ondary reactions. Competing primary reactions would include radiation breakdown of cystine to release free sulfur, oxidation of cystine to sulfate, and deamination of cystine. Secondary reactions of the primarily formed cysteine would include formation of H_2S and alanine and oxidation back to cystine.

Hydrogen sulfide formation from cystine is much smaller than from cysteine; one obvious reason is the lack of the –SH group. On the other hand, free sulfur is more readily liberated from cystine. As previously mentioned, cystine is more susceptible to radiation deamination than cysteine. The fact that NH_3 appears among the irradiation products of cystine at lower doses than alanine does shows that alanine is not a compulsory intermediate for NH_3 formation.

The amounts of cystine which have reacted and the total amounts of sulfur in the form of S and $SO_4^=$ are very similar for the same radiation doses, either in oxygen-free or oxygen-saturated solution. The large amount of $SO_4^=$ from cystine radiation, especially that from the oxygen-saturated solution, is a good indication that the $SO_4^=$ comes from the progressive oxidation of the sulfur from -1 oxidation state in cystine through a number of intermediates to the $+6$ oxidation state in $SO_4^=$. No significant *p*H changes were found in the solutions of irradiated cystine.

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Carbon-14 Tracer Studies of the Nitrolysis of Hexamethylenetetramine

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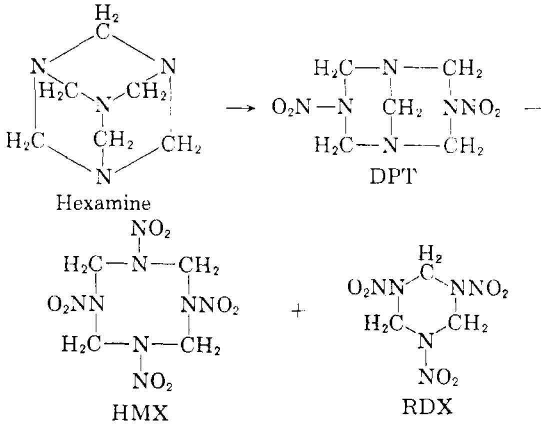
RECEIVED MAY 16, 1959

The path of carbon atoms in the nitrolysis of hexamethylenetetramine (hexamine) to a mixture of the homologous cyclic methylenenitramines,1,3,5,7-tetranitro-1,3,5,7-tetraazacycloöctane (HMX) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), was traced using carbon-14. Under conditions employed in this research both cyclic methylenenitramines are derived from the complete non-selective degradation of the hexamine molecule to fragments containing chemically equivalent methylene groups. When paraformaldehyde [$(CH_2O)_x$] is included in the nitrolysis medium, its methylene groups can enter into a common pool with those from hexamine for the formation of final products. 1,5-Dinitroendomethylene-1,3,5,7-tetraazacycloöctane (DPT) is a partial nitrolysis product which can be isolated by quenching the reaction mixture at an intermediate stage. This compound, upon further nitrolysis, also degrades completely and non-selectively to species containing chemically equivalent methylene groups with subsequent recrystallization to the final insoluble cyclic methylenenitramines.

Introduction

Bachmann and Sheehan at the University of Michigan[1] developed a new method of preparing RDX containing small quantities of HMX (RDX/HMX). The method involves the nitrolysis of hexamine with ammonium nitrate–nitric acid solution and acetic anhydride. By varying parameters of temperature and acid strength, together with quantities of ammonium nitrate and acetic anhydride, it was shown[2] that the ratios of RDX to HMX could be altered. These results led Bachmann and co-workers[3] to prepare mixtures rich in HMX (HMX/RDX). The optimum yields obtained represented 82% conversion of hexamine to HMX/RDX containing 73% HMX.

The formation of RDX and/or HMX molecules from the nitrolysis of hexamine has been postulated to take place *via* two separate paths. One involves the selective cleavage of the hexamine molecule[4] and the other, the combination of methylene and amino type fragments.[5] However, direct evidence in support of either of these possible paths of nitrolysis to HMX/RDX has been lacking. Regardless of the over-all mechanism involved, the formation of DPT has been postulated[2] as a possible precursor to the final products, equation 1.



(1)

The nitrolysis of hexamine to HMX/RDX has been studied in these laboratories and using essentially the same conditions as reported by Bachmann,[3] similar yields of HMX/RDX were obtained. It was observed that by including a small quantity of paraformaldehyde in the reaction mixture, there resulted a higher yield of mixed products to the extent of approximately 10%. This observation suggested that paraformaldehyde or its methylene groups in some manner can take part in this reaction to form cyclic methylenenitramine molecules. At the same time it also sug-

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[1] W. E. Bachmann and J. C. Sheehan, THIS JOURNAL, **71**, 1842 (1949).

[2] (a) W. E. Bachmann, *et al.*, unpublished work at the University of Michigan reported in Office of Scientific Research and Development (OSRD) Report No. 5186; (b) S. Epstein and C. A. Winkler, *Can. J. Chem.*, **30**, 734 (1952).

[3] W. E. Bachmann, *et al.*, unpublished work at the University of Michigan as reported in OSRD Report No. 1981.

[4] G. F. Wright, *et al.*, *Can. J. Chem.*, **27**, 520 (1949).

[5] C. A. Winkler, *et al.*, *ibid.*, **29**, 725 (1951).

