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# The Reaction of β-Hydroxyalkylmercuric Perchlorate with Sodium Formate in an Aqueous Solution

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The reaction of 2-hydroxy-1-propylmercuric perchlorate with sodium formate in an aqueous solution was found to be a redox-type reaction: $CH_3CH(OH)CH_2HgClO_4 + HCOONa = CH_3CH{=}CH_2 + Hg(0) + CO_2 + H_2O + NaClO_4$. The concentration of the mercurial coordinated by the formate ion was determined *in situ* by analyzing the geminal $^{199}Hg$–$^1H$ spin-coupling constant. By changing the ratio of $[CH_3CH(OH)CH_2HgClO_4]/[HCOONa]$, the initial reaction rate was confirmed to be first-order with respect to the formato-mercurial: $v = k[CH_3CH(OH)CH_2HgOCOH]$. From the variation in $k$ with the temperature, the values of $E_a = 17.5$ kcal mol$^{-1}$ and $A = 4.0 \times 10^8$ s$^{-1}$ were obtained. On the grounds of the kinetic isotope effect for DCOONa and the stereochemical study with *threo-* and *erythro-*$CH_3CH(OH)CHCH_3HgClO_4$, a mechanism is proposed in which the reaction proceeds solely through the unimolecular redox-decomposition of the formato-mercurial, involving an anti-elimination of olefin coupled with a two-electron transfer from the formate ligand to the mercurial.

A number of inorganic ions are known to oxidize formic acid in solution, and various mechanisms have been postulated for the redox processes.[1–5] In view of the ready redox-decomposition of β-hydroxyalkylmercurials,[6–9] it seemed of interest to investigate further the reactivity of the organomercurials through reactions with formate ions in aqueous media.

One of the unique features of the organomercurial is that it exhibits satellite peaks in the PMR spectra due to proton-mercury ($^{199}Hg$; $I = 1/2$, natural abundance 16.84%) spin-spin interactions. In particular, the geminal proton-mercury coupling constants are useful in discriminating the dissociation or coordination of ligands, since they depend characteristically on the ligand species.[10–13] Accordingly, a quantitative analysis of formate-ion coordination during the reaction becomes possible. In the present work, we wish to report the application of geminal coupling constants of organomercurials to reaction kinetics, together with an elucidation of the reaction mechanism on the grounds of the rate expression, the isotope effect, and the stereochemistry of the reaction.

## Experimental

*Reagent.* A mercuric solution was prepared by adding 28.703 g of 70% perchloric acid (0.20 mol) to 21.659 g of mercuric oxide (0.10 mol) suspended in 50 ml of water. Hydroxymercuration was effected by bubbling propene through the mercuric solution at 0 °C to obtain an aqueous 2-hydroxy-1-propylmercuric perchlorate solution quantitatively. Perchloric acid, formed stoichiometrically by the hydroxymercuration, was neutralized by an equivalent amount of sodium carbonate (5.299 g; 0.05 mol). The stock solution was prepared by diluting the solution to 100 ml with water (1.00 M; pH 0.75); the solution was then stored in a refrigerator. Aqueous *threo-* and *erythro-*3-hydroxy-2-butylmercuric perchlorate solutions were prepared in a similar manner using *cis-* and *trans-*2-butenes respectively. An aliquot of these solutions (2 to 10 ml) was used in each experiment. Sodium deuteroformate (DCOONa) of a minimum isotopic purity (atom % D) of 99% was obtained from Merck, Sharp, and Dohme of Canada, Ltd. The other chemicals were the G. R. grade, prepared by the Tokyo Kasei Co., Ltd. (Tokyo).

*Experimental Procedure.* A calculated amount of sodium formate (0.30 to 2.00 M) was added to 2 ml of the 2-hydroxy-1-propylmercuric perchlorate stock solution at 0 °C. A part of the solution maintained at 0 °C was quickly transferred to a PMR sample tube and put in the probe of the spectrometer kept at an adjusted temperature. The temperatures (45.2 to 63.2 °C) were calibrated by the relative chemical shifts of ethyleneglycol. The reaction was pursued by taking spectra in sequence with a JEOL PS-100 or a Hitachi R-20B PMR spectrometer.

