

Supporting information

Silver Oxide Reduction Chemistry in an Alkane Environment

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SUPPORTING INFORMATION

Figure S1 details

The Ag₂O sample was analyzed using thermogravimetric analysis (TGA) under N₂, which indicated minor weight loss between 120 °C and 240 °C (Figure S1), likely due to decomposition of Ag₂CO₃ contamination. The onset of reduction was observed at 400 °C. A significant weight loss, approximately 6.95%, occurred between 350 °C and 410 °C, closely matching the theoretical value of 6.90% for the conversion of Ag₂O to metallic silver. This strong correlation confirms that the weight reduction corresponds to the decomposition of Ag₂O. Based on these results, the Ag₂O was oven-treated at 220 °C for 5 h.

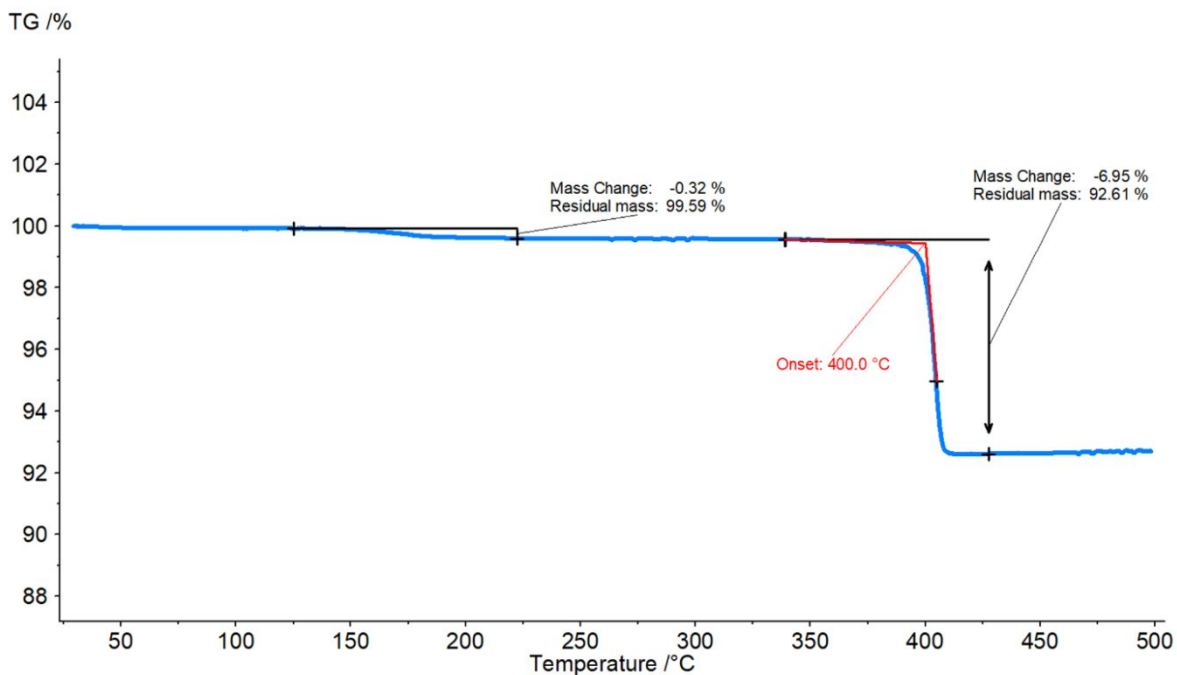


Figure S1. The TGA curve shows a gradual weight loss of pure Ag₂O as the temperature increases. Significant weight losses are observed at temperatures around 400 °C, leaving a residual mass of 92.61% (theoretical 93% for complete loss of oxygen). The heating rate is 10 °C/min and the test was run under 50 mL/min N₂ flow.

Figure S2 and S3 details

Samples of Ag_2O and pentadecane were heated at varying rates (Figure S2). Using the Ozawa-Flynn-Wall method, the activation energy was calculated to be 81.85 kJ/mol. Additionally, this method was employed to predict the conversion yields versus time at specific temperatures (Figure S3), providing the reaction kinetics.

