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Letter

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Electron Transfer Oxidation of Benzene and Aerobic Oxidation to Phenol

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ABSTRACT: The activation of very strong C-H bonds such as those found in benzene is important also in the quest for new routes for its functionalization. Using the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate as an electron transfer oxidant in > 50% aqueous H_2SO_4 as solvent the formation of a benzene radicaloid species at RT as probed by visible spectroscopy, and EPR spectroscopy recorded at X-band and W-band including ELDOR detected NMR was verified. The viability of the ET oxidation of benzene is supported by DFT calculations showing the reaction to be exergonic under these conditions. Further we show that in the presence of O_2 very selective hydroxylation to phenol took place.

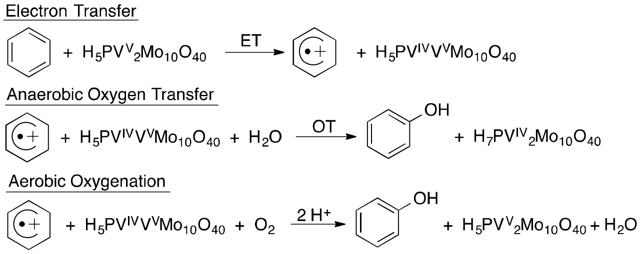
KEYWORDS – Aerobic Oxidation, Benzene, Polyoxometalate, EPR, Electron Transfer

Introduction

The direct aerobic oxidation of benzene to phenol is a challenging topic of considerable current interest against the backdrop of an industrial process that has a low atom economy.[1] The literature is abound with reports on the use of H_2O_2 as oxidant where in the majority of the cases the reactive oxidizing species is the hydroxide radical.[2] There is also a large body of research where it is likely that H_2O_2 is formed in situ under aerobic conditions, e.g. using H_2 or CO, respectively as reductants.[3,4] Successful hydroxylation of benzene with N_2O,[5] has led to numerous reports on the use of NH_3 and O_2 with the implication the N_2O is formed as an intermediate.[6] Despite the advances in using H_2O_2, and N_2O as oxidants and the mechanistically similar H_2/O_2 CO/O_2 and NH_3/O_2 combinations, there is an obvious interest in the oxidation of benzene to phenol with O_2 only. One development is the use of light in aerobic reactions.[7] However, under thermal reaction conditions the most studied system in this context is the heterogeneous oxidation over a Cu/ZSM-5 zeolite and more recently other Cu catalysts.[8] The mechanistic information for this reaction is scant but in one case there is some evidence for the formation of a benzene radical cation and then the hypothesis of the formation of a peroxide species involved in the actual hydroxylation reaction.[9] In a different approach Pd(II) in acetic acid has been used for activation of the C-H bond of benzene, formation of the acetate and/or phenol, where the co-formed Pd(0) species are reoxidized by O_2 in the presence of a co-catalyst.[10] Vanadium catalysts have also been used for the oxidation of benzene with H_2O_2 or with O_2 and a reducing agent.[11] There is also a recent report, where the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate is used together with graphitic carbon-nitride (C_3N_4) to oxidize benzene to phenol with O_2 only.[12] The authors propose here also that the reaction proceeds via electron transfer from C_3N_4 to the substrate. The combined, C_3N_4 and $H_5PV_2Mo_{10}O_{40}$, catalyst deactivates quickly apparently due to tar formation.[12]

Over the years we have promoted the use of the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate as an electron transfer (ET) and electron transfer-oxygen transfer (ET-OT) catalyst for the oxidation of hydrocarbons and related substrates, where the substrate scope was limited by the oxidation potential of $H_5PV_2Mo_{10}O_{40}$,[13] which is around 0.4-0.45 V versus SCE in many organic solvents. Recently, we have reported that in >50% aqueous sulfuric acid superior rates and increased substrate scope were found as a result of the higher oxidation potential of $H_5PV_2Mo_{10}O_{40}$ in >50% aqueous sulfuric acid.[14] For example, toluene can be oxidized to benzaldehyde through an ET-OT reaction mechanism in aqueous H_2SO_4 but there is no reaction in acetic acid or other organic polar solvents.[14b]

Scheme 1. ET oxidation of benzene by $H_5PV_2Mo_{10}O_{40}$ and subsequent pathways to phenol.



