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Chemical Reactions Mediated by Heavy Metal Ions. 2. Mercury Ligation Effects on the Hg(II)-Promoted Hydrolyses of Benzaldehyde *O*-Ethyl *S*-Ethyl and *S*-Phenyl Acetals

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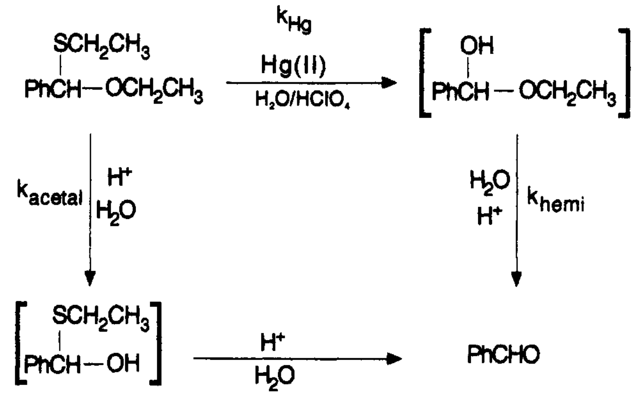
The kinetics of the mercury(II)-promoted hydrolyses of acyclic *O,S*-acetals of benzaldehyde have been measured to establish that (i) mercury(II) is a reagent, not a catalyst, in the hydrolysis reaction, (ii) the rate-limiting step can be any of the three steps in Scheme I (k_{hemi}, k_{Hg}, or k_{acetal}), depending on the concentration of mercury(II) relative to the acid, and (iii) the state of complexation of mercury(II) is critical to its reactivity. Part 1 of this series[5] established the "standard state" for all further work; this paper utilized the same controls and safeguards. The second-order rate constants for hydrolysis of benzaldehyde *O*-ethyl *S*-ethyl acetal promoted by Hg^{2+}, $HgCl^+$, $HgBr^+$, or HgI^+ is at the diffusion limit (10^9 M^{-1} s^{-1}). Rate constants for $HgCl_2$, $HgBr_2$, HgI_2, $HgCl_3^-$, and HgI_3^- are 10^6, 10^5, 10^2, 10^4, and 50 M^{-1} s^{-1}, respectively. Rate constants for hydrolysis of benzaldehyde *O*-ethyl *S*-phenyl acetal are the same, within experimental error, except for perhaps the least reactive reagents. Thus, although reagents differ in reactivity by 10^7, the reactivity toward a SEt moiety is equal to the reactivity toward a SPh moiety. A detailed mechanism is presented in which the rate-limiting step does not involve carbon–sulfur bond heterolysis, but rather one of the mercury ligation steps.

Introduction

Studies of the reactions of *O,S*-acetals have been reviewed recently.[1] The mixed acetal functionality exists in a variety of biologically important molecules, and reactions targeting sulfur are important in such systems.[2-4] Part 1 of this series[5] defined the kinetics of hydrolysis of an acyclic *O,S*-acetal promoted by mercury(II) in the presence of chloride ion. The acyclic structural feature is important because it precludes the potential return of the sulfur moiety at the spectral concentrations at which experiments are conducted, a possibility clouding some of the interpretations of earlier work which utilized cyclic organic substrates[1,6] and did not clearly delineate the acid-catalyzed process from the mercury-promoted process or rate-determining hemiacetal breakdown from rate-determining *O,S*-acetal carbon–sulfur bond breaking (k_{hemi}, k_{Hg}, and k_{acetal} in Scheme I). We have measured the kinetic constants of Scheme I and established that (1) mercury(II) is a reagent, not a catalyst in the hydrolysis reaction, (2) the rate–limiting step can be either of three steps in Scheme I (k_{hemi}, k_{Hg}, or k_{acetal}), depending on the concentration of mercury(II) relative to the acid, and (3) the state of complexation of mercury(II) is critical to its reactivity.[5] Part 1 of this series established the "standard state" for all further work; this paper employs the same controls and safeguards.

