Support Information

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

Chang Cui, [a] *Dongxiang Zhang,** [a] *Constantin Muhire,* [a] *Alemtsehay Tesfay Reda,* [a] *Jinying Li* [b, c] *and Xiyan Xu** [a]

a. *School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 102488, PR China. E-mail: boris@bit.edu.cn, xiyanxu@bit.edu.cn*
b. *Department of Radiochemistry, China Institute of Atomic Energy, Beijing, PR China.*
c. *Institute of Nuclear Technology, Chinese Nuclear Society, Beijing 100070, PR China.*

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^{Θ}	Internal energy change in ground state
ΔE_{elec}^{Θ}	electronic binding energy change of standard state
ΔE_{rot}^{Θ}	electronic rotation energy change of standard state
$\Delta E_{trans}^{\Theta}$	electronic translation energy change of standard state
ΔE_{vib}^{Θ}	electronic vibration energy change of standard state
ΔE^{Θ}	Sum of electronic energy change and thermal correction to Internal energy
ΔG^{Θ}	Gibbs free energy gap of standard state
ΔH^{Θ}	Enthalpy change of standard state
ΔS^{Θ}	Entropy change of standard state
Greek Symbols	
λ_2	The second largest eigenvalue of electron density Hessian matrix
ρ	electron density
$\lvert\nabla\rho(r)\rvert$	Module of electron density gradient

2. Chemical equations based on atomic number conservation

Based on atomic number conservation (Path1):

$$\mathbf{H_2O + 2\ IO_3^- + 5\ NO_2^- \rightarrow H_2O + 2\ IO_2^- + 3\ NO_2^- + 2\ NO_3^-} \quad \textbf{(Eq. S1)}$$

$$\mathbf{H_2O + 2\ IO_2^- + 3\ NO_2^- + 2\ NO_3^- \rightarrow H_2O + 2\ IO^- + NO_2^- + 4\ NO_3^-} \quad \textbf{(Eq. S2)}$$

$$\mathbf{H_2O + 2\ IO^- + NO_2^- + 4\ NO_3^- \rightarrow H_2O + I^- + IO^- + 5\ NO_3^-} \quad \textbf{(Eq. S3)}$$

$$\mathbf{H_2O + I^- + IO^- + 5\ NO_3^- \rightarrow 2\ OH^- + I_2 + 5\ NO_3^-} \quad \textbf{(Eq. S4)}$$

Based on atomic number conservation (Path2):

$$\mathbf{2\ HIO_3 + 5\ HNO_2 \rightarrow 2\ HIO_2 + 3\ HNO_2 + 2\ H^+ + 2\ NO_3^-} \quad \textbf{(Eq. S5)}$$

$$\mathbf{2\ HIO_2 + 3\ HNO_2 + 2\ H^+ + 2\ NO_3^- \rightarrow 2\ HIO + HNO_2 + 4\ H^+ + 4\ NO_3^-} \quad \textbf{(Eq. S6)}$$

$$\mathbf{2\ HIO + HNO_2 + 4\ H^+ + 4\ NO_3^- \rightarrow 6\ H^+ + I^- + HIO + 5\ NO_3^-} \quad \textbf{(Eq. S7)}$$

$$\mathbf{6\ H^+ + I^- + HIO + 5\ NO_3^- \rightarrow 5\ H^+ + H_2O + I_2 + 5\ NO_3^-} \quad \textbf{(Eq. S8)}$$

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
		HIO−HI	
H1			
I_2	(R2−1)2.76226		
O3	(R3−1)0.97060	(A3−1−2)54.26776	
I4	(R4−3)3.15564	(A4−3−1)148.91539	(D4−3−1−2)−77.11391
H5	(R5−3)0.97375	(A5−3−1)107.15543	(D5−3−1−2)−114.95589

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

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

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