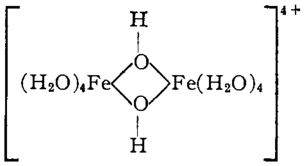
In this way k_{22} is found to be 6.7 × 10^{-3} and 33 × 10^{-3} at 15 and 51°, respectively. These are in reasonable agreement with the corresponding values (4.9 ± 0.9 × 10^{-3} and 25.1 ± 5.8 × 10^{-3}) obtained from the magnetic data. It should be noted that this method is independent of the absorbances observed at 240 mμ and is, therefore, free of the assumptions made with regard to Fe^{3+} and $FeOH^{2+}$ contributing to absorption at this wave length. The method also affords evaluation of the molar absorbancy index a_M, since this is simply 4 divided by the product of C and the intercept. The values for a_M were found to be 8.3 × 10^4 and 2.5 × 10^4 at 15 and 51°, respectively. The corresponding molar absorbancy indices calculated directly from Fig. 9 in which the concentrations of dimer derived from magnetic data are employed, are 10.0 × 10^4 and 1.5 × 10^4.

From this work it is clear that a partially hydrolyzed solution of ferric ions contains a diamagnetic species in substantial amounts. This species, which possesses a characteristic absorption spectrum, is probably, as suggested by Hedström, a binuclear complex



in which exchange interaction between adjacent irons destroys all their paramagnetism. It is to be noted that just prior to precipitation of hydrous ferric oxide the solution contains a large fraction of the iron in the form of this dimer. Furthermore, precipitation occurs without any large change of magnetic moment per atom of total iron. It seems probable, therefore, that hydrous ferric oxide owes its subnormal magnetic moment to the presence of the diamagnetic $Fe_2(OH)_2^{4+}$ built into its structure.

It also seems probable that the low magnetic moment of iron in alkaline glass, observed by Abd-El-Moneim Abou-El Azm[30] may be due in part to dispersion of some type of diamagnetic dimers in the glass, rather than entirely to colloidal ferric oxide. Mattock[31] has recently pointed out that the tendency toward dimerization by metal ions increases with the probable increase of covalence in metal–hydroxyl bonds. Without disputing this correlation, it should be pointed out, however, that metal–metal covalent bonds may influence the formation of dimers, and that no amount of covalence between metal and one or more hydroxyls could be expected to reduce the magnetic moment of the dimer, $Fe_2(OH)_2^{4+}$, below that for one unpaired electron.

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(30) Abd-El-Moneim Abou-El-Azm, *J. Soc. Glass Technol.*, **38**, 101T (1954).

(31) G. Mattock, *Acta Chem. Scand.*, **8**, 777 (1954).

Evanston, Illinois

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Studies on the Raschig Synthesis of Hydrazine: The Reaction between Aqueous Chloramine and Ammonia Solutions

By Mark M. Jones, L. F. Audrieth and Ervin Colton

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Although the reaction between chloramine and ammonia in aqueous solutions containing gelatin is shown to occur in the absence of permanent base, addition of sodium hydroxide to such a synthesis solution increases the yield of hydrazine. A spectrophotometric investigation of the synthesis solutions showed no trace of hypochlorous acid above a *p*H of 7.5. The effect of ammonium salts is shown to be due to a reduction in the basicity of the synthesis solutions. That there is no electrolyte effect in the Raschig synthesis appears probable from these experiments.

We have undertaken to define more specifically some of the factors which influence the yields of hydrazine in the Raschig synthesis. Based upon the experimental work presented in this paper supplemented by consideration of the pertinent literature it may be concluded: (a) that sodium hydroxide is not required in the Raschig synthesis although its presence increases the yield of hydrazine; (b) that hypochlorous acid is not present under conditions employed in the Raschig synthesis, in aqueous or in wet ether solutions of chloramine; (c) that the mechanism for the Raschig synthesis involving direct attack of ammonia by chloramine is to be preferred to any involving hypochlorous acid as an intermediate; and (d) that the influence of ammonium salt addition is due solely to the effect of the ammonium ion in reducing the basicity of the solution.

