

Supporting Information

Oxidation of Isoprene by Titanium Oxide Cluster Cations in the Gas Phase

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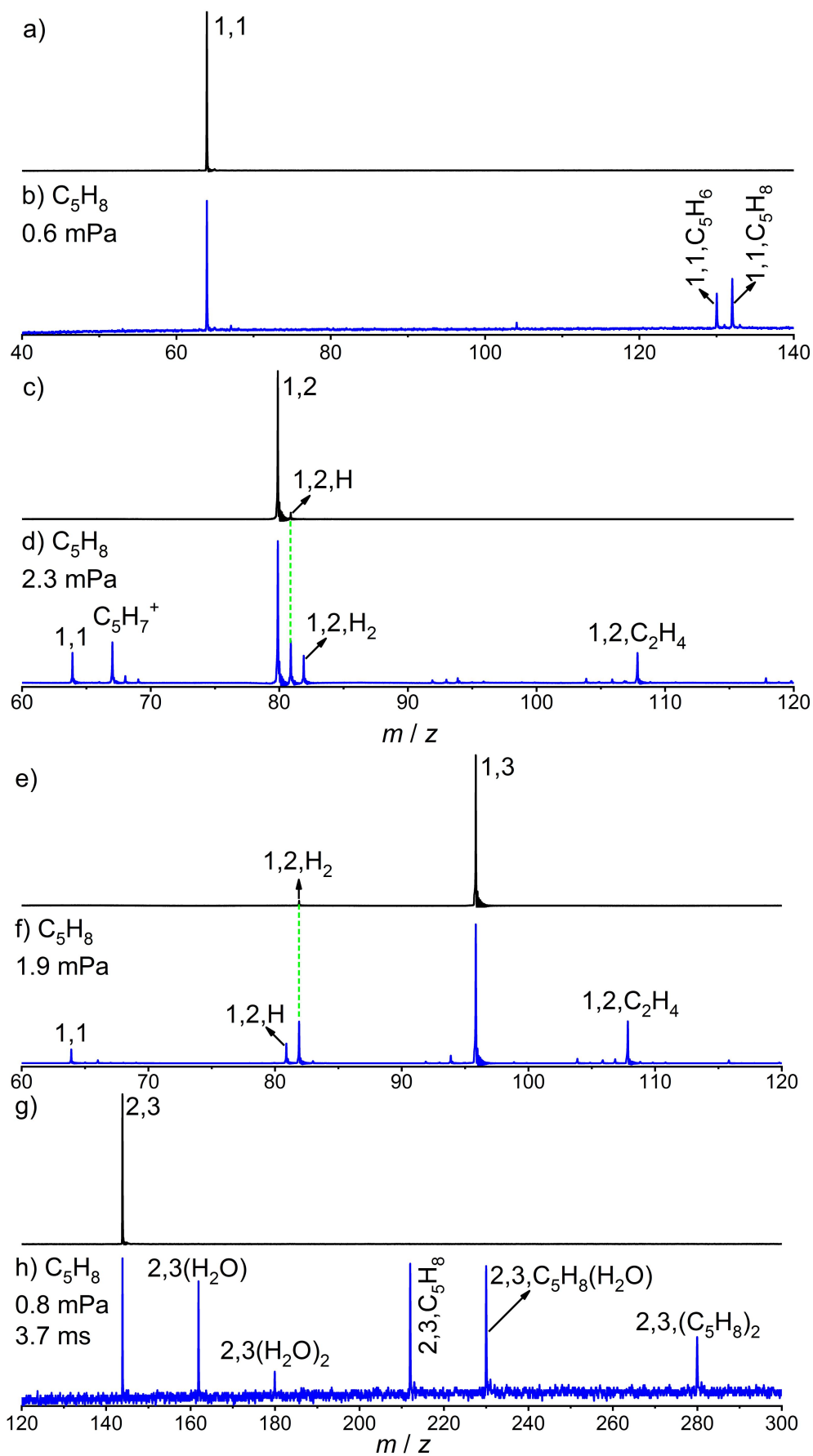
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