Hydrogen-atom attack on phenol and toluene is ortho-directed.

Supplementary Material

Olha Krechkivska,[a] Callan M. Wilcox,[a] Tyler Troy, [b,] Klaas Nauta,[a] Bun Chan,[b] Rebecca Jacob,[b] Scott A. Reid,[c] Leo Radom,[b] Timothy W. Schmidt,[a] and Scott. H. Kable [a]

a) *School of Chemistry, University of New South Wales, Kensington, NSW, 2052, Australia*

b) *School of Chemistry, University of Sydney, Sydney, NSW, 2006, Australia*

c) *Department of Chemistry, Marquette University, Milwaukee, WI, 53201, USA.*

Table of Contents

1 Experimental Results

1.1 Lifetime Scan

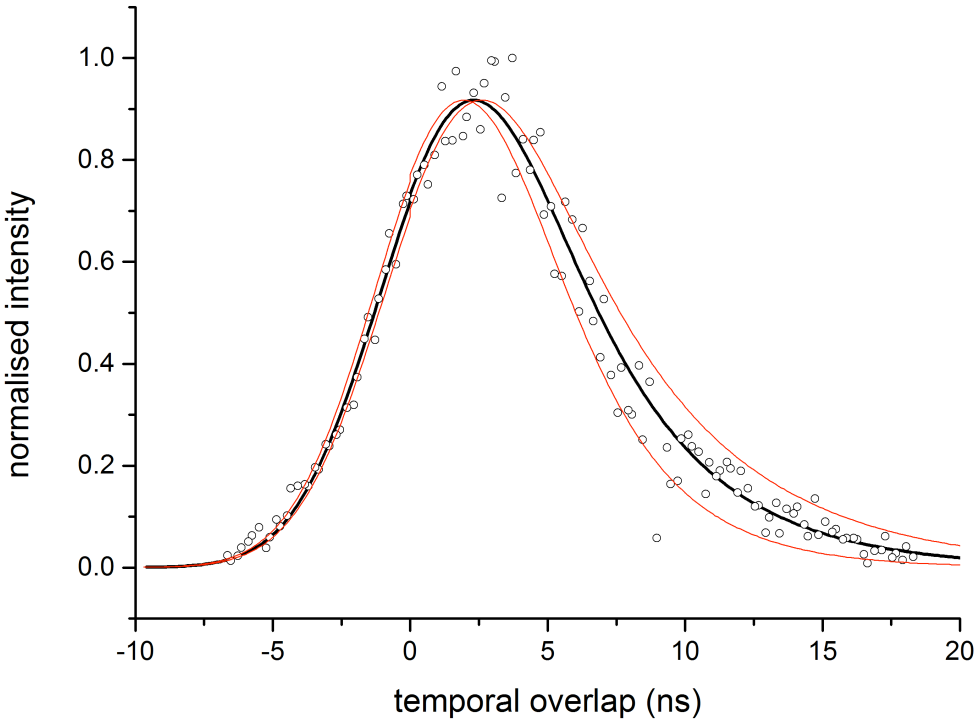

Figure S1: Lifetime scan of the lowest energy hydroxyl-CHD isomer. The data was fitted to the convolution of a Gaussian and a decaying exponential. The decay profile reveals a lifetime of 4 ± 1ns. The data were obtained by fixing the excitation laser and temporally scanning the ionization laser.

2 Computational Results

2.1 Cyclohexadienyl Radical

Table S1. Ionization Energies (IE, eV) of Cyclohexadienyl Radical

Level of theory	IE
B3-LYP/6-31G(2df,p)	6.45
B3-LYP/6-311++G(3df,3pd)	6.69
G3X(MP2)-RAD	6.86
G4(MP2)-6X	6.85
W1X-1 vibrationless	6.79
Botschwina vibrationless	6.75
W1X-1 0 K	6.84
Botschwina 0 K	6.803(5)

Geometries optimized at B3-LYP/6-31G(2df,p)

Table S2. C–H Bond Dissociation Energies (BDE, kJ mol^{-1}) for Cyclohexadienyl Radical

Level of theory	BDE
B3–LYP/6-31G(2df,p)	118.8
B3–LYP/6-311++G(3df,3pd)	114.2
G3X(MP2)-RAD	109.8
G4(MP2)-6X	107.3
W1X-1 vibrationless	109.6
Botschwina vibrationless	107 ± 1.0
G4(MP2)-6X 0 K	85
W1X-1 0 K	88.1
Botschwina 0 K	85.7 ± 2.0
G4(MP2)-6X 298 K	90
W1X-1 298 K	92.7
Botschwina 298 K	89.2

Geometries optimized at B3-LYP/6-31G(2df,p)

Table S3. Proton Affinities (PA, kJ mol^{-1}) for Benzene

Level of theory	PA
B3-LYP/6-31G(2df,p)	810.3
B3-LYP/6-311++G(3df,3pd)	787.7
G3X(MP2)-RAD	765.4
G4(MP2)-6X	765.7
W1X-1 vibrationless	767.6
G4(MP2)-6X 0 K	740
W1X-1 0 K	741.7
G4(MP2)-6X 298 K	744
W1X-1 298 K	746.3
Experimental 298 K	748.4

