types of oxygen. This is confirmed in another group of data not recorded here, in which the volatile oxygen analyses were carried out on the same samples of black as those on which the Grignard analyses were run. We therefore seem to be justified in concluding that the distribution of oxygen (other than hydroxyl) obtained from the analysis at 1000° is defined by the pyrolytic equilibrium obtaining at the temperature at which the bulk of the gases come off. It has no relationship to the distribution of bonds prevailing naturally upon the black before it is heated. The observed ratio of CO:CO_2 corresponds to an equilibrium temperature between 600 and 800°. Actually, the gases come off in differing ratios as the temperature is increased. Most of the carbon dioxide is evolved between 500 and 600° and most of the monoxide comes off between 600 and 700°. This is in accord with what one should expect from the equilibria prevailing at these different temperatures.

Acknowledgment.—Thanks are expressed to Dr. Hugh M. Smallwood for helpful advice during the prosecution of this investigation. The author is also greatly indebted to G. S. Buettner and R. R. Hampton for the proof that the gas liberated on addition of Grignard was actually methane.

Abstract

Different types of tightly bound oxygen on carbon black have been distinguished by Grignard analysis. Carbonyl oxygen tends to be from 13 to 30% greater in amount than hydroxyl oxygen for all blacks. About 26% of the total content of tightly bound oxygen is accounted for by Grignard analysis. The greater part of the oxygen on the black is thus more or less chemically inert.

RECEIVED SEPTEMBER 26, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

The Reaction between Formaldehyde and Ammonia

BY H. H. RICHMOND, G. S. MYERS AND GEORGE F WRIGHT

Although it is accepted that the final condensation product of formaldehyde and ammonia is hexamine, there have been several opinions concerning other substances which may form from these reagents and which may be intermediates in the hexamine synthesis. Thus Duden and Scharf[1] believed that formaldehyde and ammonia condensed to methylolamine, I, or methyleneimine, then trimerized to cyclotrimethylenetriamine, II. Further methylolation of this intermediate would then produce trimethylolcyclotrimethylenetriamine, III, which on condensation with ammonia would form hexamine, IV. These opinions have been endorsed by Baur and Ruetschi[2] who carried out kinetic studies on hexamine formation and designated it as a third order reaction.

Duden and Scharf found that freshly-prepared formaldehyde–ammonia mixtures did not act like aqueous hexamine solution. Thus their equimolar mixture of alkali-neutralized ammonium chloride and formaldehyde would not form 1,5-endomethylene-3,7-di-[*m*-nitrobenzenediazo]-1,3,-5,7-tetrazacycloöctane, V, as does hexamine, by reaction with diazotized *m*-nitroaniline. Furthermore this ammonia–formaldehyde solution gave, with benzoyl chloride, 1,3,5-tribenzoyl-1,3,5-triazacyclohexane, VI, and only a trace of the 1,3,5-tribenzoyl-1,3,5-triazapentane, VII, which this acid chloride gave with hexamine. Both hexamine, IV, and the Duden–Scharf solution, II, gave 1,3,5 - trinitroso - 1,3,5 - triazacyclohexane, VIII, when treated with an excess of nitrous acid, but the yield[3] from IV was only 24% and that from the solution assumed to contain II was 47% on the formaldehyde basis.[3a] We found the work of Duden and Scharf to be completely reproducible, but we have increased their yield of VI from II to 23% of theoretical, by a fortunate crystallization separation from the 12% of other product, methylene dibenzamide, IX.

Duden and Scharf believed formaldehyde–ammonia solution to consist essentially of cyclotrimethylenetriamine II. Henry,[4] on the other hand, considered that the liquid he obtained by drying an equimolar solution of aqua ammonia and formaldehyde with potassium carbonate was pure trimethylolamine, X. We have found it impossible that he could have had a pure compound, since rigorous drying with potassium carbonate removes formaldehyde and ammonia as well as water, and hexamine, IV, eventually is formed. Actually Table I shows that his solutions varied from 20–50% in water. Indeed, we found, by analysis for formaldehyde and ammonia[5] of what we shall for convenience call Henry solution, that, instead of an excess of formaldehyde, as predicted by formula X, the molar ratio of formaldehyde to ammo-

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[1] P. Duden and M. Scharf, *Ann.*, **288**, 218 (1895).

