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# Secondary Hydrogen Isotope Effects on Deoxymercuration[1]

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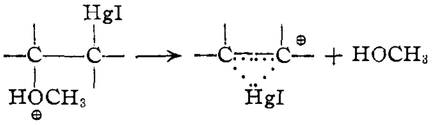
The ratio $k_H/k_D$ for acid cleavage of $CH_3OCH_2CH_2HgI$ and its 1,1,2,2-tetradeuterio analog is 1.06 ± 0.02. This isotope effect, combined with the known vibrational frequencies of the substrates and metal–olefin complexes, preclude the extensive participation of a mercuric–olefin complex in the transition state resonance hybrid. The small isotope effect also tends to preclude extensive carbonium ion character in the transition state. It can be accommodated by a substrate-like model of the transition state in which the methylene–oxygen bond is breaking.

In previous work[2] strong evidence has been presented that the rate-determining step in acid-catalyzed deoxymercuration is the reaction shown in eq. 1. Equation 1 says nothing, however, about the degree to which the protonated starting material, the mercuric iodide–olefin complex and perhaps other structures participate in the structure of the transition state. The position of the transition state along the reaction coördinate is also not known. In order to throw some light on these questions 1,1,2,2-tetradeuterio-1-iodomercuri-2-methoxyethane (II) was prepared, and its elimination rate in aqueous perchloric acid was compared with that of its undeuterated analog (I). The isotope effect turns out to be small and its magnitude is discussed.



$$-\underset{\underset{\oplus}{HOCH_3}}{\overset{|}{\underset{|}{C}}}-\overset{HgI}{\underset{|}{\overset{|}{C}}}- \longrightarrow -\overset{|}{C}\cdots\overset{|}{C}^{\oplus}- + HOCH_3 \quad (1)$$

## Results

As before,[3] good pseudo first-order kinetics were observed for both I and II. Three new determinations of $k_1$ and $k_2$ for I were made in water[4] at 25.0°. They gave an average value of $3.35 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$ for $k_2$ with an average deviation from the mean of $0.08 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$. This can be compared with a value of $3.31 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$ with a *probable error*[5] of 0.02 l. mole$^{-1}$ sec.$^{-1}$ obtained previously.[3] The new and old measurements combined gave an average value (thirteen measurements) of $3.32 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$ with a probable error[5] of $0.02 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$.

Eight separate determinations of $k_2$ were made for II under exactly the same conditions and using the same perchloric acid. These gave an average value of $3.14 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$ for $k_2$ with an average deviation from the mean of $0.08 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$ and a probable error of $0.03 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$.[5] The ratio $k_H/k_D$ is, therefore, 1.06, with a probable error of 0.02.

## Discussion

The reaction coördinate for the reaction shown in eq. 1 has previously been pictured as shown in Fig. 1. The observed isotope effect will be discussed in terms of this model and eq. 2. Equation 2 is

$$\frac{k_H}{k_D} = \frac{K_H}{K_D} \times \left(\frac{m_D^{\ddagger}}{m_H^{\ddagger}}\right)^{1/2} \times \frac{\sigma_H \sigma_D^{\ddagger}}{\sigma_H^{\ddagger} \sigma_D} \times \Pi_i \frac{\nu_{Hi}^{\ddagger} \nu_{Di}}{\nu_{Di}^{\ddagger} \nu_{Hi}} \times \frac{f_H^{\ddagger} f_D}{f_D^{\ddagger} f_H} \times \exp\left\{\frac{h}{2kT} \sum_i (\nu_{Hi} + \nu_{Di}^{\ddagger} - \nu_{Di} - \nu_{Hi}^{\ddagger})\right. \quad (2)$$

obtained by rearranging and expanding the equations of Bigeleisen and Mayer[6] without introducing any new assumptions or approximations.

In eq. 2, $K$ is a transmission coefficient, $m^{\ddagger}$ is a reduced mass for motion along the reaction coördinate, $\sigma$ is a symmetry number, $\nu_i$ is a fundamental frequency and $f$ is a vibrational partition function.[7] The ratio $K_H/K_D$ is assumed to be unity and tunneling has been neglected. Both of these seem to be fairly valid approximations for secondary isotope effects.[5c,8] The symmetry numbers of all the molecules and transition states being discussed are unity. On the basis of the model an estimate of $(m_D^{\ddagger}/m_H^{\ddagger})^{1/2}$ can be obtained by assuming that the two hydrogen atoms on the carbon whose bond to oxygen is breaking move along with that carbon and that no atoms other than these and the oxygen atom move. Thus $m_H^{\ddagger}$ is obtained by multiplying the mass of the oxygen atom by the mass of the $CH_2$ group and dividing this product by the sum of these same two masses. In this way the value 1.035 is obtained for $(m_D^{\ddagger}/m_H^{\ddagger})^{1/2}$. It is neither a maximum nor a minimum. The maximum value, 1.069, is obtained by assuming that the mass moving along with the oxygen (methyl group and solvent molecules) is infinite by comparison with the mass of the methylene group. The minimum value, 1.000, would be obtained by assuming that the hydrogen atoms do not move along with the carbon atom.

