Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information.

Photodissociation of $CH_2BrCHBrC(O)Cl$ at 248 nm : Probing Br_2 as Primary Fragment by Cavity Ring-Down Spectroscopy

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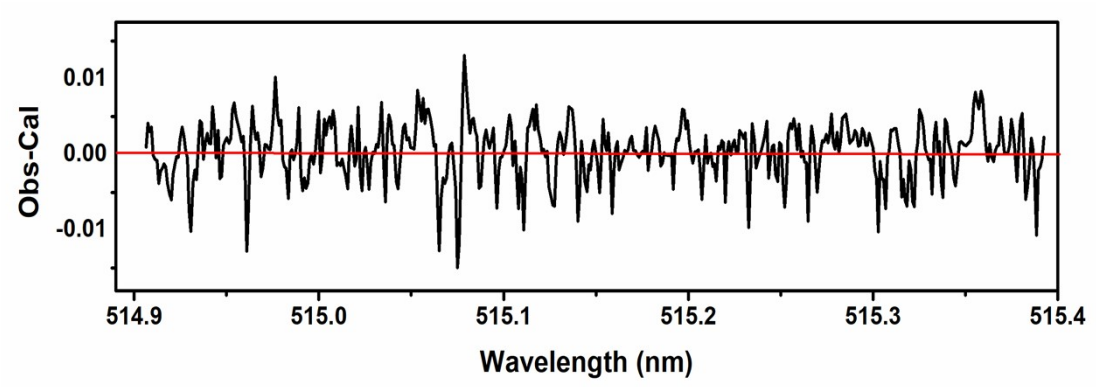


Fig.SI-1: The agreement between the experimental spectra and simulated spectra was measured with help of residual spectra as can be seen.

Table-SI-1: Coordinates of the optimized geometries (Reactant, transition states and products)

2,3-DBPC:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
C	-0.57948	-0.92045	-0.52561
H	-0.41869	-0.50716	-1.51940
H	-0.49817	-2.00534	-0.54679
C	0.37429	-0.34236	0.49127
H	0.22390	-0.76832	1.48276
C	0.31316	1.17135	0.63924
O	0.31552	1.74195	1.67718
Cl	0.27576	2.05240	-0.90427
Br	-2.39202	-0.49121	0.01860
Br	2.18725	-0.79441	-0.04976

TS_Br_2:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
C	-0.095743	-0.944034	1.438647
H	0.520485	-0.895036	2.327679
H	-0.303225	-1.921231	1.022439
C	-1.002389	0.103847	1.207016
H	-1.119817	0.902555	1.932930
C	-2.196629	-0.076897	0.338308
O	-3.219140	0.516925	0.470690
Cl	-1.998863	-1.290335	-0.949498
Br	1.905806	-0.763053	-0.039677
Br	0.391477	1.483524	-0.269207

TS_BrCl:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
C	0.328053	-1.887964	0.064737
H	0.863740	-2.207426	-0.825656
H	0.062758	-2.720684	0.715642
C	0.979730	-0.729736	0.817835
H	1.585364	-1.005266	1.683491
C	-0.259083	0.022397	1.285129
O	-0.707890	0.459869	2.245169
Cl	-1.641264	1.967112	-0.338065
Br	-1.307187	-0.865783	-0.450047
Br	2.014631	0.419650	-0.315494

TS1_HBr:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
C	0.769965	-0.679335	-0.327589
H	0.580818	-1.340476	-1.166224
H	0.221715	0.461110	-0.628398
C	-0.162154	-0.553194	0.702472
H	0.100124	-0.152973	1.677216
C	-1.527105	-1.168202	0.632514
O	-2.146954	-1.435820	1.610278
Cl	-2.099514	-1.554920	-0.987218
Br	2.586901	-0.300721	-0.006886
Br	-0.944601	1.825204	-0.051014

