

Thermogravimetric analysis of commercial tungsten molecular precursors for vapor phase deposition processes

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Table of contents

1.	Thermogravimetric analysis of $W(CO)_6$	S2-S4
2.	Thermogravimetric analysis of BTBMW.....	S5-S7
3.	Thermogravimetric analysis of (1,5-cod) $W(CO)_4$	S8-S10
4.	Thermogravimetric analysis of $WH_2(iPrCp)_2$	S11-S13
5.	Thermogravimetric analysis of $WH_2(Cp)_2$	S14-S16
6.	Thermogravimetric analysis of $[WCl_5]_2$	S17-S19
7.	Thermogravimetric analysis of WCl_6	S20-S22
8.	Thermogravimetric analysis of (mes) $W(CO)_3$	S23
9.	Comparison of TGA-derived values for all precursors.....	S24

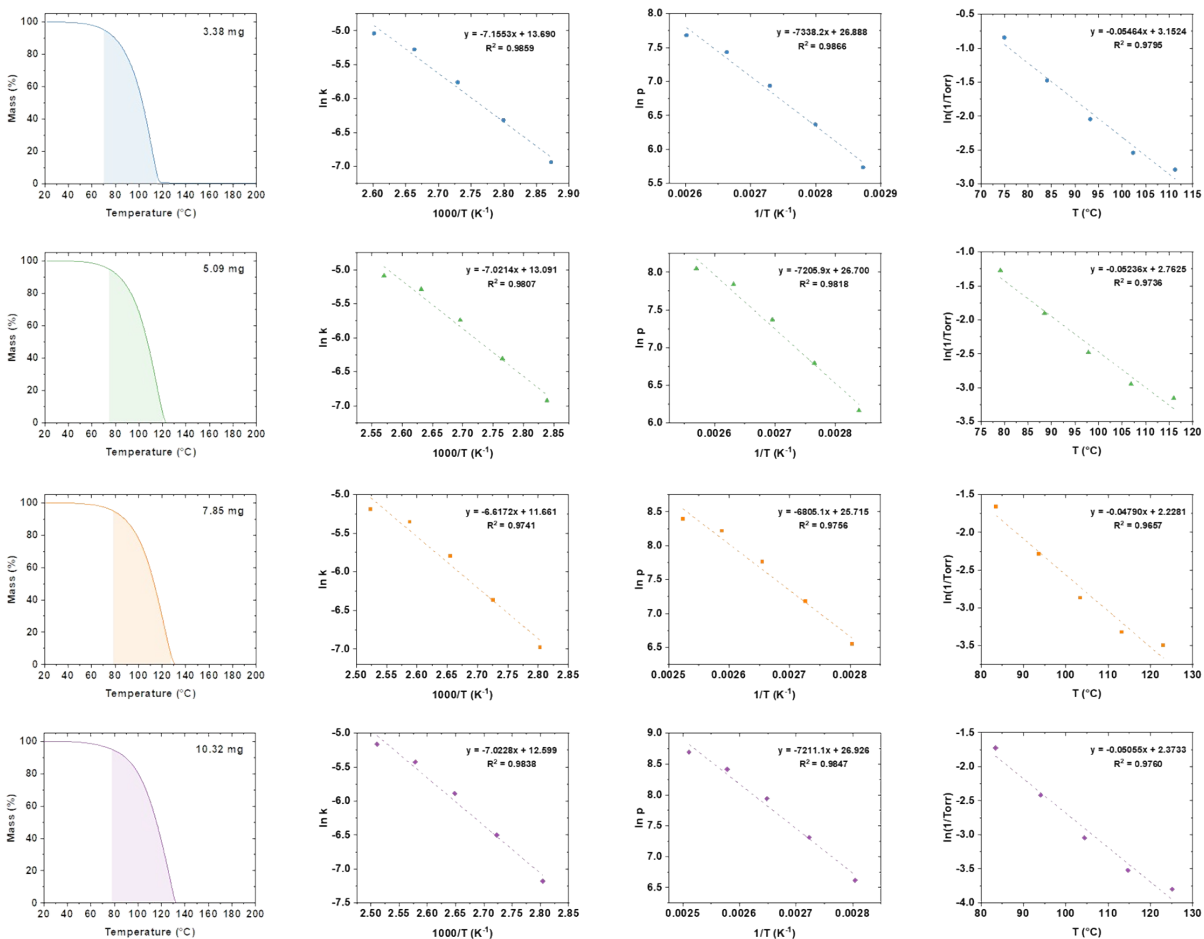


Figure S1. Thermogravimetric analysis of $W(CO)_6$. TG traces at constant temperature ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and nominally 3 (blue), 5 (green), 8 (orange), and 10 (purple) mg (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

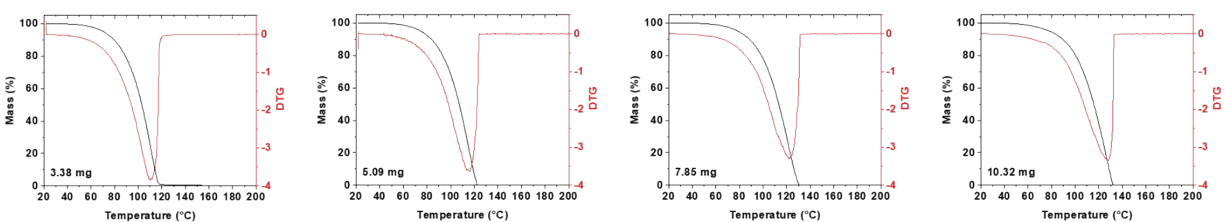


Figure S2. Thermogravimetric analysis of $W(CO)_6$. TG traces at constant temperature ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and variable masses with derivative thermogravimetric (DTG) traces shown.

Table S1. Measured and calculated thermophysical parameters from TGA of $W(CO)_6$ at constant temperature ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and variable masses.

Sample mass (mg)	3.38	5.09	7.85	10.32
Slope (Arrhenius plot)	-7.16	-7.02	-6.62	-7.02
R^2 (Arrhenius plot)	0.99	0.98	0.97	0.98
E_a (J/mol)	59.49	58.38	55.02	58.39
R^2 (Clausius-Clapeyron plot)	0.99	0.98	0.98	0.98
ΔH_{sub} (kJ/mol)	61.01	59.91	56.58	59.96
T at 1 Torr ($^\circ\text{C}$)	57.69	52.76	46.52	46.95
T window ($^\circ\text{C}$)	71-116	75-120	79-128	78-130
Residual mass (%)	0.00	0.00	0.00	0.00

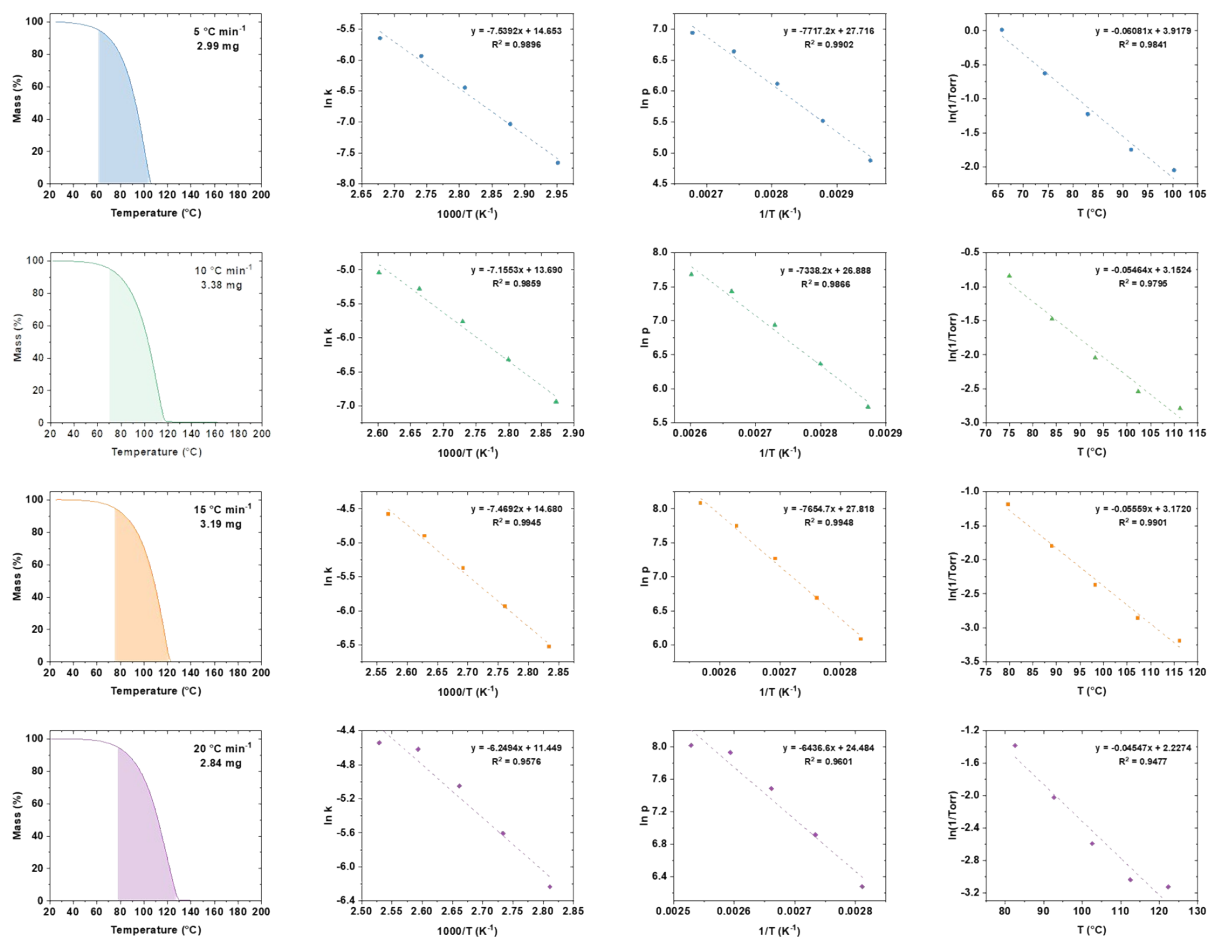


Figure S3. Thermogravimetric analysis of $W(CO)_6$. TG traces at nominally 3 mg and variable temperature ramp rates of 5 (blue), 10 (green), 15 (orange), and 20 (purple) $^\circ\text{C}/\text{min}$ (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(p/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

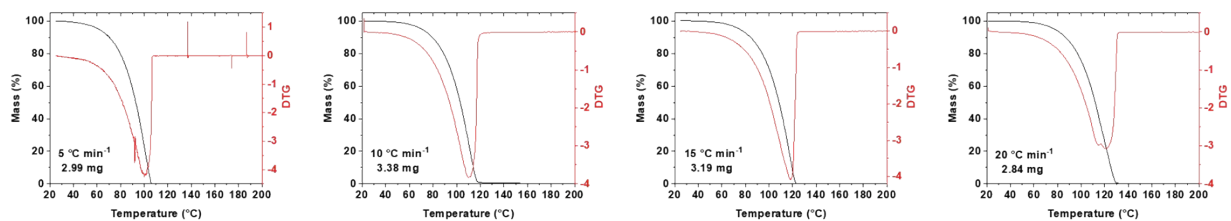


Figure S4. Thermogravimetric analysis of $W(CO)_6$. TG traces at nominally 3 mg and variable temperature ramp rates with derivative thermogravimetric (DTG) traces shown.

Table S2. Measured and calculated thermophysical parameters from TGA of $W(CO)_6$ at nominally 3 mg and variable temperature ramp rates.

