Supporting Information to

Comprehensive Quantum Chemical Analysis of the McLafferty Rearrangement of Methyl Valerate

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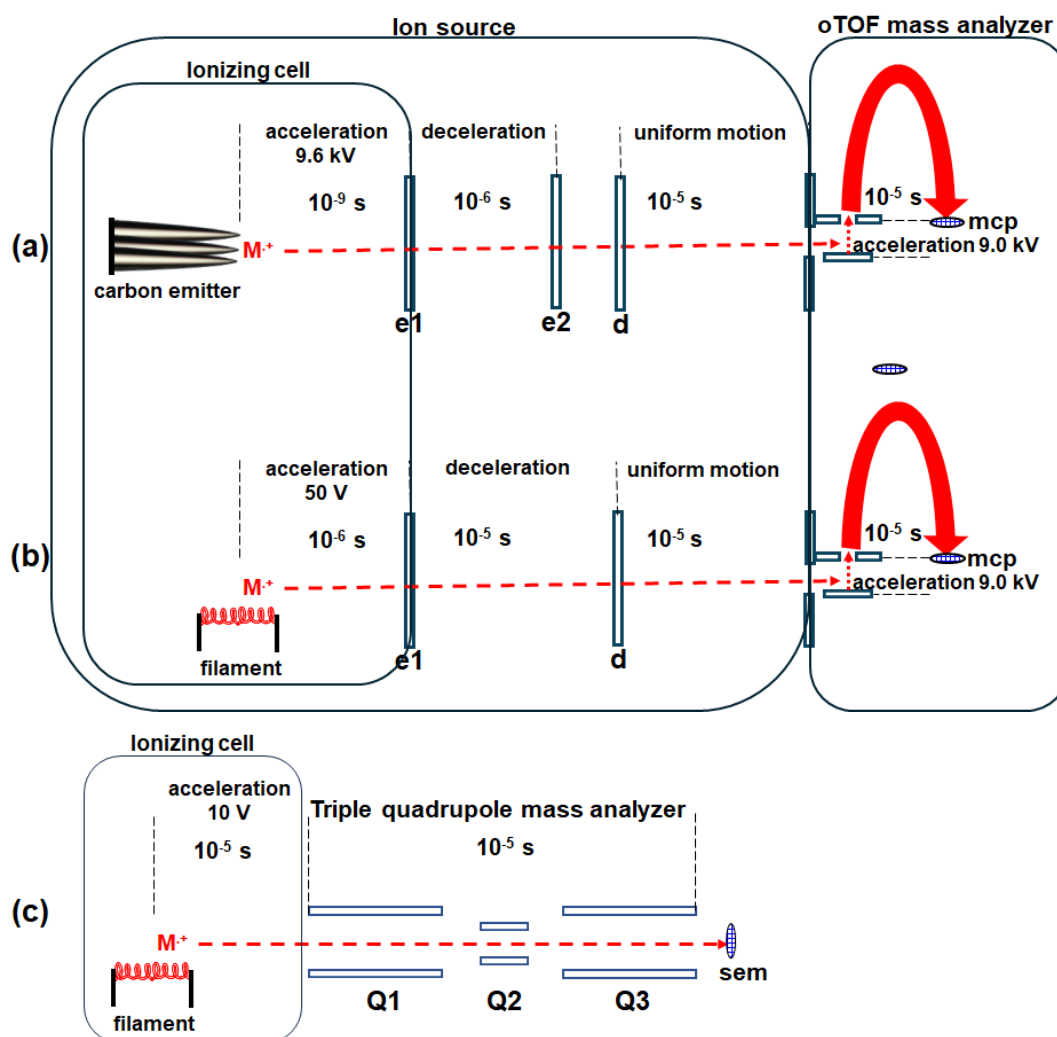
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Fig. S1 The residence times (sec) for the ions in the ion source of (a) strong field tunnel ionization (SFTI) and (b) electron ionization (EI), orthogonal time-of-flight (oTOF) and (c) triple quadrupole mass analyzer equipped with EI. e1 and e2 are retarding electrode, d is deflector electrode, and the mcp represents microchannel plate ion detector. Q1 and Q2 are quadrupole mass analyzer and Q2 is a quadrupole collision cell, and the abbreviation "sem" represents a secondary electron multiplier detector.

