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New Synthesis Routes for Energetic Materials Using Dinitrogen Pentoxide [and Discussion]

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New synthesis routes for energetic materials using dinitrogen pentoxide

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The harsh and unselective nature of conventional nitrating agents, based on nitric-sulphuric acid mixtures or pure nitric acid, has led to the development of new nitration methodologies based on dinitrogen pentoxide (N_2O_5) that overcome many of the drawbacks of conventional media, especially when dealing with sensitive substrates.

Two principal nitration systems have been developed: (i) N_2O_5 in pure nitric acid, and (ii) N_2O_5 in organic solvents, mainly chlorinated hydrocarbons. The former system possesses strength similar to mixed acid (HNO_3–H_2SO_4) systems and is therefore potent, but displays advantages such as ease of generation of the nitration reagent by electrolysis and compatibility with nitramine products, facilitating the synthesis of nitramine explosives as well as certain aromatic nitro compounds.

The second system (N_2O_5/organic solvent) encompasses a much wider range of nitrations, and with suitable choice of substrate permits the generation of polynitrated species directly without the formation of acidic by-products, an important environmental consideration. These conditions are also compatible with sensitive substrates, particularly those possessing strained-ring heterocyclic skeletons; thus the nitration of such compounds with N_2O_5 permits precursors for energetic polymers (e.g. polyNIMMO) to be prepared by selective nitration. Likewise, nitrated derivatives of suitably functionalized elastomeric pre-polymers (e.g. NHTPB) can also be manufactured; both of the latter category of compound find important application as energetic binders for novel explosive and propellant compositions, notably low-vulnerability (LOVA) propellant charges.

1. Introduction

The majority of energetic materials (explosives, propellants, etc.) are organic compounds which derive their energy from the nitro group, $-NO_2$. These nitro compounds encompass a wide variety of materials of greatly differing physical and chemical properties which can be small (i.e. low molecular weight) molecules or macromolecules, in other words polymers. The nitro substituents can be classified according to the nature of the atom to which they are attached: carbon, nitrogen or oxygen. Hence energetic materials are frequently described as being C-nitro **1** (or simply 'nitro', e.g. trinitrotoluene), N-nitro **2** (or 'nitramine', e.g. HMX), or O-nitro **3** (or 'nitrate ester', e.g. PETN), according to which functionality they contain (Urbanski 1967, 1984).

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All of these functionalities are introduced into precursor or substrate molecules by a process called nitration (Schofield 1980; Olah *et al.* 1989), which classically has used either pure nitric acid or nitric–sulphuric acid mixtures. The aim of this work is to show how a novel nitrating agent, dinitrogen pentoxide or N_2O_5 can complement or even replace some of these classical procedures.

2. Nitration potential of N_2O_5 and its applications to energetic materials synthesis

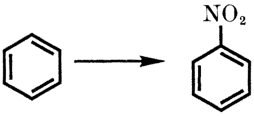
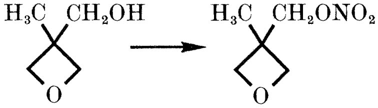
N_2O_5 is an agent capable of introducing nitro groups into substrate molecules (Addison & Logan 1973; Fisher 1990), in other words a nitrating agent, and, although it had been prepared as early as 1849 (Deville 1849), it was largely neglected as a nitrating agent until the 1920s, when the first systematic study of this type was undertaken (Haines & Adkins 1925). Presumably this neglect was a result of the difficulty in obtaining the reagent in a pure form as well as problems in storage resulting from its poor thermal stability (Addison & Logan 1973), aspects which will be covered in more detail presently. The current resurgence of interest within this research group has demonstrated the versatility of N_2O_5, which can be used to generate all three classes of energetic grouping from suitable precursors in clean, specific and frequently high-yielding reactions.

Nitration reactions, of any of the types mentioned here, are believed to proceed via the nitronium ion, NO_2^+, and we can immediately subdivide the nitrating ability of N_2O_5 according to the medium used. On the one hand 100% nitric acid, with high nitronium ion concentration on account of the high degree of dissociation of N_2O_5 arising from the high polarity of the solvent (Ingold & Miller 1950; Odokienko *et al.* 1978). On the other the organic solvents, typically chlorinated hydrocarbons (e.g. CH_2Cl_2 or freons), where a low nitronium ion concentration is found owing to the essentially undissociated nature of N_2O_5 in this environment (Chedin 1935).

Thus, the first medium provides a potent, unselective nitration system akin to mixed acid but with some advantages over the classical system, while the second enables gentler conditions to be achieved, which are essentially non-acidic and hence useful for nitrating acid-sensitive substrates or for performing selective nitrations. To show instances of reactions where the various types of energetic groups may be introduced, and how these correlate with the two types of nitrating system, the examples shown here (table 1) are illustrative. Thus, the harsher nitric acid system is more suitable for aromatic nitrations or nitrolyses to yield nitramines from their N-acyl precursors (although, under suitable conditions, these transformations can sometimes also be effected in appropriate organic solvent media), while on the other hand, the organic media, particularly chlorinated hydrocarbons or freons, are essential to enable the ring cleavage or selective nitration reactions to be carried out. With some substrates possessing both strained rings and labile groups, the reaction can be ‘fine-tuned’ to enable selective nitration of these compounds to be attained: this important aspect of N_2O_5 chemistry will be covered in more detail later (§6). It should be emphasized that, although reaction in the first two categories can sometimes be effected under organic solvent conditions as well, the latter two categories require exclusively organic solvent conditions, also preferably free from adventitious acid in certain cases.

