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Electronic supporting information

Deville rebooted – Practical N₂O₅ synthesis.

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1 Experimental

Abbreviations

Chemglass 40ml Daily Vacuum Sublimator assembly = CS
Chemglass 40ml Daily Vacuum Sublimator cold finger = CF
Huber Minichiller 300 OLE = Chiller
Magnetic stirrer = MS
Hotplate = HP
Fume Cupboard = FC
Round bottom flask = RBF
PTFE = Polytetrafluoroethylene

1.1 Instruments

Single-crystal (SCXRD) and powder diffraction (PXRD): Data were collected on an Agilent SuperNova Dual Atlas diffractometer with a mirror monochromator using either Mo ($\lambda = 0.71073 \text{ \AA}$) or Cu ($\lambda = 1.5418 \text{ \AA}$) radiation. Crystal structures were solved and refined using SHELXS1, 2 and refined using SHELXL2. Non-hydrogen atoms were refined with anisotropic displacement parameters.

1.2 Apparatus

Deville' apparatus

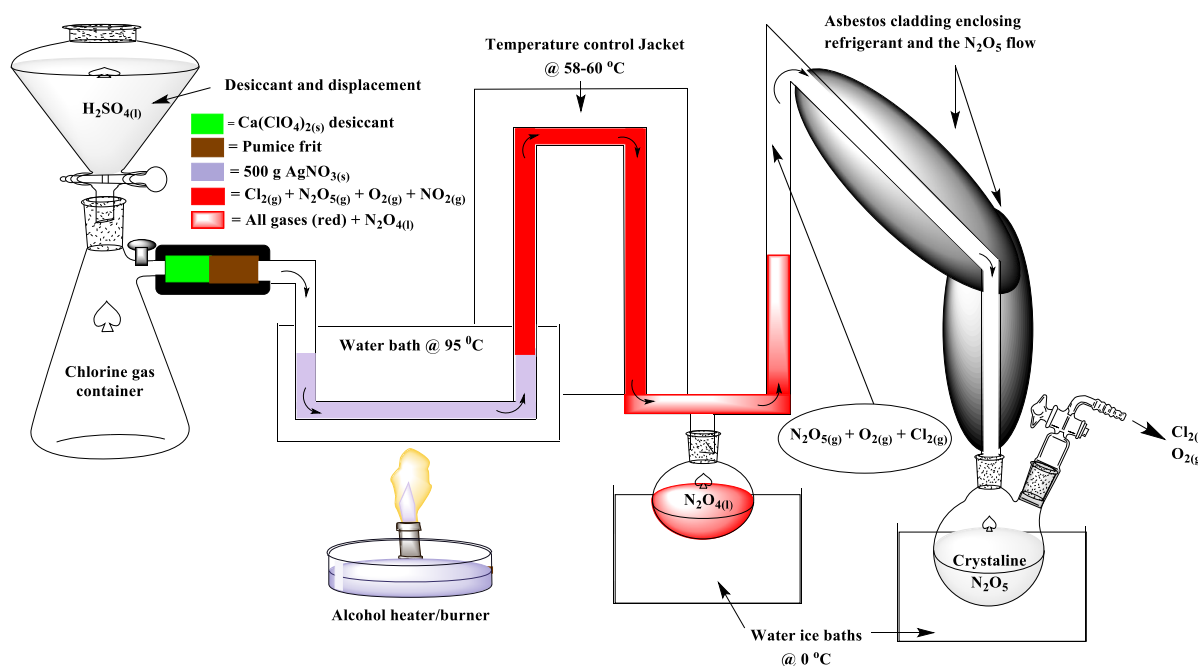


Figure S1: A diagram of Deville' original 1840's N_2O_5 synthesis apparatus as described in Deville' original 1849 publication.¹

Apparatus for N_2O_5 synthesis for the dehydration of nitric acid from phosphorous pentoxide

