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ELECTROCHEMICAL REDUCTION OF π-TRICARBONYLCHROMIUM-PHENYLDIMETHYLSULFONIUM TETRAFLUOROBORATE IN DIMETHYL SULFOXIDE

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Summary

The mechanism of the electrochemical reduction of π-tricarbonylchromium-phenyldimethylsulfonium tetrafluoroborate in anhydrous DMSO has been investigated, together with that of the free phenyldimethylsulfonium tetrafluoroborate. On varying the reduction potential and the protonating power of the medium the number of electrons transferred changes together with the nature and the yield of the products. It is suggested that formation of an intermediate sulfonium ylid by a two-electron process is followed by an acid-base reaction.

Introduction

Phenyldimethylsulfonium tetrafluoroborate, $PDMS^+ BF_4^-$, reacts with potassium t-butoxide in dimethyl sulfoxide (DMSO) to give a reactive ylid intermediate, which in the presence of benzophenone gives 94% yield of 1,1-diphenylethylene oxide and no 1,1-diphenylethylene, the Wittig product (path a) [1]. Complexation of the phenyl ring with tricarbonylchromium (TCC) changes the course of the reaction: under identical conditions, both the oxirane and the olefin were found, with the latter as major product (path b) [1]. In most cases, complexation of an aromatic ring with TCC markedly changes the rates of the reactions taking place at the side-chain even though the mechanisms are not substantially modified [2]. In the case of the homogeneous reaction of complexed phenyldimethylsulfonium tetrafluoroborate the sulfonium ylid is still formed, (eq. 1) but, in contrast to the corresponding free ligand, the sulfur in the intermediate betaine is sufficiently electrophilic in character to undergo preferential attack by the negatively charged oxygen.

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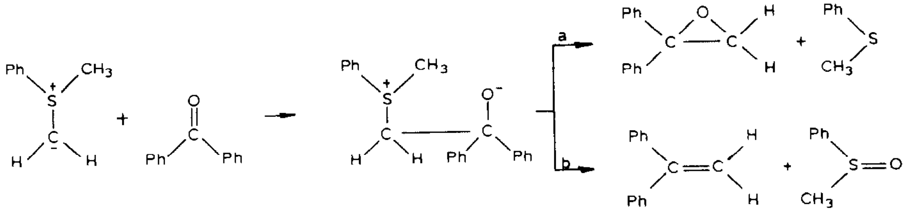
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Cathodic formation of ylid intermediates by reduction of benzyl(alkyl)sulfonium salts in DMSO was suggested on the basis of the nature of products (oxiranes) obtained in the presence of carbonyl compounds [3]. Such a process is not unlikely in view of the fact that the cathode can substitute for t-butoxide as a nucleophile, but whether the ylid would be formed electrochemically by a single electron transfer [3], or chemically after a two-electron process is still unclear. For example, formation of the ylid in the electrochemical reduction of cyanomethyldimethylsulfonium ion in DMSO is the result of proton abstraction by the cyanomethyl anion produced in the two-electron reduction of the onium salt [4].

The present report describes a comparison of the electrochemical behaviour of tricarbonylchromium-phenyldimethylsulfonium tetrafluoroborate (TCC-PDMS$^+$ BF$_4^-$) with that of the free ion. The objective was to ascertain whether or not the sulfonium ylids are intermediates of the reduction and to find out how the tricarbonylchromium group affects the electrode process mechanism.

Results and discussion

The polarographic behaviour of the free phenyldimethylsulfonium tetrafluoborate was investigated in anhydrous DMSO with TBAP as supporting electrolyte at 21°C. The salt exhibits one rather distorted wave at ca. − 1.20 V because of maxima formation (Fig. 1). Simpler behaviour is shown at the stationary Pt electrode in cyclic voltammetry (CV), a single peak being observed (Fig. 2), the height of which

