Kinetics of the Belousov-Zhabotinsky Reaction

By Mary Jost

Mentors- Dr. Rainer Glaser and Dr. Carmen Chicone

Our Goals

We would like to find a model using *Mathematica* that accurately depicts the oscillating reaction.

We need to do two things to accomplish this

1) Understand the chemistry of the reaction
2) Accurately model our oscillating reaction

This week we'll focus on the first topic.

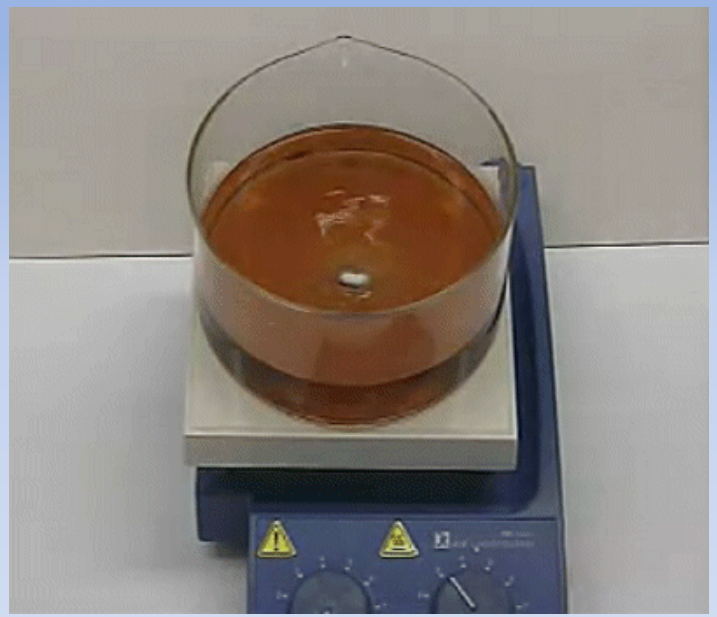
Belousov-Zhabotinsky Reaction

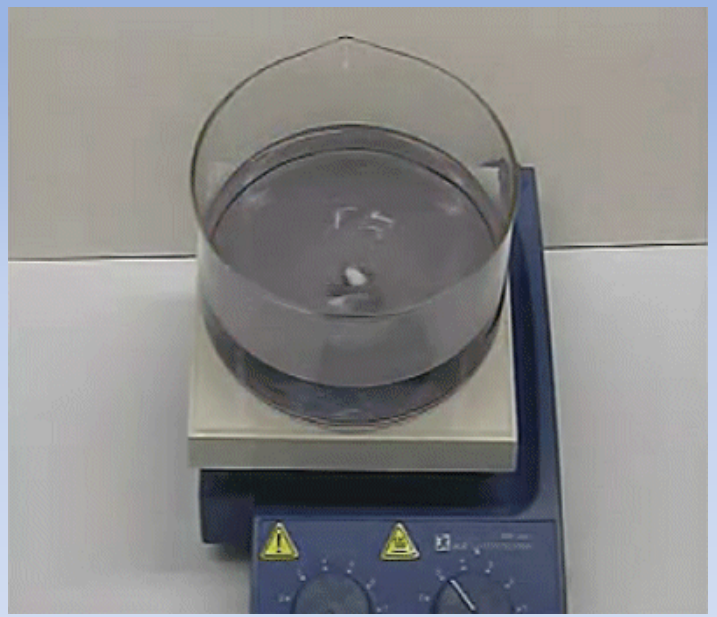
The BZ reaction is the most famous oscillating reaction. Players- Br_2, BrO_3^-, $BrO_2\bullet$, H^+, Br^-, $HBrO_2$, Ce^{4+}, Ce^{3+}, HOBr

Starting Materials- Potassium Bromide, Potassium Bromate, Malonic Acid, and Concentrated Sulfuric Acid. And later added Iron (2+).

The first reaction will be yellow and then change to clear in about 90 seconds.

Belousov-Zhabotinsky Reaction



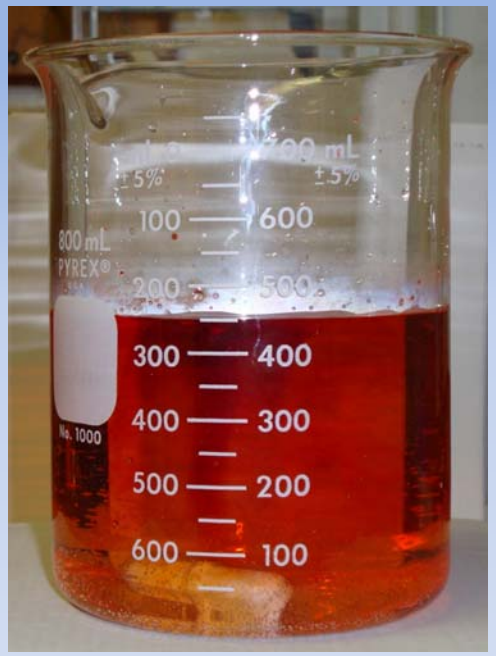


http://www.uni-regensburg.de/Fakultaeten/nat_Fak_IV/Organische_Chemie/Didaktik/Keusch/D-oscill-e.htm

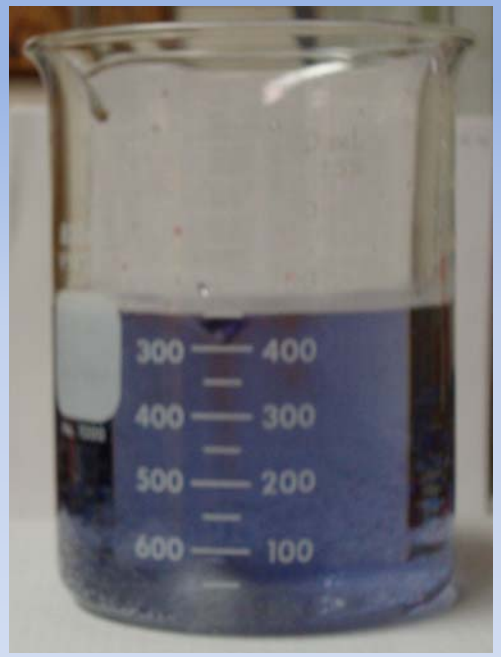
Belousov-Zhabotinsky Reaction

Once the solution is clear we add the Fe^{2+}. This indicator will show us the reaction oscillating. The solution turns bright red which lasts for about 2 minutes and then turns a light blue. This can repeat for an hour.

