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GROUP TRANSFERS 4. ARYLSELENIDE ANIONDIARYL DISELENIDE EXCHANGE

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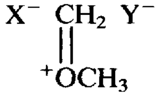
ABSTRACT

Barriers for group transfers between nucleophiles have been postulated to be lowered when the transferring group can carry a considerable negative charge. Furthermore, anions readily subject to one electron oxidation appear to lead to lower barriers than do those of high oxidation potential. These suggestions are pursued here on the identity reaction $ArSe^- + ArSeSeAr \longrightarrow ArSeSeAr + ArSe^-$. Indeed the reaction is very fast, as shown by the appearance of only a single peak in the ^{77}Se-NMR in an acetonitrile solution containing both ArSeNa and ArSeSeAr. The rate constant can be only very roughly estimated at low temperatures and dilute solutions, and is likely diffusion controlled for Ar = phenyl and *p*-methoxyphenyl. A stable intermediate $(ArSe)_3^-$, analogous to Br_3^-, is indicated, but quantitative stability could not be determined, from either the NMR or the UV spectra. Some properties of ^{77}Se-NMR are discussed.

INTRODUCTION

Previous work on group transfers[1,2,3,4] between nucleophiles has revealed that the transferring group can carry a substantial charge in the transition state, even though it is formally neutral in the reagent and the product. When this charge is considerable, the reaction rate is faster than a related transfer with a nearly neutral transition state group. Thus the methoxymethyl group is transferred faster than a methyl group[5] because the T. S. is stabilized by a major contribution from structures like **1**, and the transfer of phenacyl groups is fast because of enolate contribution to the T. S.[4] The case of stabilization by negative charge on the transferring group is of interest here. Two factors appear relevant; such stabilization is favored by a transferring group well able to tolerate the negative charge, as phenacyl compared to methyl, and also by attacking and leaving groups for which the free nucleophile is most easily oxidized to the corresponding radical, as in $ArSe^-$ compared to $ArSO_3^-$.[3] The important favorable contribution to the transition state is the structure **2**.



$$X^- \underset{{}^+OCH_3}{\overset{CH_2}{\|}} Y^-$$

1

$$X\bullet\, G^-\bullet\, X$$

2

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The extreme of a group for which the anion is favored is halogen as the transferring group. There are, however, few quantitative data on the rates of halogen transfers, although they are certainly very fast.

A new feature appears when we try to combine the two factors. Thus, when iodide ion attacks iodine, although the reaction is believed to be diffusion controlled, the typical transition state for bimolecular nucleophilic substitution has disappeared; I_3^- is instead a stable hypervalent species. Such intermediates are believed to exist for a substitution on atoms below the first row, including silicon,[6] phosphorus,[7] and others. None of these are hypervalent in the sense of violating the rules of valence, only that structures cannot be written that conform to the octet rule.

In this paper we attack the identity reaction of selenide anions with diselenides, reaction (1)

$$\mathrm{ArSe^-} + \mathrm{ArSeSeAr} \longrightarrow \mathrm{ArSeSeAr} + \mathrm{ArSe^-} \tag{1}$$

We have earlier noted that identity reaction rates can be measured by isotopic labelling and by interpolation from conventionally measured near-identity reaction rates using an LFER of some sort. The possibility of using NMR was mentioned, but the only example among methyl transfers is a somewhat uncertain study on the methyl iodide-dimethyliodonium ion reaction.[8] However, ^{77}Se-NMR has turned out to be the only handle on the rate of reaction (1). Reaction (1) is analogous to the identity reaction of thiophenoxide ion with diphenyl disulfide, which has been studied in a different solvent by Fava,[9] who used a radioactive tracer to follow the rate, with $k = 0{\cdot}49\ \mathrm{M^{-1}s^{-1}}$ at 20°C in methanol, which is far slower than the rate here observed. In structure **2**, X• is less accessible with sulfur than with selenium.