Experimental

Preparation of Chloramine Solutions.—A cold aqueous solution of chloramine, prepared by mixing aqueous sodium hypochlorite and ammonia in equimolar amounts, was shaken with diethyl ether resulting in the extraction of up to 80% of the haloamine in the non-aqueous phase. The ether extract was then shaken with an equal volume of distilled water and the two liquid layers again separated. Approximately one-half of the chloramine is found in each layer. Aqueous solutions of chloramine were thus prepared covering a large range of concentrations. The solutions were analyzed iodometrically.[1] These solutions were found to be sufficiently stable to ensure that less than 1% of the chloramine suffered decomposition between the time of analysis and the completion of the desired reaction.

Reaction of Chloramine and Ammonia in Aqueous Solution.—Previous work from this Laboratory has shown that the yields of hydrazine formed by interaction of both ammonia[2] and urea[3] with *t*-butyl hypochlorite are markedly increased by the addition of sodium hydroxide to the synthesis solution. Sisler and co-workers[4] have recently shown that good conversions of chloramine into hydrazine can be

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(1) W. Marckwald and M. Wille, *Ber.*, **56**, 1319 (1923).

(2) L. F. Audrieth, E. Colton and M. M. Jones, This Journal, **76**, 1428 (1954).

(3) E. Colton, M. M. Jones and L. F. Audrieth, *ibid.*, **76**, 2572 (1954).

(4) H. H. Sisler, C. E. Boatman, F. T. Neth, R. Smith, R. W. Shellman and D. Kelmers, *ibid.*, **76**, 3912 (1954).

achieved, in the absence of sodium hydroxide, using large excesses of ammonia (*i.e.*, saturated aqueous ammonia at 0°). Information is presented here to define more clearly the role that "permanent base" (NaOH) may play in the Raschig synthesis.

Solutions of chloramine in distilled water and aqueous ammonia–gelatin solutions, both with and without added sodium hydroxide, were mixed in the desired proportions and heated. All experiments were carried out under identical conditions to assure comparable results in the yields of hydrazine. To 100 ml. of a solution containing 13.9% NH_3 and 1.36% gelatin, 50 ml. of a NH_2Cl solution of known molarity was added. A comparable series of experiments was carried out in which 10 ml. of a 1 molal NaOH solution was added to each reaction mixture. Each solution was heated on the steam-bath for exactly 20 minutes,[5] after which it was removed and cooled to room temperature. A 10-ml. aliquot was analyzed by the direct iodate[6] procedure and the total hydrazine yield calculated.

Results are presented graphically in Fig. 1 in which hydrazine yields are plotted as a function of the NH_2Cl/NH_3 mole ratio. It is evident that chloramine does react in aqueous solution with ammonia to yield hydrazine, but that such yields are significantly larger in the presence of added permanent base, especially at the higher NH_2Cl/NH_3 mole ratios. Although the Raschig synthesis takes place in aqueous solution only in the presence of hydroxyl ion (regardless of its source) addition of sodium hydroxide aids in keeping the *p*H in the proper alkaline range even when relatively large amounts of ammonia have been driven off by heating. Reference is made to the fact that presence of gelatin makes it possible to eliminate the effects of trace dissolved metal impurities upon hydrazine yields.

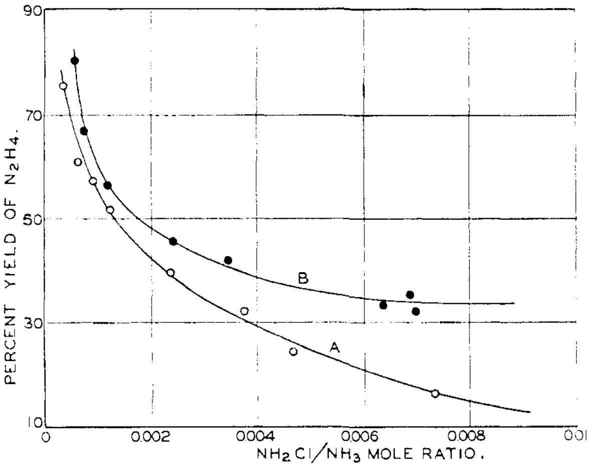

Fig. 1.—Reaction of chloramine with aqueous ammonia. Effect of chloramine/ammonia ratios on the yield of hydrazine in solutions containing no caustic (A) and added caustic (B).