This previous research has led to the presently addressed research questions. (1) Can benzene be oxidized to a radical cation by $H_5PV_2Mo_{10}O_{40}$ in H_2SO_4 through an ET step? and (2) can the resulting benzene radical cation be oxidized anaerobically via oxygen transfer from the polyoxometalate or aerobically oxygenated to phenol, potentially setting the stage for a novel benzene to phenol reaction pathway? These questions related to the research theme are summarized in Scheme 1.

Results and Discussion

Formation of a benzene radical cation. An initial indication for an electron transfer interaction between benzene and $H_5PV_2Mo_{10}O_{40}$ was manifested in the visible spectrum, Figure 1. In 80% aqueous H_2SO_4 where the oxidation potential of $H_5PV_2Mo_{10}O_{40}$ is very significantly increased,~1.17 V versus SCE, Figure S1, two peaks emerge in the visible spectrum that can be assigned to a benzene related charge transfer peak at 520 nm and a peak at 680 nm associated to the reduced polyoxometalate.[15]

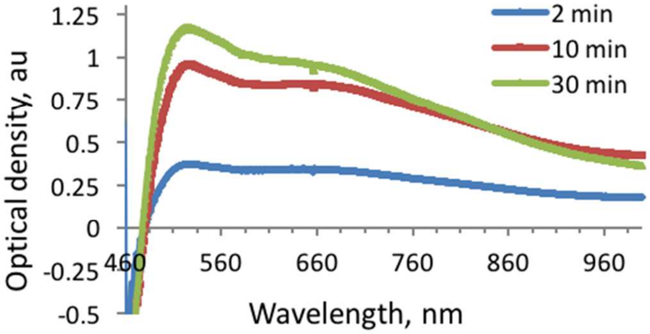


Figure 1. Visible spectrum of a mixture of 1 μL benzene with 0.1 mM $H_5PV_2Mo_{10}O_{40}$ in 80% H_2SO_4.

Buoyed by this observation, we sought for direct evidence for the presence of a benzene radical cation by EPR spectroscopy. Based on a previous study where it was observed that the radical cation of anthracene could be stabilized by the presence of hexafluoro-*i*-propanol (HFIP),[16] HFIP was also added to the $C_6H_6/H_5PV_2Mo_{10}O_{40}$ in 80% H_2SO_4 mixtures. Three samples were prepared: (i) $H_5PV_2Mo_{10}O_{40}$ which was reduced by H_2, (ii) natural isotope abundance benzene, nominally $^{12}C_6H_6$ with $H_5PV_2Mo_{10}O_{40}$ and (iii) $^{13}C_6H_6$ with $H_5PV_2Mo_{10}O_{40}$.

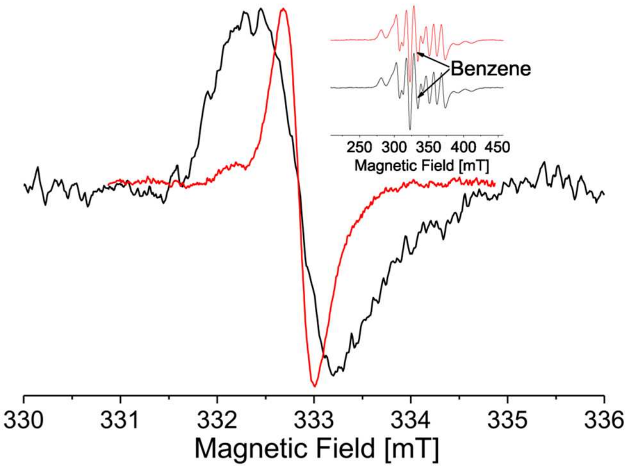


Figure 2. CW X-band EPR spectra of 1 μL C_6H_6/0.1 mM $H_5PV_2Mo_{10}O_{40}$ in 80% H_2SO_4; 50 μL HFIP. Red-$^{12}C_6H_6$; Black-$^{13}C_6H_6$.