Belousov-Zhabotinsky Reaction



Fe^{2+}



Fe^{3+}

Belousov-Zhabotinsky Reaction
Noyes-Field-Koros 1972b Model

$BrO_3^- + Br^- + 2\,H^+$	⇆	$HBrO_2 + HOBr$	(R3) slow
$HBrO_2 + Br^- + H^+$	⇆	$2\,HOBr$	(R2)
$HOBr + Br^- + H^+$	⇆	$Br_2 + H_2O$	(R1)
$2\,HBrO_2$	⇆	$BrO_3^- + HOBr + H^+$	(R4)
$BrO_3^- + HBrO_2 + H^+$	⇆	$2\,BrO_2\bullet + H_2O$	(R5) slow
$BrO_2\bullet + Ce^{3+} + H^+$	⇆	$HBrO_2 + Ce^{4+}$	(R6)
$BrO_2\bullet + Ce^{4+} + H_2O$	⇆	$BrO_3^- + Ce^{3+} + 2H^+$	(R7)

Field, R. J.; Koros, E.; Noyes, R. N. *J. Am. Chem. Soc.* **1972**, *94*, 8649-8664.

Initial Concentrations (Mol/L)

$[Br^-] = 0.012$

$[BrO_3^-] = 0.0891$

$[HOBr] = 0$

$[Br_2] = 0$

$[MA] = 0.1653$

$[HBr] = 0$

$[BMA] = 0$

$[Mred] = 0.0017$

$[Mox] = 0$

$[HCO_2H] = 0$

$[CO_2] = 0$

$[H^+] = 0.7931/2$

Assumes only one Hydrogen is deprotonation.

Rate Constants

TABLE I: FKN Rate Constants

reactn	$k_{forward}$	$k_{reverse}$	K_{equil}
R1	$k_1 = 8 \times 10^9\ M^{-2}\ s^{-1}$	$k_{-1} = 110\ s^{-1}$	$7.3 \times 10^7\ M^{-2}$
R2	$k_2 = 2 \times 10^9\ M^{-2}\ s^{-1}$	$k_{-2} = 5.0 \times 10^{-5}\ M^{-1}\ s^{-1}$	$4.0 \times 10^{13}\ M^{-1}$
R3	$k_3 = 2.1\ M^{-3}\ s^{-1}$	$k_{-3} = 1 \times 10^4\ M^{-1}\ s^{-1}$	$2.1 \times 10^{-4}\ M^{-2}$
R4	$k_4 = 4 \times 10^7\ M^{-1}\ s^{-1}$	$k_{-4} = 2 \times 10^{-10}\ M^{-2}\ s^{-1}$	$2.0 \times 10^{17}\ M$
R5 = R5′ + R5″	$k_5 = 1 \times 10^4\ M^{-2}\ s^{-1}$	$k_{-5} = 2 \times 10^7\ M^{-1}\ s^{-1}$	$5.0 \times 10^{-4}\ M^{-1}$
R6	$k_6 = 6.5 \times 10^5\ M^{-2}\ s^{-1}$	$k_{-6} = 2.4 \times 10^7\ M^{-1}\ s^{-1}$	$2.7 \times 10^{-2}\ M$
R7	$k_7 = 9.6\ M^{-1}\ s^{-1}$	$k_{-7} = 1.3 \times 10^{-4}\ M^{-3}\ s^{-1}$	$7.4 \times 10^4\ M^2$

TABLE II: Revised Rate Constants and Thermodynamic Data[a]

reactn	$k_{forward}$	$k_{reverse}$	K_{equil}	$\Delta G°$ (±1),[b] kJ/mol
R1	$k_1 = 8 \times 10^9\ M^{-2}\ s^{-1}$	$k_{-1} = 110\ s^{-1}$	$7.3 \times 10^7\ M^{-2}$	−44
R2	$k_2 = 3 \times 10^6\ M^{-2}\ s^{-1}$	$k_{-2} = 2 \times 10^{-5}\ M^{-1}\ s^{-1}$	$1.5 \times 10^{11}\ M^{-1}$	−63
R3	$k_3 = 2\ M^{-3}\ s^{-1}$	$k_{-3} = 3.2\ M^{-1}\ s^{-1}$	$0.6\ M^{-2}$	+1
R4	$k_4 = 3000\ M^{-1}\ s^{-1}$	$k_{-4} = 1 \times 10^{-8}\ M^{-2}\ s^{-1}$	$3 \times 10^{11}\ M$	−64
R5′	$k_{5'} = 42\ M^{-2}\ s^{-1}$	$k_{-5'} = 2.2 \times 10^3\ s^{-1}$	$1.9 \times 10^{-2}\ M^{-2}$	+10
R5″	$k_{5''} = 7.4 \times 10^4\ s^{-1}$	$k_{-5''} = 1.4 \times 10^9\ M^{-1}\ s^{-1}$	$5.3 \times 10^{-5}\ M$	+24
R5 = R5′ + R5″	$k_5 = 42\ M^{-2}\ s^{-1}$	$k_{-5} = 4.2 \times 10^7\ M^{-1}\ s^{-1}$	$1 \times 10^{-6}\ M^{-1}$	+34
R6	$k_6 = 8 \times 10^4\ M^{-2}\ s^{-1}$	$k_{-6} = 8.9 \times 10^3\ M^{-1}\ s^{-1}$	$9\ M^{-1}$	−5
R7	$k_7 \simeq 0$	$k_{-7} \simeq 0$	$1.2 \times 10^5\ M^2$	−29

