Electronic Supplementary Information

Theoretical Study on Molecular Mechanism of Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformyfuran Catalyzed by VO_2^+ with Counterpart Anion in N,N-Dimethylacetamide Solution

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NOTES: Evaluation of rate constants:

The rate constants k(T) were evaluated according to conventional transition state theory k'(T), including the tunneling correction κ(T) based on Wigner's formulation as follows:[1]

$$k' = \frac{k_B T}{hc^0} \bullet e^{\frac{-\Delta G^{\neq}}{RT}}$$

$$\kappa（T） = 1 + \frac{1}{24}|\frac{w^{\neq} h}{k_B T}|^2$$

$$k = \kappa（T） \times k'$$

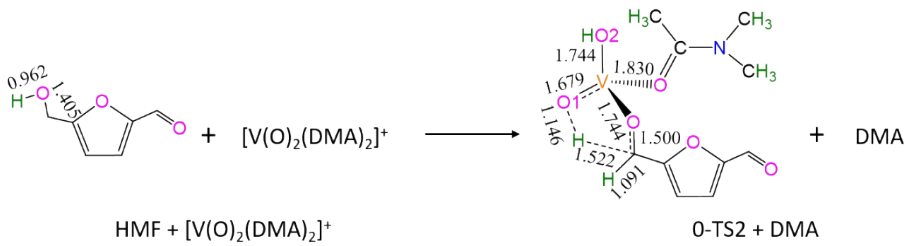
$$\ln k = -\frac{E_a}{RT} + \ln A$$

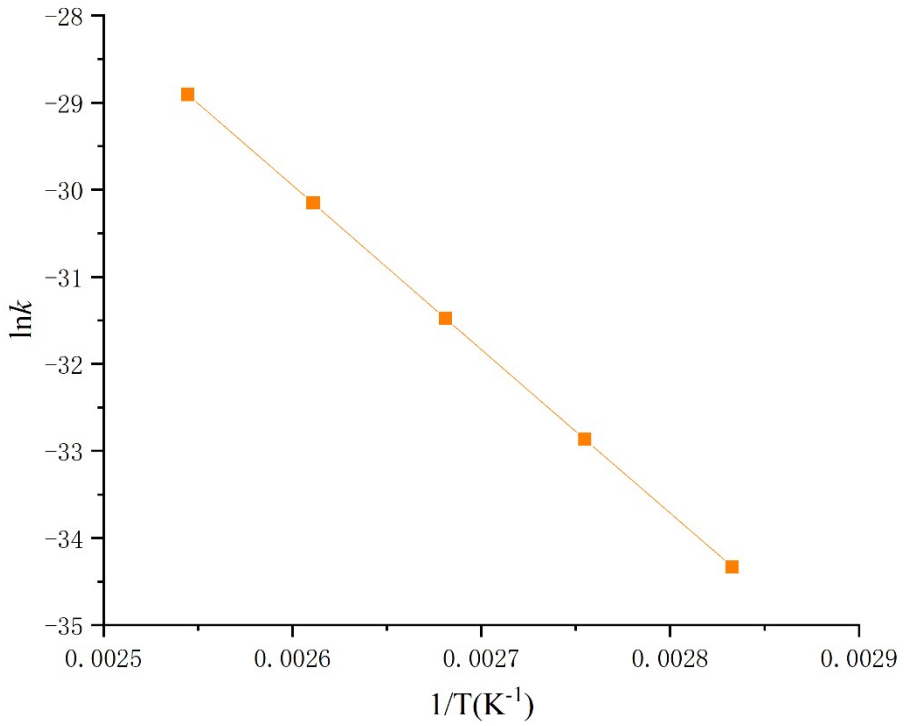
$$k = A \bullet e^{\frac{-E_a}{RT}}$$

where k_B is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, c^0 is the standard concentration (1 mol dm^{-3}), $\Delta G^{\neq}$ is the activation Gibbs free energy barrier and $\omega^{\neq}$ is the imaginary frequency of the TS.

References:

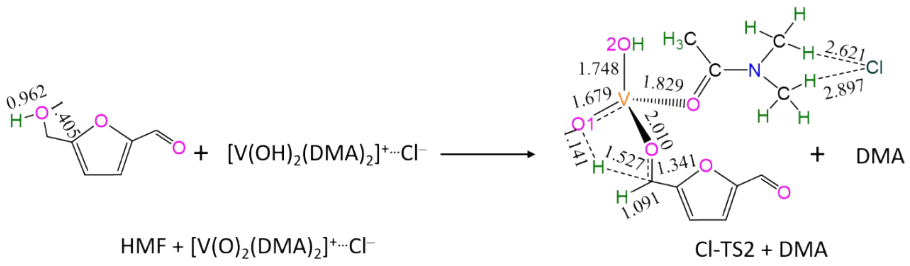
1. E. Wigner, *J. Chem. Phys*., 1937, **5**, 720–723.

