follow the rate equation

$$\frac{1}{k_1} = \frac{1}{k_4} + \frac{k_{-4}}{k_4 \Sigma k_b [B]} \qquad (2)$$

Accordingly, the values for k_1 were analyzed to give equation 3 which is plotted as the curve in Fig. 2.

$$\frac{1}{k_1} = \frac{1}{8.18 \times 10^{-6}} + \frac{1}{1.7 \times 10^{-7} + 2.78 \times 10^{-4} [OAc^-]} \qquad (3)$$

In the denominator of the second term appear the ratios $k_4 k_b / k_{-4}$ for the bases water and acetate ion. These rate constants cannot be separated; it is certain, however, that k_4/k_{-4} is very small and k_5 large.

At low base concentration, proton removal is rate controlling and the rate linear in base concentration. As the amount of base becomes large, hydration becomes rate controlling and k_1 approaches the limiting value k_4. The isotope effect on k_1 in the absence of acetate would be determined by the nucleophilic strength of D_2O in the hydration step, its basicity in the second step, the usual effect on the breaking of a carbon–hydrogen bond, and finally the effect of changing the medium from H_2O to D_2O. The observed value of k_H/k_D seems consistent with this mechanism.

The rate constant k_2 for the second stage of the reaction would be $K_2 k_6 / [H^+]$, which seems to account for k_2 above pH 4. It is quite reasonable that an acid-catalyzed dehydration would become significant below pH 4.

Preliminary studies of more basic solutions (pH 11 to 13) showed a hydroxyl-ion catalyzed fading of the nitrostyrene color. This reaction differs from the hydrolysis already described in that the nitrostyrene is regenerated if the solution is reacidified immediately. If an acidic partially hydrolyzed solution of nitrostyrene is treated with base for a minute or two, acidification restores only the concentration of nitrostyrene recently present. Longer exposure to base yields piperonal. These experiments indicate a hydroxyl ion adduct other than the form IIb if our formulation of the intermediate II is correct. One possibility would be $I \underset{H^+}{\overset{OH^-}{\rightleftarrows}} IIa$. These acid–base reactions deserve further study.

The Arrhenius Parameters of the Deuterium Isotope Rate Effect in a Base-promoted Elimination Reaction[1]: Evidence for Proton Tunnelling

BY V. J. SHINER, JR.,[2] AND MORRIS L. SMITH[3]

The rates of reaction of 1-bromo-2-phenylpropane and the 2-deuterio analog with sodium ethoxide in ethanol have been determined from 5 to 55°. The reaction product was shown to be quantitatively α-methylstyrene with no competing substitution reaction. By reference to the infrared spectra taken with a lithium fluoride prism instrument the tertiary carbon–hydrogen and carbon–deuterium vibrational stretching frequencies of these compounds were assigned as 2904 and 2160 cm.$^{-1}$, respectively. The approximately doubly-degenerate bending frequencies of these bonds were tentatively assigned as 1299 and 934 cm.$^{-1}$, respectively. The experimentally determined Arrhenius equations are: $\log k_H = 11.033 - (20,655/2.303 RT)$; $\log k_D = 11.443 - (22,406/2.303 RT)$; $\log (k_H/k_D) = -0.437 + (1,790/2.303 RT)$. An upper limit for the isotope activation energy effect, neglecting tunnelling, was estimated using the observed ground state vibrational frequencies and found to be significantly less than that obtained experimentally. The frequency factors are abnormal in that the one for the deuterium compound is almost three times that for the hydrogen analog. These apparent discrepancies between the experimental and theoretical activation parameters are rationalized on the basis of non-classical barrier penetration by the proton. The proton tunnelling through the potential barrier effectively increases the activation energy difference for the two isotopes. The general utility of the deuterium isotope rate effect in mechanistic studies is not greatly altered by the occurrence of tunnelling.

The hydrogen isotope rate effect has been developed into a fairly general and powerful tool for the investigation of reaction mechanism.[4] Application of the absolute rate theory[5] allows the theoretical calculation of the magnitude of the isotope rate effect[6,7] providing that the configurations and vibrational frequencies of the initial and transition states are known. Since the frequencies of the initial state and the isotope rate effect are subject to experimental observation while the transition state frequencies are not, the theory is generally used to infer something about the latter from the first two. In addition, where independent information on the structure of the transition state is available, observation of the isotope rate effect provides a test of the absolute rate theory.

A much more exacting test of the theory is provided by a comparison of the observed and predicted isotope Arrhenius parameters. Little definitive evidence of this type is available in spite of the wide interest in deuterium isotope effects. One obvious difficulty is the experimental one of measuring rates

(1) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) Alfred P. Sloan Research Fellow.

