

Study on the Nitrolysis of Hexamethylenetetramine by NMR-Spectrometry^(*), Part IV: A Novel Mechanism of the Formation of RDX from HA

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Untersuchung der Nitrolyse von Hexamethylenetetramin mittels NMR-Spektrometrie, Teil IV: Ein neuer Mechanismus der RDX-Bildung aus HA

Der Mechanismus der Nitrolyse von Hexamethylenetetramin (Hexamin oder HA) mit Salpetersäure und mit einer Mischung aus Salpetersäure und Ammoniumnitrat bei der Synthese von 1,3,5-Trinitro-1,3,5-triazacyclohexan (Hexogen oder RDX) wurde mittels NMR-Aufzeichnung untersucht. Es wurde gefunden, daß HA sofort verschwindet, während RDX nach und nach gebildet wird. Dies zeigt, daß einige Zwischenprodukte bei der HA-Nitrolyse entstehen. Die chemische Verschiebung der Peaks bei der ¹H- und ¹³C-NMR Spektrenaufzeichnung stimmt nicht überein mit der Ringstruktur der möglichen Zwischenprodukte, wie sie von Wright und Mitarbeitern vorgeschlagen wurde. Ein Vergleich der ¹³C-NMR Spektren zeigte, daß die Nitrolyse-Bruchstücke des K-Prozesses für die Bildung von RDX in Frage kommen können. Aufgrund dieser Ergebnisse werden Strukturen der Zwischenprodukte vorgeschlagen. All diese Befunde legen einen neuen Mechanismus der RDX-Bildung aus HA nahe, d.h. die Nitrolyse von HA ergibt zuerst einige offenkettige Methylen-nitramin-Zwischenprodukte, dann erfolgt die Kondensation der letzteren unter Bildung von RDX bei bestimmten Bedingungen.

Etude de la nitrolyse de l'hexaméthylènetétramine au moyen de la spectrométrie RMN, partie IV: un nouveau mécanisme de formation de RDX à partir de HA

Le mécanisme de nitrolyse de l'hexaméthylènetétramine (hexamine ou HA) avec de l'acide nitrique et un mélange d'acide nitrique et de nitrate d'ammonium lors de la synthèse de 1,3,5-trinitro-1,3,5-triazacyclohexane (hexogène ou RDX) a été étudié au moyen d'enregistrements RMN. On a montré que le HA disparaissait immédiatement alors que le RDX était formé progressivement. Ceci montre que certains produits intermédiaires se forment lors de la nitrolyse de HA. Le décalage chimique des pics lors de l'enregistrement des spectres par RMN ¹H et ¹³C ne correspond pas à la structure cyclique des éventuels produits intermédiaires proposée par Wright et ses collaborateurs. Une comparaison des spectres RMN ¹³C a montré que les fragments de nitrolyse dans le processus K peuvent être utilisés pour former du RDX. Compte tenu de ces résultats, on propose des structures de produits intermédiaires. Tous ces résultats suggèrent un nouveau mécanisme de formation de RDX à partir de HA, à savoir, la nitrolyse de HA donne d'abord quelques produits intermédiaires méthylènenitramine à chaîne ouverte, puis on a ensuite condensation de ces derniers avec formation de RDX dans certaines conditions.

Summary

The mechanisms of the nitrolysis of hexamethylenetetramine (hexamine or HA) with nitric acid, and with the mixture of nitric acid and ammonium nitrate to form 1,3,5-trinitro-1,3,5-triazacyclohexane (hexogen or RDX) were studied by NMR tracing. It was found that HA immediately disappeared, while RDX was formed gradually, which indicates the formation of some intermediates in the HA nitrolysis to give RDX. The chemical shifts of the peaks in the ¹H- and ¹³C-NMR tracing spectra disagreed with the possible cyclic-structure intermediates proposed by Wright and co-workers. Comparison of the ¹³C-NMR spectra showed that the nitrolysis fragments in K process can be used to form RDX. Based on the results, structures of intermediates were proposed. All the evidences mentioned above suggested a novel mechanism of the formation of RDX from HA, i.e., the nitrolysis of HA first gives some open-chain methylenenitramine intermediates, and the condensation of the latter gives RDX under certain conditions.

