

## Supplementary Information

### The protonation of carbenes structural effects on the $\alpha$ -proton acidity of carbocations

J. R. Keeffe and R. A. More O’Ferrall<sup>a</sup>

<sup>a</sup>*School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland and Department of Chemistry and Biochemistry, San Francisco State University, 1600 Holloway Avenue, San Francisco, California 94132*

*E-mail: [rmof@ucd.ie](mailto:rmof@ucd.ie)*

#### Contents

1. G3(MP2) Enthalpies and Free Energies of Carbocations, Carbocation Precursors, and Related Species (hartrees).<sup>a</sup> Point Groups<sup>b</sup> and Selected Geometric Features S2
2. Calculated MP2/6-311+G\* Electronic Energies<sup>1</sup>, Zero Point Vibrational Energies<sup>2</sup>, and Imaginary Frequencies<sup>2</sup> for Dimethoxycarbene and Dimethoxycarbenium Conformers S5
3. Dimethoxycarbene and Dimethoxycarbenium Ion,: Selected Geometric Features<sup>1</sup> for the Skeletal Framework: C1-O2-C3-O4-C5calculated at the MP2/6-311+G\* level S6
4. Experimental<sup>a</sup> and G3(MP2) Calculated<sup>b</sup> Gas Phase Enthalpies and Free Energies of Reaction S7
5. G3MP2 Enthalpies of Deprotonation ( $\Delta H_{\text{ACID}}$ ) and HIA Values for Some Carbocations. Enthalpies of Hydrogenation ( $\Delta H_{\text{HYDROG}}$ ) of the Corresponding Singlet Carbenes (kcal/mol, 298K). Gas Phase Substituent Constants.<sup>1</sup> S10

**Table 1. G3(MP2) Enthalpies and Free Energies of Carbocations, Carbocation Precursors, and Related Species (hartrees).<sup>a</sup> Point Groups<sup>b</sup> and Selected Geometric Features.**

Carbocation and Precursors (Point Group)	H (298K, 1 atm.) <sup>c</sup>	G (298K, 1 atm.) <sup>c</sup>	Geometric Feature(s) <sup>d</sup>
<sup>1</sup> dimethylcarbene (C <sub>2v</sub> )	-117.555846	-117.584265	$\Phi = 110.1$
<sup>3</sup> dimethylcarbene ((C <sub>1</sub> /C <sub>2v</sub> ))	-117.552875	-117.585962	$\Phi = 130.5$
	*	*	*
<i>tert</i> -butyl <sup>+</sup> (C <sub>1</sub> )	-157.206518	-157.242001	
isobutane (C <sub>3v</sub> )	-158.112675	-158.146020	
2-methyl-2-propanol (C <sub>1</sub> )	-233.262722	-233.299403	
isobutylene (C <sub>1</sub> /C <sub>2v</sub> )	-156.903982	-156.937671	
benzyl <sup>+</sup> (C <sub>1</sub> /C <sub>2v</sub> )	-270.148084	-270.183853	$\Theta(\text{ring}, \text{C}^+\text{H}_2) = 0.0$
toluene (C <sub>s</sub> )	-271.058922	-271.097378	
benzyl alcohol (C <sub>1</sub> )	-346.196280	-346.235909	
<sup>1</sup> phenylcarbene (C <sub>1</sub> /C <sub>s</sub> )	-269.733859	-269.769278	$\Phi(\text{HCC}_{\text{RING}}) = 106.4$
<sup>3</sup> phenylcarbene (C <sub>s</sub> )	-269.737248	-269.774168	$\Phi(\text{HCC}_{\text{RING}}) = 132.2$
	*	*	*
1-phenylethyl <sup>+</sup> (C <sub>1</sub> /C <sub>s</sub> )	-309.398541	-309.438369	$\Phi(\text{CC}^+\text{C}_{\text{RING}}) = 128.7$ $\Theta(\text{ring}, \text{CH}^+\text{CH}_3) = 0.0$
ethylbenzene (C <sub>1</sub> )	-310.291540	-310.332061	
1-phenylethanol (C <sub>1</sub> )	-385.436496	-385.479033	
styrene (C <sub>1</sub> )	-309.082102	-309.121210	$\Theta(\text{ring}, \text{CH}=\text{C}) = 26.6$
<sup>1</sup> methylphenylcarbene (C <sub>1</sub> )	-308.976428	-309.016947	$\Phi(\text{CCC}_{\text{RING}}) = 114.6$ $\Theta(\text{ring}, \text{CHCH}_3) = 32.2$
<sup>3</sup> methylphenylcarbene (C <sub>s</sub> )	-308.977731	-309.019702	$\Phi(\text{CCC}_{\text{RING}}) = 133.3$ $\Theta(\text{ring}, \text{CHCH}_3) = 0.0$