(3) Abstracted in part from a thesis submitted by Morris L. Smith to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree.

(4) For a general review see K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(5) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 153–201.

(6) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

(7) L. Melander, *Arkiv. Kemi.*, **2**, 211 (1950).

accurately enough over a wide enough range of temperature to give the Arrhenius parameter effects with the required accuracy. Another difficulty is that many of the reactions which have been studied, such as the gas phase photochemical decomposition and formation of the hydrogen halides[8] and the photolytic, pyrolytic and thermal decomposition of numerous organic compounds,[9] are mechanistically complicated radical processes which are difficult to analyze. The only definitive results in solution reactions are those of Bell, Fendley and Hulett[10] who measured the Arrhenius parameters of the isotope effect for the proton transfer involved in the base-catalyzed bromination of 2-carbethoxycyclopentanone-2-d. This work will be referred to again in the discussion below.

One of the important relevant theoretical problems which such studies would elucidate is that of proton tunnelling in chemical reactions. The wave nature of the proton suggests that there is a finite probability of systems with less energy than the potential barrier appearing on the other side; thus there exists the possibility of non-classical leakage or tunnelling through the barrier. The possibility is greatest when the particle mass is small and the barrier narrow. The applicability of the hydrogen isotopes to this problem is apparent when it is considered that isotopic molecules have essentially identical electronic potential barriers and that the greater mass of the deuteron makes its tunnelling probability of the order of only 10^{-4} that of the proton.[11]

The base-promoted elimination reaction of an alkyl halide is ideal for the measurement of deuterium Arrhenius parameter effects because it is known that these reactions have a high activation energy[12] and a large deuterium isotope rate effect.[13] The mechanism has been extensively studied and is known to be a one-step process involving the breaking of the carbon–hydrogen bond.[14] The rate of such a reaction can be directly measured accurately by a sensitive potentiometric halide ion titration[15] if there is no concurrent competing substitution reaction. Thus the compound chosen for study should give only an elimination reaction under the conditions chosen and, further, in order to avoid secondary isotope effects, the elimination should proceed through a tertiary hydrogen atom.

For this purpose 1-bromo-2-phenylpropane and 1-bromo-2-phenylpropane-2-d were prepared as described in the Experimental section. Both compounds were prepared from the same precursor in the same series of reactions except in the prepara-

(8) E.g., see E. M. Magee, This Journal ,79, 5375 (1957), and other reference therein.

(9) E.g., see (a) T. W. Newton and G. K. Rollefson, J. Chem. Phys., 17, 718 (1949); (b) J. R. McNesby, T. W. Davis and A. S. Gordon, This Journal, 76, 823 (1954); (c) 80, 261 (1958), and leading references therein.

(10) R. P. Bell, J. A. Fendley and J. R. Hulett, Proc. Roy. Soc. (London), 235A, 453 (1956).

(11) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953, pp. 29–30.

(12) V. J. Shiner, Jr., M. J. Boskin and M. L. Smith, This Journal, 77, 5525 (1955).

(13) V. J. Shiner, Jr., ibid., 74, 5285 (1952).

(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Ch. VIII.

(15) V. J. Shiner, Jr., and M. L. Smith, Anal. Chem., 28, 1043 (1956).

tion of the deuterated compound the ethyl 2-phenylpropionate was subjected to repeated exchanges with ethanol-d. The results of the deuterium analyses for all the deuterated compounds prepared are listed in Table I. Both the protonated and deuterated bromides smoothly underwent second-order elimination of hydrogen bromide when treated with sodium ethoxide in absolute alcohol. The protonated bromide, 1-bromo-2-phenylpropane, yielded 99.6% α-methylstyrene at 25°: the 2-deuterio analog gave 99.8% α-methylstyrene at 25° and 99.0% at 5°. The products from both compounds were shown to be identical to each other and to authentic α-methylstyrene by reference to boiling points, infrared spectra, freezing points and mixed freezing points, all of which were the same. It was further demonstrated by using standard solutions of α-methylstyrene that the procedure for olefin analysis gave quantitative results.

TABLE I
DEUTERIUM ANALYSES

Compound	Atom deuterium per molecule
Ethyl 2-phenylpropionate-2-d	0.997
2-Phenylpropanol-2-d	.997
1-Bromo-2-phenylpropane-2-d	.999
α-Methylstyrene[a]	.00

[a] Isolated as reaction product from the deuterated bromide.

