Electronic Supporting Information

for

Isomerization of Methoxy Radical Revisited: Impact of Water Dimer

Pradeep Kumar[a], Partha Biswas[b] and Biman Bandyopadhyay[a]

[a]*Department of Chemistry, Malaviya National Institute of Technology Jaipur, J. L. N. Marg, Jaipur – 302017, India.*
[b]*Department of Chemistry, Scottish Church College, 1 & 3 Urquhart Square, Kolkata-700006, India.*

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Rate Calculations:

Isomerization of MR can be written in terms of the bimolecular encounters between MR and catalyst, say X (X = WM, WD, FA and SA) to give HM, as:

$$MR + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RC \xrightarrow{k_2} PC \longrightarrow HM + X$$

In the above reaction scheme RC is assumed to be in equilibrium with MR and X and subsequently RC undergoes unimolecular isomerization through TS to form PC. Under this assumption, the reaction rate (ν) can be expressed as:

$$\nu = \frac{k_1}{k_{-1}} k_2 [MR][X] = K_{eq} k_2 [MR][X] = k[MR][X]$$

$$where \quad K_{eq} = \frac{k_1}{k_{-1}} \quad and \quad k = K_{eq} k_2$$

Where, K_{eq} = equilibrium constant of RCs ,

k_2 = rate constant for the unimolecular reaction of RCs leading to PCs.

K_{eq} and k_2 have been computed by using TST as shown below:

$$K_{eq} = \frac{Q_{RC}}{Q_{MR} \cdot Q_X} e^{\frac{-(E_{RC} - E_{MR})}{RT}}$$

$$k_2 = \sigma \Gamma \frac{k_B T Q_{TS}}{\mathrm{h} \ Q_{RC}} e^{\frac{-(E_{TS} - E_{RC})}{RT}}$$

Where, Q = The product of electronic, translational, rotational and vibrational canonical partition functions of the respective species referenced to the zero-point energy (ZPE),

E = ZPE corrected energies of the respective species,

= reaction path number or reaction degeneracy,

Γ = tunneling correction for the reaction (it has been taken into account by assuming unsymmetrical Eckart barrier.[y]

k_B = Boltzmann constant

h = Planck constant

T = temperature in Kelvin

R = ideal gas constant.

The inherent assumption behind this approximation is that the time scale to established the equilibrium is significantly different (fast) as compared to the time scale of second step of reaction (unimolecular conversion). This assumption will work well if the catalyst molecules are present at sufficiently large concentration. Calculations of the rate constants were carried out by use of TheRate program package.[1]

It is evident from reaction rate (v) equation that if all other conditions remain same, then $k[X]$ (where, k is the rate constant and [X] is the concentration of the catalyst) can be considered as an effective rate constant: $k_{eff} = k[X]$

To further assess the pre-equilibrium approximation, we have also carried out the rate calculations using MESMER software.[2] MESMER solves a multi grain master equation to obtain the phenomenological rate constants which is known as Bartis-Widom phenomenological rate coefficients.

Table S1 Relative energies (kcal mol^{-1}) of all species with respect to the isolated reactants calculated using two different levels of theory

Catalyst	Species	MP2/aug-cc-pVTZ	CCSD(T)/aug-cc-pVTZ
None	MR	0	0
	TS	30.0	32.7
	HM	-14.1	-8.7
WM	MR-WM	-5.1	-5.2
	TS_{WM}	19.7	22.9
	HM-WM	-20.8	-15.4
WD	MR-WD	-8.1	-8.4
	TS_{WD}	5.3	7.8
	HM-WD	-25.8	-20.5
FA	MR-FA	-8.5	-8.8
	TS_{FA}	3.8	4.4
	HM-FA	-24.1	-18.9
SA	MR-SA	-11.4	-11.8
	TS_{SA}	1.3	1.8
	HM-SA	-25.5	-20.3

Table S2 Rate constants (molecule^{-1} cm^{3} s^{-1}) in presence of the four catalysts calculated using results obtained from CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory