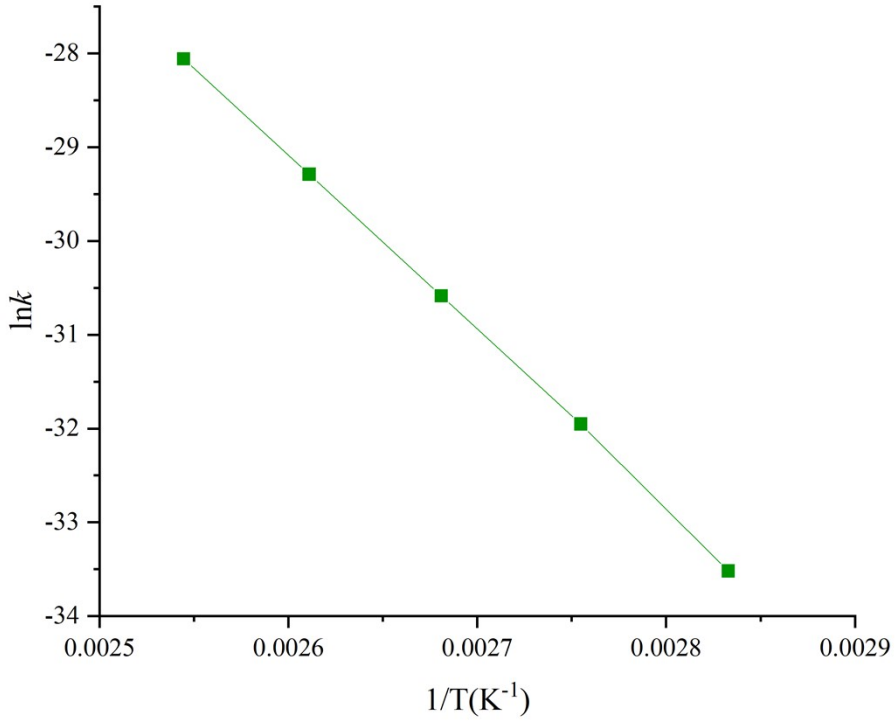




$$k = 1.45 \times 10^{8} \exp\left(-155946/RT\right)$$

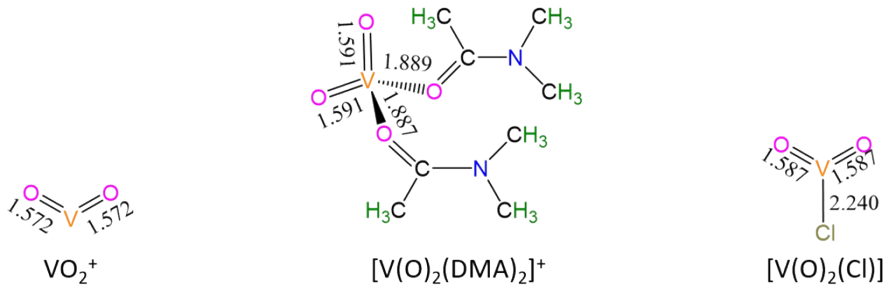
Figure S1: Arrhenius plots of rate constants for the crucial reaction step of HMF + $[V(O)_2(DMA)_2]^+$ → 0-TS2 + DMA in the reaction of 2HMF + O_2 → 2DFF + $2H_2O$ catalyzed over $[V(O)_2(DMA)_2]^+$ in N,N-Dimethylacetamide (DMA) Solution.





$$k = 2.74 \times 10^{8} \exp\left(-155189/RT\right)$$

Figure S2: Arrhenius plots of rate constants for the crucial reaction step of HMF + $[V(O)_2(DMA)_2]^+ \ldots Cl^-$ → Cl^- TS2 + DMA in the reaction of 2HMF + O_2 → 2DFF + $2H_2O$ catalyzed over $[V(O)_2(DMA)_2]^+ \ldots Cl^-$ in N,N-Dimethylacetamide (DMA) Solution



VO_2^+ $[V(O)_2(DMA)_2]^+$ $[V(O)_2(Cl)]$

(a)

Reaction	△G(kJ/mol)
$VO_2^+ + 2*DMA \rightarrow [V(O)_2(DMA)_2]^+$	−164.0
$VO_2^+ + Cl^- \rightarrow [V(O)_2(Cl)]$	−147.8

(b)

Table S1. The optimized geometric structures (a) and the formed Gibbs free energies (b) (Gr, kJ mol $^{-1}$) of $[V(O)_2(DMA)_2]$ and $[V(O)_2(Cl)]$ complexes in the DMA solution. Bond lengths are reported in Å.

