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Note

Determination of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane in microgram quantities

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Although 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) may be readily analyzed by vapor-phase chromatography (VPC)[1,2], this is not true for 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX). This fact may be partially explained on the basis of the surprisingly lower vapor pressure of HMX compared with RDX[3]. At 155°, for example, RDX has a retention time of 6.3 min on an Apiezon M column[1], but HMX failed to elute even with temperatures as high as 220°. Furthermore, HMX failed to elute under a variety of VPC conditions with columns containing different liquid phase loadings and supports, column temperatures and gas flow-rates.

It occurred to us that perhaps HMX could be quantitatively hydrolyzed to a specific product such as nitrite or nitrate, which then could be determined by some sensitive method. If the method were sufficiently sensitive, microgram quantities of HMX could be separated and determined from complex mixtures by thin-layer chromatography[4]. In this connection we have recently developed a procedure for the determination of microgram quantities of nitrite and nitrate ions[5]. We wish now to report a method for the microgram determination of HMX by basic hydrolysis.

EXPERIMENTAL

Basic hydrolysis of HMX

Ten to one thousand micrograms of HMX in acetone were put into a 25-ml (or 50-ml) volumetric flask. The acetone was removed by evaporation on a hot plate. To the dry flask was added 1.0 ml of a 50% (19 *M*) aqueous sodium hydroxide solution and the mixture heated to boiling for approximately 1 min with occasional swirling until a clear solution was obtained. The flask was cooled and analyzed for nitrite/nitrate by the following two methods.

Analysis of HMX hydrolysate for total nitrite/nitrate content —gas chromatographic method

The detailed procedure for the determination of nitrite and nitrate ions by conversion to nitrobenzene has been previously reported[5] and will not be repeated here. However, in some cases, a 4 ft. × 1/4 in. glass column packed with 2.95% Dexsil 300 GC on Chromosorb W AW DMCS, 80–100 mesh, was used rather than the Apiezon M column to determine nitrobenzene. Other conditions were: column tem-

perature, 175°; carrier gas, argon–methane (95:5); flow-rate, 192 ml/min; ^{63}Ni detector temperature, 300°; injection port temperature, 180°; pulse, 150 μsec; attenuation, ×80. Under these conditions *p*-nitrotoluene (*p*-NT) must be used as internal standard because the *o*-nitrotoluene (*o*-NT) peak is not resolved from the nitrobenzene (NB) peak. Retention times for NB and *p*-NT under these conditions were 16 and 24 sec, respectively. Fifty micrograms ($1.68 \cdot 10^{-7}$ moles) of HMX after hydrolysis and VPC analysis yielded $4.6 \cdot 10^{-7}$ moles NB with a sulfuric acid blank (for nitrate) of $0.3 \cdot 10^{-7}$ moles NB (6.5%).

Analysis of HMX hydrolysate for nitrite-ion content by the Griess method[6]

Because of the excess sodium hydroxide present after HMX hydrolysis, a somewhat modified Griess procedure was used. One milliliter of sulfanilic acid reagent (0.60 g sulfanilic acid per 100 ml of 20% aq. HCl) was mixed immediately before use with 1.7 ml of concentrated HCl and added in one portion to a 50-ml flask containing the HMX hydrolysis products. After allowing three minutes for diazotization, 1.0 ml of α-naphthylamine reagent (0.60 g α-naphthylamine per 100 ml of 1% aq. HCl) and 1.0 ml of 20% aq. sodium acetate (to buffer pH to 2.0–2.5) were added. Under these conditions, 40 min were necessary for full color development at which time the absorbance was read at 520 nm with a Cary 16 spectrophotometer. The extinction coefficient for nitrite ion for this procedure was $4.27 \pm 0.04 \cdot 10^4$. A solution of 25.0 μg ($0.847 \cdot 10^{-7}$ moles) of HMX after hydrolysis and and Griess determination gave an absorbance of 0.198 at 520 nm with a blank of 0.0056 (2.8%) to yield $2.25 \cdot 10^{-7}$ moles nitrite ion.

Applications

To test the utility of the hydrolysis method for the analysis of HMX in complex mixtures, the following procedures were carried out.