[a] All calculations were carried out at 293.15 K. [b] These $\Delta G°$ values were calculated from the equilibrium constant in the preceding column using $\Delta G° = -RT \ln K$. Because of roundoff errors (and in the cases of reactions R1 and R3 corrections for nonideality) they will differ slightly from $\Delta G°$ values calculated directly from the following $\Delta G_f°$ values. Free energies of formation in kJ/mol used are, Br^- = −102.8,[c] Br_2 = +4.1,[c] HOBr = −83.3,[c] $BrO_2^\bullet \simeq 144 \pm 1$,[c] BrO_2^- = 27,[c] $HBrO_2 \simeq -0.4 \pm 1$,[d] BrO_3^- = 18,[c] BrO_4^- = 118.3,[e] H_2O = −237.1.[c] The values for $BrO_2^\bullet$ and $HBrO_2$ are estimated from kinetic measurements and must be uncertain by at least ±1 kJ/mol. [c] Tyson, J. J. In *Oscillations and Traveling Waves in Chemical Systems*"; Field, R. J., Burger, M., Eds.; Wiley-Interscience: New York, 1985. [d] This work. [e] Schreiner, F.; Osborne, D. W.; Pocius, A. V.; Appleman, E. H. *Inorg. Chem.* **1970**, *9*, 2320. This quantity is not used in the calculations reported here but is included for completeness. Reaction R5′ is assumed to be rate determining for reaction R5 in both the forward and the reverse directions.

$HBrO_2$ Destruction & Steady State

$$2\ HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+ \qquad (R4)$$

$$[HBrO_2]_d'(t) = -2k_4\ [HBrO_2]^2$$

Steady State: rate of formation & rate of destruction are equal

$$[HBrO_2]_f'(t) = [HBrO_2]_d'(t)$$

$$+k_5\ [BrO_3^-]\ [HBrO_2]\ [H^+] = -2k_4\ [HBrO_2]^2$$

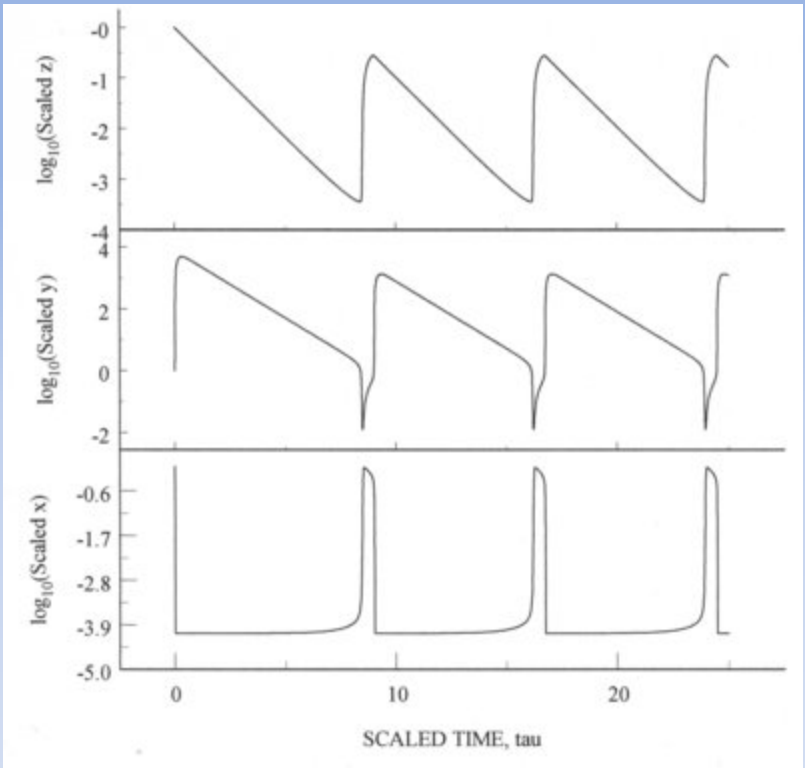
$$[HBrO_2]_{ss}'(t) = (k_5/2k_4)\ [BrO_3^-]\ [H^+]$$

Oscillating Species: Oregonator

Z = Ce(IV)

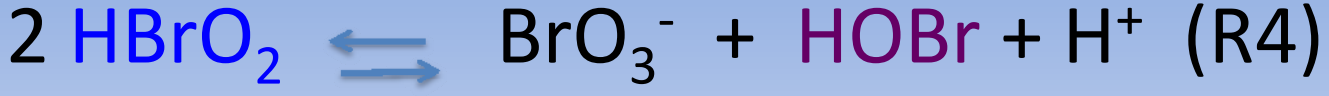
Y = Br^-

X = $HBrO_2$



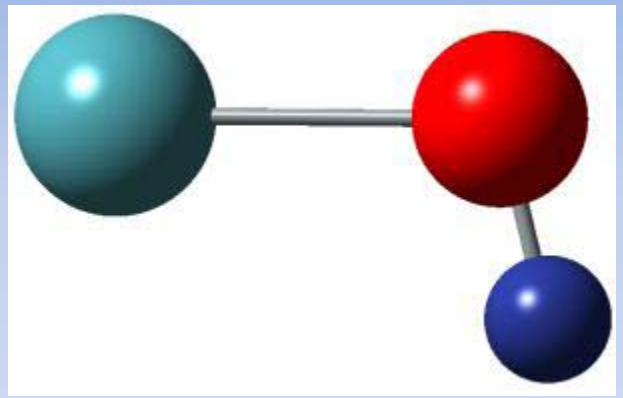
http://www.scholarpedia.org/article/Oregonator