**Table 1. G3(MP2) Enthalpies and Free Energies of Carbocations, Carbocation Precursors, and Related Species (hartrees).<sup>a</sup> Point Groups<sup>b</sup> and Selected Geometric Features.**

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

**Table 1. G3(MP2) Enthalpies and Free Energies of Carbocations, Carbocation Precursors, and Related Species (hartrees).<sup>a</sup> Point Groups<sup>b</sup> and Selected Geometric Features.**

Carbocation and Precursors (Point Group)	H (298K, 1 atm.) <sup>c</sup>	G (298K, 1 atm.) <sup>c</sup>	Geometric Feature(s) <sup>d</sup>
methoxyethylene (C1)	-192.792.408	-192.826461	$\Theta = 158.6$
ethyl methyl ether (C1)	-194.002110	-194.036497	
	*	*	*
dimethoxymethyl <sup>+</sup> (C1/C2)	-268.274132	-268.312094	$\Phi = 121.6, \Theta = 0.0$
<sup>1</sup> dimethoxycarbene (C1/C2)	-267.898677	-267.936473	$\phi = 104.3, \Theta = 180.0$
dimethoxymethane (C1)	-269.130363	-269.168036	

<sup>a</sup>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 thermochemical 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. <sup>b</sup>A slash indicates the species has virtually the higher symmetry. <sup>c</sup>A scaling factor of 0.9135 was used for vibrations. <sup>d</sup>Distances (d) are in Å; angles ( $\Phi$ ) and dihedrals ( $\Theta$ ) are in degrees. <sup>e</sup>This is the experimental electronic energy of the hydride ion. <sup>f</sup>The experimental values for the angles are  $\sim 102^\circ$  for the singlet and  $\sim 137^\circ$  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. <sup>g</sup>Ethyl<sup>+</sup> is a symmetrically bridged cation. <sup>h</sup>The rings are tilted from the line defined by the C<sup>+</sup>-H bond of the cation by  $19.5^\circ$ , from the plane defined by C<sub>Ar</sub>-C-C<sub>Ar</sub> in the singlet carbene by  $30.7^\circ$ , and from the plane defined by C<sub>Ar</sub>-C-C<sub>Ar</sub> in the triplet carbene by  $25.2^\circ$ . <sup>i</sup>These values were obtained using the G3MP2B3 method.

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

Conformer (point group) <sup>3</sup>	Electronic Energy (hartrees)	ZPVE(kcal/mol)	iv (cm <sup>-1</sup> )
Dimethoxycarbenes			
1 W form (C <sub>2</sub> )	-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 <sup>+</sup> HW <sup>+</sup> form	-268.0296472	68.48	NA
7 <sup>+</sup> HW <sup>+</sup> → HZ <sup>+</sup> ts	-268.0060496	67.72	-289.1
8 <sup>+</sup> HZ <sup>+</sup> form (C <sub>s</sub> )	-268.0346935	68.71	NA
9 <sup>+</sup> HZ <sup>+</sup> → HU <sup>+</sup> ts	-268.0061695	67.85	-227.3
10 <sup>+</sup> HU <sup>+</sup> form	-268.0192260	68.66	NA

