Supporting information for:

Reaction of the hydrogen atom with nitrous oxide in aqueous solution - pulse radiolysis and theoretical study

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A. Modelling spur chemistry

Table A1. The reaction scheme assumed to simulate evolution of the average radiation spur in N_2O saturated 0.1 M HCl solution. [a)]

Reaction		Reaction	
(R1)	$e_{aq}^- + H^+ \rightarrow H^\bullet$	(R9)	$^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O$
(R2)	$e_{aq}^- + {}^\bullet OH \rightarrow OH^-$	(R10)	$H^\bullet + H_2O_2 \rightarrow {}^\bullet OH + H_2O$
(R3)	$e_{aq}^- + e_{aq}^- \xrightarrow{+2H_2O} H_2 + 2OH^-$	(R11)	$H^+ + OH^- \rightarrow H_2O$
(R4)	$e_{aq}^- + H^\bullet \xrightarrow{+H_2O} H_2 + OH^-$	(R12)	$e_{aq}^- + N_2O \xrightarrow{H_2O} {}^\bullet OH + OH^- + N_2$
(R5)	$e_{aq}^- + H_2O_2 \rightarrow {}^\bullet OH + OH^-$	(R13)	$^\bullet OH \xrightarrow{+Cl^-} Cl_2^{\bullet -}$
(R6)	$H^\bullet + {}^\bullet OH \rightarrow H_2O$	(R14)	$H^\bullet + Cl_2^{\bullet -} \rightarrow H^+ + 2Cl^-$
(R7)	$H^\bullet + H^\bullet \rightarrow H_2$	(R15)	$Cl_2^{\bullet -} + Cl_2^{\bullet -} \rightarrow Cl_2 + 2Cl^-$
(R8)	$^\bullet OH + {}^\bullet OH \rightarrow H_2O_2$		

[a)] The calculated G-values showed very low sensitivity to the contribution of the reactions: $H^\bullet + N_2O \rightarrow {}^\bullet OH + N_2$, $H^\bullet + Cl_2 \rightarrow H^+ + Cl_2^{\bullet -}$, $Cl_2^{\bullet -} + H_2O_2 \rightarrow HO_2^\bullet + H^+ + 2Cl^-$.

The reactions with the scavengers (N_2O, H^+, Cl^-) homogeneously distributed in the bulk solutions were treated as the first order reactions. The temperature dependencies for k_{R1}-k_{R11} were assumed based on [Elliot A. J., Bartels, D.M., Report AECL-153-127160-450-001, Chalk River Laboratories, Canada 2009]. Details on the temperature dependence for the reaction rate constants k_{R12}-k_{R15} are given in the text and in Table 2.

Spur parameters. According to the extended diffusion-kinetic model [Swiatla-Wojcik D., Buxton G.V. (2000) Phys. Chem. Chem. Phys. 2 (2000) 5113] the average radiation spur initially contains: e_{aq}^-, $H^\bullet$, $^\bullet OH$, H_2, H_2O_2, H_3O^+, OH^-. The initial distribution of e^-_{aq} and the products of the dissociative attachment of sub-excitation electrons (e^-_{sub}), $e^-_{sub} + H_2O \rightarrow {}^\bullet OH + H^- \xrightarrow{+H_2O} {}^\bullet OH + H_2 + OH^-$, were described by the Gaussian function with the standard deviation of 3.8 nm, whereas the distribution of the other species by the Gaussian with the standard deviation of 1.13 nm. The average energy deposited per spur was 83 eV. The initial yields of $H^\bullet$, $^\bullet OH$, H_2O_2, H_3O^+ and OH^- were defined by four independent parameters presented in Table A2: G^o_{ex} - the initial yield of excitations, $G^o(e^-_{aq})$ - the initial yield of e^-_{aq}, $G^o_1(H_2)$ - the initial yield of H_2 formed in the dissociative attachment of e^-_{sub}, and $G^o_2(H_2)$ - the initial yield of H_2 resulting from the dissociative decay of H_2O^*,

Table A2. The initial yields G^o in 10^{-7} mol J^{-1} assumed to simulate evolution of the average radiation spur in N_2O saturated 0.1 M HCl solution. [a)]

Parameter	Value	Process
G^o_{ex}	0.78	$H_2O \xrightarrow{h\nu} H_2O^*$
$G^o(e^-_{aq})$	4.35	$e^- \xrightarrow{H_2O} e^-_{aq}$
$G^o_1(H_2)$	0.26	Dissociative attachment of dry electrons
$G^o_2(H_2)$	0.05	$H_2O^* \rightarrow H_2 + O^\bullet \xrightarrow{H_2O} H_2 + {}^\bullet OH + {}^\bullet OH$

[a)] for more details of the extended diffusion-kinetic model see [Swiatla-Wojcik D., Buxton G.V. Phys. Chem. Chem. Phys. 2 (2000) 5113 ; ibid. 5771; J. Phys. Chem. 99 (1995) 11464].

