# THE REACTION BETWEEN COPPER AND NITROGEN PEROXIDE.[1]

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As far as can be found in the literature, Sabatier and Senderens[2] are the only scientists who have investigated this reaction. They prepared powdered copper by the reduction of cupric oxide in a stream of hydrogen or of carbon monoxide, preferably the former. When a stream of nitrogen peroxide which had been purified by allowing it to pass through a litharge and then a phosphorus pentoxide tower, was allowed to pass over this copper at a temperature of $25°$, they reported the formation of a compound, $Cu_2NO_2$. This compound was unaffected in dry air, evolved nitrogen peroxide at $70°$, leaving a residue of copper and copper oxide, and when put into water reacted violently with the evolution of nitric oxide and the formation of cupric nitrate and a small quantity of cupric nitrite. *Sixty per cent. of the copper was found in the free state* in the undissolved residue.

This apparent failure of the compound to behave as a unit and the unlikelihood of the valence relations as indicated by the assigned formula suggested further research. It was also hoped that a study of the formation of this compound might throw some light upon the so-called "induction period" of the action of nitric acid upon copper.

## Experimental.

The plan of this investigation was to prepare pure nitrogen peroxide, to pass it over pure copper powder at a temperature of $25°$ and to study the products formed.

## I. Preparation of Materials.

(a) **Nitrogen Peroxide.**—Crude nitrogen peroxide was prepared by condensing in a freezing mixture the vapors evolved when c. p. nitric acid reacts with c. p. arsenious oxide. Nitrous anhydride was oxidized by passing oxygen through the liquid until the deep green color had been displaced by the light straw color of nitrogen peroxide. Nitric acid was removed by fractional distillation in all glass apparatus followed by double distillation over an excess of phosphorus pentoxide, the vapor of nitrogen peroxide being led through a tube containing first litharge and second phosphorus pentoxide and finally condensed in the bulb from which it was to be used.

(b) **Finely Divided Copper.**—An attempt was made to prepare copper by displacement from copper sulfate by zinc dust. An impure product such as Mylius and Fromm[3] have described, was secured. The anomalous behavior of this product with nitrogen peroxide is probably due to the presence of hydrated cuprous oxide.

[2] Sabatier and Senderens, *Ann. chim. phys.*, [7] (A) **7**, 399 (1896); *Bull. soc. chim.*, [3] **9**, 669 (1893); *Compt. rend.*, **115**, 236 (1892); **116**, 756 (1893).

[3] Mylius and Fromm, *Ber.*, **27**, 647 (1894).

For purposes of comparison, copper was prepared by 2 entirely independent methods. In the first method pure electrolytic test sheet copper was dissolved in c. p. nitric acid, the solution evaporated to dryness and the residue ignited for 3 hours with a blast lamp. The copper oxide secured contained 81.71% copper. No impurities were present which would not volatilize during reduction. The finely divided copper was prepared just previous to each run by reduction with carbon monoxide of a weighed sample of the copper oxide. The copper was kept in an atmosphere of dry nitrogen with which the reducing agent was displaced. Exposure to the air results in the immediate formation of a superficial coating of one of the oxides of copper.

The second method employed for preparing copper was carried out as follows: Chemically pure cuprous chloride was dissolved in conc. c. p. hydrochloric acid and reduced until colorless by heating with electrolytic test copper. The solution was then filtered through an acid-washed asbestos pad into distilled, oxygen-free water. The precipitated cuprous chloride was filtered off and reprecipitated in the same manner. The cuprous chloride was then dissolved in dil. hydrochloric acid and the colorless solution poured slowly and with stirring into a dilute solution of sodium hydroxide. The reaction which occurs may be represented as follows: $8CuCl + 8NaOH \longrightarrow 4Cu_2O, H_2O + 8NaCl + 3H_2O$. The insoluble hydrated cuprous oxide was washed by decantation until the alkalinity was completely removed and a 1-gram sample dissolved in nitric acid showed no cloudiness when treated with silver nitrate. The cuprous oxide was then filtered and dried *in vacuo* over phosphorus pentoxide. It was free from sodium. The copper content of the 3 samples prepared was found to be 87.24%, 85.9% and 85.7%, respectively. The average composition corresponds fairly closely to the theoretical composition for $4Cu_2O, H_2O$ (copper = 86.11%). The differences in composition are evidently due to the temperature and method of drying of the product. A higher temperature gives a slightly darker product which contains a higher percentage of copper. Powdered copper was prepared from the oxide by reduction with carbon monoxide in the manner explained above.