Table S2. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) relative to HMF-1 for eight configurations of 5-hydroxymethylfurfural (HMF) at M06/6-311++G(d,p) level in N,N-Dimethylacetamide (DMA) Solution under experimental temperature and pressure (383.0K and 1.0 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
HMF-1	0.11135	-457.63672	0.06464	-457.68343	0.0	0.0
HMF-2	0.11175	-457.63677	0.06516	-457.68336	-0.1	0.2
HMF-3	0.11162	-457.63616	0.06501	-457.68277	1.5	1.7
HMF-4	0.11158	-457.63554	0.06508	-457.68203	3.1	3.7
HMF-5	0.11152	-457.63497	0.06489	-457.68160	4.6	4.8
HMF-6	0.11195	-457.63655	0.06605	-457.68245	0.4	2.6
HMF-7	0.11077	-457.63582	0.06572	-457.68087	2.4	6.7
HMF-8	0.11163	-457.63542	0.06512	-457.68192	3.4	4.0

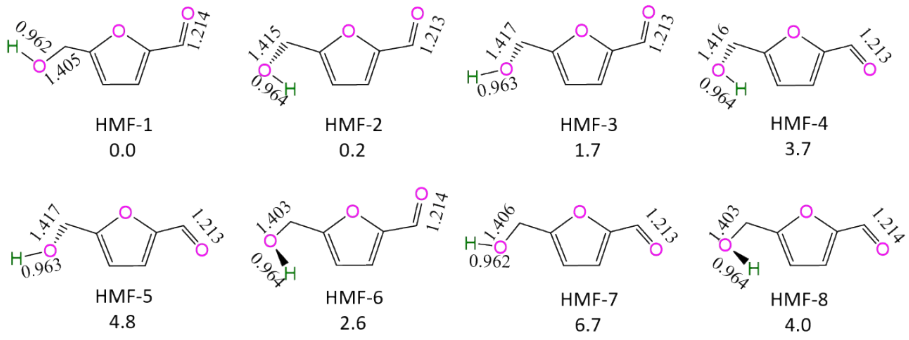


Figure S3. The geometric structures and the relative Gibbs free energy (ΔG, kJ mol^{-1}) relative to HMF-1 for eight configurations of 5-hydroxymethylfurfural (HMF) at M06/6-311++G(d,p) level in N,N-dimethylacetamide (DMA) solution under ambient temperature and pressure (383 K and 1 atm). For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

Table S3. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) relative to DFF-1 for three configurations of 2,5-Diformyfuran (DFF) at M06/6-311++G(d,p) level in N,N-Dimethylacetamide (DMA) Solution under experimental temperature and pressure (383.0K and 1.0 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
DFF-1	0.08823	-456.45115	0.04344	-456.49594	0.0	0.0
DFF-2	0.08878	-456.45252	0.04399	-456.49731	-3.6	-3.6
DFF-3	0.08840	-456.45200	0.04345	-456.49694	-2.2	-2.4