Before giving details of the preparation of N_2O_5 and further examples of how these nitration systems may be used to synthesise specific energetic compounds,

Table 1. *Summary of* N_2O_5 *nitrations*
(Key: A = nitric acid system, O = organic solvent system.)

reaction type	conditions	examples	product name
aromatic nitration	A/O		(C-)nitro compound
nitrolysis	A(O)	$R_2N{-}COCH_3 \longrightarrow R_2N{-}NO_2$	nitramine
ring cleavage	O		nitrate ester or nitramine-nitrate
selective nitration	O		nitrate ester derivative of strained-ring compound

applications to which these four basic reaction types, two in nitric acid medium and two in organic solvent medium, may be put are now discussed and are detailed below (table 2).

To date, the formation of polymer precursors, either by selective nitration forming energetic monomers (e.g. 3-hydroxymethyl-3-methyloxetane nitrate, NIMMO **53**, §6), or by nitration of pre-formed polymers (e.g. nitrated hydroxy-terminated polybutadiene, NHTPB **52**, §6), has made the greatest impact, simply because of the dearth of energetic polymers suitable for binder applications; each of these examples will be covered in more detail later. N_2O_5 nitration chemistry, however, can also furnish a wide variety of products of interest to the energetic materials community: energetic plasticizers for propellants and polymer bonded explosives (PBX), crystalline high explosives with intermediate melting points suitable for high performance melt cast explosives, and thermally stable high explosives for specialist applications. The applicability of the various types of nitration reactions in each field are indicated in table 2.

3. Preparation of N_2O_5

Two main routes are currently in use for the preparation of N_2O_5, both in our laboratories and industrially:

$$(a)\quad 2HNO_3 \xrightarrow[-2e-]{N_2O_4} N_2O_5 + H_2O; \qquad (b)\quad N_2O_4 \xrightarrow{O_3} N_2O_5.$$

cell membrane

The first, by electrolysis of nitric acid in the presence of N_2O_4, is based on a process developed in the Lawrence Livermore National Laboratory (Harrar & Pearson 1983) and subsequently developed in this country. This generates a solution of N_2O_5

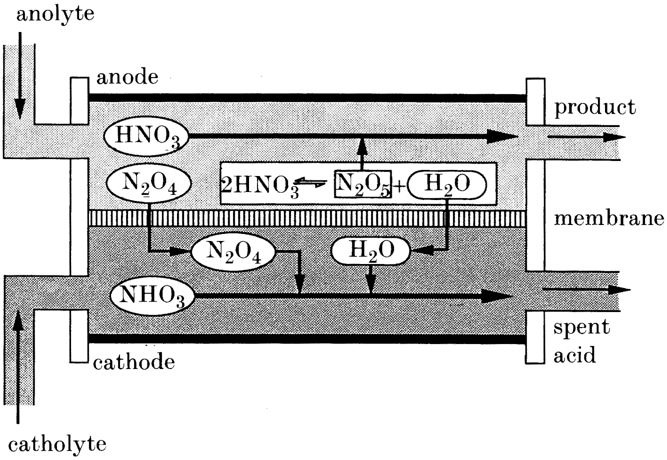


Figure 1. Electrolytic cell for generating N_2O_5 (schematic).

Table 2. *Applications of* N_2O_5 *nitrations* (*in nitric acid or organic solvent*)
(Key: + = application feasible; ( ) = application to be implemented.)

	product type	plasticizers[a]	crystalline HE[b]	thermally stable HE[c]	polymer precursors[d]
aromatic nitrations	$C–NO_2$	+		+	
nitrolysis	$N–NO_2$		+	+	(+)
ring cleavage	$N–NO_2$ $O–NO_2$	+	+		+
selective nitrations	$O–NO_2$ $(N–NO_2)$				+

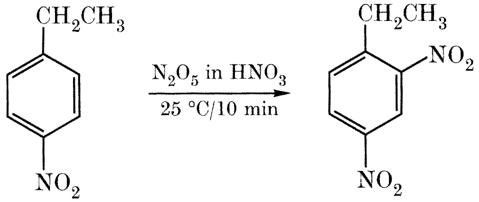
Compound types: [a] nitrate esters/nitroaromatics; [b] nitramines/nitramine-nitrates; [c] nitramines/nitroaromatics; [d] nitrate esters (nitramines).

of some 15–20% (mass/vol.) strength in anhydrous nitric acid. Rates of production of several kilograms per day are currently available and scale-up to higher production levels poses no serious technical problems (Bagg *et al.* 1991); the electrolytic cell employed is shown in figure 1. N_2O_5 generated in this way finds application mainly in the first two types of nitration reaction: aromatic nitration and especially nitrolysis to generate HMX (see §4).

