

Addition/Correction to “High-Level Ab Initio Predictions of Thermochemical Properties of Organosilicon Species: Critical Evaluation of Experimental Data and a Reliable Benchmark Database for Extending Group Additivity Approaches”

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Recently, we reported thermochemical properties of a number of organosilicon species calculated at the W1X-1 level of theory.¹ We have since come to the realization that the atomic reference values used in our original work (Table S1, ESI) were inadvertently based on unrestricted MP2 energies even though the composite W1X-1 protocol uses restricted open-shell wave functions throughout.^{2,3} In this Addition/Correction, we report the revised thermochemical data and demonstrate that they do not change the conclusions of the original paper. The results do, however, provide a cautionary note on the calculation of high-level thermochemical properties for molecules with many heavy (non-hydrogen) atoms.

The performance of restricted open-shell, unrestricted, unrestricted spin contamination corrected, and unrestricted Brueckner doubles variants of the original W1 theory have been discussed in detail by Petersson and co-workers.⁴ The four slightly different methods were found to be virtually indistinguishable on the basis of the data calculated for the G2/97 test set. Though this is certainly true and holds in general for small molecules, even sub-kJ mol⁻¹ level systematic variations in atomic reference energies can lead to large differences when the size of the system in question increases considerably. This is clearly shown by our work even though only one of the components of the W1X-1 methodology was based on an unrestricted reference determinant.

Table 1 includes the W1X-1(UMP2) and CBS-QB3 gas phase standard enthalpies of formation published in our original contribution along with the revised W1X-1(ROMP2) values. A comparison of the two W1X-1 data sets shows that the different atomic reference values lead to enthalpies based on restricted open-shell MP2 wave functions being systematically more exothermic (mean absolute difference of 4.2 kJ mol⁻¹) compared to the values calculated with the unrestricted formalism. The difference is naturally the smallest for systems with the least number of heavy atoms (e.g., SiH₄, 0.8 kJ mol⁻¹) and grows with respect to the molecular size (e.g., SiPh₂(OMe)₂, 8.5 kJ mol⁻¹). As a consequence, the revised W1X-1(ROMP2) enthalpies are now in excellent harmony with the CBS-QB3 values for monosilanes I, with a positive mean signed deviation (MSD) of only 3 kJ mol⁻¹. However, the opposite is true for all other compound classes II–V, VI–IX, X–XII, and XIII and

XIV, and the associated MSD values, –5, –8, –17, and –21 kJ mol⁻¹, respectively, are now significantly more negative than those based on the prior W1X-1(UMP2) data.

Table 2 lists well-established experimental gas phase standard enthalpies of formation for 13 reference silicon compounds used in our original paper along with the calculated values. Unsurprisingly, the W1X-1(UMP2) and W1X-1(ROMP2) values are nearly identical for the structurally simplest alkylsilanes and silanols, with larger differences observed for systems with multiple methyl and ethyl substituents, such as Si₂Me₆ and Si(OEt)₄, in which case the W1X-1(ROMP2) and W2 data are in good agreement with each other. The conclusions in our original paper are unaffected by the changes in the calculated values, and we continue to stress the importance of obtaining accurate experimental thermochemical data on compounds such as SiMe₄ and Si(OEt)₄ for which large differences between reference values and W2 level calculations are observed.

In our original paper, we noted significant differences between our W1X-1(UMP2) values for the methylsilane series and the G4 enthalpies reported by Janbazi et al.,^{7,8} +26.2, –87.3, –160.0, and –233.6 kJ mol⁻¹, for SiH₃Me, SiH₂Me₂, SiHMe₃, and SiMe₄, respectively. These differences persist even after our data have been adjusted to use atomic energies based on restricted open-shell MP2 wave functions (see Table 2). Considering the identical values given by W1X-1(ROMP2) and W2 for the standard enthalpy of formation of SiMe₄, –212.4 and –212.8 kJ mol⁻¹, respectively, the G4 prediction by Janbazi et al. remains questionable even though it matches the well-established experimental value, –233.2 ± 3.2 kJ mol⁻¹.

The last effort reported in our original contribution focused on using the calculated W1X-1 thermochemical data to derive Benson group contributions for 60 silicon-based groups and group pairs. The revised group values based on the W1X-1(ROMP2) energies are given in Tables 3 and 4. We note that the values in Table 3 are nearly, within a few kJ mol⁻¹, identical with the original data. In line with the discussion in the original paper, these values can be considered superior over those reported by Janbazi et al. and Becerra and Walsh. The values for group pairs given in Table 4

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Table 1. Calculated Gas Phase Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol⁻¹) of Monosilanes 1–42, Polysilanes 43–49, Silanols and Alkoxysilanes 50–80, Acyclic Siloxanes 81–150, Cyclic Siloxanes 151–158, and Silylamine 159^a