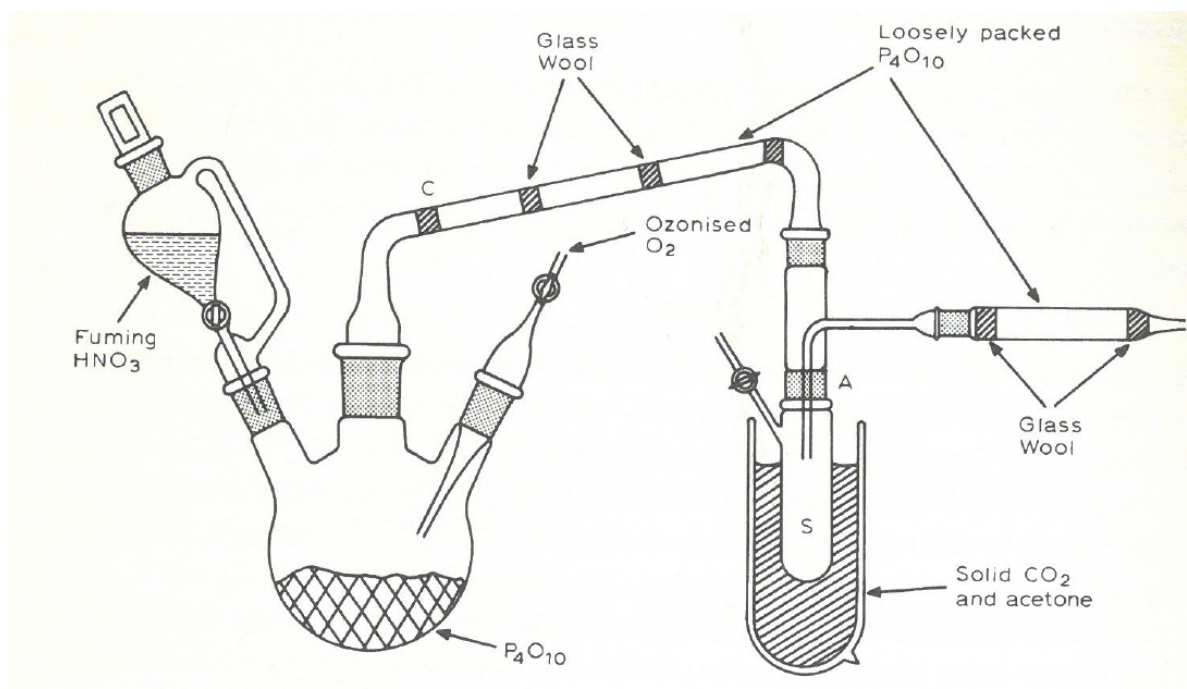
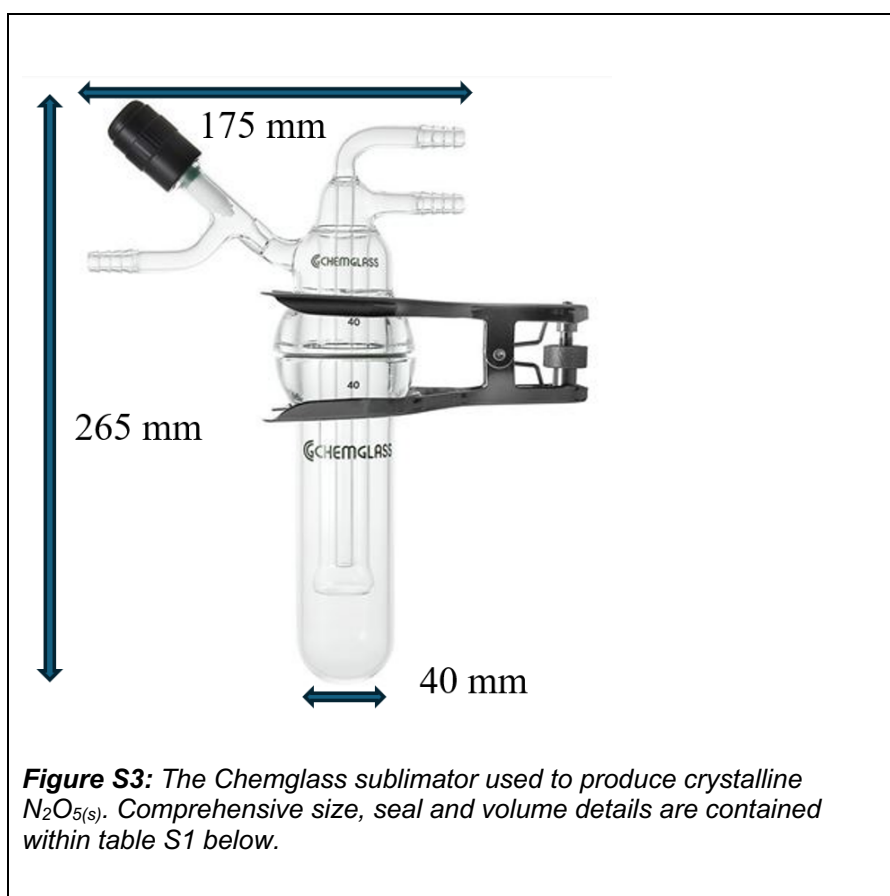