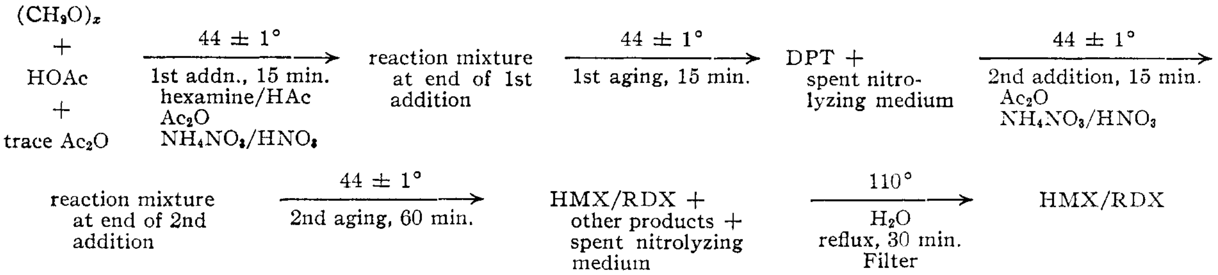

Fig. 1.—Flow diagram for the nitrolysis of hexamine.

gested a means to study the possible path of carbon atoms, or methylene groups, in the nitrolysis of hexamine through the use of carbon-14. Accordingly, a study was carried out in which either hexamine or paraformaldehyde was tagged with carbon-14 and the distribution of radioactivity in the cyclic methylenenitramine products was traced during the course of nitrolysis.

Results and Discussion

The preparation of HMX/RDX as discussed in this paper is a modification of the original Bachmann process for the nitrolysis of hexamine. Briefly, the preparation is: To a flask containing a slurry of paraformaldehyde, acetic acid and a trace of acetic anhydride, the following reagents are added simultaneously at controlled rates over a 15-minute period: (a) a solution of hexamine in glacial acetic acid, (b) acetic anhydride, (c) a solution of ammonium nitrate in nitric acid. The reaction temperature is maintained at 44 ± 1° throughout this procedure. The mixture is aged for 15 minutes and a second portion of acetic anhydride and ammonium nitrate–nitric acid is added again over a 15-minute period. This reaction mixture is aged for another 60 minutes. Hot water is then added and the slurry is refluxed for 30 minutes. The HMX/RDX product is obtained by chilling and filtering this mixture. This procedure is diagrammatically illustrated in Fig. 1.

Preliminary experiments with carbon-14 were conducted using either tagged hexamine and inactive paraformaldehyde or the reverse. The HMX/RDX product was isolated, qualitatively separated into its components, and each component assayed for radioactivity using a liquid scintillation counting technique.[6] These nitrolyses were repeated, as indicated in Table I, to show the reproducibility of the data. Without exception, the specific activities of the HMX and RDX were found to be the same and independent of the small variations in yield of combined product. The observed specific radioactivity of each cyclic methylenenitramine was compared to the calculated value assuming complete dilution of carbon atoms between hexamine and paraformaldehyde. In all of the experiments, the observed values were almost identical to the calculated values (see Calculations). It must therefore be concluded that such complete equilibration of carbon atoms or methylene groups does occur under these nitrolyses conditions.

Table I

Nitrolysis of Hexamine Using Carbon-14 as a Tracer

C^{14}-Compound	No. of runs	Yield, %[c] HMX/RDX	Obsd. spec. act., c.p.m./600 mg.		
			HMX	RDX	Calcd.[a]
Hexamine[b,d]	4	80 ± 3	175,000 ± 2455	174,860 ± 2510	
Hexamine[d]	5	90 ± 2	156,260 ± 2195	156,780 ± 940	155,600
$(CH_2O)_x$[e]	6	90 ± 2	19,510 ± 435	19,670 ± 170	19,150

[a] Of either HMX or RDX, assuming complete equilibration of carbon atoms from hexamine and paraformaldehyde. [b] Control experiment. [c] Based on 1 mole of HMX from 1 mole of hexamine. [d] 0.216 gram-atom of carbon. [e] 0.028 gram-atom of carbon.

At this point, it was of interest to determine the existence of DPT as an intermediate in order to make possible a more detailed study of the processes involved in the nitrolysis reaction. The formation of this compound from the nitrolysis of the nitric acid salt of hexamine with acetic anhydride has been reported previously.[4] The same workers also synthesized HMX starting directly with DPT. However, the isolation of DPT as an intermediate in the direct nitrolysis of hexamine to HMX/RDX has never been reported.

The isolation of this intermediate was accomplished by quenching the nitrolysis reaction after the first aging period. The quenching was performed by chilling the reaction mixture to 12° followed by rapid separation of solid material by filtration. These nitrolyses were conducted both with and without the presence of paraformaldehyde in the reaction mixture. It is significant to note that in the presence of paraformaldehyde, the yield of DPT isolated was approximately 65% of theory based on hexamine, whereas in the absence of this reactant only half that yield was obtained. Since DPT is slightly soluble and has also been observed to decompose in an acid medium, quantitative isolation of this intermediate by this quenching method was unlikely. It is probable, therefore, that the formation of this compound took place to a greater extent than indicated by the isolated yields.

