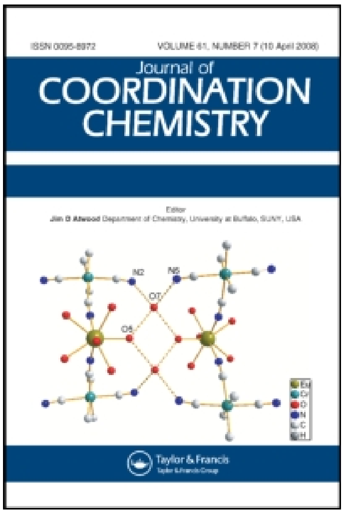

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A COMPARISON OF THE NUCLEOPHILICITY OF SULFOXIDES TOWARDS TETRACHLOROPLATINATE(II) AND TETRABROMOPLATINATE(II) ANIONS

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A COMPARISON OF THE NUCLEOPHILICITY OF SULFOXIDES TOWARDS TETRACHLOROPLATINATE(II) AND TETRABROMOPLATINATE(II) ANIONS

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The second order rate constants for the reaction

$$[PtBr_4]^{2-} + RR'SO \longrightarrow [PtBr_3(RR'SO)]^- + Br^- \qquad (1)$$

($R = CH_3$; $R' = CH_3, C_2H_5, n\text{-}C_3H_7, 2\text{-}ClCH_2CH_2, C_6H_5, 4\text{-}CH_3\text{-}C_6H_4, 4\text{-}CH_3O\text{-}C_6H_4, 4\text{-}Cl\text{-}C_6H_4$: $R = R' = C_2H_5, n\text{-}C_3H_7$: $RR' = -(CH_2)_4-$) have been measured in methanol/water (95/5 v/v) at 25.0°C. In general, the rate constants are approximately one order of magnitude greater than those for the corresponding reaction of $[PtCl_4]^{2-}$ and mainly reflect the difference in the *trans* effects of chloride and bromide. Although the rate constants are very sensitive to the bulk of the substituents R and R′ on the sulfoxide there are no enhanced steric effects arising from the replacement of Cl by Br. This is in direct contrast to the reactions of $[AuX_4]^-$ with amines where only the X = Br complex shows steric hindrance in its reaction with 2− and 2,6− substituted heterocyclic nitrogen bases.

Key words: sulfoxides, substitution, kinetics, halides

INTRODUCTION

In attempting to gain information about the detailed nature of the mechanism of substitution of d^8 metal complexes, a change of substrate from $[MCl_4]^{n-}$ to $[MBr_4]^{n-}$ is not expected to give rise to much difference other than that due to the change in the nature of the ligand *trans* to the leaving group. However, we recently showed that, in reactions of the type

$$[Au(am)X_3] + X^- \longrightarrow [AuX_4]^- + am$$

(where am is a heterocyclic base), the system where X = Br was sensitive to steric hindrance effects[1] while that with X = Cl was not.[2] Having shown recently[3] that the reactivity of sulfoxides RR′SO towards $[PtCl_4]^{2-}$ depended upon the bulk of R + R′ rather than their electron displacement properties, it seemed worthwhile to examine the consequences of the increased bulkiness resulting from the change of Cl to Br. For this reason we have examined the reaction between RR′SO and $[PtBr_4]^{2-}$ and the results are reported in this note.

EXPERIMENTAL

Materials

K_2PtCl_4 was a pure commercial sample (Engelhard). K_4PtBr_4 was obtained from the tetrachloro complex by treatment with excess HBr in water for 24 hours and recrystallization from 0.5 M HBr.

$(Et_4N)_2PtBr_4$

Stoichiometric amounts of K_2PtBr_4 and $(NH_4)Br$ were suspended in CH_2Cl_2 with stirring for 24 hours. The precipitated KBr was filtered off, the solution concentrated and the product precipitated by addition of ethyl ether. Yield > 95%. [Anal.; Calc: C, 24.79; H, 5.20; N, 3.61; Br, 41.22%. Found: C, 24.55; H, 5.14; N, 3.6; Br, 41.3%].

$K[PtBr_3(Me_2SO)]$

Equimolar amounts of K_2PtBr_4 and $Pt(Me_2SO)_2Br_2$ were reacted in water until the neutral complex had dissolved completely. After filtration, the solution was evaporated to dryness in vacuum in the presence of P_2O_5. Yield 100%. [Anal.; Calc: C, 4.68; H, 1.18; Br, 3.11%. Found: C, 4.66; H, 1.22; Br, 3.2%].