Geometries optimized at B3-LYP/6-31G(2df,p)

Table S4. Dissociation Energies (kJ mol^{-1}) for $C_6H_7^+ \rightarrow C_6H_6^+ + H$

Level of theory	DE
UB3LYP/6-31G(2df,p)	352.1
B3LYP/6-311++G(3df,3pd)	350.6
G3X(MP2)-RAD	354.8
G4(MP2)6X	352.6
W1X-1 vibrationless	355.5
W1X-1 0 K	322.9
G4(MP2)-6X 0 K	322
W1X-1 298 K	329.6
G4(MP2)-6X 298 K	328
Expt (298 K)	328.2

Table S5. Barriers (kJ mol^{-1}) for a Degenerate 1,2-Shift in Cyclohexadienyl Radical

Level of theory	Barrier
B3-LYP/6-31G(2df,p)	210.1
B3-LYP/6-311++G(3df,3pd)	205.1
G3X(MP2)-RAD	208.3
G4(MP2)-6X	199.4
W1X-1	205.7
W1X-1 0 K	193.4
W1X-1 298 K	193.3

Geometries optimized at B3-LYP/6-31G(2df,p)

Table S6. Barriers (kJ mol^{-1}) for a Degenerate 1,2-Shift in Cyclohexadienyl Cation

Level of theory	Barrier
B3-LYP/6-31G(2df,p)	51.1
B3-LYP/6-311++G(3df,3pd)	51.0
G3X(MP2)-RAD	40.8
G4(MP2)6X	38.6
W1X-1	39.8
W1X-1 0 K	34.3
W1X-1 298 K	32.9

Geometries optimized at B3-LYP/6-31G(2df,p)

2.2 Substituted Cyclohexadienyl Radicals

Table S7. Relative Energies (kJ mol^{-1}) for Isomers of Substituted Cyclohexadienyl Radicals

Species	Level of theory	ortho	meta	para	ipso
Methyl-	B3-LYP/6-31G(2df,p)	0.0	6.1	5.4	17.2
	B3-LYP/6-311++G(3df,3pd)	0.0	6.1	6.1	14.7
	G3X(MP2)-RAD	0.0	5.0	6.6	10.2
	G4(MP2)-6X	0.0	5.4	6.5	10.5
OH-	B3-LYP/6-31G(2df,p)	0.0	13.0	11.4	45.0
	B3-LYP/6-311++G(3df,3pd)	0.0	13.1	12.6	37.8
	G3X(MP2)-RAD	0.0	12.2	13.2	31.9
	G4(MP2)-6X	0.0	13.5	13.1	32.0

Geometries optimized at B3-LYP/6-31G(2df,p)

Table S8. Relative Energies (kJ mol^{-1}) for Isomers of Substituted Cyclohexadienyl Cations

Species	Level of theory	ortho	meta	para	ipso
Methyl-	B3-LYP/6-31G(2df,p)	5.5	20.9	0.0	39.2
	B3-LYP/6-311++G(3df,3pd)	5.7	21.7	0.0	38.8
	G3X(MP2)-RAD	6.3	19.7	0.0	34.3
	G4(MP2)-6X	5.9	19.7	0.0	33.7
OH-	B3-LYP/6-31G(2df,p)	11.5	70.4	0.0	131.0
	B3-LYP/6-311++G(3df,3pd)	11.5	68.2	0.0	124.6
	G3X(MP2)-RAD	14.6	72.5	0.0	123.6
	G4(MP2)-6X	14.4	73.3	0.0	123.7

Geometries optimized at B3-LYP/6-31G(2df,p)

Table S9. Ionization Energies (eV) for Isomers of Substituted Cyclohexadienyl Radicals

Species	Level of theory	ortho	meta	para	ipso
Methyl-	B3-LYP/6-31G(2df,p)	6.21	6.31	6.10	6.38
	B3-LYP/6-311++G(3df,3pd)	6.44	6.54	6.32	6.63
	G3X(MP2)-RAD	6.63	6.72	6.50	6.82
	G4(MP2)-6X	6.63	6.72	6.50	6.81
Both G3X(MP2)-RAD G4(MP2)-6X	vibrationless	6.63	6.72	6.50	6.82
	0 K	6.67	6.76	6.54	6.85
	298 K	6.68			
	0K, empirical correction	6.59	6.68	6.42	6.77
OH-	B3-LYP/6-31G(2df,p)	5.95	6.43	5.72	6.73
	B3-LYP/6-311++G(3df,3pd)	6.26	6.71	6.01	7.04
	G3X(MP2)-RAD	6.40	6.87	6.11	7.20
	G4(MP2)-6X	6.39	6.86	6.11	7.19
G3X(MP2)-RAD	vibrationless	6.40	6.87	6.11	7.2
	0 K	6.47	6.94	6.19	7.27
	298 K	6.46			
	0K, empirical correction	6.39	6.86	6.11	7.19

Geometries optimized at B3-LYP/6-31G(2df,p)

