considerably smaller, about 2.3 at the boiling point. This assumes that E_{vap} can be calculated reasonably well by using a Trouton constant of 21.5. If it is assumed that E_{vis} represents the energy necessary for the formation of a hole for the molecule that is moving, then this energy requirement is nearly twice that needed by organic compounds.

The ratio $E_{\text{vap}}/\Delta F^{\ddagger}$ approximates 1.7 to 1.8 for all of the compounds. For most organic compounds this ratio is 2.45.

Burger and Cady[1] found in the case of the perfluoropentanes that $E_{\text{vap}}/E_{\text{vis}}$ at about the boiling point ranged from 2.0 to 2.7 and $E_{\text{vap}}/\Delta F^{\ddagger}$ from 1.7 to 1.9.

Effects of Oxygen Atoms.—The effect of the oxygen atoms in perfluoro straight chain ethers in producing compounds having lower viscosities and temperature coefficients of viscosity than fluorocarbons of the same molecular weight, could be explained by assuming that internal rotation about the carbon–oxygen bond is freer than rotation about carbon–carbon bonds, and that the ether molecule is thus more flexible and requires less energy of activation than the fluorocarbon. However, a comparison of the data on perfluoro cyclic ethers and perfluoro cyclic fluorocarbons shows that the oxygen atom is as effective in reducing the viscosities and temperature coefficients of viscosity in cyclic compounds as it is in the perfluoro straight chain monoethers. This is evident from the data in Table III and is illustrated in Fig. 1. It is difficult to see how ease of rotation about the C–O bond can have much meaning in these rigid ring compounds.

The similarity of the magnitude of the effects in the two classes of compounds suggests a common cause, and, since increased internal flexibility does not appear to explain the results on the cyclic compounds, it might be imagined that it is not the explanation for the results on the straight chain compounds either.

Effects of Nitrogen Atoms.—The effectiveness of the nitrogen atom in perfluoro tertiary amines in reducing viscosity and temperature coefficients of viscosity is about the same as that of the oxygen atom, judging by the data on $(C_3F_7)_2NC_2F_5$, particularly the relation of its E_{vis} to that of the normal fluorocarbons.

Acknowledgment.—We would like to thank Dr. P. W. Trott for the samples of the pure isomers of $C_5F_{10}O$, Mr. R. A. Guenthner for most of the other compounds, and Dr. H. E. Freier and Dr. W. E. Keiser of the Analytical Section for the numerous analyses.

ST. PAUL, MINN.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

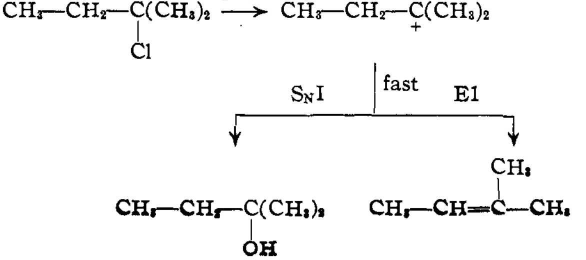
Solvolysis Rates of Some Deuterated Tertiary Amyl Chlorides

BY V. J. SHINER, JR.[1]

RECEIVED JANUARY 24, 1953

Three different β-deutero tertiary amyl chlorides, containing approximately 2, 6 and 8 deuterium atoms per molecule, have been synthesized and their rates of solvolysis and proportion of olefin formation in "80%" aqueous alcohol at 25° have been measured. The octa-deutero compound solvolyzed at a rate *ca.* two-fifths as fast as the undeuterated one while the less extensively deuterated compounds fell in the intervening range roughly spaced in proportion to the amount of β-deuteration. Deuteration of the methylene group was slightly more effective in reducing the rate than deuteration of a methyl group. Methylene deuteration cut the olefin proportion by a factor of *ca.* 1.5 while methyl deuteration showed no experimentally significant effect on this constant. This behavior is contrasted with that previously reported in a study of the effect of β-deuteration on the S_N2 and E2 reactions of isopropyl bromide. A tentative explanation in terms of mechanism is advanced to account for the reported isotope effects.