Temperatures	WM	WD	FA	SA
298	3.55×10^{-29}	2.82×10^{-21}	3.65×10^{-16}	2.80×10^{-13}
259	3.55×10^{-29}	2.82×10^{-21}	6.20×10^{-16}	1.28×10^{-12}
230	9.08×10^{-31}	8.46×10^{-22}	1.40×10^{-15}	7.13×10^{-12}
213	7.08×10^{-32}	3.39×10^{-22}	2.89×10^{-15}	2.74×10^{-11}
216	1.91×10^{-32}	2.15×10^{-22}	2.50×10^{-15}	2.11×10^{-11}
219	2.38×10^{-32}	2.30×10^{-22}	2.18×10^{-15}	1.65×10^{-11}
224	2.97×10^{-32}	2.49×10^{-22}	1.76×10^{-15}	1.11×10^{-11}
235	4.37×10^{-32}	2.85×10^{-22}	1.17×10^{-15}	5.06×10^{-12}
250	1.07×10^{-31}	3.94×10^{-22}	7.61×10^{-16}	2.04×10^{-12}
280	6.56×10^{-30}	1.64×10^{-21}	4.39×10^{-16}	5.16×10^{-13}
290	1.68×10^{-29}	2.22×10^{-21}	3.92×10^{-16}	3.61×10^{-13}
300	4.27×10^{-29}	2.98×10^{-21}	3.60×10^{-16}	2.64×10^{-13}
310	1.06×10^{-28}	3.96×10^{-21}	3.38×10^{-16}	2.00×10^{-13}
320	2.57×10^{-28}	5.20×10^{-21}	3.18×10^{-16}	1.56×10^{-13}

Table S3 Concentration of the four catalysts (in molecules cm^{-3}) within 280 K to 320 K temperature range at 0 km altitude. (% H stands for relative humidity)

Catalyst		280	290	298	300	310	320
WM[a]	20% H	5.16×10^{16}	9.56×10^{16}	1.55×10^{17}	1.72×10^{17}	2.92×10^{17}	4.70×10^{17}
	40% H	1.03×10^{17}	1.91×10^{17}	3.09×10^{17}	3.43×10^{17}	5.84×10^{17}	9.40×10^{17}
	60% H	1.55×10^{17}	2.87×10^{17}	4.64×10^{17}	5.15×10^{17}	8.77×10^{17}	1.41×10^{18}
	80% H	2.07×10^{17}	3.82×10^{17}	6.18×10^{17}	6.86×10^{17}	1.17×10^{18}	1.88×10^{18}
	100% H	2.58×10^{17}	4.78×10^{17}	7.73×10^{17}	8.58×10^{17}	1.46×10^{18}	2.35×10^{18}
WD[a]	20% H	8.18×10^{12}	2.36×10^{13}	5.44×10^{13}	6.50×10^{13}	1.63×10^{14}	3.71×10^{14}
	40% H	3.27×10^{13}	9.46×10^{13}	2.18×10^{14}	2.60×10^{14}	6.52×10^{14}	1.48×10^{15}
	60% H	7.36×10^{13}	2.13×10^{14}	4.90×10^{14}	5.85×10^{14}	1.46×10^{15}	3.33×10^{15}
	80% H	1.31×10^{14}	3.78×10^{14}	8.70×10^{14}	1.04×10^{15}	2.60×10^{15}	5.90×10^{15}
	100% H	2.04×10^{14}	5.91×10^{14}	1.36×10^{15}	1.62×10^{15}	4.06×10^{15}	9.24×10^{15}
FA[b]	High	2.61×10^{11}	2.52×10^{11}	2.45×10^{11}	2.43×10^{11}	2.36×10^{11}	2.28×10^{11}
	Average	2.02×10^{10}	1.95×10^{10}	1.90×10^{10}	1.89×10^{10}	1.83×10^{10}	1.77×10^{10}
	Low	2.61×10^{11}	2.52×10^{11}	2.45×10^{11}	2.43×10^{11}	2.36×10^{11}	2.28×10^{11}
SA[c]		3.94×10^{8}	3.80×10^{8}	3.70×10^{8}	3.68×10^{8}	3.56×10^{8}	3.45×10^{8}