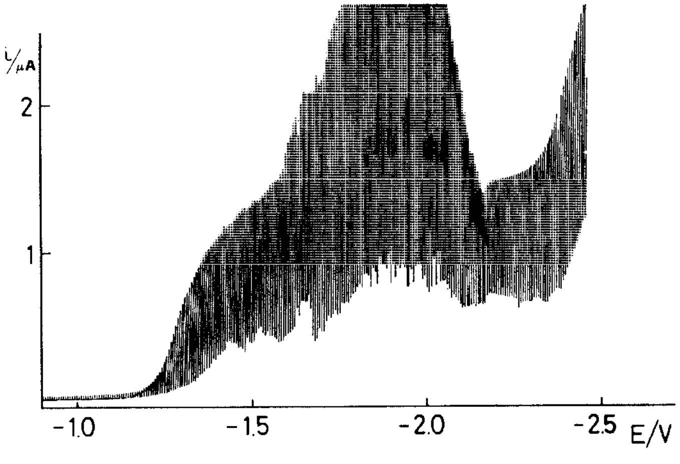


Fig. 1. D.C. polarogram of PDMS$^+$ BF$_4^-$ (c 10^{-3} M in DMSO 0.1 M TBAP at 21°C).

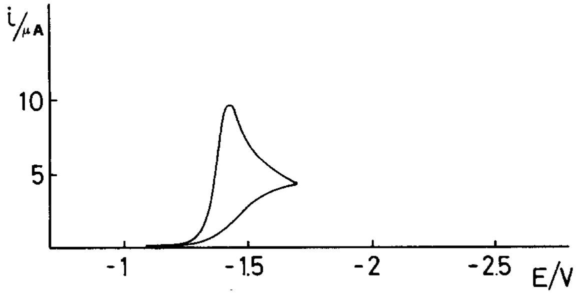


Fig. 2. Potential sweep voltammetry of PDMS$^+$ BF$_4^-$ (c 2×10^{-3} M in DMSO 0.2 M TBAP at 21°C, v 150 mV s^{-1}).

increases linearly with the scan rate, v. The plot of peak potential (E_p) vs. $\log v$ gives a straight line at scan rates lower than 1 V s^{-1} with a 30.2 ± 1.1 mV slope (Fig. 3). This value agrees with that calculated at 21°C, $RT/2F \ln 10 = 29.2$ mV, from the equation characteristic of a reversible one-electron transfer followed by fast chemical reactions [5]. The addition of a stoichiometric amount of phenol as a protonating agent to the solution does not cause any significant change in the polarographic pattern. The potentiostatic exhaustive electrolysis of a 5×10^{-2} M solution of PDMS$^+$ carried out at -1.50 V requires the comsumption of one electron per molecule whichever is used as cathode (Hg or Pt). The reduction gives phenylmethyl sulfide in 95% yield as measured by high pressure liquid chromatographic analysis; moreover, neither dimethyl sulfide nor benzene were detected, whereas dimethylmercury was found after reduction at the mercury pool (see Experimental).

The exhaustive electrolysis at a more negative potential, -2.20 V, without and with added phenol, still affords phenylmethyl sulfide in almost quantitative yield; anisole is also formed in the presence of phenol. In both cases, the current consumption exceeds one electron per molecule.

Finally, the electrolyses of three differently substituted phenylmethyl(alkyl)-sulfonium ions, where alkyl = isobutyl, isopropyl, and benzyl, were run in DMSO at -1.50 V. The product analysis showed that of the two sulfides which can be formed, viz. phenylmethyl and phenylalkyl sulfide, the percentage of the phenylmethyl

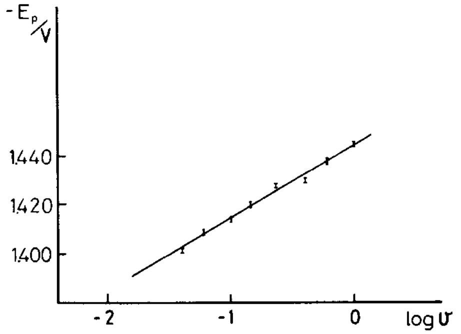
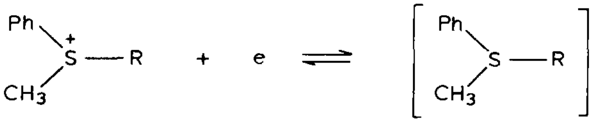