The extreme reactivity of Hg(II) and the attenuation of that reactivity on replacing aquo ligands with chloride called for an investigation of the generality of this attenuation as well as possible substrate specificities. The present study found a surprising absence of substrate specificity, at least for the more reactive combinations of reagents and substrates. The ligand effect is predictably evident over the halide series, based on the notions of hard and soft acids and bases (HSAB).

Scheme I



Experimental Section

Materials. The *O,S*-acetals were synthesized by procedures reported earlier;[5,7] benzaldehyde diethyl acetal was prepared from benzaldehyde and triethyl orthoformate.[8a] Treatment of the diethyl acetal with thionyl chloride made the α-chloro ether which, after removal of volatiles, was distilled into a cold solution of ethyl thiolate in DMF (prepared just prior to use by slow addition of ethane thiol to a stoichiometric amount of NaH in DMF). The product was characterized by proton magnetic resonance and UV spectroscopy.

All reagents were reagent grade and used as supplied, except that the perchloric acid used for conditions $<10^{-3}$ M chloride ion concentration was supplied by GFS Chemicals; this 70% perchloric acid had been double-distilled from Vycor and assayed as containing <0.00001% chloride and <0.000001% heavy metals.

Distilled water was further purified for these experiments using a Milli-Pore Milli-Q water purification system, complete with charcoal and ion-exchange cartridges; resistance of the water so purified was >10 Ω^{-1} cm.

Kinetic Methods. The standard, general computational procedures used have been described previously.[8] All rate constants were obtained using a Dionex triple-mixer stopped-flow

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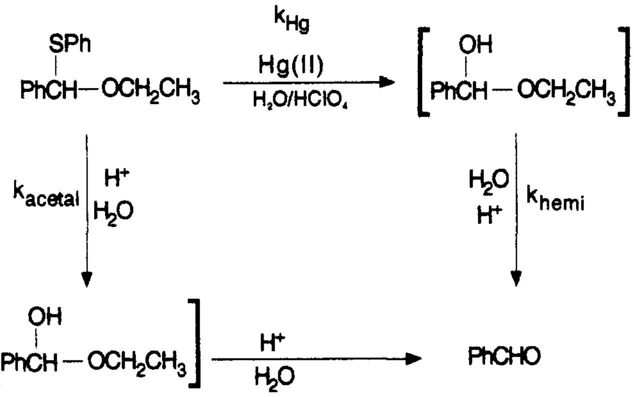
Table I. Second-Order Rate Constants for Acid-Catalyzed Hydrolyses of Substrate Acetals and Hemiacetals[a]

substrate	k_{H^+}(acetal), $M^{-1}\,s^{-1}$	k_{H^+}(hemi), $M^{-1}\,s^{-1}$
PhCH(SEt)OEt (Scheme I)	1.2[b]	600[d]
PhCH(SPh)OEt (Scheme II)	0.12[c]	600[d]

[a] Measured at 25 °C in dilute $HClO_4$ solutions (10^{-3} to 2 M); monitored at 249 nm. [b] Lit.[7] value: 1.3 $M^{-1}\,s^{-1}$ at μ = 1.0. [c] Lit.[7] value: 0.11 $M^{-1}\,s^{-1}$ at μ = 1.0. [d] Lit.[16] value: 900 $M^{-1}\,s^{-1}$ at μ = 0.1 and 30 °C.

