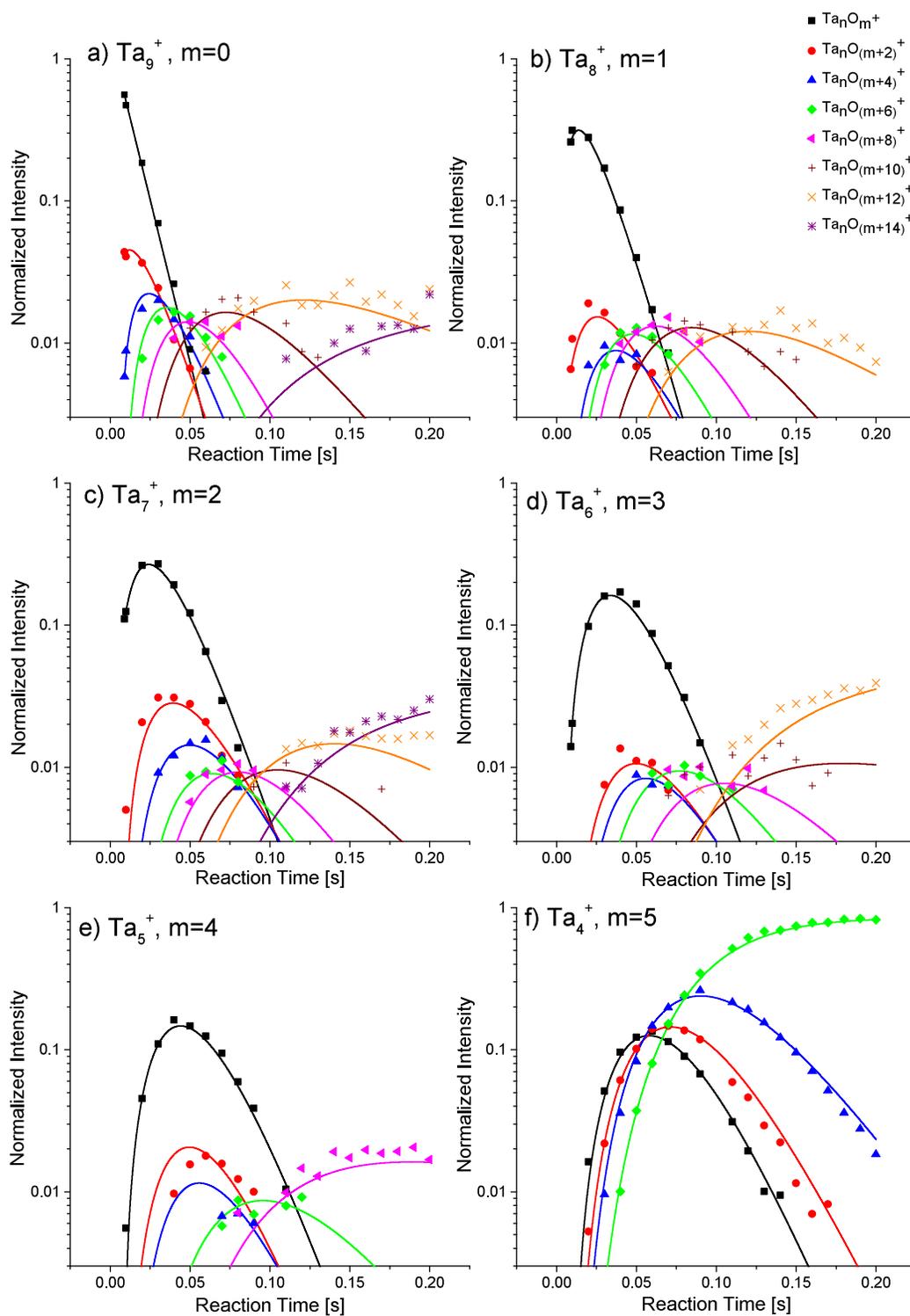


## Electronic Supplementary Information

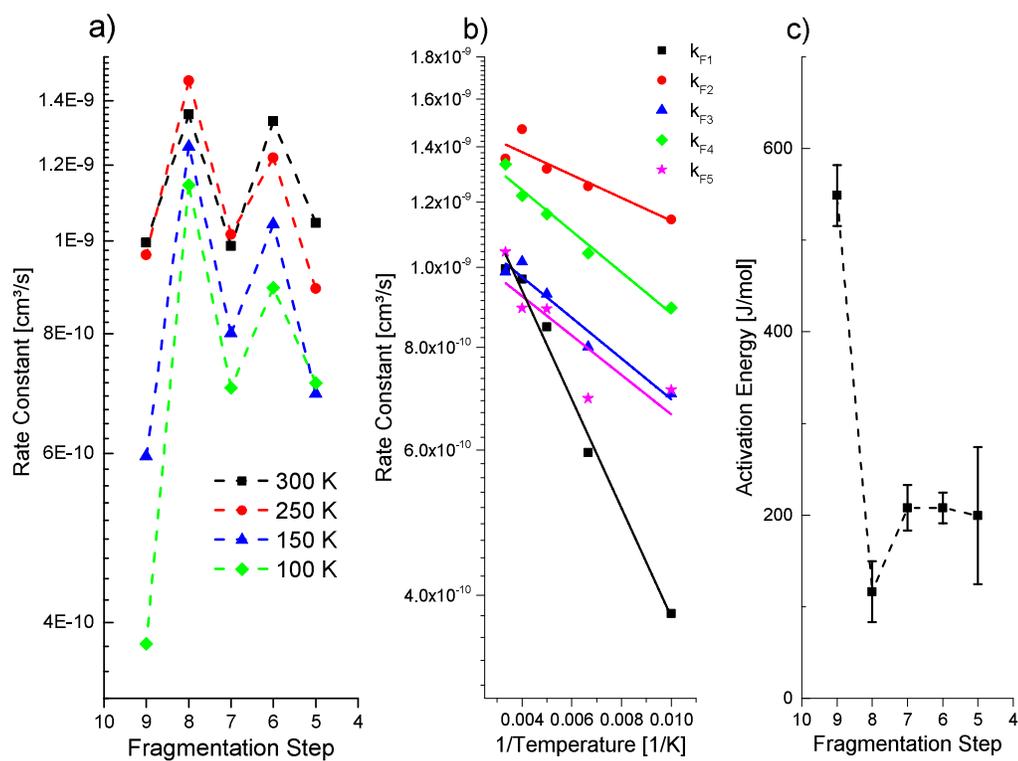
### **From oxidative degradation to direct oxidation: Size regimes in the consecutive reaction of cationic tantalum clusters with dioxygen**

