[Supplementary Information]

Kinetics of IO radicals with ethyl formate and ethyl acetate: A study using cavity ring-down spectroscopy and theoretical methods

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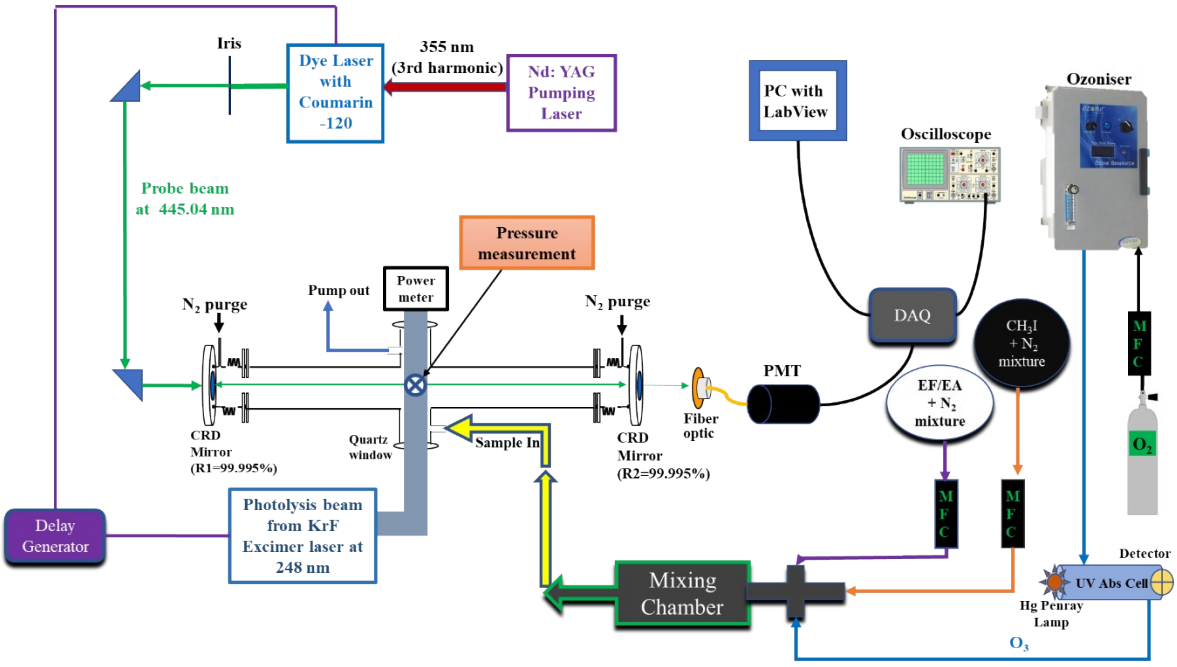

Figure S1. Schematic diagram of the pulsed laser photolysis cavity ring-down spectroscopy (CRDS) setup used for studying the kinetics of the reaction of IO radicals with EF and EA. MFC: mass flow controller; PMT: photomultiplier tube; DAQ: data acquisition card.

