The mechanism of the electroreduction of alkenyldimethylsulfonium salts

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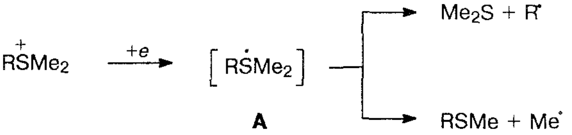
The potential of the electroreduction of alkenyldimethylsulfonium salts and the preferable direction of C—S bond cleavage are determined to a considerable extent by the position of the double bond in the alkenyl substituent.

Key words: sulfonium salts; electroreduction; mercury cathode.

In the previous communication[1] we thoroughly discussed the preparative electroreduction (ER) of allyldimethylsulfonium salts and the possible mechanism of the process at a mercury cathode. It is known[2] that the structure of substituents in sulfonium salts affects their ER potentials. For example, the cathodic reduction potentials were reported to decrease[3] when electron-accepting substituents were present in sulfonium salts; in particular, a significant shift of $E_{1/2}$ from that of the vinyl analog was observed when the double bond was in the allyl position relative to the sulfur atom.

According to the classical scheme, the reductive cleavage of sulfonium salts involves two consecutive one-electron steps[3,4] and occurs according to the *ECE*-mechanism. The first step (Scheme 1) involves the transfer of one electron and the formation of an intermediate radical, **A**, whose subsequent decay results in sulfides (RSMe and Me_2S) and radical species ($R^{\cdot}$ and $Me^{\cdot}$). The elimination of the more stable radical is preferable both in electrochemical (or photochemical)[5] and in chemical[6] reductive cleavage. The second electrochemical step is assumed to involve the reduction of the radical species to give the corresponding hydrocarbons. It was of interest to compare these data with those obtained from the preparative cathodic potentiostatic electrolysis of sulfonium salts containing alkenyl substituents of various structures.

Scheme 1



Results and Discussion

The ER potentials of alkylsulfonium salts are so high that attempts have been made[4] to use them as supporting electrolytes in electrochemical processes. Salt **1** (Table 1), which contains a substituent with a homoallyl double bond, undergoes reduction similarly to alkylsulfonium salts. The ER gives hydrocarbon **1a** and sulfide **1b**, and the charge passed (Q) is 2 F mol^{-1}. Although elimination of the bulky alkenyl radical is somewhat preferable, the composition of the ER products indicates an approximately equal probability of the cleavage of the S—Me and S—R bonds. Obviously, the reduction of radical species ($Me^{\cdot}$ and $R^{\cdot}$) occurs at a much lower cathodic potential than the potential of the first electrochemical step. Therefore, the reduction of salt **1** is actually a one-step two-electron process.

The ER of salt **2** (see Table 1), in which the double bond in the alkenyl substituent occupies the vinyl position, occurs at a somewhat more positive potential than that of salt **1**. In this case, the corresponding sulfide **2a** is practically the only product (Q = 2 F mol^{-1}). Probably, the electron-withdrawing effect of the double bond is decreased owing to additional interaction of the π-electrons of the vinyl double bond with the positive charge at the sulfur atom. The transfer of one electron to this sulfonium cation results in an intermediate that is more stable than that in the case of salt **1**, and in which an unpaired electron is delocalized over the $[C{=}C{-}\ddot{S}]^{\cdot}$ conjugated system. The decay of this radical should involve preferential elimination of $Me^{\cdot}$, which results in the high selectivity of the electrochemical process for salt **2**. The appearance of a similar transition state named a "π-ligand radical anion of a sulfonium salt cation"[6] during the chemical reduction of arylalkylsulfonium salts explains the elimination of the most stable radical along with retention of the C—S bond with the aryl substituent. Formally, the results of the preparative ER of salts **1** and **2** do not contradict the classical scheme of the reductive cleavage of sulfonium salts. However, this is actually a one-step process, since