Fig. 3. Sweep rate dependence of the peak potential for the cathodic peak of PDMS$^+$ BF$_4^-$ (c 2×10^{-3} M in DMSO 0.2 M TBAP at 21°C).

sulfide increases from 34.5 for R = Bu^i to 89.5 for R = Pr^i to 100% for R = $PhCH_2$. This trend indicates that the distribution of the sulfides is governed by the relative stabilities of the alkyl radicals. A similar leaving group propensity, benzyl > > secondary > primary > methyl > phenyl group, has recently been observed in the chemical reduction of phenyl(alkyl)sulfonium salts [6]. In the case of phenylmethylbenzylsulfonium ion, dibenzylmercury was detected.

These findings suggest that the main reduction step involves the one-electron transfer to form a neutral intermediate (eq. 2), followed by the cleavage to the stable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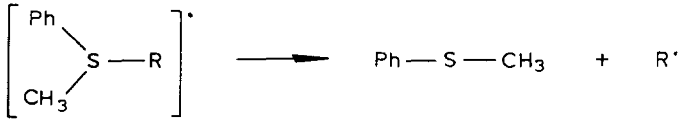
sulfide and a carbon radical (eq. 3), which may react with the cathodic material to give alkylmercury compounds. This mechanism is common to most of the reported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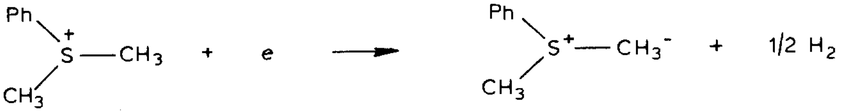
[7] electrochemical reductions of sulfonium ions; in addition, recent results on the chemical reductions of phenyl(alkyl)sulfonium salts have established that this reaction has an identical mechanism [6]. It is interesting to observe that a similar formation of radicals has also been noted in reactions of triarylsulfonium salts with strong bases in alcohols [8].

On the basis of our data and those available in the literature, formation of ylid intermediates at the electrodes seems unlikely. Ylid, might conceivably be produced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by a hydrogen discharge reaction (eq. 4), but such a process would not be consistent

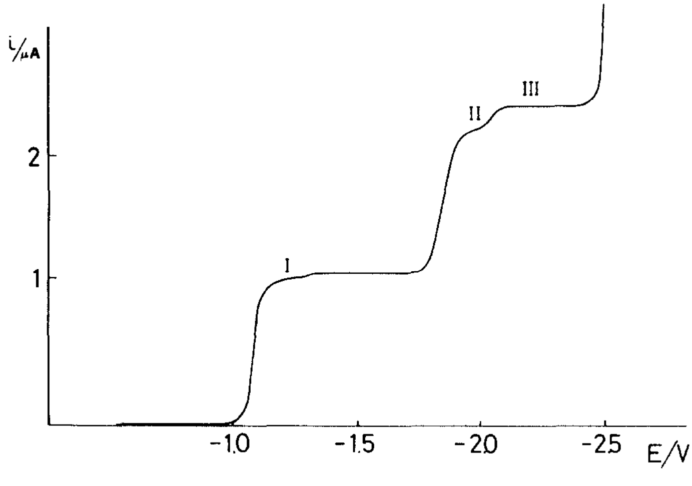


Fig. 4. D.C. polarographic pattern for TCC-PDMS$^+$ BF_4^- (c 10^{-3} M in DMSO 0.1 M TBAP at 21°C).

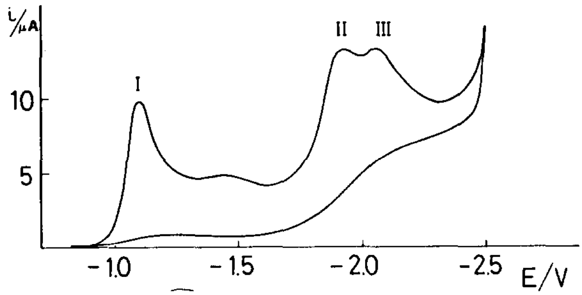


Fig. 5. Potential sweep voltammetry of TCC-PDMS$^+$ BF_4^- (*c* 2×10^{-3} *M* in DMSO 0.2 *M* TBAP at 21°C, v 150 mV s^{-1}).

with the following experimental features: (a) a substantial independence of the electrochemical results with respect to the nature of the cathodic metal, whereas path 4 is favoured at Pt; (b) no influence of proton donors, which should be catalytically reduced via the protonation of the ylid.

