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# Fluoroalkylation of thiophenols with Freons using conjugated electron transfer mediator systems composed of methylviologen-SO<sub>2</sub> and $I_2$ -SO<sub>2</sub>

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# Abstract

Methylviologen-sulfur dioxide and iodine (iodide)-sulfur dioxide have been shown to mediate electron transfer from thiophenols to Freons and perform the fluoroalkylation of thiophenols under mild conditions. © 1999 Elsevier Science S.A. All rights reserved.

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#### 1. Introduction

It is rather well known that the popular use of Freons as aerosols, coolants, etc. has caused a significant reduction of the stratospheric ozone layer. However, an alternative use of these harmful chemicals involves their utilization in the preparation of intermediates in organic synthesis, particularly in the synthesis of fluoroalkyl compounds [1-3]. It has been shown that methylviologen can serve as an effective catalyst in the preparation of perfluoroalkylsulfides from the reaction of perfluoroalkyliodides with thiophenols [4]. A direct transfer of electron from thiophenol to Freons in the presence of viologen has been deemed not possible. However, it has been demonstrated that SO<sub>2</sub> can serve as an effective mediator in electron transfer from a cathode to CF<sub>3</sub>Br and thereby lead to the electrochemical trifluoromethylation of thiophenols [5,6]. In view of the poor affinity of SO<sub>2</sub> for electrons, it is difficult for SO<sub>2</sub> to accept an electron from thiophenol and transfer it to CF<sub>3</sub>Br in the absence of potential, high pressure and temperature. In so far as each of the above-mentioned mediators perform only half of the function, namely either to accept an electron from the nucleophile (thiophenol) or to transfer it to Freon, it was considered interesting to explore the mutually complementary use of these mediators to activate Freons via a cascade electron transfer from the nucleophile to Freons (R<sub>F</sub>X). The highly reactive R<sub>F</sub> radicals thus generated can then be used in the perfluoroalkylation of thiophenols under mild homogeneous conditions as shown below:

F13B1 (CF<sub>3</sub>Br) and F113 (CFCl<sub>2</sub>CF<sub>2</sub>Cl), and thiophenol and *p*-thiocresol were used in this study as Freons and nucleophiles, respectively. This reaction was conducted in a 1:1 mixture of dimethylformamide (DMF) and pyridine to enhance the nucleophilicity of thiophenols.

### 2. Results and discussion

As shown by spectrophotometric results, both  $MV^{+\bullet}$  iodides and chlorides react with thiophenols via the formation of the corresponding radical cation (Diagram 1, step 1). The immediate appearance of the intense absorption bands at  $\lambda_{max} = 398$  and 609 nm, characteristic of  $MV^{+\bullet}$  when  $MV^{2+}$  was added to solutions of thiophenols, serves as the evidence for this phenomenon. The rate of single-electron reduction of methylviologen diiodide with thiophenols to  $MV^{+\bullet}$ , spectrophotometrically recorded for  $MV^{+\bullet}$  by the  $\lambda_{max} = 609$  nm adsorption band intensity, is described by a kinetic equation of the second-order with first-order for each of the reagents:

$$v = k_2 [\text{PhSH}] [\text{MV}^{2+}2\text{I}^{-}]$$

for C<sub>6</sub>H<sub>5</sub>SH and *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SH, with  $k_2^{30} = 4.6$  and 7.2 l mol<sup>-1</sup> s<sup>-1</sup>, correspondingly. The kinetic data show that the interaction of thiophenols with MV<sup>2+</sup> proceeds with a rather high rate. When adding F13B1 and F113 Freeons into

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Fig. 1. Cyclic voltammetry of  $MV^{2+}2I^-\text{-}SO_2$  in  $DMF+Py+0.1\,M$   $Bu_4NBF_4$  at  $25^\circ\text{C}.$  (a)  $MV^{2+}2I^ (5\times10^{-4}\text{ mol})$  alone; (b)  $MV^{2+}2I^ (5 \times 10^{-4} \text{ mol})$  after addition of SO<sub>2</sub> ( $2.5 \times 10^{-3} \text{ mol}$ ); and (c) after further bubbling of the excess of  $CF_3Br$ . Scan rate: 0.2 v s<sup>-1</sup>.

the solution of the MV<sup>+•</sup> cation radical, the concentration of MV<sup>+•</sup> does not change.

