Ammonium Pertechnetate in Mixtures of Trifluoromethanesulfonic Acid and Trifluoromethanesulfonic Anhydride

Markus Zegke*, Dennis Grödler, Maximilian Roca Jungfer, Alexander Haseloer, Meike Kreuter, Jörg M. Neudörfl, Thomas Sittel, Christopher M. James, Jörg Rothe, Marcus Altmaier, Axel Klein, Martin Breugst, Ulrich Abram, Erik Strub*, and Mathias S. Wickleder*

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Supporting Information

Table of Contents

General information ........................................................................................................... 3
Chemicals ............................................................................................................................ 3
General procedure .............................................................................................................. 3
Precautions and safety ....................................................................................................... 3
Instrumentation .................................................................................................................. 3
UV-vis absorption .............................................................................................................. 3
Liquid Scintillation Counting (LSC) .................................................................................. 4
XRD .................................................................................................................................... 4
NMR .................................................................................................................................... 5
XANES ............................................................................................................................... 5
MS ....................................................................................................................................... 5
EPR ..................................................................................................................................... 5
IR ........................................................................................................................................ 5
Experiments ....................................................................................................................... 6
1. Reactions in Tf₂O or Tf₂O/HOTf mixtures ...................................................................... 6
1.1. NH₄TcO₄ with Tf₂O .................................................................................................... 6
1.2. NH₄TcO₄ with 1.5 ml Tf₂O and 200 µl HOTf ............................................................ 6
1.3. NH₄TcO₄ with 1.5 ml Tf₂O and 10 µl HOTf ............................................................. 6
1.4. NH₄TcO₄ with 1.5 ml Tf₂O and 20 µl HOTf ............................................................. 6
1.5. NH₄TcO₄ with 1.5 ml Tf₂O and 40 µl HOTf ............................................................. 6
1.6. NH₄TcO₄ with 3.62 µl Tf₂O and 0.38 µl HOTf in 16 µl Et₂O .................................... 7
1.7. NH₄TcO₄ with 90.5 µl Tf₂O and 8.5 µl HOTf ......................................................... 7
1.8. NH₄TcO₄ with 290.5 µl Tf₂O and 8.5 µl HOTf ....................................................... 7
1.9. NH₄TcO₄ with 590.5 µl Tf₂O and 8.5 µl HOTf ....................................................... 7
1.10. NH₄TcO₄ with 890 µl Tf₂O and 10 µl HOTf ......................................................... 8
1.11. NH₄TcO₄ with 581 µl Tf₂O and 19 µl HOTf at 60 °C for 0.5, 1, 2 and 4 h .............. 8
1.12. NH₄TcO₄ with 1162 µl Tf₂O and 38 µl HOTf at 60 °C for 0.5, 1, 2 and 4 h .......... 8
1.13. NH₄TcO₄ with 581 µl Tf₂O and 10, 19, 38 and 76 µl HOTf at 60 °C for 0.5 h .... 9
1.14. NH₄TcO₄ with 581 µl Tf₂O and 19 µl HOTf at 80 °C for 0.5 h .......................... 9
1.15. NH₄TcO₄ with 581 µl Tf₂O and 19 µl HOTf at 100 °C for 10 min ................. 9
1.16. NH₄TcO₄ with 19 µl Tf₂O and 581 µl HOTf at r.t ............................................ 9
2. Reactions in neat HOTf ............................................................................................... 10
2.1. Reactions of ammonium and alkaline pertechnetates at room temperature.......................... 10
2.2. Reactions of ammonium and alkaline pertechnetates at low temperatures.......................... 10
2.3. Reaction of tetrabutylammonium pertechnetate at room temperature................................. 10
2.4. Reaction of tetrabutylammonium pertechnetate at low temperature................................. 10
2.5. Reaction of ammonium pertechnetate with aqueous HBF$_4$............................................... 10
2.6. Reaction of ammonium pertechnetate with conc. H$_2$SO$_4$............................................... 10
2.7. Hydrolysis of (NH$_4$)$_2$[TcO(OTf)$_3$] and [TcO$_3$(OTf)]: formation of solid (NH$_4$)$_4$[TcO(OTcO$_3$)$_4$]$\cdot$10H$_2$O................................................................. 11
Spectra ........................................................................................................................................ 12
  UV-vis spectra .......................................................................................................................... 12
  Powder XRD ........................................................................................................................... 14
  Single crystal XRD .................................................................................................................. 15
  NMR Spectra .......................................................................................................................... 15
  EPR Spectra ............................................................................................................................ 19
  XANES spectra ....................................................................................................................... 20
Computations ............................................................................................................................. 22
  Computational Details ........................................................................................................... 22
  Control Calculations ............................................................................................................. 22
  Calculated Spectra ................................................................................................................ 23
  Coordinates of Different Tc Complexes ............................................................................... 25
Proposed reduction mechanism for the reduction ................................................................. 27
Heat energy calculation ........................................................................................................... 27
References ................................................................................................................................. 28
General information

Chemicals

Trifluoromethanesulfonic acid (HOTf) and trifluoromethanesulfonic anhydride (Tf₂O) were purchased from ABCR and used as received without further purification.

⁹⁹Tc was provided as an aqueous solution of 2 g NH₄TcO₄ in ca. 20 ml of water. The sample is a stock solution dated 1965 and produced at the Oak Ridge National Laboratories, USA.

General procedure

All reactions and analyses were performed using standard Schlenk techniques under Ar (4.6 (99.996%)), using 10 ml DURAN® culture tubes with a PTFE lined DIN thread and PBT screw cap. All glassware was oven dried at 150 °C overnight or using an external heat gun at 550 °C for several minutes.

Prior to the experiment, 20 µl (2 mg, 11.0 µmol, 0.693 MBq) of an aqueous NH₄TcO₄ solution were added to a 10 ml DURAN® culture tube inside a Schlenk flask and evacuated to dryness overnight. To the colourless solid HOTf and Tf₂O were added (as detailed in the respective experiments below) using oven dried FORTUNA® pipettes flushed with Ar or Eppendorf microliter pipettes.

Precautions and safety

The work was carried out at the certified radiochemical laboratories of the University of Cologne and Freie Universität Berlin and the Institute for Nuclear Waste Disposal at the Karlsruhe Institute of Technology.

