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A COMPARATIVE STUDY OF LIGAND EFFECTS ON THE REACTIONS OF β-HYDROXYALKYLMERCURIALS. THE REDOX DECOMPOSITION OF β-HYDROXYPROPYLMERCURIALS AND THE PROTODEMERCURATION OF β-HYDROXYISOBUTYLMERCURIALS

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Summary

Ligand effects on the redox decomposition of β-hydroxypropylmercurials (I) ($CH_3CH(OH)CH_2HgL$ (I) $\rightarrow$ $CH_3COCH_3 + Hg^0 + H^+ + L^-$) and the protodemercuration of β-hydroxyisobutylmercurials (II) ($(CH_3)_2C(OH)CH_2HgL$ (II) $+ H^+ \rightarrow (CH_3)_3COH + Hg^{2+} + L^-$), where L = aquo ($OH_2$) and carboxylato ($OCOCF_3^-$, $OCOCHCl_2^-$, $OCOCH_2Cl^-$, $OCOCH_3^-$), have been investigated by monitoring the reaction in situ by PMR spectroscopy. The amounts of the mercurial coordinated by the aquo-ligand and the carboxylato-ligand were determined by the geminal $^{199}Hg—^1H$ spin coupling constant, $^2J(HgH)$, and the reaction rates were obtained from the peak heights in time-sequential PMR spectra. Ligand effects on the redox decomposition of I and the protodemercuration of II have been found to be opposite to each other, reflecting the different modes in the C—Hg bond dissociation. The values of $^2J(HgH)$ are useful for characterizing the ligands as the reactivity parameter for alkylmercurials.

Introduction

Hydroxymercurated olefins (β-hydroxyalkylmercurials) [1], which are formed very rapidly [2] by the reaction of olefins with aqueous mercuric salts (eqn. 1), are known as the intermediates in olefin oxidation by mercuric ions [3] in aqueous solution. Under certain reaction conditions, saturated ketones are formed exclusively [4] by the redox decomposition of the β-hydroxyalkylmercurials, which involves both an intramolecular hydrogen shift [5] and a two-electron transfer [6]. For example, propene is oxidized stoichiometrically to acetone via

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β-hydroxypropylmercurial (I) (eqn. 2). However, β-hydroxyisobutylmercurial (II) undergoes protodemercuration, yielding t-butanol (eqn. 3), instead of redox decomposition because of the lack of a migrating hydrogen.

$$R(CH_3)C{=}CH_2 + Hg^{2+} + H_2O \rightleftharpoons R(CH_3)C(OH)CH_2Hg^+ + H^+ \qquad (1)$$

(I) R = H, (II) R = CH_3

$$\underset{(I)}{CH_3CH(OH)CH_2HgL} \rightarrow CH_3COCH_3 + Hg^0 + H^+ + L^- \qquad (2)$$

$$\underset{(II)}{(CH_3)_2C(OH)CH_2HgL} + H^+ \rightarrow (CH_3)_3COH + Hg^{2+} + L^- \qquad (3)$$

The β-hydroxyalkylmercurials are so stable that the reactions can be pursued by PMR spectroscopy in situ [4,7,8] at appropriate temperatures. One of the unique features of the organomercurials is the satellite peaks appearing in PMR spectra due to the spin—spin interaction with mercury (^{199}Hg; $I = 1/2$, natural abundance 16.84%). In particular, the geminal mercury—proton spin coupling constants, $^2J(HgH)$, are very sensitive to the ligand species [9]. Accordinly, the extent of aquo-ligand coordination to the β-hydroxyalkylmercurials in aqueous solutions can be determined quantitatively, since the ligand exchange rates are sufficiently rapid on the PMR time scale. Taking advantage of this feature, we have previously investigated the reaction of mercurial I with nitrite ion [7] and formate ion [8]. We report here a comparative study of ligand effects on the redox decomposition of I (eqn. 2) and the protodemercuration of II (eqn. 3), by utilizing the values of $^2J(HgH)$ to characterize the ligands. These reactions are contrasted with each other with respect to the modes of C—Hg bond dissociation, since the former undergoes $C^+\cdots Hg^0$ heterolysis and the latter $C^-\cdots Hg^{2+}$ heterolysis.