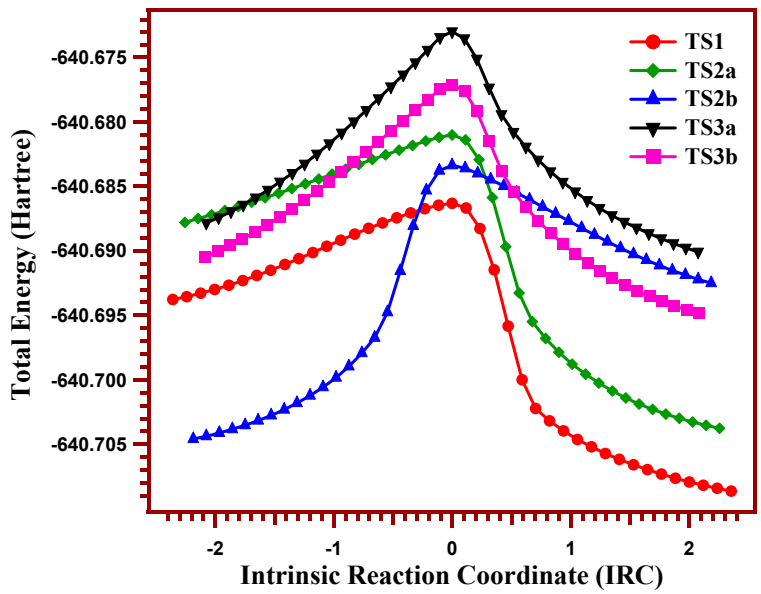

Figure S2. IRC plots of the reaction pathways (TS1, TS2a, TS2b, TS3a and TS3b) obtained for the reaction between IO radicals and EF at M06-2X/def2-SV(P) level of theory.

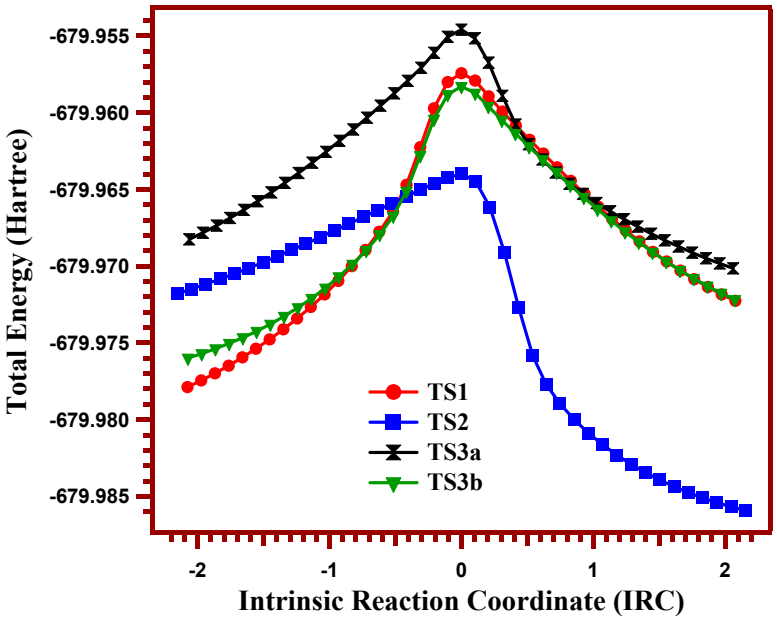

Figure S3. IRC plots of the reaction pathways (TS1, TS2, TS3a and TS3b) obtained for the reaction between IO radicals and EA at M06-2X/def2-SV(P) level of theory.

Table S1. T1 diagnostic values for all the stationary points involved in the reaction of IO radicals with EF at CCSD(T)//M06-2X/def2-SV(P) level of theory.

Stationary Points	T1 Diagnostic Values
EF (R1)	0.014
IO (R2)	0.035
PRC1	0.015
TS1	0.027
TS2a	0.023
TS2b	0.023
TS3a	0.019
TS3b	0.020
P1	0.017
P2	0.017
P3a	0.015
P3b	0.015
HOI	0.009

Table S2. T1 diagnostic values for all the stationary points involved in the reaction of IO radicals with EA at CCSD(T)//M06-2X/def2-SV(P) level of theory.

Stationary Points	T1 Diagnostic Values
EA (R1)	0.013
IO (R2)	0.035
PRC2	0.027

TS1	0.020
TS2	0.021
TS3a	0.033
TS3b	0.018
P1	0.016
P2	0.016
P3a	0.014
P3b	0.014
HOI	0.009

Table S3. Cartesian coordinates of the optimized geometries of reactants, TSs and products for the reaction of IO radicals with EF at M06-2X/def2-SV(P) level of theory.