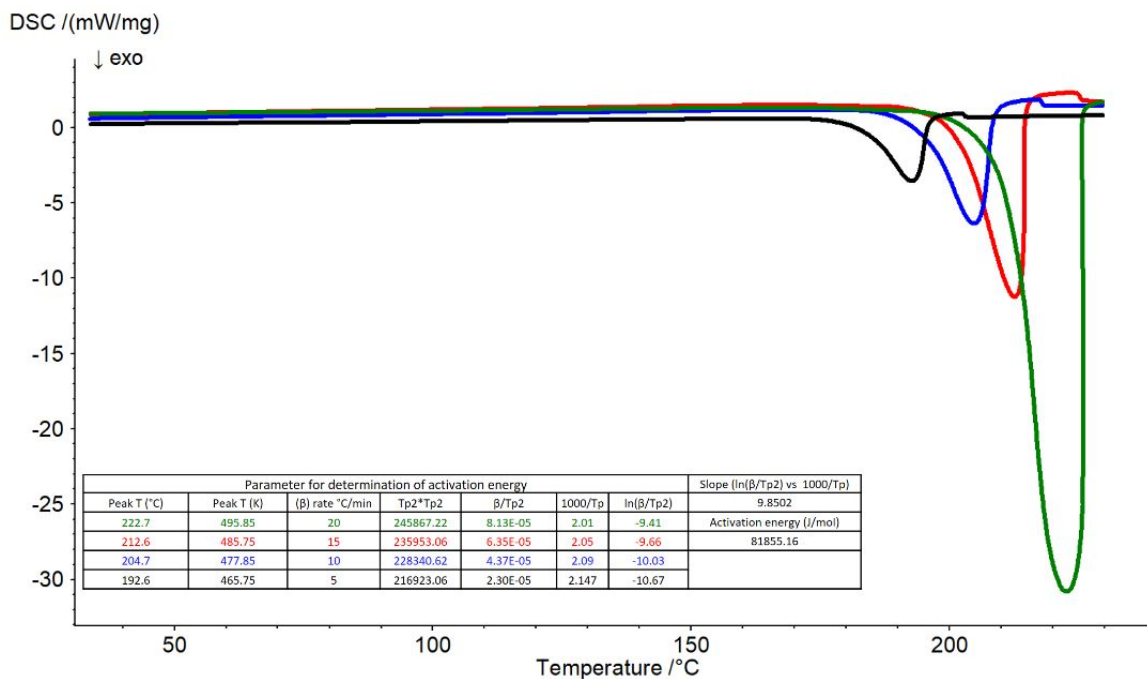


Figure S2. 5 mg of a 1:1 mole ratio of Ag_2O and pentadecane sample was analyzed at different heating rates of 5, 10, 15, and 20 °C/min (from 25 to 230 °C) under a N_2 flow of 50 mL/min. The table presents the parameters used for calculation of the activation energy.

