change for phenylacetic acid in the range of concentrations studied appears to be too small to be measured by this method at its present state of development.

The mean value D_0, $(8.44 \pm 0.14) \times 19^{-6}$, is thought to best represent the diffusion coefficient of phenylacetic acid in aqueous mixtures at concentrations below 0.01 g./cc. and at a temperature of 25°. The value calculated by use of the Stokes–Einstein equation based upon the viscosity of water and the mean radius of a Fisher–Hirschfelder model of the phenylacetic acid molecule is 7.7×10^{-6}. Because their molecules are disk-like rather than spherical in shape, aromatic compounds have usually been observed to diffuse more rapidly than predicted by the Stokes–Einstein equation. For example, *o*-hydroxybenzyl alcohol was found to have a diffusion coefficient of 7.2×10^{-6} in dilute aqueous solutions at 20°.[11] This corresponds approximately with a value of 8.3×10^{-6} at 25°, and is in good agreement with the value reported here for phenylacetic acid.

Acknowledgment.—The authors are grateful to Dr. C. E. Vanderzee for valuable suggestions pertaining to the conduct of this study.

[11] "International Critical Tables," McGraw–Hill Book Co., New York, N. Y., Vol. V, p. 71.

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The Raschig Synthesis of Hydrazine

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It has been possible to fit existing yield data for the Raschig synthesis by assuming simple rate laws. Hydrazine is formed by a bimolecular reaction between ammonia and chloramine and destroyed by a bimolecular reaction between hydrazine and chloramine. The latter reaction rate constant is about 18 times that of the former reaction, and therefore large excesses of ammonia are needed to make the first reaction predominate. The role of copper can be explained by assuming that copper catalyzes the destruction of hydrazine, again as a bimolecular reaction involving copper and hydrazine. In terms of these mechanisms the role of gelatin in increasing yield is that of complexing copper. This copper complex of gelatin appears to be unstable below *p*H 11.

Today the most useful synthesis of hydrazine is the Raschig synthesis. It consists of oxidizing excess ammonia with alkaline hypochlorite. Yields based on hypochlorite, are low unless glue or gelatin is added to the reaction mixture and even then large excesses of ammonia have to be used.

Much practical work has been done in search of conditions for maximizing yield. The qualitative conclusion reached from these are that the reaction proceeds in three steps

$$NH_3 + OCl^- = NH_2Cl + OH^- \qquad (1)$$

$$NH_2Cl + NH_3 + OH^- = N_2H_4 + Cl^- + H_2O \qquad (2)$$

$$2NH_2Cl + N_2H_4 + 2OH^- = N_2 + 2NH_3 + 2Cl^- + 2H_2O \qquad (3)$$

The first reaction is fast and proceeds to completion rapidly. The second and third reactions are of comparable rates and the qualitative conclusions are that anything increasing the rate of the second or decreasing the rate of the third will increase the yield of hydrazine. Hence large excesses of ammonia are necessary.

The purpose of this paper is to show that the above qualitative conclusions can in fact be expressed quantitatively in terms of simple rate laws and that the role of the other variables can then be determined unequivocally.

Bodenstein[2] has measured the rate of reaction between ammonia and chloramine to give nitrogen and has found it to be first order in chloramine and ammonia. We can assume therefore that reaction 2 obeys this same rate law and if we assume that reaction 3 also proceeds as a bimolecular reaction, first order in hydrazine and chloramine, then the rate at which hydrazine is produced will be the difference between the rate of creation by reaction 2 and destruction by reaction 3.

$$dN_2H_4/dt = k_2(NH_3)(NH_2Cl) - k_3(N_2H_4)(NH_2Cl) \qquad (4)$$

and the rate at which chloramine is used up is

$$-dNH_2Cl/dt = k_2(NH_3)(NH_2Cl) + 2k_3(N_2H_4)(NH_2Cl) \qquad (5)$$

Combining these two equations we get

$$-\frac{dN_2H_4}{dNH_2Cl} = \frac{1 - (k_3N_2H_4/k_2NH_3)}{1 + 2\,(k_3N_2H_4/k_2NH_3)}$$

which can be integrated, assuming the ammonia concentration to remain constant, over the course of the reaction, using as limits 0 and N_2H_4 ($t = \infty$) for the hydrazine and NH_2Cl ($t = 0$) and 0 for the chloramine. This gives the implicit relation

$$\left(1 - \frac{k_3 y}{k_2 r}\right)^3 = \exp \frac{k_3}{k_2 r}(1 + 2y) \qquad (6)$$

where y is the yield of hydrazine on hypochlorite and r is the ratio of the final[3] ammonia concentration to initial chloramine concentration. Figure 1

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[1] Institute for the Study of Metals, University of Chicago.

