$$\frac{X_0}{X_f} = \frac{\left[\dfrac{\text{area under X peak}}{\text{area under chlorobenzene peak}}\right]_{\text{initial}}}{\left[\dfrac{\text{area under X peak}}{\text{area under chlorobenzene peak}}\right]_{\text{final}}}$$

the number of mmoles originally present of the X-substituted neopentylbenzene and neopentylbenzene, respectively; H_f and X_f are the corresponding terms for the final number of mmoles present. The above ratios may be directly obtained from the chromatographic analysis using the relationship shown.

Acknowledgments. We wish to thank Mr. Victor R. Koch for obtaining the nmr spectra needed for this investigation.

Deuterium Isotope Effects in the Acid-Catalyzed Hydration of 1-Phenyl-1,3-butadiene[1]

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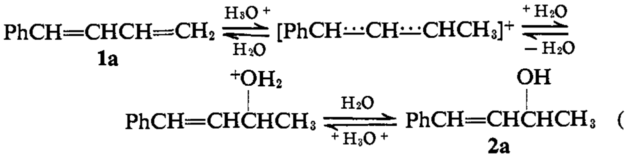
Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. *Received June 16, 1969*

Abstract: The kinetics of the acid-catalyzed hydration of 1-phenyl-1,3-butadiene and the acid-catalyzed dehydration of 1-methyl-3-phenylallyl alcohol have been studied in aqueous sulfuric acid and deuteriosulfuric acid starting with both deuterated and nondeuterated substrates. The rate constants obtained can be rationalized by a consideration of the component processes involved in the approach to equilibrium. From such a treatment the isotope effects were calculated as follows. In the forward reaction (hydration) the primary solvent isotope effect is 2.97 and the secondary isotope effect using 1-phenyl-4,4-dideuterio-1,3-butadiene is too small to be observed. In the reverse reaction the combined primary and secondary isotope effect arising from complete deuterium substitution in the terminal methyl group of 1-methyl-3-phenylallyl alcohol is 5.5. These results are shown to be consistent with the previously postulated mechanism for the hydration of 1-phenyl-1,3-butadiene and the dehydration of the adduct.

In a previous paper[3] it was shown that the mechanism of the acid-catalyzed hydration of 1-phenyl-1,3-butadiene (**1a**) to yield 1-methyl-3-phenylallyl alcohol (**2a**) involves the following steps, of which the slowest (rate-determining) step is the protonation of **1a**.



$$\underset{\mathbf{1a}}{PhCH{=}CHCH{=}CH_2} \underset{H_2O}{\overset{H_3O^+}{\rightleftharpoons}} [PhCH{\cdots}CH{\cdots}CHCH_3]^+ \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} PhCH{=}CH\overset{\overset{+}{O}H_2}{\overset{|}{C}}HCH_3 \underset{+H_3O^+}{\overset{H_2O}{\rightleftharpoons}} \underset{\mathbf{2a}}{PhCH{=}CH\overset{OH}{\overset{|}{C}}HCH_3} \quad (1)$$

Whether or not a π complex is involved in the protonation, as Taft[4a] has suggested, has not been indisputably proven, but it is probably not necessary for the interpretation of the experimental data in the present case.[4b] Similar conclusions have been reached in studies of analogous reactions, namely the dehydration of 1,2-diphenylethanol[5] and the hydration of styrene[6,7] and variously substituted styrenes.[8]

As a continuation of the study of the reactions of **1a** and **2a** we have followed the kinetics of the hydration of **1a** and the dehydration of **2a** using deuteriosulfuric acid as solvent and also using 1-phenyl-4,4-dideuterio-1,3-butadiene (**1b**) and 1-trideuteriomethyl-3-phenylallyl alcohol (**2b**) as substrates. This has enabled us to study the effect of deuterium on both forward and reverse reaction rates directly. Since the systems studied earlier[5-7] reach equilibria which are essentially completely on one side or the other, it has not been possible until now to study the deuterium isotope effects on alkene–alcohol equilibration from both directions.

Experimental Section

Preparation of Materials. 1-Phenyl-1,3-butadiene and 1-methyl-3-phenylallyl alcohol were prepared as previously described.[3]

1-Trideuteriomethyl-3-phenylallyl Alcohol. To 5 g of *trans*-4-phenyl-3-buten-2-one (Eastman) was added 20 ml of 2 *M* sodium deuterioxide in deuterium oxide, and the mixture was stirred for 8 hr at room temperature, extracted with ether, the ether layer dried over calcium sulfate, filtered, and the ether evaporated. This procedure was repeated 3 times, each time using fresh sodium deuterioxide solution, until the nmr spectrum of the product showed that the terminal methyl group was 97% deuterated (yield 4.5 g). This deuterated ketone was dissolved in 25 g of methanol, cooled to −10°, 1.5 g of sodium borohydride was added neat, and the mixture was allowed to stand for 30 min. The mixture was added to 100 ml of water, extracted with ether, the ether layer dried over sodium sulfate, filtered, and the ether evaporated. The resulting 1-trideuteriomethyl-3-phenylallyl alcohol was distilled, bp 82–84° (0.6 mm), yield 2.9 g. The nmr spectrum of the product showed 97% deuterium in the terminal methyl group.