A logical extension of the recently reported work[2] on the isotope rate effect of deuterium substitution in the bimolecular reactions, S_N2 and E2, of a typical alkyl halide is the investigation of this effect in the solvolysis reaction in a case where conditions are known to be near limiting[3] or conducive to the unimolecular mechanism.[4] The present enigmatic state of our knowledge of this apparently simple but actually extremely complex organic reaction makes it, of course, the more interesting of the two cases. The theory of isotope rate effects has been presented in detail before[5–7] and experiments have confirmed that this is a particularly powerful tool in the investigation of reactions involving bonds between hydrogen and some other element, for it is in the case of the isotopes of hydrogen that the largest differences in zero point energies appear. The well-known Hughes-Ingold S_N1–E1 mechanisms at first sight appear to allow a simple prediction of the nature of the isotope effects in the reactions to which they pertain



$$CH_3{-}CH_2{-}C(Cl)(CH_3)_2 \xrightarrow{\text{slow}} CH_3{-}CH_2{-}\overset{+}{C}(CH_3)_2$$

$$CH_3{-}CH_2{-}C(OH)(CH_3)_2 \qquad CH_3{-}CH{=}C(CH_3){-}CH_3$$

---

[1] Department of Chemistry, Indiana University, Bloomington, Indiana. Du Pont Postdoctoral Fellow, Harvard University, 1951–1952.

[2] V. J. Shiner, Jr., THIS JOURNAL, **74**, 5285 (1952).

[3] S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

[4] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

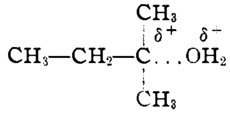
[5] O. Reitz, *Z. physik. Chem.*, **A179**, 119 (1937); **A184**, 429 (1939).

[6] H. G. Urey and G. K. Teal, *Rev. Modern Phys.*, **7**, 34 (1935).

[7] L. Melander *Arkiv Kemi*, **2**, 213 (1950).

Since the β-C–H bonds are not directly involved in any step save the non-rate-determining step, the deuterium analog should give approximately the same over-all rate but a lowered olefin fraction. A more careful consideration would allow for the effect of deuterium substitution on the inductive and hyperconjugative roles played by the alkyl group, but the nature of this influence is not easily evaluated (see later discussion).

It would seem that the views of Swain,[8] which emphasize the similarity of the S_N1 and S_N2 mechanisms might predict that the isotope effects would operate in the same fashion in both cases. The elimination reaction would then have to be independent of the substitution reaction and would be slowed down by deuterium substitution, while the substitution rate would be unaffected.[2] The role of the elimination reaction in the Swain scheme has not yet been commented on by that author and the question of its relationship to substitution appears to be one of the principal problems of his system. One possible explanation would be that the first substitution product is one of only fleeting existence, such as



$$CH_3\text{—}CH_2\text{—}\overset{\overset{CH_3}{|}\ \delta^+}{\underset{\underset{CH_3}{|}}{C}}\overset{\delta^-}{...OH_2}$$

which then, in a pair of rapid competitive steps, may lose either a proton from the oxygen or one from a β-carbon in conjunction with loss of the H_2O group from the central carbon atom. The C–O bond is dotted because it is doubted that the observed relative rates of the fast steps would be consistent with the chemistry of the conjugate acid of the tertiary alcohol. If such an intermediate is postulated in the "termolecular" mechanism then the prediction of the isotope effect of β-deuterium substitution would be the same as that predicted from the S_N1–E1 mechanisms.

Deuterated acetone was prepared by exchange as previously described[2] and ethyl-α-d_2 bromide was made from the corresponding alcohol obtained by reducing acetic anhydride with lithium aluminum deuteride. Using these two compounds and their protium analogs in different combinations in the Grignard reaction *t*-amyl-d_2, -d_6, and -d_8 alcohols were prepared. The chlorides were easily obtained from the tertiary alcohols. In a preliminary experiment, the treatment of *t*-amyl alcohol with deuterium chloride in deuterium oxide gave *t*-amyl chloride containing enough deuterium to suggest that roughly 20% of the reaction had proceeded *via* elimination of water and addition of deuterium chloride. This result would be expected on the basis of the known behavior of carbonium ions in solution as evidenced in particular in the exchange studies of Otvos, Stevenson, *et al.*,[9] on isobutane in sulfuric acid.