Heating rate (°C/min)	5	10	15	20
Sample mass (mg)	2.99	3.38	3.19	2.84
Slope (Arrhenius plot)	-7.54	-7.16	-7.47	-6.25
R^2 (Arrhenius plot)	0.99	0.99	0.99	0.96
E_a (J/mol)	62.68	59.49	62.10	51.96
R^2 (Clausius-Clapeyron plot)	0.99	0.99	0.99	0.96
ΔH_{sub} (kJ/mol)	64.16	61.01	63.65	53.52
T at 1 Torr (°C)	64.43	57.69	57.06	48.99
T window (°C)	64-104	71-116	75-121	78-127
Residual mass (%)	0.00	0.00	0.00	0.08

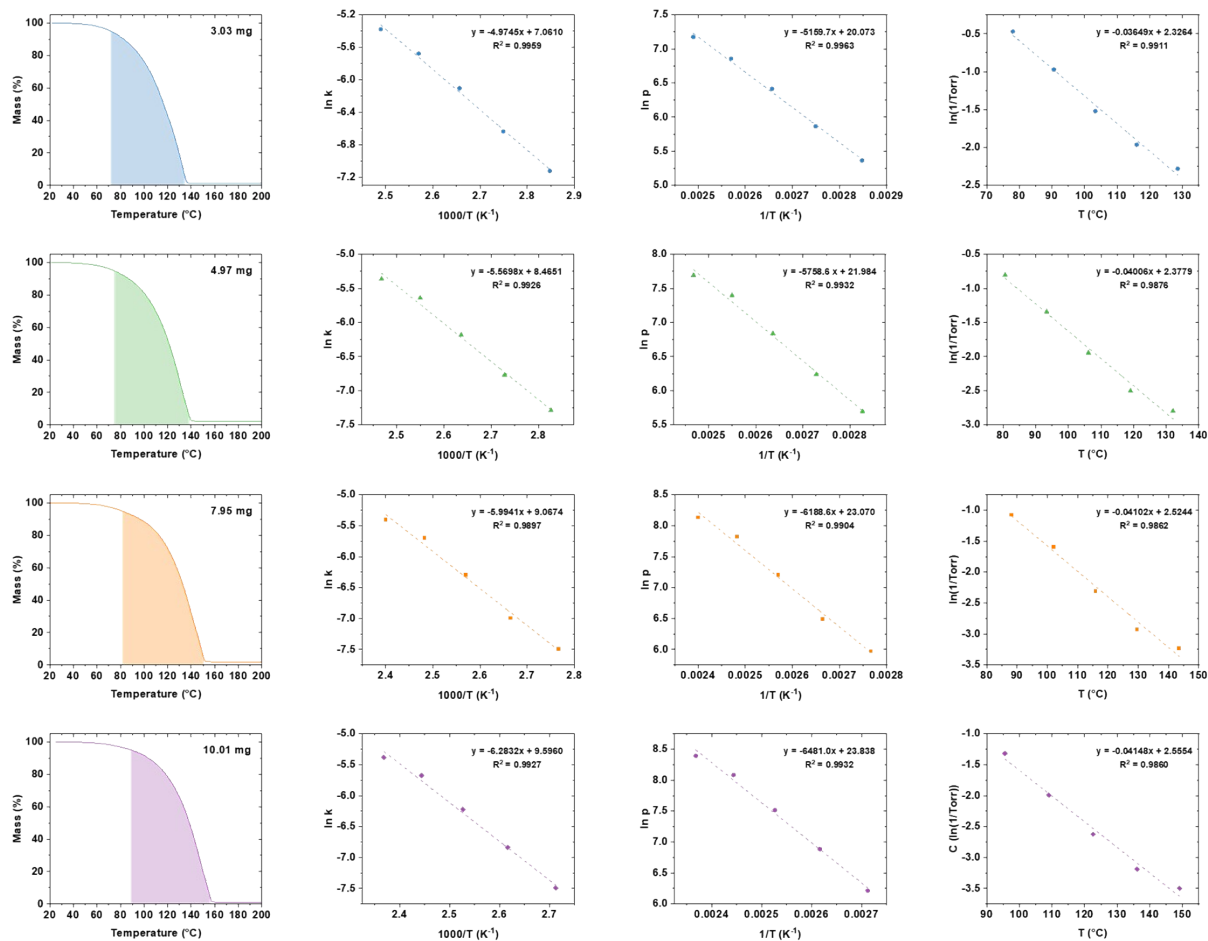


Figure S5. Thermogravimetric analysis of BTBMW. TG traces at constant temperature ramp rate of 10 °C/min and nominally 3 (blue), 5 (green), 8 (orange), and 10 (purple) mg (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

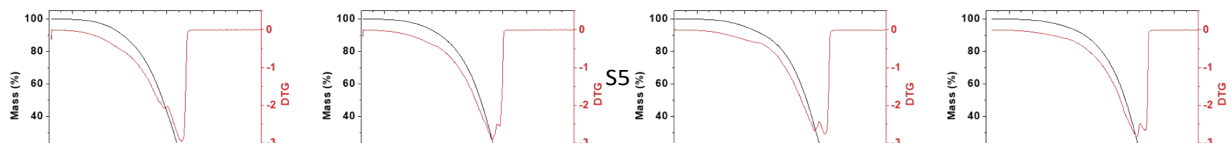


Figure S6. Thermogravimetric analysis of BTBMW. TG traces at constant temperature ramp rate of 10 °C/min and variable masses with derivative thermogravimetric (DTG) traces shown.

Table S3. Measured and calculated thermophysical parameters from TGA of BTBMW at constant temperature ramp rate of 10 °C/min and variable masses.

Sample mass (mg)	3.03	4.97	7.95	10.01
Slope (Arrhenius plot)	-4.97	-5.57	-5.99	-6.28
R ² (Arrhenius plot)	1.00	0.99	0.99	0.99
E _a (J/mol)	41.36	46.31	49.83	52.24
R ² (Clausius-Clapeyron plot)	1.00	0.99	0.99	0.99
ΔH _{sub} (kJ/mol)	42.90	47.88	51.46	53.89
T at 1 Torr (°C)	63.75	59.36	61.54	61.61
T window (°C)	72-135	74-139	81-150	89-156
Residual mass (%)	1.23	2.09	1.64	0.92

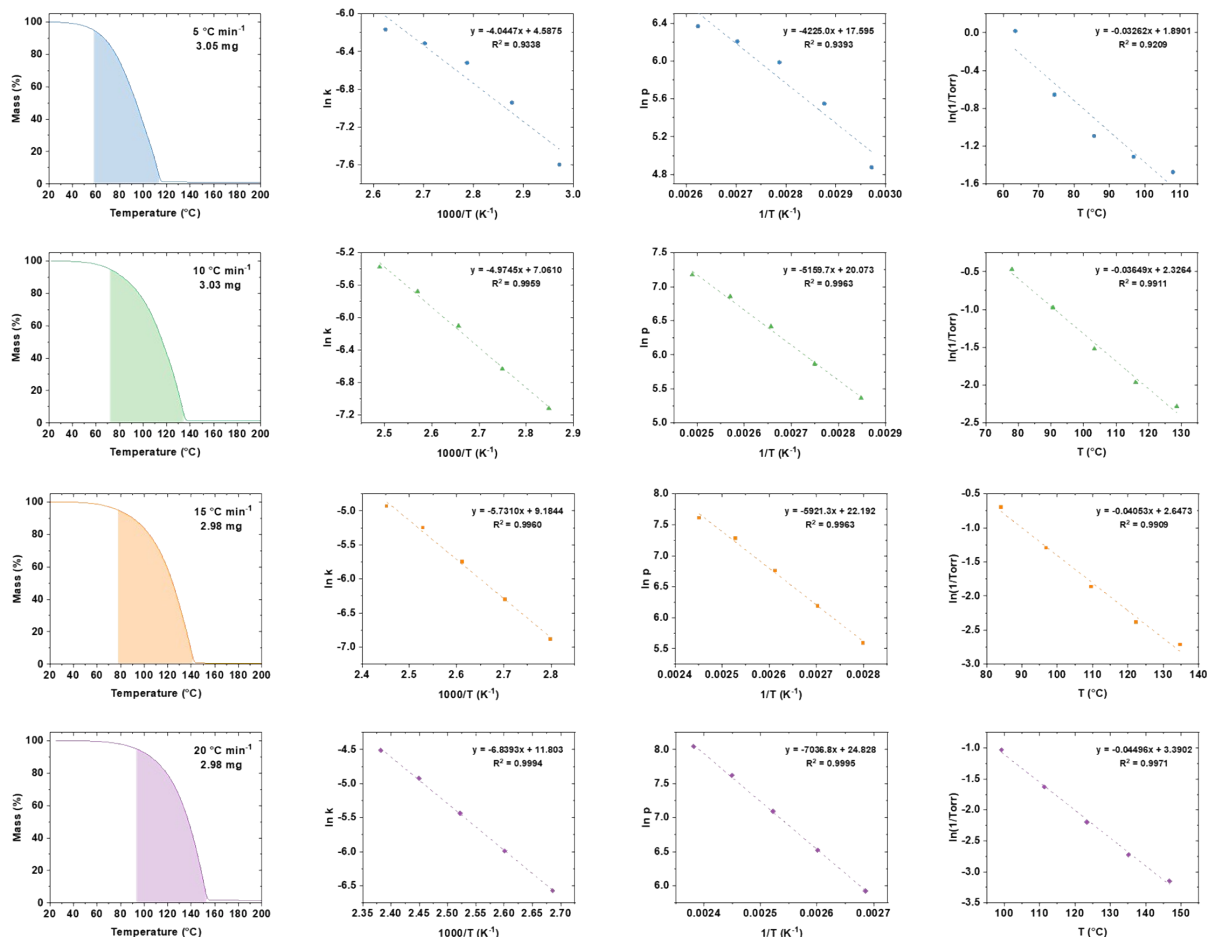


Figure S7. Thermogravimetric analysis of BTBMW. TG traces at nominally 3 mg and variable temperature ramp rates of 5 (blue), 10 (green), 15 (orange), and 20 (purple) °C/min (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of ln k vs 1000/T, ln p vs 1/T, and ln(1/Torr) vs T used to derive E_a, ΔH_{sub}, and T at 1 Torr, respectively. Equation of line of best fit and R² value displayed on each of these plots.

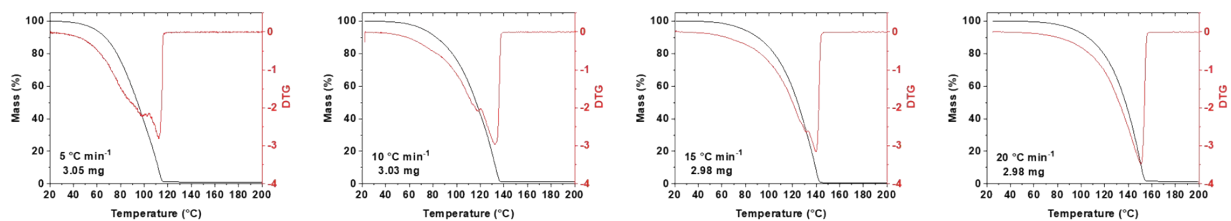


Figure S8. Thermogravimetric analysis of BTBMW. TG traces at nominally 3 mg and variable temperature ramp rates with derivative thermogravimetric (DTG) traces shown.

Table S4. Measured and calculated thermophysical parameters from TGA of BTBMW at nominally 3 mg and variable temperature ramp rates.

