

## **Cyclization Reactions in Isoprene Derived $\beta$ -Hydroxy Radicals: Implications for the Atmospheric Oxidation Mechanism**

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Table IS. Optimized geometry of isomer IIa.

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	-1.221772	-1.255195	-0.324242
6	-0.382183	-0.050810	-0.011811
6	0.991919	-0.184490	-0.651060
6	2.146345	0.023523	-0.020562
6	-1.065277	1.243870	-0.503983
1	-1.000893	-1.911378	-1.159761
1	-2.148380	-1.400944	0.222834
1	0.986910	-0.463980	-1.705284
1	2.169941	0.318099	1.024759
1	3.099922	-0.079971	-0.530634
1	-2.068289	1.323587	-0.072890
1	-0.472318	2.108159	-0.186893
1	-1.147965	1.251542	-1.595199
8	-0.287311	0.114257	1.413583
1	0.065362	-0.720563	1.764353

Table IIS. Optimized geometry of transition state species IIts1.

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	0.933825	-0.557314	1.332475
6	0.400409	-0.051684	0.019649
6	-0.945981	0.598342	0.314689
6	-2.159530	0.155588	-0.018862
6	1.352276	0.986552	-0.603641
1	0.638317	-1.543773	1.672443
1	1.446548	0.105724	2.022458
1	-0.865618	1.515762	0.896517
1	-2.338991	-0.755000	-0.589346
1	-3.054596	0.697190	0.272501
1	2.314103	0.512209	-0.820922
1	0.929053	1.367746	-1.538124
1	1.523278	1.828387	0.076940
8	0.316974	-1.146102	-0.899016
1	-0.613874	-1.348334	-1.066201

Table IIIS. Optimized geometry of isomer IIb.

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	0.167713	-0.791894	1.083892
6	-0.512543	0.064265	0.076663
6	0.819251	-0.616153	-0.309090
6	2.032342	0.164410	-0.487117
6	-1.796054	-0.377929	-0.592151
1	-0.253760	-1.765140	1.323048
1	0.652572	-0.281650	1.910634
1	0.713297	-1.476842	-0.967034
1	2.203920	1.061046	0.097549
1	2.799936	-0.153450	-1.183082
1	-2.657567	-0.126158	0.037644
1	-1.926536	0.122337	-1.560905
1	-1.802374	-1.458544	-0.770725
8	-0.458093	1.439223	0.368960
1	-0.328999	1.908422	-0.471994

Table IVS. Optimized geometry of transition state species II<sub>ts</sub>2.

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	0.257231	-0.584844	1.087922
6	-0.637647	0.083865	0.119515
6	1.063079	-0.656564	-0.179560
6	2.114764	0.195270	-0.500263
6	-1.796933	-0.592250	-0.548305
1	-0.084265	-1.534315	1.504835
1	0.662580	0.075783	1.855270
1	0.893625	-1.533671	-0.800209
1	2.387791	1.025469	0.143724
1	2.634800	0.105863	-1.448670
1	-2.723997	-0.454332	0.031031
1	-1.979494	-0.187824	-1.554196
1	-1.622331	-1.668007	-0.650173
8	-0.669677	1.458788	0.214416
1	-0.814261	1.827872	-0.672795

Table VS. Optimized geometry of isomer IIc.

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	0.297959	-0.745959	0.195690
6	-0.937501	0.029392	-0.158026
6	1.554712	-0.222055	-0.456772
6	2.675401	0.094083	0.190373
6	-2.302132	-0.566776	-0.004393
1	0.133409	-1.788676	-0.113962
1	0.447394	-0.770709	1.291526
1	1.509748	-0.112823	-1.540796
1	2.753511	0.009889	1.272621
1	3.557268	0.452765	-0.333771
1	-2.634193	-0.605910	1.050350
1	-3.059108	0.011447	-0.554893
1	-2.328456	-1.590372	-0.392438
8	-0.807775	1.380595	0.103335
1	-1.648007	1.817517	-0.106551

Table VIS. Optimized geometry of isomer IIIa.

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	0.126269	-0.217261	-0.735266
6	-0.625776	-0.077248	0.585430
1	-1.583918	-0.612301	0.483823
6	-0.904416	1.355818	0.907466
1	-1.810260	1.835563	0.551000
1	-0.110159	1.981796	1.303958
6	1.568988	0.219567	-0.745321
1	2.013763	0.084005	-1.735762
1	2.148119	-0.357294	-0.016494
1	1.670700	1.276489	-0.467695
6	-0.498926	-0.690336	-1.817732
1	-1.535138	-1.018588	-1.784935
1	0.004062	-0.767316	-2.778443
8	0.178130	-0.689652	1.602780
1	-0.219043	-0.448371	2.454847

Table VIIS. Optimized geometry of transition state species IIIts1.