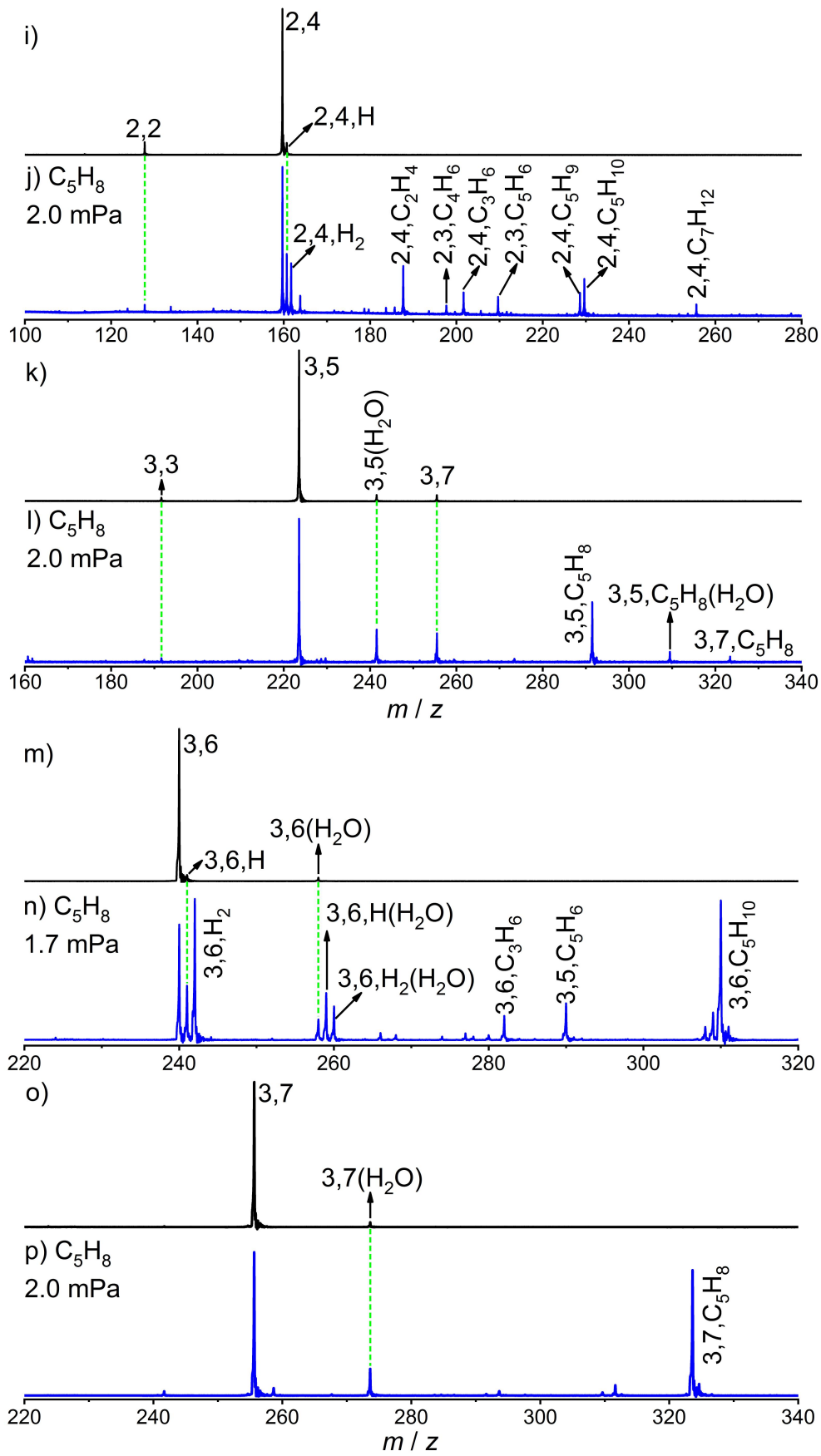
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