In the determination of reaction rate the sealed tube method was used. All of the tubes were filled with an aliquot of the same sodium ethoxide solution in ethanol from the same automatic pipet. Half of these were then filled with an aliquot of the same solution of the hydrogen compound from the same pipet and the other half likewise filled with aliquots of a solution of the deuterium compound. Thus for all runs the ethoxide ion concentration was identical and the initial alkyl bromide concentration was identical for all hydrogen compound runs and for all deuterium compound runs. The reaction rate was measured at 5°, 15°, 25°, 35°, 45° and 55° and the kinetics strictly obeyed the second-order rate law followed to ca. 95% completion. The average rate constants and the standard deviations are summarized in Table II.

TABLE II
SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF 1-BROMO-2-PHENYLPROPANE AND THE 2-d-ANALOG WITH SODIUM ETHOXIDE

Temp., °C.	1-Bromo-2-phenylpropane k_2, l. mole^{-1} sec.$^{-1}$ × 10^6	Std. dev.	1-Bromo-2-phenylpropane-2-d k_2, l. mole^{-1} sec.$^{-1}$ × 10^7	Std. dev.	k_H/k_D
5	6.401	0.055	6.819	0.032	9.387
15	23.29	.27	28.05	0.10	8.303
25	79.17	.80	105.4	4.2	7.510
35	237.7	1.6	363.4	3.0	6.542
45	689.4	7.0	1118	11	6.165
55	1933	48	3293	46	5.868

Calculation of the experimental activation energy, ΔE_{exp}, and log of the frequency factor (log A) by the method of least squares was carried out utilizing the data in Table II. The parameters were calculated both for the individual reactions and from the ratio of the rates to give directly $\Delta\Delta E_{exp}$.
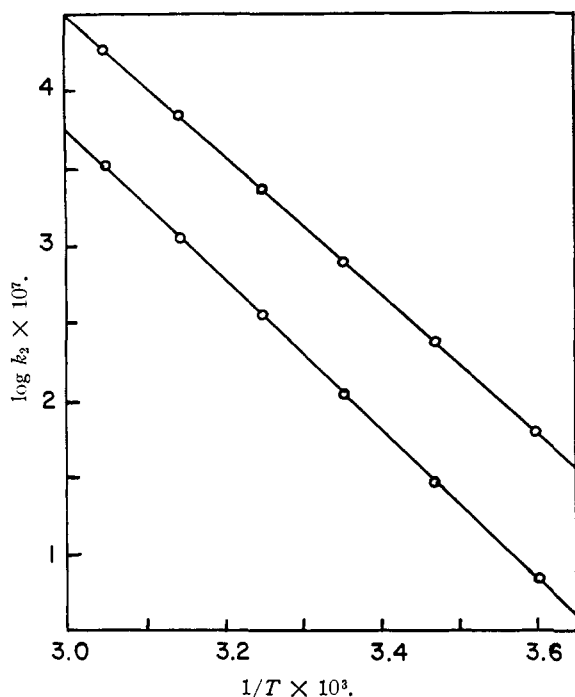
Fig. 1.—Arrhenius plots for the reaction of 1-bromo-2-phenylpropane (upper line) and 1-bromo-2-phenylpropane-2-d (lower line) with sodium ethoxide.

and log (A_D/A_H). The results are summarized in Table III.

TABLE III

EXPERIMENTAL ARRHENIUS PARAMETERS FOR THE REACTION OF 1-BROMO-2-PHENYLPROPANE AND THE 2-d-ANALOG WITH SODIUM ETHOXIDE

Parameter	1-Bromo-2-phenylpropane	1-Bromo-2-phenylpropane-2-d
ΔE_{exp}, kcal. mole^{-1}	20.655	22.406
Std. dev.	0.074	0.083
log A	11.033	11.443
Std. dev.	0.008	0.009
$\Delta\Delta E_{exp.} = \Delta\Delta E^{\ddagger}$, kcal. mole^{-1}	1.79	
Std. dev.	0.11	
log (A_D/A_H)	.437	
Std. dev.	.053	

The Arrhenius plots for the reactions are illustrated in Figs. 1 and 2. As can be seen these are excellent straight lines and show no deviation from linearity over the temperature range studied.

