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Kinetics and Mechanism of the Mercury(II)-Assisted Hydrolysis of Methyl Iodide

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The kinetics and mechanism of the reaction of aqueous Hg(II) with methyl iodide have been investigated. The overall reaction is best described as Hg(II)-assisted hydrolysis, resulting in quantitative formation of methanol and, in the presence of excess methyl iodide, ultimately, HgI_2 via the intermediate HgI^+. The kinetics are biexponential when methyl iodide is in excess. At 25 °C, the acceleration provided by Hg^{2+} is 7.5 times greater than that caused by HgI^+, while assistance of hydrolysis was not observed for HgI_2. Thus, the reactions are not catalytic in Hg(II). The kinetics are consistent with an S_N2-M^+ mechanism involving electrophilic attack at iodide. As expected, methylation of mercury is not a reaction pathway; traces of methylmercury(II) are artifacts of the extraction/preconcentration procedure used for methylmercury analysis.

Introduction

Methyl iodide plays a key role in the natural cycling of iodide and is the principal source of iodide to the atmosphere.[1,2] A product of both exo- and endocellular biological processes in the marine environment,[3] its annual production in seawater is estimated to be 4 × 10^{10} kg.[4] Reported concentrations of methyl iodide in open ocean waters range from 1.2 to 235 ng/L,[5] but levels can be thousands of times higher in coastal areas with intensive biomass production. Methyl iodide has been implicated in the mobilization[6] as well as the methylation[7,8] of metal ions in the environment. It has been shown to liberate metals from contaminated sediments and has been proposed as a means to recover metals from their naturally occurring ores as well as scrap.[7,9,10]

Methyl iodide reacts with metal ions in several distinct ways. With reduced metals, oxidative addition results in methylation of the metal. Reaction of methyl iodide with ores containing metal chalcogenides and pnictides results in methylation of the main group anion, illustrated by the reaction with iron(II) sulfide:[7]

$$\mathrm{FeS + 2MeI \leftrightarrows FeI_2 + Me_2S} \tag{1}$$

In cases where both ligand metathesis and metal oxidation are possible, methylation of both constituents may be observed, as is the case for tin(II) sulfide:[8]

$$\mathrm{SnS + 4MeI \leftrightarrows MeSnI_3 + Me_3S^+ + I^-} \tag{2}$$

The precise role of methyl iodide in the biogeochemical cycle of mercury has not been resolved.[11−14] In particular,

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(1) Yokouchi, Y.; Nojiri, Y.; Barrie, L. A.; Toom-Sauntry, D.; Fujinuma, Y. *J. Geophys. Res. [Atmos.]* **2001**, *106*, 12661−12668.
(2) Moore, R. M.; Groszko, W. *J. Geophys. Res. [Oceans]* **1999**, *104*, 11163−11171.
(3) Ehrich, H. L. *Geomicrobiology*; Dekker: New York, 1981.
(4) Lovelock, J. E. *Nature* **1975**, *256*, 193−194.
(5) Craig, P. J.; Rapsomanikis, S. *Environ. Sci. Technol.* **1985**, *19*, 726−730.
(6) Krishnamurthy, S. *Chem. Environ.* **1992**, *69*, 347−350.
(7) Thayer, J. S.; Olson, G. J.; Brinckman, F. E. *Environ. Sci. Technol.* **1984**, *18*, 726−729.
(8) Manders, W. F.; Olson, G. J.; Brinckman, F. E.; Bellama, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 538−540.
(9) Thayer, J. S. *Adv. Organomet. Chem.* **1975**, *13*, 1−5.
(10) Craig, P. J.; Laurie, S. H.; McDonagh, R. *Appl. Organomet. Chem.* **1998**, *12*, 237−241.
(11) Craig, P. J. *Organometallic Compounds in the Environment*; Longman: London, 1986.
(12) Weber, J. H. *Chemosphere* **1993**, *26*, 2063−2077.
(13) Hall, B.; Bloom, N. S.; Munthe, J. *Water Air Soil Pollut.* **1995**, *80*, 337−341.
(14) Tokos, J. J. S.; Hall, B.; Calhoun, J. A.; Prestbo, E. M. *Atmos. Environ.* **1998**, *32*, 823−827.