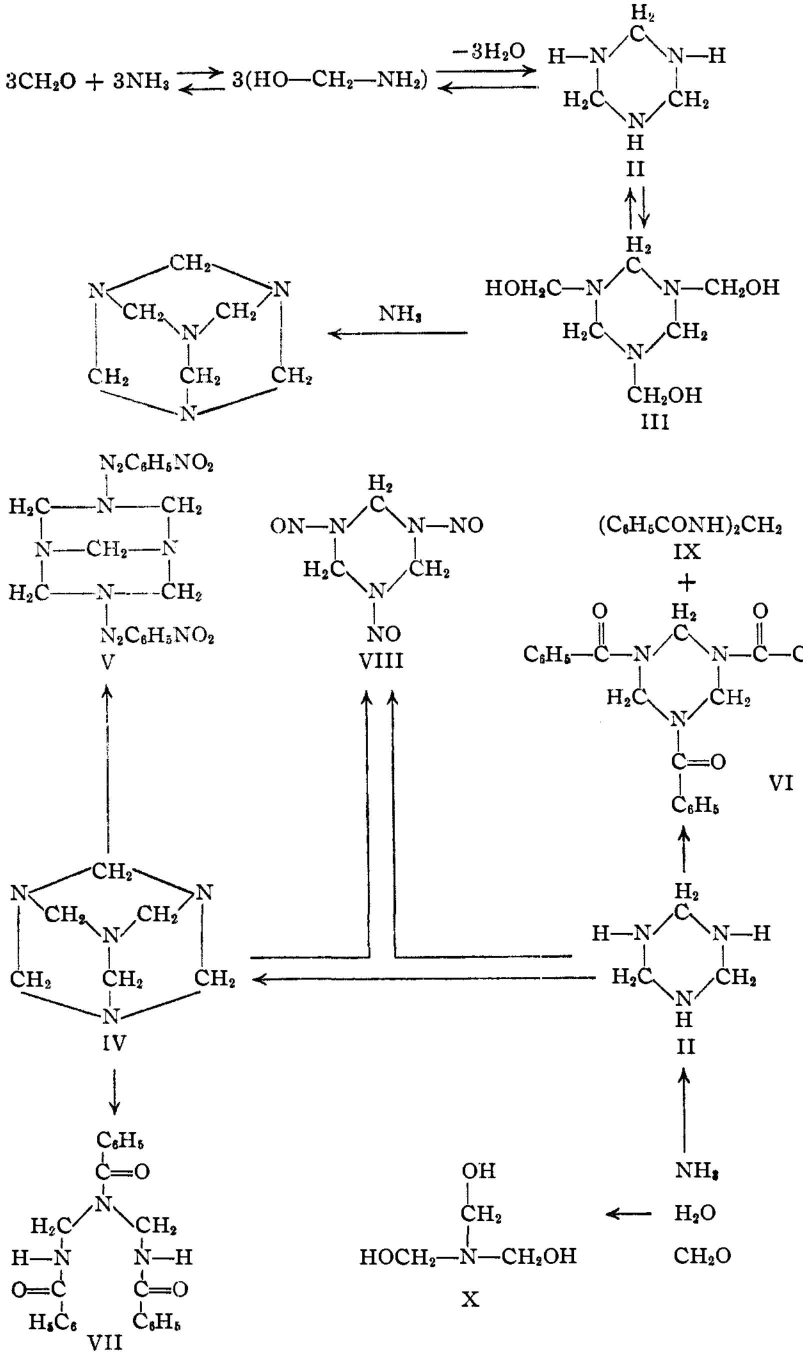
[2] E. Baur and W. Ruetschi, *Helv. Chim. Acta*, **24**, 754 (1941).

[3] F. Mayer, *Ber.*, **21**, 2883 (1888).

[3a] This latter contrast may not be entirely valid since Duden and Scharf, unlike Mayer, skimmed off the unstable trinitroso compound before it could decompose. The difference in manipulation does not, however, in our experience, account for the entire yield difference.

[4] L. Henry, *Bull. acad. roy. méd. Belg.*, 721 (1902).

[5] Hans Meyer, "Nachweis und Bestimmung organischer Verbindungen," Springer, Berlin, 1933, p. 51. We are indebted to Drs. Carmack, Kuehl and Leavitt, University of Pennsylvania, for advice on applicability of this method to our compounds.



nia was 1:1 within 3%. Since the potassium carbonate tends to force formaldehyde and ammonia from solution and the 1:1 ratio may have been fortuitous we repeated the preparation of Henry solution at higher initial dilution; the ratio of CH_2O:NH_3 still remained 1:1. Again, the same final ratio (1:1) was obtained if we started initially with $2NH_3$:$1CH_2O$. The data are included in Table I. These variations indicate strongly that Henry solution is largely cyclotrimethylenetriamine, II, rather than X which Henry thought it to be.

