Electron Transfer to Sulfenate Esters

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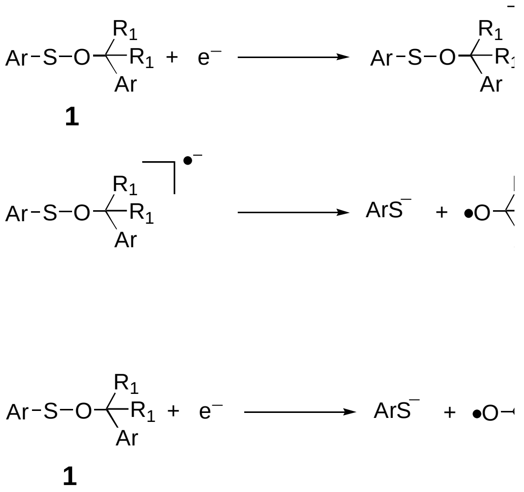
Our groups' interest has been the study of dissociative electron transfer (ET) reactions, specifically those of endoperoxides. We have employed various electrochemical techniques in our investigations of ET to endoperoxides. The endoperoxide systems represent the ultimate concerted dissociative ET system and are characterized by large intrinsic barriers due to the contribution of the bond dissociation energy. (Donkers, Workentin *Chem. Eur. J.* **2001**, 18, 4012). ET to disulfides, on the other hand, has been observed to occur via a stepwise dissociative pathway (Daasbjerg et al. *J. Am. Chem. Soc.* **1999**, 121, 1750), though a large intrinsic barrier is also observed because of significant bond lengthening that accompanies ET. We have initiated preliminary studies into ET to sulfenate esters (**1**), compounds that contain an S-O moiety, which is structurally reminiscent of both peroxides and disulfides. These studies will reveal what similarities and differences may exist upon ET to these compounds compared to O-O and S-S species and provide important new insights into dissociative ET mechanisms.



R_1 = Ar or H