This observation suggests that in the absence of other mediators, the radical cation cannot transfer the electron from thiophenol to Freon. To see whether the electron transfer can occur from methylviologen to SO2, cyclic voltammetry has been used to monitor the transfer process for MV+ iodides and chlorides both in the presence and absence of SO<sub>2</sub>. As shown in Fig. 1(a),  $MV^{2+}$  dication in the absence of SO<sub>2</sub> is reversibly reduced in DMF to the corresponding cation at the potential of -0.4 V. On adding SO<sub>2</sub>, which is difficult to reduce under similar conditions  $(E_p = -0.9 \text{ V})$  from the MV<sup>2+</sup> cyclic voltagram, there is an increase in the cathode current peak and a decrease in anodic current relative to the MV+\* cation radical (Fig. 1(b)). The observed changes suggest that at the electrochemical stage in the homogenous reaction, the MV<sup>+•</sup> cation radical can reduce the SO2 molecule and as such can serve as a mediator of electron transfer from cathode to SO<sub>2</sub>. The ability of MV<sup>+•</sup> cation radical to transfer an electron to

SO<sub>2</sub> is reflected in the results obtained spectrophotometrically. During the addition of  $SO_2$  to the  $MV^{+\bullet}$  cation radical solution, a rapid disappearance of the characteristic MV<sup>+•</sup> absorption band and the appearance of a new absorption band as  $\lambda_{max} = 434 \text{ nm}$  can be seen. It is possible to regenerate the MV<sup>+•</sup> cation radical electrochemically or chemically, for example, by adding zinc to reduce  $MV^{2+}$  to  $MV^{+\bullet}$ .

According to the results of the examination of the electrochemical processes involved (Fig. 1(c)), the addition of CF<sub>3</sub>Br to the system containing  $MV^{2+}$  and SO<sub>2</sub> will decrease the catalytic current at the reduction potential of MV<sup>+•</sup>, which is probably caused by the interaction of the SO<sub>2</sub> anion radical being formed with Freon (Diagram 1, step III). A possibility of realizing this electron transfer channel has already been described by us [6] and others [5].

This system of two mutually complementary mediators, MV<sup>2+</sup>-SO<sub>2</sub>, is able to activate Freons under mild conditions via a cascade of electron transfer from the nucleophile to Freon (Diagram 1) and can be used on a preparative scale. When bubbling F13B1 Freon through the solution of thiophenol or *p*-thiocresol in the mixture of DMF and pyridine containing catalytic amounts of MV2+2I- (3-4% of thiophenol) and SO<sub>2</sub>, the yields of  $C_6H_5SCF_3$  and p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SCF<sub>3</sub> were 74% and 41%, respectively. The simultaneous formation of other compounds such as trifluoromethanesulfinic acid (CF<sub>3</sub>SO<sub>2</sub>H) was also noticed. As shown in the case of thiophenol (Table 1), the variation in PhSH and SO<sub>2</sub> concentration ratios allow an activation process directed towards the synthesis of both C<sub>6</sub>H<sub>5</sub>SCF<sub>3</sub> and CF<sub>3</sub>SO<sub>2</sub>H in rather high yields. The following mechanism describes the involved processes:

- 1.  $PhS^{-} + MV^{2+} \rightarrow PhS^{\bullet} + MV^{+\bullet}$ 2.  $MV^{+\bullet} + SO_2 \rightleftharpoons MV^{2+} + SO_2^{-\bullet}$ 3.  $SO_2^{-\bullet} + CF_3Br \rightarrow SO_2 + CF_3Br^{-\bullet} \rightarrow CF_3^{\bullet} + Br^{-}$ 4.  $CF_3^{\bullet} + PhS^{-} \rightarrow [CF_3SPh]^{-\bullet}$ 5.  $[CF_3SPh]^{-\bullet} + MV^{2+} \rightarrow CF_3SPh + MV^{+\bullet}$ 6.  $[CF_3SPh]^{-\bullet} + SO_2 \rightarrow CF_3SPh + SO_2^{-\bullet}$ 7.  $CF_3^{\bullet} + SO_2^{-\bullet} \rightarrow CF_3SO_2^{-\bullet}$

Steps 1-3 show a cascade of electron transfer from the nucleophile to Freons and step 4-6 show the interaction between trifluoromethyl radicals formed during Freon activation with thiophenolate by radical-chain mechanism

Table 1

The dependence of trifluoromethylphenylsulfide and trifluoromethylsulfinic acid yields on sulfur dioxide concentration in the F13B1 activation process using a system of electron transfer mediators,  $MV^{2+}$ -SO<sub>2</sub>  $([C_6H_5SH] = 10^{-3} \text{ M}, [MV^{2+}2Cl^{-}] = 5 \times 10^{-5} \text{ M})$ 

[SO <sub>2</sub> ] (M)	C <sub>6</sub> H <sub>5</sub> SCF <sub>3</sub> yields (%)	CF <sub>3</sub> SO <sub>2</sub> H yields (%)
$5 \times 10^{-4}$	12	5
$1 \times 10^{-3}$	74	21
$1.4 \times 10^{-3}$	65	78
$2.0  imes 10^{-3}$	56	76



Fig. 2. Cyclic voltammetry of  $I_2$ -SO<sub>2</sub> in DMF + Py +0.1 M Bu<sub>4</sub>NBF<sub>4</sub> at 25°C. (a)  $I_2 (1 \times 10^{-4} \text{ mol})$  alone and (b) after addition of  $2 \times 10^{-3} \text{ mol}$  SO<sub>2</sub>. Scan rate: 0.2 v s<sup>-1</sup>.