Scheme II



spectrophotometer using a Nicolet Explorer IIIA oscilloscope to acquire time–absorbance data. The oscilloscope was interfaced to a HP 9825T desktop microcomputer equipped with a HP 7470A printer–plotter.[9] Rate constants reported are means of four kinetic runs, each consisting of a calculation based on 50–100 points. The software contains an adaptation of a classic[10] "optimization" subroutine, which treats the "infinity" absorbance as a variable in order to maximize the linear fit of the other data points to the first-order kinetic equation. It has been shown[11] that this optimization process does a good job of calculating the pseudo-first-order rate constant at the initial concentration condition in cases where ideal pseudo-first-order concentration conditions are not employed (e.g., where reactant ratios are 2:1, rather than the ideal 10:1). Of course, when the optimization calculations are employed under ideal conditions, the changes in "fit" are within experimental error. We have used this same sort of calculation previously when the "infinity" value was not experimentally accessible.[12]

Results

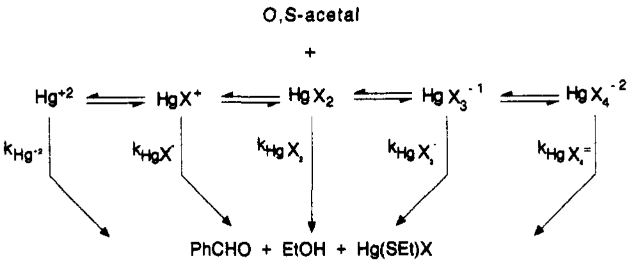
Identifying the Rate-Limiting Step. Experiments were conducted in the presence and absence of Hg(II) so as to assure that the expected kinetic orders could be experimentally observed. The reaction to be studied is the mercury-promoted hydrolysis of the *O,S*-acetal (cf. Scheme I), yet production of product requires acid so that the breakdown of the hemiacetal intermediate is sufficiently fast to assure that the mercury reaction is rate limiting. However, the *O,S*-acetal hydrolyzes slowly by an acid-catalyzed pathway, so that too high an acid concentration leads to hydrolysis by the k_{acetal} process. Thus, Table I reports the two rate constants needed for each substrate in order to assure that k_{Hg} is rate limiting.

In addition, although it does not complicate our analysis, the two hemiacetals occupying the corners of Scheme I need not be different;[7] such is the case for the hydrolysis of benzaldehyde *O*-ethyl *S*-phenyl acetal, as diagrammed in Scheme II.

Chart I

		X = Cl	X = Br	X = I
$Hg^{2+} + X^- = HgX^+$	log K_1 =	6.74	9.05	12.87
$HgX^+ + X^- = HgX_2$	log K_2 =	6.48	8.28	10.95
$HgX_2 + X^- = HgX_3^-$	log K_3 =	0.85	2.41	3.67
$HgX_3^- + X^- = HgX_4^{2-}$	log K_4 =	1.00	1.26	2.37

Scheme III



The rate constants are designated as k_{acetal} for the acid-catalyzed hydrolysis of the *O,S*-acetal, k_{hemi} for the acid-catalyzed breakdown of the hemiacetal, the k_{Hg} for the mercury-promoted step. The equations relating Schemes I and II to our experimental data are given below.

$$k_{acetal} = k_{H^+}(\text{acetal})[H^+] \qquad (1)$$

$$k_{hemi} = k_{H^+}(\text{hemi})[H^+] \qquad (2)$$

$$k_{Hg} = k_{Hg(II)}[Hg(II)] \qquad (3)$$

Using the procedures defined previously,[5] all rate constants reported herein have been unambiguously identified as k_{Hg}. Values measured for k_{H^+}(acetal) and k_{H^+}(hemi) are given in Table I.

Measurement of Ligation Effects. These experiments consisted of three series (chloride, bromide, and iodide) for each of the two *O,S*-acetals. Measurement of rate constants for a given series of mercury(II) halide complexes requires knowledge of the reactive forms of the reagents involved in the reaction. The concentrations of the various complexes can be calculated from the known equilibrium constants.[13] The various equilibria and related constants are defined by Chart I. While these equilibrium constants have been reported,[13] the error limits require that our data lose more than one significant digit in the calculations to follow. While unfortunate, this does not impact our findings because of the very large differences in reactivities observed.

