Spectroscopic Studies of Charge Transfer Complexes

XII. Diphenyl Selenium Oxide and Iodine

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The charge transfer complex between diphenyl selenium oxide and iodine was studied in the ultraviolet, visible, and infrared regions. For dilute solutions in dichloromethane the complex was of the 1:1 type. Spectral data and thermodynamic functions have been determined. The infrared data suggest that the iodine is bonded to the oxygen atom. The higher basicity of diphenyl selenium oxide compared to the corresponding sulphoxide has been discussed.

Recent studies have shown that the sulphoxides form 1:1 complexes with iodine [1-4] and iodine cyanide.[5] The infrared observations revealed that the complex bond was formed from the oxygen, while the lone pair electrons on the sulphur were not available for donation to these acceptors. In the present study we have extended the investigations to the selenium oxides. However, the aliphatic compounds R_1R_2SeO have only been incompletely described in the literature [6-7] and we did not succeed in synthesizing diethyl selenium oxide. The derivatives with electronegative substituents like the halogens or phenyl groups are more stable [7] and can be easily prepared. Thus, we restricted our study to diphenyl selenium oxide (DPSeO). Some introductory studies of the selenium oxychloride-iodine system showed that the interaction was too weak to be investigated by ordinary spectroscopic methods. This is in agreement with the calorimetric studies by Lindqvist and Zackrisson [8] who reported that selenium oxychloride was a very much weaker donor to antimony penta-chloride than DPSeO. Sheldon and Tyree [9] reported freezing point diagrams of selenium oxychloride with different metal halide acceptors and studied infrared spectral changes of the Se—O stretching frequency upon complex formation.

In the present paper we report the spectroscopic data for the DPSeO-iodine system as obtained in the ultraviolet, visible and infrared regions together with the calculated thermodynamic functions.

EXPERIMENTAL

DPSeO was prepared [10] by reaction between magnesium bromobenzene and selenium oxychloride (from British Drug House). The Grignard complex was treated with dilute sulphuric acid and separated by shaking with diethyl ether. The product was brominated and later hydrolyzed with 15 % potassium hydroxyde, washed and dried. After fractional crystallization from alcohol the compound had the melting point at 113.5°C. Reagent grade iodine and dichloromethane, *Uvasole*, for ultraviolet spectroscopy, from Merck, were used as the acceptor and the solvent, respectively.

The ultraviolet and visible spectra were obtained with a Beckman DK-1 recording spectrophotometer equipped with a thermostated cell holder. Matched pairs of 1 cm and 5 cm silica cells with tight ground glass stoppers were used in the ultraviolet and the visible regions, respectively. The infrared spectra were recorded in the region 4000−650 cm⁻¹ with a Perkin-Elmer model 21 spectrometer having sodium chloride optics and sealed cells of thickness 0.5 mm.

RESULTS

Ultraviolet region. Nonpolar solvents such as heptane, cyclohexane or carbon tetrachloride dissolve very small amounts of DPSeO. However, dichloromethane dissolves DPSeO readily and was used as solvent for the quantitative studies although it is less "inert" than heptane or carbon tetrachloride. DPSeO has a strong ultraviolet absorption band at 228 mμ and a shoulder at 270 mμ when dissolved in ethanol.[11] In dichloromethane, DPSeO has the band at approximately 268 mμ and iodine has a broad, weak absorption band at 280 mμ. The mixed solutions of DPSeO and iodine absorb strongly in the region around 290 mμ. This absorption band was assigned as the DPSeO-iodine charge transfer (CT) band superposed on the DPSeO and the iodine absorptions. A spectrum was recorded with the mixed solution in the sample beam and with blanks containing the same concentrations of DPSeO and iodine in two separate cells in the reference beam. The CT band had a peak absorption at 288 mμ at the following donor and acceptor concentrations: [DPSeO] = 2.34 × 10⁻⁴ and [I$_2$] = 9.76 × 10⁻⁴ M. At this wave length, DPSeO dissolved in dichloromethane has a molar extinction coefficient of 520 M⁻¹ cm⁻¹. Thus, quantitative calculations of the formation constants which are generally carried out with a large excess of donor, cannot be based upon absorption data at the CT maximum.