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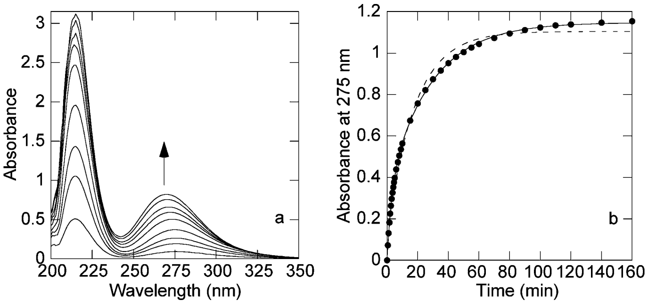

Figure 1. (a) Evolution of the UV spectrum of 0.20 mM Hg(II)(aq) in the presence of 4.0 mM MeI at 38.8 °C and pH 2.0 ($HClO_4$). (b) Kinetic profile for the reaction, showing single exponential (dashed line) and double exponential (solid line) curve fits.

its potential to methylate mercury is of concern because of the high toxicity of methylmercury(II) and its propensity for bioaccumulation and biomagnification in the food chain. Present as a thiolate complex (likely with cysteine),[15] methylmercury(II) represents up to 95% of total mercury in top predators. Methylation of Hg(II) by methyl iodide has been reported,[16] in addition to methylation of various reduced forms of mercury.[14] As part of our efforts to investigate rates and mechanisms of abiotic mercury methylation in natural waters, we undertook to examine the reaction of methyl iodide with Hg(II).

Results and Discussion

Products of the Reaction between Methyl Iodide and Hg(II). Aqueous solutions of methyl iodide kept in the dark are stable for several days, consistent with the low reported rate for uncatalyzed hydrolysis, $k_0 = 7.4 \times 10^{-8}$ s^{-1} at 25 °C.[17] No other organic components were detected by GC/FID in a methyl iodide solution incubated for 16 h at ca. 40 °C. However, in the presence of Hg(II) ions, methanol is formed rapidly. With methyl iodide in excess (2.0 mM) over Hg(II) (0.050−0.20 mM), the methanol yield was twice that of the initial concentration of Hg(II). After 12−24 h, the solutions were analyzed for monomethylmercury(II). None was detected in methyl iodide solutions in the absence of added mercury. In the presence of Hg(II), the yield was very low, <0.1%. Longer reaction times, up to 17 days, did not result in greater yields of methylmercury.

The UV spectral changes observed upon mixing weakly absorbing Hg(II) with MeI are shown in Figure 1a. They are consistent with the sequential formation of intensely absorbing mercury−iodide complexes: HgI^+ exhibits peaks at 217 and 275 nm, while maxima for HgI_2 occur at 210 and 265 nm.[18,19] The apparent displacement of the lower energy peak maximum in Figure 1a from 275 to 265 nm as the reaction proceeds suggests the initial formation of HgI^+, followed by its subsequent conversion to HgI_2. Since the corresponding spectra of HgI_3^- and HgI_4^{2-} extend further into the visible region,[19] their presence can be confidently ruled out.

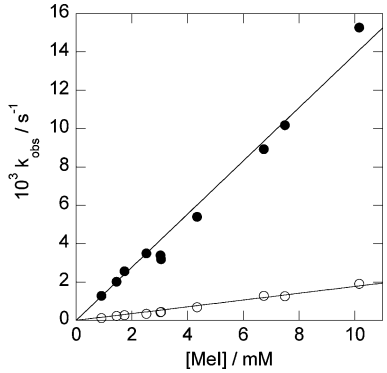

Figure 2. Dependence of pseudo-first-order rate constants k_{1obs} (filled circles) and k_{2obs} (open circles) for the aqueous reaction between Hg(II) and excess MeI on the concentration of MeI at 38.8 °C and pH 2.0 ($HClO_4$).

