Supporting Information for the manuscript "Formation Enthalpies of C_3 and C_4 Brominated Hydrocarbons: Bringing Together Classical Thermodynamics, Modern Mass Spectrometry, and High-Level *Ab Initio* Calculations"

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Computed geometries

The computed geometries for the compounds considered in this work are provided in the compressed folders DFTgeo.zip and MP2geo.zip for B3LYP-D3(BJ)/def2-TZVP and DF-MP2/aug-cc-pVQZ optimizations, respectively. The files are provided in xyz format[1] and include all considered conformations. The file naming follows the identifiers given in Table S1. The table also contains computed enthalpies of formation at 298.15 K and 0 K. **It should be emphasized that the value at 298.15 K is the primary model result. Enthalpies of formation at 0 K were derived from those at 298.15 K using computed $\Delta_0^T H$ (also listed) and are given solely for the reference.**

Effect of explicit treatment of internal rotations on thermal enthalpy $\Delta_0^T H$

In the model presented in the main manuscript, a compound was treated as an equilibrium mixture of its conformers with each conformer described with the rigid rotor/harmonic oscillator approximation. Alternatively, the conformers connected via internal rotation can also be described as a single compound with a hindered rotor. Both approaches are approximations. For alkanes, the barriers to internal rotation are reasonably high and the "mixture of conformers" approximation is usually sufficient for evaluation of thermal enthalpy at room temperature. To test the sensitivity to the chosen model for brominated compounds, hindered rotor treatment was considered for two representative cases, 1,2-dibromoethane and 3-bromopropene. Rotational potentials and the corresponding rotational constants were obtained with relaxed rotational angle scans using B3LYP-D3(BJ)/def2-TZVP. The final energies were computed with LCCSD(T)/aug-cc-pVQZ//B3LYP-D3(BJ)/def2-TZVP. The results are shown in Fig. S1.

Rotational potential obtained here for 1,2-dibromoethane agrees with the calculations of
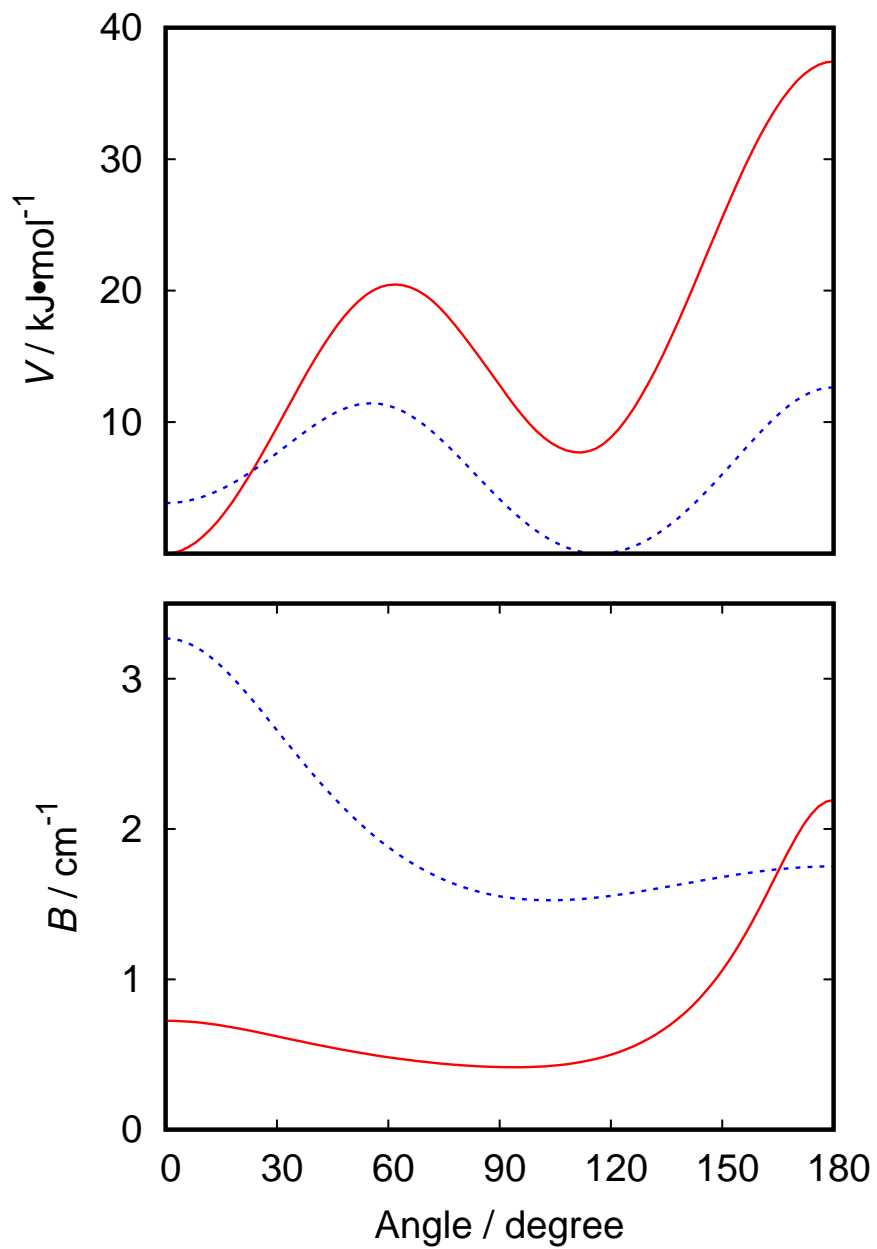
Figure S1: Computed rotational potentials (top) and constants (bottom). Solid (red) line: 1,2-dibromoethane, dotted (blue) line: 3-bromopropene. Rotational constants were evaluated following Pitzer.[2] The portion beyond 180° is omitted due to mirror symmetry.