It may be remarked here that the literature on the composition of the yellow hydrated form of cuprous oxide is somewhat indefinite. Mitscherlich[1] reports a compound of the formula $4Cu_2O, H_2O$. Gröger[2] believes it to be an amorphous cuprous oxide gel containing different amounts of water. The hydrated oxide has never been secured in a definite crystalline form. The results reported here, however, appear to confirm the work of Mitscherlich.

(c) **Carbon Monoxide.**—The results of Graham[3] and of Bartlett and Merrill[4] show that copper may absorb a considerable volume of hydrogen. Moreover, this occluded hydrogen is very difficult to remove even on long heating in an inert atmosphere. Hence, it was deemed much safer to reduce the oxide with carbon monoxide which was not known to be absorbed or to form any compound directly with copper.

Carbon monoxide was prepared by adding 50 g. of crystalline sodium formate to a cold mixture of 150 g. of water and 300 g. of concd. sulfuric acid. It was only necessary to warm this solution to secure a steady stream of carbon monoxide. The impurities, consisting of acid fumes and moisture, were removed by bubbling the gas first through conc. sodium hydroxide solution and lastly through sulfuric acid. It was further dried by passing through a column of phosphorus pentoxide.

(d) **Hydrogen.**—In order to duplicate the work of Sabatier and Senderens and to

[1] Mitscherlich, *J. prakt. Chem.*, **19**, 450 (1840).

[2] Gröger, *Z. anorg. Chem.*, **31**, 326 (1902); Abegg and Auerbach, "Handbuch der Anorg. Chem.," Bd. II, Abteilung 1, **1907**, pp. 583-4.

[3] Graham, *Phil. Mag.*, [4] **32**, 523 (1866).

[4] Bartlett and Merrill, *Am. Chem. J.*, **17**, 185 (1895).

ascertain the cause of the discrepancy between their work and that reported here, it was necessary to prepare pure hydrogen for use as a reducing agent for the copper oxide. This was done by allowing 8% hydrochloric acid which contained a trace of copper sulfate in solution to react with chemically pure zinc. The hydrogen was passed through a train of wash bottles containing in order, saturated solution of mercuric chloride, acidified potassium permanganate, strong sodium hydroxide solution and lastly sulfuric acid.

(e) Nitrogen.—After reduction, the copper was cooled in nitrogen, with which it does not react. The gas was prepared from air using an apparatus like that described by Badger,[1] and was washed with conc. sulfuric acid, colorless hydrochloric acid solution of cuprous chloride, alkaline pyrogallate, and finally with conc. sulfuric acid again. The cuprous solution remained colorless after weeks of use, showing that all oxygen had been removed; argon, etc., of course, remained.

## II. The Apparatus Used.

As shown in Fig. 1 the apparatus consisted of a reaction tube through which could be led carbon monoxide, hydrogen, atmospheric nitrogen or nitrogen peroxide as desired. All connections above the dotted line were rubber tubing, all below were fused
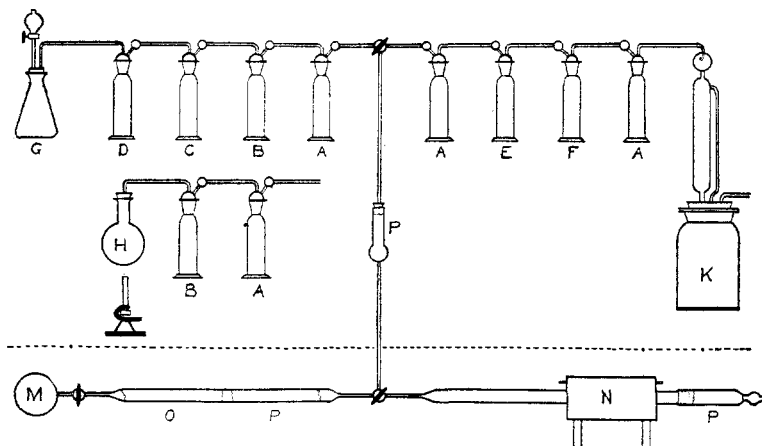


