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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; $R^4 = H$, $R^5 = p \cdot CH_3O \cdot C_6H_4$) as a chemopreventive agent of lung cancer. 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/Bu₄NBF₄ 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 ${\bf 1b}$ 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.

Dimerization Dimerization
$$\frac{1}{R^4}$$
 Solve $\frac{1}{E}$ Results $\frac{$

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