The yield of HgI_2(aq) was determined from the final UV spectra of the reaction mixtures, using its extinction coefficient $\epsilon_{265} = 5500$ M^{-1} cm^{-1}. HgI_2 was found to be formed quantitatively (within experimental error). The overall reaction stoichiometry can therefore be represented by eq 3:

$$2MeI + Hg^{2+} + 2H_2O \rightarrow 2MeOH + HgI_2 + 2H^+ \quad (3)$$

Kinetics of the Reaction between Excess Methyl Iodide and Hg(II). At ca. 40 °C, changes in the UV spectrum occur on a sufficiently rapid time scale to allow ready monitoring of the kinetics. The course of the reaction was monitored as the increase in absorbance at 275 nm, Figure 1b. The time evolution of the absorbance change is poorly described by a single-exponential function but is better described by a biexponential function:[20]

$$A_t = A_\infty + \alpha e^{-k_{1obs}t} + \beta e^{-k_{2obs}t} \quad (4)$$

Two pseudo-first-order rate constants, k_{1obs} and k_{2obs}, were obtained from a five-parameter (Abs$_\infty$, α, β, k_{1obs}, k_{2obs}) nonlinear least-squares fit of the experimental data to eq 4. Both observed rate constants depend linearly on the concentration of excess methyl iodide, Figure 2. From the slopes of these curves, the values of the second-order rate constants are $k_{fast} = 1.31 \pm 0.06$ M^{-1} s^{-1} and $k_{slow} = 0.176 \pm 0.003$ M^{-1} s^{-1} at 38.8 °C and pH 2.0.

The biexponential form of the kinetics for the reaction of Hg(II) when methyl iodide is in excess indicates a mechanism involving consecutive reactions. Furthermore, the shift in peak maximum from 275 nm (characteristic of HgI^+) to 265 nm (characteristic of HgI_2) as the reaction proceeds suggests that these two complexes are formed sequentially:

$$Hg^{2+} + MeI + H_2O \rightarrow HgI^+ + MeOH + H^+ \quad (5)$$

$$HgI^+ + MeI + H_2O \rightarrow HgI_2 + MeOH + H^+ \quad (6)$$

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(15) Harris, H. H.; Pickering, I. N.; George, G. N. *Science* **2003**, *301*, 1203.

(16) Ebinghaus, R.; Wilken, R. D. *Appl. Organomet. Chem.* **1993**, *7*, 127−135.

(17) Rudakov, E. S.; Zamashchikov, V. V.; Belyaev, V. D.; Gushchina, E. G. *Reakts. Sposobn. Org. Soedin.* **1971**, *8*, 219−236.

(18) Templet, P.; McDonald, J. R.; McGlynn, S. P. *J. Chem. Phys.* **1973**, *56*, 5746.

(19) Griffiths, R.; Anderson, R. A. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2361−2374.

(20) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1981; p 281.

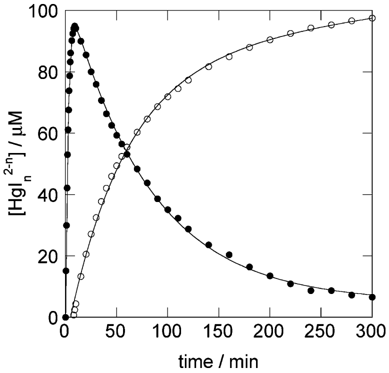

Figure 3. Kinetic profiles for the formation of HgI^+ (filled circles) and HgI_2 (open circles) extracted from the UV absorbance spectra in the reaction of 0.10 mM Hg(II) with 2.0 mM MeI at 38.8 °C, pH 2.3 ($HClO_4$), and 0.010 M ionic strength ($HClO_4$/$NaClO_4$). Solid lines are 5-parameter fits to eq 4 (see text).

The kinetic profiles are insensitive to the presence or absence of oxygen, implying that methyl radicals are not involved. Both rate constants are independent of the initial concentration of the limiting reagent, Hg(II), and the ionic strength. The latter is consistent with a mechanism involving at least one uncharged reactant, i.e., MeI.

