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Deville rebooted – practical N_2O_5 synthesis†

Lee E. Edwards,[a] Benson M. Kariuki,[a] Matthew Didsbury,[b]
Christopher D. Jones[c] and Thomas Wirth*[a]

Dinitrogen pentoxide (N_2O_5), the anhydride of nitric acid, was synthesised by Henri Étienne Sainte-Claire Deville in Paris in 1849 using silver nitrate and chlorine gas. Herein, we revisit, optimise, and modify Deville's method using photocatalysis to enable a safe, clean, practical, and reproducible alternative for N_2O_5 synthesis in quantitative yields. Moreover, it is predicted that the modifications can accommodate an industrial scale-up, but the silver chloride generated must be recycled.

Nitro compounds are used extensively in the pharmaceutical, agricultural and energetic materials industries.[1] Dinitrogen pentoxide is of great interest to the energetic materials community as it has its own specific qualities for the nitration of organic compounds.[2–5] It is a much milder nitrating agent and has proven to be far more selective than mixed or concentrated nitric acid.[2] N_2O_5 has the potential of reducing considerable amounts of waste and side products traditionally associated with energetic materials manufacture while improving safety at the same time. However, N_2O_5 is not commercially available due to its thermal instability. N_2O_5 readily sublimes with a vapour pressure of 1 atm at 33 °C and has a half-life of 10 days at 0 °C and 10 hours at 20 °C as it decomposes through releasing NO_2 and oxygen: $N_2O_5 \rightarrow 2\ NO_2 + O_2$.[6–8] Therefore, it is necessary to synthesise N_2O_5 on demand. In this context we revisited the work of Deville, the original discoverer of N_2O_5.[9,10] It is relevant to the current work to appreciate Deville's original methodology to understand why the method has been left to history. We report on our modifications and enhancements and provide images of N_2O_5 crystals in Fig. 1 and 2 synthesised by our improved method. The improved method is reproducible and used routinely and safely within our laboratories.

In the 1840s Deville was working on metal chloride analysis and characterisation. During this time, he discovered dinitrogen pentoxide and reported its synthesis in 1849.[9] Deville used a U-shaped tube filled with silver nitrate as the reaction vessel. Dry chlorine gas was passed through the silver nitrate at 95 °C and the reaction to N_2O_5 and solid silver chloride occurred. Some N_2O_5 decomposition was evident as NO_2 and its liquid dimer N_2O_4 was condensing immediately after the exit from the silver nitrate at the cooling section in the second U-shaped tube which was at a temperature of around 0 °C (Fig. 3).

Deville stated that the silver nitrate was primed by drying at 180 °C while being purged with carbon dioxide. The system was attached to a glass bottle containing the chlorine gas. The bottle had a system to drop feed concentrated sulfuric acid

Fig. 1 Single N_2O_5 crystal cluster from the current work. This cluster was 1.2 cm across at its longest point.

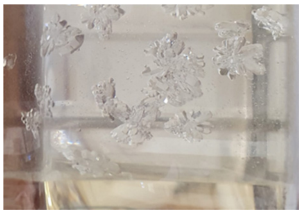

Fig. 2 A collection of N_2O_5 crystal clusters. Note that the clusters are usually up to 1–1.5 cm across.

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[a] *Cardiff University, School of Chemistry, Cardiff, CF10 3AT, UK. E-mail: wirth@cf.ac.uk*
[b] *BAE Systems Land UK, Glascoed, Usk, Monmouthshire, NP15 1XL, UK*
[c] *Falcon Project Ltd, The Magazine Area, Westcott Venture Park, Aylesbury, Bucks, HP18 0XB, UK*

† Electronic supplementary information (ESI) available: Synthesis of N_2O_5; original Deville method; optimised methods with pictures; methods of N_2O_5 recovery. See DOI: **https://doi.org/10.1039/d4cc01403k**