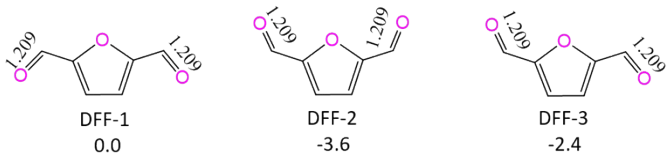
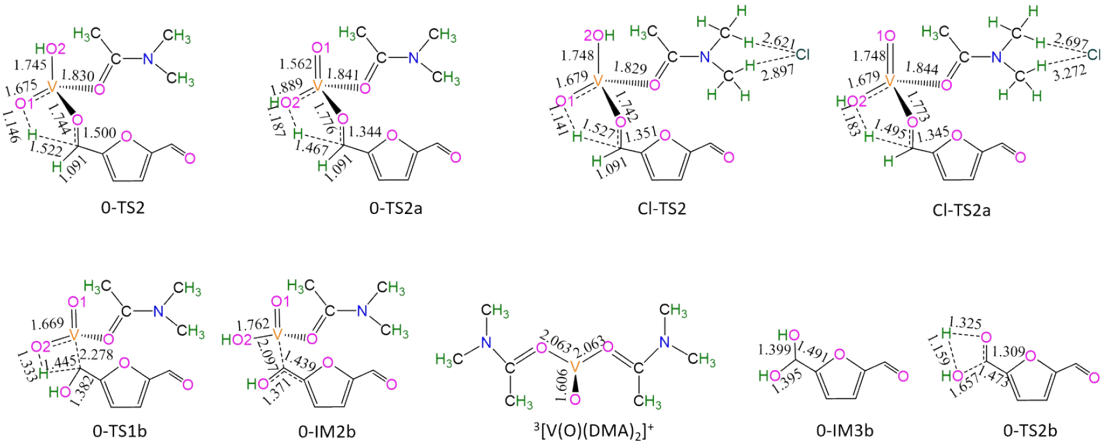
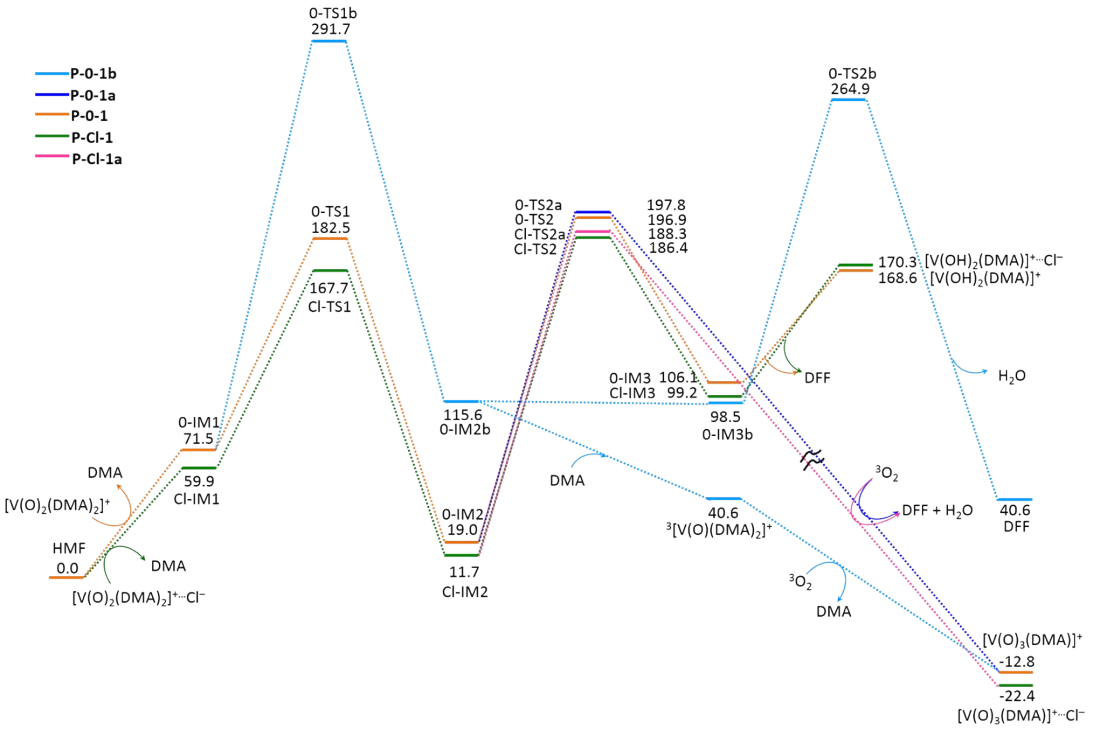


Figure S4. The geometric structures and the relative Gibbs free energy (ΔG, kJ mol^{-1}) relative to DFF-1 for three configurations of 2,5-diformylfuran (DFF) at M06/6-311++G(d,p) level in N,N-dimethylacetamide (DMA) solution under ambient temperature and pressure (383 K and 1 atm). For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.



(a)



(b)

Figure S5: The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the first HMF oxidation to DFF catalyzed by [V(O)$_2$(DMA)$_2$]$^+$ without/with Cl$^-$ in the DMA solution. For clarity, the hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