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[1] Supported in part by grants from the National Science Foundation (NSF GP-5103) and the Petroleum Research Fund (PRF 2043-A4) administered by the American Chemical Society. Grateful acknowledgment is made to the donors of these funds.

[2] To whom inquiries should be directed.

[3] Y. Pocker and M. J. Hill, *J. Amer. Chem. Soc.*, **91**, 3243 (1969).

[4] (a) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *ibid.*, **82**, 4729 (1960), and references therein. (b) However, it should be noted that the vapor pressure of hydrogen chloride solutions in nitromethane is decreased by the addition of alkenes even before hydrogen exchange and/or addition take place. Such interactions could be due to π-complex formation between molecular HCl and alkene although for addition proper, fully developed carbonium ions were shown to be the crucial intermediates (Y. Pocker and K. D. Stevens, *ibid.*, **91**, 4205 (1969); Y. Pocker, K. D. Stevens, and (the late) J. McKee, unpublished observations).

[5] D. S. Noyce, D. R. Hartter, and R. M. Pollack, *ibid.*, **90**, 3791 (1968).

[6] Y. Pocker and A. E. Miller, unpublished observations; A. E. Miller, Ph.D. Thesis, University of Washington, 1968.

[7] W. M. Schubert, B. Lamm, and J. R. Keefe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964); W. M. Schubert and B. Lamm, *ibid.*, **88**, 120 (1966).

[8] N. C. Deno, F. A. Kish, and H. J. Peterson, *ibid.*, **87**, 2157 (1965).

Table I. Observed First-Order Rate Constants for Hydration of **1** and Dehydration of **2**

	Substrate	Solvent	10^4k_{obsd}, sec^{-1}								% **2** at equil	K_{eq}
Acid, M			4.18	3.91	3.84	3.47	3.19	3.14	2.68	2.27		
$-H_0$, $-D_0$[a]			1.93	1.82	1.78	1.62	1.47	1.45	1.22	1.02		
Case I	**1a, 2a**	H_2O	26.3	20.4	18.2[b]	11.8[b]	7.6[b]	7.2	3.8[b]	2.19	83	4.88
Case II	**1b, 2b**	D_2O	9.9[b]	7.4[b]	6.6	4.4	2.95	2.75[b]	1.51	0.91	75	3.0
Case IIIa	**1b**	H_2O	24.7	19.0				6.7		2.04	89	8.1
Case IIIb	**2b**	H_2O	22.3	17.4				6.2		1.88	96	2.4
Case IVa	**1a**	D_2O			10.4	6.6	4.6		2.3		46[b]	0.85
Case IVb	**2a**	D_2O			14.0	9.2	6.3		3.0		35[b]	5.4

[a] H_0 values from M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957). D_0 values from E. Hogfeldt and J. Bigeleisen, *J. Amer. Chem. Soc.*, **82**, 15 (1970). [b] Extrapolated value.

Table II. Derived Rate Constants for Component Processes

Acid, M		4.18	3.91	3.84	3.47	3.19	3.14	2.68	2.27
$-H_0$, $-D_0$		1.93	1.82	1.78	1.62	1.47	1.45	1.22	1.02
Case I	$10^4\,k_{\text{h}}$ sec^{-1}	21.8	16.9	15.1	9.8	6.3	6.0	3.1	1.82
	$10^4\,k_{\text{d}}$ sec^{-1}	4.5	3.5	3.1	2.0	1.3	1.2	0.65	0.37
Case II	$10^4\,k_{\text{h}}$ sec^{-1}	7.4	5.6	4.9	3.3	2.21	2.06	1.03	0.68
	$10^4\,k_{\text{d}}$ sec^{-1}	2.5	1.8	1.65	1.1	0.74	0.69	0.38	0.23
Case IIIa	$10^4\,k_{\text{h}}$ sec^{-1}	22.0	16.9				5.9		1.82
	$10^4\,k_{\text{d}}$ sec^{-1}	2.7	2.1				0.8		0.22
Case IIIb	$10^4\,k_{\text{h}}$ sec^{-1}	21.4	16.7				5.9		1.80
	$10^4\,k_{\text{d}}$ sec^{-1}	0.9	0.7				0.3		0.08
Case IVa	$10^4\,k_{\text{h}}$ sec^{-1}			4.8	3.0	2.1		1.06	
	$10^4\,k_{\text{d}}$ sec^{-1}			5.6	3.6	2.5		2.2	
Case IVb	$10^4\,k_{\text{h}}$ sec^{-1}			4.9	3.5	2.2		1.05	
	$10^4\,k_{\text{d}}$ sec^{-1}			9.1	5.7	4.1		2.0	