Figure S2: Apparatus for the synthesis of N_2O_5 via HNO_3 , P_2O_5 and ozone for reference.²

Apparatus for the current work



GPE Scientific – Chemglass 40ml Daily Vacuum Sublimator (Figure S3). Total inner gas volume = 190 mL. Dimensions given below in Table 1. The replacement O rings for use between the upper and lower assemblies: Item #: CG-305-226, O ring Viton #226. Be aware: Maximum gas is pressure 0.8 bar and this pressure must not be exceeded. Exceeding this limit for this apparatus will result in the sublimator separating at the joint under excess pressure to relieve excess pressure and vent the chlorine into the FC.

Using the ideal gas law equation ($PV = nRT$), 190 mL of gas in the sublimator at 25 °C gives 6.132×10^{-3} mol of $\text{Cl}_{2(g)}$ which is 1.22633×10^{-2} mol of Cl. Therefore, there is just 1.432×10^{-3} mol of chlorine left at the end of the reaction which is not enough to register on the $\text{Cl}_{2(g)}$ detector.

Item #:	H x W (mm)	Capacity (Solid) (mL)	Joint Size	O-Ring Size	Clamp Size	Gas Volume mL	Valve Size (mm)
CG-3034-02	265 x 175	40	40	226	65	190	0-4

Table S1: Table of the Chemglass 40 mL Daily Vacuum Sublimator dimensions.

PTFE N_2O_5 recovery cylinder. Length 152 mm. Inside diameter 31 mm. Inside depth 140 mm. Outside diameter 41 mm, reduced to 39 mm @ 30 mm from the open-ended top. The very top then has a 45 ° taper to allow a good seat inside the sublimator (Figures S4 and S5) Displaces 40 mL of solvent with the cold finger of the sublimator inserted (Figure S6).

PTFE N_2O_5 recovery cylinder base. Inside diameter 41 mm. Outside diameter 80 mm. Height 28 mm. Used for supporting the PTFE N_2O_5 recovery cylinder during use to prevent it toppling over (Figures S4, S5, and S6).



Figure S4: Separate PTFE recovery cylinder and base.



Figure S5: Assembled PTFE recovery cylinder and base.



Figure S6: Assembled PTFE recovery cylinder and base with the CF inserted. Note the attached septum used for evacuating the system before priming with chlorine.

Chlorine gas detector. Crowcon Gasman Cl_2 .