Table S10. C–H Bond Dissociation Energies (BDE, kJ mol^{-1}) for Isomers of Substituted Cyclohexadienyl Radicals

Species	Level of theory	ortho	meta	para	ipso
Methyl-	B3-LYP/6-31G(2df,p)	126.1	119.9	120.7	108.8
	B3-LYP/6-311++G(3df,3pd)	121.6	115.5	115.5	106.9
	G3X(MP2)-RAD	116.4	111.4	109.8	106.2
	G4(MP2)-6X	115.2	109.8	108.7	104.7
G4(MP2)-6X	0 K	92.6	87.9	87.1	81.0
	298 K	97.8	92.8	91.5	86.5
OH-	B3-LYP/6-31G(2df,p)	129.3	116.2	117.9	84.3
	B3-LYP/6-311++G(3df,3pd)	125.8	112.7	113.2	88.0
	G3X(MP2)-RAD	120.3	108.1	107.2	88.5
	G4(MP2)-6X	119.4	105.9	106.4	87.4
G4(MP2)-6X	0 K	96.6	85.0	84.7	65.8
	298 K	101.2	89.2	88.9	69.8

Table S11. Proton Affinities (PA, kJ mol^{-1}) for Phenol

Level of theory	ortho	meta	para	ipso
B3-LYP/6-31G(2df,p)	868.2	809.3	879.7	748.7
B3-LYP/6-311++G(3df,3pd)	840.9	784.2	852.4	727.7
G3X(MP2)-RAD	820.5	762.7	835.1	711.5
G4(MP2)-6X	821.6	762.7	836.0	712.3
W1X-1 vibrationless	821.7	763.3	836.3	
W1X-1 0 K	792.2	738.2	806.4	
W1X-1 298 K	797.3	742.8	811.8	
Expt	817.3			
Benzene	750.4 (expt), 746.3 (W1X-1, 298 K)			

Table S12. Proton Affinities (PA, kJ mol^{-1}) for Toluene

Level of theory	ortho	meta	para	ipso
B3-LYP/6-31G(2df,p)	840.2	824.8	845.7	806.6
B3-LYP/6-311++G(3df,3pd)	818.9	803.0	824.7	785.9
G3X(MP2)-RAD	794.0	780.6	800.3	765.9
G4(MP2)-6X	794.4	780.6	800.3	766.6
W1X-1 vibrationless	796.7	782.2	802.8	
W1X-1 0 K	770.3	756.0	776.8	
W1X-1 298 K	775.0	760.9	781.5	
Expt	784.0			
Benzene	750.4 (expt), 746.3 (W1X-1, 298 K)			

Table S13. Barriers (kJ mol^{-1}) for a Degenerate 1,2-Shift in Isomers of Substituted Cyclohexadienyl Radical

		Relative energies				1-2 shift TS energies with respect to ortho		
Species	**Level of theory**	**ortho**	**meta**	**para**	**ipso**	**Ortho to ipso**	**Ortho to meta**	**Meta to para**
Methyl-	B3-LYP/6-31G(2df,p)	0.0	6.1	5.4	17.2	218.1	212.2	213.5
	B3-LYP/6-311++G(3df,3pd)	0.0	6.1	6.1	14.7	212.0	206.7	208.7
	G3X(MP2)-RAD	0.0	5.0	6.6	10.2	213.8	208.9	211.3
	G4(MP2)-6X	0.0	5.4	6.5	10.5	205.5	200.9	203.3
OH-	B3-LYP/6-31G(2df,p)	0.0	13.0	11.4	45.0	248.8	215.0	224.6
	B3-LYP/6-311++G(3df,3pd)	0.0	13.1	12.6	37.8	240.0	210.7	219.1
	G3X(MP2)-RAD	0.0	12.2	13.2	31.9	240.9	214.4	222.6
	G4(MP2)-6X	0.0	13.5	13.1	32.0		207.7	215.6

Table S14. Barriers (kJ mol^{-1}) for a Degenerate 1,2-Shift in Isomers of Substituted Cyclohexadienyl Cation

						1-2 shift TS		
Species	**Level of theory**	**ortho**	**meta**	**para**	**ipso**	**Ortho to ipso**	**Ortho to meta**	**Meta to para**
Methyl-	B3-LYP/6-31G(2df,p)	5.5	20.9	0.0	39.2	16.4	16.4	16.0
	B3-LYP/6-311++G(3df,3pd)	5.7	21.7	0.0	38.8	16.4	16.5	16.1
	G3X(MP2)-RAD	6.3	19.7	0.0	34.3	13.4	14.0	13.6
	G4(MP2)-6X	5.9	19.7	0.0	33.7	12.9	13.4	13.1
OH-	B3-LYP/6-31G(2df,p)	11.5	70.4	0.0	131.0	135.1	107.7	100.7
	B3-LYP/6-311++G(3df,3pd)	11.5	68.2	0.0	124.6	129.3	106.0	98.9
	G3X(MP2)-RAD	14.6	72.5	0.0	123.6	128.0	103.6	96.4
	G4(MP2)-6X	14.4	73.3	0.0	123.7	128.1	102.2	95.0