In the determination of the amount of gas evolution, the solution of the reactants was introduced into a 100-ml flask connected to a vacuum line, and the amount was determined manometrically. A Hitachi RMU-6 mass spectrometer was used for the analysis of the gas-phase components. The amounts of *cis-* and *trans-*2-butenes were determined by gas chromatography using a column of 20% dimethylsulfolane on Celite.

## Results and Discussion

*Stoichiometry of the Reaction of $CH_3CH(OH)CH_2HgClO_4$ with Sodium Formate.* The aqueous solution of 2-hydroxy-1-propylmercuric perchlorate (**1**) mixed with an equimolar amount of sodium formate was stable at 0 °C, but both the evolution of gas and the precipitation of elemental mercury were observed at *ca.* 50 °C. The reaction was pursued by taking the PMR spectra of a solution containing various concentrations (0.30 to 2.00 M) of sodium formate *in situ* after the temperature of the solution had been abruptly raised from 0 °C. The concentrations of the reactants were determined from the doublet peak ($CH_3$-; δ 1.21) for the mercurials and the singlet peak (HCO-; δ 9.12) for the formate ions respectively, in comparison with the peak intensity of the external tetramethylsilane reference. Some typical representative spectra are shown in Fig. 1, in which no other absorption peaks are obviously detected.

The time-course of the respective concentrations of the reactants is presented in Fig. 2, which evidently confirms the following equations:

$$[CH_3CH(OH)CH_2Hg^+]_0 - [CH_3CH(OH)CH_2Hg^+] = [HCOO^-]_0 - [HCOO^-] \quad (1)$$

$$d[CH_3CH(OH)CH_2Hg^+]/dt = d[HCOO^-]/dt \quad (2)$$

A mass-spectrometric analysis of the evolved gas showed that the gas-phase composition was an equi-

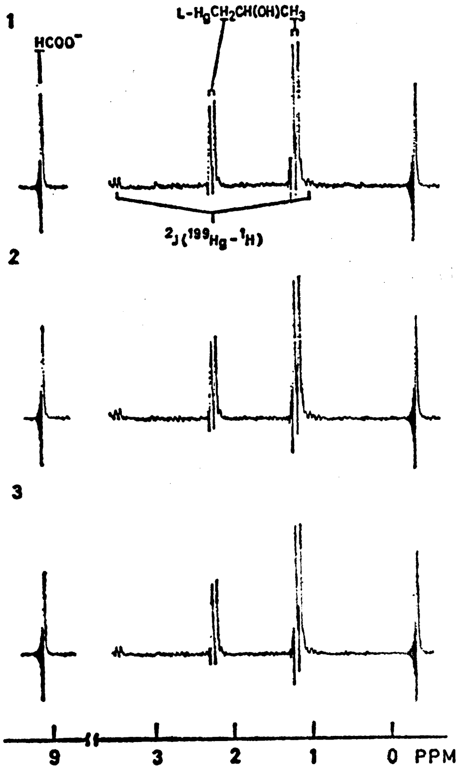

Fig. 1. The time-sequential PMR spectra obtained *in situ* for the reaction of 2-hydroxy-1-propylmercuric perchlorate with sodium formate in an aqueous solution at 51.0 °C. The unchanged singlet peak at −0.32 ppm is an absorption due to an external tetramethylsilane reference. Initial concentrations of the mercurial and sodium formate were 1.00 M and 0.70 M, respectively. These spectra were taken after (1) 14.0 min, (2) 37.0 min, (3) 136.3 min from the moment of raising the solution temperature.