In past work of this sort the vibrational frequencies have been divided into two classes: the carbon–hydrogen stretching and bending frequencies, for which it has been assumed that $\nu_H$ is $1.35\nu_D$; and all other frequencies, which have been assumed to be unchanged by the isotopic

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[1] This work was supported, in part, by the Air Force Office of Scientific Research through Contract no. AF 49(638)711 and, in part, by the National Science Foundation through grant no. NSF-G5434. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] Maurice M. Kreevoy and Frances R. Kowitt, THIS JOURNAL, **82**, 739 (1960); see O. W. Berg, W. P. Lay, A. Rodgman and G. F. Wright, *Can. J. Chem.*, **36**, 359 (1958), for a contrary view, however.

[3] Maurice M. Kreevoy and Leroy T. Ditsch, *J. Org. Chem.*, **25**, 134 (1960).

[4] Compound I and II were dispensed as solutions in methanol, so the aqueous solutions referred to actually contained 2% of methanol. This much methanol has been shown to have a negligible effect on the rate of such reactions and, in any event, was a constant factor in the present measurements.

[5] R. Livingston, "Physico Chemical Experiments," The Macmillan Co., New York, N. Y., 1957, Chap. I.

[6] (a) J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947); (b) J. Bigeleisen, *ibid.*, **17**, 675 (1949); (c) J. Bigeleisen and M. Wolfsberg, *Adv. Chem. Phys.*, **1**, 15 (1958).

[7] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 85.

[8] Reference 7, p. 94.

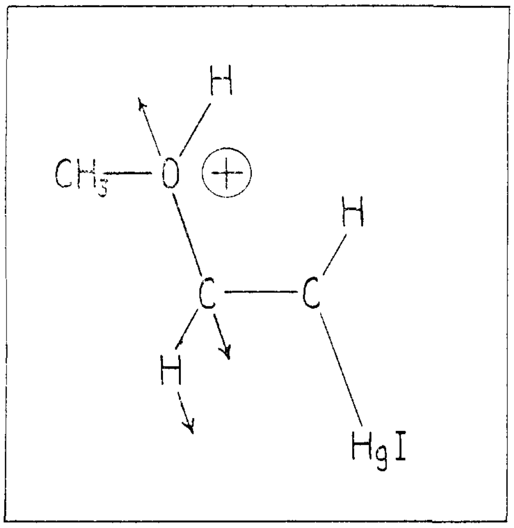

Fig. 1.—A rough pictorial representation of the reaction coördinate for acid deoxymercuration. The arrows are vectors representing the direction and, crudely, the relative size of the atomic motions.

substitution.[9] Most of the fundamental frequencies of I and II have been identified,[10] so that these approximations need not be made in the present case. The 23 assigned vibrational frequencies of I and II have been used (including the three skeletal deformations which occur in the methylene deformation region) and only the ten unassigned frequencies have been assumed equal in I and II. The unassigned frequencies are all low-lying skeletal vibrations which should not be strongly coupled to the methylene deformations. It was assumed that the 1110 cm.$^{-1}$ frequency in I and the 1050 cm.$^{-1}$ frequency in II are the methylene-oxygen stretching frequencies and that these go to zero in the two transition states.[11] The carbon-hydrogen vibrations of the methyl group do not undergo significant isotopic shifts in the starting states and it seems reasonable that this will be true also in the transition states. The methyl-oxygen frequency and the hydrogen-oxygen frequencies in the transition state are coupled to methylene groups only through the carbon-oxygen bond which is breaking. They should, therefore, undergo very little change when the methylene groups are deuterated and it is assumed that they undergo none. The low-lying structural deformation frequencies are assumed to be the same in the two transition states.

