Supplementary Information

Kinetic fall-off behavior for the Cl + Furan-2,5-dione ($C_4H_2O_3$, maleic anhydride) reaction

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Table S1. Summary of experimental conditions, fit parameters, and kinetic results obtained in this work for the Cl + $C_4H_2O_3$ (MA) ↔ $C_4H_2O_3Cl$• (adduct) reaction with N_2 bath gas

Temperature (K)	Pressure (Torr, N_2)	[$C_4H_2O_3$] (10^{14} molecule cm^{-3})	Q	$-\lambda_1$	$-\lambda_2$	S_0	k_d (s^{-1})	k_{loss} (s^{-1})	k_f (10^{-11} cm^3 $molecule^{-1}$ s^{-1})	k_r (s^{-1})	K_p (10^6 atm^{-1})
323	200	1.10	2813.9	5068.8	95.5	2016.5	15	190	2.12	2624	0.184
		3.27	3083.9	10240.9	122.1	1919.9		166	2.22	2918	0.173
		1.77	3205.1	7293.5	107.3	1989.6		176	2.36	3029	0.178
		2.40	3093.9	8123.3	107.9	1934.6		161	2.15	2879	0.170
	100	3.51	2667.1	8989.4	130.9	1125.1	118	136	1.80	2531	0.162
		2.37	2642.3	7491.9	138.2	1285.9		148	2.06	2494	0.188
		1.74	2572.2	6170.0	130.0	1256.2		138	2.08	2434	0.194
		1.31	2311.5	4785.3	141.8	1285.8		162	1.90	2149	0.201
		0.98	2420.1	4493.1	140.3	1315.0		164	2.14	2256	0.216
	50	5.39	2195.5	9862.3	107.0	1322.0	80	114	1.43	2081	0.156
		3.43	2112.4	7305.0	104.0	1458.0		113	1.52	1999	0.173
		3.09	2085.8	6529.5	103.7	1458.1		114	1.44	1972	0.166
		2.02	2008.6	4848.9	105.8	1505.4		123	1.42	1885	0.171
		1.27	1986.7	3893.9	102.5	1637.4		125	1.52	1862	0.186
	50	2.51	2005.8	5331.4	91.0	1383.5	51	114	1.34	1892	0.161
		1.15	1938.1	3565.2	83.9	1647.1		121	1.44	1818	0.181
		4.02	1924.4	7042.1	91.2	1323.5		106	1.28	1819	0.161
		1.86	2032.2	4869.7	90.4	1705.3		117	1.54	1915	0.183
		0.99	2083.7	3530.8	85.9	1829.5		133	1.49	1951	0.174
	25	7.72	1673.8	10354.7	138.1	1015.8	170	132	1.12	1541	0.165
		5.62	1701.2	7668.3	146.4	1026.2		140	1.06	1561	0.154
		4.71	1770.3	7486.7	154.9	1295.8		151	1.21	1620	0.170
		3.42	1731.8	5821.3	150.9	1292.2		144	1.19	1588	0.170
		2.50	1633.0	4418.4	157.0	1397.0		150	1.11	1483	0.170
	15	10.99	1393.4	11509.0	148.2	980.4	250	136	0.911	1257	0.165
		10.63	1329.8	9980.3	174.5	1077.2		164	0.807	1165	0.157
		9.32	1463.6	9478.0	231.7	1117.8		229	0.858	1235	0.158
		2.47	1333.5	3522.2	205.7	1640.8		182	0.867	1151	0.171
Global fit: K_p (323 K) = 0.17 ± 0.01											
308	500	2.24	2515.0	7623.8	1251.2	2069.4	250	1458	2.73	1057	0.617
		1.83	2502.8	6695.0	1159.8	1998.6		1399	2.79	1103	0.602
		1.30	2392.5	5213.3	1020.9	2168.8		1315	2.76	1077	0.611
	200	2.42	1405.3	7406.4	187.8	2047.3	66	212	2.53	1193	0.505
		2.14	1341.2	6529.0	191.9	1947.9		219	2.49	1122	0.528
		1.46	1364.4	5057.5	173.5	2061.9		207	2.60	1157	0.536
		1.22	1326.8	4337.7	182.3	2088.4		225	2.56	1102	0.554
		0.64	1324.4	3090.3	195.7	2118.9		273	2.95	1051	0.669
	100	4.64	1152.2	11736.6	125.6	1103.8	96	128	2.28	1024	0.532
		3.84	1197.0	9458.5	131.0	1142.8		136	2.16	1062	0.485
		2.90	1067.3	6978.3	124.4	1164.2		129	2.05	938	0.521
		2.09	1160.8	5939.4	126.0	1261.0		132	2.30	1028	0.532
		1.05	1073.9	3505.6	118.6	1355.7		128	2.34	946	0.589
	50	3.56	875.0	7168.9	115.0	1490.5	59	122	1.78	753	0.565
		2.62	869.5	5559.1	115.9	1695.7		125	1.81	745	0.579
		2.30	910.8	4886.7	116.8	1627.1		128	1.76	783	0.535
		2.06	934.9	4420.1	127.5	1754.9		143	1.72	792	0.520
		1.44	848.8	3333.8	112.2	1841.5		128	1.76	721	0.582
		0.948	849.3	2459.0	107.7	1780.2		130	1.75	720	0.579
	25	3.69	760.7	5872.9	185.7	1496.0	84	197	1.41	564	0.597
		2.90	706.0	4640.3	151.4	1508.0		161	1.38	545	0.604