B. DFT calculations

Table B1. Geometries and vibrational frequencies of the stationary points of H + N_2O reaction obtained using UB3LYP/cc-pVTZ for vacuum. [a)]

	H + N_2O	*cis*-HNNO	*trans*-HNNO	OH + N_2
r_{NH}	-	1.0341	1.0210	-
r_{NN}	1.1217	1.2216	1.2393	1.0914
r_{NO}	1.1834	1.2075	1.1985	-
r_{OH}	-	-	-	0.9746
$H\hat{N}N$	-	110.6	107.9	-
$N\hat{N}O$	180.0	139.6	132.5	-
ω_1	620.8	593.7	671.2	3696.4 (OH)
ω_2	620.8	760.2	776.8	2450.0 (N_2)
ω_3	1329.6	1222.3	1271.3	-
ω_4	2348.5	1338.3	1363.6	-
ω_5	-	1731.3	1714.1	-
ω_6	-	3234.5	3440.9	-

[a)] Distances (r) are in Å, angles in degrees, and frequencies (ω_i) in cm^{-1}.

Table B2. Geometries and vibrational frequencies of the transition states of H + N_2O reaction obtained using UB3LYP/cc-pVTZ for vacuum. [a)]

	[H-NNO]‡	[H-ONN]‡	[NNOH]‡	[*cis/trans*-HNNO]‡
r_{NH}	1.6404	-	1.2586	1.0491
r_{NN}	1.1370	1.1311	1.2017	1.2130
r_{NO}	1.1854	1.2235	1.4317	1.2003
r_{OH}	-	1.4663	1.3783	-
$H\hat{N}N$	113.8	-	90.2	111.2
$N\hat{N}O$	172.2	161.0	96.5	177.3
$H\hat{O}N$	-	115.5	76.7	-
$O\hat{H}N$	-	-	96.6	-
ω_1	964.6*i*	1330.8*i*	1841.9*i*	858.3*i*
ω_2	388.5	469.8	607.0	507.7
ω_3	624.1	578.3	898.3	1157.2
ω_4	677.2	806.5	1011.5	1269.4
ω_5	1293.4	1199.3	1653.1	1950.6
ω_6	2228.3	2174.8	2053.2	2899.5

[a)] Distances (r) are in Å, angles in degrees, and frequencies (ω_i) in cm^{-1}.

Table B3. Geometries and vibrational frequencies of the stationary points of H + N_2O reaction obtained using UB3LYP/cc-pVTZ using C-PCM water-solvent model. [a)]

	25°C, ε = 78.355				70°C, ε = 63.677			
	H + N_2O	*cis*-HNNO	*trans*-HNNO	OH + N_2	H + N_2O	*cis*-HNNO	*trans*-HNNO	OH + N_2
r_{NH}	-	1.0333	1.0216	-	-	1.0333	1.0216	-
r_{NN}	1.1204	1.2194	1.2340	1.0914	1.1204	1.2194	1.2340	1.0911
r_{NO}	1.1829	1.2096	1.2027	-	1.1829	1.2095	1.2027	-
r_{OH}	-	-	-	0.9754	-	-	-	0.9754
$H\hat{N}N$	-	111.2	108.6	-	-	111.2	108.6	-
$N\hat{N}O$	180.0	139.7	132.7	-	180.0	139.7	132.7	-
ω_1	618.9	594.9	674.5	3688.6 (OH)	618.9	594.9	674.5	3688.7 (OH)
ω_2	618.9	756.5	773.5	2450.0 (N_2)	618.9	756.5	773.5	2452.0 (N_2)
ω_3	1325.8	1222.9	1250.3	-	1325.8	1222.9	1250.4	-
ω_4	2334.9	1329.1	1369.1	-	2334.9	1329.1	1369.0	-
ω_5	-	1708.2	1693.8	-	-	1708.3	1693.9	-
ω_6	-	3256.7	3444.4	-	-	3256.7	3444.4	-

[a)] Distances (r) are in Å, angles in degrees, and frequencies (ω_i) in cm^{-1}.

