Temperature Effect on Activation Rate Constants in ATRP – New Mechanistic Insights into the Activation Process

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General

The reactions were followed by using a Hellma immersion probe. The temperature was controlled in a jacketed beaker with a Haake K50 thermostat unit (-25 - $+60$ °C). Reactions at even lower temperatures were conducted in an acetone/dry ice bath. At 20 °C each initiator/catalyst system was studied at least three times at different initiator concentrations. Plots of the obtained pseudo-first-order rate constants yielded straight lines from which the activation rate constants were determined. Kinetic experiments at all other temperatures were only performed once.

Cu(I)Br(PMDETA) + TEMPO without initiator

No	T / °C	[Cu(I)Br/PMDETA] ₀ / mM	[TEMPO] ₀ / mM
TM60	20	3.35	33.5
TM60-2	20	3.35	-

The experiments show the slow oxidation of the Cu(I)Br(PMDETA) complex by air. Addition of TEMPO does not influence this process.

BrPN

BrPN is a very reactive initiator, which means that the reactions with CuBr(PMDETA) have to be performed under much diluted conditions and at low temperatures.

No	T / °C	[Cu(I)Br/PMDETA] ₀ / mM	[BrPN] ₀ / mM	[TEMPO] ₀ / mM	<i>k</i> _{obs} / s ⁻¹	<i>k</i> _{act} / M ⁻¹ s ⁻¹
FS145	-41	1.68	17.3	17.2	1.82 × 10 ⁻²	1.05
FS146	-36.5	1.68	17.0	17.2	2.35 × 10 ⁻²	1.38
FS154	-39	1.24	12.7	13.4	1.45 × 10 ⁻²	1.14
FS155	-32	1.24	12.7	13.4	2.29 × 10 ⁻²	1.81
FS156	-28.5	1.25	12.9	13.5	2.65 × 10 ⁻²	2.05
FS157	-23	1.25	12.9	13.5	3.61 × 10 ⁻²	2.80
FS158	-15	1.25	12.9	13.5	5.99 × 10 ⁻²	4.64

$$\Delta H^\ddagger = (26.0 \pm 0.9) \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = (-131 \pm 4) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E_a = (28.1 \pm 0.9) \text{ kJ mol}^{-1}$$

$$\ln A = 14.6 \pm 0.4$$

BrAN

No	T / °C	[Cu(I)Br/PMDETA] ₀ / mM	[BrAN] ₀ / mM	[TEMPO] ₀ / mM	<i>k</i> _{obs} / s ⁻¹
FS237	20	0.98	10.1	12.2	3.69 × 10 ⁻²
FS238	20	0.97	13.0	12.0	4.66 × 10 ⁻²
FS239	20	0.95	16.2	11.8	5.87 × 10 ⁻²
FS247	20	1.06	19.0	13.2	7.18 × 10 ⁻²

First-order kinetics:

No	T / °C	[Cu(I)Br] ₀ / mM	[PMDETA] ₀ / mM	[BrAN] ₀ / mM	[TEMPO] ₀ / mM	$k_{\text{act}} / \text{M}^{-1} \text{s}^{-1}$
FS281	-40	3.43	3.43	36.1	34.3	1.40×10^{-1}

Second-order kinetics:

No	T / °C	[Cu(I)Br] ₀ / mM	[PMDETA] ₀ / mM	[BrAN] ₀ / mM	[TEMPO] ₀ / mM	$k_{\text{act}} / \text{M}^{-1} \text{s}^{-1}$
FS70	-20	4.21	4.21	4.21	42.6	4.93×10^{-1}
FS72	0	3.90	3.90	3.90	38.9	1.56
FS75	40	3.52	3.52	3.52	35.2	7.88

$$\Delta H^\ddagger = (28.7 \pm 0.6) \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = (-136 \pm 2) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E_a = (30.9 \pm 0.6) \text{ kJ mol}^{-1}$$

$$\ln A = 14.0 \pm 0.2$$

EtBriB

No	T / °C	[Cu(I)Br/ PMDETA] ₀ / mM	[EtBriB] ₀ / mM	[TEMPO] ₀ / mM	$k_{\text{obs}} / \text{s}^{-1}$
FS240	20	1.25	12.8	15.5	2.10×10^{-2}
FS241	20	1.23	18.9	15.2	3.11×10^{-2}
FS242	20	1.12	23.8	13.9	4.11×10^{-2}
FS243	20	1.10	29.4	13.7	4.97×10^{-2}

Second-order-kinetics:

No	T / °C	[Cu(I)Br] ₀ / mM	[PMDETA] ₀ / mM	[EtBrIB] ₀ / mM	[TEMPO] ₀ / mM	$k_{\text{act}} / \text{M}^{-1} \text{s}^{-1}$
FS69	−20	5.24	5.24	5.23	52.4	3.47×10^{-1}
FS67	0	5.08	5.08	5.09	51.1	8.83×10^{-1}
FS99	40	3.91	3.91	3.90	40.9	4.08

