

Table S1. Initial and reaction conditions for the LS experiments and experimental k_1 .

$P_1 /$ Torr	$T_1 /$ °C	$P_2 /$ Torr	$T_2 /$ K	$k_1 /$ s ⁻¹
2% MA 120 Torr				
5.4	21.4	124	1704	41124.01
5.85	21.4	119	1550	12233.58
6.15	21.4	121	1510	8008.485
5.11	20.8	126	1797	122213.5
4.9	20.8	122	1814	177321.6
4.75	20.8	125	1896	166306.7
4.75	20.8	126	1909	288720.5
4.9	21.1	126	1862	179032.2
4.9	21.1	126	1863	180385.8
4.65	21	127	1962	325480.9
4.5	21	123	1959	253689.1
4.25	21	120	2020	365638.8
4.05	21	120	2090	530668.9
4.1	21	121	2088	447180.3
4% MA 120 Torr				
$P_1 /$ Torr	$T_1 /$ °C	$P_2 /$ Torr	$T_2 /$ K	$k_1 /$ s ⁻¹
5.8	20.6	129	1492	4284.935
5.4	20.6	129	1574	11848.71
5	20.6	124	1622	18977.71
4.8	20.6	120	1632	18988.05
5.1	20.6	121	1567	10829.34
5.25	20.6	122	1539	8086.15
4.55	20.6	121	1703	44869.4
4.7	20.6	119	1648	30421.67
4.8	20.3	123	1660	25959.87
4.6	20.3	123	1714	50968.47
4.45	20.7	122	1746	61713.97
4.5	20.6	124	1753	52296.95
4.3	20.6	121	1790	81504.36
4.15	20.6	120	1819	103880.5
4.05	20.6	118	1831	122613.6
4.05	20.6	118	1815	126569.5
4.1	20.6	120	1838	163163.9
4.1	20.6	121	1851	133830.5
4.05	20.6	124	1901	243353.8

$P_1 /$ Torr	$T_1 /$ °C	$P_2 /$ Torr	$T_2 /$ K	$k_1 /$ s ⁻¹
2% MA 60 Torr				
2	21	62	2188	439208.6
1.8	21	58	2262	514201
2.1	21	63	2113	401778.7
2.2	21.1	65	2082	437149.7
2.25	21.1	65	2052	376440.2
2.25	21.1	64	2030	335510.3
2.3	21.1	64	1979	224716.1
2.35	21.1	64	1947	207769
2.4	21.2	64	1922	157895.3
2.45	21.2	64	1892	115078.4
2.55	21.2	64	1834	95006.6
2.6	21.2	64	1796	70250.28
2.65	21.2	64	1777	53403.82
2.75	21.2	63	1704	43494.68
2.9	21.3	63	1639	18872.89

$P_1 /$ Torr	$T_1 /$ °C	$P_2 /$ Torr	$T_2 /$ K	$k_1 /$ s ⁻¹
4% MA 60 Torr				
2.3	20.7	63	1743	55944.09
2.15	20.7	62	1811	79341.19
2.35	20.7	62	1704	30791.87
2.15	20.7	61	1789	59085.39
2.05	20.9	60	1847	117636.3
2.05	20.9	60	1839	156434.2
2.1	20.9	63	1888	158115.6
2.05	20.9	63	1915	189850.3
2	20.9	62	1922	280782
1.9	20.9	59	1924	271659.1
1.85	20.9	62	2037	438364.2
1.95	20.9	62	1968	236210.9
1.9	20.9	63	2041	398985.9
1.8	20.9	60	2042	401076.9
1.75	20.9	61	2113	505809.4
1.7	20.9	60	2143	648421

Table S2. Arrhenius parameters calculated from RRKM/ME for dissociation of methyl acetate .

	Pressure (atm)	A / s	n	Ea/R
MA <=> CH3 + CH3 + CO2				
	3.95E-02	6.59E+82	-19.52	6.08E+04
	7.89E-02	3.71E+82	-19.34	6.13E+04
	1.58E-01	9.06E+81	-19.07	6.16E+04
	3.16E-01	8.45E+80	-18.68	6.19E+04
	5.00E-01	9.67E+79	-18.35	6.19E+04
	1.00E+00	1.35E+78	-17.74	6.18E+04
	1.50E+00	6.11E+76	-17.31	6.17E+04
	2.50E+00	6.40E+74	-16.69	6.14E+04
	5.00E+00	3.92E+71	-15.71	6.07E+04
	1.00E+01	6.12E+67	-14.57	5.98E+04

	Pressure (atm)	A / s	n	Ea/R
MA <=> CH3OCO + CH3				
	3.95E-02	1.47E+82	-19.58	6.26E+04
	7.89E-02	4.24E+82	-19.58	6.33E+04
	1.58E-01	5.39E+82	-19.48	6.40E+04
	3.16E-01	2.70E+82	-19.28	6.45E+04
	5.00E-01	9.56E+81	-19.07	6.48E+04
	1.00E+00	7.41E+80	-18.64	6.51E+04
	1.50E+00	9.05E+79	-18.32	6.51E+04
	2.50E+00	3.20E+78	-17.84	6.51E+04
	5.00E+00	9.12E+75	-17.02	6.48E+04
	1.00E+01	5.28E+72	-16.02	6.42E+04

	Pressure (atm)	A / s	n	Ea/R
MA <=> CH3OH + CH2CO				
	3.95E-02	2.90E+75	-17.93	5.59E+04
	7.89E-02	1.64E+74	-17.5	5.59E+04
	1.58E-01	3.72E+72	-16.97	5.58E+04
	3.16E-01	3.10E+70	-16.31	5.56E+04
	5.00E-01	7.15E+68	-15.8	5.53E+04
	1.00E+00	9.49E+65	-14.93	5.47E+04
	1.50E+00	1.15E+64	-14.35	5.43E+04
	2.50E+00	2.54E+61	-13.56	5.36E+04
	5.00E+00	2.42E+57	-12.38	5.25E+04
	1.00E+01	8.51E+52	-11.08	5.12E+04

	Pressure (atm)	A / s	n	Ea/R
MA <=> CH2COHOCH3				
	3.95E-02	3.90E+72	-17.26	5.40E+04
	7.89E-02	1.21E+71	-16.76	5.40E+04
	1.58E-01	1.52E+69	-16.16	5.37E+04
	3.16E-01	7.17E+66	-15.45	5.33E+04
	5.00E-01	1.16E+65	-14.9	5.30E+04
	1.00E+00	9.59E+61	-13.98	5.23E+04
	1.50E+00	9.25E+59	-13.38	5.17E+04
	2.50E+00	1.62E+57	-12.57	5.10E+04
	5.00E+00	1.28E+53	-11.37	4.98E+04
	1.00E+01	4.37E+48	-10.07	4.85E+04