group	molecule	chemical formula	$\Delta_f H^\circ_{298K}$			
			CBS-QB3	W1X-1(UMP2)	W1X-1(ROMP2)	
I	1	SiH ₄	27.0	35.9	36.7	
	2	SiH ₃ Me	-27.6	-23.8	-22.5	
	3	SiH ₃ Et	-34.4	-32.8	-31.1	
	4	SiH ₃ Vi	94.3	96.9	98.6	
	5	SiH ₃ Ph	130.6	124.8	131.0	
	6	SiH ₃ ⁱ Pr	-52.7	-52.7	-50.5	
	7	SiH ₃ ^t Bu	-70.2	-72.3	-69.6	
	8	SiH ₃ (3-Pe)	-86.8	-90.6	-87.4	
	9	SiH ₂ Me ₂	-85.1	-85.9	-84.1	
	10	SiH ₂ EtMe	-91.9	-94.8	-92.6	
	11	SiH ₂ MeVi	35.9	34.0	36.2	
	12	SiH ₂ MePh	70.5	63.3	67.4	
	13	SiH ₂ Me ⁱ Pr	-110.7	-114.9	-112.2	
	14	SiH ₂ Me ^t Bu	-128.0	-134.2	-131.0	
	15	SiH ₂ Me(3-Pe)	-143.8	-151.7	-148.0	
	16	SiH ₂ Et ₂	-98.8	-103.7	-101.0	
	17	SiH ₂ EtPh	62.9	52.7	58.3	
	18	SiH ₂ Vi ₂	156.6	153.5	156.2	
	19	SiH ₂ Ph ₂	223.4	210.3	216.8	
	20	SiHMe ₃	-145.2	-149.9	-147.7	
	21	SiHEtMe ₂	-152.1	-158.7	-156.0	
	22	SiHMe ₂ Vi	-24.8	-30.6	-28.0	
	23	SiHMe ₂ Ph	8.5	-2.2	2.4	
	24	SiHMe ₂ ⁱ Pr	-171.0	-178.7	-175.6	
	25	SiHMe ₂ ^t Bu	-188.4	-197.9	-194.3	
	26	SiHMe ₂ (3-Pe)	-204.3	-215.3	-211.2	
	27	SiHEtMePh	-0.8	-12.7	-7.7	
	28	SiHMeVi ₂	95.1	88.2	91.4	
	29	SiHMePhVi	127.2	115.7	120.8	
	30	SiHVi ₃	215.4	207.8	211.5	
	31	SiHPhVi ₂	247.5	234.9	240.4	
	32	SiMe ₄	-207.4	-215.0	-212.4	
	33	SiEtMe ₃	-214.4	-223.7	-220.6	
	34	SiMe ₃ Vi	-87.6	-96.5	-93.3	
	35	SiMe ₃ Ph	-55.2	-68.4	-63.4	
	36	SiMe ₂ Vi ₂	31.8	21.9	25.5	
	37	SiEtMe ₂ Ph	-64.9	-78.8	-73.3	
	38	SiMe ₂ PhVi	63.2	49.1	54.6	
	39	SiMe ₂ Ph ₂	94.0	76.0	83.4	
	40	SiMeVi ₃	150.1	139.9	143.9	
	41	SiMePhVi ₂	180.4	166.1	172.1	
	42	SiEt ₄	-238.8	-251.9	-247.4	
II	43	Si ₂ H ₆	74.2	81.1	82.7	
	44	Si ₂ H ₅ Me	20.1	22.9	24.9	
	45	Si ₂ H ₄ Me ₂	-33.4	-34.6	-32.1	
46	Si ₂ Me ₆	-267.3	-280.3	-275.9		
III	47	Si ₃ H ₈	113.7	120.4	122.7	
IV	48	Si ₄ H ₁₀	151.7	158.4	161.5	
V	49	Si ₅ H ₁₂	189.4	196.1	200.0	
VI	50	SiH ₃ OH	-286.7	-280.1	-278.7	
	51	SiH ₂ MeOH	-352.4	-350.7	-348.9	
	52	SiH ₂ EtOH	-359.3	-359.3	-357.0	
	53	SiHMe ₂ OH	-417.7	-419.7	-417.4	
	54	SiMe ₃ OH	-483.4	-488.2	-485.4	
	55	SiH ₃ OMe	-253.7	-245.8	-243.9	
	56	SiH ₂ Me(OMe)	-319.7	-316.4	-314.1	
	57	SiHMe ₂ (OMe)	-384.9	-385.0	-382.3	
	VII	58	SiH ₂ (OH) ₂	-633.2	-628.7	-626.8

