A Calorimetric Investigation of Bromo and Iodo Complexes of Mercury(II) in Dimethyl Sulfoxide

R. ARNEK and D. POCEVA *

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm, Sweden

The equilibrium constants and enthalpy changes for the reactions between HgX_2 and X^- , where $\text{X} = \text{Br}$ and I , in dimethyl sulfoxide (1 M NaClO_4 , 25°C) have been obtained from calorimetric data. The stepwise formation constants for HgBr_3^- and HgBr_4^{2-} are $K_3 = 10^{5.6 \pm 0.1} \text{ M}^{-1}$ and $K_4 = 10^{2.66 \pm 0.03} \text{ M}^{-1}$ and the enthalpy changes $\Delta H^\circ_3 = -26.9 \pm 0.2 \text{ kJ mol}^{-1}$ and $\Delta H^\circ_4 = -22.7 \pm 0.5 \text{ kJ mol}^{-1}$. The corresponding values for HgI_3^- and HgI_4^{2-} are $K_3 = 10^{6.1 \pm 0.1} \text{ M}^{-1}$, $K_4 = 10^{2.58 \pm 0.03} \text{ M}^{-1}$, $\Delta H^\circ_3 = -26.8 \pm 0.1 \text{ kJ mol}^{-1}$ and $\Delta H^\circ_4 = -22.8 \pm 0.3 \text{ kJ mol}^{-1}$.

Solutions of mercury(II) halide complexes in dimethyl sulfoxide (DMSO) are being studied in this laboratory by X-ray diffraction.¹ The iodide complexes have been found to be mononuclear with HgI_4^{2-} regularly tetrahedral, HgI_3^- pyramidal and HgI_2 approximately linear.² The related calorimetric investigation reported here was performed in order to obtain thermodynamic data for the mercury(II) bromide and iodide complexes in DMSO. As the solvating properties of the dipolar aprotic solvent DMSO are markedly different from those of a protic medium, such as water, it is of considerable interest to compare the thermodynamic parameters for complex formation in the two media, DMSO and water. Data for the mercury(II) halide complexes in aqueous solution are available in literature.³

Earlier investigations of mercury(II) iodide complexes in DMSO have been made by Buckingham and Gasser⁴ (conductance and spectrophotometry), Peterson, Lingane and Reynolds⁵ (spectrophotometry), Foll, Le

Demézét and Courtot-Coupez⁶ (potentiometry), Gorenbein *et al.*^{7–9} (freezing point depression and calorimetry) and Samoilenko *et al.*¹⁰ (potentiometry).

Data on mercury(II) bromide complexes in DMSO have been reported by Le Demézét *et al.*,⁶ Gorenbein *et al.*⁹ and Samoilenko *et al.*¹⁰

EXPERIMENTAL

Chemicals. The solvent *dimethyl sulfoxide* (Mallinckrodt, analytical reagent) was distilled under reduced pressure at about 60°C over calcium hydride, the first and the last fraction of the distillate being discarded. The water content of the DMSO, measured by Karl Fischer titration, was found to be less than 0.05 %.

Sodium perchlorate was prepared by neutralizing sodium carbonate with perchloric acid. The crystals obtained were recrystallized once from water and then dried to constant weight at 125°C.

Mercury(II) bromide and iodide, sodium bromide and iodide were all of analytical grade and were carefully dried before using.

Apparatus. The measurements were carried out with an automatic calorimeter of the isothermal jacket type.¹¹ The calorimeter is wholly immersed in a thermostat bath of type LKB 7603A, maintained at $25.000 \pm 0.001^\circ\text{C}$. The calorimeter was initially charged with 100.0 cm³ (V_0) of a solution S containing HgX_2 and usually in addition some amount of NaX. Successive additions were made to the solution S of v cm³ of another thermostated solution T containing NaX. Before each addition from the buret the same amount of solution (v cm³) was removed from the calorimeter vessel, as should be added, so that the final volume was always 100.0 cm³. The solutions used in the experiments were prepared by dissolving weighed amounts of the reagents in DMSO. The concentration range of HgX_2 studied was 0.005–0.200 M for

* Present address: Faculty of Technology and Metallurgy, Skoplje, Yugoslavia.