The stoichiometry of the DPSeO-iodine complex was determined by the method of continuous variation.[12] The free DPSeO and iodine absorptions were subtracted from the total optical density of the mixed solutions, and this was plotted against the mole fraction of iodine. When the sum of the DPSeO and iodine concentrations was 0.004001 M the curves in Fig. 1 were obtained. Distinct maxima appeared for [DPSeO] = [I$_2$] indicating a 1:1 complex. The symmetrical shape of the curves seems to rule out any significant amount of higher complexes at least for this concentration range.

Different series of DPSeO-iodine solutions were recorded at 9, 19, and 30°C. The iodine concentration was kept at approximately 2.9 × 10⁻⁴ M and the donor concentration varied from 0.005 to 0.05 M, using 1 cm cells. When the spectra were rerun after 5 h negligible changes were observed. Thus, no secondary reactions occurred at these concentrations nor did any significant
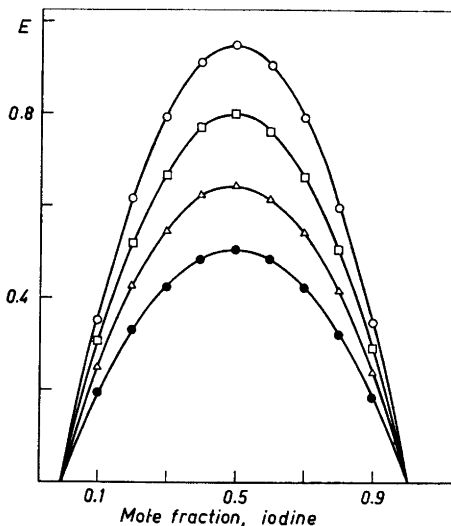
Fig. 1. Method of continuous variation of the diphenyl selenium oxide-iodine system in dichloromethane at 20°C. The absorbance of the solution minus the calculated absorbance of the components at the following wave lengths: (O) 295, (□) 300, (△) 305, and (●) 310 mμ is plotted *versus* the mole fraction of iodine. The total concentration of DPSeO plus iodine was 0.004001 M.

amount of the volatile solvent evaporate. In this concentration range the Scott equation [13] was valid and was used to determine the molecular formation constants. Only the absorption data at the long wave length tail below 305 mμ could be used for the quantitative calculations. After correcting for the DPSeO absorption, Scott plots were constructed at 305, 310, and 315 mμ and straight lines fitted by the least squares method. The formation constants and molecular extinction coefficients calculated at the different temperatures are listed in Table 1. From these data the thermodynamic functions were calculated by standard procedure. The peak extinction coefficient at 288 mμ was estimated to approximately 10 000 M^{-1} cm^{-1}.

Visible region. Iodine has an absorption peak at 505 mμ when dissolved in dichloromethane, and DPSeO has no absorption in the visible region. The mixed solutions of iodine and DPSeO showed an absorption peak at 432 mμ assigned as the blue shifted (*BS*) iodine band. Series of mixed solutions with constant iodine concentration passed through an isosbestic point at 479 mμ.

Various series of DPSeO-iodine solutions were recorded in the visible region using 5 cm absorption cells in order to keep the iodine concentration low. We calculated the formation constants and extinction coefficients by the Scott representation, using the absorption data at the peak and at two other wave lengths and correcting for the overlapping free iodine absorption. These data are listed in Table 2 with the corresponding thermodynamic functions.

Infrared region. DPSeO is fairly soluble in carbon disulphide and the infrared spectrum was recorded in the region 4000—650 cm^{-1} in a 0.5 mm cell. The Se—O stretching vibration has been assigned [14] to the sharp band at 838 cm^{-1} when DPSeO was dissolved in carbon disulphide; elsewhere the spectrum was closely related to the one obtained for diphenyl sulphoxide. When iodine was added this band was reduced in intensity and a new band appeared at 782 cm^{-1}, assigned as the Se—O stretching band of the complex.

