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Secondary Deuterium Isotope Effects in the Intramolecularly-competing Methoxymercuration of Ethylene-1,1-d_2 and *cis*-2-Butene-2-d_1

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Synopsis. Secondary deuterium isotope effects in the intramolecularly-competing methoxymercuration of ethylene-1,1-d_2 and *cis*-2-butene-2-d_1, determined from the rate ratio (k(β-deuteriomercurial)$/k$(α-deuteriomercurial)$=1.12$, 1.06), indicate that the transition state for the methoxymercuration of ethylene and *cis*-2-butene does not have a symmetrical structure such as a mercurinium ion, but is accompanied by considerable C–O bond formation.

The oxymercuration of olefins followed by reductive demercuration with sodium borohydride is a synthetically important method for the synthesis of alcohols and ethers.[1] The remarkable feature of the oxymercuration is that the reaction has almost all the usual features of an electrophilic addition but structural rearrangement, substitution, and conjugate addition do not accompany the reaction.[2] The process is strictly a 1,2-addition in the Markownikov sense and occurs in a stereospecific anti fashion for unstrained simple olefins.[3]

Although extensive studies have been accumulated,[4] there is still dissension regarding the mechanism of this reaction, as was comprehensively reviewed by Ambidge *et al.* recently.[5] One convincing line of approach has involved an application of a linear free-energy relationship,[6] but the interpretation of the rate data seems rather diverse, and depends on the category of olefins selected. In order to remove the ambiguity in the mechanistic problem, it is important to determine accurately the mechanism for the most simple olefin, ethylene.

From this viewpoint, we utilized here the secondary deuterium isotope effect to elucidate the transition-state structure for the methoxymercuration of ethylene together with *cis*-2-butene. Isotopic substitution is unique in that it generates no variation of electronic potential-energy surfaces for molecules.[7] When ethylene-1,1-d_2 (**1**) or *cis*-2-butene-2-d_1 (**2**) is oxymercurated, two isomeric adducts are obtained, *i.e.*, α- and β-deuterio-oxymercurials where the designation of α and β is made from the mercurated carbon. Because the formation of these isomers is competitive, the ratio of the product isomers is equivalent to the corresponding rate constants, k_β/k_α.

$$CH_2{=}CD_2 \xrightarrow[\text{2) aq NaCl}]{\text{1) Hg(OAc)}_2\text{-MeOH}} \underset{\mathbf{1\alpha}}{CH_2(OMe)CD_2HgCl} + \underset{\mathbf{1\beta}}{CD_2(OMe)CH_2HgCl}$$

$$cis\text{-}CH_3CH{=}CDCH_3 \xrightarrow[\text{2) aq NaCl}]{\text{1) Hg(OAc)}_2\text{-MeOH}} \underset{\mathbf{2\alpha}}{threo\text{-}CH_3CH(OMe)CDCH_3HgCl} + \underset{\mathbf{2\beta}}{threo\text{-}CH_3CD(OMe)CHCH_3HgCl}$$

Scheme 1.

Secondary deuterium isotope effects on reaction rates have been generally recognized as evidence of hybridization change at the position of isotopic substitution between reactant and transition state.[7,8] Accordingly, we can directly deduce the symmetry concerning the hybridization of α- and β-carbons in the transition state by examining the value of k_β/k_α.

Results and Discussion

Methoxymercuration of **1** and **2** was effected at 25 °C by standard procedures (Scheme 1).[9] In the absence of mineral acid, oxymercuration of olefins with mercury(II) acetate gives kinetically controlled products,[10] and there was no possibility of discrepancies of temperature or other conditions in the formation of the two isomers. The ratio of the product isomers was determined by using PMR spectroscopy carefully for the quantitative analysis.

The PMR spectrum of the methoxymercurials formed from **1** is shown in Fig. 1. Obviously two peaks with unequal intensity appear at δ 2.16 and 3.60; deuterium decoupling did not alter the peak ratio. It is evident from Fig. 1 that **1β** (δ 2.16) was formed in preference to **1α** (δ 3.60). The isomer ratio for the methoxymercuration of **2** was determined with methyl peaks. The results are tabulated in Table 1.

