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Hydrocarbon Cation Radical Formation by Reduction of Peroxydisulfate

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We report evidence for the formation of hydrocarbon radical cations upon oxidation by sulfate radical anions that are generated during the electrochemical reduction of peroxydisulfate. Although counter-intuitive, oxidation reactions can be driven by a reduction reaction. This happens when the product of a one-electron reduction undergoes a bond cleavage reaction to produce a species that is much easier to reduce (i.e., is a stronger oxidant) than the original species. In electrochemical parlance, this is called an ECE-reaction. Such a mechanism is the basis of the coreactant scheme in electrogenerated chemiluminescence (ECL) studies where homogeneous reduction of peroxydisulfate anion ($S_2O_8^{2-}$) leads to the formation of a strong oxidant, the sulfate radical anion ($SO_4^{\bullet-}$).[1] In ECL, this radical anion reacts with a reduced species, $R^{\bullet-}$, which is formed during the same reduction step, to produce an excited state via electron transfer.[1] The following overall reaction mechanism has been proposed:

$$R + e^- \rightarrow R^{\bullet-} \tag{1}$$

$$R^{\bullet-} + S_2O_8^{\ 2-} \rightarrow R + SO_4^{\ 2-} + SO_4^{\ \bullet-} \tag{2}$$

$$R^{\bullet-} + SO_4^{\ \bullet-} \rightarrow R^* + SO_4^{\ 2-} \tag{3}$$

A question that arises is whether an alternative path, in which $SO_4^{\bullet-}$ reacts with R to form the radical cation as an intermediate, occurs:

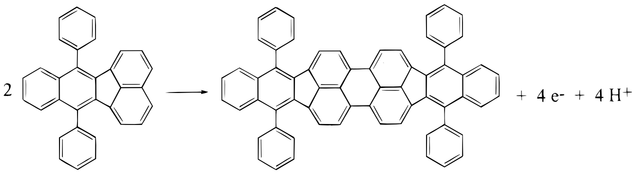
$$R + SO_4^{\ \bullet-} \rightarrow R^{\bullet+} + SO_4^{\ 2-} \tag{4}$$

$$R^{\bullet-} + R^{\bullet+} \rightarrow R^* + R \tag{5}$$

Studies aimed at demonstrating this possibility, for example, by searching for oxidation products of R during the reduction of peroxydisulfate, have never been successful because of the inability to trap a strong oxidant in either the presence of strong reductants such as $R^{\bullet-}$ or in the reducing environment near the cathode.

By using aromatic hydrocarbons whose cation radicals undergo a rapid dimerization reaction for R, we can now demonstrate through both electrochemical and ECL measurements that reaction 4 does in fact occur. The structure of the two compounds employed in this investigation, diphenylbenzo[*k*]fluoranthene (PBF) and 7,14-diphenyloacetonaphthol[1,2-*k*]-fluoranthene (ANF) are given in Schemes 1 and 2. For PBF (Scheme 1), the radical cation that is formed upon electrochemical oxidation at potentials greater than 1.60 V vs SCE, rapidly dimerizes ($k = 7500$ M^{-1} s^{-1}) via radical cation-radical cation coupling to form bis-4,4′-diphenylbenzo[*k*]fluoranthene.[2] Fluorescence and ECL measurements showed that the PBF monomer emits ~444 nm while the PBF dimer emits ~646 nm. In the case of ANF (Scheme 2), soluble oligomers are formed during electrochemical oxidation of the monomer at 1.6 V vs SCE. Further oxidation of these oligomers leads to intramolecular reactions to form ladder structures within the chains and the formation of an insoluble polymer that precipitates on the electrode.[3]

