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Electrochemical initiation by sulfur dioxide of radical-chain trifluoromethylation processes of thiophenols with bromotrifluoromethane

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Abstract

Sulfur dioxide may serve as an efficient catalyst for the electrochemical trifluoromethylation of thiophenols by Freon F13B1 (CF_3Br), which enables implementation of trifluoromethylation in an energy-saving radical-chain regime.

Keywords: Electrochemical trifluoromethylation; Thiophenols; Radical-chain processes; Bromotrifluoromethane; Sulfur dioxide catalyst

1. Introduction

Perfluoroalkyl sulfides are used for the synthesis of dyes, insecticides, etc. Typically, in the production of such sulfides, perfluoroalkyl halides, R_F Hal, are utilized as perfluoroalkylating agents, capable, when chemically [1–3] or electrochemically [4] reduced, of generating active radicals R_F .

 $R_{F}Hal \xrightarrow{+e} R_{F}Hal^{-} \longrightarrow R_{F} \cdot + Hal^{-}$

Among the perfluoroalkyl halides, iodides have been the most extensively exploited for the alkylation of thiophenols despite the fact that R_FCl and R_FBr would appear to be more attractive candidates as they are cheaper and more readily available. However, their reactions frequently proceed with much lower yields and call for more arduous conditions [1,5]. Since electrochemical activation of Freon F13B1 (CF₃Br) occurs at rather high potential (compared to CF₃I) [6], the much lower yields of trifluoromethylated products observed may be related to the capacity of CF₃ radicals to undergo reduction in the near-electrode layer. This impedes creation in the solution of a sufficient concentration of radicals for an effective and extensive radical-chain substitution process.

2. Results and discussion

In this paper, we report the possibility of the effective electrochemical trifluoromethylation of thiophenols under the action of CF_3Br using sulfur dioxide as the electron carrier. The use of SO_2 makes it possible to lower the potential of CF_3Br activation and shift the process from the near-electrode layer to the solution.

The electrosynthesis of p-XC₆H₄SCF₃ (X=H, Cl, Br, NHCOOCH₃, NO₂) was performed potentiostatically at the SO₂ reduction potential. The results of the investigations conducted are listed in Table 1. As follows from the data in the table, the Faraday yield of trifluoromethylaryl sulfides considerably exceeded 100% (except for X = NO₂), and the product yields approached quantitative values in going from X=NO₂ to X= NHCOOCH₃.

Table 1

The influence of substituents on the products and Faraday yields of p-XC₆H₄SCF₃

Substituent X in p -XC ₆ H ₄ SCF ₃	Product yield of thioether (%)	Faraday yield of thioether (%)
NHCOOCH ₃	94	376
н	78	312
Br	64	256
Cl	60	240
NO ₂	24	96

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The yield of trifluoromethylaryl sulfides was critically dependent both on the concentration of SO₂ mediator and the amount of electricity passed. Specifically, in the case of p-bromothiophenol, a decrease in the SO₂ content relative to thiophenol led to a perceptible decline in the yields of p-XC₆H₄SCF₃. (For [SO₂]/[p- BrC_6H_4SH = 1, the yield of *p*-BrC₆H₄SCF₃ was equal to 64% while for $[SO_2]/[p-BrC_6H_4SH] = 0.3$, the yield was 18%). A decrease in the quantity of electricity passed (Q) from the value needed for the complete one-electron reduction of SO₂ ($Q=1 \text{ F mol}^{-1}$) to Q = 0.25 F mol⁻¹ had little effect on the yield of $BrC_6H_4SCF_3$ (70% and 64%, respectively), with the current yields being well in excess of 100%. When Qdecreased further (0.125 F mol⁻¹) the yield of Br- $C_6H_4SCF_3$ fell to 26%, whereas the Faraday yield remained quite high (208%).

The fact that the Faraday yield of the trifluoromethylation products (except for the *p*-nitro derivative) was well over 100% for the processes explored indicates an electrochemically initiated radical-chain substitution mechanism which may be depicted as follows:

- (a) $SO_2 + e \longrightarrow SO_2^{-}$
- (b) $SO_2^- + CF_3Br \longrightarrow SO_2 + CF_3 \cdot + Br^-$
- (c) $CF_3 \cdot + SO_2^- \longrightarrow CF_3SO_2^-$
- (d) $CF_3 \cdot + XC_6H_4S^- \longrightarrow XC_6H_4SCF_3^-$
- (e) $XC_6H_4SCF_3^- + SO_2 \longrightarrow XC_6H_4SCF_3 + SO_2^-$

As can be seen from the scheme, the CF₃ radicals generated may be involved in competitive interactions: some of them are likely to be added to form trifluoromethanesulfinic acid (CF₃SO₂H) with yields of 5%-15% [7-9], whose presence in the systems under investigation has been verified by ¹⁹F NMR spectroscopy. Other CF₃ radicals are added to thiophenolate (step d), the resulting stable $XC_6H_4SCF_3^-$ ion-radical transferring an electron to the acceptor (evidently SO₂) and being transformed to trifluoromethylaryl sulfide. Increasing the accepting capacity of the X substituent in the nucleus of thiophenol and XC₆H₄SCF₃ reduces the probability of step d as the nucleophilicity of the thiophenolate is lowered, impeding the electron transfer to the acceptor in step e and thus bringing about a reduced yield of product. This occurs in the case of nitrothiophenol.

3. Experimental details

Electrolysis was conducted in both glass filter-divided and undivided cells with platinum electrodes (S = 5.5 cm^2) with stirring. A weighed sample of p-XC₆H₄SH $(1.6 \times 10^{-3} \text{ mol})$ and SO₂ solution in DMFA (5 ml, 1.6×10^{-3} mol) were added to an argon-purged solution of dimethyl formamide (25 ml) and pyridine (5 ml) containing Et_4NClO_4 (4×10⁻³ mol) as the supporting electrolyte. The electrolysis was run potentiostatically at a cathode potential of -0.9 to -1.0 V vs. Ag/ AgNO₃, while bubbling 5–10-fold excess of CF₃Br using a peristaltic pump. After passing a given amount of electricity (Q = 0.125 - 1 F mol⁻¹) the process was stopped. The reaction product was discharged into 3-4fold excess of water and extracted with chloroform; the organic layer was rinsed successively with sodium hydroxide solution, dilute hydrochloric acid and water, dried and the chloroform distilled. The product yield was determined by ¹⁹F NMR spectroscopy (CXP-90, Bruker) and by GLC methods (1.5 m SE-30 on Chromatotron column).

All the resulting products are well-documented compounds, and their characteristics (¹H, ¹⁹F NMR), melting (boiling) temperatures and refractive indices were consistent with literature data.

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