The polarographic pattern and the cyclic voltammogram at low scan rate of the TCC-PDMS$^+$ tetrafluoroborate in DMSO are shown in Fig. 4 and Fig. 5, respectively. The first polarographic wave (I) occurs at less negative potentials (half-wave potential, $E^{\rm I}_{1/2} = -1.07 \pm 0.01$ V) than for the free ligand. The plot of the log $\dfrac{i^{\rm I}_{\rm l} - i}{i}$, where $i^{\rm I}_{\rm l}$ is the limiting diffusion current, is a straight line with a slope of 58.3 ± 0.7 mV. In CV, a cathodic peak corresponding to the wave I appears, while no peak is observed in the anodic branch. On increasing the scan rate, v, within the interval 0.040 to 5 V s^{-1} the peak potential, $E^{\rm I}_{\rm p}$, shifts cathodically by 29.8 ± 1.0 mV per unit of log$v$; moreover the ratio of the peak current, $i^{\rm I}_{\rm p}$, to $v^{1/2}$ is effectively constant. Even when the voltammogram is carried out at the highest values of v (100 V s^{-1}), no anodic peak is observed.

These findings suggest that the first reduction wave is diffusion controlled, and that, as for the free ligand, the process is a one-electron reversible transfer followed by a fast chemical reaction.

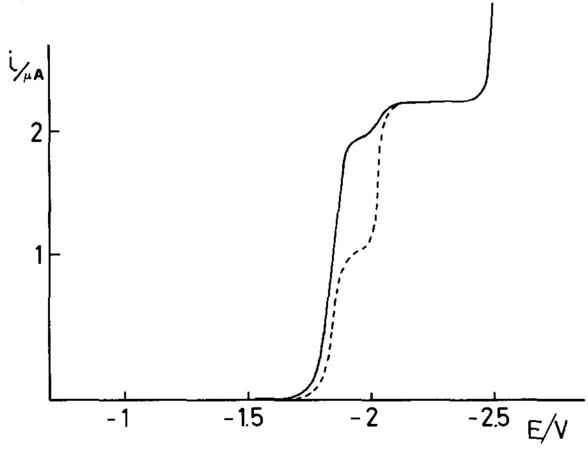


Fig. 6. D.C. polarographic pattern for TCC-PDMS$^+$ BF_4^- (*c* 10^{-3} *M* in DMSO 0.1 *M* TBAP at 21°C) after exhaustive electrolysis in the range -1.10 to -1.20 (———) and at *E* -1.80 V (- - - - - -).

In Fig. 4 a second wave, II, having a height comparable with that of the first, starts from ca. − 1.80 V, and a third wave, III, lower than the others, ranges from ca. −2.00 V up to the background discharge. A slight current increase is also observed at − 1.30 V. In CV, two irreversible cathodic peaks appear, corresponding to the polarographic waves II and III.

In order to establish the nature of the chemical reactions following the electron transfer, we ran a series of exhaustive electrolyses under various sets of conditions.

Potentiostatic exhaustive electrolyses of 10^{-3} M solutions of TCC-PDMS$^+$ carried out in the range − 1.10 ÷ − 1.20 V lead to complete disappearance of the first wave, with a current consumption of one electron per molecule; at the same time, wave II almost doubles its height and III is still low (Fig. 6). Moreover, the electrolyses of 5×10^{-2} M solutions at the same potentials enabled identification of the reduction products by HPLC. The reduction gives TCC-phenylmethyl sulfide in $\geqslant 78\%$ yield and TCC-benzene in $\leqslant 10\%$ yield. The polarographic analysis in DMSO of an authentic sample of these two complexes showed that they are reduced by a single two-electron wave at − 1.80 V for the sulfide and another at − 2.00 V for the benzene. Taking account of these results, the waves II and III of the polarogram of Fig. 4 can be safely ascribed to the reduction of TCC-phenylmethyl sulfide and TCC-benzene, respectively.