Experimental

The PMR spectra were recorded on a Hitachi R-20B spectrometer. The probe temperatures were calibrated by the relative chemical shifts of ethylene glycol.

All the reagents and the solvents were of a G.R. grade and were used without further purification. A mercuric ion solution was prepared by adding perchloric acid to mercuric oxide suspended in water. Hydroxymercuration was effected by passing the olefin (propene or isobutene) through the solution of mercuric perchlorate at 0°C to obtain an aqueous solution of the β-hydroxyalkylmercurial *. In the kinetic experiments, a quarter of equimolar amount of aqueous mercuric perchlorate was added to the solution of the mercurial in order to retain its quantitative yield, preventing the deoxymercuration. Calculated amounts of

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* It has been found that the hydroxymercuration equilibria (eqn. 1) are displaced far to the right even in strongly acidic solutions and that the equilibrium constants (25°C), K_{eq}, for propene and isobutene are 1.2×10^7 and $>1.6 \times 10^6$, respectively [10]. On the basis of these values of K_{eq} and the saturation concentration of olefin in water (ca. 0.005 M) [11], the upper limit of unreacted mercuric perchlorate can be estimated as $<2 \times 10^{-4}$ M.

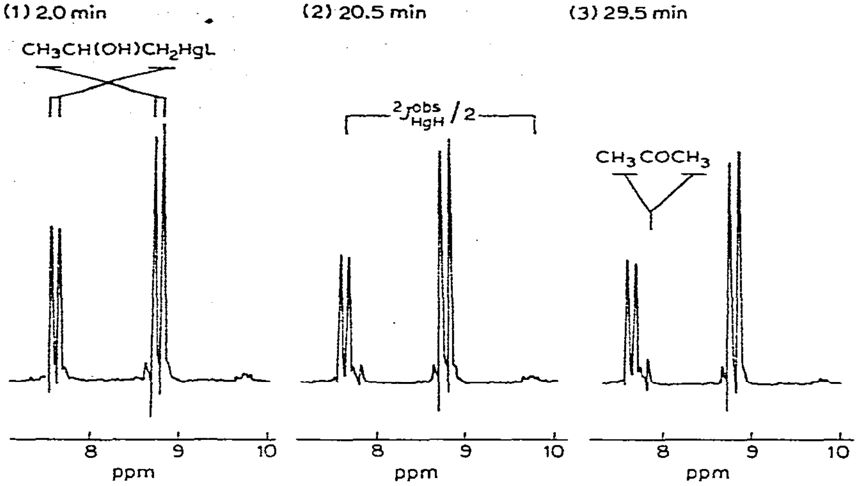


Fig. 1. The time-sequential PMR spectra obtained in situ for the redox decomposition of β-hydroxypropylmercurial in an aqueous solution at 60.0°C. Initial concentrations were 1.00 mol kg^{-1} for $CH_3CH(OH)CH_2HgClO_4$, $NaOCOCF_3$ and $HClO_4$. These spectra were taken after (1) 2.0 min, (2) 20.5 min, (3) 29.5 min from the moment of raising the solution temperature.

aqueous sodium carboxylate, NaL (L = $OCOCF_3^-$, $OCOCHCl_2^-$, $OCOCH_2Cl^-$ and $OCOCH_3^-$), prepared by the neutralization of sodium hydroxide with the corresponding carboxylic acid, except for sodium acetate, were added to the aqueous solution of the β-hydroxyalkylmercurial at 0°C. A part of the solution was transferred into a PMR tube and kept in a Dry Ice/ethanol trap. The reaction was started by inserting the tube into the probe of the PMR spectrometer; by this means the solution temperature was raised to the probe temperature and the reaction was pursued by taking the spectra in sequence.