The isotope free energy effects, $\Delta\Delta F^{\ddagger}$, were calculated from the rate ratio by the familiar relationship given in eq. 1.

$$\Delta\Delta F^{\ddagger} = \Delta F_D^{\ddagger} - \Delta F_H^{\ddagger} = RT \ln (k_H/k_D) \quad (1)$$

The isotope effect on the entropy of activation was calculated from eq. 2 to be 2.00 e.u.

$$\Delta\Delta S^{\ddagger} = \Delta S_D^{\ddagger} - \Delta S_H^{\ddagger} = 2.303\ R \log A_H/A_D$$

A knowledge of the initial state vibrational frequencies is necessary for an application of the isotope rate effect theory. These assignments were made possible only by utilization of a lithium fluoride prism instrument which has high dispersion in the 5000 to 1667 cm.$^{-1}$ region. The spectra in the C–H stretching region for 1-bromo-2-phenyl-
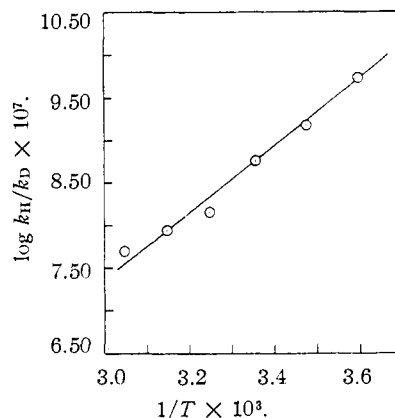

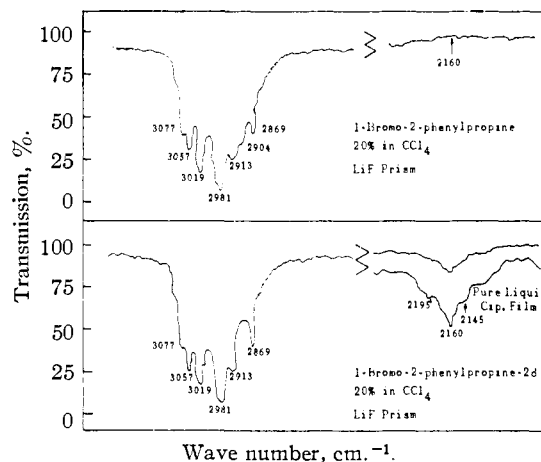Fig. 2.—Arrhenius plot of rate ratios of 1-bromo-2-phenylpropane and the 2d analog with sodium ethoxide.

Wave number, cm.$^{-1}$.

Fig. 3.—Infrared absorption spectra obtained with LiF prism of C–H, C–D stretching frequencies.

propane and the 2-d analog are shown in Fig. 3. The methyl and methylene C–H stretching frequencies are easily assigned by reference to standard works,[16] but the band for the tertiary C–H stretching is not obvious. A direct assignment for this mode of this group has apparently never been made, although indirect estimates place it around 2890 cm.$^{-1}$. From inspection of Figure 3, the only peak near this frequency present in the protium compound but completely absent in the deuterium compound is the shoulder at 2904 cm.$^{-1}$. Since this shoulder is due entirely to a single tertiary C–H stretching frequency, the differences in the two are very significant. Similar comparisons made on the protonated and deuterated precursors (ethyl 2-phenylpropionate, 2-phenylpropanol and the 2-d analogs) do not exhibit this marked difference. In the alcohol, the 2904 cm.$^{-1}$ region is swamped by the strong asymmetrical methylene and symmetrical methyl C–H stretching. In the ester, there is a very faint shoulder near 2902 cm.$^{-1}$ that does not seem to be present in the deuterio analog, but this is questionable and would scarcely be noticed except for the definite illustration in the spectra of the bromides. There seems to be no doubt that the 2904 cm.$^{-1}$ peak is due to the tertiary

(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 13–71.

C–H stretching mode. From Figure 3, the tertiary C–D stretching frequency is easily assigned since it is a triplet appearing alone with the major peak at 2160 cm.$^{-1}$ and two minor shoulders at 2195 and 2145 cm.$^{-1}$. Thus the ratio of C–H to C–D stretching frequencies is 1.344. This is close to the value of 1.363 predicted by the harmonic oscillater approximation, but significantly different. The assignments of all of the peaks in Fig. 3 are summarized in Table IV.

