

Supplemental Materials

Fuel-Specific Influences on the Composition of Reaction Intermediates in Premixed Flames of Three C₅H₁₀O₂ Ester Isomers

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Supplemental Material-Part 1 (pdf file): Figures S1-S3 and Table S1-S4

Figure S1: PIE spectra for mass 30 and 40 in the three ester flames

Figure S2: C₄ species detected in the three ester flames, as well as the modeling results for C₄H₆

Figure S3: Mole fraction profiles for oxygenated intermediates detected in the three ester flames

Table S1: Photon energies used and photoionization cross-sections for detected flame species

Table S2: Kinetic reaction mechanism for ethyl propanoate.

Table S3: Methyl isobutanoate mechanism, including submechanism for methyl methacrylate

Table S4: Rate expressions for H atom abstraction reactions by OH, H, and HO₂ radicals in functional groups of importance in the present study

Supplemental Material-Part 2 (Excel file): Table S5

Measured temperature profiles and measured mole fractions for the three ester flames are provided in the file: Supp2.xlsx.

Fig. S1. PIE spectra for mass 30 and 40 in the three ester flames.

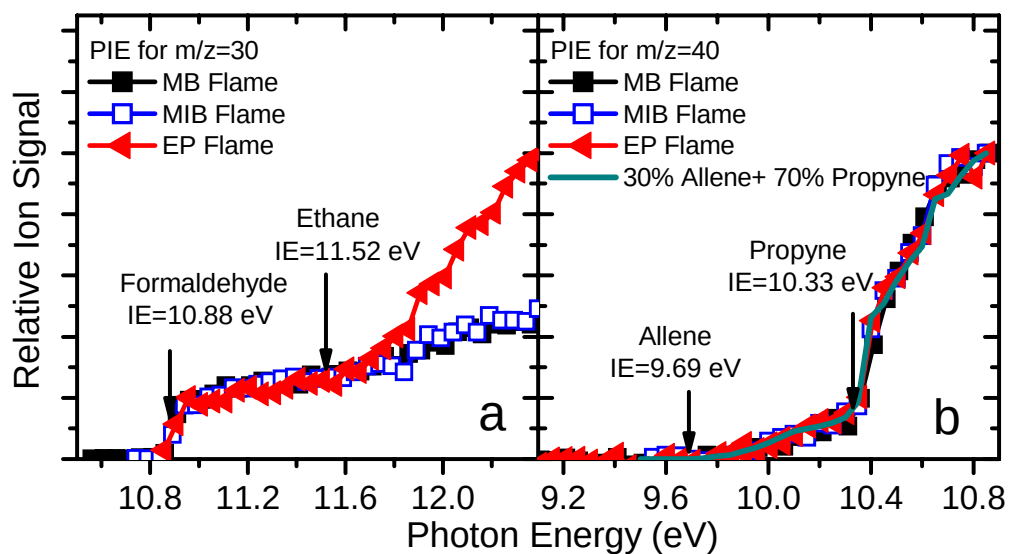


Fig. S2. C_4 species detected in the three ester flames, as well as the modeling results for C_4H_6 .

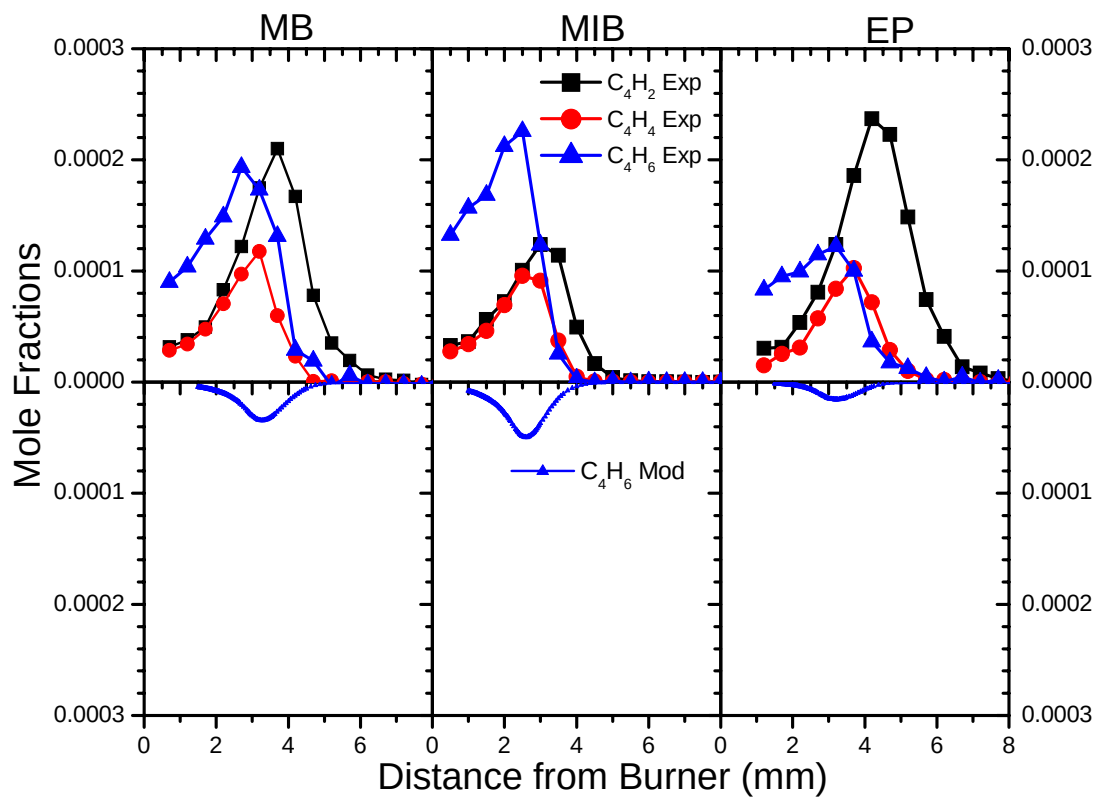


Fig. S3. Mole fraction profiles for oxygenated intermediates detected in the three ester flames.

