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Electrochemical Investigation of the Reaction between Sodium Benzenesulfinate and *p*-Halonitrobenzenes

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Abstract: *Electrochemical evidence suggests that sodium benzenesulfinate reacts with the four p-halonitrobenzenes in a S_NAr-reaction, and not in a $S_{RN}2$-reaction, as claimed by other authors.*[1]

Recently Denney and Denney[1] claimed that the $S_{RN}1$-mechanism is unable to explain a number of experimental observations, which instead could be interpreted in the framework of a $S_{RN}2$-mechanism. Their arguments were based mainly on a reinterpretation of work done by other researchers, but they also investigated the reaction between sodium benzenesulfinate and the four *p*-halonitrobenzene derivatives.

Scheme 1.

$RX + e^-$	$\rightarrow$	$RX^{-\cdot}$	(1)
$RX^{-\cdot}$	$\rightarrow$	$R^\cdot + X^-$	(2)
$Nu^- + R^\cdot$	$\rightarrow$	$NuR^{-\cdot}$	(3)
$NuR^{-\cdot} + RX$	$\rightarrow$	$NuR + RX^{-\cdot}$	(4)

The $S_{RN}1$-mechanism of nucleophilic substitution is represented in Scheme 1. In the first step (Eqn. 1) the substrate accepts an electron from a suitable electron donor, depending on the mode of initiation, to produce the corresponding anion radical, which cleaves (Eqn. 2) to afford an anion and a radical. The radical subsequently couples with a nucleophile (Eqn. 3) to give the anion radical of the product, which is oxidized by a molecule of the substrate (Eqn. 4) yielding the neutral substitution product and an anion radical of the substrate. Eqns. 2-4 thus constitute a chain mechanism, Eqn. 1 serving merely as an initiation step. This mechanism was initially put forward by Kornblum[2] and Russell[3] the substrates being nitro-containing aliphatic halides, and later the mechanism was also extended to aromatic[4] and vinylic[5] substrates. Since the initial discovery this mechanism has been found to apply in numerous cases, and excellent reviews have appeared on the subject.[6]

Scheme 2.

$RX + e^-$	$\rightarrow$	$RX^{-\cdot}$	(1)
$Nu^- + RX^{-\cdot}$	$\rightarrow$	$NuR^{-\cdot} + X^-$	(2')
$NuR^{-\cdot} + RX$	$\rightarrow$	$NuR + RX^{-\cdot}$	(4)

The $S_{RN}2$-mechanism (Scheme 2) is not a novel idea, and indeed Russell has invoked this mechanism in some cases of nucleophilic substitution on nitro-containing aliphatic halides.[7] The $S_{RN}2$-mechanism has, however, never before been found to apply in aromatic nucleophilic substitution, although it has been looked for.[8] Denney and Denney argue that *all* reactions previously thought to follow the $S_{RN}1$-mechanism are in fact better described as $S_{RN}2$-reactions. This conclusion has been rejected both on quantum-mechanical[9] and kinetic[10] grounds, and furthermore the $S_{RN}2$-mechanism is unable to explain the finding of dimerization,[11] cyclization[12] and scrambling[6d,13] products, which are strong evidence of free radicals, so the $S_{RN}1$-mechanism seems in most cases to be strongly supported by experimental facts. It is however still possible that the $S_{RN}2$-mechanism may apply in *some* cases. Inasmuch as the difference between the two mechanisms is whether or not the intermediate substrate anion radical cleaves (Eqn. 2) before coupling with the nucleophile (Eqns. 3 or 2'), it would be most likely to find $S_{RN}2$-type reactions with substrates having relatively stable anion radicals. This is the case for the four *p*-halonitrobenzene-derivatives, where the first-order rate-constants for the cleavage of the anion radical have been reported to be $9 \cdot 10^{-1}$, $4 \cdot 10^{-3}$ and 10^{-2} s^{-1} respectively for the iodo-, bromo- and chloroisomers (in N,N-dimethylformamide, DMF, at 23 °C),[14] and for the fluoro derivative the cleavage is probably even slower. Denney and Denney investigated the reaction between sodium benzenesulfinate and the four *p*-halonitrobenzenes in dimethylsulfoxide (DMSO) and in hexamethylphosphoric triamide (HMPA) (Eqn. 5), which they found to be stimulated by light and inhibited by galvinoxyl, a known radical scavenger.[1]

$$\underset{\mathbf{1}}{C_6H_5\text{-}SO_2^-Na^+} + \underset{\begin{array}{l}\mathbf{2}\text{: X=}\textit{para}\text{-F}\\ \mathbf{3}\text{: X=}\textit{para}\text{-Cl}\\ \mathbf{4}\text{: X=}\textit{para}\text{-Br}\\ \mathbf{5}\text{: X=}\textit{para}\text{-I}\end{array}}{X\text{-}C_6H_4\text{-}NO_2} \rightarrow \underset{\mathbf{6}\text{: }\textit{para}\text{-isomer}}{O_2N\text{-}C_6H_4\text{-}SO_2\text{-}C_6H_5} + NaX \qquad (5)$$

