Studies on Polythionates. V. The Action of the Cyanide Ion on Aromatic Sulfinates of Divalent Sulfur and Selenium in Acetonitrile

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Aromatic sulfinates of divalent sulfur and selenium have been found to react quantitatively with ionic cyanide in acetonitrile. Reaction mechanisms have been suggested on the basis of experiments carried out by varying the concentration of the nucleophile and measuring the formation of the corresponding pseudohalide ion by means of IR. The reaction mechanisms conform favourably with each other. The results are discussed in relation to previous studies on the corresponding polythionates-cyanide reactions in acetonitrile.

A method for analysing sulfinates of divalent sulfur and selenium by means of ionic cyanide and IR has been described.

In previous papers [1–4] we have reported reactions between polythionates and ionic cyanide in the dipolar aprotic solvent acetonitrile. From kinetic studies the reaction mechanisms have been described. Aromatic sulfinates of divalent sulfur [5] and selenium [6] constitute another series of polythionic compounds that exhibits much the same chemical properties as do the polythionates. We have therefore found it of interest to study the action of ionic cyanide on these compounds.

In contrast to the polythionates, reactions concerning nucleophilic attack by ionic cyanide on sulfinates of divalent sulfur and selenium have not been studied earlier. The reason may be that these compounds are nearly insoluble in aqueous solution. Acetonitrile has been found to be a convenient solvent for studying these reactions, because in this solvent both the substrates and the nucleophilic reagent, tetraphenylarsonium cyanide, appear to be very soluble. Furthermore, no hydrolysis can take place, which facilitates the determination of the reaction mechanism.

The following substrates will be discussed in this paper:

$$\mathrm{Ph-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-(X)_{\mathit{n}}-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-Ph}$$

(X = S and Se, n = 1 and 2)

RESULTS

The stoichiometry of the reactions between the cyanide ion and the various sulfinates has been determined by changing the concentration of the nucleophile and measuring the formation of the corresponding pseudohalide ion by means of IR. Contrary to the polythionate-cyanide reactions, the reactions between the sulfinates and the cyanide ion appear to be very fast in acetonitrile, and no kinetic experiments applying IR could be performed.

During all the reactions examined, the nucleophilic reagent was always added to the substrate. The experimental data are collected in Table 1.

The sulfur disulfinate-cyanide reaction. From Table 1 it is seen that 1 mol of sulfur di(benzenesulfinate) consumes 2 mol of the nucleophile in order to form 1 mol of ionic thiocyanate. Upon mixing the reactants in the mol ratio of 1:1 only ½ mol of the pseudohalide ion was found, indicating that the reaction passes through two steps.

There are three potential electrophilic centres in the sulfur disulfinate molecule, *i.e.*, the divalent sulfur atom and both of the sulfonyl sulfur atoms. Considering the sulfonyl sulfur

Table 1. Determination of the stoichiometry of the reaction between the cyanide ion and different aromatic sulfinates of divalent sulfur and selenium in acetonitrile.

Reaction	Amount of XCN^- formed
$\mathrm{Ph-SO_2-S-SO_2-Ph+CN^-}$	½ mol SCN^-
$\mathrm{Ph-SO_2-S-SO_2-Ph+2\,CN^-}$	1 mol SCN^-
$\mathrm{Ph-SO_2-S-S-SO_2-Ph+CN^-}$	½ mol SCN^-
$\mathrm{Ph-SO_2-S-S-SO_2-Ph+2\,CN^-}$	1 mol SCN^-
$\mathrm{Ph-SO_2-Se-SO_2-Ph+CN^-}$	½ mol $SeCN^-$
$\mathrm{Ph-SO_2-Se-SO_2-Ph+2\,CN^-}$	1 mol $SeCN^-$
$\mathrm{Ph-SO_2-Se-Se-SO_2-Ph+CN^-}$	2/3 mol $SeCN^-$
$\mathrm{Ph-SO_2-Se-Se-SO_2-Ph+2\,CN^-}$	4/3 mol $SeCN^-$
$\mathrm{Ph-SO_2-Se-Se-SO_2-Ph+3\,CN^-}$	2 mol $SeCN^-$

