

Oxygenation of Methylarenes to Benzaldehyde Derivatives by a Polyoxometalate Mediated Electron Transfer-Oxygen Transfer Reaction in Aqueous Sulfuric Acid

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Supporting Information

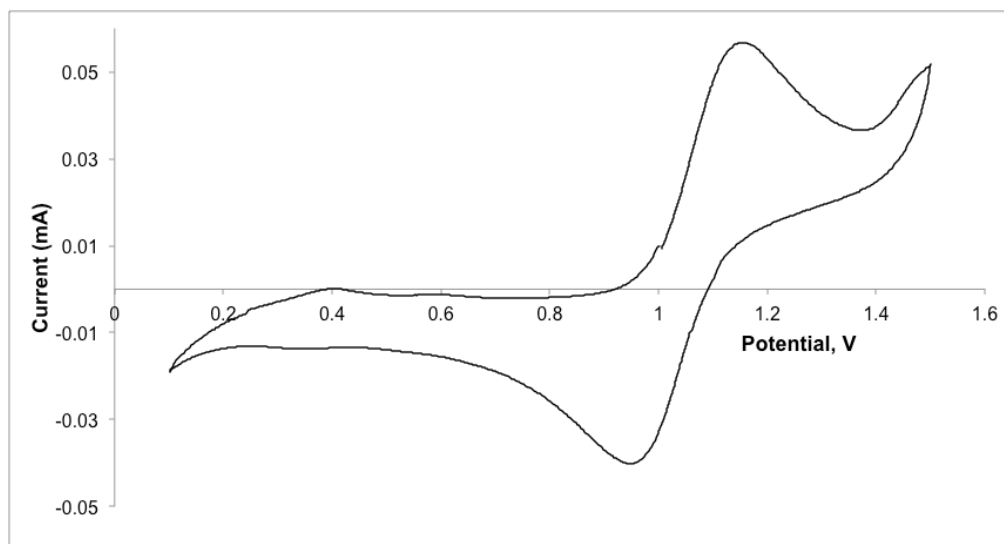


Figure S1. Cyclic voltammogram of the reaction solution.

Cyclic voltammogram versus SCE of a reaction solution containing reduced polyoxometalate after oxidation of toluene originally containing 0.10 M $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ in 50 % H_2SO_4 . Glassy carbon -working electrode, Pt wire - counter electrode and calomel - reference electrode with a scan rate of 50 mV/sec.

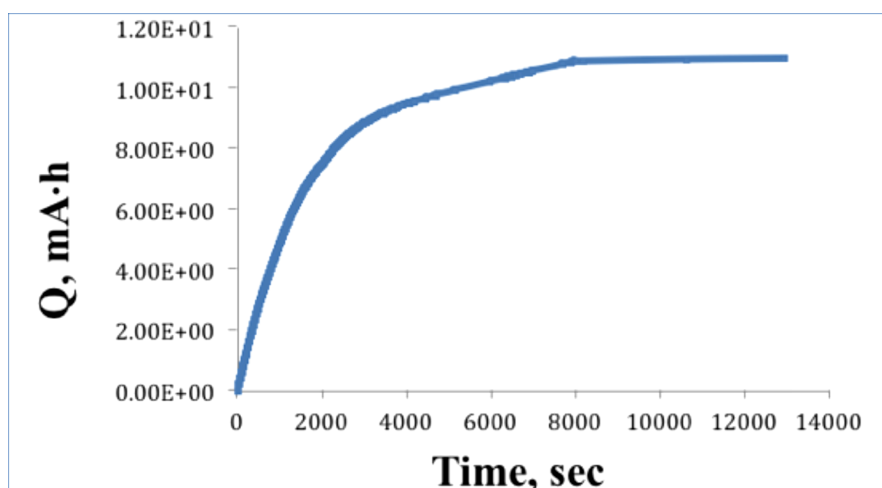


Figure S2. Electrolysis of 0.23 mmol of reduced $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ after reaction with toluene. The electrolysis of 0.225 mmol $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \cdot 32\text{H}_2\text{O}$ in 50% H_2SO_4 was carried out at 1.3 V in a glass cell using a Pt gauze ($2 \times 2 \text{ cm}^2$) working electrode and platinum wires as counter and reference electrode to yield H_2 . The calculations show involvement of 1.95 ± 0.05 electrons per polyoxometalate anion.