1-Phenyl-4,4-dideuterio-1,3-butadiene.[9] To 21 g of benzoyl chloride heated to 160° were added dropwise a solution of 3 ml of deuterium oxide and 5 ml of dry dioxane. The resultant deuterium chloride gas[10] was passed through a Dry Ice-acetone trap and into an ether (500 ml) solution of 1-trideuteriomethyl-3-phenylallyl alcohol (2.9 g) protected from atmospheric moisture by a Drierite drying tube. After all the deuterium oxide was used up the mixture was allowed to stand for 4 hr, and then was washed first with sodium carbonate solution and then with water. The ether solution was dried over sodium sulfate, filtered, and the ether removed. The resulting 1-trideuteriomethyl-3-phenylallyl chloride was distilled, bp 65–70° (0.6 mm), yield 1.0 g.

To this chloride was added 40 ml of pyridine and the mixture was refluxed for 2 hr. On cooling, 100 ml of water was added and the mixture was extracted with ether, the ether dried as above and the ether removed, yielding 0.2 g of pure 1-phenyl-4,4-dideuterio-1,3-butadiene, bp 55° (0.3 mm). Comparison of the nmr spectra of this compound and normal 1-phenyl-1,3-butadiene showed no detectable hydrogen at the terminal carbon, and was otherwise consistent with the structure. The ultraviolet spectrum of the deuterated alkene is very similar to that of the undeuterated species, except that the peak at 305 mμ now appears as a shoulder rather than a well-defined peak.

Deuterium oxide used in synthesis and kinetics was from Bio-Rad Lab and had 99.84% D.

Deuteriosulfuric acid was obtained from Stohler Isotope Chemicals and was 96.6% in deuteriosulfuric acid, 3.4% in deuterium oxide, and 99% D over-all. The solutions used in kinetic runs were made up in an atmosphere of dry nitrogen by weighing out quantities of deuteriosulfuric acid into volumetric flasks and making up to the mark with deuterium oxide. The acidities were further checked at the end of kinetic runs by titration *vs.* standard sodium hydroxide solutions.

Kinetic Methods. The hydration of **1** and the dehydration of **2** were followed spectrophotometrically as previously described.[3] Because of the limited solubility of **1** in water it was necessary to use fairly dilute solutions for kinetic runs to avoid precipitation from solution. However, solutions with an absorbance of up to 0.4 (280 mμ, 1-cm cell) may be used without difficulty. In the cases where the reaction proceeded with exchange of hydrogen for deuterium, or *vice versa*, the equilibrium value shifted with time, and the same procedure for extrapolation of infinity values as before was used.[3] It should be noted that although this method gave pseudo-first-order plots with good straight lines, inasmuch as the actual slopes of these lines may depend somewhat on the exact method of extrapolation, every effort was made to be consistent in the application of this procedure so that both the absolute and the relative magnitudes of the rate constants are reliable.

Results and Discussion

The observed rate constants ($k_{\text{obsd}} = k_{\text{h}} + k_{\text{d}}$) are summarized in Table I and Figure 1, and the component rate constants k_{h} and k_{d} derived from these are presented in Table II. The different combinations of deuterated and nondeuterated solvent and substrates

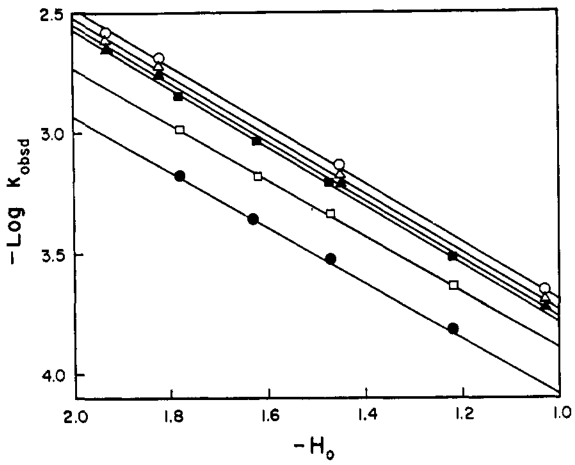

Figure 1. Plots of log k_{obsd} *vs.* H_0 for hydration of **1a** and dehydration of **2a** in sulfuric acid (○), hydration of **1b** and dehydration of **2b** in deuteriosulfuric acid, (●), hydration of **1b** in sulfuric acid (△), dehydration of **2b** in sulfuric acid (▲), dehydration of **2a** in deuteriosulfuric acid (□), and hydration of **1a** in deuteriosulfuric acid (■).

