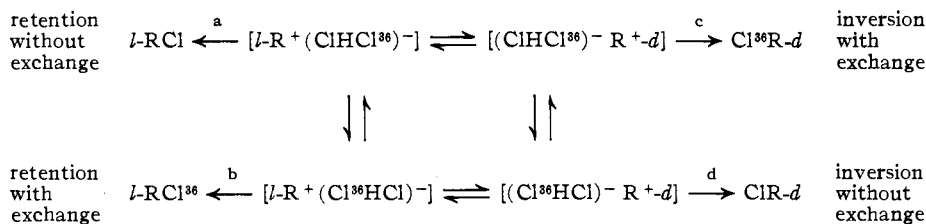SCHEME II

pyridine and NEt_4Cl acting as bases: $k_1^D = 0.29 \times 10^{-5}$ sec.$^{-1}$. This indicates that whatever the stoichiometry of these unimolecular processes, substitution or elimination, the rates are controlled by a common process which is identified as the rate of production of chemically capturable 1-phenylethyl cations, this rate being slower than the racemization process.

The component of exchange which is first order in alkyl chloride and first order in HCl cannot be an S_N2 process, because $k_2^\alpha = k_2^E$. It appears that, in contrast to NEt_4Cl^{36},[5] the HCl^{36} molecule is intervening in the rate-controlling step of the second-order process by virtue of its capacity to form a hydrogen bond with the chlorine of 1-phenylethyl chloride, and thus assists electron transfer and bond heterolysis.[6] The intermediates involved in k_2^E cannot be *tight* ion pairs because the collapse of $R^+(ClHCl^{36})^-$ if occurring on the same side of R^+ would lead to $k_2^E > k_2^\alpha$. This can be seen from Scheme I. Even if we were to allow for rapid reorganization of the ion pair in the solvent cage prior to collapse as indicated in Scheme II, we would find that statistically two routes lead to inversion (c and d) and two routes lead to exchange (b and c). Such a mechanism would lead to $k_2^\alpha = 2k_2^E$.

The experimentally found equality between k_2^α and k_2^E requires for kinetic reasons that the equilibration of radiochlorine between bichloride ion and the HCl^{36} in solution

$$R^+(ClHCl^{36})^- + HCl^{36} \rightleftharpoons R^+(Cl^{36}HCl^{36})^- + HCl$$

be faster than the recombination (collapse) of the carbonium ion with one of the chlorines of the hydrogen bichloride ion. This isotopic equilibration can be achieved either if the ion pairs in question are long lived to allow time for diffusion through the solvent cage or if both k_2^E and k_2^α represent the rate constants for the formation of kinetically free R^+ and $(ClHCl^{36})^-$.

The rates of racemization and exchange of *p*-methylbenzhydryl chloride in nitromethane increase linearly with $[HCl^{36}] < 0.11$ M. At 44.6°, V_α and V_E follow eq. 1 and 2, respectively, with $k_1^\alpha \simeq 48 \times 10^{-5}$ sec.$^{-1}$; $k_1^E \simeq 2.28 \times 10^{-5}$ sec.$^{-1}$; and $k_2^\alpha = k_2^E = 0.47$ l. mole^{-1} sec.$^{-1}$. We take the ratio $k_2^\alpha/k_2^E = 1.0$ to mean that the energy barriers for HCl^{36} catalyzed racemization and exchange are the same and that consequently they measure a common process, *e.g.*, the formation of loosely associated or possibly dissociated species of the type $R^+ + (ClHCl^{36})^-$ or $(CH_3-$

$NO_2 \cdot R)^+ + (ClHCl^{36})^-$,[8] in which the $(ClHCl^{36})^-$ group rapidly exchanges chloride with other labeled HCl^{36} molecules.

(8) It is interesting to compare these observations with those reported for $HgCl_2$ assisted ionization of *p*-chlorobenzhydryl chloride in acetone [A. Ledwith, M. Hojo, and S. Winstein, *Proc. Chem. Soc.*, 241 (1961)].

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Primary and Secondary Solvent Isotope Effects

Sir:

We wish to describe the quantitative separation and evaluation of the primary and secondary solvent isotope effects on the acid cleavage of allylmercuric iodide. In aqueous solutions containing 10^{-4}–10^{-5} M substrate, an equimolar amount of sodium iodide, and 10^{-3}–10^{-1} M perchloric acid, 1 mole of propene (measured manometrically and identified mass spectroscopically) and 1 mole of mercuric iodide (identified and measured by its ultraviolet spectrum) are produced from each mole of starting material. When crotylmercuric iodide is used as the substrate, 95% of the gaseous product is 1-butene. (The other 5% is *cis*-2-butene.)