$$Q = 11.7 \text{ mA} \cdot \text{h} = 42.12 \text{ A} \cdot \text{s} = 42.12 \text{ C}$$

$$N = 42.12 \text{ C} / (1.602 \times 10^{-19} \text{ C/electron} \times 6.023 \times 10^{23} \text{ electron/mol}) = 0.437 \text{ mmol}$$

$$0.437 \text{ mmol electron} / 0.225 \text{ mmol polyoxometalate} = 1.94$$

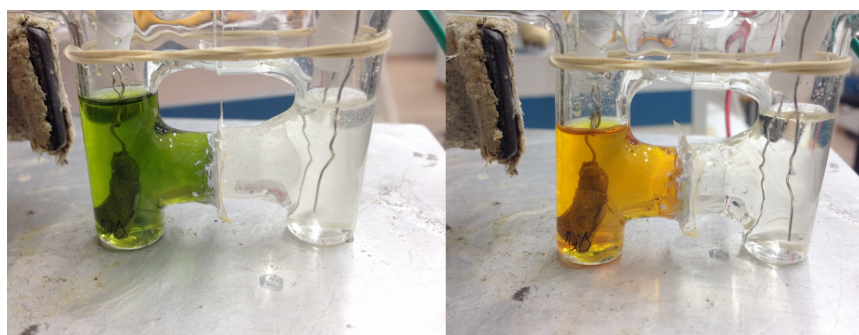


Figure S3. Electrolysis of the reduced solution of the polyoxometalate (0.23 mmol in 4 mL 50 % H_2SO_4), that is after toluene oxidation in a 2 half-cell setup. Left - before the electrolysis. Right - after the electrolysis. Electrolysis was carried out in presence of Pt gauze as working electrode, and Pt wire as counter and reference electrode at different potential starting from 1.3 to 1.5 V. The higher the potential the faster is the reoxidation reaction. The two half cells were separated by a Nafion 212 membrane washed with 5% wt H_2O_2 and 8% H_2SO_4 consecutively. The formation of H_2 was observed only at the counter electrode (cathode, right half cell).