Electrolyses in the range − 1.40 to − 1.80 V still require one electron per molecule for the exhaustive reduction; however, as the potential is shifted towards more negative values, the ratio of the heights of wave III and II after electrolysis increases until it reaches unity at a working potential of − 1.80 V (Fig. 6); this indicates that the amount of TCC-benzene increases and that of TCC-phenylmethyl sulfide decreases until the two yields become equal. GLC analysis of the electrolyzed solution showed that dimethyl sulfide is formed, in an amount which increases in parallel to that of the TCC-benzene.

When the electrolysis of TCC-PDMS$^+$ is carried out at − 1.90 V, the overall

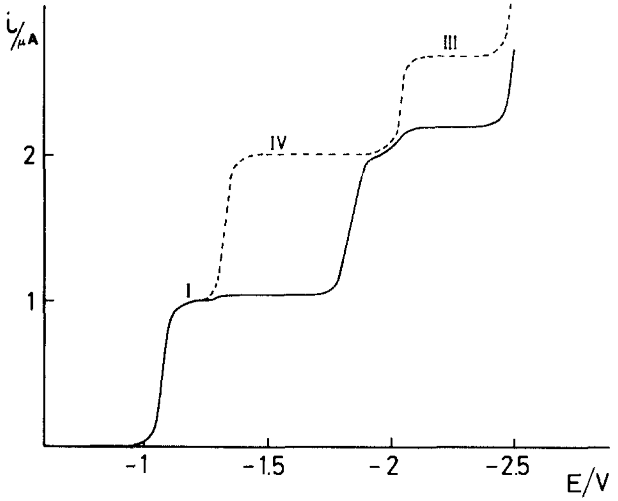


Fig. 7. D.C. polarographic pattern for TCC-PDMS$^+$ BF_4^- (c 10^{-3} M 0.1 M TBAP at 21°C) with phenol 5×10^{-3} M added (- - - - - -).

reduction requires two electrons per molecule and TCC-benzene and dimethyl sulfide are the only products. The two compounds do not arise from the reduction of TCC-phenylmethyl sulfide, as neither of them has been found in the reduction of a pure sample of the complexed sulfide at the same potential i.e. in the absence of the sulfonium complex.

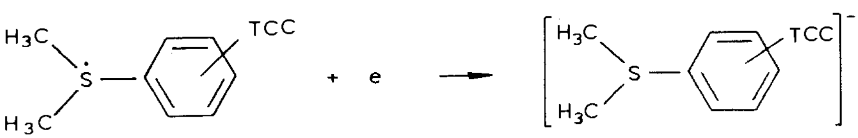
The presence of phenol at concentrations higher than the depolarizer, causes no change in the polarogram of TCC-PDMS$^+$ till -1.30 V; a new well defined wave, IV, the height of which is comparable to I, arises at ca. -1.30 V and, at the same time, wave II disappears and wave III reaches its maximum value (Fig. 7). Under these conditions the polarographic reduction of TCC-phenyldimethyl sulfide is no longer observed.

In order to clarify the nature of the reduction step IV we ran some exhaustive electrolyses at various potentials in the presence of excess phenol. In the range -1.10 to 1.20 V the reduction requires one electron per molecule. The final polarographic pattern is similar to that obtained in electrolysis at the same potentials in the absence of phenol. Thus, the complexed sulfide was found to be the main product, along with a small amount of complexed benzene. In the range -1.40 to 1.80 V two electrons per molecule are required to complete the reduction; both the final polarogram and analysis of the products showed that the TCC-benzene and the dimethyl sulfide are the main products, with only a small amount of complexed sulfide.

Finally, some electrolyses were carried out at -1.45 V in the presence of 4,4′-dimethylbenzophenone as a scavenger for any ylid formed. (It is noteworthy that the ketone is electrochemically inactive under the electrolysis conditions, and therefore cross-coupling processes involving reduction intermediates of the ketone with sulfonium salt must be ruled out.) After the passage of 1,4 electrons per molecule through an equimolar solution (1.5×10^{-3} M) of sulfonium complex and 4,4′-dimethylbenzophenone, the presence of 1,1-di(4-tolyl)ethylene was detected by GLC.