Wong et al.[3] performed at the similar (CCSD(T)//MP2) level of theory with smaller (cc-pVTZ) basis set. The results for 3-bromopropene are also consistent with G4 calculations of Tucceri et al.[4] The comparison of computed $\Delta_0^T H$ using two different approaches for both compounds is presented in Table S2.

As seen, the difference between the models is small in both cases.

References

(1) XYZ file format. `http://en.wikipedia.org/wiki/XYZ_file_format`, accessed: October 16, 2023.

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(3) Wong, B. M.; Fadri, M. M.; Raman, S. Thermodynamic Calculations for Molecules with Asymmetric Internal Rotors. II. Application to the 1,2-Dihaloethanes. *J. Comput. Chem.* **2008**, *29*, 481–487.

(4) Tucceri, M. E.; Badenes, M. P.; Bracco, L. L.; Cobos, C. J. Thermal Decomposition of 3-Bromopropene. A Theoretical Kinetic Investigation. *J. Phys. Chem. A* **2016**, *120*, 2285–2294.

(5) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation*; Blackwell Science: Oxford, U.K., 1985.

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Table S1: Listing of bromine-containing compounds used in computations[a]

ID[b]	name	CAS registry	$\Delta_f H_m^\circ(298.15\ \mathrm{K})^c$	$\Delta_0^T H$	$\Delta_f H_m^\circ(0\ \mathrm{K})^d$
01	hydrogen bromide	10035-10-6	−36.1 ± 2.5	8.64	−28.3
02	bromomethane	74-83-9	−36.0 ± 2.5	10.65	−20.6
03	bromine fluoride	13863-59-7	−59.8 ± 2.6	9.02	−52.1
04	bromoethane	74-96-4	−63.7 ± 2.6	13.49	−41.6
05	(Z)-1-bromopropene	590-13-6	39.1 ± 2.6	15.93	59.7
06	(E)-1-bromopropene	590-15-8	41.1 ± 2.6	16.14	61.5
07	2-bromopropene	557-93-7	32.9 ± 2.6	15.56	53.9
08	3-bromopropene	106-95-6	44.2 ± 2.6	15.85	64.9
09	bromocyclopropane	4333-56-6	79.6 ± 2.6	13.93	102.2
10	1-bromopropane	106-94-5	−85.6 ± 2.6	16.89	−57.5
11	2-bromopropane	75-26-3	−96.6 ± 2.6	16.88	−68.5
12	bromodifluoromethane	1511-62-2	−424.0 ± 2.6	13.04	−410.7
13	bromocyclobutane	4399-47-7	32.6 ± 2.6	16.38	62.4
14	1-bromo-2-methylpropane	78-77-3	−114.3 ± 2.6	20.47	−80.2
15	2-bromo-2-methylpropane	507-19-7	−131.7 ± 2.6	20.40	−97.5
16	1-bromobutane	109-65-9	−106.2 ± 2.6	21.14	−72.8
17	2-bromobutane	78-76-2	−117.9 ± 2.6	21.55	−84.9
18	bromotrifluoromethane	75-63-8	−649.5 ± 2.8	14.64	−637.5
19	bromine	7726-95-6	34.7 ± 2.6	9.74	49.5
20	2-bromophenol	95-56-7	−76.1 ± 2.6	20.60	−52.7
21	4-bromophenol	106-41-2	−67.6 ± 2.6	20.90	−44.4
22	1-bromo-2-methoxybenzene	578-57-4	−41.0 ± 2.6	25.54	−12.9