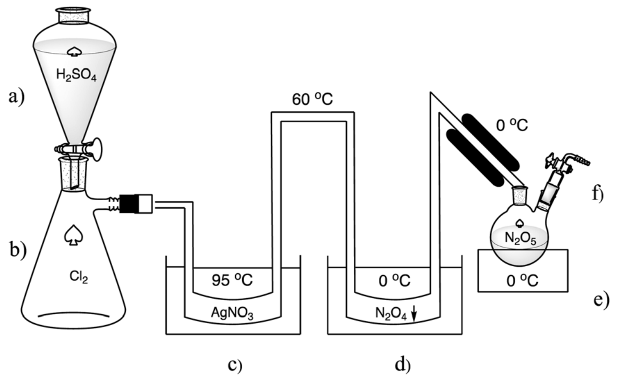

Fig. 3 Deville's experimental apparatus for the synthesis of N_2O_5: (a) H_2SO_4 for Cl_2 desiccant and displacement. (b) Chlorine gas. (c) Water bath at 95 °C to heat $AgNO_3$ at the bottom of the U-shaped tube. (d) Cold trap at 0 °C for NO_2 condensation. (e) Cold trap at 0 °C for crystallising N_2O_5. (f) Vent for O_2 and unreacted Cl_2. A more detailed diagram based on Deville's description is shown in the ESI† (Fig. S1).

that both dried and displaced the chlorine through a valve. The chlorine had to pass through calcium hypochlorite for further drying and chlorine enrichment and finally through pumice which acted as a frit. The chlorine was then introduced by the displacement with sulfuric acid at a rate of 2–3 mL min^{-1}. The chlorine gas passed through the silver nitrate, and some reacted to form N_2O_5 and AgCl. The N_2O_5 and unreacted chlorine was then passed through the cooled tubing and the N_2O_5 finally condensed into crystal clusters of approximately 1 cm size which were subsequently collected in glass vials sealed with heat in a CO_2 atmosphere for storage. It was noted that thermal decomposition often resulted in gas pressure destruction of theses vials. However, Deville' system of N_2O_5 synthesis was able run continuously for days at a time with just the sulfuric acid, water bath and fuel for the heater having to be maintained. It is our understanding that Deville' method is the only one to date describing crystals of translucent N_2O_5 similar to the size and clarity shown in Fig. 1 and 2. All other methods of N_2O_5 synthesis since 1849 use cold traps that rapidly precipitate the N_2O_5 as much finer crystals or synthesised in solvents such as HNO_3 or trifluoroacetic anhydride. While Deville's method was successful in generating N_2O_5, there was also the issue of chlorine, and NO_x being constantly vented, and the conversion of Cl_2 and $AgNO_3$ to AgCl and N_2O_5 was not efficient.

After Deville' discovery, the most widely used method of synthesising N_2O_5 is the dehydration of nitric acid with phosphorous pentoxide (P_4O_{10}) (Fig. 4, eq. 1).[11] This method is further illustrated in the ESI† (Fig. S2).[7] HNO_3 is added dropwise to P_2O_5 that has a supply of ozonised oxygen to oxidise any evolved NO_2/N_2O_4 to N_2O_5. The N_2O_5 sublimes and is condensed collected as a fine white solid in a cold trap at −78 °C.[7] Yields for this method are typically around 50%. Another method that is challenging to reproduce is the dehydration of nitric acid with trifluoroacetic anhydride.[12] The most popular method of N_2O_5 synthesis is the direct ozonolysis of N_2O_4 (Fig. 4, eq. 2). Again, the N_2O_5 is condensed after the reaction and collected as a fine white solid in a cold trap at −78 °C. Here the yield is reported to be quantitative as indicated by the red stream of NO_2/N_2O_4 becoming immediately colourless when mixing with ozone.[13,14] However, this method is completely reliant upon a supply of NO_2/N_2O_4, and this can pose significant challenges. However, ozonolysis of nitric oxide has also been reported with a yield of greater than 99%.[15] Ozone has been used frequently in N_2O_5 synthesis, and this is likely due to the ease at which ozone can oxidise NO_2/N_2O_4 to N_2O_5. Other examples include bubbling ozone through picryl pyridinium nitrate or catalytic amounts of picric acid in fuming nitric acid solutions at temperatures up to 65 °C. The N_2O_5 sublimes and is subsequently collected in a cold trap at −78 °C with yields reported of 87% and 50%, respectively.[16] N_2O_5 has also been synthesised from FNO_2 and lithium nitrate in quantitative yield, albeit only on mmol scale and temperatures of −190 °C (Fig. 4, eq. 3).[17] Dinitrogen pentoxide is electrochemically synthesised on a large scale through the oxidation of N_2O_4 to N_2O_5 in nitric acid which was first reported in 1983. Work in this area is significant, with several patents and publications, including electrolysis of N_2O_4 in a dual cell setup with a membrane (Fig. 4, eq. 4). The investigators quote yields of $>30\%$ N_2O_5 by mass in nitric acid.[18,19] The mixture of N_2O_5 in nitric acid provides a separate and unique option for nitration reactions.[20] But also this electrochemical approach requires N_2O_4 with the above highlighted challenges.

