

CROSS-PLATFORM MASS SPECTROMETRY ANNOTATION IN BREATHOMICS OF OESOPHAGEAL-GASTRIC CANCER

By

Sung-Tong Chin, Andrea Romano, Sophie LF Doran, George B. Hanna*

Division of Surgery, Department of Surgery and Cancer, Imperial College London, London W2 1NY,
United Kingdom.

Supplementary Information

FIGURE S-1. Representative total ion chromatogram of breath VOC obtained using GC-EI-MS, GC-PCI-MS and mass spectrum of SIFT-MS of breath obtained in H₃O⁺ scan mode.

TABLE S-1. Molecular details of VOC standards identified using GC, EI-MS, PCI-MS and SIFT-MS analysis. Volatile components were loaded onto TD tube using CSLR prior to MS analysis. All analysis was conducted on each different MS platforms in triplicate.

TABLE S-2. Demographic details of OG cancer patients recruited for breath analysis.

TABLE S-3. Database of SIFT-MS kinetic entries comprising number of reagent ions and product ions, and their kinetic coefficients correspondingly.

FIGURE S-1. Representative total ion chromatogram of breath VOC obtained using GC-EI-MS, GC-PCI-MS and mass spectrum of SIFT-MS of breath obtained in H_3O^+ scan mode.

