

Support Information

Molecular reaction and dynamic mechanism of iodate reduction to molecular iodine by nitrous acid in acidic solution

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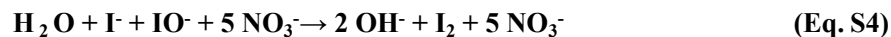
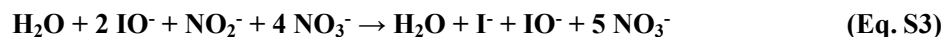
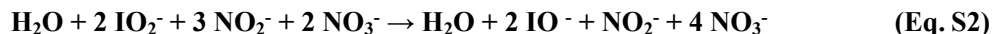
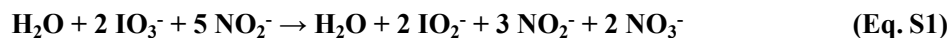
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1. Nomenclature

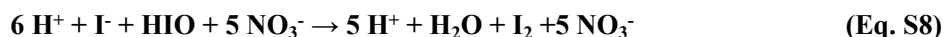
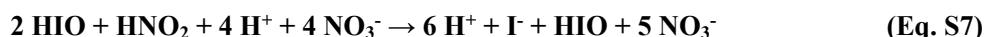
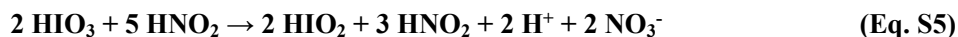
Acronyms	
AIMD	ab initio molecular dynamics
ADCH	Atomic Dipole moment corrected Hirshfeld Population method
aug-cc-pVTZ-PP	Dunning's correlation consistent basis sets with diffuse functions
CCSD (T)	Coupled cluster theory with single, double, and perturbative triple excitations
CSVR	thermal bath of Canonical Sampling Through Velocity Rescaling
def2-TZVPP	Triple zeta valence of two polarization functions basis sets
DFT	density functional theory
ESP	electrostatic potential
IRC	intrinsic reaction coordinate
IRI	interaction regional indicator
M06-2x	global hybrid functional in Minnesota series functional
NVT	ensemble at constant volume and temperature
TS	transition state
vdW	van der Waals
k_{TST}	The reaction rate parameter of molecular reaction calculated by TS theory
ZPE	zero point energy of vibration
ΔE_0^\ominus	Internal energy change in ground state
$\Delta E_{\text{elec}}^\ominus$	electronic binding energy change of standard state
$\Delta E_{\text{rot}}^\ominus$	electronic rotation energy change of standard state
$\Delta E_{\text{trans}}^\ominus$	electronic translation energy change of standard state
$\Delta E_{\text{vib}}^\ominus$	electronic vibration energy change of standard state
ΔE^\ominus	Sum of electronic energy change and thermal correction to Internal energy
ΔG^\ominus	Gibbs free energy gap of standard state
ΔH^\ominus	Enthalpy change of standard state
ΔS^\ominus	Entropy change of standard state
Greek Symbols	
λ_2	The second largest eigenvalue of electron density Hessian matrix
ρ	electron density
$ \nabla\rho(\mathbf{r}) $	Module of electron density gradient

2. Chemical equations based on atomic number conservation

Based on atomic number conservation (Path1):



Based on atomic number conservation (Path2):



3. Optimized structure parameters of reactants and products

Table 1 Optimized structure parameters of reactants and products

Symbol	Bond(Å)	Angle (°)	Dihedral (°)
HIO ₃ -NO ₂			
I1			
O2	(R2-1)2.03825		
O3	(R3-1)1.74002	(A3-1-2)92.07045	
O4	(R4-2)2.78260	(A4-2-1)41.94017	(D4-2-1-3)103.35657
H5	(R5-2)0.97913	(A5-2-1)108.13694	(D5-2-1-3)-157.20270
H6	(R6-4)0.97766	(A6-4-2)75.66109	(D6-4-2-1)-138.39639
N7	(R7-2)1.96297	(A7-2-1)156.19467	(D7-2-1-3)35.18472
O8	(R8-7)1.17434	(A8-7-2)110.41544	(D8-7-2-1)-7.17642
O9	(R9-7)1.17815	(A9-7-2)113.72823	(D9-7-2-1)174.06450
HIO ₂ -HNO ₂			
I1			
O2	(R2-1)1.93017		
O3	(R3-2)4.62745	(A3-2-1) 82.40432	
H4	(R4-2)0.96757	(A4-2-1)107.70274	(D4-2-1-3) 97.11972
H5	(R5-3)3.10477	(A5-3-2) 47.42174	(D5-3-2-1) 28.83261
N6	(R6-3)1.20970	(A6-3-2) 76.39539	(D6-3-2-1) 17.29833
O7	(R7-6)1.21259	(A7-6-3)123.46799	(D7-6-3-2)-178.04113
O8	(R8-6)1.96470	(A8-6-3)115.89510	(D8-6-3-2) -8.75427
HIO-HNO ₂			
I1			
O2	(R2-1)2.20189		
O3	(R3-2)2.81794	(A3-2-1)157.14602	
H4	(R4-2)0.97211	(A4-2-1)97.43186	(D4-2-1-3)-80.08153
N5	(R5-3)1.21560	(A5-3-2)38.63330	(D5-3-2-1)174.40868
O6	(R6-5)1.21407	(A6-5-3)122.45189	(D6-5-3-2)-166.12128

H7	(R7-2)2.80045	(A7-2-1)35.09262	(D7-2-1-5)-57.04799
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HIO-HI

H1

I ₂	(R2-1)2.76226
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O3	(R3-1)0.97060	(A3-1-2)54.26776
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I4	(R4-3)3.15564	(A4-3-1)148.91539	(D4-3-1-2)-77.11391
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H5	(R5-3)0.97375	(A5-3-1)107.15543	(D5-3-1-2)-114.95589
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4. The change of standard thermodynamic parameters

Table S2 The change of standard thermodynamic parameters of the proposed two reaction pathways of iodate reduction by nitrous acid under temperatures of 298–373 K.

Reaction path	Path1	Path2
298 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-120.624	-166.811
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-85.930	-143.160
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.829	1.771
303 k		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-120.752	-166.977
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-85.347	-142.765
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.834	1.777
308 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-120.879	-167.144
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-84.761	-142.369
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.840	1.782
313 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-121.004	-167.311
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-84.175	-141.970
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.845	1.788
318 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-121.126	-167.477
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-83.586	-141.568
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.850	1.793
323 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-121.246	-167.641
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-82.996	-141.164
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.855	1.798
328 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-121.364	-167.805

$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-82.403	-140.758
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.860	1.803
333 K		333
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-121.481	-167.969
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-81.809	-140.348
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.865	1.809
338 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-121.594	-168.131
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-81.211	-139.938
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.870	1.814
343 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-121.707	-168.292
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-80.614	-139.523
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.875	1.819
348 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-121.815	-168.453
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-80.016	-139.107
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.879	1.824
353 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-121.924	-168.613
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-79.413	-138.690
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.884	1.829
358 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-122.029	-168.771
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-78.812	-138.269
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.889	1.834
363 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-122.132	-168.928
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-78.208	-137.846
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.894	1.839
368 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-122.233	-169.084
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-77.602	-137.422
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.898	1.844

373 K		
$\Delta E_0^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-113.595	-159.650
$\Delta E^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-143.770	-194.950
$\Delta H^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-122.330	-169.239
$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	-76.995	-136.995
$\Delta S^\ominus/(\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	1.903	1.849