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The Formation Constants of Triiodo- and Tetraiodomercurate(II) Ions in Dimethyl Sulfoxide

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Received July 31, 1969

Although there is qualitative evidence[1-10] for the formation of a number of transition metal complexes in dimethyl sulfoxide (DMSO) solution, there have been only a few quantitative[11-14] determinations of such formation constants. In particular, the existence of HgI_3^- and HgI_4^{2-} in DMSO solutions containing mercury(II) iodide and potassium iodide was inferred by Buckingham and Gasser[9] from conductance and spectrophotometric data. In this note we report the stepwise formation constants of HgI_3^- and of HgI_4^{2-} and the molar absorptivities of HgI_2, HgI_3^-, and HgI_4^{2-} at 286, 304, and 334 nm.

Experimental Section

Reagent grade chemicals and DMSO were used; the DMSO contained less than 0.05% water.

The absorbances of DMSO solutions containing different concentrations of mercury(II) iodide and potassium iodide were measured with a Beckman DU spectrophotometer at 25°. The solutions were prepared by diluting aliquots of HgI_2 and KI solutions and did not contain a third electrolyte to maintain the ionic strength constant.

The stepwise formation constants and the molar absorptivities of all three mercury species were refined simultaneously using Gaussian least-squares procedures.[15] The computations recognized that the errors in the data for a common solution are correlated at the three wavelengths because concentration errors are common;[15] however, neglecting this correlation did not change the values calculated for the parameters significantly.

Results and Discussion

In agreement with Buckingham and Gasser[9] it was found that spectra of solutions of HgI_2 without added iodide showed a shoulder at 286 nm on an absorption peak which extended into the region cut off by solvent absorption. With decreasing HgI_2 concentration this shoulder shifted to longer wavelengths. This shift has been attributed[9] to disproportionation of HgI_2 to HgI^+ and HgI_3^-.

If we assume a limiting equivalent conductance of about 40 for the fully dissociated HgI_2,[16] we estimate from the conductance data of Buckingham and Gasser[9] that HgI_2 is only 5% dissociated at the concentrations employed in this study. Consequently, we have neglected the disproportionation in our analysis of the data.

TABLE I
MOLAR ABSORPTIVITIES OF MERCURY(II)-IODIDE COMPLEXES IN DMSO AT 25°

	Molar extinction coeff, M^{-1} cm^{-1}		
Species	286 nm	304 nm	334 nm
HgI_2	7,140 ± 70	6,680 ± 80	2,630 ± 50
HgI_3^-	9,680 ± 7	13,700 ± 110	7,520 ± 80
HgI_4^{2-}	23,400 ± 360	7,170 ± 110	21,700 ± 350

The spectra of HgI_2 solutions with KI:Hg(II) mole ratios in the range of 1–12 showed an increasing absorption maximum at 304 nm attributed[9] to HgI_3^-. At KI:Hg(II) mole ratios greater than approximately 20, the maximum at 304 nm decreased and an absorption maximum at 334 nm appeared which has been attributed[9] to HgI_4^{2-}. At these mole ratios an isosbestic point was observed at 314 nm which is consistent with the data given in Table II which show that the fraction of HgI_2 present is very small at these KI:Hg(II) mole ratios. The positions of the maxima found for HgI_3^- and HgI_4^{2-} in DMSO were very close to the positions of the maxima attributed to these two ions in acetonitrile, methyl formate, ethyl acetate, dichloromethane, and N,N-dimethylformamide.[17] The existence of the isosbestic point strongly suggests that no polynuclear mercury(II) complexes are formed in the concentration ranges employed. Indeed, Gaizer and Johansson[18] found no evidence of such complexes at much higher mercury(II) concentrations and lower KI:Hg(II) ratios.