[2] M. Bodenstein, *Z. physik. Chem.*, **139A**, 397 (1928).

[3] In the derivation of eq. 6 the ammonia concentration is assumed constant during the course of the reaction. This assumption is valid except at low values of yield and r. The equation then reduces to

$$y = (k_2/k_3)r \text{ or } (N_2H_4)(t = \infty) = (k_2/k_3)(NH_3)$$

This is the same result if one assumes that the reaction has reached a steady state with respect to hydrazine in eq. 4

$$d(N_2H_4)/dt = 0 = k_2(NH_3)(NH_2Cl) - k_3(N_2H_4)(NH_2Cl)$$

or

$$N_2H_4 = (k_2/k_3)(NH_3)$$

so if one uses the final ammonia concentration in eq. 6, a fit is obtained in the low yield range.

gives the yield curve based on eq. 6 with $k_3/k_2 = 18$ compared with the data of Joyner.[4] The agreement is quite good. The equation also agrees with the experimental fact that yield depends only on the ammonia to hypochlorite ratio and not on the absolute concentrations.

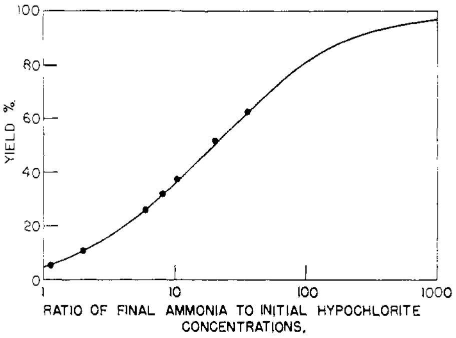

Fig. 1.—The effect of the ratio of ammonia to hypochlorite concentrations on yield: ●, the data of Joyner; —, equation 6.

Møller[5] has stated that while hypochlorite oxidized hydrazine rapidly, chloramine does so only slowly. Hence he concludes that the reacting species in eq. 3 must be hypochlorite and not chloramine and that therefore excess ammonia inhibits reaction 3, thus increasing yield. It can be shown now that this statement is contrary to experimental fact. From eq. 1 we get an equilibrium constant

$$(\mathrm{NH_2Cl})(\mathrm{OH^-})/(\mathrm{NH_3})(\mathrm{OCl^-}) = K_1$$

Hence

$$(\mathrm{OCl^-}) = (\mathrm{NH_2Cl})(\mathrm{OH^-})/K_1(\mathrm{NH_3})$$

and if reaction 3 obeyed the rate law

$$\text{Rate} = k_3'\,(\mathrm{N_2H_4})(\mathrm{OCl^-}) = \frac{k_3'\,(\mathrm{OH^-})}{K_1\,(\mathrm{NH_3})}\,(\mathrm{NH_2Cl})(\mathrm{N_2H_4})$$

we can repeat the previous integration, substituting $k_3'(\mathrm{OH^-})/K_1(\mathrm{NH_3})$ for k_3. This then gives an expression in which the yield depends much more strongly on the ammonia concentration and which is no longer independent of the absolute concentrations of ammonia and hypochlorite.

The Effects of Copper and Gelatin

Bodenstein[2] and Møller[5] have shown that no gelatin or glue is necessary if extreme precautions are taken to purify the reagents. They found that in the absence of glue or gelatin almost no hydrazine is formed if as little as 10^{-6} *M* cupric ion is present.

Bodenstein also measured the rate of the reaction between chloramine and ammonia and found that cupric ions did not influence it. Apparently then cupric ions catalyze the oxidation of hydrazine by chloramine. What then is the rate law governing this?