<sup>1</sup>Electronic energies were calculated by optimization at the MP2/6-311+G\*\* level. <sup>2</sup>Frequencies and zero point vibrational energies were calculated at the HF/6-311+G\*\* level. <sup>3</sup>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 interconvert

**Table 3. Dimethoxycarbene and Dimethoxycarbenium Ion.: Selected Geometric Features<sup>1</sup> for the Skeletal Framework: C1-O2-C3-O4-C5 calculated at the MP2/6-311+G\* level**

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

<sup>1</sup>All geometries were optimized at the MP2/6-311+G\*\* level. <sup>2</sup>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<sup>a</sup> and G3(MP2) Calculated<sup>b</sup> Gas Phase Enthalpies and Free Energies of Reaction for Some Reactions of Carbocations, kcal/mol, 298K, 1 atm.**

Reactions	$\Delta H_{\text{RXN}}$ (exp) <sup>c</sup>	$\Delta H_{\text{RXN}}$ (calc) <sup>c</sup>	$\Delta G_{\text{RXN}}$ (calc)
<b>1.</b> $^1\text{CH}_2 \rightarrow ^3\text{CH}_2$	-9 <sup>d</sup>	-9.4	-9.9
$^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$		-118.1	-108.7
$^3\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$	-110.2	-108.7	-98.8
$\text{CH}_3^+ \rightarrow \text{H}^+ + ^1\text{CH}_2$	205.2	205.2	205.0
$\text{CH}_3^+ + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{H}^+$	113.6	113.4	123.2
$^1\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH}$	-91.6	-91.8	-81.8
$\text{CH}_3^+ + \text{H}^- \rightarrow \text{CH}_4$	-314.5	-313.9	-313.9
	* * *		
<b>2.</b> $^1\text{CH}_3\text{CH} \rightarrow ^3\text{CH}_3\text{CH}$	-3 to -5	-2.9	-4.2
$^1\text{CH}_3\text{CH} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3$		-106.0	-96.4
$^1\text{CH}_3\text{CH} \rightarrow \text{CH}_2=\text{CH}_2$		-75.3	-74.4
$\text{C}_2\text{H}_5^+ \rightarrow \text{H}^+ + \text{CH}_2=\text{CH}_2$	162.6	160.3	161.6
$\text{C}_2\text{H}_5^+ \rightarrow \text{H}^+ + ^1\text{CH}_3\text{CH}$		235.7	236.0
$\text{C}_2\text{H}_5^+ + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}^+$		150.3	161.4
$^1\text{CH}_3\text{CH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$		-85.3	-74.6
$\text{C}_2\text{H}_5^+ + \text{H}^- \rightarrow \text{CH}_3\text{CH}_3$	-276.7	-269.3	-268.7
	* * *		
<b>3.</b> $^1(\text{CH}_3)_2\text{C} \rightarrow ^3(\text{CH}_3)_2\text{C}$	1.5	1.9	-1.1
$^1(\text{CH}_3)_2\text{C} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3$		-97.1	-89.6
$^1(\text{CH}_3)_2\text{C} \rightarrow \text{CH}_2=\text{CHCH}_3$		-69.1	-70.2
$(\text{CH}_3)_2\text{CH}^+ \rightarrow \text{H}^+ + \text{CH}_2=\text{CHCH}_3$	179.6	176.8	176.3
$(\text{CH}_3)_2\text{CH}^+ \rightarrow \text{H}^+ + ^1(\text{CH}_3)_2\text{C}$		245.9	246.5
$(\text{CH}_3)_2\text{CH}^+ + \text{H}_2\text{O}$ $\rightarrow (\text{CH}_3)_2\text{CHOH} + \text{H}^+$		165.2	175.8
$^1(\text{CH}_3)_2\text{C} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{CHOH}$		-80.7	-70.7
$(\text{CH}_3)_2\text{CH}^+ + \text{H}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3$	-250.0	-250.2	-251.4
	* * *		
<b>4.</b> $(\text{CH}_3)_3\text{C}^+ \rightarrow \text{H}^+ + (\text{CH}_3)_2=\text{CH}_2$	191.7	189.8	191.0
$(\text{CH}_3)_3\text{C}^+ + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{H}^+$		176.9	189.6
$(\text{CH}_3)_3\text{C}^+ + \text{H}^- \rightarrow (\text{CH}_3)_3\text{CH}$	-232.0	-235.5	-234.2

