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Behaviour of Some Selenium Bases in Disulphuric Acid. Conductometric and Cryoscopic Studies of Selenides, Selenoxides and Selenones in Disulphuric Acid

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Dimethylselenoxide is fully ionized in disulphuric acid whereas diphenyl selenoxide and its nitro derivatives behave as weak bases. In the case of selenones, alkyl selenones are completely ionized in disulphuric acid, diphenyl selenone and its nitro derivatives behave as weak electrolytes. From the extent of protonation it is observed that selenones are stronger bases than the corresponding sulphones. Amongst the selenides, diphenyl selenide is sulphonated whereas its nitro derivatives behave as weak bases in it.

In a continuation of our investigations,[1–5] we report here a study on the behaviour of selenides and compounds containing selenium–oxygen bonds in disulphuric acid. These data may be helpful in determining their relative basic strengths and also in determining their basicity with respect to sulphones. Szmant and Lapinski[6] and Szmant and Brost,[7] from their cryoscopic and spectroscopic studies on diphenyl sulphoxide in sulphuric acid concluded that it formed diphenyl sulphedium ion. This conclusion has been refuted by various workers.[8–9] Most alkyl sulphones behave as non electrolytes in sulphuric acid[9] and are protonated in disulphuric acid,[10] consequently their relative strengths have been differentiated in fluorosulphuric acid.[11] In the present study, the behaviors of selenides, selenoxides and selenones have been investigated and comparative studies with the analogous sulphur compounds have been made.

Results and Discussion

Disulphuric acid is a molecularly dissociated and slightly self ionized solvent. Its mode of dissociation and ionization may be represented[12] as in Eq. (1).

$$2H_2S_2O_7 \longrightarrow H_2SO_4 + H_2S_3O_{10} \rightleftarrows H_3SO_4^+ + HS_3O_{10}^- \qquad (1)$$

Because of its high acidic nature, most of the solutes behave as bases in it. The behaviour of a base in disulphuric acid may be represented by the general Eq. (2).

$$\text{Solute} + sH_2S_2O_7 \longrightarrow aX^+ + aHS_3O_{10}^- + bY + cH_2SO_4 \qquad (2)$$

where Y represents uncharged species. Sulphuric acid formed in the reaction does not contribute significantly to the value of γ, the number of $HS_3O_{10}^-$ ions, or to ν, the number of particles or ions produced per mole of solute as it is one of the products of self dissociation of the acid. Methods of determining the values of γ, ν and c have been discussed in detail in the experimental section.[10,11,13–15] In the case of the compounds which are not fully protonated in disulphuric acid, dissociation constants have been determined by a method, already used by various workers.[16,17]

Interpolated values of the specific conductance and the depression in freezing points of various solutes at different concentrations are given in Tables 1 and 2 respectively. The dissociation constants for solutes which are not fully ionised have been determined and are reported in Table 4. In order to compare the relative basic strength of selenium compounds with those of sulphur compounds, dissociation constants previously reported for sulphur compounds are also included in Table 4.

Like dimethyl sulphoxide, dimethyl selenoxide is stable in disulphuric acid and forms a highly conducting stable solution. From the values of γ, ν, and c, it is evident that it is completely protonated as:

$$(CH_3)_2SeO + 2H_2S_2O_7 \longrightarrow (CH_3)_2SeOH^+ + HS_3O_{10}^- + H_2SO_4 \qquad (3)$$

The solutions are colourless which suggests that there is no disproportionation to form elemental selenium which would have produced a green or yellow solution.[18] But in the case of diphenyl selenoxide, conductances of the solutions are quite low and increase

Table 1. Specific conductances of solutions of various solutes in disulphuric acid at 25 °C

Specific Conductance $\times 10^3$ (ohm^{-1} cm^{-1})

Solute	Molality $\times 10^2$								
	2	4	6	8	12	14	16	18	20
Dimethyl selenoxide	4.186	4.703	5.342	5.983	6.932	7.689	8.324	9.164	9.866
Diphenyl selenoxide	3.824	3.958	4.088	4.390	4.713	5.127	5.396	5.682	5.27
4′-Nitrodiphenyl selenoxide	3.952	4.386	4.624	4.936	5.292	5.634	6.012	6.824	7.397
4,4′-Dinitrodiphenyl selenoxide	3.908	4.214	4.438	4.729	5.032	5.724	5.938	6.318	6.874
Dimethyl selenone	4.187	4.704	5.343	5.984	6.938	7.701	8.324	9.165	9.867
Diethyl selenone	4.186	4.703	5.344	5.983	6.937	7.698	8.326	9.164	9.866
4-Nitrodiphenyl selenone	3.964	4.392	4.701	5.014	5.438	5.826	6.134	7.012	7.523
4,4′-Dinitrodiphenyl selenone	3.987	4.362	4.582	4.864	4.986	5.598	5.762	6.468	6.682