By reasoning similar to the above it can be shown that in the presence of cupric ions reaction 3 does not follow a rate law of the type

$$k_3[1 + k(\mathrm{Cu\ II})](\mathrm{NH_2Cl})(\mathrm{N_2H_4})$$

Let us therefore assume that in the presence of cupric ions the reaction proceeds by the rate law

$$k_3(\mathrm{NH_2Cl})(\mathrm{N_2H_4}) + k_3''(\mathrm{Cu(II)})(\mathrm{N_2H_4})$$

leading to

$$\mathrm{dN_2H_4}/\mathrm{d}t = k_2(\mathrm{NH_3})(\mathrm{NH_2Cl}) - k_3(\mathrm{N_2H_4})(\mathrm{NH_2Cl}) - k_3''(\mathrm{Cu(II)})(\mathrm{N_2H_4})$$

$$-\,\mathrm{dNH_2Cl}/\mathrm{d}t = k_2(\mathrm{NH_3})(\mathrm{NH_2Cl}) + 2k_3(\mathrm{N_2H_4})(\mathrm{NH_2Cl}) + 2k_3''(\mathrm{Cu(II)})(\mathrm{N_2H_4}) \quad (7)$$

At high copper concentrations the middle term will be small compared to the last term, and if we neglect it the above equation is easily integrated to give the following expression for the yield

$$y = \frac{1}{(2r)^{1/2}} \exp\left[-\,\frac{1+r}{s}\left(\frac{\pi}{2} - \tan^{-1}\frac{1-r}{s}\right)\right] \quad (8)$$

where y is the yield based on chloramine, $s = (10r - r^2 - 1)^{1/2}$, and $r = k_3''(\mathrm{Cu(II)})/k_2(\mathrm{NH_3})$. This one parameter expression is plotted on Fig. 2.

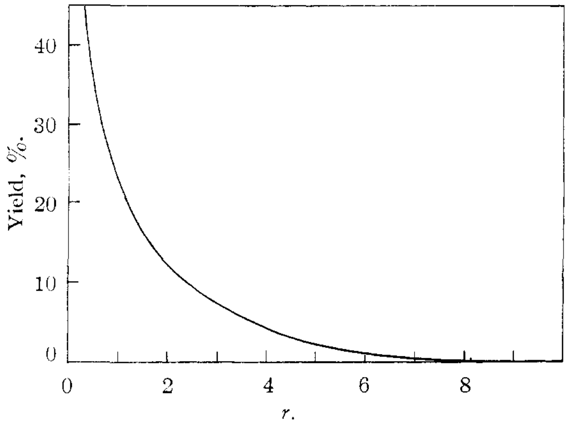

Fig. 2.—Theoretical curve, equation 8.

Møller has investigated the yield obtained when he added copper ions to very pure reagents. We can determine the value of r from his yield data by using eq. 8 and plotting it against added copper (Fig. 3). It is seen that r is linear in copper concentration. The fact that the line drawn through the data does not go through the origin is in agreement with the fact that Møller was unable to purify his reagents completely since adding gelatin doubled

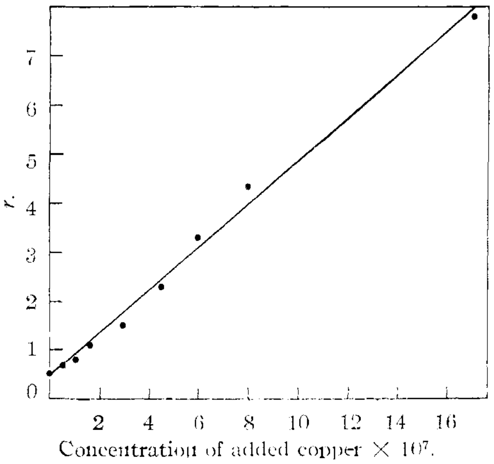

Fig. 3.—The effect of yield of added copper, data of Møller.

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

(5) M. Møller, *Kgl. Danske, Vidensk. Selsk. Math-fys. Medd.*, **12**, no. 16 (1934).

his yield. We can estimate his residual impurity catalysts to be equivalent to about 10^{-7} *M* copper. k_3''/k_2 is equal to 1.9×10^7.

The data available in the literature about the role of gelatin suggests strongly that it complexes or scavenges the copper or similar impurity catalysts. However, no estimation of their nature or concentration was ever made, nor has there been an attempt to keep their concentration constant in a series of runs evaluating the role of gelatin.