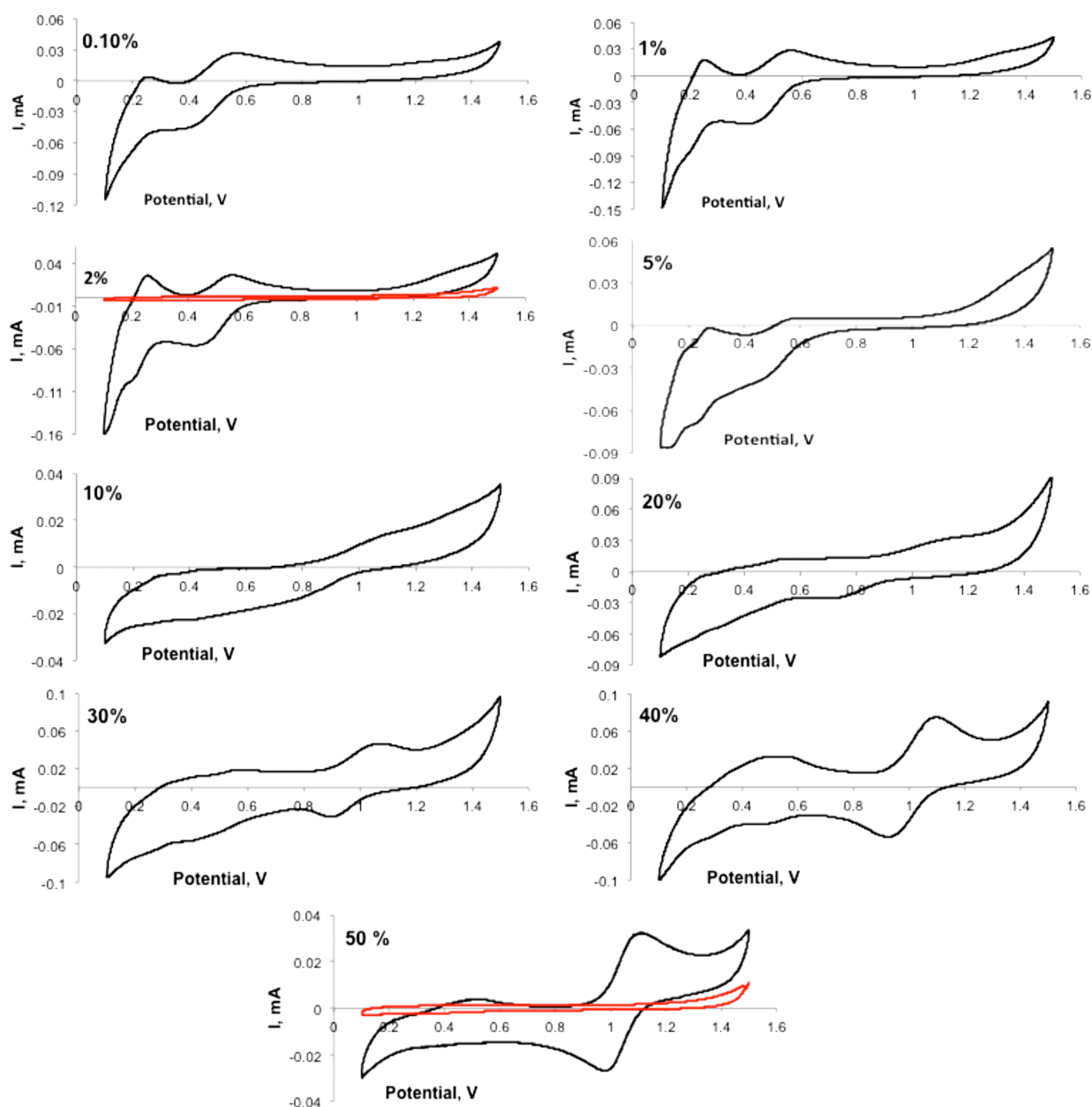


Figure S4. Cyclic voltammograms of 2 mM $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ at various concentrations of aqueous H_2SO_4 . The measurements were carried out at 2 mM $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ using a glassy carbon working electrode, a platinum wire counter electrode and a calomel reference electrode; scan rate 50 mV/sec. The red line traces are exemplary control cyclic voltammograms of solvent only.

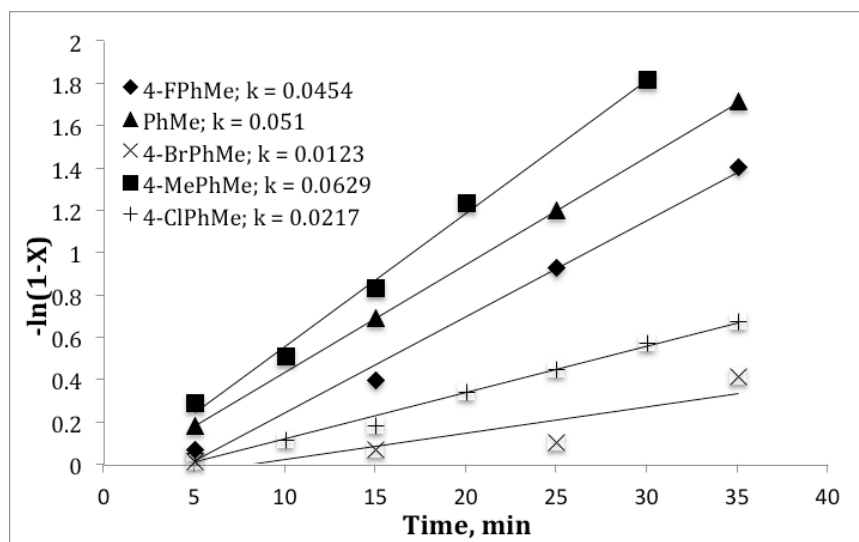


Figure S5. The oxidation of various toluene derivatives as a function of time. $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \cdot 32\text{H}_2\text{O}$ (2g, 0.922 mmol) was dissolved in 12 mL 50% H_2SO_4 and reacted with substrate (0.461 mmol) at 60 °C. The conversion (X) to product was followed by GC FID. First order rate constants (k) were obtained for each substrate.

