

Hydrolysis of $(\text{CH}_3)\text{Hg}^+$ in Different Ionic Media: Salt Effects and Complex Formation

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The hydrolysis of monomethylmercury(II) was studied potentiometrically, in NaNO_3 , Na_2SO_4 , and NaCl aqueous solution, in a wide range of ionic strengths (NaNO_3 , $0 \leq I \leq 3.25$; Na_2SO_4 , $0 \leq I \leq 1$; NaCl , $0 \leq I \leq 3 \text{ mol dm}^{-3}$) and at $t = 25^\circ\text{C}$. For the reaction $(\text{CH}_3)\text{Hg}^+ = (\text{CH}_3)\text{Hg}(\text{OH})^\circ + \text{H}^+$, we found $\log K_1 = -4.528$ ($I = 0 \text{ mol dm}^{-3}$). The species $[(\text{CH}_3)\text{Hg}]_2(\text{OH})^+$ was also found, with $\log \beta_2 = -2.15$. Monomethylmercury(II) forms quite strong complexes with Cl^- ($\log K = 5.45$, $I = 0 \text{ mol dm}^{-3}$) and SO_4^{2-} ($\log K = 2.64$, $I = 0 \text{ mol dm}^{-3}$). The dependence on ionic strength of formation constants was considered by using a Debye–Hückel type equation. Hydrolysis and complex formation constants (at different ionic strengths) obtained were used to calculate the interaction parameters of Pitzer equations.

Introduction

The impact of organomercury in the natural environment has been one of the prime causes of the growth of scientific interest and social concern in environmental matters. In general, organometallic compounds are defined as compounds that contain a metal carbon covalent bond. They may enter the environment as such, or they may be formed there. The most important source of organometals is their direct input from synthesis products used in pest control and from industries using organometals in their processes (for example, the organotin compounds, which have been used as bodices, in plastics and oil stabilizers, and as catalysts for polymerization). Other organometallic compounds in the environment result from the action of living organisms themselves on some metallic ions dissolved in water or adsorbed on mineral substrates. The production of methylmercury in the environment is considered to be a biological process occurring in water, soils, and sediments via bacterial methylation on inorganic mercury. The presence of mercury in aquatic organisms is well-documented, but the identity of mercury species accumulated in biological tissues is still a matter of debate. From recent reports, it seems clear that all mercury in fish and seafood is present as monomethylmercury. The speciation problems of organometallic compounds in the environment have been discussed recently by Pelletier (1995).

The toxicity of organometallic compounds is usually higher than that of the inorganic compounds of the same metal, because the organic groups confer lipid solubility. The mercury–methyl bond, in particular, is very stable in most organisms, and the addition of the alkyl group confers lipid solubility, allowing penetration of the blood–brain barrier and cell membranes. In addition to the direct toxicity of alkylmercury compounds, a slow decomposition to inorganic mercury(II) ions may lead to secondary toxic effects as for inorganic mercury.

Many studies on methylmercury toxicity and biochemistry have been made in the last 10 years, but data on the chemical behavior of this compound are relatively few. The monomethylmercury(II) cation can be considered as a “soft” Lewis acid. The hydrolysis and the stability of a large number of monomethylmercury(II) complexes have been

studied by Schwarzenbach and Schellenberg (1965) in $0.1 \text{ mol dm}^{-3} \text{KNO}_3$ and at $t = 20^\circ\text{C}$. No systematic study has been reported on the medium effect on the hydrolysis of $(\text{CH}_3)\text{Hg}^+$. The most important inorganic anions Cl^- and SO_4^{2-} (for natural fluids) form quite stable complexes with monomethylmercury(II).

In this work we report a potentiometric study (H^+ -glass and ISE-Cl electrodes) on the hydrolysis and Cl^- and SO_4^{2-} complex formation of $(\text{CH}_3)\text{Hg}^+$ in a wide range of ionic strengths, at $t = 25^\circ\text{C}$.

