BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(12), 2948—2952 (1974)

Deuterium Isotope Effects on the Redex Decomposition of Hydroxymercurated Propene and 2-Butenes in an Aqueous Solution

Sumio Shinoda and Yasukazu Saito

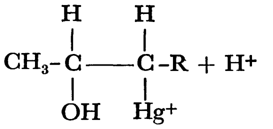
Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received May 20, 1974)

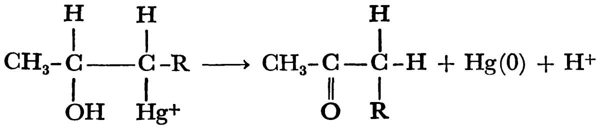
Kinetic deuterium isotope effects on the redox decomposition of hydroxymercurated propene, *cis*-, and *trans*-2-butenes in an aqueous solution ($CH_3CH(OH)CHRHg^+ \rightarrow CH_3COCH_2R + Hg(0) + H^+$; R=H, CH_3) were determined by following the reaction *in situ* by means of PMR spectroscopy. Taking advantage of the PMR characteristics, the identity of the reaction conditions was confirmed by comparing the rates for the reactant mixtures (*e.g.*, $CH_3CH(OH)CH_2Hg^+ + CH_3CD(OH)CH_2Hg^+$). The mercurials, deuterated on either β-carbon ($CH_3CD(OH)CH_2Hg^+$, $CH_3CD(OH)CHCH_3Hg^+$) or α-carbon ($CH_3CH(OH)CDHHg^+$, $CH_3CH(OH)CDCH_3Hg^+$), gave primary and secondary deuterium isotope effects of 1.35—1.40 and 1.17—1.19 respectively. A possible structure of the activated complex was proposed in accord with the observed nature of the intramolecular hydrogen shift.

The oxidation of olefins by aqueous mercuric salts[1] is known to produce unsaturated aldehydes,[2–5] saturated aldehydes,[3,4] allylic alcohols,[5] or saturated ketones[6] under various reaction conditions. In the case of milder conditions, it has been found[6,7] that propene and 2-butenes are oxidized stoichiometrically to acetone and methyl ethyl ketone respectively. The overall reaction consists of a fast[8] hydroxymercuration of the olefins[9] (Eq. (1)), followed by a rate-limiting redox decomposition of the mercurials thus formed into corresponding ketones (Eq. (2)):

$CH_3CH{=}CHR + Hg^{2+} + H_2O \longrightarrow$



$$CH_3\text{-}\underset{\displaystyle OH}{\overset{\displaystyle H}{C}}\text{——}\underset{\displaystyle Hg^+}{\overset{\displaystyle H}{C}}\text{-}R + H^+ \tag{1}$$



$$CH_3\text{-}\underset{\displaystyle OH}{\overset{\displaystyle H}{C}}\text{——}\underset{\displaystyle Hg^+}{\overset{\displaystyle H}{C}}\text{-}R \longrightarrow CH_3\text{-}\underset{\displaystyle O}{\overset{\|}{C}}\text{—}\underset{\displaystyle R}{\overset{\displaystyle H}{C}}\text{-}H + Hg(0) + H^+ \tag{2}$$

where R=H, CH_3

The intermediate mercurials are so stable that the second process can be pursued by PMR spectroscopy *in situ*[6] at appropriate temperatures. Prior articles reported data concerning the stoichiometry,[6] the rate equation,[6,7] the rate dependence on the added electrolytes,[7] product analysis from the D_2O solution,[10] and the alkyl-substituent effect on the rate.[11] In the present paper, we wish to report on deuterium isotope effects in the redox decomposition of hydroxymercurated propene and 2-butenes.

In order to measure the kinetic isotope effect accurately, it is desirable to determine the rates for both the labeled and unlabeled reactants in mixed solutions, because the identity of the reaction conditions is thus best assured. As far as the deuterium isotope effect is concerned, PMR spectroscopy appears especially suited for the analysis of reactions on account of its reasonable facility in differentiation between deuterated and undeuterated reactants *in situ*.[12]

With regard to olefin oxidation by other metal ions in an aqueous solution, similar reaction schemes have also been postulated for Pd(II),[13] Tl(III),[13] and Rh(III),[14] for which, in contrast to Hg(II), the redox decomposition of hydroxymetallation adducts has been claimed to occur after the rate-limiting (*e.g.*, hydroxymetallation) process. In view of the established usefulness of isotope effects in the elucidation of reaction mechanisms,[15] it seemed of particular interest to determine directly the isotope effects on the redox-decomposition process, which is possible only in the case of Hg(II) oxidation.