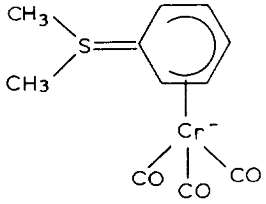
The results on the complexed sulfonium ion can be explained by the following mechanism. In the range -1.00 to -1.30 V, the ion is reduced to the neutral complexed radical (a step equivalent to eq. 2), which quickly decays to produce mainly TCC-phenylmethyl sulfide and methyl radicals (eq. 3). However, the cleavage of the sulfur–methyl bond is not the only process, as it was for the corresponding free ligand cation. The distinct amount of TCC-benzene among the reduction products is also evidence for the breaking of the sulfur–phenyl bond. Thus, while competition between S–methyl and S–phenyl bond rupture does not occur in the ligand ion because of the much higher S–phenyl than S–alkyl bond dissociation energy (for example, for phenylmethyl sulfide D^0_{298} (Ph–SCH$_3$) 60.0 kcal mol^{-1} [9] and D^0_{298} (Ph–SCH$_3$) 84.7 kcal mol^{-1}, calculated from ΔH^0_f of the radicals and ΔH^0_f of PhSCH$_3$), in the complex the strength of the two bonds becomes comparable. The characteristics of the TCC group, which have been clearly shown to excert a strong electron withdrawing effect through the σ-skeleton of benzene [2], would account for the lower strength of the S–phenyl bond.

The mechanism of the electrochemical reduction of TCC-PDMS$^+$ at more negative potentials can be inferred with the aid of the results obtained in the presence of phenol. The arising of wave IV in the polarogram of Fig. 7 and the coulombic balance (2 electrons per molecule) of the exhaustive electrolyses carried out at the

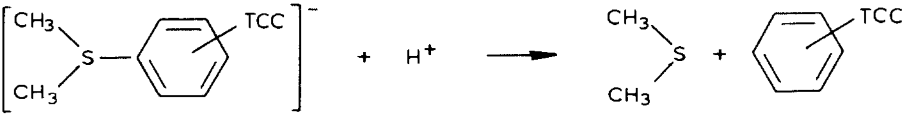


(5)

top of IV indicate that the neutral sulfur radical is further reduced to an anion before its chemical decay (eq. 5), in an overall two-electron process, (eq. 2 + 5). The collapse of the anion to reaction products is a process connected with that of protonation, and the site of protonation, in turn, depends upon the negative charge distribution in the anion. Spectroscopic and kinetic studies on chromiumtricarbonyl carbanions have shown that the negative charge is located mainly on the carbonyls and the chromium atom [10], and that a cyclohexadienyl electronic structure such as

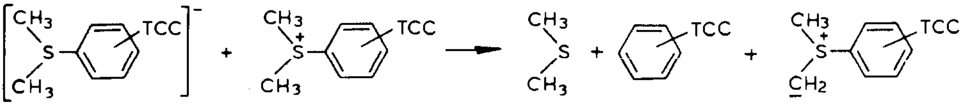


that depicted above represents satisfactorily the charge situation in the anion. Thus, protonation at chromium followed by migration of the proton from the metal to the aryl ring would on collapse give TCC-benzene and dimethyl sulfide (eq. 6).



(6)

In anhydrous DMSO in the absence of proton donors, the two-electron process still occurs at potential between − 1.30 and − 1.80 V; however, the protons required for step 6 are supplied by the depolarizer itself, to form TCC-benzene, dimethyl sulfide, and the unstable ylid (eq. 7).



