

Electronic Supplementary Information

Decomposition of Nitric Oxide by Rhodium Cluster Cations at High Temperatures

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1. Distribution maps of $\text{Rh}_{6-9}\text{N}_x\text{O}_y^+$ after reaction with NO

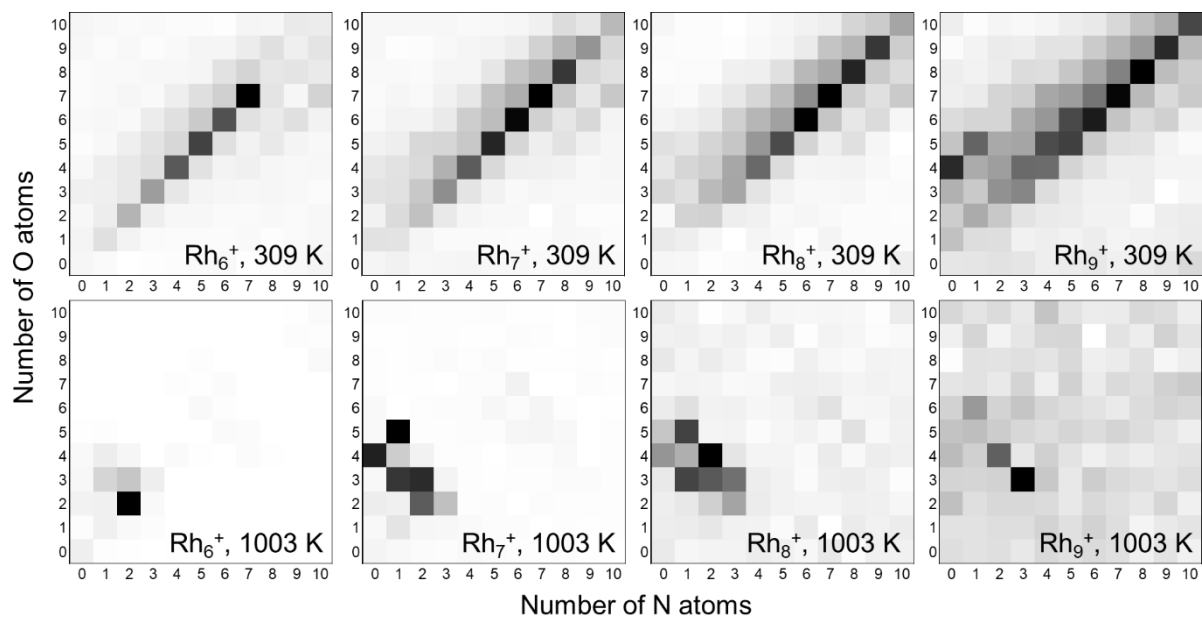


Figure S1. Ion intensity distribution maps of $\text{Rh}_{6-9}\text{N}_x\text{O}_y^+$ after reaction with NO at 309 K and those after heating to 1003 K. Note that although the map of Rh_9^+ at 309 K shows intense existence of Rh_9O_4^+ and Rh_9NO_5^+ , these are not real signals but are contributed by other compositions that have m/z close to theirs, e.g., $\text{Rh}_7\text{N}_9\text{O}_9^+$ ($m/z = 990.3$) contributes to Rh_9O_4^+ ($m/z = 990.1$). Such misassigned signals have been removed in the temperature dependence figures.