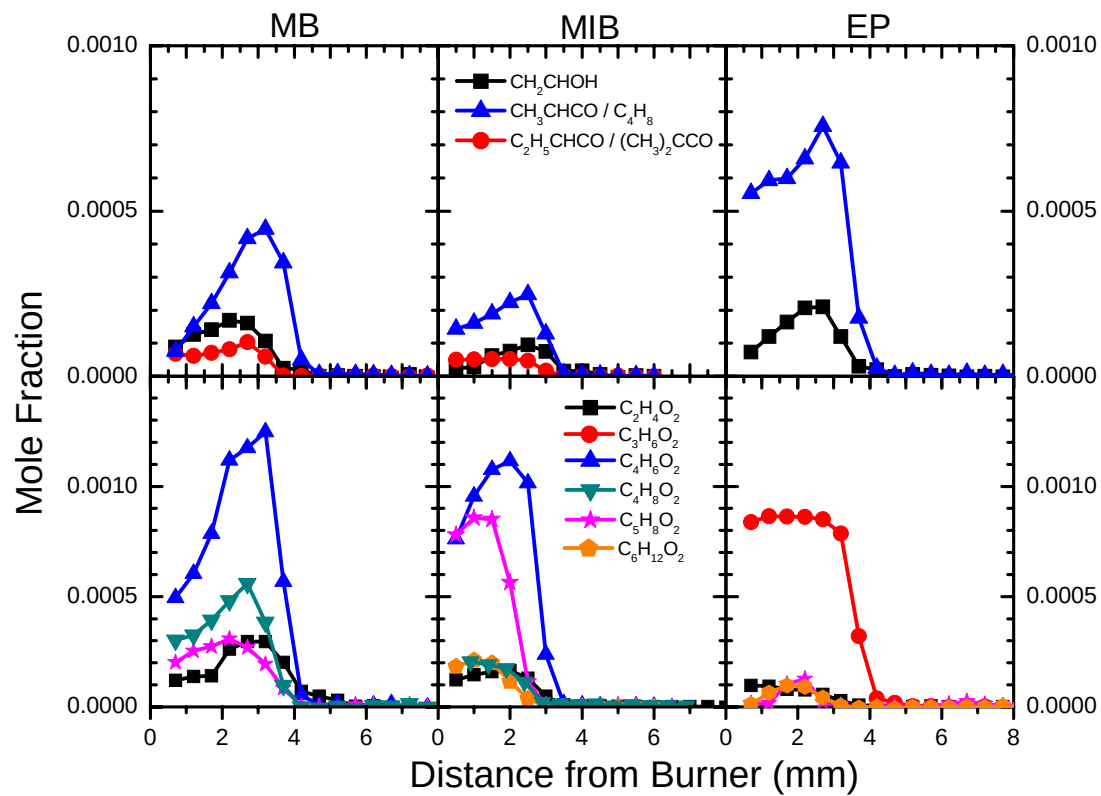


Table S1. Photon energies used (**E**) and photoionization cross-sections (**$\sigma(E)$**) for detected flame species.

M/z	Formula	Species	E	IP	$\sigma(E)$
			eV	eV	Mb [Ref]
2	H ₂	Hydrogen	16.2	15.43	X ^a
15	CH ₃	Methyl radical	11.5	9.84	7 [1]
16	CH ₄	Methane	13.2	12.61	5 [2]
18	H ₂ O	Water	13.2	12.62	X ^a
26	C ₂ H ₂	Acetylene	13.2	11.4	39 [3]
28	CO	Carbon Monoxide	14.35	14.01	X ^a
28	C ₂ H ₄	Ethylene	11.5	10.51	8 [3]
30	CH ₂ O	Formaldehyde	11.5	10.88	10.2 [3]
30	C ₂ H ₆	Ethane	12.3	11.52	13.3 [2]
32	O ₂	Oxygen	13.2	12.07	X ^a
32	CH ₃ OH	Methanol	11.5	10.84	9.6 [3]
39	C ₃ H ₃	Propargyl radical	10.0	8.67	8.8 [4]
40	Ar	Argon	16.2	15.76	X ^a
40	C ₃ H ₄	Allene	10.0	9.69	6.6 [5]
40	C ₃ H ₄	Propyne	11.5	10.36	42.1 [5]
41	C ₃ H ₅	Allyl radical	10.0	8.18	6.2 [6]
42	C ₃ H ₆	Propene	10.0	9.73	8.5 [7]
42	C ₂ H ₂ O	Ketene	10.0	9.62	21 [8]
44	CO ₂	Carbon Dioxide	14.35	13.78	X ^a
44	C ₂ H ₄ O	Ethanol	10.0	9.33	6.4 [5]
44	C ₂ H ₄ O	Acetaldehyde	11.5	10.23	9.7 [5]
50	C ₄ H ₂	Diacetylene	11.5	10.17	34 [3]
52	C ₄ H ₄	Vinylacetylene	11.5	9.58	39 [3]
54	C ₄ H ₆	1,3-Butadiene	11.5	9.07	24 [7]
56	C ₄ H ₈	Cis-2-Butene	10.0	9.09	9.10 [2]
56	C ₃ H ₄ O	Methyl Ketene	10.0	8.95	20 Est ^b
58	C ₃ H ₆ O	Acetone	10.5	9.70	11.2 [3]
60	C ₂ H ₄ O ₂	Acetic Acid	11.5	10.65	19.4 [8]
60	C ₂ H ₄ O ₂	Methyl formate	11.5	10.83	7.64 [9]
70	C ₄ H ₆ O	Ethyl ketene	9.7	8.80	20 EST ^b
70	C ₄ H ₆ O	Dimehtyl ketene	9.7	8.38	20 EST ^b
74	C ₃ H ₆ O ₂	Propanoic acid	11.5	10.44	19.4 EST ^b
86	C ₄ H ₆ O ₂	Methyl propenoate	10.5	10.0	2.28 [9]