Huber Minichiller 300 OLE

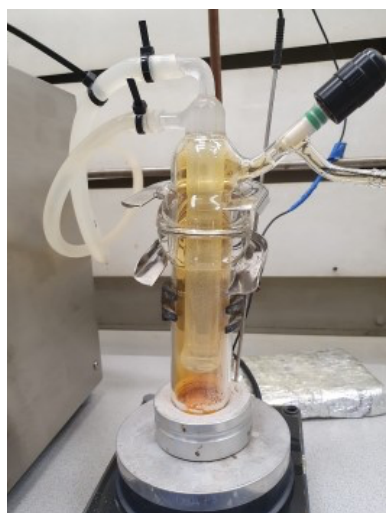
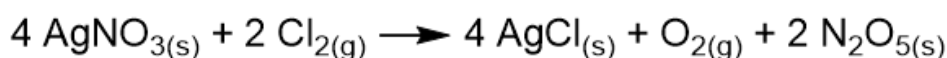
Technical specification; Fill Volume, 1.4 ; Temp Range °C, -20 to +40 (80) ; Temp Stability °C, ± 0.5 .

Retrofitting with neoprene hosing to fit to the inlet/outlet for the Chemglass Sublimator cold finger.

UVITEC Cambridge UV Lamp. Switchable 365 and 254 nm UV light. Use the 365 nm lamp. Lamp power is 12 W.

ERB Gas Solutions – Chlorine Gas regulator with needle valve a dry N₂ purge line. Details:
1 x 0-3 Bar Single Stage Stainless Steel Regulator c/w Inlet Tee Purge – BS6 316L Cylinder Connection – 1/8 OD Compression.
1 x Outlet Stainless Steel Needle Valve.
Regulator inlet gauge changed to suit low cylinder pressure inlet. Regulator PRV (pressure reducing valve) removed and plugged.
Flexible PTFE hose (from the needle stainless steel needle valve) with stainless needle and tap at the very end for chlorine delivery to septum on the sublimator fitted by Cardiff University School of Chemistry Workshops.

1.3 Synthesis Dinitrogen Pentoxide (N₂O₅) following the Deville Method at 95 °C



72 hours and 95 °C



Figure S7: Images of the CS post reaction. Note the colour of the gas has changed from that of chlorine to nitrogen dioxide. The high reaction temperature does cause decomposition of the dinitrogen pentoxide in the manner that Deville described during his synthesis.

The precursor, AgNO₃ (Sigma-Aldrich, Reagent Grade), was ground by pestle and mortar into a fine powder and transferred with a magnetic stirrer to a Chemglass sublimator. The sublimator had an inner diameter of 40 mm, an inner volume of 190 mL and was fitted with Viton seals capable of withstanding chlorine and N₂O₅. The sublimator was assembled and a septum was secured in the sublimator valve.

The sublimator with AgNO₃ was then completely evacuated of air before securing the apparatus on a hotplate with the tip of the sublimator containing the silver nitrate was immersed in sand contained within an aluminium heater block fitted with a thermocouple. The inlet and outlet pipes of the sublimator were secured to a Huber 3000 chiller set at 4 °C. The chiller was then immediately switched on to get to temperature. The chlorine gas system was then prepared. This system consisted of a chlorine cylinder (BOC Material number: 158321-E3, Cylinder size: E3 (980mm x 219mm - 32 liquid litre capacity) Nominal pressure (bar): 4.9 @ 15°C Contents: 39kg Valve outlet: BS6) and regulator (ERB Gas Solutions Ltd (Nottingham, UK), 0-3 Bar Single Stage Stainless Steel Regulator c/w Inlet Tee Purge –BS6 316L Cylinder Connection –1/8 OD Compression) and needle valve (ERB Gas Solutions Ltd, Outlet Stainless Steel Needle Valve). The outlet for the needle valve was connected to a needle via a length of PTFE tubing to allow the delivery of gasses via a septum in the sublimator. The tee connection the