To reduce contamination, all work was monitored with appropriate detectors. All surfaces were wiped clean before and after use. Standard PPE was worn at all times. NMR samples were measured in double containment technique with the sample inside a PTFE inlay within the actual NMR tube. Even closed samples containing triflic acid of triflic anhydride have been handled in a double containment system, e.g. placing the vial in a beaker, in order to avoid contamination by leakages due to occasional gas evolution. After the experiments, residual triflic acid was carefully diluted in acetone and neutralised with organic bases.

Instrumentation

UV-vis absorption

UV-vis spectra were recorded using a VWR UV-1600PC spectrophotometer. The spectrometer was equipped with a cuvette holder that was connected to a thermostat to cool or heat the samples. These DURAN® vials were directly used as reaction vessels and cuvettes in the spectrometer. Because the vials are taller than the standard cuvettes, an additional lid was added to the spectrometer to ensure a lightproof cover of the vials during measurement. A vial filled with HOTf was used as a blank before the experiment commenced.

As the control program did not allow automated measurements to obtain timed series, repeated spectra were obtained using the GS Auto Clicker program. In analogy to a scene from a popular TV series, we refer to this automation technique as "Simpsons Woodpecker Spectroscopy" (SWS).
Liquid Scintillation Counting (LSC)

LSC measurements were performed using a HIDEK SL-300 TDCR counter. For yield control, typically 20 µL aliquots of supernatant were taken and diluted with 10 mL H₂O to obtain a suitable pH value for LSC. Of this dilutions, again 20 µL aliquots were pipetted into 20 mL LSC PP vial containing 5 mL H₂O and 10 mL scintillation cocktail (Perkin Elmer Ultima Gold). Using this procedure resulted in samples with typical count rates of several hundred to several thousand cpm (counts per minute). Samples were measured for 5-10 minutes.

XRD

Single crystal data of \([\text{TcO}_3(\text{OTf})], (\text{NH}_4)_2[\text{TcO}(\text{OTf})_2] \cdot (\text{HOTf})\) and \(\text{Na}_2[\text{TcO}(\text{OTf})_5] \cdot 2 (\text{HOTf})\) were collected at 100 K with a Bruker D8 Venture diffractometer (Cu-Kα₁ radiation, \(λ = 1.5406 \text{ Å}\)) equipped with a Bruker APEX-II CCD detector. A suitable single crystal was selected and immersed in an inert oil. The crystal was then mounted on a MicroLoop. The crystal was cooled to 100 K by an Oxford Cryostream low temperature device. The single crystal data of \((\text{NH}_4)_4[\text{TcO}(\text{OTcO}_3)_{4}] \cdot 10 \text{ H}_2\text{O}\) were collected on a Bruker D8 Venture instrument with Mo Kα radiation. The crystal was stored in liquid N₂ until it was directly mounted into the diffractometers cryostream. The full data set was recorded and the images processed using APEX3. Structure solution by direct methods or intrinsic phasing was achieved through the use of SHELXS programs, and the structural model refined by full matrix least squares on F² using SHELXL-2014. Semi-empirical absorption correction form equivalents (multiscan) was executed using SADABS-2016/2. Molecular graphics were plotted using Mercury. Editing of CIFs and construction of tables and bond lengths and angles was achieved using WC and PLATON, or Olex2 program. All non-hydrogen atoms were refined anisotropically. Where possible, hydrogen atoms were placed according to residual electron density peaks, otherwise placed using idealised geometric positions and allowed to move in a “riding model” along with the atoms to which they are attached, and refined isotropically.

Powder X-ray diffraction was attempted to be measured on a P-XRD Stoe Stadi-P equipped with a Mythen 1 K detector and measured from 3 to 60° in 3° steps and 60 s exposure time in transmissions using Mo-Kα radiation. The sample was prepared using Scotch tape and cling film, with traces of Fomblin® oil but decomposed to NH₄TcO₄ on the tape (Figure S 1). Another sample was attempted to be measured between two microscope slide cover glasses, and visually the yellow material did not decompose. However, the absorption of the glass was too strong and no reflections attributable to the complex were observed. Due to the very small amount of material, the low stability and the radioactive nature of the compound, we could not measure the material inside a sealed glass capillary.

Figure S 1. Pertechnetyl triflate immediately after preparation on Scotch tape (left) and five minutes after inserting into mounting disk (right). Only reflections of NH₄TcO₄ were observed. The brown material is attributed to TcO₂.
NMR

NMR samples of the Tf₂O/HOTf reactions were flame-sealed under vacuum with a CuAl insert and measured on a Bruker Avance III 400 spectrometer operating at 400.18 MHz for ¹H and 90.07 MHz for ⁹⁹Tc at 300 K. The spectrometer was equipped with a broadband observe probe (BBFOplus) with direct x-magnetisation detection for proton and heteronuclear detection experiments. Chemical shifts are referenced internally to TMS (δ(TMS) = 0 ppm) for ¹H and to Na⁹⁹TcO₄⁻ with δ(Na⁹⁹TcO₄⁻) = 0 ppm for ⁹⁹Tc. For all spectra, standard Bruker pulse sequences were used. 1D spectra of ¹H and ⁹⁹Tc were recorded with 32k data points and were zero filled to 64k data points.

The ⁹⁹Tc NMR spectra of the reactions in neat HOTf and other acids without the addition of Tf₂O and that of [TcOCl₄]⁻ were measured on a Jeol JNM-ECA400II (400 MHz ECA II) spectrometer and referenced internally to TcO₄⁻.

XANES

Tc K-edge X-ray absorption near-edge structure (XANES) spectra were collected from the same flame-sealed solutions as used for the NMR (see above) at the INE-Beamline, KIT synchrotron source (KARA storage ring, KIT Campus North), using the conventional fluorescence yield XAS setup.[¹¹] The Tc Kα-line was detected by combining the signal of a 4-pixel and a single-pixel SDD (Vortex) detector (Hitachi, USA), using an Ar-filled ionisation chamber at ambient pressure as Is monitor. The double crystal monochromator was equipped with a pair of Ge<422> crystals. The energy scale was calibrated by assigning the first inflection point in the rising K-edge absorption of a Mo metal foil (20 µm) to the 1s-energy (E₁s (Mo⁰): 20000.0 eV).

MS

Head space gas chromatography for O₂ detection was attempted by using a Trace 1300 Chromatograph equipped with a TriPlus RSH auto sampler from Thermo Scientific with a thermal conductivity detector. The capillary column used was a Shin carbon ST 100/120 1.0 mm x 2 m 1/16” OD silico. The carrier gas was helium. An attempt at calibrating the equipment with HOTf and Tf₂O resulted in a blockage and malfunctioning of the device, rendering the O₂ detection impossible.