The best values obtained for the molar absorptivities are listed in Table I. The best values obtained for the formation constants K_3 and K_4, defined by eq 1 and 2, are (5.5 ± 1.2) × 10^5 M^{-1} and 75.7 ± 4.0 M^{-1}, respectively. These values were obtained assuming a spectrophotometric error of 0.005 transmittance unit and a concentration error of 0.5%. Assumption of a

$$K_3 = \frac{[HgI_3^-]}{[HgI_2][I^-]}\frac{f_-}{f_0 f_{I^-}} \qquad (1)$$

$$K_4 = \frac{[HgI_4^{2-}]}{[HgI_3^-][I^-]}\frac{f_{2-}}{f_- f_{I^-}} \qquad (2)$$

spectrophotometric error of 0.005 absorbance unit and the same concentration error did not result in any significant change in any of the parameters calculated. The error associated with each parameter is the square root of the appropriate diagonal element in the inverse matrix times an internal estimate of the variance of unit weight. For the 115 degrees of freedom the value

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TABLE II

SUMMARY OF THE MERCURY(II)–IODIDE DATA IN DMSO[a]

SOLN	TOTAL IODIDE	MOLE FRACTION HGI2	HGI3	HGI4	EXPERIMENTAL ABSORBANCES 286	304	334 NM	CALCULATED RESIDUALS 286	304	334 NM
11*	7.500E-05	1.000	.000	.000	.276	.270	.112	.008	.020	.014
21*	7.500E-05	1.000	.000	.000	.262	.246	.100	-.006	-.004	.002
1	1.000E-04	1.000	.000	.000	.366	.330	.125	.008	-.004	-.006
16	1.000E-04	1.000	.000	.000	.347	.325	.132	-.011	-.009	.001
26	1.000E-04	1.000	.000	.000	.351	.317	.122	-.007	-.017	-.009
2	1.100E-04	.809	.191	.000	.390	.394	.167	.008	-.007	-.011
27	1.187E-04	.646	.354	.000	.386	.473	.220	-.016	.014	.002
3	1.200E-04	.622	.378	.000	.412	.466	.218	.007	-.001	-.006
17	1.250E-04	.532	.468	.000	.427	.508	.248	.010	.009	.002
4	1.300E-04	.445	.554	.000	.439	.548	.274	.011	.018	.007
12*	1.000E-04	.405	.595	.000	.335	.419	.210	.010	.011	.002
22*	1.000E-04	.405	.595	.000	.311	.410	.215	-.014	.002	.007
28	1.374E-04	.327	.673	.000	.439	.579	.303	-.004	.007	.007
5	1.400E-04	.290	.710	.000	.449	.600	.313	.002	.015	.008
18	1.500E-04	.174	.826	.001	.471	.632	.338	.009	.006	.004
29	1.561E-04	.128	.871	.001	.456	.629	.341	-.012	-.013	-.004
23*	1.250E-04	.101	.898	.001	.329	.454	.250	-.025	-.034	-.014
13*	1.253E-04	.099	.899	.001	.358	.494	.271	.004	.005	.007
19	1.750E-04	.061	.937	.002	.488	.676	.369	.011	.011	.006
30	1.749E-04	.061	.937	.002	.462	.657	.354	-.015	-.008	-.009
14*	1.500E-04	.044	.953	.003	.367	.512	.283	.007	.009	.007
24*	1.500E-04	.044	.953	.003	.350	.484	.265	-.010	-.019	-.011
20	2.000E-04	.034	.962	.004	.491	.690	.384	.009	.016	.013
15*	1.750E-04	.028	.967	.005	.369	.519	.289	.006	.012	.009
25*	1.750E-04	.028	.967	.005	.354	.489	.271	-.009	-.018	-.009
31	6.000E-04	.004	.960	.036	.516	.661	.396	.008	-.013	-.005
32	1.100E-03	.002	.921	.077	.552	.660	.430	.016	-.001	-.000
33	1.600E-03	.001	.882	.116	.580	.648	.454	.017	-.001	-.005
34	2.090E-03	.001	.846	.153	.601	.640	.483	.012	.003	-.002
35	2.590E-03	.001	.810	.189	.628	.632	.510	.014	.007	-.000
36	3.590E-03	.000	.744	.255	.639	.591	.550	-.020	-.012	-.007
37	5.019E-03	.000	.662	.338	.722	.579	.604	.015	.010	-.004
6	8.500E-03	.000	.511	.489	.834	.531	.736	.015	.005	.013
38	1.010E-02	.000	.459	.541	.874	.521	.747	.019	.012	-.013
7	1.690E-02	.000	.311	.689	.987	.459	.882	.030	-.001	.017
39	1.760E-02	.000	.300	.700	.989	.462	.859	.025	.005	-.014
8	2.530E-02	.000	.214	.786	.979	.423	.960	-.045	-.005	.026
40	2.520E-02	.000	.214	.786	1.008	.443	.921	-.015	.014	-.013
9	3.370E-02	.000	.158	.842	1.028	.402	.990	-.034	-.008	.016
10	3.370E-02	.000	.158	.842	1.006	.404	.995	-.056	-.006	.021
41	3.770E-02	.000	.140	.860	1.075	.408	1.000	.003	.005	.015
42	5.030E-02	.000	.101	.899	1.108	.388	1.002	.007	-.003	-.013