Results

*Primary Deuterium Isotope Effect on the Decomposition of Hydroxymercurated Propene-*2-d_1. It was previously confirmed that the redox decomposition of hydroxymercurated olefins involves an intramolecular shift of β-hydrogen to α-carbon (Eq. (2)),[1,11] and that the decomposition rate is first order with respect to the mercurial.[6,7] Therefore, if the first-order rate constants for hydroxymercurated propene, $CH_3CH(OH)CH_2Hg^+$ (**1**), and hydroxymercurated propene-2-d_1, $CH_3CD(OH)CH_2Hg^+$ (**2**), are designated by k_H and k_D^{prim} respectively, k_H/k_D^{prim} represents the primary deuterium isotope effect for the intramolecular 1,2-hydrogen shift in the redox decomposition of **1**:

$$CH_3CH(OH)CH_2Hg^+ \xrightarrow{k_H} CH_3COCH_3 + Hg(0) + H^+ \tag{3}$$

$$CH_3CD(OH)CH_2Hg^+ \xrightarrow{k_D^{prim}} CH_3COCDH_2 + Hg(0) + H^+ \tag{4}$$

Figure 1 shows the time-sequential PMR spectra for the decomposition of **1** and **2** in a mixed solution (1.5 m, $[\mathbf{2}]_0/[\mathbf{1}]_0$: 0.20). It is obvious from Fig. 1 that the difference in the rate of decomposition is not very large between **1** and **2**. The concentrations of the reactants during the reaction were determined from the doublet peak for **1** ($CHC\underline{\underline{H}}_3$; δ 1.21) and the singlet peak for **2** ($CDC\underline{\underline{H}}_3$; δ 1.20) by planimetry on an expanded scale. The absence of H-D exchange between **2** and the H_2O solvent was confirmed by following the decomposition of **2** alone under identical conditions; no doublet peak appeared at δ 1.21.

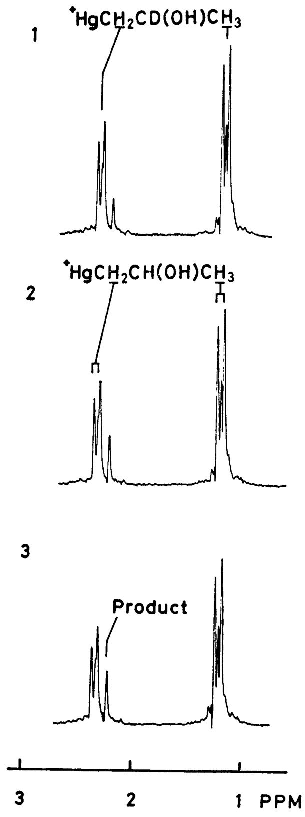


Fig. 1. The time-sequential PMR spectra obtained *in situ* for the redox decomposition of $CH_3CD(OH)CH_2Hg^+$ and $CH_3CH(OH)CH_2Hg^+$ at 38.0 °C in the mixed solution. These spectra were taken with deuterium irradiation at 15.349390 MHz after (1) 9.4 min, (2) 20.5 min, (3) 31.3 min from the moment of raising the solution temperature.

From the time-dependence of the concentrations of **1** and **2**, based on the first-order rate equations (Eqs. (5) and (6)), Eq. (7) is obtained as a formula to give the value of k_H/k_D^{prim}:

$$\log([\mathbf{1}]/[\mathbf{1}]_0) = -k_H t \tag{5}$$

$$\log([\mathbf{2}]/[\mathbf{2}]_0) = -k_D^{prim} t \tag{6}$$

$$\frac{k_H}{k_D^{prim}} = \frac{\log([\mathbf{1}]/[\mathbf{1}]_0)}{\log([\mathbf{2}]/[\mathbf{2}]_0)} \tag{7}$$

Figure 2 is a plot of the right-hand side of Eq. (7) *vs.* the time for solutions of the reactant mixture (1.5 m, $[\mathbf{2}]_0/[\mathbf{1}]_0$: 0.20 and 0.32); from the figure k_H/k_D^{prim} was determined to be 1.40 (±0.05; standard deviation).

