Supporting Information for:

Thermal Decomposition of 3-Bromopropene. A Theoretical Kinetic Investigation.

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Table S1. Structural parameters for 3-bromopropene and its transition state calculated at different levels of theory (bond lengths in Angstroms and angles in degrees).

parameters	BMK	M06-2X	B3LYP	CBS-QB3	G4	Exp.[a]
	3-bromopropene (gauche)					
r(C–Br)	1.969	1.962	1.996	2.006	1.997	1.976
r(–C(Br)–H) $_{avg}$	1.086	1.085	1.085	1.087	1.089	1.095
r(C–H)	1.085	1.084	1.084	1.086	1.087	1.080
r(=C–H)$_{avg}$	1.083	1.082	1.082	1.085	1.085	1.080
r(C–C)	1.492	1.485	1.482	1.485	1.485	1.486
r(C=C)	1.327	1.324	1.328	1.331	1.330	1.354
∠(C–C–Br)	110.8	110.4	111.2	111.3	111.1	108.1
∠(C=C–H)	120.5	120.6	120.2	120.3	120.5	
∠(=C–C–H)	112.3	112.3	112.9	112.9	112.8	
∠(C=C–C)	123.2	123.2	123.5	123.5	123.5	121.6
∠(C=C–C–Br)	116.4	116.5	115.8	115.8	115.9	121.1
	transition state channel (1)					
r(C–Br)	3.365	3.272	3.451	3.451	3.408	
r(–C(Br)–H) $_{avg}$	1.085	1.083	1.083	1.085	1.086	
r(C–H)	1.144	1.144	1.135	1.139	1.138	
r(=C–H)$_{avg}$	1.084	1.082	1.082	1.085	1.085	
r(C–C)	1.364	1.361	1.362	1.365	1.366	
r(C=C)	1.365	1.359	1.366	1.369	1.368	
∠(C–C–Br)	64.4	65.8	63.2	63.4	64.0	
∠(C=C–H)	119.7	119.8	118.9	118.7	119.0	
∠(=C–C–H)	118.8	118.6	119.1	118.9	119.0	
∠(C=C–C)	128.3	128.8	128.6	128.9	128.9	
∠(C=C–C–Br)	172.2	169.1	173.8	174.9	173.0	

[a] Niide, Y.; Takano, M.; Satoh, T.; Sasada, Y. Microwave Spectrum, Molecular Structure, and Nuclear Quadrupole Coupling Constants of 3-Bromopropene. *J. Mol. Spectrosc.,* **1976**, *63*, 108−119.

Table S2. Reaction and activation enthalpies at 0 K (in kcal mol^{-1}) for the 3-bromopropene decomposition channels at the G4 and M06-2X/6-311++G(3df,3pd) (in brackets). (a: Fission simple reaction with ΔH_r (0 K) = $\Delta H^{\#}_0$). (The numbers I, II and III are equivalent to 1, 2 and 3 in the Manuscript).

reaction channel		ΔH_r (0 K)	$\Delta H^{\#}_0$
CH_2=CH-CH_2Br → CH_2=C=CH_2 + HBr	(I)	25.0 (24.1)	56.5 (63.8)
CH_2=CH-CH_2Br → CH_2=CH-CH_2 + Br	(II)	55.1 (56.7)	a
CH_2=CH-CH_2Br → CH_2=CH-CH + HBr	(III)	78.1 (76.2)	95.7 (95.2)
CH_2=CH-CH_2Br → CH_2=C=CHBr + H_2	(IV)	39.8 (39.9)	103.8 (104.2)
CH_2=CH-CH_2Br → CH≡C-CH_2Br + H_2	(V)	40.9 (41.7)	110.9 (107.6)
CH_2=CH-CH_2Br → C=CH-CH_2Br + H_2	(VI)	131.6 (131.2)	---
CH_2=CH-CH_2Br → CH_2=CH-CBr + H_2	(VII)	86.4 (86.4)	---

Table S3. Harmonic vibrational frequencies (in cm^{-1}), rotational constants (in cm^{-1}), and torsional barrier (in kcal mol^{-1}) for the CH_2=CH-CH_2 radical calculated with the G4 method.