$(Et_4N)[PtBr_3(Me_2SO)]$

Equimolar amounts of $K[PtBr_3(Me_2SO)]$ and $(Et_4N)Br$, dissolved in CH_2Cl_2 were reacted with stirring for 24 hours. After filtering the precipitated KBr, the solution was concentrated in a rotavapor and the salt precipitated by adding ethyl ether. Yield > 95%. [Anal.; Calc: C, 18.67; H, 4.07; N, 2.18; Br 37.27%. Found: C, 18.7; H, 4.05; N, 2.21; Br 37.3%].

Dimethylsulfoxide, tetramethylenesulfoxide, (methyl)phenylsulfoxide and di-(*n*-propyl)sulfoxide were commercial products (Aldrich), which were purified by distillation or silica-gel chromatography when necessary. Diethylsulfoxide, (2-chloroethyl)methylsulfoxide, (ethyl)methylsulfoxide, (methyl)*n*-propylsulfoxide, (*p*-methylphenyl)methylsulfoxide, (*p*-chlorophenyl)methylsulfoxide and (*p*-methoxyphenyl)methylsulfoxide were obtained, with a method previously described[4] by oxidation of the corresponding thioethers in a $MeOH/H_2O$ mixture with hydrogen peroxide in the presence of a catalytic amount of sodium tungstate dihydrate. The products thus obtained were chromatographed on silica gel S (150–230 mesh ASTM) by elution with CH_2Cl_2 or $CHCl_3$. The characterization and purity of the products was checked by TLC, IR and ^1H nmr measurements by comparison with data from the literature.[5]

The required organic sulphides (ethyl)methylsulphide, (2-chloroethyl)methylsulphide, diethylsulphide were used as supplied by Fluka while (methyl)-*n*-propylsulphide, (*p*-methylphenyl)-methylsulphide, (*p*-chlorophenyl)-methylsulphide and (*p*-methoxyphenyl)-methylsulphide were synthetized by alkylation of the corresponding thiols (Aldrich or Fluka), following a standard method.[6] Methanol was reagent grade (Hoechst).

The infrared spectra were recorded on a Perkin-Elmer 683 IR spectrophotometer. ^1H nmr spectra were measured on a Varian FT80A spectrometer using $CDCl_3$ as solvent with internal standard Me_4Si. Thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60 F254 plates which were generally developed with petroleum ether or petroleum ether/$CHCl_3$ (9:1, v/v) for thioethers and $CHCl_3$/ether (6:4, v/v) for sulfoxides. Spots were developed with iodine vapour and visualised using a UV lamp.

TABLE I
First order rate constants, k_{obs}, for reaction (*I*) in $MeOH/H_2O$ (95/5 v/v) at 25°C[a]

RR'SO	$[Br^-]$ *V* mol dm^{-3}	[RR'SO] *V* mol dm^{-3}	$10^5 \times k_{obs}$, s^{-1}
Me_2SO[b]	1	0.25	1440 ± 40
		0.125	710 ± 30
		0.0625	370 ± 10
		0.03125	185 ± 5
		0.0156	87 ± 3
	3.3×10^{-3}	0.263	1570 ± 30
		0.1315	795 ± 15
		0.0658	440 ± 10
		0.0329	235 ± 6
		0.0164	125 ± 3
Me_2SO	1	0.488	299 ± 4
		0.244	155 ± 2
		0.122	75 ± 2
$(CH_2)_4SO$	0.1	0.0803	158 ± 2
		0.0481	88.1 ± 3
		0.0321	66.6 ± 1
		0.012	28.3 ± 2
	0.01	0.0798	152 ± 3
		0.0479	91.1 ± 2
Et-SO-Me	0.01	0.396	270 ± 4
		0.262	182 ± 2
		0.198	151 ± 3
		0.099	81 ± 2
		0.0396	30 ± 0.5
*n*Pr-SO-Me	0.01	1.005	450 ± 10
		0.67	297 ± 5
		0.502	250 ± 3
		0.251	128 ± 2
		0.1	60.5 ± 1
Et_2SO	0.1	0.1	34.1 ± 0.3
		0.085	28.5 ± 0.6
		0.0666	23.4 ± 0.5
		0.5	20.5 ± 0.2
		0.033	14 ± 0.2
$ClCH_2CH_2$-SO-Me	0.01	0.5015	535 ± 10
		0.251	278 ± 3
		0.125	150.5 ± 1
		0.5015	61 ± 0.5
nPr_2SO	0.1	0.5	44.5 ± 2
		0.4	35 ± 1
		0.2	25 ± 0.3
		0.0955	14.7 ± 0.5
		0.08	13 ± 0.3
		0.05	9.45 ± 0.4
	0.01	0.09	13.5 ± 0.5
C_6H_5-SO-Me	0.1	0.5	146 ± 1
		0.4	120 ± 1
		0.3	95 ± 0.5
		0.2	65 ± 0.5
		0.1	35 ± 0.3
		0.05	18 ± 0.3
p-CH_3*p*-CH_3-C_6H_4-SO-Me	0.1	0.505	125 ± 2
		0.432	113 ± 4
		0.404	107.5 ± 0.7
		0.303	84.5 ± 0.3
		0.202	57 ± 0.4
		0.101	31 ± 0.4
		0.0505	20 ± 0.2