The k_{Hg} defined by eq 3 is actually a composite rate constant; it is the sum of terms comprised of each of the rate constants for each of the five states of mercury defined by Chart I multiplied by the respective concentrations. This situation is diagrammed in Scheme III, and the second-order rate constants are defined in eq 4.

$$k_{Hg} = k_{Hg^{2+}}[Hg^{2+}] + k_{HgX^+}[HgX^+] + k_{HgX_2}[HgX_2] + k_{HgX_3^-}[HgX_3^-] + k_{HgX_4^{2-}}[HgX_4^{2-}] \qquad (4)$$

Inspection of Scheme III, Chart I, and eq 4 leads to the obvious conclusion the the pseudo-first-order rate constant measured for the mercury-promoted hydrolysis, k_{Hg}, will be a function of the halide concentration provided the five mercuric species exhibit different reactivities. In particular, the large differences between log K_2 and log K_3 should

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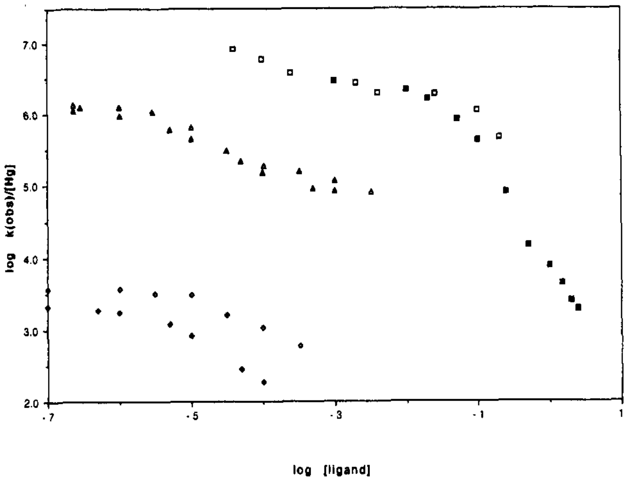


Figure 1. Effect of ligation on Hg(II)-promoted hydrolyses of benzaldehyde *O*-ethyl *S*-phenyl and *S*-ethyl acetals. Key: ■, SEt acetal, chloride ligand; □, SPh acetal, chloride ligand; ▲, SEt acetal, bromide ligand; △, SPh acetal, bromide ligand; ◆, SEt acetal, iodide ligand; ◇, SPh acetal, iodide ligand.

be evident. The change in k_{Hg} with changing $[X^-]$ for the two acetals studied is recorded in Figure 1; in all six instances (3 ligands × 2 acetals) a plateau is evident over the concentration range where HgX_2 is the predominant species. At higher ligand concentrations the rate falls off, but not as sharply as if the reactive species were limited to HgX_2; that is, other than in the plateau region, at least two terms in eq 4 contribute to the observed rate constant.

There were several experimental limitations which made it impossible to extend the curves in Figure 1 to provide data over a wider concentration range. (i) Hg(II) is a reagent; therefore, its concentration must exceed that of the *O,S*-acetal; our instrumentation required 5×10^{-6} M substrate in order to produce a reasonable signal-to-noise ratio (i.e., a minimum absorbance change of about 0.1 A was required). Thus, the Hg(II) concentration limit, coupled with the dead time of the stopped-flow instrument, placed an upper limit on rate constant measurements at low halide concentrations. (ii) The tri- and tetrahalide complexes exhibit an absorption in the UV (iodide > bromide > chloride at 250 nm); this obviates working at higher Hg(II) concentrations at high bromide or iodide concentrations. (iii) The very large size of K_1 and K_2 for iodide made it impractical to work with species other than dihalide and trihalide.

Discussion

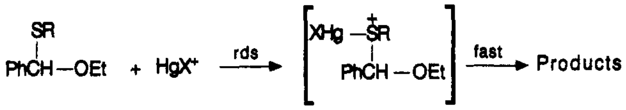
A best fit of our data (Figure 1) to eq 4 was constructed using the literature values for the complexation constants (Chart I). Because of (i) the substantial differences in the complexation constants, and (ii) the "plateau" region arising from the dominance of HgX_2 as both a reactive reagent and major species, the fit was easily done using SuperCalc 3 on an IBM PC and the calculated lines generated by the fitting procedure passes through all of the experimental points in Figure 1. The second-order rate constants defined by eq 4 are listed in Table II; their certainty is less than one significant digit because of the complexation constants on which their calculation is based. However, the significance of the results are not limited by this because of the very large changes in reactivity.