Since DPT has been shown to be the primary stable intermediate at the end of the first aging period, the nitrolysis of hexamine to HMX/RDX under the above conditions can be regarded as taking place in two separate steps. A study was therefore made of the paths of methylene carbons during the course of the first and second stages of nitrolysis by adding paraformaldehyde prior to the first and second addition of reactants, and de-

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(6) S. Helf and C. G. White, *Anal. Chem.*, **29**, 13 (1957).

termining the carbon atom equilibration in the DPT and HMX/RDX, respectively.

For the study of the first stage of reaction, hexamine–C^{14} was nitrolyzed both in the absence and presence of inactive paraformaldehyde. The reaction mixture was quenched by chilling 15 minutes after the first addition of reactants and the maximum isolatable yield of DPT was obtained in each case. The specific activities of the DPT products were compared. Where no paraformaldehyde was used, 2.5 g. of DPT with a specific activity of 2.41×10^5 counts per minute (for a 600 mg. sample) was isolated. Where the paraformaldehyde was included, 5.0 g. of DPT with a specific activity of 2.16×10^5 counts per minute was isolated. For the latter experiment the calculated specific activity of the DPT intermediate, assuming complete dilution of hexamine carbon atoms by paraformaldehyde carbon atoms, was 2.15×10^5 counts per minute. It is thus apparent that the methylene carbons from paraformaldehyde and hexamine undergo equilibration in the formation of DPT during the first stage of nitrolysis.

When the paraformaldehyde was added prior to the second addition of reactants, *i.e.*, at the beginning of the second reaction phase, it is seen from Table II, that the resulting equilibration of methylene groups was the same as when it was included initially.

TABLE II

VARIATION OF PARAFORMALDEHYDE ADDITION TIME DURING HEXAMINE-C^{14} NITROLYSIS[a]

		Obsd. specific activity, c.p.m./600 mg.		
Addn. of $(CH_2O)_x$	HMX/RDX % yield	HMX	RDX	Calcd.
None	78	176,000	177,270	(Control)
Initial	90	157,150	156,720	158,000
After 1st aging	89	156,635	157,035	158,000

[a] All data reported are an average of two experiments.

The beneficial effect of paraformaldehyde on the yield of final products was thus the same when this reagent was added either initially or prior to the second reaction stage. The observed specific activities of the HMX and RDX, in both cases, were again the same as calculated, assuming complete equilibration of carbon atoms. Therefore, it must be concluded that when paraformaldehyde was added after the DPT had formed, a complete equilibration of carbon atoms (or methylene groups) between DPT and paraformaldehyde took place in the formation of both HMX and RDX molecules.

To check for this occurrence more directly a quantity of pure DPT was synthesized separately and was added to a "pseudo" spent acid medium containing paraformaldehyde-C^{14}. This medium simulated the end of the first aging period (see Experimental procedure). The second addition of reactants, *i.e.*, addition of the remainder of the acetic anhydride and ammonium nitrate–nitric acid solution, was performed according to the normal nitrolysis conditions for the preparation of HMX/RDX. The results of duplicate runs gave a 76% yield of HMX/RDX (based on DPT) with radioactivities (c.p.m./600 mg.) of 21,060 for HMX and RDX, respectively. The calculated radioactivity of these molecules, on the basis of complete equilibration of carbon atoms, is 21,900 c.p.m./600 mg. The expected equilibration between DPT and paraformaldehyde during the second period of addition and aging of reactants was thus substantiated.

The complete equilibration of methylene groups between hexamine and paraformaldehyde during nitrolysis to HMX/RDX, as illustrated so conclusively in the above experiments, can be satisfied by any one of the following paths: I. isotopic carbon atom exchange prior to other chemical reaction between: (a) paraformaldehyde and hexamine, (b) paraformaldehyde and the intermediate DPT and (c) paraformaldehyde and HMX/RDX; II. independent condensation of paraformaldehyde with ammonium nitrate to form HMX and RDX; III. chemical equivalence of methylene groups from hexamine and paraformaldehyde during nitrolysis. A consideration of each of these possible modes of reaction is treated in the ensuing discussion.

I. Carbon Atom Exchange Studies. (a) Paraformaldehyde and Hexamine.—The complete dilution of methylene groups from hexamine by those from paraformaldehyde during nitrolysis could occur *via* isotopic carbon atom exchange prior to any subsequent chemical reaction. Such exchange would obviously mask any other possible interpretation of the carbon-14 tracer data. To explain the complete equilibration of methylene groups in the nitrolysis reaction on this basis, the rate of isotopic exchange would of necessity have to be faster than the rate of hexamine consumption. The isolation of unreacted hexamine in the presence of paraformaldehyde-C^{14} was therefore attempted during the first stage of nitrolysis. It was reasoned that if rapid isotopic exchange occurred, unreacted hexamine would contain radioactivity.

Accordingly, the usual reagents were added rapidly and simultaneously to the reaction mixture containing the paraformaldehyde-C^{14} and quenched at 44° at different time intervals by the addition of carbon tetrachloride. Hexamine was isolated under anhydrous conditions as the mercuric chloride complex[7] (identified from its infrared spectrum), directly after the rapid addition of reagents and after 2 and 4 minutes of reaction and found to contain no activity. In the 4-minute run, DPT was also isolated with a specific activity representing complete carbon atom equilibration. At the end of 8 and 15 minutes of reaction no hexamine was isolated and the DPT had the same specific activity as in the 4-minute experiment. Direct evidence was thus obtained for the absence of isotopic carbon atom exchange between unreacted hexamine and paraformaldehyde during nitrolysis conditions.