The rate, measured by following the disappearance of the substrate ultraviolet spectrum, is accurately first order in substrate to >95% of completion, and the usual integrated form of the first-order rate law[1] was used to evaluate pseudo-first-order rate constants, k_1. In 10^{-3} to 10^{-1} M perchloric acid solutions $k_1/(H^+)$ is constant apart from a small electrolyte effect. The infinite dilution value of $k_1/(H^+)$, k_H, is 4.0 ± 0.1 × 10^{-2} l. mole^{-1} sec.$^{-1}$ at 35°.[2] Although iodide ion is catalytic, it increases $k_1/(H^+)$ by <5% at 10^{-4} M.

In solutions containing methyldi(β-cyanoethyl)amine and its perchloric acid salt in a fixed ratio, with the ionic strength held constant by added sodium perchlorate, k_1 showed a linear dependence on the buffer concentration, implying general acid catalysis.

A value of 1.23 ± 0.06 × 10^{-2} l. mole^{-1} sec.$^{-1}$ was obtained for k_D, by the same means used to determine k_H but with 99.7% D_2O as solvent. The greater fractional uncertainty may be due to the sensitivity of the derived k_D to contamination of the solvent with atmospheric moisture. This leads to a value of 3.25 for k_H/k_D.

These facts show, beyond reasonable doubt, that the rate-determining step is proton transfer to the γ-carbon

(6) Molecular hydrogen chloride is a recognized electrophilic catalyst for such ionic processes as the rearrangement of camphene hydrochloride in nitrobenzene [P. D. Bartlett and I. Pöckel. *J. Am. Chem. Soc.*, **60**, 1585 (1938); Y. Pocker, *Proc. Chem. Soc.*, 216 (1960)] and for the ionization of *t*-butyl chloride in nitromethane [Y. Pocker, *J. Chem. Soc.*, 1972 (1960)].

(7) A kinetically free $(ClHCl^{36})^-$ would rapidly equilibrate its chlorines with those of HCl^{36}.

(1) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 27–31.

(2) This value is the average of ten determinations, corrected for the electrolyte effect. The uncertainty is the average deviation from the mean.
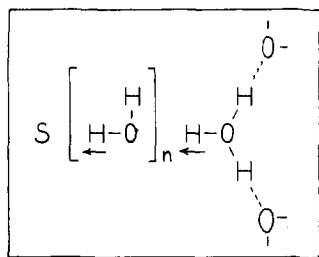
Fig. 1.—A generalized view of the transition state; n may be zero or a small integer.

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 deuteron 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	$\mathfrak{IC}_H/\mathfrak{IC}_D$
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-

$$S + H\cdot(M_2O)_{n+1}^+ \longrightarrow SH^+ + (n+1)M_2O \quad (1)$$

$$S + D\cdot(M_2O)_{n+1}^+ \longrightarrow SD^+ + (n+1)M_2O \quad (2)$$
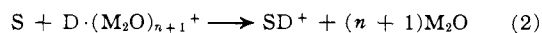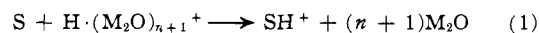
terium, but must be the same in eq. 1 and 2. Since the steps represented in eq. 1 and 2 determine the products, the product ratio in a mixed solvent is given by eq. 3. Since all the protons in an aqueous

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

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

$$H\cdot(M_2O)_{n+1}^+ + DOM \overset{\lambda}{\rightleftharpoons} D\cdot(M_2O)_{n+1}^+ + HOM \quad (4)$$
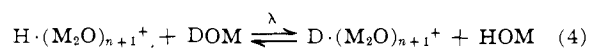
[3] C. A. Bunton and V. J. Shiner, *J. Am. Chem. Soc.*, **83**, 3214 (1961).
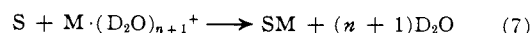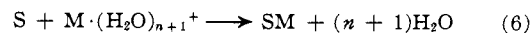
eq. 5 it is readily predicted that the quantity (RH)/(RD) × (D)/(H) should be a constant. That constant, designated $\mathfrak{IC}_H/\mathfrak{IC}_D$, is tabulated in Table I,

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

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 $\mathfrak{IC}_H/\mathfrak{IC}_D$, 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

$$S + M\cdot(H_2O)_{n+1}^+ \longrightarrow SM + (n+1)H_2O \quad (6)$$

$$S + M\cdot(D_2O)_{n+1}^+ \longrightarrow SM + (n+1)D_2O \quad (7)$$

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 Onwood[6] 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. Kretchmer, *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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The Secondary Isotope Effect on Proton Transfer from the Hydronium Ion in Aqueous Solution[1]

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