$$6\,HNO_3 + 0.5\,P_4O_{10} \longrightarrow 3\,N_2O_5 + 2\,H_3PO_4 \qquad (1)$$
$$N_2O_4 + O_3 \longrightarrow N_2O_5 + O_2 \qquad (2)$$
$$FNO_2 + LiNO_3 \longrightarrow N_2O_5 + LiF \qquad (3)$$
$$N_2O_4 + 2\,NO_3^- \longrightarrow 2\,N_2O_5 + 2\,e^- \qquad (4)$$

Fig. 4 Other methods for the synthesis of N_2O_5.

Herein we describe our investigations to simplify the Deville method, by removing the NO_2/N_2O_4 contamination issue and by operating at lower temperatures through the utilisation of additional photocatalysis.

Assessing the practicalities Deville' method, it became clear that there was a requirement to create a closed system with gas/vacuum access through a valve. This simplified the operation while ensuring the protection of N_2O_5. The $AgNO_3$ had to be heated in this system, while the N_2O_5 reaction product had to be condensed at a temperature that would not condense $NO_{2(g)}$ to $N_2O_{4(l)}$. Furthermore, the cooling should be well above the temperature to freeze $N_2O_{4(s)}$ (−11.1 °C). Finally, the temperature of the condenser had to be above 0 °C to prevent condensation if exposed to atmosphere. These requirements were all met with a Chemglass Sublimator (full details of this device are in the ESI†). This apparatus is built of 2 halves. The upper half contains the cold finger with the glass pipework to enable a flow of coolant from a chiller, and a sealed valve to enable evacuation of the sublimator to a full vacuum, then the subsequent addition of the chlorine for the reaction. The lower half of the sublimator contains $AgNO_3$ as a fine powder, and a small magnetic stirrer. The two halves have a Viton seal between them, and the assembly is clamped together and evacuated and sealed. The sublimator is then positioned on a hotplate/stirrer and cooled to 4 °C. Dry chlorine (0.8 bar) is introduced *via* a septum on the sublimator and the opened valve. This is the point where our modifications to Deville' method diverge, and they will be described separately. Firstly, the $AgNO_3$ was heated in a sand bath to 60 °C. After 72 hours there was no reaction. The temperatures were subsequently increased until a successful reaction at 95 °C. This was the temperature that Deville reported for heating the $AgNO_3$ before immediately cooling the outward flow of gas to 60 °C in an attempt to control the decomposition of N_2O_5 which was noted as being considerable. After cooling the $AgNO_3$ to room temperature the formation of crystalline N_2O_5 was observed. It should be noted that the reaction takes 72 hours at 95 °C to convert all $AgNO_3$ to AgCl. The N_2O_5 was characterised by single crystal XRD which was identical to the structure described in the literature.[9,21] The full conversion of $AgNO_3$ to complete and single phase AgCl was confirmed by powder XRD. Both results are graphically illustrated in Fig. S11, S12 and S13 (ESI†), respectively, with the full details in the ESI.† Further confirmation of full conversion was provided by solubility examination. $AgNO_3$ is highly soluble in water whereas AgCl is practically insoluble. The full mass of AgCl was always recovered from water by filtration and drying. The yield was >95% after titration of the recovered material in dichloromethane as described in the literature.[2] Furthermore, confirmation of the N_2O_5 product was provided by a repeat of the work of Maksimowski *et al.* with the selective formation of mono- and dinitrotoluene with 1, 2 or 3 equivalents of N_2O_5 from toluene.[2]

These results demonstrated that this safe, and much simplified modification to Deville's method could be used to enable dinitrogen pentoxide chemistry to those who previously found access a roadblock due to the previously acknowledged requirement for either NO_2/N_2O_4 or an ozone generator, or both. However, at this point it was acknowledged that 72 hours and thermal decomposition was an issue (Fig. 5).

