Supplementary Information

The protonation of carbenes structural effects on the α-proton acidity of carbocations

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Table 1. G3(MP2) Enthalpies and Free Energies of Carbocations, Carbocation Precursors, and Related Species (hartrees).[a] Point Groups[b] and Selected Geometric Features.

Carbocation and Precursors (Point Group)	H (298K, 1 atm.)[c]	G (298K, 1 atm.)[c]	Geometric Feature(s)[d]
^{1}dimethylcarbene (C2v)	-117.555846	-117.584265	$\Phi = 110.1$
^{3}dimethylcarbene ((C1/C2v)	-117.552875	-117.585962	$\Phi = 130.5$
	* * *		
tert-butyl^{+} (C1)	-157,206518	-157.242001	
isobutane (C3v)	-158.112675	-158.146020	
2-methyl-2-propanol (C1)	-233.262722	-233.299403	
isobutylene (C1/C2v)	-156.903982	-156.937671	
benzyl^{+} (C_1/C_{2v})	-270.148084	-270.183853	Θ(ring, $C^{+}H_2$) = 0.0
toluene (C_s)	-271.058922	-271.097378	
benzyl alcohol (C_1)	-346.196280	-346.235909	
^{1}phenylcarbene (C_1/C_s)	-269.733859	-269.769278	$\Phi(HCC_{RING}) = 106.4$
^{3}phenylcarbene (C_s)	-269.737248	-269.774168	$\Phi(HCC_{RING}) = 132.2$
	* * *		
1-phenylethyl^{+} (C_1/C_s)	-309.398541	-309.438369	$\Phi(CC^{+}C_{RING}) = 128.7$ Θ(ring, $CH^{+}CH_3$) = 0.0
ethylbenzene (C_1)	-310.291540	-310.332061	
1-phenylethanol (C_1)	-385.436496	-385.479033	
styrene (C_1)	-309.082102	-309.121210	Θ(ring, CH=C) = 26.6
^{1}methylphenylcarbene (C_1)	-308.976428	-309.016947	$\Phi(CCC_{RING}) = 114.6$ Θ(ring, $CHCH_3$ = 32.2
^{3}methylphenylcarbene (C_s)	-308.977731	-309.019702	$\Phi(CCC_{RING}) = 133.3$ Θ(ring, $CHCH_3$ = 0.0

Table 1. G3(MP2) Enthalpies and Free Energies of Carbocations, Carbocation Precursors, and Related Species (hartrees).[a] Point Groups[b] and Selected Geometric Features.

Carbocation and Precursors (Point Group)	H (298K, 1 atm.)[c]	G (298K, 1 atm.)[c]	Geometric Feature(s)[d]
2-phenylpropyl$^+$ (C_1/C_2)	-348.643870	-348.688300	Θ(ring, C(CH$_3$)$_2$ = 7.3
2-phenylpropane (C_1)	-349.526107	-349.569427	
2-phenyl-2-propanol (C_s)	-424.673963	-424.719200	
α-methylstyrene (C_1)	-348.318479	-348.360816	Θ(ring, C(C)=C) = 40.6
	*	* *	
diphenylmethyl$^+$ (C1/C2)	-500.828936	-500.876468	d(C-C$_{RING}$) = 1.411, ϕ(C$_{Ar}$-C-C$_{Ar}$) = 129[h]
diphenylmethane (C1/C2)	-501.706233	-501.755817	d(C-C$_{RING}$) = 1.510, ϕ(C$_{Ar}$-C-C$_{Ar}$) = 112
^{1}diphenylcarbene (C1/C2)	-500.401930	-500.449636	d(C-C$_{RING}$) = 1.439, ϕ(C$_{Ar}$-C-C$_{Ar}$) = 115[h]
^{1}diphenylcarbene (C1/C2)	-500.436746[i]	-500.485720[i]	
^{3}diphenylcarbene (C1/C2)	-500.397719	-500.447984	d(C-C$_{RING}$) = 1.419, ϕ(C$_{Ar}$-C-C$_{Ar}$) = 136[h]
^{3}diphenylcarbene (C1/C2)	-500.429371[i]	-500.476537[i]	
	*	* *	
methoxymethyl$^+$ (C1/Cs)	-153.856324	-153.886692	Θ = 180.0
^{1}methoxycarbene (C1/Cs) extended form	-153.486245	-153.516175	ϕ = 101.4, Θ = 180.0
methoxymethane (C1/C2v)	-154.764705	-154.795430	
1-methoxyethyl$^+$ (C1/Cs)	-193.118961	-193.153791	Φ = 120.1, Θ = 180.0
^{1}methoxymethylcarbene (C1/Cs)	-192.732530	-192.767564	Φ = 106.3, Θ(COCC) = 180.0