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Evidence for the formation of the ylid comes from the presence of the Wittig product, 1,1-di(4-tolyl)ethylene, when TCC-PDMS$^+$ is reduced in the presence of the scavenger 4,4′-dimethylbenzophenone. Probably, the ylid is no longer reducible, and chemically decays to TCC-phenylmethyl sulfide *. Thus, although the reduction between − 1.30 and − 1.80 V is really a two-electron one, polarographically it

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* A 10^{-2} *M* solution of TCC-PDMS$^+$ BF_4^- in DMSO was treated with an excess of anhydrous tetrabutylammonium hydroxide. Polarographic analysis of the solution carried out immediately after the addition of the base showed the disappearance of the wave of the sulfonium salt and the appearance of the wave characteristic of the TCC-phenylmethyl sulfide, which was also detected by HPLC.

appears as an overall one-electron process owing to the autoprotonation which supplies half of the depolarizer for the reduction. The occurrence of reaction 7 is supported by reports mentioned in the Introduction relating to ylid formation from sulfonium salts and strong bases. The electrochemical reduction of cyanomethyldimethylsulfonium ion [4] is a similar process, the electron-withdrawing effect of the CN group being comparable to that of a π-coordinated $Cr(CO)_3$.

It should be pointed out that the two-electron reduction in anhydrous DMSO implies the formation of TCC-phenylmethyl sulfide and TCC-benzene in 1/1 ratio. This was actually observed after electrolyses at -1.30 to -1.80 V of TCC-PDMS$^+$, by measuring both the heights of polarographic waves II and III and the yields of the two products by HPLC. The proposed mechanism also accounts for the observed 1/1 ratio of waves I and II in the polarogram of complexed sulfonium ion. However, a puzzling aspect of the same mechanism is represented by the lower height of wave III compared with that of wave II in the same polarogram. A reasonable explanation is that the formation of TCC-phenylmethyl sulfide from the ylid is a fast process while the rearrangement and the collapse of protonated anion is a slow process compared with the polarographic times, both the processes being fast compared with the electrolytic times.

In conclusion, the reduction mechanism of TCC-PDMS$^+$ BF_4^- changes on variation of the working potential. At less negative potentials the ion is reduced by a one-electron step to the neutral radical which collapses to products. This mechanism is similar to that for the ligand ion; however, the coordination of the phenyl ring with TCC shifts the reduction process to more positive potentials (~ 0.3 V) and makes feasible some fission of the phenyl–sulfur bond in the radical intermediate.

As the potential becomes more negative the salt is reduced by a two-electron process to the anion, which in turn forms the complexed ylid by reaction with the depolarizer itself. Thus, as in the homogeneous reaction, the ylid is produced by an acid-base process. Electrochemical production of anionic species through a two-electron process is a feature common to many chromium-tricarbonyl substrates [11], and in the case of charged species, a relevant example is that of the complexed tropylium ion, which, in contrast to the ligand ion, undergoes a two-electron reduction to form the TCC-cycloheptatrienyl anion which couples with the depolarizer itself [12].

Experimental

Materials

Melting points are uncorrected. NMR spectra were recorded on a Bruker HFX-90 MHz spectrometer with TMS as internal standard. Dimethyl sulfide, anisole, 4,4′-dimethylbenzophenone and tricarbonylchromiumbenzene were commercial grade reagents. 1,1-Di(4-tolyl)ethylene was prepared by reaction of 4,4′-dimethylbenzophenone with CH_3MgI in diethyl ether followed by hydrolysis with NH_4Cl. M.p. 60–61°C (lit. [13], 61°C).

Sulfides

Phenylmethyl, phenylisopropyl, phenylisobutyl and phenylbenzyl sulfides were prepared by standard methods [14]. Their NMR spectra were consistent with their structures.

Tricarbonylchromium-phenylmethyl sulfide

TCC-phenylmethyl sulfide was prepared by refluxing for 12 h under nitrogen a solution of the free sulfide in anhydrous, oxygen-free diethyleneglycol dimethyl ether with an excess of freshly sublimed $Cr(CO)_6$. Crystallization from diethyl ether/hexane 1/1 gave yellow crystals. Yield 27%; m.p. 102–103°C (lit. [15], 101°C).

Phenyl(alkyl)sulfonium tetrafluoroborates

Phenyldimethyl, phenylmethylisopropyl, phenylmethylisobutyl and phenylmethylbenzylsulfonium tetrafluoroborates were prepared by methylation with Me_3O^+ BF_4^- of the appropriate sulfide in anhydrous CH_2Cl_2 at room temperature [15].