Since it was well known that most of the elimination takes place in the methylene branch of the *t*-amyl group,[10] it was obvious that where the alcohol had a deuterated methylene group it would have to be converted to the chloride with deuterium chloride to minimize isotopic dilution at this position. The deuterium analyses of the intermediates in the several preparations, given in Table I, did not indicate any appreciable dilution.

TABLE I

AVERAGE NUMBER OF ATOMS OF DEUTERIUM PER MOLECULE IN THE VARIOUS ORGANIC COMPOUNDS

Compound prepared	Ethyl alcohol	Acetone	*t*-Amyl alc.	*t*-Amyl chloride
CH_3–CH_2–$CCl(CH_3)_2$	1.80	0.00	1.84	1.80
CH_3–CH_2–$CCl(CD_3)_2$	0.00	5.85	5.71	5.81
CH_3–CD_2–$CCl(CD_3)_2$	1.91	5.88	7.65	7.87

The solvolysis rate constants and their standard deviations, given in Table II, were obtained from the slope of the least squares plot of t *vs.* $\log b/b - x$. While the standard deviations were of the order of 1%, the k's apparently varied between repeated runs within the limits of ±3%. The olefin fractions were reproducible to within ±0.02 unit and determinations of isoamylene in standard solutions made up by weight showed slightly less error. The constants obtained for *t*-amyl chloride agree within the limits of experimental error with those hitherto reported.[11,12]

TABLE II

RATE DATA FOR THE SOLVOLYSIS OF DEUTERATED *t*-AMYL CHLORIDES

Run	1	2	3	4	5[a]
Deuterated groups	None	–CD_2–C	–$C(CD_3)_2$	–CD_2–$C(CD_3)_2$	
No. of points	11	12	13	13	12
k (10^{-6} sec.$^{-1}$)[b]	15.72	11.19	8.83	6.69	6.30
Std. dev.[b] of K	0.15	0.12	0.10	0.07	0.30
Olefin fraction	0.36	0.25	0.37	0.23	0.23

[a] All reactions were carried out in 80% aqueous ethyl alcohol at 25° in initially neutral solution, except run 5 which contained slightly more than enough NaOH to remain alkaline throughout the reaction. [b] Rate constants and their standard deviations were determined by the least squares method.

The following points are evident from the data in Table II: 1. The over-all rate was slowed down, roughly in proportion to the amount of β-deuteration. 2. Deuteration of the methylene group was slightly more effective in reducing the rate than deuteration of one of the methyl groups. 3. Deuteration of the methylene group was effective in lowering the olefin fraction but deuteration of the methyl groups was relatively ineffective.

Since over 80% of the elimination reaction is known to proceed toward the methylene group,[10] it is understandable why deuteration of the methyl groups had relatively little effect on the olefin fraction. The fact that this change slowed down the over-all rate indicates that substitution and elimination in *t*-amyl chloride proceed in the rate-determining step to a common species intermediate to both reactions and that there is an appreciable

---

(8) C. G. Swain and W. P. Langsdorf, Jr., THIS JOURNAL, **73**, 2813 (1951).

(9) J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, *ibid.*, **73**, 5741 (1951).

(10) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

(11) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949); **72**, 1223 (1950).

(12) E. D. Hughes and B. J. McNulty, *J. Chem. Soc.*, 1283 (1937).

isotope rate effect on this step. The S_N1–E1 mechanisms fit this requirement, of course.

Melander[7] has given an extensive theoretical treatment of the isotope effect on reaction rate in terms of the theory of absolute reaction rates and has shown that the effect of zero point energy is by far the largest factor and that the partition function and activity coefficient factors in general operate in a direction opposing the zero point energy effect. Therefore, there appears ample justification, for purposes of approximate assessment of bond characteristics in the transition state, to assume that all of the rate differences between the isotopic molecules observed in the present work arise from differences in activation energy which come as a result of zero point energy differences between the initial and transition states. From the equation $\Delta E_a = 2.303\ RT \log k_1/k_2$ the differences in activation energy due to the different kinds of isotopic substitution were calculated. Table III gives the change in activation energy due to substitution of D for H in the two positions considered. The two comparisons possible in each case show the reasonable agreement of the experimental data.

