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THE REACTION OF HYDROXYMERCURATED PROPENE WITH SODIUM NITRITE IN AN AQUEOUS SOLUTION

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Summary

The reaction of hydroxymercurated propene with sodium nitrite in aqueous solution [$CH_3CH(OH)CH_2HgClO_4 + NaNO_2 \rightarrow CH_3CH(NO_2)CH_2$-$HgClO_4 + NaOH$] has been investigated by following the reaction in situ by PMR. The amount of the mercurial coordinated by the nitrite ions was evaluated by analyzing the geminal $^{199}Hg—^{1}H$ spin-coupling constant, and thereby rate equations were determined for both aquo- and nitrito-mercurials. The observed values of secondary deuterium isotope effects are explained in conformity with the mercurinium ion mechanism suggested previously. Activation parameters for aquo- and nitrito-mercurials are discussed in terms of ligand properties.

Introduction

In the previous communication [1], it was concluded that hydroxymercurated olefins, formed very rapidly [2] by the reaction of olefins with aqueous mercuric salts, were converted gradually into the corresponding nitromercurials in the presence of nitrite ions in aqueous media. The observed stereospecificity (retention) strongly suggested a mercurinium-ion mechanism for this substitution reaction.

As is usually observed, addition of extra salts to the solution of metallic or organometallic ions leads to the formation of different kinds of complexes, which sometimes makes the kinetic analysis of the reaction in solutions rather difficult. In the case of organomercurials, formation of complexes is conspicuously reflected in the value of geminal proton—mercury (^{199}Hg; $I = 1/2$, natural abundance 16.84 %) spin-coupling constant, ^{2}J(HgH), since it varies specifically with the type of ligand [3]. Taking advantage of this feature, analysis of the ligand during the reaction becomes possible [4].

We report here the kinetic analysis of the reaction of hydroxymercurated propene with sodium nitrite, achieved by following the reaction in situ by PMR;

the ligand species were evaluated quantitatively by monitoring the value of ^2J(HgH). In order to interpret the activation parameters for the rate constants obtained, a transition-state structure was estimated on the grounds of secondary deuterium isotope effects, which were determined in mixed-reactant solutions to ensure the identity of the reaction conditions.

Results and discussion

Proton magnetic resonance spectra

An aqueous 2-hydroxy-1-perchloratomercuripropane (I) solution was obtained quantitatively by passing propene through an aqueous solution of mercur-

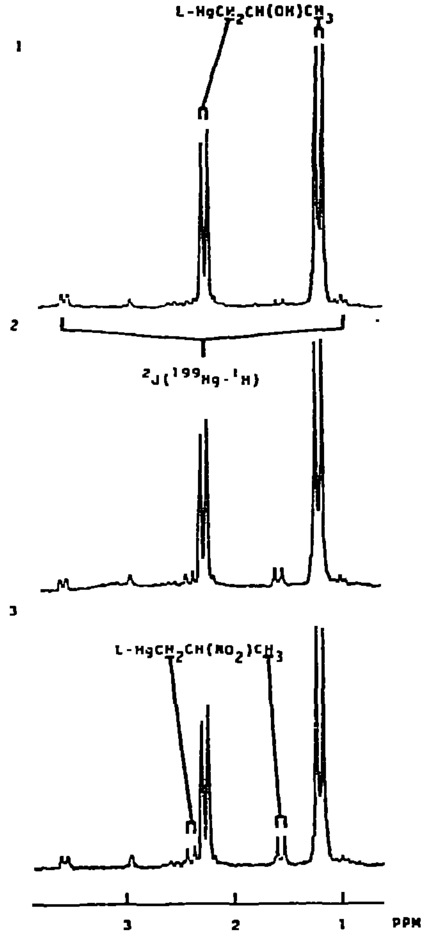


Fig. 1. The time-sequential PMR spectra obtained in situ for the conversion of the propene hydroxymercurial into the propene nitromercurial in an aqueous solution at 10.0°. Initial concentrations were chosen as 0.333 M ($CH_3CH(OH)CH_2HgClO_4$), 0.133 M ($NaNO_2$), and 0.433 M ($HClO_4$). These spectra were taken after (1) 9.3 min, (2) 56.1 min, (3) 109.2 min from the moment of raising the solution temperature.

ic perchlorate (eqn. 1). As reported previously [1], addition of sodium nitrite to this solution caused quantitative conversion of I into 2-nitro-1-perchloratomercuripropane (II) (eqn. 2). Typical representative spectra to show the process of the reaction are given in Fig. 1.