Heating rate (°C /min)	5	10	15	20
Sample mass (mg)	3.05	3.03	2.98	2.98
Slope (Arrhenius plot)	-4.04	-4.97	-5.73	-6.84
R ² (Arrhenius plot)	0.93	1.00	1.00	1.00
E _a (J/mol)	33.63	41.36	47.65	56.86
R ² (Clausius-Clapeyron plot)	0.94	1.00	1.00	1.00
ΔH _{sub} (kJ/mol)	35.13	42.90	49.23	58.51
T at 1 Torr (°C)	57.94	63.75	65.32	74.27
T window (°C)	58-114	72-135	78-141	93-153
Residual mass (%)	0.86	1.23	0.58	1.49

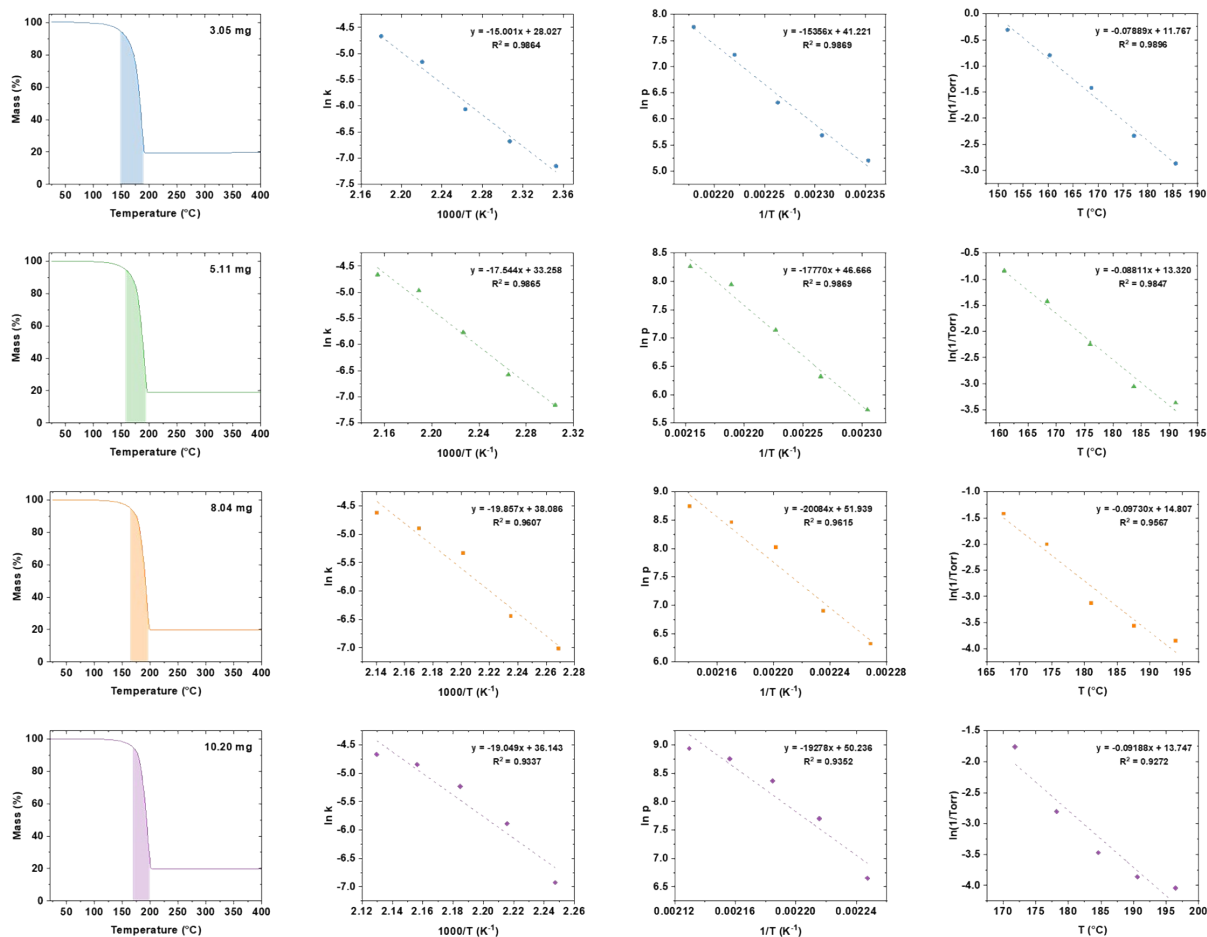


Figure S9. Thermogravimetric analysis of $(1,5\text{-cod})\text{W}(\text{CO})_4$. TG traces at constant temperature ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and nominally 3 (blue), 5 (green), 8 (orange), and 10 (purple) mg (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

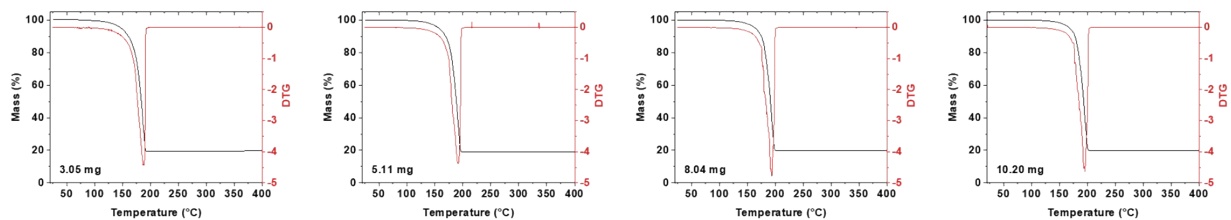


Figure S10. Thermogravimetric analysis of $(1,5\text{-cod})\text{W}(\text{CO})_4$. TG traces at constant temperature ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and variable masses with derivative thermogravimetric (DTG) traces shown.

Table S5. Measured and calculated thermophysical parameters from TGA of (1,5-cod)W(CO)₄ at constant temperature ramp rate of 10 °C/min and variable masses.

Sample mass (mg)	3.05	5.11	8.04	10.20
Slope (Arrhenius plot)	-15.00	-17.54	-19.86	-19.05
R ² (Arrhenius plot)	0.99	0.99	0.96	0.93
E _a (J/mol)	124.72	145.86	165.09	158.37
R ² (Clausius-Clapeyron plot)	0.99	0.99	0.96	0.94
ΔH _{sub} (kJ/mol)	127.68	147.75	166.99	160.29
T at 1 Torr (°C)	149.16	151.17	152.18	149.62
T window (°C)	148-190	157-195	164-197	169-199
Residual mass (%)	19.67	18.97	19.65	19.75

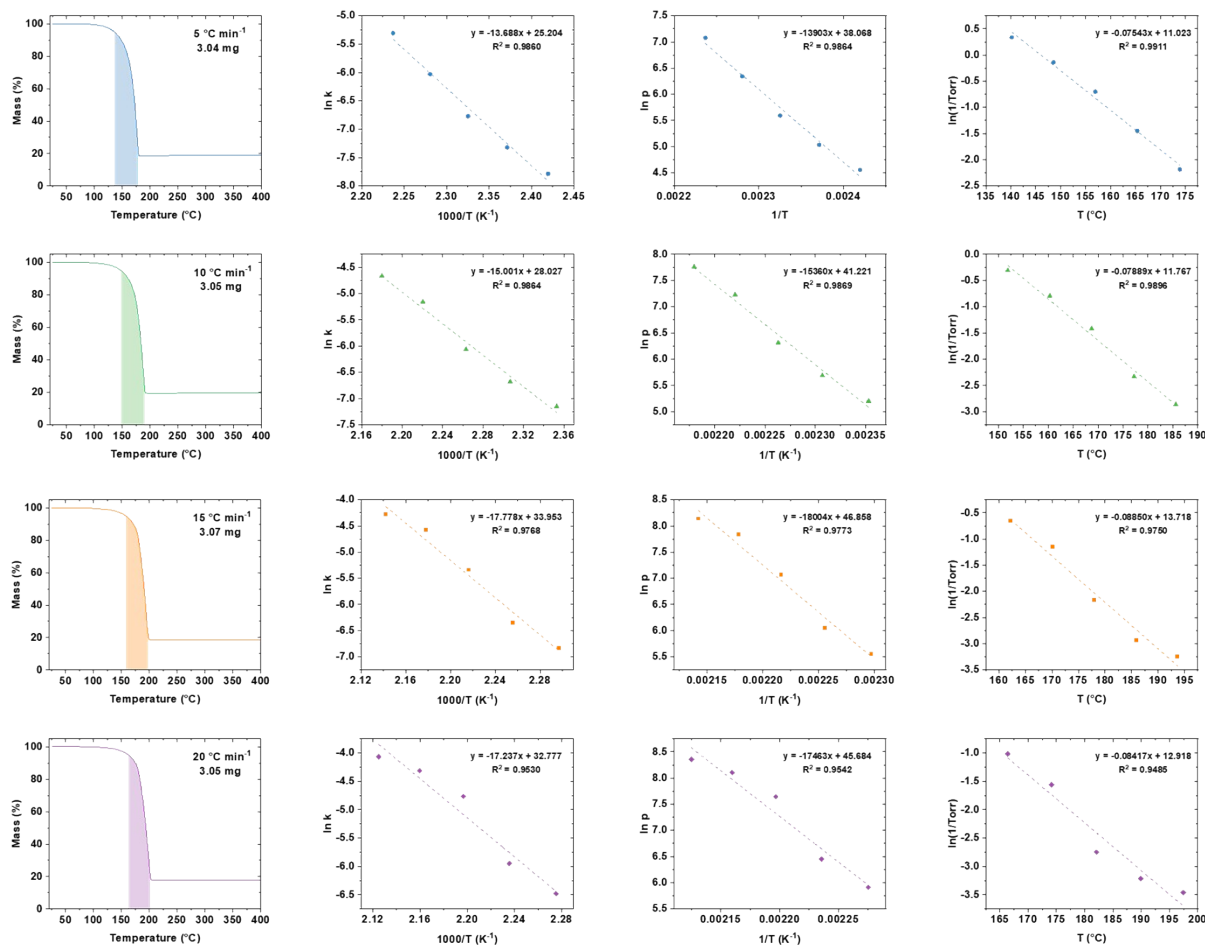


Figure S11. Thermogravimetric analysis of (1,5-cod)W(CO)₄. TG traces at nominally 3 mg and variable temperature ramp rates of 5 (blue), 10 (green), 15 (orange), and 20 (purple) °C/min (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

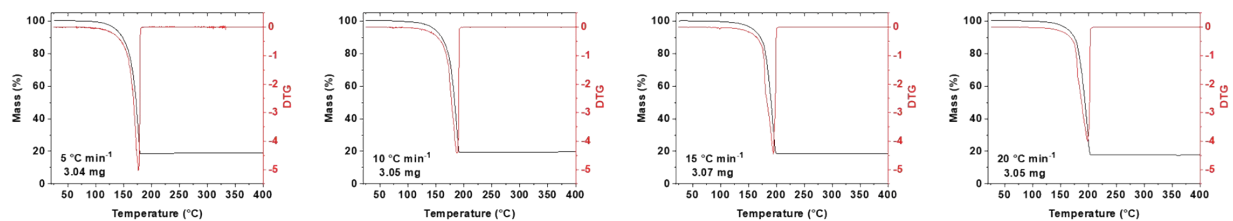


Figure S12. Thermogravimetric analysis of (1,5-cod)W(CO)₄. TG TG traces at nominally 3 mg and variable temperature ramp rates with derivative thermogravimetric (DTG) traces shown.

Table S6. Measured and calculated thermophysical parameters from TGA of (1,5-cod)W(CO)₄ at nominally 3 mg and variable temperature ramp rates.