(b) **Paraformaldehyde and DPT.**—The occurrence of rapid exchange of carbon atoms between DPT and paraformaldehyde would also account for the results of the carbon-14 tracer experiments. The absence of such exchange was demonstrated by suspending DPT-C^{14} in glacial acetic acid for 24 hours at 25° in the presence of inactive para-

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[7] (a) B. Grutzner, *Arch. Pharm.*, **236**, 370 (1898); *Chem. Zentr.*, **69**, II, 663 (1898); (b) P. Dobriner, *Z. anal. Chem.*, **36**, 44 (1897).

formaldehyde. The specific activity of the DPT remained the same as that of a control sample suspended in the same medium in the absence of paraformaldehyde. To more closely approximate conditions of nitrolysis, inactive DPT was then suspended for a period of (a) 1 hour at 30° with paraformaldehyde-C^{14} in a simulated reaction medium and (b) 30 minutes at 44° in an actual spent reaction medium which existed at the end of the first aging period. In both cases, the DPT isolated from the medium contained no radioactivity.

(c) **Paraformaldehyde and HMX-RDX.**—Another possible path for methylene group equilibration was isotopic exchange between HMX/RDX and paraformaldehyde. Hence, HMX and RDX were added separately as glacial acetic acid slurries, in lieu of the normal hexamine–glacial acetic acid solution in the regular process of nitrolysis. The paraformaldehyde in the reaction flask was labeled with carbon-14 in both experiments. In each case, the cyclic methylenenitramine was recovered quantitatively and found to contain no radioactivity. In addition to showing the absence of exchange, these experiments demonstrated the stability of cyclic methylenenitramines in a strong nitrolyzing medium. It had been previously demonstrated[8] that these compounds are also stable in spent nitrolyzing media.

From these investigations, it was concluded that the equilibration of methylene carbon atoms between hexamine and paraformaldehyde in the formation of HMX and RDX was not the result of isotopic exchange but of chemical reaction alone.

II. Independent Condensation of Paraformaldehyde with Ammonium Nitrate to Form HMX and RDX.—The independent condensation of the paraformaldehyde with ammonium ion to form HMX and RDX would also account for the results of the carbon-14 tracer experiments. This independent formation could occur either through the intermediate formation of hexamine and/or DPT or directly *via* nitrolysis. This was stoichiometrically possible since ammonium nitrate was added in sufficient excess for these separate reactions to occur. Products formed in this manner would be indistinguishable from the same products formed independently from the original hexamine. As initial evidence for the failure of this independent formation from paraformaldehyde and ammonium nitrate, the experiments on isotopic exchange between paraformaldehyde and HMX–RDX in a nitrolysis medium in the absence of hexamine can be cited. In addition to demonstrating the absence of isotopic exchange, the lack of activity in the HMX and RDX isolated also indicated that paraformaldehyde-C^{14} did not contribute independently to these products.

A specific examination of the possible independent formation of HMX/RDX was made in the following manner. An acetic acid slurry of paraformaldehyde and ammonium nitrate in quantities equivalent, respectively, to the methylene and amino nitrogen concentrations of hexamine was substituted for the hexamine solution in a normal nitrolysis experiment. Despite the fact that no other variable was introduced, no insoluble products were isolated. It was therefore evident that in the absence of hexamine, HMX/RDX was not formed independently from paraformaldehyde and ammonium nitrate under these specific conditions.

It was desired, however, to also demonstrate the failure of this independent formation in the presence of hexamine, in order to duplicate as closely as possible the conditions existing in the carbon-14 tracer experiments. If HMX/RDX were formed *via* such independent condensation then the extent of carbon atom equilibration would be dependent on the concentration of paraformaldehyde. Experiments were therefore conducted in which the paraformaldehyde was varied in such a manner as to include both an excess and a deficiency of total methylene content relative to the total amino nitrogen content. The stoichiometric ratio present in HMX and/or RDX is one methylene group to one amino nitrogen atom. The results of these experiments are given in Table III.

Table III

Nitrolysis of Hexamine-C^{14} in the Presence of Various Quantities of Paraformaldehyde

$(CH_2O)_x$ added, g.	Total methylene: amino N ratio	HMX/RDX yield, %	Specific activities, c.p.m./600 mg. Obsd. HMX	Calcd. HMX	Obsd. RDX	Calcd. RDX
None	0.8	80.0	175,000	Control	174,800	Control
0.85	0.9	91.1	155,840	155,000	153,250	155,000
1.70	1.0	88.0	138,190	138,500	138,200	138,500
2.55	1.1	88.0	127,800	125,600	126,500	125,600

The observed specific activities of both the HMX and RDX products for all runs were found to be as calculated, assuming complete dilution of methylene groups between hexamine and paraformaldehyde. In the concentration range studied, the quantity of paraformaldehyde obviously has no effect on this equilibration. The data in Table III are most significant since they demonstrate that complete equilibration of methylene groups occurs even when there is an excess of total methylene groups over amino nitrogen atoms. From these data it was concluded that, under these conditions of nitrolysis, paraformaldehyde does not react independently with ammonium nitrate to form HMX or RDX.

