ten to fifteen minutes and then the alcohol was distilled. This step was found desirable because otherwise charring occurred when acetone was added to recrystallize the product. The residue was recrystallized from boiling acetone; yield, 106.3 g. (88%). By concentrating the acetone filtrate, a second crop of crystals (4.5 g.) was obtained, bringing the total yield up to 92%. McCombie and Purdie[2] made trichlorotriethylamine hydrochloride directly from triethanolamine and thionyl chloride, using chloroform as a solvent, and obtained a yield of 73.8%.

The free trichlorotriethylamine, obtained in the usual way from the hydrochloride, had a b. p. of 143–144° at 15 mm., which is 6° higher than that reported by McCombie and Purdie[2] at the same pressure.

Anal. Calcd. for $C_6H_{12}Cl_3N$: Cl, 52.1; mol. wt., 204.5. Found: Cl, 51.6, 51.8; mol. wt. (benzene), 205.9.

The amine was almost colorless when freshly distilled, but turned to a light brown color on standing for sixty hours. The color darkened on longer standing. Crystals, which were not identified, appeared in the liquid after standing for a month. Ether solutions of the amine darkened more slowly and no crystals were observed. Instead, a small amount of dark brown material was deposited from an ether solution which had been kept for two months. No attempt was made to identify this material.

[2] McCombie and Purdie, *J. Chem. Soc.*, 1217 (1935).

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RECEIVED SEPTEMBER 3, 1938

The Catalytic Reaction between Sodium Nitrite and Dichlorodiethylenediamine Cobaltic Chloride

BY J. P. MCREYNOLDS AND JOHN C. BAILAR, JR.

In the course of stereochemical studies on the complex inorganic compounds, it was observed that racemic dichlorodiethylenediamine cobaltic chloride reacts almost instantaneously with sodium nitrite according to the equation $[Coen_2Cl_2]^+ + 2NaNO_2 \longrightarrow [Coen_2(NO_2)_2]^+ + 2NaCl$[1] but that the material which has been resolved into its optical antipodes reacts very slowly. This resolution is carried out through the α-bromocamphor-π-sulfonate, which is reconverted to the chloride by means of hydrochloric acid in alcohol and ether. The active product is then washed with alcohol and ether.[2] It was found that washing the racemic material with alcohol and ether caused it to lose its reactivity toward sodium nitrite. The washings contained cobaltous ion. That cobaltous ion catalyzes the reaction in question was demonstrated easily.[3]

Werner has noted[4] briefly that traces of acids catalyze this reaction but no other example of such catalytic substitution has been reported for compounds of this type. A study was therefore made to determine the mechanism of the reaction. Two compounds which seemed possible intermediates are sodium cobaltinitrite, $Na_3Co(NO_2)_6$, and sodium cobaltonitrite, $Na_2Co(NO_2)_4$. Sodium cobaltinitrite was found to have no catalytic effect in this reaction. On the other hand, the cobaltonitrite ion could be precipitated (as the potassium salt) from mixtures which had been catalyzed artificially by addition of cobaltous ion. This seems to point to the intermediate formation of sodium cobaltonitrite.

The mechanism postulated for this catalysis must explain the very rapid replacement of chloro by nitro groups and the apparent absence of oxygen to cobalt linkages at any step in the reaction. This latter requirement is evidenced by the fact that at no time is there any indication of a red coloration such as is found in nitrito cobalt compounds. The isolated intermediate and the almost instantaneously formed product both have the yellow color characteristic of the nitrogen to cobalt bond. Further, nitrite complexes of trivalent cobalt have been prepared and characterized. They are stable in solution for a considerable period, changing to nitro complexes quite slowly.

The explanation offered here involves a shift of the electrons upon the nitrogen to allow it to form a coördinate bond to both trivalent and bivalent cobalt. This is a very unstable arrangement and is broken up immediately, leaving the nitrogen attached to the trivalent cobalt. This latter step seems quite logical since the trivalent cobalt complexes are very much more stable than those of bivalent cobalt. It must be assumed that

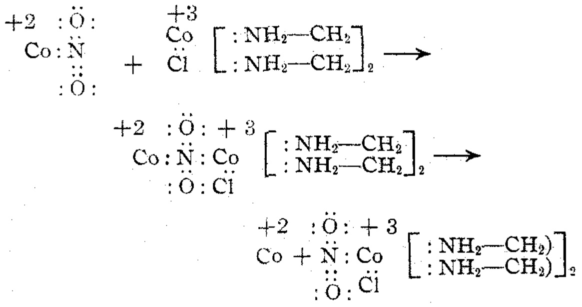
[1] The symbol "en" represents ethylenediamine.