Heating rate (°C/min)	5	10	15	20
Sample mass (mg)	3.04	3.05	3.07	3.05
Slope (Arrhenius plot)	-13.69	-15.00	-17.78	-17.24
R ² (Arrhenius plot)	0.99	0.99	0.98	0.95
E _a (J/mol)	113.80	124.72	147.81	143.31
R ² (Clausius-Clapeyron plot)	0.99	0.99	0.98	0.95
ΔH _{sub} (kJ/mol)	115.60	127.71	149.69	145.20
T at 1 Torr (°C)	146.14	149.16	155.01	153.48
T window (°C)	136-178	148-190	158-197	163-201
Residual mass (%)	19.10	19.67	18.68	17.65

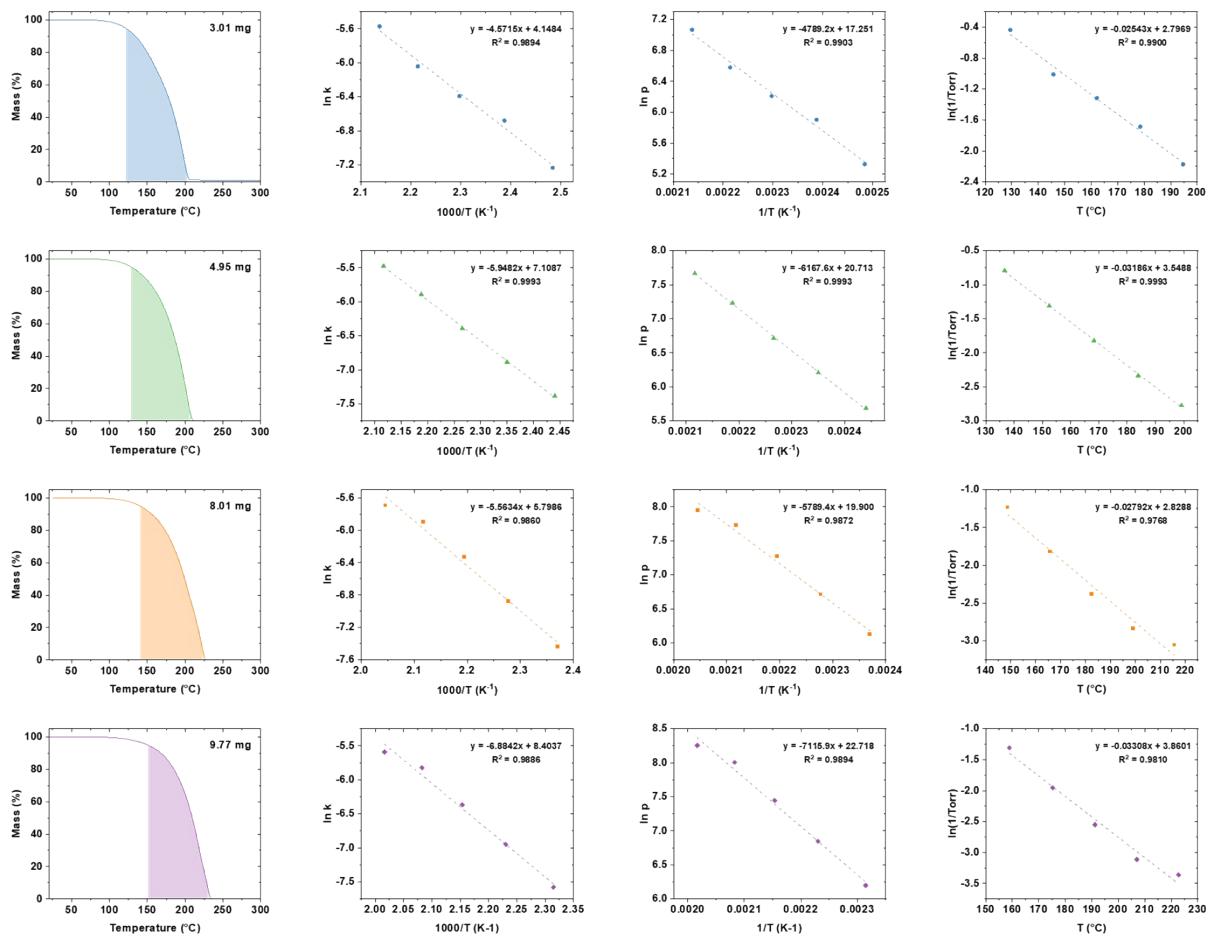


Figure S13. Thermogravimetric analysis of $\text{WH}_2(\text{iPrCp})_2$. TG traces at constant temperature ramp rate of $10^\circ\text{C}/\text{min}$ and nominally 3 (blue), 5 (green), 8 (orange), and 10 (purple) mg (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

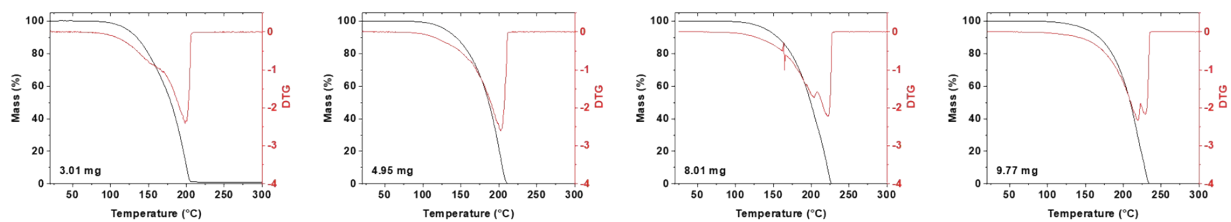


Figure S14. Thermogravimetric analysis of $\text{WH}_2(\text{iPrCp})_2$. Thermogravimetric analysis of $\text{W}(\text{CO})_6$. TG traces at constant temperature ramp rate of $10^\circ\text{C}/\text{min}$ and variable masses with derivative thermogravimetric (DTG) traces shown.

Table S7. Measured and calculated thermophysical parameters from TGA of $\text{WH}_2(\text{iPrCp})_2$ at constant temperature ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and variable masses.

Sample mass (mg)	3.01	4.95	8.01	9.77
Slope (Arrhenius plot)	-4.57	-5.95	-5.56	-6.88
R^2 (Arrhenius plot)	0.99	1.00	0.99	0.99
E_a (J/mol)	38.01	49.45	46.25	57.24
R^2 (Clausius-Clapeyron plot)	0.99	1.00	0.99	0.99
ΔH_{sub} (kJ/mol)	39.82	51.28	48.14	59.17
T at 1 Torr ($^\circ\text{C}$)	109.98	111.39	101.32	116.69
T window ($^\circ\text{C}$)	121-203	129-207	140-224	151-231
Residual mass (%)	0.80	0.13	0.30	0.08

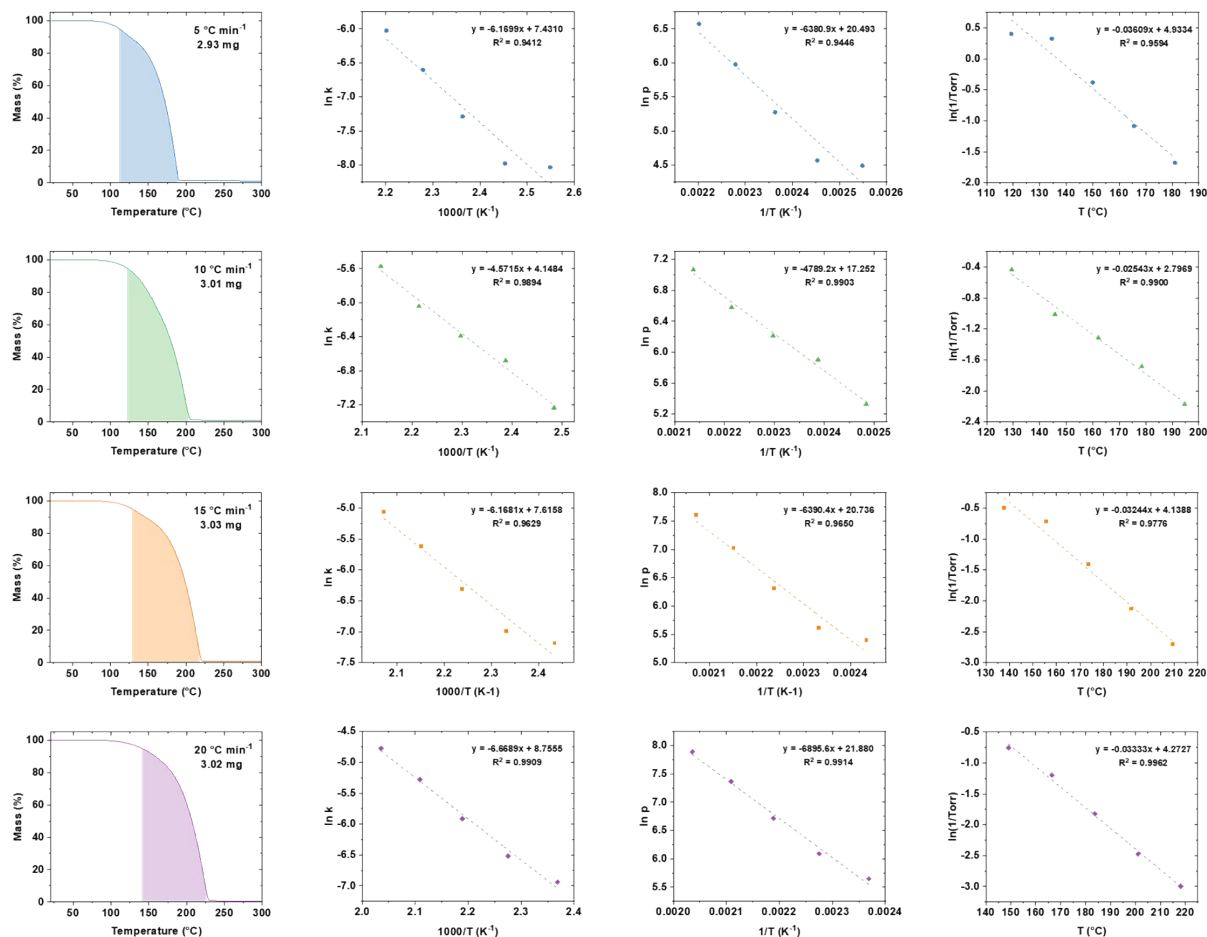


Figure S15. Thermogravimetric analysis of $\text{WH}_2(\text{iPrCp})_2$. TG traces at nominally 3 mg and variable temperature ramp rates of 5 (blue), 10 (green), 15 (orange), and 20 (purple) $^\circ\text{C}/\text{min}$ (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

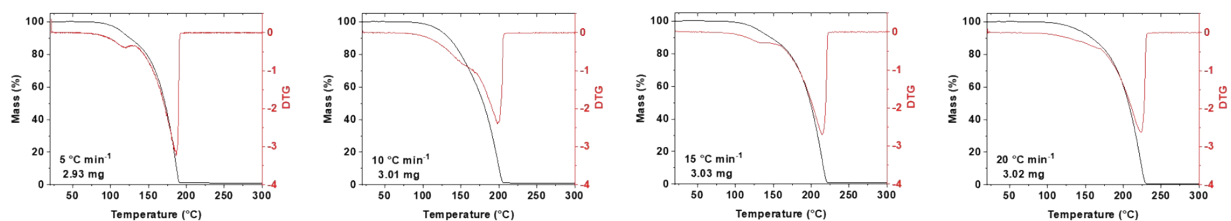


Figure S16. Thermogravimetric analysis of $\text{WH}_2(\text{iPrCp})_2$. TG traces at nominally 3 mg and variable temperature ramp rates with derivative thermogravimetric (DTG) traces shown.

Table S8. Measured and calculated thermophysical parameters from TGA of $\text{WH}_2(\text{iPrCp})_2$ at nominally 3 mg and variable temperature ramp rates.