Henry solution may contain methyleneimine, CH_2=N—H, or methylolamine, $HOCH_2NH_2$, in equilibrium with II, but it probably contains no hexamine since it will not form V with diazotized *m*-nitroaniline. A very concentrated solution does, however, decompose to give hexamine after several weeks, and the ordinary solution in long contact with excess potassium carbonate finally sets to a gelatinous mass.

It has been found that styphnic acid forms a useful monosalt with hexamine which is only 0.25% soluble in the aqueous alcoholic mother liquor and which, within limits, tends not to be contaminated with the more soluble ammonium styphnate, even when it is precipitated from an ammoniacal solution. Henry solution does not form this styphnate when less than one equivalent of styphnic acid is added, even after several hours. An excess of styphnic acid (or simply acidification of the Henry–styphnic acid solution with nitric acid) does, however, produce hexamine styphnate immediately. Henry solution is evidently unstable in acidic media.

Table I

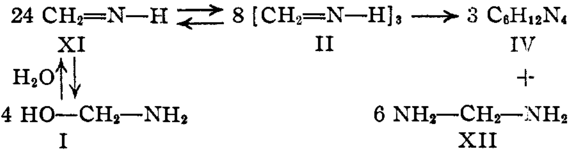
Analysis of Henry Solution

Sample	Put in, mole NH_3	CH_2O	Found wt. % NH_3	CH_2O	Ratio CH_2O: NH_3 by wt.	Age before analysis	Concn. cyclotrimethylenetriamine in aqueous solution
1	0.38	0.31	26.0	45.0	1.73	8 days	45
1	.38	.31	25.4	45.4	1.78	9 days	45
2	2.77	2.47	19.8	34.5	1.74	2 days	24
3	0.25	0.123	31.3	53.0	1.71	3 hours	53.5

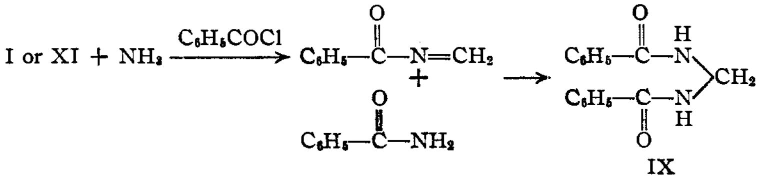
Henry solution, like that of Duden and Scharf, reacts with an excess of nitrous acid to give a 52% yield of 1,3,5-trinitroso-1,3,5-triazacyclohexane rather than the 24% yield obtainable from hexamine. All three solutions, Duden–Scharf, Henry and hexamine, give 1,5-endomethylene-3,7-dinitroso-1,3,5,7-tetrazacycloöctane when an excess of nitrous acid is not used. A higher yield of the dinitroso compound is also obtained with Henry solution than with hexamine solution. These nitrosation data serve only to indicate that Henry solution is more labile with respect to formaldehyde–ammonia availability than is hexamine.

A further proof demonstrates that hexamine is not present in fresh Henry solution. When the latter is treated with benzoyl chloride, it yields 13% of 1,3,5-tribenzoyl-1,3,5-triazacyclohexane, VI, 3.5% of methylenedibenzamide and none of the VII obtained from hexamine. These are the same products which Duden and Scharf obtained from their solution. It would seem that Henry's solution is essentially the same as that of Duden and Scharf but differs perhaps in relative amounts of several formaldehyde–ammonia condensation products. The difference in concentration could account for this. Neither of the solutions contain hexamine, however, when they are fresh.