chlorine regulator was connected via a valve tap to a regulator on a dry nitrogen cylinder. The nitrogen was in place to purge the gas system before and after the experiments. At the start of the experiment, the dry nitrogen was allowed to flow for several minutes to dry the system before switching off the gas flow. The gas was then switched to chlorine and the chlorine was then allowed to flow momentarily into the back of the fume cupboard to ensure an outlet pressure of 0.8 bar, and to prime the system. The needle valve was set to $\frac{1}{4}$ - $\frac{1}{2}$ a turn out to ensure gentle release of gas. The valve closest the delivery needle was then closed. The needle from the needle valve was then inserted into the septum of the sublimator valve. The delivery needle valve partially opened. The sublimator inlet valve was then opened and chlorine was observed immediately filling the sublimator. Note the safe working pressure of the sublimator is 0.8 bar, and *should not* be exceeded beyond 0.8 bar for this particular CS to prevent chlorine gas release from the CS joint in to the FC (it is entirely possible that with a suitable replacement sublimator capable of safely working at higher pressures could improve the reaction rate).



Figure S8: The needle from the high vacuum line being inserted into the septum of the CS. Note the cable tie securing the septum in place which is entirely satisfactory.



Figure S9: The evacuated CS is secured in place on the HP and the coolant lines from the chiller are attached and the chiller. The CS inlet valve is opened, then the fom the needle valve connected via PTFE tubing) is inserted into the septum. Then the valve at the needle (just below the thumb of the right hand) is opened to fill the CS with chlorine to a pressure of 0.8 bar (pressure set at the regulator). Both the valve on the needle and CS are closed and the needle withdrawn. The CS is than completely isolated from the chlorine gas supply and monitored with gas detection.

The gas system was kept under 2 bar of dry N_2 pressure when not in use. With the sublimator filled with chlorine (cold finger at 4 °C), isolated from the main gas lines and with the gas detector at 0 ppm, the stirrer was switched on at 250 rpm and the heat set to 95 °C and left to continue at this temperature for up to 96 hours. By this time, the green/yellow colour of the chlorine was being replaced by the red/brown of the decomposition NO_2 product (Figure S7) of N_2O_5 . Also, the $AgNO_3/AgCl$ was much finer and had begun to coat the inside of the sublimator. These observations indicated the reaction was complete (Figure S7). The 95 °C heat was switched off and allowed to return to room temperature. During cooling, small clusters of geometrical translucent N_2O_5 crystals began forming all over the cold finger of the sublimator. This crystallisation was allowed to continue for 2 hours before the opening the sublimator under an argon atmosphere for crystal recovery for XRD analysis and N_2O_5 recovery in excellent yield in dry DCM for subsequent yield calculations and nitration synthesis.

1.4 Synthesis Dinitrogen Pentoxide (N₂O₅) following the Deville Method at 65 °C

Synthesis procedure was that of section 2.1, except the temperature was maintained at 65 °C. The reaction was continued to 72 hours with no reaction.

1.5 Synthesis of dinitrogen pentoxide (N₂O₅) the modified Deville method incorporating AgNO₃ exposure with 365 nm UV light and a temperature of 65 °C.



<18 hours and 65 °C



Figure S10: The apparatus with or UV photocatalysis modification to the Deville method. Note that the colour has no NO₂ character and that the N₂O₅ condensers immediately after it has been liberated and recombined after being liberated from the silver.

Synthesis procedure was that of section 2.1, but with the following modifications. The temperature was reduced from 95 °C to 65 °C. The addition of 365 nm UV light @ 12 W facing directly and only (top half of the UV lamp was left covered) into the lower portion of the sublimator containing the AgNO₃ which was switched on upon the temperature of the cold finger in the sublimator reaching 4 °C and the hot plate reaching the required 65 °C. The reaction apparatus was then completely enclosed for safety considerations with UV light. The reaction was complete within 18 hours, which was evident from the chlorine colour becoming being practically translucent, no apparent NO₂ formation and the change in powder consistency as discussed in section 2.1. However, the most obvious indicator of reaction completion was that N₂O₅ crystal cluster were clearly evident mostly on the tip of the sublimator (Figure S10). The 30 °C decrease in temperature required for the experiment described in 2.1 without UV light allows for the immediate recrystallisation of the N₂O₅ in excellent to quantitative yield. Yield was determined from titration against NaOH and phenolphthalein after recovering the N₂O₅ from the DCM recovery solvent. Leaving the reaction for longer periods only led to the decomposition of the N₂O₅, evident from the NO₂ evolution and the visible degradation/erosion and reduction of the previously well-formed crystals.