Fig. 1.—A, conc. $H_2SO_4$; B, conc. NaOH; C, acidified $KMnO_4$ solution; D, saturated $HgCl_2$ solution; E, alkaline pyrogallol; F, solution CuCl in HCl; G, hydrogen generator; H, CO generator; K, nitrogen generator; M, nitrogen peroxide; N, electric furnace; O, litharge; P, phosphorus pentoxide.

glass wherever possible. Connections which had to be changed frequently were of tight glass sleeves with a final seal of dry paraffin. Careful tests showed that paraffin does not react with nitrogen peroxide.

## III. A Sample Run.

The copper oxide was weighed into 2 boats and placed in the reaction tube near the 3-way stopcock. The phosphorus pentoxide tube was slipped on and sealed. The 3-way cocks were turned so that carbon monoxide could be passed over the oxide. Carbon monoxide was now passed through the tube until the air was displaced. Then the

[1] Badger, *J. Ind. Eng. Chem.*, 11, 1052 (1919).

electric furnace was shoved over the portion of the tube containing the oxide and a gentle heat applied. The temperature was regulated by a lamp bank in series with the furnace and the reduction accomplished at the lowest possible temperature. Then the stopcock at the upper part of the illustration was turned and the carbon monoxide displaced by nitrogen. The furnace was now moved to the right and the current of nitrogen continued until all traces of moisture were swept out of the reaction tube. After the tube had cooled to room temperature (25–27°) the lower stopcock was turned and the nitrogen peroxide allowed to pass over the copper. In the case of copper reduced by carbon monoxide it was often 3 or 4 hours before a noticeable darkening took place, several days being required for the reaction; while copper reduced by hydrogen reacted immediately and at a fairly rapid rate. The copper first darkened to a chestnut-brown and finally turned green in places. Apparently, the same end product was secured with copper reduced by hydrogen or by carbon monoxide.

## IV. Experimental Results.

The first experiments were to determine the quantity of nitrogen peroxide which would unite with copper, this being shown by the gain in weight. The results are given in Table I.

TABLE I.

Absorption of Nitrogen Peroxide by Copper.

(Preliminary Experiments.)

| Substance. | Reduced by. | Wt. Cu. taken. G. | Product obtained. G. | Gain in wt. G. | N. and O. in product. %. | Time of action. Days. |
|---|---|---|---|---|---|---|
| CuO | H₂ | 0.5259 | 0.6362 | 0.1103 | 17.3 | 1/2 |
| | | 0.4406 | 0.5666 | 0.1260 | 22.2 | 2/3 |
| | | 0.6195 | 0.6666 | 0.0471 | 7.1 | 1 |
| 4Cu₂O,H₂O | CO | 0.1783 | 0.2074 | 0.0291 | 14.1 | 1/8 |
| | | 0.2051 | 0.2233 | 0.0182 | 8.2 | 1/8 |
| | | 0.2694 | 0.3699 | 0.1005 | 27.2 | 7 |
| | | 0.1658 | 0.2352 | 0.0694 | 25.2 | 7 |
| | | 0.2806 | 0.3332 | 0.0526 | 15.8 | 2 |
| | | 0.1476 | 0.1712 | 0.0236 | 13.8 | 2 |

The gain must be either nitrogen or oxygen or both, since these are the only elements present. The rate and amount of gain in weight was very variable, ceasing in many cases in 2 or 3 days.

The absorption of nitrogen peroxide by copper from a saturated solution of nitrogen peroxide in dry benzene was tried. In spite of the increased concentration of nitrogen peroxide the amount absorbed never exceeded 5%. Hence this method was discarded.

Since preliminary experiments failed to show any stoichiometric relation between the weight of copper and of gain in weight, a ratio between the number of atoms of nitrogen and the number of atoms of oxygen ab-

sorbed, was sought. By flooding the product with a concentrated solution of sodium hydroxide, all evolution of gas could be prevented and the nitrogen retained in the form of nitrate or nitrite. Devarda's method for the determination of total nitrogen proved satisfactory. The amount of copper and of nitrogen being known, the oxygen was determined by difference. From these values the atomic ratios were calculated.