Phenyldimethylsulfonium tetrafluoroborate. White solid. Yield 90%, m.p. 132–133°C. Analysis: Found: C, 42.70; H, 4.50; $C_8H_{11}BF_4S$ calcd.: C, 42.40; H, 4.80%. NMR (CD_3COCD_3): δ 7.78 (m, 5H, aromatic ring protons), 3.43 (s, 6H, CH_3 protons).

Phenylmethylisopropylsulfonium tetrafluoroborate. Oil for which a satisfactory elemental analysis was not obtained. NMR (CD_3COCD_3): δ 7.78 (m, 5H, aromatic ring protons), 4.13 (sept, 1H, methine proton), 3.43 (s, 3H, $\overset{+}{S}-CH_3$ protons), 1.58 and 1.33 (2d, 3H each, diastereotopic CH_3 protons).

Phenylmethylisobutylsulfonium tetrafluoroborate. Oil for which satisfactory elemental analysis was not obtained. NMR (CD_3COCD_3): δ 8.20–7.85 (m, 5H, aromatic ring protons), 3.84 and 3.76 (m, 2H, CH_2 protons), 3.44 (s, 3H, $\overset{+}{S}-CH_3$ protons), 1.92 (m, 1H, CH proton), 1.13 and 1.06 (2d, 3H each, diastereotopic CH_3 protons).

Phenylmethylbenzylsulfonium tetrafluoroborate. White solid. Yield 89%, m.p. 123–124°C (lit. [16], 120–121°C). NMR (CD_3COCD_3): δ 8.03–7.67 (m, 5H, $\overset{+}{S}-C_6H_5$ protons), 7.35 (s, 5H, others C_6H_5 protons), 5.26 and 5.04 (AB-q, J_{AB} 12.5 Hz, 2H, CH_2 protons), 3.49 (s, 3H, $\overset{+}{S}-CH_3$ protons).

Tricarbonylchromium-phenyldimethylsulfonium tetrafluoroborate. The complex was prepared by methylation with Me_3O^+ BF_4^- of TCC-phenylmethyl sulfide, as reported [15]. Yellow solid. Yield 80%, m.p. 168–171°C (from ethanol) (lit. [15]), dec. 170–180°C). NMR (CD_3COCD_3): δ 6.60–5.60 (m, 5H, aromatic ring protons), 3.56 (s, 6H, $\overset{+}{S}-CH_3$ protons).

Dimethyl sulphoxide was dried over CaH_2 and distilled under reduced pressure immediately before use. Tetrabutylammonium perchlorate (TBAP) was dried under vacuum and stored under nitrogen.

Apparatus

Polarographic and potential sweep voltammetric experiments were carried out with an Amel Model 448 three-electrode apparatus. An Ag, AgCl, tetramethylammonium chloride saturated solution in MeCN was used as reference electrode.

After each run its potential was measured against a standard calomel electrode (SCE), the difference being constant within the experimental error, $E_{Ag,AgCl,Cl^-} - E_{SCE} = -0.260 \pm 0.005$ V. A mercury pool was used as the counter electrode, and a dropping mercury electrode with mechanical control of the drop time or a hanging Pt microelectrode as the working electrode.

Controlled potential electrolyses and coulometric measurements were performed with an Amel Model 557 potentiostat equipped with an Amel Model 558 integrator;

the working electrode was a mercury pool and/or platinum gauze.

The main electrolysis products, i.e. free and coordinated sulfides and TCC-benzene, were identified and quantitatively determined by high pressure liquid chromatography by use of authentic samples and internal standards. The HPLC chromatogram of the electrolyzed solution of the phenylmethylbenzylsulfonium tetrafluoroborate showed, in addition to the peak for the phenylmethyl sulfide, a second well-defined peak. The unknown product was quantitatively separated by preparative HPLC on a C_{18}-ODS column and identified as dibenzylmercury by NMR and mass spectrometry. A Perkin–Elmer Sigma 3B gas chromatograph equipped with a flame ionization detector and a 1m 20% SE-30 on Chromosorb column was used for testing for the presence of volatile products. Dimethylmercury also was identified by gas chromatographic and mass spectrometric analysis.

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