		2.29	783.3	4010.2	174.6	1693.8		191	1.45	592	0.584
		1.60	708.5	2876.6	148.2	1657.4		164	1.39	544	0.610
		0.756	702.1	1761.4	141.2	1667.1		170	1.48	532	0.661
	15	8.80	782.1	10018.0	307.2	2093.9	126	316	1.07	466	0.548
		6.56	845.2	8047.7	342.8	2166.8		358	1.13	488	0.553
		5.83	896.6	7221.8	382.2	2317.4		402	1.13	494	0.545
		4.04	730.5	4844.6	300.2	2485.1		318	1.06	413	0.613
		2.40	802.0	3456.0	302.2	2587.2		333	1.18	469	0.600
		1.93	714.4	2646.5	287.3	2652.0		320	1.08	394	0.657
											Global fit: K_p (308 K) = 0.57 ± 0.02
296	500	1.36	1295.7	4901.1	674.4	2515.4	16	770	3.14	525	1.48
		3.02	360.6	9425.3	-63.8	2504.7		-	2.97	428	1.72
		0.96	1134.4	3510.5	588.2	2900.5		694	3.07	440	1.73
		3.42	2177.5	10515.0	1592.6	2504.7		1686	2.90	492	1.46
		2.42	678.6	7863.4	181.1	2843.8		192	3.03	486	1.55
		1.88	510.1	110.5	6097.9	2644.5		-	3.02	-	-
	200	5.37	-13.77	15298.0	-465.6	3150.4	16	-	2.76	467	1.47
		3.45	1288	10302.0	591.1	3348.5		633	2.78	655	1.05
		1.68	681.7	5052.5	185.3	3547.0		204	2.70	478	1.40
		2.66	700.0	7425.6	182.9	3555.3		196	2.59	505	1.27
	100	1.00	554.1	2891.7	126.7	3937.2	30	144	2.42	411	1.47
		2.16	564.6	5672.2	135.9	3733.1		145	2.42	420	1.43
		4.74	1327.1	11737.0	861.9	3462.9		896	2.37	431	1.37
		3.68	2219.9	9716.4	1452.5	3556.1		-	2.42	-	-
		6.58	-905.1	16505.0	-1156.8	3272.7		-	2.47	-	-
	100	4.11	1071.8	10447.0	472.0	3621.8	78	496	2.38	576	1.02
		2.31	671.41	6034.5	197.1	3953.9		207	2.37	464	1.27
		1.05	611.99	3064.8	166.9	3967.0		182	2.41	430	1.39
		3.27	870.93	500.3	7891.7	3443.6		521	2.27	350	1.61
		2.58	677.36	6987.9	179.7	3163.4		188	2.49	490	1.26
		5.62	6984.5	13730.0	6440.8	3459.5		-	2.33	-	-
		4.71	3191	11752.0	2434.8	3448.3		-	2.32	-	-
	50	1.33	456.2	3062.6	92.8	2827.7	33	101	2.00	355	1.40
		2.60	300.47	-26.0	5604.5	2624.0		-	2.02	330	1.52
		2.00	300.5	4342.0	77.4	2499.3		81	1.98	335	1.47
		0.92	444.3	2268.5	96.3	2701.7		108	2.05	336	1.52
	25	2.20	448.23	3733.9	157.1	3417.7	43	167	1.55	281	1.36
		0.85	425.9	1585.1	152.9	3557.4		177	1.50	249	1.49
		3.34	876.53	5364.3	561.73	3037.2		594	1.50	282	1.32
		4.25	-1157	6464.5	-1243.9	2773.9		-	1.49	-	-
	15	1.60	494.9	2436.4	237.8	3904.2	61	259	1.32	236	1.39
		2.57	668.5	3792.0	369.7	3658.5		396	1.34	272	1.22
		3.56	-474.7	4385.0	585.3	3434.8		-	1.18	-	-
		5.39	409	6637.7	264.7	2809.2		-	1.19	-	-
											Global fit: K_p (296 K) = 1.41 ± 0.06
283	500	2.99	3553.4	11376.0	3091.7	1667.0	12	3222.2	3.65	331	2.86
		2.04	2143.4	7160.7	1879.4	1733.5		1951	3.38	192	4.56
		1.61	2091.3	1803.2	5699.1	1780.8		1898.8	3.35	193	4.52
	200	1.27	389.9	4082.9	212.8	2696.7	6	222	3.07	168	4.76
		0.55	311.8	1901.4	137.3	2555.5		151	3.13	161	5.04
		1.86	4342.3	6096.5	3868.9	2773.9		4195	3.02	148	5.30
		3.22	3995.8	10841.0	3621.1	2654.7		3751	3.24	245	3.43
		2.63	3657.3	3654.3	7958.6	2535.7		-	3.02	-	-
	100	0.83	261.5	2422.0	116.7	3053	15	123	2.72	138	4.87
		1.52	2052.4	4239.0	1780.6	3138.6		1902	2.61	150	4.30
		1.22	740.7	3592.1	569.0	3141.5		597	2.79	144	4.82
		2.01	3005.7	6072.9	2568.6	3153.9		2767	2.80	239	2.91