Diffusion-Controlled Reactions. Two decades ago, Eigen and Eyring[14] measured the rate of reaction of $HgCl^+$ with Cl^- in water and recommended 7×10^9 M^{-1} s^{-1} as the diffusion limit. Thus, the rate of 1×10^9 M^{-1} s^{-1} calculated for reaction of HgX^+ with the *O,S*-acetal in water seems to be at the diffusion limit, considering the uncertainties in complexation constants, the uncertainties in Eigen's value, and the difference in size between chloride and *O,S*-acetal. Hence the value of $k_{Hg^{2+}}$ is listed in Table II as 10^9 M^{-1} s^{-1}, indicating that it is at the diffusion limit as well. Our data does not afford a measured value because even at the low halide concentrations employed, $[Hg^{2+}]$ is much less than $[HgCl^+]$ which also reacts at the diffusion limit.

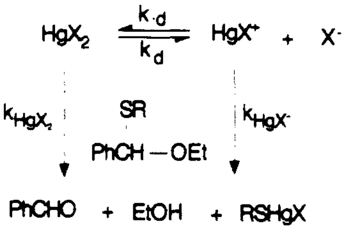
Scheme IV

	k_{diss}, s^{-1}		
	X = Cl	X = Br	X = I
$HgX^+ \rightarrow Hg^{2+} + X^-$	1.3×10^3	6.2	9.4×10^{-4}
$HgX_2 \rightarrow HgX^+ + X^-$	2.3×10^3	37	7.9×10^{-2}

Scheme V



Scheme VI



where k_{-d} and k_{HgX^+} are diffusion controlled $[10^9 M^{-1} s^{-1}]$

Using a diffusion-controlled rate constant of 7×10^9 M^{-1} s^{-1} for the reaction of the Hg^{2+} and HgX^+ species with halide and the equilibrium constants in Chart I, the first-order rate constants for the dissociation of HgX_2 and HgX^+ species may be calculated. The equations and rates of dissociation are presented in Scheme IV. These values of k_{diss} are all sufficiently slow so as to require that all mechanisms take into account possible kinetic consequences arising from such dissociations contributing to the determination of the rate-limiting step. It would be useful to know the k_{diss} values for the mercuric trihalide complex; however, since the association of the neutral HgX_2 with halide is surely far below the diffusion limit, these values cannot be calculated exactly. The relatively small values of the equilibrium constants would indicate that k_{diss} values may not be that much larger for the trihalide than for the mono- and dihalide complexes.

It is interesting to note that the rates of dissociation do not follow the "leaving group ability", as would be the case for an S_N1 reaction, for example. Rather, the rates parallel the "softness" of the ligand: chloride dissociates 10^4 to 10^6 faster than iodide, and bromide is intermediate between the two. It is also interesting to note that the more reactive chloride complexes show little difference in k_{diss} (1.8-fold), whereas the less reactive iodide complexes show a substantially greater difference in k_{diss} (84-fold). Thus, these dissociations demonstrate the general characteristics expected from the reactivity–selectivity principle.[15]

The data in Table II clearly show that the rate-limiting step for the hydrolysis of both substrates promoted by