[a] *Reference 3 (concentration of WM and WD has directly been taken from this reference where the authors computed WD concentration from WM concentration and calculated equilibrium constant for WM to WD transformation)* [b] *Reference 4* [c] *Reference 5*

Table S4 Effective rate constants (s^{-1}) in presence of the four catalysts within 280 K to 320 K temperature range at 0 km altitude calculated by TheRate. (% H stands for relative humidity)

Catalyst	Conc.	280	290	298	300	310	320
WM	20% H	3.38×10^{-13}	1.61×10^{-12}	5.50×10^{-12}	7.34×10^{-12}	3.10×10^{-11}	1.21×10^{-10}
	40% H	6.76×10^{-13}	3.22×10^{-12}	1.10×10^{-11}	1.46×10^{-11}	6.19×10^{-11}	2.41×10^{-10}
	60% H	1.02×10^{-12}	4.83×10^{-12}	1.65×10^{-11}	2.20×10^{-11}	9.30×10^{-11}	3.62×10^{-10}
	80% H	1.36×10^{-12}	6.43×10^{-12}	2.19×10^{-11}	2.93×10^{-11}	1.24×10^{-10}	4.83×10^{-10}
	100% H	1.69×10^{-12}	8.05×10^{-12}	2.74×10^{-11}	3.66×10^{-11}	1.55×10^{-10}	6.04×10^{-10}
WD	20% H	1.34×10^{-8}	5.25×10^{-8}	1.53×10^{-7}	1.94×10^{-7}	6.46×10^{-7}	1.93×10^{-6}
	40% H	5.37×10^{-8}	2.10×10^{-7}	6.14×10^{-7}	7.76×10^{-7}	2.58×10^{-6}	7.70×10^{-6}
	60% H	1.21×10^{-7}	4.74×10^{-7}	1.38×10^{-6}	1.75×10^{-6}	5.78×10^{-6}	1.73×10^{-5}
	80% H	2.15×10^{-7}	8.41×10^{-7}	2.45×10^{-6}	3.10×10^{-6}	1.03×10^{-5}	3.07×10^{-5}
	100% H	3.35×10^{-7}	1.31×10^{-6}	3.83×10^{-6}	4.83×10^{-6}	1.61×10^{-5}	4.81×10^{-5}
FA	High	1.14×10^{-4}	9.87×10^{-5}	8.95×10^{-5}	8.75×10^{-5}	7.95×10^{-5}	7.26×10^{-5}
	Average	8.87×10^{-6}	7.65×10^{-6}	6.94×10^{-6}	6.79×10^{-6}	6.17×10^{-6}	5.63×10^{-6}
	Low	1.14×10^{-7}	9.87×10^{-8}	8.95×10^{-8}	8.75×10^{-8}	7.95×10^{-8}	7.26×10^{-8}

SA	2.03×10^{-4}	1.37×10^{-4}	1.04×10^{-4}	9.69×10^{-5}	7.10×10^{-5}	5.37×10^{-5}

Table S5 Effective rate constants (s^{-1}) in presence of the four catalysts within 280 K to 320 K temperature range at 0 km altitude calculated by MESMER. (% H stands for relative humidity)

