

STUDIES OF RDX AND RELATED COMPOUNDS  
III. THE REACTION TO FORM RDX FROM AMMONIUM NITRATE  
AND FORMALDEHYDE IN ACETIC ANHYDRIDE<sup>1</sup>

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**Abstract**

This reaction at 35°C. exhibits a behavior indicative of the presence of an intermediate in the reaction. Reaction of paraformaldehyde and ammonium nitrate in glacial acetic acid resulted in the isolation of hexamine dinitrate. Evidence is presented to indicate that formation of hexamine dinitrate, accompanied by the production of nitric acid, is responsible for the production of RDX in the acetic anhydride system.

**Introduction**

Kinetic studies of the direct nitrolysis of hexamine with concentrated nitric acids to produce *cyclo*-trimethylenetrinitramine (RDX) have been reported in previous papers from this laboratory (6, 8). The present paper gives some of the results obtained by investigation of an alternative method of preparation involving the interaction of ammonium nitrate and paraformaldehyde in acetic anhydride (4, 7).

**Experimental**

The procedure, usually, was to place the desired amounts of ammonium nitrate and paraformaldehyde (expressed as moles of formaldehyde) in 125 ml. Erlenmeyer flasks, which were suspended in a thermostat from a shaker oscillating at about 140 cycles per minute. The temperature of the water bath was controlled to within  $\pm 0.1^\circ\text{C}$ . Acetic anhydride was then added, the time of its addition being taken as zero time for the reaction. The reaction was stopped, after the desired time interval, by the addition of about 20 ml. of water, the flask removed from the thermostat, and the mixture boiled for 15–20 min. After cooling, the flask was filled with water and allowed to stand, usually overnight. Precipitated RDX was collected in a sintered glass crucible, washed with water, dried in an air oven at  $90^\circ\text{C}$ . for two to three hours and weighed. In general, the weight of crude RDX was considered to be the yield and was calculated as per cent of the theoretical on a formaldehyde basis.

**Results and Discussion**

*Presence of an Intermediate in the Reaction*

RDX was produced only after an induction period, the length of which varied from two to six hours depending on the source of paraformaldehyde, when 0.02 mole paraformaldehyde, 0.04 mole ammonium nitrate, and 5 cc. acetic anhy-

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dride were allowed to react at 35°C. The presence of acetic or trichloroacetic acid reduced the induction period somewhat, but neither acid had any appreciable effect on the rate of reaction following the induction period. It appeared from these results that an intermediate was formed during the reaction, the rate of its formation, but not the rate of its conversion to RDX, being influenced by the presence of acetic or trichloroacetic acid.

A series of experiments was made in which the various reactants were individually withheld from reaction mixtures at 35°C. for a period equal to the induction period (3.5 hr.), followed by addition of the missing component and further reaction for 3.5 hr. No RDX was produced, hence no intermediate was formed, unless all three reactants were present.

The relative amounts of intermediate present at various times were determined as follows. Seven reaction mixtures, containing 13% acetic acid, were allowed to react for different times, after which they were filtered and six aliquots of each filtrate taken. The RDX content of one of these was determined by immediate dilution, that of the others after further periods of reaction at 35°C. The amounts of intermediate present at various times, expressed in terms of the amount of RDX it was capable of producing, are shown in Fig. 1. The top curve, for example, indicates the amount of intermediate present at the time of filtering, when filtration was made two to six hours after the experiment was started. The second curve from the top gives the amount of intermediate present one half hour after filtration when filtration was made at the same time intervals after start of the experiment; and similarly

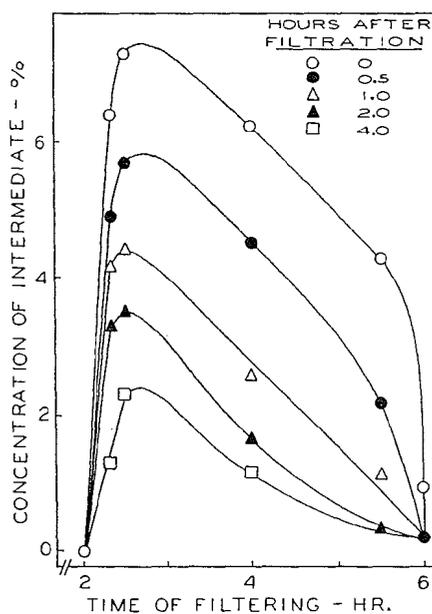


FIG. 1. Relative amounts of intermediate present at various times.

for the other curves. The results show that negligible amounts of intermediate were formed during the first two hours, while the maximum amount was present about 2.5 hr. after the start of the reaction. The RDX yield reached its maximum value at about six hours, after which time the amount of intermediate present was negligible.

The activation energy for conversion of the intermediate to RDX was determined by allowing paraformaldehyde and ammonium nitrate to react to the end of the induction period (2.5 hr.) at 35°C. in 7.5 cc. acetic anhydride containing 13% acetic acid, after which the mixtures were filtered and the filtrates allowed to react further at 25°, 30°, 35°, and 40°C. From initial rates, an activation energy of roughly 18.5 kcal. was obtained.