$$\underset{}{CH_3CH{=}CH_2 + Hg(ClO_4)_2 + H_2O \rightarrow \underset{\text{(I)}}{CH_3CH(OH)CH_2HgClO_4} + HClO_4} \qquad (1)$$

$$CH_3CH(OH)CH_2HgClO_4 + NaNO_2 \rightarrow \underset{\text{(II)}}{CH_3CH(NO_2)CH_2HgClO_4} + NaOH \qquad (2)$$

It was found, however, that the presence of hydronium ions was required in the solution for the substitution reaction to occur, since neutralization of the acid, formed stoichiometrically in the hydroxymercuration, with sodium carbonate inhibited the reaction completely. This feature of reaction was also pointed out for other exchange reactions of β-substituents of solvo-mercurials [5-9].

Concerning the effect of adding sodium nitrite to the neutralized solution of I, the value of ^2J(HgH) of the hydroxymercurial decreased from the initial value (258.0 Hz) gradually [10], and apparently became constant (237.5 Hz) (Fig. 2).

As was shown by Raman spectroscopy [11], methylmercuric perchlorate dissociates completely in water into perchlorate ions and $[CH_3HgOH_2]^+$ cations [ν(Hg—O) = 463 cm^{-1}]. This is also the case for I, because the Raman spectrum

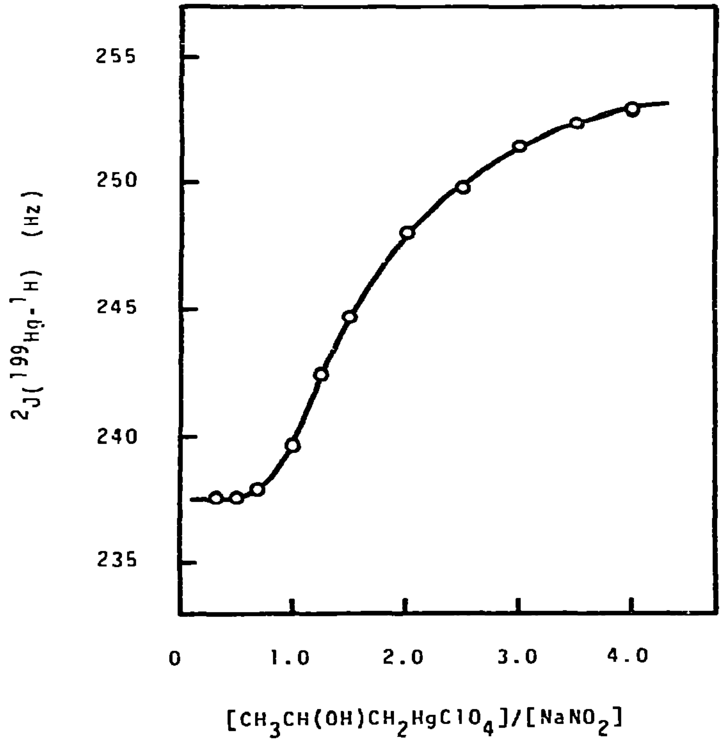


Fig.2. Variation of geminal ^{199}Hg—^{1}H spin-coupling constant with the amount of added sodium nitrite. The concentration of $CH_3CH(OH)CH_2HgClO_4$ was commonly chosen as 1.000 *M*.

showed only one absorption band at 463 cm^{-1} for the corresponding mercury—ligand stretching vibration. Accordingly, the value of 258.0 Hz is considered to be a specific value of ^2J(HgH), J_a, for the aquo-complex, $CH_3CH(OH)CH_2HgOH_2^+$ (III). The effect of the addition of sodium nitrite on the value of ^2J(HgH) is attributable to the formation of the nitrito-complex, $CH_3CH(OH)CH_2HgONO$ (IV), since the symmetric stretching vibration band of free nitrite ions (1335 cm^{-1}) in the Raman spectrum of aqueous sodium nitrite disappeared by adding an excess of I and new absorptions at 1390 and 1046 cm^{-1} appeared, which can be assigned to stretching vibrations of N=O and N—O of the nitrito-ligand, respectively [12]. We can, therefore, obtain a specific value of ^2J(HgH) for IV, J_n, by extrapolating the plot in Fig. 2 to the intercept (237.5 Hz).