[a] Data weighted assuming a spectrophotometric error of 0.005 transmittance unit and concentration errors of 0.5%. The Hg(II) concentration is 0.05 m*M* except where asterisks indicate [Hg(II)] = 0.0375 m*M*.

TABLE III

PARTIAL CORRELATION COEFFICIENTS FOR THE MERCURY(II)–IODIDE SYSTEM IN DMSO[a]

	K_3	K_4	ϵ_{HgI_2} 286 nm	304 nm	334 nm	ϵ_{HgI_3} 286 nm	304 nm	334 nm	ϵ_{HgI_4} 286 nm	304 nm	334 nm
K_3	...	−0.01	−0.06	−0.13	−0.18	−0.18	−0.42	−0.59	−0.00	−0.00	−0.01
K_4		...	−0.00	0.00	−0.00	−0.17	0.28	−0.24	−0.43	0.48	−0.58
ϵ_{HgI_2} 286 nm			...	0.09	0.12	−0.25	0.02	0.02	−0.00	0.00	0.00
304 nm				...	0.37	0.02	−0.20	0.04	0.00	−0.00	0.00
334 nm					...	0.02	0.05	−0.24	0.00	0.00	0.00
ϵ_{HgI_3} 286 nm						...	0.08	0.09	−0.21	0.01	0.02
304 nm							...	0.10	0.04	−0.29	0.04
334 nm								...	0.02	0.01	−0.23
ϵ_{HgI_4} 286 mn									...	0.07	0.06
304 nm										...	0.08
334 nm											...

[a] Data weighted assuming a spectrophotometric error of 0.005 transmittance unit and a concentration error of 0.5%.

of $(\chi^2/115)$ was equal to 2.7. This minimum is unique within wide variations of the initial estimates for the formation constants and of the initial estimates for the spectra.

The variation of the activity coefficients with changes in the ionic strength was included in the calculations *via* the equation

$$-\log f_i = Az_i^2\left(\frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.3\mu\right) \qquad (3)$$

where the constant A is 1.11 in DMSO at 25°. The validity of this equation has been reviewed by Davies.[19] Although not tested for DMSO, it was selected because it has no adjustable parameters. For the calculation of the ionic strength, all possible ion pairs were assumed completely dissociated. This is known to be true for KI in DMSO.[16]

Activity coefficients were also estimated *via* the extended Debye–Hückel equation in which the ion-size parameter was varied over wide limits for all species.

(19) C. W. Davies, "Ion Association," Butterworth and Co. Ltd., London, 1962.

In no case are the values of the parameters changed significantly. However, the values of K_3, K_4, and the absorptivities of HgI_4^{2-} changed by 10–15% if all activity coefficients were set equal to unity. Since $\chi^2/115$ did not increase appreciably, this suggests that the fit is, statistically, equally good whether or not activity corrections are included. Since the weight of chemical experience requires that the variation of the activity coefficients be included over this ionic strength range ($0 < \mu < 0.05$), we regard the results obtained with the Davies equation as the more accurate.

The distribution of Hg(II) among the three iodide complexes is given in Table II along with the experimental absorbances of the solutions and the calculated residuals. A residual is the amount to be subtracted from the measured absorbance to give agreement with the absorbance calculated from the best values of the equilibrium constants and the molar absorptivities. More than 90% of the calculated absorbances agree with the measured values to within better than 5% over the more than 1000-fold change in ligand concentration.

