ESI of

$HO_2^{\bullet}$ as a potential reactant for the bimolecular reaction of tert-butoxy radical in the atmosphere

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Table S1: Cartesian coordinates and all normal mode frequencies of the optimized geometries calculated at M062X/aug-cc-pVTZ level of theory.

Species	Cartesian coordinate (Å)				Frequencies (cm^{-1})			
	O	0.055047	-0.599984	0.000000				
$HO_2^\bullet$	O	0.055047	0.708041	0.000000	1253.4	1459.6	3690.2	
	H	-0.880751	-0.864454	0.000000				
	C	-0.682607	-1.226327	-0.435446				
	H	-0.205244	-2.108659	-0.014019				
	H	-1.735875	-1.221114	-0.162375	182.1	247.6	260.1	331.5
	H	-0.593082	-1.253404	-1.521177	331.9	384.7	412.2	430.0
	C	0.011290	0.055192	0.072287	763.4	902.4	904.4	935.3
$tBuO^\bullet$	C	1.497128	0.027822	-0.283531	962.6	1003.6	1026.0	1189.6
	H	1.995737	0.904813	0.128587	1201.8	1271.8	1378.7	1382.8
	H	1.964493	-0.864009	0.131027	1416.2	1468.1	1482.3	1488.3
	H	1.632456	0.031812	-1.365336	1494.7	1496.1	1521.4	3061.7
	C	-0.684610	1.292399	-0.493448	3066.0	3070.9	3135.8	3141.2
	H	-0.591573	1.321751	-1.579310	3147.6	3148.8	3153.0	3161.4
	H	-1.740123	1.282764	-0.226160				
	H	-0.231033	2.195166	-0.084986				
	O	-0.161785	-0.016138	1.440979				
	C	2.439591	-0.416985	-0.319422				
	H	2.560247	-1.499238	-0.280987	42.7	71.6	91.9	122.5
	H	2.710715	-0.069913	-1.315037	188.8	212.0	260.6	263.7
	H	3.114168	0.030752	0.409810	328.8	344.4	413.8	419.3
	C	0.995679	-0.038418	-0.004483	469.0	610.0	758.2	861.9
	C	0.555506	-0.512842	1.378932	927.5	937.2	968.5	1019.7
	H	-0.466158	-0.194485	1.580823	1037.7	1161.8	1220.0	1268.3

RC	H	0.610797	-1.599792	1.437295	1284.1	1375.5	1388.7	1418.1
	H	1.213283	-0.095125	2.140655	1466.1	1484.9	1490.1	1491.7
	C	0.798531	1.496383	-0.125379	1499.5	1522.6	1556.3	3065.2
	H	1.443797	1.960055	0.620396	3069.0	3072.2	3140.1	3145.6
	H	1.087567	1.838739	-1.116472	3152.3	3154.9	3157.6	3174.5
	H	-0.238924	1.755794	0.072272	3351.5			
	O	0.148823	-0.522591	-0.983469				
	O	-2.510267	-0.589205	-0.370423				
	H	-1.564993	-0.692664	-0.643717				
	O	-2.539349	0.536427	0.293526				
TS_H	C	-2.325685	-0.562737	0.144488				
	H	-2.449644	-1.434326	-0.493949	-1030.6	26.4	82.6	105.2
	H	-2.513609	-0.836431	1.179824	173.8	189.6	263.2	265.7
	H	-3.023804	0.216064	-0.161641	329.0	336.4	361.7	401.9
	C	-0.893648	0.018460	-0.008137	461.0	533.1	750.7	827.9
	C	-0.623981	0.371732	-1.469028	922.0	926.9	966.8	986.7
	H	0.395402	0.738977	-1.581676	1035.1	1112.1	1160.3	1195.7
	H	-0.756303	-0.508340	-2.096940	1265.4	1370.5	1381.1	1414.4
	H	-1.309258	1.150836	-1.802212	1464.6	1481.2	1487.4	1494.4
	C	-0.723302	1.219979	0.924091	1497.4	1522.3	1539.5	1728.5
	H	-1.401101	2.019695	0.626138	3066.6	3070.1	3072.2	3144.5
	H	-0.940769	0.930385	1.950736	3148.6	3153.1	3156.7	3158.4
	H	0.298933	1.590799	0.866428	3171.9			
	O	-0.102623	-1.032431	0.409856				
	O	2.334353	-0.685704	0.161779				
	H	1.319293	-0.886232	0.244389				
	O	2.490839	0.559882	-0.106582				

PC	C	2.620874	0.120703	-0.015811				
	H	2.949502	0.547610	-0.962707	25.2	41.3	51.1	57.8
	H	2.949820	0.775264	0.790558	70.2	201.7	268.3	277.7
	H	3.086524	-0.856447	0.111032	315.6	346.6	351.7	421.8
	C	1.106636	-0.003499	0.000403	466.9	472.4	771.0	925.5
	C	0.624047	-0.878388	-1.151401	938.9	962.7	963.5	1035.6
	H	-0.466393	-0.939819	-1.154629	1051.2	1167.0	1258.8	1275.3
	H	0.948820	-0.456173	-2.101785	1365.5	1399.9	1410.2	1426.3
	H	1.017768	-1.891435	-1.063263	1473.6	1483.9	1487.1	1500.2
	C	0.624290	-0.557420	1.336674	1509.0	1520.0	1754.4	3053.2
	H	1.018338	-1.559553	1.508553	3056.6	3067.2	3121.2	3126.8
	H	0.948990	0.092402	2.148557	3139.3	3140.0	3145.2	3146.6
	H	-0.466071	-0.616249	1.355741	3864.3			
	O	0.618448	1.328130	-0.171187				
	O	-2.697211	0.609444	-0.073659				
	H	-0.342563	1.305076	-0.172371				
	O	-3.108714	-0.498705	0.059986				
tBuOH	C	-0.717550	-1.250377	-0.545948				
	H	-0.274679	-2.155480	-0.131838	201.9	267.0	280.2	306.0
	H	-1.786990	-1.263594	-0.338680	344.8	347.6	420.5	465.5
	H	-0.567461	-1.246080	-1.625067	471.9	771.1	925.0	938.9
	C	-0.080476	-0.023819	0.085037	961.6	963.9	1035.0	1051.0
	C	1.425242	-0.013293	-0.153914	1165.9	1259.6	1275.4	1364.7
	H	1.883193	0.853072	0.328378	1399.5	1409.4	1426.2	1473.9
	H	1.875022	-0.915763	0.258551	1484.1	1487.6	1500.3	1509.5
	H	1.650883	0.036892	-1.219401	1520.1	3050.3	3054.3	3067.8