TABLE III

APPROXIMATE SOLVOLYSIS ACTIVATION ENERGY DIFFERENCES DUE TO DEUTERIUM SUBSTITUTION

Change	Runs compared	ΔE_a	Av. ΔE_a per C–H bond
CH_2 to	1 and 2	200	95
CD_2	3 and av. of 4 + 5	182	
$(CH_3)_2$ to	1 and 3	343	56
$(CD_3)_2$	2 and av. of 4 + 5	324	

Using the equations, (1) relating zero point energy and vibration frequency, $E = {}^1/_2 h\nu$ and (2) relating (approximately) the mass of the atom, the bond force constant and the vibration frequency, $k = 4\pi^2\nu^2 m$ and (3) relating (approximately) the bond force constant and bond length, kr_e^6 = a constant,[13] the changes in force constant, vibration frequency, zero point energy and bond length of the β-C–H bonds in the activation process can be calculated. With the further simplifying approximation that all of the zero point energy change occurred in the bond stretching mode of vibration, the following equation was derived from the above equations, to calculate $(k_i - k_t)$ the difference in force constant between the initial and transition states where ΔE_a is the difference in activation energy between the deuterium and protium analog. Values for k_i (4.8×10^{-5} dyne/cm.) and r_i (1.099 Å.) were assumed but the differences calculated do not strongly depend on the exact values taken.

$$\Delta E_a = \frac{h}{4\pi}\left(k_i^{1/2} - k_t^{1/2}\right)\left(\frac{1}{m_h^{1/2}} - \frac{1}{m_d^{1/2}}\right)$$

The difference in the other constants given in Table IV was then a straight-forward calculation from the value of $(k_i - k_t)$.

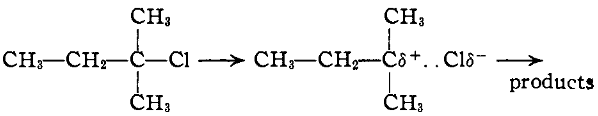
TABLE IV

APPROXIMATE CHANGE IN β-C–H BOND CHARACTERISTICS IN THE PROCESS OF ACTIVATION IN THE SOLVOLYSIS OF TERTIARY AMYL CHLORIDE

Subscript t refers to the transition state and subscript i refers to the initial state.

C–H bond in	$k_i - k_t$, 10^{-5} dynes/cm.	$\nu_i - \nu_t$, cms.$^{-1}$	$E^0_i - E^0_t$, cal.	$r_t - r_i$, Å.
CH_2 group	0.739	228	326	0.031
CH_3 group	.443	134	193	.018

This change in the nature of the β-C–H bonds must be due to the electron redistribution which accompanies the activation process.



$$CH_3\text{—}CH_2\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—}Cl \longrightarrow CH_3\text{—}CH_2\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\delta^{+}\ldots Cl\delta^{-} \longrightarrow \text{products}$$

Transition state

It would seem that an inductive withdrawal of electrons from the β-C atom would essentially act to increase the electronegativity of this atom and cause the β-C–H bonds to become shorter. It has been predicted from theoretical considerations that a hyperconjugative removal of some of the electron density of a C–H bond results in the lengthening of the bond.[14] Unfortunately the calculated C–H restoring force constants for a number of different compounds,[15] where one would hope to find experimental evidence of the effects of different types of substitution on the strength of neighboring C–H bonds, do not show clear cut and definite trends for inductive and hyperconjugative substituents. The calculated change in force constant of the β-C–H bond on activation is rather large but not as large as the range of magnitudes covered by different organic compounds if one takes the extreme cases[15]

Compound	C_2H_2	$CH_2{=}CH_2$	CH_3—NO_2	CH_3—CH_3
Force constant of CH bond in dynes/cm. $\times 10^{-5}$	5.9	5.1	5.1	4.8

However, in the activation process being considered the changes take place not on the carbon bearing the hydrogen atom but on the adjacent one and for this type of change the observed variation seems large.