Experience during these experiments highlighted the photocatalytic properties of $AgNO_3$. The decomposition of silver nitrate when exposed to light to silver, NO_2 and oxygen is well known and documented and has been used to create silver nanoparticles,[22] and its main use for many years was in photography. However, the undesirable product of this decomposition was NO_2 so this, at first, seemed detrimental. The literature photochemistry of dinitrogen pentoxide is sparse and is centred entirely on the cycle of N_2O_5 in the upper atmosphere.[23,24] The thesis of P. Steele Connell did shed some light on the possibility of photocatalysis using Deville's method.[24] Steele Connell stated that N_2O_5 absorbs in the UV range of 210–385 nm, and that in the presence of nothing but N_2O_5, light will reversibly dissociate N_2O_5 to NO_2 and NO_3 with the equilibrium much faster on the recombination. But, if NO is introduced, it will react with the NO_3 to irreversibly generate 2 NO_2 which will deplete the N_2O_5 recombination partner. For the current work, with the tightly controlled environment of the Chemglass sublimator with just silver nitrate and chlorine present, there would be no chance of side reactions. This led to a further successful modification of Deville's method.

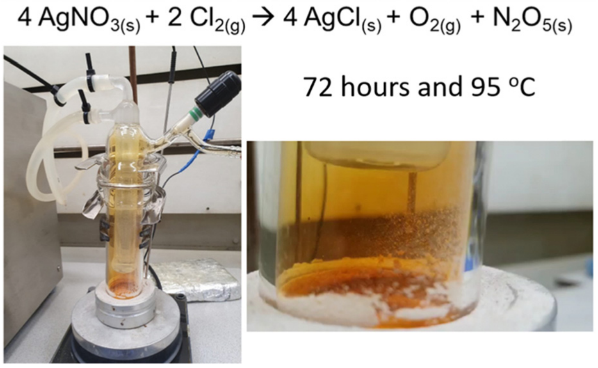

Fig. 5 The apparatus post reaction and with the hotplate temperature at 95 °C. This temperature is too high for N_2O_5 to condense on the cold finger. The condensation occurs after the hotplate is switched off. Note the deep brown colour from the N_2O_5 thermal decomposition to NO_2 and O_2. Deville experienced this decomposition and had to accommodate it with additional cooling steps and traps.

The experiment was performed with the following modifications (Fig. 6). After the addition of the chlorine to the sublimator, a UVITEC Cambridge UV Lamp was placed in front of the apparatus irradiating the lower part of the sublimator containing the $AgNO_3$. The wavelength of 365 nm was selected as the literature[23] reports the generation of N_2O_3 from N_2O_5 at shorter wavelengths, and Steele Connell stated that the upper absorption limit is 385 nm. The apparatus was then placed in a light proof box, with the $AgNO_3$ being heated at 65 °C. After 18 hours, the cold finger had deposits of clusters on N_2O_5 formed mainly around the bottom of the cold finger and on the opposite side to the UV light, so the decomposition hypothesis proved to be correct. Furthermore, there was no visible NO_2 decomposition product present. Subsequent analysis was carried out as previously described and demonstrated full conversion of $AgNO_3$ to AgCl and N_2O_5 in >95% yield. Running the reaction for longer led to N_2O_5 decomposition. An additional

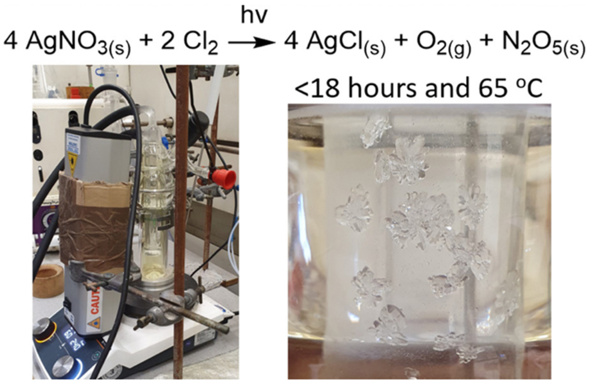

Fig. 6 The apparatus with the UV modification to the Deville method. Note that the colour has no NO_2 character and that the N_2O_5 condensers immediately after it has been produced. The UV lamp (left side) has been partially blocked to only irradiate the lower part of the sublimator with the silver nitrate.

experiment at 50 °C with radiation at 365 nm converted ~50% $AgNO_3$ to AgCl, but there was a significant amount of N_2O_5 decomposition in the form of NO_2. The method at 65 °C with UV irradiation at 365 nm has now been used routinely numerous times with reproducible results. As most of the chlorine is consumed during the reaction, the only other side products are O_2 and AgCl. The latter can be recycled by reduction to silver with H_2O_2 and NaOH and then nitrating with nitric acid.[25] The only waste being sodium chloride which seems to be an acceptable waste product considering other waste such as H_2SO_4/oleum and fuming HNO_3 generated during traditional nitration reactions.