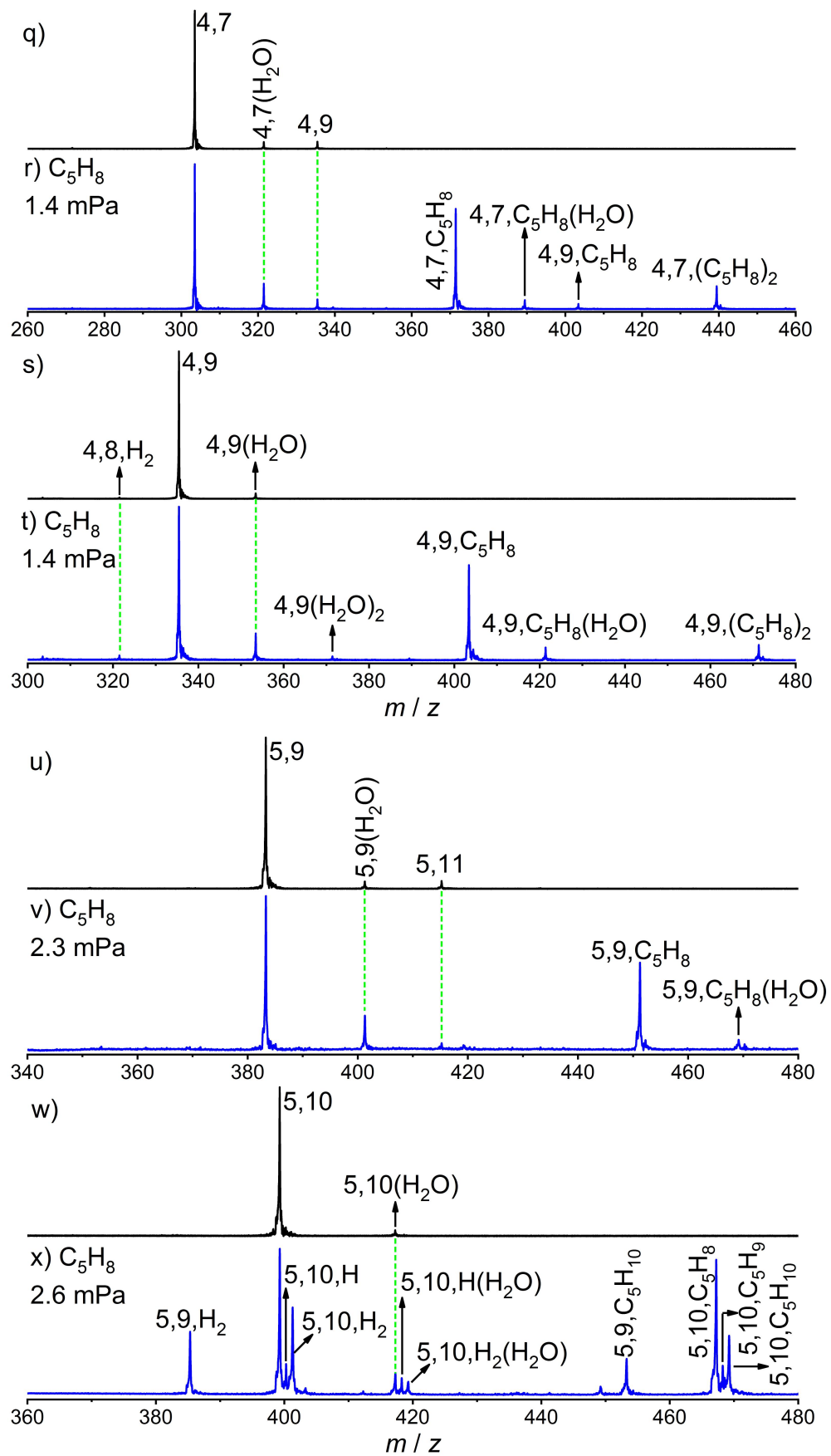
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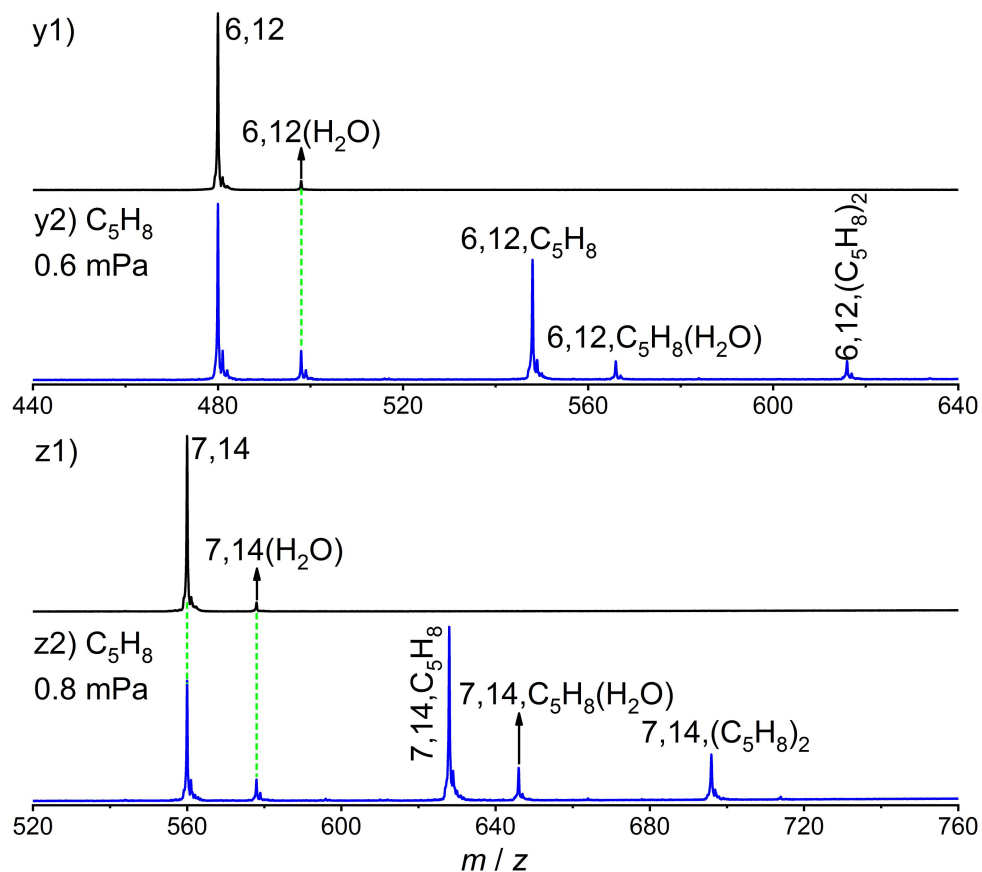