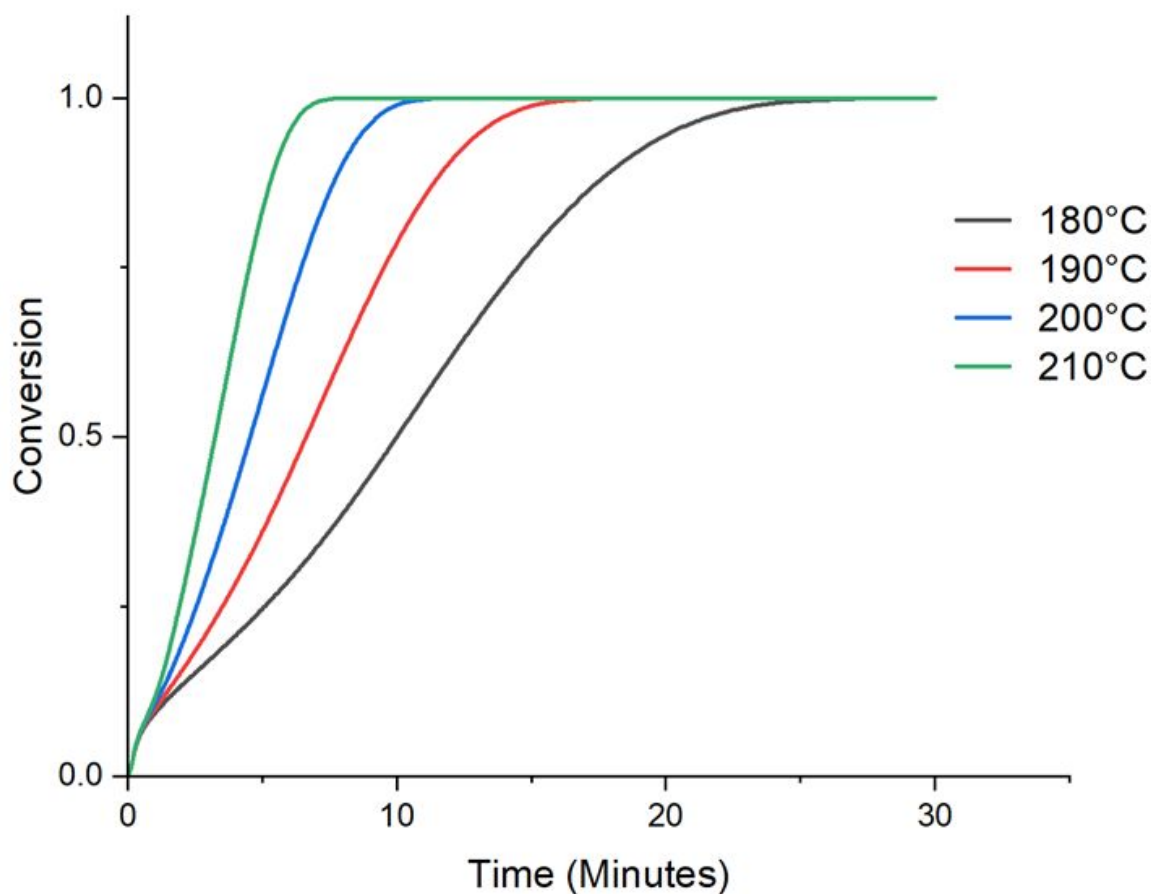


Figure S3. Predicted reaction time using the Ozawa-Flynn-Wall method.

S4 and S5 details

To capture the byproducts, the setup shown in Figure S4 was adopted. Furthermore, the setup used to quantify the amount of CO₂ is depicted in Figure S5. In this, an argon carrier flow (20 mL/min) was bubbled through the stirred reaction solution at a constant temperature of 145 °C, which is deliberately selected below the peak transition temperature (i.e., 193°C) to obtain a slower conversion and allowed for the acquisition of more data points for integration. The gas outlet was connected to a GC (Micro GC Fusion, Inficon, Switzerland) equipped with three columns: Rt-Molsieve, Rt-QBond, and Rt-U-Bond (Restek, USA). The gases then flowed at a set rate of 20

mL/min to the TCD detector, with each measurement interval taking 2 min. The TCD detector was calibrated to detect the gases of interest, and the amount of CO₂ produced was quantified by integrating the area under the curve of concentration versus time.