1. Introduction

In Hale process, we have first proved⁽¹⁾ that in the nitrolysis of hexamethylenetetramine (hexamine or HA) the methylene group which cannot be used to form

1,3,5-trinitro-1,3,5-triazacyclohexane (hexogen or RDX) appears in the form of dioxymethylenenitronitrate, O₂N(CH₂O)₂ONO₂, and reported⁽²⁾ some new evidences that the intermediate, NH(NO₂)CH₂OH, acts as a possible precursor to RDX both in Hale and in K process. Our recently ¹⁵N study⁽³⁾ shows that the intermediates to RDX, forming both in Hale and in K process, were composed of various kinds of open-chain methylenenitramines. As a continuation of this study we now report the experimental results by NMR tracing the course of nitrolysis of HA to form RDX in Hale and in K process, and the direct evidenced for proving the mechanism according to the ¹H- and ¹³C-NMR spectra of the nitrolysis of HA in Hale and in K process. Finally, we suggested a novel mechanism of the formation of RDX from HA.

2. Experimental

¹H- and ¹³C-NMR spectra were determined on a JNM-FX90Q spectrometer. Chemical shift measurements are referenced to TNT (2,4,6-trinitrotoluene): δ(¹H) 2.73 ppm, δ(¹³C) 15.37 ppm, in HNO₃ or HNO₃-NH₄NO₃ solutions.

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A mixture of HA and HNO₃ was prepared as required to obtain various HA-HNO₃ ratios, various temperatures and various HNO₃ concentrations. ¹H-NMR spectra were determined at various intervals (Fig. 1).

Since a lot of NH₄NO₃ was used in K process, the ¹H spectrum was influenced by the triplet peaks of NH₄⁺ in the nitrolysis liquors (Fig. 2). In addition the nitrolysis liquor of K process at room temperature was not a clear solution. We determined the ¹³C-NMR spectra of the nitrolysis liquors at 40°C (Fig. 3). The reaction mixture was stirred and heated on the water bath to different temperatures. After chilling to 40°C ¹³C-NMR spectra were determined at same temperature (Fig. 4).

3. Results and Discussion

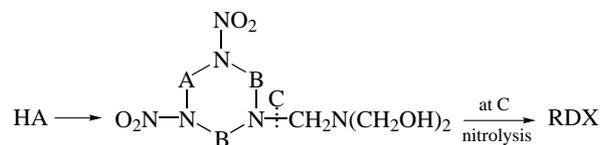
3.1 Course of Nitrolysis of HA to form RDX in Hale Process

The ¹H-NMR spectrum (Fig. 1) showed that HA immediately disappeared, while RDX was formed gradually, which indicates the formation of some intermediates in the HA nitrolysis to give RDX.

We suggested the observed peak, M1, represents an intermediate to form RDX. So, the whole reaction course seems to be as follows:



Wright⁽⁵⁾ proposed a course for the HA to give RDX:



According to the reaction course the intermediate M1 would have the cyclic-structure and the main incidence of nitrolysis, however, is postulated at C of M1 to yield cyclonite. But the chemical shifts of the peaks in the ¹H spectra of nitrolysis liquor (Fig. 1) disagreed with those structures suggested by Wright. If M1 had the cyclic-structure mentioned above, it would exhibit two bands A, B, whose intensity ratios A : B = 1 : 2 in ¹H-NMR spectra and whose chemical shifts of methylene group δ(¹H) 5.90–6.10 for A, and δ(¹H) 5.00–5.20 for B⁽⁴⁾. In addition, there is also not an “AB” quartet in the ¹H-NMR spectra of Hale process. This indicated that DPT was not an intermediate to form RDX under this condition, too. According to Refs. 1–4 and the discussions above we believed that the M1 has not the cyclic-structure. One of the possible structures of the intermediate M1 has been deduced from the new evidences⁽²⁾.