A Closer Look At Step 4

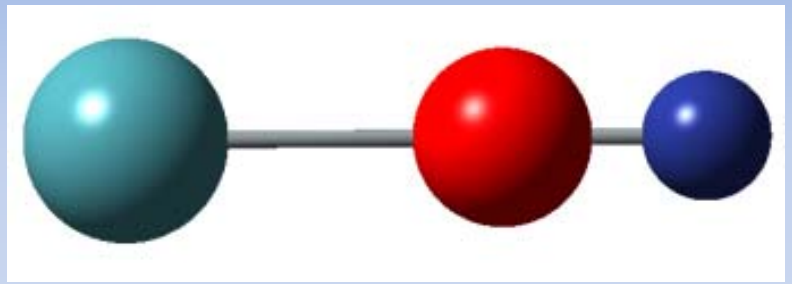


There are multiple options for each molecule that will affect the successfulness of the reaction.

HOBr

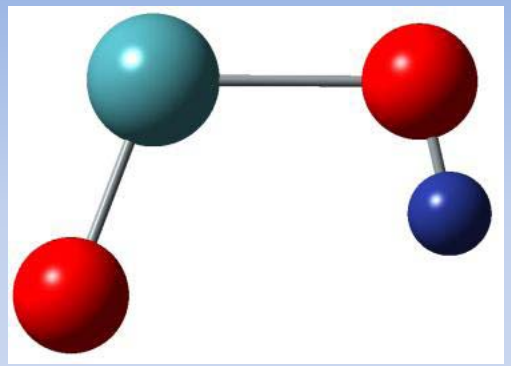


HOBr, Cs, 1a

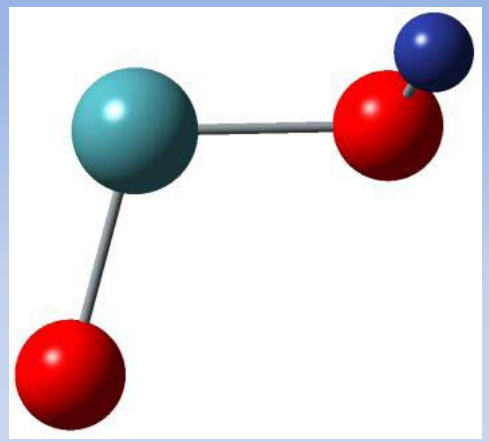


HOBr, C∞h, 1b

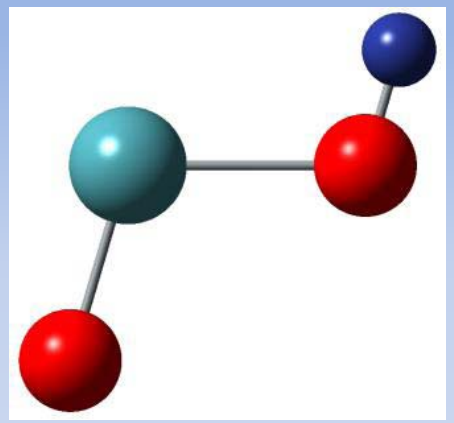