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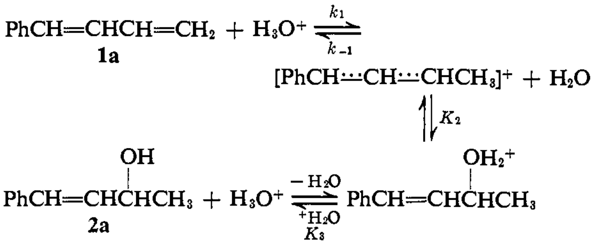
(9) Modification of the 1-phenyl-1,3-butadiene synthesis of I. E. Muskat and M. Herman, *ibid.*, **53**, 252 (1931).

(10) Method of H. C. Brown and C. Groot, *ibid.*, **64**, 2223 (1942).

are broken down into four categories for the purpose of discussing the isotope effects on each reaction.

Case I. Hydration of 1a and Dehydration of 2a in Sulfuric Acid



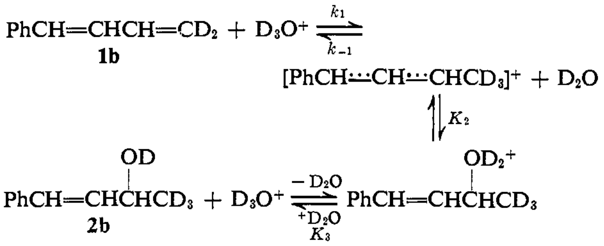
$$\underset{\mathbf{1a}}{PhCH{=}CHCH{=}CH_2} + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [PhCH{\cdots}CH{\cdots}CHCH_3]^+ + H_2O \quad (2)$$

$$\Big\Updownarrow K_2$$

$$\underset{\mathbf{2a}}{PhCH{=}CH\overset{OH}{\overset{|}{C}}HCH_3} + H_3O^+ \underset{+H_2O,\ K_3}{\overset{-H_2O}{\rightleftharpoons}} PhCH{=}CH\overset{OH_2^+}{\overset{|}{C}}HCH_3$$

This is a straightforward reaction with no isotope effects involved.

Case II. Hydration of 1b and Dehydration of 2b in Deuteriosulfuric Acid



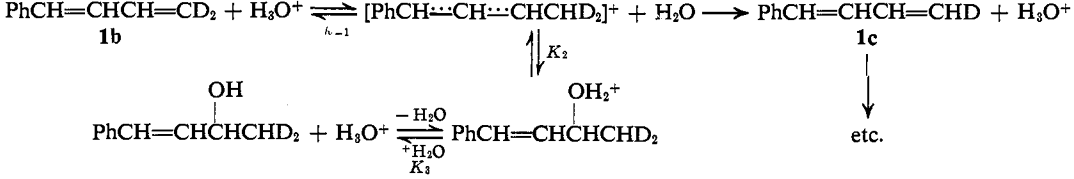
$$\underset{\mathbf{1b}}{PhCH{=}CHCH{=}CD_2} + D_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [PhCH{\cdots}CH{\cdots}CHCD_3]^+ + D_2O \quad (3)$$

$$\Big\Updownarrow K_2$$

$$\underset{\mathbf{2b}}{PhCH{=}CH\overset{OD}{\overset{|}{C}}HCD_3} + D_3O^+ \underset{+D_2O,\ K_3}{\overset{-D_2O}{\rightleftharpoons}} PhCH{=}CH\overset{OD_2^+}{\overset{|}{C}}HCD_3$$