EF (R1)

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-1.33148	0.282733	0.000028
8	-0.13254	-0.30662	-0.000037
8	-2.35404	-0.32308	0.000002
6	1.011346	0.541524	-0.000034
6	2.241667	-0.3352	0.000031
1	3.149311	0.282504	0.000031
1	2.250873	-0.97767	-0.89013
1	2.250827	-0.9776	0.890239
1	0.991644	1.18941	0.891875
1	0.991692	1.189347	-0.89199
1	-1.27091	1.39731	0.000112

IO (R2)

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
53	0	0	0.253459
8	0	0	-1.67917

PRC1

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	1.967657	-1.20028	-0.08216
8	2.753657	-0.15673	-0.02033
8	2.170604	-2.25095	-0.57401
6	2.262619	1.047496	0.605893
6	2.035508	2.107852	-0.44681
1	1.710061	3.04163	0.031604
1	1.254585	1.789633	-1.15126
1	2.959924	2.303119	-1.00656
1	3.041371	1.345177	1.319451
1	1.34274	0.808863	1.157712
1	0.048662	-1.1372	1.210686
8	-0.59299	-0.46679	1.50401
53	-1.55853	0.058757	-0.17548

TS1

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-1.43596	1.09167	0.175541
8	-2.69337	0.717919	0.031035
8	-0.99988	2.170138	-0.04756
6	-3.0377	-0.64081	0.34873
6	-4.22569	-1.03174	-0.49747
1	-4.53107	-2.05912	-0.25922
1	-3.97166	-0.97875	-1.56428
1	-5.07344	-0.36079	-0.30661
1	-3.27539	-0.68987	1.421607
1	-2.16685	-1.28439	0.155414
1	-0.71211	0.179899	0.535256
8	0.180851	-0.85405	0.586333
53	1.887279	-0.14328	-0.08871

TS2a

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.106031	-1.36933	-0.0697
8	2.607372	-0.13406	0.012607
8	2.736827	-2.34548	0.178297
6	1.738552	0.946126	-0.3142
6	2.513195	2.232612	-0.14969
1	1.87742	3.093988	-0.3929
1	3.386447	2.238445	-0.81506
1	2.866122	2.334371	0.884914
1	0.723848	0.926062	0.455895

1	1.381773	0.832665	-1.35121
1	1.037794	-1.3871	-0.39427
8	-0.38176	0.869375	1.027463
53	-1.6815	-0.11346	-0.09307

TS2b

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.066765	-1.23435	0.25337
8	2.133302	-0.03549	-0.37203
8	2.447381	-2.23353	-0.25898
6	1.842843	1.104203	0.376221
6	1.693699	2.296769	-0.52035
1	1.433895	3.18688	0.06587
1	0.906521	2.112369	-1.26549
1	2.634568	2.486157	-1.05905
1	2.546147	1.239276	1.215527
1	0.774528	0.91567	0.946615
1	1.605677	-1.1658	1.26375
8	-0.3783	0.440308	1.402513
53	-1.45548	-0.1348	-0.15084

TS3a

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	3.574107	-0.74608	-0.02346
8	3.221056	0.508603	-0.33289
8	4.689907	-1.06219	0.229909
6	1.838273	0.77549	-0.53523
6	1.184855	1.212808	0.749215
1	-0.02249	1.444924	0.42039
1	1.547542	2.168425	1.145949
1	1.10939	0.433581	1.51978
1	1.33556	-0.11748	-0.94403
1	1.782443	1.567053	-1.29185
1	2.711805	-1.45522	-0.04154
8	-1.1216	1.455587	-0.14202
53	-1.93137	-0.35303	0.000154

TS3b

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-2.32323	-1.0144	-0.2167
8	-2.77117	0.253935	-0.17858
8	-2.93267	-1.92034	0.246421
6	-1.93614	1.275541	-0.68117

6	-1.21991	1.976433	0.437717
1	-0.53842	2.77499	0.118805
1	-0.48005	1.099594	0.962808
1	-1.8752	2.267535	1.267987
1	-2.58443	1.981647	-1.22453
1	-1.21687	0.865495	-1.41351
1	-1.34685	-1.1133	-0.74448
8	0.147153	0.042087	1.206591
53	1.610773	-0.15673	-0.12079

P1

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-1.35815	0.342126	0.000449
8	-0.16983	-0.2677	-0.00052
8	-2.39111	-0.24548	0.000044
6	0.988865	0.560491	-0.00018
6	2.203232	-0.33812	0.00026
1	3.12199	0.262895	0.00047
1	2.201123	-0.98073	-0.88989
1	2.200597	-0.98057	0.890522
1	0.979752	1.208459	0.89179
1	0.980307	1.208333	-0.89225