		3.30	-16588	9164.8	-16589	2927.6		-	2.77	-	-
	50	0.65	459.4	1805.4	280.0	1772.2	26	308	2.45	151	4.03
		1.70	767.4	521.3	4380.3	1649.6		551	2.41	216	2.76
		1.20	497.1	3082.7	305.2	1740.7		324	2.38	173	3.41
		2.04	2917.5	2779.4	4874.2	1705.7		-	2.31	-	-
		3.06	1200.8	8081.5	811.7	1641.3		-	2.51	-	-
	25	0.82	736.5	1985.4	499.6	2082.9	34	564	2.08	173	3.13
		0.48	283.5	1152.8	164.3	2317.3		180	2.06	104	5.17
		1.16	1054.9	2678.2	778.8	2173.9		866	2.04	189	2.80
		2.56	1663.3	1219.4	5882.2	2001.3		-	2.11	-	-
		1.86	2828	4740.1	2042.3	2113.4		-	2.11	-	-
		3.96	3810.9	4957.4	6121.0	1923		-	1.83	-	-
	15	1.20	971.8	2127.6	799.2	3276	42	2883.9	1.59	104.2	3.97
		0.75	236.9	1276.7	172.1	3389.9		179.4	1.56	57.6	7.05
		1.48	1319.3	2602.2	1106.0	3288.2		1202.7	1.58	116.6	3.52
		1.81	6326.1	6431.2	2674.0	3264.4		-	1.52	-	-
		2.38	4916.7	5424.7	3349.1	3073.4		-	1.60	-	-
Global fit: K_p(283 K) = 4.16 ± 0.49											

Table S2. Summary of experimental conditions, fit parameters, and kinetic results obtained in this work for the Cl + $C_4H_2O_3$ (MA) ↔ $C_4H_2O_3Cl$• (adduct) reaction with He bath gas

