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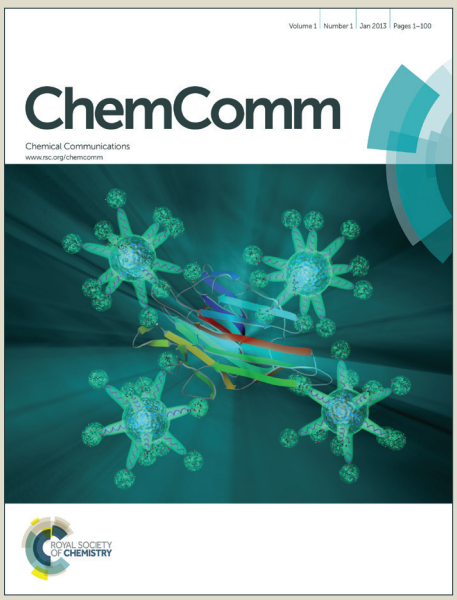

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Biomimetic oxidation of pyrene and related aromatic hydrocarbons. Unexpected electron accepting abilities of pyrenequinones.

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We present a mild catalytic method to oxidize PAHs and, in particular, pyrene. The pyrenediones are much better electron acceptors than benzoquinone in the gas phase and present similar accepting abilities in solution.

Polycyclic aromatic hydrocarbons (PAHs) have attracted a great deal of attention in areas of research as diverse as biochemistry,[1] astrochemistry[2] and materials science.[3] In this last field, PAHs have received part of the shock wave from the recent explosion of research in graphene,[4,5] due to their structural similarities.[6] Among PAHs, pyrene is probably one of the best-known organic chromophores. Its unique absorption and, in particular, its monomer/excimer emission properties have made it the fluorophore of choice for applications ranging from molecular recognition[7] to structural biology.[8] Due to its extended aromatic surface, it has also been utilized in the supramolecular association of carbon nanotubes[9] and graphene.[10] Therefore, synthetic methodologies for the structural variation of pyrene are in high demand.[11] Given their intrinsic stability, the chemical modification of pristine PAHs often relies on harsh conditions, like the utilization of strong oxidizing agents and/or acids. For instance, pyrene can be nitrated with HNO_3/CH_3COOH,[12] brominated with Br_2[13] or sulfonylated with SO_3.[14]

In nature, PAHs are metabolized by cytochrome P450 enzymes (CYPs) to form oxygen-containing electrophilic species, which are known to be carcinogenic.[15] Taking pyrene as an example, it is considered a priority environmental pollutant by the United States Environment Protection Agency, and its oxidation is an established method for its detoxification.[16] Pyrene can be oxidized to form mixtures of 1,6 and 1,8 pyrenediones (**1** and **2** in Table 1) by several microorganisms under aerobic conditions.[17] In a synthetic laboratory setting, a similar outcome can be obtained using extreme conditions, namely $K_2Cr_2O_7$ in 4M H_2SO_4 under reflux for 3 hours, which yield a modest 40% of the mixture of both diones.[18] Alternatively, $Na_2Cr_2O_7 \bullet 2H_2O$ in acetic anhydride and acetic acid can also be utilized to oxidize pyrene at room temperature. This last method requires 24 hours of reaction time and extensive purification to yield 31% and 18% of **1** and **2**, respectively.[19]

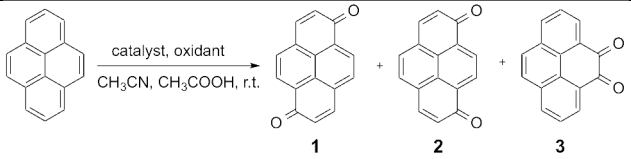
Here, we present a mild and fast method to oxidize pyrene to the corresponding quinoid 1,6- and 1,8-diketones with hydrogen peroxide, utilizing a non-heme iron complex as catalyst. This type of complexes have been successfully utilized as catalysts in the C−H oxidation of a variety of substrates,[20] including alkanes,[21] alkenes[22] and a few arenes[23] under relatively mild, environmentally friendly conditions, typically utilizing H_2O_2 as oxidant. Considering these precedents, we decided to investigate the oxidation of pyrene utilizing the following non-heme iron catalysts: $Fe(bpmen)(OTf)_2$, $Fe(bpycen)(OTf)_2$, and $Fe(pymcy)_2(OTf)_2$, where bpmen = N,N'-bis-(2-pyridylmethyl)-N,N'-dimethyl-1,2-ethylenediamine, bpycen = N,N'-bis(pyridin-2-ylmethylene)ethane-1,2-diimine, pymcy = N-(pyridin-2-ylmethylene)cyclohexanamine, and OTf = trifluoromethasulfonate (see Figure S1 in the ESI† for the structures).

