

Fig. 1.—A generalized view of the transition state; n may be zero or a small integer.

of the allyl group. A generalized picture of the transition state is shown in Fig. 1.

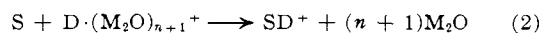
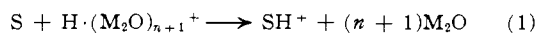
It is clear that k_H/k_D measures at least two different kinds of isotope effects: that produced by changing the proton being transferred to carbon to a deuterium and that produced by changing the remaining protons to deuterons. The former has been called the primary solvent isotope effect, $(k_H/k_D)_I$, and the latter the secondary solvent isotope effect, $(k_H/k_D)_{II}$.³ To separate these a series of reactions have been carried out in partially deuterated solvent, the propylene isolated, and the propylene-monodeuteriopropylene ratio determined by mass spectroscopy at low-ionizing voltage. The results obtained at 35° are shown in Table I.

TABLE I
ISOTOPE EFFECT BY COMPETITION

(D/H) solv.	(RH/RD) product	$\mathcal{R}_H/\mathcal{R}_D$
0.677	10.57	7.16
1.09	6.70	7.34
1.60	4.61	7.37
1.90	3.78	7.18
2.75	2.63	7.24
3.15	2.36	7.44
4.50	1.52	6.83 ^a
10.47	0.703	7.36
	Av. ^a	7.30 ± .09

^a The average and the average deviation from the mean omit the value 6.83, which was the result of the first measurement and varies from the mean by 5 average deviations.

The primary hydrogen isotope effect, $(k_H/k_D)_I$, is the ratio of rate constants for the reactions shown in eq. 1 and 2. The M's can be either protium or deu-



terium, but must be the same in eq. 1 and 2. Since the steps represented in eq. 1 and 2 determine the products, the product ratio in a mixed solvent is given by eq. 3. Since all the protons in an aqueous

$$\frac{RH}{RD} = \frac{(S)\{H \cdot (M_2O)_{n+1}^+\}}{(S)\{D \cdot (M_2O)_{n+1}^+\}} \times \left(\frac{k_H}{k_D}\right)_I \quad (3)$$

acid solution are in rapid equilibrium, the ratio $\{H \cdot (M_2O)_{n+1}^+\}/\{D \cdot (M_2O)_{n+1}^+\}$ can be related to the isotopic content of the solvent by eq. 4, the equilibrium constant for which is λ . Combining eq. 3 and 4 in



(3) C. A. Bunton and V. J. Shiner, *J. Am. Chem. Soc.*, **83**, 3214 (1961).

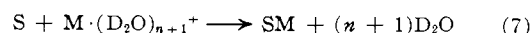
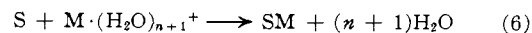
eq. 5 it is readily predicted that the quantity $(RH)/(RD) \times (D)/(H)$ should be a constant. That constant, designated $\mathcal{R}_H/\mathcal{R}_D$, is tabulated in Table I,

$$\frac{(RH)}{(RD)} = \frac{(HOM)}{(DOM)} \times \frac{1}{\lambda} \times \left(\frac{k_H}{k_D}\right)_I \quad (5)$$

which confirms its invariance under changes in isotopic composition of the solvent.

If $n \neq 0$ the H of $H \cdot (MeO)_{n+1}^+$ has an environment very similar to that in the bulk of the solvent, and it is likely that λ is close to unity. In that case $\mathcal{R}_H/\mathcal{R}_D$, 7.30, becomes, also, $(k_H/k_D)_I$. If $n = 0$, then λ is l , the isotopic fractionation constant for protons between bulk solvent and the H_3O^+ unit of aqueous acids, thought to be around 0.7.^{4,5} In that case $(k_H/k_D)_I$ is 5.1.

The secondary hydrogen isotope effect, $(k_H/k_D)_{II}$, is the ratio of rate constants for the reactions shown in eq. 6 and 7. Since k_H/k_D is the ratio of rate constants for the reactions in which all the pertinent protons are replaced with deuterons, k_H/k_D is the product of $(k_H/k_D)_I$ and $(k_H/k_D)_{II}$. This gives the latter the value



0.64 if $n = 0$ and 0.45 if $n \neq 0$. The former value is in good accord with that obtained by Kresge and Onwood⁶ for a similar system, assuming $n = 0$. It is very similar to the value predicted by Bunton and Shiner.³ Application of the data of Kresge and Onwood to the model with $n \neq 0$ would give results similar to those obtained here. Qualitatively the present results are similar to those reported for vinylmercuric iodide,⁷ but imprecision in some of the data and uncertainty in interpreting results in moderately concentrated sulfuric acid prevented the quantitative interpretation of the earlier results.^{7a}

(4) A. J. Kresge and A. L. Allred, *ibid.*, **85**, 1541 (1963).