Using the halochromic compounds of Conant and Hall (3), it was possible to estimate, despite rapid fading of the indicators, that the pH (HAc) of a normal reaction mixture started at about zero but changed to a value of about -3 as reaction progressed. Comparison with a pH (HAc) value of -3.2 determined for sulphuric acid (one drop) in acetic acid (5 cc.) containing acetic anhydride gave clear indication that a strong acid, as well as the intermediate discussed above, was formed during reaction.

When paraformaldehyde (0.02 mole) and ammonium nitrate (0.04 mole) were allowed to react in glacial acetic acid (6 cc.) for 11 hr. at 35°C., followed by addition of acetic anhydride (6 cc.) and further reaction for one hour, production of RDX occurred without an induction period following the addition of anhydride. It appeared from this that the intermediate had been formed by reaction of paraformaldehyde and ammonium nitrate in acetic acid. The rate of conversion to RDX of intermediate so formed was increased by the addition of a few drops of sulphuric or perchloric acid, while the yield of RDX obtained was adversely affected by the presence of formaldehyde in excess of a mole ratio of approximately 1.5:1 with ammonium nitrate.

The activation energy for the formation of RDX subsequent to the addition of anhydride to a glacial acetic acid preparation of the intermediate was found to be about 19.5 kcal. Comparison of this value with that recorded previously for conversion, also in acetic acid - acetic anhydride media, of the intermediate present in the filtrates from reaction mixtures suggests that the same substance is involved in the two cases.

When paraformaldehyde and ammonium nitrate reacted at 35°C. in glacial acetic acid, it was observed that the mixture gradually cleared as the paraformaldehyde reacted, until at the end of 2.5 hr. only excess ammonium nitrate remained. An hour later there appeared a dense white precipitate. The excess ammonium nitrate was removed by further reaction with a slight excess of paraformaldehyde, the precipitate filtered off, washed with glacial acetic acid and acetone, and dried in a vacuum desiccator. Elemental analysis gave\*: C, 27.4, 27.5; H, 5.3, 5.4; N, 30.7, 30.8%. For hexamine dinitrate, C, 27.1;

\*We are indebted to Dr. G. F Wright, University of Toronto, for the analyses.

H, 5.3; N, 31.6%. The precipitate gave an X-ray powder photograph which showed only the characteristic pattern for hexamine dinitrate. The formation of hexamine by reaction of formaldehyde and ammonia in acidic media has been reported previously by Baur and Ruetschi (2).

Isolation of hexamine dinitrate from the paraformaldehyde - ammonium nitrate reaction in glacial acetic acid, and comparison of the behavior of this system in the presence of acetic anhydride with the characteristics of the reaction to produce RDX from paraformaldehyde, ammonium nitrate, and acetic anhydride, give strong indication that hexamine dinitrate is the intermediate formed during the latter reaction. On this basis, the observed deleterious effect of excess paraformaldehyde on RDX yield may be readily explained, since hexamine is decomposed by formaldehyde in glacial acetic acid at a rate which increases with increased mole ratio of formaldehyde to hexamine (5).

Nitric acid is undoubtedly the strong acid revealed by the Conant - Hall indicators to be formed in the paraformaldehyde - ammonium nitrate - acetic anhydride reaction mixtures. Formation of nitric acid simultaneously with hexamine dinitrate in the reaction mixtures must be assumed to account for the nitrolysis reaction to produce RDX, unless the presence of another intermediate capable of promoting nitrolysis can be demonstrated. Rather exhaustive examination of the system failed to indicate any such alternative agent for nitrolysis.

While one of the functions of acetic anhydride is almost certainly to remove water formed during the initial production of hexamine and nitric acid, and thus maintain the nitric acid concentration at a high level favorable for nitrolysis (7), it seems likely that it also has the role of a "fast" solvent for the reaction. This was revealed by studies in which 6 cc. of various solvents were added to 3 cc. of filtrate obtained from the reaction of ammonium nitrate and paraformaldehyde in acetic acid. The solvent - filtrate mixture was allowed to react with 3 cc. acetic anhydride for 30 min. at 35°C., after which 0.5 gm. hexamine dinitrate was added. The rates of production of RDX, determined in the usual manner, were in the following order for the solvents listed: acetic anhydride  $\gg$  propionic anhydride  $>$  nitromethane  $>$  acetic acid  $>$  acetone  $>$  benzene  $>$  propionic acid  $\gg$  dioxane.

Since the present studies gave strong indication that the paraformaldehyde - ammonium nitrate - acetic anhydride reaction to produce RDX consists essentially of the production of hexamine followed by its nitrolysis, investigation of this system was abandoned in favor of studies on the Bachmann reaction (1) in which hexamine and nitric acid are among the starting materials. The results of several studies with the Bachmann system will be reported in subsequent papers.

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