3.2 Course of Nitrolysis of HA to form RDX in K Process

For the reasons given in the experimental section we determined the ¹³C-NMR spectra of the nitrolysis liquors of K process at 40°C (Figs. 3–4).

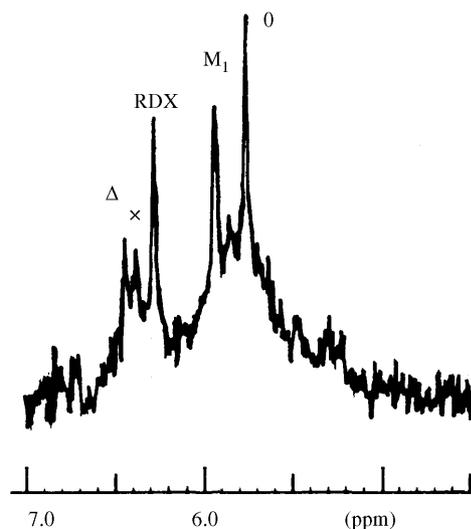


Figure 1. ¹H spectrum of reactant of Hale process determined at 27°C; reaction time = 85 s, concentration: [NA] = 21.17 mol/l, [HA] = 0.21 mol/l; (NA = nitric acid).

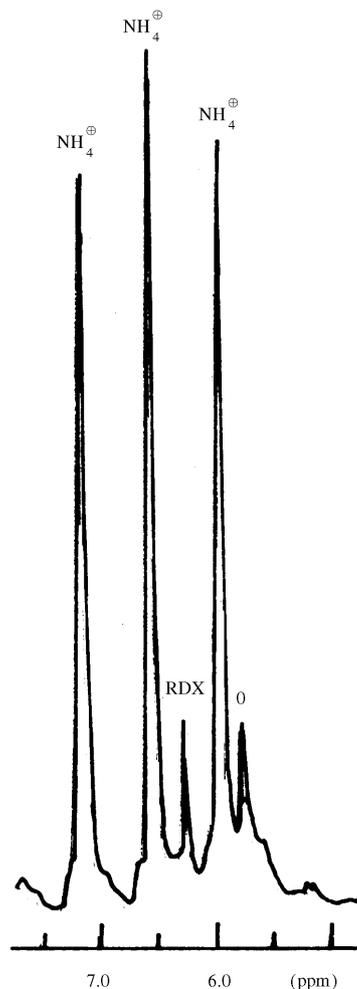


Figure 2. ¹H spectrum of reactant of K process determined at 27°C; concentration: [NA] = 23.81 mol/l, [AN] = 8.33 mol/l.

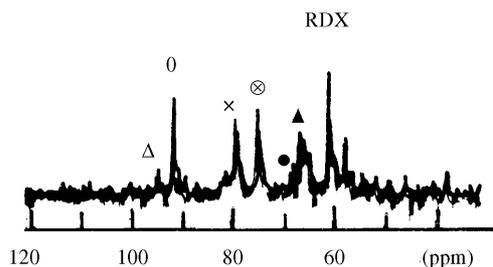


Figure 3. ^{13}C spectrum of reactant of K process at 40°C (accumulated 100×25 times), concentration: $[\text{NA}] = 23.67 \text{ mol/l}$, $[\text{AN}] = 15.36 \text{ mol/l}$, $[\text{HA}] = 0.63 \text{ mol/l}$.