Two limiting assumptions can be made for the four carbon-hydrogen stretching frequencies, the eight deformation frequencies of the methylene groups and the carbon-carbon stretching frequency. It can be assumed that their starting state frequencies are unchanged except that the five frequencies in II (bending, wagging and carbon-carbon stretching) which lie close to the carbon-oxygen stretching frequencies and have the same symmetry are multiplied by a factor of $(1.085)^{-1/5}$. Or it can be assumed that the transition state frequencies resemble those of a metal-olefin complex.[12] The latter resemble each other[12] and also those of ethylene[13] quite closely.

The factor $(1.085)^{-1/5}$—0.9838—enters because the Teller-Redlich product rule[14] requires that the pre-exponential frequency ratio be very close to unity for each symmetry class. The transition state molecular weights are nearly identical with those of the starting states and the moments of inertia must be very similar because there is little change in geometry. When the methylene deformations and the carbon-carbon stretching frequency are uncoupled from the carbon-oxygen stretching frequencies, the former must change sufficiently so that the product rule will still be obeyed. The introduction of the factor 0.9838 distributes this change evenly over those frequencies of II in the neighborhood of the carbon-oxygen stretching frequencies which have the proper symmetry. It would make very little difference to the calculated isotope effect (a factor of about 1.005) if the decrease were concentrated in one or two frequencies instead of being evenly distributed.

In the second transition state model the ethylene-like frequencies were taken from those of Ziese's salt —$K[Pt(C_2H_4)Cl_3]\cdot H_2O$.[12] The ratios $\nu_H/\nu_D$ were assumed to be the same as in ethylene.[13] In Ziese's salt there is a torsional oscillation which is a molecular rotation in ethylene. The isotopic ratio in that case was assumed to be 1.408, which makes the pre-exponential frequency ratio unity.

With the first set of assumptions the partition function ratio is 1.000 and the exponential zero-point energy factor is 1.005, so that the calculated isotopic ratio, $k_H/k_D$, is 1.040. With the second set of assumptions the partition function ratio is 0.942 and the exponential factor is 0.632, so that the calculated isotopic rate ratio is 0.616. The former is in very reasonable agreement with the observed value (1.06 ± 0.02) while the latter is very far removed. It can, therefore, be concluded that the transition state probably resembles the protonated substrate, and bears very little resemblance to the mercuric-olefin complex.

The second model fails primarily because of the substantial increase in the carbon-hydrogen stretching frequencies that accompanies the conversion of the substrate to a metal-olefin complex (or to ethylene, for the matter). The agreement with the predictions of the first model is not critically de-

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[9] A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, THIS JOURNAL, **80**, 2326 (1958).

[10] M. M. Kreevoy and L. T. Ditsch, *ibid.*, **82**, 6124 (1960); The vibrational assignments were made for the solids but the spectroscopic results strongly suggest that the bulk of the material retains the solid state geometry and vibrational frequencies at least in solutions in carbon tetrachloride and carbon disulfide.

[11] The carbon-carbon stretching frequency, the methylene-oxygen stretching frequency and the methyl-oxygen stretching frequency were not originally identified[10] but it seems reasonable that the carbon-carbon frequency should undergo the largest isotopic shift, the methylene-oxygen frequency the next largest, and the methyl-oxygen frequency the smallest. Accordingly the 1090 cm.$^{-1}$ frequency in I and the 975 cm.$^{-1}$ frequency in II are considered the carbon-carbon stretching frequencies, 1110 cm.$^{-1}$ and 1050 cm.$^{-1}$ the methylene-oxygen stretching frequencies, and 1135 cm.$^{-1}$ and 1106 cm.$^{-1}$ the methyl-oxygen stretching frequencies.

[12] D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **13**, 69 (1958).

[13] B. L. Crawford, J. E. Lancaster and R. E. Inskeep, *J. Chem. Phys.*, **21**, 678 (1953).

[14] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 232.

pendent on the assigned frequencies of I and II because most of these cancel out. It is interesting to note that most of the calculated isotope effect is temperature independent.

For a number of reactions involving carbonium ion-like transition states it has been shown that $k_H/k_D$ is substantially greater than unity for both α- and β-deuterium substitution.[9,15–17] Values, ranging from 1.05 to 1.3 *per isotopic substitution* have been reported. The small isotope effect found in the present case (about 1.015 per substitution) along with the ability of a substrate-like model to reproduce the effect militates strongly against any large degree of carbonium ion character in the transition state. If the small excess of observed effect over that predicted is real, however, it may be due to a slight degree of carbonium ion character in the transition state.

## Experimental

The preparation of I and II have been described previously.[3,10] Rate constants were measured as before.[3]

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(15) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(16) K. B. Wiberg, *ibid.*, **55**, 713 (1955).