Although kinetic ambiguity precludes the direct assignment of fitted values for k_{fast} and k_{slow} to individual elementary reactions in a consecutive mechanism,[20] it is reasonable to assume that k_{fast} corresponds to the reaction of excess methyl iodide with Hg^{2+}, since its affinity for iodide ($K_1 = 6.4 \times 10^{12}$) is higher than that of HgI^+ ($K_2 = 1.3 \times 10^{11}$).[21] The concentrations of each mercury−iodide complex were calculated from absorbance values at 275 and 265 nm in individual spectra recorded during the course of the reaction with methyl iodide, using measured extinction coefficients for HgI^+ and HgI_2 at each wavelength. Figure 3 shows the initial formation of HgI^+, whose concentration passes through a maximum and then decreases as it is converted to HgI_2. The latter begins to appear after a short induction period, corresponding to the time at which [HgI^+] passes through its maximum. Biexponential curve fits of each of the individual concentration profiles yield the same values for k_{1obs} and k_{2obs} as biexponential fits to the overall absorbance time profile.

Effect of Iodide. The kinetic profiles remain distinctly biphasic, and the magnitudes of the second-order rate constants are unchanged by the addition of small amounts of iodide ion, up to 0.32 mM in a 0.50 mM Hg^{2+} solution. However, when 0.50 mM iodide was added to a 0.50 mM Hg(II) solution, the kinetics of the reaction upon addition of 10.0 mM methyl iodide became pseudo-first-order, Figure 4. Under these conditions, Hg(II) is immediately converted to HgI^+, which is responsible for the high initial absorbance (ca. 0.8) at 275 nm. The primary reaction occurring in these solutions is that shown in eq 6. From the fitted value of k_{obs} = 0.001 52 ± 0.000 02 s^{-1}, the second-order rate constant is calculated to be 0.160 ± 0.002 $M^{-1}\ s^{-1}$, in reasonable agreement with the value for k_{slow}, 0.115 $M^{-1}\ s^{-1}$, obtained under biphasic reaction conditions at this pH (see below). This further confirms our assignment of rate constants in the consecutive mechanism, eqs 5 and 6.

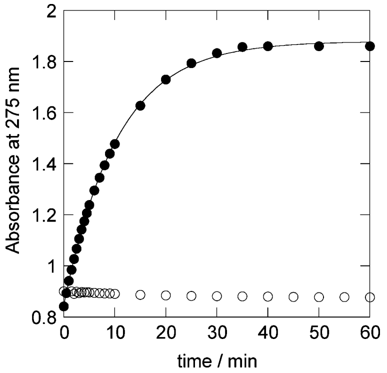

Figure 4. Kinetic profiles for the reactions of (a) 0.50 mM HgI^+ with 10.0 mM MeI (filled circles) and (b) 0.20 mM HgI_2 with 5.0 mM MeI (open circles), at 38.8 °C, pH 2.3, and $\mu = 0.10$ M ($HClO_4$/$NaClO_4$). The solid line is the single-exponential fit to the experimental data.

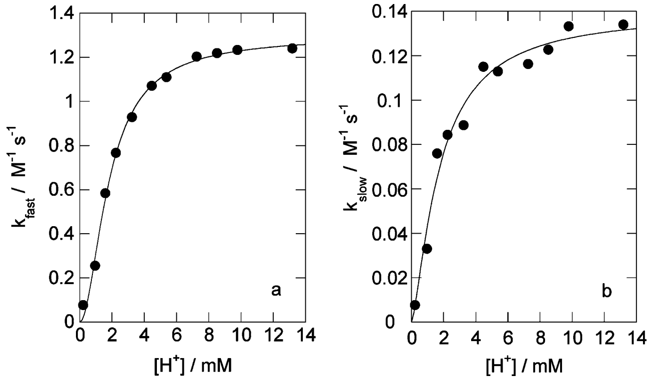

Figure 5. Dependence of the second-order rate constants k_{fast} and k_{slow} for the aqueous reaction of Hg(II) with MeI on the concentration of hydrogen ion, at 38.8 °C and 0.050 M ionic strength ($HClO_4$/$NaClO_4$). The solid lines are nonlinear curve fits to eqs 10 and 11, respectively (see text).