	C	-0.720902	1.252836	-0.448285	3118.7	3124.7	3139.8	3140.9
	H	-0.568208	1.345995	-1.523785	3145.1	3148.1	3864.5	
	H	-1.791074	1.246953	-0.244394				
	H	-0.282034	2.130428	0.031433				
	O	-0.343468	-0.144394	1.483918				
	H	0.041656	0.611591	1.935452				
O_2	O	0.000000	0.000000	0.594930		1754.4		
	O	0.000000	0.000000	-0.594930				
	C	0.066257	0.000017	-0.022338				
	C	-1.210896	-0.000351	-0.814405	-1851.0	178.9	233.8	309.5
	C	0.898844	-1.261436	-0.123257	336.0	357.2	409.0	470.1
	C	0.897755	1.262214	-0.123019	650.3	830.5	883.9	921.3
	O	-0.725289	-0.000518	1.188997	956.4	977.5	1022.7	1027.8
	H	-1.720122	-0.000911	0.414255	1116.2	1175.7	1293.4	1310.3
TS_I	H	-1.517800	0.927159	-1.282898	1404.4	1412.7	1433.5	1474.7
	H	-1.516760	-0.927612	-1.284061	1489.1	1496.2	1507.2	1974.0
	H	0.263393	-2.141434	-0.031325	3043.7	3047.6	3117.9	3119.3
	H	1.424045	-1.300879	-1.078164	3124.3	3129.3	3131.2	3231.2
	H	1.637241	-1.284864	0.678553				
	H	1.421998	1.302726	-1.078408				
	H	0.261637	2.141598	-0.029899				
	H	1.636920	1.285702	0.678083				
	C	-0.038150	0.029445	0.014058				
	C	-1.114346	0.020996	-1.019411	86.1	231.7	278.5	317.4
	C	0.772692	-1.262193	-0.031632	328.2	349.9	410.6	449.9
	C	0.872411	1.242839	-0.159156	471.6	545.7	783.5	919.6
	O	-0.620515	0.191855	1.312498	946.1	950.3	1002.7	1023.7

	H	-1.282861	-0.495317	1.431372	1139.3	1239.1	1278.7	1346.3
(OH)tBu$^{\bullet}$	H	-1.889270	0.772413	-0.971198	1395.0	1410.2	1455.0	1478.5
	H	-1.044342	-0.606913	-1.894995	1486.2	1499.8	1509.3	3056.0
	H	0.123885	-2.124782	0.130219	3064.3	3127.0	3139.8	3146.9
	H	1.259229	-1.378563	-1.000495	3151.1	3165.4	3275.5	3855.2
	H	1.533828	-1.246946	0.747036				
	H	1.383412	1.202421	-1.120220				
	H	0.284261	2.157761	-0.107771				
	H	1.613912	1.258222	0.640188				
	C	0.707690	1.287667	-0.480101				
	H	0.224911	2.139859	-0.008351	-588.3	134.8	219.2	230.6
	H	1.787478	1.389104	-0.348992	239.5	248.2	385.9	450.2
	H	0.496757	1.277451	-1.547730	508.1	616.4	642.3	789.4
	C	0.284427	0.000000	0.211402	901.6	959.4	968.7	1076.5
TS$_D$	C	-1.717849	0.000000	-0.339965	1081.2	1228.7	1387.1	1393.4
	H	-2.055292	-0.916180	0.120919	1421.3	1437.8	1472.7	1473.5
	H	-2.055292	0.916180	0.120919	1478.9	1492.6	1578.8	3060.3
	H	-1.627199	0.000000	-1.417570	3064.0	3111.6	3131.3	3135.9
	C	0.707690	-1.287667	-0.480101	3168.3	3170.4	3271.4	3282.0
	H	0.496757	-1.277452	-1.547730				
	H	1.787477	-1.389104	-0.348992				
	H	0.224911	-2.139859	-0.008351				
	O	0.103468	0.000000	1.439809				
	C	1.282300	-0.610596	-0.000020				
	H	2.137008	0.058802	-0.000170				
	H	1.315530	-1.258313	0.877272	39.5	146.8	384.1	494.3
	H	1.315478	-1.258766	-0.876963	541.1	806.8	889.1	898.6