Catalyst	Conc.	280	290	298	300	310	320
WM	20% H	3.77×10^{-13}	1.74×10^{-12}	5.81×10^{-12}	7.71×10^{-12}	3.19×10^{-11}	1.22×10^{-10}
	40% H	7.52×10^{-13}	3.47×10^{-12}	1.16×10^{-11}	1.54×10^{-11}	6.34×10^{-11}	2.45×10^{-10}
	60% H	1.13×10^{-12}	5.21×10^{-12}	1.74×10^{-11}	2.31×10^{-11}	9.59×10^{-11}	3.67×10^{-10}
	80% H	1.51×10^{-12}	6.94×10^{-12}	2.32×10^{-11}	3.08×10^{-11}	1.28×10^{-10}	4.89×10^{-10}
	100% H	1.88×10^{-12}	8.68×10^{-12}	2.9×10^{-11}	3.85×10^{-11}	1.6×10^{-10}	6.11×10^{-10}
WD	20% H	1.31×10^{-8}	5.05×10^{-8}	1.46×10^{-7}	1.85×10^{-7}	6.09×10^{-7}	1.80×10^{-6}
	40% H	5.22×10^{-8}	2.02×10^{-7}	5.86×10^{-7}	7.39×10^{-7}	2.44×10^{-6}	7.20×10^{-6}
	60% H	1.18×10^{-7}	4.56×10^{-7}	1.32×10^{-6}	1.66×10^{-6}	5.45×10^{-6}	1.62×10^{-5}
	80% H	2.09×10^{-7}	8.09×10^{-7}	2.34×10^{-6}	2.95×10^{-6}	9.71×10^{-6}	2.87×10^{-5}
	100% H	3.26×10^{-7}	1.26×10^{-6}	3.65×10^{-6}	4.6×10^{-6}	1.51×10^{-5}	4.49×10^{-5}
FA	High	7.93×10^{-5}	7.44×10^{-5}	7.1×10^{-5}	7.12×10^{-5}	6.71×10^{-5}	6.44×10^{-5}
	Average	6.14×10^{-6}	5.76×10^{-6}	5.5×10^{-6}	5.46×10^{-6}	5.20×10^{-6}	5.00×10^{-6}
	Low	7.93×10^{-8}	7.44×10^{-8}	7.1×10^{-8}	7.12×10^{-8}	6.71×10^{-8}	6.44×10^{-8}

SA	2.95×10^{-5}	2.66×10^{-5}	2.45×10^{-5}	2.4×10^{-5}	2.16×10^{-5}	1.95×10^{-5}

Table S6 Optimized geometries in Cartesian coordinates and normal mode frequencies of all species calculated at MP2/aug-cc-pVTZ level of theory

Species	Cartesian coordinate (Å)				Vibrational frequencies (cm^{-1})		
MR	C	0.581872	0.000089	-0.010498			
	H	0.865280	-0.004096	1.050892	807.7226	968.7007	1127.056
	H	0.999450	0.903630	-0.458822	1415.008	1432.323	1539.404
	H	0.999079	-0.900437	-0.465240	3006.008	3090.193	3131.184
	O	-0.794380	0.000046	-0.007980			
HM	C	0.684714	0.027438	-0.066480			
	H	1.113909	0.987547	0.173444	433.6348	621.2987	1067.206
	H	1.229154	-0.882854	0.109015	1212.753	1367.984	1509.170
	O	-0.670357	-0.125781	0.021718	3194.145	3343.541	3854.749
	H	-1.088491	0.736930	-0.057321			
TS	C	-0.628082	0.000001	0.006767			
	H	-1.151053	0.934246	-0.171669	-2108.122	844.6455	1031.746
	H	-1.151052	-0.934234	-0.171728	1149.538	1191.385	1502.643
	O	0.742190	0.000004	-0.084151	2602.608	3112.367	3229.723
	H	0.133075	-0.000051	0.976004			
MR-WM	C	-1.304759	-0.496026	-0.011360			
	H	-0.603971	-1.187156	-0.482799	69.9095	6.5984	113.9642
	H	-2.305564	-0.564287	-0.438409	179.4596	350.26	437.0240
	H	-1.365238	-0.771375	1.050999	935.9952	1025.52	1123.5392
	O	-0.824776	0.798388	-0.008100	1411.271	1435.192	1535.8440
	H	1.119029	0.407694	0.017476	1642.0936	3004.88	3097.0467
	H	2.646450	0.355046	-0.003530	3149.0056	3727.8958	3915.5858
	O	1.867007	-0.206359	-0.001346			
HM-WM	C	1.594154	0.453076	-0.049929			
	H	2.647667	0.262332	0.057840	64.1035	80.9239	154.5240
	H	1.164833	1.393885	0.260395	185.1505	236.92	288.9752
	O	0.817172	-0.661979	-0.001150	584.6835	774.30	1116.4078
	H	-2.475492	-0.249859	0.639227	1233.4945	1436.24	1508.4694
	H	-0.114948	-0.389470	0.012611	1629.4883	3183.95	3330.1810
	H	-2.324381	0.137155	-0.828992	3666.6407	3813.7576	3935.3650
	O	-1.874998	0.177916	0.020961			