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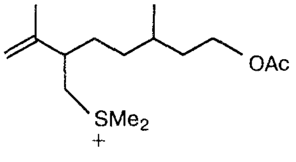
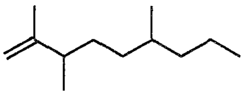
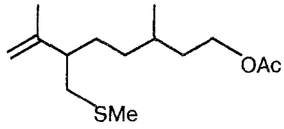
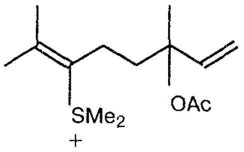
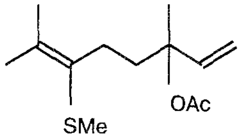
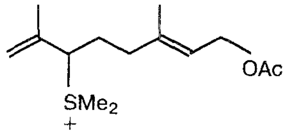
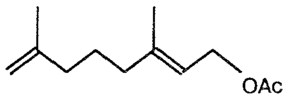
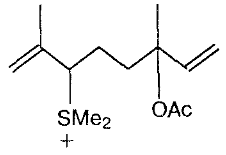
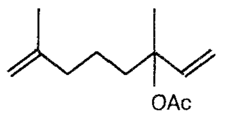
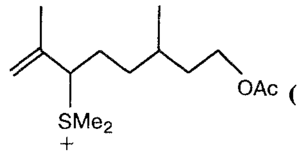
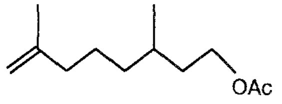
Table 1. Results of preparative electroreduction of $RSMe_2ClO_4$ salts (supporting electrolyte, 0.3 *M* $LiClO_4$ in DMF—10 % H_2O) on a mercury cathode

Cation	*E*/V	Main products*	
		Structure	Yield (%)
 **(1)**	−2.0**	 **(1a)**	28
		 **(1b)**	45
 **(2)**	−1.8÷1.9	 **(2a)**	72
 **(3)**	−1.2	 **(3a)**	42
 **(4)**	−1.2÷−1.5	 **(4a)**	66
 **(5)**	−1.2	 **(5a)**	55
5	−1.2÷−1.7	**5a**	80

* The amounts of CH_4 and Me_2S formed were not determined.
** Supporting electrolyte: 0.1 *M* $LiClO_4$ in DMF—1 % H_2O.

both electrochemical steps occur at the same potential.

In contrast, allyldimethylsulfonium salts **3**—**5** undergo reduction at relatively low cathodic potentials, and the process involves two separate steps. The electrolysis at the first step ($E = -1.2$ V) involves predominant formation of the corresponding hydrocarbons **3a**—**5a** (in ~50 % yield, Q ~1 F mol^{-1}), while sulfides RSMe are not detected at all. Electrolysis initially at $E = -1.2$ V and then at gradually increasing potentials makes it possible to obtain the hydrocarbons in higher yields (see Table 1). For example, the yield of product **5a** in the ER of salt **5** reaches 80 % ($E_{final} = -1.7$ V, $Q \approx 2$ F mol^{-1}) with retention of the α-position of the double bond in the alkenyl radical (the admixture of the β-isomer is 5—10 %). We believe that the high selectivity of the process is related to the reaction of the allyl radical with the mercury cathode rather than to the stability of the radical itself. This allows us to explain the almost complete absence of isomerization, *i.e.*, the retention of the α-position of the double bond in the end products **3a**—**5a**. It has been shown[7] that the $E^1_{1/2}$ values for salt **5** on platinum and mercury cathodes are close. However, the processes occurring at the second-wave potentials differ significantly: the positive shift of

$E^{II}_{1/2}$ on a mercury cathode and the appearance of additional waves suggest a change in the ER mechanism when the platinum cathode is replaced by a mercury cathode. The presence of an allyl substituent in the sulfonium cation induces such a significant anodic shift of the first-wave potential ($E = -1.2$ V) that desorption of the intermediate radical **A** from the mercury electrode surface is unlikely to occur at this potential. Probably, the subsequent transformations of this radical involve the elimination of Me_2S and the formation of organomercury intermediates[1] whose reduction at E = −1:2 to −1.7 V results in hydrocarbon RH. We believe that the above considerations are the only ones that explain the relatively high selectivity of the cathodic electrolysis of allyldimethylsulfonium salts.

Thus, in cases when the ER of sulfonium salts is complicated by chemical transformations of an intermediate radical **A**, the potentials of the first and second reduction waves differ significantly. A change in the position of the double bond in the alkenyl substituents of alkenyldimethylsulfonium salts can both favor a significant shift in the ER potential and change the preferential direction of the cleavage of the S—R or S—CH_3 bonds.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer, and mass spectra were obtained on a Varian MAT CH-6 spectrometer. The R_f values refer to a fixed Silufol silica gel layer in an ether—hexane (1 : 4) system. Polarographic monitoring was performed on a mercury dropping electrode using a PU-1 polarograph and a saturated calomel reference electrode.