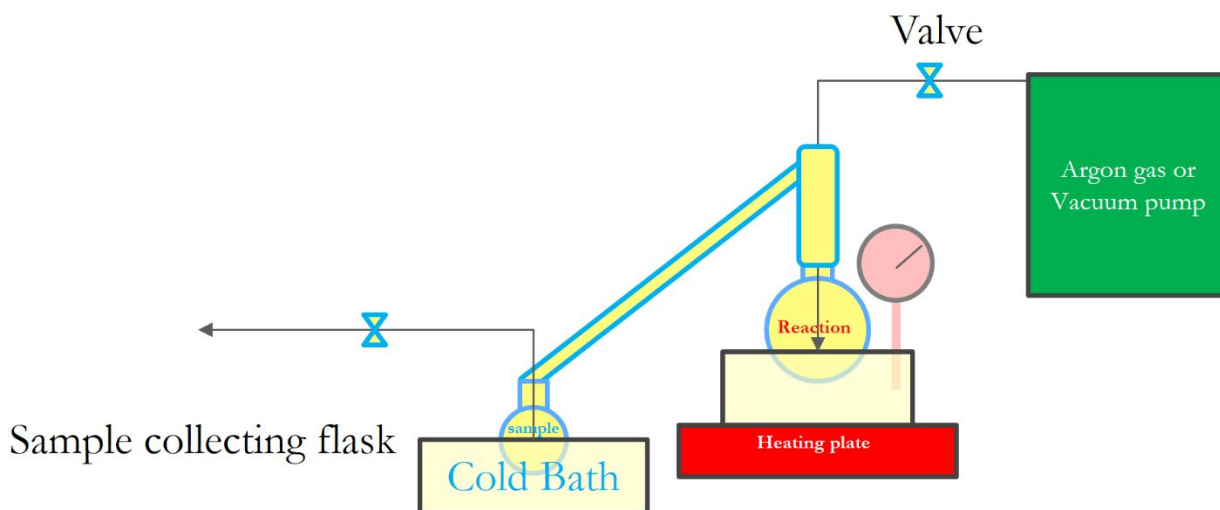


Figure S4. The setup used to collect reaction vapors. The reaction flask was kept at 180 °C for 30 min. the cold bath (acetone/ice slurry) was maintained at -78 °C. a constant flow of Ar.

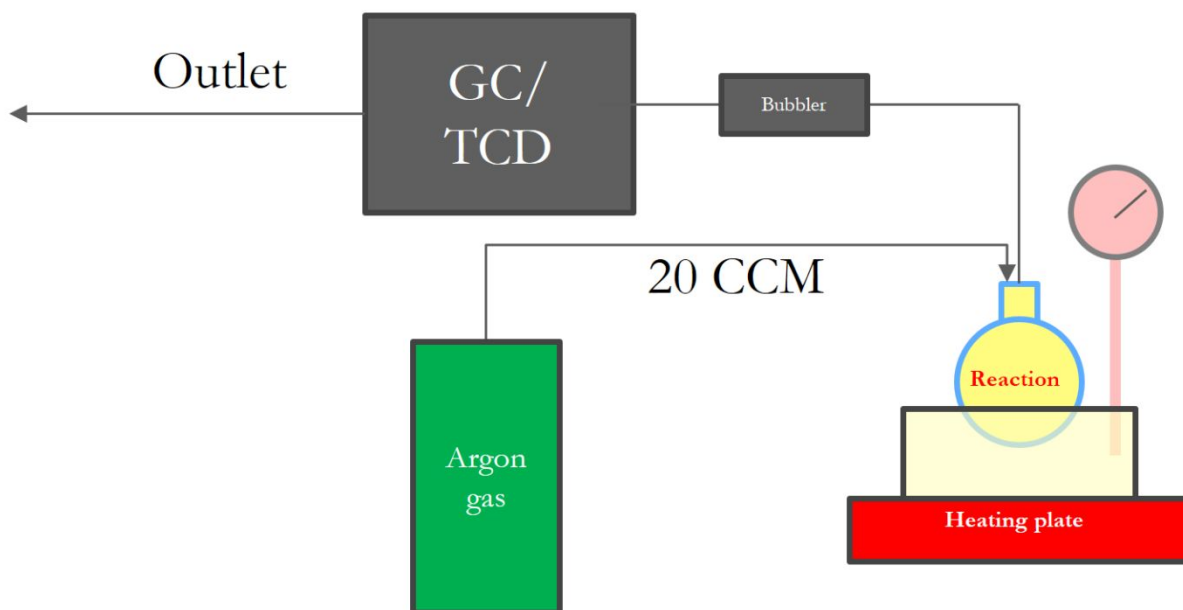


Figure S5. Schematic representation of the GC/TCD setup used for gas measurements, purge flow is set at 20 mL/min.

S6 details

From the GC-TCD measurements, an H₂O signal was observed (Figure S6). However, the setup was not designed to quantify the amount of H₂O.