The X-band CW spectrum, at RT gave a narrow EPR signal at g = 2.0057 typical for an organic radical, Figure 2 (red plot). A second sample of $^{13}C_6H_6/H_5PV_2Mo_{10}O_{40}$ in 80% H_2SO_4 benzene, Figure 2 (black plot) was measured as well in order to better identify the radical cation by the expected hyperfine splitting from the interaction of the free electron with the 13-C nuclei. Instead, however, the broad featureless spectrum was obtained probably due to slow tumbling rate of the benzene molecule, which is likely ion-paired or bound to $H_5PV_2Mo_{10}O_{40}$. For better resolution and confirmation, W-band (95 GHz) EPR measurements were carried out at 20 K. While $H_5PV_2Mo_{10}O_{40}$ reduced by H_2 exhibited only the expected V(IV) EPR spectrum the $^{12}C_6H_6/H_5PV_2Mo_{10}O_{40}$ and $^{13}C_6H_6/H_5PV_2Mo_{10}O_{40}$ gave two nicely resolved signals, one from V(IV) and the other, which was much weaker, from an organic radicaloid species situated at g = 2.0057 as also observed in the X-band spectrum, Figure 3.

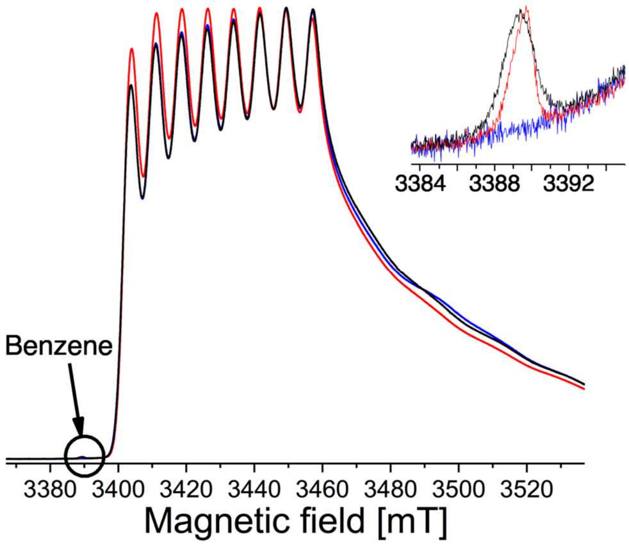


Figure 3. W-band EPR spectra. Blue $H_5PV_2Mo_{10}O_{40}/H_2$, red-$^{12}C_6H_6/H_5PV_2Mo_{10}O_{40}$, black-$^{13}C_6H_6/H_5PV_2Mo_{10}O_{40}$.

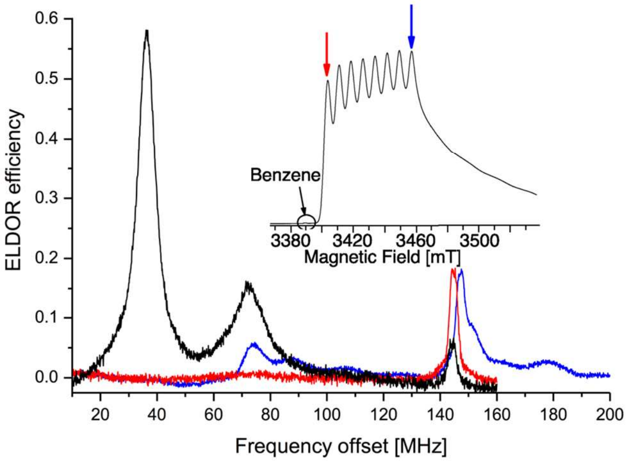


Figure 4. ELDOR detected NMR of $^{13}C_6H_6/H_5PV_2Mo_{10}O_{40}$. The color of the spectrum corresponds to the field positions according to the arrows.