EPR

EPR spectra were recorded on glassy frozen solutions in HOTf at 78 K in the X-band on a Miniscope MS400 spectrometer (Magnetech). Simulations have been done with Easyspin.[¹²]

IR

IR spectra were measured from KBr pellets on a Shimadzu Affinity-1 FTIR spectrometer and verified by a direct measurement on a Nicolet iS10 FT-IR.
Experiments

1. Reactions in Tf₂O or Tf₂O/HOTf mixtures

1.1. NH₄TcO₄ with Tf₂O

2.0 mg NH₄TcO₄ (0.011 mmol, 1.0 eq.) were treated with 1.5 ml (1237.6 mg, 8.92 mmol, 810.6 eq) Tf₂O. The material does not dissolve, and the mixture does not change colour, even after repeated heating for a total of 5 hours at 80 °C with freezing periods in between.

1.2. NH₄TcO₄ with 1.5 ml Tf₂O and 200 µl HOTf

2.0 mg NH₄TcO₄ (0.011 mmol, 1.0 eq.) were treated with 1.5 ml (1237.6 mg, 8.92 mmol, 810.6 eq) Tf₂O, followed by the addition of 200 µl (372 mg, 2.6 mmol, 234 eq.) HOTf. After one hour of heating to 80 °C a green solution was obtained.

1.3. NH₄TcO₄ with 1.5 ml Tf₂O and 10 µl HOTf

A suspension of 2.0 mg NH₄TcO₄ (0.011 mmol, 1.0 eq.) in 1.5 ml (1237.6 mg, 8.92 mmol, 810.6 eq) Tf₂O was treated with 10 µl (18.6 mg, 0.13 mmol, 11.7 eq.) of HOTf. After one hour of heating to 80 °C a deep purple solution was obtained. The colour intensified over the course of 3 hours. After 5 d at -15 °C green needles suitable for X-ray crystallography could be isolated.

1.4. NH₄TcO₄ with 1.5 ml Tf₂O and 20 µl HOTf

A suspension of NH₄TcO₄ in 1.5 ml (1237.6 mg, 8.92 mmol, 810.6 eq) Tf₂O was treated with 20 µl (37.2 mg, 0.26 mmol, 23.4 eq.) HOTf. After one hour of heating to 80 °C a dark purple solution was obtained. From this solution green crystals of (NH₄)₂[TcO(OTf)₃] could be isolated.

1.5. NH₄TcO₄ with 1.5 ml Tf₂O and 40 µl HOTf

A suspension of NH₄TcO₄ in 1.5 ml (1237.6 mg, 8.92 mmol, 810.6 eq) Tf₂O was treated with 40 µl (74.4 mg, 0.52 mmol, 46.8 eq.) of HOTf. After one hour of heating to 80 °C a dark purple solution was obtained. The solution was kept at -15 °C for one night. Yellow crystals of [TcO₃(OTf)] suitable for X-ray crystallography were isolated.
1.6. \( \text{NH}_4\text{TcO}_4 \) with 3.62 µl Tf\(_2\)O and 0.38 µl HOTf in 16 µl Et\(_2\)O

A solution of 0.38 µl HOTf (0.65 mg, 0.004 mmol, 0.4 eq.) and 3.62 µl (6.07 mg, 0.022 mmol, 2.0 eq.) Tf\(_2\)O in 16.0 µl Et\(_2\)O were added to 2.0 mg NH\(_4\)TcO\(_4\) (0.011 mmol, 1.0 eq.) and was heated for 4 h at 60 °C. All volatiles were removed under reduced pressure for 18 h leaving a brown solid as a residue, supposedly TcO\(_2\).

1.7. \( \text{NH}_4\text{TcO}_4 \) with 90.5 µl Tf\(_2\)O and 8.5 µl HOTf

A solution of 8.5 µl (15.8 mg, 0.11 mmol, 10.0 eq.) HOTf and 90.5 µl (151.77 mg, 0.54 mmol, 49.1 eq.) Tf\(_2\)O were added to 2.0 mg NH\(_4\)TcO\(_4\) (0.011 mmol, 1.0 eq.) and was heated for 3 h at 60 °C. The reaction mixture started to turn purple after 10 min and remained deep purple after 3 h of heating. After 3 d at −15 °C no crystallisation of [TcO\(_3\)(OTf)] was observed.

1.8. \( \text{NH}_4\text{TcO}_4 \) with 290.5 µl Tf\(_2\)O and 8.5 µl HOTf

A solution of 8.5 µl (15.8 mg, 0.11 mmol, 10.0 eq.) HOTf and 290.5 µl (487.2 mg, 1.73 mmol, 118.2 eq.) Tf\(_2\)O were added to 2.0 mg NH\(_4\)TcO\(_4\) (0.011 mmol, 1.0 eq.) and was heated for 3 h at 60 °C. The reaction mixture started to turn purple after 30 min and remained deep purple after 3 h of heating. After 3 d at −15 °C no crystallisation of [TcO\(_3\)(OTf)] was observed.

1.9. \( \text{NH}_4\text{TcO}_4 \) with 590.5 µl Tf\(_2\)O and 8.5 µl HOTf

A solution of 8.5 µl HOTf (15.8 mg, 0.11 mmol, 10.0 eq.) and 590.5 µl (487.2 mg, 3.51 mmol, 319.1 eq.) Tf\(_2\)O were added to 2.0 mg NH\(_4\)TcO\(_4\) (0.011 mmol, 1.0 eq.) and was heated for 2 h at 60 °C. The NH\(_4\)TcO\(_4\) reacted under formation of yellow oily droplets, which dissolved after 30 min. The reaction mixture stayed colourless at 60 °C but darkened to purple at room temperature. After additional 3 h of heating at 60 °C the mixture stayed purple at given temperature. After 3 d at −15 °C no crystallisation of [TcO\(_3\)(OTf)] was observed.