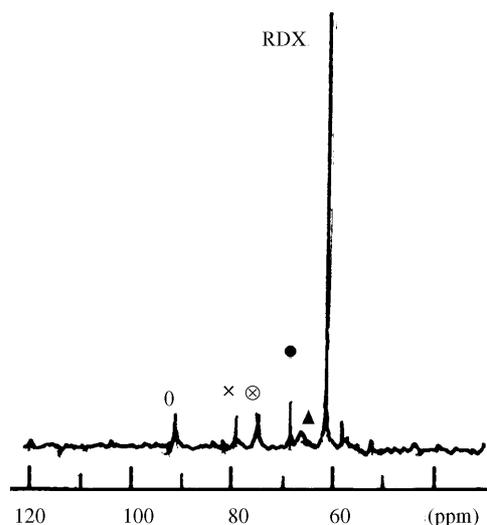


Figure 4. ^{13}C spectrum of the same reactant as in Fig. 3 (accumulated 100×25 times), heated to 80°C for 30 min and determined after chilling to 40°C .

The results of the assignments of ^{13}C peak to the methylene groups of the products and the intermediates in K process are given in Table 1.

According to the results given in Table 1 and the fact that RDX can be formed from condensation of open-chain methylenenitramines⁽³⁾, in much the way that we explained in the section 3.1, we can rule out the possibility that the intermediates have the cyclic-structure proposed by Wright and co-workers.

Table 1. Assignment of ^{13}C Peaks to the Methylene Groups of the Products and the Intermediates in K Process

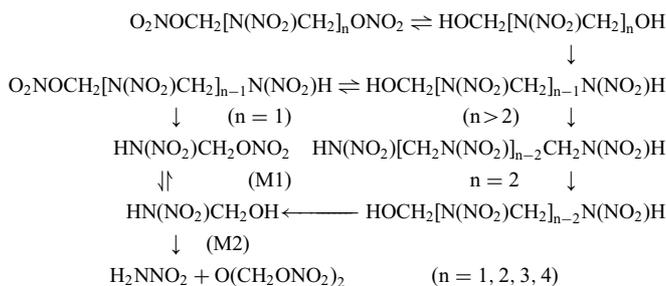
Structure	$\delta(^{13}\text{C})\text{ppm}$	Signs
$\text{CH}_2(\text{ONO}_2)_2$	93	Δ
$\text{O}_2\text{NO}(\text{CH}_2\text{O})_2\text{NO}_2$	89–91	\circ
RDX	61–62	RDX
$\text{RN}(\text{NO}_2)\text{CH}_2\text{ONO}_2$ ($\text{R} \neq \text{H}$)	~ 79	X
$\text{R}_1\text{N}(\text{NO}_2)\text{CH}_2\text{N}(\text{NO}_2)\text{R}_2$ ($\text{R}_1, \text{R}_2 \neq \text{H}$)	58–65	\blacktriangle
$\text{RN}(\text{NO}_2)\text{CH}_2\text{OH}$ ($\text{R} \neq \text{CH}_2\text{OH}$)	69	\bullet
$\text{O}_2\text{NN}(\text{CH}_2\text{OH})_2$	74	\otimes

The comparison of the peaks between Figs. 3–4 which are assumed to be open-chain methylenenitramines decreased with the peak in Fig. 4 which represents RDX increased, shows that the nitrolysis fragments in K process can be used to form RDX by heating the reaction mixture to higher temperature.

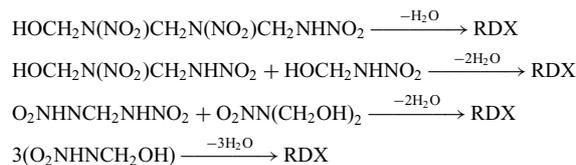
4. The Mechanism of Nitrolysis of HA

All the evidences mentioned above suggested a novel mechanism of the formation of RDX from nitrolysis of HA. The nitrolysis of HA first gives some open-chain methylenenitramine intermediates, and the condensation of the latter gives RDX under certain conditions. The hypothesis embraces the following three points:

- (1) In Hale- and K process, the nitrolysis of HA first gives some open-chain methylenenitramine fragments, and the fragments in the nitrolysis liquor exist in the equilibria as in the following equations:



- (2) The fragments can be converted to the useful intermediates to form RDX. The probable mechanisms are proposed as follows:



- (3) The main role of NH_4NO_3 is the protection of the intermediates from the oxidation in K process.

5. References

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