Let us assume that gelatin complexes copper and that the equilibrium concentration of active copper is

$$\frac{(\text{active copper})\,(\text{gelatin})}{(\text{copper complex})} = K$$

or by rearrangement

$$(\text{active copper}) = (\text{total copper})\,\frac{(K)}{(\text{gelatin}) + (K)}$$

By using eq. 8 we can evaluate the *r* from the yield, and by comparing 1/*r* *vs.* the gelatin concentration we see that according to eq. 9 we should obtain a straight line whose intercept with the abscissa should give us the reciprocal of the impurity catalyst concentration times $k_2(\text{NH}_3)/k_3''$ and whose slope is 1/*K* times that. Figure 4 shows the series 1 and 3 of Joyner's data of the effect of gelatin on yield.

The Effect of *p*H on Yield

Joyner has investigated the effect of adding ammonium ions to the reaction mixture and also the effect of adding sodium hydroxide, all at constant ammonia to hypochlorite ratio and in the presence of gelatin. The data can be interpreted in terms of an effect of *p*H on yield. The drop in yield as a function of *p*H is much too rapid to be explained in terms of a *p*H effect on k_3/k_2, but can be explained in terms of a *p*H effect on k_3''/k_2, although the data are very meager. The interpretation of this is that apparently the copper gelatin complex is unstable below *p*H 11. The data are plotted on Fig. 4 with the ordinate expanded so that the three points coincide approximately with the gelatin data. The scatter of Joyner's data is tremendous and it must be kept in mind that he made no attempt to keep his impurity catalyst concentrations constant. It would be desirable to repeat this work with known concentrations of impurity catalysts. There is, however, polarographic evidence[6] that the copper gelatin complex is unstable at lower *p*H's. At *p*H 9.55 gelatin acts as a normal maxima suppressor for copper; at *p*H 14 very small quantities of gelatin shift the half-wave potential by about one volt.

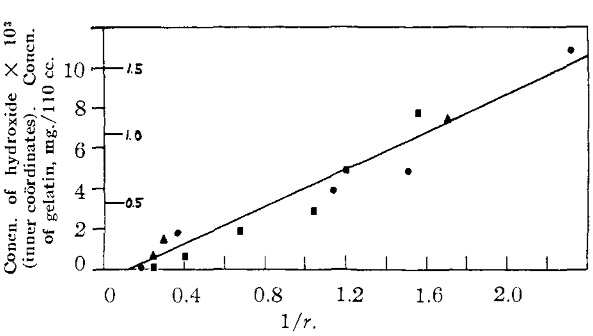

Fig. 4.—The effect on yield of added gelatin and *p*H; the data of Joyner; ● series 1, ■ series 3 on gelatin; ▲ data on added ammonium ion.

The Effect of Temperature

Bodenstein has measured the effect of temperature on yield on solutions of fairly high purity without using gelatin. Unfortunately, these solutions were not pure enough because the yield at 80° was only about half of what it would have been had gelatin been used. This indicates that at 80° about half the hydrazine was oxidized by impurities and in all probability his data measure nothing more than the temperature dependence of k_3''/k_2. More meaningful data were obtained by Nagasawa[7] who reports little temperature dependence on yield, indicating k_3/k_2 is constant with temperature.

The Mechanism of the Raschig Synthesis

The mechanism which we propose as a result of these considerations is

$$\text{NH}_3 + \text{OCl}^- = \text{NH}_2\text{Cl} + \text{OH}^- \text{ fast}$$

$$\text{NH}_2\text{Cl} + \text{NH}_3 = (\text{N}_2\text{H Cl}) \xrightarrow{\text{OH}^-} \text{N}_2\text{H}_4 + \text{Cl}^- + \text{H}_2\text{O}$$

$$\text{NH}_2\text{Cl} + \text{N}_2\text{H}_4 = (\text{N}_3\text{H}_6\text{Cl}) \xrightarrow[\text{NH}_2\text{Cl}]{2\text{OH}^-} \text{N}_2 + 2\text{NH}_3 + 2\text{Cl}^- + 2\text{H}_2\text{O}$$

The second reaction is a simple bimolecular displacement reaction. The nature of the intermediates in the third reaction is open. Preliminary experiments with isotopically labeled hydrazine indicate that N_3H_5 probably is not formed. In other words, chloramine does not add to the hydrazine as it adds to the ammonia in the second reaction.

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[6] L. Meites, THIS JOURNAL, **71**, 3269 (1949).

[7] Nagasawa, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **69**, 17 (1948).