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Figure S 2 High resolution image of the packing of [TcO\(_3\)(OTf)].
1.10. NH₄TcO₄ with 890 µl Tf₂O and 10 µl HOTf

A solution of 10.0 µl HOTf (17.1 mg, 0.114 mmol, 10.4 eq.) and 890 µl (1.492 g, 5.29 mmol, 480.9 eq.) Tf₂O were added to 2.0 mg NH₄TcO₄ (0.011 mmol, 1.0 eq.) and was heated for 2 h at 60 °C. The NH₄TcO₄ reacted under formation of yellow oily droplets, which dissolved after 30 min. The reaction mixture stayed colourless at 60 °C but darkened to purple at room temperature. After additional 5 h of heating at 60 °C, the mixture stayed purple at the given temperature. After 3 d at −15 °C no crystallisation of [TcO₃(OTf)] was observed.

1.11. NH₄TcO₄ with 581 µl Tf₂O and 19 µl HOTf at 60 °C for 0.5, 1, 2 and 4 h

Four solutions of 19.0 µl HOTf (32.5 mg, 0.216 mmol, 19.6 eq.) and 581 µl (974 mg, 3.45 mmol, 313.9 eq.) Tf₂O were added to 2.0 mg NH₄TcO₄ (0.011 mmol, 1.0 eq.) respectively and were heated for 0.5 h (11a), 1 h (11b), 2 h (11c) and 4 h (11d) at 60 °C. The reaction supernatant was analysed by UV-Vis spectroscopy at room temperature to monitor the reaction process. After 3 d at −15 °C crystallisation of [TcO₃(OTf)] was observed in all batches but in different yields.

Yields (wrt [TcO₃(OTf)]): 11a: 97%; 11b: 81%; 11c: 48%; 11d: 44%

Figure S 3. Reaction vials of 11a, 11b, 11c and 11d.

1.12. NH₄TcO₄ with 1162 µl Tf₂O and 38 µl HOTf at 60 °C for 0.5, 1, 2 and 4 h

Four solutions of 38.0 µl HOTf (65.0 mg, 0.432 mmol, 39.2 eq.) and 1162 µl (1.948 g, 6.90 mmol, 627.3 eq.) Tf₂O were added to 2.0 mg NH₄TcO₄ (0.011 mmol, 1.0 eq.) respectively and were heated for 0.5 h (12a), 1 h (12b), 2 h (12c) and 4 h (12d) at 60 °C. The reaction supernatant was analysed by UV-Vis spectroscopy at room temperature to monitor the reaction process. After 3 d at −15 °C crystallisation of [TcO₃(OTf)] was observed in moderate yields (LSC).

Yields (wrt [TcO₃(OTf)]): 12a: 47%; 12b: 42%; 12c: 49%; 12d: 37%

Figure S 4. Reaction vials of 12a, 12b, 12c and 12d.
1.13. NH₄TcO₄ with 581 µl Tf₂O and 10, 19, 38 and 76 µl HOTf at 60 °C for 0.5 h

Four solutions of either 10.0 µl (17.1 mg, 0.114 mmol, 10.4 eq.) (13a), 19.0 µl (32.5 mg, 0.217 mmol, 19.7 eq.) (13b), 38.0 µl (65.0 mg, 0.432 mmol, 39.2 eq.) (13c) or 76.0 µl (130.0 mg, 0.866 mmol, 78.7 eq.) (13d) HOTf in 581 µl (974 mg, 3.45 mmol, 313.7 eq.) Tf₂O were added to 2.0 mg NH₄TcO₄ (0.011 mmol, 1.0 eq.) and were heated for 0.5 h at 60 °C. The reaction supernatant was analysed by UV-Vis spectroscopy at room temperature to monitor the reaction process. After 3 d at -15 °C crystallisation of [TcO₃(OTf)] was observed in the first two batches in different yields (LSC).

Yields (wrt [TcO₃(OTf)]): 13a: 82%; 13b: 68%; 13c: 44%; 13d: 11%

![Figure S 5. Reaction vials of 13a, 13b, 13c and 13d.](image)

1.14. NH₄TcO₄ with 581 µl Tf₂O and 19 µl HOTf at 80 °C for 0.5 h

A solution of 19.0 µl HOTf (32.5 mg, 0.216 mmol, 19.6 eq.) and 581 µl (974 mg, 3.45 mmol, 313.9 eq.) Tf₂O were added to 2.0 mg NH₄TcO₄ (0.011 mmol, 1.0 eq.) and was heated for 0.5 h at 80 °C. The reaction supernatant was analysed by UV-Vis spectroscopy at room temperature to monitor the reaction process. After 3 d at -15 °C crystallisation of [TcO₃(OTf)] was observed in a yield of 71%.

1.15. NH₄TcO₄ with 581 µl Tf₂O and 19 µl HOTf at 100 °C for 10 min

A solution of 19.0 µl HOTf (32.5 mg, 0.216 mmol, 19.6 eq.) and 581 µl (974 mg, 3.45 mmol, 313.9 eq.) Tf₂O were added to 2.0 mg NH₄TcO₄ (0.011 mmol, 1.0 eq.) and was heated for 10 min at 100 °C. The reaction supernatant was analysed by UV-Vis spectroscopy at room temperature to monitor the reaction process. After 3 d at -15 °C crystallisation of [TcO₃(OTf)] was observed in a yield of 97%.

1.16. NH₄TcO₄ with 19 µl Tf₂O and 581 µl HOTf at r.t.

A solution containing 581 µl HOTf (993 mg, 6.6 mmol, 600 eq.) and 19 µl (31 mg, 0.11 mmol, 10 eq.) Tf₂O was added to 2.0 mg NH₄TcO₄ (0.011 mmol, 1.0 eq.). The mixture was left standing at room temperature. The solid turned yellow, and the supernatant turned purple within 30 min. After three days, the solution showed a pale green colour.
2. Reactions in neat HOTf
K[TcO₄], Cs[TcO₄], Ag[TcO₄] and NBu₄[TcO₄] were prepared by salt metathesis between NH₄[TcO₄] in a minimum amount of water with KOH, Cs₂CO₃, AgNO₃ and NBu₄Cl following standard procedures.

2.1. Reactions of ammonium and alkaline pertechnetates at room temperature
NH₄TcO₄, KTCO₄, AgTcO₄ and CsTcO₄ (0.07 mmol) react with neat, fuming triflic acid (0.5 ml) at room temperature (20 – 30°C) under a colour change to yellow and the formation of a purple solution. The purple solution contained a transient, paramagnetic Tc(VI) species. After storage overnight, pure, yellow [TcO₃(OTf)] crystallises from such solutions as verified by X-ray diffraction. This material is highly reactive towards an open atmosphere due to the hygroscopic nature of the adhered residual HOTf on the surface of the crystals. Under strictly anhydrous conditions, the yellow crystals of [TcO₃(OTf)] gradually dissolve under intensification of the purple colour, but ultimately form bright green solutions of [TcO(OTf)₅]²⁻. Such solutions turn reddish-orange when partially exposed to the atmosphere, forming the polyoxometallate [{TcO(OTcO₃)₄}₄⁴⁻, which crystallises after prolonged time.