The isotope effect on the elimination step is smaller than would be expected on the basis of the large observed effect in the E2 reaction,[2] (H/D rate ratio of 6.7), even allowing for the fact that the C–H bonds are already stretched slightly. The fact that the olefin fraction is near the same for (a) both the di- and octa-deutero compounds and (b) for the hexa-deutero compound and the undeuterated one, indicates that the effect of the β-deuterium substitution on the fast substitution step is small and that the only appreciable effect on the olefin fraction is the isotope effect in the C–H bond being broken in the fast elimination step. With this assumption the ratio of the rate of H elimination to that of D elimination is calculated to be 1.8.

If we consider the reaction

---

(13) J. W. Linnett, *Quart. Rev.*, **1**, 73 (1947).

(14) C. A. Coulson, "Valence," Oxford University Press, London. 1952, p. 310.

(15) J. W. Linnett, *Trans. Faraday Soc.*, **41**, 223 (1945).

$$\underset{\text{I}}{CH_3—CH_2—\overset{+}{C}(CH_3)_2} \rightleftarrows CH_3—CH=C(CH_3)_2 + H^+$$

it is obvious that the *t*-amyl carbonium ion is acting as an acid or a pseudo-acid. Since the above reaction is fast enough to compete successfully with the substitution reaction, which is a combination of ions, it seems that I is a true acid. If this is the case it might be hydrogen bonded, at the β-H atoms, in solution. This would explain the low isotope effect in the elimination, because the proton transfer, being assisted by prior hydrogen bonding, is a rapid low activation energy process and the transition state would show a relatively high conservation of zero point energy. If the β-situated hydrogen atoms serve as sites for solvation of the carbonium ion through the formation of ion-dipole bonds it is apparent that this solvation energy might be relayed, by hyperconjugation, to the central carbon atom and could contribute to the breaking of the C–Cl bond in the solvolysis. This hypothesis would explain the apparent stretching of the β-C–H bonds in the activation process. It also provides definite sites of action for some of the many solvent molecules apparently involved in the solvolytic process.

Thus far, although it has been considered for some time that substitution and elimination in this type of reaction have a common precursor formed in the rate-determining step, attention (certainly for no *a priori* reason!) has been drawn principally to the "substitution type" driving forces which might force the reaction, *i.e.*, ionic or covalent bond formation at the halogen and at the central carbon atom. These data indicate that the common precursor may be a true intermediate between substitution and elimination and that "elimination type" driving forces such as internal stabilization of the double bond and bonding (probably only ionic, here) to the β-hydrogen atoms may also be important in the *rate-determining solvolytic step.* Thus the CH bonds of the CH_2 group were stretched more than those of the CH_3 group because the double bond, already partially developed by hyperconjugation in the carbonium ion, was more stable in that branch. It may be anticipated that factors which stabilize olefin formation may act in the manner described to speed up the solvolytic step even though the double bond is only completely formed by total loss of the appropriate proton in a subsequent step. The carbonium ion may thus be viewed as a species whose electron distribution and bonding situation is intermediate between that required for final elimination and that required for final substitution, the actual nearness to one or the other being dependent on the relative stabilities of various possible contributing mesomers. The destiny of each molecule then is dependent on a later collision (or activation) which can send it either to substitution or elimination. This view is thought to differ from that of Hughes and Ingold only in being somewhat more specific concerning the role of the solvent but it of course fits the general S_N1–E1 scheme. The importance of elimination type driving forces which is stressed here has been considered before mainly through the hyperconjugative type of internal electron redistribution. Recent work of Hughes, Ingold and Rose[16] on the solvolysis reactions of menthyl and *neo*-menthyl chlorides which in the first case gave 32% Δ^2- and 68% Δ^3-menthene and in the latter almost wholly Δ^3-menthene indicates the importance of elimination type driving forces in those solvolyses.