Temperature (K)	Pressure (Torr, He)	$[C_4H_2O_3]$ (10^{14} molecule cm^{-3})	Q	$-\lambda_1$	$-\lambda_2$	S_0	k_d (s^{-1})	k_{Loss} (s^{-1})	k_f (10^{-11} cm^3 $molecule^{-1}$ s^{-1})	k_r (s^{-1})	K_p (10^6 atm^{-1})
323	300	3.58	3024.5	10050.7	149.0	3381.6	59	185	1.99	2839	0.159
		3.18	2964.6	8989.2	154.9	3559.3		199	1.92	2765	0.158
		2.55	2894.1	7657.9	146.8	3518.1		196	1.90	2698	0.160
		2.01	2827.0	6668.3	133.9	2938.5		186	1.95	2641	0.168
		1.27	2738.1	5051.3	134.3	3644.4		216	1.89	2522	0.170
	100	3.63	1891.4	6614.6	85.7	3546.6	48	100	1.31	1791	0.166
		3.23	1920.3	6095.1	84.5	3466.5		100	1.30	1820	0.163
		2.56	1856.4	5012.3	83.9	3312.1		104	1.25	1752	0.162
		1.97	1885.2	4462.9	83.6	3470.0		108	1.32	1777	0.169
		0.91	1841.0	3016.2	78.8	4293.9		124	1.33	1717	0.176
											Global fit: K_p (323 K) = 0.17 ± 0.01
308	100	5.81	870.8	10003.0	110.9	4087.8	120	110.2	1.57	760.7	0.492
		5.49	860.3	9375.4	125.4	4136.5		125.8	1.55	734.4	0.504
		4.22	849.5	7311.9	120.2	4810.7		120.2	1.53	729.3	0.501
		3.04	835.6	5883.4	127.9	4977.6		129.0	1.66	706.6	0.562
		2.40	830.1	4792.6	117.8	4732.0		117.3	1.65	712.8	0.552
		1.13	815.8	2680.3	115.3	4971.3		113.5	1.65	702.2	0.559
											Global fit: K_p (308 K) = 0.53 ± 0.03
296	500	2.49	2101.2	7617.5	1473.8	1328.6	124	1597	2.76	504	1.36
		2.15	720.0	6823.9	222.5	1776.7		230	2.89	490	1.46
		1.75	792.3	5843.7	240.3	2043.6		253	2.96	540	1.36
		1.33	775.9	4582.9	264.2	1693.9		282	2.96	493	1.49
		0.97	704.3	3330.0	205.4	1760.8		220	2.79	484	1.40
	300	5.83	614.9	1946.3	159.9	3725.7	37	198	2.49	416	1.48
		3.64	645.0	9486.8	184.7	4153.3		192	2.47	453	1.35
		3.16	665.7	8261.1	178.7	3882.5		188	2.45	478	1.27
		2.45	648.6	6548.2	178.5	4223.2		190	2.46	459	1.33
		2.20	624.0	5741.6	167.6	3720.3		179	2.38	445	1.33
		1.69	616.7	4624.2	174.1	3360.0		189	2.45	428	1.42
		0.95	604.1	2780.8	163.1	3390.2		187	2.42	417	1.44
	100	9.12	310.7	15617.8	45.7	5538.2	106	45	1.67	266	1.56
		6.88	392.2	12001.5	80.4	7102.7		80	1.68	312	1.34
		4.91	432.2	8773.2	119.0	7737.3		120	1.70	312	1.35
		3.36	417.3	6276.2	112.7	9118.3		113	1.74	304	1.42
		1.66	390.4	3453.9	87.2	9518.9		85	1.83	305	1.49
		0.97	419.6	2126.3	112.0	8322.6		113	1.76	306	1.42
	100	4.43	456.2	7923.5	123.4	2845.3	69	126	1.70	330	1.27
		3.16	442.8	6127.7	90.3	2002.2		92	1.81	351	1.28
		3.06	436.1	5535.8	120.9	2986.0		124	1.68	312	1.34
		2.04	418.8	4010.4	76.5	2080.2		77	1.76	342	1.28
		1.03	401.1	2219.0	82.2	2147.4		84	1.77	317	1.39
		0.95	422.5	1903.9	121.9	3275.2		132	1.62	290	1.38
	100	3.03	448.9	5480.0	151.8	2494.2	80	156	1.68	293	1.43
		2.11	466.2	4164.9	145.4	2673.2		151	1.78	315	1.40
		3.03	448.9	5480.0	151.9	2494.2		156	1.68	293	1.43
		1.24	473.3	2596.4	146.8	2908.0		157	1.77	317	1.39
	50	3.94	369.5	5637.7	98.2	1914.0	63	100	1.35	270	1.24
		3.63	369.7	5078.5	91.8	1857.6		94	1.30	276	1.17
		2.93	322.6	3967.3	101.6	2089.3		104	1.26	219	1.42
		2.73	342.9	3858.8	86.5	1816.2		88	1.30	255	1.26
		1.67	333.9	2524.3	87.1	1782.9		90	1.33	244	1.34
											Global fit: K_p (296 K) = 1.37 ± 0.03

Table S3. Computed CBS-QB3 enthalpies at 298 K (in au) and B3LYP/6-311G(2d,d,p) geometries (atomic number and Cartesian coordinates in 10^{-10} m) for Cl, $C_4H_2O_3$ (MA) and $C_4H_2O_3$•Cl (adduct).

For $C_4H_2O_3$ (MA), the rotational constants are B = 6.86, 2.46 and 1.81 GHz.
For $C_4H_2O_3$•Cl (adduct), the rotational constants are B = 2.80, 1.44 and 1.04 GHz.

Cl atom

CBS-QB3 Enthalpy= -459.681232

Maleic anhydride

CBS-QB3 Enthalpy = -378.780589

6	0.000000000	1.131875000	0.159628000
6	0.000000000	0.665536000	-1.256735000
6	0.000000000	-0.665536000	-1.256735000
6	0.000000000	-1.131875000	0.159628000
8	0.000000000	0.000000000	0.971021000
8	0.000000000	-2.238041000	0.598153000
8	0.000000000	2.238041000	0.598153000
1	0.000000000	1.356406000	-2.086671000
1	0.000000000	-1.356406000	-2.086671000

Cl adduct

CBS-QB3 Enthalpy = -838.491388

6	-1.618170000	-0.386090000	-0.038391000
6	-0.525931000	-1.077731000	0.616960000
6	0.638620000	-0.188314000	0.687514000
6	0.097264000	1.138565000	0.124657000
8	-1.193034000	0.932542000	-0.310253000
8	0.648259000	2.186547000	0.063652000
8	-2.715952000	-0.762210000	-0.325777000
1	-0.580051000	-2.105350000	0.942027000
1	1.084920000	-0.051442000	1.671889000
17	2.001780000	-0.800989000	-0.375255000

Table S4. Computed B3LYP/6-311G(2d,d,p) vibrational frequencies for $C_4H_2O_3$ (MA) and $C_4H_2O_3Cl$• (Cl adduct), in cm^{-1} and scaled by 0.99.