In order to conclusively verify that the peak at g = 2.0057 is indeed from benzene and not some impurity or other artifact, further W-band ELDOR detected NMR spectra were recorded at different magnetic field positions within the EPR spectrum, Figure 4. The ELDOR detected NMR spectra recorded on the first (red) and the eighth (blue) line of the V(IV) species shows signals at the Larmor frequency of hydrogen atoms from the solution situated at 144.1 MHz and 147.3 MHz respectively. These signals are assigned to the protons from the polyoxometalate and solvent. The ELDOR detected NMR spectrum recorded at the g = 2 peak shows a signal at 36 MHz associable to the Larmor frequency of 13-C atoms. The peak at 72 MHz is assigned to the sum frequencies, and the signal at 144.1 MHz is associable to hydrogen atoms. All these easily detected strong signals are consistent with the presence of a benzene radicaloid species. In addition, on the blue trace there are six additional peaks ranging from 75 MHz to 180 MHz. These peaks are assigned to the 51-V transitions as reported previously.[17] A 13-C Mims ENDOR spectrum was also measured, Figure S2, at the field position of the benzene species further verifying that the 13-C signal could only originate from isotopically labeled benzene and not from any other source.

Oxygenation of benzene to phenol. Initial attempts at the anaerobic oxidation of benzene with $H_5PV_2Mo_{10}O_{40}$ via the electron transfer (benzene to polyoxometalate) oxygen transfer (polyoxometalate to benzene) mechanism[14b,16] in 80 % H_2SO_4 at 100 °C yielded phenylmaleic anhydride, as the major product, without discernable formation of phenol. One can assume that this compound is formed via the lower temperature homogeneous $H_5PV_2Mo_{10}O_{40}$ version of the classic Mars-van Krevelen type oxidation reaction of diphenyl,[16,18] the latter being formed *in situ* as an intermediate. Dilution of the reaction mixture to 50 % aqueous H_2SO_4 showed no product formation up to 170 °C. Above this temperature, one could observe the formation of diphenylsulfone as the major product in increasing amounts as a function of temperature, via sulfonation reactions unrelated to oxygenation. One can conclude, therefore, that there appears to be no kinetically feasible anaerobic ET-OT pathway from benzene to phenol, see Scheme 1 (middle), despite the fact that such a reaction is clearly exergonic, see below.

Table 1. Aerobic Oxidation of Phenol and Derivatives

Substrate	Conversion, mol%	ArOH, mol%	2-/4-ratio	Others, mol%
PhH	65±5^a	95	---	PhOPh, 5
PhH^b	10	97	---	PhOPh, 3
PhF	78	80	55/45	$C_6H_3FO_2$, 20^c
PhCl	62	70	60/40	$C_6H_4Cl_2$, 30
$PhNO_2$	68	60	13/87	$C_6H_4(NO_2)_2$, 40