In the SFTI source in Fig. S1(a), analyte molecules are ionized by an electron transfer at the time scale of 10^{-16} s *via* a tunneling effect in the vicinity of the tip of the needle of the carbon emitter. The resulting molecular ions ($M^{+.}$) and fragment ions ($m^{+.}$) are accelerated by the potential at 9.6 kV

in the 2 mm distance from the tip of the emitter to electrode e1 (acceleration region). In this instrument, the fragment ions produced by the field dissociation within 10^{-14} to 10^{-12} s to complete a couple of vibrations on the tip of the emitter could potentially be reachable to the entrance of the oTOF. It should be noted that the fragment ions produced along the way in the acceleration region may potentially be deflected by the deflector electrode d, due to the reduction in kinetic energy from $Mv^2/2$ to $(m/M)v^2/2$. This could result in such ions becoming unreachable to the entrance of oTOF. It would appear that the residence time of the ions accelerated by a potential of 9.6 kV in the acceleration region is approximately 10^{-9} s. The ions which pass through this region are decelerated to a kinetic energy of 10 or 20 eV and then transverse into the entrance at a constant kinetic energy. It is estimated that the residence time of the ions in the transverse region at the uniform motion is around 10^{-5} s. It is possible that a part of the molecular and fragment ions reached in the transverse region may degrade due to its excess internal energy within the metastable time scales of 10^{-6} to 10^{-5} s. It may be the case that the degraded fragment ions can be detected by the detector mcp of the oTOF mass analyzer. It may therefore be concluded that the oTOF instrument, equipped with the SFTI source, is capable of detecting stable ions produced within a timescale of 10^{-14} to 10^{-12} s in the vicinity of the carbon emitter tip, as well as fragment ions produced by metastable decay of molecular ions with a lifetime of 10^{-6} to 10^{-5} s in the transverse region.

In the EI source in Fig. S1(b), the molecular ions may be formed by electron impact at a time scale of 10^{-16} s in the ionizing cell. It seems that fragment ions may have been accumulated over a range of time scales, from 10^{-14} to 10^{-5} s, in the accelerating, decelerating, and transverse regions. As a result, it would appear that the instrument used in the EI source does not provide much information about the timeframe of the fragmentation.