86	C ₄ H ₆ O ₂	Vinyl acetate	10.5	9.31	18.0 [9]
88	C ₄ H ₈ O ₂	Methyl propanoate	10.5	10.06	7.9 [9]
88	C ₄ H ₈ O ₂	Ethyl acetate	10.5	9.95	6.18 [9]
100	C ₅ H ₈ O ₂	Methyl crotonate	10.5	9.7	8.5 [9]
100	C ₅ H ₈ O ₂	Ethyl propenoate	10.5	9.9	4.5 [9]
102	C ₅ H ₁₀ O ₂	Methyl butanoate	10.5	9.85	3.4 [9]
102	C ₅ H ₁₀ O ₂	Methyl isobutynate	10.5	9.74	16.9 [9]
102	C ₅ H ₁₀ O ₂	Ethyl propanoate	10.5	9.85	9.68 [9]
116	C ₆ H ₁₂ O ₂		10.5		10 Est ^b

a) "X" in the table indicates that photoionization cross sections are not used for the mole fraction determination; b) "Est" in the table indicates that the cross section data is estimated.

References:

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Table S2. Kinetic reaction mechanism for ethyl propanoate. Based on Metcalfe et al.³³ with modifications made for reaction rates written in bold. Submechanism for epvd is new in this study.

ethyl propanoate abbreviations

Species	Name	Formula
Ep	ethyl propanoate	CH ₃ CH ₂ (CO)OCH ₂ CH ₃
ep3j	ethyl propanoate radical 1	•CH ₂ CH ₂ (CO)OCH ₂ CH ₃
ep2j	ethyl propanoate radical 2	CH ₃ •CH(CO)OCH ₂ CH ₃
epej	ethyl propanoate radical 3	CH ₃ CH ₂ (CO)O•CHCH ₃
epmj	ethyl propanoate radical 4	CH ₃ CH ₂ (CO)OCH ₂ •CH ₂
ee2j	ethyl propanoate radical	•CH ₂ (CO)OCH ₂ CH ₃
mpmj	methyl propanoate radical	CH ₃ CH ₂ (CO)O•CH ₂
ep2d	ethyl propenoate	CH ₂ =CH(CO)OCH ₂ CH ₃
epvd	vinyl propanoate	CH ₃ CH ₂ (CO)OCH=CH ₂
ep2dej	ethyl propenoate radical 1	CH ₂ =CH(CO)O•CHCH ₃
ep2dmj	ethyl propenoate radical 2	CH ₂ =CH(CO)OCH ₂ •CH ₂
ep2dvj	ethyl propenoate radical 3	•CH=CH(CO)OCH ₂ CH ₃
epvd2j	vinyl propanoate radical 1	CH ₃ •CH(CO)OCH=CH ₂
epvd3j	vinyl propanoate radical 2	•CH ₂ CH ₂ (CO)OCH=CH ₂
epvdivj	vinyl propanoate radical 3	CH ₃ CH ₂ (CO)OCH=•CH

Reaction	A	n	Ea
ep3j + h(+m) = ep(+m)	1.00E+14	0	0.00E+00
ep2j + h(+m) = ep(+m)	1.00E+14	0	0.00E+00
epej + h(+m) = ep(+m)	1.00E+14	0	0.00E+00
epmj + h(+m) = ep(+m)	1.00E+14	0	0.00E+00
ep(+m) = c2h5cooh + c2h4(+m)	6.00E+13	0	5.00E+04
ep(+m) = c2h5cooh + c2h4(+m)	1.60E+13	0	5.00E+04
ep(+m) = ee2j + ch3(+m)	5.73E+23	-2.3	8.77E+04
ep(+m) = c2h5oco + c2h5(+m)	2.63E+27	-3.2	9.47E+04
ep(+m) = c2h5co + c2h5o(+m)	1.65E+24	-2	1.00E+05
ep(+m) = c2h5co2 + c2h5(+m)	5.73E+25	-2.8	9.21E+04
ep(+m) = mpmj + ch3(+m)	3.39E+21	-1.6	9.21E+04
ep + o2 = ep3j + ho2	3.00E+13	0	5.23E+04
ep + o2 = ep2j + ho2	2.00E+13	0	4.43E+04
ep + o2 = epej + ho2	2.00E+13	0	4.82E+04
ep + o2 = epmj + ho2	3.00E+13	0	5.23E+04

ep	+	h	=	ep3j	+	h2	1.33E+06	2.54	6.76E+03
ep	+	h	=	ep2j	+	h2	5.04E+13	0	7.30E+03
ep	+	h	=	epej	+	h2	3.25E+05	2.4	2.58E+03
ep	+	h	=	epmj	+	h2	1.88E+05	2.8	6.28E+03
ep	+	h	=	ep3j	+	h2	6.60E+05	2.54	6.76E+03
ep	+	h	=	ep2j	+	h2	2.52E+14	0	7.30E+03
ep	+	h	=	epej	+	h2	1.20E+06	2.4	2.58E+03
ep	+	h	=	epmj	+	h2	6.66E+05	2.8	6.28E+03
ep	+	o	=	ep3j	+	oh	1.96E+06	2.43	4.75E+03
ep	+	o	=	ep2j	+	oh	4.40E+12	0	3.28E+03
ep	+	o	=	epej	+	oh	2.81E+13	0	5.20E+03
ep	+	o	=	epmj	+	oh	1.03E+14	0	7.88E+03
ep	+	o	=	ep3j	+	oh	9.81E+05	2.43	4.75E+03
ep	+	o	=	ep2j	+	oh	2.20E+13	0	3.28E+03
ep	+	o	=	epej	+	oh	7.66E+05	2.41	1.14E+03
ep	+	o	=	epmj	+	oh	9.81E+05	2.43	4.75E+03
ep	+	oh	=	ep3j	+	h2o	1.06E+10	0.97	1.59E+03
ep	+	oh	=	ep2j	+	h2o	2.29E+10	0.51	6.30E+01
ep	+	oh	=	epej	+	h2o	2.29E+10	0.51	6.30E+01
ep	+	oh	=	epmj	+	h2o	1.05E+10	0.97	1.59E+03
ep	+	oh	=	ep3j	+	h2o	5.28E+09	0.97	1.59E+03
ep	+	oh	=	ep2j	+	h2o	1.15E+11	0.51	6.30E+01
ep	+	oh	=	epej	+	h2o	1.15E+11	0.51	6.30E+01
ep	+	oh	=	epmj	+	h2o	5.28E+09	0.97	1.59E+03
ep	+	ch3	=	ep3j	+	ch4	4.53E-01	3.65	7.15E+03
ep	+	ch3	=	ep2j	+	ch4	2.00E+11	0	7.90E+03
ep	+	ch3	=	epej	+	ch4	1.20E-09	6.36	8.93E+02
ep	+	ch3	=	epmj	+	ch4	4.53E-01	3.65	7.15E+03
ep	+	ho2	=	ep3j	+	h2o2	2.38E+04	2.55	1.65E+04
ep	+	ho2	=	ep2j	+	h2o2	4.32E+12	0	1.44E+04
ep	+	ho2	=	epej	+	h2o2	7.22E+03	2.55	1.05E+04
ep	+	ho2	=	epmj	+	h2o2	2.38E+04	2.55	1.65E+04
ep	+	ho2	=	ep3j	+	h2o2	2.38E+04	2.55	1.65E+04
ep	+	ho2	=	ep2j	+	h2o2	2.16E+12	0	1.44E+04