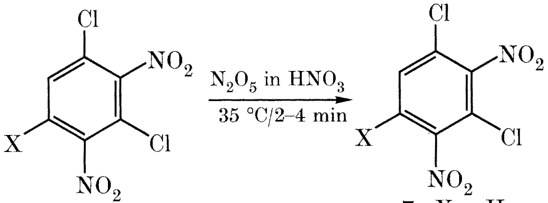
The second route, ozonation of N_2O_4, although known for some decades (Harris *et al.* 1967), was not, to our knowledge, developed into a viable large-scale synthetic process until the inception of work in our laboratories. The gas-phase reaction of ozone (as a 5–10% mixture with oxygen) with N_2O_4 generates essentially acid-free N_2O_5 which is trapped as a solid and can be stored at low temperature for lengthy periods until required. Its dissolution in organic solvents, typically chlorinated hydrocarbons (e.g. dichloromethane) or freons, gives a mild nitrating agent useful in ring cleavage and selective nitrations. Currently around 1 to 1.5 kg per week can be made on our laboratory scale apparatus but there is no intrinsic limitation to scale-up, high output ozonizers being available commercially.

4. N_2O_5–Nitric-acid nitrations

Turning now to specific examples of reactions in each of the four above categories, the utility of N_2O_5 nitrations in energetic materials chemistry is illustrated. First, aromatic nitrations: compounds **5** (2,4-dinitroethylbenzene, an energetic plasticizer ingredient), **7a** (2,4-diamino-1,3,5-trinitrobenzene, explosive) and **7b** (2,4,6-triamino-1,3,5-trinitrobenzene, explosive) are formed cleanly and in essentially quantitative yield.



4 **5**

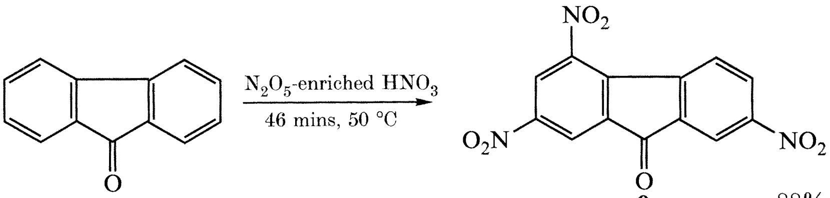


6

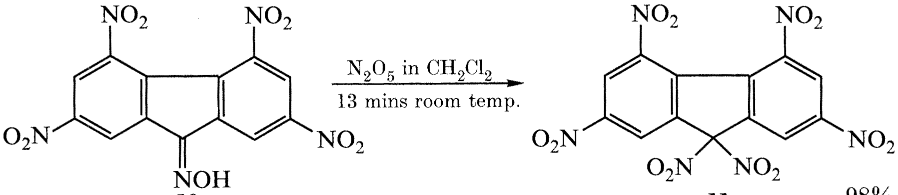
7a X = H

7b X = Cl

Furthermore, polynitrofluorenes (e.g. **11**), which are novel thermally stable explosives, have been made for the first time (Honey 1991). Interestingly, in this reaction N_2O_5 effects the introduction of a gem-dinitro moiety.



8 **9** 88%



10 **11** 98%

A remarkable phenomenon has been discovered in N_2O_5–nitric-acid nitrations of aromatic substrates, namely an unexpected rate enhancement (figure 2) of up to 30 times at high N_2O_5 concentration over that which would be expected from nitric-acid–sulphuric-acid systems of similar concentration (Moodie & Stephens 1987; Moodie *et al.* 1990, 1991). This feature gives N_2O_5–nitric acid solutions unique nitration potential which will be exploited in future studies.

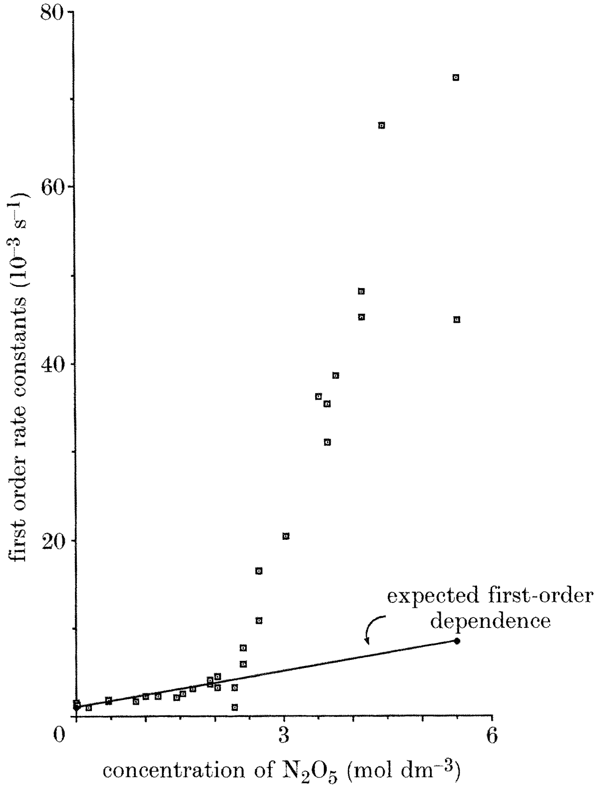
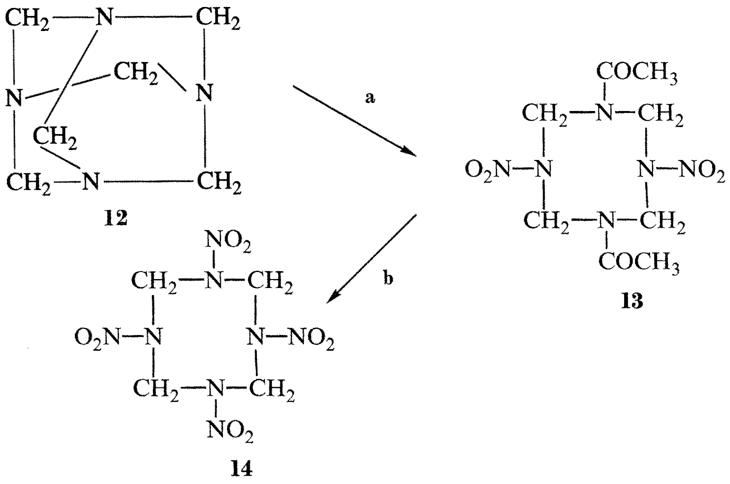