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	-0.630818	0.009964	-0.108672
6	0.757015	-0.509515	-0.311789
1	0.798983	-1.368132	-0.993266
6	0.541731	-0.875018	1.106150
1	0.230470	-1.876407	1.375890
1	0.794379	-0.176640	1.894600
6	-0.806595	1.454484	0.318413
1	-1.698885	1.574258	0.942190
1	-0.929081	2.088273	-0.568337
1	0.058954	1.833116	0.865295
6	-1.736841	-0.732737	-0.521665
1	-2.746556	-0.383263	-0.331283
1	-1.625162	-1.712247	-0.977635
8	1.725990	0.471380	-0.610049
1	2.562020	0.166933	-0.221685

Table VIIS. Optimized geometry of isomer IIIb.

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	-0.589902	-0.002180	0.035744
6	0.790693	-0.573347	-0.317319
1	0.792570	-1.424882	-1.000105
6	0.253770	-0.783698	1.063586
1	-0.081516	-1.775044	1.357821
1	0.698447	-0.194825	1.862768
6	-0.704699	1.502324	0.224086
1	-1.474315	1.739407	0.968068
1	-0.984390	1.987213	-0.718746
1	0.243565	1.935488	0.549368
6	-1.762236	-0.668483	-0.531473
1	-1.787700	-1.746392	-0.658559
1	-2.609165	-0.093872	-0.890149
8	1.832299	0.340792	-0.530406
1	2.618352	-0.001119	-0.074960

Table IXS. Optimized geometry of transition state species III<sub>ts</sub>2.

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	-0.760761	-0.003596	0.108549
6	0.951701	-0.617140	-0.307809
1	0.913465	-1.408482	-1.046186
6	0.232966	-0.728594	0.978546
1	-0.050674	-1.732471	1.301846
1	0.651576	-0.149766	1.808130
6	-0.760211	1.510003	0.146144
1	-1.158926	1.881961	1.100045
1	-1.385133	1.916201	-0.655910
1	0.247228	1.921963	0.016830
6	-1.824874	-0.693371	-0.482609
1	-1.932146	-1.769493	-0.379995
1	-2.517608	-0.185703	-1.146151
8	1.986576	0.268298	-0.502090
1	2.306691	0.575595	0.361184

Table XS. Optimized geometry of transition state species III<sub>c</sub>.

Atomic Number	Coordinates (Angstroms)		
	x	y	z
6	-0.998751	-0.020989	0.100826
6	1.409932	-0.724773	-0.271841
1	1.371302	-1.159908	-1.266710
6	0.204964	-0.799130	0.623278
1	-0.072973	-1.852480	0.749638
1	0.478707	-0.425988	1.626012
6	-0.858966	1.480124	0.063144
1	-0.710759	1.885550	1.075087
1	-1.746142	1.958440	-0.362941
1	0.014790	1.780968	-0.528048
6	-2.100266	-0.650435	-0.321942
1	-2.190185	-1.733723	-0.287912
1	-2.953328	-0.105448	-0.719187
8	2.207965	0.396803	-0.260393
1	2.203401	0.769380	0.636426

Table XIS. Frequencies of isomer II, its isomers, and transition state species ( $\text{cm}^{-1}$ ).  
 The imaginary frequencies of transition state species are indicated by *i*.

IIa	IIIs1	IIb	IIIs2	IIc
116.5505	421.1774 <i>i</i>	187.5619	519.0532 <i>i</i>	58.7710
125.7830	76.1868	207.5682	157.2357	84.4112
248.7298	167.5949	213.1639	167.1045	167.7469
285.5611	252.8581	243.5630	218.5420	212.0726
301.8700	283.3870	305.0972	316.7480	341.7793
319.2441	298.7382	364.5818	359.6586	358.0009
380.5773	348.9760	410.2843	391.9196	369.5591
417.6284	400.8695	437.0555	448.2876	415.6092
436.1928	435.4210	476.5983	451.5772	471.5390
525.7997	506.6632	551.1038	504.5856	624.3467
578.2846	567.9758	655.6541	649.2463	833.5028
702.7703	682.0618	794.1119	779.8694	916.5523
742.0788	744.2266	855.8728	876.9626	934.1459
892.5397	902.8564	900.1653	901.5910	941.1197
951.8474	912.7055	935.8257	957.1470	1008.7221
963.6279	928.8558	1000.7968	994.5830	1029.5950
996.0277	969.2205	1032.6962	1030.0979	1038.6142
1034.6878	1026.2444	1057.3604	1070.7855	1129.4419
1044.5250	1050.2064	1102.7580	1168.9883	1137.4829
1051.7745	1116.3600	1117.0953	1198.9805	1225.8866
1206.5303	1206.3884	1199.8616	1216.5738	1309.5615
1261.4108	1246.6938	1257.3597	1272.9590	1334.6943
1329.8891	1314.3032	1284.2395	1338.9465	1354.8607
1349.3406	1364.2133	1376.5221	1418.6135	1418.8314
1417.2418	1423.5398	1421.9755	1425.0301	1440.8291
1455.5951	1462.8145	1441.5807	1443.8559	1470.2926
1474.0140	1479.4901	1491.5319	1497.2731	1487.6551
1512.0353	1515.7209	1499.2120	1507.0048	1502.7973
1519.4473	1521.8610	1515.6831	1524.9197	1520.3164
1726.1387	1712.7764	1529.9969	1536.8069	1733.3581
3057.3758	3056.1981	3038.1798	3000.4349	2944.1329
3135.6210	3128.6925	3099.5783	3052.1137	2951.2690
3138.5087	3142.1204	3121.5815	3097.1280	3035.0036
3148.1324	3147.1263	3146.3775	3121.2002	3036.1531
3167.2807	3164.9899	3155.5346	3162.9334	3115.0952
3172.2032	3170.9292	3183.8803	3169.6852	3148.6145
3250.9544	3230.0013	3238.5694	3178.3604	3158.9994
3273.9141	3281.2710	3282.5240	3256.4994	3234.6967
3717.1739	3784.5717	3710.8450	3699.1493	3743.9568