TABLE 1. RATE RATIO FOR THE INTRAMOLECULARLY-COMPETING METHOXYMERCURATION OF DEUTERIO-OLEFINS

Olefin	k_β/k_α
$CH_2{=}CD_2$	1.21
cis-$CH_3CH{=}CDCH_3$	1.06

For unsymmetrically deuterium-substituted symmetrical olefins such as **1** or **2**, the olefinic carbons are equivalent on the electronic potential-energy surface. If the transition state for the methoxymercuration of ethylene or *cis*-2-butene is symmetrical, retaining the equivalence of the two carbons, the secondary deuterium isotope effect would be identical for the two isomers. The observed substantial deviation of k_β/k_α from unity, therefore, indicates that the symmetrical transition state such as **3** or **4** is unfavorable for ethylene and *cis*-2-butene, despite the symmetry in substituents.

An intervention of oxy-addendum in the transition state has been claimed by several authors on the basis of the substituent effect on the rate of oxymercuration[2,11] On the assumption of the inverse α-deuterium

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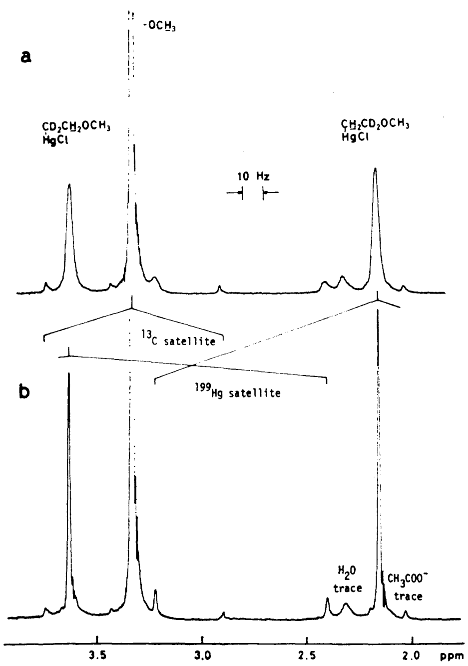
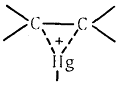


Fig. 1. PMR spectrum of the methoxymercurials of ethylene-1,1-d_2 at 25 °C and 100 MHz in $CDCl_3$ solution; (a) without deuterium irradiation; (b) with deuterium irradiation at 15.349345 MHz which corresponds to the center of the α- and β-deuterium resonance.

isotope effect ($k_H/k_D<1$), which has been usually observed when there is a change from sp^2 to sp^3 in the carbon bond hybridization,[7,8] the observed magnitude of the rate ratio for the intramolecularly-competing process, k_β/k_α, directly shows that the C–O bond is considerably formed in the transition state. Hence, the transition-state structure for the methoxymercuration of ethylene and *cis*-2-butene would be represented as **5**. The position of mercury along the C–C bond axis may be of interest, but seems to be a complicated problem since the molecular orbital calculation[12] suggests that rather small energy is required to shift the mercury along that axis (as compared with halonium ions), and that the ease of the displacement depends appreciably on the kind of the ligand bonded to mercury(II). The "mercurinium ion" intermediate, formulated frequently as **3** in analogy to olefin-Ag(I) π-complex or bromonium ion,[12] may be involved in the reaction path, possibly in the pre-rate-determining step equilibria,[13] but its formation is not a rate-determining step.[14]

It is noteworthy that **5** is similar to the transition-state structure proposed by Kreevoy and coworkers for the deoxymercuration reaction.[15] In view of the reversible nature of the oxymercuration of olefins and the deoxymercuration of the formed adducts, it is reasonable that their transition-state structures resemble each other, although the content of C–Hg and C–O bond formation may be variable with the kind of olefin substituents or mercury ligands.



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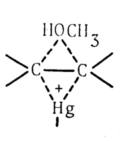

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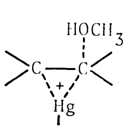

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Experimental

Preparations of **1** and **2** were described elsewhere.[16,17] All the reagents and solvents were commercially available. PMR spectra were recorded on a JEOL PS-100 spectrometer. Deuterium decoupling was carried out with a JEOL OA-1 synthesizer.

In determining the isomer ratios, both radio-frequency power and sweep rate were selected to avoid saturation of signal intensity. Spectra were obtained in both the frequency-increasing and -decreasing conditions ten times on a 4- or 10-fold expanded scale of the standard sweep width, so as to secure the precision of area measurement. Reported values were the avarage of three independent runs with an error of 3% (standard deviation) for the total measurement.

Methoxymercuration was performed by introducing **1** or **2** *via* a vacuum line into the solution consisting of methanol (5 cm^3) and mercury(II) acetate (2 mmol) at 25 °C, which was stirred by a magnetic stirring bar until all the mercury(II) ions were consumed to yield a homogeneous solution. Mercurials were isolated in the form of chloride by the method described by Ichikawa *et al.*[9]

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