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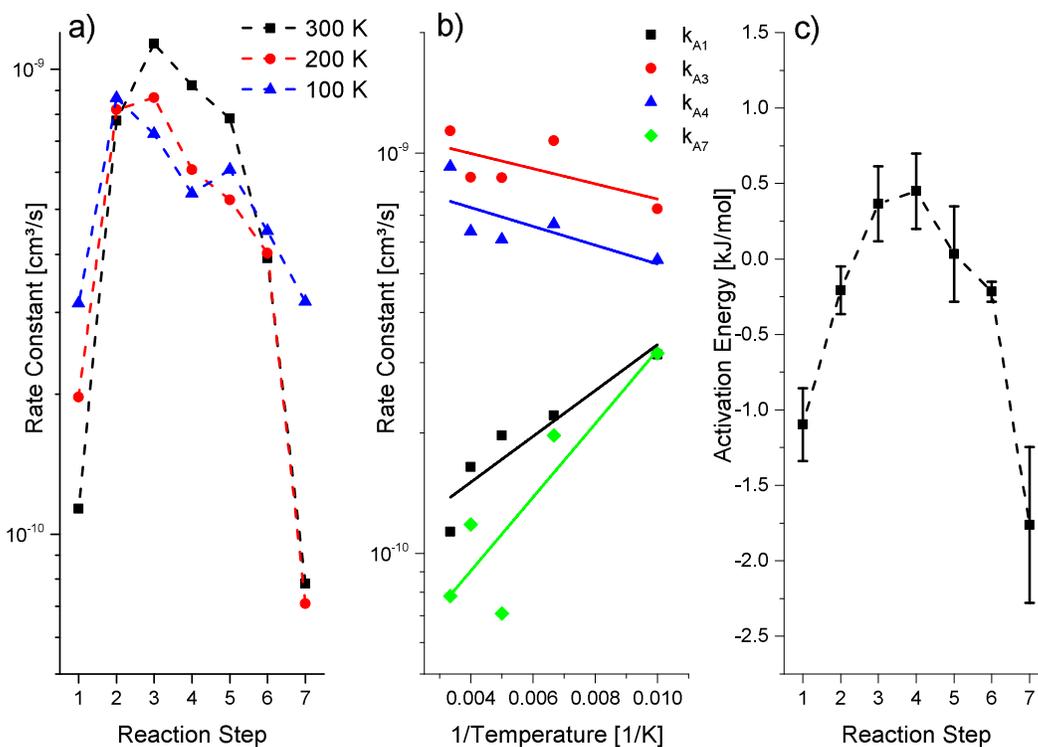
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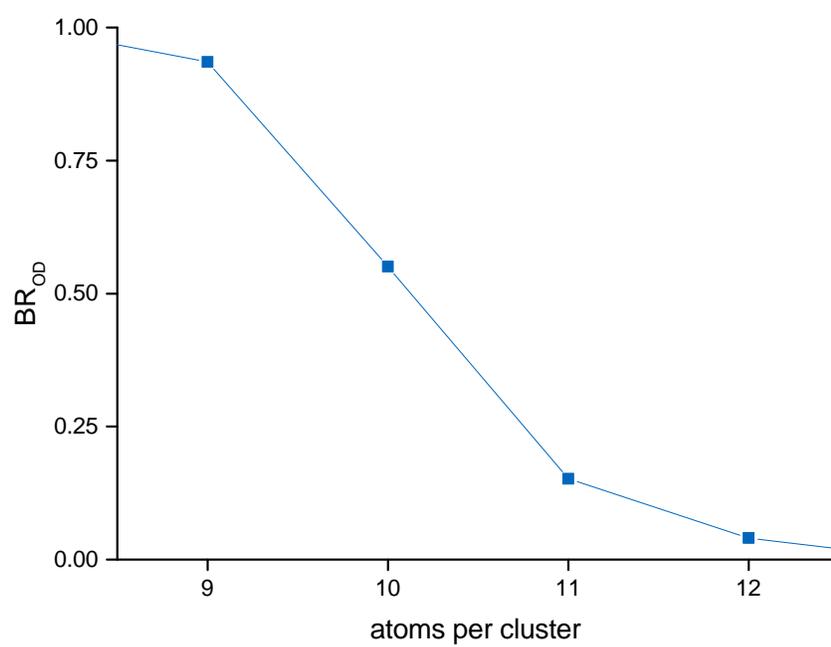
**Fig. S 1** Intermediate and product cluster abundances in the oxidation of Ta<sub>9</sub><sup>+</sup> as a function of reaction time. Symbols represent measurement points and results of the kinetic simulation are depicted as solid lines. Intact oxidation products of Ta<sub>9</sub><sup>+</sup> are shown in a), while the corresponding species of the first fragmentation product, Ta<sub>8</sub>O<sup>+</sup> are shown in b). Consequently, c-f) show intact oxidation products of Ta<sub>7</sub>O<sub>2</sub><sup>+</sup> through Ta<sub>4</sub>O<sub>5</sub><sup>+</sup>.



**Fig. S 2** Bimolecular rate constants  $k_{F1-F5}$  and apparent activation energies of the five oxidative degradation steps in the main reaction channel of  $\text{Ta}_9^+$ . In these plots, “fragmentation step 9”, for example, denotes the reaction step from  $\text{Ta}_9^+$  to  $\text{Ta}_8\text{O}^+$ , “fragmentation step 8” refers to the degradation of  $\text{Ta}_8\text{O}^+$  to  $\text{Ta}_7\text{O}_2^+$  and so on. The change of rate constants as a function of the reaction step is shown for various temperatures in a). An Arrhenius plot is depicted in b) for the five rate constants. Corresponding apparent activation energies are extracted from the respective slope in the Arrhenius plot and are shown in c).