atoms as the electrophilic centres, the stoichiometry with respect to ionic thiocyanate may be explained by a first step according to eqn. 1,

$$\mathrm{Ph{-}SO_2{-}S{-}SO_2{-}Ph + CN^- \longrightarrow Ph{-}SO_2{-}CN + Ph{-}SO_2{-}S^-} \qquad (1)$$

followed by a fast removal of a sulfur atom from the thiosulfinate ion by a second cyanide ion, eqn. 2.

$$\mathrm{Ph{-}SO_2{-}S^- + CN^- \xrightarrow{fast} Ph{-}SO_2^- + SCN^-} \qquad (2)$$

However, separate experiments proved that ionic benzenethiosulfonate did not react with the cyanide ion in a fast reaction in acetonitrile. After 2 h at room temperature no ionic thiocyanate could be detected using 5.0×10^{-3} M solutions of each of the reactants. From these observations the mechanism involving nucleophilic substitution at the sulfonyl atoms can be rejected as a possible first step in the sulfur di (benzenesulfinate)-cyanide reaction.

The electrophilic centre thus has to be the divalent sulfur atom, and the following two mechanisms are in agreement with the data of Table 1.

$$\mathrm{Ph{-}SO_2{-}S{-}SO_2{-}Ph + CN^- \xrightarrow{slow} Ph{-}SO_2{-}SCN + Ph{-}SO_2^-}$$

$$\mathrm{CN^- \downarrow fast}$$

$$\mathrm{Ph{-}SO_2{-}CN + SCN^-}$$

Scheme 1a.

$$\mathrm{Ph{-}SO_2{-}S{-}SO_2{-}Ph + CN^- \overset{fast}{\rightleftharpoons} Ph{-}SO_2{-}SCN + Ph{-}SO_2^-}$$

$$\mathrm{CN^- \downarrow slow}$$

$$\mathrm{Ph{-}SO_2{-}CN^- + SCN^-}$$

Scheme 1b.

Mechanism 1a involves a nucleophilic attack by the cyanide ion at the divalent sulfur atom to displace ionic benzenesulfinate in the rate determining step. The stoichiometry requires that the intermediate, benzenesulfonyl thiocyanate, once formed reacts with any additional cyanide ion, *i.e.*, the cyanide ion prefers the intermediate to the original reactant. Otherwise cyanide would be tied up in the intermediate and not quantitatively delivered as benzenesulfonyl cyanide and thiocyanate.

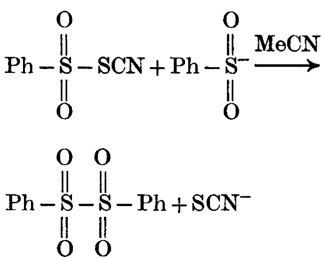
Mechanism 1b involves a fast reversible first step with a small equilibrium constant. Under these circumstances no appreciable accumulation of the intermediate can take place and the stoichiometry with respect to ionic thiocyanate will be the same. The second step is thought to be rate determining, irreversible, product formation.

In order to determine which of these two mechanisms really takes place, separate reactions between the intermediate, $PhSO_2SCN$, and ionic cyanide and ionic benzenesulfinate were carried out.

1 mol of benzenesulfonyl thiocyanate was found to react quantitatively with 1 mol of ionic cyanide to give ionic thiocyanate and benzenesulfonyl cyanide in a fast reaction, eqn. 3-

$$\mathrm{Ph{-}SO_2{-}SCN + CN^- \xrightarrow{MeCN} Ph{-}SO_2{-}CN + SCN^-} \qquad (3)$$

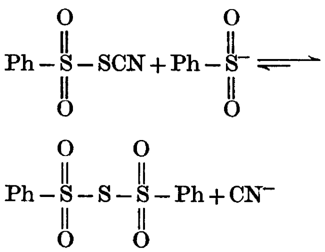
Experiments have also shown that the benzenesulfinate ion rapidly reacts with benzenesulfonyl thiocyanate in acetonitrile, giving quantitatively 1 mol of ionic thiocyanate and probably disulfon, eqn. 4.