For this process both forward and reverse rates were found to be slower than in Case I. However, the reverse reaction (dehydration) was retarded less than the forward reaction (hydration), an effect that can be explained by the consideration of three factors. It has previously been shown that a reaction involving a rapid preequilibrium protonation is accelerated in deuterated solvents in the absence of other isotope effects,[11] as, for example, in the acid-catalyzed enolization of acetone,[12,13] the acid-catalyzed dehydration of 1-methyl-1-cyclopentanol,[14] and the deoxymercuration of 1-iodomercury-2-propanol.[15] Consequently, one would expect that the equilibrium constant for the preequilibrium protonation (K_3 in eq 3) will be increased; values as large as 3.3 have been reported for K_D/K_H in the demethoxymercuration of 1-iodomercury-2-methoxypropane,[16] so a value of 3.0 for K_D/K_H in this case is not unreasonable and in fact has been observed for similar systems.[11a] However, because the substrate is deuterated, both k_1 and K_2 will show isotope effects tending to slow the reaction down. In the acid-catalyzed dehydration of 2-deuterio-1,2-diphenylethanol, Noyce, *et al.*,[5] found that the equilibrium constant for carbonium ion formation was decreased by about 17%, and Shiner[17] reported $k_H/k_D = 1.4$ for the solvolyses of tertiary butyl halides containing one completely deuterated methyl group. In the solvolyses of 1-phenylethyl halides Shiner reported a β-d_3 isotope effect of only 1.2 in water.[18] Similarly, the β-d_3 isotope effect on E1 elimination from 1-phenylethyl chloride in nitromethane is 1.25,[19] but in these cases the reactions are not limiting SN1–E1 processes[20] and one would expect a smaller isotope effect than in completely unimolecular dissociations.[21] Indeed, the β-d_3 isotope effect on carbonium ion formation from the corresponding alcohol is about double that of the chloride.[22] The present elimination is entirely unimolecular, as the rates of ^{18}O-exchange and racemization of **2** are the same,[3] so a value of K_H/K_D for K_2 of 1.5 is reasonable. Finally, the rate-determining step is the abstraction of a proton or deuteron, implying that a primary isotope effect is operative on this step. Since the forward reaction shows a mean isotope effect of 3.0, a value of 3.7 for the combined primary and secondary isotope effects for k_1 is not unreasonable. Thus because $k_d = k_1 \times K_2 \times K_3$, the ratio of k_d for Case I and for Case II should be $1/3.7 \times 1/1.5 \times 3.0 = 1.85$. Examination of Table II will show that this is indeed the case. Similarly, since $K_{eq} = k_h/k_d$, one can predict K_{eq} from these isotope effects and the value of K_{eq} for Case I (4.88). Thus $K_{eq} = 4.88 \times 1/3.0/(1/3.7 \times 1/1.5 \times 3.0) = 3.0$, which also agrees with the experimentally observed value (Table I).

Case IIIa. Hydration of 1b in Sulfuric Acid



$$\underset{\mathbf{1b}}{PhCH{=}CHCH{=}CD_2} + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [PhCH{\cdots}CH{\cdots}CHCHD_2]^+ + H_2O \longrightarrow \underset{\mathbf{1c}}{PhCH{=}CHCH{=}CHD} + H_3O^+ \quad (4)$$

$$\Big\Updownarrow K_2 \qquad\qquad \Big\downarrow \text{etc.}$$

$$PhCH{=}CH\overset{OH}{\overset{|}{C}}HCHD_2 + H_3O^+ \underset{+H_2O,\ K_3}{\overset{-H_2O}{\rightleftharpoons}} PhCH{=}CH\overset{OH_2^+}{\overset{|}{C}}HCHD_2$$

In this and the following cases, the interpretation of the results must take into account the reversibility of the reaction, as return from alcohol to alkene involves the partitioning of the carbonium ion between the abstraction of a proton (leading back to **1b**) or of a deuteron (leading on to **1c**), as in eq 4. Since the ultraviolet spectra of the deuterated compounds are essentially indistinguishable from those of the nondeuterated compounds, the exchange is only observed as a drift in the equilibrium position, which is corrected for by extrapolation of the infinity values back to the times at which readings were taken.

Since return to **1b** proceeds *via* proton abstraction it is reasonable to assume that it occurs at a rate at least competitive with that of advance to **1c**. In that case one would expect that isotopic exchange is fairly slow, and that during the time that the reaction is followed (two half-lives), eq 4 is an adequate description of the reaction. Taking the experimentally observed (at ten half-lives) equilibrium constants, one can

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(11) (a) F. A. Long and J. Bigeleisen, *Trans. Faraday Soc.*, **55**, 2077 (1959); F. A. Long, *Ann. N. Y. Acad. Sci.*, **84**, 596 (1960); (b) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., p 214 (1959); K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(12) O. Reitz, *Naturwissenschaften*, **24**, 814 (1936); *Z. Elektrochem.*, **43**, 659 (1937); *Z. Phys. Chem.*, **A179**, 119 (1937).

(13) F. A. Long and D. Watson, *J. Chem. Soc.*, 2019 (1958).

(14) E. L. Purlee and R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **78**, 5807 (1956).

(15) M. M. Kreevoy, *ibid.*, **81**, 1099 (1959).

(16) M. M. Kreevoy and L. T. Ditsch, *J. Org. Chem.*, **25**, 134 (1960).

(17) V. J. Shiner, Jr., *Tetrahedron*, **5**, 243 (1959).

(18) V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamatry, *J. Amer. Chem. Soc.* **90**, 418 (1968).