2.2. Reactions of ammonium and alkaline pertechnetates at low temperatures
NH₄TcO₄, KTCO₄, AgTcO₄ and CsTcO₄ (0.07 mmol) react with neat, fuming triflic acid (0.5 ml) between -20° and +5°C under a colour change to yellow and the formation of a yellow solution. After storage overnight, the formation of yellow crystals of [TcO₃(OTf)] was observed in all cases. No dissolution of the crystals and formation of a purple or green solution was observed. Exposure to the atmosphere, however, resulted in a change of colour to the orange-red of the polyoxometallate [{TcO(OTcO₃)₄}₄⁴⁻, which crystallises after prolonged time.

2.3. Reaction of tetrabutylammonium pertechnetate at room temperature
NBu₄TcO₄ (0.07 mmol) dissolved in neat, fuming HOTf (0.5 ml) at room temperature in a violent reaction. The initially yellow solution heated to boiling before changing its colour to purple through red and finally yellow within seconds. No formation of solid [TcO₃(OTf)] was observed.

2.4. Reaction of tetrabutylammonium pertechnetate at low temperature
NBu₄TcO₄ (0.07 mmol) was dissolved in neat, fuming HOTf (0.5 ml) to give a yellow solution.

2.5. Reaction of ammonium pertechnetate with aqueous HBF₄
NH₄TcO₄ (0.07 mmol) was dissolved in aqueous BF₄ (0.5 ml, 45-50%) giving a colourless solution.

2.6. Reaction of ammonium pertechnetate with conc. H₂SO₄
NH₄TcO₄ (0.07 mmol) was dissolved in conc. H₂SO₄ (0.5 ml) giving a yellow solution.
2.7. Hydrolysis of \((\text{NH}_4)_2[\text{TcO(OTf)}_3]\) and \([\text{TcO}_3(\text{OTf})]\): formation of solid \((\text{NH}_4)_4\{[\text{TcO(OTcO)}_3]_4\}_4 \cdot 10\text{H}_2\text{O}\)

\(\text{NH}_4\text{TcO}_4\) (12 mg, 0.07 mmol) was added to neat, fuming triflic acid (0.5 ml) at room temperature in a screw-lid glass vial. The vial was closed and carefully shaken resulting in a purple solution with yellow sediment. Overnight, large yellow crystals of \([\text{TcO}_3(\text{OTf})]\) formed. The crystals dissolved within one week and during this time a colourless liquid condensed on the sides of the vial above the solution. The condensed liquid turned reddish-purple and red-green dichroic and highly hygroscopic crystals of \((\text{NH}_4)_4\{[\text{TcO(OTcO)}_3]_4\}_4 \cdot 10\text{H}_2\text{O}\) slowly formed upon slow exposure to the atmosphere. After three weeks, the bottom solution had turned orange and crystals of \((\text{NH}_4)_4\{[\text{TcO(OTcO)}_3]_4\}_4 \cdot 10\text{H}_2\text{O}\) deposited. The vial was opened under \(\text{Ar}\) and the crystals were filtered off via a reverse frit under \(\text{Ar}\). They were washed with dry, degassed pentane and diethyl ether. They were then transferred to an \(\text{Ar}\)-filled, tared screw-lid vial as a suspension in dry diethyl ether. The diethyl ether was evaporated in vacuum. The thus obtained green-red dichroic crystals of \((\text{NH}_4)_4\{[\text{TcO(OTcO)}_3]_4\}_4 \cdot 10\text{H}_2\text{O}\) were stored under \(\text{Ar}\).

Yield: 3.2 mg (1 \(\mu\)mol, 31\%). Melting point: ca. 30°C. FT-IR: 3493 (broad, \(\nu_{\text{OH}}\)), 3211 (broad, \(\nu_{\text{NH}_4}\)), 2961 (m, \(\nu_{\text{NH}_4}\)), 2916 (w, \(\nu_{\text{NH}_4}\)), 2849 (w, \(\nu_{\text{NH}_4}\)), 1618 (w, \(\nu_{\text{NH}_4/\nu_{\text{OH}}}\)), 1402 (m, \(\nu_{\text{CO}}\)), 1089 (m, \(\nu_{\text{CO}}\)), 1026 (m, \(\nu_{\text{CO}}\)), 910 (vs, \(\nu_{\text{CO}}\)), 788 (broad, \(\nu_{\text{CO}}\)).

The highly hygroscopic crystals form a deep brown-red oil upon exposure to moisture, while dilute solutions in acetone, ethanol or water show a range of colours from red-brown via orange to yellow depending on the concentration. Crystals suitable for X-ray diffraction were obtained by slow hydrolysis of the initial purple solution and some of the \([\text{TcO}_3(\text{OTf})]\) crystals on a glass plate. Due to the highly hygroscopic nature and the low melting point, the crystals were stored in liquid nitrogen until the measurement.

![Figure S6. Ellipsoid plot of \((\text{NH}_4)_4\{[\text{TcO(OTcO)}_3]_4\}_4 \cdot 10\text{H}_2\text{O}\) including the partially disordered solvent water molecules.](image-url)
Spectra

UV-vis spectra

**Figure S 7.** Absorption spectrum of experiment 1.11.

**Figure S 8.** Absorption spectrum of experiment 1.12.
Figure S 9. Absorption spectrum of experiment 1.13.

Figure S 10. Absorption spectra of experiments 1.14 and 1.15.
Figure S 11. Powder diffractogram of the brown material, which formed when pertechnetyl triflate was mounted onto Scotch tape (cf. Fig S 1). The observed reflections can only be attributed to NH₄TcO₄.
**Table S 1. Crystal data and refinement parameters.**