It may be significant that no methylenedibenzamide IX is formed by benzoylation of hexamine. This might be interpreted as evidence that both Duden–Scharf and Henry solutions contain methylenediamine, XII, which might be in equilibrium with substances having other formaldehyde–ammonia ratios. Alternatively methylenediamine might be a concomitant product if these solutions decompose to form hexamine.


$$\begin{array}{ccccc} 24\,CH_2{=}N{-}H & \rightleftarrows & 8\,[CH_2{=}N{-}H]_3 & \longrightarrow & 3\,C_6H_{12}N_4 \\ XI & & II & & IV \\ H_2O \updownarrow & & & & + \\ 24\,HO{-}CH_2{-}NH_2 & & & & 6\,NH_2{-}CH_2{-}NH_2 \\ I & & & & XII \end{array}$$

The formation of methylenedibenzamide, IX, can of course be explained without postulating the presence of methylenediamine. Thus a stepwise formation from methyleneimine, XI or methylolamine, I (perhaps in equilibrium with II) is quite as reasonable if ammonia is present as an equilibrium component. The formation of IX from benzamide and formalin is known.[6]

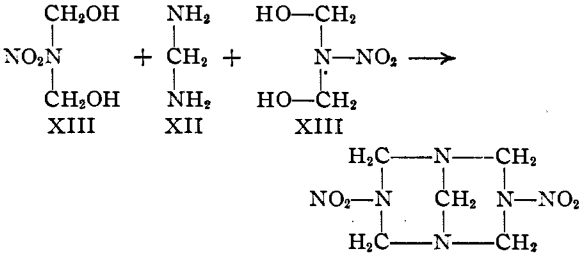

$$I \text{ or } XI + NH_3 \xrightarrow{C_6H_5COCl} C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}N{=}CH_2 + C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \longrightarrow \begin{array}{l} C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}\overset{H}{N} \\ \qquad\qquad\quad \rangle CH_2 \\ C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}\underset{H}{N} \end{array}$$

IX

Other evidence does, however, favor the equation series I → XII outlined above. For example, we have treated a 43% Henry solution with 60% sulfuric acid and obtained a sulfate salt. This salt had the same chemical properties as that designated methylenediamine sulfate by Knudsen[7] (who reported his compound in 50% yield from methylenediformamide in 50% sulfuric acid) but the salt from Henry solution (13% yield) gave a fair analysis for the neutral sulfate while that prepared by us from methylenediformamide evidently contained a variable amount of the acid salt. Our analyses gave a ratio of methylenediamine:sulfuric acid of 5:6, while Knudsen suggested the ratio 3:4. Neither Knudsen's salt nor that from Henry solution gave styphnates under conditions where hexamine styphnate would have formed.

When methylenediamine sulfate was filtered from the strongly acidified Henry solution, the filtrate gave no hexamine styphnate. This does not invalidate the reaction II → IV + XII as impossible in neutral or weakly acid solution, since it is known[2] that hexamine is not formed from formaldehyde and ammonia in strongly acid aqueous solution. It does indicate that cyclotrimethylenetriamine exhibits a tendency to decompose into methylenediamine and the elements of hexamine. Under strongly acid conditions these fragments are partially stabilized as the salts. In weakly acid or basic solution, the fragments combine to give hexamine. Decomposition of methylenediamine in the latter media probably also contributes to hexamine formation.

Confirmation that our salt contained the same base as that of Knudsen was established by the preparation of a compound which, on the basis of its analysis, should be 1,5-endomethylene-3,7-dinitro-1,3,5,7-tetrazacycloöctane (DPT). This



DPT

compound can also be prepared by admixture of a solution of nitramide in aqueous formaldehyde (shown as dimethylolnitramide, XIII) with a solution of formaldehyde and ammonia. The base from Knudsen's methylenediamine sulfate was shown to react in the same manner with dimethylolnitramide, but more rapidly. The slower reaction with formaldehyde and ammonia would imply that methylenediamine was available from this mixture.

The formation of DPT from our methylenediamine sulfate prepared from Henry solution is as rapid as that from Knudsen's compound. Precipitation is immediate, whereas about a minute elapses before it occurs from formaldehyde–ammonia at 10°. The yields from the two sulfates also are identical at 95% of theoretical on the formaldehyde basis. Despite the discrepancy in the analyses, the two salts seem then to contain

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(6) A. Einhorn, *et al.*, *Ann.*, **343**, 207 (1905).

(7) P. Knudsen, *Ber.*, **47**, 2698 (1914).

the same base with respect to the characterizing reaction leading to DPT.

On the other hand, the addition of dimethylolnitramide to Henry solution in neutral solution gives a 55% yield of DPT, but precipitation does not occur before three to four minutes at 10°. The decomposition of Henry solution to methylenediamine would therefore seem to be slower than the formation of methylenediamine from formaldehyde–ammonia. This could indicate that formaldehyde–ammonia solution contained less trimer (cyclotrimethylenetriamine) than Henry solution. In neither case would there appear to be a significant amount of methylenediamine in the equilibrium system.