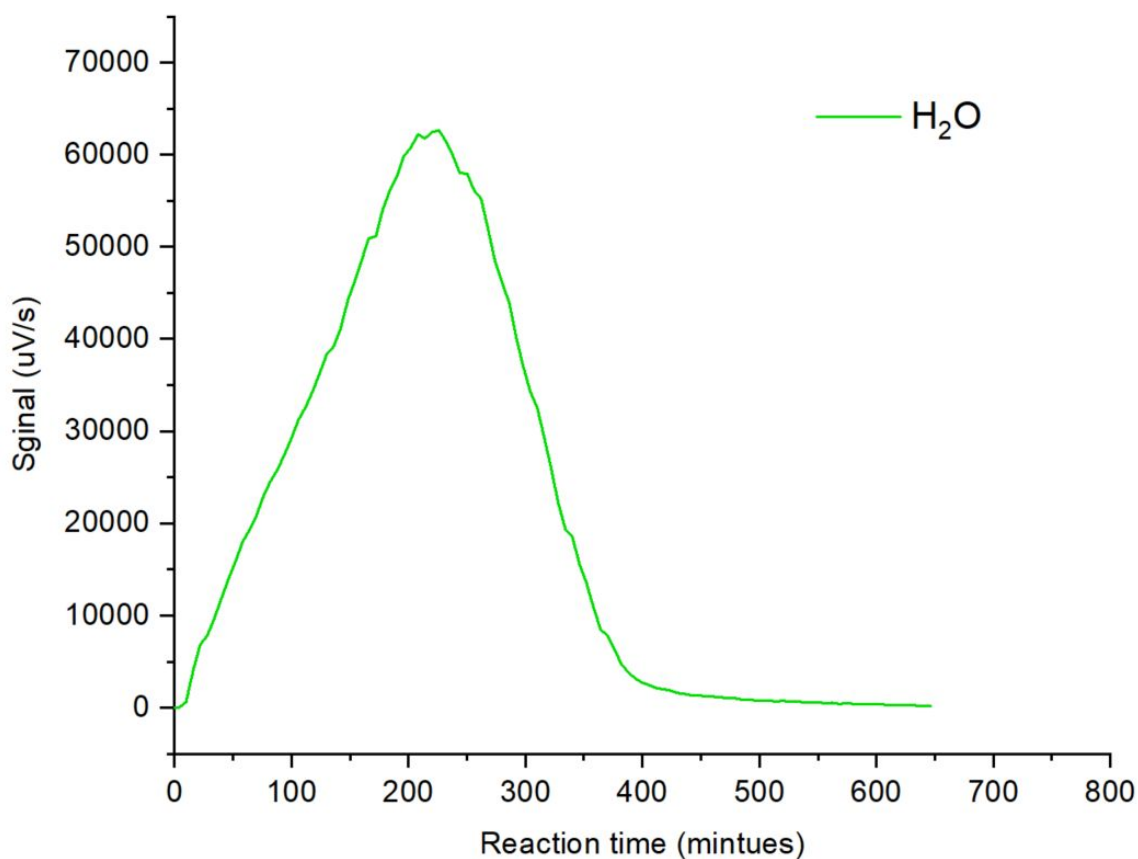


Figure S6. H₂O signal intensity versus time, observed in the reduction of Ag₂O in pentadecane at 145°C using GC-TCD (sampling rate: 2 min). Although the system was not calibrated for H₂O, signal strength directly relates to the concentration of H₂O in the gas stream.

S7 details

A 0.2 mL sample of pentadecane was placed in a 20 mL vial, prepared in open air. The vial was then sealed and placed in the GC-MS agitator. The agitator heated and agitated the vial at 70 °C for 120 min. After this period, a headspace sample was taken to measure the amount of CO₂ produced. The amount of CO₂ present in the air was also measured as a control. The results showed that no CO₂ was produced when pentadecane was heated in the presence of oxygen.