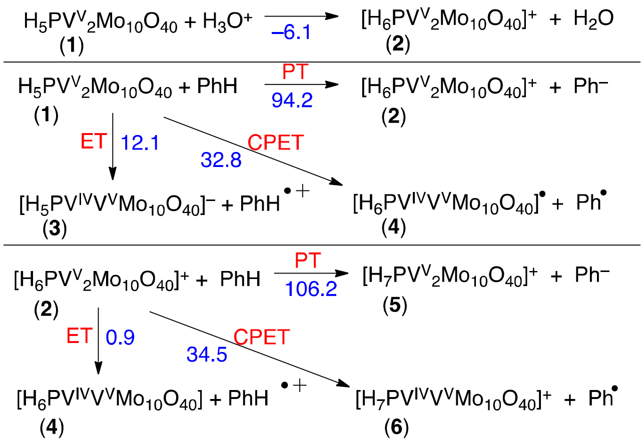
Reaction conditions: 0.5 mmol ArH, 0.46 mmol $H_5PV_2Mo_{10}O_{40}{\bullet}32H_2O$, 5 mL 50% H_2SO_4, 10 bar O_2, 170 °C, 6 h. Analyses were done by GC-MS, GC-FID, using *p*-xylene as external standard. (a) average of 5 runs; (b) 5 bar O_2. (c) 2-fluoro-1,4-benzoquinone.

In order to further probe phenol formation from benzene with $H_5PV_2Mo_{10}O_{40}$ in 50 % aqueous H_2SO_4, we turned to aerobic reactions, Table 1. For benzene, the reaction proceeded sluggishly at 10 bar O_2 with a good selectivity to phenol with some formation of diphenylether. No sulfate esters were observed presumably because there was sufficient water present to shift the equilibrium to phenol. At lower O_2 pressure the reaction was much less efficient; there was no oxygenation with 10 bar air. Some substituted substrates, PhX, where X = F, Cl, and NO_2 were also reacted. The phenols were formed as an isomeric mixture. Interestingly for benzene as substrate no 1,4-benzoquinone was observed, but for fluorobenzene significant amounts of 2-fluoro-1,4-benzoquinone were found. Chlorobenzene and nitrobenzene also reacted to yield the corresponding phenols, but acid catalyzed disproportionation reactions became significant.[19] For PhBr and PhI (not shown) this disproportionation was essentially the only reaction observed. It should be noted that although 10 bar O_2 was used in the reaction, the amount of O_2 in solution was in fact very low due to poor solubility of O_2 in the reaction medium (~1 mM), leading to a $H_5PV_2Mo_{10}O_{40}/O_2$ ratio of 100:1 in the reaction (see the SI for the relevant calculation). Since the results show that a reaction between the reduced polyoxometalate and O_2 is needed for oxygenation to occur, the low concentration in the solution phase of O_2 is the likely reason for the slow oxygenation reaction. It should be noted that after the reaction $H_5PV_2Mo_{10}O_{40}$ can be recovered unchanged, although during the reaction several forms of the catalyst may be present as previously discussed.[20]

Computational DFT analysis. The free energy of reactions in 50% H_2SO_4 were analyzed by DFT calculations, Scheme 2, show that reactions between neutral $H_5PV^V{}_2Mo_{10}O_{40}$ and benzene are all significantly endergonic. On the other hand, protonation of $H_5PV^V{}_2Mo_{10}O_{40}$ to yield $[H_6PV^V{}_2Mo_{10}O_{40}]^+$, **2**, is exergonic making an electron transfer process between **2** and benzene feasible

(ΔG_{298} = 0.9 kcal/mol). Protonation of **4** can further stabilize the interaction by 3.5 kcal/mol. These results support an affirmative answer to the first question addressed in the Introduction, i.e. whether the first reaction in Scheme 1 is possible in highly acidic media. Notably CPET reactions are not realistic.

Scheme 2. ΔG_{298} of Outer Sphere Reactions (in blue) Between Benzene and $H_5PV_2Mo_{10}O_{40}$ in 50% H_2SO_4.