Table 1. continued

group	molecule	chemical formula	$\Delta_{\mu}H^{\circ}_{298K}$		
			CBS-QB3	W1X-1(UMP2)	W1X-1(ROMP2)
VIII	59	SiH ₂ (OMe) ₂	-565.7	-557.7	-554.9
	60	SiHMe(OMe) ₂	-635.1	-630.3	-627.0
	61	SiHVi(OMe) ₂	-513.6	-509.5	-505.7
	62	SiHPh(OMe) ₂	-482.7	-483.3	-477.6
	63	SiMe ₂ (OMe) ₂	-705.1	-702.3	-698.5
	64	SiMeVi(OMe) ₂	-584.6	-582.4	-578.1
	65	SiMePh(OMe) ₂	-555.0	-556.8	-550.6
	66	SiVi ₂ (OMe) ₂	-464.3	-462.6	-457.9
	67	SiPhVi(OMe) ₂	-435.4	-437.4	-430.7
	68	SiPh ₂ (OMe) ₂	-406.9	-412.4	-403.9
	69	SiH(OH) ₃	-988.7	-985.9	-983.5
	70	SiMe(OMe) ₂ OH	-992.3	-986.6	-982.7
	71	SiEt(OMe) ₂ OH	-999.1	-994.3	-990.0
	72	SiMe(OMe) ₃	-957.0	-948.6	-944.3
IX	73	SiEt(OMe) ₃	-964.3	-956.7	-951.9
	74	Si(OH) ₄	-1344.2	-1341.7	-1338.7
	75	Si(OMe) ₃ OH	-1243.4	-1232.3	-1227.8
	76	Si(OEt)(OMe) ₂ OH	-1277.0	-1267.5	-1262.6
	77	Si(OEt) ₂ (OMe)OH	-1310.8	-1302.8	-1297.4
	78	Si(OMe) ₄	-1209.9	-1195.8	-1190.9
	79	Si(OEt)(OMe) ₃	-1243.8	-1231.3	-1225.9
X	80	Si(OEt) ₄	-1345.7	-1337.7	-1330.9
	81	O(SiH ₃) ₂	-356.3	-339.7	-337.6
	82	O(SiMe ₃)(SiH ₃)	-556.8	-550.7	-547.1
	83	O(SiF ₃)(SiH ₃)	-1620.9	-1605.9	-1602.9
	84	O(SiH ₂ Me)(SiH ₃)	-422.3	-410.7	-408.1
	85	O(SiH ₂ Vi)(SiH ₃)	-300.1	-289.3	-286.2
	86	O(SiH ₂ Ph)(SiH ₃)	-265.8	-259.6	-254.7
	87	O(SiH ₂ F)(SiH ₃)	-774.9	-759.8	-757.3
	88	O(SiHMe ₂)(SiH ₃)	-489.3	-481.0	-477.9
	89	O(SiHVi ₂)(SiH ₃)	-248.0	-241.3	-237.3
	90	O(SiHF ₂)(SiH ₃)	-1204.1	-1190.3	-1187.6
	91	O(SiHMePh)(SiH ₃)	-335.7	-332.7	-327.3
	92	O(SiH ₂ Me) ₂	-488.3	-481.4	-478.3
	93	O(SiHMe ₂)(SiH ₂ Me)	-555.1	-550.7	-548.0
	94	O(SiH ₂ Ph)(SiH ₂ Me)	-330.6	-329.9	-324.5
	95	O(SiMe ₃)(SiH ₂ Me)	-622.5	-621.2	-617.2
	96	O(SiHMe ₂) ₂	-621.7	-621.6	-617.6
	97	O(SiMe ₃)(SiHMe ₂)	-689.1	-690.8	-686.3
	98	O(SiMe ₃) ₂	-756.2	-760.0	-755.0
	99	O(SiH ₂ Vi) ₂	-244.5	-238.9	-234.9
XI	100	O(SiH ₂ F) ₂	-1192.1	-1179.1	-1176.4
	101	O(SiHF ₂)(SiH ₂ F)	-1619.7	-1607.7	-1604.6
	102	O(SiF ₃)(SiH ₂ F)	-2035.4	-2022.4	-2019.0
	103	O(SiHF ₂) ₂	-2045.5	-2034.6	-2031.3
	104	O(SiF ₃)(SiHF ₂)	-2460.7	-2448.8	-2445.2
	105	O(SiF ₃) ₂	-2874.1	-2861.4	-2857.4
	106	SiH ₂ (OSiH ₃) ₂	-771.7	-746.1	-742.7
	107	SiH ₂ (OSiH ₂ Me)(OSiH ₃)	-838.0	-816.3	-812.4
	108	SiH ₂ (OSiH ₂ Vi)(OSiH ₃)	-716.0	-695.9	-691.5
	109	SiH ₂ (OSiH ₂ Ph)(OSiH ₃)	-680.3	-665.7	-659.4
	110	SiH ₂ (OSiH ₂ F)(OSiH ₃)	-1190.8	-1166.0	-1162.2
	111	SiH ₂ (OSiMe ₃)(OSiH ₃)	-973.7	-958.5	-953.6
	112	SiH ₂ (OSiHMe ₂)(OSiH ₃)	-905.8	-888.5	-884.1
	113	SiH ₂ (OSiHF ₂)(OSiH ₃)	-1620.1	-1596.1	-1592.0
	114	SiH ₂ (OSiF ₃)(OSiH ₃)	-2036.7	-2011.9	-2007.5
	115	SiH ₂ (OSiH ₂ Me) ₂	-904.2	-888.2	-883.8
	116	SiH ₂ (OSiHMe ₂)(OSiH ₂ Me)	-972.0	-959.5	-954.7
	117	SiH ₂ (OSiMe ₃)(OSiH ₂ Me)	-1039.9	-1029.4	-1024.0