$HBrO_2$



HBrO2, Cs, cis, TS, **2b**

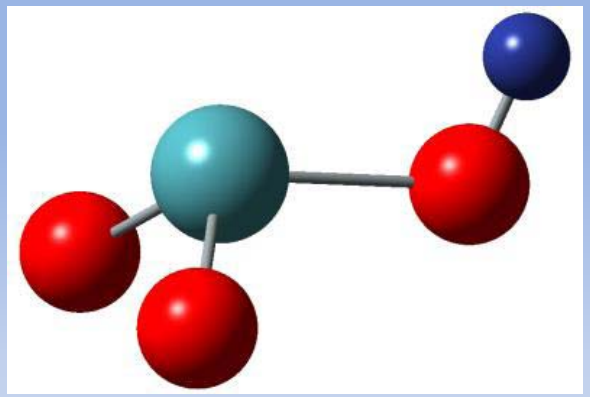


HBrO2, C1, **2a**

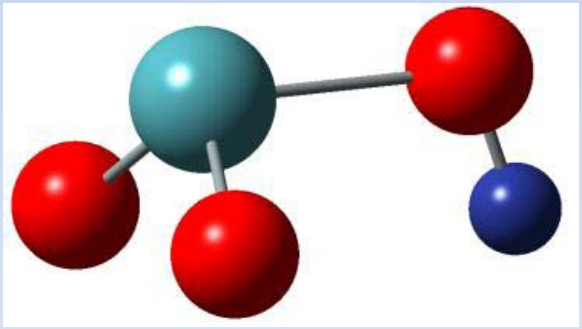


HBrO2, Cs, trans,TS,**2c**

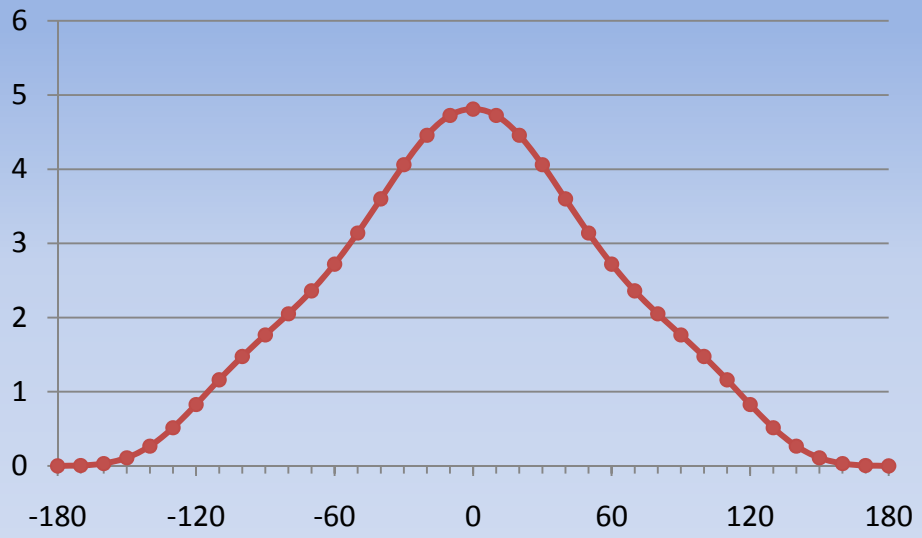
BrO_3^-



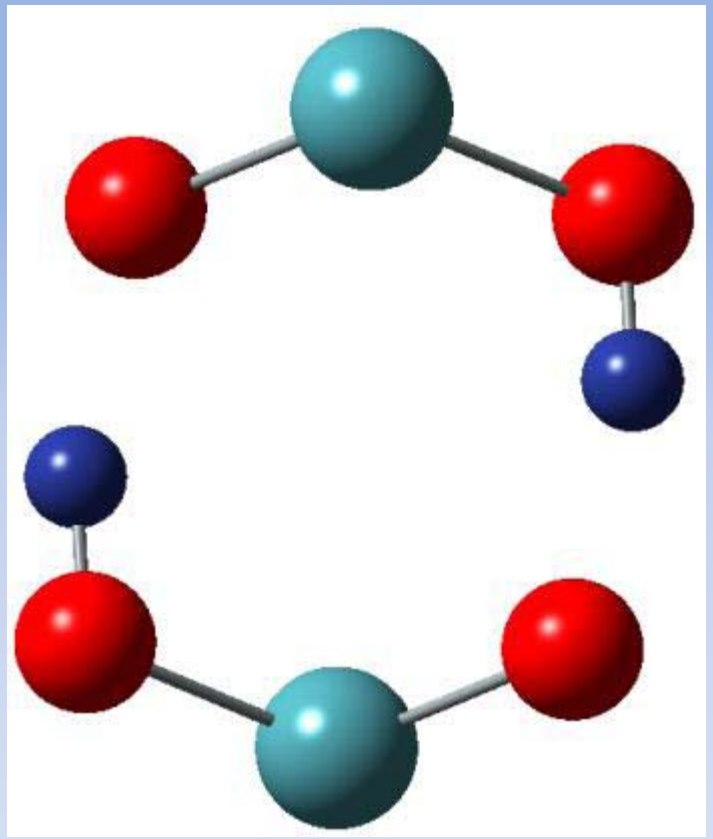
HBrO3, Cs, syn, TS, **3a**

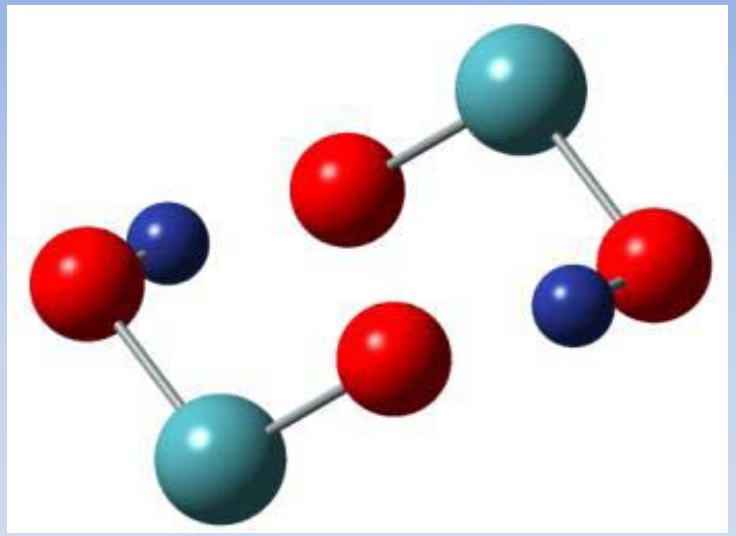