TABLE IV

PEAK ASSIGNMENT OF C–H AND C–D STRETCHING FREQUENCIES OF 1-BROMO-2-PHENYLPROPANE AND THE 2-d ANALOG (LiF PRISM)

1-Br-2-phenyl-propane	1-Br-2-phenyl-propane-2-d	Stretching assignment
3077	3077	Aromatic C–H
3057	3057	Aromatic C–H
3019	3019	Aromatic C–H
2981	2981	Asym. methyl C–H
2913	2913	Asym. methylene C–H
2904	..	Tertiary C–H
2869	2869	(Overlapping sym. methyl and methylene C–H)
..	2160	Tertiary C–D

The spectra from 5000 to 650 cm.$^{-1}$, taken with the NaCl prism, of the two bromides are identical and assignable in a regular way with the exception of four peaks in the 1300 to 900 cm.$^{-1}$ region. Of these only two can be seriously considered to be related to the C–H and C–D bending vibrations; these are 1299 cm.$^{-1}$ for C–H and 934 cm.$^{-1}$ for C–D. The literature assignments for tertiary C–H bending are indefinite. There should be a total of two each of these fundamentals, but only one peak at 1299 cm. is resolved; thus, it must be assumed they are approximately doubly degenerate and the single 1299 peak represents this degeneracy. If the 1299 peak is so assigned, then the related C–D peak should be near 966 cm. and one is found at 934 cm.$^{-1}$ of similar intensity. Accordingly, 1299 and 934 cm.$^{-1}$ are tentatively assigned to the doubly-degenerate tertiary C–H and C–D bending modes.

The most detailed theoretical treatments of the effect of isotopic substitution on reaction rates have been given by Bigeleisen[6] and Melander[7] and are founded upon the absolute rate theory.[5] The problem is fundamentally an evaluation of the complete partition functions. This is simplified by assuming anharmonicity to be insignificant and applying the Teller–Redlich product rule. The ratio of rate constants for hydrogen and deuterium given by Bigeleisen becomes 3 if the ratio of symmetry numbers and transmission coefficients are set equal to unity; m^* is equal to the effective mass of the molecule along the reaction coördinate u_i is equal to $h\nu_i/kT$ where ν_i are vibrational frequencies, Δu_i is equal to $h(\nu_{iH} - \nu_{iD})/kT$, and the asterisks (*) refer to quantities for the transition state.

$$\frac{k_H}{k_D} = \left(\frac{m_D^*}{m_H^*}\right)^{1/2} \prod_i \frac{u_{iD}}{u_{iH}} e^{\Delta u_i/2} \left(\frac{1 - e^{-u_{iH}}}{1 - e^{-u_{iD}}}\right)$$
$$\prod_i \frac{u_{iH}^*}{u_{iD}^*} e^{\Delta u_i^*/2} \left(\frac{1 - e^{-u^*_{iD}}}{1 - e^{-u^*_{iH}}}\right) \quad (3)$$

From the infrared spectra, the ν_i can be obtained for the ground state, but none are available for the

transition state. Therefore, any calculation of the relative rates of the alkyl bromide and the 2-d analog must of necessity make certain assumptions about the frequencies in the transition state. The simplest calculation is that which would obtain if the isotopic atoms were essentially free in the activated complex and there were no bonding between the atoms undergoing reaction. Under this assumption the total product term (equation 3) of the transition state becomes unity as all ν_i^* involving directly the isotopic atoms approach zero and all other frequencies in the deuterium transition state become equal to those of the hydrogen transition state. The equation for the maximum isotope effect then becomes

$$\frac{k_H}{k_D} = \left(\frac{m_D^*}{m_H^*}\right)^{1/2} \prod_i \frac{u_{iD}}{u_{iH}} \times e^{\Delta u_i/2} \left(\frac{1 - e^{-u_{iH}}}{1 - e^{-u_{iD}}}\right) \quad (4)$$

and the equation for the maximum isotope effect on ΔE^* can be written as

$$\Delta \Delta E^* = kT^2 \sum_i \frac{1}{T} \left[\frac{u_{iD}(e^{\Delta u_i} - 1) - \Delta u_i}{e^{u_{iH}}} - \frac{\Delta u_i}{2}\right] \quad (5)$$

Using the frequencies assigned for the C–H and C–D stretching and bending, the values obtained from eq. 4 and 5 are given in Table V.

TABLE V

COMPARISON OF THEORETICAL AND EXPERIMENTAL QUANTITIES

Temp., °C.	—Theoretical maximum $k_H/k_D{}^a$—			Exptl. k_H/k_D
	Stretching	One bending	Stretching and one bending[b]	
5	6.787	2.544	17.27	9.387
15	6.350	2.463	15.64	8.304
25	6.019	2.417	14.55	7.510
35	5.632	2.322	13.08	6.542
45	5.334	2.263	12.07	6.165
55	5.068	2.208	11.19	5.868
ΔE_a, cal./mole	1090	500	1590	1789

^{a} Associated with loss of the designated frequencies. ^{b} The apparent discrepancy arising from the experimental ΔE_a being greater than the total theoretical ΔE_a while the experimental k_H/k_D are less than the theoretical values arises from the log (A_H/A_D) being equal to -0.437 while the product of the corresponding terms of eq. 4, i.e., all except the $e^{\Delta u_i/2}$ terms, is close to one.