| Complex | \((\text{NH}_4)_2[\text{TcO(OTf)}_5] \bullet \text{HOTf}\) | \([\text{TcO}_2(\text{OTf})]_{\bullet 2}\text{HOTf}\) | \((\text{NH}_4)_4[\{\text{TcO(OTC)}_3\}_{\bullet 4}] \bullet 10\text{H}_2\text{O}\) |
|----------|----------------------------------|----------------------------------|----------------------------------|
| CCDC Number | 2114967 | 2114965 | 2114966 |
| Empirical formula | \(\text{C}_6\text{H}_9\text{F}_{18}\text{N}_2\text{O}_{19}\text{S}_6\text{Tc}_2\) | \(\text{C}_2\text{F}_6\text{O}_2\text{S}_2\text{Tc}_2\) | \(\text{H}_{36}\text{N}_4\text{O}_{78}\text{Tc}_{20}\) |
| Formula weight | 1045.51 | 590.14 | 3300.33 |
| Temperature/K | 100.0 | 100.0 | 100.0 |
| Crystal system | orthorhombic | monoclinic | triclinic |
| Space group | \(\text{Pbca}\) | \(\text{P}2_1/c\) | \(\text{P}-1\) |
| \(a/\text{Å}\) | 9.4625(2) | 8.7221(5) | 11.328(2) |
| \(b/\text{Å}\) | 24.2120(5) | 8.8945(6) | 12.833(2) |
| \(c/\text{Å}\) | 26.4840(6) | 9.1632(6) | 13.987(2) |
| \(\alpha/°\) | 90 | 90 | 71.842(6) |
| \(\beta/°\) | 90 | 115.3430(10) | 69.144(6) |
| \(\gamma/°\) | 90 | 90 | 74.378(6) |
| Volume/\(\text{Å}^3\) | 6067.6(2) | 642.46(7) | 1776.5(5) |
| \(Z\) | 8 | 2 | 1 |
| \(\rho_{\text{calc}}/\text{g/cm}^3\) | 2.289 | 3.051 | 3.085 |
| \(\mu/\text{mm}^{-1}\) | 9.552 | 22.027 | 3.886 |
| \(F(000)\) | 4096.0 | 560.0 | 1548 |
| Crystal size/mm³ | 0.207 × 0.124 × 0.06 | 0.1 × 0.1 × 0.1 | 0.09 × 0.03 × 0.02 |
| Radiation | \(\text{CuK}_\alpha (\lambda = 1.54178)\) | \(\text{CuK}_\alpha (\lambda = 1.54178)\) | \(\text{MoK}_\alpha (\lambda = 0.71073)\) |
| 2\(\theta\) range for data collection/° | 6.67 to 144.25 | 11.22 to 143.85 | 2.35 to 25.94 |
| Index ranges | \(-10 \leq h \leq 11, -29 \leq k \leq 29, -32 \leq l \leq 32\) | \(-10 \leq h \leq 10, -10 \leq k \leq 10, -11 \leq l \leq 11\) | \(-13 \leq h \leq 13, -15 \leq k \leq 15, -17 \leq l \leq 17\) |
| Reflections collected | 59485 | 14565 | 45155 |
| Independent reflections | 5971 [\(R_{\text{int}} = 0.0945, R_{\text{sigma}} = 0.0263\)] | 1262 [\(R_{\text{int}} = 0.0559, R_{\text{sigma}} = 0.0243\)] | 6745 [\(R_{\text{int}} = 0.0559, R_{\text{sigma}} = 0.0243\)] |
| Data/restraints/parameters | 5971/9/505 | 1262/0/109 | 645/720/643 |
| Goodness-of-fit on \(F^2\) | 1.040 | 1.234 | 1.085 |
| Final R indexes \([I>2\sigma(I)]\) | \(R_1 = 0.0255, wR_2 = 0.0651\) | \(R_1 = 0.0235, wR_2 = 0.0585\) | \(R_1 = 0.0588, wR_2 = 0.1263\) |
| Final R indexes \([\text{all data}]\) | \(R_1 = 0.0291, wR_2 = 0.0662\) | \(R_1 = 0.0242, wR_2 = 0.0588\) | \(R_1 = 0.0701, wR_2 = 0.1312\) |
| Largest diff. peak/hole/e Å⁻³ | 2.08/-0.84 | 0.52/-0.99 | 2.01/-1.27 |
NMR Spectra

Figure S 12. $^{99}$Tc-NMR of purple sample obtained from experiment 1.5.
Figure S 13. $^{99}$Tc-NMR spectra of NH$_4$TcO$_4$ and NBu$_4$TcO$_4$ in different, highly acidic media. Pertechnetate did not react with HBF$_4$ (experiment 2.5): the $^{99}$Tc NMR spectrum shows only the resonance of TcO$_4^-$. It is assumed that the dissolution of pertechnetate in H$_2$SO$_4$ (experiment 2.6) gives probably the water adduct [TcO$_3$(OSO$_3$H)(OH$_2$)$_2$] ($\delta = 273$ ppm, $\nu_{1/2} = 8316$ Hz). When water-free TcO$_4$ is dissolved in triflic acid (experiments 2.1 and 2.4), the narrow resonance of [TcO$_3$(OTf)] is observed ($\delta = 204$ ppm, $\nu_{1/2} = 350$ Hz). When such solutions are exposed to moisture or moisture is present in the starting materials, a resonance similar to that of [TcO$_3$(OSO$_3$H)(OH$_2$)$_2$] was observed. It can be attributed to [TcO$_3$(OSO$_2$CF$_3$)(OH$_2$)$_2$] ($\delta = 269$ ppm, $\nu_{1/2} = 6565$ Hz) and the intensity of the resonance of [TcO$_3$(OTf)] eventually vanishes.
Figure S14. $^{99}$Tc-NMR spectra of NBu$_4$[TcOCl$_4$] ($\delta = 4951$ ppm, $\nu_{1/2} = 12.1$ kHz) in CH$_2$Cl$_2$ and neat HOTf compared to an in situ sample of [TcO(OTf)$_5$]$^2^-$ ($\delta = 6601$ ppm, $\nu_{1/2} = 17.8$ kHz).

