Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information: The Kinetics and Mechanism of the Oxidation of Pyruvate ion by Hypochlorous Acid

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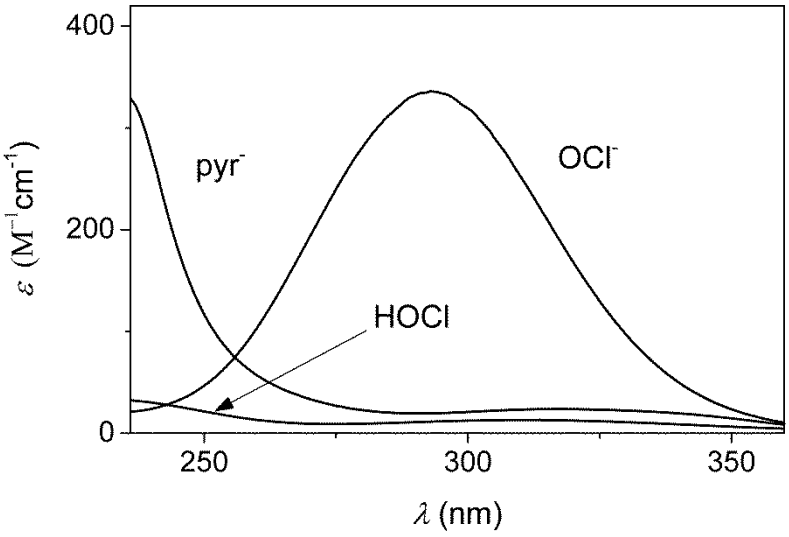

Figure S1. The molar absorbtivity of the reactants

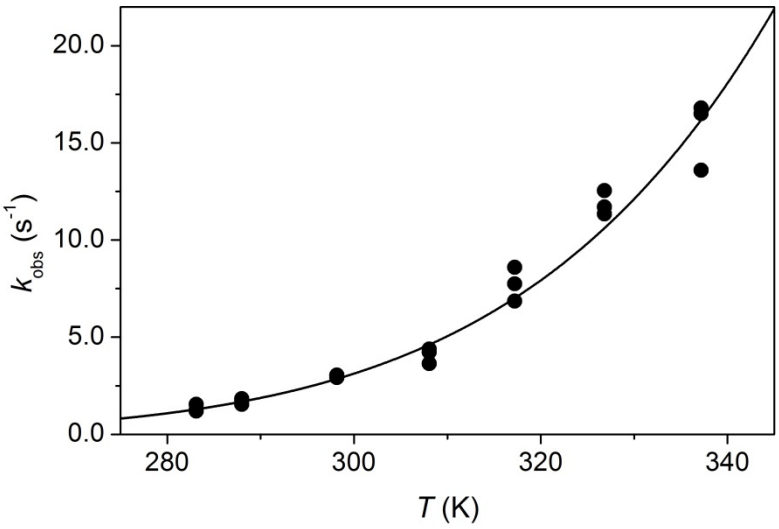

Figure S2. The pseudo first order rate constant as a function of temperature. The experimental data (dots) were fitted to the Eyring equation (solid line), $k_{obs} \approx k_{HOCl}$. pH = 2.8, I = 1.0 M ($NaClO_4$) $\Delta H_{HOCl}^{\neq} = 34.6 \pm 1.2$ kJmol^{-1}, $\Delta S_{HOCl}^{\neq} = -120.3 \pm 3.6$ Jmol^{-1}K^{-1}. The pre-exponential factor of the Arrhenius equation was calculated from $\Delta S_{HOCl}^{\neq}$: $A_{HOCl} = 8.8 \times 10^6$ s^{-1}.