In the triple quadrupole mass analyzer, it seems that the molecular ion of MetVal is selected by Q1, the fragment ions are produced from the molecular ion by colliding with nitrogen gas in Q2, and the fragment ions can
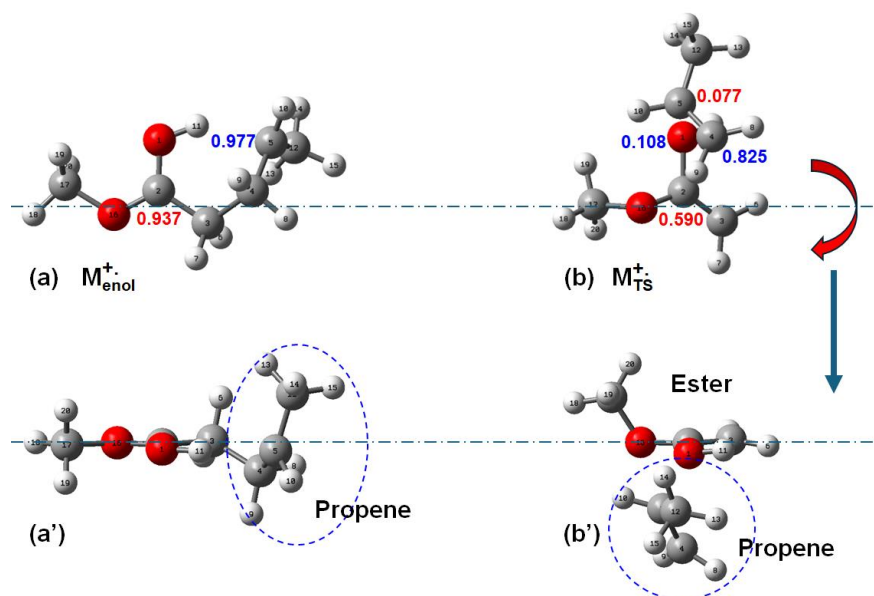
be analyzed by Q3, with a time scale of 10^{-5} s through both the ionizing cell and the mass analyzer.
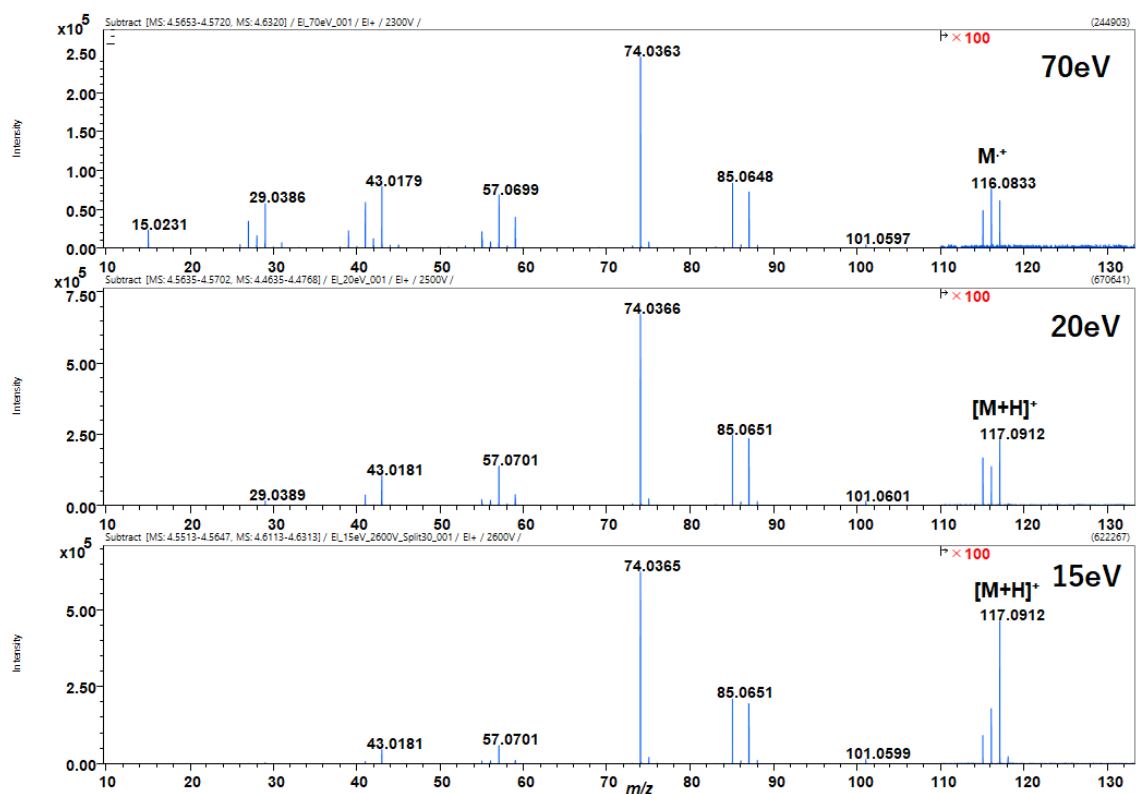

Fig. S2 The EI mass spectra of methyl valerate obtained with (a) 70 eV, (b) 20 eV, and (c) 15 eV electron energy.
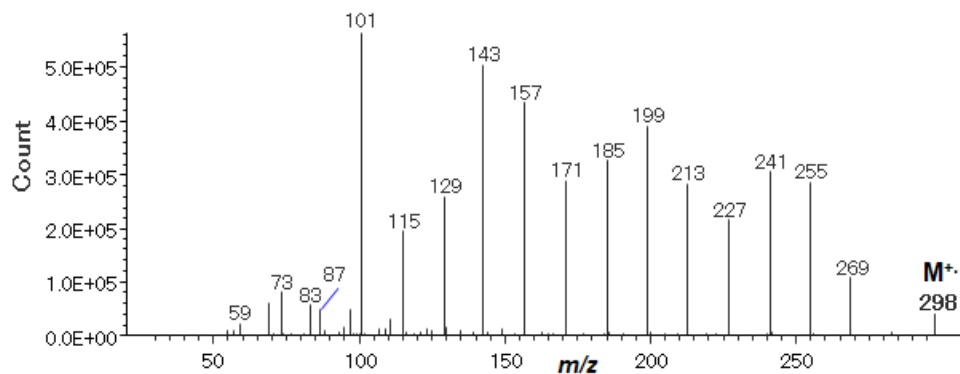
Fig. S3 The CID spectrum of molecular ion at m/z 298 of methyl stearate.