The present scheme differs from that of Swain[8] in that the formation of ion-dipole bonds, by attack of solvent,[17] is envisaged at each center which can receive a substantial fraction of the developed charge by conjugation, hyperconjugation and/or rearrangement. Hydrogen bonds are apparently unique among ion-dipole bonds in that evidence indicates that they are saturable and directional.[18]

Therefore, there is reason to believe that the attack on partially positive hydrogen is limited to one solvating species. Such considerations apparently would not apply to partially positive carbon and these centers would be subject to attack by as many near solvent molecules as steric considerations permit. The work here reported does not furnish any new evidence concerning the solvation attack on the developing anion, which is evidently of great importance also.

While the data here presented do not bear directly on the non-limiting solvolytic reactions it is of interest to inquire whether the above mechanism in the limiting case, where substitution, elimination and rearrangement forces may all be in play in the passage of each molecule into the transition state, could possibly be a part of a "hybridized" intermediate type mechanism which combines both bimolecular and unimolecular mechanisms.[3] This would be possible in an intermediate type reaction where there might be as many different transition states as there are products corresponding to complete nucleophilic attack at the different possible sites. The principal attack in each case would have partial covalent character but fairly large charges would nevertheless be developed and could by conjugation and hyperconjugation be transferred to other centers to be dissipated by ion-dipole bond formation. These transition states could be denoted as substitution with solvation and elimination with solvation. One can visualize a case where subsequent activation might interchange the roles of the principal nucleophile and one of the solvating species so that each reaction could have some "limiting" character in this sense.[19]

Thus there is no *a priori* reason why the limiting S_N1–E1 behavior, as herein postulated, could not, in non-limiting solvolyses, be "hybridized," in almost any proportion demanded by the situation, with the S_N2–E2 scheme. The data and treatment of Winstein, Grunwald and Jones[3] indicate that the

---

[16] E. D. Hughes, C. K. Ingold and J. B. Rose, private communication (J. B. R. Thesis, University College, London, 1951).

[17] Some confusion in the use of the terms nucleophilic and electrophilic appears inevitable. This terminology has been applied not only to denote the electronic character of the species in question but also to indicate that the attack has substantial covalent character.[9] Swain[8] does not limit these terms according to the latter criterion, which is admittedly purely formal, but there appears justification for keeping the usage in its original stricter sense.

[18] C. A. Coulson, ref. 14, p. 298.

[19] *Cf.* "evidence for an intermediate," ref. 3.

borderline solvolyses actually do take place through a mechanism into which the characteristics of both the extreme cases are merged.

Additional experiments designed to test the hypothesis of "elimination-type" driving forces, and to elucidate further the mechanism of these and other isotope rate effects are underway.

Experimental

Kinetic Method.—About 0.6 ml. of the alkyl chloride was added to 125 ml. of "80%" aqueous alcohol at 0°. A 5.00-ml. aliquot of this solution was measured with an automatic pipet into each of twenty-four tubes. This operation was carried out in a 0° room and each tube after filling was placed in an ice-bath. The tubes were then in turn sealed off quickly, placed in a tube holder and returned to the ice-bath. Then the entire lot was immersed in a −80° bath for storage. At zero time for the kinetic run twenty-one of the tubes were immersed in a 25.00 ± 0.01° thermostat and shaken vigorously for one minute to reduce the warm-up time. The three tubes not previously removed from the −80° bath were used to obtain the zero titration. At appropriate time intervals the tubes were removed from the thermostat, chilled quickly to −80° and stored for subsequent titration of amount of developed acid. The infinity titration was determined by averaging the results of the titration of several tubes which were allowed to stand ten or more half-lives at 25.0°. The plot of log $b/(b - x)$ *vs.* t (where x represents the difference in the amount of acid developed between the tube taken out at time t and the zero tube, and b is the value of x for the infinity tubes) gave a good straight line. The uncertainty in the value of b, which may be the cause of some of the difference between the reproducibility and the error calculated by the deviation from linearity,[20] was of the order of ±1% or less. The reactions were followed to 75–80% completion in each case. The rate constants and their standard deviations were determined for each run from the least squares calculation of the slope of the above plot.