Fig. S1 TOF mass spectra for the reactions of mass-selected Ti_xO_y^+ cations (panels a, c, e, g, i, k, m, o, q, s, u, w, y1, and z1) with C_5H_8 (panels b, d, f, h, g, l, n, p, r, t, v, x, y2, and z2). The time periods for the reactions are 3.7 ms in h) and 1.7 ms in the other panels. The C_5H_8 pressures are given. The $\text{Ti}_x\text{O}_y\text{Z}^+$ ($Z = \text{C}_2\text{H}_4, \text{C}_4\text{H}_6,$ or other C_mH_n) species are labeled as “x,y,Z”.

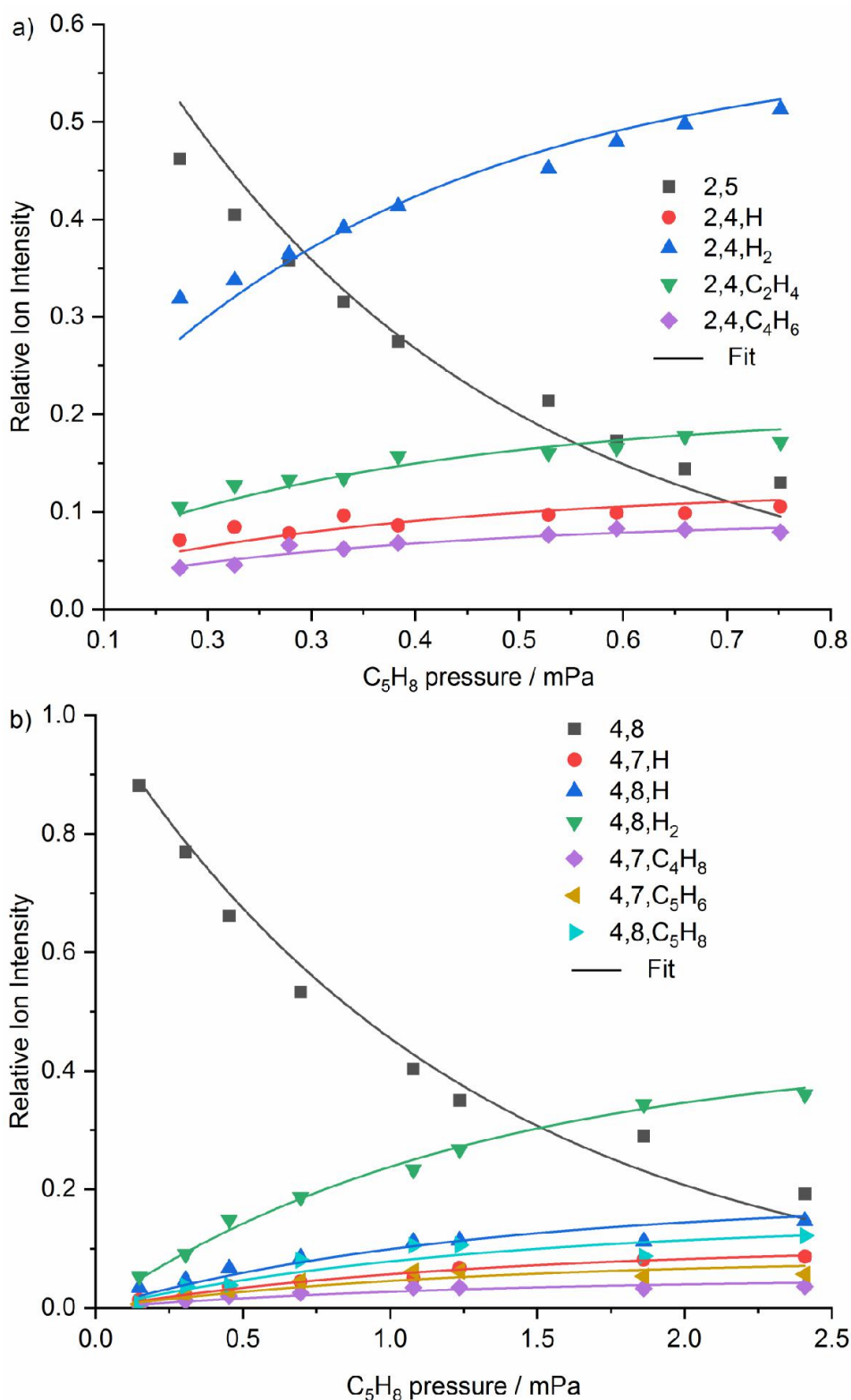


Fig. S2 Variations of the relative ion intensities with respect to the C_5H_8 pressures in the reactions of (a) $Ti_2O_5^+$ and C_5H_8 for 3.7 ms, (b) $Ti_4O_8^+$ and C_3H_6 for 1.7 ms, respectively. The $Ti_xO_yZ^+$ ($Z = C_2H_4, C_4H_6, C_4H_8, C_5H_6, \text{ or } C_5H_8$) species are labeled as “ x,y,Z ”.

Table S1. The reaction channels of Ti_xO_y^+ clusters with isoprene and the pseudo first-order rate constants (k_1) (in $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