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Scheme VII

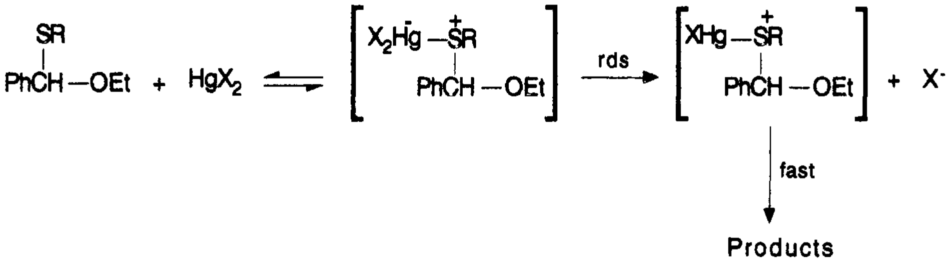

Table II. Second-Order Rate Constants for Hg(II)-Promoted Hydrolyses in the Presence of Halide[a]

	X = Cl	X = Br	X = I
Benzaldehyde *O*-Ethyl *S*-Ethyl Acetal			
$k_{Hg^{2+}}$, M^{-1} s^{-1}	10^9[b]	10^9[b]	10^9[b]
k_{HgX^+}, M^{-1} s^{-1}	1×10^9	1×10^9	9×10^8
k_{HgX_2}, M^{-1} s^{-1}	1×10^6	9×10^4	2×10^2
$k_{HgX_3^-}$, M^{-1} s^{-1}	2×10^4	*c*	5×10^1
$k_{HgX_4^{2-}}$, M^{-1} s^{-1}	*c*	*c*	*c*
Benzaldehyde *O*-Ethyl *S*-Phenyl Acetal			
$k_{Hg}{}^{2+}$, M^{-1} s^{-1}	10^9[b]	10^9[b]	10^9[b]
k_{HgX^+}, M^{-1} s^{-1}	1×10^9	1×10^9	1×10^9
k_{HgX_2}, M^{-1} s^{-1}	2×10^6	1×10^5	9×10^2
$k_{HgX_3^-}$, M^{-1} s^{-1}	1×10^4	*c*	3×10^2
$k_{HgX_4^{2-}}$, M^{-1} s^{-1}	*c*		

[a] Substrate concentrations 10^{-5} to 10^{-6} M. Second-order rate constants were calculated from data in Figure 1, based on eq 4 and Chart I. Precision is limited by the literature *K* values (Chart I) to one significant digit. [b] Not calculable from our data, but represents the diffusion limit.[14] [c] Cannot be distinguished from zero; not calculable from the data, which is limited by solubility, salt effects, etc.

Hg^{2+} and HgX^+ is association of the mercury reagent with the *O*,*S*-acetal. Thus for these reagents, the product is determined by what amounts to a trapping process as shown in Scheme V, using HgX^+ as reagent. Because the process is diffusion controlled for the HgX^+ species, there is no ligand effect evident. The kinetics are more complicated than simply Scheme V, however, because at the most dilute chloride concentrations employed, $HgCl_2$ is still the dominant species present. Thus, the k_{diss} processes defined by Scheme IV play a dominant kinetic role. The chemistry and kinetics are as shown in Scheme VI.

The velocity of the k_{HgX_2} process is less than the k_{diss} process at the concentrations of mercury(II) and substrate employed; hence, the kinetics are determined by the competition of X^- and substrate for HgX^+; since both of these processes are diffusion controlled, the fate of HgX^+ is simply a matter of the relative concentrations of substrate and X^-. The appropriate rate equation, based on this scenario, is derived as follows:

$$d[PhCHO]/dt = k_{HgX^+}[HgX^+][substrate] \qquad (5)$$

applying the steady state approximation to HgX^+ in the usual way

$$d[HgX^+]/dt = 0 = -k_{HgX^+}[HgX^+][substrate] - k_{-d}[HgX^+][X^-] + k_d[HgX_2] \qquad (6)$$

solving for $[HgX^+]$ in (6) and substituting into (5)

$$\frac{d[PhCHO]}{dt} = \frac{k_d k_{HgX^+}[HgX_2][substrate]}{k_{-d}[X^-] + k_{HgX^+}[substrate]} \qquad (7)$$