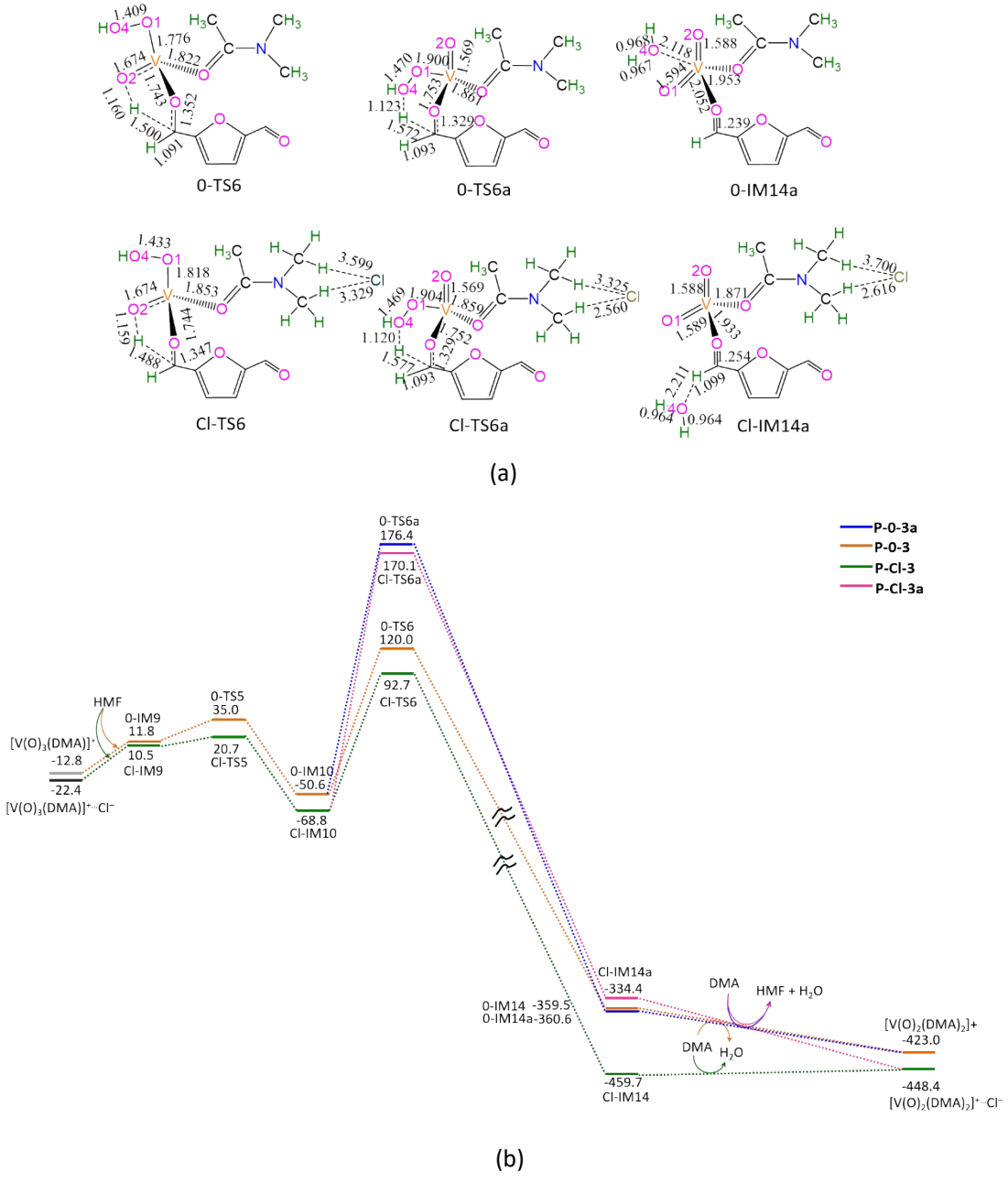


Figure S6: The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the oxidative dehydration of the second HMF to DFF by $[V(O)_3(DMA)]^+$ without/with Cl^- in the DMA solution. For clarity, the hydrogen atoms on carbon are not shown. Bond lengths are reported in Å