p-CH_3O-C_6H_4-SO-Me	0.1	0.5	110 ± 1
		0.4	94 ± 0.3
		0.397	91 ± 0.5
		0.3	75 ± 0.3
		0.2	54 ± 0.3
		0.1	33 ± 0.3
		0.05	18.2 ± 0.2
p-Cl-C_6H_4-SO-Me	0.1	0.406	215 ± 2
		0.4	213 ± 2
		0.3	167 ± 2
		0.2	106 ± 0.5
		0.1	63.8 ± 0.4
		0.05	37 ± 0.4

[a]Substrate concentration always less than 10^{-4} mol dm^{-3}. [b]Measurements in H_2O.

Kinetics

The kinetics were followed with a Varian-Cary 219 spectrophotometer by periodically scanning the spectrum of the reaction mixture in the range 250–350 nm. The values of the first-order rate constants k_{obs} (Table I) were determined from the slopes of $\log(A_t - A_\infty)$ *vs* time, A_∞ and A_t being the absorbances at the chosen wavelength at time t and at the end of the reaction respectively, by a weighted non-linear regression analysis based on the Gauss-Newton algorithm[7] with three optimized parameters, A_0, A_∞ and k_{obs}.

RESULTS

In order to avoid complication[8] from extensive solvolysis of the substrate and dimerization to $[Pt_2Br_6]^{2-}$ the reactions were always initiated by adding finely powdered $[Et_4N]_2[PtBr_4]$ to a solution containing all the other reagents. Of the sulfoxides used, only Me_2SO was sufficiently soluble in water for this solvent to be used. In order to survey the group of sulfoxides available it was necessary to use $MeOH/H_2O$ (95/5 v/v).).

In aqueous solution containing excess LiBr and Me_2SO, the spectrum of a solution of $[PtBr_4]^{2-}$ changes smoothly to that of an authentic sample of $[Pt(Me_2SO)Br_3]^-$ without any indication of the presence of other intermediate species absorbing in the wavelength range 250–350 nm.

Variation of $[Br^-]$ from 3×10^{-3} mol dm^{-3} to 1.0 mol dm^{-3} had no significant effect upon the nature of the spectral changes. Within the range of Me_2SO concentrations used there was no indication of any further reaction to give bis- or higher Me_2SO species, nor was there any evidence that the reaction was reversible, as suggested by Kukushkin.[9] The rate constant for the reaction was therefore computed by treating the change of absorbance as a single first-order process in the way described above. The reaction between $[PtBr_4]^{2-}$ and Me_2SO in $MeOH/H_2O$ (95/5 v/v) follows exactly the same form and is likewise a single substitution that yields $[Pt(Me_2SO)Br_3]^-$ with no detectable amount of intermediate species or subsequent reaction.

No attempt was made to isolate or otherwise characterize the products of reaction with the other sulfoxides but the general similarity of the spectra and spectral changes suggested that the same type of reaction, $[PtBr_4]^{2-} + RR'SO \rightarrow [Pt(RR'SO)Br_3]^- + Br^-$, was being followed and there was no complication arising from solvolysis, dimerization or subsequent reaction.

DISCUSSION

As in the case of the reaction with $[PtCl_4]^{2-}$, the rate law for substitution contains a [RR'SO] dependent term. The rate constants are slightly effected by the amount of excess bromide present but this does not effect the linearity of the plot of k_{obs} *vs* [RR'SO] or even the slope and arises from a reduction in the magnitude of the nucleophilic independent term in the rate law $k_{obs} = k_1 + k_2[RR'SO]$. In the case of the reaction with Me_2SO in water k_1 is almost zero; $(2 \pm 5) \times 10^{-5}$ when $[Br^-] = 1.0$ mol dm^{-3} and $(4 \pm 0.9) \times 10^{-4}$ s^{-1} when $[Br^-]$ is 0.0033 mol dm^{-3}, the latter rate constant agreeing within experimental error with the literature values of $(1.9 \pm 0.2) \times 10^{-4}$ (25°C, $[Br^-] = 0$) and 2.2×10^{-4} s^{-1} (25°C, $[Br^-] = 3 \times 10^{-3}$ mol dm^{-3})[10] for the solvolytic rate constant for $[PtBr_4]^{2-}$ in water at 25°C. The disappearance of this term when $[Br^-] = 1$ mol dm^{-3} is due to the supression of the substitution pathway by way of the solvato complex as a result of the capture of this intermediate.

