first prepared by Rojoski.[1] Bourson[2] gives, as the best method for its preparation, the addition of a concentrated solution of sodium bisulfite to a solution of cupric sulfate, filtration from the slight precipitate, and gentle warming of the filtrate. Sulfur

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[1] *Jahresber.*, **1851**, 366.

[2] *J. prakt. Chem.*, **25**, 399 (1842).

dioxide is evolved and the red compound crystallizes out. Rammelsberg[1] believed this compound to be a cuprous-cupric sulfite, $Cu_2SO_3.CuSO_3.2H_2O$, but Étard[2] declares that the original conception of it is correct. It is also known in the form of a white isomer (Étard[3]).

Berzelius[4] recognized the existence of cuprous sulfate in solution as probable from the fact that cooling a mixture, made by passing sulfur dioxide into hot cupric sulfate solution, produces a slight precipitate of metallic copper on cooling. This precipitate he attributed to a decomposition in the sense of the equation: $Cu_2SO_4 \longrightarrow Cu + CuSO_4$. Two derivatives of cuprous sulfate were made before the mother-substance, itself, was isolated. Joannis[5] prepared a carbon monoxide addition product, $Cu_2SO_4.(CO)_4.H_2O$, by reduction of copper sulfate with copper in the presence of carbon monoxide. An ammoniated compound was prepared by Pechard[6] by reduction of cupric sulfate in ammoniacal solution with hydroxylamine sulfate and precipitating with alcohol, by Bouzat[7] by the action of ammonium sulfate on cuprous oxide in ammoniacal solution, and by Foerster and Blankenberg[8] by electrolysis of an ammoniacal solution of cupric sulfate. It is a white crystalline compound of the formula $Cu_2SO_4.5NH_3$. The free cuprous sulfate cannot be obtained by driving out the gaseous constituents of either of these derivatives; but it has been made by Recoura[9] by the action of cuprous oxide on methyl sulfate:

$$Cu_2O + (CH_3)_2SO_4 \longrightarrow Cu_2SO_4 + (CH_3)_2O$$

It is described as a grayish white powder, stable in dry air and to heat (at least up to a temperature of 188°, since it was made by boiling with an excess of methyl sulfate), but it is quickly decomposed by moisture and in the sense supposed by Berzelius:

$$Cu_2SO_4 + aq \longrightarrow Cu + CuSO_4 + 21\text{Cal.}$$

Acid cuprous thiosulfate, shining, golden needles, prepared by adding a solution of cupric sulfate to a solution of somewhat more than two mols of sodium thiosulfate, falls partly within this class. Its formula is $Cu_2H_4(S_2O_3)_3$. Cuprous metaphosphate in solid solution in excess of metaphosphoric acid was prepared by Auger.[10] Cuprous acetate is briefly mentioned by Pechard[3] as a white crystalline compound, $Cu_2(C_2H_3O_2)_2$,

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[1] *Pogg. Ann.*, **67**, 245 (1846).

[2] *Compt. rend.*, **95**, 36 and 137 (1882).

[3] *Loc. cit.*

[4] *Lehrbuch*, 4 Aufl., **4**, 562 (1836).

[5] *Compt. rend.*, **125**, 948 (1897).

[6] *Ibid.*, **136**, 504 (1903).

[7] *Ibid.*, **146**, 75 (1908).

[8] *Ber.*, **39**, 4428 (1909).

[9] *Compt. rend.*, **148**, 1105 (1908).

[10] *Ibid.*, **144**, 199 (1907).

resulting from reduction of cupric acetate in ammoniacal solution with hydroxylamine sulfate. Ammoniated cuprous formate, $Cu_2(HCO_2)_2.4NH_3.1/2H_2O$, and ammoniated cuprous benzoate, $Cu_2(C_7H_5O_2)_2.5NH_3$, were prepared by Joannis[1] by the action of the ammonium salts of the respective acids on cuprous oxide—both reagents in liquid ammonia solution.

Experimental.

The cuprous salts of some organic acids were desired for purposes which, if accomplished, will be reported later, and an attempt was made to prepare the oxalate by reducing the cupric compound with sulfur dioxide in the presence of oxalic acid or of alkali oxalate. No change could be obtained, possibly on account of the very slight solubility of the cupric oxalate, but, when the latter was dissolved in ammonia and sulfur dioxide was passed in to acid reaction, some interesting color changes and precipitations took place, and there was left an insoluble mixture containing a brown substance now believed to be the desired salt. This procedure was not studied, since a new and simpler process was found.

Cuprous sulfite was sprinkled little by little into a hot solution of an excess of oxalic acid; the solid changed from bright red to brown and much sulfur dioxide was evolved. The precipitate was almost as fine and difficult to filter as calcium oxalate, but became coarser by continued warming. It was filtered off, washed with water and finally with alcohol and tested qualitatively, as follows:

1. Hydrochloric acid, diluted (1:2), was freed from dissolved oxygen by warming in a stream of carbon dioxide and a little of the compound was thrown into the hot acid while still protected from air by the stream of gas. Immediate solution took place, indicating absence of free copper and only a faint color was present, indicating absence of cupric salt.

2. The compound dissolved in concentrated ammonia with considerable blue color which rapidly increased in intensity; that there was no free copper in the substance was proven by the absence of insoluble residue.

