Solvent Effects on Kinetics and Reaction Mechanisms. The Formation of Sulphonium and Selenonium Salts

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Second-order rate constants and activation parameters for the methylation of methyl phenyl sulphide and methyl phenyl selenide by dimethyl sulphate have been measured in 14 aprotic solvents covering a wide range of dielectric constants. The same reactivity order is observed with both substrates in the various solvents. The analysis of the medium effects on the reactivity was performed by the Koppel–Palm multiparameter approach. The results indicate that the polarization and electrophilicity of the solvents are responsible for the rates of both reactions. The higher reactivity of methyl phenyl selenide has been ascribed to the higher polarizability and softness of the selenium atom in comparison with the sulphur atom.

In the past few years we have been interested in the solvent kinetic effects of a variety of chemical processes.[1] Following a recent study on the formation of a phosphonium salt from benzyl chloride and triphenylphosphine,[2] we now report kinetic data on the formation of sulphonium and selenonium salts from methyl phenyl sulphide and methyl phenyl selenide with dimethyl sulphate in 14 aprotic solvents covering a wide range of dielectric constants.

This work is aimed at elucidating which solvent properties are responsible for the rate of formation of 'onium salts of the Group VIB elements. For this purpose the methodology of correlation analysis was applied. In particular, we have used the Koppel–Palm equation (1),[3] in which the solvent effects on the observed reactivity are described in detail by four standard empirical parameters.

$$\log k = yY + pP + eE + bB + \log k_0 \qquad (1)\,\dagger$$

The formation of the 'onium salts is a very suitable system for a quantitative study of solvent effects, because a single product is formed and the kinetics of the reaction are easy to follow in a sufficiently large number of solvents, thus allowing an accurate statistical analysis of the experimental results.

The substituent effects on the rate of methylation of aryl methyl sulphides have been recently studied,[5] but no information concerning solvent effects in the alkylation of sulphides and selenides is available, differently from that of tertiary amines (Menschutkin reaction) which has been widely investigated.[6,7]

Results and Discussion

Whereas tertiary amines and phosphines react readily with alkyl halides, methyl phenyl sulphide and methyl phenyl selenide remain unreactive under these experimental conditions. Therefore, the more effective dimethyl sulphate has been used with these substrates.

Table 1. Rate constants for the reaction of methyl phenyl sulphide (MPS) with dimethyl sulphate (DMS) in acetonitrile at 80 °C

No.	Initial [MPS]/M	Initial [DMS]/M	10^3k_{obs}/ min^{-1}	10^4k_2 [a]/ l mol^{-1} s^{-1}
1	0.0318	0.196	3.92	3.33
2	0.0291	0.253	4.73	3.11
3	0.0318	0.303	6.25	3.43
4	0.0297	0.401	7.54	3.14
5	0.0390	0.260	5.22	3.34
6	0.0471	0.260	4.97	3.18
7 [b]	0.0297	0.255	4.94	3.23

[a] Average k_2 = 3.27 (± 0.16) × 10^{-4} l mol^{-1} s^{-1}. [b] In the presence of 0.02 mol l^{-1} of dimethylphenylsulphonium methyl sulphate.

It is well known that sulphides and selenides have smaller nucleophilic power than amines and phosphines, as indicated by nucleophilic constants n_{MeI}, which vary in the order P > N > Se > S.[8]

The kinetics of alkylation have been carried out in the presence of excess of dimethyl sulphate with respect to the sulphide or selenide (*ca.* 10 : 1, mol : mol) and the reaction was followed by determining the unreacted substrate by g.l.c., after separation of the 'onium salt formed. The reaction obeys the pseudo-first-order rate law to at least 80% completion. The k_{obs} values result correlated with the linear concentration of the dimethyl sulphate (excess) indicating overall second-order kinetics.

Table 1 reports k_2 values for the methylation of methyl phenyl sulphide in acetonitrile at 80 °C on changing the reagent concentrations. The presence of added 'onium salt does not interfere with kinetics. Second-order rate constants and activation parameters for the methylation of methyl phenyl sulphide and methyl phenyl selenide are reported in Tables 2 and 3, respectively.