Figure S15. $^{99}$Tc-NMR spectra of a red-orange solution of (NH$_4$)$_4$[TcO(OTcO$_3$)$_4$]$\cdot$10H$_2$O in triflic acid (experiment 2.7). The solvent fuming HOTf had turned into non-fuming (dilute/aqueous) HOTf over the course of the storage. After dissolution of [[TcO(OTcO$_3$)$_4$]$\cdot$4 several low-intensity Tc(V) resonances are observed with chemical shifts between those observed for the reference compounds [TcOCl$_4$]$^-$ and [TcO(OTf)$_5$]$^2^-$. In addition, a considerably broadened TcO$_4^-$ resonance ($\nu_{1/2} = 400$ Hz) was observed. The main Tc(V) species in the sample gives an extremely broad resonance at $\delta = 6530$ ppm with $\nu_{1/2} = 48$ kHz. The presence of several technetium(V) species suggests that different substitution equilibria under exchange of the pertechnetato ligands play a role upon dissolution of the tetrameric polyoxotechnetate anion.
EPR Spectra

Purple reaction solutions between \(\text{NH}_4\text{TcO}_4\) and neat fuming HOTf allow the detection of EPR spectra. The concentrations of the paramagnetic species are generally low and reach a maximum with the intensity of the purple colour. The course of the reaction (reduction of the Tc(VII) complex \([\text{TcO}_3\text{(OTf)}]\)) depends on the ratio of the starting materials and the moisture, which was allowed to enter the reaction vessel. Generally, the appearance of intermediate Tc(VI) species was observed for all reactions performed, but the intensity of the observed spectra were highest, when small amounts of moisture were present. In such cases, also the signals of more than one Tc(VI) species appeared in the EPR spectra. However, one species, which we assume to be the triflato complex \([\text{Tc}^\text{VI}\text{O(OTf)}_5]\) dominates in all measured spectra.

Figure S 16 depicts the X-band EPR spectrum of \([\text{Tc}^\text{VI}\text{O(OTf)}_5]^+\) (\(S = 1/2\)) recorded for a frozen-glass sample of the complex in HOTf at 78 K. The spectrum shows an axial symmetry with well resolved \(^{99}\text{Tc}\) hyperfine interactions in parallel and perpendicular parts. In the centre of the spectrum, some signals of a second species are visible. The formation of a minor second species has also been found during reactions of \(\text{TcNCl}_4^-\) with HOTf and \(\text{CH}_3\text{SO}_3\text{H}\).\(^{[13,14]}\)

![EPR Spectrum Image]

Figure S 16. Frozen solution X-band EPR spectrum of \([\text{Tc}^\text{VI}\text{O(OTf)}_5]^+\) in HOTf, \(T = 78\) K.

The spectral parameters of \([\text{Tc}^\text{VI}\text{O(OTf)}_5]^+\) are close to those of the previously studied nitrido complexes \([\text{TcN(OTf)}_5]^2-\) and \([\text{TcN(CH}_3\text{SO}_3)_5]^2-.\)^{[14]} They are compared in Table S 2. It is evident that the \(^{99}\text{Tc}\) couplings are generally smaller for the oxido complexes. This effect is also observed for corresponding chloride complexes and the corresponding spectral parameters are contained in Table S 2.

**Table S 2.** EPR parameters of \([\text{Tc}^\text{VI}\text{O(OTf)}_5]^+\) and related compounds

| Compound                | \(g_\parallel\) | \(g_\perp\) | \(A_{\parallel}^{\text{Tc}}\) (10\(^{-4}\) cm\(^{-1}\)) | \(A_{\perp}^{\text{Tc}}\) (10\(^{-4}\) cm\(^{-1}\)) | Ref. |
|------------------------|----------------|-------------|--------------------------|--------------------------|-----|
| \([\text{TcO(OTf)}_5]^+\) | 1.712          | 1.950       | 312                      | 155                      | This work. |
| \([\text{TcN(OTf)}_5]^2-\) | 1.895          | 1.995       | 360                      | 174                      | \([13]\) |
| \([\text{TcN(CH}_3\text{SO}_3)_5]^2-\) | 1.900          | 1.985       | 352                      | 165                      | \([13]\) |
| \([\text{TcOCl}_5]^2-\) | 2.057          | 1.936       | 230                      | 96                       | \([14]\) |
| \([\text{TcNCl}_4]^+\) | 2.016          | 2.003       | 295                      | 137                      | \([15]\) |
XANES spectra

Six consecutive measurements (scans) were taken of the “green” compound, and eight consecutive measurements (scans) of the “purple” compound, both in triflic acid solution. In all measurements, a Mo foil was measured as a reference. The raw spectra of the purple compound showed only a very low absorption in the X-ray range (underlining the strong absorption in the visible range), which made a correct determination of the exact edge energy for this sample impossible.

All raw spectra were loaded into the XASviewer program of the Larch package. Larch is distributed under an open-source license that is nearly identical to the BSD license. It is under active and open development centered at the GeoScoilEnviroCARS sector of Center for Advanced Radiation Sources at the University of Chicago.

All Mo XANES spectra were plotted as normalised $\mu(E)$ and then recalibrated by auto aligning the Mo K edges to the edge of the first scan. The spectra of the six scans were summed up. The turning point of the resulting K edge was found at 20002.8 eV. The Tc XANES spectra were plotted as normalised $\mu(E)$. The energy shifts determined from the Mo K edges were applied manually to the respective spectrum (0 eV, 0.440 eV, 0.408 eV, 0.647 eV, 0.977 eV, and 2.551 eV, respectively). The Tc spectra 1-6 were summed up to obtain a single XANES spectrum of the green solution.

Reference spectra of Tc(VII) and Tc(IV) were obtained from a previous measurement in which the turning point of the Mo K edge had been fixed at 20000.0 eV. Hence, to enable a comparison, the sum spectrum of the green solution was again shifted by -2.8 eV. All 3 spectra are plotted in Figure S 17.

![Figure S 17. XANES spectra of Tc(IV), Tc(VII) and the unknown compound ("green" solution).](image)

From the data it can be seen that the green sample is exhibiting an oxidation state well below +VII, indicating the presence of a reduced Tc species. The absorption is clearly in between the edges of the
Tc(IV) and the Tc(VII). A closer look at an enlarged section (Figure S 18) shows a difference of +1.4 eV between the Tc(IV) reference and the green solution and of -5.2 eV with respect to the Tc(VII) reference. We conclude that the most probable oxidation state of the green solution is Tc(V), although the shift is slightly below the average value of 2.2 eV per oxidation state.