The β-hydroxypropylmercurial (I) and the β-hydroxyisobutylmercurial (II) gave acetone (eqn. 2) and t-butanol (eqn. 3) as the sole products, respectively, under the reaction conditions adopted. The stoichiometry of the redox decomposition and the protodemercuration was ascertained by comparing the PMR peak intensities of the reactant and the product with that of the external tetramethylsilane reference in situ, as reported previously [4]. The typical time-sequential PMR spectra of the redox decomposition of I are shown in Fig. 1. Observed rate constants were determined from the peak height analysis. A doublet peak of the methyl group of I and a singlet peak of acetone were used for the redox decomposition of I, whereas the singlet peaks of the methyl groups of both II and t-butanol were utilized for the protodemercuration of II.

Results

The values of $^2J(HgH)$ and the stability constants for β-hydroxypropylmercurials (I)

It has been ascertained by Raman spectroscopy [8] that the β-hydroxypropylmercurial (I), formed by the reaction of propene with aqueous mercuric perchlorate, dissociates completely into an aquo-coordinated mercurial and free perchlorate ion, as was found for the methylmercurial [12]. Upon addition of sodium carboxylate, NaL, I is converted into a mixture of an aquo-mercurial and a carboxylato-mercurial in a rapid equilibrium as shown in eqn. 4, with the stability constant, K_s, given by eqn. 5, where the 2-hydroxypropyl group,

$$RHg^+(OH_2) + L^- \overset{K_s}{\rightleftarrows} RHgL + H_2O \tag{4}$$

$$K_s = [RHgL]/RHg^+(OH_2)][L^-] \tag{5}$$

$CH_3CH(OH)CH_2$, is abbreviated as R for the sake of simplicity. Since protons are formed stoichiometrically by the hydroxymercuration reaction (see eqn. 1), such an equilibrium as eqn. 6 exists also in the solution.

$$H_3O^+ + L^- \overset{K_h}{\rightleftarrows} HL + H_2O \tag{6}$$

$$K_h = [HL]/[H_3O^+][L^-] \tag{6a}$$

The material balance of the solution was therefore described by eqn. 7—9 (The subscript t indicates total).

$$[H^+]_t = [H_3O^+] + [HL] \tag{7}$$

$$[RHg^+]_t = [RHg^+(OH_2)] + [RHgL] \tag{8}$$

$$[L^-]_t = [L^-] + [HL] + [RHgL] \tag{9}$$

Since the aquo- and the carboxylato-ligands exchange with each other rapidly on the PMR time scale (eqn. 4), the observed value of $^2J(HgH)$, J_{obs}, is expressed as a function of the mole fractions (eqn. 10), where J_A and J_L are the inherent

$$J_{obs} = J_A x + J_L(1 - x) \tag{10}$$

values of $^2J(HgH)$ for the aquo- and the carboxylato-mercurials, respectively, and x is the mole fraction of the former. Therefore, we can adequately evaluate the amounts of these two species, using eqn. 11, from the observed value of $^2J(HgH)$ in situ, as far as we know both J_A and J_L.

$$\begin{aligned} x &= (J_{obs} - J_L)/(J_A - J_L) \\ 1 - x &= (J_A - J_{obs})/(J_A - J_L) \end{aligned} \tag{11}$$

In addition, the use of the reported values for K_h [13] (eqn. 6) makes it possible to determine the amounts of the other species (eqn. 7—9) and hence K_s of I (eqn. 5).