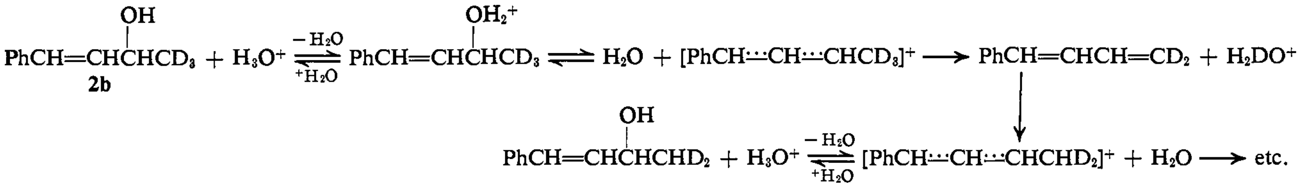
(19) Y. Pocker, F. Naso, and G. Tocchi, Proceedings XIXth International Congress of Pure and Applied Chemistry, London, 1963.

(20) E. Grunwald, A. Heller, and F. S. Klein, *J. Chem. Soc.*, 2604 (1957).

(21) E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press, New York, N. Y., 1964, p 209.

(22) Y. Pocker, F. Naso, and G. Tocchi, unpublished observations.

Case IIIb

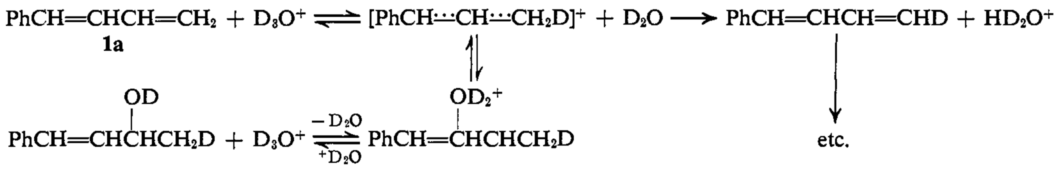


$$\underset{\mathbf{2b}}{\mathrm{PhCH{=}CH\overset{OH}{C}HCD_3}} + \mathrm{H_3O^+} \xrightleftharpoons[+\mathrm{H_2O}]{-\mathrm{H_2O}} \mathrm{PhCH{=}CH\overset{OH_2^+}{C}HCD_3} \rightleftharpoons \mathrm{H_2O} + [\mathrm{PhCH\text{⋯}CH\text{⋯}CHCD_3}]^+ \longrightarrow \mathrm{PhCH{=}CHCH{=}CD_2} + \mathrm{H_2DO^+}$$

$$\downarrow$$

$$\mathrm{PhCH{=}CH\overset{OH}{C}HCHD_2} + \mathrm{H_3O^+} \xrightleftharpoons[+\mathrm{H_2O}]{-\mathrm{H_2O}} [\mathrm{PhCH\text{⋯}CH\text{⋯}CHCHD_2}]^+ + \mathrm{H_2O} \longrightarrow \text{etc.} \qquad (5)$$

Case IVa

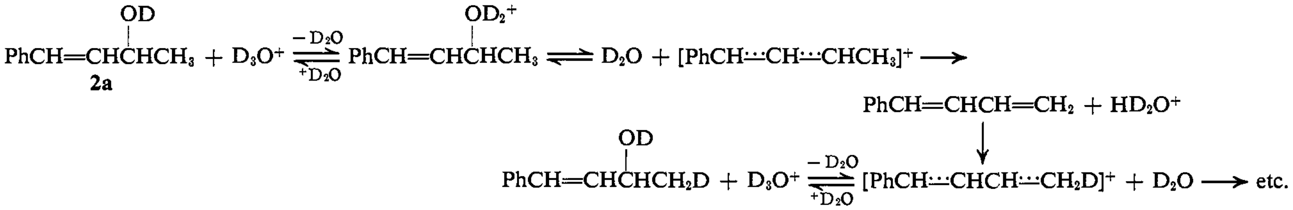


$$\underset{\mathbf{1a}}{\mathrm{PhCH{=}CHCH{=}CH_2}} + \mathrm{D_3O^+} \rightleftharpoons [\mathrm{PhCH\text{⋯}CH\text{⋯}CH_2D}]^+ + \mathrm{D_2O} \longrightarrow \mathrm{PhCH{=}CHCH{=}CHD} + \mathrm{HD_2O^+}$$

$$\upharpoonleft\!\downharpoonright \qquad\qquad \downarrow$$

$$\mathrm{PhCH{=}CH\overset{OD}{C}HCH_2D} + \mathrm{D_3O^+} \xrightleftharpoons[+\mathrm{D_2O}]{-\mathrm{D_2O}} \mathrm{PhCH{=}\overset{OD_2^+}{C}HCHCH_2D} \qquad \text{etc.} \qquad (6)$$