Scheme 1



Scheme 2

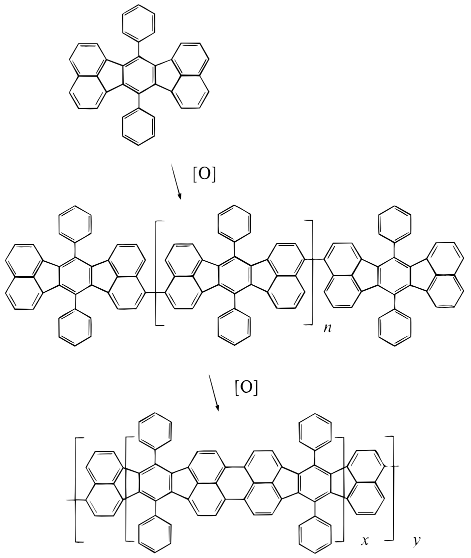


Figure 1 shows the voltammograms of a 2.5 mM solution of PBF (A) and a 2 mM solution of ANF (B) before (a) and after (b) the addition of 8 mM peroxydisulfate anion, $S_2O_8^{2-}$. With both compounds, the first reduction wave, at $E_p = -1.9$ V vs SCE for PBF and $E_p = -1.62$ V vs SCE for ANF, went from a one-electron reversible wave to a multi-electron irreversible catalytic wave in the presence of peroxydisulfate. This catalytic response indicates regeneration of the neutral fluoranthene derivative upon the homogeneous electron transfer from the electrochemically generated radical anion to peroxydisulfate anion (eq 2). The resulting sulfate radical ion can then undergo a number of homogeneous electron transfers with the neutral species and radical ions of both compounds near the surface of the electrode. These reactions (eqs 3−5), in turn, lead to the formation of the excited state for ECL emission as well as the possibility of generating the radical cation from the neutral monomer leading to either the dimer or polymer (Schemes 1 and 2).

For ANF, radical cation-radical cation coupling results in a thin polymer film, which is electrochemically active on the surface of the electrode; therefore, the presence of the polymer film after reduction in a solution containing peroxydisulfate confirms the formation of radical cations. A solution of 2 mM ANF and 8 mM $(TBA)_2S_2O_8$ was cycled between −0.5 and −2.15 V vs SCE until the polymer film was electrochemically detected. Afterward, the Pt electrode was rinsed in electrolyte solution, followed by a rinse in benzene and then immersion in a solution of supporting electrolyte. A cyclic voltammogram (CV) obtained under these

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(1) (a) White, H. S.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6891. (b) Richards, T. C.; Bard, A. J. *Anal. Chem.* **1995**, *67*, 3140. (c) Richter, M. M.; Bard, A. J. *Anal. Chem.* **1996**, *68*, 2641.

(2) (a) Debad, J. D.; Morris, J. C.; Magnus, P.; Bard, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 2374. (b) Debad, J. D.; Morris, J. C.; Magnus, P.; Bard, A. J. *J. Org. Chem.* **1997**, *62*, 530.

(3) Debad, J. D.; Bard, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 2476.

10.1021/ja000307y CCC: $19.00

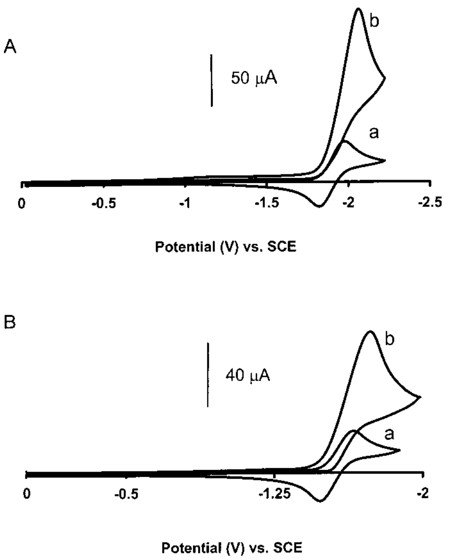

Figure 1. Cyclic voltammogram of 2.5 mM diphenylbenzo[*k*]fluoranthene (A) and 2 mM of 7,14-diphenyloacetonaphthol[1,2-*k*]-fluoranthene (B) in 4:1 benzene/CH_3CN containing 0.2 M $TBAPF_6$ as an electrolyte (a) before and (b) after the addition of 8 mM $(TBA)_2S_2O_8$ at a scan rate of 500 mV/s.

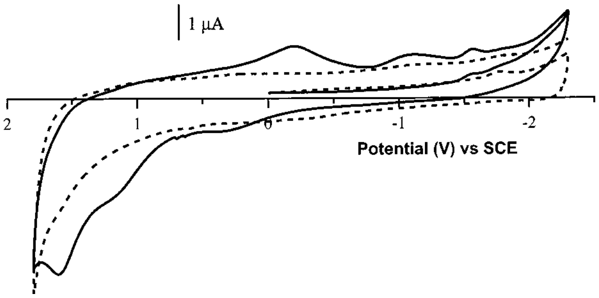

Figure 2. Cyclic voltammogram of a thin film of the ANF polymer, previously deposited on Pt disk electrode by cycling between −0.5 and −2.1 V vs SCE in a solution of 2 mM ANF and 8 mM $(TBA)_2S_2O_8$, in a 4:1 benzene/CH_3CN solution containing 0.2M $TBAPF_6$ at a scan rate of 200 mV/s (solid line). A cyclic voltammogram obtained under the same experimental conditions in the absence of $(TBA)_2S_2O_8$ (dashed line).