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Carbocation and Precursors (Point Group)	H (298K, 1 atm.)[c]	G (298K, 1 atm.)[c]	Geometric Feature(s)[d]
methoxyethylene (C1)	-192.792.408	-192.826461	Θ = 158.6
ethyl methyl ether (C1)	-194.002110	-194.036497	
	* * *		
dimethoxymethyl$^+$ (C1/C2)	-268.274132	-268.312094	Φ = 121.6, Θ = 0.0
^{1}dimethoxycarbene (C1/C2)	-267.898677	-267.936473	ϕ = 104.3, Θ = 180.0
dimethoxymethane (C1)	-269.130363	-269.168036	

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[a] One hartree = 627.51 kcal/mol. GAUSSIAN 03, Revision B.04, Frisch, M. J, et al., Gaussian, Inc., Pittsburgh PA, 2003. The G3 method uses a composite "…recipe involving a variety of different models with the purpose of providing accurate themochemical data." See Hehre, W. J. *A Guide to Molecular Mechanics and Quantum Chemical Calculations*; Wavefunction, Inc.: Irvine, CA, 2003, p 252. Results are estimated to be accurate within about 2 kcal/mol or less. [b] A slash indicates the species has virtually the higher symmetry. [c] A scaling factor of 0.9135 was used for vibrations. [d] Distances (d) are in Å; angles (Φ) and dihedrals (Θ) are in degrees. [e] This is the experimental electronic energy of the hydride ion. [f] The experimental values for the angles are ~102^o for the singlet and ~137^o for the triplet. See (a) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485. (b) Shavitt, I. *Tetrahedron* **1985**, *41*, 1531. Also See Moss, R. A.; .Platz, M. S.; Jones, M., Jr., Eds., *Reactive Intermediate Chemistry*; Wiley-Interscience: New York, 2004, p 277. This volume has five chapters covering various aspects of carbene chemistry. [g] Ethyl$^+$ is a symmetrically bridged cation. [h] The rings are tilted from the line defined by the C^+-H bond of the cation by 19,5^o, from the plane defined by C_{Ar}-C-C_{Ar} in the singlet carbene by 30.7^o, and from the plane defined by C_{Ar}-C-C_{Ar} in the triplet carbene by 25.2^o. [i] These values were obtained using the G3MP2B3 method.

Table 2. Calculated MP2/6-311+G* Electronic Energies[1], Zero Point Vibrational Energies[2], and Imaginary Frequencies[2] for Dimethoxycarbene and Dimethoxycarbenium Conformers

Conformer (point group)[3]	Electronic Energy (hartrees)	ZPVE(kcal/mol)	iν (cm^{-1})
	Dimethoxycarbenes		
1 W form (C2)	-267.6440703	59.40	NA
2 W → Z ts	-267.6163288	58.85	-259.4
3 Z form	-267.6406846	59.62	NA
4 Z → U ts	-267.6071099	58.66	-201.8
5 U form	-267.6115868	59.30	
	Dimethoxycarbenium ions		
6^+ HW^+ form	-268.0296472	68.48	NA
7^+ $HW^+ \rightarrow HZ^+$ ts	-268.0060496	67.72	-289.1
8^+ HZ^+ form (Cs)	-268.0346935	68.71	NA
9^+ $HZ^+ \rightarrow HU^+$ ts	-268.0061695	67.85	-227.3
10^+ HU^+ form	-268.0192260	68.66	NA

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[1] Electronic energies were calculated by optimization at the MP2/6-311+G** level. [2] Frequencies and zero point vibrational energies were calculated at the HF/6-311+G** level. [3] Conformer symbols: the W form is the fully extended conformer; the Z form has the two methoxy units *anti* to one another; the U form has them approximately *syn* to one another; ts stands for the rotational transition states by which the specified stable conformers interconver

Table 3. Dimethoxycarbene and Dimethoxycarbenium Ion,: Selected Geometric Features[1] for the Skeletal Framework: C1-O2-C3-O4-C5calculated at the MP2/6-311+G* level

