

## Supplementary information

### Cl-initiated oxidation of methacrolein under NO<sub>x</sub>-free conditions studied by VUV photoionization mass spectrometry†

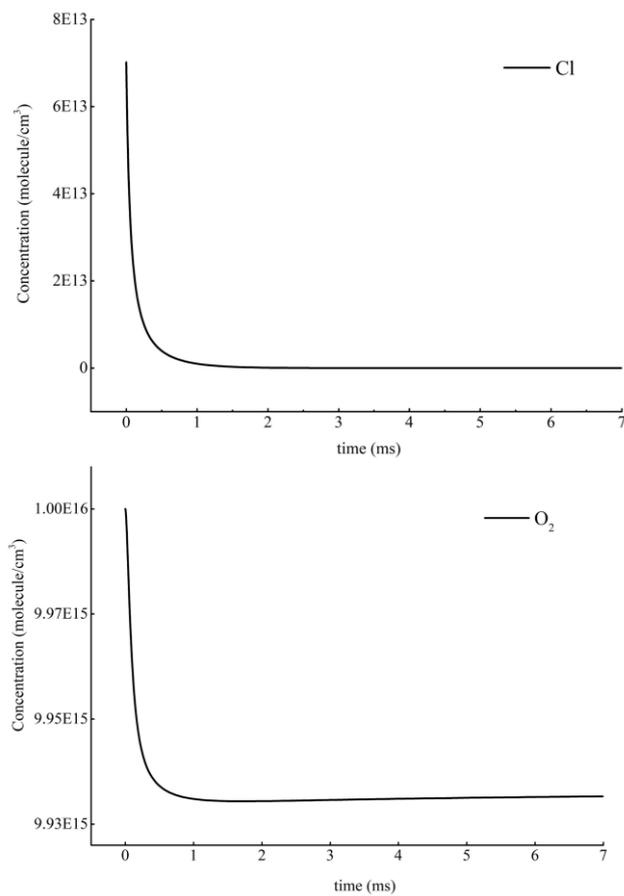
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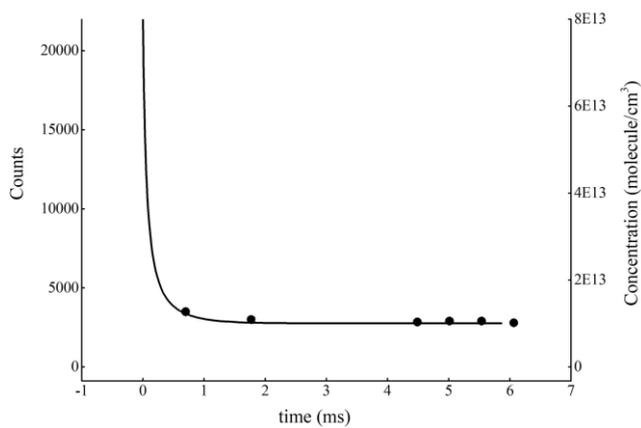
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**Table S1.** Assignment of the mass peaks of the secondary products and their fragment ions

m/z	molecular formula	assignment
140	C <sub>4</sub> H <sub>6</sub> O <sup>35</sup> Cl <sub>2</sub>	
142	C <sub>4</sub> H <sub>6</sub> O <sup>35</sup> Cl <sup>37</sup> Cl	C <sub>4</sub> H <sub>6</sub> OCl + Cl <sub>2</sub> → C <sub>4</sub> H <sub>6</sub> OCl <sub>2</sub> + Cl
144	C <sub>4</sub> H <sub>6</sub> O <sup>37</sup> Cl <sub>2</sub>	
111	C <sub>3</sub> H <sub>5</sub> <sup>35</sup> Cl <sub>2</sub>	C <sub>4</sub> H <sub>6</sub> OCl <sub>2</sub> <sup>+</sup> fragment:
113	C <sub>3</sub> H <sub>5</sub> <sup>35</sup> Cl <sup>37</sup> Cl	C <sub>3</sub> H <sub>5</sub> Cl <sub>2</sub> <sup>+</sup> [-CHO]
115	C <sub>3</sub> H <sub>5</sub> <sup>37</sup> Cl <sub>2</sub>	
76	C <sub>3</sub> H <sub>5</sub> <sup>35</sup> Cl	C <sub>4</sub> H <sub>6</sub> OCl <sub>2</sub> <sup>+</sup> fragment:
78	C <sub>3</sub> H <sub>5</sub> <sup>37</sup> Cl	C <sub>3</sub> H <sub>5</sub> Cl <sup>+</sup> [-CHOCl]
104	C <sub>4</sub> H <sub>5</sub> O <sup>35</sup> Cl	
106	C <sub>4</sub> H <sub>5</sub> O <sup>37</sup> Cl	C <sub>4</sub> H <sub>5</sub> O + Cl <sub>2</sub> → C <sub>4</sub> H <sub>5</sub> OCl + Cl



**Fig. S1.** The theoretical time behavior of reactants (O<sub>2</sub> and Cl atoms) in the Cl-initiated oxidation of MACR.



**Fig. S2.** The experimental (dots) and theoretical (lines) time behavior of reactant (MACR) in the Cl-initiated oxidation of MACR.