Case IVb



$$\underset{\mathbf{2a}}{\mathrm{PhCH{=}CH\overset{OD}{C}HCH_3}} + \mathrm{D_3O^+} \xrightleftharpoons[+\mathrm{D_2O}]{-\mathrm{D_2O}} \mathrm{PhCH{=}CH\overset{OD_2^+}{C}HCH_3} \rightleftharpoons \mathrm{D_2O} + [\mathrm{PhCH\text{⋯}CH\text{⋯}CHCH_3}]^+ \longrightarrow$$

$$\mathrm{PhCH{=}CHCH{=}CH_2} + \mathrm{HD_2O^+} \qquad (7)$$

$$\downarrow$$

$$\mathrm{PhCH{=}CH\overset{OD}{C}HCH_2D} + \mathrm{D_3O^+} \xrightleftharpoons[+\mathrm{D_2O}]{-\mathrm{D_2O}} [\mathrm{PhCH\text{⋯}CHCH\text{⋯}CH_2D}]^+ + \mathrm{D_2O} \longrightarrow \text{etc.}$$

obtain k_h and k_d from k_{obsd} as before (Table II). It should be noted that k_h here turns out to be the same as for Case I, that is, the protonation of the alkene does not show any appreciable isotope effect due to the deuterium substitution on the terminal carbon. This has also been observed in the acid-catalyzed hydration of styrene.[7]

Considering the values obtained for k_d, it will be noted that they lie between the k_d values for Cases I and II, as one might expect. However, attempts at rationalizing the magnitudes of the k_d values in this case by expressing k_d as a weighted average of the k_d values for Cases I and II prove to be difficult, for two reasons. First, it is necessary to estimate the secondary isotope effects on proton and deuteron removal from the $-CHD_2$ group. As mentioned previously, Noyce, *et al.*,[5] obtained values for the secondary isotope effects on proton abstraction from the carbonium ion derived from 2-deuterio-1,2-diphenylethanol due to the presence of a β-deuterium, and it is likely that similar values also apply to deuteron abstraction. Second, one should use some kind of statistical weighting factor to allow for the uneven distribution of protons and deuterons on the $-CHD_2$ group, and this is more complex than might appear at first sight. In the hydration of isobutene in water–deuterium oxide mixtures, Gold and Kessick[23] found that aside from the kinetic isotope effect there was also an isotope effect on the distribution of hydrogen and deuterium in the product, namely the proportion of hydrogen in the product was about 3.9 times the proportion of hydrogen in the solvent, implying that the distribution of protons and deuterons between hydronium ions and water molecules was not a simple random arrangement. Thus quite apart from the differences in kinetic acidities of (for example) $HDO^+–H$ and $HDO^+–D$ there are other factors influencing the choice of proton or deuteron for attack by the organic base. By the principle of microscopic reversibility these same factors must play a role in the reverse step of the reaction under consideration, rendering it difficult to predict *a priori* what the partitioning factors between proton and deuteron abstraction will be. Assigning values of 1.6 and 1.2 for the isotope effects on k_1 and K_3 compared with Case I gives nice agreement with experiment, as a K_{eq} value of 9.3 (90.4% **2**) is obtained.

Case IIIb. Dehydration of 2b in Sulfuric Acid

Dividing up k_{obsd} for this case into its components as before, it may be seen that k_h is essentially the same as k_h for Cases I and IIIa, for the same reasons as indicated above. On the other hand, k_d is about three times smaller than the corresponding rate constant in Case II, because here, although the primary and secondary isotope effects are operating on k_1 and K_2, there is no solvent isotope effect on K_3, and the corresponding rate enhancement is lacking. Calculating K_{eq} from this standpoint gives a value of $4.88 \times 3.7 \times 1.5 = 27$, compared with the observed value of 24.

Case IVa. Hydration of 1a in Deuteriosulfuric Acid

In Cases IVa and IVb proton abstraction leads to exchange rather than retention of the original label as in Cases IIIa and IIIb, so exchange is faster than before. Thus the observed equilibrium constants at ten half-lives do not so nearly represent the initial equilibrium in eq 6, and extrapolated values are given in Table I. Using these values to calculate k_h and k_d (Table II), it will be noted that k_h is very nearly the same as in Case II, again arguing that in the hydration step there is no secondary effect of any significance, and that only the primary effect is observed. As far as the reverse process is concerned, again since it involves partitioning, rationalization of the magnitudes of k_d is difficult. However, assignment of values of 1.3 and 1.2 for the isotope effects on k_1 and K_2 yields a K_{eq} value of 0.85, which exactly matches the value in Table I.

Case IVb. Dehydration of 2a in Deuteriosulfuric Acid

As in Case IVa, here k_h is similar to k_h in Case II (see Table II). The k_d values in the table are about three times as large as those for Case I, as there is no primary isotope effect to overshadow the accelerative effect of

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[23] V. Gold and M. A. Kessick, *Discussions Faraday Soc.*, **39**, 84 (1965); *J. Chem. Soc.*, 6718 (1965).

the solvent in this instance. Calculation of K_{eq} gives $K_{eq} = 4.88 \times 1/30/(1 \times 1 \times 3.0) = 0.54$, agreeing with the value in Table I.