Finally hexamine, in contrast to Henry solution or formaldehyde–ammonia solution, will not react with dimethylolnitramide to give DPT. The formation of DPT therefore provides a useful test for completion of the reaction of formaldehyde and ammonia to hexamine, and this reaction occurs over a measurable time at low temperatures.

Both Duden–Scharf and Henry solutions are essentially identical in composition except that the former contains sodium chloride and is more dilute. This high dilution evidently accelerates the conversion to hexamine, since the Duden–Scharf solution turns into hexamine solution more rapidly than Henry solution. In order to study this conversion, we diluted a Henry solution (nineteen hours old) five-fold with water. The *p*H of this diluted solution was 11.6 but it decreased on aging at 20° as shown

Time, hours	0	1	2	4	6
*p*H	11.6	11.3	10.9	10.7	10.4

Time hours	17	20	26	31	43	60
*p*H	10.1	10.0	9.9	9.8	9.5	9.1

It may be seen that the decomposition is still very slow. Insofar as hexamine formation is concerned, this system is starved with respect to formaldehyde and may be contrasted to a system containing sufficient formaldehyde to react completely in the 6:4 ratio required for hexamine. This contrast was afforded by the following experiment.

The *p*H of 0.2 mole of concd. ammonia in an equal volume (13.4 cc.) of water was found at 0° to be 12.5 according to the Coleman glass electrode. If this solution was chilled to −15° while 0.3 mole of ice-cold 40% formalin was added over three minutes, the temperature did not rise above +15° and then receded rapidly to 0° where it was maintained. It may be seen from the change in *p*H after this initial reaction

Time, min. after mixing	0	3	6	8
*p*H	11.0	10.4	10.1	9.8

Time, min. after mixing	11	52	274	332
*p*H	9.5	9.0	7.3	7.3

that most of the ammonia, as such, was used up immediately during the mixing process, since the *p*H had dropped to 11.0 by the time the first measurement could be taken. Conversion to hexamine was, however, evidently slight at this initial *p*H because the solution would still enhance the yield of DPT when it was treated with dimethylolnitramide, over the minimal 20% obtainable if the latter compound was treated with ammonia alone.[8a] Furthermore the *p*H (11) was much higher than that of a solution of hexamine at the same concentration (*p*H 7.2). However, the *p*H decreased to approximately this value (7.3) over about four hours. The solution then did not enhance the yield of DPT, so it evidently contained only hexamine.

In consideration of these two experiments, we assume that the fast reaction which occurs during mixing is I → II as outlined in our first formulation. This confirmation of the Duden and Scharf opinion would imply that the resulting excess of formaldehyde would add more slowly to give IV by some path which might involve III. In view of the considerable difference in rate between formation of II and its subsequent conversion to IV, the third order kinetics of Baur and Ruetschi[2] would not seem to fit the mechanism which they adopted from Duden and Scharf.

It will be noted that all steps in the alkaline reaction series $\mathrm{I} \rightleftarrows \mathrm{II} \rightleftarrows \mathrm{III} \rightarrow \mathrm{IV}$ of the first formulation are represented as reversible except for the last step. This conforms with our observation that hexamine in aqueous solution is not in measurable equilibrium with the substances from which it is prepared. This has been demonstrated by repetition of another of Henry's experiments in which he obtained two phases by saturation of aqueous hexamine with potassium carbonate. The lighter phase would have been Henry solution ($CH_2O:NH_3$, 1:1) if fresh aqueous formaldehyde and ammonia had been saturated with potassium carbonate. In the experiment with hexamine the lighter phase contained only hexamine, since it would not enhance the minimal yield of DPT from one mole of nitramide and one mole of formaldehyde.

The experiment was then elaborated by maintaining a solution of one mole of hexamine and 2 moles of ammonia in 420 cc. of water at 25° for thirty-five minutes, and then saturating it with 16 g. of potassium carbonate for ten minutes. After filtration of the oily top layer it was analyzed to discover a ratio $CH_2O:NH_3$ of 0.96. The ratio in the original solution was 1:1. The layer was, however, still hexamine–ammonia. (This invalidates Henry's claim that it is trihydroxymethylamine.) Thus, it did not enhance the DPT yield from a 1:1 nitramide–formaldehyde solution. Conditions for the condensation were correct, since subsequent addition of Henry solution did furnish a 55% yield of DPT instead of the minimal 20%. Furthermore the oily upper layer

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[8a] This 20% yield without added formaldehyde evidently is formed because formaldehyde-nitramide in aqueous solution is not entirely dimethylolnitramide.

yielded hexamine sulfate (identified as the styphnate) when it was treated with 60% sulfuric acid. Under these conditions, a Henry solution (from formaldehyde–ammonia) would have yielded methylenediamine sulfate. In summary, therefore, it would seem that hexamine formation is not measurably reversible in alkaline media, at least with respect to the final step (III → IV) of the reaction.