Table 1. Formation constants, extinction coefficients and thermodynamic functions for the diphenyl selenium oxide-iodine complex in dichloromethane obtained from the *CT* band by the Scott representation.*

Temp. °C	305 mμ		310 mμ		315 mμ	
	K_c M^{-1}	ε $M^{-1} cm^{-1}$	K_c M^{-1}	ε $M^{-1} cm^{-1}$	K_c M^{-1}	ε $M^{-1} cm^{-1}$
9	39.2	6.900	39.6	5.200	40.4	3.700
19	29.7	6.700	29.5	5.100	30.8	3.600
30	21.4	6.600	21.4	5.000	21.9	3.550
$-\Delta H^\circ$	4.9		5.0		4.9	
$-\Delta G_{25}^\circ$	1.90		1.90		1.92	
$-\Delta S^\circ$	10.0		10.6		9.9	

Mean value $-\Delta H^\circ = 4.9$ kcal/mole; $-\Delta G_{25}^\circ = 1.91$ kcal/mole; $-\Delta S^\circ = 10.2$ e.u.

* The values were calculated from absorption data of 11 different DPSeO-I_2 solutions. [I_2] = 2.872 × 10⁻⁴ M, [DPSeO] varied from 0.004749 M to 0.04749 M, using 1 cm cells.

This band overlapped partly the strong aromatic doublets at 737 and 729 cm⁻¹ but appeared broader and more intense than the free Se—O stretching band in DPSeO. Moreover, some smaller changes occurred in the infrared bands at 691 and 663 cm⁻¹ upon addition of iodine. The former was displaced 2 cm⁻¹ towards longer wave lengths and the latter 1 cm⁻¹ with a two-fold increase in intensity. These bands seem to correspond with those observed at 687 and

Table 2. Formation constants, extinction coefficients and thermodynamic functions for the diphenyl selenium oxide-iodine complex in dichloromethane, obtained from the *BS* band by the Scott representation.*

Temp. °C	410 mμ		420 mμ		432 mμ	
	K_c M^{-1}	ε $M^{-1} cm^{-1}$	K_c M^{-1}	ε $M^{-1} cm^{-1}$	K_c M^{-1}	ε $M^{-1} cm^{-1}$
9	41.4	1220	42.9	1400	43.2	1480
19	32.1	1200	32.6	1380	33.3	1450
30	23.5	1180	24.1	1340	24.2	1420
$-\Delta H^\circ$	4.6		4.7		4.7	
$-\Delta G_{25}^\circ$	1.95		1.96		1.97	
$-\Delta S^\circ$	8.8		9.1		9.1	

Mean value $-\Delta H^\circ = 4.7$ kcal/mole; $-\Delta G_{25}^\circ = 1.96$ kcal/mole; $-\Delta S^\circ = 9.0$ e.u.

* The values were calculated from absorption data of 10 different DPSeO-I_2 solutions. [I_2] = 2.226 × 10⁻⁴ M, [DPSeO] varied from 0.004758 M to 0.03356 M, using 5 cm cells.

673 cm^{-1} in the diphenyl sulphoxide spectrum for which very similar perturbations occurred upon complex formation.[5] Following Lappert and Smith[15] the DPSeO bands at 691 and 663 cm^{-1} can probably be assigned to an asymmetrical ring deformation and a C—Se stretching mode, respectively.

For comparison, the infrared spectrum of selenium oxychloride dissolved in carbon disulphide was investigated when the solution was saturated with iodine. No change was observed in the Se—O stretching frequency[9] at 975 cm^{-1}, probably because of negligible complex formation. However, if the stronger acceptor iodine monochloride was added, the 975 cm^{-1} band decreased in intensity and a new band assigned to the Se—O stretching in the complex appeared at 942 cm^{-1}.

DISCUSSION

The thermodynamic functions calculated for the DPSeO-iodine system demonstrate that DPSeO is a fairly strong donor towards iodine. The relative basicities observed for the sulphoxides[1-4] suggest that eventual aliphatic selenium oxides should interact even stronger with iodine. No direct comparison can be made with the corresponding sulphoxides which were all investigated in carbon tetrachloride solutions. However, de Maine and co-workers[16] in their extensive studies of donor-acceptor complexes in different solvents have generally found higher values for K_c and $-\Delta H°$ in carbon tetrachloride than in more polar solvents like chloroform. We obtained the following data[3] for the diphenyl sulphoxide-iodine complex in carbon tetrachloride: $-\Delta H° = 2.8$ kcal/mole, $-\Delta G_{25}° = 0.78$ kcal/mole, and $-\Delta S° = 6.9$ e.u. Thus, the values listed in Table 1 and 2 indicate that DPSeO is a considerably stronger base. The same conclusion[17] can be drawn from the blue shifts of the visible iodine peak upon complex formation to diphenyl sulphoxide and DPSeO, which were 58[3] and 73 mμ, respectively.