TS_{WM}	C -1.006422 0.515997 0.008835 H 0.363026 0.769681 0.015035 H -1.340918 1.026908 0.923637 H -1.273163 1.033722 -0.925034 O -0.828801 -0.748636 0.010748 H 0.860446 -0.683665 -0.087404 H 1.987319 0.057738 0.739278 O 1.509028 0.086090 -0.100563	-1381.2761 188.7210 373.6247 402.1024 553.3765 617.1818 821.99 1138.1143 1197.4839 1211.1802 1375.31 1519.3544 1597.7765 1713.9734 2960.7275 3041.2434 3088.2784 3817.0573
MR-WD	C 1.624684 -0.646780 0.278440 H 0.804341 -1.286595 -0.080653 H 1.429840 -0.490348 1.342557 H 2.584594 -1.132864 0.108322 O 1.495613 0.535310 -0.419639 H -1.423292 2.153358 -0.328180 H -0.163054 1.336766 -0.008796 H -1.597196 -0.355781 -0.013842 H -2.365144 -1.677582 0.120264 O -1.098996 1.445287 0.235062 O -1.523891 -1.313881 -0.166712	49.1017 65.67 66.66 120.7245 155.12 197.34 199.9369 211.02 357.20 397.2183 574.04 656.67 843.5776 1042.37 1178.97 1394.6224 1455.05 1529.90 1646.36 1665.91 2986.39 3081.95 3148.86 3617.99 3659.85 3900.18 3909.37
HM-WD	C 1.577060 -0.508740 0.410319 H -0.420104 -1.413993 -0.124840 H 1.208372 -0.314004 1.409347 H 2.474859 -1.088068 0.269558 O 1.371977 0.433125 -0.539185 H -1.583649 2.017965 -0.260571 H 0.583193 0.957832 -0.288149 H -1.443934 0.524452 0.106303 H -1.763657 -1.978221 0.348706 O -1.055633 1.406411 0.260073 O -1.381023 -1.296227 -0.211171	78.43 105.78 142.10 200.42 216.04 228.7773 274.09 281.06 320.8114 398.46 550.56 699.1170 760.90 899.91 1140.4513 1251.08 1478.58 1510.4094 1632.48 1651.60 3159.2826 3306.63 3489.52 3602.5402 3669.16 3894.81 3898.1470
TS_{WD}	C -1.552565 0.225967 0.177216 H -0.474998 1.003292 -0.016289 H -1.632392 0.400059 1.263376 H -2.319457 0.738103 -0.418138 O -1.092684 -0.893167 -0.241631 H 1.889932 -1.540721 -0.454687 H 0.464068 -1.171925 0.082117 H 1.244853 0.563144 -0.089663 H 1.060237 2.003150 0.551133 O 1.444328 -0.984749 0.191039 O 0.783749 1.459054 -0.197052	-1075.77 71.22 186.2543 314.6233 318.9303 349.1730 387.4418 470.8772 539.1420 582.0361 599.9233 907.2542 1072.7153 1136.1818 1198.7408 1241.9055 1352.1661 1508.8484 1586.5513 1647.0529 1694.1074 2876.3894 2947.9467 3052.1656 3101.5656 3831.9969 3884.0190