Table B4. Geometries and vibrational frequencies of the transition states of H + N_2O reaction obtained using UB3LYP/cc-pVTZ using C-PCM water-solvent model. [a)]

	25°C, ε = 78.355				70°C, ε = 63.677			
	[H-NNO]‡	[H-ONN]‡	[NNOH]‡	[*cis/trans*-HNNO]‡	[H-NNO]‡	[H-ONN]‡	[NNOH]‡	[*cis/trans*-HNNO]‡
r_{NH}	1.6330	-	1.2576	1.0453	1.6330	-	1.2576	1.0453
r_{NN}	1.1359	1.1301	1.1994	1.2120	1.1359	1.1301	1.1994	1.2120
r_{NO}	1.1851	1.2230	1.4381	1.2031	1.1851	1.2230	1.4381	1.2031
r_{OH}	-	1.4574	1.3818	-	-	1.4575	1.3818	-
$H\hat{N}N$	113.7	-	90.6	111.4	113.7	-	90.6	111.4
$N\hat{N}O$	172.2	161.0	96.3	177.5	172.2	161.0	96.3	177.5
$H\hat{O}N$	-	115.6	76.6	-	-	115.6	76.6	-
$O\hat{H}N$	-	-	96.5	-	-	-	96.5	-
ω_1	983.7i	1412.2i	1845.0i	863.9i	983.7i	1411.9i	1845.0i	863.9i
ω_2	392.3	479.7	579.9	497.4	392.3	479.7	580.0	497.5
ω_3	622.9	578.7	891.4	1164.2	622.9	578.7	891.5	1164.2
ω_4	679.5	808.5	997.3	1260.1	679.5	808.5	997.4	1260.1
ω_5	1286.7	1193.9	1664.2	1927.8	1286.7	1193.9	1664.2	1927.9
ω_6	2212.2	2159.9	2047.8	2984.4	2212.3	2159.9	2047.8	2984.2

[a)] Distances (r) are in Å, angles in degrees, and frequencies (ω_i) in cm^{-1}.

Table B5. Geometries and vibrational frequencies of the stationary points of H + N_2O reaction obtained using UB3LYP/cc-pVTZ using IEF-PCM water-solvent model. [a)]

	25°C, ε = 78.355				70°C, ε = 63.677			
	H + N_2O	*cis*-HNNO	*trans*-HNNO	OH + N_2	H + N_2O	*cis*-HNNO	*trans*-HNNO	OH + N_2
r_{NH}	-	1.0333	1.0216	-	-	1.0333	1.0216	-
r_{NN}	1.1204	1.2194	1.2340	1.0911	1.1204	1.2194	1.2341	1.0911
r_{NO}	1.1829	1.2096	1.2027	-	1.1829	1.2096	1.2027	-
r_{OH}	-	-	-	0.9754	-	-	-	0.9754
$H\hat{N}N$	-	111.2	108.6	-	-	111.2	108.6	-
$N\hat{N}O$	180.0	139.7	132.7	-	180.0	139.7	132.7	-
ω_1	618.9	594.5	674.6	3688.6 (OH)	618.9	594.4	674.6	3688.7 (OH)
ω_2	618.9	756.2	773.5	2452.0 (N_2)	618.9	756.2	773.6	2452.0 (N_2)
ω_3	1325.8	1222.7	1250.4	-	1325.8	1222.6	1250.6	-
ω_4	2334.9	1328.8	1369.0	-	2334.9	1328.7	1369.0	-
ω_5	-	1708.4	1694.0	-	-	1708.5	1694.1	-
ω_6	-	3256.6	3444.3	-	-	3256.6	3444.3	-

[a)] Distances (r) are in Å, angles in degrees, and frequencies (ω_i) in cm^{-1}.

Table B6. Geometries and vibrational frequencies of the transition states of H + N_2O reaction obtained using UB3LYP/cc-pVTZ using IEF-PCM water-solvent model. [a)]

	25°C, ε = 78.355				70°C, ε = 63.677			
	[H-NNO]‡	[H-ONN]‡	[NNOH]‡	[*cis/trans*-HNNO]‡	[H-NNO]‡	[H-ONN]‡	[NNOH]‡	[*cis/trans*-HNNO]‡
r_{NH}	1.6331	-	1.2576	1.0454	1.6331	-	1.2576	1.0454
r_{NN}	1.1359	1.1302	1.1994	1.2120	1.1359	1.1302	1.1995	1.2120
r_{NO}	1.1851	1.2230	1.4381	1.2031	1.1851	1.2230	1.4380	1.2031
r_{OH}	-	1.4575	1.3818	-	-	1.4576	1.3818	-
$H\hat{N}N$	113.7	-	90.6	111.4	113.7	-	90.6	111.4
$N\hat{N}O$	172.2	161.0	96.3	177.5	172.2	161.0	96.3	177.5
$H\hat{O}N$	-	115.6	76.6	-	-	115.6	76.6	-
$O\hat{H}N$	-	-	96.5	-	-	-	96.5	-
ω_1	983.7i	1411.7i	1844.9i	863.8i	983.7i	1411.2i	1844.9i	863.8i
ω_2	392.3	480.0	580.0	497.5	392.3	480.0	580.2	497.5
ω_3	622.9	578.7	891.5	1164.2	622.9	578.7	891.5	1164.1
ω_4	679.4	808.5	997.6	1260.1	679.4	808.5	997.7	1260.2
ω_5	1286.7	1194.0	1664.1	1928.0	1286.7	1194.0	1664.1	1928.1
ω_6	2212.2	2159.9	2047.8	2984.0	2212.3	2160.0	2047.9	2983.6