The basic question involved in the application of absolute rate theory to this problem is what fraction of the total zero-point energy is utilized in getting over the energy barrier? The transition state can reasonably be viewed as a three-body problem since in the rate-determining step the proton is being removed by the base and the transition state would appear as

EtO --- H --- C—R$_3$
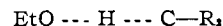
It has been shown[5] that for simple reactions of type X + YZ = XY + Z the three component system X, Y and Z has the lowest potential energy when the three atoms are in a straight line. In this model only a stretching frequency contributes to the energy required to surmount the barrier and the zero-point energy of the bending vibrations is conserved in the transition state. It seems extremely unrealistic to visualize any configuration that would require loss of all of the zero-point energy in the transition state. Even if a linear model is dis-

carded and it is assumed that some of the potential energy due to the bending vibration is utilized, then some portion of the energy due to stretching will not be used (stretching and bending are normal to one another) and thus be conserved in the transition state. The fact that the bending frequencies of strongly hydrogen bonded hydrogen atoms are very nearly normal, e.g., in FHF$^-$ it is 1225 cm.$^{-1,17}$ reinforces the conclusion that the bending zero point energy would be largely conserved in the transition state.

Bell[18] has given an excellent discussion of the theory and evidence relating to the tunnelling of protons through electronic potential barriers including especially a consideration of the evidence obtained from a study of the hydrogen isotope effect. It was concluded that a frequency factor ratio, A_D/A_H, above the classical limit of unity (or possibly an extreme limit of 2) can be attributed to tunnelling. All of the arguments invoked by Bell, Fendley and Hulett[10] in support of the observation of tunnelling in the fluoride ion-catalyzed ionization of 2-carbethoxycyclopentanone apply equally well to the present case except that the frequency factor discrepancy is not quite so large.

However, one objection to the use of the isotope frequency factor effect criterion for tunnelling is the observation[19] of a value of 2.1 for this effect in the solvolysis of 2,3-dimethyl-2-chlorobutane-3-d. In this first-order solvolytic reaction the rate-determining step does not involve rupture of the carbon-hydrogen bond. It is extremely difficult therefore to visualize any contribution of the tunnel effect in this reaction. The frequency factor ratio is nevertheless above the classical limit.

A second argument for tunnelling can be based on an analysis of the isotope activation energy effect. If the proton can tunnel through the barrier much more effectively than the deuteron, then the activation energy of the hydrogen compound relative to the deuterium compound will be lower than otherwise expected. Thus tunnelling seems to offer the only reasonable explanation of the abnormally high isotope activation energy effect observed in this study. The value of 1790 cal./mole could only be accommodated without all tunnelling if all stretching and bending vibrational energy of the isotopic atom were lost in activation. The high probability that the bending zero point energy would be largely conserved in the transition state leads to a theoretical maximum value of $\Delta\Delta E^*$ around 1200 to 1300 cal./mole and a discrepancy with the experimental value well outside of experimental error. One somewhat disturbing relationship is that the abnormality in the frequency factor effect just about cancels the abnormality in the activation energy effect and the rate ratios are near the expected maximum values. This situation is fairly common in kinetic studies of organic reactions and usually finds its rationalization in solvation effects. However, isotope effect theory as presently understood seems to allow no such combina-

tion of these abnormalities other than through the tunnel effect. Thus, since the results are outside the limits set by the isotope rate effect theory if the tunnelling is neglected, and no other source of the discrepancy seems apparent, either the theory needs modification or tunnelling is significant. The latter seems the most likely.

A more detailed check of this conclusion would be provided by the collection of the relevant data including activation energy and entropy effects involving the third isotope, tritium. Neither of the heavier isotopes should tunnel appreciably and no large abnormalities in the activation energy difference between deuterium and tritium should appear. The transition state frequencies could be assigned so as to explain one of the isotope effects and the second could be used as a check. Very few comparisons of tritium and deuterium rate effects have been made and no activation parameter effects are available. A study of tritium effects in the elimination reaction reported in this paper is now being attempted.

Experimental

Kinetic Procedure.—The kinetic method and procedure, the constant temperature baths, the olefin analyses procedure, and the bromide analyses have all been described previously.[12,13,15]

Infrared Spectra.—The infrared spectra for all compounds used in this work were taken, in a demountable cell or in 10–20% carbon tetrachloride solution in a 0.1 mm. cell, with the Perkin–Elmer model 21 recording spectrophotometer in the region from 5000 to 650 cm.$^{-1}$ with a sodium chloride prism. In addition spectra for those compounds containing deuterium and their protium analogs were taken from 5000 to 1667 cm.$^{-1}$ using the lithium fluoride prism.