P2

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	1.316721	0.302185	-0.001
8	0.107951	-0.29092	-0.03928
8	2.329995	-0.31375	0.031043
6	-1.01729	0.488589	-0.09377
6	-2.29311	-0.25	0.033943
1	-3.1409	0.41794	-0.1627
1	-2.42335	-0.68054	1.044041
1	-2.32747	-1.08471	-0.68175
1	-0.89933	1.526425	0.232141
1	1.249545	1.413635	-0.00086

P3a

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-1.25334	0.277542	0.000297
8	-0.04886	-0.29973	-0.00047
8	-2.26993	-0.33795	0.000027
6	1.086867	0.559678	-0.00033
6	2.325231	-0.30556	0.000395

1	2.340638	-0.94824	-0.88957
1	2.340044	-0.9476	0.890835
1	1.060098	1.207405	0.891461
1	1.060719	1.2068	-0.89258
1	-1.20375	1.393038	0.001243

P3b

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	1.051041	0.175884	0.269758
8	0.144808	-0.60028	-0.33952
8	2.177266	0.265153	-0.09723
6	-1.17788	-0.56602	0.184066
6	-1.86603	0.712402	-0.12473
1	-2.72552	1.02892	0.465475
1	-1.68139	1.189143	-1.08826
1	-1.16492	-0.75987	1.271172
1	-1.68428	-1.42822	-0.28226
1	0.636686	0.717426	1.153236

HOI

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
53	0.014879	-0.29048	0
8	0.014879	1.680295	0
1	-0.90763	1.952876	0

Table S4. Cartesian coordinates of the optimized geometries of reactants, TSs and products for the reaction between IO radicals and EA at M06-2X/def2-SV(P) level of theory.

EA (R1)

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-2.13224	-0.87989	0.000012
1	-3.10131	-0.37254	-0.00157
1	-2.03483	-1.52335	-0.88431
1	-2.03668	-1.52091	0.886324
6	-1.03064	0.14557	-0.000081
8	0.177103	-0.43722	-0.000045
8	-1.18186	1.335773	-0.000043
6	1.298683	0.445242	0.000122
6	2.551268	-0.39917	-0.000049
1	3.441286	0.244019	0.000098

1	2.584139	-1.04105	-0.89067
1	2.584123	-1.04143	0.89029
1	1.239454	1.097998	0.884074
1	1.23944	1.098351	-0.88357

IO (R2)

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
53	0	0	0
8	0	0	1.869838

PRC2

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	1.36508	-2.34146	0.67636
1	0.920301	-3.17697	0.126556
1	2.295165	-2.63918	1.173602
1	0.659233	-1.99101	1.443893
6	1.596159	-1.18608	-0.25649
8	2.502899	-0.33421	0.229045
8	1.015221	-1.00646	-1.29481
6	2.665441	0.886011	-0.49202
6	3.626705	1.753508	0.285571
1	3.777243	2.710916	-0.23102
1	4.600536	1.256456	0.392701
1	3.227652	1.955676	1.288724
1	1.677808	1.359797	-0.59761
1	3.033435	0.659681	-1.50445
8	-0.22736	0.544904	0.819622
53	-1.92524	0.218092	-0.02649

TS1

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-1.02029	-0.80994	0.056106
1	0.049422	0.12842	-0.01085
1	-0.70381	-1.26611	0.970791
1	-0.45538	-0.96017	-0.84012
6	-2.28882	0.062822	0.029532
8	-3.44564	-0.47811	-0.22055
8	-2.20671	1.299097	0.249654
6	-4.62356	0.332309	-0.24523
6	-5.83645	-0.51158	0.188776
1	-6.71783	0.094817	0.170312
1	-5.67788	-0.88025	1.180664
1	-5.95635	-1.33566	-0.4831

1	-4.78213	0.700974	-1.23711
1	-4.50366	1.156386	0.426654
8	1.057344	0.856669	-0.1293
53	2.794762	-0.1038	0.008475