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

Reactions	$\Delta H_{\text{RXN}}$ (exp) <sup>c</sup>	$\Delta H_{\text{RXN}}$ (calc) <sup>c</sup>	$\Delta G_{\text{RXN}}$ (calc)
<b>5.</b> $^1\text{PhCH} \rightarrow ^3\text{PhCH}$	-2.3 <sup>d</sup>	-2.1	-3.1
$\text{PhCH}_2^+ \rightarrow ^1\text{PhCH} + \text{H}^+$		259.9	260.1
$^1\text{PhCH} + \text{H}_2 \rightarrow \text{PhCH}_3$		-99.4	-92.1
$\text{PhCH}_2^+ + \text{H}_2\text{O} \rightarrow \text{PhCH}_2\text{OH} + \text{H}^+$	184.2	182.0	192.9
$^1\text{PhCH} + \text{H}_2\text{O} \rightarrow \text{PhCH}_2\text{OH}$		-78.0	-67.2
$\text{PhCH}_2^+ + \text{H}^- \rightarrow \text{PhCH}_3$	-239.5	-240.5	-242.1
	*   *   *		
<b>6.</b> $^1\text{PhCCH}_3 \rightarrow ^3\text{PhCCH}_3$	-2.0 (heptane) <sup>e</sup>	-0.8	-1.7
$^1\text{PhCCH}_3 \rightarrow \text{PhCH}=\text{CH}_2$		-66.3	-63.7
$^1\text{PhCCH}_3 + \text{H}_2 \rightarrow \text{PhCH}_2\text{CH}_3$		-93.2	-83.9
$\text{PhCHCH}_3^+ \rightarrow ^1\text{PhCCH}_3 + \text{H}^+$		264.9	264.4
$\text{PhCHCH}_3^+ \rightarrow \text{PhCH}=\text{CH}_2 + \text{H}^+$	200.6	198.6	199.0
$\text{PhCHCH}_3^+ + \text{H}_2\text{O}$ $\rightarrow \text{PhCH}(\text{OH})\text{CH}_3 + \text{H}^+$		188.4	200.1
$^1\text{PhCCH}_3 + \text{H}_2\text{O} \rightarrow \text{PhCH}(\text{OH})\text{CH}_3$		-76.5	-64.4
$\text{PhCHCH}_3^+ + \text{H}^- \rightarrow \text{PhCH}_2\text{CH}_3$	-227.8	-229.3	-229.7
	*   *   *		
<b>7.</b> $\text{PhC}(\text{CH}_3)_2^+ \rightarrow \text{PhC}(\text{CH}_3)=\text{CH}_2 + \text{H}^+$	206.5	204.2	205.5
$\text{PhC}(\text{CH}_3)_2^+ + \text{H}_2\text{O}$ $\rightarrow \text{PhC}(\text{CH}_3)_2\text{OH} + \text{H}^+$		193.3	206.2
$\text{PhC}(\text{CH}_3)_2^+ + \text{H}^- \rightarrow \text{PhCH}(\text{CH}_3)_2$	-221.3	-222.5	-221.8
	*   *   *		
<b>8.</b> $^1\text{Ph}_2\text{C} \rightarrow ^3\text{Ph}_2\text{C}$	-3.6 (cyclohexane) <sup>e</sup>	2.6 (4.6)	1.0 (5.8)
$^1\text{Ph}_2\text{C} + \text{H}_2 \rightarrow \text{Ph}_2\text{CH}_2$		-86.4	-78.3
$\text{Ph}_2\text{CH}^+ \rightarrow ^1\text{Ph}_2\text{C} + \text{H}^+$		268.0	267.8
$\text{Ph}_2\text{CH}^+ + \text{H}^- \rightarrow \text{Ph}_2\text{CH}_2$		-217.4	-218.7