Acetone	C	0.000000	0.186064	0.000013	1087.3	1126.4	1251.1	1388.8
	C	-1.282300	-0.610596	-0.000020	1398.1	1462.6	1468.9	1473.7
	H	-1.315478	-1.258766	-0.876963	1492.9	1848.5	3063.4	3069.0
	H	-1.315530	-1.258313	0.877272	3125.0	3131.9	3180.6	3181.6
	H	-2.137008	0.058802	-0.000170				
	O	0.000000	1.390916	-0.000014				
	C	0.000000	-0.000471	0.000000				
$CH_3^{\bullet}$	H	-0.535164	0.058870	0.932152	421.7	1413.2	1413.2	3141.2
	H	-0.535164	0.058870	-0.932152	3317.2	3318.1		
	H	1.070327	-0.114913	0.000000				
	C	-0.201207	-0.154536	-0.528725				
	H	-1.163185	-0.233281	0.324792				
	H	-0.671098	0.737134	-0.951733				
	H	-0.399017	-1.100176	-1.023183	-2669.3	14.94	87.77	110.4
	C	1.189604	0.013334	0.002985	194.29	204.13	242.77	343.54
TS_β	C	2.187424	-1.061213	-0.37426	355.78	382.86	459.53	483.97
	H	3.042934	-1.018943	0.299951	587.86	681.49	786.48	887.32
	H	1.730319	-2.045842	-0.29274	920.94	956.03	978.18	1020.29
	H	2.545861	-0.914296	-1.393175	1055.32	1175	1195.11	1309.72
	C	1.756052	1.416938	-0.051161	1337.29	1408.26	1415.57	1421.23
	H	2.106404	1.652587	-1.05621	1469.01	1477.63	1488.92	1500.15
	H	0.998449	2.141228	0.243483	1509.9	1575.07	3046.17	3063.56
	H	2.599053	1.498187	0.63499	3067.61	3136.44	3141.7	3149.49
	O	0.475637	-0.26273	1.163066	3152.32	3202.21		
	O	-2.511988	-0.187319	0.503999				
	O	-3.011269	0.199583	-0.551966				
	C	1.393067	-1.015851	0.101897				

	H	1.705112	-1.397714	-0.872222				
	H	2.268831	-0.783668	0.700148	62.41	133.22	226.55	239.25
	H	0.802964	-1.800123	0.57767	390.1	531.68	597.7	777.46
	C	0.556978	0.222461	-0.107418	807.1	940.39	982.59	1008.65
Butanone	C	-0.823007	0.020887	-0.695427	1107.79	1120.66	1230.38	1288.39
	H	-1.085196	0.916948	-1.254999	1344.86	1391.65	1408.55	1465.12
	H	-0.821983	-0.834465	-1.372456	1478.91	1488.01	1506.13	1511.55
	C	-1.830098	-0.205429	0.436553	1844.79	3063.87	3068.24	3077.94
	H	-2.832154	-0.347515	0.036418	3125.54	3128.11	3145.43	3151.53
	H	-1.575308	-1.088183	1.023544	3181.2			
	H	-1.843867	0.654954	1.103725				
	O	0.949995	1.318419	0.205568				

Table S2: Cartesian coordinates of the optimized geometries and all normal mode frequencies of the species involved in tBuO$^{\bullet}$ + $HO_2^{\bullet}$ reaction, calculated at M062X/def2TZVP level of theory.

Species	Cartesian coordinate (Å)				Frequencies (cm^{-1})			
	O	0.055087	-0.598373	0.000000				
$HO_2^{\bullet}$	O	0.055087	0.706771	0.000000	1263.8	1461.9	3674.8	
	H	-0.881390	-0.867186	0.000000				
	C	-0.682952	-1.227003	-0.435974				
	H	-0.205304	-2.109839	-0.013835				
	H	-1.736840	-1.221846	-0.162077	180.3	248.2	259.9	332.2
	H	-0.594213	-1.255364	-1.522536	332.6	382.3	411.9	431.4
	C	0.011291	0.055071	0.071532	763.8	901.8	907.8	935.8
tBuO$^{\bullet}$	C	1.497848	0.027819	-0.283302	962.5	1002.1	1025.8	1191.2
	H	1.996424	0.905731	0.129003	1202.0	1273.4	1378.5	1382.3
	H	1.965580	-0.863962	0.133007	1416.0	1466.1	1479.9	1486.1

	H	1.635027	0.030868	-1.365677	1492.6	1494.0	1519.2	3063.4
	C	-0.684995	1.293028	-0.493392	3067.9	3072.8	3139.5	3144.8
	H	-0.593709	1.323306	-1.580174	3151.3	3152.8	3156.9	3165.3
	H	-1.740854	1.283961	-0.224267				
	H	-0.230516	2.196263	-0.084833				
	O	-0.161614	-0.015965	1.439617				
RC	C	2.438420	-0.421880	-0.324433				
	H	2.554166	-1.505670	-0.292044				
	H	2.708264	-0.071623	-1.320120	50.7	70.5	91.5	120.3
	H	3.118430	0.018998	0.405062	189.1	212.1	260.8	265.9
	C	0.996477	-0.037716	-0.004107	329.9	345.1	416.4	420.3
	C	0.555177	-0.522169	1.375681	468.9	592.6	759.6	868.2
	H	-0.461240	-0.191017	1.587024	928.0	937.9	969.1	1021.2
	H	0.593657	-1.611350	1.420635	1037.0	1164.2	1221.8	1269.3
	H	1.222111	-0.124600	2.141320	1293.8	1376.0	1388.8	1418.3
	C	0.807491	1.498713	-0.112944	1464.4	1483.0	1488.2	1490.0
	H	1.452990	1.955242	0.638146	1497.9	1520.9	1553.4	3067.4
	H	1.100215	1.848114	-1.101436	3071.2	3074.4	3143.9	3149.4
	H	-0.229951	1.762228	0.084102	3156.8	3159.1	3161.9	3177.3
	O	0.148935	-0.510751	-0.987119	3370.9			
	O	-2.518867	-0.588463	-0.367101				
	H	-1.576101	-0.699063	-0.647079				
	O	-2.538560	0.538846	0.289121				
	C	2.326959	-0.567174	-0.121214				
	H	2.450397	-1.418601	0.545600				
	H	2.515989	-0.876291	-1.147187				
	H	3.027779	0.219360	0.160475	-1189.9	14.2	81.0	104.4