At higher concentrations (i.e., [I^-] > [Hg(II)]), iodide inhibits the reaction with methyl iodide completely. Thus no reaction was detected when a solution containing 0.20 mM Hg(II) and 0.40 mM I^- was mixed with 5.0 mM CH_3I, Figure 4. Under these conditions, mercury is initially converted to HgI_2, which is unreactive toward methyl iodide.

pH Dependence of the Rate Constants. Both second-order rate constants k_{fast} and k_{slow} depend on the concentration of hydrogen ion and show saturation behavior at high [H^+], Figure 5. The pH dependence of the rate constants implies that the Hg(II) reactants are subject to preequilibrium hydrolysis:

$$Hg^{2+} + H_2O \leftrightarrows HgOH^+ + H^+ \quad K_{a1} \tag{7}$$

$$HgOH^+ + H_2O \leftrightarrows Hg(OH)_2 + H^+ \quad K_{a2} \tag{8}$$

$$HgI^+ + H_2O \leftrightarrows Hg(I)(OH) + H^+ \quad K_{a3} \tag{9}$$

According to this scheme, the acid dependence of the rate constants will be described by eqs 10 and 11, assuming that Hg^{2+} and HgI^+ are reactive species, while

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(21) Hepler, L. G.; Olofsson, G. *Chem. Rev.* **1975**, *75*, 585−602.

Table 1. Temperature Dependence of Intrinsic Second-order Rate Constants[a] for the Reactions of Hg(II) with MeI

temp, °C	k_1, M^{-1} s^{-1}	k_2, M^{-1} s^{-1}
11.5	0.165 ± 0.003	0.019 ± 0.001
20.6	0.382 ± 0.004	0.045 ± 0.002
29.5	0.83 ± 0.02	0.115 ± 0.001
38.8	1.43 ± 0.06	0.234 ± 0.003
48.1	2.31 ± 0.03	0.456 ± 0.004

[a] Calculated by correcting k_{fast} and k_{slow} for their $[H^+]$ dependence using eqs 10 and 11, using fitted values for K_{a1}, K_{a2}, and K_{a3} determined at 38.8 °C.

$HgOH^+$ and Hg(I)(OH) are not:

$$k_{fast} = k_1[H^+]^2/(K_{a1}K_{a2} + K_{a1}[H^+] + [H^+]^2) \qquad (10)$$

$$k_{slow} = k_2[H^+]/(K_{a3} + [H^+]) \qquad (11)$$

The three-parameter fit of the data in Figure 5a to eq 10 yields the intrinsic rate constant $k_1 = 1.34 \pm 0.02$ M^{-1} s^{-1} and the acid dissociation constants $K_{a1} = (3 \pm 2) \times 10^{-4}$ and $K_{a2} = (2.3 \pm 0.4) \times 10^{-3}$, at 38.8 °C and $\mu = 0.050$ M. (Note: equilibrium constants are dimensionless. They are defined in terms of relative activities, $a = C/C^0$, using the standard state for solutes $C^0 = 1$ mol/L.) The fitted values of K_{a1} and K_{a2} are comparable to literature values for the sequential hydrolysis of Hg^{2+} at 25 °C, 2.6×10^{-4} and 2.6×10^{-3}.[21] The unusual ordering $K_{a1} < K_{a2}$ is well-known[22] and is likely a consequence of the change in coordination number from $Hg(H_2O)_6^{2+}$ to $Hg(OH)_2$.[23] The two-parameter fit of the data in Figure 5b to eq 11 yields $k_2 = 0.16 \pm 0.01$ M^{-1} s^{-1} and $K_{a3} = (2.2 \pm 0.4) \times 10^{-3}$. The fitted value of K_{a3} is somewhat greater than the literature value 1.2×10^{-4} calculated from the reported equilibrium constants for the binding of iodide to Hg^{2+}, 6.4×10^{12}, and the formation of Hg(I)(OH) from Hg^{2+}, I^-, and H_2O, 7.9×10^8, at 25 °C.[21] Instead, our results suggest that the acidities of $HgOH^+$ and HgI^+ are similar (i.e., $K_{a2} \approx K_{a3}$).

