Thin-layer Chromatography of Some Nitramine-Explosives

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During the investigations of formation of the high explosive hexogen by nitrolysis of hexamethylene tetramine a number of nitramines closely related to hexogen were discovered. These compounds are of interest as possible reaction intermediates or side products which if present may adversely affect the properties of hexogen.

Very few papers deal with methods for chromatographic separation of these compounds. Malmberg *et al.*¹ described a column chromatographic procedure for the separation of various nitramines. This method, however, is rather tedious and does not lend itself to routine examinations. Yasuda and Rogers² deal with the separation of hexogen and octogen (HMX) on paper impregnated with formamide, for the determination of RDX in HMX.

The scope of this investigation was to establish if thin-layer chromatography is a suitable method for separating some of the more well-known nitramines.

Of special interest is, of course, the separation of hexogen, hexahydro-1,3,5-trinitro-*s*-triazine (III) and HMX, octahydro-1,3,5,7-tetranitro-*s*-tetrazine (V) as hexogen manufactured by the Bachmann process usually contains a few per cent of HMX. For investigation of different steps in the manufacturing process BSX, 2,4,6-

trinitro-2,4,6-triazaheptane-1,7-dioldiacetate (I) AcAn, 2,4,6,8-tetranitro-2,4,6,8-tetrazanonane-1,9-dioldiacetate (II). SEX, 1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-s-tetrazine (VI) and DPT, 3,7-dinitro-1,3,5,7-tetrazabicyclo-[3,3,1]-nonane (VII) were of interest and therefore included in this study.

Experimental. The thin-layer plates were prepared by coating silica gel G (Merck) on glass plates using Stahl's technique and activated at 110° for an hour. All substances tested were prepared in our laboratories and purified by several recrystallisations in suitable solvents. All spots were applied in acetone solution with an Agla burette.

The number of solvents usable for chromatography are limited as the nitramine compounds are not easily soluble in most organic solvents except for ketones. The latter, however, are so strong eluants that all substances follow the front. By addition of less polar solvents to, *e.g.*, acetone the solubility is so decreased that problems with tailing spots may easily arise. The most promising combinations of solvents were mixtures of aliphatic hydrocarbons with acetone or ethylmethylketone. With a mixture of petroleum ether (b.p. 40–60°C) and acetone, 2:1.2, as the moving phase the most efficient separation was obtained. The solubility of the nitramines in this solvent was, however, so low that spots containing more than 50 µg of each substance caused tailing.

Detection of spots. The usual way of detecting nitramines is with the Franchimont reagent¹. This, however, is less suitable in thin-layer chromatography as the zinc-powder used is difficult to remove completely from the surface and thus may hide weak spots. The sensitivity of this reagent is otherwise excellent (approx-

I $n=2$

II $n=3$

mately 0.5 μg). With fluorescence indicators (fluorescein or diphenylbenzidine) it is possible to detect 1–2 μg by noting the reduction in the fluorescent background when irradiating with ultraviolet light.

The photochemical reaction between diphenylamine and nitrates proposed by Coldwell³, with the nitrate ion resulting in a strongly yellow product consisting of 2- and 4-nitrodiphenylamine⁴, is said to give only a very faint yellow colour difficult to distinguish from the background if applied to RDX. When spots of nitramines on silica-gel plates were sprayed with a 1 % solution of diphenylamine in ethanol and exposed for 5 min to radiation from a standard 125 W mercury lamp (black glass bulb removed) strong blue-violet spots appeared making 0.5 μg of nitramines easily detectable against a faint brownish background. The nature of this reaction is still unknown but the reaction product could be separated by chromatography into at least four compounds, two of which were violet and two yellow, the latter presumably the two nitrodiphenylamines isolated by Coldwell. By visual comparison of colour intensities with spots obtained from known standard amounts a semiquantitative estimation of nitramines was possible.

Results. Fig. 1 shows the separation of five different nitramines. About 30 μg substance was applied in each spot. The plates were developed for about 45 min at room temperature. To obtain constant R_F values the temperature is rather critical with this type of solvent. It is therefore advisable to

Fig. 1. Chromatogram of different nitramines 1.) HMX. 2.) BSX. 3.) From top BSX, RDX, DPT, HMX and SEX. 4.) RDX. 5.) From top HMX and SEX.

Fig. 2. To the left chromatogram of waste product from the Bachmann process. To the right reference chromatogram.

use a reference spot of RDX. The separation was, however, always good. The two substances BSX and AcAn were not separable with this solvent. This is quite understandable due to their similar structure.

Fig. 2 shows to the left a chromatogram of a product isolated from a waste liquor of the Bachmann process. About 200 μg was applied. To the right a reference mixture of HMX and SEX was applied. The by-product was treated in such a manner that neither BSX or DPT could be present. It was evident that RDX, HMX and SEX were present. The third spot from the top is, however, still unknown, but is believed to be TAX, 1-acetylhexahydro-3,5-dinitro-s-triazine (IV). This has, however, not yet been proved as pure TAX is not available and no method for synthesis of this compound seems to have been published. Work is in progress to isolate the substance and to prove its identity.

Thin-layer chromatography has showed to be a most valuable tool for rapid separation of nitramines of interest in the manufacture of hexogen. No doubt further types may be separated in this way and a better quantitative estimation of the different substances after elution of the spots seems to be possible with Yasuda's colorimetric micromethod².

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