DMF was purified by storage with K_2CO_3 and subsequent distillation. Sulfonium salt **1** was obtained by a standard procedure.[8] Salts **3—5** were synthesized by a known procedure.[9] Salt **2**, a by-product of the synthesis of salt **4** (content 10—15 %), was isolated from the reaction mixture after the ER of salt **4**. The alkenyldimethylsulfonium salts **1—5** were purified as described previously.[9]

The preparative electrolysis at a controlled potential was performed in a cell with a porous glass diaphragm using a P-5848 potentiostat until the starting reagent was exhausted. Bottom mercury (~16 cm^2) was used as the cathode, a platinum grid served as the anode, and a saturated calomel electrode served as the reference electrode. The catholyte volume was 14 mL. When the electrolysis was completed, the solution was diluted with water, acidified with aqueous HCl, and extracted with ether. The extract was dried with $MgSO_4$.

The electroreduction of (7-acetoxy-2-isopropenyl-5-methylheptyl)dimethylsulfonium perchlorate (1). The electrolysis of salt **1** (0.25 g) was carried out for 3 h at $E = -2.0$ V in a 0.1 *M* solution of $LiClO_4$ in DMF containing 1 % H_2O. After the usual work-up, the ethereal extract was concentrated *in vacuo* and the residue was separated on a column with SiO_2 (20 g). Gradient elution from hexane to ether (up to 20 % of the latter) gave 40 mg (28 %) of 3,6,7-trimethyl-7-octen-1-ol acetate (**1a**) and 78 mg (45 %) of 3,7-dimethyl-6-methylthiomethyl-7-octen-1-ol acetate (**1b**) as colorless liquids with R_f 0.63 and 0.51, respectively.

^{1}H NMR for **1a** ($CDCl_3$), δ: 0.88 (d, 3 H, CH_3, J = 6 Hz); 0.98 (d, 3 H, CH_3, J = 6.5 Hz); 1.2—1.7 (m, 7 H, $CHCH_2$); 1.64 (br.s, 3 H, $CH_3C{=}C$); 1.96 (m, 1 H, CHC=C); 2.04 (s, 3 H, $OCOCH_3$); 4.06 (m, 2 H, CH_2O); 4.66 (br.s, 2 H, $H_2C{=}C$). MS (EI, 70 eV), *m/z*: 152 [M−AcOH]$^+$. Mol. weight for $C_{13}H_{24}O_2$: 212.3.

Sulfide **1b** obtained was identical to an authentic sample whose characteristics were reported in Ref. 9.

The electroreduction of (6-acetoxy-2,6-dimethylocta-2,7-dien-3-yl)dimethylsulfonium perchlorate (2). Salt **2** (0.130 g) was electrolyzed for 40 min (I_{init} = 50 μA) at $E = -1.8$ to −1.9 V in a 0.3 *M* solution of $LiClO_4$ in DMF containing 10 % H_2O until the wave at $E_{1/2} = -1.9$ V disappeared completely (polarographic monitoring). Standard treatment followed by purification on a column with SiO_2 (20 g) using gradient elution from hexane to ether (up to 20 % of the latter) gave 63 mg (72 %) of 2,6-dimethyl-3-(methylthio)octa-2,7-dien-6-ol acetate (**2a**), R_f 0.43, as a colorless liquid. IR ($CHCl_3$), ν/cm^{-1}: 2980 and 2930 (C—H), 1730 (C=O), 1605 (C=C—S), 1240 (C—O). ^{1}H NMR ($CDCl_3$), δ: 1.54 (s, 3 H, CH_3); 1.72 and 1.88 (both s, 6 H, $CH_3C{=}C$); 1.99 (s, 3 H, $OCOCH_3$); 2.11 (s, 3 H, CH_3S); 1.7—2.25 (m, 4 H, CH_2); 5.14 (m, 2 H, $CH_2{=}C$); 5.96 (dd, 1 H, CH=S, J = 18.5 Hz and 11 Hz). MS (EI, 70 eV), *m/z*: 242 [M]$^+$, 182 [M−AcOH]$^+$, 167 [M−AcOH−Me]$^+$, 135 [M−AcOH−SMe]$^+$. Mol. weight for $C_{13}H_{22}O_2S$: 242.4.

The procedure for the preparative electrolysis of salts **3—5** has been reported previously.[1] The characteristics of the main products, **3a—5a**, have been published.[10]

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