TS_H	C	0.895550	0.017023	0.010672	170.2	189.3	264.1	266.4
	C	0.619250	0.425016	1.455103	333.5	337.6	387.6	407.3
	H	-0.396926	0.808254	1.548847	467.2	535.1	754.2	841.4
	H	0.736431	-0.434714	2.115117	921.0	928.4	961.9	967.0
	H	1.310906	1.207357	1.769590	1043.0	1112.8	1166.0	1206.8
	C	0.725551	1.184135	-0.967517	1270.4	1369.8	1384.2	1415.2
	H	1.405655	1.992931	-0.697904	1463.2	1478.8	1485.3	1492.8
	H	0.942460	0.855799	-1.983228	1496.5	1520.6	1544.3	1710.4
	H	-0.296401	1.559665	-0.923011	3068.9	3072.7	3075.0	3147.9
	O	0.101796	-1.043112	-0.379357	3153.4	3156.4	3161.1	3163.9
	O	-2.334299	-0.689122	-0.143943	3175.2			
	H	-1.316478	-0.899451	-0.193148				
	O	-2.490455	0.561196	0.091124				
PC	C	2.654057	0.143855	-0.037854				
	H	2.974311	0.430773	-1.039695				
	H	2.970359	0.919258	0.660200	5.9	28.0	37.2	37.9
	H	3.139726	-0.794330	0.232804	50.2	203.7	269.6	281.0
	C	1.142117	-0.004811	0.001318	310.1	346.6	349.0	421.0
	C	0.674869	-1.050796	-1.005513	467.0	472.8	771.7	924.9
	H	-0.415120	-1.131630	-0.996408	939.2	959.9	965.8	1036.1
	H	0.991052	-0.769048	-2.010210	1049.2	1169.0	1261.8	1276.0
	H	1.086300	-2.033524	-0.769558	1366.8	1398.0	1409.6	1426.4
	C	0.669531	-0.360296	1.407145	1471.2	1481.4	1484.7	1497.8
	H	1.081725	-1.317975	1.729050	1506.9	1517.8	1764.8	3054.1
	H	0.980930	0.411416	2.111596	3057.5	3069.9	3123.5	3129.1
	H	-0.420422	-0.436029	1.437513	3143.4	3144.3	3149.7	3151.1
	O	0.630577	1.276247	-0.366299	3858.3			

	O	-2.763421	0.582816	-0.163897				
	H	-0.331114	1.233990	-0.358200				
	O	-3.229805	-0.469139	0.131738				
tBuOH	C	-0.718055	-1.251445	-0.546804				
	H	-0.274970	-2.156857	-0.131550				
	H	-1.788094	-1.264458	-0.338538	203.4	270.1	282.0	312.2
	H	-0.568707	-1.248713	-1.627104	346.0	349.3	421.0	467.2
	C	-0.080733	-0.024420	0.084475	473.1	771.8	925.7	939.8
	C	1.425562	-0.013030	-0.153301	961.9	966.2	1035.4	1050.8
	H	1.883026	0.854471	0.329346	1167.6	1261.9	1276.6	1365.8
	H	1.875625	-0.915576	0.260944	1399.5	1410.2	1426.4	1472.1
	H	1.653569	0.036494	-1.219250	1481.7	1485.2	1498.5	1508.0
	C	-0.720927	1.253302	-0.447706	1517.8	3051.2	3055.3	3069.1
	H	-0.569932	1.348076	-1.524231	3121.4	3127.5	3142.9	3143.8
	H	-1.791624	1.247861	-0.242022	3149.0	3150.7	3858.0	
	H	-0.280857	2.131085	0.032503				
	O	-0.343688	-0.145080	1.482716				
	H	0.042958	0.613258	1.931979				
O_2	O	0.000000	0.000000	0.594124		1765.5		
	O	0.000000	0.000000	-0.594124				

Figure S1: Comparison of potential energy surface along with optimized geometries of stationary points for tBuO$^\bullet$ + $HO_2^\bullet$ reaction, obtained at CCSD(T)/CBS//M062X/aug-cc-pVTZ level of theory with the same calculated at CCSD(T)/CBS//M062X/def2TZVP level of theory. The energetics at CCSD(T)/CBS//M062X/def2TZVP level of theory are shown in paranthesis. Similarly, bond lengths at M062X/def2TZVP level of theory are shown in paranthesis (Å).