TS2

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	3.453703	-1.80124	0.497572
1	3.331035	-2.85013	0.23135
1	4.431204	-1.43708	0.172354
1	3.399697	-1.68502	1.583644
6	2.366425	-0.98867	-0.14096
8	2.557782	0.368339	0.083657
8	1.403987	-1.40599	-0.78433
6	1.567757	1.272523	-0.41835
6	1.969791	2.694894	-0.12545
1	1.176579	3.378959	-0.43772
1	2.890072	2.952362	-0.66342
1	2.147602	2.826279	0.944841
1	0.512422	1.036572	0.24547
1	1.277247	1.030407	-1.44591
8	-0.477	0.777528	0.959578
53	-1.94698	-0.19314	-0.02979

TS3a

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-5.5713	-0.81143	-0.13136
1	-6.49844	-0.25277	-0.28872
1	-5.42339	-1.5435	-0.93616
1	-5.61415	-1.36628	0.815146
6	-4.40966	0.145134	-0.1015
8	-3.25075	-0.50196	0.088723
8	-4.47998	1.336216	-0.22723
6	-2.07916	0.311645	0.134903
6	-0.8933	-0.59798	0.353921
1	0.178453	0.071075	0.400945
1	-0.80824	-1.32533	-0.46461
1	-0.99934	-1.15023	1.29734
1	-2.18908	1.050695	0.9428
1	-1.99946	0.87688	-0.80591
8	1.16716	0.823351	0.461137
53	2.897789	-0.07369	-0.09581

TS3b

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	3.39506	-2.01374	-0.09789
1	4.377479	-2.43652	0.131358
1	2.635486	-2.41625	0.585148
1	3.092893	-2.27845	-1.11974
6	3.450864	-0.51583	0.038023
8	2.262488	0.042441	-0.23415
8	4.417893	0.123729	0.346645
6	2.201449	1.464919	-0.13647
6	0.793131	1.89146	-0.47758
1	0.702578	2.983971	-0.41423
1	-0.03481	1.372196	0.323868
1	0.530846	1.577622	-1.49688
1	2.943932	1.902182	-0.82094
1	2.490191	1.765775	0.8819
8	-0.89163	0.816697	1.028579
53	-2.30362	-0.28857	-0.05954

P1

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.129498	-0.91976	0.00005
1	1.889274	-1.97014	0.000002
1	3.15177	-0.5811	0.000125
6	1.082061	0.078254	-0.000011
8	-0.14651	-0.47296	-0.00012
8	1.274597	1.272321	-0.000002
6	-1.23639	0.454656	0.000018
6	-2.51538	-0.34624	0.000038
1	-3.3725	0.32597	0.000171
1	-2.57235	-0.97981	0.883915
1	-2.57246	-0.9796	-0.88399
1	-1.15363	1.094259	-0.87934
1	-1.1535	1.094088	0.8795

P2

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-2.2146	-0.28746	0.289218
1	-2.90654	0.558388	0.242586
1	-2.53416	-1.08584	-0.39316
1	-2.1951	-0.70831	1.303518
6	-0.8356	0.177743	-0.08869
8	0.027675	-0.86585	-0.10131
8	-0.5207	1.301291	-0.35334
6	1.36698	-0.67268	-0.35266

6	2.137252	0.361922	0.386058
1	3.207851	0.230765	0.184447
1	1.983354	0.269851	1.477532
1	1.837065	1.378831	0.099055
1	1.827547	-1.60434	-0.68031

P3a

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-2.2201	-0.27552	0
1	-2.80415	-1.20036	0
1	-2.45879	0.32999	0.884106
1	-2.45879	0.32999	-0.88411
6	-0.75273	-0.6104	0
8	0	0.499274	0
8	-0.28682	-1.716	0
6	1.412859	0.297931	0
6	2.073168	1.656475	0
1	1.779827	2.228306	0.890532
1	1.779827	2.228306	-0.89053
1	1.688731	-0.29667	-0.88407
1	1.688731	-0.29667	0.884067

P3b

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.09426	-0.85161	0.016764
1	3.051531	-0.32286	-0.0058
1	2.019341	-1.47108	0.920158
1	2.004662	-1.51976	-0.84988
6	0.970298	0.148455	-0.00105
8	-0.22425	-0.46173	0.02737
8	1.092525	1.341373	-0.03532
6	-1.36233	0.397162	0.007417
6	-2.58542	-0.43541	0.012807
1	-3.54695	0.024054	0.236442
1	-2.55748	-1.42769	-0.4364
1	-1.29578	1.046382	-0.8876
1	-1.32234	1.082257	0.871002

HOI

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
53	0.014879	-0.29048	0
8	0.014879	1.680295	0
1	-0.90763	1.952876	0

Table S5. Vibrational frequencies (cm^{-1}) of reactants, TSs and products for the reaction of IO radicals with EF at M06-2X/def2-SV(P) level of theory. 'i' represents single imaginary wavenumber of the corresponding TS.

