Supporting information for:

Characterization of the *t*-Butyl Radical and its Elusive Anion

Alexander Yu. Sokolov,* Samyak Mittal, Andrew C. Simmonett, and

Henry F. Schaefer III

Center for Computational Quantum Chemistry, The University of Georgia, Athens, GA, 30602

E-mail: alex@ccqc.uga.edu

*To whom correspondence should be addressed

Table S1: Focal point analysis of the C_s transition state energy of *t*-butyl radical relative to the C_{3v} global minimum structure (ΔE_v, kcal mol^{-1}).[a]

Basis Set	ΔE_e[ROHF]	δ[MP2]	δ[CCSD]	δ[CCSD(T)]	ΔE_e[CCSD(T)]
cc-pVDZ	+1.55	−0.24	−0.06	+0.02	[+1.27]
cc-pVTZ	+1.66	−0.46	−0.01	−0.00	[+1.19]
cc-pVQZ	+1.70	−0.47	−0.01	−0.00	[+1.22]
cc-pV5Z	+1.71	−0.47	−0.00	+0.00	[+1.24]
CBS limit	[+1.72]	[−0.47]	[+0.00]	[+0.00]	**[+1.26]**
ΔE_v (final) = ΔE_e[CBS CCSD(T)] + Δ_{core}[CCSD(T)/cc-pCVTZ] + Δ_{ZPVE}[CCSD(T)/cc-pCVTZ] + Δ_{rel}[CCSD(T)/cc-pCVTZ] = +1.26 − 0.00 − 0.41 + 0.00 = **+0.85 kcal mol^{-1}**					
Fit Function	$a+be^{-cX}$	$a+bX^{-3}$	$a+bX^{-3}$	$a+bX^{-3}$	
Points (X)	3,4,5	4,5	4,5	4,5	

[a]The symbol δ denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory in the hierarchy ROHF→MP2→CCSD→CCSD(T). Square brackets signify results obtained from basis set extrapolations or additivity assumptions. Final predictions are boldfaced.

Table S2: Focal point analysis of the C_s transition state energy of *t*-butyl anion relative to the C_{3v} global minimum structure (ΔE_v, kcal mol^{-1}).[a]

Basis Set	ΔE_e[RHF]	δ[MP2]	δ[CCSD]	δ[CCSD(T)]	ΔE_e[CCSD(T)]
cc-pVDZ	+5.16	+0.97	−0.50	+0.14	[+5.77]
cc-pVTZ	+5.16	+0.77	−0.52	+0.11	[+5.51]
cc-pVQZ	+5.20	+0.73	−0.51	+0.10	[+5.51]
cc-pV5Z	+5.18	+0.67	−0.49	+0.08	[+5.45]
CBS limit	[+5.15]	[+0.61]	[−0.46]	[+0.06]	**[+5.37]**
ΔE_v (final) = ΔE_e[CBS CCSD(T)] + Δ_{core}[CCSD(T)/cc-pCVTZ] + Δ_{ZPVE}[CCSD(T)/cc-pCVTZ] + Δ_{rel}[CCSD(T)/cc-pCVTZ] = +5.37 + 0.05 − 0.37 + 0.00 = **+5.05 kcal mol^{-1}**					
Fit Function	$a+be^{-cX}$	$a+bX^{-3}$	$a+bX^{-3}$	$a+bX^{-3}$	
Points (X)	3,4,5	4,5	4,5	4,5	

[a]The symbol δ denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory in the hierarchy RHF→MP2→CCSD→CCSD(T). Square brackets signify results obtained from basis set extrapolations or additivity assumptions. Final predictions are boldfaced.

Table S3: Focal point analysis of the C_{3h} transition state energy of *t*-butyl anion relative to the C_{3v} global minimum structure (ΔE_v, kcal mol^{-1}).[a]

Basis Set	ΔE_e[RHF]	δ[MP2]	δ[CCSD]	δ[CCSD(T)]	ΔE_e[CCSD(T)]
cc-pVDZ	+16.04	+1.46	−0.36	+0.52	[+17.65]
cc-pVTZ	+17.46	+1.39	−0.45	+0.54	[+18.94]
cc-pVQZ	+18.29	+1.53	−0.59	+0.59	[+19.83]
cc-pV5Z	+18.69	+1.60	−0.58	+0.61	[+20.32]
CBS limit	[+18.99]	[+1.67]	[−0.57]	[+0.62]	**[+20.72]**
ΔE_v (final) = ΔE_e[CBS CCSD(T)] + Δ_{core}[CCSD(T)/cc-pCVTZ] + Δ_{ZPVE}[CCSD(T)/cc-pCVTZ] + Δ_{rel}[CCSD(T)/cc-pCVTZ] = +20.72 − 0.16 − 2.94 + 0.06 = **+17.68 kcal mol^{-1}**					
Fit Function	$a+be^{-cX}$	$a+bX^{-3}$	$a+bX^{-3}$	$a+bX^{-3}$	
Points (X)	3,4,5	4,5	4,5	4,5	

[a]The symbol δ denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory in the hierarchy RHF→MP2→CCSD→CCSD(T). Square brackets signify results obtained from basis set extrapolations or additivity assumptions. Final predictions are boldfaced.

Table S4: Harmonic vibrational frequencies (ω_e, in cm^{-1}) and infrared intensities (in km mol^{-1}) of the *t*-butyl radical (C_{3v} global minimum structure) computed at the CCSD(T)/cc-pCVTZ level of theory.

Symmetry	Mode	ω_e	IR Intensity
a_1	ω_1	3060	41
	ω_2	2959	66
	ω_3	1499	18
	ω_4	1423	2
	ω_5	1108	1
	ω_6	771	1
	ω_7	263	3
a_2	ω_8	3105	0
	ω_9	1476	0
	ω_{10}	967	0
	ω_{11}	132	0
e	ω_{12}	3109	40
	ω_{13}	3059	16
	ω_{14}	2953	29
	ω_{15}	1500	2
	ω_{16}	1480	3
	ω_{17}	1401	6
	ω_{18}	1307	4
	ω_{19}	1016	2
	ω_{20}	936	0
	ω_{21}	369	0
	ω_{22}	148	0

Table S5: Harmonic vibrational frequencies (ω_e, in cm^{-1}) and infrared intensities (in km mol^{-1}) of the *t*-butyl anion (C_{3v} lowest-energy structure) computed at the CCSD(T)/cc-pCVTZ level of theory.

Symmetry	Mode	ω_e	IR Intensity
a_1	ω_1	2977	62
	ω_2	2656	866
	ω_3	1477	4
	ω_4	1369	7
	ω_5	1081	151
	ω_6	792	113
	ω_7	394	21
a_2	ω_8	3011	0
	ω_9	1470	0
	ω_{10}	928	0
	ω_{11}	295	0
e	ω_{12}	3016	134
	ω_{13}	2971	136
	ω_{14}	2589	195
	ω_{15}	1474	1
	ω_{16}	1460	10
	ω_{17}	1347	13
	ω_{18}	1208	4
	ω_{19}	1017	11
	ω_{20}	967	0
	ω_{21}	370	0
	ω_{22}	311	2