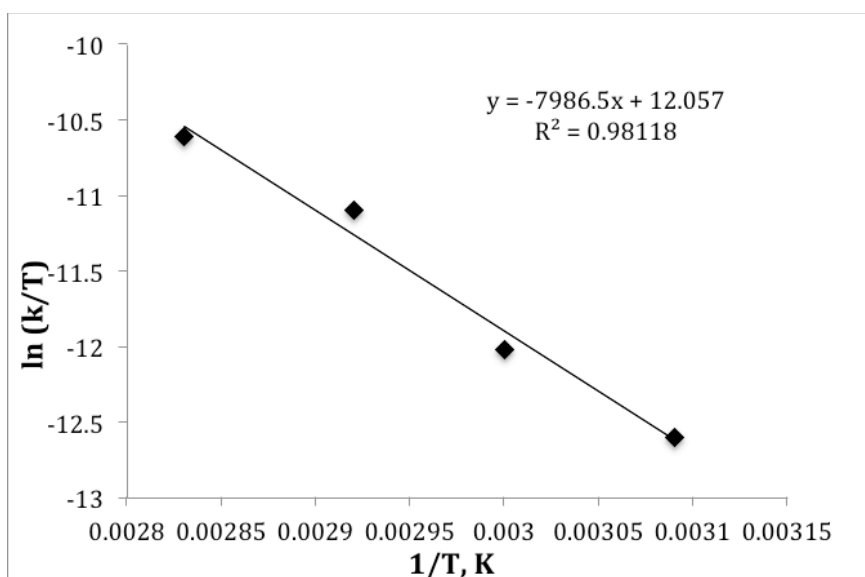


Figure S6. The oxidation of toluene by $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ as a function of temperature. $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \cdot 32\text{H}_2\text{O}$ (2g, 0.922 mmol) was dissolved in 12 mL 50% H_2SO_4 and reacted with toluene (0.461 mmol) at temperatures between 323-353 K. The conversion of toluene to benzaldehyde was followed by GC FID. First order rate constants (k) were obtained at each temperature and the results were plotted according to the Eyring equation:

$$\ln(k/T) = -\Delta H^\ddagger/R(1/T) + \ln(k_B/h) + \Delta S^\ddagger/R.$$

$$\Delta H^\ddagger_{298} = 15.8 \text{ kcal/mol}; \Delta S^\ddagger_{298} = -23.3 \text{ cal/mol K}; \Delta G^\ddagger_{298} = 22.8 \text{ kcal/mol}$$

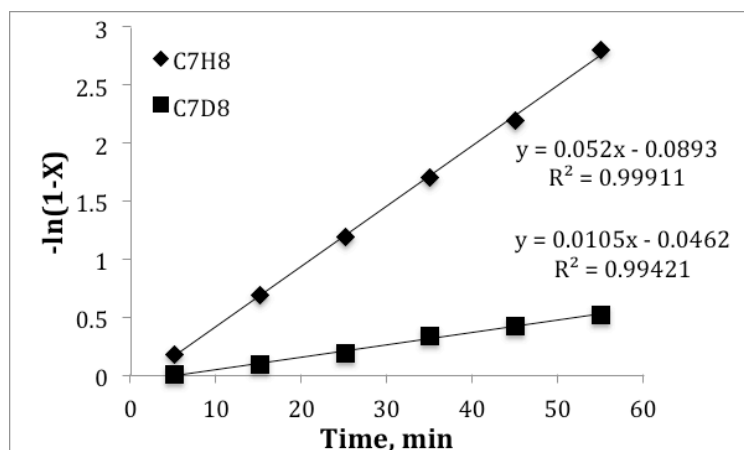


Figure S7. Measurement of the kinetic isotope effect for the oxidation of toluene to benzaldehyde.

$\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \cdot 32\text{H}_2\text{O}$ (2g, 0.922 mmol) was dissolved in 12 mL 50% H_2SO_4 and reacted with either toluene- H_8 or toluene- D_8 (0.461 mmol) at 60 °C. The conversion (X) to product was followed by GC-FID. First order rate constants (k) were obtained for each reaction.