Experimental[8b]

Tribenzoylcyclotrimethylenetriamine.—To a solution of 0.10 mole ammonium chloride (5.3 g.) in 25 cc. water was added 0.12 mole (4.8 g.) of sodium hydroxide with stirring at 10°. To this solution was added dropwise 0.06 mole of 37% formalin (4.5 cc.) and finally 0.09 mole (12.6 g.) of benzoyl chloride was added dropwise at 10° over ten minutes. The granular precipitate turned to a white sirup after fifteen minutes of stirring. This sirup was washed thrice with water by decantation and was then digested at 60° with 25 cc. of ethanol, and filtered hot. The ethanol-insoluble material was further extracted with hot chloroform to leave 0.53 g. of chlorine-containing white solid, m. p. 205°. The hot chloroform-soluble fraction crystallized on cooling to yield 1.8 g. (23% theory on formaldehyde basis) of tribenzoylcyclotrimethylenetriamine, m. p. 222°; prisms after recrystallization from chloroform-ether.

The ethanol extract on cooling yielded 1.8 g. (12% on formaldehyde basis) of methylenedibenzamide, m. p. 221°, fine needles. A mixed melting point between the two major products was depressed.

The preparation was repeated using the same molar quantities of Henry solution with respect to formaldehyde content. A 13% yield of tribenzoylcyclotrimethylenetriamine and a 3.5% yield of methylenedibenzamide were obtained. The Henry solution showed no test for hexamine when it was treated with diazotized *m*-nitroaniline.

Preparation of Henry Solution (Sample I, Table I).—Into 25 g. (0.31 mole) of 37% formalin at 0° was passed 6.5 g. (0.38 mole) of gaseous ammonia. To the cold solution was added 8 g. of potassium carbonate with stirring at 10° until two layers separated. The top layer was decanted after centrifuging, weight 14.5 g. To this was added 5 g. of potassium carbonate. The mixture was stirred thoroughly, cooled in the refrigerator, again centrifuged and the top layer decanted. After repetition with 5 g. more potassium carbonate, the top layer (wt. 4.8 g.) was much more viscous than a hexamine solution of the same formaldehyde content, nor did it freeze to a crystalline mass at −30°, as did a hexamine solution. Analyses carried out by the method of Carmack, Kuehl and Leavitt[5] checked within 3%.

As Table I shows, the final $CH_2O:NH_3$ ratio was approximately the same when more dilute formalin, or more ammonia, was used in the preparation outlined above. If Henry solution is allowed to stand too long over potassium carbonate it sets to a gelatinous mass, and a clear, very concentrated solution finally deposits hexamine after several weeks.

Decomposition of Henry Solution by Acid.—To 2 cc. of Henry solution (0.0101 mole of cyclotrimethylenetriamine) was added 55 cc. of a saturated aqueous styphnic acid solution (0.00204 mole). No precipitate was formed.

On the other hand, a 5-cc. aliquot (containing 0.00087 mole of cyclotrimethylenetriamine) was added to 0.00204 mole of saturated aqueous styphnic acid. A precipitate of hexamine styphnate, weighing 0.17 g. and melting at 197° (dec.) was formed immediately. This represents a 98% yield if two moles of cyclotrimethylenetriamine give one mole of hexamine.

In the same manner, acidification with nitric acid of the basic solution of styphnic acid in Henry solution immediately gave hexamine styphnate.

Preparation of Hexamine Styphnate.—One equivalent of hexamine was added to a saturated aqueous solution of styphnic acid. The precipitate of hexamine mono-styphnate was quantitative; if the styphnic acid was saturated into ethanol instead of water the loss by solubility in 1:1 water–ethanol was only 0.25 g. per 100 cc. solution. The melting point was 196° (6° per minute rise). If the material was impure, it could be crystallized from nitromethane (90° to 25°), m. p. 196° or 197–198° by fast heating of the m. p. bath.