parameters	CH_2=CH-CH_2
	G4
vibrational frequencies	
	3203
	3200
	3109
	3103
	3094
	1497
	1487
	1400
	1252
	1201
	1026
	1008
	918
	796
	773
	548
	529
	416
rotational constants	
A	1.840
B	0.345
C	0.290
torsional barrier	11.9

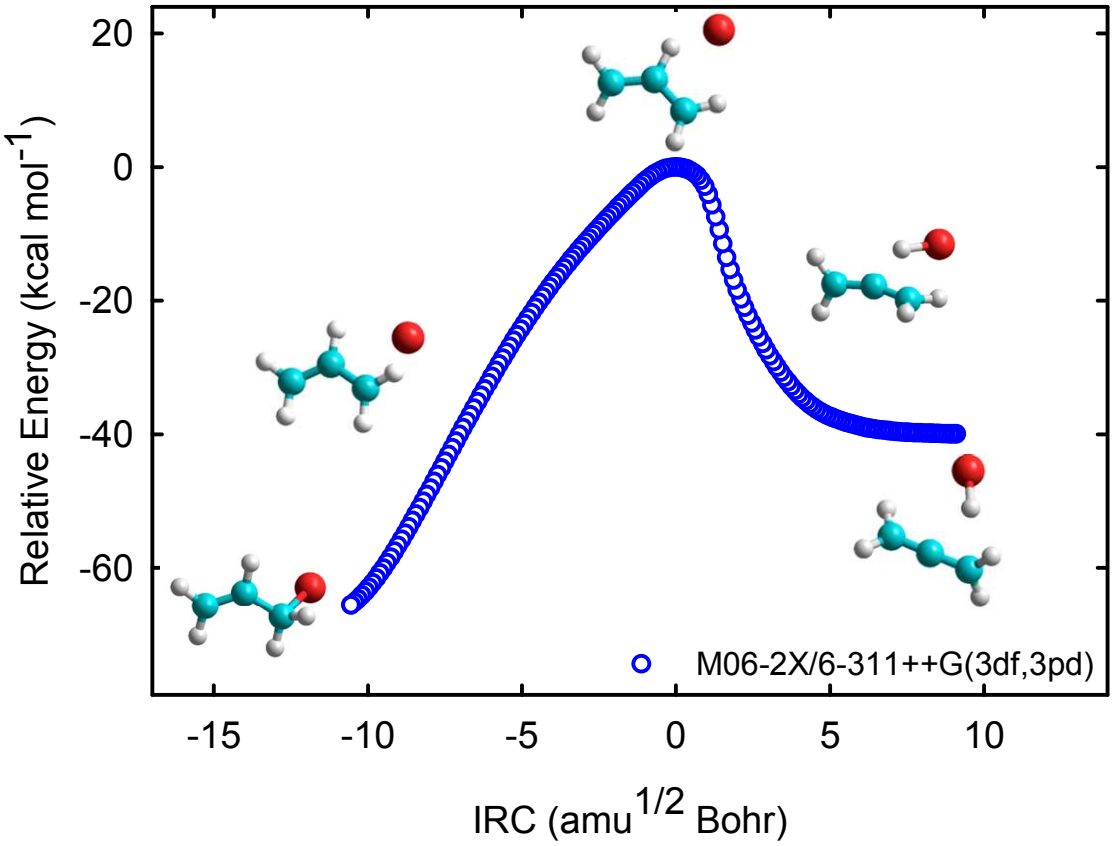

Figure S1. Relative energy along the intrinsic reaction coordinate for channel (1).