As aquo- and nitrito-complexes exchange with each other rapidly on the PMR time scale (eqn. 3), any value of ^2J(HgH) observed in the course of the reaction, J_{obs}, is expressed as a function of their mole fractions (eqn. 4). On this basis, we can adequately evaluate the amounts of both III and IV in situ by applying eqn. 5 to the monitored value of J_{obs}.

$$\underset{\text{(III)}}{CH_3CH(OH)CH_2HgOH_2^+} + NO_2^- \rightleftharpoons \underset{\text{(IV)}}{CH_3CH(OH)CH_2HgONO} + H_2O \quad (3)$$

$$J_{obs} = J_a x + J_n(1 - x) \quad (4)$$

$$x = (J_{obs} - J_n)/(J_a - J_n),\ 1 - x = (J_a - J_{obs})/(J_a - J_n) \quad (5)$$

x and $(1 - x)$ are mole fractions of III and IV, respectively.

Rate expression

Addition of perchloric acid to the aqueous solution of I containing sodium nitrite caused a marked increase of the value of ^2J(HgH). This is understandable in terms of coordinated nitrite ions being withdrawn by the added protons to form nitrous acid, due to its low acidity (dissociation constant: 6×10^{-4} at 30°). If excess amounts of perchloric acid were added, mercurials were present predominantly in the form of the aquo-complex, as was confirmed by measuring ^2J(HgH). Under such a condition, initial rates were determined for the solutions with various concentrations of both sodium nitrite and perchloric acid (Table 1). These results indicate that the initial rate is proportional to both the concentrations of the aquo-complex and added sodium nitrite and is independent of the concentration of perchloric acid.

$$v_0 = k_a[NaNO_2]\ [CH_3CH(OH)CH_2HgOH_2^+] \quad (6)$$

$(k_a = 5.0 \times 10^{-3}\ M^{-1}sec^{-1};\ 35.0°)$

On the other hand, if the added amount of sodium nitrite was greater than that of perchloric acid, the value of ^2J(HgH) showed that mercurials were present predominantly in the form of the nitrito-complex. Under such a condition, initial rates were determined for the solutions with various concentrations of both sodium nitrite and perchloric acid (Table 2). In contrast to the former case, these results indicate that the initial rate is proportional to both the concentrations of the nitrito-complex and added perchloric acid and is independent of

TABLE 1

KINETIC DATA AT 35.0° SHOWING THE DEPENDENCE OF THE INITIAL RATE ON THE CONCENTRATIONS OF SODIUM NITRITE AND PERCHLORIC ACID[a]

$[NaNO_2]$ (*M*)	$[HClO_4]$ (*M*)	$v_0 \times 10^4$ [b] (*M* sec^{-1})
0.050	0.333	0.69
	0.433	0.80
	0.533	0.72
	0.667	0.87
	average	0.77
0.083	0.333	1.25
	0.433	1.40
	0.533	1.27
	0.667	1.32
	average	1.31
0.117	0.333	1.75
	0.433	1.81
	0.533	1.77
	0.667	1.90
	average	1.81

[a] Total mercurial concentrations were commonly chosen as 0.333 *M*, where mole fractions of the aquo-complex were at least 0.90 as was confirmed by the value of ^2J(HgH). [b] Initial rates were calculated from the initial linear slopes of the plots of the conversion (below 5%) vs. the time.

the concentration of sodium nitrite.

$$v_0 = k_b[HClO_4]\ [CH_3CH(OH)CH_2HgONO] \qquad (7)$$

$$(k_b = 14.3 \times 10^{-3}\ M^{-1}sec^{-1};\ 35.0°)$$

Taking into account the common-ion effect on the dissociation of weak

TABLE 2

KINETIC DATA AT 35.0° SHOWING THE DEPENDENCE OF THE INITIAL RATE ON THE CONCENTRATIONS OF SODIUM NITRITE AND PERCHLORIC ACID[a]

$[HClO_4]$ (*M*)	$[NaNO_2]$ (*M*)	$v_0 \times 10^4$ [b] (*M* sec^{-1})
0.050	0.500	2.32
	0.567	2.40
	0.633	2.50
	0.700	2.24
	average	2.36
0.067	0.500	3.38
	0.567	3.25
	0.633	3.37
	0.700	3.02
	average	3.26
0.100	0.500	4.65
	0.567	4.75
	0.633	4.60
	0.700	5.00
	average	4.75