Figure 2. Rate profile for an aromatic nitration. The nitration of phenyltrimethyl ammonium perchlorate (PTMAP) by N_2O_5/HNO_3 shows an unexpected rate enhancement.

Nitrolysis reactions to form nitramines again offer improvements over existing methodology, largely due to the instability of these products in media containing sulphuric acid (Wright 1969). The route of greatest practical utility so far is, of course, the production of HMX (**14**) via DADN (**13**) (Siele *et al.* 1981), which is now being utilized in this country on pilot scale and is under development for production scale in the U.S.A.:

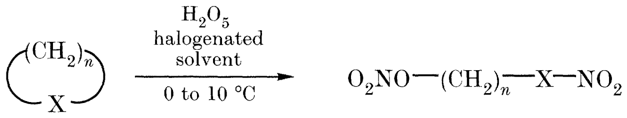


The reaction steps are (*a*) acetylation followed by mild nitration, (*b*) vigorous nitration by N_2O_5/HNO_3.

5. N_2O_5–Organic solvent nitrations

These types of reaction embrace two distinct but related areas of chemical synthesis, namely ring-cleavage reactions and selective nitrations, and each will be dealt with in turn.

The ring cleavage reactions shown below constitute an entire family of novel reactions discovered by the Synthetic Chemistry Section at R.A.R.D.E. in the early 1980s (Golding *et al.* 1988*a*,*b*), and enable the preparation of multifarious nitrated compounds of high-energy content (viz. **16a**, **16b**, **17a**, **17b**), which are applicable in all fields of energetic materials technology except, perhaps, those areas requiring ultimate thermal stability.



15
$n = 2$ or 3
X = O or NR (R = alkyl, etc.)

16a X = O, $n = 2$
16b ,, , $n = 3$
17a X = NR, $n = 2$
17b ,, , $n = 3$

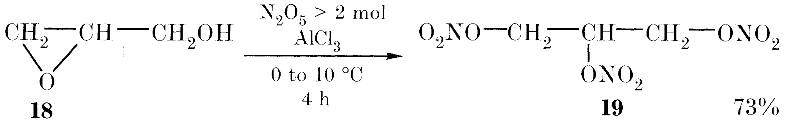
The substrates (**15**) are strained-ring heterocycles with three- or four-membered rings containing either oxygen or nitrogen heteroatoms, making a total of four possible sets of reactions. It should be noted that these reactions possess a common feature, namely, the simultaneous introduction of two energetic groups, either similar (nitrate in the case of the oxygen heterocycles) or dissimilar (nitramine-nitrates in the case of the nitrogen heterocycles). Thus the reaction is a new type of nitration, namely an addition reaction, which features complete utilization of the nitrating agent, unlike the more usual substitutive nitration where, with N_2O_5, half of the nitrating agent would be wasted. These reactions are generally high yielding and encompass a wide range of compounds, the main limitation being that R is not equal to H or certain other groups for the nitrogen heterocycles (see below).

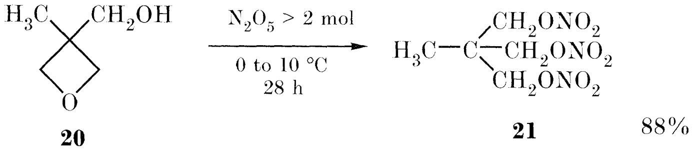
As a new nitration method, these reaction sequences possess in common several advantages over conventional nitration routes using mixed acids:

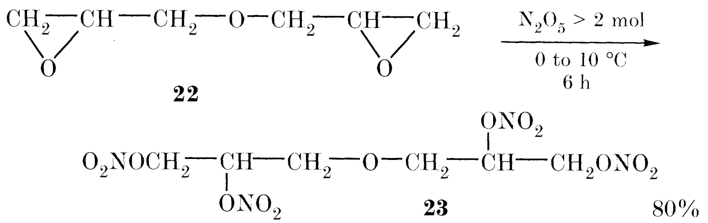
(*a*) absence of waste acids for disposal;
(*b*) simple product separation (evaporation of solvent often suffices);
(*c*) ease of temperature control (reactions are essentially non-exothermic);
(*d*) high selectivity in position of attack with polyfunctional substrates.