Fig. S4 The structures of the enol-form molecular ion $[M_{enol}]^{+\cdot}$ (a, a') and the transition state $[M_{TS}]^{+\cdot}$ (b, b') of methyl valerate optimized at the M06-2X/6-31+G(d) level of theory. The numerical values in red and blue represent the charge and spin sites, respectively. The structures (a') and (b') correspond to those obtained with the 90-degree rotation around (a) and (b) the axis. The dotted circle represents the propene moiety of the methyl valerate ion.
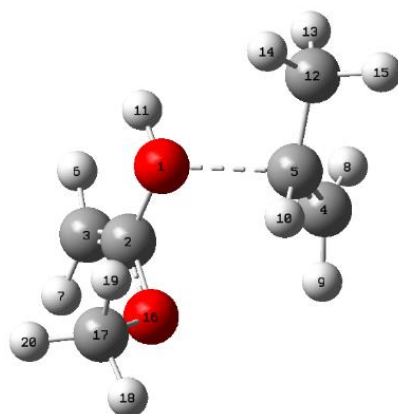
Fig. S5 The transition state (TS) structure of methyl valerate, which was not initially anticipated, was obtained with the GRRM program and then reoptimized at the M06-2X/6-31+G(d) level of theory. It would appear that there is an imaginary frequency associated with the bond between the enol oxygen (O1) and the propene carbon (C5), which is negative in sign.

Table S1. The data of bond frequency and infrared intensity for partial modes of the transition state (TS) of methyl valerate molecular ion. The mode 1 involves imaginary frequency having negative sign of -117.1946 and IR intensity of 81.4395.

	Mode #	Frequency	Infrared
1	1	-117.19	81.4395
2	2	44.11	0.7694
3	3	70.81	3.7064
4	4	81.36	8.1590
5	5	119.07	3.2343
6	6	158.55	4.3368
7	7	222.66	4.2063
8	8	252.25	11.7043
9	9	258.31	7.5285
10	10	296.11	2.6886
11	11	347.15	0.4339
12	12	424.64	1.0244
13	13	450.43	4.6970
14	14	534.35	53.2484
15	15	606.86	25.1526
16	16	711.31	1.0369
17	17	734.75	12.7816
18	18	857.10	45.1604
19	19	890.02	12.2173
20	20	908.73	89.5132
21	21	913.11	33.3765
22	22	931.37	14.6075

Table S2. The atomic coordinates in the transition state (TS) involving one imaginary frequency of methyl valerate molecular ion.

Atom	X	Y	Z
1 O	-0.124573	0.159332	-0.888508
2 C	1.018990	0.570761	-0.175753
3 C	1.507365	1.802456	-0.234820
4 C	-1.479192	0.472741	1.395569
5 C	-1.595301	-0.441996	0.313066
6 H	1.043163	2.582572	-0.827505
7 H	2.411498	2.032171	0.314848
8 H	-2.101201	1.361517	1.436304
9 H	-0.751023	0.305251	2.181396
10 H	-1.086855	-1.396262	0.427898
11 H	-0.414514	0.850514	-1.513892
12 C	-2.736736	-0.389315	-0.635998
13 H	-3.078109	0.631545	-0.826668
14 H	-2.506813	-0.904509	-1.571501
15 H	-3.570001	-0.935844	-0.170179
16 O	1.438229	-0.424799	0.605868
17 C	2.085702	-1.520831	-0.079207
18 H	2.357520	-2.233550	0.696516
19 H	1.401682	-1.980959	-0.797424
20 H	2.980433	-1.151615	-0.585809