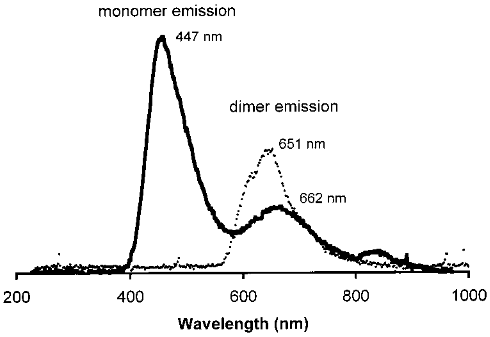

Figure 3. Electrogenerated chemiluminescence emission spectrum of 2.5 mM diphenylbenzo[*k*]fluoranthene (solid line) and 0.5 mM bis-4,4′-diphenylbenzo[*k*]fluoranthene (dotted line) in 4:1 benzene/acetonitrile containing 0.2 M $TBAPF_6$ as an electrolyte. All spectra were obtained with an integration time of 10 min.

experimental conditions is shown in Figure 2 (solid line). Also shown is a CV obtained after cycling in a solution containing only 2 mM ANF and no peroxydisulfate (dashed line). Upon comparing these two CVs, one can see that there is marked difference between an electrode repeatedly reduced in the presence of peroxydisulfate to one repeatedly reduced without peroxydisulfate. On the first cathodic sweep, two weak waves appear around −1.6 and −1.8 V. On the anodic sweep, three waves are seen around 0.35, 1.15 and 1.64 V. The two latter waves coincide with those assigned to polymer films of ANF formed by electrochemical oxidative coupling.[3] Upon sweep reversal, no reduction wave corresponding to the oxidations at 1.15 and 1.64 V is seen; instead, two broad peaks at −0.20 and −1.13 V are observed. On the second and all following scans, the CV remains basically the same, although the current slowly decreases indicating loss of the polymer film upon repeated oxidation and reduction. This electrochemical behavior has been previously observed with these polymer films. Thus, a polymer film is deposited during reduction only in the presence of peroxydisulfate.

Evidence of radical cation formation is also demonstrated by the appearance of dimer emission in the ECL spectrum of the PBF monomer during its reduction in the presence of peroxydisulfate. Figure 3 shows an ECL emission spectrum (solid line) obtained from a 2.5 mM PBF solution containing 8 mM $S_2O_8^{2-}$ as the working electrode was pulsed between 0.022 V and past the first reduction wave of the monomer to ∼ −2.122 V vs SCE with 100 ms steps. The main band at a λ_{max} of 447 nm corresponds to the fluorescence and ECL emission the monomer. However, a second band at a λ_{max} of 662 nm also appears. Based on our previously reported work, this band corresponds to the ECL emission of the dimer, bis-4,4′-diphenylbenzo[*k*]fluoranthene that is only formed on PBF oxidation.[2]

To confirm this assumption, ECL of a 0.5 mM dimer solution prepared by chemical synthesis was obtained with the same amount of peroxydisulfate in solution. In this experiment, the electrode was pulsed between 0.022 V and past the first reduction wave of the dimer, ∼−1.52 V vs SCE. The resulting ECL spectrum (Figure 3, dotted line) clearly indicates that the second emission band is due to the formation of the dimer during the reduction of the monomer in the presence of peroxydisulfate. In our previously reported work, PBF was shown to oxidize at potentials above 1.60 V vs SCE. This means that the $E°$ for reduction of the sulfate radical is positive of that for DBF oxidation to the radical cation. In fact, the value has been reported to be +3.2 V vs SCE.[4] Overall, the results presented here confirm that the sulfate radical anion, generated during reduction of peroxydisulfate can generate radical cations, and these may be intermediates in the formation of the singlet excited state of aromatic hydrocarbons in ECL experiments.

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(4) Memming, R. *J. Electrochem. Soc.* **1969**, *116*, 785.