EF	IO	PRC1	TS1	TS2a	TS2b	TS3a
31.7263	618.5642	20.6783	**i**	**i**	**i**	**i**
148.2796		49.8267	24.7388	33.7688	35.8876	23.8667
228.5073		63.6757	45.1518	66.2167	66.551	47.145
268.1564		88.7759	55.0734	96.6276	97.6355	67.5194
442.973		112.9118	102.0691	106.4283	117.9482	101.8323
643.2213		146.8078	127.2093	143.4292	149.7127	126.1427
814.3367		228.8772	239.7162	188.7043	212.6428	160.4841
952.8299		249.042	283.1704	224.9516	221.8945	355.7486
1063.221		346.4106	312.2532	307.9866	331.2889	384.3398
1101.837		362.8479	448.7485	437.0894	442.2833	542.4245
1171.799		410.3494	543.4191	562.4199	568.1046	591.8926
1177.701		621.3542	637.4505	645.1067	644.5806	649.4447
1268.808		630.8923	795.9583	724.0061	749.4871	700.1978
1309.664		813.366	815.2045	855.1242	875.6965	802.7008
1380.426		927.377	947.1774	964.6918	963.8591	948.9603
1421.636		1072.926	1093.036	1056.723	1054.429	1060.523
1453.351		1123.349	1140.327	1115.557	1105.675	1090.384
1459.768		1147.288	1171.411	1170.686	1168.394	1095.298
1481.13		1171.729	1190.95	1207.245	1197.928	1167.45
1508.905		1263.718	1278.84	1250.018	1243.123	1221.428
1953.745		1355.3	1330.408	1280.839	1264.873	1246.453
2988.852		1384.85	1388.415	1365.854	1356.192	1319.443
3054.101		1433.284	1437.749	1414.627	1412.167	1341.822
3081.681		1459.129	1460.558	1444.88	1423.848	1391.007
3108.629		1477.63	1475.19	1450.61	1449.618	1434.196
3180.993		1508.845	1484.262	1454.663	1451.202	1456.342
3182.473		1981.062	1511.426	1469.789	1470.054	1490.023
		3074.595	1963.216	1954.535	1951.966	1954.877
		3109.808	3080.617	3046.495	3040.547	2987.189
		3166.215	3086.184	3060.618	3065.093	3068.444
		3174.944	3148.436	3070.063	3080.224	3112.663
		3185.147	3180.046	3162.355	3153.156	3169.028
		3752.654	3182.448	3186.989	3184.539	3213.043

TS3b	P1	P2	P3a	P3b	HOI
-1509.03	38.4456	81.7568	114.0674	114.119	624.174
41.2518	199.6497	137.042	140.7829	140.6977	1101.505
80.397	218.7938	190.5623	206.3267	206.017	3857.715
92.8165	267.886	231.6885	329.1969	329.1318	
101.3107	433.6279	429.8974	446.7404	446.9299	
181.0626	623.9944	528.2834	513.5714	514.0945	
240.9783	808.4504	644.1367	652.1087	652.0904	