23	1-bromo-3-methoxybenzene	2398-37-0	−48.0 ± 2.6	24.82	−19.2
24	1-bromo-4-methoxybenzene	104-92-7	−46.3 ± 2.6	24.53	−17.2
25	1,2-dibromoethane	106-93-4	−39.1 ± 2.7	17.03	−12.6
26	4'-bromoacetophenone	99-90-1	−60.1 ± 2.7	27.11	−32.6
27	4-bromobenzoic acid	586-76-5	−271.6 ± 2.8	25.20	−247.3
28	1,1-dibromopropane	598-17-4	−53.9 ± 2.7	20.18	−21.0
29	1,2-dibromopropane	78-75-1	−72.7 ± 2.7	20.53	−40.2
30	1,3-dibromopropane	109-64-8	−64.1 ± 2.7	20.84	−31.8
31	2,2-dibromopropane	594-16-1	−68.3 ± 2.7	20.11	−35.4
32	1,2-dibromobutane	533-98-2	−94.6 ± 2.7	24.79	−56.8
33	1,3-dibromobutane	107-80-2	−97.7 ± 2.7	24.93	−60.0
34	1,4-dibromobutane	110-52-1	−86.2 ± 2.7	24.96	−48.6
35	*meso*-2,3-dibromobutane	5780-13-2	−102.5 ± 2.7	24.05	−64.0
36	*dl*-2,3-dibromobutane	598-71-0	−103.3 ± 2.7	24.26	−65.0
37	1,2-dibromo-2-methylpropane	594-34-3	−107.8 ± 2.7	24.17	−69.4
38	1,3-dibromo-2-methylpropane	28148-04-1	−93.0 ± 2.7	24.46	−54.9
39	2,3-dibromo-2-methylbutane	594-51-4	−134.6 ± 2.7	27.82	−90.3
40	2-bromofluorene	1133-80-8	209.2 ± 2.9	30.28	242.9
41	2,6-dibromophenol	608-33-3	−46.0 ± 2.8	24.36	−18.2
42	tribromomethane	75-25-2	57.4 ± 2.8	16.11	83.4
43	1,2-dibromotetrafluoroethane	124-73-2	−804.4 ± 3.0	25.07	−785.2

[a]values are given in kJ·mol^{-1}; [b]compound identifier used to label the provided xyz files; [c]computed; [d]derived from computed $\Delta_f H_m^\circ(298.15\ \mathrm{K})$ and $\Delta_0^T H$

Table S2: $\Delta_0^T H$ **computed with the "mixture-of-conformers" and hindered-rotor models**

	$\Delta_0^T H$ / kJ·mol^{-1}	
compound	mixture of conformers	hindered rotor
1,2-dibromoethane	17.0	17.3
3-bromopropene	15.9	16.0

Table S3: Non-ideality correction to the enthalpies of vaporization at T = 298.15 K (kJ·mol^{-1})

compound	Majer and Svoboda[5]	This work[a]
tribromomethane	0.01	0.01
bromomethane	0.43	0.34[b]
bromoethane	0.23	0.16[b]
1-bromopropane	0.12	0.11[c]
2-bromopropane	0.16	0.15[b]
3-bromopropene	0.12	0.10
1,2-dibromopropane	0.02	0.02
1,3-dibromopropane	0.01	0.01
1-bromobutane	0.07	0.06
2-bromobutane	0.10	0.07
1-bromo-2-methylpropane	0.08	0.07
2-bromo-2-methylpropane	0.12	0.12
1,4-dibromobutane	0.00	0.00
1,2-dibromo-2-methylpropane	0.02	0.02

[a]unless specified otherwise, second virial coefficients $B_{2,m}$ are estimated with the Pitzer-Curl method[6] and vapor pressures are evaluated by NIST TDE; [b]$B_{2,m}$ are evaluated by NIST TDE using the available experimental data; [c]both experimental data and Pitzer-Curl predictions are used in the $B_{2,m}$ evaluation