The values of J_L were determined by the same method as reported previously [7,8]. When the values of J_{obs} were plotted against $[RHg^+]_t/[L^-]_t$ (Fig. 2), J_{obs} decreased as the amount of NaL was increased and they finally converged to a constant value. In the case of $L = OCOCF_3^-$, however, extrapolation of the plot to the intercept was so inaccurate that the value of J_L was determined by the computer fitting method. A series of the input values proposed for J_L and the sets of the experimental data for J_{obs} and $[L^-]_t$ gave the corresponding

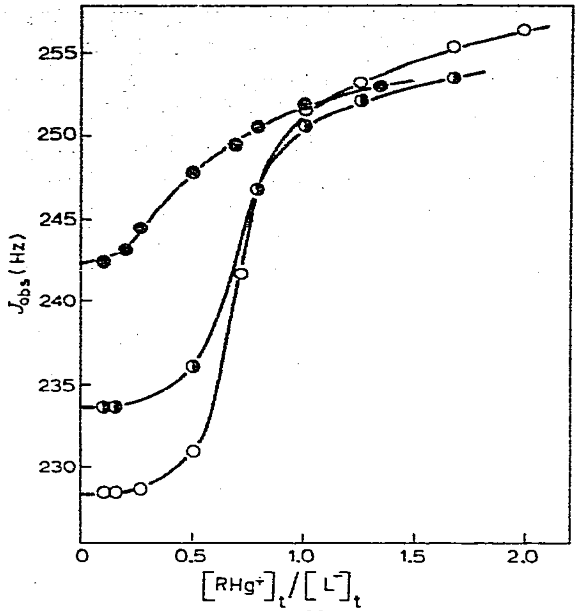


Fig. 2. Variation of geminal ^{199}Hg—^{1}H spin coupling constant with the amount of added sodium carboxylate, NaL (L = $OCOCF_3^-$ (●), $OCOCH_2Cl^-$ (◑), $OCOCH_3^-$ (○)). The total concentration of $CH_3CH(OH)CH_2Hg^+$, $[RHg^+]_t$, was commonly chosen as 1.00 mol kg^{-1}.

value of K_s, from which the series of J_{calc} were derived. The optimum value of J_L was selected so as to minimize the magnitude of $\Sigma(J_{obs} - J_{calc})^2$. The value of J_A was determined as 258.0 Hz by direct measurement of ^2J(HgH) for the aqueous solution of β-hydroxypropylmercuric perchlorate.

The geminal Hg—H coupling constants for I (J_A and J_L) and the stability constants for I (K_s) were listed in Table 1 together with the corresponding values reported for methylmercurials.

The role of carboxylato-mercurial in the redox decomposition of the β-hydroxypropylmercurials (I)

The first-order rate constants of the redox decomposition of I [4,6], k_{obs},

TABLE 1

GEMINAL ^{199}Hg—^{1}H SPIN COUPLING CONSTANTS AND LOGARITHMIC STABILITY CONSTANTS FOR β-HYDROXYPROPYLMERCURIALS (I) AND METHYLMERCURIALS

L	^2J(HgH) (Hz) [a]			log K_s [a]	
	I	CH_3HgL [b]	CH_3HgL [c]	I	CH_3HgL [b]
OH_2	258.0	260.0	(243.0) [d]	—	—
$OCOCF_3^-$	242.3	—	227.5	0.22	—
$OCOCHCl_2^-$	—	245.8	223.0	—	1.14
$OCOCH_2Cl^-$	233.7	239.2	219.0	2.31	2.19
$OCOCH_3^-$	228.3	233.3	213.5	3.82	3.18

[a] Data in H_2O solution unless otherwise stated. [b] Ref. 18. [c] Ref. 13, $CDCl_3$ solution. [d] Estimated from the linear correlation with ^2J(HgH) for I in H_2O solution.

were determined in the presence of equimolar amounts of sodium carboxylate. The rate constant for an equimolar solution of aquo-mercurial I and sodium perchlorate, k_A, was compared with the values of k_{obs}, where the initial concentrations of I were commonly chosen as 1.00 mol kg^{-1}. The logarithms of the relative observed rate constants, $\log(k_{obs}/k_A)$, were plotted against the values of ^2J(HgH) for methylmercurials, CH_3HgL, taken as the parameters indicative of σ-donor ability of the ligand L [13,14,15] (Fig. 3). It was found that the rate constant of the redox decomposition of I was proportional to ^2J(HgH). In Fig. 3 the rate constants of the protodemercuration of β-hydroxyisobutylmercurials (II) are also shown (vide infra).