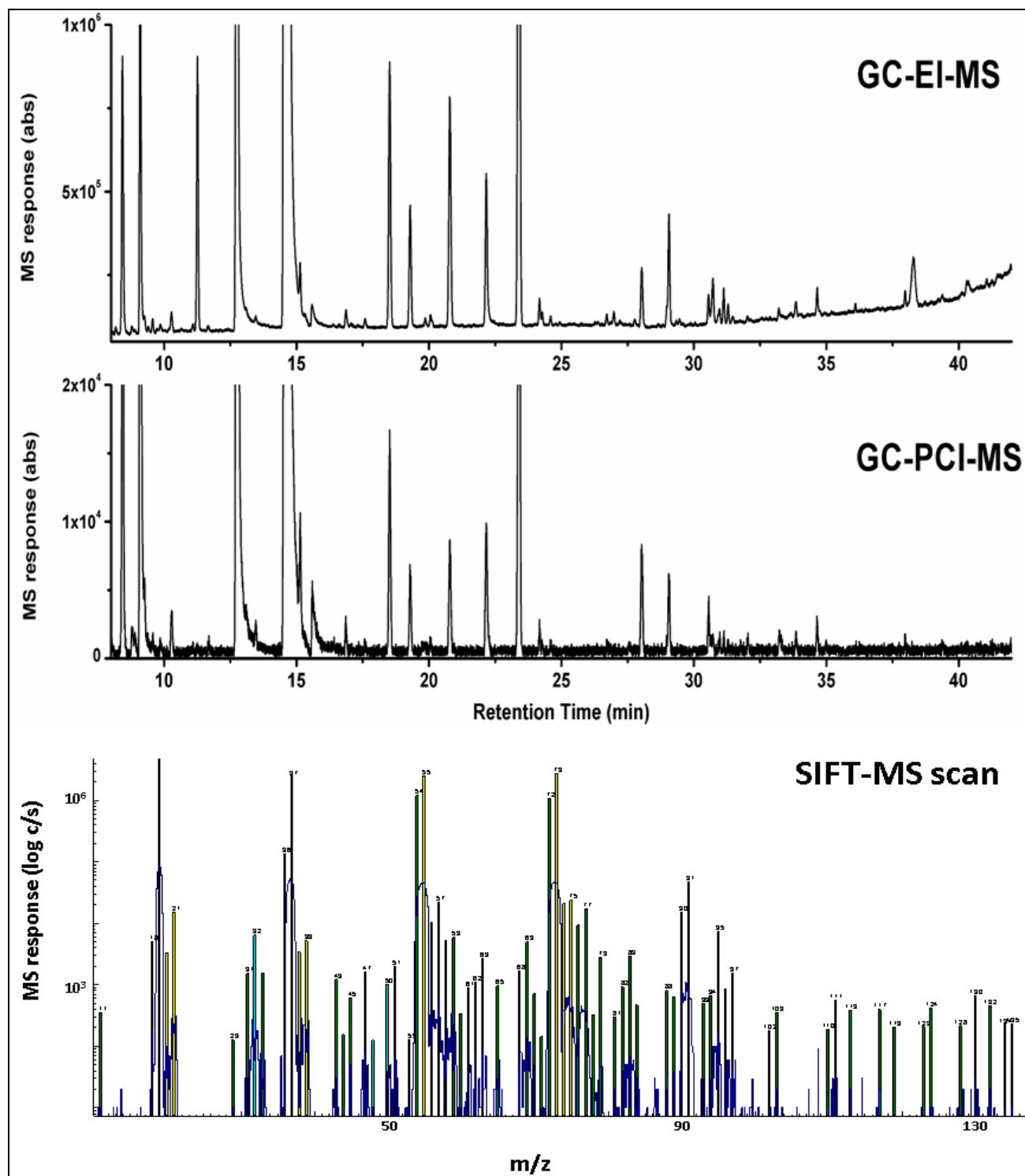


TABLE S-1. Molecular details of VOC standards identified using GC, EI-MS, PCI-MS and SIFT-MS analysis. Volatile components were loaded onto TD tube using CSLR prior to MS analysis. All analysis was conducted on each different MS platforms in triplicate.

Compound	CAS no.	RI ₆₂₄	PCI-MS Mass spectrum	EI-MS Mass spectrum	SIFT-MS [§]	
			m/z (intensity)	m/z (intensity)	Precursors	reactants
<u>Phenols</u>						
phenol	108-95-2	1158	94(999) ^a ,95(809) ^b	94(999) ^a ,66(387),65(266),39(243)	H ₃ O ⁺	95,113
					NO ⁺	94,112
4-methylphenol;	106-44-5;	1241	107(999) ^c ,108(988) ^a ,109(697)	108(999) ^a ,107(953),77(325),90(121)	H ₃ O ⁺	109,127
3-methylphenol	108-39-4		^b			
					NO ⁺	108,126
					O ₂ ⁺	108,126
2-ethylphenol	90-00-6	1286	123(999) ^b ,107(761),122(623) ^a	107(999),122(377) ^a ,77(287),79(158)	H ₃ O ⁺	123,141
					NO ⁺	122,140
					O ₂ ⁺	107,122,125,140
4-ethylphenol;	123-07-9;	1323	123(999) ^b ,107(761),122(623) ^a	107(999),122(377) ^a ,77(287),79(158)	H ₃ O ⁺	123,141
3-ethylphenol	620-17-7				NO ⁺	122,140
					O ₂ ⁺	107,122,125,140

Ketones

acetone	67-64-1	498*	59(999) ^b ,58(363) ^a	43(999),58(487) ^a	H ₃ O ⁺	59,77
					NO ⁺	88
					O ₂ ⁺	43,58
2-butanone	78-93-3	608	73(999) ^b ,57(300)	43(999),72(250) ^a ,57(80)	NO ⁺	102
2-pentanone	107-87-9	716	87(999) ^b ,58(220),71(201)	43(999),86(197) ^a ,58(98),71(97)	NO ⁺	116
2-hexanone	591-78-6	850	101(999) ^b ,58(431),85(97)	43(999),58(664),85(119),71(84),100(180) ^a	NO ⁺	130
2-heptanone	110-43-0	976	115(999) ^b ,58(401)	43(999),58(549),71(133),114(60) ^a	NO ⁺	144
2-octanone	111-13-7	1089	129(999) ^b ,58(391)	43(999),58(859),71(189),128(50) ^a	NO ⁺	158
2-nonanone	821-55-6	1190	143(999) ^b ,58(403)	43(999),58(911),71(223),142(70) ^a	nd	nd
2-decanone	693-54-9	1281	157(999) ^b ,58(409)	58(999),43(845),71(377),156(40) ^a	H ₃ O ⁺	157,175

Unsaturated Aldehydes

2-propenal	4170-30-3	479*	57(999) ^b ,55(400),56(314)	56(999) ^a ,27(954), 55(718)	H ₃ O ⁺	57,55,75,73
					NO ⁺	86,112
					O ₂ ⁺	28,55,56
2-butenal	123-73-9	683	71(999) ^b ,69(394),70(261)	41(999),39(899),70(736) ^a ,69(401)	H ₃ O ⁺	71,89
					NO ⁺	69
2-pentenal	1576-87-0	818	85(999) ^b ,84(366),55(172)	55(999),84(874) ^a ,41(508)	H ₃ O ⁺	85,103