[2] Bailar and Auten, THIS JOURNAL, **56**, 774 (1934).

[3] The traces of cobaltous ion present in the racemic material evidently are produced during the conversion of the *trans* form of the complex to the *cis* form by evaporation of the solution and subsequent heating of the residue in the oven. A dry sample of optically active material unreactive to sodium nitrite became reactive after several hours of such heating. It lost a large part of its optical activity during the heating.

[4] Werner, *Ber.*, **34**, 1734 (1901).

one chloride group ionizes from the cobaltic complex momentarily or that the coördination number of the cobaltic ion may exceed six, at least for an instant. On the first assumption, the mechanism of the catalytic reaction may be as follows



It is possible that the familiar coördination compounds of metal ions with ethylene compounds and with azo compounds are formed in the same way—by the shift of a pair of electrons from the double bond to an adjacent atom.

The catalyzed reaction, when applied to optically active starting material, lends further evidence in favor of such a mechanism since the product always has a much lower activity than that formed through the uncatalyzed reaction.

A further investigation was carried out to determine the possibilities of extending this type of catalysis to other substitutions. All attempts to catalyze the substitution of oxalate or thiocyanate groups for chloro groups by the addition of metallic ions failed to show positive results. The ions used were nickelous, ferric, aluminum, stannous and cobaltous, all of which tend to form unstable complex ions. This study showed that cobaltous ion is unique among those tried in producing the catalytic substitution of the nitro group.

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RECEIVED JULY 25, 1938

Ammonium Chloride–Sodium Sulfide Solutions for Organic Nitro Reductions and for Inorganic Qualitative Analysis

BY M. J. MURRAY AND D. E. WATERS[1]

Two disadvantages in the use of ammonium sulfide as reducing agent for organic nitro compounds have been: (1) the length of time consumed in saturating the ammonium hydroxide with hydrogen sulfide, and (2) the indefinite amounts of materials used. Both of these disadvantages are overcome by preparing a solution containing equivalent amounts of ammonium chloride and crystalline sodium sulfide ($Na_2S \cdot 9H_2O$). This solution is added to the nitro compound dissolved in ammonium hydroxide or alcohol and ammonium hydroxide. The mixture can be heated at once until excess hydrogen sulfide has escaped, and from this point the isolation of the reduction product is the same as in standard procedures.

The reagent was tested most thoroughly on the reduction of *p*-nitrobenzoic acid. The yields were consistently higher than on parallel runs using hydrogen sulfide and ammonium hydroxide. The melting point and the neutralization equivalent showed the product to be one of high purity. Reduction by sodium polysulfide, sodium sulfide alone, and sodium hydrogen sulfide gave yields inferior as to both quality and quantity. Other compounds reduced by the sodium sulfide–ammonium chloride reagent were: *p*-nitrophenylacetic acid,[2] 3-nitrophthalhydrazide,[3] and *m*-dinitrobenzene.[4] In each case the yield equaled or exceeded that reported in the reference given.

A second use of this rapid method for the preparation of ammonium sulfide is in the making up of solutions of ammonium polysulfide for inorganic qualitative analysis. A solution of approximately known strength can be prepared in a few minutes as follows: equivalent amounts of ammonium chloride and crystalline sodium sulfide ($Na_2S \cdot 9H_2O$) are dissolved in a small volume of water, powdered sulfur is added, and the mixture warmed to promote solution. Then ammonium hydroxide is added and the solution diluted to the desired strength. Concentrations are not given here because textbooks do not agree as to the optimum strength.[5] Attention should also be directed to the fact that few laboratory assistants make up the ammonium polysulfide solutions as strong as called for because of the difficulty of completely saturating the ammonium hydroxide with hydrogen sulfide. For this reason solutions prepared by the short method just described will be, in general, considerably more concentrated than ordinarily

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(1) Present address, Transylvania College, Lexington, Ky.

(2) "Organic Syntheses," Coll. Vol. I, 1932, p. 44.

(3) Huntress, Stanley and Parker, *J. Chem. Ed.*, **11**, 143 (1934).

(4) Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," 22nd edition, The Macmillan Co., New York, N. Y., 1932, p. 162.

(5) Curtman and Lehrman, *J. Chem. Ed.*, **6**, 2203 (1929), recommend a definite strength but it is doubtful whether such a high concentration is advisable in all procedures.