 $S_{RN}1$ . The interaction between trifluoromethyl radicals either with thiophenolate or with  $SO_2$  depends on the ratio of the concentration of thiophenol and  $SO_2$ , and hence leads to a preferable formation of either  $C_6H_5SCF_3$  or  $CF_3SO_2H$ . That  $MV^{2+}$ - $SO_2$  is able to activate the interaction of thiophenols with F13B1 and F113 Freons under mild conditions was definitely ascertained. In the latter case,  $C_6H_5SCF_2CFCl_2$  was obtained in 34% yield.

In the search for the catalytic systems for successive electron transfer from the nucleophile to Freon under mild conditions, it was observed that molecular iodine possesses a redox potential close to that exhibited by the methylviologen dication. As shown in Fig. 2, I<sub>2</sub> can be reduced reversibly at a potential of -0.39 V. In the presence of SO<sub>2</sub>, considerable growth of the reduction wave of I<sub>2</sub> and practically a complete disappearance of the reverse oxidation wave (Fig. 2(b)) are seen. As demonstrated spectrophotometrically, the observed catalytic effect can be caused by the electron from reduced I<sub>2</sub> getting added to SO<sub>2</sub>. It was found that the addition of an excess of SO<sub>2</sub> to KI leads to a yellow colored solution and increases the absorption of molecular iodine in electronic spectra ( $\lambda_{max} = 366$  nm).

Molecular iodine, on the other hand, can also react with thiophenol, generating I<sup>-</sup>. This phenomenon is demonstrated by a disappearance of the colour of the solution and absorption band of I2 when double the amount of thiophenol is added to the iodine solution. The above results show the conditions of mutually complementary mediation for electron transfer from iodide ion or reduced by thiophenolate- $I_2$  to  $SO_2$  to activate Freons. Indeed as was observed in the preparative scale reaction, upon bubbling of CF3Br into the solution containing equimolar quantities of thiophenol, SO<sub>2</sub> and 12% I<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>SCF<sub>3</sub> and CF<sub>3</sub>SO<sub>2</sub>H were formed in 31% and 9% yields, respectively. Instead of I<sub>2</sub>, if iodide ion is used as a co-catalyst in the reaction of CF<sub>3</sub>Br with thiophenol in the presence of KI and SO<sub>2</sub>  $([PhSH] = [SO_2] = [KI] = 0.002 \text{ mol})$ , the formation of C<sub>6</sub>H<sub>5</sub>SCF<sub>3</sub> and CF<sub>3</sub>SO<sub>2</sub>H drops to 20% and 7%, respectively. Lower yields of C<sub>6</sub>H<sub>5</sub>SCF<sub>3</sub> and CF<sub>3</sub>SO<sub>2</sub>H are obtained using I2-SO2 and I-SO2 catalytic systems as compared to  $MV^{2+}$ -SO<sub>2</sub>. The molecular I<sub>2</sub> in the I<sub>2</sub>-SO<sub>2</sub> and I<sup>-</sup>-SO<sub>2</sub> catalytic systems can serve to trap free radicals in the radical chain process of trifluoromethylation, the example being CF<sub>3</sub> radicals derived from F13B1 Freon activation. This inference is confirmed by the formation of CF<sub>3</sub>I in these systems along with C<sub>6</sub>H<sub>5</sub>SCF<sub>3</sub> and CF<sub>3</sub>SO<sub>2</sub>H. Thus, in the case of the reaction of  $C_6H_5SH + CF_3Br$  with  $I_2$ -SO<sub>2</sub> and  $I^-$ -SO<sub>2</sub> systems,  $CF_3I$ is formed in 16% and 10% yields, respectively. The above mentioned transformation can be described schematically as follows:

Here, Steps 1 and 2 serve as the initiation of the chain process, while Steps 3–5 and Steps 6–8 represent chain propagation and chain termination, respectively. Instead of  $I_2$ , if KI is used, then the initiation reaction begins with Step

