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SUPPORTING INFORMATION

Supporting Information

s-trans-isoprene (RBecke3LYP/6-31G*)

H	-0.68433	-2.19061	0.00000
C	0.37506	-1.94986	0.00000
C	0.82657	-0.68795	0.00000
H	1.06002	-2.79261	0.00000
C	0.00000	0.52576	0.00000
H	1.90311	-0.51674	0.00000
C	0.58839	1.73418	0.00000
C	-1.50208	0.37878	0.00000
H	0.01013	2.65400	0.00000
H	1.67046	1.84021	0.00000
H	-1.99548	1.35488	0.00000
H	-1.84578	-0.17729	0.88145
H	-1.84578	-0.17729	-0.88145

s-trans-isoprene (RHF6-31G*)

H	-0.67484	-2.17899	0.00000
C	0.37322	-1.93996	0.00000
C	0.82426	-0.69631	0.00000
H	1.05120	-2.77424	0.00000
C	0.00000	0.52955	0.00000
H	1.88962	-0.53285	0.00000
C	0.58978	1.71681	0.00000
C	-1.50178	0.38884	0.00000
H	0.02510	2.63197	0.00000
H	1.66129	1.81520	0.00000
H	-1.98162	1.35975	0.00000
H	-1.84180	-0.15720	0.87515
H	-1.84180	-0.15720	-0.87515

maleic anhydride (RBecke3LYP/6-31G*)

O	0.00000	0.00000	0.97188
C	0.00000	1.13206	0.15879
O	0.00000	2.24565	0.59988
C	0.00000	0.66784	-1.25826
C	0.00000	-0.66784	-1.25826
H	0.00000	1.36046	-2.08980
C	0.00000	-1.13206	0.15879
H	0.00000	-1.36046	-2.08980
O	0.00000	-2.24565	0.59988

maleic anhydride (RHF/6-31G*)

O	0.000000	0.000000	0.947496
C	0.000000	1.113988	0.167122
O	0.000000	2.203435	0.599982
C	0.000000	0.658574	-1.253196
C	0.000000	-0.658574	-1.253196
H	0.000000	1.346873	-2.073398
C	0.000000	-1.113988	0.167122
H	0.000000	-1.346873	-2.073398
O	0.000000	-2.203435	0.599982

endo T. S. (**1**) (RBecke3LYP/6-31G*)

C	1.73352	-0.64887	-0.12666
C	1.69990	-0.11376	1.15809
C	0.84813	-1.69905	-0.46099
C	-0.06289	-2.23433	0.42825
C	-1.29305	-0.34501	1.02792
C	-0.37847	0.66129	1.32764
H	1.46113	-0.73835	2.01157
H	0.73977	-1.94500	-1.51565
H	0.13751	-2.26558	1.49318
H	-0.82198	-2.92713	0.07762
C	2.52213	0.05098	-1.21109
H	2.31998	1.12856	-1.20669
H	3.60057	-0.07891	-1.05706
H	2.27497	-0.33670	-2.20366
H	2.28620	0.77243	1.38700
H	-0.15127	1.04654	2.31299
H	-1.86546	-0.93378	1.73163
C	-0.30954	1.55905	0.14579
O	0.28620	2.59108	-0.01705
O	-1.08155	0.98693	-0.86125
C	-1.80573	-0.09806	-0.33321
O	-2.66782	-0.64244	-0.96737

endo T. S. (**1**) (RHF/6-31G*)

C	1.75502	-0.55958	-0.12997
C	1.69028	-0.01340	1.14117
C	0.92951	-1.64327	-0.44590
C	0.04586	-2.19162	0.45678
C	-1.22688	-0.44109	0.99942
C	-0.39020	0.61750	1.30947
H	1.50658	-0.63640	1.99399
H	0.82106	-1.91023	-1.48287
H	0.27364	-2.23345	1.50330
H	-0.66966	-2.91922	0.11916
C	2.52301	0.15473	-1.22000
H	2.45697	1.23010	-1.10159
H	3.57420	-0.11722	-1.18329
H	2.14815	-0.09975	-2.20393
H	2.23126	0.89181	1.35433
H	-0.20856	1.01185	2.28794
H	-1.78647	-1.03219	1.69425
C	-0.41639	1.53628	0.14602
O	0.07237	2.59880	0.00500
O	-1.14042	0.93126	-0.83340
C	-1.76821	-0.18262	-0.35023
O	-2.58185	-0.76092	-0.97433

exo T. S. (2) (RBecke3LYP/6-31G*)