(5) V. Gold, *Proc. Chem. Soc.*, 141 (1963).

(6) A. J. Kresge and D. P. Onwood, *J. Am. Chem. Soc.*, **86**, 5014 (1964).

(7) M. M. Kreevoy and R. A. Kretschmer, *ibid.*, **86**, 2435 (1964).

(7a) NOTE ADDED IN PROOF.—We believe that the difference between the present views and those of Gold and Kessick (*Proc. Chem. Soc.*, 295 (1964)) lies in nomenclature and formalism rather than substance. The Gold and Kessick quantity $l^{-(1+2\alpha)}$ contains the secondary solvent isotope effect as we have formulated it.

(8) (a) Sloan Foundation Fellow, 1960–1964; (b) National Science Foundation Cooperative Graduate Fellow, 1963–1965; (c) National Science Foundation Undergraduate Research Participant, summer 1964.

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RECEIVED AUGUST 27, 1964

The Secondary Isotope Effect on Proton Transfer from the Hydronium Ion in Aqueous Solution¹

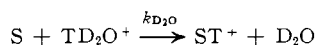
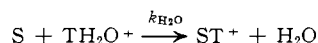
Sir:

Although proton transfer from the hydronium ion requires breaking an O–H bond of normal strength, the deuterium isotope effect on this reaction, as determined by comparing rates in H_2O and D_2O , has

(1) This research was supported in part by the Atomic Energy Commission under USAEC Contract AT(11-1)-1025 and in part by the National Institutes of Health under PHS Research Grant GM 09369-01A1.

proven to be unusually small. More than ten examples of this isotope effect measured in dilute aqueous acid have been reported so far, and in no case is the value (k_H/k_D) larger than 3. It has been suggested that these low values are the result of a sizable inverse secondary isotope effect which serves to offset a primary effect of normal magnitude.² This secondary effect cannot be observed directly in experiments which compare reaction velocities in the two waters, H₂O and D₂O, or their mixtures, but evidence pointing to its existence can be supplied by combining solvent isotope effects with product and reactant isotopic compositions.³ Use of the third isotope of hydrogen, however, allows more direct measurement of this secondary isotope effect. We wish to report here the results of such an experiment.

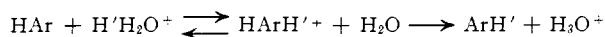
The secondary isotope effect on proton transfer from the hydronium ion has its origin in changes in the strength of the two nonreacting bonds of H₃O⁺.⁴ The isotope effect on these secondary changes can be isolated from that on the primary change, breaking of the reacting O-H bond, by keeping the isotope in the reacting bond constant while making isotopic substitution in the nonreacting bonds. This can be achieved by measuring the rates of incorporation of tracer levels of tritium into a substrate from acidified solutions of H₂O and D₂O.



The ratio of the rate constants for these two reactions is the secondary isotope effect.

$$k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = (k_H/k_D)_{\text{sec}}$$

As the system with which to perform this experiment, we chose aromatic hydrogen exchange in 1,3-dimethoxybenzene catalyzed by dilute perchloric acid. This reaction is known to occur by a two-step mechanism, the first being rate-determining proton transfer from the hydronium ion to form a phenonium ion intermediate^{2c,6}



Observed rate constants for this reaction are functions of three rate constants for individual steps

$$k_{\text{obsd}} = k_1/(1 + k_{-1}/k_2)$$

Here k_1 refers to the first forward step and k_{-1}/k_2 is an isotope effect which measures partition of the intermediate in the forward and reverse directions. To ensure that the ratio k_{-1}/k_2 was the same in the two sets

(2) (a) C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83**, 3214 (1961); (b) C. G. Swain and E. R. Thornton, *ibid.*, **83**, 3884 (1961); (c) A. J. Kresge and Y. Chiang, *ibid.*, **84**, 3976 (1962).

(3) M. M. Kreevoy and R. A. Kretchner, *ibid.*, **86**, 2435 (1964); V. Gold and M. A. Kessick, *Pure Appl. Chem.*, **8**, 421 (1964); M. M. Kreevoy, P. W. Steinwand, and W. V. Kayser, *J. Am. Chem. Soc.*, **86**, 5013 (1964).

(4) Though the hydronium ion is certainly solvated in aqueous solution and the ion H₃O₄⁺ seems to be an especially important solute species, solvent isotope effects can be described adequately in terms of H₃O⁺ alone (ref. 5).

(5) K. Heinzinger and R. E. Weston, Jr., *J. Phys. Chem.*, **68**, 744 (1964).