Equation 7 was incorporated into eq 4 in place of the $k_{HgX^+}[HgX^+]$ term for the purpose of fitting the data. Since we found that $k_{-d} = k_{HgX^+}$ (i.e., both are at the diffusion limit)

$$\frac{d[PhCHO]}{dt} = \frac{k_d[HgX_2][substrate]}{[X^-] + [substrate]} \qquad (8)$$

Equation 8 simply expresses the fact that when HgX_2 is the reservoir of mercury(II) and when the substrate is at spectral concentration, reducing the concentration of halide below that of the substrate simply produces k_{diss} as the rate-limiting step and the reaction would be first order in HgX_2, but zero order in substrate. (As discussed in the next paragraph, this is not possible experimentally because of Scheme VI). Conversely, at higher halide concentrations, the rate is first order in HgX_2 and substrate, but inverse first order in halide. The k_d values calculated are the same as those listed in Scheme IV, indicating that our assumptions are correct.

There is an interesting kinetic condition that occurs when HgX_2 is the only source of halide (i.e., in the absence of added NaX): according to Scheme VI loss of substrate is accompanied by formation of halide (since mercury becomes complexed to sulfur during the course of the reaction); hence, the sum [substrate] + $[X^-]$ is a constant throughout the course of the reaction. Because the binding of halide to mercury is so tight (cf. Scheme III), under these conditions the halide concentration at $t = 0$ is at least 1 order of magnitude less that substrate concentration. Thus $[substrate]_t + [X^-]_t = [substrate]_{t=0}$. This is why (i) first-order kinetics are observed under these condition of changing halide concentration and (ii) the rate constant measured under these conditions is simply $k_d = k_{HgX^+}$.

Relative Reactivities of Mercuric Halide Complexes. The range in reactivities shown in Table II is striking; certainly using mercury as a reagent for effecting hydrolysis of *O*,*S*-acetals requires careful control of ligand concentrations, as well as strict attention to reagent purity at lower ligand concentrations.

The rate constants in Table II show that the reactivity of mercury(II) in promoting the hydrolysis of *O*,*S*-acetals is increasingly diminished by complexation with halide ligands and that this diminution is iodide > bromide > chloride. All of the data in Table II are qualitatively explained by hard and soft acid/base (HSAB) precepts.[17] This is most easily viewed as a Lewis acid being titrated by basic ligands: as the mercury(II) Lewis acid is "titrated" by adding additional halide ligands, its Lewis acid reactivity is decreased. The "softer" iodide ligand titrates the mercury(II) more effectively than does the "harder" chloride.

Once again, the reactivity–selectivity relationship is evident; the reactivity of $HgCl_2$ is 10^3 below the diffusion limit, whereas HgI_2 is 10^7 below. The striking result no-

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[17] (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539. (b) Pearson, R. G. *J. Org. Chem.* **1989**, *54*, 1423–1430. (c) Pearson, R. G. *J. Am. Chem. Soc.* 1988, *110*, 7684–7690.

ticeable from Table II is that all mercury(II) complexes having fewer than two halide ligands react at the diffusion limit, and this high reactivity can be essentially "turned off" by loading the solution with halide ligand. Thus, while mercury(II) is noted for high reactivity toward sulfur in proteins, this is dependent upon the state of complexation of the mercury. As previously noted,[5] if mercury(II) is preincubated with sulfur ligands, the high Lewis acid reactivity disappears. Certainly in our chemical system, once the mercury(II) complexes with the sulfur moiety, it is effectively removed from the reaction scenario. Future work will examine the effect of ligands other than halide; however, a much more reactive system will have to be found to examine the more interesting case of thio ligands.

We have attempted to elucidate a quantitative relationship, using approaches often used to establish linear free energy relationships, but have been unsuccessful so far. One problem with the data in Table II is that they are not extensive enough. As additional data emerges, we are hopeful that the reactivities of metallocomplexes can be quantified.