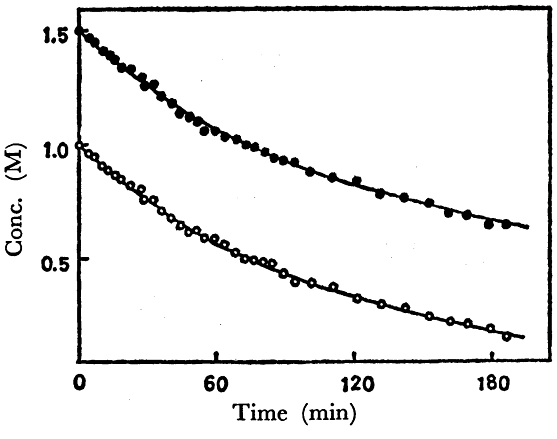

Fig. 2. The time-course of concentrations of the reactants for the reaction of 2-hydroxy-1-propylmercuric perchlorate with sodium formate in an aqueous solution at 63.2 °C. ○ and ● correspond to the mercurial and formate ions, respectively.

molar mixture of propene and carbon dioxide. No other gas, such as hydrogen or carbon monoxide, was detected by either mass-spectroscopic or gas-chromatographic analysis. It was also found by manometric measurement that the amounts of propene and carbon dioxide formed coincided (within 2%) with those of decomposed mercurials and formate ions. The stoichiometry of the reaction can, therefore, be expressed by Eq. (3), which obviously shows a redox-type reaction:

$$\begin{aligned}&\mathrm{CH_3CH(OH)CH_2HgClO_4 + HCOONa}\\&\quad = \mathrm{CH_3CH{=}CH_2 + Hg(0) + CO_2 + H_2O + NaClO_4} \qquad (3)\end{aligned}$$

*Rate Equation for the Reaction of $CH_3CH(OH)CH_2$-$HgClO_4$ with Sodium Formate.* In the solution of the reactants, mercurials are present in the forms of both an aquo-complex, $\mathrm{CH_3CH(OH)CH_2HgOH_2^+}$ (**2**),[14] and a formato-complex, $\mathrm{CH_3CH(OH)CH_2Hg}$-OCOH (**3**),[15] which are equilibrated as Eq. (4). Their ratio is reflected in the apparent value of the geminal $^{199}$Hg-$^1$H spin-coupling constant, $^2J_{\mathrm{HgH}}$, of the mercurial. Formate ions are found in the forms of ligands, free ions, and formic acid, which exchange with each other rapidly on the PMR time-scale. The peak intensities in Fig. 1 show the total amounts of the mercurials and formate ions respectively.

$$\begin{aligned}&\underset{\mathbf{2}}{\mathrm{CH_3CH(OH)CH_2HgOH_2^+}} + \mathrm{HCOO^-} \rightleftharpoons\\&\quad \underset{\mathbf{3}}{\mathrm{CH_3CH(OH)CH_2HgOCOH}} + \mathrm{H_2O} \qquad (4)\end{aligned}$$

Since any observed value of $^2J_{\mathrm{HgH}}$, $J_{\mathrm{obs}}$, is expressed as a function of the molar fractions (Eq. (5)), the amounts of both **2** and **3** can be adequately evaluated through the use of Eq. (6) by monitoring the value of $J_{\mathrm{obs}}$ *in situ*, if the inherent values of $^2J_{\mathrm{HgH}}$ for **2** and **3** ($J_{\mathrm{a}}$ and $J_{\mathrm{f}}$, respectively) are properly determined:

$$J_{\mathrm{obs}} = J_{\mathrm{a}}x + J_{\mathrm{f}}(1-x) \qquad (5)$$

$$\left.\begin{aligned}x &= (J_{\mathrm{obs}}-J_{\mathrm{f}})/(J_{\mathrm{a}}-J_{\mathrm{f}})\\1-x &= (J_{\mathrm{a}}-J_{\mathrm{obs}})/(J_{\mathrm{a}}-J_{\mathrm{f}})\end{aligned}\right\} \qquad (6)$$

where $x$ and $(1-x)$ are molar fractions of **2** and **3** respectively. As the complete dissociation of **1** had been confirmed,[14] it was possible to determine the value of $J_{\mathrm{a}}$ by simply measuring the $^2J_{\mathrm{HgH}}$ for the aqueous solution of **1** (258.0 Hz). The increase in the added amount of sodium formate caused the decrease in the value of $^2J_{\mathrm{HgH}}$ (Fig. 3). In the presence of a