HgBr₂ and 0.005–0.040 M for HgI₂.^{*} The concentration of NaX in the buret solution T was 0.2–0.35 M for NaBr and 0.2–0.5 M for NaI. The ionic strength was kept constant at 1 M by using sodium perchlorate as ionic medium.

The heat of dilution of the solution T, always less than 0.5 M in NaX, in DMSO with sodium perchlorate as ionic medium, was found by experiments to be negligible.

RESULTS AND CALCULATIONS

The reactions which have been studied are

with X = Br and I.

For reactions (1) and (2) we denote the equilibrium constants K_3 , M⁻¹ and K_4 , M⁻¹ and the enthalpy changes ΔH°_3 and ΔH°_4 , kJ/mol.

The zero superscripts used with ΔH (and also with ΔG and ΔS in the following) mean that the standard states are hypothetical ideal

^{*} Throughout this paper M = mol dm⁻³.

Table 1. Experimental results for a typical titration in the Hg(II)–Br⁻ system.^a

S: $C_{\text{HgBr}_2} = 20.445 \times 10^{-3}$ M; $C_{\text{Br}^-} = 1.298 \times 10^{-3}$ M
T: $C_{\text{Br}^-} = 0.2595$ M

v/cm^3	Q/J	$\Delta Q/J$
0.500	3.464	0.020
0.499	3.495	-0.019
0.500	3.490	-0.007
0.499	3.504	-0.028
0.499	3.505	-0.030
0.498	3.507	-0.039
0.500	3.504	-0.023
0.999	6.946	0.004
0.997	6.936	-0.015
0.997	6.847	0.003
0.499	3.227	0.046
0.500	2.909	0.029
0.999	5.246	0.003
0.998	4.964	-0.054
0.998	4.626	-0.038
0.997	4.211	-0.036
0.998	3.668	0.002
0.998	3.075	0.008
0.999	2.438	0.040

^a The complete set of experimental data are available from the authors upon request.

Table 2. Experimental results for a typical titration in the Hg(II)–I⁻ system.^a

S: $C_{\text{HgI}_2} = 20.63 \times 10^{-3}$ M;
 $C_{\text{I}^-} = 2.542 \times 10^{-3}$ M
T: $C_{\text{I}^-} = 0.5114$ M

v/cm^3	Q/J	$\Delta Q/J$
0.500	6.838	0.008
0.500	6.833	0.012
0.500	6.814	0.031
0.498	6.819	-0.003
0.499	6.830	-0.003
0.498	6.807	-0.007
0.500	6.552	0.030
0.498	5.179	0.043
0.500	4.862	0.036
0.498	4.642	-0.021
0.499	4.302	0.007
0.499	3.939	-0.028
0.500	3.438	0.007
0.498	2.943	-0.028
0.500	2.442	-0.035
0.999	3.422	0.028
0.999	2.167	-0.016

^a The complete set of experimental data are available from the authors upon request.

one molar solutions of the solutes in DMSO (1 M NaClO₄).

The experimental data from the enthalpy titrations are pairs of (v, Q) values, where Q J is the heat evolved for an addition of v cm³. The (v, Q) values for two representative titrations are given in Tables 1 and 2. (In total 11 series of measurements were performed, including 160 Q -values). By means of the least-squares program LETAGROP/KALLE¹² (calorimetric version of LETAGROP) the values for the parameters K_3 , K_4 , ΔH°_3 and ΔH°_4 were searched for which minimize the error square sum U defined by

$$U = \sum (Q_{\text{calc}} - Q)^2$$

The values for the equilibrium constants K_3 and K_4 and the enthalpy changes ΔH°_3 and ΔH°_4 which give a minimum in the error square sum U are given in Table 3.

The errors given correspond to three standard deviations. σ_Q is the standard deviation in the Q -measurements. It was found during the calculations that the function $U(K_3)$ (for both Br⁻ and I⁻) has a rather shallow minimum. Conse-

Table 3. Computed values of K_3 , K_4 , ΔH° , and ΔH°_4 in DMSO (1 M NaClO₄, 25°C).

System	X = Br	X = I
log K_3	5.6 ± 0.1	6.1 ± 0.1
log K_4	2.65 ± 0.03	2.58 ± 0.03
ΔH°_3 , kJ	-26.85 ± 0.15	-26.78 ± 0.11
ΔH°_4 , kJ	-22.68 ± 0.28	-22.84 ± 0.27
σ_Q , J	0.04	0.04

quently the values for log K_3 are relatively uncertain. In fact the constants K_3 are somewhat too high to be safely determined from calorimetric titration data. The most favourable range for determining equilibrium constants by calorimetry is usually considered to be $0 < \log K < 3$.