Maleic anhydride	Cl - MA adduct
165	63
258	147
400	191
554	305
630	394
639	525
692	562
768	586
853	605
862	700
892	724
975	789
1036	846
1065	910
1246	1009
1314	1051
1637	1175
1836	1220
1896	1276
3200	1304
3221	1762
	1896
	3075
	3218

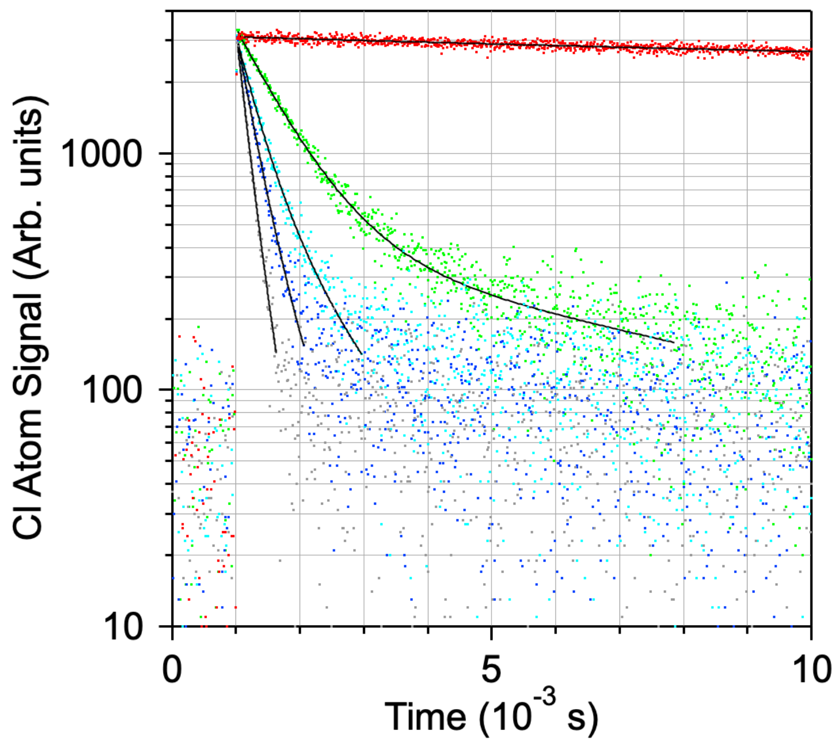

Figure S1. Representative Cl atom temporal profiles obtained for a range of $C_4H_2O_3$ (MA) concentrations at 283 K and 100 Torr (N_2). MA concentrations from top to bottom are (10^{14} molecule cm^{-3}): 0, 0.37, 0.83, 1.22, and 2.01. The lines for profiles with MA present are non-linear least-squares fits of the data to eq. I. Fit results are given in **Table S1**.