Table 1. continued

group	molecule	chemical formula	$\Delta_f H^\circ_{298K}$		
			CBS-QB3	W1X-1(UMP2)	W1X-1(ROMP2)
	118	SiH ₂ (OSiH ₂ F) ₂	-1607.1	-1585.0	-1581.0
	119	SiH ₂ (OSiHMe ₂) ₂	-1039.4	-1030.3	-1025.0
	120	SiH ₂ (OSiMe ₃)(OSiHMe ₂)	-1107.2	-1100.2	-1094.3
	121	SiH ₂ (OSiMe ₃) ₂	-1175.1	-1169.9	-1163.6
	122	SiHMe(OSiH ₃) ₂	-843.2	-821.1	-817.2
	123	SiHVi(OSiH ₃) ₂	-720.8	-699.2	-694.8
	124	SiHPh(OSiH ₃) ₂	-689.0	-671.9	-665.6
	125	SiHF(OSiH ₃) ₂	-1203.6	-1178.3	-1174.5
	126	SiHMe(OSiH ₂ Me)(OSiH ₃)	-909.5	-892.1	-887.7
	127	SiHMe(OSiHMe ₂)(OSiH ₃)	-977.0	-963.4	-958.5
	128	SiHMe(OSiMe ₃)(OSiH ₃)	-1045.1	-1033.0	-1027.7
	129	SiHMe(OSiH ₂ Me) ₂	-975.5	-962.9	-958.0
	130	SiHMe(OSiHMe ₂)(OSiH ₂ Me)	-1043.4	-1034.4	-1029.0
	131	SiHMe(OSiMe ₃)(OSiH ₂ Me)	-1111.3	-1104.1	-1098.2
	132	SiHMe(OSiHMe ₂) ₂	-1110.6	-1104.4	-1098.6
	133	SiHMe(OSiMe ₃)(OSiHMe ₂)	-1179.1	-1174.7	-1168.4
	134	SiHMe(OSiMe ₃) ₂	-1246.5	-1243.8	-1237.0
	135	SiHF(OSiH ₂ F)(OSiH ₃)	-1622.9	-1594.8	-1594.4
	136	SiHF(OSiHF ₂)(OSiH ₃)	-2051.1	-2027.1	-2022.7
	137	SiMe ₂ (OSiH ₃) ₂	-915.5	-894.7	-890.3
	138	SiMe ₂ (OSiH ₂ Me)(OSiH ₃)	-981.5	-965.5	-960.6
	139	SiMe ₂ (OSiHMe ₂)(OSiH ₃)	-1049.1	-1036.6	-1031.2
	140	SiMe ₂ (OSiMe ₃)(OSiH ₃)	-1116.9	-1106.2	-1100.4
	141	SiMe ₂ (OSiH ₂ Me) ₂	-1047.4	-1036.0	-1030.6
	142	SiMe ₂ (OSiHMe ₂)(OSiH ₂ Me)	-1115.0	-1107.2	-1101.4
	143	SiMe ₂ (OSiMe ₃)(OSiH ₂ Me)	-1182.8	-1176.7	-1170.4
	144	SiMe ₂ (OSiMe ₃) ₂	-1317.9	-1316.6	-1309.3
	145	SiMe ₂ (OSiHMe ₂) ₂	-1182.3	-1177.1	-1170.9
	146	SiMe ₂ (OSiMe ₃)(OSiHMe ₂)	-1250.4	-1246.9	-1240.1
	147	SiF ₂ (OSiH ₃) ₂	-1625.4	-1598.9	-1594.8
	148	SiF ₂ (OSiH ₂ F)(OSiH ₃)	-2043.8	-2017.1	-2012.7
	149	SiF ₂ (OSiH ₂ F) ₂	-2460.5	-2434.9	-2430.3
XII	150	O(SiH ₂ OSiH ₃) ₂	-1186.1	-1151.9	-1147.1
XIII	151	(OSiH ₂) ₃	-1215.7	-1196.3	-1192.4
	152	(OSiHMe)(OSiH ₂) ₂	-1290.0	-1273.4	-1269.0
	153	(OSiMe ₂)(OSiH ₂) ₂	-1362.9	-1348.1	-1343.2
	154	(OSiHMe) ₂ (OSiH ₂)	-1363.8	-1350.2	-1345.3
	155	(OSiMe ₂)(OSiHMe)(OSiH ₂)	-1436.6	-1424.6	-1419.1
	156	(OSiHMe) ₃	-1437.3	-1426.6	-1421.2
	157	(OSiMe ₂) ₃	-1653.8	-1648.3	-1641.5
XIV	158	(OSiH ₂) ₄	-1656.2	-1623.5	-1618.1
XV	159	NH(SiMe ₃) ₂	-454.0	-472.0	-457.5

^aUsed abbreviations: Me = methyl, Et = ethyl, ⁱPr = isopropyl, ^sBu = *sec*-butyl, 3-Pe = 3-pentyl, Vi = vinyl, and Ph = phenyl.

Table 2. Experimental (exptl) and Calculated (CBS-QB3, W1X-1(UMP2), W1X-1(ROMP2), and W2) Gas Phase Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol⁻¹) of 13 Reference Silicon Compounds^a

molecule	$\Delta_f H^\circ_{298K}$				
	exptl	CBS-QB3	W1X-1(UMP2)	W1X-1(ROMP2)	W2
SiH ₄	34.3 ± 1.2	27.0	35.9	36.7	
Si ₂ H ₆	79.9 ± 1.5	74.2	81.1	82.7	
Si ₃ H ₈	120.9 ± 4.4	113.7	120.4	122.7	
SiH ₃ Me	-29.1 ± 4.0	-27.6	-23.8	-22.5	
SiH ₂ Me ₂	-94.7 ± 4.0	-85.1	-85.9	-84.1	
SiHMe ₃	-163.4 ± 4.0	-145.2	-149.9	-147.7	
SiMe ₄	-233.2 ± 3.2	-207.4	-215.0	-212.4	-212.8
Si ₂ Me ₆	-303.7 ± 5.5	-267.3	-280.3	-275.9	-277.0
Si(OH) ₄	-1351.3 ± 1.7	-1344.2	-1341.7	-1338.7	
SiMe ₃ (OH)	-500.0 ± 3.0	-483.4	-488.2	-485.4	

Table 2. continued

molecule	$\Delta_f H^\circ_{298K}$				
	exptl	CBS-QB3	W1X-1(UMP2)	W1X-1(ROMP2)	W2
Si(OEt) ₄	-1356.0 ± 6.0	-1345.7	-1337.7	-1330.9	-1331.4
O(SiMe ₃) ₂	-777.4 ± 6.0	-756.2	-760.0	-755.0	-761.0
NH(SiMe ₃) ₂	-477.0 ± 5.0	-454.0	-472.0	-457.5	-460.8

^aExperimental data are taken from the two most recent compilations by Becerra and Walsh.^{5,6}

Table 3. Thermochemical Benson Group Contributions for Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol⁻¹), Entropies (S°_{298K} , J K⁻¹ mol⁻¹), and Heat Capacities (C_p , J K⁻¹ mol⁻¹) Derived from Results of W1X-1(ROMP2) calculations