III. Chemical Equivalence of Methylene Groups from Hexamine, DPT and Paraformaldehyde during Nitrolysis.—The results of these tracer experiments provide strong evidence that methylene groups from hexamine, DPT and paraformaldehyde are all chemically equivalent in the processes involved during this nitrolysis reaction. In the first reaction stage, methylene groups from hexamine and paraformaldehyde form a common pool for the formation of DPT molecules. Similarly, in the second stage, methylene groups from DPT and paraformaldehyde can form a common pool for the formation of HMX and RDX molecules. It must, therefore, be concluded that, during the first stage, hexamine degrades non-selectively to low molecular weight species, and the formation of DPT, under the incomplete nitrolysis conditions of this stage, is a consequence of the

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(8) W. J. Chute, D. C. Downing, A. F. McKay, G. S. Myers and G. F Wright, *Can. J. Res.*, **27**, 218 (1949).

TABLE IV

ISOLATION OF DPT WITH VARIOUS TIMES OF ADDITION OF C^{14}-LABELED PARAFORMALDEHYDE

Expt.	Addition of $(CH_2O)_x$–C^{14}	Time of contact[a] before quenching, min.	DPT isolated, g.	Specific activity of DPT c.p.m./600 mg. Obsd.	Calcd.[b]	Chem. equilibration, %
1	Initially[c]	30	4.6	29,240	29,215	100
2	After 1st addn. of reactants	15	4.3	8,080	29,215	28
3	After 1st addn. of reactants	30	4.2	9,235	29,215	32
4	After 1st age period	30	3.1	90	29,215	0
5	None added	..	3.0	....	....	..

[a] Of the paraformaldehyde with the reaction medium. [b] Assuming complete dilution of hexamine carbon atoms by paraformaldehyde carbon atoms. [c] This experiment was repeated with hexamine-C^{14} and inactive $(CH_2O)_x$. The observed specific activity of the DPT was 2.15×10^5 c.p.m./600 mg.; calculated, 2.15×10^5 c.p.m./600 mg. DPT.

recombination of these species. Similarly, the degradation of DPT during the second nitrolysis is also non-selective. Therefore, the relative ratio of HMX to RDX is not controlled by a selective cleavage of a large molecule but is more likely influenced by the particular conditions controlling the recombination of a common methylene-containing fragment. In addition to the cyclic methylenenitramines, under conditions other than those described in this paper, the hexamine molecule can be degraded to fragments forming linear products as indicated by the work of Bachman,[1,9] Wright[8] and Reed.[10]

A more detailed picture of the processes occurring in the nitrolysis reaction was obtained by observing the distribution of carbon-14 in DPT and in HMX/RDX upon varying the time of addition of the paraformaldehyde during each stage. Such data are shown in Table IV for the isolation of DPT during the first nitrolysis phase.

When the labeled paraformaldehyde was added initially to the reaction mixture, the radioactivity of the isolated DPT was indicative of complete chemical equivalence of methylene groups between hexamine and paraformaldehyde. However, when the paraformaldehyde was added at the later intervals, the radioactivity of the isolated DPT was reduced; and when it was added after the first aging period, essentially no radioactivity was present in the DPT molecules indicating that all of this compound had already formed. Thus, once DPT molecules have formed during this first nitrolysis phase, its methylene groups can no longer become chemically equivalent with those from paraformaldehyde. Experiments 2 and 3 in Table IV also demonstrate that after the addition of paraformaldehyde, the time of contact before quenching had no important effect on the extent to which the methylene groups from hexamine and paraformaldehyde became chemically equivalent. The difference in the observed radioactivities in these two experiments is not considered to be significant. It is also interesting to note that the greater the period of time elapsing before the addition of paraformaldehyde during the first stage, the smaller was the yield of DPT isolated, and that, when the paraformaldehyde was added at the end of this stage, the amount of DPT isolated was almost the same as in a run where no paraformaldehyde was included.

Reference is also made to experiment 4 in Table IV as additional evidence for the absence of interaction between ammonium nitrate and paraformaldehyde. Here, paraformaldehyde-C^{14} was added after the first aging period, *i.e.*, after DPT had formed. The time of contact with the reaction mixture containing the excess ammonium nitrate was 30 minutes. This was the time also allowed for the nitrolysis of hexamine to DPT. The DPT that was isolated under these conditions contained no activity. In addition to further demonstrating the absence of isotopic carbon atom exchange between paraformaldehyde and DPT, this experiment indicates the failure of ammonium nitrate and paraformaldehyde-C^{14} to form radioactive DPT in a nitrolysis medium.

TABLE V

VARIATION OF $(CH_2O)_x$ ADDITION TIME DURING SECOND STAGE OF HEXAMINE-C^{14} NITROLYSIS

Expt.	$(CH_2O)_x$ addn., min.	HMX/RDX yield, g.	Obsd. spec. act.,[a] c.p.m./600 mg. HMX	RDX	Chem. equilibration, %
1	None[b]	8.1	176,100	177,270	..
2	Init.[c]	9.5	157,150	157,720	100
3	15[d]	9.6	164,000	163,170	67
4	30[d]	8.8	168,900	168,810	37
5	45[d]	8.4	176,200	177,400	0

[a] Calculated specific activity of either HMX or RDX assuming complete dilution of carbon atoms, 156,800 c.p.m./600 mg. [b] Control run. [c] Prior to second addition of reactants. [d] After the second addition of reactants.