ep	+	ho2	=	epej	+	h2o2	3.61E+03	2.55	1.05E+04
ep	+	ho2	=	epmj	+	h2o2	2.38E+04	2.55	1.65E+04
ep	+	ch3o2	=	ep3j	+	ch3o2h	2.38E+04	2.55	1.65E+04
ep	+	ch3o2	=	ep2j	+	ch3o2h	4.32E+12	0	1.44E+04
ep	+	ch3o2	=	epej	+	ch3o2h	7.22E+03	2.55	1.05E+04
ep	+	ch3o2	=	epmj	+	ch3o2h	2.38E+04	2.55	1.65E+04
ep	+	c2h5	=	ep3j	+	c2h6	4.52E-01	3.65	9.14E+03
ep	+	c2h5	=	ep2j	+	c2h6	2.00E+11	0	7.90E+03
ep	+	c2h5	=	epej	+	c2h6	1.08E+00	3.46	5.96E+03
ep	+	c2h5	=	epmj	+	c2h6	4.52E-01	3.65	9.14E+03
ep	+	c2h3	=	ep3j	+	c2h4	3.02E+02	3.3	1.05E+04
ep	+	c2h3	=	ep2j	+	c2h4	4.00E+11	0	1.43E+04
ep	+	c2h3	=	epej	+	c2h4	1.81E+00	3.46	2.61E+03
ep	+	c2h3	=	epmj	+	c2h4	3.02E+02	3.3	1.05E+04
ep	+	ch3o	=	ep3j	+	ch3oh	2.17E+11	0	6.46E+03
ep	+	ch3o	=	ep2j	+	ch3oh	3.80E+10	0	2.80E+03
ep	+	ch3o	=	epej	+	ch3oh	4.58E+10	0	2.87E+03
ep	+	ch3o	=	epmj	+	ch3oh	2.17E+11	0	6.46E+03
ep3j	=	c2h4	+	c2h5oco			8.83E+15	-0.7	3.56E+04
ep2d	+	h	=	ep3j			1.00E+13	0	2.90E+03
ep2j	=	ch3chco	+	c2h5o			2.79E+22	-2.3	4.57E+04
ep2j	=	ep2d	+	h			1.32E+14	-0.2	4.09E+04
epej	=	ch3cho	+	c2h5co			1.13E+21	-1.7	4.06E+04
epvd	+	h	=	epej			1.00E+13	0	2.90E+03
epvd	+	h	=	epmj			1.00E+13	0	2.90E+03
epmj	=	c2h4	+	c2h5co2			2.33E+14	-0.2	3.30E+04
ep2d	=	c2h3	+	c2h5oco			4.28E+22	-1.7	1.08E+05
ep2d	=	c2h3co	+	c2h5o			1.38E+23	-1.8	9.02E+04
ep2d	=	mp2dmj	+	ch3			2.52E+20	-1	9.22E+04
ep2d	+	o2	=	ep2dej	+	ho2	2.00E+13	0	4.82E+04
ep2d	+	o2	=	ep2dmj	+	ho2	3.00E+13	0	5.23E+04