They concluded that the reaction could not be a $S_{RN}1$-reaction, as the cleavage of the substrate anion radical (Eqn. 2) was too slow to allow for a feasible chain reaction following Scheme 1. Another mechanism of aromatic substitution, the addition-elimination or S_NAr mechanism, was excluded by the authors because this mechanism would neither show inhibition by galvinoxyl nor be stimulated by photons. Instead the $S_{RN}2$-mechanism was invoked to explain the experimental results. We decided to reinvestigate these reactions by electrochemical methods, as this has proven to be an excellent way to investigate reactions of the $S_{RN}1/S_{RN}2$-type.[6c,8c]

Results and discussion

UV-measurements

The UV-spectrum of sodium benzenesulfinate (**1**) in DMSO shows a small absorption peak at 258.2 nm and a larger at 319.5 nm. The spectrum of **3** in DMSO shows only one peak at 276.0 nm. A mixture of **1** and **3** has a UV-spectrum which is indistinguishable from an overlay of the spectra of **1** and **3** respectively, indicating that the two compounds do not form a charge-transfer (CT) complex. In the few cases studied thoroughly, it is believed that the main fraction of photostimulation in $S_{RN}1$-type reactions is due to CT excitation.[15] As **1** and **3** do not form a charge-transfer complex, the photostimulation reported by Denney and Denney[1] does not seem to be supported by the results of our UV-measurements, although it can not be excluded that the photostimulation could arise from other than CT-excitation.

Reduction potentials

The standard potentials of **2-6** were measured in DMF, the results are shown in Table 1 together with potentials obtained in DMSO.[16]

Table 1: Standard potentials of the substrates **2-5** and of the product **6**.

Compound	E°/V^{a} (DMF)	E°/V^{a} (DMSO)
2	-1.044	-1.055[b]
3	-0.971	-0.980[b]
4	-0.963	-0.965[b]
5	-0.957	-0.960[b]
6	-0.757	-0.759

[a] vs. SCE. [b] from Ref. 16. The standard potentials were calculated as the midpoint between the reduction and oxidation peaks.

The potentials measured in DMF are very close to those obtained in DMSO, so we believe that conclusions drawn from electrochemical measurements in DMF are also valid for DMSO-solutions and vice versa. A common step in the $S_{RN}1$ and $S_{RN}2$ reactions is the electron transfer (ET) from the anion radical of the product to a substrate molecule (Eqn. 4). In the case where the ET is not dissociative (i.e. Eqns. 4 and 2 are not concerted), which is often the case when the substrate is aromatic, reaction 4 is really an equilibrium. However, in the $S_{RN}1$-reaction the cleavage of the substrate anion radical (Eqn. 3) drives this equilibrium to the right, even if the reduction potential of the substrate is more negative than that of the product. Indeed $S_{RN}1$-reactions are known where the electron transfer is uphill, although in most cases it is a downhill reaction.[6c,8c] In the case of the $S_{RN}2$-mechanism, the cleavage of the substrate anion radical, if it happens at all, will lead to a radical that goes into the $S_{RN}1$-reaction and thus does not continue the $S_{RN}2$-chain, so in this case the cleavage can not drive an uphill electron transfer in the desired direction. In principle it is possible that the coupling between the nucleophile and the substrate anion radical (Eqn. 2') could drive the equilibrium (Eqn. 4) to the right and thereby provide the driving force for the overall $S_{RN}2$-reaction.

From the data given by Denney and Denney a lower limit for the rate constant of the coupling reaction 2' in the case where Nu^- is benzenesulfinate and RX is one of the *p*-halonitrobenzene derivatives, can be estimated. Assuming that reaction 2' is rate determining, which is true when reaction 4 is a pre-equilibrium, the expression for the disappearance of the nucleophile is the following:

$$-\frac{d[Nu]}{dt} = k\,[Nu]\,[RX^{\cdot-}] \qquad (6)$$

If it is assumed that the total concentration of product and substrate anion radicals reaches a steady state of 10^{-7} M (which is probably several orders of magnitude too high an estimate) the steady state concentration of the substrate anion radical can be evaluated from the difference in the standard potential between the substrate and the product (Table 1). Thus for *p*-fluoronitrobenzene a steady state concentration of $RX^{\cdot-}$ of $\sim 1.5\cdot10^{-12}$ M is reached. The rate expression (Eqn. 6) can then be rewritten into a pseudo first-order equation:

$$-\frac{d[Nu]}{dt} = k'[Nu] \qquad \text{where } k' = k\cdot 1.5\cdot10^{-12}\,M \qquad (7)$$