(4)

In both reactions, eqns. 3 and 4, the electrophilic centre of benzenesulfonyl thiocyanate thus appears to be the sulfonyl sulfur atom.

If the mechanism of the sulfur disulfinate-cyanide reaction is of the type 1b, reaction 4 has to pass through an equilibrium first-hand, eqn. 5.



(5)

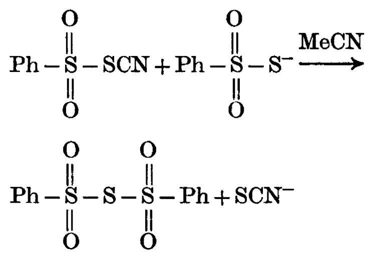
Since $PhSO_2SCN$ is present from the beginning in the reaction vessel, the reaction 3 would have converted part of the cyanide into $PhSO_2CN$, and hence the yield of ionic thiocyanate would not have been quantitative. This is not in agreement with the experimental results. Furthermore, the first step of the mechanism 1b predicts that the sulfinate ion is a better nucleophile towards divalent sulfur than the cyanide ion, contrary to what has been reported earlier.[7]

On the other hand, if the mechanism is of the type 1a, there may be a reaction path for the intermediate to react according to eqn. 4 at a rate which is inferior to the rate of reaction in the presence of ionic cyanide but still superior to the rate of the inversion of the first step. Hence, if no ionic cyanide is present, reaction 4 can give other products than the original reaction. When ionic cyanide is present, however, the second step, eqn. 3, represents the easiest path.

The sulfur di(benzenesulfinate)-cyanide reaction thus appears to follow the mechanism of the type 1a, and consequently the nucleophilicity of the cyanide ion towards sulfenyl sulfur and sulfonyl sulfur is much larger than the nucleophilicity of the benzenesulfinate ion towards the same substrates.

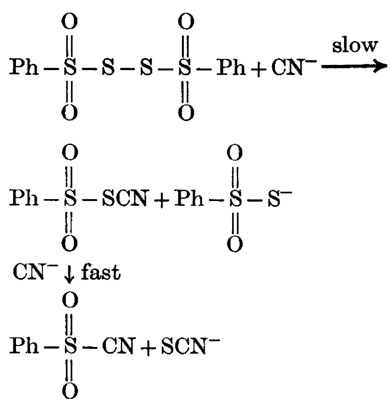
The disulfur disulfinate-cyanide reaction. Disulfur di(benzenesulfinate) has been found to react with ionic cyanide in the same mol ratio as sulfur di(benzenesulfinate), *i.e.* 1:2 (Table 1); 1 mol of ionic thiocyanate was formed. When the reaction was performed in the mol ratio of 1:1, only ½ mol of ionic thiocyanate was detected, indicating that the reaction passes through two steps.

Furthermore, the benzenethiosulfonate ion has been found to displace ionic thiocyanate quantitatively when reacted with benzenesulfonyl thiocyanate in acetonitrile. The reaction appeared to be fast, eqn. 6.



(6)

By applying the same kind of reasoning for the disulfur disulfinate-cyanide reaction as was made for the sulfur disulfinate-cyanide reaction, we arrive at the mechanism given in Scheme 2.



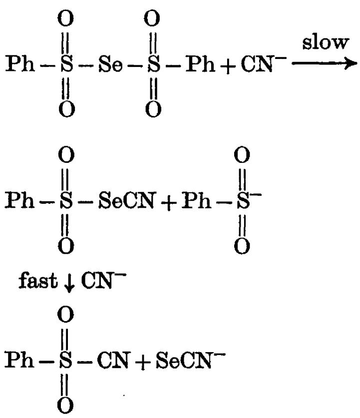
Scheme 2.