[a] Total mercurial concentrations were commonly chosen as 0.333 *M*, where mole fractions of the nitrito-complex were at least 0.96 as was confirmed by the value of ^2J(HgH). [b] Initial rates were calculated from the initial linear slopes of the plots of the conversion (below 5%) vs. the time.

acids, both $[NaNO_2]$ in eqn. 6 and $[HClO_4]$ in eqn. 7 are approximately equal to $[HNO_2]$ under the respective conditions [13]. On this basis, we can obtain eqn. 8 or eqn. 9 as a unifying rate expression, the latter showing the presence of hydronium-ion catalysis in the reaction.

$$v_0 = k_L[HNO_2]\,[CH_3CH(OH)CH_2Hg^+L] \qquad (L = H_2O, ONO^-) \tag{8}$$

$$v_0 = k_L'[H^+]\,[NO_2^-]\,[CH_3CH(OH)CH_2Hg^+L] \tag{9}$$

$$(k_L' = k_L/K;\ [H^+]\,[NO_2^-]/[HNO_2] = K)$$

Since the rate for the mixed-complex systems can be calculated by eqn. 10 in this approximation, coincidence of experimental and calculated values of the rate was examined for solutions with various ratios of two types of the mercurials to verify the validity of eqn. 8:

$$v_0 = [NaNO_2]\,(k_a[III] + k_b[IV]),\ \text{if}\ [NaNO_2] < [HClO_4] \tag{10a}$$

$$v_0 = [HClO_4]\,(k_a[III] + k_b[IV]),\ \text{if}\ [HClO_4] < [NaNO_2] \tag{10b}$$

For a ready comparison of each value, the effective rate, v_e, is defined by eqn. 11 in terms of the observed initial rate, v_0.

$$v_e = v_0/[NaNO_2],\ \text{if}\ [NaNO_2] < [HClO_4] \tag{11a}$$

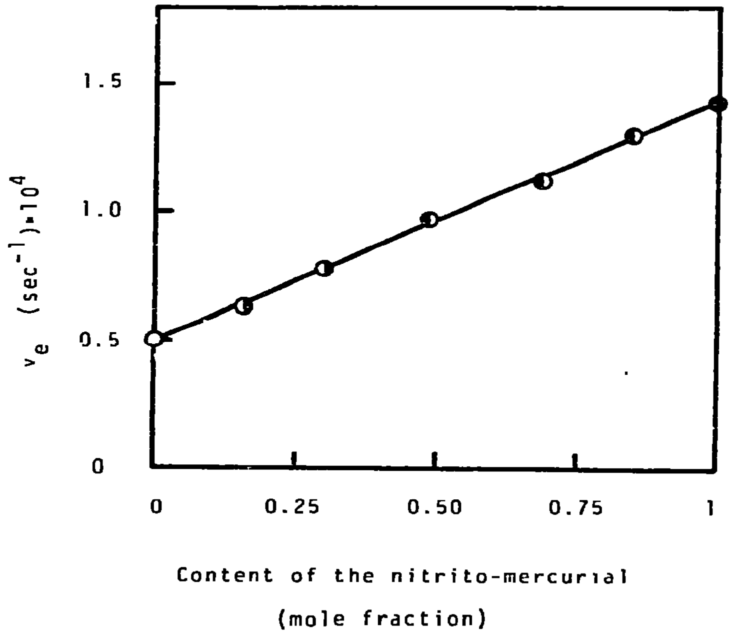


Fig. 3. Dependence of the effective rate, v_e, on the mole fraction of the nitrito-complex in the mercurial plotted in accord with eqn. 11a (◑) or eqn. 11b (◐) (35.0°, total mercurial concentration 0.333 M). The solid line represents calculated values obtained from eqn. 10 by using both the value of k_a (○) and k_b (●). Each point corresponds to the composition ($NaNO_2$ (M), $HClO_4$ (M)) of the solution: 1 (0.167, 0.200), 2 (0.333, 0.500), 3 (0.333, 0.167), 4 (0.400, 0.167), 5 (0.467, 0.167).

$$v_e = v_0/[\mathrm{HClO_4}], \text{ if } [\mathrm{HClO_4}] < [\mathrm{NaNO_2}] \qquad (11b)$$

As shown in Fig. 3, a plot of v_e vs. the composition of the mercurial was found to agree well with the calculated value (k_a[III] + k_b[IV]) represented by a solid line.