TABLE 2. FREEZING POINTS OF SOLUTIONS OF VARIOUS SOLUTES IN DISULPHURIC ACID (°C)

Solute	Molality $\times 10^2$									
	2	4	6	8	10	12	14	16	18	20
Dimethyl selenoxide	34.82	34.76	34.64	34.58	34.46	34.32	34.26	34.18	34.06	33.92
Diphenyl selenoxide	35.06	35.02	34.98	34.86	34.80	34.76	34.68	34.58	34.49	34.36
4′-Nitrodiphenyl selenoxide	35.01	34.92	34.84	34.76	34.70	34.62	34.54	34.46	34.32	34.18
4,4′-Dinitrodiphenyl selenoxide	35.04	34.98	34.86	34.79	34.70	34.62	34.58	34.48	34.38	34.24
Dimethyl selenone	34.82	34.75	34.64	34.58	34.45	34.31	34.24	34.16	34.02	33.89
Diethyl selenone	34.81	34.76	34.62	34.56	34.44	34.30	34.26	34.12	34.04	33.88
Diphenyl selenone	35.06	35.03	34.96	33.84	34.76	34.66	34.58	34.46	34.32	33.92
4-Nitrodiphenyl selenone	35.02	34.96	34.84	34.80	34.72	34.64	34.52	34.42	34.36	34.24
4,4′-Dinitrodiphenyl selenone	34.98	34.88	34.78	34.70	34.64	34.56	34.48	34.39	34.29	34.18

with time. Simultaneously the solutions develop a dirty brown color but when the solutions are poured onto crushed ice, nothing separates out. This suggests that diphenyl selenoxide is sulphonated and the sulphonated product behaves as a weak base. A slight increase in the conductance of the solution is due to the formation of sulphuric acid which is known to behave as a weak base in disulphuric acid (*loc. cit.*). There has been no indication of the existence of dipositive selenidium ions as was proposed by Szmant and Lapanski for sulphoxide (*loc. cit.*) since that would have produced highly conducting solutions.

TABLE 3. SUMMARY OF THE VALUES OF γ, ν AND c FOR VARIOUS SELENIUM COMPOUNDS IN $H_2S_2O_7$

Compound	γ	ν	c		
			Conductivity	Cryoscopy	Titration
Dimethyl selenoxide	1	2	1	1.1	1
Diphenyl selenoxide	—	1	1	—	1
Dimethyl selenone	1	2	1	1.1	1.1
Diethyl selenone	1	2	1	1.1	1.1
Diphenyl selenone	1	2.1	1	1.1	1.1
p-Nitrophenyl selenide	1	2	—	—	—
Selenyl chloride	—	1	—	—	—
Selenyl fluoride	—	1	—	—	—

TABLE 4. DISSOCIATION CONSTANTS OF VARIOUS COMPOUNDS CONTAINING SULPHUR–OXYGEN AND SELENIUM–OXYGEN BOND IN DISULPHURIC ACID

Compound	$K_b \times 10^2$
4-Nitrodiphenyl sulphoxide	86.42
4-Nitrodiphenyl selenoxide	92.38
4,4′-Dinitrodiphenyl sulphoxide	49.56
4,4′-Dinitrodiphenyl selenoxide	63.74
4-Nitrodiphenyl sulphone	78.46
4-Nitrodiphenyl selenone	82.58
4,4′-Dinitrodiphenyl sulphone	60.92
4,4′-Dinitrodiphenyl selenone	72.54

The introduction of an electron withdrawing group in one of the rings deactivates both of the rings towards sulphonation as 4-nitrodiphenyl selenoxide gives a stable pink solution in disulphuric acid. The conductance and the freezing point of the solution do not change with time. From the cryoscopic and conductance studies, it is evident that it behaves as a weak base. The dissociation constant is reported in Table 4. The introduction of a nitro group in the other ring further reduces the basicity of the Se–O group as is evident from the behavior of 4,4′-dinitrodiphenyl selenoxide, which in disulphuric acid forms an orange colored solution that becomes darker with time. However, there is no significant change with time in the values of γ, ν and c indicating that the solutions are fairly stable. From the experimental data it is evident that 4,4′-dinitrodiphenyl selenoxide behaves as a weak base. When solutions of both the mono- and di-nitro compounds are poured onto crushed ice, both the compounds are recovered quantitatively suggesting that in these compounds there is no sulphonation of the ring. From the cryoscopic and conductance data only, we do not feel qualified to specify the site of the protonation in these compounds. However, it may be reasonable to believe that the π electrons in the Se=O group are more labile and therefore the Se=O group will be protonated in preference to the ring NO_2 group. From the extent of the protonation of selenoxides, it is evident that selenoxides are more basic than sulphoxide *i.e.* the extent of the $d\pi$-$p\pi$ overlap between sulphur and oxygen is more than that between selenium and oxygen and consequently sulphoxide are less basic.