The first step is supposed to be a nucleophilic attack by the cyanide ion at one of the divalent sulfur atoms, displacing ionic benzenethiosulfonate. The second step, which appears to be much faster, is analogous to the second step of the sulfur disulfinate-cyanide reaction.

Hence, the cyanide ion is a better nucleophile towards sulfenyl sulfur and sulfonyl sulfur than is the benzenethiosulfonate ion.

The selenium disulfinate-cyanide reaction. With regard to nucleophilic substitution reactions on divalent sulfur and selenium in acetonitrile, ionic cyanide has been found to be far more reactive towards the latter.[2] From analogy with the sulfur di(benzenesulfinate)-cyanide reaction, nucleophilic attack at the sulfonyl sulfur atoms may then be rejected as a possible first step in the selenium disulfinate-cyanide reaction.

The difference in the stoichiometry with respect to ionic selenocyanate, Table 1, may indicate that selenium di(benzenesulfinate) reacts with ionic cyanide in an analogous way as the corresponding sulfur compound, Scheme 3.



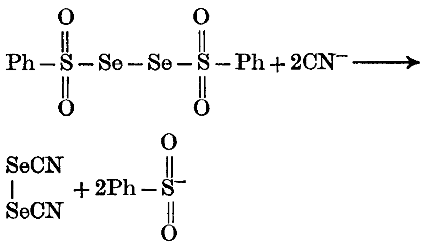
Scheme 3.

A fast reversible first step with a small equilibrium constant can hardly take place because the nucleophilicity of the cyanide ion towards divalent selenium in methanol is $\approx 10^3$ times greater than the nucleophilicity of the benzenesulfinate ion towards the same substrate.[8] In acetonitrile, however, the difference is believed to be even higher.[9]

Unfortunately, the second step of this reaction can not be separately studied since benzenesulfonyl selenocyanate has not yet been prepared.

The diselenium disulfinate-cyanide reaction. 1 mol of diselenium di(benzenesulfinate) was found to consume 3 mol of cyanide ions, giving 2 mol of ionic selenocyanate Table 1. Upon mixing the reactants in the mol ratio of 1:1, 2/3 mol of ionic selenocyanate was formed. This may indicate that the reaction passes through three steps.

Foss [6] has pointed out that in reactions of diselenium disulfinates with nucleophilic agents the sulfinate groups are the leaving groups. Nucleophiles like ionic ethylxanthate displace both of the sulfinate groups without breakdown of the selenium-selenium bond.[6] If ionic cyanide reacts in an analogous manner, selenocyanogen would be formed, eqn. 7.



(7)

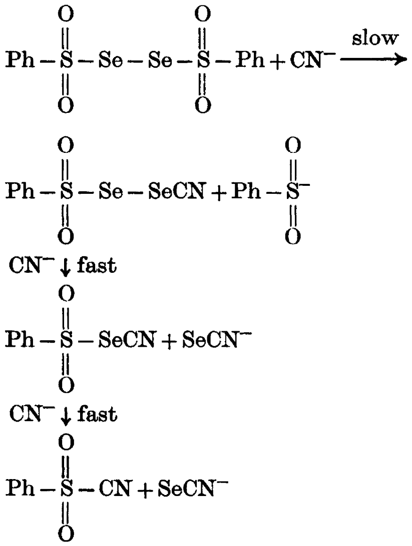
However, previous studies have shown that 1 mol of selenocyanogen consumes 4 mol of cyanide ions to give 2 mol of ionic selenocyanate, eqn. 8.[10]

$$(SeCN)_2 + 4\,CN^- \xrightarrow{MeCN} 2\,SeCN^- + (CN)_4^{2-} \quad (8)$$

The stoichiometry of the diselenium disulfinate-cyanide reaction would thus be quite different from the one experimentally observed, Table 1.

Combining the present results, the work of Foss,[6] and applying the same reasoning as for the other reactions in this series, we arrive at a possible mechanism for the diselenium disulfinate-cyanide reaction as depicted by Scheme 4.