Conformer[2]	O2-C3, O4-C3 lengths (Å)	O2,C3,O4 angle	C1-O2, C5-O4 dihedral	Rotational Progress at ts
1 **W** form	1.320, 1.320	105.6°	0.0°	NA
2 **W→Z** ts	1.360, 1.311	106.5°	110.6°	61%
3 **Z** form	1.332, 1.316	109.3°	180.0°	NA
4 **Z→U** ts	1.366, 1.311	113.1°	112.9°	84%
5 **U** form	1.330, 1.330	116.4°	45.7°	NA
6 **HW$^+$** form	1.265, 1.266	117.9°	0.0°	NA
7 **HW$^+$→HZ$^+$** ts	1.271, 1.263	119.8°	119.4°	66%
8 **HZ$^+$** form	1.270, 1.264	122.0°	180.1°	NA
9 **HZ$^+$→HU$^+$** ts	1.279, 1.263	125.0°	112.5°	62.5%
10 **HU$^+$** form	1.269, 1.270	132.5°	0.1°	NA

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[1] All geometries were optimized at the MP2/6-311+G** level. [2] Conformer symbols: the W forms are the fully extended conformers; the Z forms have the two methoxy units *anti* to one another; the U forms have them approximately *syn* to one another; ts stands for the rotational transition states by which the specified stable conformers interconvert.

Table 4. Experimental[a] and G3(MP2) Calculated[b] Gas Phase Enthalpies and Free Energies of Reaction for Some Reactions of Carbocations, kcal/mol, 298K, 1 atm.

Reactions	ΔH_{RXN} (exp)[c]	ΔH_{RXN} (calc)[c]	ΔG_{RXN} (calc)
1. $^1CH_2 \rightarrow {}^3CH_2$	-9[d]	-9.4	-9.9
$^1CH_2 + H_2 \rightarrow CH_4$		-118.1	-108.7
$^3CH_2 + H_2 \rightarrow CH_4$	-110.2	-108.7	-98.8
$CH_3^+ \rightarrow H^+ + {}^1CH_2$	205.2	205.2	205.0
$CH_3^+ + H_2O \rightarrow CH_3OH + H^+$	113.6	113.4	123.2
$^1CH_2 + H_2O \rightarrow CH_3OH$	-91.6	-91.8	-81.8
$CH_3^+ + H^- \rightarrow CH_4$	-314.5	-313.9	-313.9
	* * *		
2. $^1CH_3CH \rightarrow {}^3CH_3CH$	-3 to -5	-2.9	-4.2
$^1CH_3CH + H_2 \rightarrow CH_3CH_3$		-106.0	-96.4
$^1CH_3CH \rightarrow CH_2{=}CH_2$		-75.3	-74.4
$C_2H_5^+ \rightarrow H^+ + CH_2{=}CH_2$	162.6	160.3	161.6
$C_2H_5^+ \rightarrow H^+ + {}^1CH_3CH$		235.7	236.0
$C_2H_5^+ + H_2O \rightarrow CH_3CH_2OH + H^+$		150.3	161.4
$^1CH_3CH + H_2O \rightarrow CH_3CH_2OH$		-85.3	-74.6
$C_2H_5^+ + H^- \rightarrow CH_3CH_3$	-276.7	-269.3	-268.7
	* * *		
3. $^1(CH_3)_2C \rightarrow {}^3(CH_3)_2C$	1.5	1.9	-1.1
$^1(CH_3)_2C + H_2 \rightarrow CH_3CH_2CH_3$		-97.1	-89.6
$^1(CH_3)_2C \rightarrow CH_2{=}CHCH_3$		-69.1	-70.2
$(CH_3)_2CH^+ \rightarrow H^+ + CH_2{=}CHCH_3$	179.6	176.8	176.3
$(CH_3)_2CH^+ \rightarrow H^+ + {}^1(CH_3)_2C$		245.9	246.5
$(CH_3)_2CH^+ + H_2O \rightarrow (CH_3)_2CHOH + H^+$		165.2	175.8
$^1(CH_3)_2C + H_2O \rightarrow (CH_3)_2CHOH$		-80.7	-70.7
$(CH_3)_2CH^+ + H^- \rightarrow CH_3CH_2CH_3$	-250.0	-250.2	-251.4
	* * *		
4. $(CH_3)_3C^+ \rightarrow H^+ + (CH_3)_2{=}CH_2$	191.7	189.8	191.0
$(CH_3)_3C^+ + H_2O \rightarrow (CH_3)_3COH + H^+$		176.9	189.6
$(CH_3)_3C^+ + H^- \rightarrow (CH_3)_3CH$	-232.0	-235.5	-234.2

Table 4. Experimental[a] and G3(MP2) Calculated[b] Gas Phase Enthalpies and Free Energies of Reaction for Some Reactions of Carbocations, kcal/mol, 298K, 1 atm.