First-order-kinetics:

No	T / °C	[Cu(I)Br/PMDETA] ₀ / mM	[EtBrIB] ₀ / mM	[TEMPO] ₀ / mM	$k_{\text{obs}} / \text{s}^{-1}$	$k_{\text{act}} / \text{M}^{-1} \text{s}^{-1}$
FS68	0	2.54	26.5	25.5	2.51×10^{-2}	9.48×10^{-1}
FS282	−40	3.35	33.4	33.5	3.35×10^{-3}	1.00×10^{-1}

As can be seen from the two measurements at 0 °C, both methods – second-order and pseudo-first-order approach – yield comparable values for k_{act} .

$$\Delta H^\ddagger = (25.3 \pm 0.8) \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = (-153 \pm 3) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E_a = (27.5 \pm 0.8) \text{ kJ mol}^{-1}$$

$$\ln A = 12.0 \pm 0.3$$

MBriB

No	T / °C	[Cu(I)Br/ PMDETA] ₀ / mM	[MBriB] ₀ / mM	[TEMPO] ₀ / mM	$k_{\text{obs}} / \text{s}^{-1}$
FS244	20	1.21	12.4	15.0	2.91×10^{-2}
FS245	20	1.18	17.0	14.7	3.63×10^{-2}
FS126	20	1.85	19.0	19.5	4.26×10^{-2}
FS246	20	1.06	21.8	13.2	5.16×10^{-2}

No	T / °C	[Cu(I)Br/ PMDETA] ₀ / mM	[MBriB] ₀ / mM	[TEMPO] ₀ / mM	$k_{\text{obs}} / \text{s}^{-1}$	$k_{\text{act}} / \text{M}^{-1} \text{s}^{-1}$
FS283	-40	3.20	33.4	32.0	4.04×10^{-3}	1.21×10^{-1}
FS124	-20	2.56	26.3	25.8	1.18×10^{-2}	4.49×10^{-1}
FS125	0	2.64	27.1	27.8	3.04×10^{-2}	1.12
FS127	40	1.71	17.2	17.7	8.06×10^{-2}	4.68

$$\Delta H^\ddagger = (25.2 \pm 0.9) \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = (-151 \pm 3) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E_a = (27.5 \pm 0.9) \text{ kJ mol}^{-1}$$

$$\ln A = 12.1 \pm 0.4$$

CIPN

No	T / °C	[Cu(I)Br/ PMDETA] ₀ / mM	[CIPN] ₀ / mM	[TEMPO] ₀ / mM	$k_{\text{obs}} / \text{s}^{-1}$
FS102	20	2.26	23.1	23.0	2.03×10^{-3}
FS264	20	4.94	127.3	50.3	1.48×10^{-2}
FS265	20	4.71	202.2	48.0	2.33×10^{-2}

No	T / °C	[Cu(I)Br]/PMDETA] ₀ / mM	[CIPN] ₀ / mM	[TEMPO] ₀ / mM	$k_{\text{obs}} / \text{s}^{-1}$	$k_{\text{act}} / \text{M}^{-1} \text{s}^{-1}$
FS286	-20	4.89	257.0	49.6	2.40×10^{-3}	9.43×10^{-3}
FS285	0	4.77	219.2	48.1	8.42×10^{-3}	3.84×10^{-3}
FS277	40	3.31	35.0	34.6	8.49×10^{-3}	2.43×10^{-1}
FS278	60	3.31	35.0	34.6	1.93×10^{-2}	5.52×10^{-1}

$$\Delta H^\ddagger = (32.9 \pm 1.4) \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = (-151 \pm 5) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E_a = (35.3 \pm 1.3) \text{ kJ mol}^{-1}$$

$$\ln A = 12.2 \pm 0.6$$

PEBr

No	T / °C	[Cu(I)Br]/PMDETA] ₀ / mM	[PEBr] ₀ / mM	[TEMPO] ₀ / mM	$k_{\text{obs}} / \text{s}^{-1}$
FS248	20	4.25	59.5	42.7	5.16×10^{-3}
FS82	20	4.53	108.2	45.1	9.86×10^{-3}
FS249	20	3.94	137.9	39.7	1.28×10^{-2}

No	T / °C	[Cu(I)Br/PMDETA] ₀ / mM	[PEBr] ₀ / mM	[TEMPO] ₀ / mM	<i>k</i> _{obs} / s ⁻¹	<i>k</i> _{act} / M ⁻¹ s ⁻¹
FS78	-20	4.05	82.9	40.8	8.18 × 10 ⁻⁴	9.87 × 10 ⁻³
FS80	0	4.53	108	45.1	3.12 × 10 ⁻³	2.88 × 10 ⁻²
FS84	40	4.05	61.9	40.6	1.53 × 10 ⁻²	2.47 × 10 ⁻¹
FS86	60	4.16	45.7	41.7	2.78 × 10 ⁻²	6.08 × 10 ⁻¹

$$\Delta H^\ddagger = (34.0 \pm 1.0) \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = (-148 \pm 3) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E_a = (36.4 \pm 1.0) \text{ kJ mol}^{-1}$$

$$\ln A = 12.6 \pm 0.4$$

CIAN

No	T / °C	[Cu(I)Br/ PMDETA] ₀ / mM	[CIAN] ₀ / mM	[TEMPO] ₀ / mM	<i>k</i> _{obs} / s ⁻¹
TM17	20	4.37	81.4	44.9	4.62 × 10 ⁻³
TM18	20	4.24	126.3	43.6	7.31 × 10 ⁻³
FS89	20	4.33	170.7	45.0	9.88 × 10 ⁻³