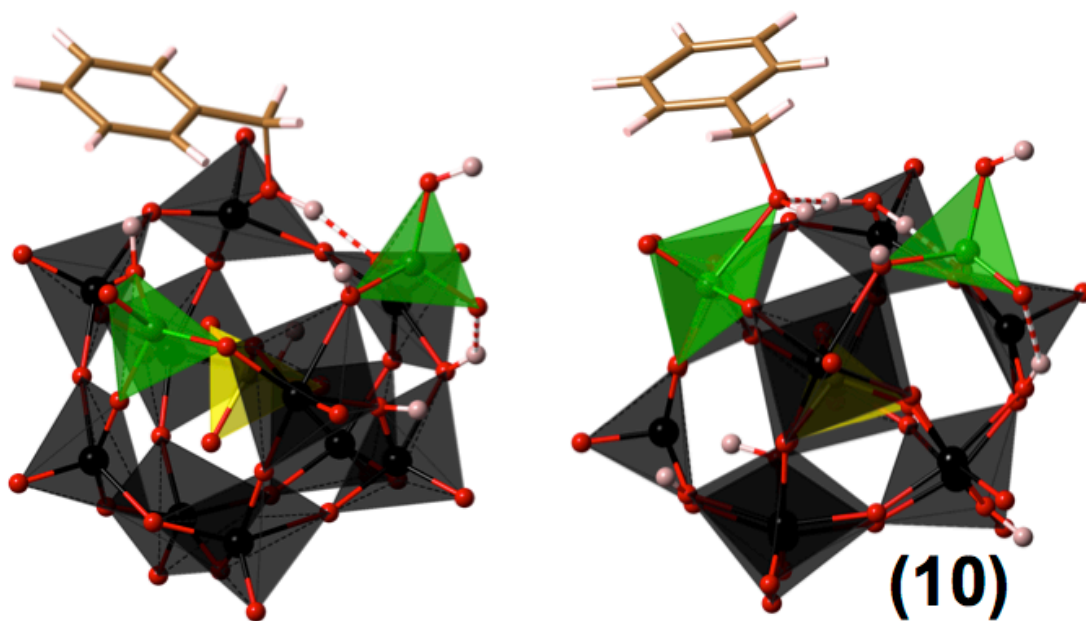


Figure S8. Coordinatively unsaturated species formed during the oxygen transfer from the polyoxometalate to toluene; without water (left) and with a coordinated water molecule (right). Green – V; black – Mo; yellow – P; red- O; brown – C; pink – H.

Table S1. Calculated proton affinity (PA, kcal/mol) and adiabatic electron affinity (EA, kcal/mol) of several PV₂ complexes in oxidized and reduced states in sulphuric acid at two temperatures (298 and 343 K)

Complex		PA ^c		EA ^d	
Composition	Notation	298 K	343 K	298 K	343 K
H ₅ PV ₂ Mo ₁₀ O ₄₀	(1)	-2.42	4.86	-139.68	-139.66
H ₆ PV ₂ Mo ₁₀ O ₄₀ ⁺	(2)	0.70	8.08	-150.25	-150.27
H ₅ PV ₂ Mo ₁₀ O ₄₀ ⁻	(3)	-12.99	-5.76		
H ₆ PV ₂ Mo ₁₀ O ₄₀	(4)	-10.39	-3.03	-136.28	-136.24
H ₇ PV ₂ Mo ₁₀ O ₄₀ ⁺	(5)	6.45	13.76	-145.56	-145.43
H ₆ PV ₂ Mo ₁₀ O ₄₀ ^{-a}	(6T)	-5.39	1.86		
H ₆ PV ₂ Mo ₁₀ O ₄₀ ^{-b}	(6S)	-5.97	1.42		
H ₇ PV ₂ Mo ₁₀ O ₄₀ ^a	(7T)	-2.42	4.86	-139.68	-139.66
H ₇ PV ₂ Mo ₁₀ O ₄₀ ^b	(7S)	0.70	8.08	-150.25	-150.27

^a triplet state; ^b singlet state; ^c PA is the energy released (negative values) or trapped (positive values) at proton transfer from H₃O⁺ to the species in sulphuric acid (for (1), PA=ΔG of reaction (2)); ^d EA is the energy released when an electron is attached to the species in sulphuric acid (EA=-ΔG of H_nPV₂Mo₁₀O₄₀^m + e⁻ → H_nPV₂Mo₁₀O₄₀^{m-1}).

Table S2. Calculated vertical and adiabatic ionization energies (IE, kcal/mol) of substituted toluene derivatives, benzyl alcohol and benzaldehyde in sulphuric acid and the corresponding Gibbs free energies (ΔG²⁹⁸ in sulphuric acid, kcal/mol) for electron transfer to oxidized (1, 2) and reduced species (4, 5) neutral (1, 4) and cationic (2, 5) polyoxometalate species.