Experimental Section

Chemicals. Monomethylmercury(II) cation was used in the form of chloride salt (from Strem Chemicals purity). Sodium nitrate, sodium chloride, and sodium sulfate (Fluka products) were used without purification. Hydrochloric acid and sodium hydroxide stock solutions (Fluka) were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. All solutions were prepared with analytical grade water ($R = 18 \text{ M } \Omega \cdot \text{cm}^{-1}$), using grade A glassware.

Apparatus. Measurements were performed by using an apparatus consisting of a potentiometer Metrohm model 605, equipped with an Orion combination glass electrode (Ross type 8102) and by a motorized buret Metrohm model 654. The estimated accuracy was $\pm 0.2 \text{ mV}$ and $\pm 0.003 \text{ cm}^3$ for emf and titrant volume readings, respectively. The apparatus was connected to a personal computer, and automatic titrations were performed by using a suitable computer program (titrant delivery, data acquisition, check for the stability of emf). When measuring pCl, a chloride electrode Orion model 9417B was used coupled with a reference electrode Ag/AgCl double-junction Orion model 9092. The measurement cells were thermostated at 25°C with an uncertainty of $\pm 0.1^\circ\text{C}$. All titrations were carried out by stirring magnetically and by bubbling purified and presaturated N_2 through the solution, in order to exclude O_2 and CO_2 inside.

Procedure. Twenty-five cubic centimeters of solution containing $(\text{CH}_3)\text{HgCl}$ (2 to 10 mmol dm^{-3}) and NaCl ($0 \leq I \leq 3 \text{ mol dm}^{-3}$) or NaNO_3 ($0 \leq I \leq 3.25 \text{ mol dm}^{-3}$) or Na_2SO_4 ($0 \leq I \leq 1 \text{ mol dm}^{-3}$) as background salts to adjust the ionic strength at different values was titrated with

standard NaOH solution up to pH 11.5 (60 to 80 points, initial pH ~ 3). For each experiment, independent titrations of acidic solutions (hydrochloric or nitric or sulfuric acids) with standard NaOH in the same ionic strength conditions as the systems to be investigated were carried out, in order to determine electrode potential (E^{ext}) and acidic junction potential ($E_j = j_a [\text{H}^+]$). The reliability of the calibration in the alkaline range was checked by calculating $\text{p}K_w$ values. In each system to be titrated, a slight excess of corresponding (hydrochloric or nitric or sulfuric) strong acid was added in order to compare the internal electrode potential (E^{int}) with the external one. Measurements with an ISE-Cl electrode were performed by adding monomethylmercury(II) to a solution containing NaNO_3 (0.01–0.1 mol dm^{-3}); calibration was performed separately by titrating with NaCl.

Calculations. The nonlinear least-squares computer program ESAB2M (De Stefano et al., 1987) was used for the refinement of all parameters of an acid–base titration (E° , K_w , coefficient of junction potential, j_a , analytical concentration of reagents). For the calculation of hydrolysis and complex formation constants, together with the parameters for dependence on ionic strength, BSTAC (De Stefano et al., 1993) and STACO (De Stefano et al., 1996) computer programs were used. Both the programs are able to analyze simultaneously pH and pCl titration data. Concentrations and hydrolysis and formation constants are given both in molar and molal scale. Regarding the measurements performed in Na_2SO_4 solutions, we have taken into account, in the calculations, the formation of both HSO_4^- and NaSO_4^- species (De Robertis et al., 1994). The LIANA (De Stefano et al., 1997) program was used to test the dependence of $\log K$ on ionic strength by different equations; the ES4ECI (De Stefano et al., 1993) program was used to draw the distribution diagrams.