Since the rate equation for the redox decomposition of I in the presence of NaL is expressed as eqn. 12, the relative rate constant, k_L/k_A, is given by eqn. 13 using the mole fractions of I.

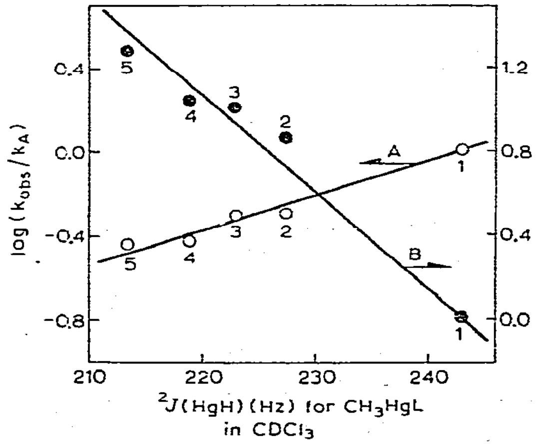
$$\begin{aligned} v &= k_{obs}\{[RHg^+(OH_2)] + [RHgL]\} \\ &= k_A[RHg^+(OH_2)] + k_L[RHgL] \end{aligned} \tag{12}$$

$$(k_L/k_A) = \{(k_{obs}/k_A) - x\}/(1-x) \tag{13}$$

The addition of NaL to the aquo-mercurial I affects the rate of the redox decomposition in two ways: one is the ligand effect caused by the coordination of L to I and the other is the neutral salt effect due to coexisting strong electrolytes, $HClO_4$ and $NaClO_4$. For the neutral salt effect, an excellent linear relationship between the rate constant of the aquo-mercurial, k_A, and the thermodynamic activities of the electrolytes was found previously (eqn. 14) [6].

$$k_A = k_{HClO_4}a_{HClO_4} + k_{NaClO_4}a_{NaClO_4} \tag{14}$$

As for L = $OCOCF_3^-$ and $OCOCH_2Cl^-$, the observed rate constants, k_{obs}, and



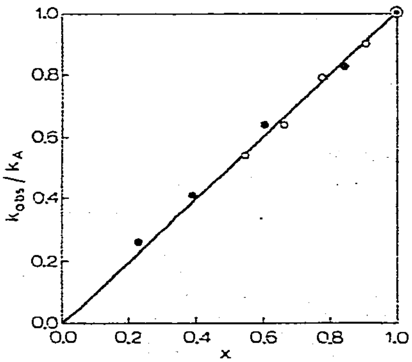


Fig. 3. Ligand effects on the reactions of β-hydroxyalkylmercurials. A: redox decomposition of β-hydroxypropylmercurials at 60.0°C. B: protodemercuration of β-hydroxyisobutylmercurials at 41.6°C. L: 1, OH_2 (aquo); 2, $OCOCF_3^-$; 3, $OCOCHCl_2^-$; 4, $OCOCH_2Cl^-$; 5, $OCOCH_3^-$.

Fig. 4. Correlation of the relative rate constant with the mole fraction of aquo-mercurial in the redox decomposition of β-hydroxypropylmercurials at 60.0°C [L = $OCOCF_3^-$ (●) and $OCOCH_2Cl^-$ (○)].

the observed geminal coupling constants, J_{obs}, were measured for the solutions in a series of the ratios of $[RHg^+]_t$ to $[L^-]_t$. The rate constants of the aquo-mercurial, k_A, with the neutral salt effects, taken into account by eqn. 14, and the mole fractions of the aquo- and the carboxylato-mercurials, calculated by eqn. 11, are summarized in Table 2. The relationships between k_{obs}/k_A and the mole fraction of the aquo-mercurial, shown in Fig. 4, were therefore represented as eqn. 15.

$$k_{obs}/k_A = x \qquad (15)$$

Since the combination of eqn. 13 and 15 leads to $(k_L/k_A) = 0$, the rate of the redox decomposition of the carboxylato-mercurial, RHgL, has been found to be negligibly slow compared with that of aquo-mercurial.