In Tables 1 and 2 the experimental data (v, Q) and the differences $\Delta Q = (Q_{\text{calc}} - Q)$ are given for two typical experiments

PREVIOUS DATA. DISCUSSION

The values for K_3 and K_4 obtained by us from calorimetric data are in reasonable agreement with those obtained by le Demézét *et al.*⁶ from potentiometric measurements in 0.1 M Et₄NClO₄ (log K_3 = 5.8, log K_4 = 2.4 for Hg(II)–Br[–]; log K_3 = 6.2, log K_4 = 2.2 for Hg(II)–I[–]). The values for Hg(II)–I[–] reported by Peterson *et al.*⁵ are markedly lower (log K_3 = 5.74 ± 0.1, log K_4 = 1.88 ± 0.02); however, those values were obtained from measurements without a sup-

porting electrolyte and with a total mercury(II) concentration not exceeding 5×10^{-5} M. Samoilenko *et al.*¹⁰ reported in 1 M NaClO₄ log K_4 = 0.9 for Hg(II)–Br[–] and log K_4 = 2.0 for Hg(II)–I[–]; the former value seems rather low.

Gorenbein *et al.*^{8,9} reported calorimetric values for ΔH_3 and ΔH_4 in DMSO without ionic medium (ΔH_3 = -23.4 kJ mol⁻¹, ΔH_4 = -13.8 kJ mol⁻¹ for Hg(II)–Br[–]; ΔH_3 = -32.2 kJ mol⁻¹, ΔH_4 = -11.3 kJ mol⁻¹ for Hg(II)–I[–]). Our values for ΔH°_3 and ΔH°_4 differ considerably from those reported by Gorenbein *et al.*^{8,9} Unfortunately the latter do not give the complex constants used in the computation of the ΔH -values.

A value $\Delta H_3 + \Delta H_4$ = -43.8 kJ mol⁻¹ in DMSO without ionic medium has been reported by Buckingham and Gasser.⁴

The thermodynamic parameters ΔG° , ΔH° and ΔS° for the formation of the complexes HgX₃[–] and HgX₄^{2–} in DMSO are collected in Table 4 together with the corresponding quantities for aqueous solution. For comparison the values of K_3 and K_4 in DMSO and water are also in Table 5. Comparing the thermodynamic parameters in DMSO for the formation of Hg(II)–bromide and iodide complexes, we find that they are strikingly similar (in aqueous solution there is a considerable difference). For both ligands the values of K_3 and K_4 are higher in DMSO than in water, the increase being most pronounced for K_3 . For the bromide complexes this is mainly an effect of the more favourable enthalpy terms in DMSO. For the iodide complexes, where the material for comparison

Table 4. The values of ΔG° , ΔH° and ΔS° at 25°C in DMSO and water for the reactions studied: (A) Hg(II)–Br[–], (B) Hg(II)–I[–].

Reaction	DMSO, 1 M NaClO ₄ ^a			H ₂ O, 0.5 M NaClO ₄		
	ΔG° / kJ mol ⁻¹	ΔH° / kJ mol ⁻¹	ΔS° / J mol ⁻¹ K ⁻¹	ΔG° / kJ mol ⁻¹	ΔH° / kJ mol ⁻¹	ΔS° / J mol ⁻¹ K ⁻¹
A. Hg(II)–Br [–]						
HgBr ₂ + Br [–] ⇌ HgBr ₃ [–]	-32.0	-26.9	+17	-12.0 ^b	-12.6 ^b	-2 ^b
HgBr ₃ [–] + Br [–] ⇌ HgBr ₄ ^{2–}	-15.1	-22.7	-25	-9.7 ^b	-17.1 ^b	-25 ^b
HgBr ₂ + 2Br [–] ⇌ HgBr ₄ ^{2–}	-47.1	-49.6	-8	-21.7 ^b	-29.7 ^b	-27 ^b
B. Hg(II)–I [–]						
HgI ₂ + I [–] ⇌ HgI ₃ [–]	-34.8	-26.8	+27	-21.6 ^c	–	–
HgI ₃ [–] + I [–] ⇌ HgI ₄ ^{2–}	-14.7	-22.8	-27	-12.7 ^c	–	–
HgI ₂ + 2I [–] ⇌ HgI ₄ ^{2–}	-49.5	-49.6	0	-34.2 ^c	-42.0 ^d	-26

^a Present work. ^b Ref. 13. ^c Ref. 14. ^d Ref. 15, 16.