Secondary Deuterium Isotope Effect on the Decomposition of Hydroxymercurated Propene-1-d$_1$. As it is bonded directly to mercury, the α-carbon of the mercurial may undergo a very drastic change during the course of redox decomposition; through this change a secondary kinetic isotope effect can be expected if a deuterium substituent is introduced at that carbon:

$$CH_3CH(OH)CDHHg^+ \xrightarrow{k_D^{sec}} CH_3COCDH_2 + Hg(0) + H^+ \tag{8}$$

In order to determine the isotope effect accurately, the decomposition rates were measured for the mixture

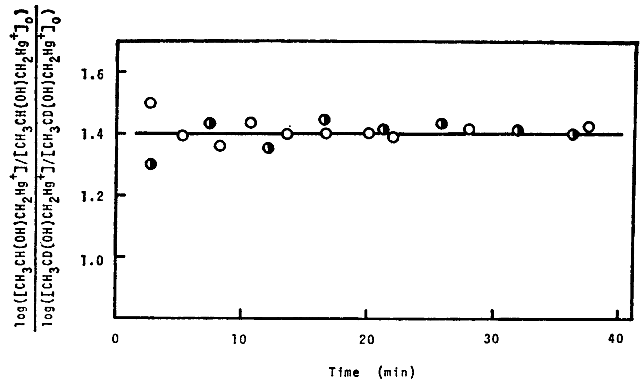


Fig. 2. Plot of $(\log([CH_3CH(OH)CH_2Hg^+]/[CH_3CH(OH)CH_2Hg^+]_0))/(\log([CH_3CD(OH)CH_2Hg^+]/[CH_3CD(OH)CH_2Hg^+]_0))$ *vs.* the time for the redox decomposition of $CH_3CH(OH)CH_2Hg^+$ and $CH_3CD(OH)CH_2Hg^+$ at 38.0 °C in the mixed solution. ○ and ◑ correspond to the ratio of initial concentrations $([CH_3CD(OH)CH_2Hg^+]_0/[CH_3CH(OH)CH_2Hg^+]_0)$ of 0.20 and 0.32 respectively.

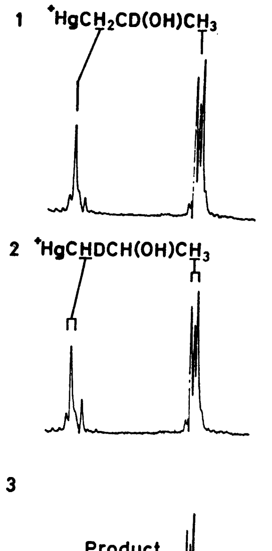
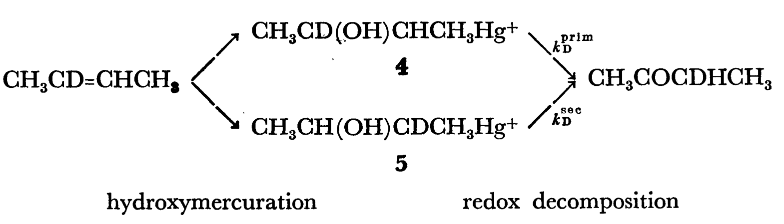


Fig. 3. The time-sequential PMR spectra obtained *in situ* for the redox decomposition of $CH_3CD(OH)CH_2Hg^+$ and $CH_3CH(OH)CDHHg^+$ at 38.0 °C in the mixed solution. These spectra were taken with deuterium irradiation at 15.349390 MHz after (1) 3.0 min, (2) 10.6 min, (3) 32.1 min from the moment of raising the solution temperature.

of **2** and $CH_3CH(OH)CDHHg^+$ (**3**) which was obtained by the hydroxymercuration of a mixed gas of propene-2-d_1 and propene-1-d_1. Figure 3 shows the time-sequential PMR spectra for the conversion of **2** and **3** into the product, acetone-d_1, in a mixed solution (1.5 m, $[\mathbf{2}]_0/[\mathbf{3}]_0$: 0.34). The concentration of **3** during the reaction was determined in the same manner



Scheme I.