The same reactivity sequence is observed with both substrates in the various solvents. The slowest reaction rate occurs in carbon tetrachloride and the highest in sulpholane. In all cases methyl phenyl selenide is more reactive than sulphide. In fact, the reactivity ratio k_{sel}/k_{sul} at 60 °C varies from 2.6 in carbon tetrachloride to 5.8 in sulpholane. The ratio $k_{CCl_4} : k_{sulpholane}$ at 60 °C is 74.5 for methyl phenyl sulphide and 163 for methyl phenyl selenide.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are both variable, thus levelling the

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† log *k* is the observed reaction rate in the solvent. *Y* represents the polarity of the solvent as Kirkwood's function of the dielectric constant $(\varepsilon - 1)/(2\varepsilon + 1)$. *P* is the solvent polarizability $(n^2 - 1)/(2n^2 + 1)$. *E* gives a measure of the electrophilic solvation of negative charges (Lewis acidity) deriving from the Dimröth–Reichardt E_T parameter[4] corrected for non-specific influences of the solvent. *B* represents a measure of the nucleophilic solvation of positive charges (Lewis basicity) deriving from i.r. stretching frequencies of MeOD. The coefficients *y*, *p*, *e*, and *b* are the sensitivities of the reaction to the change of polarity (*Y*), polarizability (*P*), electrophilicity (*E*), and basicity (*B*) of the solvents. $\log k_0$ represents the notional reaction rate in the gas phase, where *Y*, *P*, *E*, and *B* are zero.

Table 2. Second-order rate constants and activation parameters for the reaction of methyl phenyl sulphide with dimethyl sulphate in various aprotic solvents

Solvent	ε	10^4k_2/l mol^{-1} s^{-1} [a]					$\Delta H^‡$ [b]/ kcal mol^{-1}	$-\Delta S^‡$ [c]/ cal mol^{-1} K^{-1}
		50 °C	60 °C	70 °C	80 °C	100 °C		
(1) CCl_4	2.24		0.0263	0.0728	0.128		19.7	24.7
(2) Toluene	2.38		0.0353		0.161	0.848	18.8	27.0
(3) Benzene	2.28		0.0569	0.100	0.267		17.2	30.9
(4) Chlorobenzene	5.62		0.0893		0.372	1.01	14.2	38.9
(5) Ethyl acetate	6.02	0.041	0.0924	0.193			16.2	32.9
(6) 1,4-Dioxane	2.21		0.0942	0.221		1.08	14.0	39.3
(7) Anisole	4.33		0.117		0.564	2.00	16.7	30.7
(8) Acetone	20.7	0.100	0.204	0.380			13.9	38.2
(9) Propiononitrile	27.2		0.407	0.836	1.44		14.1	36.3
(10) Nitroethane	28.1		0.651		2.22	8.94	15.4	31.5
(11) Acetonitrile	37.5		0.783	1.44	3.27		15.9	29.6
(12) Nitromethane	38.6		1.21		5.29	21.4	17.0	25.4
(13) Propylene carbonate	65.1		1.52	3.46	7.87		18.6	20.1
(14) Sulpholane	44.0		1.96		9.36	38.8	15.8	27.4

[a] Maximum error ±7%. [b] Maximum error ±1.0 kcal mol^{-1}. [c] Maximum error ±2.5 cal mol^{-1} K^{-1}.

Table 3. Second-order rate constants and activation parameters for the reaction of methyl phenyl selenide (MPSe) with dimethyl sulphate in various aprotic solvents

Solvent [a]	10^4k_2 at 60 °C/ l mol^{-1} s^{-1}	$\Delta H^‡$/ kcal mol^{-1}	$-\Delta S^‡$/ cal mol^{-1} K^{-1}
(1)	0.0695		
(2)	0.121	15.9 [b]	33.2 [b]
(3)	0.153		
(4)	0.282	15.7 [c]	32.1 [c]
(5)	0.292		
(6)	0.379		
(7)	0.426		
(8)	0.824		
(9)	1.29		
(10)	2.17		
(11)	3.12	14.8 [d]	30.0 [d]
(12)	5.81		
(13)	7.12	14.4 [e]	29.6 [e]
(14)	11.4		

[a] Numbering in Table 2. [b] Obtained from k_2 values determined at 60, 80 (0.533 × 10^{-4}), and 100 °C (1.78 × 10^{-4}). [c] Obtained from k_2 at 60, 80 (1.11 × 10^{-4}), and 100 °C (4.06 × 10^{-4}). [d] Obtained from k_2 at 60, 70 (5.72 × 10^{-4}), and 80 °C (11.8 × 10^{-4}). [e] Obtained from k_2 at 50 (3.73 × 10^{-4}), 60, and 70 °C (14.8 × 10^{-4}).