Deuterium Analyses.—Combustion analyses for deuterium using the gradient density tube method were done as described in an earlier paper.[13] The analyses are reproducible within ±1% and the absolute accuracy is about ±2%.

Absolute Ethanol.—Sufficient alcohol to carry out all kinetic runs was dried and purified as before.[20]

Preparation of 2-Phenylpropionic Acid.—This was prepared by the general method of Campaigne and LeSeur.[21] The silver oxide was prepared by adding a solution of 150 g. (0.89 mole) of silver nitrate in 300 ml. of water to a solution of 70 g. (1.75 moles) of sodium hydroxide in 300 ml. of water. Continuous stirring resulted in a brown, semisolid mixture. To this mixture, contained in a 1-l. flask cooled in an ice-bath, was added 57 g. (0.425 mole) of 2-phenylpropionaldehyde[22] in small portions with stirring. The oxidation was complete in about 30 minutes after the last of the aldehyde had been added. The silver salt was removed by filtration and washed with several portions of hot water.

The silver salt was acidified with concentrated hydrochloric acid and the organic acid which was liberated extracted with ether. The ether solution was dried over anhydrous magnesium sulfate, decanted, and the solvent distilled from the crude acid which was then distilled in a 12 × 400 mm. vacuum-jacketed Vigreux column. The product was collected at 116–117° (1 mm.) and weighed 60 g. (0.4 mole) or 94% of the theoretical amount.

Preparation of Ethyl 2-Phenylpropionate.—This was prepared by the general method of Brändström.[23] To 115 g. (0.75 mole) of 2-phenylpropionic acid was added 50 ml. of chloroform, 80 g. of ethanol and 3 ml. of concd. sulfuric acid. The mixture was refluxed until the theoretical amount of water had been collected in the water separator.

(17) G. L. Coté and H. W. Thompson. Proc. Roy. Soc. (London), 210A. 206 (1951).

(18) R. P. Bell. "The Proton in Chemistry." Cornell University Press, Ithaca, N. Y., 1959, pp. 205–214.

(19) V. J. Shiner, Jr., THIS JOURNAL. 76. 1603 (1954).

(20) V. J. Shiner, Jr., and C. J. Verbanic. ibid., 79. 369 (1957).

(21) E. Campaigne and W. M. LeSeur. Org. Syntheses. 33. 94 (1953).

(22) (a) C. F. H. Allen and J. Van Allen. "Organic Syntheses," Coll. Vol. III, John Wiley and Sons. Inc., New York. N. Y., 1955, p. 727; (b) p. 733.

(23) A. Brändström. Arkiv. Kemi, 1. 481 (1950).

The crude product was distilled in a 18 × 400 ml. Nestor spinning band column and the purified product collected at 59–60° (0.3 mm.). The total yield was 121 g. (0.68 mole) or 91% of the theoretical amount.

Preparation of Ethanol-*d*.—Eastman Kodak Co. "white label" ethyl orthoformate (600 g.) was distilled until a constant b.p. of 144.2° (760 mm.) was attained to remove all ethyl formate, ethanol and water. After a generous sample of triethyl orthoformate was collected, the pot was allowed to cool. Then 50 g. (2.5 moles) of deuterium oxide (99.5%) was added to the distillation pot and distillation resumed. The ethanol-*d* was collected at 79.5° (760 mm.) and weighed 230 g. (4.9 moles) or 98% of the theoretical amount. Upon combustion analysis, the ethanol-*d* was found to contain 0.97 atom of deuterium per molecule.

Preparation of Ethyl 2-*d*-2-Phenylpropionate.—The method consisted of base-catalyzed exchange of the 2-hydrogen atom of ethyl 2-phenylpropionate with ethanol-*d*. Eighty-nine grams (0.50 mole) of ethyl 2-phenylpropionate was mixed with 94 g. (2.0 moles) of ethanol-*d* and the container flushed with nitrogen. Then 0.5 g. (0.022 mole) of sodium metal was added to make the solution *ca.* 0.01 *N* in ethoxide ion and the mixture was refluxed for 24 hours.

The ethanol was removed under diminished pressure at room temperature and another two moles of the deuterated ethanol-*d* was added and refluxed as before. This procedure was repeated with one mole of ethanol-*d* and once again with 1.25 moles of deuterated ethanol. Calculations showed that the 2-position of the ester should be fully deuterated after this extensive exchange.