In the final set of experiments, 2 sets of absorptions were run simultaneously. After the stated time of absorption, one of the boats was withdrawn and the contents immediately analyzed; the other was placed in a desiccator over calcium chloride and analyzed after the period stated. The results are given in Tables II and III.

TABLE II.

Composition of Product of the Reaction between Copper and Nitrogen Peroxide Immediately on Withdrawing from the $NO_2$.

| | Substance. | Reducing Agent. | Time of action. Days. | Wt. Cu. G. | Wt. product. G. | Gain in wt. G. |
|---|---|---|---|---|---|---|
| 1 | $4Cu_2O, H_2O$ | CO | 8 | 0.2360 | 0.3109 | 0.0749 |
| 2 | $4Cu_2O, H_2O$ | CO | 6 | 0.3798 | 0.4435 | 0.0637 |
| 3 | CuO | CO | 6 | 0.5948 | 0.6797 | 0.0849 |
| 4 | $4Cu_2O, H_2O$ | CO | 6 | 0.3763 | 0.4356 | 0.0593 |
| 5 | CuO | $H_2$ | 1 | 0.8625 | 0.9332 | 0.0707 |

| | N. and O. in product. %. | Wt. N in product. G. | Wt. O in product. G. | Atomic ratio. N to O. |
|---|---|---|---|---|
| 1..... | 24.1 | 0.0168 | 0.0581 | 3.03 |
| 2..... | 14.4 | 0.0143 | 0.0494 | 3.02 |
| 3..... | 12.5 | 0.0190 | 0.0659 | 3.03 |
| 4..... | 13.6 | 0.0138 | 0.0455 | 2.89 |
| 5..... | 7.5 | 0.0152 | 0.0555 | 3.19 |

TABLE III.

Composition of Product of the Reaction between Copper and Nitrogen Peroxide After Standing for the Time Indicated.

| | Substance. | Reducing agent. | Time of action. Days. | Wt. Cu. G. | Wt. product. G. | Gain in Wt. G. |
|---|---|---|---|---|---|---|
| 1 | $4Cu_2O.H_2O$ | CO | 8 | 0.2223 | 0.2692 | 0.0469 |
| 2 | $4Cu_2O.H_2O$ | CO | 6 | 0.3598 | 0.4706 | 0.1108 |
| 3 | CuO | CO | 6 | 0.5079 | 0.6280 | 0.1201 |
| 4 | CuO | CO | 6 | 0.7765 | 0.8979 | 0.1214 |
| 5 | $4Cu_2O.H_2O$ | $H_2$ | 1 | 0.3780 | 0.4282 | 0.0502 |

| | N and O in product. %. | Time of standing. Hrs. | Wt. N in product. G. | Wt. O in product. G. | Atomic ratio. N to O. |
|---|---|---|---|---|---|
| 1................. | 17.4 | 4 | 0.0090 | 0.0379 | 3.68 |
| 2................. | 23.5 | 3 | 0.0230 | 0.0892 | 3.39 |
| 3................. | 19.2 | 2 | 0.0258 | 0.0943 | 3.20 |
| 4................. | 13.5 | Const. wt. | 0.0254 | 0.0960 | 3.31 |
| 5................. | 11.7 | 16 | 0.0101 | 0.0401 | 3.47 |

When the product is analyzed immediately on withdrawing from the nitrogen peroxide, the ratio of the number of atoms is 1 : 3 or that of the

nitrate radical. The product loses weight on being exposed to the air and gives off a gas, nitric oxide or nitrogen peroxide. This loss indicates that the nitrogen peroxide is either adsorbed by the copper or that if a compound is formed it is very unstable. The residues obtained on standing, therefore, must contain some copper oxide which accords with the findings of Sabatier and Senderens.

Furthermore, these experimenters found that 60% of the copper remained in the free state when this product was treated with water. This was confirmed experimentally and indicates that the product is not a compound but rather a mixture. Microscopic examination also showed the product to be composed of metallic particles of copper imbedded in a matrix of brownish material.