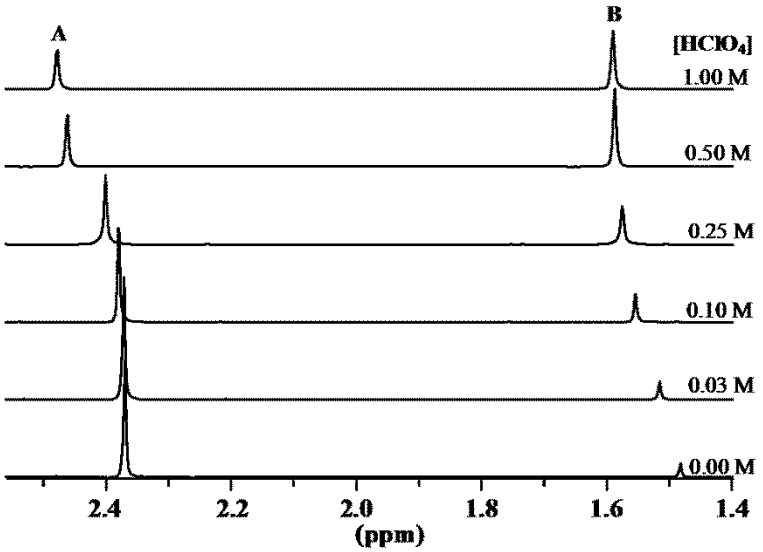

Figure S3. The ^{1}H NMR spectra of a pyruvic acid solution as a function of acid concentration: the CH_3 peak of pyruvate ion and pyruvic acid (A) and hydrated pyruvic acid (B)

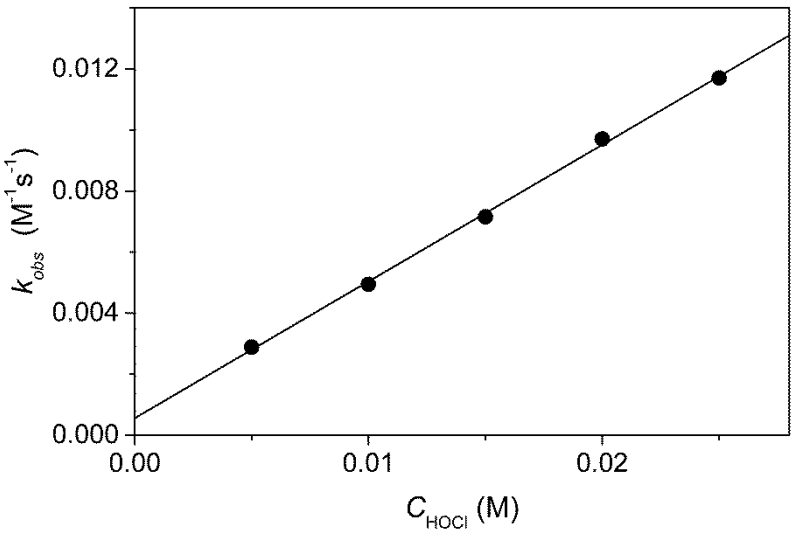

Figure S4. The pseudo-first-order rate constant as a function of HOCl concentration. Experimental data (dots) were fitted to a straight line (solid line). λ = 220 nm, [PYR] = 0.001 M, pH = 1.0, I = 1.0 M ($NaClO_4$)

nucleophilic oxygen electrophilic carbon

Figure S5. Calculated ESP Charges (Electrostatic Potential) for the transition state from two viewing angles. Red cloud: nucleophilic character; blue color: electrophilic character.

Table S1. The stoichiometry of the pyruvate ion – hydrochlorous acid reaction as a function of pH

pH	$C_{0\,PYR}$ (M)	$C_{0\,Cl(I)}$ (M)	$\Delta C_{PYR}/\Delta C_{Cl(I)}$
2.0	0.0125	0.0374	1.00
	0.0374	0.0374	0.93
	0.1120	0.0374	0.99
4.00	0.0125	0.0187	1.01
	0.0374	0.0374	0.99
	0.1120	0.0374	1.03
6.00	0.0125	0.0187	1.03
	0.0374	0.0374	0.98
	0.1120	0.0374	0.87
	0.0374	0.0374	0.94
	0.0448	0.0374	0.94
	0.0561	0.0374	0.95
	0.0747	0.0374	1.01
	0.0860	0.0374	1.01
	0.0934	0.0374	1.16
8.00	0.0125	0.0187	1.00
	0.0374	0.0374	0.95
	0.1120	0.0374	0.94
10.00	0.0125	0.0187	0.99
	0.0374	0.0374	0.95
	0.1120	0.0374	1.00
		Average	0.98 ± 0.01

The stoichiometry of the reaction is as follows.

$$CH_3COCOOH + HOCl = CH_3COOH + CO_2 + H^+ + Cl^-$$

Table S2. The calculated reaction Gibbs free energies of the pyruvate ion – HOCl and the pyruvate ion – HOCl – H_2O systems (in kJmol^{-1}).