Table 5. Values of K_3 and K_4 in DMSO and water at 25°C.

	DMSO		H ₂ O ^a	
	X = Br	X = I	X = Br	X = I
log K_3	5.6	6.1	2.1	3.8
log K_4	2.65	2.58	1.7	2.2
log K_3, K_4	8.25	8.68	3.8	6.0

^a Ref. 13, 14.

is not complete, the difference in the entropy terms seems to be as important as the difference in the enthalpy terms.

To explain, at least qualitatively, the difference in stability between the complexes in DMSO and in water one has to take into account the different solvating properties of the two media. In general anions, and especially those able to form hydrogen bonds, are more strongly solvated in water than in DMSO. The halide ions have in a protic solvent such as water, capacity to form hydrogen bonds. The capacity is more pronounced the smaller the ion; the iodide ion is probably rather weakly hydrogen bonding. In an aprotic solvent such as DMSO no hydrogen bonds can be formed.

One might thus expect the bromide ion, which can form hydrogen bonds in water, to form stronger mercury(II) complexes in DMSO than in water, provided there is not too big a difference in solvation of Hg(II) in the two media. For the iodide ion, on the other hand, which probably forms no hydrogen bonds in water, one might expect less difference in stability between the mercury(II) complexes in water and DMSO. One would furthermore expect the difference in stability between the mercury(II)–bromide and iodide complexes to be smaller in DMSO than in water. The observed stabilities of the complexes give support to the model outlined briefly above.

The stabilities of several metal halide complexes in dimethyl sulfoxide have been discussed in a recent paper by Åhrland and Björk.¹⁷

Acknowledgements. This work has been supported by the Swedish Natural Science Research Council. The English was revised by Dr. D. Lewis.

REFERENCES

1. Johansson, G. and Sandström, M. *Personal communication*.
2. Gaizer, F. and Johansson, G. *Acta Chem. Scand.* 22 (1968) 3013.
3. Sillén, L. G. and Martell, A. E., Eds., *Stability Constants*, The Chemical Society, Special Publications Nos. 17 and 25, London 1964, 1971.
4. Buckingham, A. and Gasser, R. P. H. *J. Chem. Soc. A* (1967) 1964.
5. Peterson, R. J., Lingane, P. J. and Reynolds, W. L. *Inorg. Chem.* 9 (1970) 680.
6. Foll, A., Le Demézét, M. and Courtot-Coupez, J. *Bull. Soc. Chim. Fr.* (1972) 1207.
7. Gorenbein, E. Y., Vainshtein, M. N., Trofimchuk, A. K., Abarbarchuk, I. L. and Skorobogatko, E. P. *Zh. Obshch. Khim.* 43 (1973) 495.
8. Gorenbein, E. Y., Vainshtein, M. N., Skorobogatko, E. P. and Trofimchuk, A. K. *Zh. Obshch. Khim.* 44 (1974) 1558.
9. Gorenbein, E. Y., Vainshtein, M. N. and Skorobogatko, E. P. *Ukr. Khim. Zh.* 9 (1974) 923.
10. Samoilenko, V. M., Lyashenko, V. I. and Polishchuk, N. V. *Zh. Neorg. Khim.* 19 (1974) 2984.
11. Arnek, R. and Holmqvist, E. *To be published*.
12. Arnek, R. *Ark. Kemi* 32 (1970) 81.
13. Björkman, M. and Sillén, L. G. *Trans. Roy. Inst. Technol. (Stockholm)* 1963.
14. Sillén, L. G. *Acta Chem. Scand.* 3 (1949) 539.
15. Gallagher, P. K. and King, E. L. *J. Amer. Chem. Soc.* 82 (1960) 3510.
16. Christensen, J. J., Izatt, R. M., Hansen, L. D. and Hale, J. D. *Inorg. Chem.* 3 (1964) 130.
17. Åhrland, S. and Björk, N.-O. *Coord. Chem. Rev.* 16 (1975) 115.

Received June 26, 1975.