HBrO3, Cs, anti, **3b**



5 options for 2 $HBrO_2$

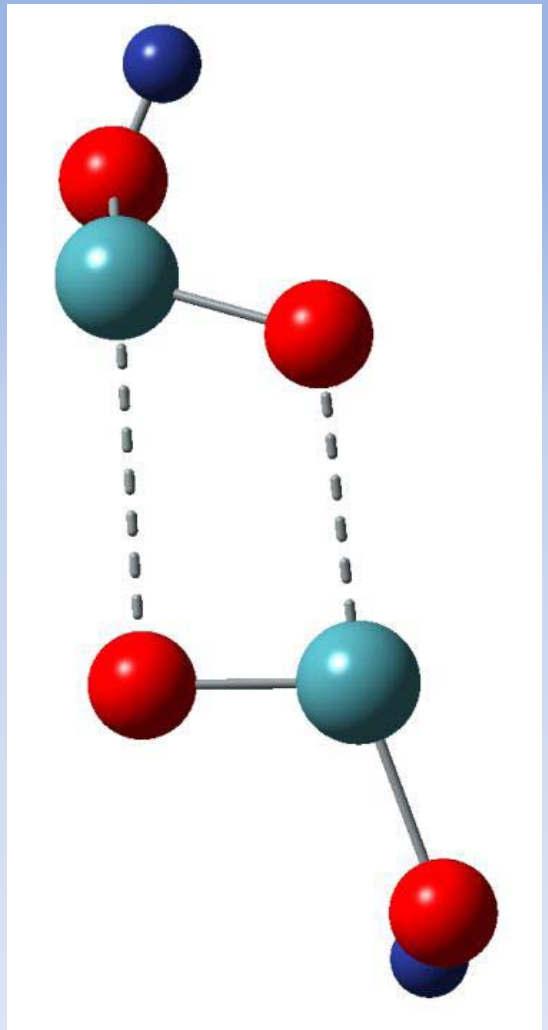




4a

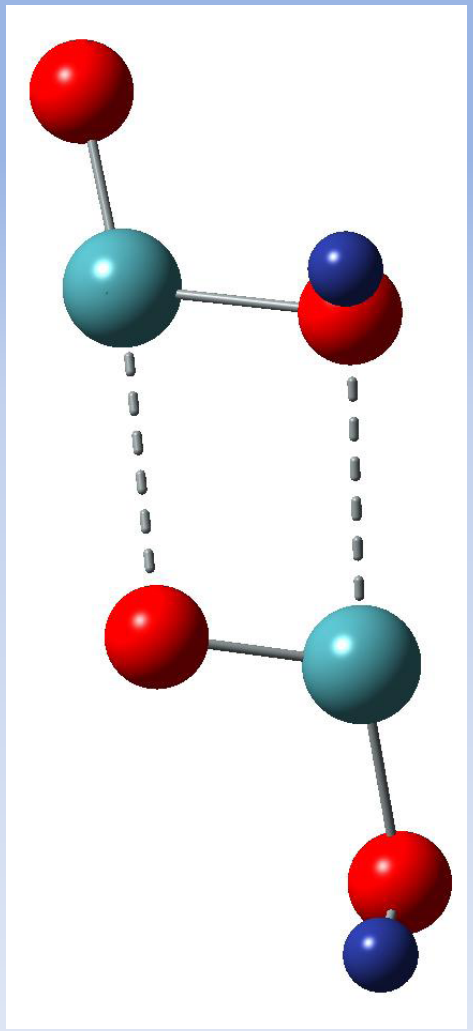
5 options for 2 $HBrO_2$

4b

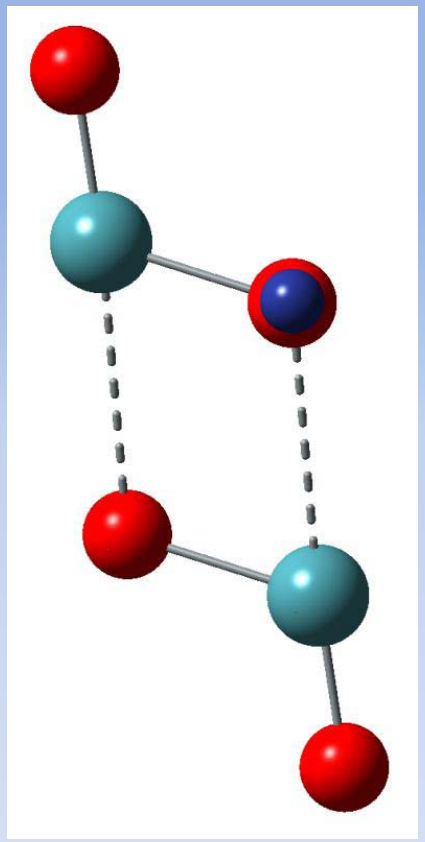


5 options for 2 $HBrO_2$

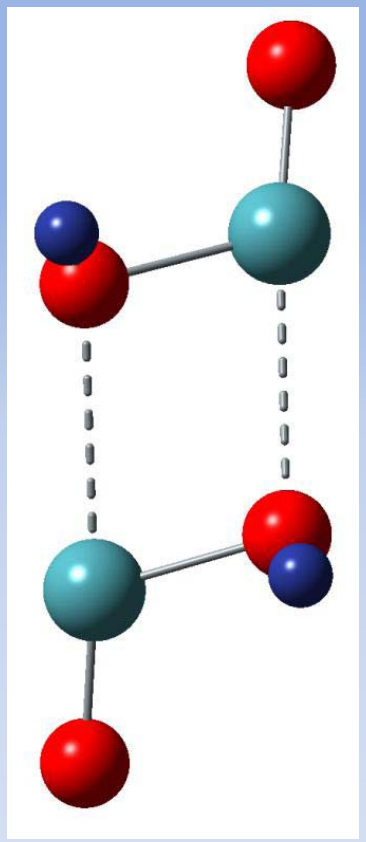
4c



5 options for 2 $HBrO_2$