The product on being heated to 70° evolves nitrogen peroxide and leaves a residue of copper and copper oxide. Sabatier and Senderens state that approximately $1/3$ of the oxygen present in the product remains in the residue. This evidently means that the residue must be 39% cupric oxide,[1] or 75% cuprous oxide, or some intermediate value if both oxides are present. Only that portion of copper which had been acted upon by nitrogen peroxide would give oxide on being heated or would react with water. The remainder, therefore, might be free copper which checks very closely with the values found.

Further, Sabatier and Senderens state that a sample of copper, on being treated with nitrogen peroxide, gained 2.300 g. in weight and that 0.180 g. of nitric oxide was formed by reduction of the nitrogen peroxide. These figures show that their so-called "nitro copper" contained at least 10% of cuprous oxide or its equivalent in cupric oxide (5.5%)[2] or some intermediate value. Since copper oxide is known to be formed in such quantities, this formula $Cu_2NO_2$ cannot properly be assigned to the product.

Although this formula was given to the product by Sabatier and Senderens, their values do not entirely bear this out. Direct combustion gave Cu 73.5%, N 7.3% and O 19.2%, in which the atomic ratio of nitrogen to oxygen is 1 : 2.3. The experiments reported in this paper indicate that the true ratio is 1 : 3 or that of the nitrate radical. On adding water to the product, 90% of the nitrogen is found in the form of nitrate while 10% is in the nitrite form, further showing the presence of nitrate radical. If a nitrate is present, it must necessarily be an anhydrous one. Since the properties do not correspond to those of an-

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[1] Sabatier and Senderen's product was 73.4% Cu, 18.5% O, 8.1% N. If $1/3$ of the oxygen remains 73.4 parts Cu would be combined with 6.2 of O; total 79.6 parts. One part of O corresponds to 8.95 parts $Cu_2O$ or 4.97 of CuO, therefore 6.2 parts O correspond to 75% $Cu_2O$ or 39% of CuO.

[2] The experimental results show that 8.65 g. of product correspond to 2.3 g. of gain; 0.180 g. NO correspond to 0.096 g. of O; 0.096 g. O correspond to 10.0% $Cu_2O$ or 5.5% CuO.

hydrous cupric nitrate which was prepared by Guntz and Mason[1] and since there is always a large excess of copper present, it would seem reasonable to assume the presence of a layer of cuprous nitrate on the surface of the copper.

It may be added, in conclusion, that the results given here would lead one to doubt the existence of the compounds which have been stated to be formed by the action of nitrogen peroxide upon other metals.[2]

## Summary.

1. Hydrated cuprous oxide has been prepared and its copper content found to confirm the formula $4Cu_2O.H_2O$.

2. It has been shown that copper nitroxyl, $Cu_2NO_2$, is not formed by the action of nitrogen peroxide on copper, but that the product is a mixture.

3. The presence of the nitrate radical is indicated and it is suggested that the reaction may be the formation of anhydrous cuprous nitrate on the surface of the copper.

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## SOLUBILITY VI. THERMODYNAMIC RELATION BETWEEN SOLUBILITY AND INTERNAL PRESSURE.

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We are accustomed to attack problems involving molecular weights and equilibria in gaseous systems upon the basis of the laws expressing the behavior of the ideal gas. In like manner do we attack the problems presented by solutions, including molecular weights, solubility, solvation and dissociation, upon the basis of some "law" supposed to express the behavior of the "ideal solution." Van't Hoff's law for osmotic pressure has served so well for the derivation of useful relationships that its historical value and plausible analogy with the gas law have obscured its inadequacy for dealing with all but very dilute solutions. Since we are always inclined to ascribe deviations from our ideal law to changes in molecular species, that is, to chemical changes, it is important that our ideal law be one which is obeyed by all systems in which chemical changes are absent, a criterion by no means fulfilled by van't Hoff's law.

It has been pointed out that Raoult's law is obeyed by more solutions and through much wider ranges of concentration than van't Hoff's law[3] besides having a simpler kinetic basis. There is, therefore, more justifica-

[1] Guntz and Mason, *Bull. soc. chim.*, 5, 1104; 7, 313 (1909).

[2] Sabatier and Senderens, *loc. cit.*

[3] G. N. Lewis, THIS JOURNAL, 30, 668 (1908); see also Hildebrand, *ibid*, 38, 1453 (1917).