C	-2.26897	0.02591	-0.26261
C	-1.32427	0.94924	-0.69488
C	-1.93040	-1.34591	-0.22010
C	-0.69086	-1.83156	-0.58724
C	0.63615	-0.66997	0.91103
C	0.28376	0.67690	0.83695
H	-0.59708	0.67836	-1.45200
H	-2.60296	-2.01083	0.32064
H	-0.10388	-1.35009	-1.36120
H	-0.42837	-2.86894	-0.40229
H	0.36741	-1.36602	1.69192
C	-3.56323	0.49246	0.36550
H	-3.85039	-0.12402	1.22458
H	-3.49563	1.53401	0.69578
H	-4.38517	0.43747	-0.36070
H	-1.52622	2.01496	-0.62981
H	-0.27976	1.22991	1.57518
C	1.90184	-0.84214	0.16479
O	2.59577	-1.81043	0.01259
O	2.22362	0.39107	-0.42373
C	1.34729	1.36566	0.05951
O	1.49989	2.53207	-0.18133

exo T. S. (2) (RHF/6-31G*)

C	-2.24379	0.01891	-0.26583
C	-1.30258	0.93559	-0.69674
C	-1.90519	-1.33728	-0.21856
C	-0.66299	-1.80609	-0.57697
C	0.60496	-0.67312	0.88561
C	0.25469	0.66540	0.81246
H	-0.60074	0.67174	-1.46334
H	-2.55994	-2.00161	0.32002
H	-0.10108	-1.34557	-1.36526
H	-0.40069	-2.83112	-0.38816
H	0.36518	-1.34916	1.67753
C	-3.53226	0.49358	0.36786
H	-3.85001	-0.15813	1.17417
H	-3.42845	1.49785	0.76340
H	-4.33095	0.51687	-0.36830
H	-1.51055	1.98917	-0.63728
H	-0.28328	1.21619	1.55436
C	1.88631	-0.82223	0.16131
O	2.57718	-1.76503	0.02419
O	2.18928	0.38589	-0.40179
C	1.33639	1.34507	0.05422
O	1.49444	2.48850	-0.17330

Table 1. Becke3LYP/6-31G* and RHF/6-31G* energies and entropies for the Diels-Alder reactions of isoprene with maleic anhydride.

		Energy (a.u)	ZPE(a.u.)	S(e.u.)	$\Delta H^{\ddagger}$(kcal/mol)[a,b]
s-trans-isoprene	B3LYP	-195.31045	0.11409	74.2	---
	RHF	-193.95723	0.12197	73.3	---
SCIPCM *s-trans*-isoprene	B3LYP	-195.30879	---	---	---
	RHF	-193.95805	---	---	---
maleic anhydride	B3LYP	-379.28955	0.05588	72.7	---
	RHF	-377.23017	0.06120	71.6	---
SCIPCM maleic anhydride	B3LYP	-379.29354	---	---	---
	RHF	-377.23637	---	---	---
maleic anhydride endo T.S. (**1**)	B3LYP	-574.57594	0.17213	103.3	15.9
	RHF	-571.12880	0.18563	99.8	37.6
maleic anhydride exo T.S. (**2**)	B3LYP	-574.57292	0.17188	106.0	17.8
	RHF	-571.12526	0.18544	101.5	39.8
SCIPCM endo T.S. (**1**)	B3LYP	-574.58163	---	---	13.8
	RHF	-571.13592	---	---	37.5
SCIPCM exo T.S. (**2**)	B3LYP	-574.57884	---	---	15.5
	RHF	-571.13244	---	---	39.7

[a]SCIPCM energies calculated with dielectric of 2.274 D (benzene, 25°C).[16]

[b]All activation enthalpies include unscaled gas-phase ZPE and thermal corrections.

Table 2. Becke3LYP/6-31G* calculated and experimental kinetic isotope effects for the Diels-Alder reaction of isoprene and maleic anhydride (298.15 K).