Spectrophotometric Examination of the Synthesis Solution.—Wiberg and Schmidt[7] have stated that formation of hydrazine in the Raschig synthesis is due (a) to hydrolysis of chloramine to hypochlorous acid followed (b) by the action of the latter in effecting oxidation of ammonia to hydrazine. This proposed mechanism is based upon the observation that anhydrous ethereal solutions of chloramine and ammonia yield no hydrazine until water is added.

A spectrophotometric examination of the various components alleged and believed to be present in the synthesis solution showed (a) that the absorption spectrum of a wet ether solution of chloramine is very similar to that of an aqueous solution giving an absorption maximum at 2450 Å.[8,9] and (b) that at a *p*H above 7.5 aqueous solutions of hypochlorite containing an excess of ammonia show only the presence of chloramine, neither hypochlorite, di-, nor trichloramine being detectable. A solution of hypochlorous acid, prepared by acidifying an aqueous solution of sodium hypochlorite to a *p*H of 6.5 with hydrochloric acid was found to give a pronounced absorption between 2800 to 3100 Å. with a maximum at about 2900 Å. A solution of hypochlorous acid in wet ether was also prepared; its spectrum was found to be completely different from that of chloramine in wet ether. It is thus evident that chloramine is in fact the important reactant leading to the formation of hydrazine. The observations of Wiberg and Schmidt are readily explainable in terms of hydroxyl ion formation by reaction of ammonia and water. If hydroxyl ion is merely necessary as catalyst then presence of water in the ether solution would be required for the synthesis of hydrazine.[10]

Role of Ammonia Salts.—It has been stated that the addition of ammonium salts to the Raschig synthesis liquor reduces the yield of hydrazine.[11] It was suspected that the acidic nature of the ammonium ion might be responsible for these observations and a series of experiments was designed to test this hypothesis. A standardized procedure for the synthesis of hydrazine was developed in which ammonia and sodium hypochlorite solutions were mixed and heated for ten minutes on a hot plate. The ratios of ammonia to hypochlorite and of hydroxide to hypochlorite were kept constant at 30:1 and 1.46:1, respectively. The initial concentrations were $[OH^-]$ = 0.174 molar, $[OCl^-]$ = 0.119 and $[NH_3]$ = 3.57 molar. Each solution was made up to a total volume of 200 ml. with distilled water. To each sample 0.5 g. of gelatin was added. Weighed amounts of NH_4Cl were introduced into one series of experimental samples; weighed amounts of sodium chloride were added to a second series. Finally, equivalent amounts of NH_4Cl and NaOH were introduced into samples representing a third group of runs. The yields of hydrazine were found to decrease after a small amount of ammonium salt had been added. This amount was approximately equivalent to the original $[OH^-]$ of the solution. In the third set of experiments, in which sodium hydroxide was added exactly equivalent to the ammonium chloride, the yield of hydrazine was unaffected. Typical data for one such group of experiments are presented in Fig. 2. It thus appears that ammonium salts act primarily as added acidic substances. The fact

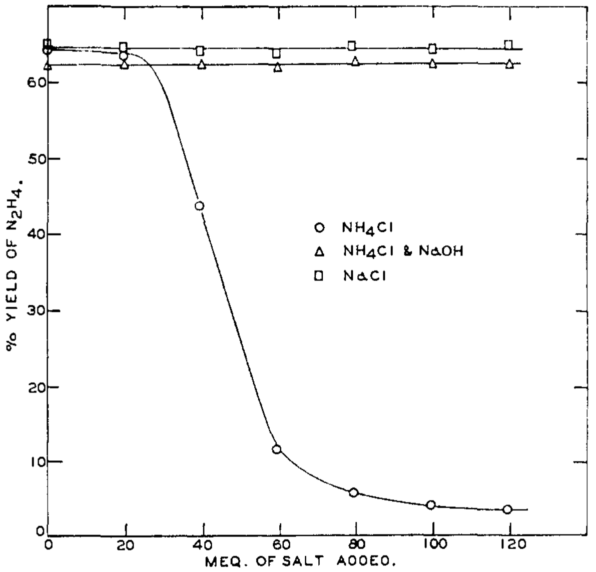

Fig. 2.—Effect of salt additions on the yield of hydrazine from chloramine and ammonia in aqueous solution.