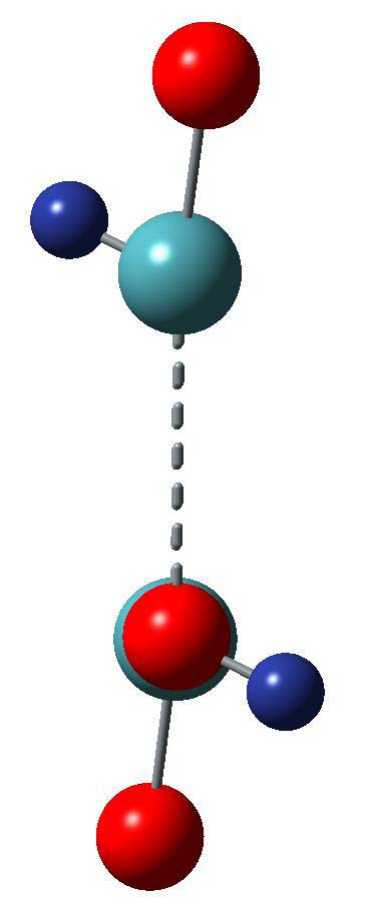


Trans-**4d**

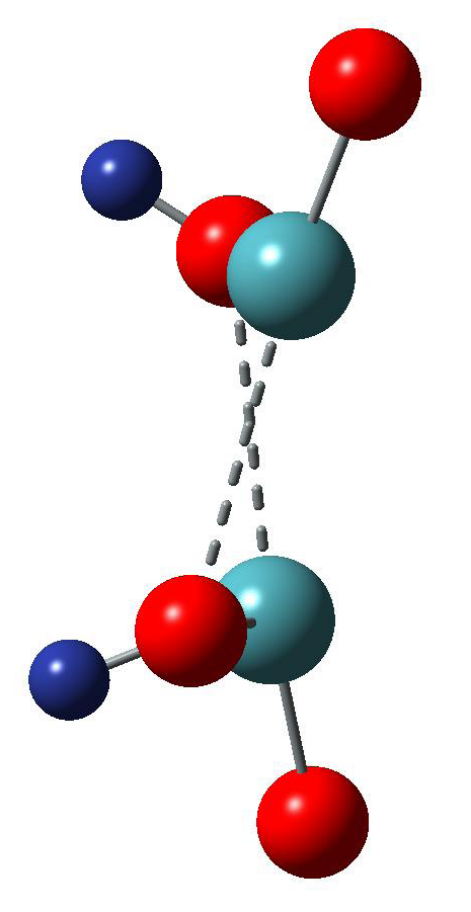


Cis-**4d**

5 options for 2 $HBrO_2$

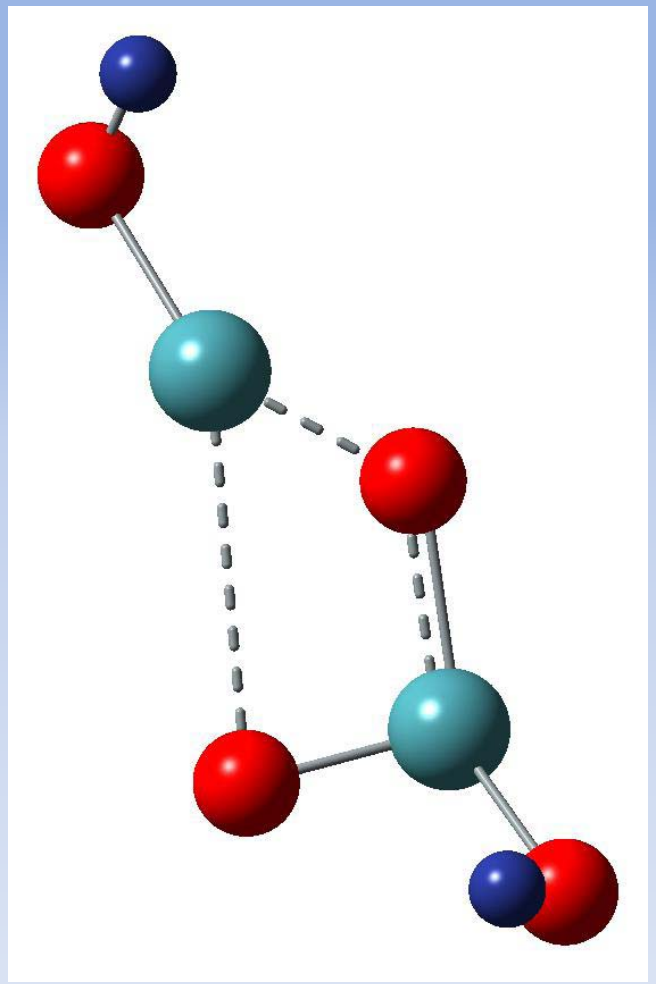


Trans-**4d**



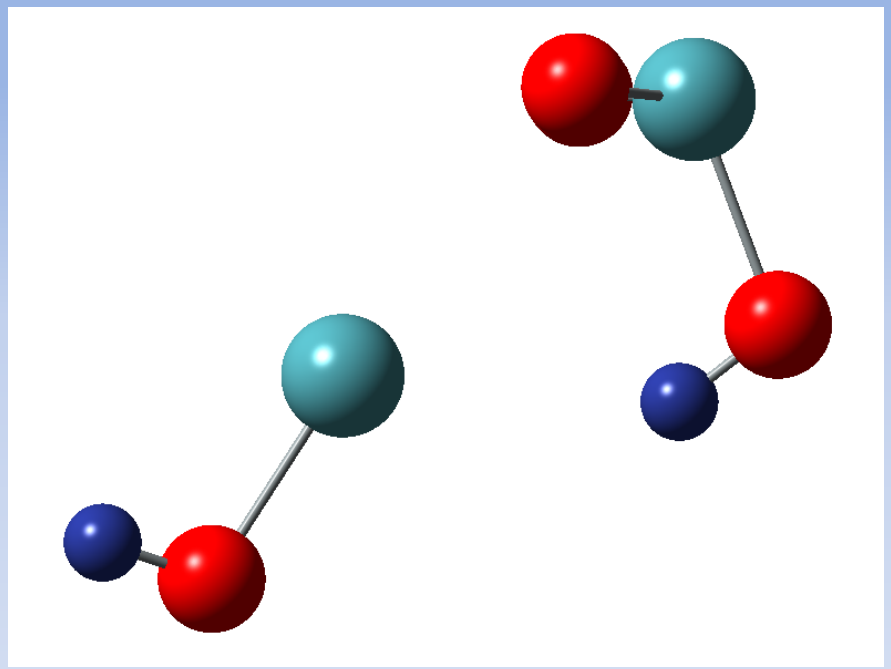
Cis-**4d**

Transition State- Oxygen Transfer

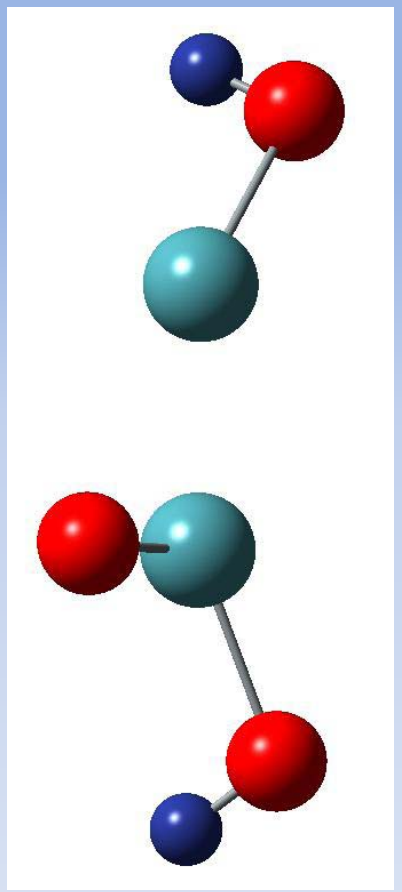


6a, TS(**4b**,**5**)