Benson group	$\Delta_f H^\circ_{298K}$	S°_{298K}	$C_{p,298K}$	$C_{p,500K}$	$C_{p,1000K}$	Benson group	$\Delta_f H^\circ_{298K}$	S°_{298K}	$C_{p,298K}$	$C_{p,500K}$	$C_{p,1000K}$
Si-(C)(H) ₃	20	156	32	45	63	Si-(C _D)(H)(O) ₂	-4	-35	27	35	39
Si-(C _D)(H) ₃	36	149	28	45	64	Si-(F)(H)(O) ₂	-421	71	43	52	58
Si-(H) ₃ (O)	39	151	30	44	63	Si-(C) ₄ ^a	-43	-85	35	33	26
Si-(H) ₃ (Si)	41	152	35	49	68	Si-(C) ₃ (O) ^a	-43	-85	35	33	26
Si-(C) ₂ (H) ₂	0	72	31	40	51	Si-(C) ₃ (C _D)	-29	-87	30	32	26
Si-(C _D) ₂ (H) ₂	31	53	25	40	52	Si-(C) ₃ (Si)	-11	-86	36	35	30
Si-(H) ₂ (O) ₂	11	56	31	41	51	Si-(C) ₂ (C _D) ₂	-15	-106	27	31	27
Si-(H) ₂ (Si) ₂	39	68	36	46	59	Si-(C) ₂ (O) ₂	-53	-104	35	33	27
Si-(C)(C _D)(H) ₂	16	63	28	40	51	Si-(C _D) ₂ (O) ₂	-19	-124	32	39	35
Si-(C)(H) ₂ (O)	11	63	30	39	50	Si-(C)(C _D) ₃	-2	-116	24	31	28
Si-(C)(H) ₂ (Si)	26	69	34	43	55	Si-(C)(O) ₃	-57	-108	36	35	29
Si-(C _D)(H) ₂ (O)	28	53	26	39	51	Si-(C)(C _D)(O) ₂	-35	-111	28	31	26
Si-(F)(H) ₂ (O)	-380	159	38	52	68	Si-(F) ₃ (O)	-1222	214	59	71	78
Si-(C) ₃ (H)	-20	-8	32	36	38	Si-(F) ₂ (O) ₂	-840	87	50	57	60
Si-(C _D) ₃ (H)	24	-34	21	34	40	Si-(O) ₄	-67	-132	43	38	30
Si-(H)(O) ₃	-30	-34	36	39	40	C-(C)(H) ₂ (Si)	-9	34	22	32	50
Si-(C) ₂ (C _D)(H)	-6	-16	28	35	39	C-(C) ₂ (H)(Si)	18	-59	19	28	39
Si-(C) ₂ (H)(O)	-16	-12	32	36	38	O-(H)(Si)	-318	117	14	22	29
Si-(C _D) ₂ (H)(O)	14	-38	25	36	40	O-(C)(Si)	-240	39	5	9	16
Si-(F) ₂ (H)(O)	-808	178	47	60	72	O-(Si) ₂	-416	38	10	17	26
Si-(C)(C _D) ₂ (H)	8	-26	26	36	40	ring strain, 6-membered ring	21	87	-5	-3	-3
Si-(C)(H)(O) ₂	-22	-26	32	37	39	ring strain, 8-membered ring	4	104	4	5	5

^aValues for the group Si-(C)₃(O) have been fixed to those of Si-(C)₄.

Table 4. Thermochemical Benson Group Pair Contributions for Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol⁻¹), Entropies (S°_{298K} , J K⁻¹ mol⁻¹), and Heat Capacities (C_p , J K⁻¹ mol⁻¹) Derived from Results of W1X-1 Calculations

Benson group	$\Delta_f H^\circ_{298K}$	S°_{298K}	$C_{p,298K}$	$C_{p,500K}$	$C_{p,1000K}$
Si-(C _B)(H) ₃ + C _B -(C _B) ₂ (Si)	62	104	35	58	83
Si-(C)(C _B)(H) ₂ + C _B -(C _B) ₂ (Si)	40	37	39	57	74
Si-(C _B)(H) ₂ (O) + C _B -(C _B) ₂ (Si)	54	31	44	62	80
Si-(C _B) ₂ (H) ₂ + C _B -(C _B) ₂ (Si)	79	-3	49	74	98
Si-(C) ₂ (C _B)(H) + C _B -(C _B) ₂ (Si)	17	-47	41	53	62
Si-(C _B)(C _D) ₂ (H) + C _B -(C _B) ₂ (Si)	46	-65	36	53	63
Si-(C _B)(H)(O) ₂ + C _B -(C _B) ₂ (Si)	18	-63	41	53	62
Si-(C)(C _B)(C _D)(H) + C _B -(C _B) ₂ (Si)	31	-60	37	52	62
Si-(C)(C _B)(H)(O) + C _B -(C _B) ₂ (Si)	23	-53	40	53	62
Si-(C) ₃ (C _B) + C _B -(C _B) ₂ (Si)	-6	-118	44	50	50
Si-(C) ₂ (C _B) ₂ + C _B -(C _B) ₂ (Si)	30	-167	55	68	73
Si-(C _B) ₂ (O) ₂ + C _B -(C _B) ₂ (Si)	22	-182	52	66	73
Si-(C) ₂ (C _B)(C _D) + C _B -(C _B) ₂ (Si)	7	-135	40	49	50
Si-(C)(C _B)(C _D) ₂ + C _B -(C _B) ₂ (Si)	20	-147	38	50	51
Si-(C)(C _B)(O) ₂ + C _B -(C _B) ₂ (Si)	-14	-143	45	52	53
Si-(C _B)(C _D)(O) ₂ + C _B -(C _B) ₂ (Si)	1	-154	55	70	74
2*Si-(C) ₃ (N) + N-(H)(Si) ₂	-204	-134	93	98	96

show, however, greater variation with respect to the original W1X-1(UMP2) data. This is to be expected because they are derived from enthalpies calculated for bigger molecules with aromatic substituents. Overall, the revised values reported herein are the most accurate ones determined to date and we recommend

their use in all estimations of thermochemical properties of organosilicon species using Benson's methodology.