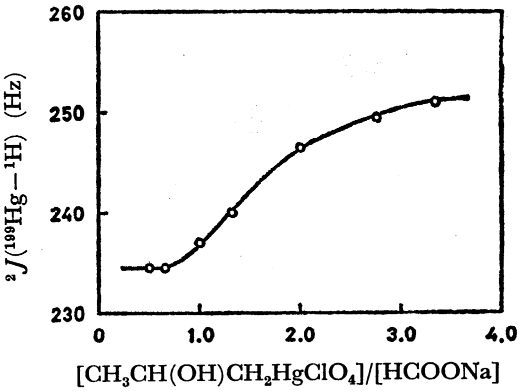

Fig. 3. Variation of geminal $^{199}$Hg-$^1$H spin-coupling constant with the amount of added sodium formate. The concentration of $\mathrm{CH_3CH(OH)CH_2HgClO_4}$ was commonly chosen as 1.00 M.

sufficient excess of sodium formate, the value became apparently constant. By extrapolating the plot to the intercept, the value of $J_f$ was determined to be 234.5 Hz. The difference in value between $J_a$ and $J_f$ is large enough for us to determine $x$ and $(1-x)$ with sufficient precision.

The reaction rates were determined for the solutions of the reactants with various ratios of [$CH_3CH(OH)$-$CH_2HgClO_4$] to [HCOONa], where the initial concentrations of the mercurial were commonly chosen as 1.00 M. The increase in the amount of added sodium formate accelerated the reaction. Further, as is shown in Fig. 4, a plot of the initial rate against the concentration of **3**, as evaluated by Eq. (6), is linear. Each of the double circles represents three experimental values of the initial rates determined for solutions with different pH values, which were controlled by added amounts of both sodium formate and perchloric acid.

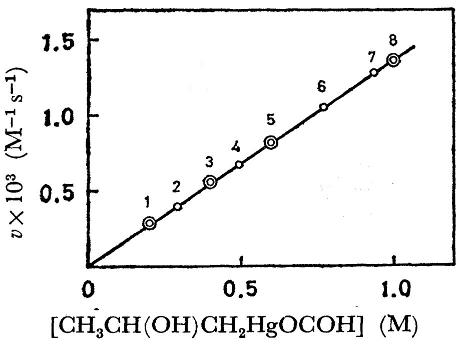

Fig. 4. Plot of initial rate *vs.* concentration of 2-hydroxy-1-propylmercuric formate at 63.2 °C.
Each point corresponds to the composition (HCOONa (M), $HClO_4$ (M)) of the solution: 1 (0.29, 0.10; pH 0.77. 0.58, 0.41; pH 0.52. 0.95, 0.82; pH 0.20), 2(0.30, 0.00; pH 1.60), 3(0.50, 0.10; pH 1.08. 0.79, 0.40; pH 0.85. 1.18, 0.80; pH 0.57), 4(0.50, 0.00; pH 1.80), 5(0.71, 0.10; pH 1.59. 1.02, 0.41; pH 1.34. 1.41, 0.81; pH 1.05), 6(0.80, 0.00; pH 2.27), 7(1.07, 0.00; pH 2.39), 8(1.50, 0.00; pH 3.41. 1.80, 0.00; pH 3.88. 2.00, 0.00; pH 4.20), where the concentration of $CH_3CH(OH)$-$CH_2HgClO_4$ was commonly chosen as 1.00 M. Initial rates were calculated from the initial linear slopes of the plots of the conversion (below 5%) *vs.* time.

The observed absence of any appreciable variation in the rate with the pH evidently shows that the reaction is zero-order in proton activity in the pH range studied.