The second nitrolysis stage was investigated in the same manner as above. Here, the hexamine was tagged with carbon-14 and inactive paraformaldehyde was added at different intervals during the last stage. These results, as listed in Table V, are clearly analogous to those obtained from the study of the first stage of the process. As the paraformaldehyde was added in later stages during the second addition of reactants, there was a decrease in the extent to which the methylene groups became chemically equivalent as observed from the radioactivities of the final products. When the paraformaldehyde was added after 45 minutes had elapsed of the normal one hour duration of the second aging period, no equilibration of methylene groups occurred, indicating that essentially all of the HMX/RDX product had already formed. Here too, as the paraformaldehyde was added during later periods of the second nitrolysis stage, the yield of cyclic methylenenitramines approached the yield obtained when this material was excluded

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(9) W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton and L. B. Scott, THIS JOURNAL, **73**, 2769 (1951).

(10) R. Reed, Jr., *ibid.*, **78**, 801 (1956).

entirely. Therefore, as the nitrolysis reagents were completely consumed to form products, the methylene groups from paraformaldehyde could no longer become chemically equivalent with those from HMX and RDX.

It can thus be postulated that paraformaldehyde increases the concentration of total methylene groups which exist in precursors to HMX/RDX. The increase in yield of combined HMX/RDX products, as a result of including paraformaldehyde, can therefore be accounted for on this basis. That the mode of reaction is more complex than is suggested by the above statements is evidenced by the fact that methylene content is not the only criterion in controlling yield or composition of the product. It is obvious that the processes involving amino groups and the formation of the nitramino structure are equally important for understanding the chemistry of the reaction. The mode of reaction involving these nitrogen species is currently being investigated using nitrogen-15 as a tracer.

Experimental

Calculations of Theoretical Specific Activity for Carbon Atom Equilibration.—The calculation of the theoretical specific activities for carbon atom equilibration between hexamine and paraformaldehyde was performed as follows: When hexamine-C^{14} was nitrolyzed the following expression was used

$$A_2 = A_1 \left(\frac{a}{a + b}\right)$$

where A_1 = specific activity of the cyclic methylenenitramine obtained from nitrolysis of hexamine-C^{14} in the absence of paraformaldehyde; A_2 = theoretical specific activity of the cyclic methylenenitramine obtained from the nitrolysis of hexamine-C^{14} in the presence of paraformaldehyde, upon complete equilibration of carbon atoms to products; a = gram atoms of carbon from hexamine molecule; b = gram atoms of carbon from paraformaldehyde.

When paraformaldehyde was labeled the following expression was used

$$B_2 = \frac{B_1}{a + b} \times W$$

where B_1 = known total activity (expressed as c.p.m. per total weight of paraformaldehyde added); B_2 = theoretical activity per unit weight of carbon of the particular cyclic methylenenitramine upon complete equilibration of carbon atoms with either hexamine or DPT to form products; W = weight of cyclic methylenenitramine carbon being counted; a = gram atoms of carbon from hexamine; b = gram atoms of carbon from paraformaldehyde.

Preparation of Hexamine-C^{14}.—To 200 ml. of formalin solution (36%) and 16 ml. of C^{14}-labeled formalin (0.01 mc./ml.), 160 ml. of ammonium hydroxide (28% ammonia) was added dropwise with stirring. Water was then removed under reduced pressure until a precipitate began to form. An additional 160 ml. of ammonium hydroxide was added and the above procedure repeated; 125 ml. of 98% ethanol was added and the mixture refluxed until the solid product was completely dissolved. The solution was transferred quantitatively by suction through a fritted disc. The precipitation of hexamine-C^{14} was completed by adding ether and chilling. The yield was 90% of theory, subl. pt. 260°, specific activity 0.18 μc./mM. (The entire synthesis was carried out in a closed system to prevent exposure to the highly volatile C^{14}-labeled formaldehyde.)

Preparation of Paraformaldehyde-C^{14}.—A solution of 100 ml. of formalin (36%) and 8 ml. of C^{14}-labeled formalin (0.01 mc./ml.) was vacuum distilled under constant agitation. After all the water was apparently removed, heat and stirring were continued for 0.5 hour. The polymerized formaldehyde was placed in a glove box and pulverized. The product was then dried over magnesium sulfate. The yield was 85% of theory (subl. pt. 143°).

Preparation of DPT-C^{14}.—To a mixture of 21 g. (0.35 mole) of acetic acid and 6 g. (0.2 mole) of paraformaldehyde solutions A containing 67 g. (0.48 mole) of hexamine-C^{14} (specific activity 0.18 μc./mM) dissolved in 110 g. (1.8 moles) of acetic acid, and B consisting of 63 g. (1.0 mole) of 98% nitric acid and 130 g. (1.3 moles) of acetic anhydride, were added dropwise. Solution B was prepared by adding the nitric acid dropwise to the acetic anhydride over a 0.5-hour period below 10° and aged for 0.75 hour. Solutions A and B were added continuously and simultaneously at 25–30° and the resulting mixture aged for 30 minutes at 30°. The DPT-C^{14} was precipitated by the addition of 267 ml. of water (65°), filtered and washed with cold water. The yield of product (m.p. 201°), represented approximately 59% of theory (specific activity, 0.13 μc./mM).