Ionic Strength Dependence of Formation Constants

Dependence on ionic strength was taken into account by using the Debye–Hückel type equation (Daniele et al., 1991; De Stefano et al., 1993)

$$\log K = \log {}^{\text{T}}K - z^* I^{1/2} (2 + 3I^{1/2})^{-1} + CI + DI^{3/2} + EI^2 \quad (1)$$

with

$$z^* = \sum (\text{charges})_{\text{reactants}}^2 - \sum (\text{charges})_{\text{products}}^2$$

(K = formation constant; ${}^{\text{T}}K$ = formation constant at infinite dilution; z = charge; C , D , and E = empirical parameters). The parameter E can be neglected at $I < 1$ mol dm^{-3} . Results of a series of investigations (Daniele et al., 1991) showed that, when all interactions are taken into account, the empirical parameters of eq 1 are given by

$$C = 0.1\text{p}^* + 0.23z^*; \quad D = -0.10z^* \quad (2)$$

$$\text{p}^* = \sum (\text{moles})_{\text{reactants}} - \sum (\text{moles})_{\text{products}}$$

The activity of water was taken into account by the simple relationship $\log a_w = -0.015I$. Both STACO and BSTAC computer programs can deal with measurements at different ionic strengths and can refine the empirical parameters of eq 1 in addition to formation constants.

Dependence on ionic strength was also taken into account by considering the Pitzer equations (Pitzer, 1973, 1991; Pitzer and Mayorga, 1973). According to the Pitzer equations, for electrolytes 1–1, 1–2 and 2–1, the activity

Table 1. Hydrolysis Constants^a of $(\text{CH}_3)\text{Hg}^+$ in NaNO_3 Aqueous Solution at Different Ionic Strengths, Both in Molar (c) and Molal (m) Scale, and $t = 25^\circ\text{C}$

$I/\text{mol dm}^{-3}$	$-\log K_c$	$I/\text{mol kg}^{-1}$	$-\log K_m$
0.01	4.529 ± 0.010^b	0.010	4.528
0.09	4.538 ± 0.005	0.090	4.535
0.25	4.556 ± 0.005	0.253	4.551
0.49	4.582 ± 0.004	0.499	4.574
0.81	4.618 ± 0.005	0.833	4.606
1.00	4.639 ± 0.008	1.035	4.624
1.44	4.687 ± 0.009	1.511	4.666
1.96	4.744 ± 0.010	2.094	4.715
2.25	4.776 ± 0.005	2.428	4.743
2.56	4.809 ± 0.008	2.793	4.771
3.24	4.882 ± 0.025	3.626	4.832

^a Reaction $(\text{CH}_3)\text{Hg}^+ + \text{H}_2\text{O} = (\text{CH}_3)\text{Hg}(\text{OH})^\circ + \text{H}^+$. ^b $\geq 95\%$ confidence interval.

coefficients of cations M or anion X can be expressed by

$$\log \gamma_M = z_M^2 f^\gamma + 2 \sum_a m_a (B_{Ma} + EC_{Ma}) + \sum_a \sum_c m_c m_a (z_M^2 B_{ca} + z_M C_{ca}) + \sum_c m_c (2\theta_{Mc} + \sum_a m_a \psi_{Mca}) + \sum_a \sum_{a'} m_a m_{a'} \gamma_{Maa'} \quad (3)$$

$$\log \gamma_X = z_X^2 f^\gamma + 2 \sum_c m_c (B_{Xc} + EC_{Xc}) + \sum_a \sum_c m_c m_a (z_X^2 B_{ca} + z_X C_{ca}) + \sum_a m_a (2\theta_{Xa} + \sum_c m_c \psi_{Xca}) + \sum_c \sum_{c'} m_c m_{c'} \psi_{Xcc'} \quad (4)$$

and for neutral species

$$\log \gamma_{MX}^0 = 2\lambda I \quad (5)$$

where m_i is the molality of the cation (c) and anion (a) in the solution, z the charge, E the equivalent molality ($E = 1/2 \sum_i m_i |z_i|$), I the ionic strength in molal scale, and