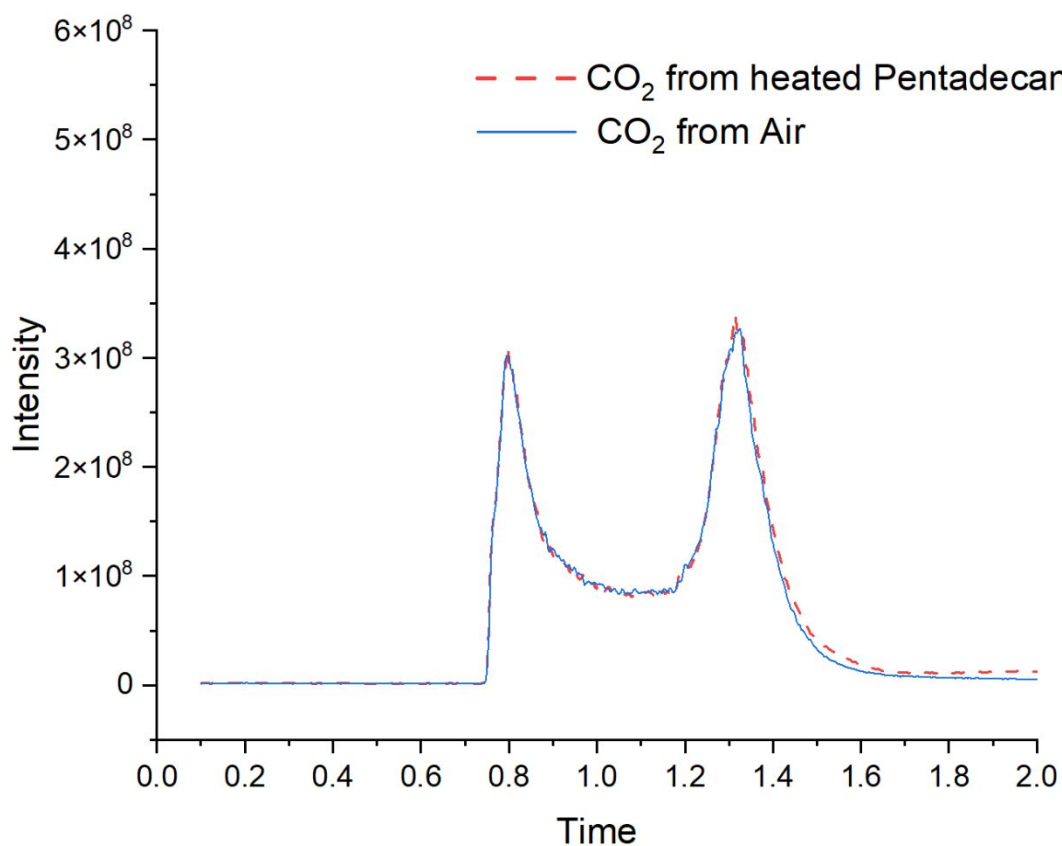


Figure S7. GC-MS measurements of two samples, highlighting the region associated with CO₂ (44 m/z). Pentadecane was heated at 70 °C in a vial containing air for 120 min (red dotted curve). Meanwhile, a vial containing only air was measured to display the background CO₂ present in the air (blue curve).

S8 details

The adduct formed by the reaction of Ag_2O with pentadecane was analyzed using GC-MS. The analysis revealed no detectable changes in the pentadecane (Figure S8).