(17) V. J. Shiner and S. Cross, THIS JOURNAL, **79**, 3599 (1957).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY, AMES, IOWA]

# Reactions of Monohaloörganosilanes and Magnesium in Tetrahydrofuran

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Monohaloörganosilanes react with magnesium in tetrahydrofuran to give essentially two classes of compounds. Products of tetrahydrofuran ring cleavage are obtained when no aromatic groups are linked to the silicon atom, whereas aryl-containing halosilanes form the corresponding disilanes. By the latter reaction, a new class of disilanes of the general formula PhRHSiSiHRPh has become readily available. The preparation of 1,1,2,2-tetraphenyldisilane, 1,2-dimethyl-1,2-diphenyldisilane and 1,2-diethyl-1,2-diphenyldisilane is described.

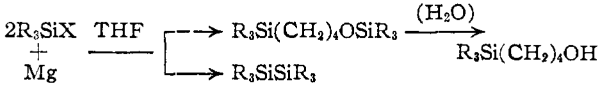
Reactions of halosilanes with magnesium have been of special interest because of the possible formation of silyl Grignard reagents with silicon directly linked to magnesium. No such reagent has been isolated; however, the intermediate formation of such compounds has been proposed by several workers.[1–3]

Eméleus, Maddock and Reid[1] suggested the formation of an unstable Grignard compound $SiH_3MgI$ from the reaction of iodosilane with magnesium in diisoamyl ether to account for the formation of monosilane and hydrogen. No disilane could be detected in their experiments. An analogous reaction between bromosilane and magnesium is reported by Van Artsdalen and Gravis.[2] Eaborn[3] reported possible formation of a transient Grignard reagent from triethyliodosilane and magnesium in ether.

Recently, strong evidence for the triphenylsilyl Grignard reagent has been shown by work of Selin and West.[4] Triphenylchlorosilane was coupled by cyclohexylmagnesium bromide and other Grignard reagents in tetrahydrofuran to give good yields of hexaphenyldisilane. Trimethylchlorosilane, under the same conditions, gave no reaction, but 1,1,1-trimethyl-2,2,2-triphenyldisilane was obtained when a mixture of trimethylchlorosilane and triphenylchlorosilane was treated with the Grignard reagent. The authors state that "apparently aromatic groups on silicon are necessary for the stabilization of the silyl Grignard reagent, just as they appear necessary for the formation of organosilylalkali compounds."[5] In this Laboratory, the direct coupling of triphenylchlorosilane by magnesium in diethyl ether proved to be unsuccessful,[6] but was eventually achieved by the use of tetrahydrofuran as the solvent.[7]

Anderson and Sprung[8] investigated the reaction of trimethylchlorosilane with magnesium in tetrahydrofuran in the presence of ethyl iodide or magnesium iodide and found that 4-trimethylsilylbutoxytrimethylsilane and 3-butenoxytrimethylsilane are formed as products of the cleavage of tetrahydrofuran. They propose a mechanism which involves the cleavage of the tetrahydrofuran ring by magnesium iodide in the presence of magnesium.

The general usefulness of tetrahydrofuran as a solvent for the preparation of organometallic compounds gave the impetus to this investigation of the behavior of various monohaloörganosilanes toward magnesium in this solvent. Under the conditions employed there are two courses the reaction may follow



$$2R_3SiX + Mg \xrightarrow{THF} \begin{cases} R_3Si(CH_2)_4OSiR_3 \xrightarrow{(H_2O)} R_3Si(CH_2)_4OH \\ R_3SiSiR_3 \end{cases}$$

One of these leads to the formation of products from the cleavage of tetrahydrofuran to give, on hydrolysis, 4-organosilyl-substituted 1-butanols as the main products. This mode of reaction was always observed when the organohalosilane did not

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(1) H. J. Eméleus, A. G. Maddock and C. Reid, *J. Chem. Soc.*, 353 (1941).

(2) E. R. Van Artsdalen and J. Gavis, THIS JOURNAL, **74**, 3196 (1952).

(3) C. Eaborn, *J. Chem. Soc.*, 2755 (1949).

(4) T. G. Selin and R. West, *Tetrahedron*, **5**, 97 (1959).

(5) H. Gilman and T. C. Wu, THIS JOURNAL, **73**, 4031 (1951).

(6) H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

(7) M. V. George, D. J. Peterson and H. Gilman, THIS JOURNAL, **82**, 403 (1960).

(8) R. P. Anderson and M. M. Sprung, WADC Technical Report 59-61, 47 (1959).