MR-FA	C	-2.052698	0.524993	0.076215			
	H	-1.306125	1.259131	-0.228755	40.3170	86.4580	125.6243
	H	-2.151417	0.606489	1.168719	155.2585	180.6970	209.6524
	H	-3.031596	0.694212	-0.370856	672.2190	807.7323	937.8172
	O	-1.604893	-0.764896	-0.134572	1042.9286	1079.5520	1142.664
	C	1.722305	0.115209	0.020609	1202.5510	1375.1448	1410.067
	O	1.153459	-1.089016	0.059260	1430.1417	1441.4301	1525.887
	H	0.176890	-0.969956	-0.010754	1771.4689	2998.9995	3100.006
	O	1.137058	1.171977	-0.078662	3109.3138	3161.6177	3426.185
	H	2.809616	0.024391	0.092494			
MA-FA	C	-1.800717	0.523674	0.354276			
	H	0.157259	1.114783	-0.120741	92.1393	132.5318	158.0052
	H	-1.429815	0.444542	1.369361	177.8394	210.0715	335.1436
	H	-2.664446	1.132478	0.144673	671.4281	745.0239	801.0968
	O	-1.676894	-0.553924	-0.455107	830.7942	1075.8084	1116.497
	C	1.608167	-0.096982	0.008791	1198.0583	1248.4473	1359.648
	O	0.945221	-1.088904	0.243429	1420.7062	1439.6606	1509.519
	H	-0.863789	-1.024344	-0.190475	1756.5087	3132.0642	3152.884
	O	1.138913	1.127501	-0.204314	3308.5377	3430.4857	3603.395
	H	2.698165	-0.105002	-0.053284			
TS_{FA}	C	-1.686233	0.469583	0.226401			
	H	-0.558927	0.990393	-0.056682	-1581.0941	111.5960	228.2984
	H	-1.532307	0.575994	1.312175	261.0540	389.4417	415.6065
	H	-2.495433	1.074226	-0.184142	544.6929	760.9463	1013.599
	O	-1.456043	-0.683456	-0.308575	1067.4046	1162.5465	1198.660
	C	1.495744	0.080996	0.008453	1242.5259	1294.9177	1317.449
	O	0.958896	-1.091916	0.150798	1406.1732	1476.9912	1541.168
	H	-0.077257	-1.042473	0.019649	1595.5030	1743.4637	2359.819
	O	0.899805	1.154806	-0.162035	2975.1113	3133.1158	3138.370
	H	2.585598	0.062917	0.058366			
MR-SA	C	-2.915023	0.496359	0.011898			
	H	-2.522735	1.068147	-0.830346	21.7927	47.5046	105.8865
	H	-2.494425	0.965032	0.913268	108.4937	137.4555	224.7016
	H	-4.002036	0.510538	0.064505	267.1392	376.4545	424.1798
	O	-2.415190	-0.790996	0.023246	507.4708	536.6131	546.5106
	O	0.131338	-0.989986	-0.786004	767.1543	827.4224	903.2702
	H	-0.813612	-0.942525	-0.472221	911.0901	1035.7410	1151.8127
	O	0.076530	1.252092	0.228191	1162.49	1212.7792	1324.3341
	S	0.951852	0.149227	-0.071781	1391.2265	1437.2317	1456.8997
	O	1.283218	-0.502939	1.357044	1528.8446	3002.8137	3100.7217
	H	2.054365	-1.079815	1.241329	3168.1656	3229.8462	3767.1996
	O	2.178972	0.295933	-0.802405			