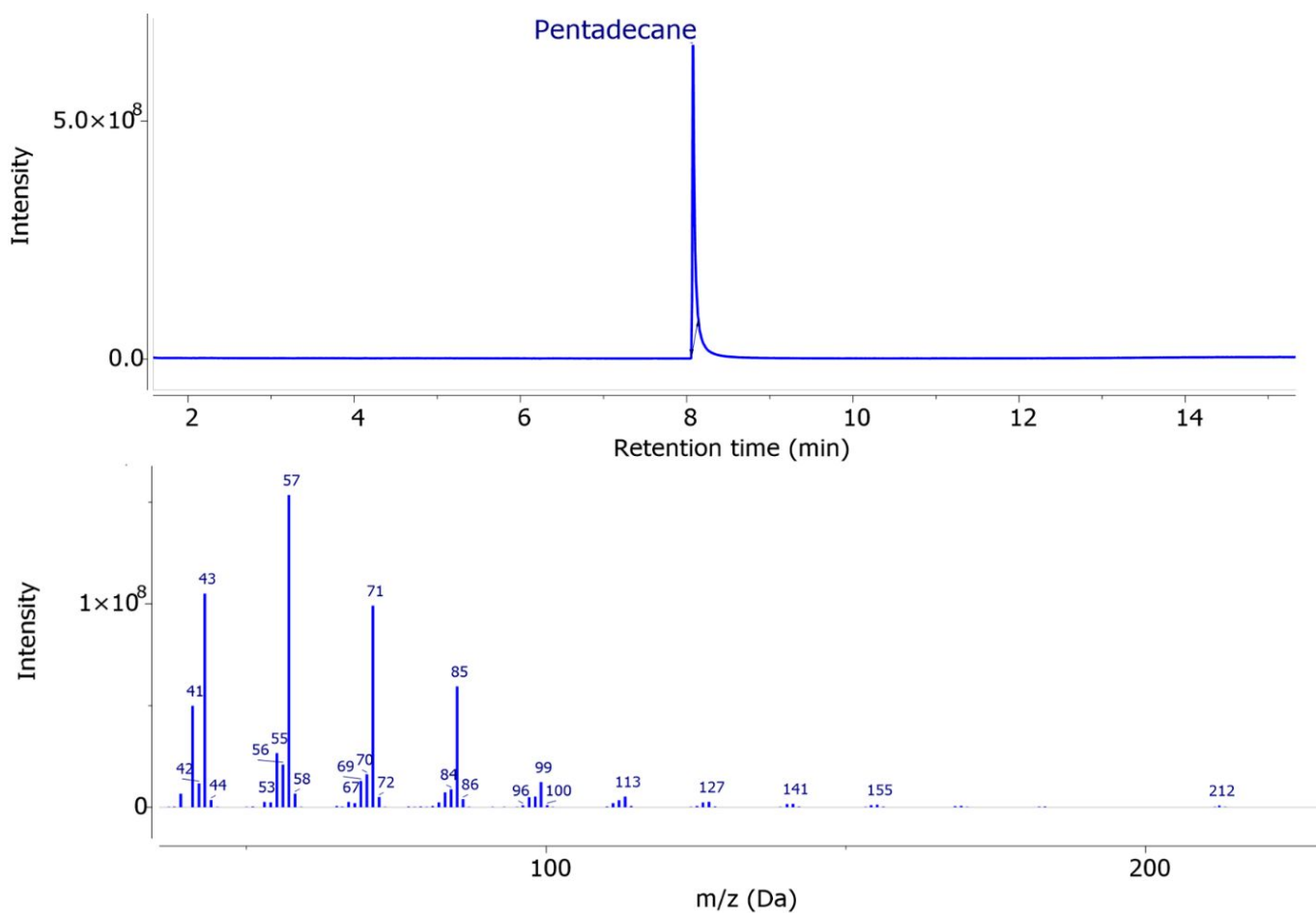


Figure S8. GC-MS analysis of the liquid adduct from the reaction between Ag_2O and pentadecane showed the presence of pentadecane only, with a retention time of 8 min and a molecular ion peak at 212 m/z .

S9 details

The mass spectra of a peak with 1.755 min retention time, from the experiment shown in Figure 10 as an example of a 1-alkene, specifically 1-hexene (Figure S9).