The mixture was then dissolved in ether, and water added to remove the sodium ethoxide. The water layer was then extracted with two 100-ml. portions of ether, all ether solutions and washings were combined, dried over anhydrous magnesium sulfate and the ether removed by distillation. The residue was distilled in an 18 × 400 mm. Nestor spinning-band column and the pure deuterated ester collected at 59–60° (0.3 mm.). The product weighed 81 g. (0.455 mole) or 90% of the theoretical amount. The ethyl 2-*d*-2-phenylpropionate was found to contain 0.997 atom of deuterium per molecule.

Preparation of 2-Phenylpropanol.—A solution of 80 g. (0.45 mole) of ethyl 2-phenylpropionate in 250 ml. of anhydrous ether was added dropwise to a slurry of 9.1 g. (0.24 mole) of lithium aluminum hydride in 500 ml. of anhydrous ether with rapid stirring. The reaction was contained in a 2-l. flask and addition carried out at a rate which maintained gentle refluxing over a period of 3 hours. Then the excess hydride was decomposed with wet ether and the complex decomposed with 400 ml. of 25% sulfuric acid.

The layers were separated and the water extracted twice with 150-ml. portions of ether. All ether solutions were then combined and dried over anhydrous magnesium sulfate. The ether was removed by distillation and the crude product distilled through the 18 × 400 mm. Nestor spinning-band column. The alcohol was collected at 65° (0.1 mm.)

and weighed 50 g. (0.366 mole) or 81.5% of the theoretical amount.

Preparation of 2-*d*-2-Phenylpropanol.—This was prepared with exactly the same procedure as described above for the protium analog using ethyl 2-*d*-2-phenylpropionate as the starting material. A yield of 83% was obtained and on analysis the alcohol was found to contain 0.997 atom of deuterium per molecule.

Preparation of 1-Bromo-2-phenylpropane.—The method of Landauer and Rydon[24] was used. A mixture of 162 g. (0.55 mole) of triphenyl phosphite (redistilled) and 85.5 g. (0.50 mole) of benzyl bromide was heated in a 500 ml. round-bottomed flask at 110° for 48 hours. Upon cooling (the mixture was almost a glass). 47.5 g. (0.35 mole) of 2-phenylpropanol was added and the reaction mixture heated to 55° and maintained at that temperature for 24 hours.

After cooling, the reaction mixture was dissolved in 300 ml. of ether and washed nine times with 200-ml. portions of ice-water. Then the ether was dried with anhydrous calcium chloride and the product distilled through a 12 × 400 mm. vacuum-jacketed Vigreux column and collected at 61° (0.1 mm.). The yield was 67 g. (0.33 mole) or 97%; freezing point obtained by cooling curve, −67.9° with a difference between initial and half-frozen points of 0.3°.

Anal. Calcd. for $C_9H_{11}Br$: C, 54.28; H, 5.58; Br, 40.14. Found: C, 54.36; H, 5.69; Br, 39.91.

Preparation of 1-Bromo-2-phenylpropane-2-*d*.—This compound was prepared in exactly the same manner as the protium analog above. The yield was 93% and when analyzed for deuterium was found to contain 0.999 atom of deuterium per molecule.

Isolation and Identification of Reaction Products of 1-Bromo-2-phenylpropane and its Deuterium Analog with Sodium Ethoxide.—To 10 g. (0.05 mole) of 1-bromo-2-phenylpropane was added 100 ml. of 1.6 *N* sodium ethoxide and the mixture refluxed for 24 hours. The reaction mixture was extracted three times with 100-ml. portions of low-boiling ligroin (35–50°) and the ligroin dried with anhydrous calcium chloride. Upon distillation through a 15 × 500 mm. vacuum-jacketed column packed with 3/32" glass helices, the product was collected at 161.3° (760 mm.).

The boiling point of α-methylstyrene is reported in the literature as 162° (760 mm.). The infrared spectrum of the product and A.P.I. infrared spectrum No. 329 of α-methylstyrene were identical. Likewise a cooling curve of the isolated olefin gave a freezing point of −24.94° as compared to the freezing point of −24.18° obtained for an authentic sample of α-methylstyrene (reported in literature −23.21°). A 50–50 mixture of the isolated olefin and α-methylstyrene gave a freezing point of −24.73°, *i.e.*, there was no depression.

The same procedure was followed again for the 1-bromo-2-phenylpropane-2-*d*. Again the product was identical to authentic α-methylstyrene. Upon analysis the olefin was found to contain 0.00 atom of deuterium per molecule; the starting material had contained 0.999 atom of deuterium per molecule.

(24) S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).