Reactions	ΔH_{RXN} (exp)[c]	ΔH_{RXN} (calc)[c]	ΔG_{RXN} (calc)
5. $^1PhCH \rightarrow {}^3PhCH$	-2.3[d]	-2.1	-3.1
$PhCH_2^+ \rightarrow {}^1PhCH + H^+$		259.9	260.1
$^1PhCH + H_2 \rightarrow PhCH_3$		-99.4	-92.1
$PhCH_2^+ + H_2O \rightarrow PhCH_2OH + H^+$	184.2	182.0	192.9
$^1PhCH + H_2O \rightarrow PhCH_2OH$		-78.0	-67.2
$PhCH_2^+ + H^- \rightarrow PhCH_3$	-239.5	-240.5	-242.1
* * *			
6, $^1PhCCH_3 \rightarrow {}^3PhCCH_3$	-2.0 (heptane)[e]	-0.8	-1.7
$^1PhCCH_3 \rightarrow PhCH{=}CH_2$		-66.3	-63.7
$^1PhCCH_3 + H_2 \rightarrow PhCH_2CH_3$		-93.2	-83.9
$PhCHCH_3^+ \rightarrow {}^1PhCCH_3 + H^+$		264.9	264.4
$PhCHCH_3^+ \rightarrow PhCH{=}CH_2 + H^+$	200.6	198.6	199.0
$PhCHCH_3^+ + H_2O$ $\rightarrow PhCH(OH)CH_3 + H^+$		188.4	200.1
$^1PhCCH_3 + H_2O \rightarrow PhCH(OH)CH_3$		-76.5	-64.4
$PhCHCH_3^+ + H^- \rightarrow PhCH_2CH_3$	-227.8	-229.3	-229.7
* * *			
7. $PhC(CH_3)_2^+ \rightarrow PhC(CH_3){=}CH_2 + H^+$	206.5	204.2	205.5
$PhC(CH_3)_2^+ + H_2O$ $\rightarrow PhC(CH_3)_2OH + H^+$		193.3	206.2
$PhC(CH_3)_2^+ + H^- \rightarrow PhCH(CH_3)_2$	-221.3	-222.5	-221.8
* * *			
8. $^1Ph_2C \rightarrow {}^3Ph_2C$	-3.6 (cyclohexane)[e]	2.6 (4.6)	1.0 (5.8)
$^1Ph_2C + H_2 \rightarrow Ph_2CH_2$		-86.4	-78.3
$Ph_2CH^+ \rightarrow {}^1Ph_2C + H^+$		268.0	267.8
$Ph_2CH^+ + H^- \rightarrow Ph_2CH_2$		-217.4	-218.7

Table 4. Experimental[a] and G3(MP2) Calculated[b] Gas Phase Enthalpies and Free Energies of Reaction for Some Reactions of Carbocations, kcal/mol, 298K, 1 atm.

Reactions	ΔH_{RXN} (exp)[c]	ΔH_{RXN} (calc)[c]	ΔG_{RXN} (calc)
9. $CH_3O{=}CH_2^+ \rightarrow {}^1CH_3OCH + H^+$		232.2	232.5
$CH_3O{=}CH_2^+ + H^- \rightarrow CH_3OCH_3$		-238.9	-237.1
${}^1CH_3OCH + H_2 \rightarrow CH_3OCH_3$		-70.2	-61.4
10. $(CH_3O)_2CH^+ \rightarrow (CH_3O)_2C + H^+$		235.6	235.7
$(CH_3O)_2CH^+ + H^- \rightarrow (CH_3O)_2CH_2$		-206.2	-204.0
$(CH_3O)_2C + H_2 \rightarrow (CH_3O)_2CH_2$		-40.8	-31.5