The leaving group in the slow step of the mechanism in Scheme 4 is the sulfinate ion. In a relatively much faster step a second cyanide ion attacks the intermediate. $Ph-S(O)_2-Se-SeCN$, to displace ionic selenocyanate. Benzenesulfonyl selenocyanate formed in the second



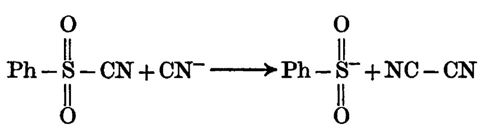
Scheme 4.

step is attacked by a third cyanide ion in a reaction similar to the second step of the selenium disulfinate-cyanide reaction.

Ionic selenocyanate is thus a better leaving group than the benzenesulfinate ion when considering nucleophilic substitution at divalent selenium in acetonitrile.

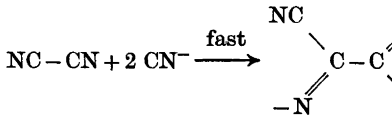
Analysis by means of ionic cyanide and IR. The cyanide method has occupied a central position in analysing polythionates in aqueous solution.[11] The amount of ionic thiosulfate formed is determined by iodometric titrations. With regard to the sulfinates of divalent sulfur and selenium studied in this work, the cyanide method may as well be applied. This may be done by reacting the sulfinate with excess ionic cyanide in acetonitrile and measuring by means of IR the amount of the corresponding pseudohalide ion formed.[12] The experimental values have been found to agree within $\pm 2-3$ % of the theoretical one.

Benzenesulfonyl cyanide which is one of the products in the reactions mentioned above is, however, attacked by excess of ionic cyanide. The electrophilic centre is the carbon atom, and ionic benzenesulfinate is displaced,[13] eqn. 9.



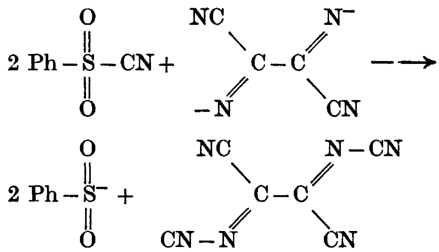
(9)

The cyanogen then rapidly adds 2 mol of cyanide ions and probably forms the diiminosuccinonitrile dianion, having strong absorption in IR at 2142 cm^{-1} and 2153 cm^{-1},[14] eqn. 10.



(10)

Separate experiments have shown that 1 mol of cyanide ions completely reacts with 1 mol of benzenesulfonyl cyanide, forming a yellowish solution that has a strong IR absorption at 2135 cm^{-1}. This may be explained by a reaction between the postulated diiminosuccinonitrile dianion and 2 mol of benzenesulfonyl cyanide according to eqn. 11.



(11)

DISCUSSION

The rate of reaction between two negatively charged ions in many cases is largely depressed in a dipolar aprotic solvent relative to a protic solvent.[1] In aqueous solution aromatic thiosulfonates can be analysed by reacting them with ionic cyanide.[15] If, however, ionic benzenethiosulfonate at all reacts with ionic cyanide in acetonitrile, the reaction has to be very slow. After 2 h at room temperature no ionic thiocyanate could be detected when using 5.0×10^{-3} M of each of the reactants.

It is of particular interest to note that benzenesulfonyl thiocyanate is much more susceptible to nucleophilic attack by the cyanide ion in acetonitrile than is the thiocyanatosulfonate ion, $^{-}O_3SSCN$.[2] The electrophilic centre in both cased is the sulfonyl sulfur atom, and ionic thiocyanate is the leaving group.

Likewise, the cyanosulfonate ion appears to be unaffected by ionic cyanide in acetonitrile,[2] while benzenesulfonyl cyanide undergoes a fast nucleophilic attack at the carbon atom by the same anion, eqn. 9.