To further analyze the fate of the benzene radical cation we calculated an ET-OT pathway, showing intermediates and a key transition state for possible formation of phenol in the absence of O_2, Figure 5 and 6. Comprehensive figures of optimized structures can be found in Figure S3 of the SI The initial ET induces high positive charge and large spin densities on the two symmetric C-atoms of benzene, Figure 5, which allows its coordination to yield **7T**, a triplet intermediate where benzene radical cation is bound to **4**. Hydrogen transfer stimulated by a charge induced interaction of a very acidic H atom bound to the coordination site in **7T** leads to **9T**, where the H atom is bound to the unfavorable terminal O atom, Figures S4, S5. Non-activated proton migration to the bridging sites yield triplet **8T** and open shell **8S** as the most stable calculated species. The calculated spin densities correlate well with the intermediate observed in the EPR experiments with only ~1% of the electron spin density on the benzene moiety, Figures S5, S6. These low free energy species represent the lowest energy points on the reaction profile and *de facto* thermodynamically preclude OT to yield phenol and the protonated reduced polyoxometalate $[H_8PV^{IV}{}_2Mo_{10}O_{40}]^+$. Thus, though the second reaction in Scheme 1 is exergonic, it is blocked by formation of adducts **8T** and **8S**.

Considering **2** as the most stable form of the polyoxometalate in 50% sulfuric acid, benzene oxidation to phenol is found to be exergonic by 14.7 kcal/mol, compared to 43.3 kcal/mol for benzene oxidation by oxygen, $C_6H_6 + ½ O_2 \rightarrow C_6H_5OH$. Thus, in the presence of oxygen as a final oxidant, transformation of **8T** and **8S** to phenol becomes exergonic by 34.0 and 30.5 kcal/mol, respectively. Without experimental evidence at this time for any intermediates in the aerobic reaction after initial formation of the benzene radical cation, it would be most speculative to delineate a specific reaction pathway. Given the strong dependence of phenol formation on the O_2 pressure, the reaction of O_2 with an intermediate to yield a superoxide and/or a peroxide by electron transfer(s) to yield an intermediate viable for oxygenation would be a reasonable assumption.

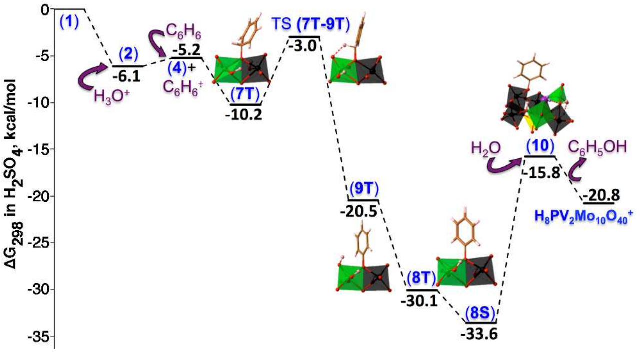


Figure 5. A free energy profile and key structures an ET-OT anaerobic mechanism showing formation of phenyl-polyoxometalate adducts **8T** and **8S** and thermodynamic interdiction of their transformation to phenol.

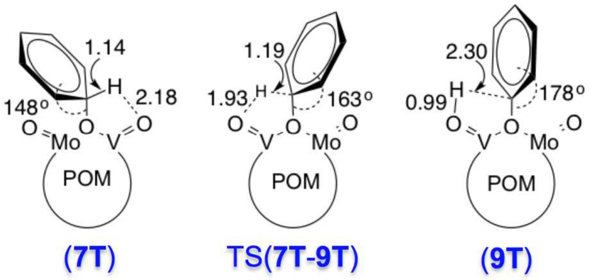


Figure 6. Detailed geometries of the initial, transition and final states of the benzene C-H bond breaking step.

In answer to the questions asked at the outset, we have shown by using visible spectroscopy and X-band and W-band EPR spectroscopy that ET oxidation of benzene is possible even at RT and that under aerobic, but not anaerobic conditions, phenol can be formed.

INFORMATION

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Present Addresses

Author Contributions

The manuscript was written through contributions of all authors.

ASSOCIATED CONTENT

Supporting Information

Supporting Information. Experimental and computational methods, and additional data. The Supporting Information is available free of charge on the ACS Publications website.

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SYNOPSIS TOC