ep2d	+	o2	=	ep2dvj	+	ho2	1.40E+12	0	6.07E+04
ep2d	+	h	=	ep2dej	+	h2	1.20E+06	2.4	2.58E+03
ep2d	+	h	=	ep2dmj	+	h2	6.66E+05	2.54	6.76E+03
ep2d	+	h	=	ep2dvj	+	h2	4.05E+05	2.5	9.79E+03
ep2d	+	o	=	ep2dej	+	oh	7.66E+05	2.41	1.14E+03
ep2d	+	o	=	ep2dmj	+	oh	9.81E+05	2.43	4.75E+03
ep2d	+	o	=	ep2dvj	+	oh	6.03E+10	0.7	7.63E+03
ep2d	+	oh	=	ep2dej	+	h2o	1.15E+11	0.51	6.30E+01
ep2d	+	oh	=	ep2dmj	+	h2o	5.28E+09	0.97	1.59E+03
ep2d	+	oh	=	ep2dvj	+	h2o	1.11E+06	2	1.45E+03
ep2d	+	ch3	=	ep2dej	+	ch4	1.20E-09	6.36	8.93E+02
ep2d	+	ch3	=	ep2dmj	+	ch4	4.53E-01	3.65	7.15E+03
ep2d	+	ch3	=	ep2dvj	+	ch4	8.40E-01	3.5	1.17E+04
ep2d	+	ho2	=	ep2dej	+	h2o2	7.22E+03	2.55	1.05E+04
ep2d	+	ho2	=	ep2dmj	+	h2o2	2.38E+04	2.55	1.65E+04
ep2d	+	ho2	=	ep2dvj	+	h2o2	3.00E+09	0	9.93E+03
ep2d	+	ch3o2	=	ep2dej	+	ch2o2h	7.22E+03	2.55	1.05E+04
ep2d	+	ch3o2	=	ep2dmj	+	ch3o2h	2.38E+04	2.55	1.65E+04
ep2d	+	ch3o2	=	ep2dvj	+	ch3o2h			
ep2d	+	c2h5	=	ep2dej	+	c2h6	1.08E+00	3.46	5.96E+03
ep2d	+	c2h5	=	ep2dmj	+	c2h6	4.52E-01	3.65	9.14E+03
ep2d	+	c2h5	=	ep2dvj	+	c2h6	1.00E+11	0	9.80E+03
ep2d	+	c2h3	=	ep2dej	+	c2h4	1.81E+00	3.46	2.61E+03
ep2d	+	c2h3	=	ep2dmj	+	c2h4	3.02E+02	3.3	1.05E+04
ep2d	+	c2h3	=	ep2dvj	+	c2h4	8.40E-01	3.5	9.68E+03
ep2d	+	ch3o	=	ep2dej	+	ch3oh	4.58E+10	0	2.87E+03
ep2d	+	ch3o	=	ep2dmj	+	ch3oh	2.17E+11	0	6.46E+03
ep2d	+	ch3o	=	ep2dvj	+	ch3oh	4.00E+01	2.9	8.61E+03
epvd	+	h	=	epvd2j	+	h2	2.52E+14	0	7.30E+03
epvd	+	h	=	epvd3j	+	h2	6.66E+05	2.54	6.76E+03
epvd	+	h	=	epvdvj	+	h2	4.05E+05	2.5	9.79E+03

epvd	+	o	=	epvd2j	+	oh	2.20E+13	0	3.28E+03
epvd	+	o	=	epvd3j	+	oh	9.81E+05	2.43	4.75E+03
epvd	+	o	=	epvdvj	+	oh	6.03E+10	0.7	7.63E+03
epvd	+	oh	=	epvd2j	+	h2o	1.15E+11	0.51	6.30E+01
epvd	+	oh	=	epvd3j	+	h2o	5.28E+09	0.97	1.59E+03
epvd	+	oh	=	epvdvj	+	h2o	1.11E+06	2	1.45E+03
epvd	+	ho2	=	epvd2j	+	h2o2	4.32E+12	0	1.44E+04
epvd	+	ho2	=	epvd3j	+	h2o2	2.38E+04	2.55	1.65E+04
epvd	+	ho2	=	epvdvj	+	h2o2	3.00E+09	0	9.93E+03
epvd	+	ch3	=	epvd2j	+	ch4	2.00E+11	0	7.90E+03
epvd	+	ch3	=	epvd3j	+	ch4	4.53E-01	3.65	7.15E+03
epvd	+	ch3	=	epvdvj	+	ch4	8.40E-01	3.5	1.17E+04
epvd	+	ch3o	=	epvd2j	+	ch3oh	3.80E+10	0	2.80E+03
epvd	+	ch3o	=	epvd3j	+	ch3oh	2.17E+11	0	6.46E+03
epvd	+	ch3o	=	epvdvj	+	ch3oh	4.00E+01	2.9	8.61E+03
epvd	+	c2h3	=	epvd2j	+	c2h4	4.00E+11	0	1.43E+04
epvd	+	c2h3	=	epvd3j	+	c2h4	3.02E+02	3.3	1.05E+04
epvd	+	c2h3	=	epvdvj	+	c2h4	8.40E-01	3.5	9.68E+03
epvd	+	c2h5	=	epvd2j	+	c2h6	2.00E+11	0	7.90E+03
epvd	+	c2h5	=	epvd3j	+	c2h6	4.52E-01	3.65	9.14E+03
epvd	+	c2h5	=	epvdvj	+	c2h6	1.00E+11	0	9.80E+03
epvd	+	ch3o2	=	epvd2j	+	ch3o2h	4.32E+12	0	1.44E+04
epvd	+	ch3o2	=	epvd3j	+	ch3o2h	2.38E+04	2.55	1.65E+04
epvd	+	ch3o2	=	epvdvj	+	ch3o2h	3.00E+09	0	9.93E+03
epvd	+	o2	=	epvd2j	+	ho2	2.00E+13	0	4.43E+04
epvd	+	o2	=	epvd3j	+	ho2	3.00E+13	0	5.23E+04
epvd	+	o2	=	epvdvj	+	ho2	1.40E+12	0	6.07E+04
ep2dej	=	ch3cho	+	ch2chco			2.42E+23	-2.7	3.33E+04
ep2dmj	=	c2h4	+	c2h3co2			1.50E+12	0.44	3.20E+04
ep2dvj	=	c2h2	+	c2h5co2			1.00E+14	0	4.50E+04
epvd2j	=	ch3chco	+	ch2cho			1.00E+14	0	4.50E+04
epvd3j	=	c2h4	+	c2h3co2			1.00E+14	0	4.50E+04
epvdvj	=	c2h2	+	c2h5co2			1.00E+14	0	4.50E+04

c2h3co2	=	c2h3	+	co2	1.00E+13	0	1.00E+04
ee2j	=	c2hco	+	c2h5o	9.36E+19	-1.9	5.64E+04

Table S3. Methyl isobutanoate mechanism, including submechanism for methyl methacrylate

methyl isobutanoate abbreviations

Species	Name	Formula
mib	methyl isobutanoate	CH ₃ CHCH ₃ (CO)OCH ₃
mibpj	methyl isobutanoate radical 1	•CH ₂ CHCH ₃ (CO)OCH ₃
mibtj	methyl isobutanoate radical 2	CH ₃ •CCH ₃ (CO)OCH ₃
mibmj	methyl isobutanoate radical 3	CH ₃ CHCH ₃ (CO)O•CH ₂
mp2j	methyl propanoate radical 2	CH ₃ •CH(CO)O/CH ₃
ocoic3h7	methyl isobutanoate radical	CH ₃ CHCH ₃ (CO)O•
mmethac	methyl methacrylate	CH ₂ =CCH ₃ (CO)OCH ₃
mmethmj	methyl methacrylate radical 1	CH ₂ =CCH ₃ (CO)O•CH ₂
mmethvj	methyl methacrylate radical 2	•CH=CCH ₃ (CO)OCH ₃
mmethpj	methyl methacrylate radical 3	CH ₂ =C•CH ₂ (CO)OCH ₃