Table S4. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the conversion of 5-hydroxymethylfurfural (HMF) to 2,5-Diformyfuran (DFF) ($2HMF + O_2 \rightarrow 2DFF + 2H_2O$) catalyzed over $[V(O)_2(DMA)_2]^+$ at M06/6-311++G(d,p)/aug-cc-pVTZ level in N,N-Dimethylacetamide (DMA) Solution under experimental temperature and pressure (383.0K and 1.0 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
DMA	0.12859	-287.59794	0.08445	-287.64208		
$^3O2$	0.00387	-150.29864	-0.02282	-150.32533		
H_2O	0.02126	-76.40546	-0.00263	-76.42935		
HMF-1 + $[V(O)_2(DMA)_2]^+$	0.38142	-2127.25036	0.26073	-2127.37105	0.0	0.0
0-IM1	0.25388	-1839.63144	0.18361	-1839.70171		
0-IM1 + DMA	0.38247	-2127.22939	0.26806	-2127.34380	55.1	71.6
0-TS1	0.24949	-1839.59343	0.18346	-1839.65946		
0-TS1 + DMA	0.37808	-2127.19137	0.26791	-2127.30154	154.9	182.5
0-IM2	0.25318	-1839.65348	0.18496	-1839.72171		
0-IM2 + DMA	0.38177	-2127.25143	0.26941	-2127.36379	-2.8	19.1
0-TS2	0.24795	-1839.58740	0.18140	-1839.65395		
0-TS2 + DMA	0.37654	-2127.18535	0.26585	-2127.29603	170.7	197.0
0-TS2a	0.24816	-1839.58675	0.18130	-1839.65362		
0-TS2a + DMA	0.37675	-2127.18470	0.26575	-2127.29570	172.4	197.8
0-IM3	0.25062	-1839.61790	0.17997	-1839.68855		
0-IM3 + DMA	0.37921	-2127.21585	0.26442	-2127.33064	90.6	106.1
$[V(OH)_2(DMA)]^+$	0.15621	-1383.11153	0.10030	-1383.16744		
$[V(OH)_2(DMA)]^+$ + DMA + DFF-2	0.37358	-2127.16199	0.22874	-2127.30683	232.0	168.6
0-IM5	0.16469	-1533.51321	0.10545	-1533.57246		
0-IM5 + DMA+ DFF-2 - $^3O_2$	0.37820	-2127.26503	0.25671	-2127.38652	-38.5	-40.6
^{3}0-IM5	0.16387	-1533.48600	0.10042	-1533.54946		
^{3}0-IM5 + DMA+ DFF-2 - $^3O_2$	0.37738	-2127.23782	0.25168	-2127.36351	32.9	19.8
0-TS3	0.16163	-1533.46586	0.10258	-1533.52491		
0-TS3 + DMA + DFF-2 - $^3O_2$	0.37513	-2127.21768	0.25384	-2127.33897	85.8	84.2
0-IM6	0.16643	-1533.51228	0.10643	-1533.57229		
0-IM6 + DMA + DFF-2 - $^3O_2$	0.37993	-2127.26410	0.25769	-2127.38634	-36.1	-40.2
0-TS4	0.16456	-1533.46841	0.10474	-1533.52823		
0-TS4 + DMA+ DFF-2 - $^3O_2$	0.37806	-2127.22023	0.25600	-2127.34229	79.1	75.5
0-IM7	0.16671	-1533.48652	0.10609	-1533.54715		
0-IM7 + DMA+ DFF-2 - $^3O_2$	0.38021	-2127.23834	0.25735	-2127.36120	31.6	25.9
$[V(O)_3(DMA)]^+$	0.14275	-1457.07992	0.09016	-1457.13251		
$[V(O)_3(DMA)]^+$ + DMA + DFF-2 + H_2O - $^3O_2$	0.37751	-2127.23720	0.23880	-2127.37591	34.6	-12.8

Continued from **Table S4**

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
0-IM9	0.25658	-1914.73542	0.18541	-1914.80658		
0-IM9 + DMA + DFF-2 + H_2O -HMF-1 - $^3O_2$	0.37999	-2127.25598	0.26941	-2127.36656	-14.8	11.8
0-TS5	0.25284	-1914.72806	0.18318	-1914.79773		
0-TS5 + DMA - $^3O_2$+ DFF-2 + H_2O - HMF-1	0.37625	-2127.24863	0.26718	-2127.35770	4.5	35.1
0-IM10	0.25745	-1914.75900	0.18610	-1914.83035		
0-IM10 + DMA - $^3O_2$ + DFF-2 + H_2O - HMF-1	0.38086	-2127.27957	0.27010	-2127.39033	-76.7	-50.6
0-TS6	0.25140	-1914.69424	0.18027	-1914.76537		
0-TS6 + DMA - $^3O_2$ + DFF-2 + H_2O - HMF-1	0.37481	-2127.21481	0.26427	-2127.32535	93.3	120.0
0-IM11	0.25537	-1914.73711	0.18335	-1914.80913		
0-IM11 + DMA - $^3O_2$ + DFF-2 + H_2O - HMF-1	0.37878	-2127.25767	0.26735	-2127.36910	-19.2	5.1
$[V(OH)(OOH)(DMA)]^+$	0.16081	-1458.23466	0.10296	-1458.29251		
$[V(OH)(OOH)(DMA)]^+$ + DMA + H_2O - HMF-1 - $^3O_2$ + 2*DFF-2	0.37301	-2127.20774	0.23095	-2127.34979	111.9	55.8
0-IM13	0.16201	-1458.40709	0.10364	-1458.46546		
0-IM13 + DMA - $^3O_2$ + 2*DFF-2 + H_2O - HMF-1	0.37421	-2127.38017	0.23164	-2127.52275	-340.8	-398.3
0-TS7	0.15918	-1458.34169	0.10304	-1458.39783		
0-TS7 + DMA - $^3O_2$ + 2*DFF-2 + H_2O - HMF-1	0.37137	-2127.31477	0.23103	-2127.45511	-169.1	-220.7
0-IM14	0.16266	-1458.39129	0.10324	-1458.45070		
0-IM14 + DMA - $^3O_2$ + 2*DFF-2 + H_2O - HMF-1	0.37485	-2127.36437	0.23123	-2127.50798	-299.3	-359.5
0-TS6a	0.24911	-1914.66720	0.17243	-1914.74388		
0-TS6a + DMA - $^3O_2$ + 2*DFF-2 + H_2O - HMF-1	0.37252	-2127.18777	0.25643	-2127.30386	164.3	176.4
0-IM14a	0.25427	-1914.87033	0.17619	-1914.94841		
0-IM14a + DMA - $^3O_2$ + 2*DFF-2 + H_2O - HMF-1	0.37768	-2127.39090	0.26019	-2127.50838	-369.0	-360.6
$[V(O)_2(DMA)_2]^+$	0.27007	-1669.61364	0.19609	-1669.68761		
$[V(O)_2(DMA)_2]^+$ - $^3O_2$ + 2*DFF-2 - HMF-1 + 2*H_2O	0.37493	-2127.39424	0.23701	-2127.53216	-377.8	-423.0