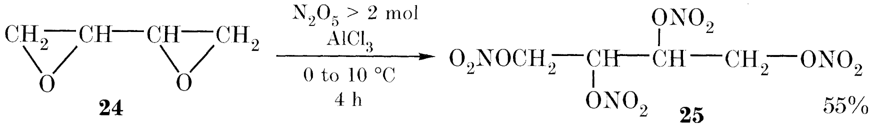
Yields are frequently high (80–98 %) and product contamination from byproducts is correspondingly low. In addition, the first two features suggest important environmental advantages, since waste liquors from conventional nitrators require tedious post-reaction treatment to prevent pollution and indeed to avoid hazard, containing labile chemical constituents such as, for instance, acetyl nitrate. The N_2O_5-strained-ring reactions, on the other hand, avoid these problems and exhibit the further advantages mentioned above. The last feature (selectivity in position of attack) is of relevance primarily to energetic binder synthesis, but before turning to this topic the ring-cleavage nitration reactions will be surveyed.

Strained-ring oxygen heterocycles (**15**, X = O) with three-membered (epoxide, $n = 2$) or four-membered (oxetane, $n = 3$) rings are cleaved cleanly and in high yield to give the corresponding dinitrate esters **16a** and **16b**, 1,2- or 1,3-dinitrates according to the substrate. The reaction is quite general and fails to give yields exceeding *ca.* 70% in only a few cases, notably heavily substituted epoxides or oxetanes substituted at the 2-position; in the latter case oxidative cleavage reactions are believed to supervene. Reaction rates may be accelerated in certain cases by catalysis (e.g. addition of Lewis acids such as $AlCl_3$).



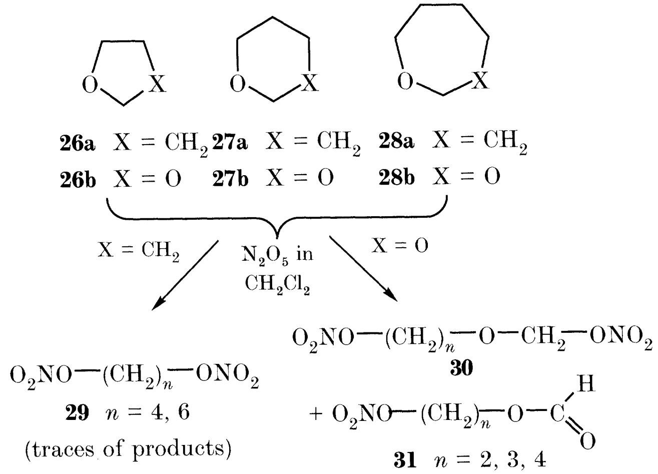






Applications to the synthesis of energetic plasticizer compounds are shown above, giving rise to both known (nitroglycerine **19** or trimethylolethane trinitrate **21**) and novel compounds (diglycerol tetranitrate **23** or erythritol tetranitrate **25**). The reactions appear to be unaffected by even moderate amounts of nitric acid, formed either from atmospheric moisture or by reaction with other functionalities in the substrate molecule (e.g. in the cases of glycerol **18** or 3-hydroxymethyl-3-methyloxetane **20**); in this respect these nitrations contrast sharply with the nitrogen heterocycle reactions, particularly those of the aziridines (see below).

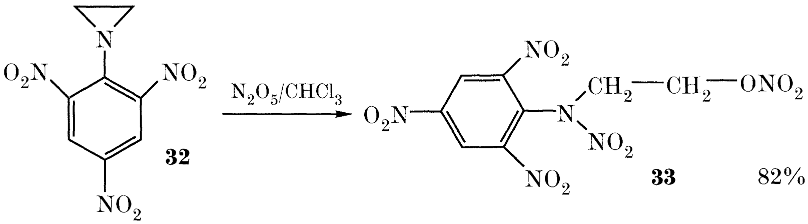
Finally, the possession of ring strain in these oxygen heterocycles has been shown to be a prerequisite for these reactions to proceed in high yield; substrates with five, six and seven membered rings, i.e. **26a**, **27a** and **28a** react sluggishly yielding generally less than 5% of the corresponding dinitrates, unless other functionalities (particularly a second oxygen atom in the 3-position) are present:

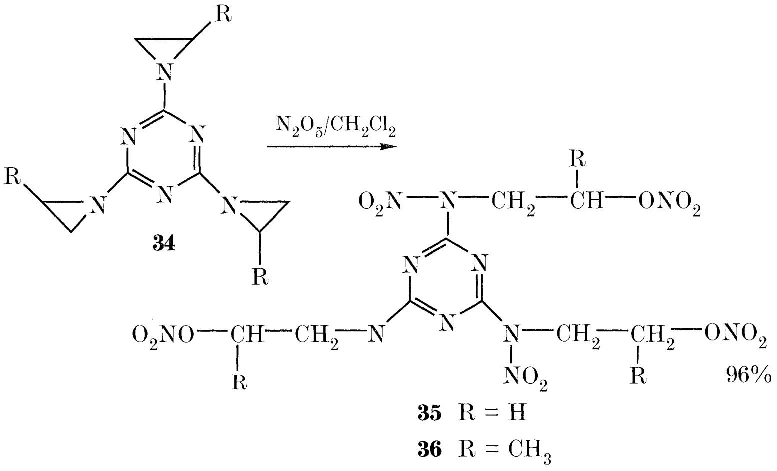


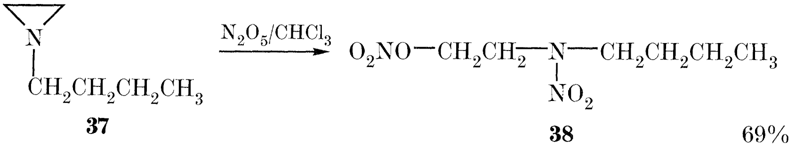
However, in such cases (compounds **26b**, **27b** and **28b**), products formed by competing reaction pathways are also found, e.g. formate-nitrates **31**, as well as the expected hemiformal nitrates **30**; the former are believed to originate from hydride abstraction, proceeding via stable dioxolenium cation intermediates (Golding *et al.* 1989).