The data reported in Tables 3 and 4 were used to estimate the standard enthalpies of formation of organosilicon species examined experimentally by Voronkov et al.⁹⁻¹⁴ An updated

Table 5. Comparison between Experimental (exptl) and Estimated (Benson) Standard Gas Phase Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol^{-1}) of Organosilicon Compounds Studied by Voronkov et al.^a

chemical formula	Benson groups ^{b,c}	$\Delta_f H^\circ_{298K}$ exptl	$\Delta_f H^\circ_{298K}$ Benson	diff
SiH(C ₄ H ₉) ₃	6*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-341.0	-298	43
SiH(C ₅ H ₁₁) ₃	9*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-402.0	-359	43
SiH(C ₆ H ₁₃) ₃	12*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-466.0	-421	45
SiH(C ₇ H ₁₅) ₃	15*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-529.0	-483	46
SiH(C ₈ H ₁₇) ₃	18*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-591.0	-545	46
SiH(C ₉ H ₁₉) ₃	21*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-651.0	-607	44
SiH(C ₁₀ H ₂₁) ₃	24*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-713.0	-669	44
SiH(<i>s</i> -C ₄ H ₉) ₃	6*C-(C)(H) ₃ , 3*C-(C) ₃ (H), 3*tert., 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-355.0	-311	44
SiH(<i>i</i> -C ₄ H ₉) ₃	6*C-(C)(H) ₃ , 3*C-(C) ₂ (H) ₂ , 3*C-(C) ₃ (H), 3*tert., 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-413.0	-373	40
SiH(CH ₃) ₂ (C ₄ H ₉) ₂	4*C-(C) ₂ (H) ₂ , 2*C-(C)(H) ₃ , C-(H) ₃ (Si), 2*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-283.0	-247	36
SiH(CH ₃) ₂ (C ₅ H ₁₁) ₂	6*C-(C) ₂ (H) ₂ , 2*C-(C)(H) ₃ , C-(H) ₃ (Si), 2*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-325.0	-289	36
SiH(CH ₃) ₂ (C ₆ H ₁₃) ₂	8*C-(C) ₂ (H) ₂ , 2*C-(C)(H) ₃ , C-(H) ₃ (Si), 2*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-366.0	-330	36
SiH(CH ₃) ₂ (C ₁₀ H ₂₁) ₂	16*C-(C) ₂ (H) ₂ , 2*C-(C)(H) ₃ , C-(H) ₃ (Si), 2*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-531.0	-495	36
SiH(C ₂ H ₅) ₂ (C ₄ H ₉) ₂	4*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-301.0	-256	45
SiH(C ₂ H ₅) ₂ (C ₅ H ₁₁) ₂	6*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-340.0	-298	42
SiH(C ₂ H ₅) ₂ (C ₆ H ₁₃) ₂	8*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-381.0	-339	42
SiH(C ₂ H ₅) ₂ (C ₈ H ₁₇) ₂	12*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-468.0	-421	47
SiH(C ₂ H ₅) ₂ (C ₁₀ H ₂₁) ₂	16*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-545.0	-504	41
SiH(C ₂ H ₅) ₂ (<i>s</i> -C ₄ H ₉) ₂	5*C-(C)(H) ₃ , 2*C-(C) ₃ (H), 2*tert., 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-315.0	-265	50
SiH(C ₂ H ₅) ₂ (<i>i</i> -C ₄ H ₉) ₂	5*C-(C)(H) ₃ , 2*C-(C) ₂ (H) ₂ , 2*C-(C) ₃ (H), 2*tert., 3*C-(C)(H) ₂ (Si), Si-(H)(C) ₃	-358.0	-306	52
Si(C ₃ H ₇) ₂ (C ₄ H ₉) ₂	6*C-(C) ₂ (H) ₂ , 4*C-(C)(H) ₃ , 4*C-(C)(H) ₂ (Si), Si-(C) ₄	-423.0	-372	51
Si(C ₃ H ₇) ₂ (C ₆ H ₁₃) ₂	7*C-(C) ₂ (H) ₂ , 4*C-(C)(H) ₃ , 4*C-(C)(H) ₂ (Si), Si-(C) ₄	-444.0	-392	52
Si(C ₃ H ₇) ₂ (OC ₂ H ₅) ₂	4*C-(C)(H) ₃ , 2*C-(C) ₂ (H) ₂ , 2*C-(C)(H) ₂ (O), 2*C-(C)(H) ₂ (Si), 2*O-(C)(Si), Si-(C) ₂ (O) ₂	-852.0	-827	25
Si(OC ₂ H ₅) ₄	4*C-(C)(H) ₃ , 4*C-(C) ₂ (H) ₂ , 4*C-(C)(H) ₂ (O), 4*O-(C)(Si), Si-(O) ₄	-1397.0	-1410	-13
Si(OC ₂ H ₉) ₄	8*C-(C) ₂ (H) ₂ , 4*C-(C)(H) ₃ , 4*C-(C)(H) ₂ (O), 4*O-(C)(Si), Si-(O) ₄	-1482.0	-1493	-11
(OSiPh ₂) ₃	30*C _B -(C _B) ₂ (H), 3*[Si-(C _B) ₂ (O) ₂ +C _B -(C _B) ₂ (Si)], 3*O-(Si) ₂ , 6-member	-880.0	-747	133
(OSiMe ₂) ₄	8*C-(H) ₃ (Si), 4*Si-(C) ₂ (O) ₂ , 4*O-(Si) ₂ , 8-member	-2138.0	-2210	-72
(OSiMe ₂) ₂ (OSiPh ₂) ₃	30*C _B -(C _B) ₂ (H), 2*C-(H) ₃ (Si), 4*O-(Si) ₂ , 3*[Si-(C _B) ₂ (O) ₂ +C _B -(C _B) ₂ (Si)], Si-(C) ₂ (O) ₂ , 8-member	-1454.0	-1317	137
(OSiMe ₂) ₂ (OSiPh ₂) ₂	20*C _B -(C _B) ₂ (H), 4*C-(H) ₃ (Si), 4*O-(Si) ₂ , 2*[Si-(C _B) ₂ (O) ₂ +C _B -(C _B) ₂ (Si)], 8-member	-1691.0	-1615	76
(OSiMe ₂) ₃ (OSiPh ₂)	10*C _B -(C _B) ₂ (H), 6*C-(H) ₃ (Si), 4*O-(Si) ₂ , 3*[Si-(C _B) ₂ (O) ₂ +C _B -(C _B) ₂ (Si)], 8-member	-1910.0	-1920	-2
(OSiMe ₂) ₄	40*C _B -(C _B) ₂ (H), 4*[Si-(C _B) ₂ (O) ₂ +C _B -(C _B) ₂ (Si)], 4*O-(Si) ₂ , 8-member	-1226.0	-1022	206
(OSiMePh ₄)	4*C-(H) ₃ (Si), 20*C _B -(C _B) ₂ (H), 4*[Si-(C)(C _B) ₂ (O) ₂ +C _B -(C _B) ₂ (Si)], 4*O-(Si) ₂ , 8-member	-1685.0	-1609	76
Si(OCH ₃) ₃ [(CH ₂) ₂ SCH ₃] ₃	3*C-(H) ₃ (O), C-(C)(H) ₂ (S), C-(H) ₃ (S), S-(C) ₂ , 3*O-(C)(Si), C-(C)(H) ₂ (Si), Si-(C)(O) ₃	-946.6	-933	15
Si(OCH ₃) ₃ [(CH ₂) ₃ SCH ₃] ₃	3*C-(H) ₃ (O), C-(C) ₂ (H) ₂ (S), C-(C)(H) ₂ (S), C-(H) ₃ (S), S-(C) ₂ , 3*O-(C)(Si), C-(C)(H) ₂ (Si), Si-(C)(O) ₃	-957.0	-954	5
Si(OCH ₃) ₃ [(CH ₂) ₄ S(CH ₂ CH ₃)] ₃	3*C-(H) ₃ (O), 2*C-(C)(H) ₂ (S), C-(H) ₃ (S), S-(C) ₂ , 3*O-(C)(Si), C-(C)(H) ₂ (Si), Si-(C)(O) ₃	-962.2	-956	8
Si(OCH ₃) ₃ [(CH ₂) ₅ S(CH ₂ CH ₃)] ₃	3*C-(H) ₃ (O), 2*C-(C)(H) ₂ (S), C-(C) ₂ (H) ₂ , C-(H) ₃ (S), S-(C) ₂ , 3*O-(C)(Si), C-(C)(H) ₂ (Si), Si-(C)(O) ₃	-979.9	-977	5
Si(OCH ₃) ₃ [(CH ₂) ₆ S(CH ₂ CH ₃)] ₃	4*C-(C)(H) ₃ , 3*C-(C)(H) ₂ (O), 2*C-(C)(H) ₂ (S), S-(C) ₂ , 3*O-(C)(Si), C-(C)(H) ₂ (Si), Si-(C)(O) ₃	-1069.0	-1055	16
Si(OCH ₃) ₃ [(CH ₂) ₇ S(CH ₂ CH ₃)] ₃	4*C-(C)(H) ₃ , 3*C-(C) ₂ (H) ₂ , 3*C-(C)(H) ₂ (O), 2*C-(C)(H) ₂ (S), S-(C) ₂ , 3*O-(C)(Si), C-(C)(H) ₂ (Si), Si-(C)(O) ₃	-1119.0	-1115	4