In the reactions in $MeOH/H_2O$ the relative errors in fixing the intercept are smallest with the least reactive sulfoxides and a value between 5×10^{-5} and 1.5×10^{-4} s^{-1} is indicated.

The second-order rate constants, k_2, are reported in Table II and compared with those for the corresponding reactions of the sulfoxides with $[PtCl_4]^{2-}$. In all cases the rate constant for the reaction with $[PtBr_4]^{2-}$ is greater by approximately one order of magnitude. This is almost entirely due to the difference in the *trans* effects of bromide and chloride. These data may be compared with those obtained by Elding[10,11] for the solvolysis of $[PtCl_4]^{2-}$ and $[PtBr_4]^{2-}$ in water at 25°C where the first-order solvolytic rate constants are 3.59×10^{-5} and 1.9×10^{-4} s^{-1}, respectively. The ratio of the rate constants for the solvolysis of the bromo and chloro complexes is somewhat smaller than that for the sulfoxide entry, varying from 8 to 21 but, in the latter case there is no systematic relation to bulk or to electron displacement of R and R'. These minor variations should not detract attention from the fact that the rate constants are very sensitive to steric hindrance from the substituents on sulphur and that this obscures any small variation due to electronic displacement effects of R. No new behaviour pattern is introduced as a result of changing the halogen from chloride to bromide.

The absence of any marked difference in response to steric effects lies in direct contrast to the $[AuX_4]^- + am \rightarrow [AuX_3(am)] + X^-$ system where the bromo complexes

TABLE II
Specific rate constants, k_1 and k_2, for the reactions (*l*) in $MeOH/H_2O$ (95/5 v/v) (in parenthesis are given the values of k_2 for the corresponding reactions at $[PtCl_4]^{2-}$)

RR'SO	$10^5 \times k_1$, s^{-1}	$10^5 \times k_2$, mol^{-1}dm^{3}s^{-1}	R[a]
Me_2SO (in H_2O)	40 ± 10	5740 ± 10 (320)	18
Me_2SO	3 ± 5	610 ± 5 (113)	5.4
$(CH_2)_4SO$	4 ± 4	1860 ± 60 (114)	16.3
Et-SO-Me	11 ± 6	660 ± 30 (66)	10
n-Pr-SO-Me	21 ± 9	430 ± 10 (35.9)	12
Et_2SO	5 ± 2	285 ± 20 (13.5)	21
2-$ClCH_2CH_2$-SO-Me	15 ± 5	1040 ± 20 (65)	16
n-Pr_2SO	7 ± 1	74 ± 4 (4.9)	15
C_6H_5-SO-Me	6 ± 2	284 ± 7 (23.7)	12
p-Me-C_6H_4-SO-Me	9 ± 2	239 ± 7 (27.9)	8.6
p-CH_3O-C_6H_4-SO-Me	12 ± 3	202 ± 6 (25.8)	7.8
p-Cl-C_6H_4-SO-Me	11 ± 3	505 ± 10 (44.2)	11

[a] $R = k_2(PtBr_4^{2-})/k_2(PtCl_4^{2-})$

are much more sensitive to *ortho*-methyl substitution in the heterocyclic base, am. While it is possible that the change in the bulk of X is insufficient to produce a significant enough effect in the coordination shell of the larger Pt(II) ion, it should not be forgotten that the intimate mechanism at Au(III) and Pt(II) differs significantly, the former being more synchronous.[12]

In a paper, published after the submission of our work, dealing with the reactions between *trans*-$[Pt(py)_2Cl_2]$ and $(4\text{-}X\text{-}C_6H_4)CH_3SO$ ($X = H, CH_3, CH_3O$), Hoover and Zipp[13] claim a greater sensitivity of the rate constant to the substituent effect, but to claim a linear dependence (slope −0.60) on the basis of three data points ($X = CH_3O$, $-\log k_2 = 3.25$, $s = -0.268$; $X = CH_3$, $-\log k_2 = 3.81$, $s = -0.170$; $X = H$, $-\log k_2 = 3.51$, $s = O$) seems a little bit optimistic. There may be some considerable interest in comparing the reactivity of sulfoxides towards different types of substrates but the work remains to be done.