	Endo (**1**)		Exo (**2**)	
	Calculated[a,b]	Experimental[c]	Calculated[a,b]	Experimental[c]
methyl-(*d1*)	0.996	0.996 (assumed)	1.006	1.006 (assumed)
H7 = D (IN)	0.920	0.904±0.005	0.905	0.913 ± 0.005
H8 = D	0.985	0.986±0.006	1.001	0.996 ± 0.006
H9 = D (IN)	0.925	0.934±0.004	0.910	0.944 ± 0.004
H10 = D (OUT)	0.961	0.964±0.005	0.961	0.974 ± 0.005
H15 = D (OUT)	0.952	0.952±0.005	0.951	0.962 ± 0.005
H16 = D	0.957	---	0.943	---
H17 = D	0.973	---	0.956	---
C11 = ^{13}C	1.001	1.001 (assumed)	1.001	1.001 (assumed)
C1 = ^{13}C	1.022	1.023±0.003	1.022	1.023 ± 0.003
C2 = ^{13}C	1.004	1.002±0.002	1.004	1.002 ± 0.002
C3 = ^{13}C	1.002	1.001±0.003	1.002	1.001 ± 0.003
C4 = ^{13}C	1.018	1.018±0.002	1.019	1.018 ± 0.002
C5 = ^{13}C	1.021	---	1.023	---
C6 = ^{13}C	1.025	---	1.026	---
C18 = ^{13}C	0.998	---	0.999	---
C21 = ^{13}C	1.000	---	1.000	---

[a]Based on the Becke3LYP/6-31G* structures **1** and **2**, with frequencies scaled by 0.963.[13a]
[b]A tunneling correction based on a one-dimensional infinite parabolic barrier model was used.[14]
[c]Recalculated from previously reported data,[20] made relative to the methyl - *d1* value which is assumed to be equal to 0.996 for **1** and 1.006 for **2**, and the methyl carbon value which is assumed to be equal to 1.001 for both **1** and **2**. These assumed values are the Becke3LYP values corrected for tunneling.

Table 3. RHF/6-31G* calculated and experimental kinetic isotope effects for the Diels-Alder reaction of isoprene and maleic anhydride (298.15 K).

	Endo (**1**)		Exo (**2**)	
	Calculated[a,b]	Experimental[c]	Calculated[a,b]	Experimental[c]
methyl-(*d1*)	0.995	0.995 (assumed)	1.004	1.004 (assumed)
H7 = D (IN)	0.919	0.903±0.005	0.909	0.912 ± 0.005
H8 = D	0.984	0.985±0.006	0.996	0.994 ± 0.006
H9 = D (IN)	0.919	0.933±0.004	0.913	0.942 ± 0.004
H10 = D (OUT)	0.943	0.963±0.005	0.946	0.972 ± 0.005
H15 = D (OUT)	0.942	0.951±0.005	0.941	0.960 ± 0.005
H16 = D	0.964	---	0.942	---
H17 = D	0.978	---	0.956	---
C11 = ^{13}C	1.001	1.001 (assumed)	1.001	1.001 (assumed)
C1 = ^{13}C	1.029	1.023±0.003	1.029	1.023 ± 0.003
C2 = ^{13}C	1.008	1.002±0.002	1.008	1.002 ± 0.002
C3 = ^{13}C	1.006	1.001±0.003	1.006	1.001 ± 0.003
C4 = ^{13}C	1.027	1.018±0.002	1.027	1.018 ± 0.002
C5 = ^{13}C	1.030	---	1.031	---
C6 = ^{13}C	1.032	---	1.033	---
C18 = ^{13}C	0.999	---	0.999	---
C21 = ^{13}C	1.000	---	1.000	---

[a]Based on the RHF/6-31G* structures **1** and **2**, with frequencies scaled by 0.8929.[13b]

[b]A tunneling correction based on a one-dimensional infinite parabolic barrier model was used.[14]

[c]Recalculated from previously reported data,[20] made relative to the methyl - *d1* value which is assumed to be equal to 0.995 for **1** and 1.004 for **2**, and the methyl carbon value which is assumed to be equal to 1.001 for both **1** and **2**. These assumed values are the RHF values corrected for tunneling.