Reaction				A	n	Ea
mibmj	+	h	= mib	1.00E+14	0	0.00E+00
mibtj	+	h	= mib	1.00E+14	0	0.00E+00
mibpj	+	h	= mib	1.00E+14	0	0.00E+00
mp2j	+	ch3	= mib	1.00E+13	0	0.00E+00
ocoic3h7	+	ch3	= mib	1.00E+13	0	0.00E+00
ch3o	+	ic3h7co	= mib	8.00E+12	0	0.00E+00
ch3oco	+	ic3h7	= mib	8.00E+12	0	0.00E+00
mib	+	h	= mibmj + h2	9.40E+04	2.8	6.28E+03
mib	+	h	= mibtj + h2	3.62E+06	2.5	6.76E+03
mib	+	h	= mibpj + h2	1.88E+05	2.8	6.28E+03
mib	+	oh	= mibmj + h2o	5.28E+09	1	1.59E+03
mib	+	oh	= mibtj + h2o	1.15E+11	0.5	6.30E+01
mib	+	oh	= mibpj + h2o	1.06E+10	1	1.59E+03
mib	+	o	= mibmj + oh	9.81E+05	2.4	4.75E+03
mib	+	o	= mibtj + oh	3.94E+05	2.4	1.15E+03
mib	+	o	= mibpj + oh	1.96E+06	2.4	4.75E+03
mib	+	ch3	= mibmj + ch4	4.53E-01	3.7	7.15E+03

mib	+	ch3	=	mibtj	+	ch4	2.72E+00	3.7	7.15E+03
mib	+	ch3	=	mibpj	+	ch4	9.06E-01	3.7	7.15E+03
mib	+	ho2	=	mibmj	+	h2o2	2.38E+04	2.6	1.65E+04
mib	+	ho2	=	mibtj	+	h2o2	7.22E+03	2.6	1.05E+04
mib	+	ho2	=	mibpj	+	h2o2	4.76E+04	2.6	1.65E+04
mib	+	o2	=	mibmj	+	ho2	3.00E+13	0	5.23E+04
mib	+	o2	=	mibtj	+	ho2	4.08E+13	0	4.14E+04
mib	+	o2	=	mibpj	+	ho2	6.00E+13	0	5.23E+04
mib	+	ch3o	=	mibmj	+	ch3oh	2.17E+11	0	6.46E+03
mib	+	ch3o	=	mibtj	+	ch3oh	3.80E+10	0	2.80E+03
mib	+	ch3o	=	mibpj	+	ch3oh	4.34E+11	0	6.46E+03
mib	+	ch3o2	=	mibmj	+	ch3o2h	2.38E+04	2.6	1.65E+04
mib	+	ch3o2	=	mibtj	+	ch3o2h	7.22E+03	2.6	1.05E+04
mib	+	ch3o2	=	mibpj	+	ch3o2h	4.76E+04	2.6	1.65E+04
mib	+	c2h3	=	mibmj	+	c2h4	3.02E+02	3.3	1.05E+04
mib	+	c2h3	=	mibtj	+	c2h4	4.00E+11	0	1.43E+04
mib	+	c2h3	=	mibpj	+	c2h4	6.03E+02	3.3	1.05E+04
mib	+	c2h5	=	mibmj	+	c2h6	4.52E-01	3.7	9.14E+03
mib	+	c2h5	=	mibtj	+	c2h6	2.00E+11	0	7.90E+03
mib	+	c2h5	=	mibpj	+	c2h6	9.04E-01	3.7	9.14E+03
ch2o	+	ic3h7co	=	mibmj			1.00E+11	0	8.20E+03
ch3o	+	ic3h6co	=	mibtj			1.00E+11	0	8.20E+03
h	+	mmethac	=	mibtj			4.00E+10	0	2.90E+03
ch3	+	mp2d	=	mibpj			1.00E+11	0	8.20E+03
ch3oco	+	c3h6	=	mibpj			5.00E+11	0	8.20E+03
h	+	mmethac	=	mibpj			5.00E+11	0	2.90E+03
ic3h7	+	co2	=	ocoic3h7			1.00E+11	0	8.20E+03
mibtj	+	o2	=	mmethac	+	ho2	3.00E-09	0	3.00E+03
mibpj	+	o2	=	mmethac	+	ho2	3.00E-09	0	3.00E+03
mmethac	+	h	=	mmethmj	+	h2	6.66E+05	2.5	6.76E+03
mmethac	+	o	=	mmethmj	+	oh	9.81E+05	2.4	4.75E+03