		ΔG_r	
Functional	Basis set	pyruvate ion – HOCl	pyruvate ion – HOCl – H_2O
B3LYP	6-31+G(d,p)	-330.1	-342.4
	6-311+G(d,p)	-365.2	-390.1
M06	6-31+G(d,p)	-371.6	-397.5
	6-311+G(d,p)	-410.2	-421.0

Table S3. Predicted parameters of activation for the pyruvate ion – HOCl and the pyruvate ion – HOCl – H_2O systems by the DFT method

Functional	Basis set	pyruvate ion – HOCl		pyruvate ion – HOCl – H_2O	
		$\Delta H^{\ddagger}$ (kJmol^{-1})	$\Delta S^{\ddagger}$ (Jmol^{-1}K^{-1})	$\Delta H^{\ddagger}$ (kJmol^{-1})	$\Delta S^{\ddagger}$ (Jmol^{-1}K^{-1})
B3LYP	6-31+G(d,p)	123.6	-34.0	116.8	-40.2
	6-311+G(d,p)	111.2	-34.9	102.5	-65.1
M06	6-31+G(d,p)	128.8	+5.0	105.6	-25.6
	6-311+G(d,p)	116.0	-12.6	101.2	-0.3

Table S4. Transition states

Transition states of the pyruvate – HOCl system (x, y, z coordinates)

B3LYP/6-31+G(d,p)

Imaginary frequency: -637.7

C	-0.89061600	0.76013300	0.37461200
O	-1.02461100	0.95912600	1.56265800
C	-0.90468200	1.84536700	-0.67238600
H	-0.25059100	2.65655300	-0.33995200
H	-0.58657400	1.46915800	-1.64321300
H	-1.92370600	2.23653300	-0.75771600
C	-1.43212500	-0.86112100	-0.17054400
O	-1.26930300	-1.75235700	0.66240900
O	-2.02041500	-0.72503000	-1.24220100
H	0.76685900	-0.90098600	0.52265400
O	0.84039800	-0.15127100	-0.09948700
Cl	2.89117600	-0.15125100	-0.11993500

B3LYP/6-311+G(d,p)

Imaginary frequency: -623.9

C	-0.92623700	0.77422800	0.36885200
O	-1.08421700	0.98491600	1.54204500
C	-0.90513800	1.83759000	-0.69793100
H	-0.28707100	2.66848800	-0.35102300
H	-0.53197300	1.44722000	-1.64095400
H	-1.92506200	2.20416800	-0.84373100
C	-1.42319300	-0.87484900	-0.17583900
O	-1.30029700	-1.74525700	0.67448400
O	-1.94782600	-0.75509800	-1.27382000
H	0.78569300	-0.90039300	0.58442500
O	0.86062200	-0.16524700	-0.04873200
Cl	2.89762200	-0.14093100	-0.11006000

M06/6-31+G(d,p)

Imaginary frequency: -700.2

C	-0.93984900	0.76679700	0.35700400
O	-1.12053000	0.99521800	1.52801300
C	-0.93802900	1.79830200	-0.72540500
H	-0.36606400	2.66515900	-0.37920000

H	-0.51722500	1.40096800	-1.64976700
H	-1.96895300	2.11730000	-0.91332900
C	-1.37224300	-0.89270000	-0.17445400
O	-1.24878400	-1.72426700	0.71482300
O	-1.86076300	-0.81818000	-1.29350300
H	0.77592500	-0.81332400	0.63648300
O	0.83692100	-0.11001100	-0.03796900
Cl	2.86601700	-0.12626900	-0.10164600

M06/6-311+G(d,p)