(6) A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **81**, 5509 (1959); **83**, 2877 (1961); A. J. Kresge and Y. Sato, unpublished work on 1,3-dimethoxybenzene.

of measurements, one in H₂O and one in D₂O, we determined initial rates only, allowing each reaction to proceed to no more than 2% completion. Under these conditions, $k_{-1}/k_2 = k_T/k_H$ in both solvents, and the ratio of observed rate constants is equal to the ratio of rate constants for the first step in the forward direction (rate-determining proton transfer from the hydronium ion).

Table I shows that these initial rates for equivalent dimethoxybenzene and tritium concentrations are directly proportional to acid concentration and that

TABLE I

RATES OF INCORPORATION OF TRITIUM INTO 1,3-DIMETHOXYBENZENE CATALYZED BY PERCHLORIC ACID AT 25°

Solvent	10 ² [Acid], M	Rate, ^a M ⁻¹ hr. ⁻¹	Rate/[acid], M ⁻² hr. ⁻¹
H ₂ O	1.32	0.288	21.8 ± 4%
H ₂ O	2.20	0.530	24.0 ± 4%
H ₂ O	4.41	1.00	22.7 ± 4%
			Av. 22.9 ± 2%
D ₂ O	1.32	0.787	59.5 ± 2%
D ₂ O	2.12	1.11	52.3 ± 2%
D ₂ O	2.87	1.53	53.4 ± 2%
D ₂ O	3.89	2.25	57.9 ± 3%
			Av. 55.7 ± 1%

$$R = (\text{rate})_{\text{H}_2\text{O}}/(\text{rate})_{\text{D}_2\text{O}} = 0.411 \pm 2.7\%$$

^a Rates were calculated by least-squares fit of kinetic data to a zero-order expression; error limits are standard deviations of the mean. The rate constants include an arbitrary factor which is a function of the method employed to measure them. The factor is the same for all rate constants and cancels in the ratio R .

the rate of any uncatalyzed reaction is negligibly low. The system, therefore, is measuring only proton transfer from the hydronium ion. The ratio, R , of the average rates in H₂O and in D₂O presented in Table I does not give the secondary isotope effect, $(k_H/k_D)_{\text{sec}}$, directly, because R compares rates at the same total acidity in H₂O as in D₂O, whereas $(k_H/k_D)_{\text{sec}}$ refers to rates at equivalent concentrations of TH₂O⁺ and TD₂O⁺. The two quantities are related by the following expression

$$R = (k_H/k_D)_{\text{sec}} [\text{TH}_2\text{O}^+]/[\text{TD}_2\text{O}^+]$$

In either solvent, tritium will be fractionated between the acid and water species, but this fractionation will not be the same in H₂O as in D₂O and the ratio $[\text{TH}_2\text{O}^+]/[\text{TD}_2\text{O}^+]$ will not be unity. Application of the rule of the geometric mean shows, however, that $[\text{TH}_2\text{O}^+]/[\text{TD}_2\text{O}^+] = l$, the D-H fractionation factor for the hydronium ion in aqueous solution.⁷ The secondary isotope effect, therefore, is equal to R/l or 0.60 ± 0.02 .⁸

This empirically determined value of the secondary isotope effect on proton transfer from the hydronium ion is in good agreement with the value of 0.61 predicted theoretically.^{2a} We believe, however, that this agreement is fortuitous, for this isotope effect cannot be expected to have a constant value. Its magnitude

(7) A. J. Kresge, *Pure Appl. Chem.*, **8**, 243 (1964).

(8) This result is calculated using $l = 0.69$ (ref. 5 and 9); the error limit is the standard deviation of the mean.

(9) A. J. Kresge and A. L. Allred, *J. Am. Chem. Soc.*, **85**, 1541 (1963); V. Gold, *Proc. Chem. Soc.*, 141 (1963).

will depend on the extent to which the strength of the nonreacting bonds of H_3O^+ changes as the proton transfer transition state is reached, and this, in turn, will be a function of the amount of proton transfer at the transition state. An upper limit of 1.00 for this isotope effect can be set for the (hypothetical) case of no proton transfer and no change in the nonreacting bonds. A lower limit is harder to fix, but an argument can be made for its being l^2 or 0.48.^{2b} It seems likely that the position which the isotope effect on a given reaction occupies with respect to these limits will constitute a valuable criterion of the extent of proton transfer at the transition state of that reaction.