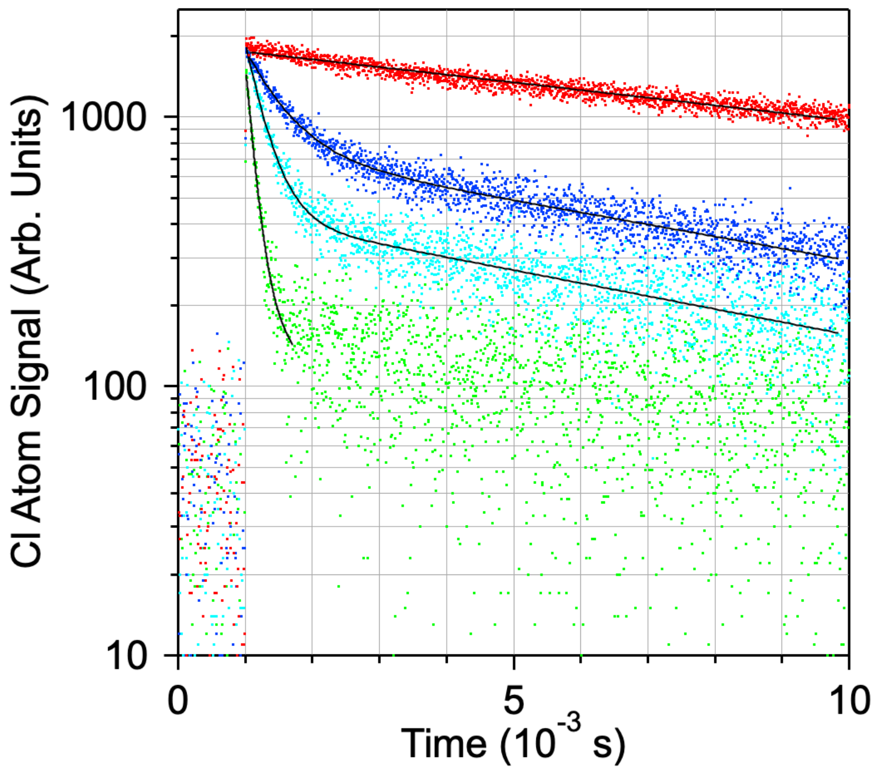

Figure S2. Representative Cl atom temporal profiles obtained for a range of $C_4H_2O_3$ (MA) concentrations at 308 K and 50 Torr (N_2). MA concentrations from top to bottom are (10^{14} molecule cm^{-3}): 0, 0.57, 1.44, and 3.56. The lines for profiles with MA present are non-linear least-squares fits of the data to eq. I. Fit results are given in **Table S1**.

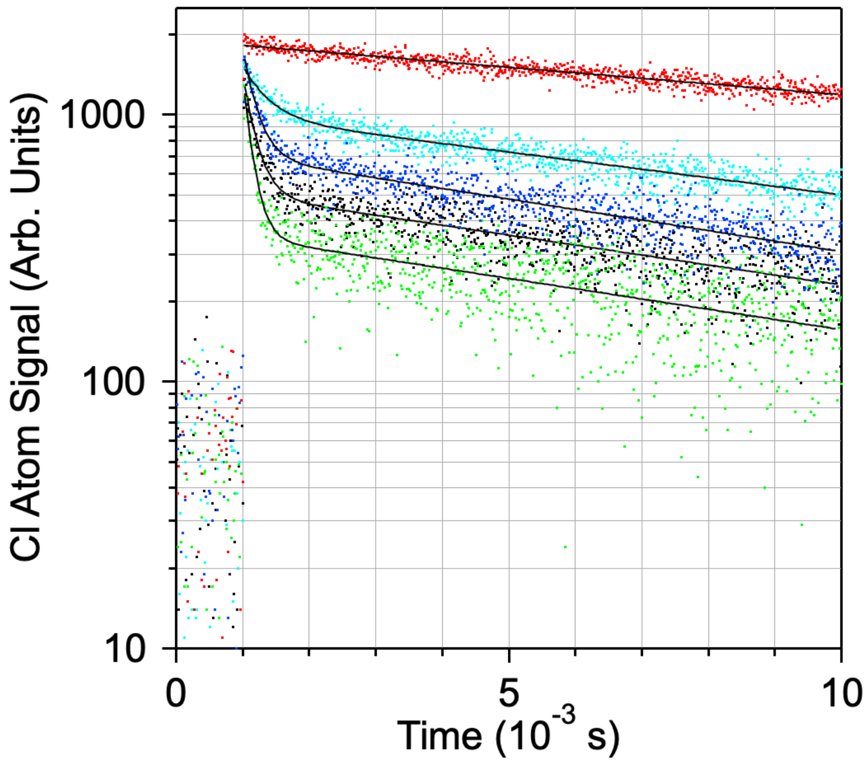

Figure S3. Representative Cl atom temporal profiles obtained for a range of $C_4H_2O_3$ (MA) concentrations at 323 K and 50 Torr (N_2). MA concentrations from top to bottom are (10^{14} molecule cm^{-3}): 0, 0.67, 1.86, 2.51 and 4.02. The lines for profiles with MA present are non-linear least-squares fits of the data to eq. I. Fit results are given in **Table S1**.

