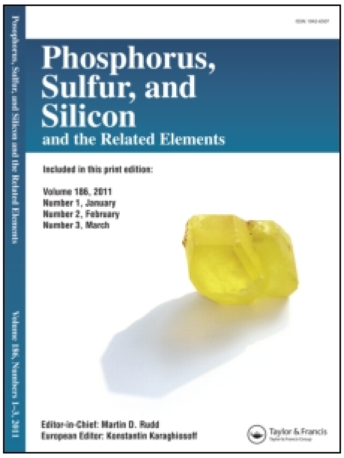

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Experimental and Theoretical Studies of Radical Intermediate Reactivity During the Electroreduction of Dithiolethiones and the Corresponding Dithiolium Cations

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Experimental and Theoretical Studies of Radical Intermediate Reactivity During the Electroreduction of Dithiolethiones and the Corresponding Dithiolium Cations

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INTRODUCTION

It is interesting to study the electron-transfer reactions involving 1,2-dithiole-3-thiones **1** and their S-alkylated derivatives, 3-methylsulfanyl-1,2-dithiolium cations **2** because derivatives **1** are known for their antioxidant and radical scavenger activities. Indeed, redox properties may be implicated in the new therapeutic use of Sulfarlem® (**1a**; $R^4 = H$, $R^5 = p\cdot CH_3O\text{-}C_6H_4$) as a chemopreventive agent of lung cancer.[1] Some electrochemical data were already available for **1** but not for **2**.[2,3]

RESULTS

The electrochemical study was realized at a platinum or glassy carbon working electrode in DMF/Bu_4NBF_4 medium. It revealed that **1** and **2** showed many close analogies in their electrochemical behavior. The

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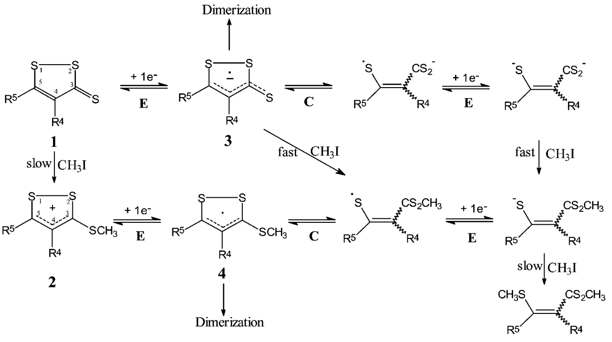
cyclic voltammetry interpretation was that radical anion **3** and radical **4** followed a dimerization route or were involved in an ECE mechanism. When the 4 position of the dithiole ring was free, the mechanism was a combination of the two pathways. When the 5 position ring was free, the mechanism mainly followed the dimerization route. Bechgaard *et al.* already observed that radical dimerization occurs in dithiolium cations substituted in position 3, 4, or 5 by alkyl or aryl groups.[4]

Density functional calculations have been carried out at the B3LYP/6-31+G(d) level of theory on 5-phenyl-1,2-dithiole-3-thione **1b** and its S_3-protonated form mainly to investigate the ECE process. The transition states for the chemical step of this mechanism appeared to be located about 3 kcal/mol above the reactants, indicating therefore that the radicals displayed an intrinsic stability toward S_1—S_2 bond cleavage.



a $R^4 = H, R^5 = p.CH_3O\text{-}C_6H_4$
b $R^4 = H, R^5 = C_6H_5$
c $R^4 = H, R^5 = p.CH_3\text{-}C_6H_4$
d $R^4 = C_6H_5, R^5 = H$
e $R^4 = p.CH_3\text{-}C_6H_4, R^5 = H$

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