Denney and Denney reported that the reaction between sodium benzenesulfinate and *p*-fluoronitrobenzene went to 64% completion after 24 h in DMSO. Assuming pseudo first-order behaviour as in Eqn. 7 this corresponds to a pseudo first-order rate constant of $1.2\cdot10^{-5}$ s^{-1} or a second-order rate constant $k = 8\cdot10^{6}$ $M^{-1}s^{-1}$. Applying the same kind of calculations second-order rate constants of $1.2\cdot10^{5}$ $M^{-1}s^{-1}$ and $8.5\cdot10^{5}$ $M^{-1}s^{-1}$ are obtained for the chloro- and bromo-isomer. These estimates of the coupling rate constants

are of course very rough, and they may be inacurate by some orders of magnitude. They are however to be considered as *lower limits* for the rate constants of reaction 2, given the potentials in Table 1 and the reaction times reported by Denney and Denney.

Such a fast S_N2-reaction (Eqn. 2') between two negatively charged species does not seem very likely,[17] although in the *p*-halonitrobenzene series the nitro-group in the para-position could withdraw so much charge-density from the reaction site, as to make the coulombic repulsion less important. In any case it was pointed out by Bunnett[9] that in the $S_{RN}2$-reaction of aromatic compounds any conceivable transition state of the coupling reaction (Eqn. 2') involves a loss of aromaticity, which would add to the barrier of the reaction. So even though the standard potentials do not provide conclusive evidence against the title reaction being of the $S_{RN}2$-type, they clearly put severe restrictions on the rate of the coupling reaction (Eqn. 2').

Cyclic voltammetry (CV)

Halonitrobenzenes have been studied electrochemically both in liquid ammonia,[18] DMF,[14,19,20,21,22] acetonitrile,[21,22] and DMSO.[15,21] We investigated the cyclic voltammetric behaviour of the four *p*-halonitrobenzenes in DMF in the absence and in the presence of the nucleophile **1**. Without added nucleophile the substrates **2-5** all show two waves in CV, the first of which being reversible at all scan rates investigated (0.02-80 Vs^{-1}), except for the iodo-isomer where the reversibility is partially lost at scan rates below 5 Vs^{-1} and completely at 0.2 Vs^{-1}. The first wave corresponds to a one-electron reduction leading to the anion radical of the substrate (Eqn. 1, the electron donor being the electrode). The $S_{RN}2$-reaction is a zero-electron process, where the electron initially put into the system (Eqn. 1) plays the role of a catalyst. Therefore, if the anion radicals of the compounds **2-5** react with **1** in a $S_{RN}2$-process, one should observe a change of the initial one-electron reversible wave to a zero-electron wave upon addition of the nucleophile to a solution of the substrate. At sufficiently high concentrations of the nucleophile and/or low scan rates, the substrate wave should disappear completely, and instead one should see a new wave corresponding to the substitution product.[6c]

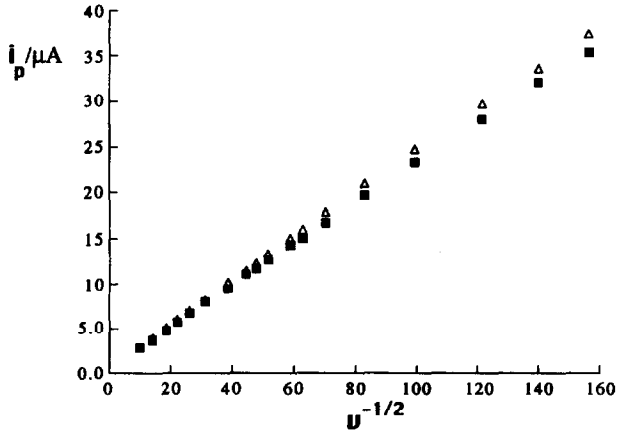

Figure 1. Cyclic voltammetry on a gold electrode (Ø 0.6 mm) in DMF containing 0.1 M $TBABF_4$. Plot of i_p vs. $v^{-1/2}$ for 2 mM p-iodonitrobenzene alone (Δ) and after addition of 10 mM sodium benzenesulfinate (■).