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} (2I)^{-1} f_1 \quad (6)$$

$$B'_{MX} = \beta_{MX}^{(1)} (2I^2)^{-1} f_2 \quad (7)$$

$$C_{MX} = C_{MX}^{(0)} (2 |z_M z_X|^{1/2})^{-1} \quad (8)$$

$$f_1 = 1 - (1 + 2I^{1/2}) \exp(-2I^{1/2}) \quad (9)$$

$$f_2 = -1 + (1 + 2I^{1/2} + 2I) \exp(-2I^{1/2}) \quad (10)$$

$$f^\gamma = -0.392 [I^{1/2} (1 + 1.2I^{1/2})^{-1} + 1.667 \ln(1 + 1.2I^{1/2})] \quad (11)$$

$\beta^{(0)}$, $\beta^{(1)}$, and $C^{(0)}$ represent interaction parameters between two ions of opposite signs, θ represents interaction parameters between two ions of the same sign, ψ represents triple interaction parameters (+ – +, – + –), and λ is the interaction parameter of neutral species. At $I \leq 3$ mol kg^{-1} , θ and ψ parameters can be neglected.

Results and Discussion

Hydrolytic Species. Monomethylmercury(II) forms in aqueous solution the main species $(\text{CH}_3)\text{Hg}(\text{OH})^\circ$ and the weak species $[(\text{CH}_3)\text{Hg}]_2(\text{OH})^+$. In aqueous millimolar conditions the dimeric species forms in quite low percentages, while significant amounts are formed in aqueous dioxane solutions (Anderegg, 1974). The hydrolysis constant of $(\text{CH}_3)\text{Hg}(\text{OH})^\circ$ species has been determined in NaNO_3 , in a wide range of ionic strengths ($0 \leq I \leq 3.25$ mol dm^{-3}). Results are reported in Table 1, both in molar and molal scale, at 25°C . Values for hydrolysis constants

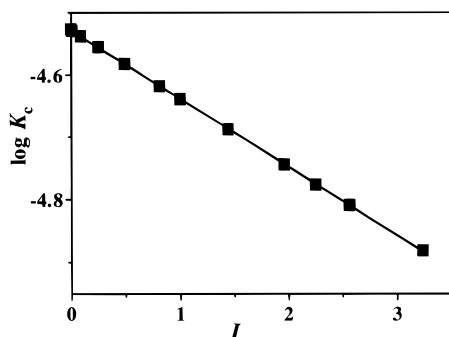


Figure 1. Hydrolysis constants of $(\text{CH}_3)\text{Hg}^+$ (monomeric species) vs $I/\text{mol dm}^{-3}$, at $t = 25^\circ\text{C}$.

Table 2. Formation Constants of $(\text{CH}_3)\text{HgCl}^\ominus$ Complex at Different Ionic Strengths, Both in Molar (c) and Molal (m) Scale, and at $t = 25^\circ\text{C}$

$I/\text{mol dm}^{-3}$	$\log K_c$	$I/\text{mol kg}^{-1}$	$\log K_m$
0.10	5.25 ± 0.03^a	0.101	5.25
0.25	5.19 ± 0.02	0.253	5.19
0.5	5.16 ± 0.02	0.510	5.15
1.0	5.13 ± 0.03	1.035	5.11
2.0	5.14 ± 0.03	2.139	5.11
3.0	5.22 ± 0.04	3.327	5.17

^a $\geq 95\%$ confidence interval.

Table 3. Formation Constants of $(\text{CH}_3)\text{Hg}(\text{SO}_4)^\ominus$ Complex at Different Ionic Strengths, Both in Molar (c) and Molal (m) Scale, and at $t = 25^\circ\text{C}$

$I/\text{mol dm}^{-3}$	$\log K_c$	$I/\text{mol kg}^{-1}$	$\log K_m$
0.09	2.54 ± 0.04^a	0.090	2.54
0.16	2.51 ± 0.04	0.161	2.51
0.25	2.51 ± 0.05	0.253	2.50
0.36	2.52 ± 0.05	0.365	2.51
0.49	2.55 ± 0.05	0.499	2.54
0.64	2.59 ± 0.05	0.655	2.58
0.81	2.63 ± 0.07	0.833	2.62
1.00	2.68 ± 0.07	1.035	2.67

^a $\geq 95\%$ confidence interval.

are fairly dependent on ionic strength, as we can see in Figure 1. The thermodynamic constant at $I = 0 \text{ mol dm}^{-3}$ was calculated by considering eq 1: $\log K_1 = -4.528$. For the species $[(\text{CH}_3)\text{Hg}]_2(\text{OH})^+$, $\log \beta_2 = -2.15 \pm 0.15$ was obtained.