Mechanism of Hydrolyses Promoted by Mercury(II). As the prior discussion emphasizes, the mechanism of these hydrolyses promoted by mercury(II) involves as much inorganic chemistry as organic; indeed, the very close similarity of the rates of hydrolysis of the *S*-ethyl and *S*-phenyl *O,S*-acetals implies that carbon–sulfur bond heterolysis is not part of the kinetics, since it is known that such heterolysis exhibits a substantial difference in reactivity toward Brønsted acids.[7] The mechanism for the diffusion controlled processes was shown in Scheme VI; the mechanism proposed for the other processes is illustrated using HgX_2.

The absence of substantial difference in rate between the two *O,S*-acetals implies that the dissociation of X^- is not concerted with carbon–sulfur heterolysis, and therefore the mechanism is shown as occurring stepwise. The plausibility of this mechanism can be demonstrated by evaluating reasonable preequilibrium constants and dissociation rate constants. The preequilibrium involves association of a soft sulfur center—a good model from Chart I would be association of a soft iodide. An estimate of 10^3 to 10^4 is reasonable. The rate constant for the rate determining step in Scheme VII will vary with X^-; using the measured rate constants from Table II and a preequilibrium constant of 10^4 gives k_{rds} of 10^2, 10, and 10^{-2} for chloride, bromide, and iodide dissociations, respectively. While these are certainly consistent with the k_{diss} values given in Scheme IV for the dihalide, they are best viewed as minimum values, since the models assumed were chosen most conservatively. The point is not to calculate the specific constants in Scheme VII but to demonstrate that perfectly reasonable values of the constants combine to produce the observed rate constant.

It is important to recognize that the rate-limiting step in Scheme VII arises because the HgX_2–acetal complex dissociates the neutral acetal preferentially to the negatively charged halide (i.e., the first step is an equilibrium) and the subsequent complex undergoes carbon–sulfur heterolysis preferentially to reassociation with halide (i.e., the second step is not reversible kinetically). We are currently examining systems which are more likely to show rate-limiting carbon–sulfur heterolysis.

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Desulfurization of Benzo- and Dibenzothiophenes with Nickel Boride

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Nickel boride, prepared from the reduction of nickel chloride hexahydrate with sodium borohydride in methanol–tetrahydrofuran, reduces benzothiophenes to alkylbenzenes and dibenzothiophenes to biphenyls. The reaction is rapid at or below room temperature and does not require protection from the atmosphere. Best results are obtained when the nickel boride is generated in situ in the presence of the sulfur compound. Hydroxyl, carboxyl, ester, and amino groups are unaffected while chloro, bromo, and nitro substituents are also reduced under these conditions. A short-lived intermediate, possibly a nickel hydride species, appears to be required in the desulfurization. Complexation of the substrate to the nickel boride surface, followed by stepwise reduction of the two C–S bonds, occurs. The faster disappearance of dibenzothiophene containing the lighter ^{32}S isotope compared to that with ^{34}S ($k(^{32}S)/k(^{34}S)$ = 1.005 to 1.006) suggests that C–S bond cleavage is the rate-determining step.

The reductive desulfurization of various types of organosulfur compounds is of importance both in the laboratory and in industry. In the former case, many synthetic procedures are based upon transformations that utilize a sulfur-containing functionality that must then be reductively removed in the final step. Moreover, the fuel processing industry is faced with increasingly stringent requirements for fuels with low sulfur content in response to mounting concerns over acid rain. Consequently, there is considerable interest in both areas in new methodology that can efficiently reduce C–S bonds to C–H bonds.

Polycyclic aromatic sulfur compounds such as benzo- and dibenzothiophenes are of special relevance because of their widespread occurrence in fossil fuels and the fact that they are particularly difficult to remove by conventional hydrodesulfurization methods.[1] Furthermore, the sulfur atom of such heterocycles has a strong directing effect towards metalations, alkylations, acylations, and other reactions.[2] Subsequent desulfurization then provides

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