Heating rate (°C/min)	5	10	15	20
Sample mass (mg)	2.93	3.01	3.03	3.02
Slope (Arrhenius plot)	-6.17	-4.57	-6.17	-6.67
R^2 (Arrhenius plot)	0.94	0.99	0.96	0.99
E_a (J/mol)	51.30	38.01	51.28	55.45
R^2 (Clausius-Clapeyron plot)	0.94	0.99	0.97	0.99
ΔH_{sub} (kJ/mol)	53.05	39.82	53.13	57.33
T at 1 Torr (°C)	136.70	109.98	127.58	128.19
T window (°C)	112-189	121-203	129-218	141-227
Residual mass (%)	1.07	0.80	0.85	0.66

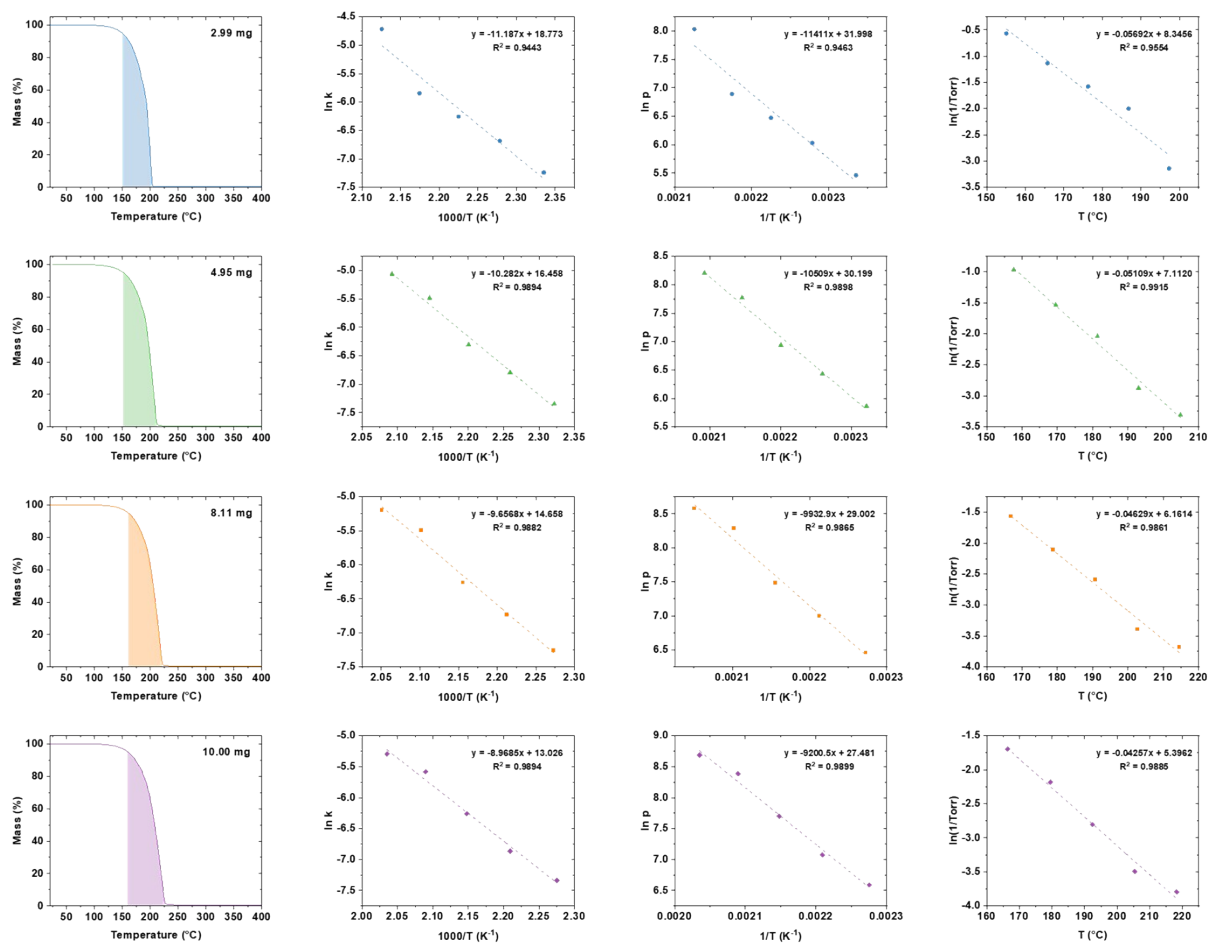


Figure S17. Thermogravimetric analysis of $\text{WH}_2(\text{Cp})_2$. TG traces at constant temperature ramp rate of $10^\circ\text{C}/\text{min}$ and nominally 3 (blue), 5 (green), 8 (orange), and 10 (purple) mg (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

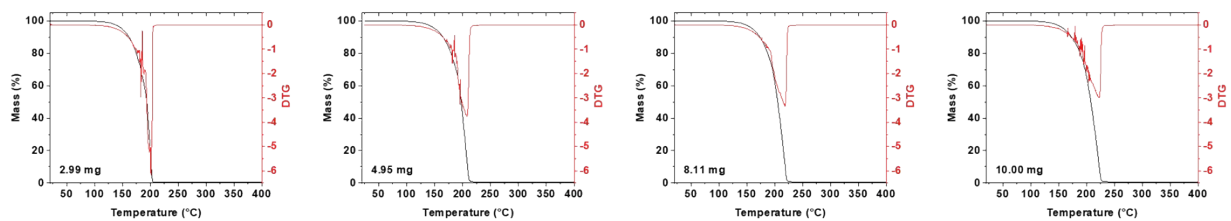


Figure S18. Thermogravimetric analysis of $\text{WH}_2(\text{Cp})_2$. TG traces at constant temperature ramp rate of $10^\circ\text{C}/\text{min}$ and variable masses with derivative thermogravimetric (DTG) traces shown.

Table S9. Measured and calculated thermophysical parameters from TGA of $\text{WH}_2(\text{Cp})_2$ at constant temperature ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and variable masses.

Sample mass (mg)	2.99	4.95	8.11	10.00
Slope (Arrhenius plot)	-11.19	-10.28	-9.66	-8.97
R^2 (Arrhenius plot)	0.94	0.99	0.99	0.99
E_a (J/mol)	93.01	85.48	80.29	74.56
R^2 (Clausius-Clapeyron plot)	0.95	0.99	0.99	0.99
ΔH_{sub} (kJ/mol)	94.88	87.38	82.59	76.50
T at 1 Torr ($^\circ\text{C}$)	146.62	139.21	133.10	126.76
T window ($^\circ\text{C}$)	150-203	152-210	161-220	160-225
Residual mass (%)	0.58	0.49	0.59	0.57

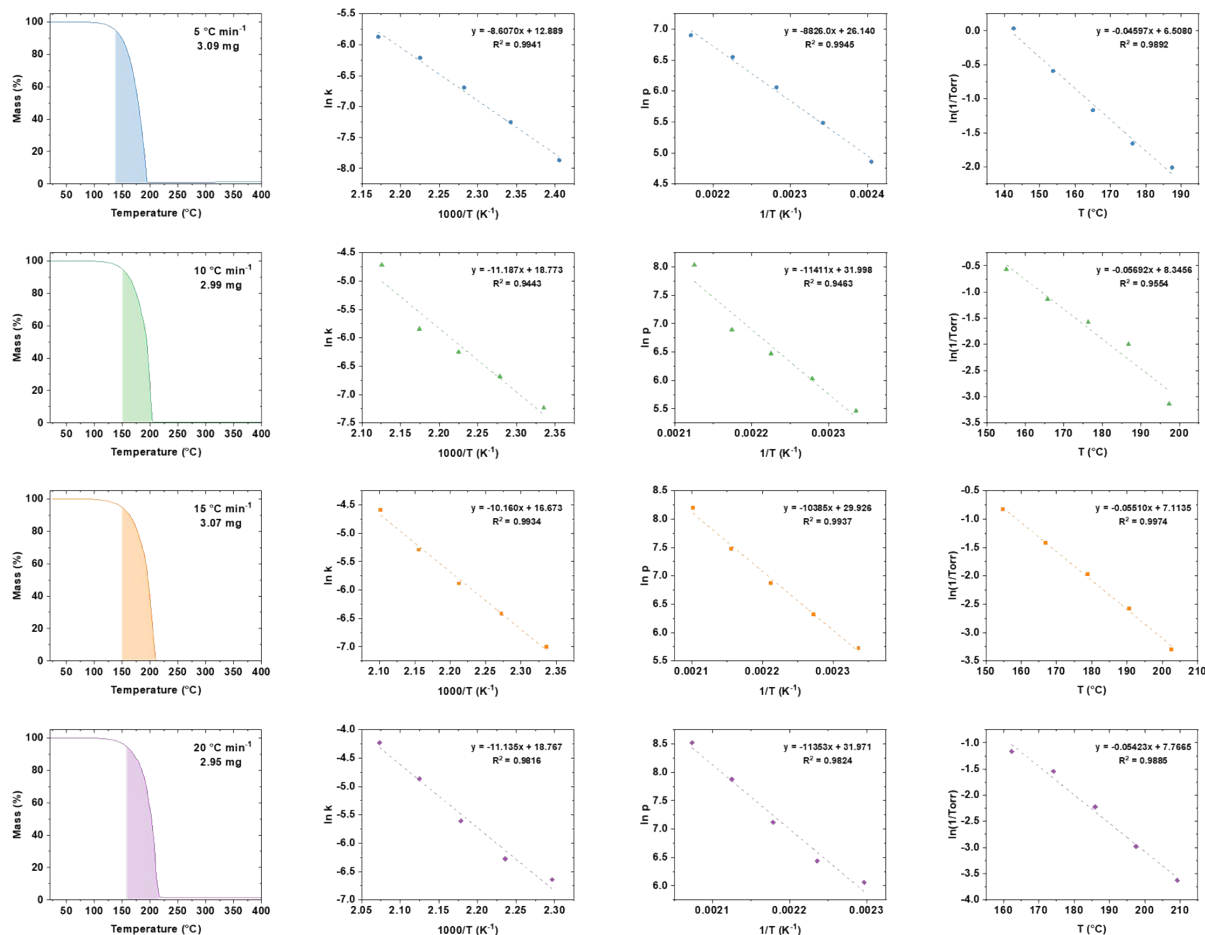


Figure S19. Thermogravimetric analysis of $\text{WH}_2(\text{Cp})_2$. TG traces at nominally 3 mg and variable temperature ramp rates of 5 (blue), 10 (green), 15 (orange), and 20 (purple) $^\circ\text{C}/\text{min}$ (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

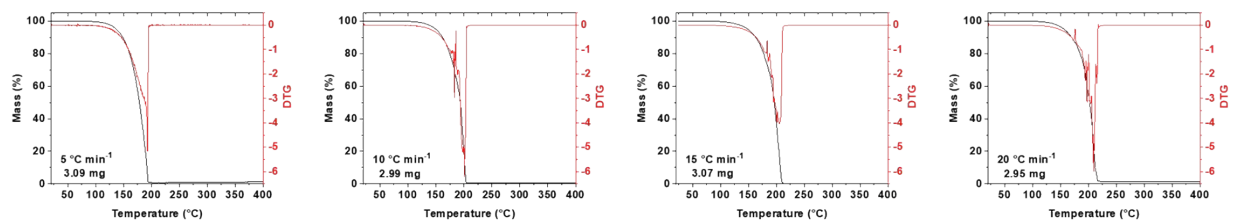


Figure S20. Thermogravimetric analysis of $\text{WH}_2(\text{Cp})_2$. TG traces at nominally 3 mg and variable temperature ramp rates with derivative thermogravimetric (DTG) traces shown.

Table S10. Measured and calculated thermophysical parameters from TGA of $\text{WH}_2(\text{Cp})_2$ at nominally 3 mg and variable temperature ramp rates.