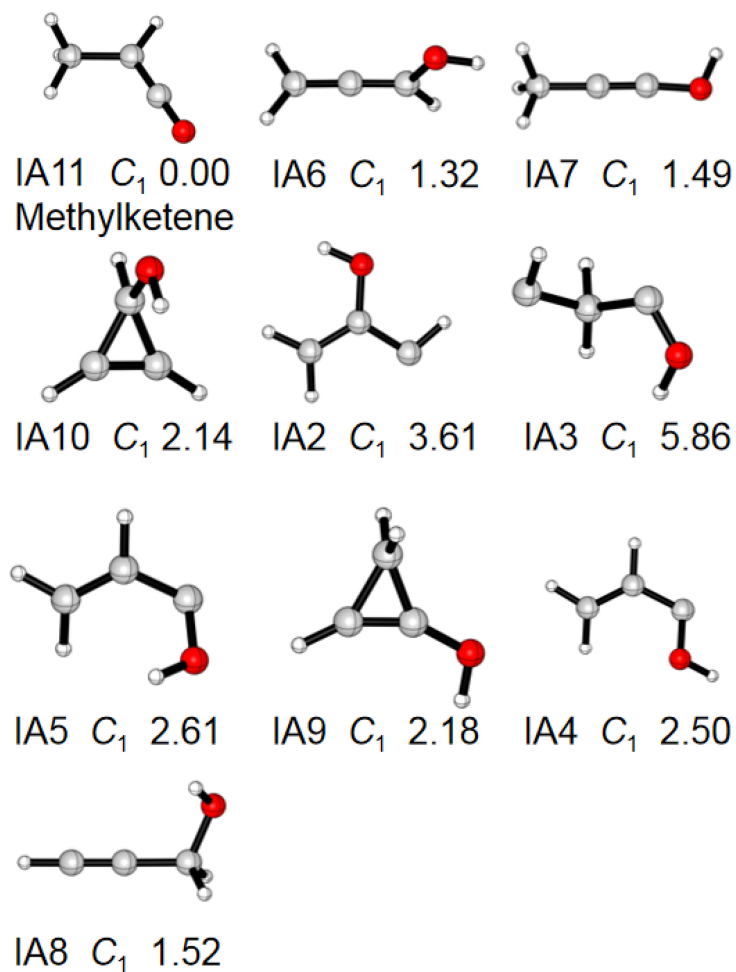
x	y	$\Delta^{[a]}$	Reaction Channel Types					k_1	$\vartheta^{[b]}$
			1	2	3	4	5		
1	1	-1	√	√	×	×	×	3.0	220%
1	2	1	×	√	√	×	×	1.8	139%
1	3	3	×	×	×	√	√	2.7	218%
2	3	-1	√	×	×	×	×		
2	4	1	×	√	√	√	√	2.8	247%
2	5	3	×	×	×	√	√	2.6	238%
3	5	-1	√	×	×	×	×		
3	6	1	×	√	√	√	×	2.6	242%
3	7	3	√	×	×	×	×		
4	7	-1	√	×	×	×	×		
4	8	1	√	√	×	√	√	2.0	196%
4	9	3	√	×	×	×	×		
5	9	-1	√	×	×	×	×		
5	10	1	√	√	×	√	×	2.7	263%
6	12	1	√	×	×	×	×		
7	14	1	√	×	×	×	×		

^[a] $\Delta=2y-nx+q$, q : the charge number, n : the highest oxidation state of element Ti.

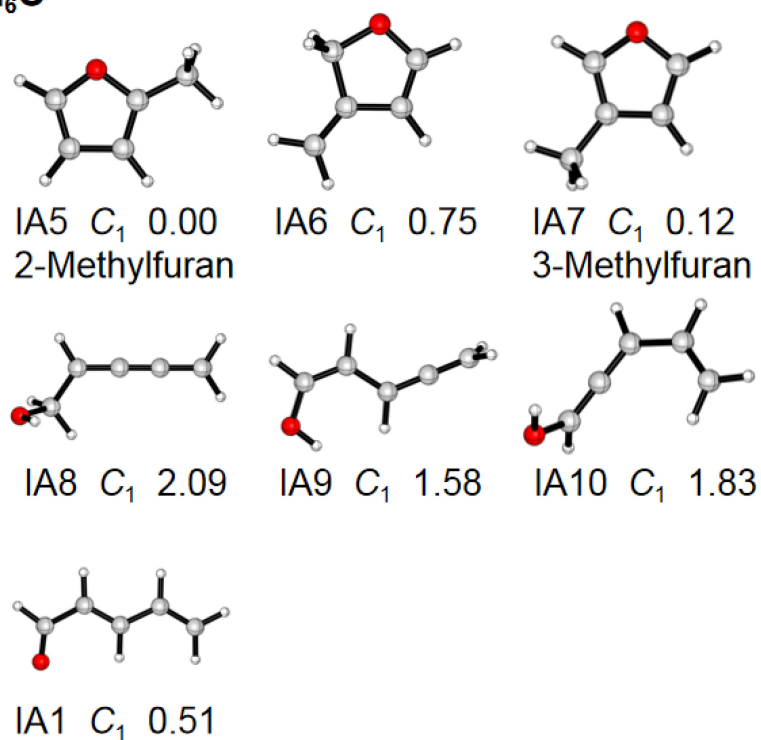
^[b] Reaction efficiency is defined as $\vartheta = (k_1/k_{\text{calc}}) \times 100\%$ and k_{calc} is the theoretical rate of collision that is calculated with $k_{\text{calc}} = 2\pi(e^2\alpha/\mu)^{1/2}$, in which e is the charge of the

cluster ion, α is the electric polarizability of the reactant molecule, and μ is the reduced mass.¹