There is no doubt that sulfoxides appear to be stronger nucleophiles relative to anionic reagents, such as Cl^-, Br^-, NCS^-, when they react with the anionic substrates $[PtX_4]^{2-}$ ($\log k_2$ for $X = Cl$ in water at 25°C $= -43.2, -2, -2.5$ for Br^-, NCS^- and Me_2SO, respectively[14]) than when they react with neutral *trans*-$[Pt(py)_2Cl_2]$ ($n^{\circ}_{Pt} = 2.67$ for Me_2SO,[15] $n^{\circ}_{Pt} = 4.18, 5.75$ for Br^- and NCS^- respectively[16]). Even the qualitative nucleophilicity sequence is different, *i.e.* $NCS^- > Me_2SO > Br^-$ and $NCS^- > Br^- > Me_2SO$ for anionic and neutral substrates, respectively.

There has been some suggestion that the apparently low nucleophilicity of sulfoxides is due to their ambidenticity and that initial attack takes place through oxygen, the subsequent Pt–O → Pt–S rearrangement being fast. This seems to be inconsistent with the sensitivity of rate towards the bulk of substituents on S. It is tempting to suggest that the sulphur end of the ligand is biphilic and to an anionic reagent such as $[PtX_4]^{2-}$ represents the best site for interaction. To a cationic substrate on the other hand this advantage is lost and the oxygen may well be the initial donor.

The absence of any noticeable dependence on the inductive effect of the substituents on S is consistent with the idea that the two opposing requirements of σ donation and π acceptance of a biphilic binding atom tend to cancel out the electron displacement properties of the substituents.

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REFERENCES

1. L. Cattalini, G. Chessa, G. Michelon, B., Pitteri, M.L. Tobe and A. Zanardo, *Inorg. Chem.*, **24,** 3409 (1985).
2. L. Cattalini and M.L. Tobe, *Inorg. Chem.*, **5,** 1145 (1966); see also L. Cattalini, M. Nicolini and A. Orio, *Inorg. Chem.*, **5,** 1674 (1966) and L. Cattalini, *M.T.P. International Review of Science, Inorganic Chemistry,* Series 1, Vol. 9, M.L. Tobe Editor, Butterworths University Park Press, Oxford, 1972.
3. G. Annibale, L. Cattalini, L. Canovese, G. Michelon, G. Marangoni and M.L. Tobe, *Inorg. Chem.*, **22,** 975 (1983).
4. L. Cattalini, G. Chessa, G. Marangoni, B. Pitteri and M.L. Tobe, *J. Chem. Soc. Dalton Trans.*, 2091 (1985).
5. D.O.C., V Edition, 1982, Chapman and Hall, New York; *ibidem,* Third supplement, 1985; C.C. Price and R.D. Gilbert, *J. Am. Chem. Soc.*, **74,** 2073 (1952); C.C. Price and R.G. Gillis, *ibid.*, **75,** 4750 (1953); A. Cerniani and G. Modena, *Gazz. Chim. Ital.* **89.** 843 (1959).
6. M.E. Peach, *"The Chemistry of the Thiol Group",* (S. Patai, Ed., Interscience, New York, N.Y., 1974) pp 721–735.

7. Y. Bard, *"Non linear parameter estimation"*, (Academic Press, New York, 1970).
8. I.E. Teggins, D.R. Gano, M.A. Tucker and D.S. Martin Jr., *Inorg. Chem.*, **6,** 69 (1967).
9. Y.N. Kukushkin and V.V. Kirillov, *Russ. J. Inorg. Chem.*, **18,** 756 (1973).
10. L.I. Elding, *Acta Chem. Scand.*, **24,** 2546 (1970).
11. L.I. Elding, *Acta Chem. Scand.*, **20,** 2559 (1966).
12. L. Cattalini, A. Orio and M.L. Tobe, *J. Am. Chem. Soc.*, **89,** 3130 (1967).
13. T. Hoover and P.A. Zipp, *Inorg. Chim. Acta*, **63,** 9 (1982).
14. L.I. Elding and A.B. Groning, *Inorg. Chim. Acta*, **31,** 243 (1978).
15. L. Cattalini, A. Threathgold and M.L. Tobe, to be published.
16. R.G. Pearson, H. Sobel and J. Songstad, *J. Am. Chem. Soc.*, **90,** 319 (1968).