					NO ⁺	83,114
2-hexenal	6728-26-3	947	99(999) ^b ,57(572),69(235), 83(326)	41(999),55(586),69(500),83(389), 98(160) ^a	H ₃ O ⁺	99,117
					NO ⁺	97,128
2-heptenal	18829-55-5	1068	113(999) ^b ,95(507),83(541), 57(593),68(158)	41(999),55(427),70(260),83(400)	H ₃ O ⁺	113,131
					NO ⁺	111,142
2-octenal	2548-87-0	1173	127(999) ^b ,109(811),57(579), 70(394),83(381)	41(999), 55(845),70(706),83(617)	H ₃ O ⁺	127,145
					NO ⁺	125,156
2-nonenal	18829-56-6	1268	141(999) ^b ,123(740),81(491), 57(477)	41(999),55(756),70(718),83(476), 96(220),122(120),140(40) ^a	H ₃ O ⁺	141,159
					NO ⁺	139,170
2,4-nonadienal	5910-87-2	1327	81(999) ^d ,139(950) ^b ,121(126)	81(999),41(201),67(164),138(77) ^a	nd	nd
2,4-decadienal	25152-84-5	1406	153(999) ^b ,81(908),135(151)	81(999),41(508),55(161),67(171), 152(60) ^a	H ₃ O ⁺	153,171
					NO ⁺	151

Alcohols

1-propanol	71-23-8	576	59(999) ^c ,61(193) ^b	31(999),42(135),59(109) ^c	H ₃ O ⁺	43,61,79,97
					NO ⁺	59,77,95,113
2-propanol	67-63-0	506	59(999) ^c ,61(818) ^b	45(999),59(40) ^c	nd	nd
1-butanol	71-36-3	698	57(999) ^d ,56(454),73(85) ^c	56(999),31(981),41(876)	H ₃ O ⁺	57,75,93

2-methyl-1-propanol	78-83-1	654	57(999) ^d ,73(123) ^c	43(999),31(376),74(141) ^a	nd	nd
1-pentanol	71-41-0	829	71(999) ^d ,55(230),87(66) ^c	55(999),42(949),70(489),31(369)	H ₃ O ⁺	71,89,107,125
2-methyl-1-butanol	137-32-6	792	71(999) ^d ,57(306),56(272)	57(999),41(877),70(423),31(369)	nd	nd

Saturated Aldehydes

propanal	123-38-6	489*	59(999) ^b ,58(512),57(315)	58(999) ^a ,29(880)	NO ⁺	55,57
butanal	123-72-8	596	73(999) ^b ,55(637),72(352)	44(999),43(786),72(734) ^a ,57(258)	NO ⁺	71
pentanal	110-62-3	724	69(999) ^d ,87(603) ^b ,58(318)	44(999),58(485),86(60) ^a	NO ⁺	85
hexanal	66-25-1	859	83(999) ^d ,56(360),101(196) ^b	44(999),56(819),43(550), 72(160),82(120)	NO ⁺	99
heptanal	111-71-7	986	97(999) ^d ,70(384),55(234), 115(135) ^b	70(999),44(883),43(836), 55(779),81(320), 96(180)	NO ⁺	113
benzaldehyde	100-52-7	1087	107(999) ^b ,105(494),106(480)	106(999) ^a ,105(950),77(889),51(495)	nd	nd
octanal	124-13-0	1099	111(999) ^d ,69(963),84(517), 129(239) ^b	43(999),44(808),56(657),84(550)	NO ⁺	127
nonanal	124-19-6	1200	69(999),57(588),83(576),98(339), 125(248) ^d ,143(208) ^b	57(999),41(893),43(879),44(715), 70(421), 98(406), 82(300)	NO ⁺	141
decanal	112-31-2	1291	83(999),57(554),97(461),69(363), 112(193),157(185) ^b	43(999),41(801),57(621),44(539), 70(471), 82(360), 112(200)	NO ⁺	155
undecanal	112-44-7	1375	61(999),97(941),83(766),71(597),	41(999),43(902),57(699),82(461),	nd	nd

111(320),171(209)^b 44(406),67(346), 126(100)