as before by using the doublet peak at δ 1.21. From a plot of the right-hand side of Eq. (9) *vs.* the time, k_D^{sec}/k_D^{prim} was determined to be 1.20 (±0.05). Accordingly, the value of the secondary deuterium isotope effect is 1.17 (1.40/1.20).

$$\frac{k_D^{sec}}{k_D^{prim}} = \frac{\log([3]/[3]_0)}{\log([2]/[2]_0)} \tag{9}$$

Deuterium Isotope Effects on the Decomposition of Hydroxymercurated 2-Butene-2-d$_1$. By the hydroxymercuration of 2-butene-2-d_1, two kinds of deuterated mercurials, $CH_3CD(OH)CHCH_3Hg^+$ (**4**) and $CH_3CH(OH)CDCH_3Hg^+$ (**5**), were obtained as an isomeric mixture. By comparing the decomposition rates of **4** and **5** for the mixture (Scheme I), the value of k_D^{sec}/k_D^{prim} was determined with sufficient accuracy.

Figure 4 shows the time-sequential PMR spectra for the redox decomposition of hydroxymercurated *cis*-2-

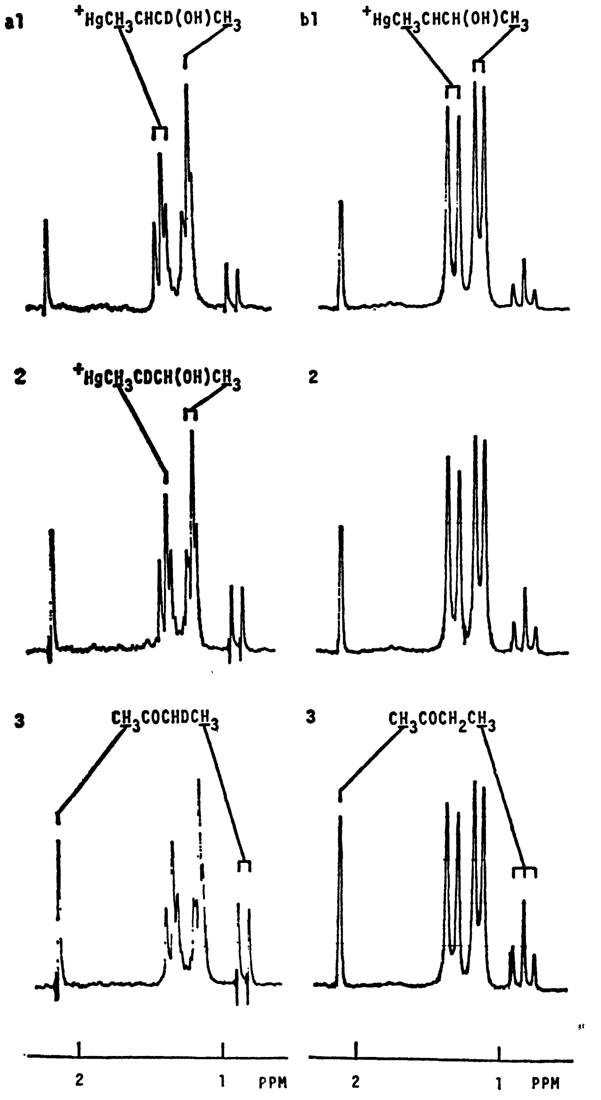


Fig. 4. The time-sequential PMR spectra obtained *in situ* for the redox decomposition of hydroxymercurated *cis*-2-butene-2-d_1 (**a**) and *cis*-2-butene (**b**) at 0.2 °C. These spectra were taken after (**a**) (1) 7.4 min, (2) 20.0 min, (3) 35.8 min with deuterium irradiation at 15.349390 MHz, and after (**b**) (1) 3.0 min, (2) 8.0 min, (3) 21.5 min from the moment of raising the solution temperature.