Continued from **Table S4**

[VO(DMA)2]+	0.26542	-1594.35696	0.19346	-1594.42892		
0-TS1c	0.24823	-1839.54952	0.17989	-1839.61786		
0-TS1c + DMA	0.37682	-2127.14746	0.26434	-2127.25995	270.1	291.7
0-IM2c	0.25110	-1839.61463	0.18079	-1839.68494		
0-IM2c + DMA	0.37969	-2127.21258	0.26525	-2127.32702	99.2	115.6
0-IM3c	0.11635	-532.85603	0.06778	-532.90460		
0-IM3c + $[VO(DMA)_2]$+	0.38177	-2127.21298	0.26123	-2127.33352	98.1	98.5
0-TS3c	0.11045	-532.79316	0.06239	-532.84123		
0-TS3c + $[VO(DMA)_2]$+	0.37587	-2127.15012	0.25584	-2127.27015	263.2	264.9

Table S5. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the conversion of 5-hydroxymethylfurfural (HMF) to 2,5-Diformyfuran (DFF) (2HMF + O_2 → 2DFF + 2H_2O) catalyzed over $[V(O)_2(DMA)_2]^+\ldots Cl^-$ at M06/6-311++G(d,p)/aug-cc-pVTZ level in N,N-Dimethylacetamide (DMA) Solution under experimental temperature and pressure (383.0K and 1.0 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
$[V(O)_2(DMA)_2]^+\ldots Cl^-$	0.26998	-2129.98487	0.18959	-2130.06526		
Cl^-	0.00000	-460.36727	-0.02006	-460.38733		
HMF-1 + $[V(O)_2(DMA)_2]^+\ldots Cl^-$	0.38133	-2587.62159	0.25423	-2587.74869	0.0	0.0
Cl-IM1	0.25388	-2300.00729	0.17737	-2300.08380		
Cl-IM1 + DMA	0.38247	-2587.60523	0.26182	-2587.72589	43.0	59.9
Cl-TS1	0.24964	-2299.96946	0.17637	-2300.04273		
Cl-TS1 + DMA	0.37823	-2587.56741	0.26082	-2587.68481	142.3	167.7
Cl-IM2	0.25392	-2300.02836	0.18014	-2300.10214		
Cl-IM2 + DMA	0.38251	-2587.62631	0.26460	-2587.74423	-12.4	11.7
Cl-TS2	0.24819	-2299.96288	0.17547	-2300.03561		
Cl-TS2 + DMA	0.37678	-2587.56083	0.25992	-2587.67769	159.5	186.4
Cl-TS2a	0.24831	-2299.96125	0.17466	-2300.03490		
Cl-TS2a + DMA	0.37690	-2587.55920	0.25911	-2587.67698	163.8	188.3
Cl-IM3	0.25159	-2299.99360	0.17635	-2300.06883		
Cl-IM3 + DMA	0.38018	-2587.59154	0.26080	-2587.71092	78.9	99.2
$[V(OH)_2(DMA)]^+\ldots Cl^-$	0.15573	-1843.48319	0.09449	-1843.54443		
$[V(OH)_2(DMA)]^+\ldots Cl^-$ + DMA + DFF-2	0.37311	-2587.53365	0.22294	-2587.68382	230.9	170.3
Cl-IM5	0.16521	-1993.88889	0.09769	-1993.95641		
Cl-IM5 + DMA+ DFF-2 - $^3O_2$	0.37872	-2587.64071	0.24895	-2587.77047	-50.2	-57.2
Cl-TS3	0.16282	-1993.83765	0.09683	-1993.90365		
Cl-TS3 + DMA + DFF-2 - $^3O_2$	0.37633	-2587.58947	0.24809	-2587.71770	84.3	81.4
Cl-IM6	0.16713	-1993.88346	0.09982	-1993.95077		
Cl-IM6 + DMA + DFF-2 - $^3O_2$	0.38064	-2587.63528	0.25108	-2587.76483	-35.9	-42.4
Cl-TS4	0.16562	-1993.83942	0.09974	-1993.90530		
Cl-TS4 + DMA+ DFF-2 - $^3O_2$	0.37913	-2587.59124	0.25101	-2587.71936	79.7	77.0
Cl-IM7	0.16801	-1993.86101	0.10181	-1993.92721		
Cl-IM7 + DMA+ DFF-2 - $^3O_2$	0.38151	-2587.61283	0.25307	-2587.74127	23.0	19.5
$[V(O)_3(DMA)]^+\ldots Cl^-$	0.14260	-1917.45184	0.08063	-1917.51381		
$[V(O)_3(DMA)]^+\ldots Cl^-$+ DFF-2 + H_2O - $^3O_2$+ DMA	0.37736	-2587.60912	0.22926	-2587.75722	32.7	-22.4
Cl-IM9	0.25622	-2375.10752	0.17902	-2375.18472		
Cl-IM9 + DMA + DFF-2 + H_2O - HMF-1 - $^3O_2$	0.37963	-2587.62809	0.26302	-2587.74469	-17.1	10.5