In conclusion, we have revisited and rebooted Deville's distinguished method by providing modifications to simplify, enhance the safety, performance, repeatability of N_2O_5 synthesis in yields >95%. The optimum conditions for a full conversion, quantitative yield and the minimum of decomposition were heating the $AgNO_3$ to 65 °C, with the cold finger at 4 °C and the $AgNO_3$ irradiated with UV light at 365 nm with a reaction time of 18 hours. The full details of the experimental and apparatus are in the ESI,† including details on the process of N_2O_5 recovery. We foresee no barriers to scaling up this method to kg scale with an appropriately sized apparatus.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1 S. Noriega, J. Cardoso-Ortiz, A. López-Luna, M. D. R. Cuevas-Flores and J. A. Flores De La Torre, *Pharmaceuticals*, 2022, **15**, 717.
2 P. Maksimowski, A. Nastała and W. Tomaszewski, *Cent. Eur. J. Energ. Mater.*, 2022, **19**, 424–437.
3 M. B. Talawar, R. Sivabalan, B. G. Polke, U. R. Nair, G. M. Gore and S. N. Asthana, *J. Hazard. Mater.*, 2005, **124**, 153–164.
4 A. K. Kharchenko, R. V. Fauziev, M. N. Zharkov, I. V. Kuchurov and S. G. Zlotin, *RSC Adv.*, 2021, **11**, 25841–25847.
5 D. Fischer, T. M. Klapötke and J. Stierstorfer, *Chem. Commun.*, 2016, **52**, 916–918.
6 F. Daniels and A. C. Bright, *J. Am. Chem. Soc.*, 1920, **42**, 1131–1141.
7 C. C. Addison and N. Logan, *Developments in Inorganic Nitrogen Chemistry*, Ed. C. B. Colburn, Elsevier, Amsterdam, 1973, vol. 2, pp. 27–69.
8 F. Daniels and E. G. Johnson, *J. Am. Chem. Soc.*, 1921, **43**, 53–71.
9 M. H. Deville, *C. R. Acad. Bulg. Sci. Paris*, 1849, **28**, 257.
10 J. Gay, *Henri Sainte-Claire Deville: sa vie et ses travaux*, Gautheir-Villars et Fils, Imprimieurs Libraries, Paris, 1889.
11 N. S. Gruenhut, M. Goldfrank, M. L. Cushing and G. V. Gaesar, in *Inorganic syntheses*, ed. L. F. Audrieth, McGraw-Hill, New York, 1950, vol. III, pp. 78–81.
12 J. H. Robson, *J. Am. Chem. Soc.*, 1955, **77**, 107–108.
13 P. A. Guye, *US Pat.*, 1348873, 1920.
14 J. C. Harris and H. B. Trebellas, *Inorg. Synth.*, 1967, **9**, 83–88.
15 N. I. Kobozev, M. Temkin and S. J. Freiberg, *Gen. Chem.*, 1933, **3**, 534.
16 K. Okon, *Biul. Wojsk. Akad. Tech.*, 1958, **7**, 3.
17 W. W. Wilson and K. O. Christie, *Inorg. Chem.*, 1987, **26**, 1631–1633.
18 J. E. Harrar and R. K. Pearson, *J. Electrochem. Soc.*, 1983, **130**, 108.
19 Q. Wang, M. Su, X. Zhang, L. Wang, J. Wang and Z. Mi, *Electrochim. Acta*, 2007, **52**, 3667–3672.
20 H. Feuer and A. T. Nielsen, *Nitro Compounds*, Purdue University Press, West Lafayette, Indiana, 1990, pp. 268–365.
21 E. Grison, K. Eriks and J. L. de Vries, *Acta Cryst.*, 1950, **3**, 290–294.
22 F. Naaz, U. Farooq, M. A. M. Khan and T. Ahmad, *ACS Omega*, 2020, **5**, 26063–26076.
23 T. G. Koch and J. R. Sodeau, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 2347–2351.
24 P. Steele Connell, *The photochemistry of dinitrogen pentoxide*, University of California, Lawrence Berkeley Laboratory, 1979.
25 P. C. Hsu, Z. Chiba, B. J. Schumacher, L. C. Murguia and M. G. Adamson, *Recovery of silver from waste silver chloride for the MEO system*, US Dept. of Energy, Technical report, 1996, DOI: 10.2172/250506.