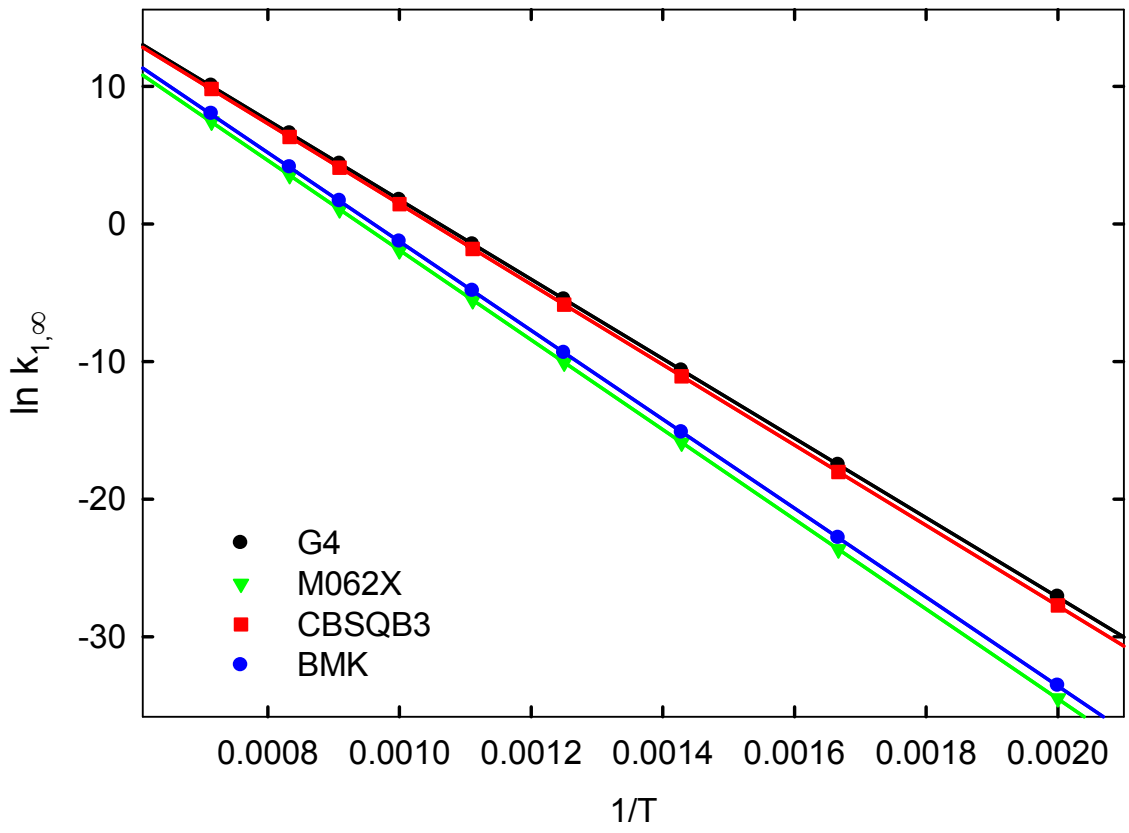

Figure S2. Temperature dependence of $k_{1,\infty}$ (in s^{-1}) at different levels of theory.