RESULTS AND DISCUSSION

The work on reaction (1) has nearly all been done with Ar = *p*-methoxyphenyl, although some studies on the unsubstituted compound are included. The use of substitutents with a substantial positive Hammett σ proved difficult because the reduction of the diselenide by sodium in liquid ammonia leads to overreduction for the case of chloro or trifluoromethyl substitutents, as well as the previously noted nitro and cyano substitutents.[3] The reduction used before on a wider variety of cases, namely the use of excess sodium borohydride, was unsuitable because it could not give known proportions of the sodium salt and the diselenide, and because of borane complexing of the anions.[10]

We attempted to prepare known mixtures of the anions with the diselenides by adding small amounts of oxidizing agents to the selenide anion solutions. These anion solutions are extremely sensitive to air, with the major product being deselenide, but the reaction is far from quantitative. It gives overoxidation products, as shown by HPLC analysis of the product. Then, bromine in carbon tetrachloride was tried, but the anion is totally destroyed by far less than one equivalent of bromine. Of course, the oxidizing agent is the carbon tetrachloride, and this is discussed in more detail below. Like air, bromine in acetonitrile also gives products other than the diselenide, so this was also unsuitable. Most of these reactions were attacked by UV methods, and the various complications such as overoxidation and the appearance of new absorptions, especially with bromine, made any quantitative interpretation difficult.

The search for $(\mathrm{ArSe})_3^-$ was conducted by both NMR and by UV. In the NMR the chemical shift of the single ^{77}Se peak, as shown in Table 1, was within the rather large experimental error, the same as the weighted mean of the anion shift and the diselenide. The presence of only a single peak shows that the reaction is very fast. The chemical shift errors were mainly

Table 1. ^{77}Se shifts for $ArSe^-$–ArSeSeAr mixtures in acetonitrile

Ar[a]	$(ArSe^-)$[b]	(ArSeSeAr)[b]	δ_{obs}[c]	δ_{calc}[c,d]	T°C[e]
Ph	0·000	0·1	456		amb
Ph	0·15	0·00	141[f]		amb
Ph	0·093	0·091	343	349	amb
Ph	0·011	0·0042	278[g]	277	−30
An	0·04	0·00	102[h]		amb
An	0·000	0·1	482		amb
An	0·179	0·096	282	299	amb
An	0·074	0·071	362	353	amb
An	0·054	0·035	319	317	amb
An	0·032	0·033	346	358	amb
An	0·008	0·0044	279[i]	301	−30

[a] An = *p*-methoxyphenyl.

[b] Concentrations in moles per liter.

[c] Chemical shifts calculated in parts per million from Me_2Se, but the actual internal standard was Ph_2Se.

[d] Calculated from the chemical shifts of the diselenide and the sodium salt weighted by the concentrations and the fact that only one of the two seleniums in the diselenide suffers a change of environment when reaction (1) occurs: $\delta_{calc} = [\delta_{ArSe^-}(ArSe^-) + 2\delta_{ArSeSeAr}(ArSeSeAr)]/[(ArSe^-) + 2(ArSeSeAr)]$.

[e] Ambient temperature in the NMR probe; *ca.* 30 °C.

[f] This value can be compared to the value in Reference 2 of 140·4 ppm in sulfolane, but the agreement appears to be fortuitously close.

[g] This line was conspicuously broadened, it had a width of 90 Hz.

[h] Reference 2 gives 93·9 in sulfolane. See note f.

[i] This line was broadened to about 220 Hz, see note g.

due to uncertainty about the composition of the mixture, arising in some cases from the unavoidable contamination of the sodium selenide by small amounts of diselenide from adventitious oxidation, and for the more dilute solutions, weighing errors. In the early stages there were major uncertainties in the chemical shifts. These were attributed to an apparent temperature dependence of the chemical shifts, shared by all the compounds. The use of an internal standard (diphenyl selenide) eliminated this problem in all the results reported here.