Determination of Amount of Reaction.—The tube, previously chilled to −80°, after reaction time t at 25.0°, was rinsed quickly with distilled water, placed in a heavy-walled wide-mouth bottle containing 100 ml. of absolute alcohol at 0° and smashed with a heavy glass rod. The resulting solution was titrated with an approximately 0.02 *N* standard aqueous sodium hydroxide solution to the end-point as shown by methyl red. In the run done in slightly alkaline solution approximately 0.02 *N* standard aqueous hydrochloric acid and methyl red were used in the titration.

Olefin Determinations.—When the kinetic run was 70 to 100% complete, six to eight tubes were removed from the thermostat and chilled to −80°. The total reaction at this time was determined as described above and the amount of olefin developed was determined by the reaction with bromine in chloroform as described previously.[2] From these values the olefin fraction was obtained.

Preparation of Ethyl-α-d_2 Alcohol and Ethyl-α-d_2 Bromide.—A solution of 4.3 g. (0.043 mole) of acetic anhydride in 25 ml. of diethyl carbitol was added slowly to an ice-cold slurry of 2.0 g. of lithium aluminum deuteride[21] in 100 ml. of diethyl carbitol. The reaction mixture was allowed to stand overnight and was then heated at 100° for several hours. After cooling, the reaction mixture was hydrolyzed with 50 ml. of mono-*n*-butyl carbitol, and the resulting ethyl-α-d_2 alcohol was removed by distillation: 3.5 g. (0.076 mole), yield 89%. This material was converted to the bromide by dropwise treatment with 8 g. (0.03 mole) of phosphorus tribromide at −10°. The reaction mixture was distilled and the product dried over potassium carbonate; recovered 7.0 g. (0.064 mole), yield 84%.

Preparation of *t*-Amyl-d_8 Chloride.—A solution of the above sample of ethyl-α-d_2 chloride in 15 ml. of ether was added slowly to 1.5 g. (0.062 mole) of magnesium in a 50-ml. three-neck flask with 15 ml. of dry ether. After the addition was complete the solution was allowed to stand several hours and then 4.0 g. (0.069 mole) of acetone-d_6, prepared as described previously,[2] by exchange with deuterium oxide, was added dropwise. The reaction mixture was allowed to stand overnight and was then hydrolyzed by pouring on excess NH_4Cl and ice. The ether layer and ether extracts of the water layer were combined and the ether removed through a helix packed column. The *t*-amyl-d_8 alcohol was purified by distillation; recovered 3.6 g. (0.041 mole), yield 66%. This product was refluxed in ether with a slight excess of sodium hydride for 24 hours. The ether was removed by distillation and evacuation. The remaining sodium hydride and the sodium *t*-amylate were hydrolyzed with 1.5 g. of deuterium oxide and then the amyl alcohol and excess deuterium oxide were removed and trapped under vacuum. This mixture was then treated with gaseous deuterium chloride in a previously evacuated system, the deuterium chloride being generated by the action of deuterium sulfate, made from the reaction of heavy water with sulfur trioxide, on sodium chloride. The resulting layers were separated and the organic layer after washing once with aqueous sodium bicarbonate was dried over anhydrous potassium carbonate and distilled; yield 3.0 g. (0.029 mole), 70%.

Preparation of Di- and Hexa-deutero *t*-Amyl Alcohols.—These compounds were synthesized in a manner similar to that described above using ethyl-α-d_2 bromide and acetone in the one case and ethyl bromide and acetone-d_6 in the other. The *t*-amyl-d_6 alcohol was converted to the chloride by treatment with concd. hydrochloric acid, while the di-deutero alcohol was converted to the alcohol-*d* and treated with deuterium oxide and deuterium chloride.

Deuterium Analyses.—The deutero organic compounds were analyzed for deuterium content in the manner previously described.[2]

Acknowledgments.—The author wishes to express his appreciation to Professor P. D. Bartlett for his advice and encouragement given throughout the progress of this work, to Professor E. D. Hughes and Dr. G. E. Dunn for several valuable suggestions, and to the du Pont Company for the Fellowship grant which made this work possible.

CAMBRIDGE, MASS.

---

[20] Suggestion of the referee.

[21] Obtained from Metal Hydrides, Inc., Beverly, Mass., on allocation from the United States Atomic Energy Commission.