Nitrolysis of Hexamine to HMX/RDX.—To 39.3 g. of acetic acid, 0.65 g. of acetic anhydride and 0.85 g. of paraformaldehyde (subl. pt. 145°) solutions consisting of: (a) 5.05 g. of hexamine dissolved in 8.25 g. of acetic acid, (b) 12.8 g. of acetic anhydride and (c) 9.0 g. of a 15/14 by weight nitric acid (98%)–ammonium nitrate solution were added continuously and simultaneously over a 15-minute period with stirring. When the addition was completed, 3.2 g. of acetic anhydride was added in bulk and the reaction mixture was aged for 15 minutes. The temperature of the reaction mixture was maintained at 44 ± 1° throughout this procedure.

After this first aging period, 24.0 g. of acetic anhydride and 13.6 g. of a 15/14 (by weight) nitric acid–ammonium nitrate solution were added over a 15-minute period. After aging for 60 min., 17.5 g. of water (75–85°) was added, and the mixture was refluxed for 30 minutes. The mixture was then cooled to 20° and approximately 100 g. of ice was added. The water-insoluble material was filtered and washed with cold water. The yield of HMX/RDX was approximately 90% of theory (based on hexamine molecule) and 85% of this mixture was HMX.

Quenching of Nitrolysis Mixture at End of First Aging Period.—A normal nitrolysis of hexamine was carried out up to the end of the first aging period. At this point the reaction mixture was chilled to 12° and filtered rapidly. The material thus isolated was washed first with ether, then acetone and finally with ice-water. The product weighed approximately 5.0 g. and was identified as DPT from its infrared spectrum and melting point (203–204°). The yield represented 65% of theory based on one mole of hexamine.

Nitrolysis of DPT in a "Pseudo" Spent Reaction Medium.—The quantities of reagents existing in the reaction medium at the end of the first aging period were calculated to be: 56.2 g. of acetic acid, 0.15 g. of nitric acid, 4.35 g. of ammonium nitrate and 7.85 g. of DPT (based on the theoretical yield of DPT from hexamine). These quantities were mixed with 0.85 g. of paraformaldehyde-C^{14} and the second addition of the nitric acid–ammonium nitrate solution plus the acetic anhydride were added in the usual quantities. The yield of HMX/RDX was 76% of theory based on the DPT.

Exchange Studies. 1. Paraformaldehyde-C^{14} and Hexamine.—To the suspension of paraformaldehyde-C^{14} in glacial acetic acid containing a trace of acetic anhydride, the usual reactants were added simultaneously and rapidly in the same proportions, but in one-tenth the quantities, given in the procedure for the nitrolysis of hexamine. The reaction mixture was quenched by the addition of 40 ml. of carbon tetrachloride directly after the introduction of reactants (designated "zero" time) and after 2,4,8 and 15 minutes of reaction at 44°. The solid resulting from the addition of CCl_4 was washed free of nitrolyzing acids with additional CCl_4. The material thus isolated was rapidly slurried with 10 ml. of glacial acetic acid, filtered and washed three times with 20 ml. portions of absolute alcohol. The remaining material was then extracted with water, leaving behind an insoluble fraction. The water extract was treated with an aqueous mercuric chloride solution (5%) to precipitate any amino compound as the addition complex. The infrared spectrum, from a solid mull, of each mercuric chloride complex was obtained using a Perkin–Elmer infrared spectrophotometer, model 21. Each spectrum was compared with that of the same complex of a hexamine standard. The mercuric chloride complexes obtained from the zero, 2- and 4-minute experiments were identified as hexamine mercuric chloride from their associated absorption maxima at 6.85, 7.25, 7.50, 8.10, 10.00, 12.45 and 14.85 μ and found to contain no radioactivity. The 8- and 15-minute experiments did not yield any precipitate upon the addition of mercuric chloride to their respective water extracts.

The water-insoluble fractions were purified from dimethyl sulfoxide and identified as DPT by infrared analysis and melting point determinations. The 4-, 8- and 15-minute experiments each contained DPT having a specific activity of 4500 c.p.m./100 mg. (0.014 μc./m *M*).

2. (a) **Paraformaldehyde and DPT-C^{14} in Acetic Acid.**—Two samples were prepared consisting of: (1) 2.18 g. (0.01 mole) of DPT-C^{14} (10,000 c.p.m./600 mg.) and 3 g. (0.10 mole) of paraformaldehyde in 25 ml. of acetic acid; (2) 2.18 g. of DPT-C^{14} (10,000 c.p.m./600 mg.) in 25 ml. of acetic acid (this served as a control). After agitating for 24 hours at 25° both samples of DPT were purified and radioassayed at 10,000/c.p.m. 600 mg.

2. (b) **Paraformaldehyde and DPT-C^{14} in Simulated Spent Reaction Medium.**—This exchange study was conducted in a medium (as calculated above) simulating conditions at the end of the first aging period of hexamine nitrolysis. Two samples were prepared using DPT-C^{14}, with and without paraformaldehyde. The mixture was agitated for 1 hour at 30°. Hot water (65°) was added and the DPT isolated from each experiment had the same specific activity, *viz.*, 10,000 c.p.m./600 mg.