Heating rate ($^{\circ}\text{C}/\text{min}$)	5	10	15	20
Sample mass (mg)	3.09	2.99	3.07	2.95
Slope (Arrhenius plot)	-8.61	-11.19	-10.16	-11.14
R^2 (Arrhenius plot)	0.99	0.94	0.99	0.98
E_a (J/mol)	71.56	93.01	84.47	92.58
R^2 (Clausius-Clapeyron plot)	0.99	0.95	0.99	0.98
ΔH_{sub} (kJ/mol)	73.38	94.88	86.35	94.39
T at 1 Torr ($^{\circ}\text{C}$)	141.57	146.62	129.10	143.21
T window ($^{\circ}\text{C}$)	137-193	150-203	149-208	157-215
Residual mass (%)	1.25	0.58	0.00	1.43

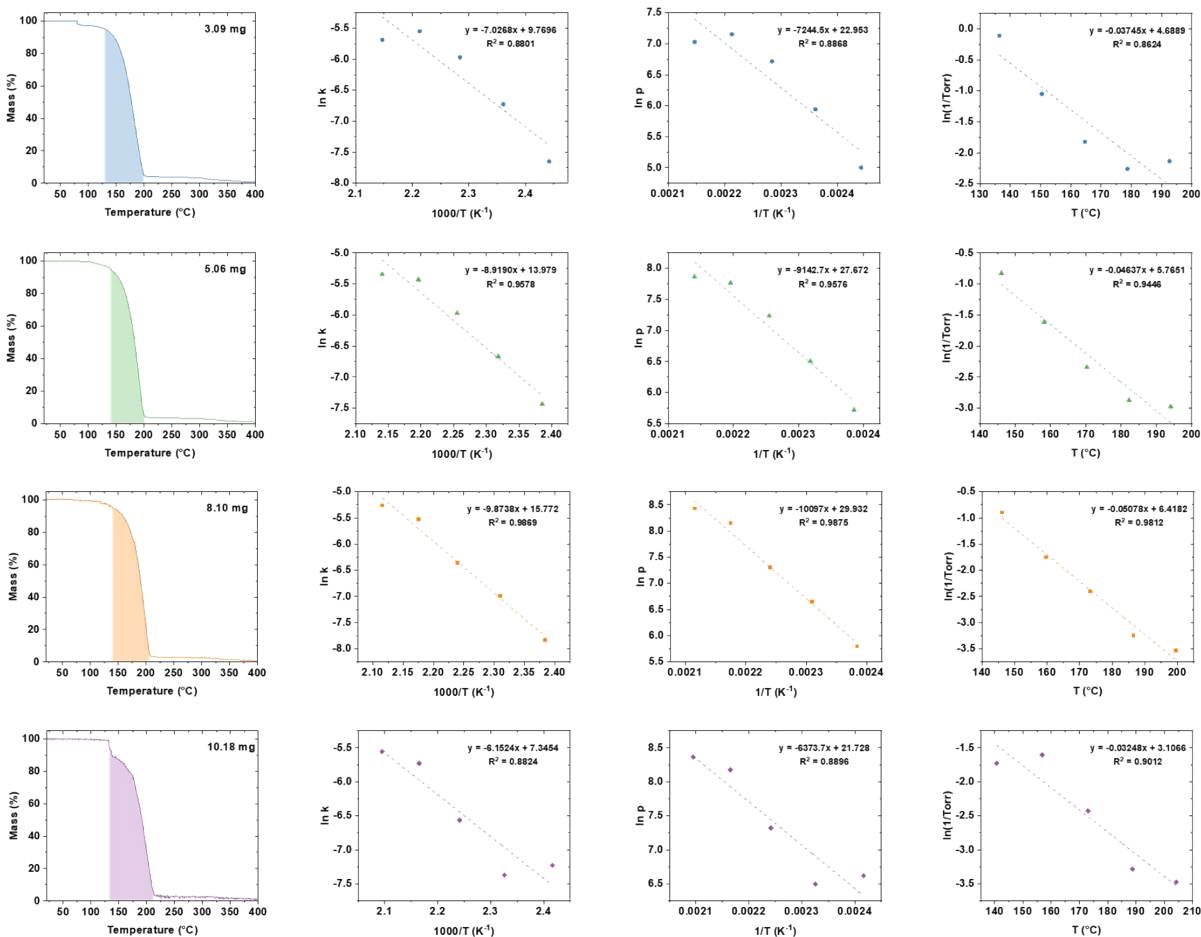


Figure S21. Thermogravimetric analysis of $[\text{WCl}_5]_2$. TG traces at constant temperature ramp rate of $10^\circ\text{C}/\text{min}$ and nominally 3 (blue), 5 (green), 8 (orange), and 10 (purple) mg (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

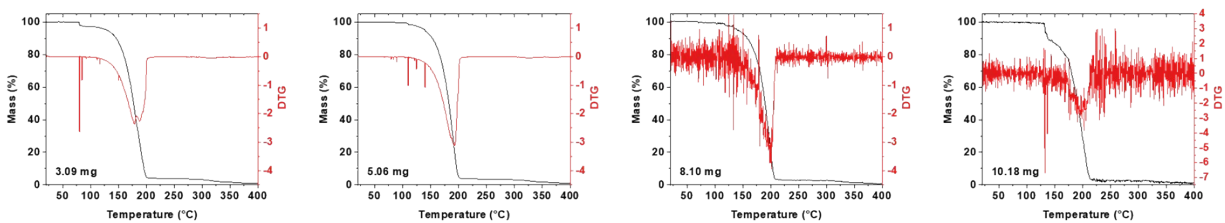


Figure S22. Thermogravimetric analysis of $[\text{WCl}_5]_2$. TG traces at constant temperature ramp rate of $10^\circ\text{C}/\text{min}$ and variable masses with derivative thermogravimetric (DTG) traces shown.

Table S11. Measured and calculated thermophysical parameters from TGA of $[\text{WCl}_5]_2$ at constant temperature ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and variable masses.

Sample mass (mg)	3.09	5.06	8.10	10.18
Slope (Arrhenius plot)	-7.03	-8.92	-9.87	-6.15
R^2 (Arrhenius plot)	0.88	0.96	0.99	0.88
E_a (J/mol)	58.42	74.15	82.09	51.15
R^2 (Clausius-Clapeyron plot)	0.89	0.96	0.99	0.89
ΔH_{sub} (kJ/mol)	60.23	76.02	83.95	52.99
T at 1 Torr ($^\circ\text{C}$)	125.20	124.33	126.39	95.65
T window ($^\circ\text{C}$)	130-200	140-200	140-206	133-212
Residual mass (%)	0.81	1.03	0.71	1.29

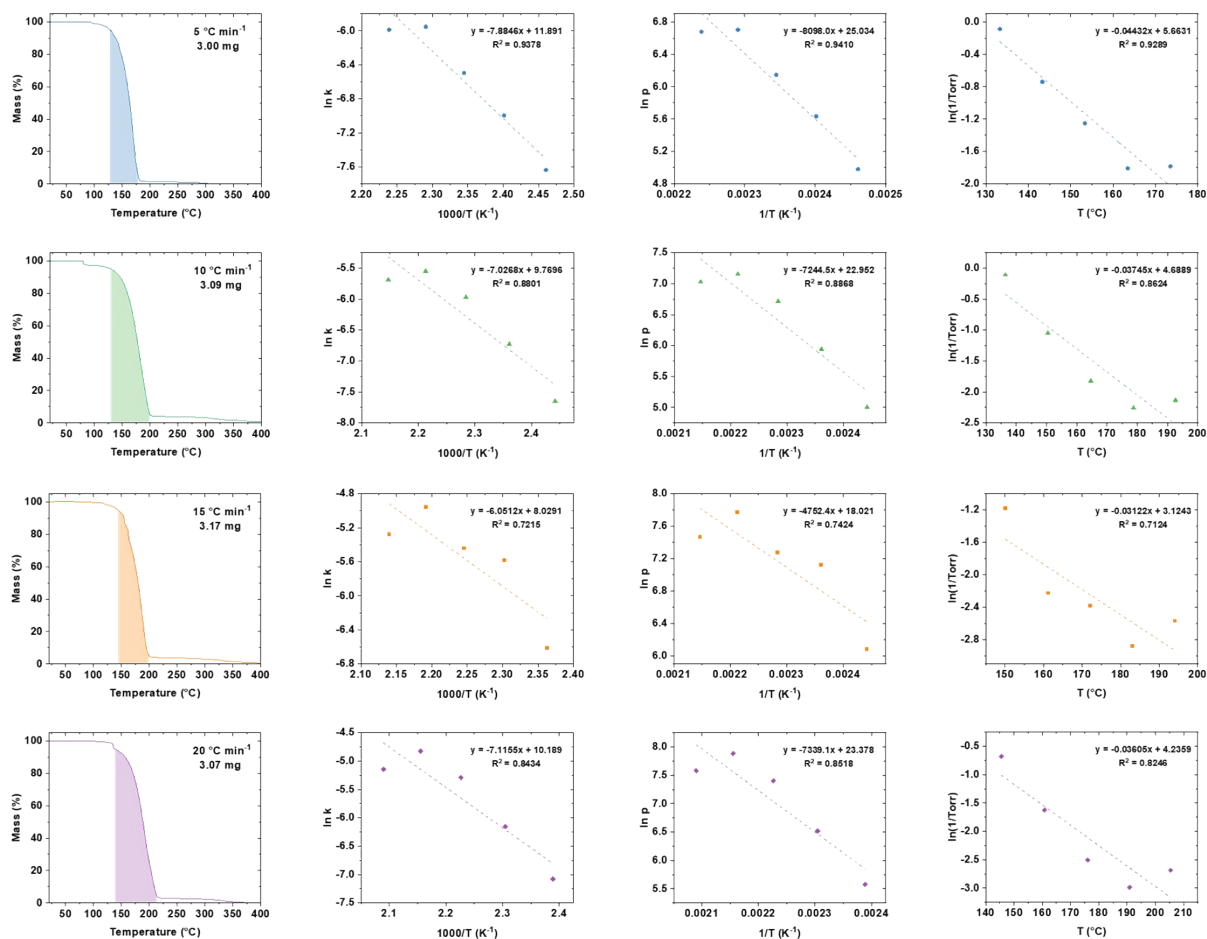


Figure S23. Thermogravimetric analysis of $[\text{WCl}_5]_2$. TG traces at nominally 3 mg and variable temperature ramp rates of 5 (blue), 10 (green), 15 (orange), and 20 (purple) $^\circ\text{C}/\text{min}$ (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

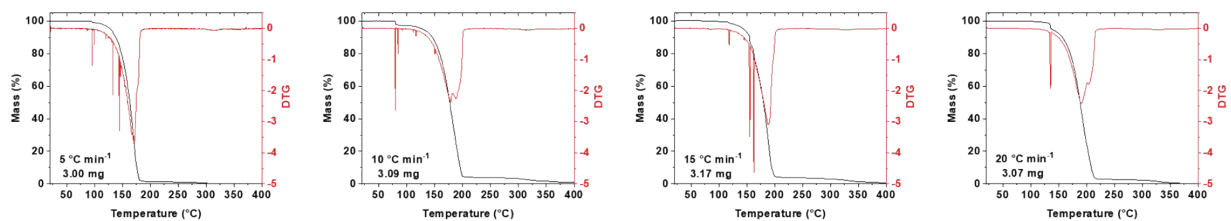


Figure S24. Thermogravimetric analysis of $[\text{WCl}_5]_2$. TG traces at nominally 3 mg and variable temperature ramp rates with derivative thermogravimetric (DTG) traces shown.

Table S12. Measured and calculated thermophysical parameters from TGA of $[\text{WCl}_5]_2$ at nominally 3 mg and variable temperature ramp rates.