1.6 Synthesis of dinitrogen pentoxide (N₂O₅) the modified Deville method incorporating AgNO₃ exposure with 365 nm UV light and a temperature of 50 °C.

Synthesis procedure was that of section 2.3 but with a lower temperature of 50 °C. The reaction was left to run for 18 hours as in section 2.3. After this time, there was N₂O₅ clearly visible on the cold finger, but there was visibly much less (≈50% less) and there was much more decomposition of the N₂O₅ evident from the swirling deep red colour of the NO₂ gas present inside the sublimator.

1.7 Recovery of the Dinitrogen Pentoxide.

N_2O_5 is a thermally labile translucent crystalline solid that exhibits a half-life of 10 days at 0 °C, and 10 hours at 20 °C. The solid readily sublimates, having a vapour pressure of 51 mm at 0 °C, 200 mm at 15 °C, 279 mm at 20 °C and 1 atm at 32.5 °C. The reaction vessel cannot be placed in a glove box as the N_2O_5 will rapidly sublime into a gas in a vacuum. Indeed, if the CS is flushed with $\text{N}_{2(g)}$ it will rapidly erode the N_2O_5 . Therefore, the following recovery procedure was developed.

Once the CS and contents have cooled and enough time (2 hours) has passed to allow the N_2O_5 to condense and crystallise, place a funnel attached to an argon gas line directly above the CS. This will dilute the air which contains moisture that will destroy the anhydride causing it to fume as per this equation:



On a stirrer plate, prepare the PTFE recovery sleeve with 40 mL of a recovery solvent such as dry DCM or fuming nitric acid. Place a stirrer in the sleeve. Ensure the argon is blowing directly over the CS. While wearing long butyl gloves, remove the clamp on the CS holding the two halves together. Remove the upper half of the CS that contains the CF coated with N_2O_5 and immediately place the CF into the sleeve. Turn off the chiller which will allow the N_2O_5 to warm and transfer to the solvent. The stirrer also aids the process. Have a 100 mL RBF with a septum that has been evacuated ready. Remove the CF from the PTFE recovery sleeve and place to one side. Use a 50 mL syringe with a long needle to collect the 40 mL solution of solvent and N_2O_5 . Transfer the solution to the evacuated 100 mL RBF through its septum, which will be aided by the vacuum. Add an argon filled balloon to the RBF to equalise the pressure. Remove 1 mL of the solution for later extraction with water in a separatory funnel for titration in 0.1 M NaOH and phenolphthalein to obtain the concentration. Remove the balloon from the septum then immediately transfer the RBF to a Dewar with dry ice for storage. N_2O_5 visibly decomposes rapidly to NO_2 and O_2 in solvents at r.t. DCM will not freeze in dry ice at -78 °C as it has a freezing point of -96.7 °C. N_2O_5 can be stored in dry ice and preserved for extended periods. Use the N_2O_5 as required when ready.

Take a sample of the $\text{AgCl}_{(s)}$ side product for PXRD analysis or solubility if desired and dispose of the rest as solid waste. Remove the upper CS from the chiller hoses and remove the water coolant. Clean up the glassware. Do not use any solvents on the Viton main seal as it will get damaged. Leave this seal in the FC overnight to vent, then place in the 150 °C oven for future work.