Effect of Temperature on the Rate Constants. Values of the pH-independent rate constants k_1 and k_2 determined between 10 and 50 °C are collected in Table 1. Both show a similar temperature dependence, in which the magnitude of each rate constant approximately doubles for each 10 °C increase in temperature. The Eyring plots are linear, Figure 6, and activation parameters were obtained from their slopes and intercepts.[20] The values of $\Delta H_1^‡$ and $\Delta S_1^‡$ (corresponding to the elementary reaction shown in eq 5) are 53 ± 3 kJ mol^{-1} and -74 ± 5 J mol^{-1} K^{-1}, respectively. For $\Delta H_2^‡$ and $\Delta S_2^‡$ (corresponding to the elementary reaction shown in eq 6), values are 64 ± 2 kJ mol^{-1} and -52 ± 2 J mol^{-1} K^{-1}, respectively. The uncertainties are based on the propagation of errors.[24]

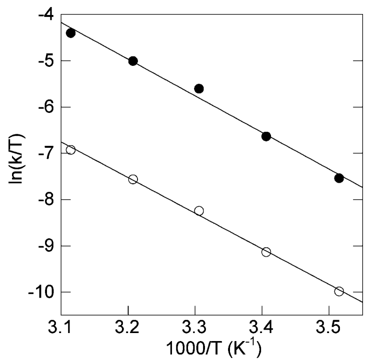

Figure 6. Eyring plots for the intrinsic second-order rate constants k_1 (filled circles: slope −6318.7 K, intercept 14.839) and k_2 (open circles: slope −7716.8 K, intercept 17.522).

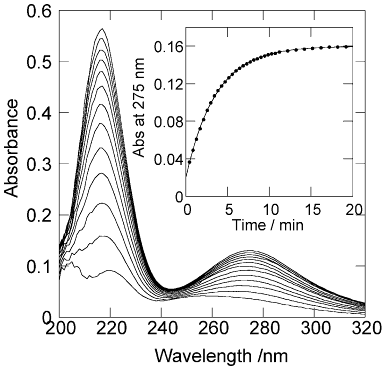

Figure 7. Evolution of the UV spectrum of an aqueous mixture of 10.0 mM Hg(II) and 0.10 mM MeI at 30.0 °C, pH 2.3 ($HClO_4$), and 0.010 M ionic strength ($HClO_4/NaClO_4$). Total time elapsed: 30 min. The inset shows the kinetic profile at 275 nm. The solid line is the single-exponential fit to the experimental data.

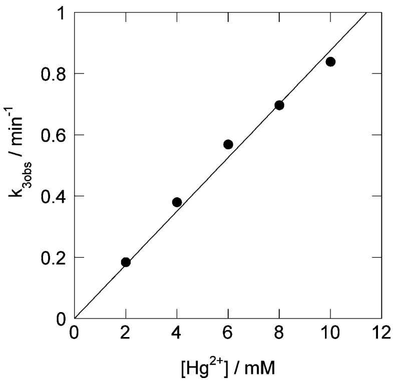

Figure 8. Dependence of the pseudo-first-order rate constants k_{3obs} for the reaction between excess Hg(II) and MeI on the concentration of Hg(II) at 30.0 °C and pH 1.0 ($HClO_4$).

Kinetics of the Reaction between Excess Hg(II) and MeI. When the pseudo-first-order condition was reversed, such that Hg(II) was in large excess over methyl iodide, the spectral changes observed were those shown in Figure 7. In contrast to the results described above, the peak maximum at 275 nm does not shift over the course of the reaction and the kinetic profile is no longer biexponential. The inset to Figure 7 shows the data fit to a single-exponential function.

Values of the pseudo-first-order rate constants k_{3obs} measured at pH 1.0, 0.10 M ionic strength, and 30.0 °C depend linearly on the concentration of Hg(II), Figure 8. These observations are consistent with the occurrence of a single reaction, corresponding to eq 5. The second-order rate constant for this reaction is 1.46 ± 0.03 M^{-1} s^{-1}, compared to 1.35 ± 0.02 M^{-1} s^{-1} obtained for k_1 under the conditions

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(22) Hietanen, S.; Sillen, L. G. *Acta Chem. Scand.* **1952**, *6*, 747−758.