* * *

Reactions	ΔH_{RXN} (exp)[c]	ΔH_{RXN} (calc)[c]	ΔG_{RXN} (calc)
11. ${}^1CH_3OCCH_3 \rightarrow CH_3OCH{=}CH_2$		-37.6	-37.0
${}^1CH_3OCCH_3 \rightarrow {}^1HOCH_2CCH_3$		23.4	23.8
${}^1HOCH_2CCH_3 \rightarrow HOCH_2CH{=}CH_2$		-66.7	-66.0
$CH_3OCH{=}CH_2 \rightarrow HOCH_2CH{=}CH_2$		-5.8	-5.3
$CH_3O{=}CH\text{-}CH_3^+ \rightarrow CH_3OCH{=}CH_2 + H^+$	205.4	204.9	205.4
$CH_3O{=}CH\text{-}CH_3^+ + H^- \rightarrow CH_3OCH_2CH_3$		221.1	-220.8

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[a] Experimental heats of reaction, and heats of formation for reactants and products were taken from or calculated from data given in the following sources: (a) Bartmess, J. E. In *NIST Standard Reference Database Number 69,* Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology (http://webbook.nist.gov): Gaithersburg, MD, 2005. (b) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98,* 2744. (c) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255. [b] GAUSSIAN 03, Revision B.04, Frisch, M. J, et al., Gaussian, Inc., Pittsburgh PA, 2003. [c] ΔH for reactions of alkenes or carbenes with H^+ provide proton affinities (PA), those of carbocations with water giving alcohols and H^+ are related to a gas phase K_{R+}, those of carbocations with hydride ion give the negative of the hydride ion affinity (HIA) of the cations. The experimental electronic energy for the hydride ion, 333.1 kcal/mol, was used in the HIA evaluations. [d] The singlet-triplet carbene energy differences are from (a) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485. (b) Shavitt, I. *Tetrahedron* **1985**, *41*, 1531. (c) Admasu, A.; Gudmundsdottir, A. D.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 3832. (d) Sugiyama, M. H.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966. Also See Moss, R. A.; .Platz, M. S.; Jones, M., Jr., Eds., *Reactive Intermediate Chemistry*; Wiley-Interscience: New York, 2004, p 279, 397. [e] ΔG value. In acetonitrile $\Delta G = -3.3$ kcal/mol and $\Delta H = -2.6$ kcal/mol: Eisenthal, K. B.; Moss, R. A.; Turro, N. J. *Science* **1984**, *225*, 1439. Values in parentheses were calculated with the G3MP2B3 method.

Table 5. G3MP2 Enthalpies of Deprotonation (ΔH_{ACID}) and HIA Values for Some Carbocations. Enthalpies of Hydrogenation (ΔH_{HYDROG}) of the Corresponding Singlet Carbenes (kcal/mol, 298K). Gas Phase Substituent Constants.[1]

Carbocation (Substituents)	ΔH_{ACID}	HIA	ΔH_{HYDROG}	$\Sigma\sigma_F$	$\Sigma\sigma_{R+}$	$\Sigma\sigma_\alpha$
1. methyl (H, H, H)	205.2	-314.5	-118.1	0	0	0
2. ethyl (Me, H, H)	235.7	-276.7	-106.0	0	-0.08	-0.35
3. isopropyl (Me, Me, H)	245.9	-250.0	-97.1	0	-0.16	-0.70
4. benzyl (Ph, H, H)	259.9	-240.5	-99.4	0.10	-0.22	-0.81
5. α-phenethyl (Ph, CH_3, H)	264.9	-229.3	-93.2	0.10	-0.30	-1.16
6. methoxymethyl (OMe, H, H)	232.2	-238.9	-70.2	0.25	-0.42	-0.17
6. diphenylmethyl	268.0	-217.4	-86.4			
7. dimethoxymethyl (OMe, OMe, H)	235.6	-206.2	-40.8	0.50	-0.84	-0.34
8. 1-methoxyethyl (OMe, Me, H)	242.5	-221.1	-64.6	0.25	-0.50	-0.52

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[1] Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

The following correlations were established using the "Solver" function within the Excel software package. The coefficients correspond to the respective ρ values and r^2 indicates the quality of the correlation

ΔH_{ACID} (G3) = $36.2\sigma_F - 11.7\sigma_{R+} - 48.7\sigma_\alpha + 213.8$ $r^2 = 0.909$

HIA (G3) = $-111.6\sigma_F - 178.5\sigma_{R+} - 34.4\sigma_\alpha - 304.1$ $r^2 = 0.945$

$\Delta H_{HYDROG} = -129.3\sigma_F - 175.5\sigma_{R+} + 14.5\sigma_\alpha - 114.7$ $r^2 = 0.985$