3. Warm dilute (1:15) nitric acid used in small quantity decomposes the substance, forming copper and copper nitrate. The solution, freed from copper by hydrogen sulfide, showed the presence of oxalic acid in large quantity.

4. Decomposed with a few drops of concentrated nitric acid and dissolved in water, the solution gave no precipitate with barium chloride, showing absence of sulfur compounds.

5. With cold, very dilute, sulfuric acid the compound remains unchanged, but it decomposes instantly on warming to about 30°, giving cupric oxalate and copper.

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[1] *Compt. rend.*, **138**, 1499 (1904).

6. Dilute nitric acid (1:15) does not change it in the cold but oxidizes it to copper nitrate by heating.

7. A sample of about 2 g. was heated in a water-jacketed air bath (about 95°) for two hours and changed in color to a dull, dark gray. This substance, when thrown into cold dilute nitric acid, changed back to the brown without any green or blue color showing in the liquid or in the solid.

8. Heated alone in a crucible, the substance changes to gray, then to greenish gray giving off traces of water, and then decomposes suddenly, almost explosively, scattering so that no residue remains in the crucible. (Silver oxalate explodes if heated quickly.[1])

Quantitative determination of the copper was made by decomposing it in a crucible with a few drops of slightly diluted nitric acid, evaporating and igniting.

0.3393 and 0.3003 g. gave 0.2148 and 0.1911 g. CuO; found: 50.57 and 50.82% Cu; Calc. for $Cu_2C_2O_4$: Cu, 53.89%; for $Cu_2C_2O_4.2H_2O$: Cu, 50.61%.

The gray sample mentioned above was analyzed with the results:

0.1132 and 0.1317 g. gave 0.0717 and 0.0872 g. CuO; found: 50.70% and 50.82% Cu.

From this, taken in connection with its behavior with dilute nitric acid, the gray substance is of the same composition as the brown.

Attempts were made to find the reducing value of the oxalic acid radical by suspending the substance in hot water, passing hydrogen sulfide through and gradually adding dilute hydrochloric acid. The excess hydrogen sulfide was removed from the filtrate by heating in a stream of carbon dioxide and the solution was titrated with permanganate. Sharp end points were obtained, but the results were very erratic, all of them, however, indicating much greater reducing power than calculated for the formula $Cu_2C_2O_4.2H_2O$, or even for the anhydrous salt formula. The substance was then decomposed in the presence of an excess of calcium nitrate with dilute nitric acid, and calcium oxalate was precipitated with an excess of ammonia. The oxalate was then titrated as usual.

The factor for the permanganate was cc. × 1.0967 = cc. 0.1 *N.* 0.2339 and 0.2107 g. required 23.14 and 20.85 cc.; found: 47.53% and 47.55% C_2O_4.

The complete analysis, as far as carried out, is Cu 50.69, C_2O_4 47.54; Calc. for $Cu_2H_2(C_2O_4)_4$: 51.14, 47.25.

A hot water extract of the salt was found to be acid to methyl orange, though this may have been due to hydrolysis rather than to acidity of the salt.

What is apparently the same substance can also be prepared by digesting cuprous oxide with a solution of two and one-half parts of oxalic

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[1] Richter's "Organic Chemistry," 3^{a} *Am. Ed.*, Vol. I, 433–4.

acid. A sample made by digesting 4 g. of the oxide with the acid for three hours was analyzed for copper:

0.2256 g. gave 0.1156 g. CuO; found: Cu 50.95%.

The reactions of many other organic acids on cuprous sulfite have been tried but, in all cases, more or less green coloration has indicated the formation of cupric compounds. Apparently, the solubility of the cuprous compound first formed is chiefly responsible for the success of the experiment. The appearance of the insoluble portions obtained in some of the experiments gives encouragement to the hope that they can be used for further transformations as cuprous salts.

Conclusions.

1. Attention has been called to an erroneous statement common in text-books of general chemistry.
2. A new method for the preparation of cuprous salts of oxygen acids has been devised, and the probable conditions of its applicability have been indicated.
3. A new compound of the class has been prepared, some of its properties described, and its probable formula determined.

LEXINGTON, KY.

[HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK CITY.]

A PRECIPITANT FOR AMMONIA.

(A SUBSTITUTE FOR NESSLER'S REAGENT.)

BY SARA STOWELL GRAVES.

Received March 3, 1915.

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I. Introduction.

Nessler's reagent for ammonia, developed in the early part of the last century, was applied to water analysis in 1867. It has stood the test of time and has come into wide use, particularly in physiological work. But with the development of colorimetry, its disadvantages, as well as its value, have become apparent and innumerable modifications of the reagent have resulted. Its instability and tendency to produce a cloud in dilute solutions are the chief difficulties. Recently efforts have been made to apply the reagent in micro-Kjeldahl[1] work (without previous distillation) with varying degrees of success, the precipitate due to salts making the accurate matching of colors extremely hard.

A probable explanation of why the colored solution produced by Nessler's reagent becomes cloudy, especially in the presence of salts, may be found in the following considerations:

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[1] Folin and Farmer, *J. Biol. Chem.*, **11**, 493 (1912); Gulick, *Ibid.*, **18**, (1914); Bock and Benedict, *Ibid.*, **20**, 47 (1914).