2 Characterisation by SCXRD

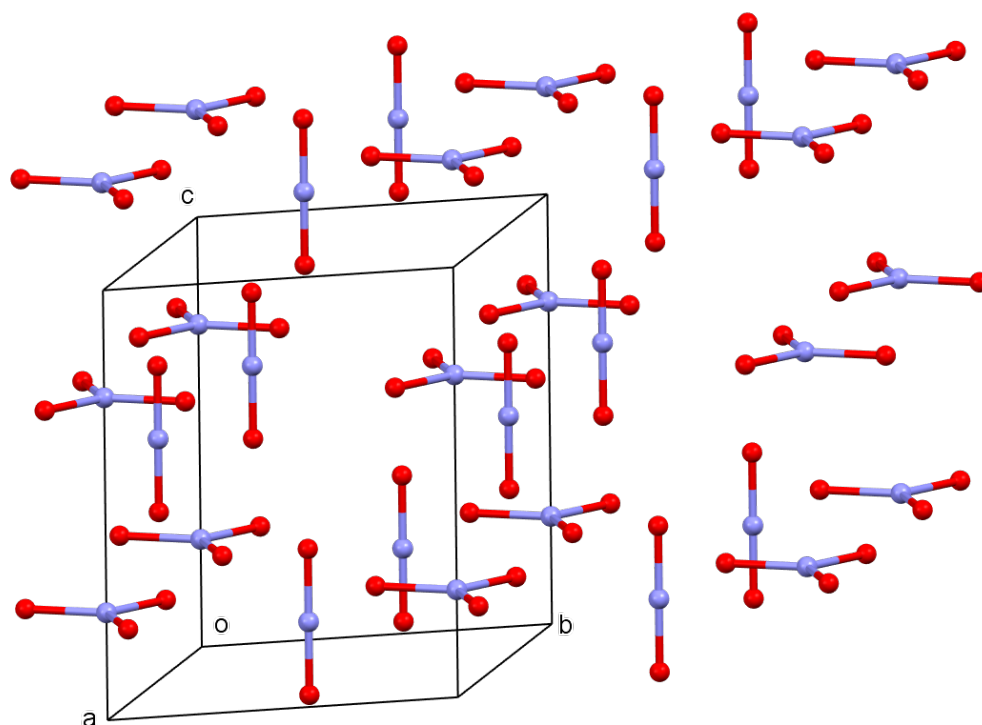


Figure S11: The structure of dinitrogen pentoxide (nitronium nitrate) that shows the linear $[\text{NO}_2]^+$ ion and planar $[\text{NO}_3]^-$ ion.³



Figure S12: A close-up photograph of a dinitrogen pentoxide crystal cluster from the current work that clearly demonstrates what Deville described as “six-sided prisms which appear dependent on a right rhombus-based prism”.¹ The crystal measures approximately 1.2 cm at its longest point.

The crystal and structure refinement data are shown in Table S2. The crystal structure is hexagonal, space group $P6_3/mmc$. In the structure the planar NO_3^- ions lie parallel to the ab plane whereas the linear NO_2^+ ions are aligned with the c axis (Figure S9). Bond lengths and angles shown in Table S3. The structure has been deposited in the data base as CSD 2332914. The structure is the same as that reported by Grison, Eriks, and de Vries in 1950.³

Table S2. Crystal data and structure refinement.

Empirical formula	N ₂ O ₅
Formula weight	108.02
Temperature	180(2) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	P 6 ₃ /m m c
a	5.4151(8) Å
b	5.4151(8) Å
c	6.5657(10) Å
α	90°.
β	90°.
γ	120°.
Volume	166.73(6) Å ³
Z	2
Density (calculated)	2.152 Mg/m ³
Absorption coefficient	0.242 mm ⁻¹
F(000)	108
Crystal size	0.560 x 0.300 x 0.140 mm ³
Reflections collected	1125
Independent reflections	107
R(int)	0.0468
Completeness to theta = 25.242°	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.214
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	107 / 0 / 13
Goodness-of-fit on F ²	1.221
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0308, wR2 = 0.0765
R indices (all data)	R1 = 0.0437, wR2 = 0.0833
Extinction coefficient	0.29(6)
Largest diff. peak and hole	0.232 and -0.199 e.Å ⁻³

Table S3. Bond lengths [Å] and angles [°].