^aSee refs 9–14 for details of the experimental work. ^bLiterature values (kJ mol^{-1}): C-(C)(H)₃(O) = C-(H)₃(Si) = -42.26, C-(C)₄ = 19.2, C-(C)₃(H) = -1.17, C-(C)₂(H)₂ = -20.63, C_B-(C_B)₂(H) = -13.81, C-(C)(H)₂(O) = -32.90, C-(C)(H)₂(S) = -23.17, S-(C)₂ = 46.99, tertiary corr = -2.26. ^cDetermined in this work (*italicized*, kJ mol^{-1}): C-(C)₂(H)₂(Si) = 18, C-(C)(H)₂(Si) = -9, Si-(C)₄ = -43, Si-(C)₃(H) = -20, Si-(C)₂(O)₂ = -53, [Si-(C)(C_B)₂(O)₂+C_B-(C_B)₂(Si)] = -14, [Si-(C_B)₂(O)₂+C_B-(C_B)₂(Si)] = 22, Si-(C)(O)₃ = -57, Si-(C)(H)(O)₂ = -22, Si-(O)₄ = -67, O-(Si)₂ = -240, O-(Si)₂ = -416, 6-member ring corr = 21, 8-member ring corr = 4.

version of Table S4 published in the Supporting Information of our original paper is presented herein as Table 5. The reported values reproduce the same trends as discussed earlier: a systematic difference of around 40 kJ mol^{-1} is seen in the data for tri- and tetrasubstituted alkylsilanes, wildly varying data are observed for longer-chain alkoxy-silanes and phenyl-substituted cyclosiloxanes, and excellent harmony between experimental and estimated enthalpies of formation is noted for trimethoxy- and triethoxysilanes with thioether substituents. Thus, we reiterate our earlier conclusion that the data reported by Voronkov et al. should be flagged in thermochemical databases and treated with caution.