Secondary deuterium isotope effects

The usefulness of secondary isotope effects in the elucidation of reaction mechanisms seems to be well established (for a review of kinetic isotope effects see ref. 14). In order to measure the kinetic isotope effect with sufficient accuracy, it is desirable to determine each of the rates for both the labeled and unlabeled reactants in mixed solutions, because the identity of reaction conditions is thus best assured. As far as deuterium isotope effects are concerned, PMR spectroscopy appears especially suited for this purpose, due to its facility in differentiating between deuterated and undeuterated reactants in situ [15].

In order to determine the α-secondary isotope effect caused by deuteration on the carbon bonded to hydroxyl group, reaction rates were measured for the mixture of I and $CH_3CD(OH)CH_2HgClO_4$ (V) which was obtained by hydroxymercuration of propene-2-d_1. Figure 4 shows a spectrum obtained in situ in the course of the conversion of I and V into the corresponding nitromercurials in the mixed solution ($[V]_0/[I]_0 = 0.38$). Concentrations of the reactants during

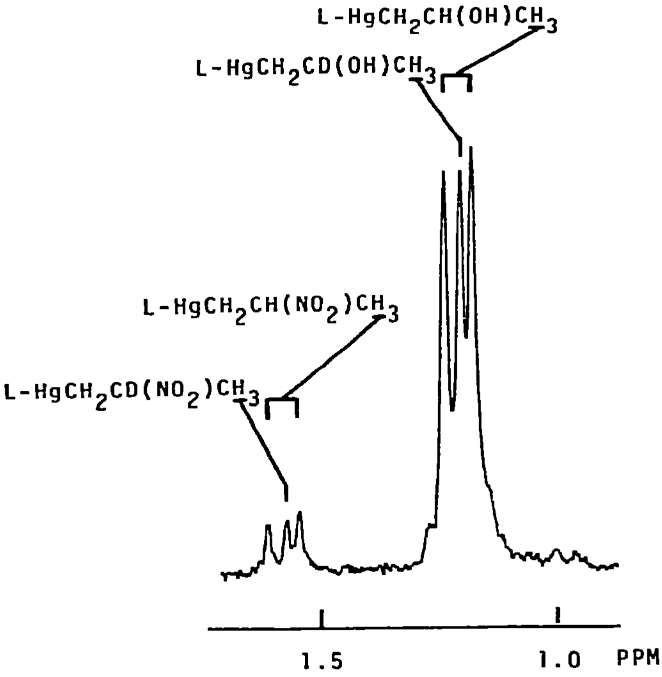


Fig. 4. The PMR spectrum obtained in situ in the course of the conversion of propene and propene-2-d_1 hydroxymercurials into the corresponding nitromercurials in the mixed solution at 14.2°. The total mercurial concentration was 0.333 *M* with the composition of aquo- (0.87) and nitrito- (0.13) complexes. This spectrum was taken with deuterium irradiation at 15.349408 MHz after 86.5 min from the moment of raising the solution temperature.

the reaction were determined from the doublet peak for I (CHC$\underline{H}_3$; δ 1.21) and the singlet peak for V (CDC$\underline{H}_3$; δ 1.20) on an expanded scale, respectively. Absence of H—D exchange between V and the solvent H_2O was confirmed by following the reaction of V alone under the identical conditions; no doublet peak appeared at δ 1.21.

If the rate constants for I and V are designated by k_H and k_D^α respectively, the value of the isotope effect, k_H/k_D^α, is obtainable in the form of a logarithmic ratio (eqn. 13) so long as the reaction rate is first order with respect to the mercurial concentration, since, by virtue of mixing, all other terms are common and cancelled out by taking the ratio:

$$\begin{aligned} &CH_3CH(OH)CH_2Hg^+ + NO_2^- \xrightarrow{k_H} CH_3CH(NO_2)CH_2Hg^+ + OH^- \\ &CH_3CD(OH)CH_2Hg^+ + NO_2^- \xrightarrow{k_D^\alpha} CH_3CD(NO_2)CH_2Hg^+ + OH^- \end{aligned} \tag{12}$$

$$k_H/k_D^\alpha = \log([I]/[I]_0)/\log([V]/[V]_0) \tag{13}$$

A plot of the right-hand side of eqn. 13 vs. the reaction time gave a constant value and k_H/k_D^α was determined to be 1.10 ± 0.05 (standard deviation).