The results of the NMR studies are shown in Table 1. There was no significant dependance of the averaged chemical shift with concentration, suggesting that the concentration of the trimer anion even in the most concentrated solutions was too small to influence the observed average chemical shift. There was a perceptible variation in peak widths of all the compounds of an apparently instrumental origin that seemed unrelated to concentration or composition. Within this uncertainty, the averaged peaks were about as sharp as the standard except for the runs reported for the most dilute solutions at lower temperatures. This broadening gives rise to a very rough estimate of the rate constant for reaction (1).

Reaction (1) is clearly very fast. In concentrated solutions, no solid evidence of broadening of the peak of the averaged signal could be seen. Cooling these solutions just short of the precipitation of the components in the hope of increasing the concentration of the trimer anion gave no significant change in the chemical shift or width of the averaged peak. However, the most dilute solutions did, on cooling to −30 °C, show a significant increase in peak width, compared to the internal standard, and to any of the other peaks seen. Because of the dilution and the broadening, these spectra required much longer accumulation times; even after 4 hours, the signal to noise ratio was so poor that widths of these lines were not determined with precision. The quality of the spectra for these reasons was not good enough to justify a detailed line shape analysis. Using just the line width, a chemical relaxation time of $2{\cdot}8 \times 10^{-7}$s was calculated for the *p*-methoxy case, and $1{\cdot}7 \times 10^{-7}$s was calculated for the unsubstituted phenyl case.[11] These then lead to rate constants of $2{\cdot}9 \times 10^{8}$ and $3{\cdot}9 \times 10^{8}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for the two cases, respectively. These are not significantly different, and are probably not below the diffusion controlled limit for acetonitrile at −30 °C. We therefore refrain from a discussion of any substitutent effect.

The UV studies are generally inconclusive. The characteristics of the spectra are presented in Table 2. In no case could a spectrum of any mixture be shown to differ from that of a combination of the individual spectra, except when the anion was oxidized with carbon tetrachloride where there were some changes with time, lasting for several minutes. Precise interpretation of the spectra was prevented by the demonstrated presence of significant side products. The high extinction coefficients prevented the study of concentrated solutions in the UV, although cells as thin as 1 mm were used. Still thinner cells did not allow adequate mixing of these very air sensitive mixtures.

In spite of all this evidence, there is still reason to suspect the existence of the trimer anion. When the two reagents are mixed the faint yellow color of the diselenide turns a visibly more intense and more orange color, although the sodium arylselenide solutions are colorless. The color is due to a long tail on the UV maximum of the diselenide, which has only a very low extinction coefficient in the visible region. The visible absorption intensity of the mixtures was slightly higher than that for the two components, but the difficulty of dealing with this featureless weak absorption in the presence of uncertain side reactions prevented any convincing quantitative instrumental demonstration of a specific interaction. Nevertheless, the visible clue is entirely reproducible and can most easily be explained by a significant interaction of the two species.

The reaction between $ArSe^-$ and CCl_4 is interesting and has an amusing consequence when a low concentration of CCl_4 is added to a solution of $ArSe^-$ in CH_3CN in an NMR tube. The absorption of the selenium anion disappears completely although that of the reference Ph_2Se is quite unaltered. After about twenty minutes the Se spectral line reappears in the new position

Table 2. UV data for diselenides and arylselenide anion in acetonitrile

Compound	λ_{max}	ε
PhSeSePh	330	700
	240	16700
PhSeSePh	329[a]	1070[a]
	240[a]	17400[a]
$PhSe^-$	295	6900
	227	8400
AnSeSeAn[b]	278(sh)	10000
	248(sh)	14200
	228	15600
$AnSe^-$	298	13400
	233(sh)	10600

[a] These data were reported by A. J. Parker, *Acta Chem. Scand.*, 855 (1962) in methanol solution.
[b] An = *p*-Methoxyphenyl.