Acids

acetic acid	64-19-7	674	61(999) ^b ,60(210)	43(999),45(903),60(747) ^a	H ₃ O ⁺	61,79,97
					NO ⁺	90
propanoic acid	79-09-4	790	75(999) ^b ,74(459),57(259)	74(999) ^a ,45(900),57(466)	H ₃ O ⁺	73,75,93,111
					NO ⁺	104,122,57,55
butanoic acid	107-92-6	900	89(999) ^b ,60(480),71(239),73(145)	60(999),73(324),41(162)	H ₃ O ⁺	89,107,125
					NO ⁺	118,136,71
pentanoic acid	109-52-4	1012	103(999) ^b ,60(423),85(253),73(194)	60(999),73(356),41(178)	H ₃ O ⁺	103,121,139
hexanoic acid	142-62-1	1112	117(999) ^b ,60(322),99(266),73(187)	60(999),73(445),87(134),41(196)	H ₃ O ⁺	117,135,153

RI₆₂₄ indicates retention index on ZB-624 column; ^a indicates M⁺; ^b indicates [M+H]⁺; ^c indicates [M-H]⁺; ^d indicates [M-17]⁺;

[§]Information for rate constant and coefficient of each precursor and reactant was listed in supplementary information;

nd indicates not detected; * denotes estimated retention index from extrapolation.

TABLE S-2. Demographic details of OG cancer patients recruited for breath analysis.

	Patient ID																				
Factor	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Age	56	71	61	78	74	44	79	43	77	61	67	61	60	66	63	56	52	65	52	48	69
Gender	M	M	M	M	M	M	M	M	F	M	F	M	M	M	M	M	M	M	M	M	M
Race	C	C	C	C	C	AR	C	C	C	C	C	C	AS	C	AS	C	AR	C	C	C	C
Smoking history (pack year)	10	10	0	30	0	20	75	0	30	20	0	20	0	10	10	15	10	5	10	10	5
Alcohol history (unit week)	10	12	30	2	8	0	5	0	5	1	0	1	3	4	0	5	0	5	16	5	10
ASA grade	3	2	2	2	3	1	3	2	2	2	2	2	1	2	2	2	1	2	1	1	2
Diabetes	N	N	N	N	Y	N	N	N	N	Y	Y	Y	N	N	N	N	N	N	N	N	N
Pulmonary impairment	N	N	N	N	N	N	Y	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Ischaemic heart disease	N	N	N	N	Y	N	Y	N	N	N	N	N	N	N	N	N	N	N	N	N	Y
Hypertension	Y	Y	Y	N	Y	N	N	N	N	Y	N	Y	Y	N	N	N	N	N	Y	Y	N
Asthma	Y	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	Y	N	N

M: Male, F: Female, C: Caucasian, AR: Arabian, AS: Asian.

TABLE S-3. Database of SIFT-MS kinetic entries comprising number of reagent ions and product ions, and their kinetic coefficients correspondingly.

2,4-decadienal(H₃O⁺)

4 precursors /rate constant: 19 /4.9e-9 1.0, 37 /3.0e-9 1.0, 55 /2.7e-9 1.0, 73 /2.6e-9 1.0

2 products /rate constant: 153 /1, 171 /1,

2,4-decadienal(NO⁺)

3 precursors /rate constant: 30 /4.2e-9 1.0, 48 /1e-9 1.0, 66 /1e-9 1.0

1 product /rate constant: 151 /1.2

butanal(NO⁺)

3 precursors /rate constant: 30 /3.3e-9 1.0, 48 /1e-9 1.0, 66 /1e-9 1.0

1 products /rate constant: 71 /1

pentanal(NO⁺)

3 precursors/rate constant: 30 /3.0e-9 1.0, 48 /1e-9 1.0, 66 /1e-9 1.0

1 product /rate constant: 85 /1.2

hexanal(NO⁺)

3 precursors /rate constant: 30 /3.0e-9 1.0, 48 /1e-9 1.0, 66 /1e-9 1.0

1 product /rate constant: 99 /1

heptanal(NO⁺)

3 precursors/rate constant: 30 /3.3e-9 1.0, 48 /1e-9 1.0, 66 /1e-9 1.0

1 product /rate constant: 113 /1

octanal(NO⁺)

3 precursors /rate constant: 30 /3.0e-9 1.0, 48 /1e-9 1.0, 66 /1e-9 1.0

1 product /rate constant: 127 /1

nonanal(NO⁺)

3 precursors /rate constant: 30 /3.3e-9 1.0, 48 /1e-9 1.0, 66 /1e-9 1.0

1 product /rate constant: 141 /1

decanal(NO⁺)

3 precursors /rate constant: 30 /3.3e-9 1.0, 48 /1e-9 1.0, 66 /1e-9 1.0

1 product /rate constant: 155 /1

acrolein(H3O+)