No	T / °C	[Cu(I)Br/PMDETA] ₀ / mM	[CIAN] ₀ / mM	[TEMPO] ₀ / mM	<i>k</i> _{obs} / s ⁻¹	<i>k</i> _{act} / M ⁻¹ s ⁻¹
FS87	-20	4.30	314	43.0	1.60 × 10 ⁻³	5.10 × 10 ⁻³
FS88	0	4.30	314	43.0	5.36 × 10 ⁻³	1.71 × 10 ⁻²
FS90	40	3.30	65.6	33.0	8.91 × 10 ⁻³	1.36 × 10 ⁻¹
FS91	60	3.37	39.1	33.7	1.14 × 10 ⁻²	2.92 × 10 ⁻¹

$$\Delta H^\ddagger = (33.4 \pm 0.8) \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = (-155 \pm 3) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E_a = (35.8 \pm 0.8) \text{ kJ mol}^{-1}$$

$$\ln A = 11.7 \pm 0.3$$

AlI₂Br

No	T / °C	[Cu(I)Br/ PMDETA] ₀ / mM	[AlI ₂ Br] ₀ / mM	[TEMPO] ₀ / mM	<i>k</i> _{obs} / s ⁻¹
FS252	20	4.25	74.1	42.7	2.80 × 10 ⁻³
FS250	20	4.04	141.0	40.6	5.11 × 10 ⁻³
FS115	20	3.98	190.8	40.1	6.67 × 10 ⁻³
FS251	20	3.76	229.7	37.8	8.76 × 10 ⁻³

No	T / °C	[Cu(I)Br/PMDETA] ₀ / mM	[AlI ₂ Br] ₀ / mM	[TEMPO] ₀ / mM	<i>k</i> _{obs} / s ⁻¹	<i>k</i> _{act} / M ⁻¹ s ⁻¹
FS120	-20	3.98	191	40.1	5.42 × 10 ⁻⁴	2.84 × 10 ⁻³
FS119	0	3.98	191	40.1	1.74 × 10 ⁻³	9.12 × 10 ⁻³
FS117	40	4.20	126	42.4	1.32 × 10 ⁻²	1.05 × 10 ⁻¹
FS118	60	4.20	126	42.4	3.74 × 10 ⁻²	2.97 × 10 ⁻¹

$$\Delta H^\ddagger = (38.7 \pm 1.2) \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = (-140 \pm 4) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E_a = (41.1 \pm 1.3) \text{ kJ mol}^{-1}$$

$$\ln A = 13.6 \pm 0.5$$

MBrP

No	T / °C	[Cu(I)Br/PMDETA] ₀ / mM	[MBrP] ₀ / mM	[TEMPO] ₀ / mM	<i>k</i> _{obs} / s ⁻¹
FS111	20	4.00	40.1	42.3	5.51 × 10 ⁻³
FS110	20	3.85	77.2	40.6	1.01 × 10 ⁻²
FS109	20	3.71	111	39.2	1.56 × 10 ⁻²
FS108	20	3.58	143	37.8	1.98 × 10 ⁻²
FS112	20	3.45	173	36.5	2.29 × 10 ⁻²

No	T / °C	[Cu(I)Br/PMDETA] ₀ / mM	[MBrP] ₀ / mM	[TEMPO] ₀ / mM	<i>k</i> _{obs} / s ⁻¹	<i>k</i> _{act} / M ⁻¹ s ⁻¹
FS77	-20	4.05	62.1	40.8	9.95 × 10 ⁻⁴	1.60 × 10 ⁻²
FS79	0	4.45	66.0	44.3	3.75 × 10 ⁻³	5.68 × 10 ⁻²
FS83	40	3.30	35.2	33.1	1.20 × 10 ⁻²	3.41 × 10 ⁻¹
FS85	60	3.98	40.7	39.9	2.96 × 10 ⁻²	7.27 × 10 ⁻¹

$$\Delta H^\ddagger = (30.8 \pm 0.6) \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = (-156 \pm 2) \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E_a = (33.2 \pm 0.6) \text{ kJ mol}^{-1}$$

$$\ln A = 11.7 \pm 0.2$$

Determination of $\Delta S^\ddagger$

Determination of the entropy of activation ($\Delta S^\ddagger$) for studied reactions by extrapolation to infinite temperatures ($1/T \rightarrow 0$).