Alkyl sulphones are known to behave as weak electrolytes in sulphuric acid[9] but behave as strong bases in both fluorosulphuric[11] and disulphuric acids.[10] Dimethyl and diethyl selenones are monoprotonated and completely ionized in disulphuric acid. Becasue of the higher acid strength of the medium, the basicity of all these alkyl selenones is leveled to that of $HS_3O_{10}^-$ and it does not seem to be possible to differentiate their relative basicity. It is also observed that as compared to diphenyl selenoxide, diphenyl selenone is more stable towards sulphonation by the solvent as the conductance and the freezing point of the solutions do not change with time. It may be that unlike selenone, the deactivating inductive effect of the selenoxide group is counter balanced by the conjugation of the shared pairs of electrons on the selenium atom with the aromatic ring. Conjugation of the Se=O with the aromatic ring may be negligible and therefore diphenyl selenoxide undergoes sulphonation whereas the selenones are comparatively stable.

From the conductance and cryoscopic studies, it is evident that diphenyl selenone bahaves as a strong base and the introduction of a deactivating group in one or both of the rings decreases the basicity of the Se=O group to a large extent as 4-nitro- and 4,4′-dinitrodiphenyl selenones behave as weak bases in disulphuric acid. Their dissociation constants have been determined and are included in Table 4. Our observations are at varience with those of Szmant and Lapinski (*loc. cit.*) who observed that the introduction of a nitro group in the *para* position of the ring increases the basicity of the SO group in sulphones and are in agreement with our earlier observations in fluorosulphuric acid. These observations are supported by the results of a theoretical molecular orbital treatment of sulphones by Koch and Moffitt[19] who have shown that there is only a slight conjugation between the double bond of S=O and the aromatic ring in diphenyl sulphone. This conclusion is supported by IR and UV spectroscopic measurements. By analogy similar arguments can be put forward for selenones.

In order to compare the basicity of compounds containing the selenium–oxygen bond and to determine the effects of substitution on their basicity, investigations have been extented to the behavior of SeO_2Cl_2, SeO_2F_2 and diethyl selenate in disulphuric acid. It is interesting to observe that the value of ν for these electrolytes is one, but there is a decrease in the conductance of the solution. This suggests that these compounds behave as non-electrolytes in disulphuric acid. This behaviour of non-electrolytes is similar to the one observed in the solvo-system sulphuric acid.[20] This decrease in the conductance of the solution may be attributed to a decrease in the mobilities of $H_3SO_4^+$ or $HS_3O_{10}^-$ ions caused by the non-electrolyte or to a reduction in the concentration of the autoprotolysis ion. A decrease in the mobilities of the characteristic solvent ions could be attributed to strong hydrogen bonding interactions between these solutes and the solvent molecules which would hinder the orientation of the latter and decrease their effectiveness in the proton-transfer conduction process. Diethyl selenate behaves as a weak base. The increase in the conductance is so insignificant that it is not possible to determine its dissociation constant.

It has been of interest to investigate the behaviour of selenides in disulphuric acid. Sulphides undergo sulphonation and oxidation in both sulphuric and disulphuric acids but in fluorosulphuric acid they are strong bases. The solutions of diphenyl selenides in disulphuric acid are not very stable as the solutions are green and the conductance of the solution changes with time. Even *p*-nitrophenyl selenide does not form stable solutions when dissolved in disulphuric acid. However, initial conductance and freezing point data indicate that it may be singly protonated. For each addition of the solute the changes in the conductance and freezing point have been observed with time and then extrapolated to zero time to get the initial conductance and freezing point. The introduction of a nitro group to each of the rings decreases the basicity of the selenide group to the extent that 4,4′-dinitrodiphenyl selenide behaves as a weak electrolyte. The solutions become intensely coloured. The intensity of the colour increases very much after 24 hr although there is no significant change in the conductance of the solution. The properties may be due to the presence of a quinonoid structure for the protonated species.

It may thus be concluded that compounds containing selenium–oxygen bonds are more basic than the corresponding compounds containing sulphur–oxygen bonds. Thus suggesting that the extent of $d\pi$-$p\pi$ overlap is greater in the sulphur–oxygen compounds than in the selenium–oxygen compounds.

Experimental

The design of the conductivity cell and the cryoscopic set up has been described earlier. Conductance measurements were made in an oil thermostat regulated at 25.00±0.02 °C using a precision measuring bridge WBR No. 108 with logarithmic indicator amplifier type TAV, IKC No. 034 (Wissenchaftlich Technische Werkstatten) Wielheim Oby/Germany. The composition of disulphuric acid was determined from its conductance in conductometric studies and from its freezing point in the cryoscopic studies. Addition of powdered solids was made with a weight burette having a wide bore tap while liquids were added with a weight dropper which was fitted with quickfit joints to avoid contact with moisture.

