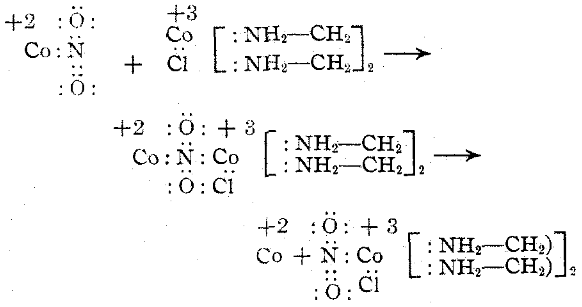
one chloride group ionizes from the cobaltic complex momentarily or that the coördination number of the cobaltic ion may exceed six, at least for an instant. On the first assumption, the mechanism of the catalytic reaction may be as follows



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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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.

made up, and it may be advisable to redetermine which strength is best for the particular scheme of analysis being used.

Ammonium polysulfide prepared by the rapid method has been used successfully in this Laboratory over a period of three years for the separation of Divisions A and B in Group II.

DEPARTMENT OF CHEMISTRY
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The Interaction between Methylene Radicals and Hydrogen

BY CHARLES ROSENBLUM

The photolysis of ketene in the presence of hydrogen points to a reaction between methylene radicals and hydrogen, in contrast with the relative stability[1] of methylene toward ketene itself and toward ether vapor. The reactants, 100 mm. of ketene and 225 mm. of hydrogen, were irradiated in a cylindrical quartz vessel (volume 130 cc.) by a "hot" mercury arc for about forty-five minutes, and the resultant gas mixture analyzed. Although a constricted arc was used throughout, a hydrogen-mercury vapor filter[2] for resonance radiation was interposed as an added precaution against the lamp as a source of hydrogen atoms. A mixture of ethylene and hydrogen did not react when exposed to the arc under these conditions.

Irradiation of ketene alone[3] results in an increase in volume due to the formation of carbon monoxide and ethylene as the sole gaseous products, this increase falling below the theoretical value after longer exposures because attendant polymerization creates a gaseous hydrocarbon deficiency. The reaction which occurs in the presence of hydrogen differs markedly from the above in that it is characterized by a volume decrease. This can be accounted for only if the gaseous hydrocarbon is saturated and some saturated liquid (or solid) hydrocarbons of low vapor pressure are formed, which implies a disappearance of hydrogen.

Analysis confirmed these expectations fully. Of the ketene decomposed in the presence of hydrogen at 35°, 1% yielded methane, 74% was recovered as a gas with an average composition[4] $C_{2.56}H_{7.12}$, and 25% yielded a residue of low volatility. At 200° the methane content corresponded to 9.6% of the decomposed ketene, the gaseous fraction with a mean composition[4] $C_{2.68}H_{7.36}$ represented 69%, and the residue accounted for 21% of the ketene present originally. In both cases, the average composition of the residual polymeric product was C_4H_{10}. The mean composition and quantity of this polymer were deduced from the carbon and hydrogen deficiencies in the balance sheet of initial and final gaseous components of the reaction system. The amounts of condensed product calculated in this manner agreed well with the observed volume decreases.

The experiments indicate that the direct association of methylene radicals and molecular hydrogen to form methane is inappreciable. The profound change in the nature of the products when hydrogen is present suggests that the interaction in question is

$$CH_2' + H_2 = CH_3 + H$$

Such a reaction yielding methyl radicals and atomic hydrogen would account for the formation of saturated and higher molecular weight hydrocarbons.[5] The methylene radical has been represented as energy rich (CH_2') since present accepted views as to bond energies would suggest that the reaction of a normal methylene radical with hydrogen would be endothermic. The energy of the radical must arise from the photoenergy absorbed during the dissociation process.

A secondary source of methyl radicals might be a reaction between methylene radicals and methane already formed

$$CH_2 + CH_4 = 2CH_3$$

This would be less endothermic than the reaction with hydrogen. The low yields of methane, increasing at higher temperatures, do not appear to support this view.

The source of methane is probably an interaction of methyl radicals with hydrogen[6] or hydrocarbons[7] which is known to take place readily at or above 150–160°. The recombination of methyl radicals to form ethane would account for the

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[1] Pearson, Purcell and Saigh, *J. Chem. Soc.*, 409 (1938).

[2] Morikawa, Benedict and Taylor, *J. Chem. Phys.*, **5**, 212 (1937).

[3] Norris, Crone and Saltmarsh, *J. Chem. Soc.*, 1533 (1933); THIS JOURNAL, **56**, 1644 (1934); Ross and Kistiakowsky, *ibid.*, **56**, 1112 (1934).

[4] Shown by cracking over a nickel catalyst in an excess of hydrogen.

[5] Summarized in Bonhoeffer and Harteck, "Grundlagen der Photochemie," Theodor Steinkopff, Dresden-Blasewitz, Germany, 1933, p. 264; also Jungers and Taylor, *J. Chem. Phys.*, **6**, 325 (1938).

[6] Cunningham and Taylor, *J. Chem. Phys.*, **6**, 359 (1938); Taylor and Rosenblum, *ibid.*, **6**, 119 (1938).

[7] Unpublished work of J. O. Smith, Princeton, 1938.