2. Relative intensities of $\text{Rh}_{6,9}\text{N}_x\text{O}_y^+$ as functions of temperature

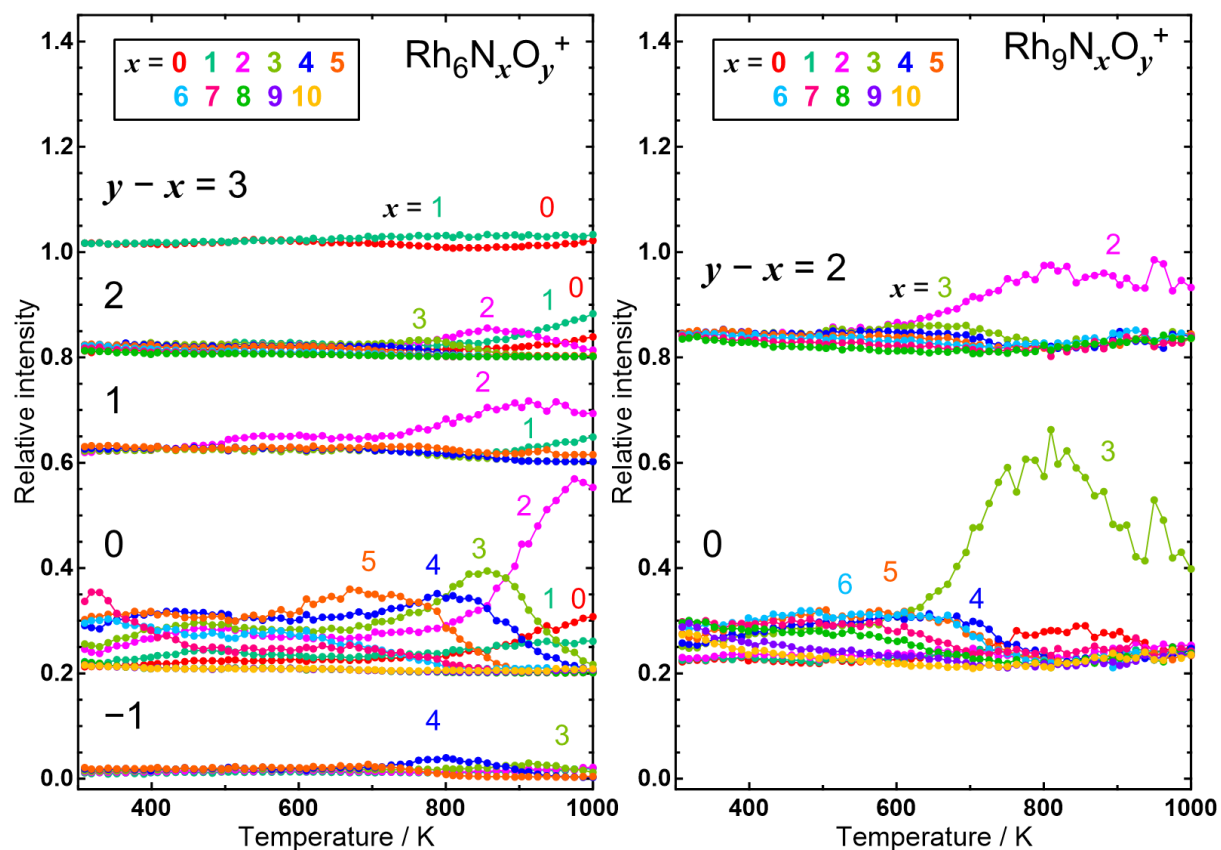


Figure S2. Relative intensities of $\text{Rh}_{6,9}\text{N}_x\text{O}_y^+$ after reaction with NO at 309 K, followed by heating as function of the heating temperature. The plots are vertically offset based on $y - x$ values for clarity. The intensity of Rh_6NO_2^+ ($m/z = 663.4$) is not evaluated below 800 K because it is considered low enough and the evaluation is disturbed by a strong signal of $\text{Rh}_5\text{N}_5\text{O}_5^+$ ($m/z = 664.5$).

3. Atomic coordinates for optimized structures

Coordinates are shown in angstrom.

$\text{Rh}_8\text{N}_3\text{O}_3^+$ (quintet)

	x	y	z
Rh	2.196841	-0.400193	1.437375
Rh	-0.488896	0.126401	-1.490993
Rh	-0.882555	0.011231	1.636104
Rh	2.633036	-0.119895	-1.281770
Rh	1.047818	1.894860	0.049978
Rh	0.260889	-1.942862	0.117018
Rh	-2.062932	1.720967	-0.024476
Rh	-2.408007	-1.406166	-0.305636
N	2.030348	-1.474506	-0.121659
O	-0.648289	2.929033	0.083352
N	0.769104	0.809423	1.599285
O	-1.256789	-2.828604	-0.625600
N	1.190428	0.985588	-1.594171
O	-3.252162	0.269699	-0.129778

$\text{Rh}_8\text{N}_2\text{O}_2^+$ (dectet)

	x	y	z
Rh	-2.294982	0.452199	-1.335940
Rh	2.597807	0.172818	-0.597190
Rh	-1.660907	-1.157619	0.791443
Rh	0.117270	1.364129	-0.721873
Rh	-0.281861	-1.119987	-1.475807
Rh	-1.875940	1.471826	1.048402
Rh	0.864312	-2.042036	0.698372
Rh	1.042288	0.399740	1.591279
N	3.574000	1.578058	-0.304606
O	1.682861	-1.476813	-1.114407
N	-0.749991	0.197497	1.765736
O	4.238702	2.504683	-0.156687

Rh ₈ NO ₃ ⁺ (septet)			
	x	y	z
Rh	-2.344210	-0.048757	1.333266
Rh	0.365466	0.040704	-1.303366
Rh	0.364914	0.040967	1.303825
Rh	-2.343690	-0.048839	-1.333900
Rh	-0.963937	-1.834485	0.000129
Rh	-0.476542	2.224884	0.000074
Rh	2.209438	-1.699436	0.000150
Rh	2.503012	1.218804	-0.000153
N	-1.975237	1.187021	-0.000298
O	0.682972	-2.775189	0.000185
O	1.394707	2.705214	0.000280
O	3.506872	-0.371517	-0.000341

4. Complete author list for ref 16

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