Table 1 summarizes the reaction conditions we have tested in this work. In all cases, pyrene was dissolved in a 0.33 M CH_3COOH solution in CH_3CN, to which three separate additions containing one third of the total catalyst and H_2O_2 in CH_3CN were added at 10 min intervals. After the last addition, the solution was allowed to stir at room temperature for 10 more minutes and quenched with a saturated $NaHCO_3$ aqueous solution.[24] No oxidation products were observed with the imine-based catalysts $Fe(pymcy)(OTf)_2$ or $Fe(bpycen)_2(OTf)_2$ (entries 1 and 2 in Table 1). However, reaction was immediately apparent when utilizing $Fe(bpmen)(OTf)_2$ (entries 3–6 in Table 1). In analogy with the biooxidation by CYPs, the main products detected by HPLC analysis were the 1,6 and 1,8 pyrenediones (**1** and **2** in Table 1) with some residual 4,5-pyrenedione (**3** in Table 1) detectable in some of the runs. All products showed spectroscopic and analytical properties (^{1}H NMR, ^{13}C NMR and MALDI-TOF) consistent with their structure and the data reported in the literature (see the ESI†). Under optimized conditions (entry 5 in Table 1), 29%, 16% and 5% isolated yields for **1**, **2,** and **3** were obtained**,** respectively. Adding more catalyst (entry 6 in Table 1) results in complex mixtures of oxidation and decreased yields for **1** and **2**. Although the isolated yields are relatively modest, the mild method proposed here compares well to the much stronger oxidation conditions reported earlier.[18-19]

Other small PAHs, like napthalene and anthracene also produce the corresponding 1,4-naphtoquinone (NQ) and 9,10-anthraquinone (AQ),

in modest to good yields (32% and 85%, respectively, entries 2 and 3 in Table 2). In both cases conversion was complete by TLC, but naphthalene yielded a mixture of oxidation products where 1,4-naphthoquinone was the main product. Unsurprisingly, the oxidation of anthracene proceeded cleanly to yield 9,10-anthraquinone. However, other substrates, such as benzene and phenanthrene (entries 1 and 4 in Table 2), did not show signs of reaction by TLC analysis.

Table 1 Non-heme iron catalyzed oxidation of pyrene.



Entry	Catalyst (mol%)	Oxidant (eq.)	Yield (%)[a] 1	2	3
1	$Fe(pymcy)_2(OTf)_2$	H_2O_2 (3 eq.)	-	-	-
2	Fe(bpycen)$(OTf)_2$ (15%)	H_2O_2 (3 eq.)	-	-	-
3	Fe(bpmen)$(OTf)_2$ (5%)	H_2O_2 (3 eq.)	14	8	-
4	Fe(bpmen)$(OTf)_2$ (10%)	H_2O_2 (3 eq.)	17	9	-
5	Fe(bpmen)$(OTf)_2$ (15%)	H_2O_2 (3 eq.)	29	16	5
6	Fe(bpmen)$(OTf)_2$ (20%)	H_2O_2 (3 eq.)	15	9	-

[a] Isolated yields, after column chromatography.

Table 2 Fe(bpmen)$(OTf)_2$ catalyzed oxidation of other PAHs.[a]

Entry	Reagent	Product	Conversion	Yield[b]
1	Benzene	-	-	-
2	Naphthalene	1,4-Naphthoquinone	100 %	32 %
3	Anthracene	9,10-Anthraquinone	100 %	85 %
4	Phenanthrene	-	-	-

[a] All reactions were run under the conditions described in entry 5 of Table 1 and the main text. [b] Isolated yields, after column chromatography.

Quinones are key electron acceptors in both biology and industry. For instance, coenzyme Q10, which features a *p*-benzoquinone (BQ) core as redox unit, is involved in the electron transport chain in aerobic respiration, and doubles as antioxidant inhibiting both the initiation and the propagation of lipid and protein oxidations.[25] From an industrial point of view, 2-alkylanthraquinones are utilized to produce hydrogen peroxide since the 1940s, and indeed the anthraquinone method still monopolises the large scale production of H_2O_2.[26] Despite these facts, research on pyrenequinones has focused on their environmental interest and their use as photosensitizers in the production of singlet oxygen for photodynamic therapy.[27] Surprisingly, the electron-accepting properties of pyrenequinones have hardly been investigated.[28]