382.5872	935.301	962.3272	869.033	869.1875	
408.9533	1088.592	1004.864	983.1109	983.0153	
508.2133	1154.34	1052.397	1057.05	1057.008	
594.4724	1175.759	1142.157	1117.031	1116.988	
650.5192	1245.68	1206.249	1136.866	1136.847	
665.817	1301.89	1267.081	1199.863	1199.919	
867.0019	1379.29	1367.525	1318.595	1318.52	
938.6286	1428.54	1423.993	1386.356	1386.352	
1058.963	1459.343	1438.286	1435.206	1435.198	
1085.731	1480.971	1450.404	1446.629	1446.612	
1090.144	1505.852	1470.517	1473.669	1473.634	
1173.368	1994.13	1953.736	1954.637	1954.65	
1219.011	3081.444	3021.76	2993.524	2993.7	
1243.343	3083.756	3022.917	3043.666	3043.736	
1321.971	3142.494	3115.822	3085.921	3085.944	
1343.535	3180.862	3175.319	3184.547	3184.419	
1389.962	3182.454	3192.493	3306.779	3306.539	
1424.306					
1438.695					
1479.779					
1956.712					
3014.629					
3044.145					
3103.979					
3118.828					
3216.858					

Table S6. Vibrational frequencies (cm^{-1}) of reactants, TSs and products for the reaction of IO radicals with EA at M06-2X/def2-SV(P) level of theory. 'i' represents single imaginary wavenumber of the corresponding TS.

EA	**IO**	**PRC2**	**TS1**	**TS2**	**TS3a**	**TS3b**
65.2727	618.5642	27.309	**i**	**i**	**i**	**i**
79.0291		53.7441	38.1254	30.8564	25.8811	30.788
153.7758		76.1578	40.949	48.5468	45.2036	39.7616
199.843		83.4867	65.2908	66.6102	60.0467	47.8453
268.798		104.0752	83.223	82.5116	77.7161	87.2445
381.004		116.1098	105.6565	98.9259	86.3855	110.4529
432.9954		158.6614	160.3843	138.9004	123.4896	123.765
604.2422		171.6898	207.7362	183.8804	193.127	200.5418
659.3904		206.1579	271.2568	204.0729	247.2724	215.5573
807.1402		284.6722	375.1979	254.6153	339.8506	379.2057
887.4391		381.901	416.9908	390.6776	410.9897	426.5347
982.686		436.3992	542.2069	436.6798	453.6411	543.9398
1011.199		596.4025	572.9487	566.6706	563.0976	567.3419
1057.055		638.8974	623.6208	601.9433	604.6867	603.7157
1127.484		664.7086	661.2967	661.7587	662.5024	661.8418
1154.996		803.7381	722.3783	726.6321	698.558	678.4422
1177.698		890.9123	806.4599	859.3139	797.4376	846.2777

1300.171		988.9067	886.3315	893.1885	927.0451	889.3795
1316.049		1019.759	970.9941	985.0664	991.2982	987.4518
1371.837		1048.235	998.4314	1017.705	1028.271	1011.296
1399.323		1127.853	1017.624	1056.787	1056.328	1058.212
1439.207		1155.356	1126.183	1154.314	1103.002	1097.406
1447.927		1179.027	1154.446	1175.694	1117.366	1139.404
1450.873		1296.502	1177.081	1195.465	1137.733	1166
1461.134		1316.361	1185.012	1249.037	1191.501	1237.596
1478.813		1366.174	1299.168	1308.316	1294.432	1272.724
1508.973		1396.457	1303.399	1355.806	1305.468	1311.432
1912.615		1435.651	1325.525	1387.15	1326.318	1322.196
3077.425		1445.036	1378.251	1397.195	1377.092	1378.071
3082.443		1459.531	1416.526	1427.647	1416.142	1408.688
3089.13		1460.918	1444.291	1444.133	1442.849	1440.478
3132.252		1479.1	1460.667	1449.628	1450.955	1445.732
3175.08		1504.505	1478.401	1453.454	1466.475	1449.989
3175.623		1893.223	1507.208	1467.901	1499.342	1484.257
3178.907		3068.835	1892.733	1920.725	1913.429	1917.247
3223.135		3076.345	3076.685	3066.816	3081.156	3051.14
		3082.273	3083.722	3089.665	3083.459	3087.582
		3135.778	3134.38	3109.866	3119.542	3118.262
		3167.346	3145.168	3157.667	3137.742	3126.16
		3168.849	3174.46	3180.459	3172.669	3177.725
		3173.34	3175.602	3186.059	3214.799	3218.912
		3210.437	3258.717	3225.226	3217.116	3222.969