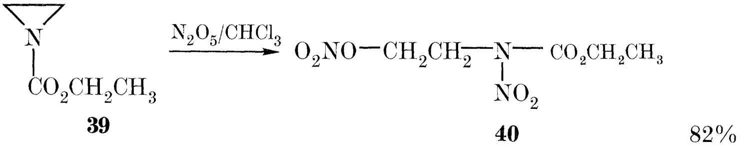
With the nitrogen heterocycles (**15**, X = NR), the three-membered (aziridine, $n = 2$) and four-membered (azetidine, $n = 3$) compounds give rise to the corresponding nitramine-nitrate products **17a** and **17b** in many cases in good to excellent yields. As mentioned earlier, the aziridine reactions are particularly susceptible to acid resulting from either adventitious moisture or from hydroxylic species within the substrate molecule, and in such cases only low yields of the desired nitramine-nitrates are obtained (R. W. Millar, N. C. Paul and D. H. Richards, unpublished results), with homopolymerization of the aziridine supervening (Dermer & Ham 1969).

The products find application as melt-castable explosives or plasticizers; thus the explosive materials pentryl **33** and Tris-X **35** (Millar *et al.* 1992) feature a high oxygen balance and the latter is an entirely novel compound, inaccessible by other routes, illustrating the utility of N_2O_5-ring cleavage reactions.



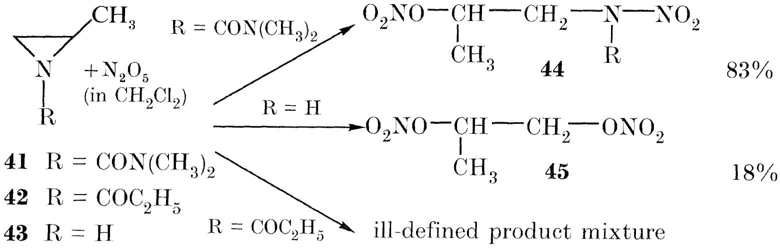


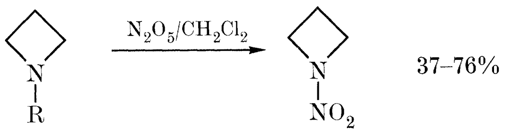




Both of these products are highly energetic and show other favourable physical properties. These strained-ring/N_2O_5 reactions can also yield energetic plasticizers, starting from nitrogen heterocycles: Bu-NENA **38**, for instance, is a component of some LOVA propellant compositions, whereas nitrocarbamates such as **40** make excellent energetic plasticizers (Olsen *et al.* 1966).

Finally, the cleavage reactions of nitrogen heterocycles have been found to be not quite as general as those of the oxygen series, with the course of the reaction being affected by the nature of the exocyclic nitrogen substituent (R) as well as the ring size:





46 R = CON$(CH_3)_2$
47 R = COC_2H_5
48 R = H

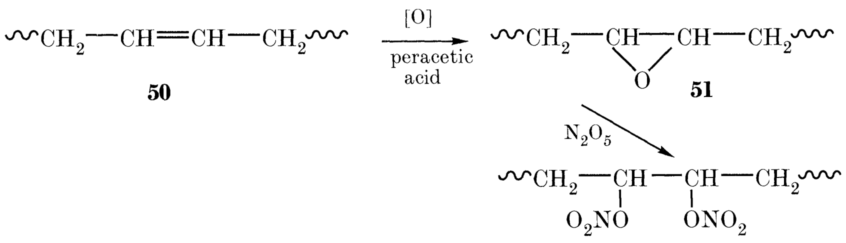
49

Thus when R is hydrogen no nitramine-nitrates are obtained: aziridines such as **43** yield 1,2-dinitrates **45** by a rearrangement reaction with expulsion of N_2O, while azetidine **48** gives the cyclic nitramine, N-nitroazetidine **49**, by a substitutive nitration (Golding *et al.* 1991). The behaviour becomes more complex with other N-acyl substituents, some aziridines (e.g. the carbamyl compound **41**) showing predominantly ring-opening behaviour giving nitramine-nitrate products (e.g. **44**) whereas others (e.g. the propionyl compound **42**) yield mixtures, indicating competing reaction pathways. The azetidines, on the other hand, tend toward deacylative nitration (nitrolysis), yielding N-nitroazetidine **49** with groups such as carbamyl (e.g. **46**) or propionyl (**47**) (Golding *et al.* 1991). Such deacylations are, of course, well known in nitration chemistry (Smith 1966; Gilbert *et al.* 1975) and reflect the lower ring strain in azetidines which permits alternative reactions to occur.