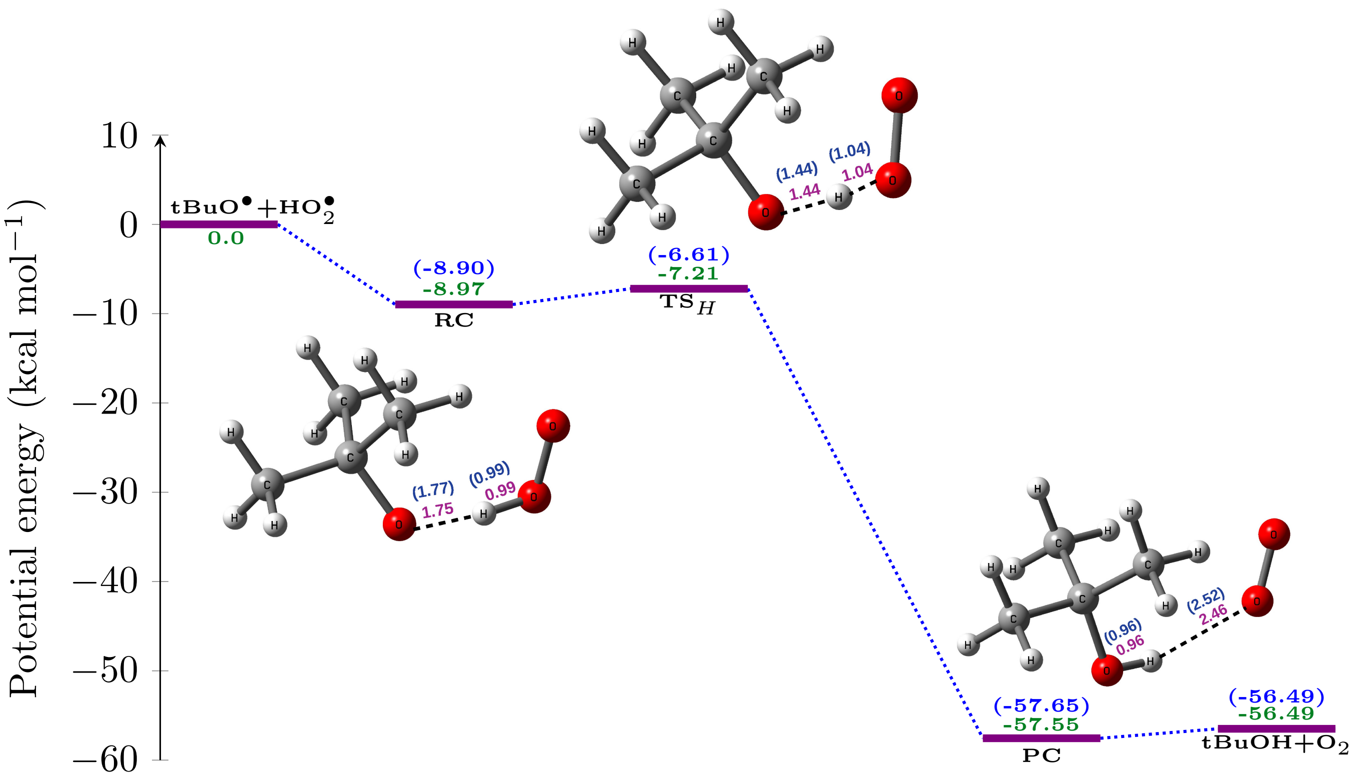

Figure S2: IRC for the transition state (TS_H) of the tBuO$^\bullet$ + $HO_2^\bullet$ reaction obtained at M062X/aug-cc-pVTZ level of theory.

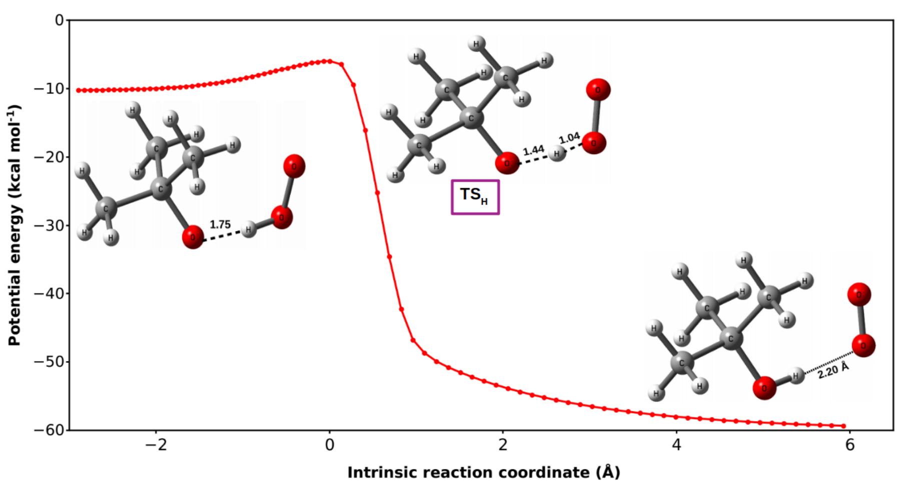

Table S3: Transition state theory rate constants (k_{TST}) for the isomerization path along with zero curvature tunneling (τ_{ZCT}), Eckart tunneling contributions (τ_{Eckart}), and small curvature tunneling (τ_{SCT}) within the temperature range 213–450 K and pressure =1.0 atm.

T	k_{TST}	τ_{ZCT}	τ_{Eckart}	τ_{SCT}
213	1.84×10^{-13}	2.40×10^{7}	1.25×10^{8}	1.28×10^{8}
216	4.30×10^{-13}	1.28×10^{7}	6.51×10^{7}	6.64×10^{7}
219	9.83×10^{-13}	6.96×10^{6}	3.47×10^{7}	3.52×10^{7}
224	3.72×10^{-12}	2.67×10^{6}	1.28×10^{7}	1.29×10^{7}
235	5.68×10^{-11}	3.97×10^{5}	1.74×10^{6}	1.73×10^{6}
250	1.59×10^{-9}	4.41×10^{4}	1.72×10^{5}	1.70×10^{5}
259	9.79×10^{-9}	1.43×10^{4}	5.18×10^{4}	5.14×10^{4}
260	1.19×10^{-8}	1.27×10^{4}	4.57×10^{4}	4.54×10^{4}
265	3.07×10^{-8}	7.24×10^{3}	2.50×10^{4}	2.49×10^{4}
270	7.64×10^{-8}	4.28×10^{3}	1.42×10^{4}	1.42×10^{4}
278	3.08×10^{-7}	1.98×10^{3}	6.15×10^{3}	6.18×10^{3}
280	4.31×10^{-7}	1.65×10^{3}	5.05×10^{3}	5.09×10^{3}
290	2.16×10^{-6}	7.19×10^{2}	2.03×10^{3}	2.07×10^{3}
298	7.24×10^{-6}	4.01×10^{2}	1.06×10^{3}	1.09×10^{3}
300	9.70×10^{-6}	3.50×10^{2}	9.14×10^{2}	9.39×10^{2}
310	3.96×10^{-5}	1.87×10^{2}	4.54×10^{2}	4.70×10^{2}
320	1.48×10^{-4}	1.09×10^{2}	2.45×10^{2}	2.57×10^{2}
350	4.96×10^{-3}	3.21×10^{1}	5.98×10^{1}	6.40×10^{1}
400	5.39×10^{-1}	9.83×10^{0}	1.48×10^{1}	1.59×10^{1}
425	3.73×10^{0}	6.82×10^{0}	9.60×10^{0}	1.02×10^{1}
450	2.09×10^{1}	5.16×10^{0}	6.91×10^{0}	7.26×10^{0}

Table S4: Pressure dependent overall bimolecular rate constants in cm^3 molecule^{-1} sec^{-1} for tBuO$^{\bullet}$ + $HO_2^{\bullet}$ reaction within temperature range of 213–450 K.