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(5) Hydrazine is lost by volatilization when aqueous solutions are heated; such losses increase with time. This loss was standardized by heating all solutions for the same length of time on the steam-bath.

(6) R. A. Penneman and L. F. Audrieth, *Anal. Chem.*, **20**, 1058 (1948).

(7) W. Wiberg and M. Schmidt, *Z. Naturforsch.*, **6B**, 336 (1951).

(8) W. S. Metcalf, *J. Chem. Soc.*, 148 (1942).

(9) J. Kleinberg, M. Tecotsky and L. F. Audrieth, *Anal. Chem.*, **26**, 1388 (1954).

(10) Such a hypothesis is not, however, tenable in those instances where hydrazine formation has been shown to occur in liquid ammonia (R. Mattair and H. H. Sisler, THIS JOURNAL, **73**, 1619 (1951)) and certain other anhydrous non-aqueous solvents (see reference 4).

(11) R. A. Joyner, *J. Chem. Soc.*, **123**, 1114 (1923).

that the upper curves in this figure are horizontal shows that added salts which act only as strong electrolytes, have very little, if any effect on the yield of hydrazine.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

Kinetics of the Oxidation of Cyclohexane with Nitrogen Pentoxide[1]

BY J. C. D. BRAND[2]

RECEIVED NOVEMBER 10, 1954

The kinetics of oxidation of cyclohexane by nitrogen pentoxide have been measured in carbon tetrachloride solution at 0 and 20°. The results are interpreted by a mechanism in which the initial attack on the hydrocarbon is by an NO_3 radical generated by dissociation of the nitrogen pentoxide, $N_2O_5 \rightleftarrows NO_2 + NO_3$, $RH + NO_3 = R\cdot + HNO_3$. The main products of the oxidation, nitrocyclohexane and cyclohexyl nitrate, are formed in bimolecular, parallel reactions of the cyclohexyl radical with nitrogen dioxide; cyclohexyl nitrite is a transient intermediate in the formation of cyclohexyl nitrate. The retardation of the reaction by nitrogen dioxide is analyzed. Induced oxidation of the solvent occurs by a mechanism analogous to radical transfer in polymerization. Relative velocity coefficients of the reactions in the assumed mechanism are calculated from the experimental results. Single-step velocity coefficients are evaluated on the assumption that certain key reactions have the same rate (and activation energy) in solution as at high pressure in the homogeneous gas phase.

The reaction of nitrogen pentoxide with saturated hydrocarbons has recently been examined in its qualitative aspects by Titov and Schitov[3] who observed that the primary oxidation products were the mononitro compound and the nitrate ester of the corresponding alcohol.

$$RH \xrightarrow{N_2O_5} RNO_2 \text{ and } RONO_2$$

This behavior was established for *n*-heptane, *n*-octane and cyclohexane. Oxidation of the *n*-alkanes occurred principally at the methylene group adjacent to the terminal methyl group.

The present study is concerned with the kinetics and mechanism of the oxidation, cyclohexane being chosen for quantitative measurements because of the equivalence of the methylene groups. The results are of interest for two reasons: firstly because the reaction serves as a useful model for the familiar vapor phase nitration process[4] and can be studied under much simpler experimental conditions; and secondly because the participation of a saturated hydrocarbon in a fast reaction at room temperature is arresting and merits examination for its own sake. The measurements in this paper refer to oxidation in carbon tetrachloride solution; the reaction is initially more rapid than the spontaneous decomposition of nitrogen pentoxide[5] but is powerfully retarded by the accumulation of nitrogen tetroxide as the oxidation proceeds. The mechanism involves consecutive, non-chain radical reactions, and radical transfer with the solvent occurs.

Experimental

Materials.—Cyclohexane was submitted to acid extraction and partial freezing, and was twice fractionated in a 60-plate Podbielniak column with a take-off ratio of 1:50. The final product had f.p. 6.60° (*cf.* 6.68 ± 0.05° extrapolated for pure cyclohexane by Aston, Szasz and Fink[6]).