[a)] Distances (r) are in Å, angles in degrees, and frequencies (ω_i) in cm^{-1}.

Table B7. Geometries and vibrational frequencies of the stationary points of H + N_2O reaction obtained using UB3LYP/cc-pVTZ using SMD water-solvent model. [a)]

	25°C, ε = 78.355				70°C, ε = 63.677			
	H + N_2O	*cis*-HNNO	*trans*-HNNO	OH + N_2	H + N_2O	*cis*-HNNO	*trans*-HNNO	OH + N_2
r_{NH}	-	1.0349	1.0236	-	-	1.0349	1.0236	-
r_{NN}	1.1203	1.2187	1.2331	1.0908	1.1203	1.2187	1.2331	1.0908
r_{NO}	1.1829	1.2104	1.2035	-	1.1829	1.2104	1.2035	-
r_{OH}	-	-	-	0.9783	-	-	-	0.9783
$H\hat{N}N$	-	111.6	108.8	-	-	111.6	108.8	-
$N\hat{N}O$	180.0	139.8	132.8	-	180.0	139.8	132.8	-
ω_1	619.1	598.8	675.7	3633.0 (OH)	619.1	598.4	675.7	3633.4 (OH)
ω_2	619.1	733.3	761.8	2454.0 (N_2)	619.1	733.1	761.8	2454.0 (N_2)
ω_3	1326.8	1213.1	1246.0	-	1326.8	1213.0	1246.2	-
ω_4	2339.4	1322.0	1372.2	-	2339.4	1321.9	1372.2	-
ω_5	-	1712.7	1694.2	-	-	1712.8	1694.3	-
ω_6	-	3249.1	3429.3	-	-	3249.1	3429.3	-

[a)] Distances (r) are in Å, angles in degrees, and frequencies (ω_i) in cm^{-1}.

Table B8. Geometries and vibrational frequencies of the transition states of H + N_2O reaction obtained using UB3LYP/cc-pVTZ using SMD water-solvent model. [a)]

	25°C, ε = 78.355				70°C, ε = 63.677			
	[H-NNO]‡	[H-ONN]‡	[NNOH]‡	[*cis/trans*-HNNO]‡	[H-NNO]‡	[H-ONN]‡	[NNOH]‡	[*cis/trans*-HNNO]‡
r_{NH}	1.6449	-	1.2649	1.0454	1.6449	-	1.2648	1.0454
r_{NN}	1.1355	1.1300	1.1987	1.2126	1.1355	1.1300	1.1988	1.2126
r_{NO}	1.1860	1.2222	1.4370	1.2038	1.1860	1.2222	1.4369	1.2038
r_{OH}	-	1.4661	1.3850	-	-	1.4661	1.3850	-
$H\hat{N}N$	113.2	-	90.7	111.4	113.2	-	90.7	111.4
$N\hat{N}O$	172.0	161.0	96.4	177.7	172.0	161.0	96.4	177.7
$H\hat{O}N$	-	115.1	76.8	-	-	115.1	76.8	-
$O\hat{H}N$	-	-	96.1	-	-	-	96.1	-
ω_1	985.6i	1413.0i	1858.2i	868.8i	985.6i	1412.4i	1858.1i	868.8i
ω_2	391.0	474.1	583.9	500.2	390.9	474.2	584.0	500.3
ω_3	621.0	579.7	889.9	1166.0	621.0	579.7	890.0	1166.0
ω_4	681.0	809.8	971.7	1266.5	680.9	809.9	971.9	1266.5
ω_5	1285.3	1197.9	1665.9	1928.4	1285.3	1198.0	1665.8	1928.5
ω_6	2216.0	2162.1	2013.1	3007.7	2216.1	2162.2	2013.4	3007.2

[a)] Distances (r) are in Å, angles in degrees, and frequencies (ω_i) in cm^{-1}.