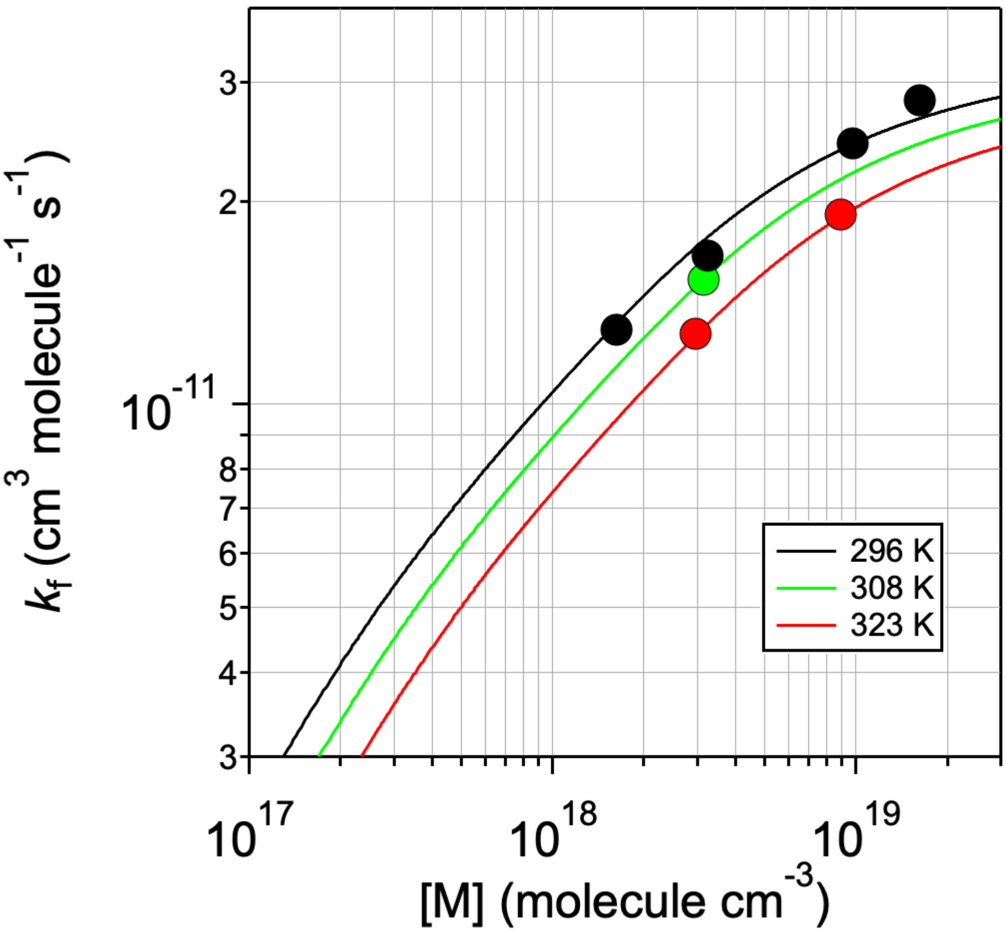

Figure S4. Fall-off data for the Cl + $C_4H_2O_3$ (MA) + M (He) reaction. Lines are a least-squares fit of the data (see **Table S2**) using the rate coefficient parameters for N_2 data after incorporating a collision efficiency ratio of 0.34.

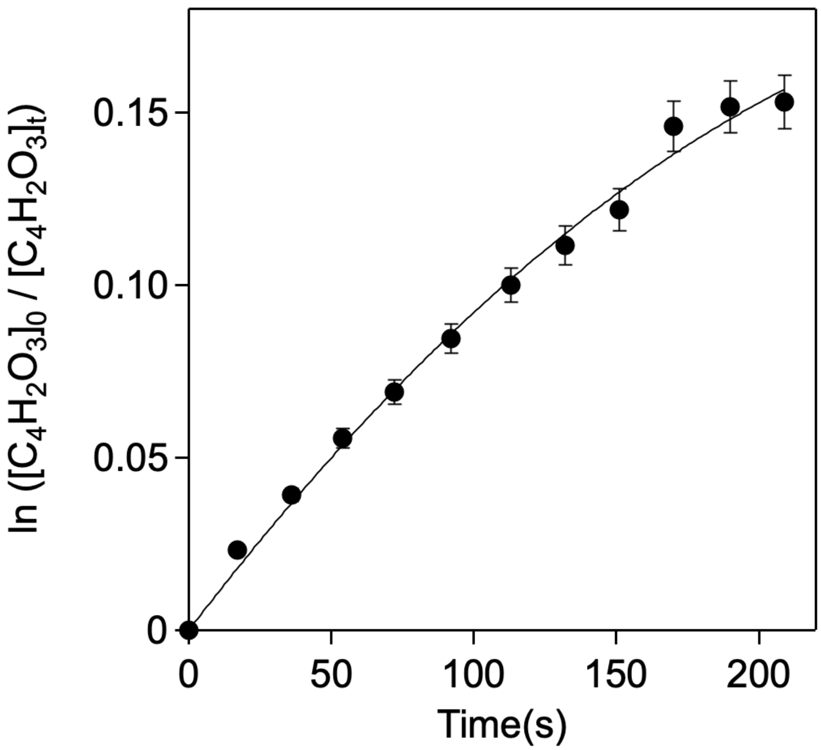

Figure S5. A representative measurement of the dark loss of $C_4H_2O_3$ (MA) in the relative rate apparatus, i.e., in the absence of Cl atom. The line is an empirical second-order polynomial least-squares fit of the data used to correct for MA loss in the relative rate kinetic measurement, e.g. see **Figure 3** in the text for the magnitude of the dark loss correction. MA loss measurements performed before and after each kinetic measurement were consistent to within 3%.