Certain discrepancies were observed between the thermodynamic functions listed in Tables 1 and 2. Generally, the data calculated from the CT band should be the most reliable, because this band usually has a much higher intensity than the BS band. However, previous calculations on the dimethyl sulphoxide-iodine system[2] revealed that the absorption data at the side of the CT-band led to less reliable data for the formation constants. For the diphenyl sulphoxide and methyl phenyl sulphoxide complexes with iodine[3] only the long wave length tail of the CT-band could be used for quantitative studies, and no reliable formation constants were obtained from this region. Thus, for the DPSeO-iodine system as well, the data derived from the BS-band are probably the more reliable.

Through the benzene rings DPSeO should be able to act as a π-donor in addition to the n-donor sites at the selenium and the oxygen. However, the π-donor ability to iodine is probably very much weaker than for benzene and does not need to be taken into consideration. No X-ray crystallographic determinations of DPSeO or selenium oxychloride have been reported. However, Raman data for selenium oxychloride can be interpreted in terms of pyramidal structure.[18] The crystal structure of DPSeO is isomorphous with that of diphenyl sulphoxide[9] indicating a pyramidal configuration.

Very little information is available about the Se—O bond in the selenium oxides. It seems reasonable, however, that the Se—O bond like the S—O bond in the sulphoxides [20] has partial double bond character. It should result from $p\pi \rightarrow d\pi$ bonding from O to Se superposed on the Se—O σ-bond. However, the larger radius and lower electronegativity of the selenium relative to the sulphur atom may lead to less effective d-orbital overlap [21] and a lower double bond character in the selenium compound. This is also suggested by the lower Se—O stretching frequency in DPSeO compared to the S—O stretching frequency in diphenyl sulphoxide (838 and 1053 cm⁻¹, respectively). In selenium oxychloride, on the other hand, the strongly electronegative chlorine atoms should lead to a more effective π-bonding in this molecule compared with DPSeO as demonstrated by the much higher Se—O stretching frequency in the former. For comparison, the sequence of the S—O stretching force constants in R_2SO, calculated by Cotton and Horrocks [22] were: 11.0, 9.69, 7.80, and 6.54 [23] m dyn/Å when R stands for F, Cl, Br, and CH_3, respectively.

Donation of electrons from the oxygen in DPSeO should lower the $p\pi \rightarrow d\pi$ bonding and thus the Se—O stretching frequency. On the other hand, complex formation from the selenium should drain electrons from this atom followed by an increased Se—O stretching frequency. Meanwhile, the kinematic effect of coupling two oscillators tends to increase the frequencies. Therefore the observed decrease in the Se—O stretching frequency in DPSeO upon complex formation to iodine strongly suggests that the oxygen atom is the donor site. Moreover, the absolute $(\varDelta\nu)$ as well as the relative $(\varDelta\nu/\nu)$ frequency shifts upon complex formation to iodine were larger for DPSeO than for diphenyl sulphoxide. Thus the decrease in π-bonding character upon complex formation to iodine should also be larger in the selenium compound. The less effective π-bonding in the selenium oxides compared to the corresponding sulphoxides results in a higher electron density on the oxygen in the former group. A stronger interaction with iodine in the selenium oxide was therefore to be expected.

In the selenium oxychloride the electron density on the oxygen is much lower than for DPSeO and the complexing ability to the halogens is small. However, selenium oxychloride can form complexes to stronger acceptors like iodine monochloride, tin tetrachloride [9] or titatium tetrachloride [9] and a decrease in the Se—O stretching frequency is observed.

The selenium oxychloride-tin tetrachloride complex was later studied by Hermodsson,[24] using X-ray crystallographic methods and complex formation over the oxygen was verified.

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