N(1)-O(1)#1	1.1148(19)
N(1)-O(1)	1.1148(19)
N(2)-O(2)#2	1.2534(18)
N(2)-O(2)	1.2535(18)
N(2)-O(2)#3	1.2535(18)
O(1)#1-N(1)-O(1)	180.0
O(2)#2-N(2)-O(2)	120.0
O(2)#2-N(2)-O(2)#3	120.0
O(2)-N(2)-O(2)#3	120.000(1)

Symmetry transformations used to generate equivalent atoms:

#1 $x, y, -z+3/2$ #2 $-x+y+2, -x+1, z$ #3 $-y+1, x-y-1, z$

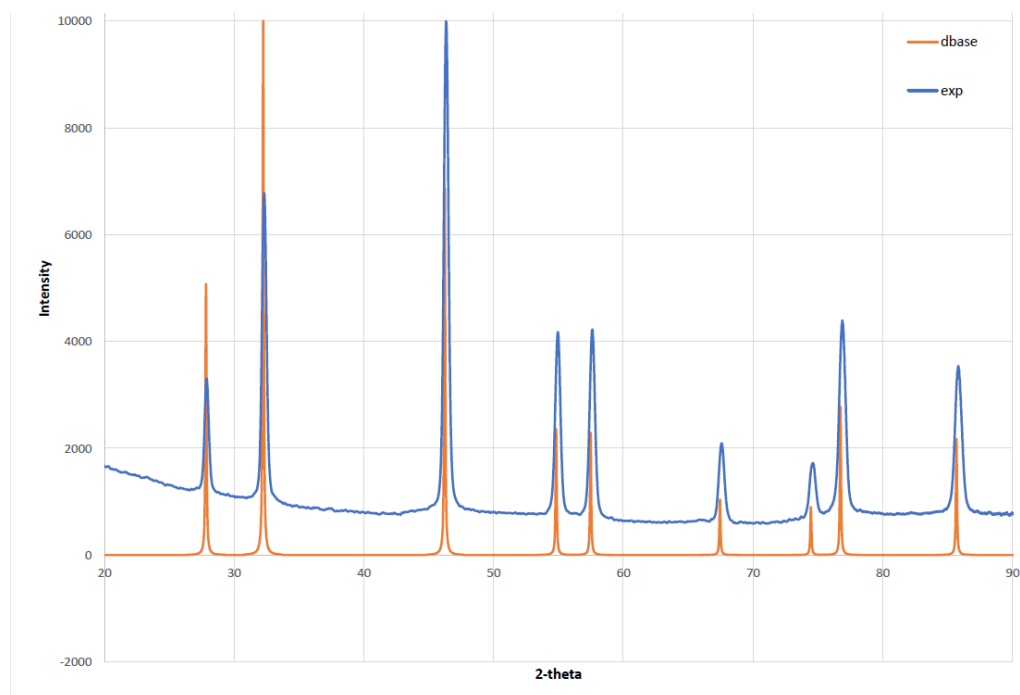


Figure S13: Powder XRD of reference of silver chloride (orange) with the powder XRD of the bulk product (blue) demonstrating the full conversion of silver nitrate to single phase silver chloride after the reaction.

3 References

1. M. H. Deville, *Compt. Rend. Acad. Sci. Paris* 1849, **28**, 257.
2. C. C. Addison and N. Logan, *Developments in Inorganic Nitrogen Chemistry*, Vol. 2, Ed. C. B. Colburn, Elsevier, Amsterdam, 1973, pp. 27–69.
3. E. Grison, K. Eriks and J. L. de Vries, *Acta Cryst.*, 1950, **3**, 290–294.