In contrast to the trithionate ion, $^{-}O_3SSSO_3^{-}$, which does not react with ionic cyanide even in boiling acetonitrile,[16] sulfur di(benzenesulfinate) reacts rapidly with ionic cyanide in the same solvent. The rate constants of the various steps of the latter reaction appear to follow the order:

$$k_2\left(\mathrm{Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CN+CN^-}\right) \ll$$

$$k_2\left(\mathrm{Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Ph+CN^-}\right) \ll$$

$$k_2\left(\mathrm{Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-SCN+CN^-}\right) \quad \text{and}$$

$$k_2\left(\mathrm{Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-SCN+Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S^-}}}\right) \ll$$

$$k_2\left(\mathrm{Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-SCN+CN^-}\right)$$

With regard to the disulfur di(benzenesulfinate), it appears to follow the same mechanism when reacted with ionic cyanide as does the tetrathionate ion, albeit the former reaction is much faster.[1] The sequence of the rate constants of the various steps is believed to be:

$$k_2\left(\mathrm{Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CN+CN^-}\right) \ll$$

$$k_2\left(\mathrm{Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Ph+CN^-}\right) \ll$$

$$k_2\left(\mathrm{Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-SCN+CN^-}\right) \quad \text{and}$$

$$k_2\left(\mathrm{Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-SCN+Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S^-}\right) \ll$$

$$k_2\left(\mathrm{Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-SCN+CN^-}\right)$$

Benzenesulfonyl selenocyanate, which has been postulated to be the intermediate of the selenium di(benzenesulfinate)-cyanide reaction, has two potential electrophilic centres; the sulfur atom and the selenium atom. The selenocyanatosulfonate ion, $^{-}O_3SSeCN$, is supposed to be attacked by ionic cyanide at the selenium atom, displacing ionic sulfite in acetonitrile.[4] If, however, benzenesulfonyl selenocyanate undergoes a nucleophilic substitution by ionic cyanide in the same manner, selenium dicyanide would also here be formed, and would immediately consume 3 mol of cyanide ions to form 1 mol of ionic selenocyanate.[14] The stoichiometry of the reactants of the selenium di(benzenesulfinate)-cyanide reaction would then be different from what is experimentally found.

The mechanism of the selenium di(benzenesulfinate)-cyanide reaction, Scheme 3, is thus different from the mechanism of the selenotrithionate-cyanide reaction in acetonitrile which is believed to follow the mechanism pictured by eqns. 12 – 14.[4]

$$\mathrm{^{-}O_3S-Se-SO_3^{-}+CN^{-}} \xrightarrow{\text{slow}} \mathrm{^{-}O_3S-SeCN+SO_3^{2-}} \quad (12)$$

$$\mathrm{^{-}O_3S-SeCN+CN^{-}} \xrightarrow{\text{fast}} \mathrm{Se(CN)_2+SO_3^{2-}} \quad (13)$$

$$\mathrm{Se(CN)_2+3\ CN^{-}} \xrightarrow{\text{fast}} \mathrm{SeCN^{-}+(CN)_4^{2-}} \quad (14)$$

These findings support our previous statement that the negative charge on the sulfonyl group of the selenocyanatosulfonate ion probably prevents the cyanide ion from attacking at the sulfur atom.[4]

The first step in the reaction between the diselenotetrathionate ion, $^{-}O_3SSeSeSO_3^{-}$, and the cyanide ion in acetonitrile is supposed to involve nucleophilic substitution on one of the selenium atoms, followed by ionic scission of the selenium-selenium bond, eqn. 15.[4]

$^{-}O_3S - Se - Se - SO_3^{-} + CN^{-} \longrightarrow {}^{-}O_3S - SeCN + SeSO_3^{2-}$ (15)

However, in nucleophilic substitutions on diselenium di(benzenesulfinate) the sulfinate groups are the leaving groups.[6] The first step in these reactions is thus different from the first step of the diselenotetrathionate-cyanide reaction.