Chloride and Sulfate Complexes. Calculations of hydrolysis constants in NaCl and Na_2SO_4 , performed without considering the complex formation between $(\text{CH}_3)\text{Hg}^+$ and Cl^- or SO_4^{2-} , do not give results. The presence of these salts influences the speciation of $(\text{CH}_3)\text{Hg}^+$ owing to the formation of chloride and sulfate complexes. In particular, the calculation of $(\text{CH}_3)\text{Hg}^+ - \text{Cl}^-$ complex formation showed the quite high stability of this species, as can be seen in Table 2, where results are reported at different ionic strengths. Calculations of the Cl^- complex formation constant were performed by considering pH and pCl measurements simultaneously. Calculations for measurements in Na_2SO_4 are also consistent with the formation of $(\text{CH}_3)\text{Hg}(\text{SO}_4)^\ominus$ species, and values for complex formation constants are reported in Table 3. Both $(\text{CH}_3)\text{HgCl}^\ominus$ and $(\text{CH}_3)\text{Hg}(\text{SO}_4)^\ominus$ species are dependent on ionic strength (Figure 2), and the parameters of eq 1 for dependence on ionic strength were also calculated and are reported in Table 4.

Pitzer Interaction Parameters. Molal values of hydrolysis and complex formation constants, reported in Tables 1–3, were used to calculate the interaction param-

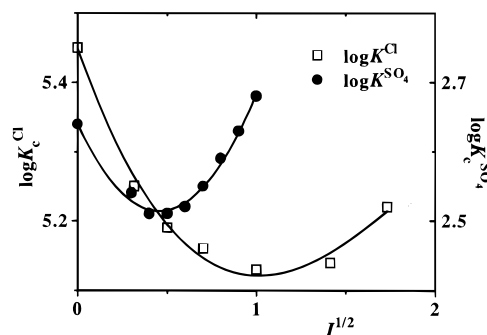


Figure 2. Formation constants of $(\text{CH}_3)\text{HgCl}^\ominus$ and $(\text{CH}_3)\text{Hg}(\text{SO}_4)^\ominus$ vs $I^{1/2}/\text{mol dm}^{-3}$, at $t = 25^\circ\text{C}$.

Table 4. Hydrolysis and Complex Formation Constants of Cl^- and $\text{SO}_4^{2-} - (\text{CH}_3)\text{Hg}^+$, at $I = 0 \text{ mol dm}^{-3}$ and $t = 25^\circ\text{C}$, Together with Parameters for Dependence on Ionic Strength (Eq 1)

species	$\log^T K$	C	E
$(\text{CH}_3)\text{Hg}(\text{OH})^\ominus$ ^a	-4.528 ± 0.012^c	0.1118	7.6×10^{-4}
$(\text{CH}_3)\text{Hg}(\text{Cl})^\ominus$ ^b	5.45 ± 0.03	0.205	0.075
$(\text{CH}_3)\text{Hg}(\text{SO}_4)^\ominus$ ^b	2.64 ± 0.05	1.24	0

^a $D = 0$. ^b $D = -0.1$ z^* . ^c $\geq 95\%$ confidence interval.

Table 5. Pitzer Interaction Parameters (Eqs 3–11), at $t = 25^\circ\text{C}$

	$(\text{CH}_3)\text{Hg}^+, \text{NO}_3^-$	$(\text{CH}_3)\text{Hg}(\text{SO}_4)^\ominus, \text{Na}^+$
$\beta^{(0)}$	0.09 ± 0.05^a	0.45 ± 0.04^a
$\beta^{(1)}$	0.57 ± 0.14	-4.36 ± 0.14
$C^{(\phi)}$	0.04 ± 0.02	0

^a $\geq 95\%$ confidence interval.

eters of Pitzer equations (eqs 3–11). Since ionic strength is lower than 3.25 mol kg^{-1} , calculations were performed neglecting the θ and ψ parameters (in Na_2SO_4 also the $C^{(\phi)}$ term). Interaction parameters of $(\text{CH}_3)\text{Hg}^+$ with NO_3^- and $[(\text{CH}_3)\text{Hg}(\text{SO}_4)^\ominus]$ with Na^+ are reported in Table 5.