6. Selective nitrations and energetic binders

Selective nitrations, as suggested earlier, are feasible in organic solvent medium and, owing to the mild nitrating power of N_2O_5 under these conditions, it is possible to allow a nitration to proceed only partly to completion where two or more functional groups of widely differing lability are present in the same molecule. Such an approach, of course, would be quite impossible with conventional strongly acid media, e.g. nitric–sulphuric acid mixtures, whereas other known mild reagents, e.g. acetyl nitrate or tetranitromethane, are impractical on large scale on account of excessive hazard and expense.

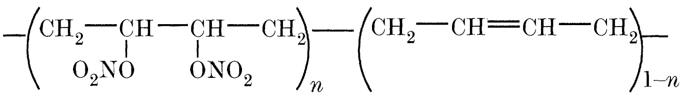
Two approaches to energetic binder macromolecules by selective nitration chemistry using N_2O_5 are illustrated by the following reactions: first, the epoxy groups in an epoxidised hydroxy-terminated polybutadiene **51** can be cleaved by N_2O_5 while leaving the chain double bonds essentially intact to yield an energetic polybutadiene containing vicinal dinitrate groups.



50

51

52

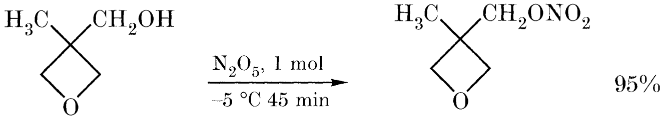


$$-\left(\underset{O_2NO}{CH_2-CH}-\underset{ONO_2}{CH}-CH_2\right)_n-\left(CH_2-CH=CH-CH_2\right)_{1-n}-$$

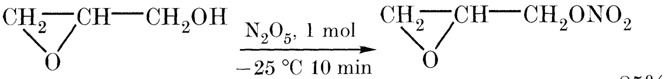
52a

This material, known as NHTPB (nitrated hydroxy-terminated polybutadiene, **52**) is currently undergoing scale-up and evaluation in collaboration with industry, since it is readily preparable on large scale from cheap precursors and shows desirable properties for binder applications (Stewart *et al.* 1990).

The second approach involves the generation of energetic monomers by selective nitration: candidate molecules such as 3-hydroxymethyl-3-methyloxetane **20** and glycidol **18** have been found to be susceptible to nitration on the hydroxyl function while leaving the strained ring unchanged and essentially quantitative yields in the nitration step have been achieved under suitable conditions (Stewart *et al.* 1990; Bagg *et al.* 1991):

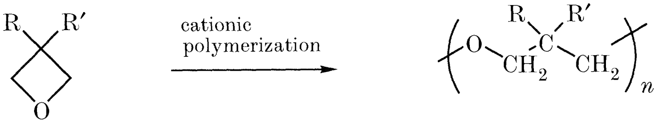


20 **53**



18 **54**

The nitrated strained-ring monomers, 3-hydroxymethyl-3-methyloxetane nitrate **53** and glycidyl nitrate **54**, are then polymerized cationically to their respective polymers resulting in materials with the desired molecular weight range and suitable hydroxyl functionality, enabling subsequent cross-linking to a polyurethane rubber to be carried out:



53 R = CH_3,
R′ = CH_2ONO_2

55

The resulting energetic rubbers constitute a significant new class of energetic materials with wide application in propellant and explosive technology, notably enabling viable high-performance low-vulnerability propellant formulations to be manufactured for the first time (Debenham *et al.* 1991), and such materials are undergoing scale-up to tonnage levels in collaboration with industry.

7. Conclusions

N_2O_5 nitrations are versatile and have much to offer the energetic materials chemist/technologist. It has been established that two essentially different but complementary systems are available: (*a*) N_2O_5 in nitric acid; and (*b*) N_2O_5 in organic solvents. The former system, now available on pilot plant scale, can effect nitrations of the aromatic and nitrolysis type, useful for generating (C-) nitro and nitramine products respectively. It is a potent nitration system which has already shown advantage over mixed acid systems, particularly in the preparation of nitramines such as HMX.

The N_2O_5 organic solvent system, on the other hand, although a milder nitration medium can nevertheless effect nitration of a wide variety of substrates, in particular the selective nitration of polyfunctional substrates and also nitration of polymers such as epoxidized HTPB. These products are of great importance industrially and have demonstrated that the future of N_2O_5 in the field of energetic materials chemistry is assured.

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Discussion

F. Volk (*Fraunhofer Institute, F.R.G.*). You produced interesting polymeric nitrate esters. I would be interested in the thermal stability of these nitrate esters. Do you have any results of long-term ageing tests?