EXPERIMENTAL

Acetonitrile and tetraphenylarsonium cyanide were purified as reported previously.[2]

Sulfur di(benzenesulfinate) was prepared by oxidation of equivalent amounts of sodium benzenesulfinate and sodium benzenethiosulfonate by means of iodine in aqueous solution.[5] The compound was recrystallized from ethanol and it melted at 134 °C as reported in the literature.[5]

Disulfur di(benzenesulfinate) was prepared in the same way as described by Foss[6] for disulfur di(*p*-toluenesulfinate). The compound was recrystallized several times from benzene-petroleum ether (b.p. 40 – 60 °C). The substance melted at 76 °C as reported by Otto and Tröger.[5]

Selenium di(benzenesulfinate) was prepared from selenium tetrachloride and sodium benzenesulfinate as reported by Foss.[6]

Diselenium di(benzenesulfinate) was prepared and purified by the method of Foss.[6]

Benzenesulfonyl thiocyanate was prepared by the action of sodium benzenesulfinate on thiocyanogen in carbon tetrachloride.[17] The substance was recrystallized from petroleum ether (b.p. 40 – 60 °C) by cooling in dry ice-acetone mixture (m.p. 28 °C). IR showed a strong sharp peak at 2165 cm^{-1}, indicating that no iso form was present.

Benzenesulfonyl cyanide was prepared from sodium benzenesulfinate and chlorocyanogen as described by Cox and Ghosh.[18] The compound was crystallized from petroleum ether (b.p. 40 – 60 °C) by cooling in dry ice-acetone mixture. IR showed a strong sharp peak at 2188 cm^{-1}.

The benzenesulfonyl thiocyanate and the benzenesulfonyl cyanide were both stored in a refrigerator.

Tetraphenylarsonium benzenethiosulfonate was precipitated from an aqueous solution of sodium benzenethiosulfonate by means of tetraphenylarsonium chloride. The compound was recrystallized from acetonitrile by adding some ether. (Found: C 64.66; H 4.47; S 11.37. Calc. for $C_{30}H_{25}O_2S_2As$: C 64.80; H 4.50; S 11.50).

Tetraphenylarsonium benzenesulfinate was prepared from tetraphenylarsonium chloride and sodium benzenesulfinate in methanol. Upon mixing the solutions made by dissolving 5.0 g of tetraphenylarsonium chloride in 10 ml of methanol and 3.0 g of sodium benzenesulfinate dihydrate in 10 ml of methanol, sodium chloride was precipitated. The sodium salt was filtered off and the solvent was removed in vacuum. The residue was dissolved in acetonitrile that had been carefully flushed with nitrogen prior to use. Excess of sodium benzenesulfinate was filtered off and ether was added, whereupon tetraphenylarsonium benzenesulfinate crystallized. (Found: C 68.45; H 4.85; S 6.01. Calc. for $C_{30}H_{25}O_2SAs$: C 68.60; H 4.77; S 6.11).

The sulfinate-cyanide reactions were studied in the concentration range $2 - 5 \times 10^{-3}$ M of the substrate. The nucleophilic reagent was always added to the substrate, and the amount of pseudohalide ions formed was measured immediately after mixing the reactants by means of IR. All the reactions were performed at room temperature.

The reactions between benzenesulfonyl thiocyanate and the various nucleophiles (ionic cyanide, ionic benzenethiosulfonate, and ionic benzenesulfinate) were quantitatively studied by measuring the amount of formed ionic thiocyanate applying IR. The nucleophile was always added to the substrate.

The benzenesulfonyl cyanide-cyanide reaction was quantitatively studied by measuring the disappearance of the peak at 2188 cm^{-1} applying IR. When excess of ionic cyanide was added to the benzenesulfonyl cyanide solution, a yellowish-red solution immediately occurred, giving strong absorption in IR at 2142 cm^{-1} and 2153 cm^{-1}. This may be due to the postulated diiminosuccinonitrile dianion. Upon mixing the reactants in the mol ratio of 1:1 the peak of the benzenesulfonyl cyanide completely disappeared. The solution turned yellowish and gave strong IR absorption at 2135 cm^{-1}. This may be due to the formation of a polycyanic compound, eqn. 11.

The IR measurements were performed on a Unicam SP 200 G Infrared Spectrophotometer applying 0.1 cm liquid cells.

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