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

Reactions	$\Delta H_{\text{RXN}}$ (exp) <sup>c</sup>	$\Delta H_{\text{RXN}}$ (calc) <sup>c</sup>	$\Delta G_{\text{RXN}}$ (calc)
9. $\text{CH}_3\text{O}=\text{CH}_2^+ \rightarrow {}^1\text{CH}_3\text{OCH} + \text{H}^+$		232.2	232.5
$\text{CH}_3\text{O}=\text{CH}_2^+ + \text{H}^- \rightarrow \text{CH}_3\text{OCH}_3$		-238.9	-237.1
${}^1\text{CH}_3\text{OCH} + \text{H}_2 \rightarrow \text{CH}_3\text{OCH}_3$		-70.2	-61.4
10. $(\text{CH}_3\text{O})_2\text{CH}^+ \rightarrow (\text{CH}_3\text{O})_2\text{C} + \text{H}^+$		235.6	235.7
$(\text{CH}_3\text{O})_2\text{CH}^+ + \text{H}^- \rightarrow (\text{CH}_3\text{O})_2\text{CH}_2$		-206.2	-204.0
$(\text{CH}_3\text{O})_2\text{C} + \text{H}_2 \rightarrow (\text{CH}_3\text{O})_2\text{CH}_2$		-40.8	-31.5
	*   *   *		
11. ${}^1\text{CH}_3\text{OCCH}_3 \rightarrow \text{CH}_3\text{OCH}=\text{CH}_2$		-37.6	-37.0
${}^1\text{CH}_3\text{OCCH}_3 \rightarrow {}^1\text{HOCH}_2\text{CCH}_3$		23.4	23.8
${}^1\text{HOCH}_2\text{CCH}_3 \rightarrow \text{HOCH}_2\text{CH}=\text{CH}_2$		-66.7	-66.0
$\text{CH}_3\text{OCH}=\text{CH}_2 \rightarrow \text{HOCH}_2\text{CH}=\text{CH}_2$		-5.8	-5.3
$\text{CH}_3\text{O}=\text{CH}-\text{CH}_3^+ \rightarrow \text{CH}_3\text{OCH}=\text{CH}_2 + \text{H}^+$	205.4	204.9	205.4
$\text{CH}_3\text{O}=\text{CH}-\text{CH}_3^+ + \text{H}^- \rightarrow \text{CH}_3\text{OCH}_2\text{CH}_3$		221.1	-220.8

<sup>a</sup>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. <sup>b</sup>GAUSSIAN 03, Revision B.04, Frisch, M. J, et al., Gaussian, Inc., Pittsburgh PA, 2003. <sup>c</sup> $\Delta H$  for reactions of alkenes or carbenes with  $\text{H}^+$  provide proton affinities (PA), those of carbocations with water giving alcohols and  $\text{H}^+$  are related to a gas phase  $K_{\text{R}^+}$ , 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. <sup>d</sup>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. <sup>e</sup> $\Delta G$  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 ( $\Delta H_{\text{ACID}}$ ) and HIA Values for Some Carbocations. Enthalpies of Hydrogenation ( $\Delta H_{\text{HYDROG}}$ ) of the Corresponding Singlet Carbenes (kcal/mol, 298K). Gas Phase Substituent Constants.<sup>1</sup>**

Carbocation (Substituents)	$\Delta H_{\text{ACID}}$	HIA	$\Delta H_{\text{HYDROG}}$	$\Sigma\sigma_{\text{F}}$	$\Sigma\sigma_{\text{R}^+}$	$\Sigma\sigma_{\alpha}$
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. $\alpha$ -phenethyl (Ph, CH <sub>3</sub> , 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

<sup>1</sup>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  $\rho$  values and  $r^2$  indicates the quality of the correlation

$$\Delta H_{\text{ACID}} (\text{G3}) = 36.2\sigma_{\text{F}} - 11.7\sigma_{\text{R}^+} - 48.7\sigma_{\alpha} + 213.8 \quad r^2 = 0.909$$

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

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