4 precursors /rate constant: 19 /4.2e-9 1.0, 37 /3.3e-9 1.0, 55 /3.0e-9 1.0, 73 2.8e-9 1.0

1 product /rate constant: 39 /1

acrolein(H3O+)

4 precursors /rate constant: 19 /4.2e-9 1.0, 37 /3.3e-9 1.0, 55 /3.0e-9 1.0, 73 /2.8e-9 1.0

4 products /rate constant: 57 /1, 55 /-0.006, 75 /1, 73 /-0.008

acrolein(NO+)

3 precursors /rate constant: 30 /2.1e-9 1.0, 48 /1.6e-9 1.0, 66 /1.5e-9 1.0

2 products /rate constant: 86 /1, 112 /1

acrolein(O2+)

1 precursors /rate constant: 32 /4.9e-9 1.0

3 products /rate constant: 28 /1, 55 /1, 56 /1

acetaldehyde(H3O+)

4 precursors /rate constant: 19 /3.7e-9 1.0, 37 /3.0e-9 1.0, 55 /2.7e-9 1.0, 73 /2.6e-9 1.0

4 products /rate constant: 45 /1.0, 63 /1.0, 81 /1.0, 99 1.0

acetaldehyde(NO+)

1 precursor /rate constant: 30 /0.6e-9 1.0

1 product /rate constant: 43 /1.0

acetone(H3O+)

4 precursors /rate constant: 19 /3.9e-9 1.0, 37 /3.3e-9 1.0, 55 /2.5e-9 1.0, 73 /2.4e-9 1.0

2 products /rate constant: 59 /1.0, 77 /1.0

acetone(NO+)

1 precursor /rate constant: 30 /2.2e-9 1.0

1 product /rate constant: 88 /1.0

acetone(O2+)

1 precursor /rate constant: 32 /3.1e-9 1.0

2 products /rate constant: 43 /1.0, 58 /1.0

ethanol(H3O+)

4 precursors /rate constant: 19 /2.7e-9 1.0, 37 /2.3e-9 1.0, 55 /2.1e-9 1.0, 73 /1e-11 1.0

3 products /rate constant: 47 /1.0, 65 /1.0, 83 /1.0

methanol(H3O+)

4 precursors /rate constant: 19 /2.4e-9 1.0, 37 /1.9e-9 1.0, 55 /1.9e-9 1.0, 73 /1e-11 1.0

3 products /rate constant: 33 /1.0, 51 /1.0, 69 /1.0

propanol(H3O+)

4 precursors /rate constant: 19 /2.7e-9 1.0, 37 /2.3e-9 -0.1, 55 /2.2e-9 -0.1, 73 /2.1e-9 -0.1

1 product /rate constant: 43 /1.0, 61 /1.0, 79 /1.0, 97 /1.0

propanol(NO+)

3 precursors /rate constant: 30 /2.4e-9 1.0, 48 /2.0e-9 1.0, 66 /1.9e-9 1.0,

4 products /rate constant: 59 /1.0, 77 /1.0, 95 /1.0, 113 /1.0

butanol(H3O+)

4 precursors /rate constant: 19 /2.8e-9 1.0, 37 /2.2e-9 1.0, 55 /1.9e-9 1.0, 73 /1.8e-9 1.0

5 products /rate constant: 57 /1.0, 55 /-0.006, 75 /1.0, 73 /-0.008, 93 /1.0

pentanol(H3O+)

4 precursors /rate constant: 19 /2.8e-9 1.0, 37 /2.2e-9 1.0, 55 /1.9e-9 1.0, 73 /1.8e-9 1.0

4 products /rate constant: 71 /1.0, 89 /1.0, 107 /1.0, 125 /1.0

phenol(H3O+)

4 precursors /rate constant: 19 /2.4e-9 1.0, 37 /1.9e-9 1.0, 55 /1.9e-9 1.0, 73 /5e-10 1.0

2 products /rate constant: 95 /1.0, 113 /1.0

phenol(NO+)

3 precursors /rate constant: 30 /2.2e-9 1.0, 48 /1.6e-9 1.0, 66 /1.3e-9 1.0

2 products /rate constant: 94 /1.0, 112 /1.0

methyl_phenol(H3O+)

4 precursors /rate constant: 19 /2.8e-9 1.0, 37 /1.7e-9 1.0, 55 /1.2e-9 1.0, 73 /5e-10 1.0