T (K)	Pressure (atm)				
	0.1	0.5	1.0	5.0	10.0
213	8.67×10^{-12}	8.67×10^{-12}	8.67×10^{-12}	8.67×10^{-12}	8.67×10^{-12}
216	8.64×10^{-12}	8.64×10^{-12}	8.64×10^{-12}	8.64×10^{-12}	8.64×10^{-12}
219	8.60×10^{-12}	8.60×10^{-12}	8.60×10^{-12}	8.60×10^{-12}	8.60×10^{-12}
224	8.52×10^{-12}	8.52×10^{-12}	8.52×10^{-12}	8.52×10^{-12}	8.52×10^{-12}
235	8.28×10^{-12}	8.28×10^{-12}	8.28×10^{-12}	8.28×10^{-12}	8.28×10^{-12}
250	7.87×10^{-12}	7.87×10^{-12}	7.87×10^{-12}	7.87×10^{-12}	7.87×10^{-12}
259	7.59×10^{-12}	7.59×10^{-12}	7.59×10^{-12}	7.59×10^{-12}	7.59×10^{-12}
260	7.55×10^{-12}	7.55×10^{-12}	7.55×10^{-12}	7.55×10^{-12}	7.55×10^{-12}
265	7.39×10^{-12}	7.39×10^{-12}	7.39×10^{-12}	7.39×10^{-12}	7.39×10^{-12}
270	7.22×10^{-12}	7.22×10^{-12}	7.22×10^{-12}	7.22×10^{-12}	7.22×10^{-12}
278	6.95×10^{-12}	6.95×10^{-12}	6.95×10^{-12}	6.95×10^{-12}	6.95×10^{-12}
280	6.88×10^{-12}	6.88×10^{-12}	6.88×10^{-12}	6.88×10^{-12}	6.88×10^{-12}
290	6.53×10^{-12}	6.53×10^{-12}	6.53×10^{-12}	6.53×10^{-12}	6.53×10^{-12}
298	6.26×10^{-12}	6.26×10^{-12}	6.26×10^{-12}	6.26×10^{-12}	6.26×10^{-12}
300	6.19×10^{-12}	6.19×10^{-12}	6.19×10^{-12}	6.19×10^{-12}	6.19×10^{-12}
310	5.85×10^{-12}	5.85×10^{-12}	5.85×10^{-12}	5.85×10^{-12}	5.85×10^{-12}
320	5.53×10^{-12}	5.53×10^{-12}	5.53×10^{-12}	5.53×10^{-12}	5.53×10^{-12}
350	4.63×10^{-12}	4.63×10^{-12}	4.63×10^{-12}	4.63×10^{-12}	4.63×10^{-12}
400	3.44×10^{-12}	3.44×10^{-12}	3.44×10^{-12}	3.44×10^{-12}	3.44×10^{-12}
425	2.99×10^{-12}	2.99×10^{-12}	2.99×10^{-12}	2.99×10^{-12}	2.99×10^{-12}
450	2.60×10^{-12}	2.60×10^{-12}	2.60×10^{-12}	2.60×10^{-12}	2.60×10^{-12}

Figure S3: Gibbs free energy profile for decomposition (panel A), isomerization (panel B), and tBuO$^\bullet$ + HO$_2^\bullet$ reaction (panel C) obtained at CCSD(T)/CBS level of theory at 298 K.