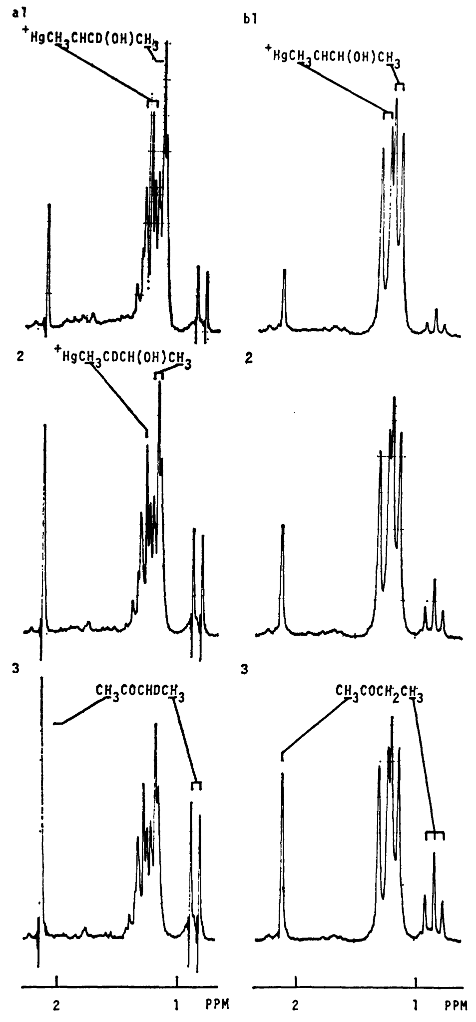


Fig. 5. The time-sequential PMR spectra obtained *in situ* for the redox decomposition of hydroxymercurated *trans*-2-butene-2-d_1 (**a**) and *trans*-2-butene (**b**) at 0.7 °C. These spectra were taken after (**a**) (1) 10.9 min, (2) 31.9 min, (3) 53.7 min with deuterium irradiation at 15.349390 MHz, and after (**b**) (1) 2.8 min, (2) 19.6 min, (3) 33.4 min from the moment of raising the solution temperature.

butene-2-d_1 (**a**) and *cis*-2-butene (**b**). Similar spectral sequences for the *trans*-isomers are shown in Fig. 5. Obviously, a marked contrast in the spectral pattern at δ 0.85 can be seen between the two sequences; this unequivocally indicates that methyl ethyl ketone-3-d_1 ($CH_3COCDHC\underline{\underline{H}}_3$; doublet) is produced by the decomposition of the deuterated mercurials. This was confirmed by a mass-spectrometric analysis of the product (d_1: 99.2%, d_0: 0.8%) and was consistent with the prior finding that no deuterium incorporation into the product was observed when D_2O was used as the solvent.[11] These facts are decisive evidence for the mechanism of the intramolecular 1,2-hydrogen shift in the redox decomposition.

From a plot of the right-hand side of Eq. (10) *vs.* the time, k_D^{sec}/k_D^{prim} was determined to be 1.15 ($\pm$0.05) for both isomers:

$$\frac{k_D^{sec}}{k_D^{prim}} = \frac{\log([\mathbf{5}]/[\mathbf{5}]_0)}{\log([\mathbf{4}]/[\mathbf{4}]_0)} \tag{10}$$

Experimental difficulties were encountered in following the reaction for mixtures of **4** or **5** with the corresponding undeuterated mercurial because of their inadequate PMR characteristics. Nevertheless, a comparison of the rate constants for deuterated and undeuterated mercurials was possible by pursuing each of the reactions in separated runs under identical reaction conditions (three determinations); a magnitude of isotope effects similar to that for propene was obtained (Table 1).

TABLE 1. KINETIC DEUTERIUM ISOTOPE EFFECTS ON THE REDOX DECOMPOSITION OF HYDROXYMERCURATED PROPENE, *cis*- AND *trans*-2-BUTENES

Olefin	Isotope effect	
	$\left(\frac{k_H}{k_D}\right)_{prim}$	$\left(\frac{k_H}{k_D}\right)_{sec}$
propene[a]	1.40	1.17
cis-2-butene[b]	1.35	1.17
trans-2-butene[c]	1.37	1.19

Reaction temperatures are (a) 38.0 °C, (b) 0.2 °C, and (c) 0.7 °C, respectively.

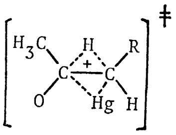
Discussion

The mechanism of the intramolecular 1,2-hydrogen shift in the redox decomposition of β-hydroxyalkyl-metal complexes has been proposed for the case of Pd(II)[13] and Rh(III)[14] as well as for the case of Hg(II).[1,10] Further, the lack of glycols in the product has commonly been interpreted as strong evidence against a simple carbonium-ion mechanism through the heterolysis of the carbon-metal σ-bond.[10,13,14] For the redox processes, some such assistance of the metals seems to be required for the hydrogen shift to occur concertedly with the two-electron transfer along the carbon-metal bond.