Speciation of $(\text{CH}_3)\text{Hg}^+$ in Aqueous Solution. The speciation of monomethylmercury(II) in aqueous solution strongly depends on the presence of different salts. This is due to the very different complexing ability of different inorganic anions. Nitrate ion does not form ion pairs with monomethylmercury(II), and this is confirmed by the slope of $\log K_1$ vs I (Figure 1); in fact the value of C (eq 1, Table 4) is very close to that found for salt backgrounds where no significant interaction occurs (Daniele et al., 1991; De Stefano et al., 1993). On the contrary, both Cl^- and SO_4^{2-} show high interaction with $(\text{CH}_3)\text{Hg}^+$ (Tables 2, 3). This fact is clearly shown in the speciation diagrams reported in Figure 3. In the pH range of most important natural and biological fluids (e.g., blood, pH 7.4; seawater, pH 8.2) monomethylmercury(II) is strongly hydrolyzed, but in the presence of Cl^- and SO_4^{2-} anions high percentages of inorganic complexes are formed (Figure 3b,c,d). It is interesting to note that in conditions of 35‰ seawater salinity (De Robertis et al., 1994), hydrolysis becomes significant at $\text{pH} > 8$, while the chloride complex is present in high percentages for $\text{pH} \leq 10$.

Literature Comparison. Few quantitative data can be found in the literature on the hydrolysis of $(\text{CH}_3)\text{Hg}^+$ and Cl^- complex formation (Alderighi et al., 1995; Anderegg, 1974; Jawaid et al., 1978; Schwazzenbach and Schellenberg, 1965; Waugh et al., 1955; Zanella et al., 1968): in Table 6 we report the most significant findings. Only constant medium hydrolytic constants have been reported, at $I \leq 1 \text{ mol dm}^{-3}$. Regarding SO_4^{2-} complex

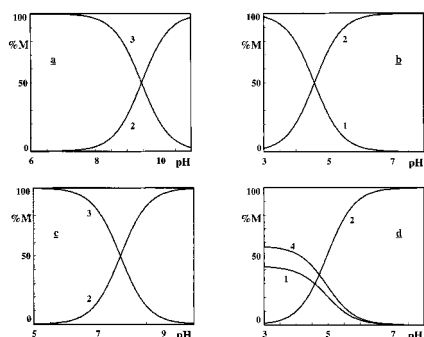


Figure 3. Speciation diagrams of $(\text{CH}_3)_3\text{Hg}^+$ (M) in different salt solutions, at $t = 25\text{ }^\circ\text{C}$: (a) artificial seawater, 35‰ salinity (NaCl 0.42, Na_2SO_4 0.029, KCl 0.011, CaCl_2 0.011, MgCl_2 0.055 mol dm^{-3} ; (b) NaNO_3 0.5 mol dm^{-3} ; (c) NaNO_3 0.5, NaCl 0.01 mol dm^{-3} ; (d) NaNO_3 0.5, Na_2SO_4 0.01 mol dm^{-3} . Species: 1, $(\text{CH}_3)_3\text{Hg}^+$; 2, $(\text{CH}_3)_3\text{Hg}(\text{OH})^+$; 3, $(\text{CH}_3)_3\text{HgCl}^+$; 4, $(\text{CH}_3)_3\text{Hg}(\text{SO}_4)^+$.