As a last note, while comparing our atomic reference energies to those reported in the original W1X-1 work, we noticed that the protocol for the determination of extrapolation exponents α for ΔCCSD and $\Delta(\text{T})$ energy components had not been described in detail.² A later publication by the same author, however, confirmed that the exponents were determined simultaneously by fitting the energies to the G2/97 set of thermochemical quantities.¹⁵ Although this leads to excellent performance based on the reported benchmark data, it does allow the ΔCCSD and $\Delta(\text{T})$ energy components to compensate for one another in a manner that might not work equally well for all possible molecular systems. Consequently, it is entirely possible that the differences between W1X-1 and CBS-QB3 values noted by us (see above) are not entirely due to deficiencies in the latter method but can also be affected by the extrapolation exponents α used in the former. More detailed investigations of the performance of W1X-1 method with respect to the original W1 and W2 variants are currently underway.

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REFERENCES

- (1) Vuori, H. T.; Rautiainen, J. M.; Kolehmainen, E. T.; Tuononen, H. M. High-Level Ab Initio Predictions of Thermochemical Properties of Organosilicon Species: Critical Evaluation of Experimental Data and a Reliable Benchmark Database for Extending Group Additivity Approaches. *J. Phys. Chem. A* **2022**, *126*, 1729–1742.
- (2) Chan, B.; Radom, L. W1X-1 and W1X-2: W1-Quality Accuracy with an Order of Magnitude Reduction in Computational Cost. *J. Chem. Theory Comput.* **2012**, *8*, 4259–4269.
- (3) Corrected atomic energies (in a.u.) are: -37.85009 , -54.60719 , -75.10585 , -99.80418 , and -289.79580 for C, N, O, F, and Si, respectively.
- (4) Barnes, E. C.; Petersson, G. A.; Montgomery, J. A., Jr.; Frisch, M. J.; Martin, J. M. L. Unrestricted Coupled Cluster and Brueckner Doubles Variations of W1 Theory. *J. Chem. Theory Comput.* **2009**, *5*, 2687–2693.
- (5) Becerra, R.; Walsh, R. Thermochemistry. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons, Ltd., 1998; Vol. 2, pp 153–180, DOI: 10.1002/0470857250.ch4.
- (6) Becerra, R.; Walsh, R. Thermochemistry of Organosilicon Compounds. In *Organosilicon Compounds*; Lee, V. Y., Ed.; Academic Press, 2017; pp 79–113, DOI: 10.1016/B978-0-12-814213-4.00003-4.
- (7) Janbazi, H.; Hasemann, O.; Schulz, C.; Kempf, A.; Wlokas, I.; Peukert, S. Response surface and group additivity methodology for estimation of thermodynamic properties of organosilanes. *Int. J. Chem. Kinet.* **2018**, *50*, 681–690.
- (8) Janbazi, H.; Schulz, C.; Wlokas, I.; Wang, H.; Peukert, S. A group additivity methodology for predicting the thermochemistry of oxygen-containing organosilanes. *Int. J. Chem. Kinet.* **2020**, *52*, 918–932.
- (9) Voronkov, M. G.; Baryshok, V. P.; Klyuchnikov, V. A.; Danilova, T. F.; Pepekin, V. I.; Korchagina, A. N. Thermochemistry of organosilicon compounds: I. Triorganyl-, tetraorganyl-, organylorganoxy- and tetraorganoxy-silanes. *J. Organomet. Chem.* **1988**, *345*, 27–38.
- (10) Voronkov, M. G.; Baryshok, V. P.; Klyuchnikov, V. A.; Korchagina, A. N.; Pepekin, V. I. Thermochemistry of organosilicon compounds: II. 1-Organylsilatranes. *J. Organomet. Chem.* **1989**, *359*, 169–177.
- (11) Voronkov, M. G.; Sorokin, M. S.; Klyuchnikov, V. A.; Shvets, G. N.; Pepekin, V. I. Thermochemistry of organosilicon compounds: III. (Organylthioalkyl)trialkoxysilanes and 1-(organylthioalkyl)silatranes. *J. Organomet. Chem.* **1989**, *359*, 301–313.
- (12) Voronkov, M. G.; Klyuchnikov, V. A.; Sokolova, E. V.; Danilova, D. F.; Shvets, G. N.; Korchagina, A. N.; Gussel'nikov, L. E.; Volkova, V. V. Thermochemistry of organosilicon compounds: IV. Thermochemical properties of Si-substituted silacyclobutanes. *J. Organomet. Chem.* **1991**, *401*, 245–248.
- (13) Voronkov, M. G.; Klyuchnikov, V. A.; Mironenko, E. V.; Shvets, G. N.; Danilova, T. F.; Khudobin, Yu. I. Thermochemistry of organosilicon compounds: V. Thermochemical properties of perorganyloligocyclosiloxanes. *J. Organomet. Chem.* **1991**, *406*, 91–97.
- (14) Voronkov, M. G.; Klyuchnikov, V. A.; Marenkova, L. I.; Danilova, T. F.; Shvets, G. N.; Tsvetnitskaya, S. I.; Khudobin, Y. I. Thermochemistry of organosilicon compounds: VI. Thermochemical properties of organosilicon compounds with a Si–N bond. *J. Organomet. Chem.* **1991**, *406*, 99–104.
- (15) Chan, B. How to computationally calculate thermochemical properties objectively, accurately, and as economically as possible. *Pure Appl. Chem.* **2017**, *89*, 699–713.