corresponding to the weighted average position of the anion and the diselenide lines. The reaction is apparently mostly the reaction (2) followed by reaction (3)

$$ArSe^- + CCl_4 \longrightarrow ArSeCl + CCl_3^- \tag{2}$$

$$ArSeCl + ArSe^- \longrightarrow ArSeSeAr + Cl^- \tag{3}$$

and the signal disappears because the reaction is slow enough so that successive pulses give a signal at a different chemical shift, and the accumulated spectrum is too broad to be seen. Either (2) or (3) could be the slow step, but we favor (2). Since no ^{77}Se signal is seen until the reaction is essentially complete, the absence of a signal due to ArSeCl must either mean that its concentration is too low, or that it is also exchanging rapidly with the $ArSe^-$ and the ArSeSeAr (for this reaction the NMR window was changed to include the chemical shift of arylselenyl chlorides, at about 1000 ppm). If its concentration is too low to see, it must mean that step (3) is relatively fast. If (3) is slow it is entirely plausible that the identity reaction (4) is very fast, since many positive halogen reactions are very fast, and this would

$$ArSe^- + ClSeAr \longrightarrow ArSeCl + {}^-SeAr \tag{4}$$

account for the invisibility of a constant chemical shift signal during the reaction. However, it is implausible that the selenium transfer reaction (3), which appears to go to completion and hence is thermodynamically favorable, would be much slower than the thermoneutral identity exchange (1). Thus the probably endothermic reaction (2) is more likely the slow reaction. The slow reaction is clearly the same as that seen in the UV.

The sequence (2) and (3) is partially confirmed by the detection of side products when more concentrated solutions are used. The compound $PhSeCCl_3$, identified primarily by its mass spectrum, was isolated; it confirms the presence of the CCl_3^- fragment. When cyclohexene was added, 7,7-dichloronorcarane was identified as a low yield product by GC comparison with an authentic sample. This further identifies the intermediate CCl_3^- by its decomposition product CCl_2. The attack on carbon tetrachloride is reminiscent of the similar attack by another very powerful nucleophile, triphenylphosphine, an essential step in the reaction of alcohols with carbon tetrachloride and triphenylphosphine.[12] Similar attacks of some carbanions on carbon tetrachloride have been reported.[13a] The mechanism of these attacks may occur with initial electron transfer; with carbanions some dimers have been detected.[13b]

NMR studies on ^{77}Se are fairly straightforward; it is more sensitive than ^{13}C. Relaxation is fast, and we do not confirm the long relaxation times for the only compound that is in common with the studies of Ellis.[14] The discrepancy is not explained. Thus spectral accumulation is easy and rapid. A reported temperature sensitivity of the chemical shifts[15] was confirmed, thus a 10 ppm shift of a diselenide line was observed over a range from 233 to 283°K. This does not seem to be a chemical effect, since the relative chemical shifts of our standard and other pure compounds are not changed. The temperature dependence is however severe enough so that heating by the decoupling signal can cause peak broadening. This problem was overcome by using Waltz decoupling.

EXPERIMENTAL

Materials

Bis-*p*-methoxyphenyl diselenide was prepared by the reaction of the Grignard reagent of *p*-bromoanisole with selenium using a procedure similar to that of Reich and Renga.[16] Sodium *p*-methoxyphenylselenide was prepared by the reduction of the diselenide by sodium in liquid ammonia.[17] Using standard Schlenk tube techniques, the ammonia solution of the salt was filtered and the ammonia allowed to evaporate under an argon atmosphere. The viscous liquid residue solidified to a fine powder after brief stirring with degassed hexane and was washed with a second portion of hexane, then ethyl ether and again with hexane. Residual solvent was pumped away and the white free-flowing salt, slightly contaminated by sodium amide, was transferred under argon to ampules that were then flame sealed. All further handling was also done under argon or on the vacuum line, for these salts are very sensitive to oxygen, especially when in solution. The ampules were opened using an apparatus similar to a Schlenk solids transfer tube. In this way there was less oxygen contamination than a glove bag or an ordinary dry box would have introduced.