Figure S 18 Enlarged XANES spectra from 21060 to 21069 eV.
Computations

Computational Details

All Tc complexes were optimised employing the GGA functional PBE\textsuperscript{[16,17]} with the corresponding pseudopotential for Tc\textsuperscript{[18]}, Grimme’s D3 correction with Becke-Johnson damping\textsuperscript{[19]} and the SMD continuum model for water\textsuperscript{[20]}. As the solvent mixture of trifluoromethanesulfonic acid and trifluoromethanesulfonic anhydride cannot be adequately modelled within Gaussian, water was chosen as the closest alternative. Density fitting was used to accelerate the calculations and an extremely fine grid with 99 radial shells per atom and 974 angular points per shell for numerical integration of the density. Subsequently, electronic energies were obtained from single point calculations with different methods (e.g., B3LYP-D3BJ, CAM-B3LYP-D3BJ, DLPNO-CCSD(T), M06-L-D3, (RI)-MP2, PBE-D3BJ, TPSSh-D3BJ, ωB97X-D3BJ, ωB2PLYP), the def2-QZVP or def2-QZVPP basis set, and the SMD model for water. UV-Vis spectra were obtained from the PBE-optimised structures relying on either time-dependent DFT (B3LYP-D3BJ, CAM-B3LYP-D3BJ, ωB97XX-D3BJ, ωB2PLP, ωB2GPPLYP) or STEOM-DLPNO-CCSD calculations, the def2-TZVP basis set, and the SMD model for water. Control reactions indicated that neither the basis set nor the number of transitions (30–100) had a significant influence on the observed spectra. All theoretical spectra were simulated by overlapping Gaussian functions for each transition and a value of σ = 0.4 eV (3226 cm\textsuperscript{-1}) was chosen for the width of the absorption band at a height of 1/e.

Control Calculations

As shown in Figure S 19 for the [TcO\textsubscript{3}]\textsuperscript{+} system for the ωB2GP-PLYP functional (a very reliable functional to calculate the UV-Vis spectra for organic compounds\textsuperscript{[21]}) different parameters had no significant effect on the resulting spectra.

![Figure S 19 Calculated UV-Vis-spectra for the [TcO\textsubscript{3}]\textsuperscript{+} system (ωB2GP-PLYP): left: different basis sets, right: different transition numbers.](image-url)
Calculated Spectra

Figure S20 Calculated UV-Vis-spectra for the [TcO$_3$]$^+$ system (wB2GP-PLYP): left: different basis sets, right: different transition numbers.

Figure S21 Calculated UV-Vis-spectra for the [TcO$_3$Cl] system.
Figure S.22 Calculated UV-Vis-spectra for the [TcO$_3$OTf] system.

Figure S.23 Calculated UV-Vis-spectra for the [TcO$_4$]$^-$ system.
Figure S 24 Calculated UV-Vis-spectra for the [TcO₄]²⁻ system.

Coordinates of Different Tc Complexes

|       | [TcO₃]⁺ |          |          |
|-------|---------|----------|----------|
| Tc    | -0.37626| 1.51746  | 6.25390  |
| O     | -0.94044| 1.09815  | 4.72395  |
| O     | -1.56775| 1.00303  | 7.33387  |
| O     | -0.36687| 3.19543  | 6.33042  |

|       | [TcO₃]Cl |          |          |
|-------|----------|----------|----------|
| Tc    | -0.47295 | 1.69790  | 6.04491  |
| O     | -1.34545 | 1.25381  | 4.65373  |
| O     | -0.52691 | 0.46407  | 7.21880  |
| O     | -0.98487 | 3.20637  | 6.63001  |
| Cl    | 1.72154  | 1.88455  | 5.41748  |
|       | Tc   | O    | O    | O    | S    | O    | F    | F    | F    |
|-------|------|------|------|------|------|------|------|------|------|
| [TcO₂]OTf |      |      |      |      |      |      |      |      |      |
| Tc    | -0.67160 | 1.68673 | 6.01049 |
| O     | -1.03537 | 0.64471 | 4.72503 |
| O     | -1.63253 | 1.22669 | 7.33046 |
| O     | -1.18072 | 3.23280 | 5.54974 |
| O     | 1.35812  | 1.71362 | 6.26980 |
| S     | 2.50778  | 2.30386 | 7.10756 |
| O     | 2.19237  | 3.60821 | 7.65861 |
| O     | 3.10033  | 1.29306 | 7.96216 |
| C     | 3.74081  | 2.59312 | 5.72369 |
| F     | 4.00355  | 1.44454 | 5.08292 |
| F     | 3.25803  | 3.48876 | 4.84961 |
| F     | 4.87641  | 3.06818 | 6.26192 |

|       | Tc    | O    | O    | O    | S    | O    | F    | F    | F    |
|-------|-------|------|------|------|------|------|------|------|------|
| Pertechnetate Anion [TcO₄]⁻ |      |      |      |      |      |      |      |      |      |
| Tc    | -1.01079 | 0.19607 | 0.01562 |
| O     | -0.41967 | 1.01414 | 1.43989 |
| O     | -0.42735 | 1.02374 | -1.40633 |
| O     | -2.74469 | 0.21863 | 0.02237 |
| O     | -0.41380 | -1.43299 | 0.00985 |

|       | Tc    | O    | O    | O    | S    | O    | F    | F    | F    |
|-------|-------|------|------|------|------|------|------|------|------|
| Technetate Anion [TcO₆]²⁻ |      |      |      |      |      |      |      |      |      |
| Tc    | -1.01301 | 0.20838 | 0.00559 |
| O     | -0.45469 | 1.12735 | 1.44066 |
| O     | -0.29575 | 1.03190 | -1.41614 |
| O     | -2.79874 | 0.14621 | 0.12047 |
| O     | -0.45410 | -1.49426 | -0.06918 |
Proposed reduction mechanism for the reduction

Scheme S 1 Proposed reduction mechanism for the reduction of the pertechnetyl cation TcO$_{3}^{3+}$ to the Tc(V) complex.

Heat energy calculation

In comparison to the work by Denden et al.$^{[22,23]}$ we would like to address the fact that the applied dose of irradiation may very well correspond to the energy applied by us during simple heating from freezing at -18 °C to +60 °C or from room temperature to 80 °C or 100 °C (average $\Delta T$ of ca. 60 – 80 K).

The applied dose corresponds to a heating of around 90K (see calculation below):

$$1 \text{ Gy} = 1 \text{ J/kg}$$

Applied dose $H$:

$$H = 360 \text{ kGy} = 360 \text{ kJ/kg} = 360 \text{ J/g}$$

Heat capacity $C_p$ of liquid water is more or less constant at $C_p = 4 \text{ J/(K*g)}$, therefore:

$$\Delta T = \frac{H}{C_p}$$

$$= \frac{360 \text{ J/g}}{4 \text{ J/(K*g)}}$$

$$= 360/4 \text{ K}$$

$$= 90 \text{ K}$$
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