TS2_HBr:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
C	0.389144	-0.050840	1.345795
H	0.931449	0.796702	1.749676
H	0.445835	-0.999763	1.866363
C	-0.569294	0.128816	0.329553
H	0.558910	-0.168619	-0.368147
C	-0.995856	1.469679	-0.142187
O	-2.018572	1.728159	-0.683342
Cl	0.252292	2.725481	0.103463
Br	2.255438	-0.687887	-0.227618
Br	-1.770311	-1.285618	-0.022067

TS_HCl:

Atoms	Coordinates (Angstroms)

	X	Y	Z
C	0.640790	-1.204854	-0.375191
H	0.541681	-2.074614	0.272719
H	0.545152	-1.494796	-1.420417
C	-0.395317	-0.136527	-0.088711
H	-0.343581	0.879870	-0.714942
C	-0.254231	0.449408	1.216550
O	-0.177397	0.849482	2.266176
Cl	-0.368343	2.679094	-0.636593
Br	2.400215	-0.448771	-0.119358
Br	-2.200492	-0.816917	-0.165230

P1_TS_$Br_{2:}$

Atoms	Coordinates (Angstroms)		
	X	Y	Z
C	1.717702	-1.160235	0.000000
H	2.761471	-1.455807	0.000000
H	0.969004	-1.945252	0.000000
C	1.384038	0.129247	0.000000
H	2.128158	0.920557	0.000000
C	0.000000	0.656209	0.000000
O	-0.282087	1.811688	0.000000
Cl	-1.306611	-0.574372	0.000000

P1_TS_BrCl:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
C	1.407234	1.248805	-0.301422
H	1.077794	1.451644	-1.317806
H	1.970568	2.047852	0.174016
C	0.455691	0.435665	0.616729
H	0.418311	0.708559	1.665784
C	1.670222	-0.158503	0.048641
O	2.335408	-1.140020	-0.090906
Br	-1.238537	-0.121248	-0.056527

P1_TS1_HBr:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
C	-0.366960	-0.238663	0.000132
H	-0.043022	-1.271938	0.000549
C	0.482413	0.787456	-0.000219
H	0.152896	1.821479	-0.000586
C	1.948726	0.618975	0.000039
O	2.731692	1.513758	0.000149
Cl	2.536534	-1.077234	-0.000057
Br	-2.213416	-0.038664	0.000003

P1_TS2_HBr:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
C	0.266842	1.855947	0.000000
H	1.290224	2.210839	0.000000
H	-0.535688	2.584333	0.000000
C	0.000000	0.551728	0.000000
C	1.038227	-0.524154	0.000000
O	0.820108	-1.690023	0.000000
Cl	2.726330	0.057479	0.000000
Br	-1.756955	-0.101522	0.000000

P1_TS_HCl:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
C	-0.510497	-0.954421	0.000333
H	-0.413147	-1.576992	-0.890792
H	-0.413528	-1.576653	0.891724
C	0.497071	0.148566	0.000226
C	0.201165	1.434303	0.000153
O	-0.009793	2.577479	0.000000
Br	-2.319814	-0.264742	-0.000080
Br	2.313487	-0.342026	-0.000069

$Br_{2:}$

Atoms	Coordinates (Angstroms)		
	X	Y	Z
Br	0.000000	0.000000	1.143769
Br	0.000000	0.000000	-1.143769

BrCl:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
Cl	0.000000	0.000000	-1.448763
Br	0.000000	0.000000	0.703685

HBr:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
Br	0.000000	0.000000	0.039264
H	0.000000	0.000000	-1.374253

HCl:

Atoms	Coordinates (Angstroms)		
	X	Y	Z
H	0.000000	0.000000	-1.209596
Cl	0.000000	0.000000	0.071153