Table 6. Literature Comparison

reaction	$t/^\circ\text{C}$	$I/\text{mol dm}^{-3}$	$\log K^a$	ref ^b
$(\text{CH}_3)_3\text{Hg}^+ + \text{OH}^-$	20	0.1 (NaNO_3)	9.37	a
	25	0.1 (KNO_3)	$[-4.56]^c$	b
	25	dil.	9.5 ± 0.1	c
	25	1 (NaNO_3)	$[-4.69]^c$	e
	25	0.1 (KNO_3)	9.00	g
	25	0.15 (NaClO_4)	9.18	h
$(\text{CH}_3)_3\text{Hg}^+ + \text{Cl}^-$	25	0	$[-4.53]^c$	this work
	20	0.1 (NaNO_3)	5.25	a
	25	0	5.45	c
	25	1 (NaClO_4)	5.32	f
$(\text{CH}_3)_3\text{Hg}^+ + \text{SO}_4^{2-}$	25	0	5.45	this work
	25	0.7 (Na_2SO_4)	0.94	d
	25	0	2.64	this work

^a Formation constants; equilibrium: $(\text{CH}_3)_3\text{Hg}^+ + \text{OH}^- = (\text{CH}_3)_3\text{Hg}(\text{OH})^+$. ^b a: Schwarzenbach and Schellenberg, 1965. b, Anderegg, 1974. c, Waugh et al., 1955. d, Rabenstein et al., 1976. e, Jawaid et al., 1978. f, Budevsky et al., 1973. g, Zanella et al., 1968. h, Alderighi, 1995. ^c Hydrolysis constants; equilibrium: $(\text{CH}_3)_3\text{Hg}^+ + \text{H}_2\text{O} = (\text{CH}_3)_3\text{Hg}(\text{OH})^+ + \text{H}^+$.

formation, only one constant has been reported (Rabenstein et al., 1976). On the whole, the agreement between our own and literature values is satisfactory. Dependence on ionic strength has never been taken into account.

Concluding Remarks. Data reported in this work allow the speciation studies of $(\text{CH}_3)_3\text{Hg}^+$ for any natural fluid to be made, in a wide range of conditions (salts and ionic strengths). The interaction of two important anions (present, e.g., in seawater), F^- and CO_3^{2-} , has not been considered here. The low concentration (seawater: F^- 0.07 mmol dm^{-3} , CO_3^{2-} 2 mmol dm^{-3}) and the reported formation constants [F^- , $\log K = 1.50$, $t = 20\text{ }^\circ\text{C}$, $I = 0.1\text{ mol dm}^{-3}$ (Schwarzenbach and Schellenberg, 1965); CO_3^{2-} , $\log K = 6.1$, $t = 25\text{ }^\circ\text{C}$, $I \leq 1\text{ mol dm}^{-3}$ (Rabenstein et al., 1976)] does not allow one to draw any conclusion about their ability to interact with $(\text{CH}_3)_3\text{Hg}^+$.

By considering our own and literature values, we can give the following recommended (R) and tentative (T) thermodynamic parameters:

(a) Hydrolysis ($I = 0.1\text{ mol dm}^{-3}$, $t = 25\text{ }^\circ\text{C}$):

$$\log K = -4.51 \pm 0.05 \quad (\text{R})$$

$$\Delta G^\circ = 25.7 \pm 0.2\text{ kJ mol}^{-1}$$

(b) Chloride complex ($I = 0\text{ mol dm}^{-3}$, $t = 25\text{ }^\circ\text{C}$):

$$\log K = 5.45 \pm 0.10 \quad (\text{T})$$

ΔH° values have been reported by Schwarzenbach and Schellenberg (1965) and by Alderighi et al. (1995). For the hydrolysis of $(\text{CH}_3)_3\text{Hg}^+$ ($I = 0.1\text{ mol dm}^{-3}$, $t = 25\text{ }^\circ\text{C}$)

$$\Delta H^\circ = 20.5 \pm 0.5\text{ kJ mol}^{-1} \quad (\text{T})$$

and

$$T\Delta S^\circ = -5.2 \pm 0.6\text{ kJ mol}^{-1} \quad (\text{T})$$

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