The conductometric factors γ ($HS_3O_{10}^-$) were obtained by comparison of the conductance at various concentrations of the solute with that of nitromethane in disulphuric acid. The temperature at which all conductance measurements were made (25 °C) was below the freezing point of all the solutions studied but since disulphuric acid super cools readily no problems were encountered with spontaneous crystallization of the solutions during the measurements.

In the case of the cryoscopic measurements, the observed freezing points were corrected for the super cooling by adding the correction ($\delta=0.014S\theta$) where S is the amount of super cooling and θ is the depression of the freezing point. The value of ν (the number of particles or ions produced per mole of the solute) has been calculated by equation:

$$\nu = \frac{\theta(1-0.178mS)}{5.9m}$$

where m is the molality, S is the number of the solvent molecules used and θ is the depression of the freezing point obtained by subtracting the observed freezing points from 35.82° which is the freezing point of a hypothetical solvent containing zero concentration of ionic self dissociation products. The factor c, the amount of sulphuric acid produced per mole of the solute has been found out by titrating these solutions against sulphur trioxide. Freezing point rises because of the reaction $H_2SO_4+SO_3\rightarrow H_2S_2O_7$, passes through a maximum and then decreases. The maximum in the freezing point represents the number of moles of sulphuric acid produced in a particular reaction. This technique has already been used by Wyatt and Dacre.

Dimethyl selenoxide was purified by fractional distillation under reduced pressure. Diphenyl selenoxide was prepared by the oxidation of diphenyl selenide with an equimolar amount of a 30% solution of hydrogen peroxide in glacial acetic acid. 4-Nitro- and 4, 4′-dinitro-diphenyl selenoxide were prepared by the oxidation of the corresponding selenides which in turn were prepared by refluxing ethanol solution of 1-chloro-4 nitrobenzene with freshly prepared concentrated solution of sodium selenide. The compounds were recrystallized from acetic acid. Diethyl selenone (Aldrich) was purified by several recrystallization from absolute alcohol. 4-Nitro- and 4,4′-dinitro-diphenyl selenones were prepared by the oxidation of the corresponding selenoxides with an excess of 30% H_2O_2 in acetic acid. Alkyl selenates were purified by distillation under reduced pressure.

References

1) R. C. Paul, V. P. Kapila, and K. C. Malhotra, *J. Chem. Soc.*, *A*, **1970**, 2267.

2) R. C. Paul, J. K. Puri, V. P. Kapila, and K. C. Malhotra, *J. Inorg. Nucl. Chem.*, **34**, 2141 (1972).

3) K. C. Malhotra and R. D. Sharma, *Ind. J. Chem.*, **10**, 430 (1972).

4) R. C. Paul, V. P. Kapila, J. K. Puri, and K. C. Malhotra, *ibid.*, **9**, 992 (1971).

5) K. C. Malhotra and S. M. Sehgal, *ibid.*, **12**, 1190 (1974).

6) H. H. Szmant and R. L. Lapinski, *J. Amer. Chem. Soc.*, **74**, 4395 (1952).

7) H. H. Szmant and G. A. Brost, *ibid.*, **74**, 5175 (1952).

8) R. J. Gillespie and R. C. Passerni, *J. Chem. Soc.*, **1956**, 3850.

9) S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964).

10) R. C. Paul, J. K. Puri, and K. C. Malhotra, *J. Inorg. Nucl. Chem.*, **33**, 991 (1971).

11) K. C. Malhotra, S. K. Sharma, and K. K. Paul, *Ind. J. Chem.*, **9**, 250 (1971).

12) R. J. Gillespie and K. C. Malhotra, *J. Chem. Soc.*, *A*, **1967**, 1994.

13) R. J. Gillespie and K. C. Malhotra, *ibid.*, **1968**, 1933.

14) R. C. Paul, D. Singh, and K. C. Malhotra, *ibid.*, **1969**, 1396.

15) R. J. Gillespie and K. C. Malhotra, *Inorg. Chem.*, **8**, 1751 (1969).

16) R. C. Paul, V. P. Kapila, J. K. Puri, and K. C. Malhotra, *Ind. J. Chem.*, **9**, 469 (1971).

17) R. C. Paul, V. P. Kapila, J. K. Puri, and K. C. Malhotra, *J. Chem. Soc.*, *A*, **1971**, 2132.

18) J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Can. J. Chem.*, **46**, 149 (1969).

19) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

20) R. J. Gillespie and C. Solomons, *J. Chem. Soc.*, **1957**, 1796.