Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Threshold Photoionization Shows No Sign of Nitryl Hydride in Methane Oxidation with Nitric Oxide

Martin Hoener,[1] Andras Bodi,[2] Patrick Hemberger,[2] Torsten Endres,[3] and Tina Kasper[1]

[1]Mass Spectrometry in Reactive Flows – Institute for Combustion and Gas Dynamics (IVG),
University Duisburg-Essen, Duisburg 47057, Germany

[2]Laboratory for Synchrotron Radiation and Femtochemistry – Paul Scherrer Institute, Villigen
5232, Switzerland

[3]Reactive Fluids - Institute for Combustion and Gas Dynamics (IVG), University Duisburg-Essen,
Duisburg 47057, Germany

EXPERIMENTAL

The experiment uses a pressurized plug-flow reactor to provide reproducible reaction conditions that can be modelled 1-dimensionally.[1] It allows the investigation of reactions at pressures of up to 6 bar. The reactor has an isothermal zone of 450 mm length and the internal reaction volume is enclosed with a fused silica liner to prevent wall interactions. The analyte is expanded through three differential pressure stages and injected into the spectrometer using a molecular beam sampling interface. Analysis is performed by double imaging photoion photoelectron coincidence spectroscopy (i^2PEPICO).[2,3] This mass resolved analytical technique uses tunable synchrotron VUV light for sample ionization. The energy selective analysis of the sample yields an additional discrimination criterion for species in conjunction with the mass selective analysis of the spectrometer and allows a direct probe into vibronic transitions of the analyzed compounds.[3,4] The grazing incidence monochromator with an energy dependent energy resolution $E/\Delta E \approx 1500$ delivers the ionizing VUV light through the beam line[2,5] to the interaction region, where species in the molecular beam are ionized. Higher harmonic contamination of the light is removed by a noble gas filter. Inlet conditions of the reactor, including volume flows and molar fractions of all reactants, are given in Table S1.

Reactant	Flow [sccm]	Mole Fraction
Ar	252.0	0.900
O_2	12.2	0.044
CH_4	13.0	0.046
NO	2.8	0.010

Table S1. Reaction conditions at an equivalence ration of $\varphi = 2.1$ with an argon dilution of 90 %, addition of 1% nitric oxide and a total flow of 280 sccm.

Table S2 gives the reactant flows for a reference measurement performed in a mixture of 4.4% Oxygen and 1% NO diluted with 94.6% argon. In these conditions, oxygen will react with NO to from NO_2 at a temperature of 723 K, comparable to the temperature used for the photon energy scan in the hydrocarbon reaction mixture.

Reactant	Flow [sccm]	Mole Fraction
Ar	265	0.946
O_2	12.2	0.044
NO	2.8	0.010

Table S2. Reaction conditions for the reference measurement at 723 K and a total flow of 280 sccm.

The photon energy scans for the reaction conditions given in Table S1 were performed between 10.4 and 12.2 eV with a scan resolution of 30 meV. The averaging time was 900 s at each photon energy. A photon energy scan was performed between 10.4 and 12.2 eV in the reference reaction conditions (Table S2) at the same scan resolution to provide a comparison between both the NO (*m*/*z* 30) and NO_2 (*m*/*z* 46) signals.

COMPUTED ENERGIES

Molecule	B3LYP/6-311++G(d,p)	CBS-QB3	G4	W1BD
trans-HONO	−205.751616	−205.475055	−205.643615	−205.810557
trans-HONO^{+}	−205.348932	−205.072518	−205.241546	−205.407969
cis-HONO	−205.750001	−205.474369	−205.642595	−205.810039
cis-HONO^{+}	−205.336489	−205.059793	−205.230143	−205.396655
O_2N–H	−205.683328	−205.462227	−205.630773	−205.796804
O_2N–H^{+}	−205.238147	−205.016240	−205.187812	−205.35188
TS *trans*-HONO^{+} ⇌ *cis*-HONO^{+}			−205.220109	
TS *trans*-HONO^{+} ⇌ /HO···NO^{+}			−205.229219	
TS *trans*-HONO^{+} ⇌ /HNO_2^{+}			−205.149045	
TS O_2N–H^{+}⇌ H···ONO^{+}			−205.154857	
TS H···ONO^{+}/*cis*-HONO^{+}			−205.155933	
HO···NO^{+}			−205.246739	
H···ONO^{+}			−205.173382	
NO^{+}			−129.519156	
$^{\bullet}$OH			−75.709475	
NO_2^{+}			−204.669929	
H			−0.50142	

Table S3. Computed energies in E_h for stable structures, transition states and dissociative ionization fragments. Known energies match literature values within a few kJ.[6,7]

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