Table-SI-3: Vibrational frequencies (cm^{-1}) of stationary points

2,3-DBPC	TS_Br2	TS_BrCl	TS1_HBr	TS2_HBr	TS_HCl
68.74	-1201.56	-371.67	-1788.00	-1714.55	-608.63
83.24	40.92	57.66	64.57	58.41	25.64
138.73	61.40	80.54	75.23	66.04	65.74
169.56	101.21	102.91	103.45	107.24	102.39
208.69	129.29	121.39	144.80	201.76	132.41
268.11	199.22	179.73	222.69	274.75	164.80
450.71	262.96	196.77	285.36	307.65	200.16
514.51	362.87	239.44	328.82	321.68	276.93
552.69	467.62	327.26	451.34	354.21	354.53
646.35	511.70	527.25	496.69	468.87	525.15
675.31	616.57	611.90	612.05	626.75	663.10
781.15	653.27	657.17	648.06	659.18	701.20
891.50	751.11	832.79	731.33	708.72	796.31
1055.06	870.44	861.62	830.15	762.54	902.74
1152.85	954.20	1027.25	951.39	927.68	979.49
1198.29	1007.40	1133.18	1084.38	967.73	1182.12
1229.25	1156.96	1191.45	1123.84	1057.48	1208.27
1293.50	1203.90	1264.43	1216.82	1178.20	1250.32
1364.76	1381.04	1364.95	1261.33	1213.13	1291.39
1490.87	1496.03	1492.09	1295.36	1371.60	1488.34
1931.55	1892.35	2244.33	1546.70	1514.83	1829.80
3156.26	3214.28	3147.20	1897.67	1916.41	2365.74
3180.25	3235.95	3220.14	3239.80	3210.20	3139.67
3230.05	3323.02	3251.72	3249.60	3324.47	3215.09

P1_TS_Br_2	P1_TS_BrCl	P1_TS1_HBr	P1_TS2_HBr	P1_TS_HCl
93.75	84.64	132.75	40.47	90.19
268.39	209.64	149.56	202.98	122.37
450.88	271.59	229.27	277.18	161.52
455.75	525.13	243.76	368.55	205.08
505.97	551.96	424.42	385.67	311.87
621.56	648.69	485.72	479.97	526.21
775.42	669.61	635.18	634.69	589.42
960.91	869.14	641.17	654.45	672.14
1008.35	1052.43	829.10	713.03	723.12
1033.38	1148.86	882.84	777.49	940.98
1179.90	1208.72	991.45	973.11	1073.94

1311.42	1268.85	1147.87	1006.27	1191.13
1448.24	1448.05	1244.61	1211.65	1295.87
1732.76	1497.19	1320.70	1431.43	1434.69
1901.20	2260.07	1698.11	1707.60	1497.42
3193.79	3149.62	1908.96	1919.90	2282.79
3215.10	3219.44	3242.71	3198.12	3117.60
3291.09	3237.23	3279.91	3298.25	3177.34