Figure 1 shows a plot of i_p vs. $\sqrt{v}$ for *p*-iodonitrobenzene alone and with addition of nucleophile. It is clear that the plot with added nucleophile is indistinguishable from the plot for *p*-iodonitrobenzene (**5**) alone, indicating that there is no change in the peak current when the nucleophile is added, even at low scan rates ($v = 100\ mVs^{-1}$), when the difference should manifest itself. This was also the case for the other 3 substrates. For unknown reasons the voltammograms tended to broaden a little at higher scan rates, much as if the iR_u-compensation was inadequate, which explains the small difference at higher scan rates. Furthermore, with none of the substrates was there any wave corresponding to the product **6**, even on repeated scanning at low scan rates. We therefore conclude that if the substrates **2** - **5** react with sodium benzenesulfinate (**1**) in a $S_{RN}2$-reaction, it must be very slow ($k < 1\ M^{-1}s^{-1}$). This clearly contradicts the conclusion drawn above based on the relative reduction potentials of the substrates and the product.

Preparative electrolysis

It is possible to trigger $S_{RN}1$ and/or $S_{RN}2$-reactions by light,[23] dissolving metal,[4,24] transition metal ions,[25] sodium amalgam[26] and by electrochemical means.[6c,8c,27] The electrochemical initiation produces the anion radical of the substrate directly either at the electrode or in the solution via redox catalysis.[28] Therefore, if the *p*-halonitrobenzenes are submitted to a preparative electrolysis at the potential of their first wave in the presence of the nucleophile **1**, it should be possible to detect the coupling product **6**, provided that the $S_{RN}2$-mechanism is true for these reactions. As the reduction potential of the product is less negative than those of the substrates, the product will be reduced to its anion radical at the working potential. In the absence of side reactions the process will thus consume 1 F/mole of substrate,[6c] and to isolate the product after electrolysis the anion radical must be reoxidized either by air during work-up or electrochemically while still in the cell.

Table 2: Yields from preparative reductions of *p*-chloronitrobenzene in DMSO with or without sodium benzenesulfinate present.

Exp.	Starting compounds/10^{-3} mol			Yield %		n
	1	**3**	**6**	**3**	**6**	F/mol
1	3.07	0.68	0	87.7	<1.0	0.98
2	0	0.72	0	98.3	-	0.87
3	1.33	0.50	0.16	63.5	68.0	1.09[a]

[a] Based on the total amount of **3** and **6** initially present.

The electrochemical reduction of the four *p*-halonitrobenzenes has been described before.[22] Table 2 summarizes the results of our preparative electrochemical reductions of *p*-chloronitrobenzene, which were carried out at ambient temperature in DMSO using a mercury pool as the cathode and 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) as the supporting electrolyte. The duration of a reduction and subsequent oxidation was generally about 4-5 hours. Each entry in Table 2 shows the result of one reduction, which is representative of at least 2 or 3 runs carried out under identical conditions except for the exact amount of starting compounds. Entry 1 shows that electrochemical reduction of **3** in the presence of the nucleophile **1** yields the same product, namely the recovered starting material, as the reduction of **3** alone (entry 2). Furthermore, a comparison of the two first entries shows that the amount of charge consumed in the reduction of **3** is not significantly affected by the presence of **1** and remains close to 1 F/mol.

It could be suggested that the failure to detect any **6** in experiment 1 (Table 2) was due to **6** not being stable under the reaction conditions, hence a reduction was carried out under conditions as in experiment 1, but with a small amount of **6** added prior to reduction (experiment 3, Table 2). In this case about two thirds of **3** and **6** were recovered. We are unable to explain the rather poor material balance, as no other products were detected, but in any case the result shows that if *any* **6** were formed in experiment 1, we would have detected at least *some* of it. In one of the runs similar to experiment 1, a small amount of **6** corresponding to 4.0 % of the initial amount of **3** was detected, but in this case the reaction mixture was left overnight before work-up, and we assume that the **6** formed stems from a polar reaction between **1** and **3**. In no other cases any **6** were detected in runs similar to experiment 1. We therefore conclude that the reaction between **1** and **3** (Eqn. (5)) does not show catalysis by electrons provided by an electrode, as predicted by Scheme 2.

It should be noted that the large recovery (up to 98 %) of **3** after reduction suggests that the stability of the *p*-chloronitrobenzene anion radical in DMSO is larger than expected from the rate constant (10^{-2} s^{-1}) reported by Danen *et al.* for the unimolecular cleavage of $\mathbf{3}^{\cdot-}$ in DMF. This point was not further investigated.