Ligand effect on the protodemercuration of the β-hydroxyisobutylmercurials (II)

The protodemercuration of the β-hydroxyisobutylmercurials (II), monitored by PMR in situ, was well analyzed on the assumption that the reaction was first-order with respect to II. The rates of the reaction of the aquo-mercurial were determined for the solutions with various concentrations of proton ($HClO_4$) and strong electrolyte ($NaClO_4$) (Table 3). A linear relationship between the observed rate constant, k_{obs}, first-order with respect to II, and the total proton concentration passing through the origin shows that the rate is also first-order with respect to proton. No appreciable variation in rate with the concentration of sodium perchlorate indicates that the reaction is zero-order in the activity of strong electrolyte in contrast with the redox decomposition of I *.

The addition of NaL to the aquo-mercurial II in aqueous solutions leads to the same situation both in equilibria (see eqn. 4—6) and in material balance (see eqn. 7—9) as found in the solution of I. The rate equation is therefore represented as eqn. 16. Eqn. 16 is convertible to eqn. 17 by using the mole fractions of II.

$$\begin{aligned} v &= k_{obs}\{[RHg^+(OH_2)] + [RHgL]\}[H^+] \\ &= \{k_A[RHg^+(OH_2)] + k_L[RHgL]\}[H^+] \qquad (16) \end{aligned}$$

$$(k_L/k_A) = \{(k_{obs}/k_A) - x[H^+]\}/(1-x)[H^+] \qquad (17)$$

Since the rate of the aquo-mercurial is independent of the added strong electrolyte, $NaClO_4$, as shown in Table 3, k_A is equal to $k_{obs}/[H^+]$ for the aqueous solution of II in the absence of NaL. The mole fractions of the aquo-mercurial (x) and the carboxylato-mercurial ($1-x$) can be evaluated from eqn. 11 in a similar manner as above. The relative rate constant, k_L/k_A, was obtained as shown in Table 4. The logarithms of k_L/k_A were plotted against the value of ^2J(HgH) for the methylmercurials (Fig. 3). It is obvious that the rate constants

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* The possibility that the reaction of II with proton involves deoxymercuration followed by acid-catalyzed hydration of the first product, isobutene, is ruled out; (1) The rate of acid-catalyzed hydration of isobutene is first-order with respect to proton [11]. Therefore, the hydroxymercuration equilibrium (eqn. 1)/hydration path should result in a second-order kinetics with respect to proton. (2) An addition of strong electrolyte causes an increase in the rate of the hydration [11].

TABLE 2

KINETIC DATA FOR THE REDOX DECOMPOSITION OF β-HYDROXYPROPYLMERCURIALS IN THE PRESENCE OF SODIUM CARBOXYLATE, NaL, AT 60.0°C

L^-	$[L^-]_t$ (mol kg^{-1})	J_{obs} [a] (Hz)	K_{obs} (10^{-5} sec^{-1})	$[H^+]$ [a] (mol kg^{-1})	$k(H)a(H)$ [b] (10^{-5} sec^{-1})	$k(Na)a(Na)$ [c] (10^{-5} sec^{-1})	k_A [d] (10^{-5} sec^{-1})	k_{obs}/k_A	x [a]
$OCOCF_3^-$	0.50	257.7	2.13	0.95	1.98	0.57	2.55	0.83	0.85
$OCOCF_3^-$	1.00	253.8	1.93	0.82	1.89	1.13	3.02	0.64	0.61
$OCOCF_3^-$	2.00	250.4	1.72	0.66	1.96	2.25	4.21	0.41	0.39
$OCOCF_3^-$	3.00	247.9	1.40	0.47	1.86	3.45	5.29	0.26	0.23
$OCOCH_2Cl^-$	0.50	257.7	1.81	0.73	1.44	0.57	2.01	0.90	0.91
$OCOCH_2Cl^-$	1.00	254.7	1.73	0.50	1.05	1.14	2.19	0.79	0.78
$OCOCH_2Cl^-$	1.25	252.0	1.40	0.36	0.78	1.41	2.19	0.64	0.67
$OCOCH_2Cl^-$	1.50	249.0	1.23	0.25	0.57	1.69	2.26	0.54	0.55