**Fig. S 3** Bimolecular rate constants  $k_{A1-A7}$  and apparent activation energies of the seven intact oxidation steps from  $\text{Ta}_9^+$  to  $\text{Ta}_9\text{O}_{14}^+$ . The change of rate constants as a function of the reaction step is shown for various temperatures in a). An Arrhenius plot is depicted in b) for four selected rate constants. Corresponding apparent activation energies are extracted from the respective slope in the Arrhenius plot and are shown in c). It should be noted that the apparent rate constants especially of the first and the seventh step become increased at lower temperatures, which is explained by the Lindeman mechanism for energy transfer: The formation of an energized intermediate  $[\text{Ta}_x\text{O}_x(\text{O}_2)^+]$ \* is independent of temperature and (in absence of a barrier for the following product formation) only the back-reaction, *i.e.* the dissociation of the energized intermediate, is affected by temperature. Decreasing the temperature will then hinder the dissociation and increase the apparent rate constant.



**Fig. S 4** Branching ratios for oxidative degradation in the first reaction step as a function of cluster size in the transitional size regime. While  $\text{Ta}_9^+$  mostly fragments, the initial  $BR_{OD}$  subsequently decreases with increasing cluster size and only a small amount of  $\text{Ta}_{12}^+$  clusters undergoes oxidative degradation.