Anal. Calcd. for $C_{12}H_{15}N_7O_8$: C, 37.5; H, 3.90; N, 25.4. Found: C, 37.7; H, 3.98; N, 25.9.

This styphnate is much more useful than the picrate as a hexamine derivative largely because ammonium styphnate is soluble in water or water–ethanol. Thus a solution containing one mole hexamine as a 50% solution plus 2 moles of ammonia gave a 98% yield of hexamine styphnate, m. p. 196°.

Preparation of Methylenediamine Sulfate.—To 8 cc. of 60% sulfuric acid cooled to 5° was added 5.0 cc. (0.025 mole) of Henry solution (analyzed as 43% cyclotrimethylenetriamine) over a five-minute period. The temperature was maintained at 10° to 15°. A crystalline product, which formed at once, was filtered after one hour at 0°, washed with 20 cc. each of ether, ethanol and ether. The product dried at 50°, weighed 0.47 g. (13%) and melted at 183–193° (dec., soft at 158°).

Anal. Calcd. for $CH_8N_2SO_4$: C, 8.34; H, 5.62; N, 19.4; SO_4, 66.6. Found: C, 8.22; H, 5.57; N, 19.4; SO_4, 68.7.

1,5-Endomethylene-3,7-dinitro-1,3,5,7-tetrazacyclooctane (DPT).—The use of DPT formation as a test for presence of formaldehyde–ammonia, cyclotrimethylenetriamine or methylenediamine was carried out by adding to 0.48 cc. (0.006 mole) of 37% formalin at 0°, 0.43 g. (0.006 mole) of nitramide (solution 1).[8] After dilution with 2 cc. of water, or with 2 cc. of the solution to be tested (solution 2) the combination of solutions 1 and 2 was carefully adjusted to *p*H 7 either with ammonia or dilute hydrochloric acid. The beginning and duration of precipitation was noted. After forty minutes at 0° the precipitate was filtered off, water-washed and dried at 50°. The yield (m. p. 202–205°, dec.) was 0.11 g. or 21% of theoretical (CH_2O basis) when water was used as solution 2.

When Henry reagent was used as solution 2 the yield was 54% of theoretical (CH_2O basis). Hexamine as solution 2 gave a yield of only 11%; this is less than that obtained when pure water was used as solution 2, but might have been expected since the presence of hexamine in the combined solutions caused less addition of ammonia for neutralization than was necessary for the formation of DPT. This was shown by neutralization of a 1:1 molar mixture of nitramide and formaldehyde with hexamine instead of ammonia. No DPT was precipitated. Likewise, a solution of 2 moles of ammonia to 3 moles of formaldehyde which had been aged for three hours at 25° gave no precipitate with 1 mole of nitramide plus 1 mole of formalin over a one-hour period. Subsequent addition of ammonia precipitated a 29% yield of DPT (CH_2O basis).

1,3,5-Trinitroso-1,3,5-triazacyclohexane, VIII.—To a solution of 2.1 g. Henry solution containing 0.031 mole ammonia and 0.031 mole formaldehyde in 2.8 cc. ice-water was added a solution of 6.8 cc. (0.080 mole) concd. hydrochloric acid in 20 cc. ice-water with stirring. To the resulting solution was added 5.0 g. (0.072 mole) of sodium nitrite in 8 cc. ice-water. After thirty minutes of stirring, a yield of 0.48 g. (52%, CH_2O basis) was filtered and washed to melt at 105° after drying *in vacuo*.

1,5-Endomethylene-3,7-dinitroso-1,3,5,7-tetrazacyclooctane.—To a fresh Henry solution containing 0.031 mole ammonia and 0.031 mole formaldehyde in 20 cc. ice-water was added at 0° with stirring a solution of 2.5 g. (0.036 mole) sodium nitrite, 2.92 cc. (0.036 mole) concd. hydrochloric acid in 12 cc. ice-water. The product weighed 0.34 g. when filtered and dried. This 36% yield (CH_2O basis) melted at 198°.

(8b) All melting points corrected against reliable standards.

(8) H. S. Booth, "Inorganic Syntheses," Vol. I, 1st ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 72.

When alternatively the Henry solution was added to the nitrous acid solution, the yield was decreased to 22%, m. p. 202°.

Summary

1. The system formaldehyde–ammonia has been re-examined. The results agree with those of Duden and Scharf, and designate cyclotrimethylenetriamine as the intermediate in the eventual formation of hexamine.