mmethac	+	oh	=	mmethmj	+	h2o	5.28E+09	1	1.59E+03
mmethac	+	ho2	=	mmethmj	+	h2o2	2.38E+04	2.6	1.65E+04
mmethac	+	ch3	=	mmethmj	+	ch4	4.53E-01	3.7	7.15E+03
mmethac	+	ch3o	=	mmethmj	+	ch3oh	2.17E+11	0	6.46E+03
mmethac	+	ch3o2	=	mmethmj	+	ch3o2h	2.38E+04	2.6	1.65E+04
mmethac	+	c2h3	=	mmethmj	+	c2h4	3.02E+02	3.3	1.05E+04
mmethac	+	c2h5	=	mmethmj	+	c2h6	4.52E-01	3.7	9.14E+03
mmethac	+	o2	=	mmethmj	+	ho2	3.00E+13	0	5.23E+04
mmethac	+	h	=	mmethvj	+	h2	4.05E+05	2.5	9.79E+03
mmethac	+	o	=	mmethvj	+	oh	6.03E+10	0.7	7.63E+03
mmethac	+	oh	=	mmethvj	+	h2o	1.11E+06	2	1.45E+03
mmethac	+	ho2	=	mmethvj	+	h2o2	3.00E+09	0	1.99E+04
mmethac	+	ch3	=	mmethvj	+	ch4	8.40E-01	3.5	1.17E+04
mmethac	+	ch3o	=	mmethvj	+	ch3oh	4.00E+01	2.9	8.61E+03
mmethac	+	ch3o2	=	mmethvj	+	ch3o2h	3.00E+09	0	9.93E+03
mmethac	+	c2h3	=	mmethvj	+	c2h4	8.40E-01	3.5	9.68E+03
mmethac	+	c2h5	=	mmethvj	+	c2h6	1.00E+11	0	9.80E+03
mmethac	+	o2	=	mmethvj	+	ho2	1.40E+12	0	6.07E+04
mmethac	+	h	=	mmethpj	+	h2	6.66E+05	2.5	6.76E+03
mmethac	+	o	=	mmethpj	+	oh	9.81E+05	2.4	4.75E+03
mmethac	+	oh	=	mmethpj	+	h2o	5.28E+09	1	1.59E+03
mmethac	+	ho2	=	mmethpj	+	h2o2	2.38E+04	2.6	1.65E+04
mmethac	+	ch3	=	mmethpj	+	ch4	4.53E-01	3.7	7.15E+03
mmethac	+	ch3o	=	mmethpj	+	ch3oh	2.17E+11	0	6.46E+03
mmethac	+	ch3o2	=	mmethpj	+	ch3o2h	2.38E+04	2.6	1.65E+04
mmethac	+	c2h3	=	mmethpj	+	c2h4	3.02E+02	3.3	1.05E+04
mmethac	+	c2h5	=	mmethpj	+	c2h6	4.52E-01	3.7	9.14E+03
mmethac	+	o2	=	mmethpj	+	ho2	3.00E+13	0	5.23E+04
mmethac	+	oh	=	mp2j	+	ch2o	1.00E+11	0	4.00E+03
mmethac	+	oh	=	ch3coch3	+	ch3oco	1.00E+11	0	4.00E+03
mmethac	+	o	=	ch3coch2	+	ch3oco	1.00E+11	0	1.05E+03
mmethmj	=	ch2o	+	ic3h5co			1.00E+14	0	4.50E+04
mmethvj	=	c3h4-p	+	ch3oco			1.00E+14	0	4.50E+04
mmethpj	=	c3h4-a	+	ch3oco			1.00E+14	0	4.50E+04
mmethac	=	ic3h5co	+	ch3o			1.00E+16	0	7.10E+04
mmethac	=	c3h5-a	+	ch3oco			1.00E+16	0	7.10E+04

Table S4. Rate expressions for H atom abstraction reactions by OH, H, and HO₂ radicals in functional groups of importance in the present study. The three C₅H₁₀O₂ methyl esters are shown in bold type. Reactions with an asterisk * indicate the final values in cases where the reaction rates were modified. Final column shows reaction rate evaluated at 1000K.

				A	n	Ea cal/mol	rate (1000K) cm ³ -mol ⁻¹ -s ⁻¹
R(CO)OCH₃							
methyl	formate	+	OH	5.27E+09	0.97	1590	1.92E+12
methyl	ethanoate	+	OH	5.27E+09	0.97	1590	1.92E+12
methyl	propanoate	+	OH	5.27E+09	0.97	1590	1.92E+12
methyl	butanoate	+	OH	7.02E+07	1.61	-35	4.83E+12
methyl	isobutanoate	+	OH	5.27E+09	0.97	1590	1.92E+12
methyl	formate	+	H	6.66E+05	2.54	6756	9.26E+11
methyl	ethanoate	+	H	9.40E+04	2.75	6280	7.09E+11
methyl	propanoate	+	H	9.40E+04	2.75	6280	7.09E+11
methyl	butanoate	+	H	1.95E+06	2.4	4471	3.26E+12
methyl	isobutanoate	+	H	9.40E+04	2.75	6280	7.09E+11
methyl	formate	+	HO ₂	2.38E+04	2.55	16490	2.64E+08
methyl	ethanoate	+	HO ₂	4.04E+04	2.5	16690	2.87E+08
methyl	propanoate	+	HO ₂	4.04E+04	2.5	16690	2.87E+08
methyl	butanoate	+	HO₂	1.23E+04	2.6	13910	7.07E+08
methyl	isobutanoate	+	HO₂	2.38E+04	2.55	16490	2.64E+08
CH₃(CO)OR							
methyl	acetate	+	OH	1.40E+10	0.51	63	4.60E+11
ethyl	acetate	+	OH	1.40E+10	0.51	63	4.60E+11
methyl	acetate	+	H	1.50E+05	2.4	2583	6.48E+11
ethyl	acetate	+	H	1.50E+05	2.4	2583	6.48E+11
methyl	acetate	+	HO ₂	9.00E+02	2.55	10532	2.01E+08
ethyl	acetate	+	HO ₂	9.00E+02	2.55	10532	2.01E+08
CH₃CH₂(CO)OR							
c2h5cooh		+	OH	5.28E+09	0.97	1586	1.93E+12
methyl	propanoate	+	OH	5.28E+09	0.97	1586	1.93E+12