(23) Cotton, A. F.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: Toronto, 1980; p 603.

(24) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646−1655.

of excess MeI at the same temperature and pH, and further confirming the attribution of rate constants in the consecutive mechanism.

Mechanism of the Reaction between Hg(II) and Methyl Iodide. Our results show that the major, if not only, interaction of Hg(II) with methyl iodide is its electrophilic promotion of hydrolysis. Methylmercury, while detected in trace amounts, is probably not a reaction product. We recently showed that the commonly used preconcentration/extraction analysis method gives methylmercury artifacts at these levels when Hg(II) solutions are analyzed, even in the absence of added methylating agent.[25]

The rates of solvolysis of alkyl halides have long been known to be strongly accelerated in the presence of certain metal electrophiles, in particular by those with high MX^{n+} stability constants, such as Ag(I), Hg(II), and Tl(III).[26−28] The rate enhancement is often accompanied by dramatic changes in selectivity, for example, in the yields of elimination, rearrangement, and racemization. In metal cation-assisted hydrolysis, the role of the electrophile is to replace the departing X^- by the better leaving group $MX^{(n-1)+}$. This is analogous to the well-known role of metal cations, especially Hg(II), in inducing the aquation of transition metal complexes via the formation of [M−X−Hg] intermediates.[29]

Although the metal cation is often described as a catalyst, it is not always clear that a catalytic effect exists.[27] For primary and secondary alkyl halides, the mechanism of electrophilically assisted hydrolysis is S_N2-M^+, and the transition state for methyl halides is described as $[H_2O^{\delta+}\cdots H_3C^{\delta+}\cdots X^{\delta-}\cdots M^{n+}]$.[26−28] Large negative values for $\Delta S_1^\ddagger$ and $\Delta S_2^\ddagger$ are consistent with the expected pre-equilibrium association of Hg(II) and methyl iodide,[28] although no UV spectral changes associated with the formation of intermediates $[MeIHg^{2+}]$ or $[MeIHgI^+]$ were detected.

The rate constant for the reaction of excess Hg^{2+}(aq) with MeI was previously reported to be 1.45 M^{-1} s^{-1} (25 °C, 0.05 M HNO_3),[17] compared to our value for k_1 (0.51 M^{-1} s^{-1}), interpolated for 25 °C using the activation parameters reported here. However, since Hg(II) was used in excess in the earlier study, it was not clear whether the role of the metal cation was catalytic. Our results show that electrophilic assistance of the hydrolysis of methyl iodide is stoichiometric, not catalytic, in Hg(II). The binding of iodide to the Hg^{2+} cation attenuates its electrophilicity, although HgI^+ is slightly more effective at promoting the hydrolysis of MeI ($k_1/k_2 = 7.5$ at 25 °C) than the ratio of the sequential formation constants for HgI^+ and HgI_2 would predict ($K_1/K_2 = 49$ at 25 °C).[21] This phenomenon has been attributed to "inductive retardation": the stronger the Lewis acid, the lower the S_N2 character of the transition state.[26] However, the fraction of hydrolysis occurring by the S_N1-M^+ mechanism (relative to the fraction of the reaction occurring as S_N2-M^+) is still expected to be very low for methyl iodide. In fact, it was estimated previously at only 0.04%.[17]

HgI_2 is ineffective in promoting the hydrolysis of methyl iodide due to its much lower iodide affinity compared to HgI^+ ($K_2/K_3 = 2.1 \times 10^7$ at 25 °C).[21] Furthermore, since HgX_2 (X = OH, Cl) is more abundant in natural (fresh) waters than electrophilic Hg^{2+} and HgX^+, we conclude that Hg(II) is unlikely to react directly with methyl iodide in the aquatic environment.

Experimental Section

Reagents. All solutions were prepared with distilled deionized (18 MΩ Milli-Q Plus) water in glass bottles and handled with all-glass syringes and analytical micropipets (Eppendorf). Glassware was soaked overnight in 10% HNO_3, rinsed with copious amounts of distilled deionized water, and stored capped and filled with deionized water until prior to use.