Heating rate ($^{\circ}\text{C}/\text{min}$)	5	10	15	20
Sample mass (mg)	3.00	3.09	3.17	3.07
Slope (Arrhenius plot)	-7.88	-7.03	-6.05	-7.12
R^2 (Arrhenius plot)	0.94	0.88	0.72	0.84
E_a (J/mol)	65.55	58.42	50.31	59.16
R^2 (Clausius-Clapeyron plot)	0.94	0.89	0.74	0.85
ΔH_{sub} (kJ/mol)	67.33	60.23	39.51	61.02
T at 1 Torr ($^{\circ}\text{C}$)	127.78	125.20	100.07	117.50
T window ($^{\circ}\text{C}$)	128-178	130-200	145-199	138-213
Residual mass (%)	0.00	0.81	0.67	0.00

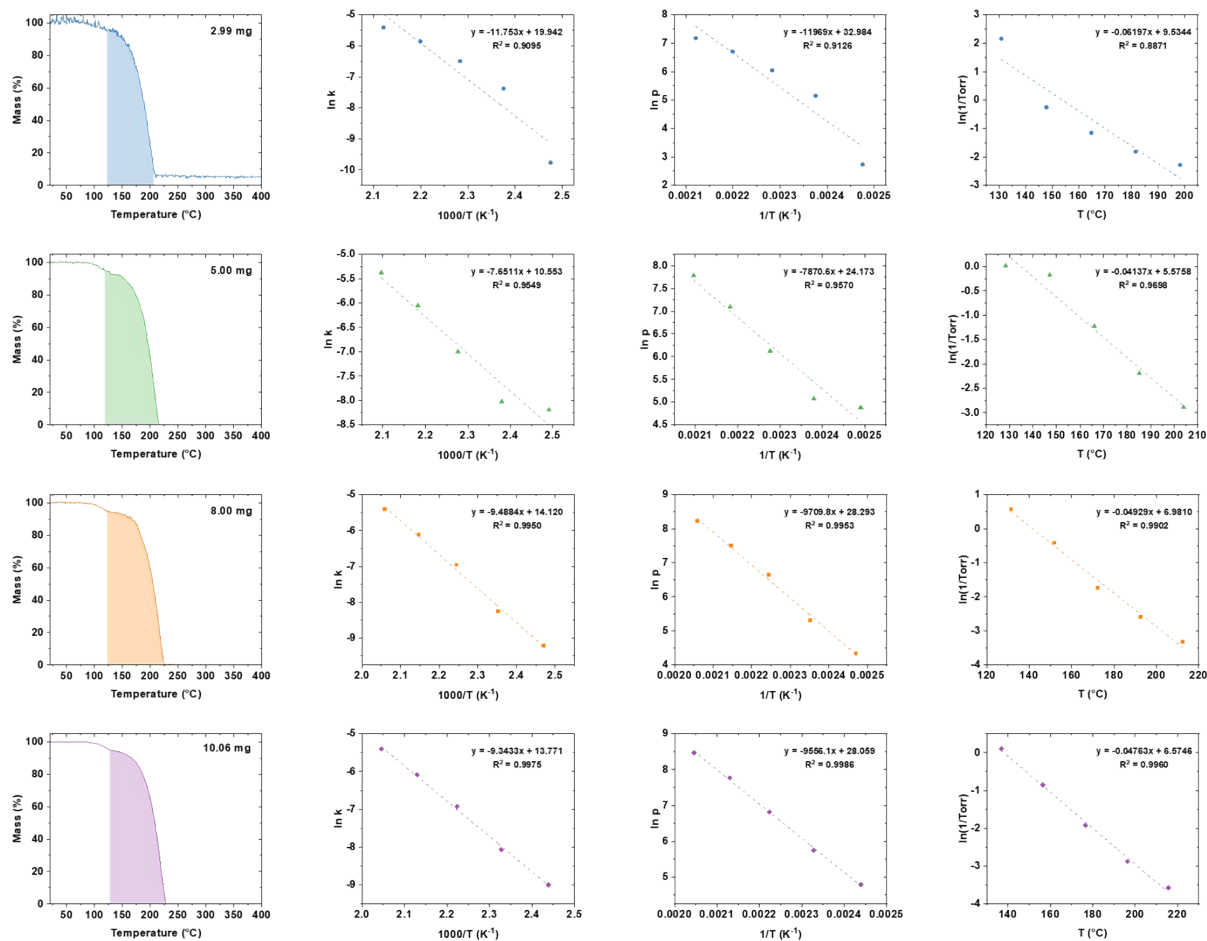


Figure S25. Thermogravimetric analysis of WCl_6 . TG traces at constant temperature ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and nominally 3 (blue), 5 (green), 8 (orange), and 10 (purple) mg (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

Figure S26. Thermogravimetric analysis of WCl_6 . TG traces at constant temperature ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and variable masses with derivative thermogravimetric (DTG) traces shown.

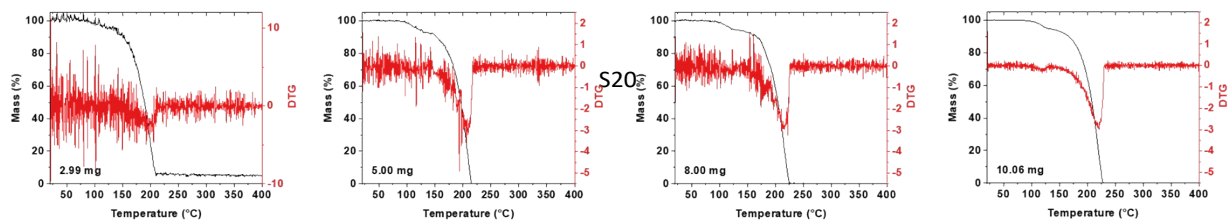


Table S13. Measured and calculated thermophysical parameters from TGA of WCl_6 at constant temperature ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and variable masses.

Sample mass (mg)	2.99	5.00	8.00	10.06
Slope (Arrhenius plot)	-11.75	-7.65	-9.49	-9.34
R^2 (Arrhenius plot)	0.91	0.95	1.00	1.00
E_a (J/mol)	97.71	63.61	78.89	77.68
R^2 (Clausius-Clapeyron plot)	0.91	0.96	1.00	1.00
ΔH_{sub} (kJ/mol)	99.52	65.44	80.73	79.45
T at 1 Torr ($^\circ\text{C}$)	153.86	134.78	141.63	138.03
T window ($^\circ\text{C}$)	122-207	119-213	122-222	127-225
Residual mass (%)	5.00	0.00	0.00	0.00

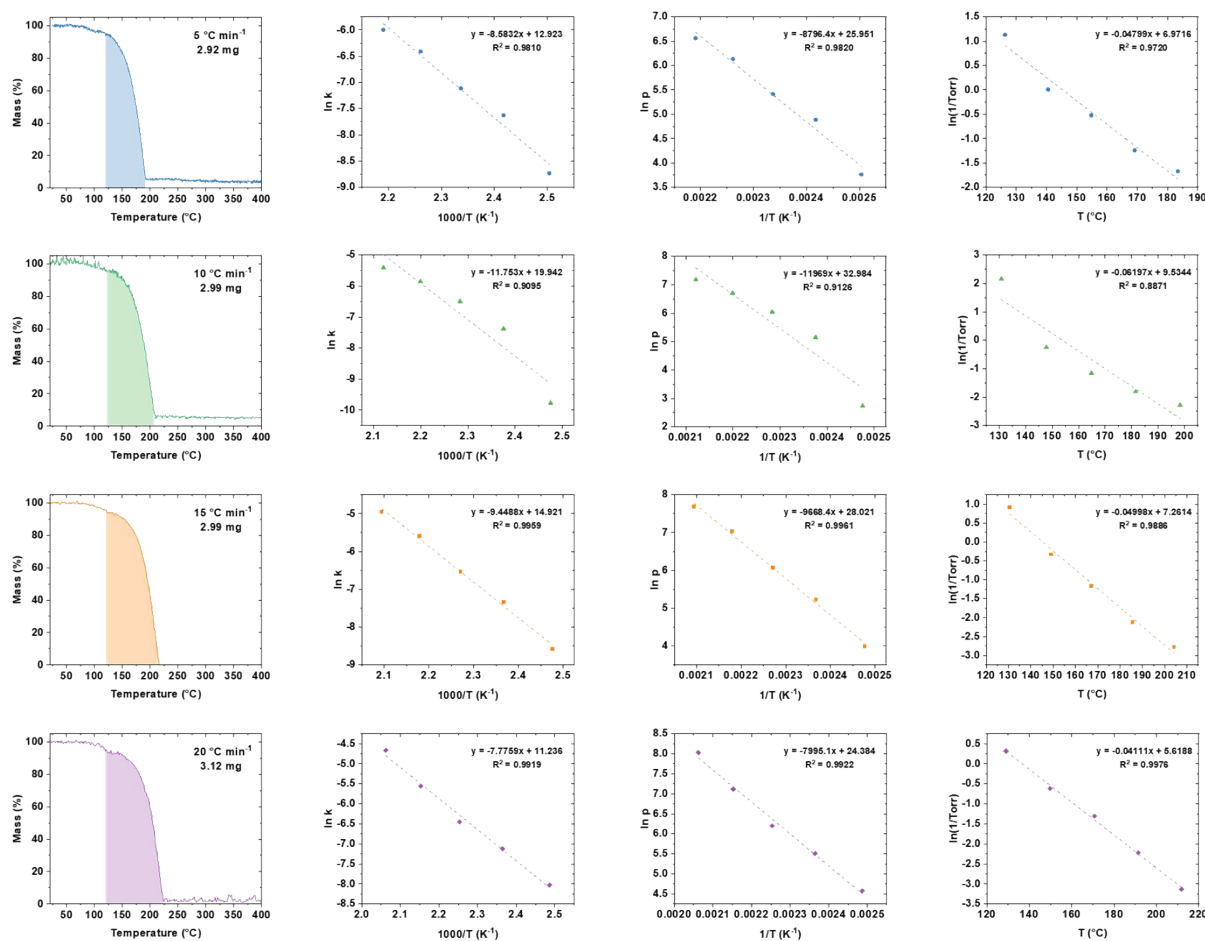


Figure S27. Thermogravimetric analysis of WCl_6 . TG traces at nominally 3 mg and variable temperature ramp rates of 5 (blue), 10 (green), 15 (orange), and 20 (purple) $^\circ\text{C}/\text{min}$ (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Plots of $\ln k$ vs $1000/T$, $\ln p$ vs $1/T$, and $\ln(1/\text{Torr})$ vs T used to derive E_a , ΔH_{sub} , and T at 1 Torr, respectively. Equation of line of best fit and R^2 value displayed on each of these plots.

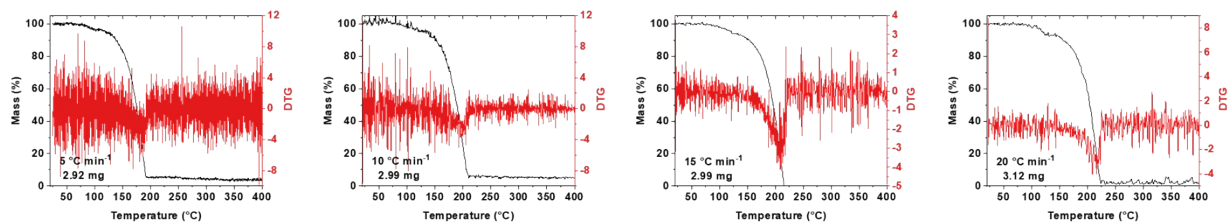


Figure S28. Thermogravimetric analysis of WCl_6 . TG traces at nominally 3 mg and variable temperature ramp rates with derivative thermogravimetric (DTG) traces shown.

Table S14. Measured and calculated thermophysical parameters from TGA of WCl_6 at nominally 3 mg and variable temperature ramp rates.