[a] Initial values before reactions occur, when initial mercurial concentrations were commonly chosen as 1.00 mol kg^{-1}. [b] $k(H) = k(HClO_4) = 2.30 \times 10^{-5}$ mol^{-1} kg sec^{-1}. [c] $k(Na) = k(NaClO_4) = 1.85 \times 10^{-5}$ mol^{-1} kg sec^{-1}. [d] k_A was calculated by eqn. 14 using the data of footenotes b and c [6].

TABLE 3

KINETIC DATA SHOWING THE DEPENDENCE OF THE RATE OF THE PROTODEMERCURATION OF β-HYDROXYISOBUTYLMERCURIAL ON THE CONCENTRATIONS OF ELECTROLYTES

Added electrolyte	[electrolyte] [a] (mol kg^{-1})	$[H^+]_t$ [b] (mol kg^{-1})	k_{obs} (10^{-4} sec^{-1})
$HClO_4$	0	1.50	0.99
$HClO_4$	0.50	2.00	1.40
$HClO_4$	1.00	2.50	1.61
$HClO_4$	1.50	3.00	1.92
$NaClO_4$	0	1.50	0.99
$NaClO_4$	0.51	1.50	1.02
$NaClO_4$	1.06	1.50	1.03
$NaClO_4$	1.41	1.50	0.99

[a] Electrolyte ($HClO_4$ or $NaClO_4$) was added to the solution containing aquo-mercurial (1.50 mol kg^{-1}) and $HClO_4$ (1.50 mol kg^{-1}) at the reaction temperature of 41.6°C. [b] Total proton concentration.

TABLE 4

LIGAND EFFECTS ON THE RELATIVE RATE CONSTANTS OF THE PROTODEMERCURATION OF β-HYDROXYISOBUTYLMERCURIALS (II) AT 41.6°C

L	[NaL] (mol kg^{-1})	[mercurial II] (mol kg^{-1})		Relative rate constant k_L/k_A
		aquo-mercurial	carboxylato-mercurial	
$OCOCF_3^-$	0.51	0.789	0.025	7.53
$OCOCF_3^-$	1.14	0.617	0.088	6.78
$OCOCF_3^-$	1.55	0.511	0.121	7.54
$OCOCHCl_2^-$	0.67	0.742	0.019	10.5
$OCOCHCl_2^-$	0.96	0.697	0.075	10.4
$OCOCH_2Cl^-$	0.70	0.642	0.078	11.5
$OCOCH_2Cl^-$	1.05	0.674	0.130	10.4
$OCOCH_3^-$	0.20	0.792	0.018	21.4
$OCOCH_3^-$	0.39	0.755	0.035	16.7

of the protodemercuration of II increase with the decrease in ^2J(HgH), in contrast with that of the redox decomposition of I.

Discussion

The values of ^2J(HgH) and the stability constants for alkylmercurials

The values of ^2J(HgH) for methylmercurials correlate linearly with those of ^2J(HgH) for β-hydroxypropylmercurials (I) (Table 1) as well as for β-methoxyisobutylmercurials, $(CH_3)_2C(OCH_3)CH_2HgL$ [15,16]. Moreover, an excellent linear relationship between the values of ^2J(HgH) and the logarithmic stability constants, $\log\{[RHgL]/[RHg^+(OH_2)][L^-]\}$, is not only pointed out for CH_3HgL [13,17,18] but also found for the mercurials I (Table 1). Thus the donor ability of the ligand L is characterized properly by the value of ^2J(HgH).