Table 4. Solvent parameters of the Koppel–Palm equation (1)

Solvent [a]	Y [b]	P [b]	E [c]	B [d]	log k_2 at 60 °C MPS	MPSe
(1)	0.226	0.215	0	0	−5.58	−5.16
(2)	0.24	0.226	1.3	58	−5.45	−4.92
(3)	0.23	0.227	2.1	48	−5.24	−4.81
(4)	0.337	0.234	0	38	−5.05	−4.55
(5)	0.385	0.185	1.6	181	−5.03	−4.53
(6)	0.223	0.203	4.2	237	−5.03	−4.42
(7)	0.345	0.232	1.4	155	−4.93	−4.37
(8)	0.465	0.18	2.1	224	−4.69	−4.08
(9)	0.473	0.183	3.2	164	−4.39	−3.89
(10)	0.474	0.193	2.8	66	−4.19	−3.66
(11)	0.48	0.174	5.2	160	−4.11	−3.51
(12)	0.481	0.189	5.1	65	−3.92	−3.24
(13)	0.489	0.202			−3.82	−3.15
(14)	0.483	0.222	2.3	157	−3.71	−2.95

[a] Numbering for solvents is that of Table 2. [b] Ref. 3. [c] Ref. 10. [d] Parameter of general Lewis basicity derived from the stretching frequencies of the free and hydrogen-bonded phenolic OH group, I. A. Koppel and A. I. Paju, *Org. React.*, 1974, **11**, 121.

differences of reactivity. However, the reactivity order observed in the various solvents is the same on changing the temperature within the range 50—100 °C, where no isokinetic temperature occurs. Therefore, the selection of 60 °C as the comparison temperature does not appear to be arbitrary.

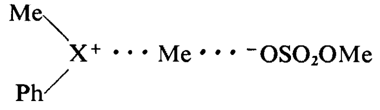
The values of k_2 at 60 °C are approximately related to dielectric constants of the solvents (Table 2), but significant deviations from linearity are observed. Particularly, in carbon tetrachloride and dioxane, which have comparable dielectric constants, very different reaction rates are measured. It is then probable that other solvent properties contribute to the reactivity.

To perform a more detailed analysis of the medium effects on kinetics we applied the Koppel–Palm treatment.[3]

The input data for the multiple linear regression are reported in Table 4, and the results of the statistical analysis are summarized in Table 5.

The correlation coefficients and the standard deviations for simple correlation on Y are statistically unreliable; an improved result is obtained with the two-parameter (Y and E) correlation; the best equation to describe the change of reactivity includes Y, P, and E parameters. No improvement is observed on including B values. The three-parameter equations are statistically reliable, the F-test values being significant for a confidence level >99.5%.

The reaction appears to be favoured by increase of polarity, polarizability, and electrophilicity of the solvents. The solvent basicity does not influence the reactivity probably because the positive charge developing in the transition state is buried among the methyl and phenyl groups as in (A).



(A) X = S, Se

The accelerating effects of the dielectric constant and of the refraction index are ascribed to electrostatic stabilization of the transition state by permanent and induced dipoles of the solvent molecules. The electrophilic solvation favours the reactivity by specific dipole–dipole interactions between the

Table 5. Correlation of the solvent effects for the formation of sulphonium and selenonium salts by Koppel–Palm equation (1)

Variables	Coefficients of regression y	p	e	b	$\log k_0$	R[a]	S[b]
Sulphonium							
Y	5.02				−6.56	0.895	0.290
Y, E	3.94		0.124		−4.49	0.931	0.240
Y, P, E	4.94	11.8	0.181		−9.42	0.975	0.155
Y, P, E, B	4.73	10.7	0.193	-7.9×10^{-6}	−9.15	0.969	0.182
Selenonium							
Y	5.33				−6.10	0.875	0.353
Y, E	4.35		0.131		−6.10	0.915	0.298
Y, P, E	5.24	13.3	0.230		−9.40	0.962	0.212
Y, P, E, B	5.25	13.9	0.225	5.0×10^{-4}	−9.58	0.963	0.221

[a] Correlation coefficient. [b] Standard deviation.

Table 6. Standardization of the Koppel–Palm regression coefficients

	Sulphonium	Selenonium	Phosphonium
Coefficients			
y	4.94	5.24	5.76
p	11.8	13.3	6.31
e	0.181	0.230	0.134
Standard deviation of variables			
${}^{s}\log k_2$	0.599	0.675	0.929
${}^{s}Y$	0.111	0.111	0.082
${}^{s}P$	0.022	0.022	0.025
${}^{s}E$	1.68	1.68	5.13
Standardized coefficients (and relative percentages)			
y'	0.915 (49.3)	0.862 (46.2)	0.508 (35.9)
p'	0.433 (23.3)	0.433 (23.2)	0.170 (12.0)
e'	0.507 (27.3)	0.571 (30.6)	0.739 (52.2)

leaving methyl sulphate anion and the electrophilic centres of the dipolar aprotic solvents.