P1	**P2**	**P3a**	**P3b**	**HOI**
76.1043	59.2627	71.3288	72.3477	624.174
150.013	86.187	80.8169	78.3254	1101.505
202.6853	113.6679	152.3324	157.3326	3857.715
269.4131	206.4083	190.3591	172.6547	
349.1908	244.8045	204.7708	201.2382	
381.2407	377.3419	389.3821	370.0228	
431.2788	452.1117	417.2924	421.1453	
597.9268	513.9521	457.4758	575.9079	
669.3031	592.9481	603.1037	604.8893	
745.2289	694.6953	660.6048	658.2753	
808.1977	865.3798	836.8594	788.3623	
878.2327	948.0212	946.5248	953.0732	
992.1641	997.9675	991.1051	989.1368	
1022.685	1018.197	1020.971	1057.668	
1136.271	1053.012	1057.497	1067.401	
1156.652	1140.669	1140.23	1122.607	
1177.344	1230.432	1147.739	1160.839	
1299.11	1306.111	1250.546	1285.757	
1329.41	1362.932	1316.885	1308.578	
1377.748	1397.063	1374	1370.629	
1423.188	1427.593	1411.092	1414.091	
1461.459	1436.532	1444.787	1445.404	
1465.468	1444.644	1450.445	1450.815	
1478.662	1450.439	1451.282	1469.788	

1509.999	1467.583	1480.529	1493.503	
1814.84	1919.352	1912.7	1909.229	
3077.173	3022.345	3008.511	3084.102	
3077.844	3088.661	3081.724	3089.851	
3126.731	3125.721	3089.424	3138.912	
3174.532	3178.123	3179.572	3180.027	
3175.515	3178.294	3192.376	3185.872	
3208.158	3223.563	3223.384	3223.314	
3343.281	3242.329	3314.179	3303.317	

Calculation of pressure dependent rate coefficients using MESMER/RRKM

To investigate the degree of influence of the respective PRCs into the pressure dependency of the kinetics of the titled reactions, MESMER[1] (Master Equation Solver for Multipotential Energy Well Reactions) 5.2 program suite was used to calculate the rate coefficients at the experimentally studied pressures using Rice-Ramsperger-Kassel-Marcus (RRKM)[2] theory. Lennard-Jones (L-J) parameters for all the species involved in the titled reactions have been tabulated in Table S7. Considering N_2 as a bath gas, the collisional energy transfer was modelled using the exponential down model with the average energy transfer the downward trajectory[3]. The obtained Bartis-Widom phenomenological rate coefficients were tested for convergence with respect to the 'size of the energy gain' (15 cm^{-1}) and 'energy above the top hill' ($25k_BT$) parameters. Inverse Laplace Transform (ILT) approach was used for obtain the final room temperature rate coefficients from the concentration profiles. Table S8 shows the calculated pressure dependent rate coefficients for both the titled reactions and the obtained data have been incorporated into Figure 5 for a better comparison.

Table S7. Calculated L-J (σ and ε) parameters of all the involved species using MESMER/RRKM method.

IO + EF			IO + EA		
Stationary points	σ (Å)	ε (K)	Stationary points	σ (Å)	ε (K)
PRC1	5.980	516.520	PRC2	6.350	540.150
TS1	5.976	516.523	TS2	6.355	540.155
P1	5.382	391.545	P2	5.82	402.94
HOI	4.825	451.905	HOI	4.825	451.905

Table S8. The calculated pressure dependent rate coefficients for the reaction of IO radicals with EF and EA at 298 K using MESMER/RRKM method. The data have been plotted in Figure 5 for comparison.

IO + EF		IO + EA	
Pressure (Torr)	k_{IO+EF}^{MESMER}(298 K) cm^3 molecule^{-1} s^{-1}	Pressure (Torr)	k_{IO+EA}^{MESMER}(298 K) cm^3 molecule^{-1} s^{-1}
39	1.50×10^{-14}	40	7.45×10^{-14}
65	1.58×10^{-14}	65	9.94×10^{-14}
87	1.64×10^{-14}	95	1.23×10^{-13}
114	1.71×10^{-14}	126	1.42×10^{-13}
143	1.74×10^{-14}	148	1.55×10^{-13}

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