Substituent	Ionization energy (IE), kcal/mol		ΔG ²⁹⁸ for ET in sulphuric acid, kcal/mol			
	Vertical ^a	Adiabatic ^b	2→4	5→7	1→3	4→6
H	162.4	144.38	-5.9	-1.2	4.7	8.1
4-F	161.2	143.78	-6.5	-1.8	4.1	7.5
4-Cl	160.9	145.25	-5.0	-0.3	5.6	9.0
4-Br	159.2	146.00	-4.3	0.4	6.3	9.7
4-Me	155.6	137.78	-12.5	-7.8	-1.9	1.5
4- <i>i</i> Pr	164.1	137.51	-12.7	-8.1	-2.2	1.2
Benzyl alcohol	161.4	147.96	-3.9	0.8	6.7	10.1
Benzaldehyde	175.2	159.46	9.2	13.9	19.8	23.2

^a the vertical ionization energy is approximated by HOMO level in sulphuric acid; ^b adiabatic ionization energy is approximated by energy required to remove an electron from the solvated molecule to infinity.

Additional Detail on Computational Methods

All computations were done using a locally modified version of the Gaussian 09 package.¹ Geometry optimizations and harmonic frequency evaluations have been performed using the nonempirical GGA density functional² PBE³ in conjunction with the PC1 basis set. The latter

is a combination of Jensen's polarization consistent pc-1 basis set^{4,5} for the main group elements with the Stuttgart-Dresden-Dolg (SDD) basis set-RECP (relativistic energy-consistent pseudopotential) combination⁶ for molybdenum and vanadium; to the latter, a single *f*-type polarization function was added, the exponent being the geometric average of the two *f*-exponents given by Martin and Sundermann.⁷ This combination is of double- ζ plus polarization quality. In order to speed up the calculations, we applied the density fitting (DF) approximation⁸ for calculating the two-electron (Coulomb) integrals. This approximation is known to speed up pure-DFT calculations on large systems by 1-2 orders of magnitude. The auxiliary basis sets required for this were generated by the automatic algorithm as implemented in Gaussian 09. Thus, geometries of all the complexes were optimized at the PBE-DF/PC1 level of theory without symmetry constraints. Subsequently, single-point calculations at the optimized geometries were performed using the empirical hybrid meta-GGA functional M06⁹ combined with the same basis set (M06/PC1), as well as using the PBE functional but combined with a larger AUG-PC1 basis set. The AUG-PC1 basis set represents a combination of the aug-pc-1 basis set on the main group elements^{10, 11} and SDD basis set with added *f* basis functions on molybdenum and vanadium. The final level of theory applied in the present work is thus the additivity approximation $E_e[\text{M06/AUG-PC1}] \approx E[\text{PBE-DF/AUG-PC1}] - E[\text{PBE-DF/PC1}] + E[\text{M06/PC1}]$.

Bulk solvent effects of the sulphuric acid medium have been calculated at the M06/PC1 level via the self-consistent reaction field (SCRF) method,¹² using the continuum solvation model COSMO as it is implemented in Gaussian 09¹³. Sulphuric acid is not a "common solvent", so its parameters are not stored internally in Gaussian 09. The main parameters that influence the calculated solvation energy are static (EPS) and optical or dynamic (EPSINF) dielectric constants. We applied EPS=100. EPSINF was calculated by squaring the refractive index ($n=1.446$ for sulphuric acid)¹⁴ of the solvent, EPSINF=2.091. The effect of ϵ is small for neutral species (the solvation energies of CH₃OH and H₂SO₄ calculated for different values of ϵ and R vary only by less than 0.7 kcal/mol in the range $1.5 < R < 2.25$ and $30 < \epsilon < 100$).¹⁵ However, stabilization of charged species, such as ionic pair, strongly depends on dielectric constant. Our calculations showed that even in this case varying the dielectric constant from 81 (pure water) to 100 (pure sulphuric acid) causes changes of less than 2 kcal/mol. Other, less important parameters were set as follows: CCl₄ was set as a similar solvent from the list of solvents determined in Gaussian 09, as recommended in the G09 manual; VMOL= 53.3 cm³/mol; DENSITY=0.011 and RSOLV =2.23.

Dispersion interactions within the computed structures were approximately taken into account by adding the D2 empirical dispersion correction term,¹⁶ with an s_6 value of 0.25, as suggested by Karton *et al.* for the M06 functional.¹⁷

Supporting References

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