Heating rate ($^{\circ}C/min$)	5	10	15	20
Sample mass (mg)	2.92	2.99	2.99	3.12
Slope (Arrhenius plot)	-8.59	-11.75	-9.45	-7.78
R^2 (Arrhenius plot)	0.98	0.91	1.00	0.99
E_a (J/mol)	71.44	97.71	78.56	64.65
R^2 (Clausius-Clapeyron plot)	0.98	0.91	1.00	0.99
ΔH_{sub} (kJ/mol)	73.14	99.52	80.39	66.48
T at 1 Torr ($^{\circ}C$)	145.27	153.86	145.29	136.68
T window ($^{\circ}C$)	119-190	122-207	121-214	119-222
Residual mass (%)	3.52	5.00	0.00	1.16

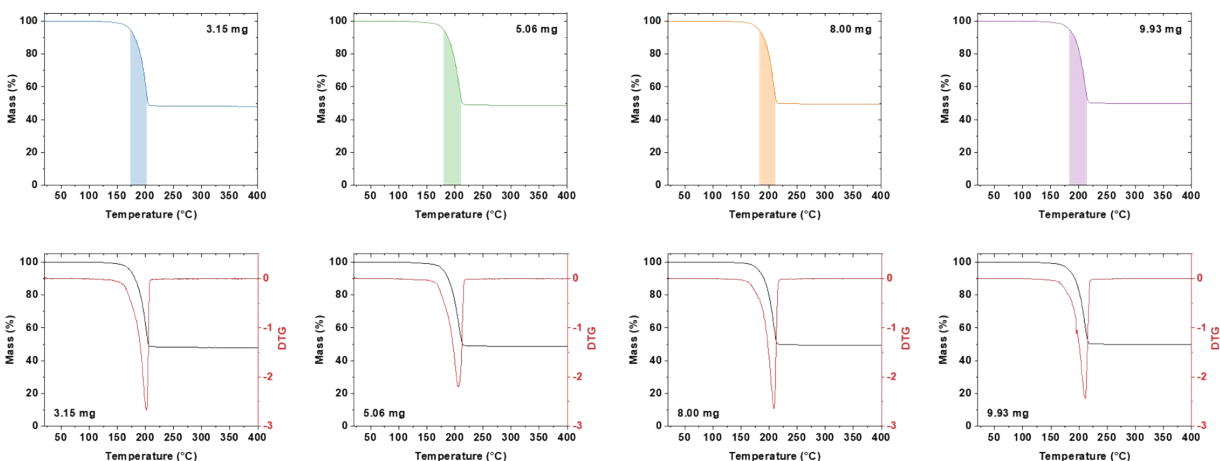


Figure S29. Thermogravimetric analysis of (mes)W(CO)₃. TG traces at constant temperature ramp rate of 10 °C/min and nominally 3 (blue), 5 (green), 8 (orange), and 10 (purple) mg (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Derivative thermogravimetric (DTG) traces also shown. Note (mes)W(CO)₃ led predominantly to decomposition products with 48.9 ± 0.8 % average residual mass precluding extraction of sublimation kinetics.

Table S15. Measured and calculated thermophysical parameters from TGA of (mes)W(CO)₃ at constant temperature ramp rate of 10 °C/min and variable masses.

Sample mass (mg)	3.15	5.06	8.00	9.93
T window (°C)	173-203	180-211	182-211	183-214
Residual mass (%)	48.00	48.57	49.43	49.77

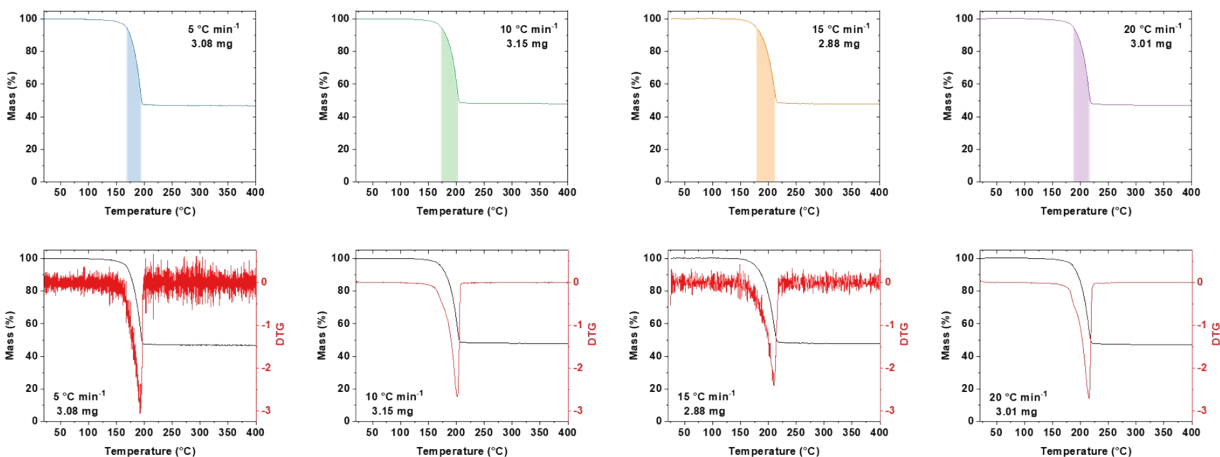


Figure S30. Thermogravimetric analysis of (mes)W(CO)₃. TG traces at nominally 3 mg and variable temperature ramp rates of 5 (blue), 10 (green), 15 (orange), and 20 (purple) °C/min (with actual masses displayed on graphs). Shaded regions underneath TG traces represent TGA temperature windows. Derivative thermogravimetric (DTG) traces also shown. Note (mes)W(CO)₃ led predominantly to decomposition products with 47.5 ± 0.6 % average residual mass precluding extraction of sublimation kinetics.

Table S16. Measured and calculated thermophysical parameters from TGA of (mes)W(CO)₃ at nominally 3 mg and variable temperature ramp rates.

Heating rate (°C/min)	5	10	15	20
Sample mass (mg)	3.08	3.15	2.88	3.01
T window (°C)	168-195	173-203	178-213	188-217
Residual mass (%)	46.82	48.00	47.87	47.16

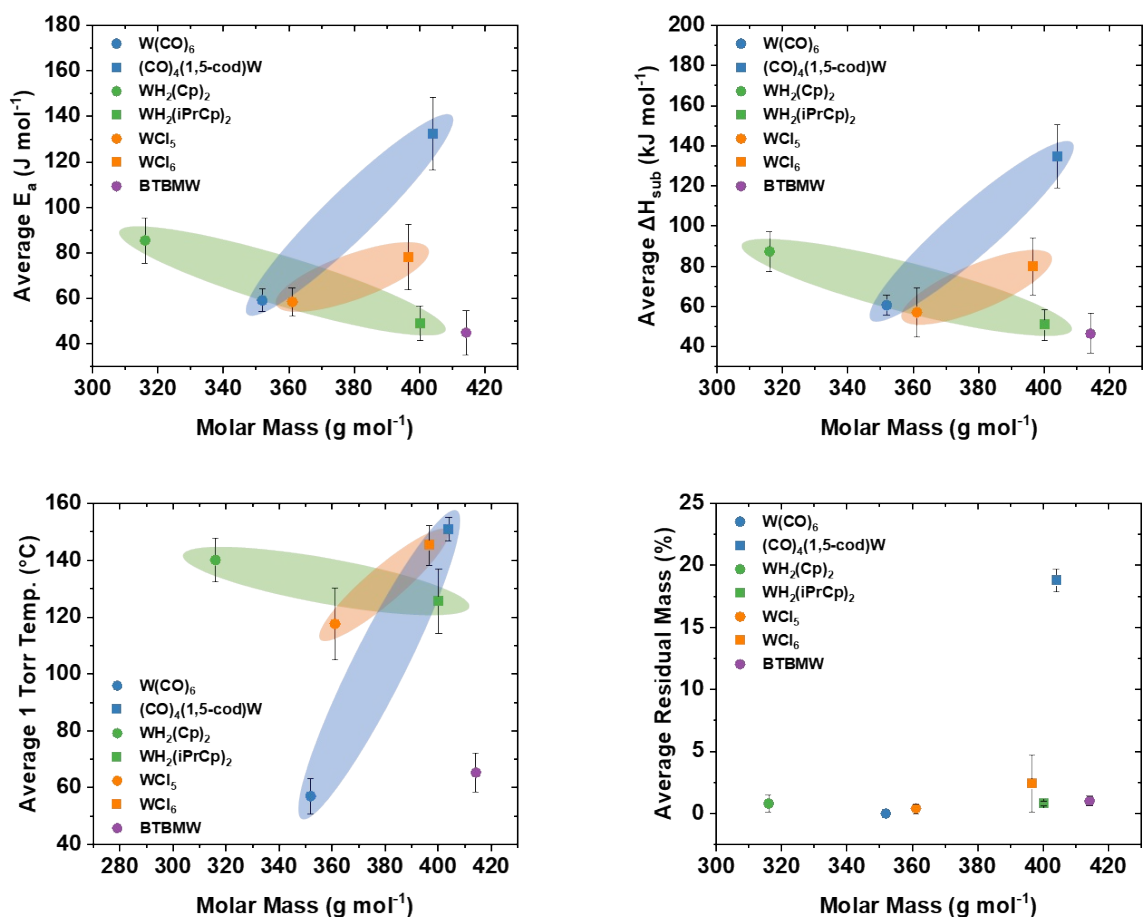


Figure S31. Plots comparing TGA-derived E_a , ΔH_{sub} , T at 1 Torr, and residual mass, respectively, of $\text{W}(\text{CO})_6$, $(1,5\text{-cod})\text{W}(\text{CO})_4$, WH_2Cp_2 , $\text{WH}_2(\text{iPrCp})_2$, WCl_6 , $[\text{WCl}_5]_2$, and BTBMW plotted against their molar masses. Thermophysical parameters are averages with error bars representing standard deviations, and based on TGA experiments in which sample loading was fixed at nominally 3 mg and temperature ramp rates were varied between 5, 10, 15, and 20 °C/min. The shaded regions group precursors together based on their ligand environments: carbonyl ligands (blue), cyclopentadienyl ligands (green), chloride ligands (orange), and amido/imido ligands (purple). Both $\text{WH}_2(\text{iPrCp})_2$ and BTBMW are liquids at RT; the rest of the precursors shown are solids. Note (mes) $\text{W}(\text{CO})_3$ led predominantly to decomposition products with $47.5 \pm 0.6\%$ average residual mass precluding extraction of sublimation kinetics.

Table S17. TGA-derived E_a , ΔH_{sub} and 1 Torr temperature values from trials varying temperature ramp rate, with fixed 3 mg sample loading.^a

Molecule	E_a (J/mol)	ΔH_{sub} (kJ/mol)	T at 1 Torr (°C)	Res. Mass (%)
$\text{W}(\text{CO})_6$	59.1 ± 4.9	60.6 ± 4.9	57.0 ± 6.3	0.0 ± 0.0
$(1,5\text{-cod})\text{W}(\text{CO})_4$	132.4 ± 15.9	134.6 ± 15.8	150.9 ± 4.1	18.8 ± 0.9
WH_2Cp_2	85.4 ± 10.0	87.3 ± 10.0	140.1 ± 7.7	0.8 ± 0.7
$\text{WH}_2(\text{iPrCp})_2$	49.0 ± 7.6	50.8 ± 7.6	125.6 ± 11.2	0.8 ± 0.2
BTBMW	44.9 ± 9.8	46.4 ± 9.9	65.3 ± 6.8	1.0 ± 0.4
WCl_6	78.1 ± 14.3	79.9 ± 14.3	145.3 ± 7.0	2.4 ± 2.3
$[\text{WCl}_5]_2$	58.4 ± 6.2	57.0 ± 12.1	117.6 ± 12.5	0.4 ± 0.4

^a Note (mes) $\text{W}(\text{CO})_3$ led predominantly to decomposition products with $47.5 \pm 0.6\%$ average residual mass precluding extraction of sublimation kinetics.