In conclusion, a self-consistent interpretation of the deuterium isotope effects on the hydration of 1-phenyl-1,3-butadiene and the dehydration of 1-phenyl-3-methylallyl alcohol is obtained in terms of the mechanism previously proposed. While this is evidence for the correctness of the mechanism, it should be borne in mind that it involves several important assumptions: first, that the solvation energies of the various species are the same in protic or deuterated solvents; second, that the solvation energies of deuterated and nondeuterated substrates are the same in a given solvent; and third, that the basicities of water and deuterium oxide toward these carbon acids are much the same. Whereas this last assumption is not generally true, it does apply to very strong acids,[24] which these carbonium ions are.

Comparison of k_h for Cases I and II gives a mean primary solvent isotope effect for hydration of 2.97, compared to 2.3–3.3 for styrene.[7] Also, comparison of k_d for Cases II and IVb or I and IIIb gives a combined primary and secondary isotope effect for dehydration of 5.5. The magnitudes of these effects are of interest, because they are a more quantitative indication of the degree of stretching of the C–H bond in the transition state.

(24) R. P. Bell, *J. Chem. Soc.*, 187 (1965).

The Mechanisms for the Acid-Catalyzed Hydrolysis of Vinyl Acetate and Isopropenyl Acetate[1]

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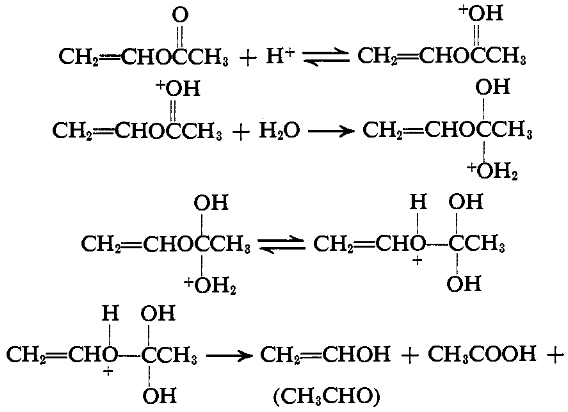
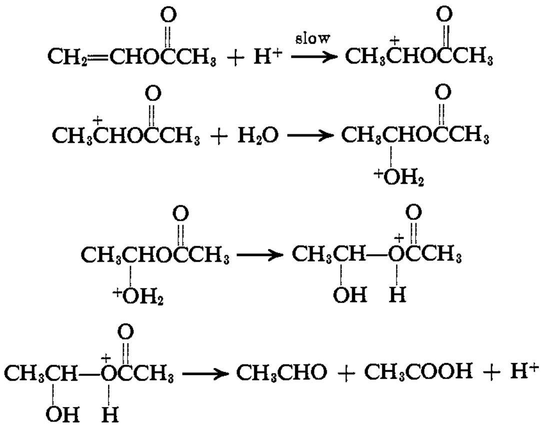
Abstract: In dilute aqueous sulfuric acid, both vinyl acetate and isopropenyl acetate hydrolyze primarily by the same mechanism as ethyl acetate. The alternative ASE2 mechanism, involving rate-determining protonation of the double bond, accounts for less than 0.5% of the rate for vinyl acetate but about 20% of the rate for isopropenyl acetate in 6% sulfuric acid. In this medium, vinyl acetate is hydrolyzed 30% faster than isopropenyl acetate and 75% faster than ethyl acetate. At higher values of the acidity, the ASE2 mechanism becomes progressively more important with the two mechanisms showing equal rates at about 13% acid for isopropenyl acetate and 50% acid for vinyl acetate. The rate of isopropenyl acetate, extrapolated to 60% acid, is about 100 times faster than vinyl acetate at the same acidity and about 1.5 times faster than α-acetoxystyrene. Observed solvent isotope effects (k_{H_2O}/k_{D_2O}) are 0.73 in 6% acid and 2.69 in 59% acid for vinyl acetate; for isopropenyl acetate the values are 1.06 in 6% acid and 3.20 in 40% acid. Effects of methyl and phenyl substitution α to a potential carbonium ion site are discussed.

Although studies of the acid-catalyzed hydrolysis of saturated esters have been extensive and the mechanisms by which these reactions occur are well understood, less work has been done on vinyl esters. Two mechanisms have been proposed for the hydrolysis of vinyl esters. Scheme I is the same as the mechanism by which the majority of saturated esters hydrolyze in acid, involving equilibrium protonation on the carbonyl carbon followed by attack of water and collapse to products. Scheme II is the ASE2 mechanism, which consists of a rate-determining protonation of the double bond with subsequent fast reaction to products in anal-

Scheme I. Mechanism for Normal Ester



Scheme II. ASE2 Mechanism



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