Products



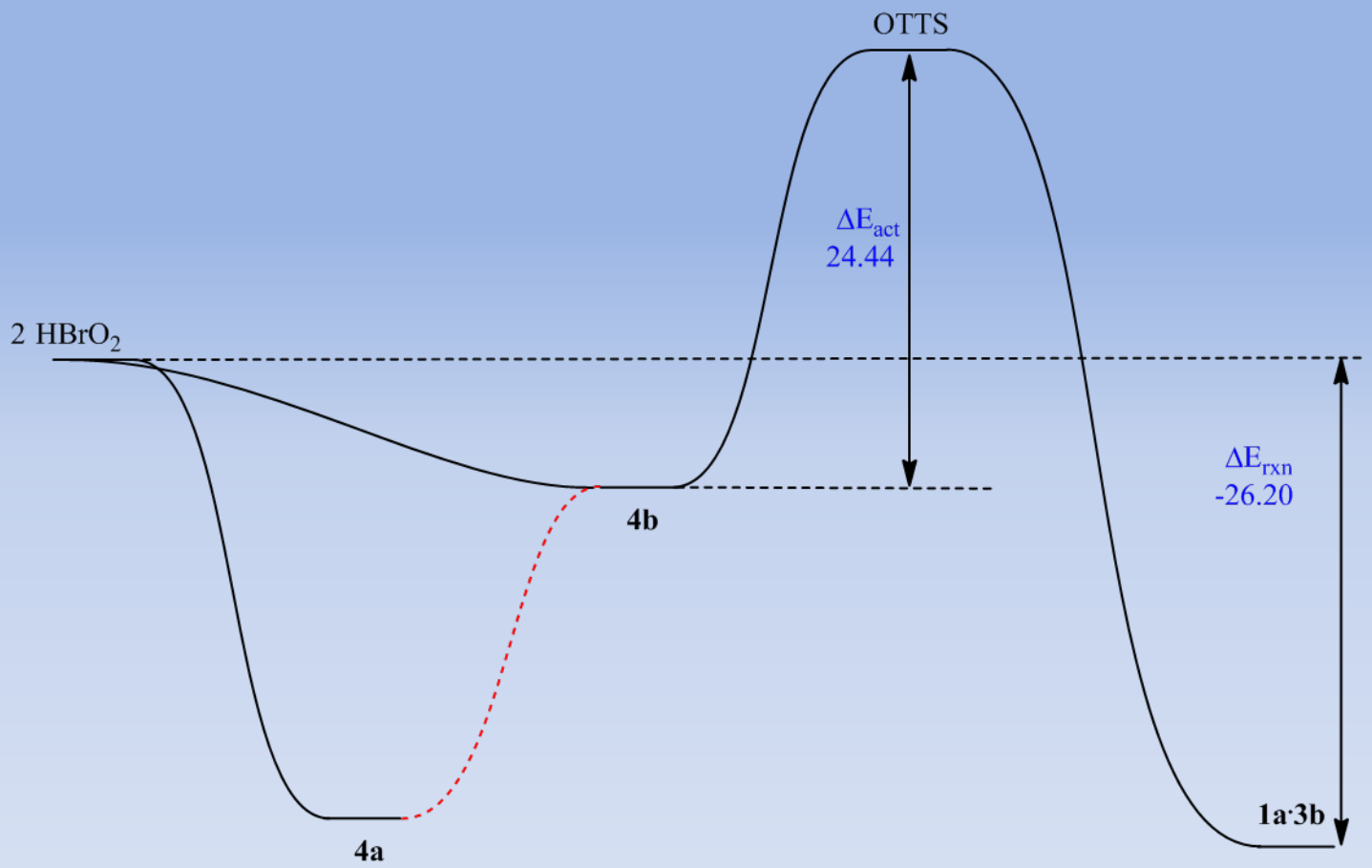
5a



5b

Table 2. Relative and Reaction Energies

Relation / Reaction	ΔE	ΔH_0	ΔH_{298}	ΔG_{298}
E_{rel}, **1b** *vs.* **1a**	46.28	45.28	44.93	46.36
E_{act}, **2a** → **2b**	3.02	2.27	2.11	2.29
E_{act}, **2a** → **2c**	8.08	7.30	7.14	7.35
E_{act}, **3b** → **3a**	4.81	4.66	4.17	5.56
E_{rel}, **4b** *vs.* **4a**	18.03	16.46	17.44	14.40
E_{rel}, **4c** *vs.* **4a**	18.11	16.43	17.44	14.64
E_{rel}, cis-**4d** *vs.* **4a**	18.90	17.12	18.16	15.49
E_{rel}, trans-**4d** *vs.* **4a**				
E_{rel}, TS(**4b**,**4c**) *vs.* **4a**				
E_{dim}, 2 **2a** → **4a**	-27.17	-24.84	-24.76	-12.41
E_{dim}, 2 **2a** → **4b**	-9.14	-8.37	-7.31	1.99
E_{rel}, **5b** *vs.* **5a**				
E_{act}, **4b** → **6a**	25.85	24.96	24.44	26.67
E_{rxn}, **4b** → **5a**	-26.50	-26.26	-26.20	-26.40
E_{diss}, **5a** → **1a** + **3b**	5.37	4.46	3.51	-5.56
E_{rxn}, 2 **2a** → **1a** + **3b**	-30.27	-30.17	-30.01	-29.97


OTTS
ΔE_{act}
24.44
2 $HBrO_2$
4b
ΔE_{rxn}
-26.20
4a
1a·3b