Imaginary frequency: -686.9

C	-0.96155300	0.77065600	0.35759500
O	-1.14154300	1.00064600	1.51841600
C	-0.95632800	1.79214500	-0.73233200
H	-0.38375800	2.66096100	-0.39557400
H	-0.53929900	1.38728200	-1.65309400
H	-1.98625400	2.11117700	-0.92036700
C	-1.36821100	-0.90498300	-0.17300400
O	-1.23568500	-1.72900100	0.71054400
O	-1.84898400	-0.83027000	-1.28625500
H	0.78267400	-0.82204800	0.62968500
O	0.85212200	-0.10879700	-0.02751800
Cl	2.87270100	-0.11440600	-0.09974700

Transition states of the pyruvate – HOCl – H_2O system(x, y, z coordinates)

B3LYP/6-31+G(d,p)

Imaginary frequency: -662.4

C	0.80852600	-0.68879700	0.69412200
O	0.93199900	-0.18242300	1.79436800
C	0.71225900	-2.17975300	0.46787200
H	-0.03863300	-2.58463600	1.15235300
H	0.45550700	-2.41583800	-0.56284300
H	1.68016400	-2.63131000	0.70823700
C	1.59734500	0.20928900	-0.63206600
O	1.75000800	1.41896300	-0.40906200
O	2.01805800	-0.57822600	-1.47552600
H	-0.81993600	0.83970100	0.03915300
O	-0.73450200	-0.10677800	-0.27318200
Cl	-2.75374700	-0.42460200	-0.35287900
O	-0.55117200	2.50566800	0.52585200

H	-0.87786600	3.16668900	-0.09947800
H	0.39055000	2.34155800	0.28235600

B3LYP/6-311+G(d,p)

Imaginary frequency: -646.6

C	0.89222100	-0.67968700	0.71308500
O	1.03414800	-0.15129100	1.78667900
C	0.81750600	-2.17089400	0.50141700
H	0.12576700	-2.59131300	1.23449300
H	0.50201500	-2.41625600	-0.50843600
H	1.80977100	-2.59474300	0.67888300
C	1.56507200	0.23695200	-0.68874500
O	1.69198700	1.44136200	-0.47407100
O	1.94590700	-0.54827800	-1.54122900
H	-0.86025800	0.80485200	0.07364300
O	-0.75968400	-0.13371900	-0.22966300
Cl	-2.77570600	-0.47902200	-0.33723000
O	-0.59055100	2.52214200	0.56451600
H	-0.94855800	3.19785200	-0.02201900
H	0.33503000	2.38303100	0.27195500

M06/6-31+G(d,p)

Imaginary frequency: -743.6

C	0.83487600	-0.64764900	0.72154700
O	0.96118900	-0.07856800	1.78363200
C	0.72887700	-2.13462700	0.56961400
H	0.00082800	-2.50328400	1.30014300
H	0.43242100	-2.41795800	-0.44041900
H	1.70291200	-2.58238100	0.79480100
C	1.55892200	0.18976500	-0.67815500
O	1.71470400	1.39721800	-0.49680800
O	1.92967400	-0.63346400	-1.50214500
H	-0.81461500	0.82380400	0.02441700
O	-0.71446100	-0.12326500	-0.26783400
Cl	-2.70459700	-0.45964500	-0.35165000
O	-0.57953000	2.50273000	0.53490300
H	-0.92813600	3.16701300	-0.06972000
H	0.35607900	2.36462500	0.27681200

M06/6-311+G(d,p)

Imaginary frequency: -706.8

C	0.95743500	-0.60660200	0.72810500
O	1.08923500	0.00102800	1.75369400
C	0.94995500	-2.09735100	0.61149800
H	0.31944700	-2.50362900	1.40749500
H	0.59478800	-2.42678200	-0.36269700
H	1.97100600	-2.46307100	0.76050700
C	1.50014300	0.26010500	-0.74918000
O	1.58249800	1.46651300	-0.57412100
O	1.85826900	-0.54874900	-1.57999200
H	-0.85322200	0.73073400	0.09347700
O	-0.73395900	-0.19772800	-0.22900500
Cl	-2.72563000	-0.55866300	-0.32074100
O	-0.70242600	2.44153800	0.59214900
H	-1.11625500	3.10860400	0.03825300
H	0.22580200	2.41368500	0.27121600