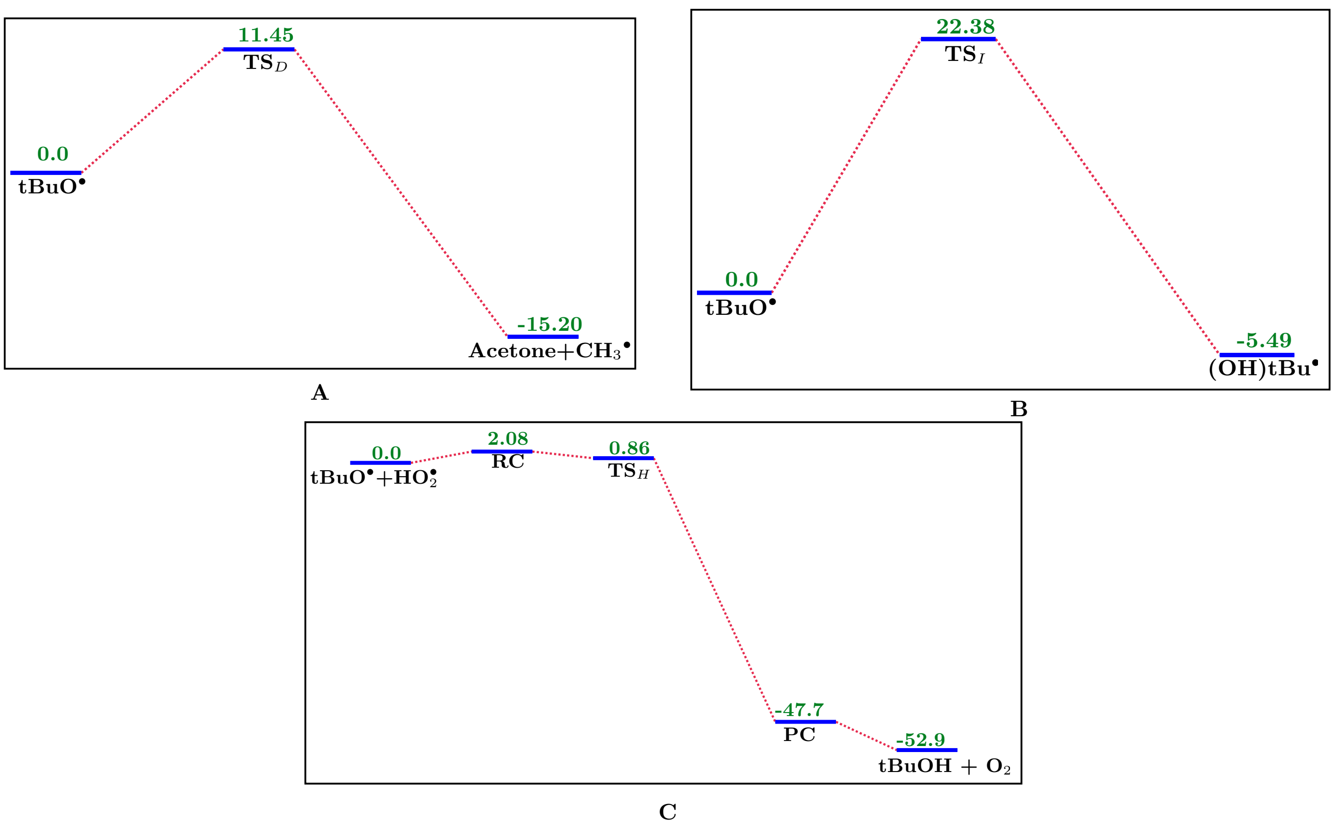

Figure S4: Potential energy surface for $tBuO^{\bullet}$+O_2 reaction (ZPE corrected) obtained at CCSD(T)/CBS//M062X/aug-cc-pVTZ level of theory.

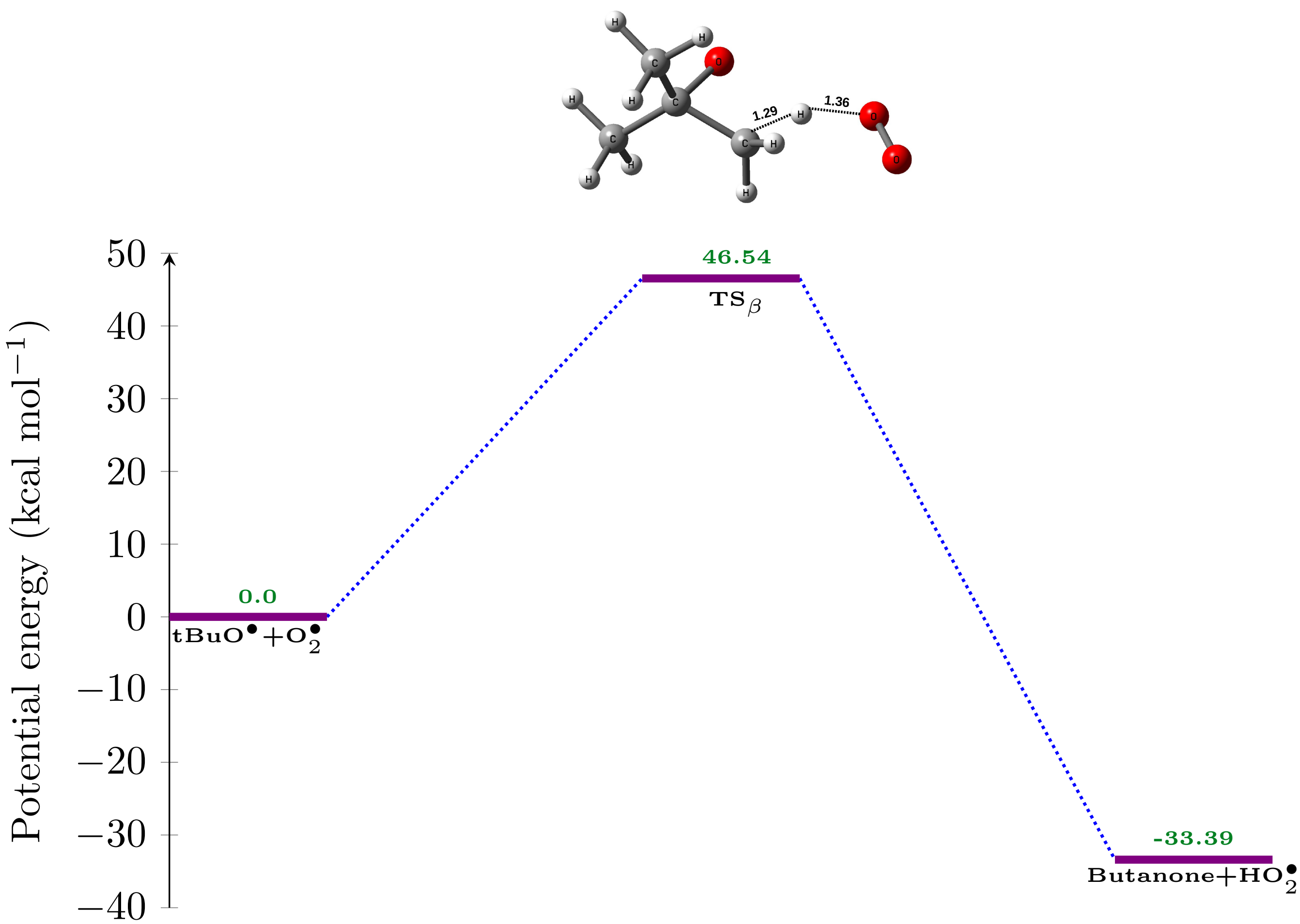

Table S5: Transition state theory rate constants augmented with Eckart tunneling contributions ($k_{TST/Eckart}$) for the $tBuO^{\bullet}+O_2$ reaction along with effective rate constants (k_{Eff}) within the temperature range 213-450 K and pressure =1.0 atm. The concentration of co-reactant (O_2) is known to be $\sim10^{18}$ molecule cm^{-3}.