Table XIIS. Frequencies of isomer III, its isomers, and transition state species ( $\text{cm}^{-1}$ ).  
 The imaginary frequencies of transition state species are indicated by *i*.

IIIa	IIIts1	IIIb	IIIts2	IIIc
71.0970	578.4633 <i>i</i>	134.6837	521.6374 <i>i</i>	74.0373
175.0798	136.5661	177.0685	164.9460	116.9755
211.2211	192.3271	215.4250	187.6177	204.7964
236.0633	263.5563	245.7425	243.7445	223.0484
276.5982	294.6762	271.5383	273.6971	338.9256
331.9823	374.8757	358.6745	369.9453	398.0772
365.6177	388.0628	382.0253	398.3840	418.2589
439.7943	446.0221	451.5837	449.0188	451.0853
522.3369	510.1753	477.7764	476.1115	557.6490
562.5810	519.9007	514.3485	511.7135	660.2828
600.2330	668.4245	707.5276	630.5355	726.1889
741.5064	673.9247	750.5209	745.2950	821.1820
784.0306	724.1886	883.7460	786.6145	899.5111
910.0500	792.3626	933.7186	908.1627	917.4181
925.0870	893.5886	952.5781	966.5184	977.9654
987.9368	971.4182	984.0250	1001.8727	1005.0024
1029.6712	1018.3306	1044.5919	1046.7072	1056.6531
1082.3362	1068.8977	1055.3483	1064.3405	1086.4862
1090.7197	1106.4549	1105.9471	1096.0244	1176.9306
1117.0771	1173.4067	1135.1663	1188.4823	1208.1660
1239.3034	1207.6321	1190.4242	1233.1829	1296.9501
1319.5382	1298.5270	1287.2850	1302.9753	1322.8046
1362.0433	1334.7143	1304.1556	1342.4256	1353.9872
1386.8436	1369.0319	1349.7975	1390.4318	1438.2959
1435.1353	1430.5959	1421.7904	1426.6767	1445.6011
1473.0247	1448.3089	1442.1181	1445.4766	1470.8732
1476.0632	1481.9444	1488.1114	1495.9870	1490.2788
1507.3123	1515.4577	1504.5884	1518.9869	1511.1649
1527.6871	1519.1496	1521.7824	1528.9364	1530.7734
1728.1043	1537.5118	1533.1425	1536.5546	1728.2730
2988.5219	3047.9228	3051.0953	3033.4288	2978.0084
3048.8874	3054.7652	3107.0867	3069.6913	3026.0700
3107.2726	3110.0540	3115.0470	3092.4272	3078.3840
3135.1020	3154.7304	3136.8933	3121.5022	3084.7713
3157.4995	3165.1906	3152.4145	3141.6634	3128.5999
3166.3145	3191.6981	3169.7259	3163.1416	3155.2166
3233.5764	3253.5052	3223.8059	3234.4192	3200.8364
3272.3794	3300.7296	3267.7241	3250.2056	3230.4984
3732.4097	3723.8872	3716.4781	3719.0076	3727.7471



Table XIIS. Moments of inertia of isomer II, its isomers, and transition state species (amu\*bohr<sup>2</sup>).

<b>IIa</b>	<b>IIts1</b>	<b>IIb</b>	<b>IIts2</b>	<b>IIc</b>
381.91701	365.90816	347.32041	335.02756	294.78588
652.38579	588.05866	583.15831	634.55521	770.07087
721.81857	698.09185	698.31373	762.28301	954.74946

Table XIVS. Moments of inertia of isomer III, its isomers, and transition state species (amu\*bohr<sup>2</sup>).

<b>IIIa</b>	<b>IIIts1</b>	<b>IIIb</b>	<b>IIIts2</b>	<b>IIIc</b>
375.47233	378.94272	339.61441	335.43110	225.60204
644.68042	648.31232	596.08554	648.81956	926.25131
649.78796	659.12210	681.90812	742.21002	1071.42785