Conclusions

The reaction between the four *p*-halonitrobenzenes and sodium benzenesulfinate, to which the $S_{RN}2$-mechanism (Scheme 2) was previously assigned,[1] was investigated by UV-spectrometry and electrochemical methods. The results do not support the reported photostimulation of reaction 5, as no evidence of CT-complex formation was found by UV-spectrometry. Reduction potentials of the substrates are more negative than that of the product, which makes the ET-step (Eqn. 4) an uphill reaction. This could be overcome if reaction 2' is very fast; however, cyclic voltammetry shows that this reaction must be extremely slow, if it happens at all. Conclusive evidence against the $S_{RN}2$-mechanism in this system is provided by preparative electrolysis, which fails to give the product predicted by Scheme 2. The electrochemical experiments thus exclude any radical or radical anion chain mechanism for the reactions investigated. A different mechanism of aromatic nucleophilic substitution which explains the experimental results must therefore be considered. A possible reaction route is the addition-elimination or S_NAr-mechanism, which was rejected by Denney and Denney on the basis of experiments showing inhibition by galvinoxyl and stimulation by photons. Inasmuch as the inhibition and stimulation effects usually encountered in $S_{RN}1$-reactions are somewhat larger than those found by Denney and Denney, the results to us seem, although puzzling, not compelling evidence against the S_NAr-mechanism. We believe that the assignment of the S_NAr-mechanism to reaction 5 is compatible with the evidence at hand, but it is possible that a further mechanism, not yet postulated in detail, may provide a better explanation for the experimental results.

We wish to emphasize that the present work does not exclude the $S_{RN}2$-mechanism as a possibility in *some* aromatic nucleophilic substitution reactions. However, the experiments we have carried out are a test, which any candidate for the $S_{RN}2$-reaction must pass, before a proper assignment of the mechanism can be done. Very recently in the literature there appeared a number of likely candidates for the aromatic $S_{RN}2$-reaction,[29,30] and it would certainly be interesting to investigate these by electrochemical means to provide further evidence in favour of or against the $S_{RN}2$-mechanism in those cases.

Experimental

Materials. Sodium benzenesulfinate (**1**) was dried by dissolving in DMF, drying over molecular sieves (4 Å) and precipitating with ether. *p*-Fluoronitrobenzene (**2**) was distilled and *p*-chloronitrobenzene (**3**) recrystallized from ethanol prior to use. **4** and **5** were used as received.

4-Nitro-diphenylsulfone (**6**) was prepared by boiling 6.0 g of each **1** and **3** in 100 ml DMF for 10 minutes. The solution was poured onto 300 ml of crushed ice and 200 ml of water, filtered with suction and washed with ether. Recrystallization of the crude product from ethanol and water yielded 5.7 g (59 %) of colourless needles, m.p. 138-140 °C (lit. 143 °C).[31] GC showed no impurities. ^{1}H NMR ($CDCl_3$): δ 7.5-7.7 ppm (m, 3H) δ 7.95-8.0 ppm (d, 2H) δ 8.1-8.17 ppm (d, 2H) δ 8.3-8.4 ppm (d, 2H).

The solvents containing supporting electrolyte were dried through a column of activated alumina before use.

UV-spectrometry. UV-measurements were carried out on a UVIKON 860 spectrometer.

CV-experiments. Cyclic voltammetric experiments were carried out using procedures and equipment previously described.[32] A gold electrode or a hanging drop mercury electrode electrolytically plated on gold was used as the working electrode. Potentials were measured against naphthoquinone (**2-5**) or benzoquinone (**6**) but reported vs. SCE. CV-experiments with sodium benzenesulfinate and the substrates (**2-5**) were conducted with a substrate concentration of 2 mM and the nucleophile in a 5 or 10-fold excess.

Preparative electrolysis. For the preparative reductions a conventional H-cell was used with a mercury pool as the cathode and a carbon rod as the anode. A silver wire in a tetrabutylammonium iodide solution served as a pseudo-reference electrode. Reductions were carried out in DMSO containing 0.1 M $TBABF_4$ as the supporting electrolyte with the potential set at -0.7 V vs. the reference (which is approximately 400 mV negative of SCE). The reaction mixture was reoxidized electrochemically at a potential of -0.2 V vs. Ag/AgI before work-up. A preparative experiment generally took around 4-5 hours. The work-up involved diluting the reoxidized catholyte with water and extracting thrice with toluene. The toluene extracts were collected, washed with water and dried over anhydrous $MgSO_4$. The original water phase was acidified with HCl and extracted with toluene, but in no case was anything but trace impurities found in these toluene extracts. Yields were determined on a HP5890 gas chromatograph using naphthalene as an internal standard and correcting for different response factors.

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