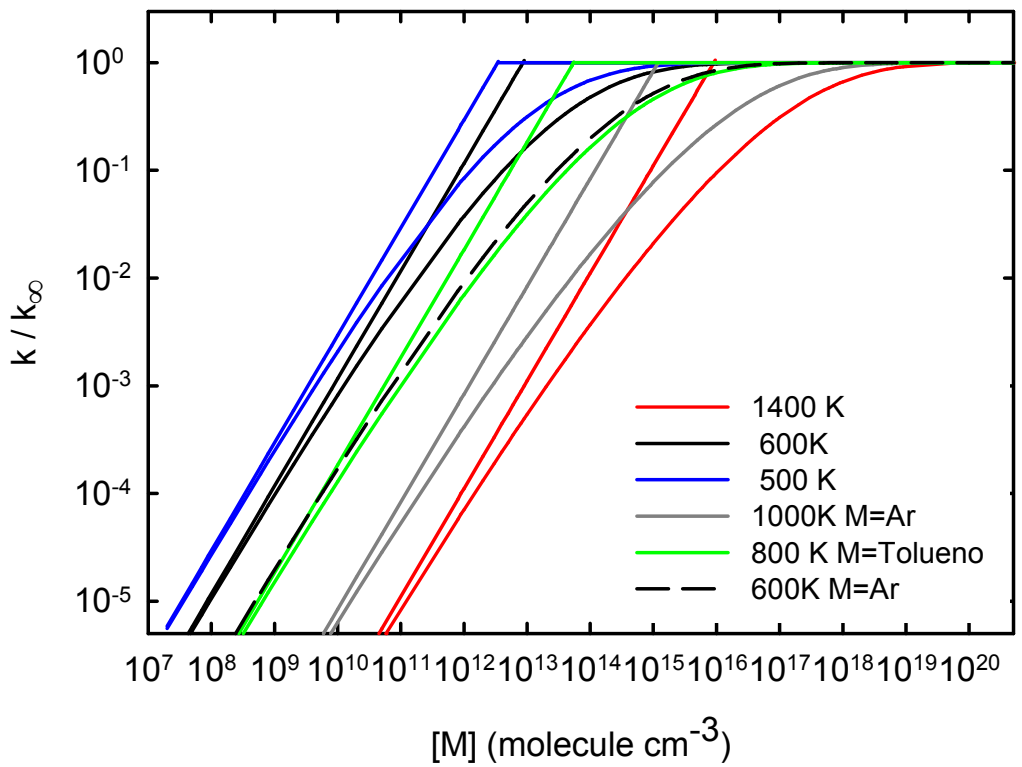

Figure S3. Reduced falloff curves for channel (1).

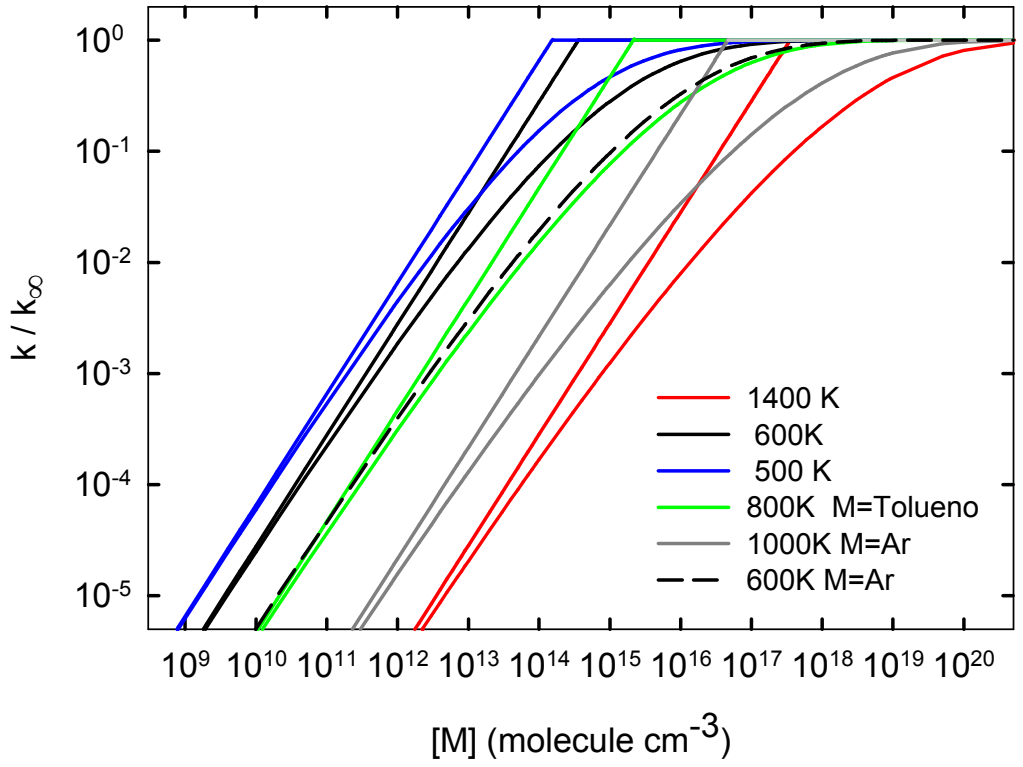

Figure S4. Reduced falloff curves for channel (2).