For the elucidation of transition-state structures, the kinetic isotope effect is considered to be one of the most important methods, since it has definitely been understood on the basis of the partition functions of the reactant and the transition state.[16] Usually, the values of the primary deuterium isotope effect for intramolecular hydrogen migration are small, along with a small angle (60°—90°) between the bonds to the migrating hydrogen in the transition state; according to the detailed calculations of O'Ferrall,[17] the values observed for the present case (1.35—1.40) can reasonably be associated with the three-membered cyclic transition state of the 1,2-hydride rearrangement. In practice, the observed values are close to those of the pinacol rearrangement ($\sim$1.6), in which the hydride rearrangement was presumed to be concerted with the breaking of a bond between carbon and a leaving group at the migration terminus; its transition-state structure has been claimed to resemble a non-classical carbonium ion.[18,19]

Secondary isotope effects are understandable in terms of force-constant changes at the position of the isotopic substitution between the reactant and the transition state;[20] substantial force-constant changes are, more or less, incident to the hybridization changes. As is typically observed in S_N1 solvolysis,[21] the secondary deuterium isotope effect of 1.1—1.3 corresponds to the hybridization change of deuterated carbon from sp^3 to sp^2.[22] Therefore, the observed magnitude of secondary deuterium isotope effects in the present case seems to be explained satisfactorily by the sp^2 character of α-carbon in the transition state; this is consistent with the previous suggestion to account for the pattern of the alkyl-substituent effect on the decomposition rate.[11]

As to the stereochemistry of the hydrogen shift in the redox decomposition of hydroxymercurials, an anti-mode with respect to the leaving mercury was strongly suggested by the product distribution (ketone or epoxide) for hydroxymercurated cyclic olefins.[23] Taking into consideration the foregoing results on deuterium isotope effects, together with the suggested stereochemistry, a structure such as is depicted below may be proposed for the transition state of the redox decomposition of hydroxymercurials. In view of the well-known affinity of mercuric ions for olefinic π-electrons,[24,26] it seems likely that mercury facilitates the *anti*-wise hydrogen shift by anchimeric assistance; this is in contrast to the case of Pd(II), for which *syn*-wise assistance through Pd(II)-hydrogen interaction has been postulated.[27]



(R = H, CH_3)

Experimental

The FMR spectra were recorded on a JEOL PS-100 spectrometer. The deuterium decoupling was carried out with a JEOL OA-1 synthesizer. The mass spectra were obtained using a Hitachi RMU-6 spectrometer.

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

Preparation of cis- *and* trans-*2-Butene-2*-d_1. The *cis*- and *trans*-2-bromo-2-butenes were prepared by the procedure of Caldwell[28] (bromination followed by the dehydrobromination of *trans*- and *cis*-2-butenes respectively). The lithiation of each 2-bromo-2-butene by metallic lithium in dry diethyl ether was effected at room temperature by standard procedures.[29] The reaction mixture was quenched at 0 °C 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 solvent ether was removed by condensation with a Dry Ice–ethanol trap fitted before the liquid-nitrogen trap. The isomeric purities of the products were determined by glpc (20% dimethylsulfolane on Celite) to be 97% and 96% for *cis*- and *trans*-2-butene-2-d_1 respectively. Mass spectral analysis at 58—68 gave 99.5% d_1 and 0.5% d_0 components for each of them.

Preparation of the Mixed Gas of Propene-1-d_1 and Propene-2-d_1. The mixture of 1- and 2-bromopropene was prepared by a similar procedure, but using propene instead of 2-butene as the starting material. The Grignard reagents formed from the mixture of bromopropenes in dry tetrahydrofuran[30] were decomposed at 0 °C with deuterium oxide. The product, a propene-1-d_1 and propene-2-d_1 mixture, was isolated in the manner described above. The isotopic purity of the product 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 the fractional distillation of the bromopropene mixture (isomeric purity of 99.7% by glpc); it was then converted into propene-2-d_1 in the same manner as in the case of the mixture. The isotopic purity of the product (99.5% d_1 and 0.5% d_0) was unchanged from the case of the mixture.