2. The formaldehyde–ammonia solution prepared by Henry is found essentially to behave as cyclotrimethylenetriamine and not as trimethylolamine, which he suggested.

3. The final stages of the hexamine synthesis from cyclotrimethylenetriamine are non-reversible in alkaline solution.

TORONTO, CANADA RECEIVED AUGUST 22, 1947

[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Hydrogenolysis of Alkyl Halides by Lithium Aluminum Hydride[1]

BY J. ENOCH JOHNSON, RONALD H. BLIZZARD AND HOMER W. CARHART

Lithium aluminum hydride is an excellent reducing agent for many types of organic compounds.[2,3] It has also been used successfully for the determination of active hydrogen.[4] The reactions using this reagent are ordinarily carried out conveniently in ethyl ether solution and usually proceed rapidly and to completion. The reaction of lithium aluminum hydride with alkyl halides is more sluggish and in some instances does not occur in a reasonable time in refluxing ethyl ether. This difficulty may be overcome by the use of solvents such as tetrahydrofuran which permit the employment of higher temperatures. The reactions have been further accelerated and yields improved by a new procedure using lithium hydride which also greatly decreases the amount of lithium aluminum hydride necessary to complete the reaction.

Experimental results indicate that not all four hydrogen atoms show the same reactivity toward alkyl halides, and that the reaction probably proceeds in at least two steps, as represented by the equations

$$LiAlH_4 + RX \longrightarrow RH + LiX + AlH_3$$
$$AlH_3 + 3RX \longrightarrow AlX_3 + 3RH$$

Of these steps, the first is presumed to be much more rapid than the second.

As may be seen from the data in Table I, when the molar ratio of reagent to the more active halides was greater than one the reactions proceeded rapidly and to completion. When the ratio was approximately 0.25 (the calculated value to replace all four hydrogens), the reactions were sluggish. The stepwise course of the reaction would account for the fact that more than one hydrogen per mole of reagent is consumed and that all four hydrogens are not replaced in a reasonable time.

Since aluminum hydride reacts with lithium hydride in ether to produce lithium aluminum hydride,[5] it was considered reasonable that alkyl halides could be hydrogenated by means of lithium hydride with only a small amount of lithium aluminum hydride present. This hydrogenolysis was found to proceed rapidly and to completion. Under these conditions the reaction may be represented as

$$RX + LiH \xrightarrow{LiAlH_4} RH + LiX$$

It is evident that lithium aluminum hydride acts as a hydrogen carrier, as shown by the fact that no reaction was found to occur with lithium hydride alone. The use of lithium hydride greatly reduces the amount of lithium aluminum hydride necessary and minimizes the possibility of the formation of aluminum halide.

In general, it was found that alkyl bromides react more readily than alkyl chlorides with lithium aluminum hydride. Primary halides react more readily than secondary halides which in turn are more reactive than tertiary halides. Alicyclic and aromatic halides proved very unreactive.

The reaction of 1,2-dibromoöctane with lithium aluminum hydride to give a moderate amount of olefin was surprising, since, with the exception of a trace of olefin in the reaction product of bromocyclohexane, olefins were not observed in the reaction products of the other alkyl halides. No attempt was made to identify this olefin.

Experimental

In order to accelerate the reaction of lithium aluminum hydride with alkyl halides, it was necessary to use temperatures higher than that of refluxing ethyl ether. This temperature should be kept below 100°, the incipient decomposition point of the reagent. Tetrahydrofuran was found to be an excellent reaction medium because it is a good solvent for the reagent,[2] it is miscible with water and has a desirable boiling point. Diisopropyl ether, although having the proper boiling point, was found to be a poor solvent for the reagent. Di-*n*-butyl ether, in which the reagent is suitably soluble, requires an externally controlled temperature for the reaction, and in one instance of its use, there was a sudden rise in temperature of the reaction mixture with consequent decomposition of reagent.

The following serves as an example of the method used.

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[1] The opinions contained herein are the authors' and are not to be construed as official or reflecting the views of the Department of the Navy.

[2] Finholt, Bond and Schlesinger, THIS JOURNAL, 69, 1199 (1947).

[3] Nystrom and Brown, *ibid.*, 69, 1197, 2548 (1947).

[4] Krynitsky, Johnson and Carhart, *ibid.*, 70, 486 (1948).

[5] H. I. Schlesinger, from an unpublished report to the Naval Research Laboratory.