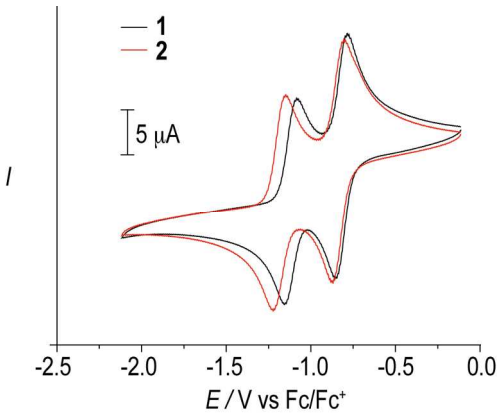


Fig. 1 Cyclic voltammograms of **1** (black) and **2** (red) in CH_3CN at room temperature. Glassy carbon as working electrode, $Ag/AgNO_3$ as reference electrode, 0.1 M $TBAPF_6$ as electrolyte.

Figure 1 displays the cyclic voltammograms of **1** and **2** in CH_3CN. Both quinones show two reversible reduction waves at half-wave potentials $E^1_{1/2} = -0.82$ V and $E^2_{1/2} = -1.12$ V for **1** and $E^1_{1/2} = -0.84$ V and $E^2_{1/2} = -1.19$ V for **2**, with respect to ferrocene/ferricenium. For comparison, BQ undergoes reduction at $E^1_{1/2} = -0.88$ V and $E^2_{1/2} = -1.47$ V, NQ at $E^1_{1/2} = -1.06$ V and $E^2_{1/2} = -1.63$ V and AQ at $E^1_{1/2} = -1.31$ V and $E^2_{1/2} = -1.89$ V under identical experimental conditions (see the ESI).

The cathodic shift of the first reduction potential along the BQ, NQ, AQ series can be easily rationalized in terms of the energy and topology calculated for the LUMO (Figure 2). The LUMO is mainly localized on the quinoid ring and suffers a destabilization along the BQ, NQ, AQ series due to the additional antibonding interactions rising from the inclusion of lateral benzene rings. In contrast, the LUMOs of **1** and **2** stand close in energy with respect to the LUMO of BQ because they resemble two BQ LUMOs with no additional destabilizing interactions. This explains, to a first approximation, the similar values obtained for the first reduction potential of **1**, **2**, and BQ.

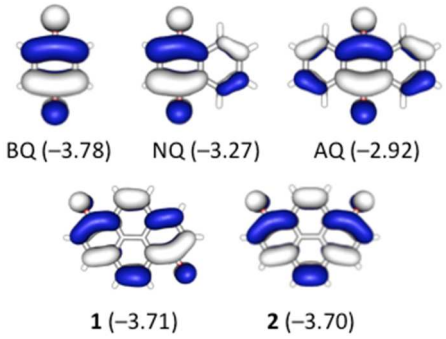


Fig. 2 Topology and energy (in eV) calculated for the lowest-unoccupied molecular orbital (LUMO).

Although reduction potentials are usually considered a valid method to evaluate the electron acceptor ability of molecules, their electron affinity (EA) is a direct measurement of it. Table 3 gives the adiabatic EA values computed at room temperature using the G3(MP2) procedure (see the ESI† for full computational details). The G3(MP2) method provides an EA of 1.92 eV for BQ in very good agreement with the experimental value of 1.91 eV.[29] Likewise, the EA values calculated for NQ (1.83 eV) and AQ (1.66 eV) reproduce accurately the experimental values of 1.81 and 1.59 eV, respectively.[29] Therefore, the electron-accepting ability decreases with the size of the system along the BQ, NQ, AQ series. In contrast, the EA values calculated for **1**

(2.32 eV) and **2** (2.34 eV) indicate that the pyrenediones are remarkably stronger electron acceptors than BQ. To rationalize the apparent mismatch between the theoretical EAs, calculated in gas phase, and the experimental $E_{1/2}$ values, measured in CH_3CN, the first half-wave reduction potentials were estimated theoretically using the expression[30]

$$E_{1/2} = \Delta G_{red}/(-nF) + E_{ref}$$

where ΔG_{red} is the free energy difference for the one-electron attachment reaction in solution (i.e. $\Delta G_{red} = \Delta G_g + \Delta\Delta G_{solv}$), n is the number of electrons transferred (n = 1 in this case), F is the Faraday constant and E_{ref} is the potential of the reference electrode.