2 products /rate constant: 109 /1.0, 127 /1.0

methyl_phenol(NO+)

3 precursors /rate constant: 30 /2.2e-9 1.0, 48 /1.6e-9 1.0, 66 /1.3e-9 1.0

2 products /rate constant: 108 /1.0, 126 /1.0,

methyl_phenol(O2+)

1 precursor /rate constant: 32 /2.2e-9 1.0

2 products /rate constant: 108 /1.0, 126 /1.0

ethyl_phenol(H3O+)

4 precursors /rate constant: 19 /2.8e-9 1.0, 37 /1.7e-9 1.0, 55 /1.2e-9 1.0, 73 /5e-10 1.0

2 products /rate constant: 123 /1.0, 141 /1.0

ethyl_phenol(NO+)

3 precursors /rate constant: 30 /2.3e-9 1.0, 48 /1.6e-9 1.0, 66 /1.3e-9 1.0

2 products /rate constant: 122 /1.0, 140 /1.0

ethyl_phenol(O2+)

1 precursor /rate constant: 32 /2.2e-9 1.0

4 products /rate constant: 107 /1.0, 122 /1.0, 125 /1.0, 140 /1.0

acetic_acid(H3O+)

4 precursors /rate constant: 19 /2.6e-9 1.0, 37 /1.9e-9 1.0, 55 /1.9e-9 1.0, 73 /1.8e-9 1.0

3 products /rate constant: 61 /1.0, 79 /1.0, 97 /1.0

acetic_acid(NO+)

3 precursors /rate constant: 30 /1.5e-9 1.0, 48 /5e-10 1.0, 66 /5e-10 1.0

1 product /rate constant: 90 /1.0

propanoic_acid(H3O+)

4 precursors /rate constant: 19 /2.7e-9 1.0, 37 /1.9e-9 1.0, 55 /1.9e-9 1.0, 73 /1.9e-9 1.0

4 products /rate constant: 73 /-0.008, 75 /1.0, 93 /1.0, 111 /1.0

butyric_acid(H3O+)

4 precursors /rate constant: 19 /2.9e-9 1.0, 37 /1.9e-9 1.0, 55 /1.9e-9 1.0, 73 /1.9e-9 1.0

3 products /rate constant: 89 /1.0, 107 /1.0, 125 /1.0

pentanoic_acid(H3O+)

4 precursors /rate constant: 19 /2.4e-9 1.0, 37 /1.9e-9 1.0, 55 /1.9e-9 1.0, 73 /1.7e-9 1.0

3 products /rate constant: 103 /1.0, 121 /1.0, 139 /1.0

hexanoic_acid(H3O+)

4 precursors /rate constant: 19 /2.4e-9 1.0, 37 /1.9e-9 1.0, 55 /1.9e-9 1.0, 73 /1.7e-9 1.0

3 products /rate constant: 117 /1.0, 135 /1.0, 153 /1.0

propionic_acid(NO+)

3 precursors /rate constant: 30 /1.5e-9 1.0, 48 /5e-10 1.0, 66 /5e-10 1.0

4 products /rate constant: 104 /1.0, 122 /1.0, 57 /1.0, 55 /-0.006

butyric_acid(NO+)

3 precursors /rate constant: 30 /1.9e-9 1.0, 48 /7e-10 1.0, 66 /7e-10 1.0

3 products /rate constant: 118 /1.0, 136 /1.0, 71 /1.0

formaldehyde

1 precursor /rate constant: 19 /2.7e-9 1.0

1 product /rate constant: 31 /1.0

noise(H3O+)

1 precursor /rate constant: 19 /3.1e-9 1.0

3 products /rate constant: 10 /1.0, 24 /1.0, 150 /1.0

butanone(NO+)

1 precursors /rate constant: 30 /2.5e-9 1.0

1 product /rate constant: 102 /1.0

pentanone(NO+)

1 precursors /rate constant: 30 /2.5e-9 1.0,

1 product /rate constant: 116 /1.0

hexanone(NO+)

1 precursors /rate constant: 30 /2.5e-9 1.0

1 product /rate constant: 130 /1.0

heptanone(NO+)

1 precursors /rate constant: 30 /2.5e-9 1.0

1 product /rate constant: 144 /1.0

octanone(NO+)

1 precursors /rate constant: 30 /2.5e-9 1.0

1 product /rate constant: 158 /1.0