Kinetic Studies in the Redox Decomposition of the Hydroxymercurials. Olefins were transferred *via* a vacuum line into an aqueous solution consisting of 3.00 M of mercuric perchlorate at 0 °C until all the mercuric ions had been consumed by hydroxymercuration. The solutions of hydroxymercurated olefins were diluted with identical amounts of a 3.00 M aqueous mercuric perchlorate solution. 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 ethyleneglycol), and the reaction was pursued by taking the spectra in sequence. For the mixed-reactant systems, the overlapped portions of their peaks were reasonably resolved, as was confirmed by the agreement of the resolved and synthesized line shapes, since each of the spectra was separately obtainable under identical measuring conditions.

During the reaction, no evolution of gas due to olefin formation by deoxymercuration[9] was observed. The PMR-spectral parameters of the hydroxymercurated propene and 2-butenes were tabulated in a prior paper.[6]

The authors wish to express their gratitude to Professor Yukio Yoneda for his helpful discussions and encouragement, and to Professor Richard L. Schowen for his valuable suggestions.

References

1) For a recent review of oxidation of olefins with mercuric salts, see H. Arzoumanian and J. Metzger, *Synth.* 527 (1971).

2) B. C. Fielding and H. L. Roberts, *J. Chem. Soc., A*, **1966**, 1627.

3) J. C. Strini and J. Metzger, *Bull. Soc. Chim. Fr.*, **1966**, 3145, 3150.

4) B. Charavel and J. Metzger, *ibid.*, 4865 (1968).

5) H. B. Tinker, *J. Organometal. Chem.*, **32**, C25 (1971).

6) Y. Saito and M. Matsuo, *ibid.*, **10**, 524 (1967).

7) M. Matsuo and Y. Saito, This Bulletin, **44**, 2889 (1971).

8) J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).

9) W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

10) M. Matsuo and Y. Saito, *J. Org. Chem.*, **37**, 3350 (1972).

11) Y. Saito, "Some Theoretical Problems of Catalysis," ed. by T. Kwan, G. K. Boreskov, and K. Tamaru, University of Tokyo Press, Tokyo (1973), p. 241.

12) D. D. Maness and L. D. Turrentine, *Tetrahedron Lett.*, 755 (1973).

13) P. M. Henry, *Advan. Chem. Ser.*, **70**, 126 (1968).

14) B. R. James and M. Kastner, *Can. J. Chem.*, **50**, 1698 (1972).

15) For a recent review of kinetic isotope effects, see "Isotope Effects in Chemical Reactions," ed. by C. J. Collins and N. S. Bowman, Van Nostrand Reinhold, New York, N. Y. (1970).

16) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 15 (1958).

17) R. A. M. O'Ferrall, *J. Chem. Soc. B*, **1970**, 785.

18) W. B. Smith, R. E. Bowman, and T. J. Kmet, *J. Amer. Chem. Soc.*, **81**, 997 (1959).

19) W. B. Smith, T. J. Kmet, and P. S. Rao, *ibid.*, **83**, 2190 (1961).

20) M. Wolfsberg, *Ann. Rev. Phys. Chem.*, **20**, 449 (1969).

21) R. E. Weston, Jr., *Ann. Rev. Nucl. Sci.*, **11**, 439 (1961).

22) A. Steritwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

23) R. A. Kretchmer, R. A. Conrad, and E. D. Mihelich, *J. Org. Chem.*, **38**, 1251 (1973).

24) R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

25) M. Matsuo and Y. Saito, *J. Organometal. Chem.*, **27**, C41 (1971).

26) K. Ichikawa, S. Fukushima, H. Ouchi, and M. Tsuchida, *J. Amer. Chem. Soc.*, **80**, 6005 (1958).

27) P. M. Henry, *ibid.*, **86**, 3246 (1964).

28) R. A. Caldwall, *J. Org. Chem.*, **35**, 1193 (1970).

29) R. G. Jones and H. Gilman, "Organic Reactions," Vol. 6, ed. by R. Adams, John Wiley & Sons, Inc., New York, N. Y. (1951), p. 339.

30) D. Seyferth, *Progr. Inorg. Chem.*, **3**, 129 (1962).