The free energy difference in gas phase (ΔG_g) and the free energy of solvation ($\Delta\Delta G_{solv}$) were computed at the G3(MP2) level and using a continuum solvation model (PCM with acetonitrile), respectively (see the ESI†). ΔG_g follows the same trend as the EA values (Table 3) because entropy effects are computed as small as 0.5 cal/mol·K. The origin of the larger EAs calculated for **1** and **2** compared to BQ stems from the larger π-electron delocalization in the LUMO of the formers at nearly the same molecular orbital energy (Figure 3). On the other hand, the $\Delta\Delta G_{solv}$ stabilization term is computed to be 0.4 eV larger for BQ than for **1** and **2**. The decrease (in absolute value) of the $\Delta\Delta G_{solv}$ term along the BQ > NQ > AQ > **1** = **2** series (Table 3) is mainly due to the fact that solvation effects stabilize to a larger extent the anion of BQ (–2.25 eV) than the anions of NQ (–2.13 eV), AQ (–2.03 eV), **1** (–1.94 eV) and **2** (–1.95 eV) (Table S1). EA and solvation stability differences between BQ and the two pyrenediones cancel each other and result in similar ΔG_{red} values for the three systems (Table 3). The final theoretical $E_{1/2}$ values are computed to be –0.90, –0.89 and –0.87 V for BQ, **1** and **2**, respectively, in very good agreement with the experimental data. Accurate values are also predicted for NQ and AQ (Table 3). Calculations therefore support the electron-acceptor capabilities measured in solution for pyrenediones **1** and **2**, and ascribe $E_{1/2}$ values similar to BQ due to the cancellation of two competing terms: i) the larger EAs computed for **1** and **2** in gas phase and ii) the less stabilizing solvation term ($\Delta\Delta G_{sol}$) in the pyrenediones. This result contrasts with the empirical linear-regression procedure usually employed to relate $E_{1/2}$ and EA ($E_{1/2}$ = EA – $\Delta\Delta G_{solv.}$ + E_{ref}), where $\Delta\Delta G_{solv}$ is considered to be constant for a given family of structurally similar compounds.[31]

Table 3. Thermochemical (in eV) and electrochemical (in V) data calculated for the one-electron attachment $A + e^- \rightarrow A^-$ reaction. Experimental first half-wave reduction potentials are also included.

	BQ	NQ	AQ	**1**	**2**
$EA_{298K,\,theor}$ [a]	1.92	1.83	1.66	2.32	2.34
$EA_{298K,\,exp}$ [b]	1.91	1.81	1.59	-	-
$\Delta G_{g,298K}$ [c]	–2.07	–1.97	–1.80	–2.48	–2.49
$\Delta\Delta G_{solv}$	–2.02	–1.91	–1.81	–1.62	–1.62
ΔG_{red}	–4.09	–3.88	–3.61	–4.09	–4.12
$E^1_{1/2,theor}$ [d]	–0.90	–1.11	–1.37	–0.89	–0.87
$E^1_{1/2,exp}$	–0.88	–1.06	–1.31	–0.82	–0.84

[a] Zero-point energy and thermal corrections are included. [b] Experimental values extracted from reference 29. [c] Corrected values taking into account the free electron as an ideal monoatomic gas, 5/2 RT,[32] and the correction for the change in standard state from 1 atm to 1 mol·L^{-1}.[33] [d] E_{ref} = –4.99 V (reduction potential of Fc^+/Fc).[34]

Conclusions

In conclusion, we have described a mild oxidation method for pyrene and other small PAHs, based on the use of a non-heme iron catalyst, $Fe(bpmen)(OTf)_2$, with H_2O_2 as oxidant. Our method affords mainly 1,6- and 1,8-pyrenediones, in analogy with the oxidation of pyrene by natural CYPs. Although modest, the isolated yields of pyrenequinones are synthetically useful, and comparable to those recently reported for the catalytic oxidation of smaller PAHs.[35] To the best of our knowledge, this constitutes the first example of Fe-catalyzed C-H oxidation of PAHs.

The electron accepting properties of both pyrenequinones were investigated experimentally through cyclic voltammetry, which showed that **1** and **2** are slightly better acceptors than BQ in solution. A detailed theoretical investigation revealed that the pyrenequinones show much higher EAs than BQ, approximately by 0.4 eV. By calculating the theoretical reduction potentials in solution, we showed that the difference in EA is cancelled out by a significantly decreased $\Delta\Delta G_{solv}$ in the case of **1** and **2** with respect to BQ. Our results suggest that the commonly accepted practice of assuming that $\Delta\Delta G_{solv}$ remains constant for a family of structurally related compounds,[31] such as the quinones under study, can sometimes lead to significant errors.

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Notes and references

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