T(K)	$k_{TST/Eckart}$	k_{Eff}
213	5.70×10^{-37}	5.70×10^{-19}
216	6.46×10^{-37}	6.46×10^{-19}
219	7.34×10^{-37}	7.34×10^{-19}
224	9.06×10^{-37}	9.06×10^{-19}
235	1.45×10^{-36}	1.45×10^{-18}
250	2.80×10^{-36}	2.80×10^{-18}
259	4.19×10^{-36}	4.19×10^{-18}
260	4.38×10^{-36}	4.38×10^{-18}
265	5.49×10^{-36}	5.49×10^{-18}
270	6.89×10^{-36}	6.89×10^{-18}
278	9.96×10^{-36}	9.96×10^{-18}
280	1.09×10^{-35}	1.09×10^{-17}
290	1.75×10^{-35}	1.75×10^{-17}
298	2.56×10^{-35}	2.56×10^{-17}
300	2.81×10^{-35}	2.81×10^{-17}
310	4.56×10^{-35}	4.56×10^{-17}
320	7.45×10^{-35}	7.45×10^{-17}
350	3.40×10^{-34}	3.40×10^{-16}
400	4.94×10^{-33}	4.94×10^{-15}
425	2.01×10^{-32}	2.01×10^{-14}
450	8.54×10^{-32}	8.54×10^{-14}

Details of the kinetics

The mechanism of $tBuO^{\bullet}$ + $HO_2^{\bullet}$ reaction can be represented as follows:

$$\mathrm{tBuO^{\bullet} + HO_2^{\bullet} \xrightarrow{k_{asso}} RC \xrightarrow{k_{disso}} tBuOH + O_2^{\bullet}} \tag{R1}$$

This reaction occurs in two steps; in the first step, a barrierless association of $tBuO^{\bullet}$ and $HO_2^{\bullet}$ takes place which forms RC, and in the next, RC undergoes unimolecular dissociation to form products. The overall rate constants for $tBuO^{\bullet}$ + $HO_2^{\bullet}$ reaction have been computed using master equation as implemented in the MESMER software package.[1] MESMER uses inverse laplace transformation (ILT) method for the barrierless association process, and for the unimolecular dissociation process, MESMER uses Rice-Ramsperger-Kassel-Marcus (RRKM) theory. The ILT method (for the first step) requires an Arrhenius pre-exponential factor for the barrierless association, which has been computed using KTOOLS program as implemented in the MultiWell suite of programs.[2] Lennard-Jones (L-J) model is used to calculate the collisional frequency between reactants and bath gas, and as a bath gas, air is employed to mimic the atmospheric environment with L-J parameters, σ=3.68 $\mathring{A}$ and ϵ=86.2 K. For the L-J parameters of RC, we need L-J parameters of reactants, i.e., $tBuO^{\bullet}$ and $HO_2^{\bullet}$. Zhang et al.[3] recommended the L-J parameters for $tBuO^{\bullet}$ to be σ=5.85 $\mathring{A}$ and ϵ=326.6 K, whereas for $HO_2^{\bullet}$, we have taken the L-J parameters of O_2 (σ=3.39 $\mathring{A}$ and ϵ=121.7 K) due to their similar sizes. Thus, using the combining rule,[4] L-J parameters for RC can be calculated using following equations:

$$\sigma_{\mathrm{RC}} = \frac{1}{2}(\sigma_{\mathrm{tBuO^{\bullet}}} + \sigma_{\mathrm{HO_2^{\bullet}}})$$

$$(\epsilon/\mathrm{k_B})_{\mathrm{RC}} = [(\epsilon/\mathrm{k_B})_{\mathrm{tBuO^{\bullet}}}(\epsilon/\mathrm{k_B})_{\mathrm{HO_2^{\bullet}}}]^{1/2}$$

The L-J parameters for RC using above equations turns out to be, σ=4.62 $\mathring{A}$ and ϵ=199.37 K. A single-exponential down model is used to describe the collisional energy transfer probability with an energy grain size of 100 cm^{-1} and ΔE_{down}= 200 cm^{-1}.

Table S6: Bimolecular rate constants, k_b (in cm^3 $molecule^{-1}$ sec^{-1}) and effective rate constants, k_{eff} (in sec^{-1}) for $tBuO^{\bullet}$ + $HO_2^{\bullet}$ reaction using MESMER software package within 213–450 K and pressure =1.0 atm.

T(K)	k_b	k_{eff}
213	2.04×10^{-12}	6.13×10^{-4}
216	2.04×10^{-12}	6.12×10^{-4}
219	2.04×10^{-12}	6.12×10^{-4}
224	2.04×10^{-12}	6.11×10^{-4}
235	2.03×10^{-12}	6.09×10^{-4}
250	2.02×10^{-12}	6.07×10^{-4}
259	2.02×10^{-12}	6.06×10^{-4}
260	2.02×10^{-12}	6.06×10^{-4}
265	2.02×10^{-12}	6.05×10^{-4}
270	2.02×10^{-12}	6.05×10^{-4}
278	2.01×10^{-12}	6.04×10^{-4}
280	2.01×10^{-12}	6.03×10^{-4}
290	2.01×10^{-12}	6.02×10^{-4}
298	2.00×10^{-12}	6.01×10^{-4}
300	2.00×10^{-12}	6.01×10^{-4}
310	2.00×10^{-12}	5.99×10^{-4}
320	1.99×10^{-12}	5.98×10^{-4}
350	1.98×10^{-12}	5.93×10^{-4}
400	1.95×10^{-12}	5.85×10^{-4}
425	1.94×10^{-12}	5.81×10^{-4}
450	1.92×10^{-12}	5.76×10^{-4}

References

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