Thin-layer separation and analysis of HMX in RDX–HMX mixtures. Fifty microliters of an acetone solution containing HMX (0.71 μg/μl) and RDX (1.4 μg/μl) were spotted in a series of ten spots on each of four 0.3-mm thick silica gel HF-254 plates. The plates were simultaneously developed with benzene–acetone (4:1) in an ascending manner. After air drying, zones for HMX and RDX were located under 254-nm UV light; R_F values for HMX and RDX were 0.3 and 0.4, respectively. Zones containing the HMX were scraped off and extracted with acetone, the acetone evaporated in a 25-ml volumetric flask, and the basic hydrolysis of HMX carried out as previously described.

The number of moles of HMX may be calculated from that of NB (or nitrite) as moles NB/(3·0.93), where 0.93 is the hydrolysis yield in the formation of three moles of nitrite for each mole of HMX hydrolyzed. The recovery of the HMX applied to the four plates in the RDX–HMX mixture was 101 ± 4%.

Analysis of aqueous HMX solutions. Ten milliliters of an aqueous solution of HMX were extracted four times with 10-ml portions of benzene. The extract was placed in a 100-ml round-bottomed flask and the benzene removed under vacuum at 25° by means of a water aspirator. The contents were taken up in acetone, transferred to a 25-ml volumetric flask and analyzed for HMX by basic hydrolysis and conversion of the nitrite formed to nitrobenzene as described above. A total of 26 ± 2 μg was found and therefore the aqueous solution had a calculated concentration of 2.6 ± 0.2

ppm HMX. An independent check on the hydrolysis procedure for the HMX determination was made by taking another 10 ml of the aqueous HMX solution, extracting as described, and analyzing on TLC plates by the spot-area method of analysis[4] with known concentrations of HMX. By this procedure, a total of 25 ± 2 μg of HMX was found in the extract of the 10 ml aqueous solution (2.5 ± 0.2 ppm HMX, calculated), which is in excellent agreement with the result of the hydrolysis procedure.

RESULTS AND DISCUSSION

Three moles of nitrite ion are formed for each mole of HMX reacted in the heterogeneous hydrolysis of HMX by strong (50%, 19 *M*) aqueous sodium hydroxide. A constant hydrolysis yield of 92 ± 3% was found for the formation of nitrite ion over a hundred-fold change in initial HMX. Nitrite ion was analyzed both by the direct Griess spectrophotometric procedure and the indirect gas chromatographic method by conversion to NB. From the results obtained (Table I) only nitrite ion (and no nitrate ion) was formed during the HMX basic hydrolysis because the Griess method is specific for nitrite ion.

Although both the VPC and Griess methods give identical analytical results for the nitrite ion produced in the basic hydrolysis of HMX, the VPC method is considerably faster. The nitrite oxidation and nitration step for the formation of nitrobenzene requires only 6–7 min and another 30 sec for analysis, whereas 40 min are required for full color development for the Griess spectrophotometric determination of nitrite. Theoretically, the VPC method employing the ^{63}Ni detector is much more sensitive than the Griess method for the nitrite analysis. Practically, however, the blanks encountered with the chromatographic method set a lower limit of about ten micrograms for HMX, which is also the lower limit for the Griess determination.

TABLE I

HYDROLYSIS YIELD OF NITRITE ION FORMED IN THE HETEROGENEOUS HYDROLYSIS OF HMX IN 50% (19 *M*) AQUEOUS SODIUM HYDROXIDE AS A FUNCTION OF HMX

Initial HMX		*NO_2^- Formed*	*Method*	*Mole ratio*	*Yield**
μg	*10^{-7} moles*	*(10^{-7} moles)*		*NO_2^-/HMX*	*(%)*
9.97	0.337	0.91	VPC	2.7	90
20.0	0.678	1.78	Griess	2.6	87
25.0	0.847	2.41	Griess	2.9	95
25.0	0.847	2.25	Griess	2.7	88
28.1	0.950	2.7	VPC	2.8	92
49.7	1.68	4.4	VPC	2.6	87
50.0	1.69	4.62	Griess	2.7	91
99.7	3.37	10	VPC	3.0	100
99.7	3.37	9.2	VPC	2.7	90
997	33.7	94	VPC	2.8	92
997	33.7	101	VPC	3.0	100
1000	33.8	98.9	Griess	2.9	97
			Average	2.8 ± 0.1	92 ± 3

* Based on the theoretical ratio of NO_2^-/HMX = 3.

We are at present investigating the determination of RDX by basic hydrolysis as an alternative to the VPC method.

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