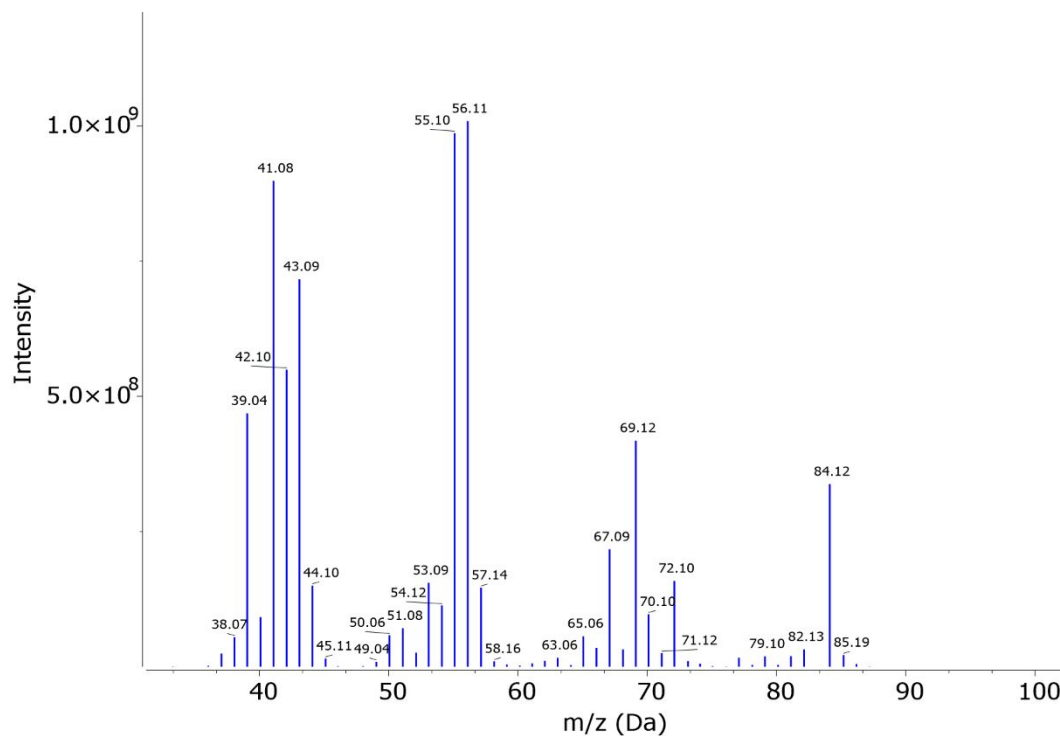


Figure S9. Exemplary mass spectrum of 1-hexene with a retention time of 1.755 min. The main peaks are observed at 84, 69, 56, and 41 m/z.

S10 details

Illustration of the formation of the DMPO adducts (DMPO-OOH, DMPOX and DMPO-PNO) is shown in S10.

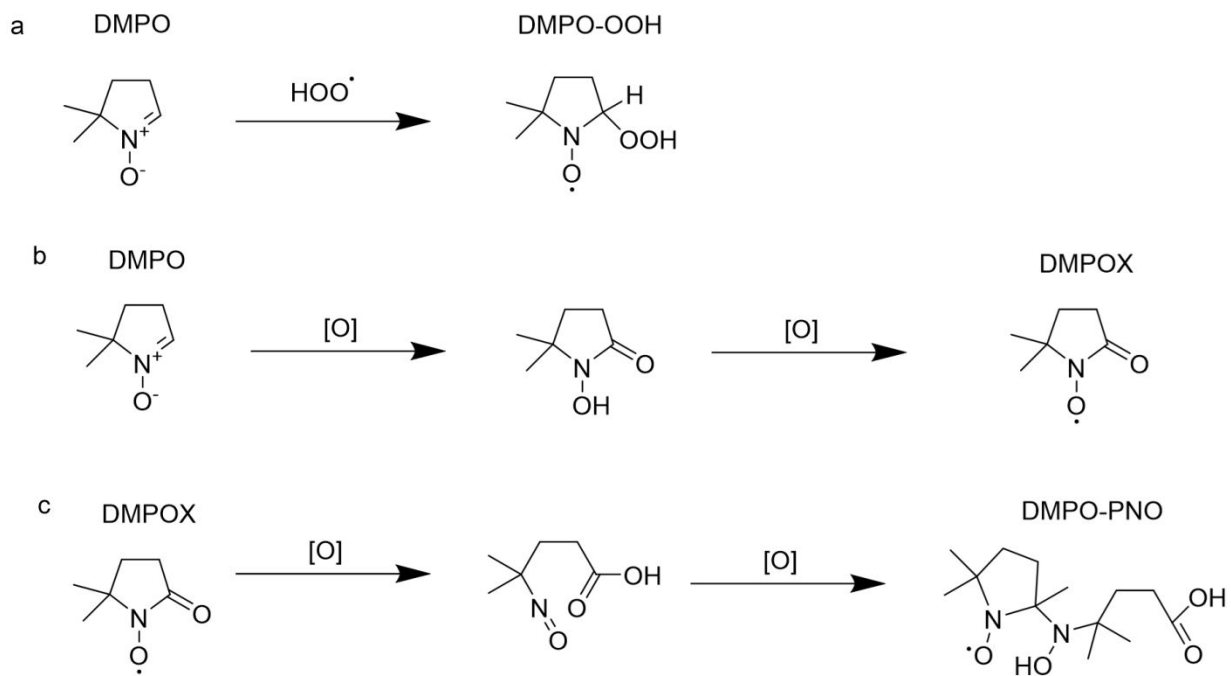


Figure S10. Formation mechanisms of (a) DMPO-OOH (analogous for other adducts, such as DMPO-OOR, DMPO-OH, DMPO-H etc.), (b) DMPOX and (c) DMPO-PNO.