Stock solutions of 20 mM mercury(II) perchlorate were prepared by dissolving red HgO (99.999%, Aldrich) in 0.2 M $HClO_4$ (Analr, 70%) followed by dilution with water. These solutions were standardized by titration with KSCN (Baker ACS reagent) to the ferric alum end point.[30] Stock solutions were diluted daily, prior to kinetic experiments. Solutions of potassium iodide and HgI_2 were prepared by dissolving a measured amount of KI (Aldrich ACS reagent 99%,) or red HgI_2 (Aldrich ACS reagent 99%), respectively, in water. HgI_2 solutions were stirred for ca. 2 h at ca. 50 °C to ensure complete dissolution and were prepared at concentrations lower than the reported solubility (6 g/100 g of water).[31] HgI^+ solutions were prepared by mixing the appropriate volumes of solutions of mercury(II) perchlorate and KI. The methylmercury standard was prepared by dissolving approximately 20 mg of MeHgCl (Aldrich, ACS reagent, 99%) in 20 mL of methanol (EM Science, ACS reagent, 99.91%) to yield a stock solution of approximately 1000 ppm. Further dilutions with water were made as needed.

Methyl iodide (99%, Aldrich) was vacuum-distilled at room temperature to a liquid nitrogen trap to remove traces of adventitious iodide. Stock solutions were prepared daily in glass bottles sealed with white rubber septa and minimal headspace, to minimize losses due to volatilization. Due to its limited solubility in water, concentrations were limited to less than 80 mM. Dilute perchloric acid solutions were prepared from concentrated $HClO_4$ (EM Science, ACS 30% solution). Ionic strength was established with $NaClO_4$ (Aldrich, ACS reagent, 99%).

Kinetics and Reaction Products. The kinetics of HgI_2 formation were measured at constant temperature using a sample holder thermostated to ±0.1 °C with a circulating water bath. UV spectra were recorded on a Cary-300 UV−visible spectrophotometer in 1 cm square quartz cuvettes capped with white rubber septa (Aldrich). For variable-pH experiments, the pH was measured using a Thermo-Orion model 525 A+ pH-meter. The instrument was calibrated using two standard buffers with pH 7 and 10 (Thermo-Orion applications solutions). Solutions were stirred continuously during the pH measurements. Kaleidagraph 3.5 (Synergic Software) was used for nonlinear regression analysis of kinetic curves. An HP

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(25) Celo, V.; Ananth, R. V.; Scott, S. L.; Lean, D. R. S. *Anal. Chim. Acta* **2004**, *516*, 171−177.

(26) Rudakov, E. S.; Kozhevnikov, I. V.; Zamashchikov, V. V. *Russ. Chem. Rev.* **1974**, *43*, 305−316.

(27) Kevill, D. N. In *The Chemistry of Functional Groups*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1983; Suppl. D, pp 933−984.

(28) Zamashchikov, V. V.; Rudakov, E. S.; Bezbozhnaya, T. V. *React. Kinet. Catal. Lett.* **1984**, *24*, 65−69.

(29) Banerjee, R. *Coord. Chem. Rev.* **1985**, *68*, 145−167.

(30) Kolthoff, M.; Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*; Macmillan: New York, 1952.

(31) Choi, S. S.; Tuck, D. G. *J. Chem. Soc.* **1962**, 4080.

6890 GC/FID equipped with a DB-1 capillary column operating isothermally at 40 °C was used directly for methanol quantitation without additional sample preparation. CH_3OH (Fisher Scientific, HPLC grade) was used as a calibration standard, with CH_3CN (Fisher Scientific, HPLC grade) as the internal standard.

For determination of methylmercury, solid-phase extraction in sulfhydryl cotton fiber (SCF) was used, followed by capillary gas chromatography−atomic fluorescence spectroscopy detection, according to a previously described procedure.[25] Analysis was performed on a HP 6890 Plus GC attached to a PS Analytical AFS mercury analyzer. A calibration curve was run with every set of experiments using methylmercury standards treated in exactly the same way as samples.

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Supporting Information Available: Values of the pseudo-first-order rate constants k_{1obs}, k_{2obs}, and k_{3obs} measured under a variety of experimental conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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