The β-secondary isotope effect associated with deuteration on the carbon bonded to mercury is obtainable by comparing the reaction rates for I and $CH_3CH(OH)CDHHgClO_4$ (VI). Reaction analysis was made for a mixture of V and VI which was obtained by hydroxymercuration of mixed gas of propene-2-d_1 and propene-1-d_1. Figure 5 shows a spectrum obtained in situ in the course of

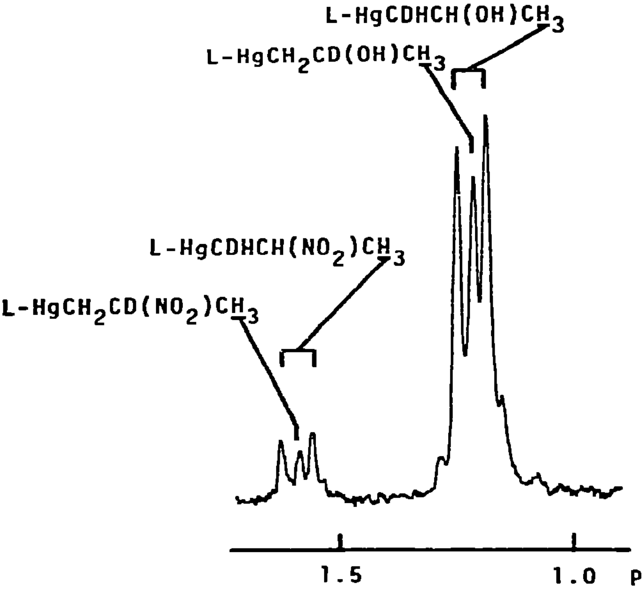


Fig. 5. The PMR spectrum obtained in situ in the course of the conversion of propene-1-d_1 and propene-2-d_1 hydroxymercurials into the corresponding nitromercurials in the mixed solution at 14.2°. The total mercurial concentration was 0.533 M with the composition of aquo- (0.87) and nitrito- (0.13) complexes. This spectrum was taken with deuterium irradiation at 15.349408 MHz after 75.3 min from the moment of raising the solution temperature.

the conversion of V and VI into the corresponding nitromercurials in the mixed solution ($[(V]_0/[VI]_0 = 0.34$).

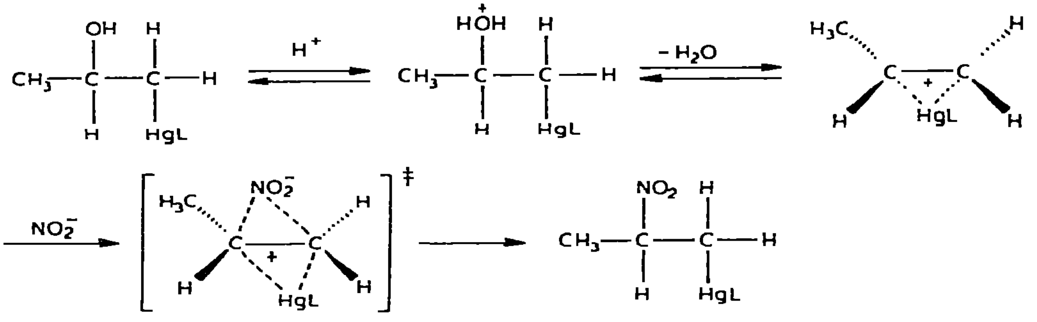
$$CH_3CH(OH)CDHHg^+ + NO_2^- \xrightarrow{k_D^\beta} CH_3CH(NO_2)CDHHg^+ + OH^- \qquad (14)$$

$$k_D^\alpha/k_D^\beta = \log([V]/[V]_0)/\log([VI]/[VI]_0) \qquad (15)$$

From a plot of the right-hand side of eqn. 15 vs. the reaction time k_D^α/k_D^β was determined to be 1.03 ± 0.05 (standard deviation). Accordingly, the β-secondary deuterium isotope effect, k_H/k_D^β, is 1.13 ± 0.10.

As typically observed in S_N1 solvolysis, the secondary deuterium isotope effect of 1.1-1.3 corresponds to the hybridization change of the deuterated carbon from sp^3 to sp^2 along the reaction coordinate [16]. Therefore, the observed magnitude of isotope effects seems to support a transition-state structure involving a nucleophilic attack of a nitrite ion to the mercurinium ion [1], since it requires more or less the sp^2 character for both α- and β-carbons (Scheme 1) [5-9]. The rate equation (eqn. 9) is consistent with Scheme 1 because of the first-order dependence on both $[H^+]$ and $[NO_2^-]$.