2. The results of the present investigation show that the system of mutually complementary mediators  $MV^{2+}$ -SO<sub>2</sub> and  $I^{-}/I_{2}$ -SO<sub>2</sub> are capable of realizing a subsequent electron transfer from the nucleophile to F13B1 and F113 Freons. This process permits the fluoroalkylation of thiophenols under mild conditions, and especially if methylviologen diiodide is used as a co-catalyst, two channels of electron transfer to SO<sub>2</sub> can be opened: one from thiophenol through MV<sup>+•</sup> intermediate cation radical and the second with  $MV^{2+}$  iodide ion. Apparently, the above-described system of complementary mediators activates Freons through a path of electron transfer not only from thiophenols but also from other nucleophiles, provided the nucleophile oxidation potential is close to or more negative as compared to the reduction potential of the mediator conjugated with  $SO_2$ .

## 3. Experimental

Electrochemical investigation has been carried out using the potentiostat PI-50-1 and programmer PR-8 in a thermostated three-electrode cell with spot platinum electrode (0.7 mm), the reference electrode Ag/AgCl, and supporting electrolyte, Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M), recrystallized from an ethylacetate-pentane mixture. The NMR-19F spectra were recorded on a 235-MHZ Bruker spectrometer CXP-90, and the <sup>19</sup>F chemical shifts are given in ppm by reference to  $C_6F_6$ . The yields of the products have been determined by NMR-spectroscopy. The electron spectra have been recorded with the aid of spectrophotometer Specord M-10 in 10 mm quartz cuvettes in dimethylformamide. Thiophenol was purified by distillation and *p*-thiocresol was purified by acid precipitation from its alkaline solution and subsequent recrystallization. DMF and pyridine were purified as described elsewhere [7].

Cyclic voltammograms were recorded over the range -0.1--0.6 V under pure argon in a cell containing 3 ml DMF + 2 ml of pyridine for methylviologen (MV<sup>2+</sup>2X<sup>-</sup>, X = Cl, I; [MV<sup>2+</sup>2I<sup>-</sup>] = 5 × 10<sup>-4</sup> mol) whilst adding SO<sub>2</sub> to this solution ( $2.5 \times 10^{-3}$  mol) and also whilst bubbling to MV<sup>2+</sup>-SO<sub>2</sub> solution of an excess of F13B1 Freon ( $1 \times 10^{-2}-2 \times 10^{-2}$  mol). An analogous technique was used to record the cyclic voltammograms of I<sub>2</sub> ( $1 \times 10^{-4}$  mol), I<sub>2</sub> + SO<sub>2</sub> ( $2 \times 10^{-3}$  mol) and I<sub>2</sub> + SO<sub>2</sub> + CF<sub>3</sub>Br (excess,  $1 \times 10^{-2}-2 \times 10^{2}$  mol) in the same mixture of solvents.

# 3.1. Perfluoroalkylation of thiophenols in the presence of methylviologen and sulfur dioxide

To the solution of  $MV^{2+}2I^{-}$  (3 × 10<sup>-3</sup> mol) in 3 ml DMF and 1.5 ml of pyridine under argon, was added 1 × 10<sup>-3</sup> mol of thiophenol or *p*-thiocresol (blue colour), 1 × 10<sup>-3</sup> mol of sulfur dioxide (yellow colour), and an excess of F13B1 bubbled for 4–6 h. From <sup>19</sup>F-NMR, the yields of C<sub>6</sub>H<sub>5</sub>SCF<sub>3</sub> ( $\delta = 120$  ppm) and CF<sub>3</sub>SO<sub>2</sub>H ( $\delta = 76$  ppm) have been calculated. The reaction mixture was diluted with water, extracted with ether or chloroform, and the organic layer washed with alkali water, then acidified, dried and fractionated. The physical parameters (such as boiling or melting point), refractive indices, spectra (<sup>1</sup>Hand <sup>19</sup>F-NMR) of the trifluoromethylalkylsulfides agreed with the literature data [3].

The fluoroalkylation of thiophenols with F113 Freon and the isolation of the products were similarly conducted but with  $1 \times 10^{-2}$ – $2 \times 10^{-2}$  mol of F113 instead of CF<sub>3</sub>Br. The same technique was used for the trifluoromethylation of thiophenols with F13B1 Freon in the presence of iodine and SO<sub>2</sub>. The concentration of the starting substrates were as follows: [PhSH] (or [*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SH]) =  $2 \times 10^{-3}$  mol; [I<sub>2</sub>], 10–12% of the quantity of thiophenol; [SO<sub>2</sub>] =  $2 \times 10^{-3}$  mol; and [CF<sub>3</sub>Br] =  $1 \times 10^{-2}$ – $1.5 \times 10^{-2}$  mol.

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