The relative contributions of each solvent parameter to the changes of reactivity of methyl phenyl sulphide and selenide have been determined by calculations of standardized partial regression coefficients.[9] The results are reported in Table 6 together with the data of the benzylation of triphenylphosphine in 18 protic and aprotic solvents,[2] recalculated by the new E values.[10]

The parameters governing the rate of the 'onium salt formation are qualitatively similar in all cases. The polarity is the most important solvent parameter in the methylation of sulphide and selenide, while the electrophilicity makes the predominant contribution to the formation of the phosphonium salt. In this case it is probable that elimination of the small chloride anion is more sensitive to electrophilic solvation in comparison with the other reactions, where the negative charge is dispersed towards the bulky methyl sulphate anion. However, the correlation for phosphonium salt formation involves both aprotic and protic solvents, whereas that of sulphonium and selenonium involves only the former. The solvent series are thus not strictly comparable and the greater importance of the electrophilicity term in the phosphonium salt formation could be connected with this.

The application of the Taft-Kamlet treatment [11] would be helpful to check these results, but it cannot be used in this case because the α values of hydrogen bond donation are zero for most of the aprotic solvents employed.

The higher reactivity of methyl phenyl selenide may be ascribed to the higher polarizability of the selenium atom in comparison with that of the sulphur atom. In fact, the formation of the 'onium salt of the Group VI elements involves the large and polarizable *p*-orbitals (3*p* and 4*p*-electrons for sulphur and selenium, respectively), different from the formation of the 'onium salt of the Group V elements, in which the *s*-orbitals are involved.[12]

The higher reactivity of methyl phenyl selenide appears to be justified on the basis of the HSAB principle,[13] since the selenium atom is softer than sulphur atom, and then co-operative effects are expected with the soft CH_3^+ electrophilic reagent.

Experimental

Materials.—Methyl phenyl sulphide, dimethyl sulphate, and the various solvents are commercial products (AnalaR grade) distilled before use. Peroxide-free 1,4-dioxane was purified by the literature method [14] and kept over sodium.

Methyl phenyl selenide has been prepared by methylation of the corresponding selenophenate,[15] which was obtained by Grignard reaction by phenylmagnesium bromide and selenium,[16] yield 80%, b.p. 200—201 °C.[17]

The 'onium salts have been synthesized from equimolar amounts of sulphide or selenide and dimethyl sulphate in chlorobenzene at 70 °C. During the reaction a liquid layer heavier than chlorobenzene is formed. After cooling the solidified layer was collected, dried under vacuum, and crystallized. Dimethylphenylsulphonium methyl sulphate had m.p. 78—80 °C from acetonitrile–dioxane.[18] Dimethylphenylselenonium methyl sulphate had m.p. 107—108 °C from acetonitrile.[18]

Kinetic Measurements.—To a series of stoppered test tubes containing thermostatted solutions of dimethyl sulphate (1 ml), thermostatted solutions of sulphide or selenide (1 ml) were added. The final concentrations of the reagents were *ca.* 2.5×10^{-2} mol l^{-1} for the substrate and *ca.* 0.25 mol l^{-1} for dimethyl sulphate. At suitable intervals, the tubes were chilled and 2 ml of a solution of 1,2,4-trichlorobenzene (g.l.c. standard) in benzene of known concentration was added. The sulphonium (or selenonium) salt formed was then extracted with water (3 × 10 ml). The benzene solution containing sulphide and standard was analysed by g.l.c. The concentration of the residual reagent ($a - x$) was calculated from the corrected peak areas. This procedure was checked by determining known concentrations of sulphide and selenide. The deviation between found and calculated values did not exceed 5%. The reaction strictly follows the pseudo-first-order rate law. Plots of log $(a - x)$ *versus* time were linear to at least 80% completion.

Catalytic effects of the salt formed on the reaction rate were not observed on changing the initial concentrations of the reagents. The uncertainty of k_2 did not exceed $\pm 6\%$ of the average value.

Other solvents were not included in this work because of experimental difficulties leading to unreliable k_2 values. In fact, protic solvents partly react with dimethyl sulphate and some other solvents interfere with g.l.c. analysis.

Acknowledgements

We thank the CNR, Rome, for financial support.

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Received 8*th October* 1982; *Paper* 2/1744