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Hyperconjugative Deuterium Isotope Effects on the Redox Decomposition of Hydroxymercurated 2-Butenes in an Aqueous Solution

Miharu Kosaki, Sumio Shinoda, and Yasukazu Saito

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

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Synopsis. The relative magnitude of the isotope effects of the deuterium atoms at the positions hyperconjugative to α- and β-carbons has been determined for the title reaction by monitoring the reaction of 2-butene-1,1,1,3-d_4 by PMR. On the basis of our results, the cation character in the transition state is concluded for both of the carbons, in support of the structure proposed previously.

The oxidation of olefins by aqueous mercuric salts is known to produce unsaturated aldehydes, saturated aldehydes, or allylic alcohols.$^{1)}$ It has been found, however, that, under certain reaction conditions, saturated ketones are formed exclusively$^{2)}$ by the redox decomposition of intermediate hydroxymercurated-olefins, which involves both an intramolecular hydrogen shift$^{3)}$ and a two-electron transfer.$^{4)}$ Recently an investigation from the viewpoint of kinetic deuterium isotope effects$^{5)}$ was performed in order to elucidate the transition-state structure; the cation character was suggested on the basis of the secondary deuterium isotope effect for α-carbon, $CH_3CHOHC\mathit{H}CH_3Hg^+$, which receives the migrating hydrogen and repels the reduced mercury during the reaction.$^{6)}$

With regard to β-carbon, $CH_3\mathit{C}HOHCHCH_3Hg^+$, however, it has no hydrogen other than the migrating one. In order to obtain complementary information about this carbon, 2-butene-1,1,1,3-d_4 is used in the present study, since the hyperconjugative isotope effects also reflect the cation character of the carbon at the reaction center.

Results and Discussion

Since the oxymercuration reaction of 2-butenes proceeds stereospecifically,$^{7)}$ *cis*- and *trans*-2-butenes are hydroxymercurated into *threo*- and *erythro*-oxymercurials respectively. When unsymmetrically deuterated 2-butenes are used, two regio isomers are formed with respect to the position of the deuterium substituents.

The process of the formation of 2-butanone-d_4 from a mixture of the hydroxymercurated 2-butene-d_4's was followed by PMR *in situ*:

$$CH_3CDOHCHCD_3Hg^+ \longrightarrow CH_3COCHDCD_3 + Hg(0) + H^+ \qquad (1)$$

$$CD_3CHOHCDCH_3Hg^+ \longrightarrow CD_3COCHDCH_3 + Hg(0) + H^+ \qquad (2)$$

Some representative spectra taken in a time sequence are shown in Fig. 1. The methyl protons of *threo*- and *erythro*-$CD_3CHOHCDCH_3Hg^+$ were observed at δ 1.38 and δ 1.30 respectively, whereas those of *threo*- and *erythro*-$CH_3CDOHCHCD_3Hg^+$ coincidentally both appeared at δ 1.19. The singlet peak observed at δ 2.13 was assigned to the methyl protons of 2-butanone-3,4,4,4-d_4.$^{2)}$

Peak-area analyses were made for the mixture of the reactants in a manner reported previously.$^{6)}$ By comparing each spectrum with preceeding ones, it was ascertained that the peak decrease at δ 1.19 was equal to the peak increase at δ 2.13; this feature can be expected from the stoichiometry of Reaction (1). From the semi-logarithmic time dependence of the peak-height at δ 1.19, the first-order$^{4)}$ rate constant was obtained as $(6.23\pm0.21)\times10^{-5}\ s^{-1}$ for Reaction (1). By using the sum of the peaks at δ 1.38 and δ 1.30, the first-order rate constant was obtained as $(6.14\pm0.24)\times10^{-5}\ s^{-1}$ for Reaction (2). Since all the reactants were present in the same solution, these rate constants could be obtained under completely identical reaction conditions. Therefore, it was confirmed that the relative magnitudes of isotope effects had been determined accurately.$^{6)}$

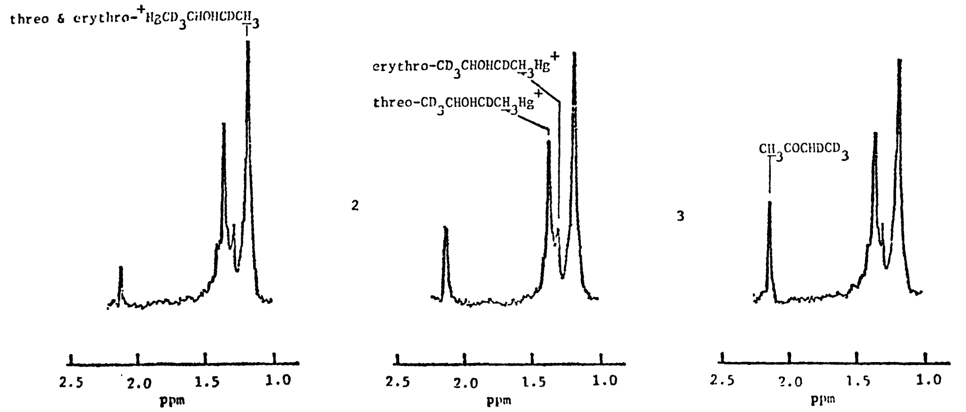


Fig. 1. The time sequential PMR spectra obtained *in situ* for the redox decomposition of the mixture of *threo*- and *erythro*-$CH_3CDOHCHCD_3Hg^+$ and -$CD_3CHOHCDCH_3Hg^+$ at 3.0 °C in an aqueous solution. These spectra were recorded after (1) 0.0 min, (2) 30.9 min and (3) 49.3 min.