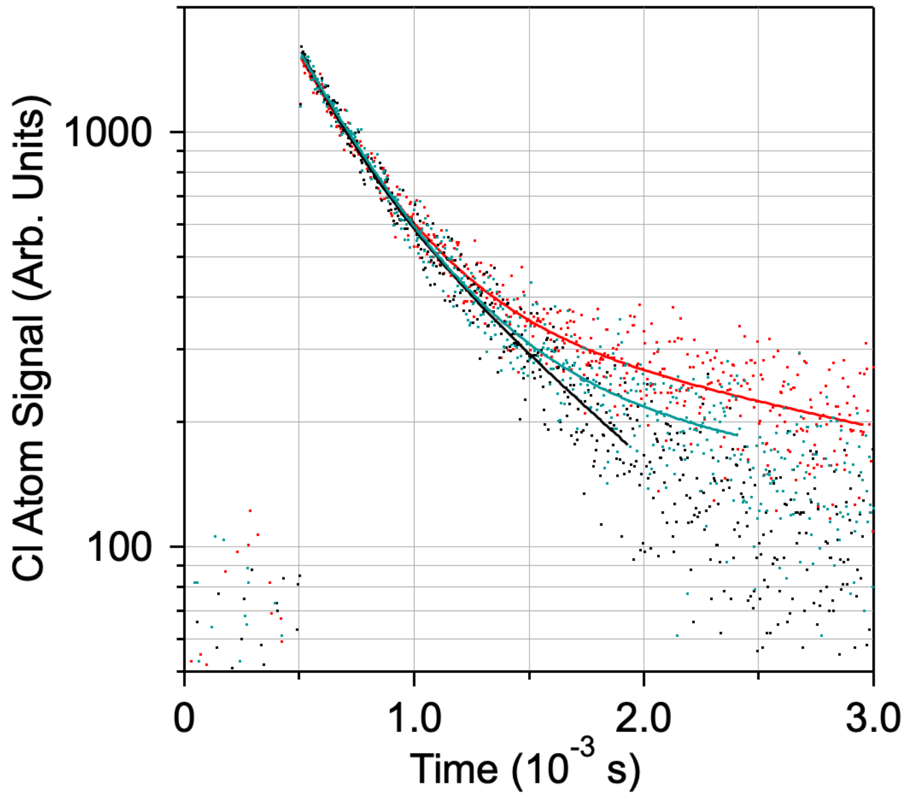

Figure S6. Representative Cl atom temporal profiles obtained for a range of O_2 concentrations with a $C_4H_2O_3$ (MA) concentration of $(6.22 \pm 0.10) \times 10^{13}$ molecule cm^{-3} at 296 K and 40 Torr (N_2). O_2 concentrations from top to bottom profile are (10^{14} molecule cm^{-3}): 0, 1.27, and 4.03. The lines are non-linear least-squares fits of the data to eq. I. Not all measured Cl atom profiles are shown for clarity, see **Figure 6**.

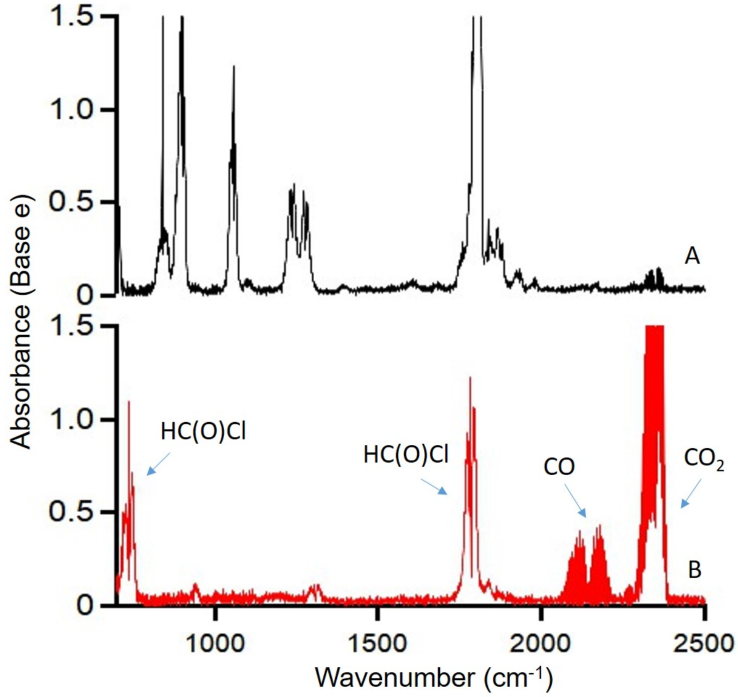

Figure S7. Infrared spectra of reaction products formed in the Cl + $C_4H_2O_3$ reaction. Experiments were performed at 296 K with 630 Torr syn. Air bath gas. Panel A is the initial MA spectrum. Note the high initial MA concentration resulted in saturated absorbance at 1805 cm^{-1}. Panel B is the spectrum recorded after ~3 mins of reaction with MA subtracted, ~90% MA loss.