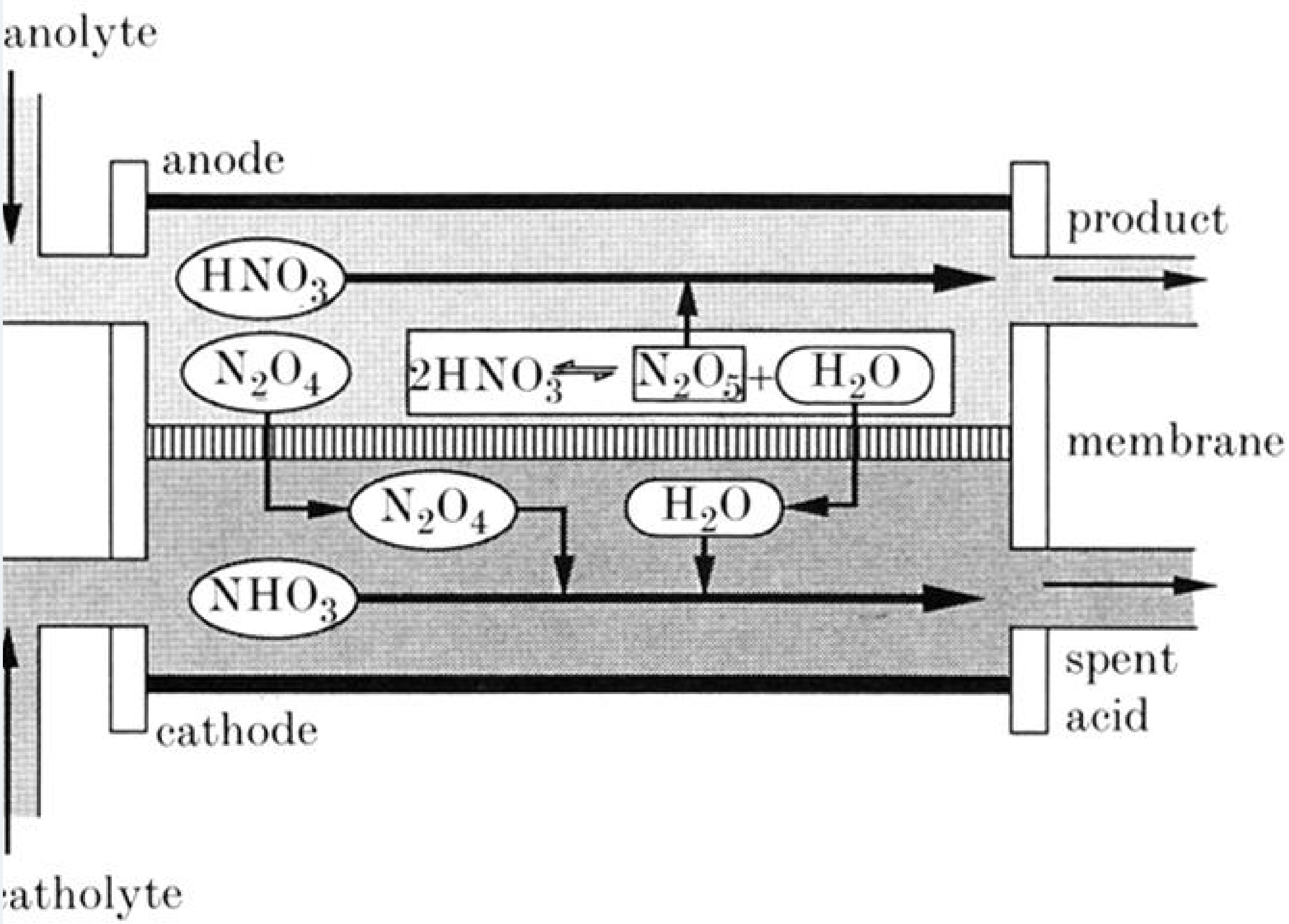
R. W. Millar. We have found polyNIMMO to possess good thermal stability in the vacuum stability test, with figures (for the uncured material) of around 1 cm^3/40 h/5 g polymer at 100 °C being typical (up to 2.5 cm^3 is acceptable). Notably, it is significantly more stable than liquid nitrate esters such as nitroglycerine. The only long-term ageing results available relate to accelerated ageing tests of polyNIMMO cured with Desmodur N100 and stabilized with 2-nitrodiphenylamine (1%): this material displayed a reduced rate of nitrate ester breakdown (compared with unstabilized material) and chain scission of the polymer backbone was greatly retarded, demonstrating that its stability is comparable with that of binders currently used in propellant compositions.

B. J. Thomson (*Health and Safety Executive, U.K.*). Conventional batch nitration reactions feature highly among the incidents occurring in batch processes because of their strongly exothermic nature; so the low exothermicity of N_2O_5 nitrations can be viewed as a step towards minimizing the risk associated with nitration. But conventional batch nitration mixtures can also be detonable in their own right, when examined by conventional tests, such as the BAM U.N. 50/60 Tube Test. What are the detonability or explosive characteristics of the N_2O_5 nitration systems, particularly the N_2O_5/organic solvent systems?

R. W. Millar. First, to clear up a possible misconception, only N_2O_5-*ring opening* nitrations show by exothermicity; N_2O_5-hydroxyl group reactions are strongly exothermic, and to overcome this potential problem we use flow reactor technology.

This also greatly reduces the bulk medium risk since very little energetic material is present in the flow reactor zone at any given time.

Concerning the question of detonability of N_2O_5-organic solvent mixtures, particularly for large-scale batch reactions, in these circumstances we keep the N_2O_5 concentration down to around 10 mass/vol. % since this is considered by our hazards section to be outside the detonable range of concentrations.



igure 1. Electrolytic cell for generating N_2O_5 (schematic).