*	ethyl	propanoate	+	OH	5.28E+10	0.97	1586	1.93E+13
	ethyl	propanoate	+	OH	1.06E+10	0.97	1586	3.88E+12
	c2h5cooh		+	H	5.28E+09	0.97	1586	1.93E+12
	methyl	propanoate	+	H	6.66E+06	2.54	6756	9.26E+12
	ethyl	propanoate	+	H	6.66E+05	2.54	6756	9.26E+11
*	ethyl	propanoate	+	H	1.33E+06	2.54	6756	1.85E+12
	c2h5cooh		+	HO2	2.38E+04	2.55	16490	2.64E+08
	methyl	propanoate	+	HO2	2.38E+04	2.55	16490	2.64E+08
	ethyl	propanoate	+	HO2	2.38E+04	2.55	16490	2.64E+08
CH3CH2(CO)OR								
	c2h5cooh		+	OH	1.15E+11	0.51	63	3.78E+12
	methyl	propanoate	+	OH	1.15E+11	0.51	63	3.78E+12
	ethyl	propanoate	+	OH	1.15E+11	0.51	63	3.78E+12
*	ethyl	propanoate	+	OH	2.29E+10	0.51	63	7.52E+11
	c2h5cooh		+	H	2.54E+14	0	7300	6.45E+12
	methyl	propanoate	+	H	6.66E+06	2.54	6756	9.26E+12
	ethyl	propanoate	+	H	2.52E+14	0	7300	6.40E+12
*	ethyl	propanoate	+	H	5.04E+13	0	7300	1.28E+12
	c2h5cooh		+	HO2	4.32E+12	0	14400	3.08E+09
	methyl	propanoate	+	HO2	2.16E+12	0	14400	1.54E+09
	ethyl	propanoate	+	HO2	4.32E+12	0	14400	3.08E+09
CH3CHCH3(CO)OR								
	methyl	isobutanoate	+	OH	2.93E+04	2.53	-1659	2.63E+12
	isobutane		+	OH	2.93E+04	2.53	-1659	2.63E+12
	2-methyl	butane	+	OH	5.73E+10	0.51	63	1.88E+12
	methyl	isobutanoate	+	H	6.02E+05	2.54	2583	6.84E+12
	isobutane		+	H	6.02E+05	2.54	2583	6.84E+12
	2-methyl	butane	+	H	6.02E+05	2.54	2583	6.84E+12
	methyl	isobutanoate	+	HO2	7.22E+03	2.55	10530	1.61E+09
	isobutane		+	HO2	2.80E+12	0	16010	8.87E+08
	2-methyl	butane	+	HO2	2.80E+12	0	16010	8.87E+08

CH₃CHCH₃(CO)OR

methyl	isobutanoate	+	OH	1.06E+10	0.97	1586	3.88E+12
isobutane		+	OH	6.65E+04	2.67	-1689	1.59E+13
2-methyl	butane	+	OH	1.05E+10	0.97	1590	3.85E+12
methyl	isobutanoate	+	H	1.88E+05	2.75	6280	1.42E+12
isobutane		+	H	1.81E+06	2.54	6756	2.52E+12
2-methyl	butane	+	H	1.21E+06	2.54	6756	1.68E+12
methyl	isobutanoate	+	HO₂	4.76E+04	2.55	16490	5.29E+08
isobutane		+	HO ₂	6.12E+01	3.59	17160	6.40E+08
2-methyl	butane	+	HO ₂	1.68E+13	0	20440	5.73E+08

R(CO)OCH₂CH₃

	ethyl	formate	+	OH	1.05E+10	0.97	1586	3.84E+12
	ethyl	acetate	+	OH	1.05E+10	0.97	1586	3.86E+12
	ethyl	propanoate	+	OH	5.28E+09	0.97	1586	1.93E+12
*	ethyl	propanoate	+	OH	1.06E+10	0.97	1586	3.88E+12
	ethyl	formate	+	H	1.88E+05	2.75	6280	1.42E+12
	ethyl	acetate	+	H	6.66E+05	2.54	6756	9.26E+11
	ethyl	propanoate	+	H	6.66E+05	2.54	6756	9.26E+11
*	ethyl	propanoate	+	H	1.88E+05	2.8	6280	2.00E+12
	ethyl	formate	+	HO ₂	1.68E+13	0	20430	5.75E+08
	ethyl	acetate	+	HO ₂	2.38E+04	2.55	16490	2.64E+08
	ethyl	propanoate	+	HO₂	2.38E+04	2.55	16490	2.64E+08

R(CO)OCH₂CH₃

	ethyl	formate	+	OH	1.16E+07	1.61	-35	7.98E+11
	ethyl	acetate	+	OH	2.29E+10	0.51	63	7.52E+11
	ethyl	propanoate	+	OH	1.15E+11	0.51	63	3.78E+12
*	ethyl	propanoate	+	OH	1.16E+07	1.61	-35	7.98E+11
	ethyl	formate	+	H	3.25E+05	2.4	4471	5.43E+11
	ethyl	acetate	+	H	1.20E+05	2.4	2583	5.18E+11
	ethyl	propanoate	+	H	1.20E+06	2.4	2583	5.20E+12
*	ethyl	propanoate	+	H	3.25E+05	2.4	2583	1.40E+12
	ethyl	formate	+	HO ₂	5.60E+12	0	17700	7.58E+08

	ethyl	acetate	+	HO2	7.22E+03	2.55	10530	1.61E+09
	ethyl	propanoate	+	HO2	7.22E+03	2.55	10530	1.61E+09
*	ethyl	propanoate	+	HO2	3.61E+03	2.5	10530	5.70E+08
CH3CH2CH2(CO)OCH3								
	methyl	butanoate	+	OH	1.15E+11	0.51	63	3.78E+12
*	methyl	butanoate	+	H	2.00E+05	2.4	2583	8.64E+11
	methyl	butanoate	+	H	6.00E+05	2.4	2583	2.59E+12
	methyl	butanoate	+	HO2	1.23E+04	2.6	13910	7.07E+08
CH3CH2CH2(CO)OCH3								
	methyl	butanoate		OH	4.68E+07	1.61	-35	3.22E+12
	methyl	butanoate	+	H	1.30E+06	2.4	4471	2.17E+12
	methyl	butanoate	+	HO2	8.19E+03	2.6	13910	4.71E+08
CH3CH2CH2(CO)OCH3								
	methyl	butanoate	+	OH	5.28E+09	0.97	1586	1.93E+12
	methyl	butanoate	+	H	6.66E+05	2.54	6756	9.26E+11
	methyl	butanoate	+	HO2	2.02E+04	2.55	16490	2.24E+08