It has been claimed that the Fermi contact mechanism is dominant for the geminal Hg—H coupling constants for both the methylmercurials [19,20] and the β-oxyalkylmercurials [16]. As reported previously [15], the ligand influence on ^1J(HgC) and ^2J(HgH) for these alkylmercurials is correlated closely to the mutual polarizability of the valence *s* orbitals [21] and the C—Hg σ-bond overlap population. The value of ^2J(HgH) is therefore a good measure of the strength of the carbon—mercury σ-bonding in a series of alkylmercurials.

Ligand effects on the redox decomposition of β-hydroxypropylmercurial (I) and the protodemercuration of β-hydroxyisobutylmercurial (II)

The rates of the redox decomposition of cyclohexylmercurials (eqn. 18) were reported to decrease in the order of L = ClO_4^- > $OCOCH_3^-$ > Br^- [22], while the values of ^2J(HgH) for CH_3HgL with these ligands also decrease in the same order [9,19].

$$C_6H_{11}HgL \xrightarrow{HOAc} C_6H_{10} + C_6H_{11}OAc + Hg^0 + HL \qquad (18)$$

With respect to the redox decomposition of I, it has been found that the carboxylato-mercurial is virtually inactive in the presence of the aquo-mercurial. Therefore, the C—Hg bond cleavage apparently proceeds more easily for the mercurials with the ligands exerting larger ^2J(HgH) values, when the two-electron transfer from carbon to mercury ($C^+\cdots Hg^0$ heterolysis) takes place. It is to be noted here that the logarithms of the rate constants for the redox decomposition of aquo-coordinated β-hydroxyalkylmercurials [23] increase with an increase in the values of ^1J(HgC) for the corresponding β-methoxyalkylmercuric chlorides [24].

On the other hand, both the deoxymercuration, i.e., the reverse reaction of the oxymercuration (eqn. 1) and the protodemercuration of alkylmercurials [25] and II accompany the C—Hg bond cleavage of the type of $C^-\cdots Hg^{2+}$ heterolysis. In the deoxymercuration, the addition of NaL (e.g., L = ClO_4^-, $OCOCF_3^-$, Cl^- and Br^-) to the aqueous solution of the aquo-mercurial I in the presence of proton at room temperature results in the bond cleavage, yielding propene, for the cases of L = Cl^- and Br^-, while no reaction occurs for the cases of L = ClO_4^- and $OCOCF_3^-$ [26]. The values of ^2J(HgH) for CH_3HgL are as follows (units in Hz for chloroform or benzene solution) [13,19,24,28]: L = ClO_4^- (259.8, Bz) > $OCOCF_3^-$ (227.5, $CDCl_3$) > Cl^- (203.6, $CDCl_3$; 203.1, Bz) > Br^- (196.9, $CDCl_3$). As for the protodemercuration of alkylmercurials, Nugent and Kochi have recently reported the rate of the following reactions [25]. The logarithm of the rate constant increases linearly with the decrease in ^1J(Hg—CH_3) and

$$CH_3HgR + HOAc \rightarrow CH_4 + RHgOAc \qquad (19)$$

^2J(Hg—CH_3) for CH_3HgR [25]. In the protodemercuration of II, the logarithm of the relative rate constant for the aquo- and the carboxylato mercurial, log (k_L/k_A), also increases linearly with the decrease in ^2J(HgH) for CH_3HgL (Fig. 3). It is therefore concluded that the smaller the values of ^2J(HgH) and hence the weaker the C—Hg bond, the easier the $C^-\cdots Hg^{2+}$ heterolysis.

In summary, the value of ^2J(HgH) is a good parameter for measuring both the strength of the C—Hg bond and its reactivity, whereas the ligand effects on the $C^+\cdots Hg^0$ heterolysis of the C—Hg bond (eqn. 2 and 18) and the $C^-\cdots Hg^{2+}$ heterolysis (eqn. 3 and 19) are in a marked contrast to each other.

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