The rate equation for the reaction of **1** with sodium formate in an aqueous solution is, therefore, given by Eq. (7). This equation shows that the reaction proceeds only when the formate ligand is coordinated:

$$v = -d[CH_3CH(OH)CH_2Hg^+]/dt = -d[HCOO^-]/dt$$
$$= k[CH_3CH(OH)CH_2HgOCOH] \qquad (7)$$
$$(k = 1.35\times10^{-3}\ s^{-1}\ \text{at}\ 63.2\ ^\circ C)$$

*Kinetic Isotope Effect for the Reaction of $CH_3CH(OH)$-$CH_2HgClO_4$ with Sodium Formate.* Experiments with DCOONa indicated a kinetic isotope effect, $k_H/k_D$, of 2.1±0.1 (the mean of three experimental values), at 51.0 °C. This effect is similar in magnitude to those for the inorganic ions,[1,2] although considerably smaller than that for $Hg^{2+}$ (3.4 at 46.5 °C).[2] The existence of the kinetic isotope effect confirms that the C–H bond of the formate ion is actually broken in the rate-determining step. Therefore, we can exclude a possible alternative path in which the slow deoxymercuration of the mercurial is succeeded by the fast oxidation of the formate ion by the free mercuric ion formed, even though this path is consistent with the data in Fig. 2. In fact, oxy-ligands are far less effective for the deoxymercuration than halo-ligands;[16] moreover, the reaction rate has been claimed to be first-order in proton activity in the case of deoxymercuration.[17,18]

*Stereochemistry of the Reactions of $CH_3CH(OH)CHCH_3$-$HgClO_4$ with Sodium Formate.* *Threo*- and *erythro*-3-hydroxy-2-butylmercuric perchlorate, obtained by the hydroxymercuration of *cis*- and *trans*-2-butenes[19] respectively, were used to determine the stereochemical nature of the reaction. Both the evolution of gas and the precipitation of elemental mercury were also observed for the reactions of these mercurials with sodium formate. The gas-chromatographic analyses of the evolved 2-butenes showed that the stereo-isomerism was completely retained in comparison with the respective starting 2-butenes. This clearly indicates that the reaction involves the stereospecific anti-elimination of olefins.

*Activation Parameters for the Decomposition of $CH_3CH$-$(OH)CH_2HgOCOH$.* From the variation in $k$ in Eq. (7) with the temperature (45.2 to 63.2 °C), the values of $E_a=17.5$ ($\pm0.5$) kcal $mol^{-1}$ and $A=4.0$ $(\pm0.9)\times10^8\ s^{-1}$ were obtained as activation parameters for the unimolecular decomposition of **3**. The activation energy, $E_a$, is of a magnitude similar to those for the inorganic ions.[1,2] The value of the pre-exponential factor, $A$, reported for the unimolecular decomposition of the $Tl^{3+}$-formate ion adduct,[2] lies near to the normal magnitude of $A$ ($\sim10^{13}\ s^{-1}$) for simple unimolecular reactions in solutions.[20] Therefore, the comparatively large reduction of $A$ for the unimolecular decomposition of **3** strongly suggests a restricted structure of the transition state.

*Structural Consideration of the Activated Complex.* Taking into consideration the results of the kinetic isotope effect and stereochemistry, the structure of the activated complex represented in Fig. 5 is proposed for the decomposition of the formato-mercurial, where the hydroxyl ion and the elemental mercury are eliminated in an anti-manner, coupled with two-electron transfer processes. The magnitude of $A$ seems to be

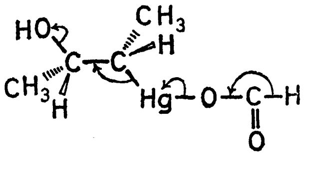

Fig. 5. Proposed structure of the activated complex for the redox decomposition of *threo*-3-hydroxy-2-butylmercuric formate.

compatible with this sterically-restricted structure. The observed stereospecificity of the reaction may be correlated with the predominant preference of antiperiplanar elimination in the $E2$ reactions.[21]

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