SCHEME 1



Consideration on the activation parameters

From the variation in k_a and k_b with the temperature (14.0-35.0°), activation parameters shown in Table 3 were obtained for each type of the complex. In view of Scheme 1, these results show that the nitrito-ligand is more effective than the aquo-ligand for the activation of mercurials from the σ-bonded reactant to the π-bonded activated state. This seems in accord with their values of ^2J(HgH), since halooxymercurials, being subject to deoxymercuration quite easily via mercurinium-ion intermediates [17,18], have much lower ^2J(HgH) values (e.g.,

TABLE 3

GEMINAL ^{199}Hg—^{1}H SPIN-COUPLING CONSTANTS AND ACTIVATION PARAMETERS FOR TWO TYPES OF THE MERCURIAL

Ligand	^2J(HgH) (Hz)	E_a (kcal/mol)	log A
H_2O	258.0	15.7	8.8
ONO^-	237.5	12.9	7.3

219.0 and 210.5 Hz for $CH_3CH(OH)CH_2Hg$-Cl and -SCN, respectively; solvent H_2O/DMSO ratio 1/2) [19]. Taking into consideration the fact that the carbon—mercury σ-bond becomes weak with decreasing ^2J(HgH) value [20,21], it is reasonable that formation of the mercurinium ion becomes easy for the ligand with low ^2J(HgH) value.

Experimental

PMR spectra were recorded on a JEOL PS-100 or a Hitachi R-20B spectrometer. Deuterium decoupling was carried out with a JEOL OA-1 synthesizer. Laser Raman spectra were recorded on a JEOL S-1 spectrometer equipped with an argon ion laser. Mass spectra were obtained using a Hitachi RMU-6 spectrometer.

All the reagents and solvents were of a G.R. grade. The tetrahydrofuran was dried over calcium chloride, refluxed with metallic sodium, and distilled immediately before use.

Preparation of the mixed gas of propene-1-d_1 and propene-2-d_1

The mixture of 1- and 2-bromopropenes was prepared by bromination followed by dehydrobromination of propene [22]. The Grignard reagents formed from the mixture of bromopropenes in dry tetrahydrofuran were decomposed at 0° with deuterium oxide (Merck, 99.75 atom % deuterated) under a dry nitrogen gas stream, with the gas-phase components trapped by a Dewar condenser of liquid nitrogen. The vapor of the solvent tetrahydrofuran was removed by condensation with a Dry Ice—ethanol trap fitted before the liquid nitrogen trap. Isotopic purity of the products was confirmed by mass spectrometry as 99.5 % d_1 and 0.5 % d_0.

Preparation of propene-2-d_1

2-Bromopropene was obtained by fractional distillation of the bromopropene mixture (isomeric purity of 99.7 % by GLPC), which was converted into propene-2-d_1 in the same manner as the case of the mixture. Isotopic purity of the product was confirmed by mass spectrometry as 99.5 % d_1 and 0.5 % d_0.

Procedure

A mercuric solution was prepared by adding 28.703 g of 70% perchloric acid (0.200 mol) to 21.659 g of mercuric oxide (0.100 mol) suspended in 50 ml of water. Hydroxymercuration was effected by passing propene through the mercuric solution at 0° to obtain an aqueous 2-hydroxy-1-perchloratomercuripropane solution quantitatively. The perchloric acid, formed stoichiometrically by the hydroxymercuration, was neutralized by an equivalent amount of sodium carbonate (5.299 g, 0.050 mol). The stock solution was prepared by diluting the solution to 100 ml with water (1.000 *M*); the solution was then stored in a refrigerator. Calculated amounts of sodium nitrite and perchloric acid were added to an aliquot of the properly-diluted stock solution at 0°. A part of the solution was transferred into a PMR sample 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 up to the probe temperature (calibrated by the relative chemical shifts of ethylene glycol), and the reaction was pursued by taking the spectra in sequence. During the course of the reaction, no evolution of gas due to olefin formation by deoxymercuration was observed. For the spectral analysis of the mixed-reactant systems, the overlapped portions of their peaks were reasonably resolved, which was confirmed by the agreement of the resolved and synthesized line shapes by using each of the spectra obtained separately under identical measuring conditions. The PMR spectral parameters of both hydroxymercurated and nitromercurated propenes were tabulated in a prior paper [1].

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