HM-SA	C 2.510875 0.680962 0.050198 H 0.795983 0.576275 1.022455 H 2.004345 1.188305 -0.763026 H 3.315531 1.172627 0.572400 O 2.654199 -0.660886 -0.028989 O -0.008152 -0.880376 -0.871317 H 1.898349 -1.011354 -0.529868 O -0.139467 0.345177 1.273393 S -0.907671 -0.146997 -0.013395 O -1.175219 1.21807 -0.807261 H -1.951734 1.643462 -0.409544 O -2.156985 -0.684880 0.436762	39.5454 92.0279 133.9790 157.3991 193.4639 273.6392 339.8196 382.3827 424.2778 503.4366 536.7415 547.1142 657.9004 732.0890 831.6837 851.1883 901.8792 1106.0538 1161.4534 1207.9206 1254.4039 1271.2194 1407.9641 1454.8035 1508.6361 3147.9997 3237.1761 3304.7289 3686.2906 3759.2855
TS_{SA}	C -2.450647 0.565668 -0.020888 H -1.457484 0.758118 -0.733978 H -2.050967 1.184776 0.796835 H -3.358948 0.928019 -0.493884 O -2.324418 -0.723092 0.097017 O -0.008582 -1.075531 0.623297 H -1.135673 -0.952674 0.453688 O 0.036471 0.650509 -1.128048 S 0.844939 -0.052198 -0.120732 O 2.110185 -0.610565 -0.504571 O 1.104439 1.098098 0.975020 H 1.843171 0.807569 1.532654	-1703.5797 35.0188 114.6252 211.4644 219.0340 337.9861 378.8078 409.2606 452.8162 479.6697 548.1197 562.8545 675.8058 818.4387 900.9640 1002.4573 1074.7410 1151.5177 1196.6273 1220.2323 1253.6144 1324.6264 1365.2764 1403.8972 1519.71 1602.4591 1743.6568 2993.2428 3186.3530 3765.2460
WM	O 0.000000 0.000000 0.118189 H 0.000000 0.758025 -0.472754 H 0.000000 -0.758025 -0.472754	1627.7612 3824.7050 3950.6090
WD	O -1.385097 0.000601 0.110496 H -1.746597 -0.763119 -0.349950 H -1.747854 0.758911 -0.357831 O 1.512857 -0.000695 -0.121976 H 0.559405 0.000611 0.048517 H 1.912972 0.004353 0.751104	127.0098 147.1099 154.9316 184.1613 360.4078 630.2965 1629.3162 1650.2617 3718.7825 3813.9011 3915.1798 3935.2566
FA	C 0.000000 0.422392 0.000000 H -0.376774 1.447695 0.000000 O 1.163418 0.108154 0.000000 O -1.034994 -0.439528 0.000000 H -0.650614 -1.331055 0.000000	625.952 674.778 1058.557 1130.131 1301.324 1408.906 1794.039 3125.306 3741.349
SA	H 1.683905 -0.014800 1.107699 O 0.659484 1.084346 -0.827065 O 1.034771 -0.687872 0.848480 S 0.000058 0.000064 -0.159243 O -1.035291 0.687175 0.848517 H -1.684504 0.013827 1.106801 O -0.659005 -1.083655 -0.828259	242.8958 328.1320 367.2603 431.4837 485.9993 531.5543 542.2237 821.4432 873.6608 1155.1241 1170.0433 1219.2879 1469.2375 3760.6034 3764.8107

Table S7 Absolute energies (in Hartree) of all species involved in isomerization of MR calculated at the two different levels of theory

Species	MP2/aug-cc-pVTZ	CCSD(T)/aug-cc-pVTZ
MR	-114.84396077	-114.885062
TS	-114.79613291	-114.8328949
HM	-114.86634476	-114.8988607
MR-WM	-191.18101248	-191.2357163
TS_{WM}	-191.14159052	-191.1909453
HM-WM	-191.20605728	-191.2519222
MR-WD	-267.52313693	-267.5914694
TS_{WD}	-267.50181805	-267.5656003
HM-WD	-267.55128696	-267.6106135
MR-FA	-304.34423196	-304.4168392
TS_{FA}	-304.32465040	-304.395769
HM-FA	-304.36904354	-304.4328489
MR-SA	-814.28172138	-814.3693943
TS	-814.26141531	-814.3478167
HM-SA	-814.30415433	-814.3829675

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