Kinetic deuterium isotope effects have been considered to be almost precisely multiplicative. The mechanisms of the retro-Diels-Alder reaction of 9,10-dihydro-9,10-ethanoanthracene[8)] and the base-induced dehydrotosylation and dehydrobromination of cyclohexyl derivatives[9)] were discussed accordingly. With respect to the present reaction, the rate constant of Reaction (1) should be affected cumulatively by both migrating deuterium and the methyl deuterium of CD_3CHg; their effects are expressed in terms of the primary deuterium isotope effect, $(k_H/k_D)^{\text{prim}}$, and the hyperconjugative deuterium isotope effect, $(k_H/k_D)^{\text{hyp(Hg)}}$, respectively. As for Reaction (2), the effects of both α-deuterium (CDHg) and the other methyl deuterium (CD_3COH) should also be imposed on the rate cumulatively; the rate is affected by both the α-secondary deuterium isotope effect, $(k_H/k_D)^{\alpha}$, and the hyperconjugative deuterium isotope effect, $(k_H/k_D)^{\text{hyp(OH)}}$.

The ratio of the rate constants for Reactions (1) and (2) is, therefore, given as follows:

$$\frac{k(1)}{k(2)} = \frac{k_H/k(2)}{k_H/k(1)} = \frac{(k_H/k_D)^{\alpha}}{(k_H/k_D)^{\text{prim}}} \times \frac{(k_H/k_D)^{\text{hyp(OH)}}}{(k_H/k_D)^{\text{hyp(Hg)}}} \qquad (3)$$

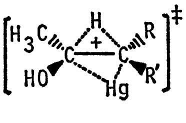
where k_H is the rate constant of $CH_3CHOHCHCH_3Hg^+$.

As far as the value of $(k_H/k_D)^{\text{prim}}/(k_H/k_D)^{\alpha}$ is concerned, the value of 1.15 was previously obtained for *cis*- and *trans*-2-butene.[6)] By substituting the observed value of both $k(1)/k(2)$ and $(k_H/k_D)^{\text{prim}}/(k_H/k_D)^{\alpha}$ into Eq. (3), the ratio of the hyperconjugative isotope effects concerning the α- and β-carbons, $(k_H/k_D)^{\text{hyp(OH)}}/(k_H/k_D)^{\text{hyp(Hg)}}$, was calculated to be 1.17 ± 0.10, where the error limit was determined in view of those for both the rate constants and the isotope effects.

As is well known, the magnitude of the hyperconjugative deuterium isotope effect increases proportionally to the extent of the positive charge on the reacting carbon in the transition state.[10)] With regard to the S_N1 solvolysis reactions, such magnitudes have been reported as 1.33[11)], 1.34[12)], and 1.40[12)] per CD_3 at 25 °C. In contrast, values as small as 1.05 per CD_3 were found at 60.56 °C[13)], 73.88 °C[13)], and 105.02 °C[14)] for the radical decomposition reactions.

Taking into account the considerable cation character of the α-carbon ($CH_3CHOH\mathit{C}HCH_3Hg^+$) in the present reaction,[6)] it is now possible to estimate the extent of the β-carbon ($CH_3\mathit{C}HOHCHCH_3Hg^+$) by using the ratio of the hyperconjugative isotope effects, since it represents the relative extent of the cation character of these carbons. If the β-carbon had no cation character at all in the transition state, the ratio would be less than unity (*e.g.*, 1/1.3). The observed ratio of 1.17 ± 0.10, therefore, strongly suggests that the cation character of the β-carbon (COH) is almost comparable to, or rather larger than, that of the α-carbon (CHg).

The transition-state structure for the redox decomposition reaction of hydroxymercurated 2-butene proposed previously[6)] is thus supported from the point of view of the hyperconjugative deuterium isotope effects.



(R, R′=H, CH_3)

Experimental

All the reagents and solvents were of a G. R. grade. The diglyme was dried by refluxing it with lithium aluminum hydride before use. The alumina catalyst (spherical, 1/8 mesh) was supplied by ALCOA (F-110). The BET surface area (N_2 adsorption) was 190 m^2/g. The catalyst (20.0 g) was loaded in a flow reactor, evacuated at 350 °C for 2 hr, and then exposed to the vapor of deuterium oxide (Merck, 99.75 atom % deuterated) at 200 °C.

Preparation of 2-Butene-1,1,1,3-d_4. 2-Butanone-1,1,1,-3,3-d_5 was obtained by the hydrogen-deuterium exchange of 2-butanone by a keto-enol equilibrium in a deuterium-oxide solution of potassium carbonate at 80 °C. Isotopic purities of 98% were ascertained by PMR analysis for both methyl and methylene groups. The hydrogenation of 2-butanone-1,1,1,3,3-d_5 by lithium aluminum hydride was effected in diglyme at 50 °C to obtain 2-butanol-1,1,1,3,3-d_5, which was then dehydrated into deuterated *n*-butenes catalytically at 170 °C by the use of the flow reactor, with a nitrogen-gas carrier. The analysis of the product by glpc (20% dimethylsulfolane on Celite) confirmed the composition of *cis*-2-butene (54.1%), *trans*-2-butene (14.6%) and 1-butene (31.3%).

Kinetic Studies of the Redox Decomposition. The gaseous olefin was introduced *via* a vacumm 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 solution of hydroxymercurated *n*-butenes was 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 (3.0 °C; calibrated by the relative shifts of ethylene glycol); the reaction was then pursued for 60 min, with fifteen spectrum charts taken in sequence. During the reaction, no evolution of gas due to olefin formation by deoxymercuration was observed.

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