Br_2	BrCl	HBr	HCl
350.79	464.44	2656.78	3000.03

Fig-SI-2: UV-visible spectrum of 2,3-DBPC at various concentrations

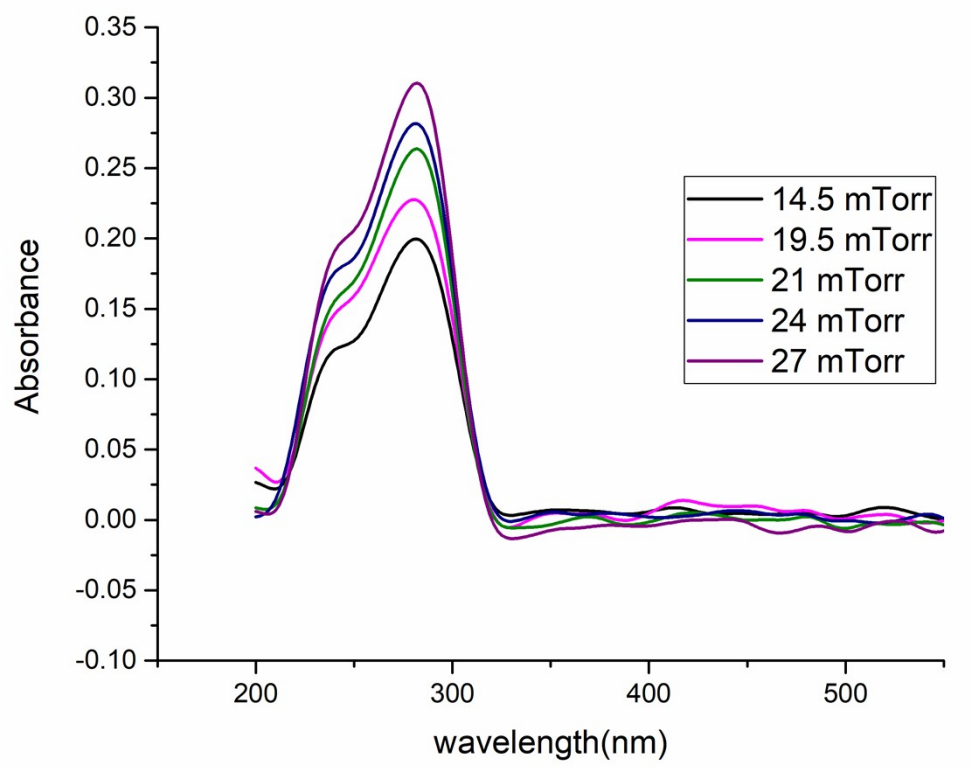
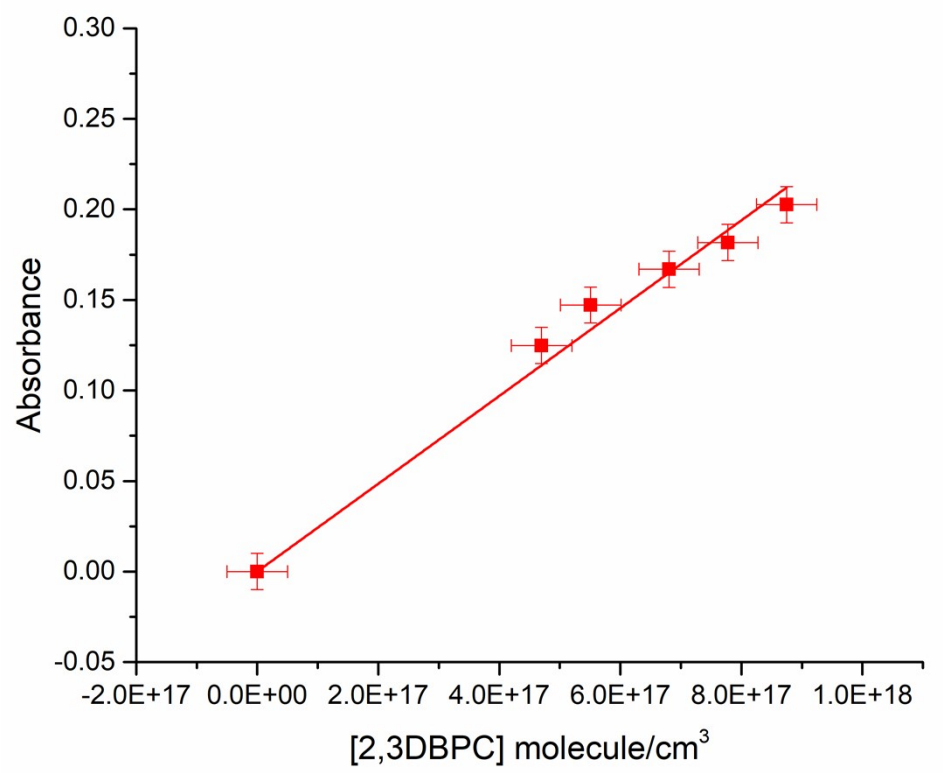


Fig-SI-3: Plot of absorbance of 2,3-DBPC at 248nm at various concentration of 2,3-DBPC


0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
Absorbance
-2.0E+17
0.0E+00
2.0E+17
4.0E+17
6.0E+17
8.0E+17
1.0E+18
[2,3DBPC] molecule/cm3