Examination of the partial correlation coefficients[20] indicates that the parameters are not strongly correlated. This is a consequence of the widely separated values of K_3 and K_4 which minimizes the overlap of species as the iodide ion concentration is increased. As may be seen from Table II, 12% of the solutions contain mainly HgI_2, nearly 20% contain over 90% HgI_3^-, and the solutions at the higher KI concentrations are mainly HgI_4^{2-}. Because the parameters are not strongly correlated, the errors quoted above are probably realistic estimates of the 50% confidence intervals for the parameters.

Acknowledgments.—R. J. Peterson wishes to thank the NSF Undergraduate Research Participation Program for its support, and P. J. Lingane wishes to thank the University of Minnesota Computing Center for a grant of computer time.

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A Potentiometric Study of Cobalt(III) Perchlorate Solutions[1a]

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Received August 28, 1969

There is some uncertainty, and even controversy,[2] concerning the species present in acidic cobalt(III) perchlorate solutions. There seems to be fairly general agreement that solutions of $[Co^{III}] \gtrsim 10^{-2}\ M$ and $[H^+] < 0.5\ M$ contain di- and/or polynuclear hydrolyzed species.[3] However, it has also been suggested on the basis of kinetic studies[2] that a (hydrated) dimer of Co^{III} predominates even in solutions of $[Co^{III}] \lesssim 1 \times 10^{-3}\ M$ at high acidities.

Also, there is a paucity of standard potential ($E°_{Co}$) data for the Co^{III}–Co^{II} couple in perchlorate solutions. Two values, at 25° in 4 M $HClO_4$—1.92 ± 0.02 V (measured directly)[4] and 1.95 ± 0.10 V (indirect estimate)[5]—are the only ones found in the literature.

If cobalt(III) exists in solution in the form of dimeric ions, this should be supported by electromotive force measurements with the (reversible) Co^{III}–Co^{II} redox electrode; the "Nernst slope" would be half of that expected for monomeric cobalt(III) (at constant cobalt(II) concentration).[6,7]

If both monomeric and dimeric Co^{III} species are present in equilibrium

$$2Co^{III} \rightleftharpoons Co^{III}_2 \qquad (1)$$

one has

$$[Co^{III}_2][Co^{III}]^{-2} = K_D \qquad (1a)$$

Here brackets are used to denote concentrations, and K_D is an overall dimerization quotient. If hydrolysis occurs, K_D will be a constant at constant $[H^+]$ ($\equiv h$). If K_D in eq 1 is finite, then the Nernst equation for the emf, E (expressed as a reduction potential), is given by

$$E = E_0 + \frac{RT \ln 10}{F} \log \{[(1 + 8K_D[Co^{III}]_T)^{1/2} - 1]/4K_D[Co^{2+}]\} \qquad (2)$$

where E_0 is a constant, which includes *inter alia* the reference half-cell emf and liquid junction potentials (assumed to be constant); $[Co^{III}]_T$ is the total concentration of Co^{III}; other symbols have their conventional meaning. For the case of a very high K_D (practically all dimer) eq 2 reduces to

$$E = E_0 + \frac{RT \ln 10}{2F} \log ([Co^{III}]_T/2K_D[Co^{2+}]^2) = E_0' + \frac{RT \ln 10}{2F} \log ([Co^{III}]_T/[Co^{2+}]^2) \qquad (2a)$$

Experimental Section

Cobalt(III) perchlorate solutions in 3 M $(Na^+,H^+)ClO_4^-$ were prepared by electrolytic oxidation near 0° of cobalt(II) perchlorate which had been prepared from reagent grade cobalt carbonate and perchloric acid. Sodium perchlorate was prepared from chloride-free sodium carbonate and perchloric acid. Water was triply distilled. Other reagents were of reagent grade.

The cell used for the emf measurements was

$$\text{ref electrode}\,|\,|\,h\ M\ H^+,\ 3\ M\ ClO_4^-\,|\,|\,h\ M\ H^+,\ 3\ M\ ClO_4^-,\ Co^{III},\ Co^{2+}(Ag^+)\,|\,Au(s)$$

The reference electrode was a commercial calomel electrode in which the KCl had been replaced with 4.0 M NaCl. An $HClO_4$–

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[1] (a) Work performed under the auspices of the U. S. Atomic Energy Commission. (b) On leave from the Royal Institute of Technology, Stockholm, Sweden.

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