C.P. carbon tetrachloride was purified by treatment with Hg and by extraction with concd. H_2SO_4 and concd. KOH; it was deaerated by refluxing in a current of nitrogen, and freshly distilled from P_2O_5 before use.

Nitrogen pentoxide was prepared from nitrogen dioxide (Matheson) and excess ozone.[7] The crystals were purified by sublimation twice from P_2O_5 in a stream of ozone.

Cyclohexyl nitrate (*cf.*[3,8]) was obtained by esterification of cyclohexanol with nitric acid in 85% sulfuric acid at −5°; b.p. 76° (12 mm.), after washing with 85% phosphoric acid. Cyclohexyl nitrite was prepared by the method of Hunter and Marriott.[9]

Velocity Measurements.—All experiments were conducted in a medium of carbon tetrachloride. Oxygen, which interfered with the course of the reaction, was swept out of the apparatus with a current of dry nitrogen after the final sublimation of the nitrogen pentoxide; the dissolution of the pentoxide in carbon tetrachloride and the subsequent manipulation of the solution was conducted under nitrogen in a closed apparatus. Commencement of the reaction was timed from the addition of cyclohexane. Velocity measurements were made at 0 and 20°.

To follow the reaction, aliquot samples were withdrawn by automatic pipet and were delivered into a measured volume of dilute sodium carbonate solution. After shaking, the aqueous phase (*p*H 9–10) was analyzed for nitrite and chloride and the carbon tetrachloride layer was separated, dried (Na_2SO_4) and examined by infrared methods. The nitrite (from N_2O_4) present in the aqueous phase was estimated with ceric sulfate; the chloride, formed by hydrolysis of phosgene generated by induced oxidation of the solvent, was analyzed by the Volhard method. Nitrogen pentoxide was estimated by delivery of the solution in carbon tetrachloride into acetone containing a few per cent. of water, the nitric acid liberated being titrated potentiometrically with alkali; when present, nitrogen tetroxide contributed to the total nitric acid and was determined by a simultaneous analysis for nitrite by the previous procedure. In the potentiometric titration nitric acid was estimated independently of nitrous acid which, in the acetone medium, was very weakly acidic.

Infrared Spectra.—The infrared spectra confirmed that the major products of the reaction were nitrocyclohexane and cyclohexyl nitrate, as reported by Titov and Schitov.[3] The most prominent bands of these two absorbers in CCl_4 solution were at: nitrocyclohexane, 6.44 and 7.26 μ; cyclohexyl nitrate, 6.11, 7.84 and 11.55 μ. Relatively smaller amounts of chlorocyclohexane and trichloronitromethane were identified by the following bands (excluding bands unresolved from bands of unreacted cyclohexane, or obscured by solvent absorption): for $C_6H_{11}Cl$, 7.89, 8.24, 10.06, 11.25 and 14.60 μ; for CCl_3NO_2, 6.19, 7.41, 7.65, 11.10, 11.61, 11.88 and 14.93 μ. These bands were clearly seen if the major reaction products were first removed from

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[1] This research was supported by the United States Air Force under Contract No. AF 33(038)-23976 monitored by the Office of Scientific Research. Report Control Number OSR-TN-54-19.

[2] The University, Glasgow W. 2, Scotland.

[3] A. I. Titov and N. V. Schitov, *Doklady Akad. Nauk*, **81**, 1085 (1951).

[4] G. B. Bachman, L. Addison, J. V. Hewett, L. Kohn and A. Millikan, *J. Org. Chem.*, **17**, 906 (1952).

[5] H. Eyring and F. Daniels, THIS JOURNAL, **52**, 1472 (1930).

[6] J. G. Aston, G. J. Szasz and H. L. Fink, *ibid.*, **65**, 435 (1943).

[7] J. H. Smith and F. Daniels, *ibid.*, **69**, 1735 (1947).

[8] Fr. Fichter and A. Petrovich, *Helv. Chim. Acta*, **24**, 256 (1941).

[9] L. Hunter and J. A. Marriott, *J. Chem. Soc.*, 285 (1936).