(a) C_3H_4O



(b) C_5H_6O



(c) C₅H₇O

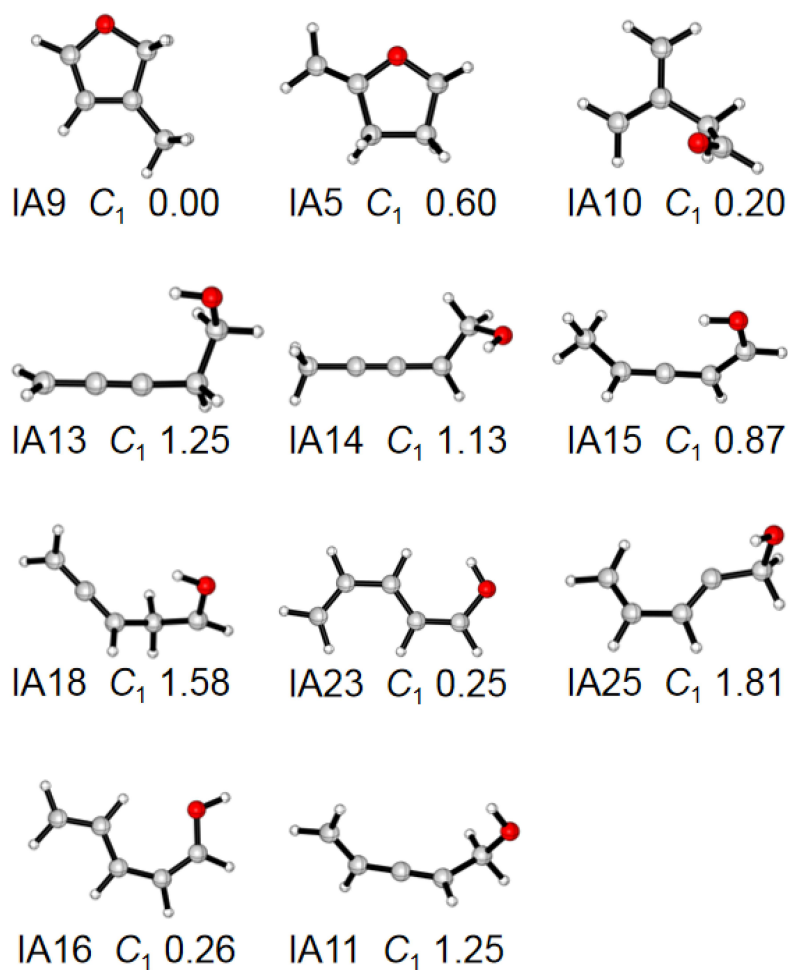


Fig. S3 DFT-calculated structures of neutral products (a) C₃H₄O, (b) C₅H₆O, and (c) C₅H₇O of the reaction $\text{Ti}_2\text{O}_5^+ + \text{C}_5\text{H}_8$. The spin states of (a) C₃H₄O and (b) C₅H₆O are singlet, and that of (c) C₅H₇O is doublet. The zero-point vibration-corrected energies ($\Delta H_{0\text{K}}$ in eV) of the possible products with respect to the separated reactants Ti_2O_5^+ and C_5H_8 are given.

Table S2. Comparison of neutral products of C₅H₈ oxidation mediated by Ti_xO_y⁺ cations and TiO₂ surfaces.

Product Type	Neutral Products	
	Ti _x O _y ⁺ + C ₅ H ₈	TiO ₂ surfaces
Hydrocarbon Compounds	C ₅ H ₇	Propanal
	C ₅ H ₆	
	C ₂ H ₂ (Acetylene)	
	C ₃ H ₄ (Propyne)	
	C ₃ H ₆ (Propylene)	
Carbonyl Compounds	CH ₂ O (Formaldehyde)	CH ₂ O (Formaldehyde)
		Butanal/butanone
		methacrolein, MACR
		Pentanal
		Acetone
	C ₃ H ₄ O (Methylketene)	methyl vinyl ketone, MVK
Others	CO	CO ₂
	H ₂ O	
	C ₅ H ₆ O (2-Methylfuran)	
	C ₅ H ₇ O	Acetaldehyde

References

1. G. Kummerlowe and M. K. Beyer, *Int. J. Mass Spectrom.*, 2005, **244**, 84-90.