2. (c) **Paraformaldehyde-C^{14} and DPT in an Actual Spent Reaction Medium.**—The nitrolysis of hexamine was performed in the usual manner but without the inclusion of paraformaldehyde and carried out to the end of the first aging period. At this interval, 0.85 g. of paraformaldehyde-C^{14} was added and the mixture was agitated for an additional 30 minutes at 44°. The reaction mixture was chilled and the DPT was isolated as described above. Radioanalysis showed the DPT to be free of activity.

3. **Paraformaldehyde-C^{14} and HMX-RDX.**—Five grams each of inactive HMX and RDX were added separately in place of the hexamine-acetic acid solution and a usual nitrolysis was carried out in the presence of paraformaldehyde-C^{14}. The HMX and RDX in each case were isolated quantitatively at the end of the experiment and found to contain no activity.

Isolation of Pure HMX from HMX/RDX.—Two grams of inactive HMX/RDX containing 0.02 g. of RDX-C^{14} (0.13 μc./m*M*) was dissolved in 100 ml. of C.P. acetone in an erlenmeyer flask. Acetone was then evaporated until a precipitate began to form. The mixture was cooled to 25° and the supernatant liquid decanted. The precipitate was washed with two 10-ml. portions of chilled acetone. Two additional recrystallizations by this procedure were required for the isolation of HMX (m.p. 274.5–275°) free of activity and hence free of RDX. This proven method was used for the isolation of HMX-C^{14} samples for radioassay.

Isolation of Pure RDX from HMX/RDX.—A glass tube 5.7 cm. in diameter and 52 cm. in length was filled to a height of 47 cm. with a 2:1 silicic acid–Celite mixture (Mallinckrodt silicic acid, Johns-Mansville Hyflo-Supercel). The column was prewashed with the following sequence of solvents: a, 0.2 *V* ml. of ether; b, 1.0 *V* ml. of acetone-ether (1:1); c, 0.6 *V* ml. of ether; d, 2.0 *V* ml. of hexane where $V = 900$ ml. Five grams of inactive HMX/RDX containing 0.05 g. of HMX–C^{14} (0.13 μc./m*M*) was dissolved in a mixture of 25 ml. of dimethyl sulfoxide (Stepan Chemical Co.) and 100 ml. of benzene was applied to the column. Benzene containing 2% (by volume) dimethyl sulfoxide was used as the developer. The first four *V*'s were collected and the benzene was evaporated. Only the third and fourth concentrates, consisting of the residual dimethyl sulfoxide solutions, yielded precipitates upon the addition of water. Each precipitate was separately washed with ethanol–ether and recrystallized from dioxane (1 g./16 ml.). Both RDX fractions (m.p.'s 204°) were found to be free of activity, denoting the absence of HMX. In the actual isolation of RDX-C^{14} samples for radioassay by the above proven procedure, the third and fourth *V*'s were combined.

Liquid Scintillation Counting Procedure.—A Tricarb liquid scintillation counter (Packard Instrument Co.) consisting of 2 refrigerated photomultiplier tubes in a coincidence circuit was used to radioassay all samples. The lower and upper discriminators were fixed at 10 and 50 volts, respectively. The high voltage was set at 1180 volts. All samples were assayed using 70 ml. Kimble Exax weighing bottles. The same counting system was used for C^{14}-labeled RDX, DPT and HMX. It contained: (a) 600 mg. of C^{14}-labeled cyclic methylenenitramine, (b) 35 ml. of toluene containing 4 g. of diphenyloxazole per liter (Tol/PPO), (c) 14 ml. of tetrahydrofuran, (d) 16 ml. of dimethyl sulfoxide, (e) 0.5 ml. of water containing 9 mg. of inactive formaldehyde per ml. The inclusion of tetrahydrofuran was needed to prevent the dimethyl sulfoxide from freezing out of solution. The cyclic methylenenitramine was first dissolved in dimethyl sulfoxide. This was followed by the addition of tetrahydrofuran, the formalin, and finally the Tol/PPO. The counting system for paraformaldehyde-C^{14} was the same as the above with the following exceptions: The DPT, HMX or RDX were inactive and the formalin solution was prepared from the hydrolyzed paraformaldehyde-C^{14}. From the radioactivity measurements in counts per minute, the specific activities of the carbon atoms were determined.

Analysis of HMX/RDX Mixture for HMX and RDX Content.—The HMX/RDX mixture was analyzed by the method developed by Wright.[11] An aqueous solution of sodium nitroso ferricyanide was added to an acetone solution of a weighed sample of HMX/RDX and the resultant solution was made alkaline. The solution was allowed to stand 20 minutes in order to develop a blue-green color caused by the reaction of RDX with the reagent. The transmittance of the solution at 625 mμ was then measured. By comparing the transmittance value with a standard curve, the percentage of RDX in the mixture was calculated. The HMX content was then determined by difference.

Acknowledgment.—The authors wish to express their gratitude to Professors John W. Irvine, Jr., and Ludwig F. Audrieth for their helpful comments during this investigation. They are indebted to the Army Ordnance Corps for granting the release of this article for publication.

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[11] S. B. Wright, U. S. Defense Corporation, Control No. 20-T-17, Series A (1953).