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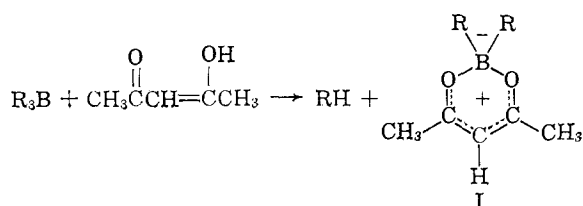
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RECEIVED AUGUST 27, 1964

Cyclic Dialkylboronium Acetylacetonates

Sir:

We wish to report the general synthesis of cyclic dialkylboronium acetylacetonates of structure I and related cyclic compounds.¹ The reaction of trialkylboranes with acetylacetonate produces the corresponding dialkylboronium acetylacetonate and the hydrocarbon derived from the trialkylborane in virtually quantitative yield. The reaction undoubtedly proceeds through



the enol form of the β -dicarbonyl compound in a manner analogous to the known reaction of carboxylic acids with trialkylboranes.² Other β -dicarbonyl compounds such as dibenzoylmethane and ethyl acetoacetate gave products analogous to I with trialkylboranes as did 2-imino-4-pentanone.

In a typical preparation, the trialkylborane is mixed with a 50% excess of acetylacetonate and heated under nitrogen at 70–75° for 24 hr. The excess acetylacetonate, hydrocarbon product, and dialkylboronium acetylacetonate are recovered by fractional distillation at reduced pressure. Yields of chelate and hydrocarbon most often exceed 95%. Triphenylborane did not react with acetylacetonate under these conditions. Table I reports pertinent characterization data. All products gave satisfactory elemental analyses.

The simple dialkylboronium acetylacetonates are bright yellow, distillable liquids or low melting solids. They are stable toward water and atmospheric oxygen for moderate periods of time. Treatment of these compounds with aqueous base at the reflux temperature followed by acidification and distillation afforded the

(1) W. Gerrard, M. F. Lappert, and R. Shaffer, *J. Chem. Soc.*, 3648 (1958), have prepared di-*n*-butylboron ethyl acetoacetate and diphenylboron ethyl acetoacetate from the corresponding organoboron chlorides and ethyl acetoacetate.

(2) H. C. Brown and K. Murray, *J. Am. Chem. Soc.*, **81**, 4108 (1959).

TABLE I

Trialkylborane	Dicarbonyl compound	Yield, %	B.p. (mm.) or m.p., °C.
<i>n</i> -Butyl	Acetylacetonate	98.3	86 (0.1)
Isobutyl	Acetylacetonate	98.3	75 (0.1)
2-Butyl	Acetylacetonate	98.5	71 (0.15)
<i>n</i> -Hexyl	Acetylacetonate	98.3	120 (0.1)
Cyclohexyl	Acetylacetonate	98.5	65.5–66.0
<i>n</i> -Butyl	2-Imino-4-pentanone	89.6	84 (0.1)
Isobutyl	Dibenzoylmethane	90	70–71
Isobutyl	Ethyl acetoacetate	92	87 (1.0)

corresponding dialkylborinic anhydrides in high yield. This method is attractive for the large scale synthesis of the latter compounds.

Bromination of dialkylboronium acetylacetonates with elemental bromine in carbon tetrachloride solution at room temperature apparently produces unstable dibromides which spontaneously dehydrobrominate to produce monobromo derivatives which contain no vinylic hydrogen and two equivalent methyl groups in their ¹H n.m.r. spectra. Unsubstituted dialkylboronium acetylacetonates exhibited vinylic hydrogen at τ 4.6 to 4.8 and two equivalent methyl groups at τ 8.00 relative to tetramethylsilane. These results confirm the cyclic structure I assigned to the dialkylboronium acetylacetonates and the monobromo derivatives. The infrared spectra of the dialkylboronium acetylacetonates contained absorption bands at 6.25, 6.55, 7.25, 9.00, and 13.0 μ . Their ultraviolet spectra were characterized by two principal absorption bands between 320–345 and 220–270 $m\mu$.

Further work dealing with the chemistry of the dialkylboronium acetylacetonates is in progress and will be reported elsewhere.

Acknowledgment.—The authors wish to thank the Petroleum Research Fund administered by the American Chemical Society for generous financial support.

(3) Alfred P. Sloan Research Fellow.

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The Thermal Isomerization of C-Phenyldicarbaundecaborate(12)

Sir:

We wish to report the thermal rearrangement of the C-phenyldicarbaundecaborate(12) (I) derived from C-phenyl-*o*-dicarbaclododecaborane(12)¹ (II) to an isomeric ion III which was also prepared directly by basic degradation of C-phenyl-*m*-dicarbaclododecaborane(12) (IV). The latter material (m.p. 55.1–55.6°) was prepared in 70% yield by thermal rearrangement² of the *ortho* isomer at 410° and was characterized by its mass spectrum. The mass spectrum contained a sharp cutoff at $m/e = 223$ which corresponds to ¹¹B₁₀¹²C₇¹³C¹H₁₆. The ratios of the $m/e = 222$ and 223 intensities for this material and the *ortho* isomer

(1) R. A. Wiesboeck and M. R. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

(2) (a) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963); (b) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).