Continued from **Table S5**

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
Cl-TS5	0.25292	-2375.10360	0.17558	-2375.18094		
Cl-TS5 + DMA - $^3O_2$ + DFF-2 + H_2O - HMF-1	0.37633	-2587.62417	0.25958	-2587.74091	-6.8	20.4
Cl-IM10	0.25717	-2375.13445	0.17671	-2375.21492		
Cl-IM10 + DMA - $^3O_2$ + DFF-2 + H_2O - HMF-1	0.38058	-2587.65502	0.26071	-2587.77489	-87.8	-68.8
Cl-TS6	0.25280	-2375.07684	0.17699	-2375.15265		
Cl-TS6 + DMA - $^3O_2$ + DFF-2 + H_2O - HMF-1	0.37621	-2587.59741	0.26099	-2587.71262	63.5	94.7
Cl-IM11	0.25501	-2375.11550	0.17922	-2375.19130		
Cl-IM11 + DMA - $^3O_2$ + DFF-2 + H_2O - HMF-1	0.37842	-2587.63607	0.26322	-2587.75127	-38.0	-6.8
$[V(OH)(OOH)(DMA)]^+…Cl^-$	0.16122	-1918.60625	0.09441	-1918.67306		
$[V(OH)(OOH)(DMA)]^+…Cl^-$-$^3O_2$ + DMA + H_2O - HMF-1 +2*DFF-2	0.37341	-2587.57933	0.22240	-2587.73034	110.9	48.2
Cl-IM13	0.16420	-1918.79928	0.10346	-1918.86002		
Cl-IM13 + DMA - $^3O_2$ + H_2O + 2*DFF-2 - HMF-1	0.37640	-2587.77236	0.23146	-2587.91730	-395.8	-442.7
Cl-TS7	0.15918	-1918.72986	0.09567	-1918.79337		
Cl-TS7 + DMA - $^3O_2$ + H_2O + 2*DFF-2 - HMF-1	0.37138	-2587.70294	0.22367	-2587.85065	-213.6	-267.7
Cl-IM14	0.16471	-1918.80434	0.10256	-1918.86649		
Cl-IM14 + DMA - $^3O_2$ + H_2O + 2*DFF-2- HMF-1	0.37690	-2587.77742	0.23055	-2587.92377	-409.1	-459.7
Cl-TS6a	0.24942	-2375.03997	0.16546	-2375.12393		
Cl-TS6a + DMA - $^3O_2$ + H_2O + 2*DFF-2- HMF-1	0.37283	-2587.56053	0.24946	-2587.68390	160.3	170.1
Cl-IM14a	0.25278	-2375.22521	0.16191	-2375.31609		
Cl-IM14a + DMA - $^3O_2$ + H_2O + 2*DFF-2- HMF-1	0.37619	-2587.74577	0.24591	-2587.87606	-326.0	-334.4
$[V(O)_2(DMA)_2]^+…Cl^-$	0.26998	-2129.98487	0.18959	-2130.06526		
$[V(O)_2(DMA)_2]^+…Cl^-$ - $^3O_2$ + 2*DFF-2 - HMF-1 + 2*H_2O	0.37493	-2587.76151	0.21695	-2587.91949	-367.4	-448.4