Sodium phenylselenide was prepared in an analogous fashion from commercial diphenyldiselenide and handled in the same way. Attempts to prepare sodium *p*-chlorophenylselenide or *p*-trifluoromethylphenylselenide by this method gave salt mixtures with at least some of the halogen missing, presumably having been reductively removed. Mixtures of diselenide and the sodium aryl selenide were made up by weight, but since the salts were always kept under argon, and the apparatus to be weighed was rather heavy, the precision of weighing the salt was only about ±1 mg, which was a significant error for the most dilute solutions.

The sodium salts were freely soluble in sulfolane or acetonitrile, but completely insoluble in ethyl ether and benzene. Neither crown ether (up to 8 equivalents of 18-crown-6) nor cryptand (1·5 equivalents of Kryptofix 222) increased the solubilities in the latter two solvents, although in ethyl ether the salt and cryptand mixture did liquify. Acetonitrile was the solvent used for almost all the work, since sulfolane is difficult to distill and is much more viscous; acetonitrile was conventionally purified and degassed. The solvent was distilled into the sample on the vacuum line. For the NMR work it was mixed with about 5% CD_3CN for a lock signal.

Reaction with CCl_4

The reaction of the sodium *p*-methoxyphenylselenide with CCl_4 appeared to be clean in very dilute solutions, ($<10^{-4}$ M) with yields of diselenide approaching 98% by HPLC. However, in more concentrated solutions, there were side reactions, with several additional bands appearing in the HPLC and amounting to as much as 20% of the material. With sodium phenylselenide even dilute solutions showed appreciable side reaction and concentrated solutions yielded a major product (about 40%) besides the diselenide. Flash chromatography of this raw product afforded a white crystalline material, mp 71–72 °C. From its mass spectrum and ^{13}C and ^{77}Se NMR we identified this as phenyl trichloromethyl selenide (lit mp 70°[18]). ^{13}C-NMR ($CDCl_3$) δ 79·46, 129·36, 130·39, 131·14, 137·69; ^{77}Se-NMR ($CDCl_3$) δ 920; mass spectrum isotopic abundances for $C_7H_5Cl_3Se$; found *m/e* 270, 13%; 272, 46%; 274(M) 100%; 276, 86%; 278, 31%; 280, 6% calcd. on the basis of isotopic abundances M-4, 13·2%; M-2, 43·2%; M, 100%; M + 2, 86·3%; M + 4, 33·5%; M + 6, 6·0%.

To test the possible formation of dichlorocarbene, a sample of sodium *p*-methoxyphenylselenide in acetonitrile was mixed successively with 6 equivalents of cyclohexene and then an excess of CCl_4. After concentration of the solution, all volatiles were distilled trap-to-trap, and injection of a sample of the distillate onto a capillary GC column showed the presence of a small amount of 7,7-dichloronorcarane (by comparison to, and co-injection with, an authentic sample).

NMR details

The ^{77}Se spectra were taken on an IBM AF300 instrument operating at 7·01 Tesla, with a selenium resonance at 57·23 MHz. Chemical shifts are referenced to dimethyl selenide assuming a chemical shift for diphenylselenide of 402 ppm.[19] The spectra are all proton decoupled using Waltz decoupling to minimize sample heating. Typically, 512 64K scans were aquired in 1·31 second intervals over a spectral window of 436·75 ppm (25000 Hz) using a 90° pulse angle (8·5 μ-seconds), without recycle delay. A line broadening of 3 Hz was used to weight and transform the FID. T_1 and T_2 values were not measured, but fast measurements using Inversion-Recovery and CPMG show that both the diselenides and the anions have values <1sec.

Spectra were taken in sealed 10 mm NMR tubes which were degassed by a freeze–thaw cycle three times before sealing.

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